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Washington State Ferry Biodiesel Project

Literature Review Report for September 05, 2007

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Summary

Biodiesel is a mixture of methyl esters of long chain fatty acids, produced typically by alkali-catalyzed transesterification from vegetable oils. For biodiesel quality, the most critical fuel quality parameter is the total glycerin content. Another set of important quality parameters are the levels of sulfur, phosphorus, sodium, potassium, calcium and magnesium. Biodiesel products in the U.S. must meet ASTM D6751 quality standard specification. In this specification, values of physical properties and impurities for commercial products are set out, including viscosity, water and sediment, cetane number, cloud point, acid number, glycerin, phosphorus, etc. One of the important parameters, oxidation stability, current ASTM D6751 addresses this although European standard EN 14212 require a higher level of oxygen stability.

Other factors affecting biodiesel quality are environmental conditions, which are mainly the cold flow properties. Biodiesel has a relatively higher cloud point and pour point, which limits its application as B100 in low temperature conditions. In addition, biodiesel has a strong tendency to absorb moisture due to its chemical properties. This can be a significant concern for biodiesel applications in high humidity marine environment.

When running engines on biodiesel blends, fuel filter clogging is a recurring theme. Biodiesel users describe symptoms similar to those on the WSF vessels were reported, such as white milky fluid in fuel bowls, black deposits between filter pleats and a general increase in filter servicing and change-out. None were reported to have occurred at the extreme levels reported by WSF, and centrifugal separators were not mentioned in other applications.

1. Introduction

This document serves as a literature review report for the Washington State Ferry Biodiesel Project (Contract No. 200700001). The purpose of this project is to develop and test new fuel specifications for biodiesel and biodiesel blended fuels, as well as biodiesel product handling guidelines for use in a marine environment. To test the fuel specification and product handling guidelines, a work plan was developed and then implemented on board Washington State Ferries (WSF) vessels for a period of one year. In order to develop a successful project work plan for the fuel test, the project team reviewed specific scientific studies and technical documents related to the topic. This literature review report includes a brief introduction and overviews of the following topics listed in separate sections: (1) fuel quality specification and test methods, (2) characterization of biodiesel fuel and alternate test methods, (3) fuel usage in both marine and land-based applications, (4) the effects of environmental conditions on fuel quality, (5) fuel storage, stability, transport, and blending, (6) the effects of biodiesel production on its quality, and (7) other related biodiesel research.

2. Fuel Quality Specification and Test Methods

2.1 Biodiesel standard specifications

Biodiesel is typically produced from vegetable oils. The biodiesel products must meet some standards established in various countries and regions around world, including the United States (ASTM D6751), Europe (EN 14214) etc. Table 1 lists the standard specifications of biodiesel in the United States (ASTM 6751-07a), Europe (14214-225), Japanese Industrial Standard, and the U.S. Department of Defense (B19-B21 specification).

Table 1 Biodiesel standard specifications

		EUROPE	**USA**	**Japan**	**Dept of Defense**
	Specification units	EN 14214:2005	ASTM 6751-07a	Japanese Industrial Std.	B19-B21 Spec
				(voluntary spec)	
Fatty Acid Methyl Ester Content	% (V/V)	100	100	100	19.0-20.0
Density 15°C	g/cm³	0.86-0.90		0.86-0.90	
Viscosity 40°C	mm²/s	3.5-5.0	1.9-6.0	3.5-5.0	1.3 - 4.1
Distillation	90% @ °C		360		343
Flashpoint	°C	120 min	130 min	120min	38min
CFPP (Plug Point)	°C	Country spec		*report	
Cloud point	°C		* report		
Sulphur	mg/kg	10 max	15 max	10 max	0.015 / 0.05 / 0.5
Carbon Residue(B100 dist.residue)	%mass		0.05 max		
Carbon residue (B10 dist.residue)	%mass	0.3 max		0.3 max	.35 max
Sulphated ash	%mass	0.02 max	0.02 max	0.02 max	
Ash content	%mass				0.01
Water (dissolved)	mg/kg	500 max	500 max	500 max	
Water and Sediment					0.05
Total contamination	mg/kg	24 max		24 max	

Copper corrosion@50 C, for 3h	3h/50°C	No.1	No.3	No.1	No.3
Oxidation stability	hrs;110°C	6 hours min	3	record	
Cetane number		51 min	47 min	51 min	40
Acid value	mgKOH /g	0.5 max	0.5 max	0.5 max	0.200
Methanol	%mass	0.20 max	0.20 max	0.20 max	
Ester content	%mass	96.5 min		96.5	
Monoglyceride	%mass	0.8 max		0.8 max	
Diglyceride	%mass	0.2 max		0.2 max	
Triglyceride	%mass	0.2 max		0.2 max	
Free glycerol	%mass	0.02 max	0.02 max	0.02 max	
Total glycerol	%mass	0.25 max	0.24 max	0.25 max	
Iodine value	g I/100g	120 max		120	
Linolenic acid ME	%mass	12 max		12 max	
C(x:4) & greater unsaturated esters	%mass	1 max			
Phosphorus	mg/kg	10 max	10 max	10 max	
Alkalinity	mg/kg				
Gp I metals (Na, K)	mg/kg	5 max	5 max	5 max	
GpII metals (Ca, Mg)	mg/kg	5 max	5 max	5 max	
Storage Stability, total insolubles,	mg/100ml				4 max
Thermal Stability, 90 mins	pad % reflectance, min				70 min
Aromaticity	%mass				35
Lubricity / wear	µm at 60°C				

*agreement between producer and customer

2.2. Biodiesel industry steps up quality enforcement efforts in US

The American society of Testing and Materials (ASTM) has continued to refine quality guidelines for Biodiesel since original specification guideline created in December 2001. Since 2004, there have been three revisions:

D6751 06 (June 2006)
D6751 06b (Jan 2007)
D6751 07a (Mar 2007) Current

Several specifications have been added or made more stringent reflecting a movement toward the more mature knowledge base of the European specs as well as developing knowledge in the US industry. These changes include:

- Metals added: Gp I (Na, K) and Gp II (Ca, Mg). No metals testing previously.
- Water: New test to insure extremely low water content
- Methanol: More accurate method to insure minimal methanol content; hence a higher flashpoint.
- Oxidation Stability: Newly added to assure stability of product/shelf life

The National Biodiesel Board (NBB) is the national not-for-profit trade association representing the biodiesel industry as the coordinating body for advocacy, research and development in the United States.

The NBB is undertaking a project to work with states to catalog information regarding their authority to regulate fuels; their status in adopting ASTM D6751 as the fuel specification for biodiesel; enforcement procedures; and to assess their capacity to analyze samples.

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, which began in 2004, is a unique 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 inadequate 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.

In the interim period since the original Washington State Ferries biofuel test of 2004-05, there have been continued improvements in manufacturing and handling processes and the monitoring of these systems as indicated in Section 2.1 above.

Also, in 2004, the feedstocks available to the U.S. Biodiesel market were largely limited to soy and animal fat, and available only out of the Midwest. There are now other feedstocks in use such as Canola, and producers located in the Pacific Northwest broadening source options for local consumers. Additionally, there are now local testing laboratories established specifically for Biodiesel analysis.

2.3. References

Quality Specifications
EN: http://www.ebb-eu.org
ASTM: nbb.org
JIS: http://www.dieselet.com/standards/jp/fuel_biodiesel
DOD: http://www.desc.dla.mil/DCM/Files/DESC%20-%20Biodiesel%20Specs%20_%20Northern%20Usage.pt#287,7,slide7

Industry Quality Enforcement Efforts
www.astm.org
www.biodiesel.org
www.bq9000.org

3. Characterization of Biodiesel Fuel and Alternate Test Methods

3.1. Biodiesel physical properties and their characterizations

Viscosity is one of the most important biodiesel fuel physical properties. Ranges of acceptable kinetic viscosity at 40 ^{o}C are 1.9 – 6.0 mm^{2}/s as required by ASTM D6751 specification. The kinetic viscosity of fatty compounds (such as those found in biodiesel fuel) is significantly influenced by compound structure, including chain length, the position, number, and nature of double bonds, and the nature of oxygenated moieties [1]. Biodiesel viscosity is also dependent on temperature. It is reported that biodiesel viscosity can be calculated in the range from 273 K to 303 K with one equation [2].

Another important physical property of biodiesel fuel is solubility. Intersolubility of the biodiesel components in ethanol, methanol and diesel fuel was characterized [3]. For instance, rapeseed oil ethyl and methyl esters are soluble in ethanol and diesel fuel without limitation. However, an increase in moisture levels in ethanol results in decreasing intersolubility of biodiesel components, which suggests avoiding increased moisture content during fuel storage.

3.2. Biodiesel chemical properties and their characterizations

Oxidation stability is one of the most important chemical properties of biodiesel. Because of its chemical structure, biodiesel is sensitive to oxidative degradation, which results in the formation of corrosive acids and deposits. The main factors affecting biodiesel stability are natural antioxidant content, polyunsaturated fatty ester content, and the level of mono- and diglycerides. However, there was no oxidation stability requirement in the US biodiesel standard specification ASTM D6751, although European standard EN 14212 does contain one. The lack of agreement on which oxidation stability test method specified was the primary reason for the absence of an oxidation stability requirement in the ASTM D6751 specification [4]. Modified ASTM Test Method D2274 and European Rancimat test were considered for an oxidation stability test in U.S. Now the current ASTM D6751-07a specification has the oxidation stability requirement, setting three hours using Rancimat method instead of the six hours standard used in Europe.

A modified version of ASTM Test Method D2274 may distinguish between stable and unstable B100 samples in some cases. Consideration of Test Method D2274 for biodiesel oxidation stability means selection of three parameters: test temperature between 95 ^{o}C and 110 ^{o}C; test time (e.g. 16 hours); and the ratio of aged B100 to non-polar solvent (iso-octane) for measuring solubility effects.

The most appropriate testing conditions are at 95^{o}C for 16 hours. The test temperature ranging from 95^{o}C to 110 ^{o}C has almost no effect on the measured total insoluble but a very marked effect on the amount of iso-octane insoluble [5]. These results suggest the significant ability of B100 to solubilize polymers formed during oxidation. This test gives no induction period, presuming that all antioxidant capacity in the B100 is consumed during the test. Thus this test is a measure of the tendency of B100 to form polymers and insolubles.

Unlike D2274, Rancimat in Europe tests using an induction period, which is the amount of time from the beginning of the air purge until a sharp increase in the measurement is observed. This method does not give any measure of polymer forming tendency. The induction period prior to the onset of rapid oxidation is measured. The European specification requires Rancimat Induction Period at 110 ^{o}C to be more than six (6) hours. One significant difference for use of the Rancimat test is the biodiesel origin. Most of the biodiesel produced in Europe is rapeseed-based, but most of the biodiesel produced in the U.S. is made from soybeans or yellow grease. The rapeseed biodiesel tends to have significantly longer Rancimat induction periods than either the soy or yellow grease biodiesel because of different polyunsaturated content. Many U.S. biodiesel users reported have induction periods of 1-4 hours less than the 6 hours minimum requirement of the European specification [4, 5].

Antioxidants as additives in the biodiesel can protect against oxidation. Biodiesel blends with ultra low sulfur diesel (ULSD) may tend to be more susceptible to oxidation as natural inhibitors are removed along with the sulfur compounds.

3.3. Alternate test methods for biodiesel fuel

3.3.1. Test Methods Using Modern Techniques

High concentrations of monoglycerides and diglycerides in biodiesel not only affect the fuel quality, but also indicate incomplete reactions during production. The levels of these compounds were determined using advanced methods such as infrared spectrometry (FT-IR), Raman spectra, NMR, gel permeation chromatography (GPC), HLPC, and gas chromatography-mass spectrometry (GC-MS), etc. [6, 7]. It is reported that this approach using the advanced modern techniques is superior to typical methods in terms of the short time required and greater information gathered on the molecular structure level.

Trace elements in biodiesel are often required but must be monitored. For example, the phosphorus concentration is limited to below 10 mg/kg according to the ASTM D6751 standard. It is suggested to monitor the sodium, potassium, calcium, and magnesium levels in biodiesel due to their ability to form undesirable compounds in the engines. In this study, the determination of calcium, chlorine, potassium, magnesium, sodium, and phosphorus in biodiesel was investigated by using advanced inductively coupled plasma (ICP) technique [8]. The results demonstrated that this method can detect these elements to very low levels (e.g., μg/kg concentrations for sodium and potassium).

3.3.2. Field Test Methods Using Test Kits

Some field test methods are available for testing fuel quality. In Washington State Department of Agriculture (WSDA)'s motor fuel quality program, several tests from several companies are considered. These tests include Titra-Lube TAN test for total acid number values [9], pHLip test for B100 quality [10], Fleet Biodiesel tests [11], and InfraCal Filtometer [12], etc. The WSF biodiesel project did not use field test kits because the sample methods are operationally difficult to employ and provide limited scientific value.

3.4. References

1. Kinetic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Gerhard Knothe, Kevin R. Steidley, ***Fuel***. **2005,** 84:1059-1065.
2. Measurement of the temperature dependent viscosity of biodiesel fuels. S. Kerschbaum, and G. Rinke, ***Fuel***. **2004**, 83:287-291.
3. Solubility of multi-component biodiesel fuel systems. Violeta Makareviciene, Egle Sendzikiene, Prutenis Janulis, ***Bioresource Technology*. 2005,** 96:611-616.
4. An evaluation and comparison test of methods to measure oxidation stability of neat biodiesel: September 2003 – May 2005. S. R. Westbrook, ***National Renewable Energy Laboratory*. 2005**.
5. Stability of biodiesel and biodiesel blends: interim report. R.L. McCormick, T.L. Alleman, J.A. Waynick, S.R. Westbrook, S. Porter, ***National Renewable Energy Laboratory*. 2006**.
6. Analysis of monoglycerides and diglycerides in biodiesel fuel by GC-MS and FTIR. Ngee Sing Chong, Subathra Ramamoorthy, Christopher Ashford, Avrill Buerstetta, Kiran Donthula, and Beng Guat Ooi, ***The 233rd ACS National Meeting***, Chicago, IL, USA, March 25-29, **2007**.
7. Application of Raman spectroscopy to monitor and quantify ethyl esters in soybean oil transesterification. Grace F. Chesti, Julio L. de Macedo, Valdeilson S. Braga, Antonio T.C.P. de Souza, Vincente C.I. Parente, Esdras S. Figueredo, Ines S. Resck, Jose A. Dias, Silva C. L. Dias. ***Journal of the American Oil Chemists' Society***. **2006,** 83:597-601.
8. Analysis of biodiesel by argon-oxygen mixed-gas inductively coupled plasma optical emission spectrometry. M. Edlund, H. Visser, P. Heitland, ***Journal of Analytical Atomic Spectrometry*. 2002,** 17:232-235.

9. Titra-Lube TAN test Kit: Quantitative test kit to determine total acid number values between 0 and 2 in petroleum products and lubricating oils. ***Dexsil***, **2006**.
10. Field test kit for B100 quality: pHLip test. ***Cytoculture International Inc.***, **2007**.
11. Biodiesel Field Test Kits. ***Fleet Biodiesel***, **2007**.
12. Measuring the biofuel blend ratios in gasoline and diesel fuel, Wikls Enterprise Inc., 2006.

4. Fuel Usage in Marine and Land-Based Applications

4.1 Marine applications including fuel quality challenges and solutions

Several pilot tests have been performed under marine conditions. The results of these tests, in particular for filter clogging problems, are presented below.

Case 1: BioMer project "biodiesel demonstration and assessment for tour boats" in Canada in 2004.

This project was conducted in the Old Port of Montreal and Lachine Canal National Historic Site in Canada by the BioMer team from mid-May to mid-October 2004. The BioMer project had three objectives: (1) to test the use of neat biodiesel (B100) and various blends as alternative fuels for tour boats of various sizes; (2) to asses the economic viability and benefits of the use of biodiesel to the industry's routine operations; and (3) to measure the various environmental impacts (e.g. polluting emissions, biodiesel biodegradability and toxicity) resulting from use of biodiesel.

The biodiesel was supplied by Rothsay's Sainte-Catherine plant in Quebec. The 12 boats used, in various boat capacity sizes from 12 to 750 passengers, consumed a total of 116,685 liters of cooking-oil-based biodiesel, primarily B100, and in certain instances in B5, B10, and B20 blends with petrodiesel (low-sulfur-500 ppm) throughout this project. Biodiesel CP was not an issue in this project because the project was conducted during the summer. It is to be noted that all on-board fuels tanks were NOT cleaned before fueling with biodiesel.

In spite of higher cloud point for the biodiesel used (origin of recycled cooking oil), there were no serious filter-plugging issues. Although filter plugging problems did occur in some trials (leading to more frequent filter change), customer service was not impacted. The conclusions and recommendations made by the BioMer project team included:

- Begin using B20 before going on to Bl00 to ensure a smooth conversion to biodiesel and give users time to become familiar with the biofuel (use, maintenance, precautions, etc.).
- Verify with engine manufacturers whether guarantees remain valid after converting to biodiesel Note that weaker blends (from B5 to B20) are more widely accepted by engine manufacturers than Bl00.
- Use B20 since it offers excellent performance and maximizes engine efficiency without affecting fuel consumption.
- Tune diesel engines, e.g., by adjusting injection timing and duration, to optimize efficiency and performance before any use of Bl00. Note that after such tuning, the engine must only run on B100 and must be retuned to run again on petrodiesel
- Thoroughly clean on board and dockside fuel tanks to reduce the release of buildup due to the fuel's solvent action before starting to use biodiesel blends stronger than 5%.
- Schedule three or four additional filter changes during the cleansing period if prior cleaning is not feasible.
- Check the filtering process from tank to boat engine to make sure that large filters with the same mesh size are used at all stages, if possible, in order to counter the effects of buildup release.
- Benefit from a lower concentration like B20, which yields a very significant reduction in emissions with no pronounced increase in NOx emissions, even though B100 leads to a more impressive reduction.
- Use more competitively priced B20 rather than higher-cost B100.
- Respond to any biodiesel spill with the same measures as for a petrodiesel spill since biodiesel, even though generally less environmentally harmful than petrodiesel, is still a fuel and can have an environmental impact should a major spill in water occur.

Fuel Filter Clogging Issues

Fuel filter clogging was reported six weeks after converting to biodiesel for the BioMer project, which required the changing of fuel filters frequently. In order to understand the clogging origins, the project team has conducted a series of tests and analyses to answer three key questions:

(1) Does biodiesel adversely affect fuel filters? (Yes.)
(2) Was standard biodiesel delivered during this period? (Yes. It met ASTM D6751.)
(3) Was the clogging merely due to the solvent and cleansing effects of biodiesel? (No. mold was present, too.)

The most plausible reason for filter clogging may be the release of tank buildup as a result of biodiesel solvent properties. In order to prove that, two samples (one for B100 and another for B10) were taken directly from the clogged filters. QETE conducted tests (e.g., acid number, water and sediment, water content, mold and bacteria present, and gum test) to identify components of the sludge. The results of the B100 sample showed that filter clogging was caused by a large amount of sediment, primarily composed of gums and varnishes. The B100 tests did not detect water, mold or bacteria in the sample. However, analysis of the B10 sample indicated that water and traces of mold and bacteria were present in this sample. The source of water was not clear. The water may provide favorable conditions for bacteria and mold to grow in the fuel.

It was concluded that biodiesel use gave rise to only minor incidents due to fuel filter problems. Fuel filters clogged quickly and frequent filter changes were required for a certain period of time. The clogging that occurred six weeks after the biodiesel was introduced was caused by the solvent properties of biodiesel.

Case 2: Biodiesel tests in ferry fleet in San Francisco Bay in 2002 and 2005.

A ferry operated by Blue & Gold Fleet on San Francisco Bay, California, was tested for diesel engine emissions from August 2001 to April 2002, using three types of fuels: neat diesel, B20, and B100 soybean biodiesel. The test vessel Oski was equipped with two identical Detroit Diesel engines at port and starboard. For each fuel type, the test engine RPM ranged from approximately 600 RPM to approximately 1,700 RPM. The results were not conclusive due to test methodology questions.

A project of “Biodiesel on the Bay: Feasibility of Operating San Francisco Bay Ferries on Biodiesel and Installing a Marine Biodiesel Fueling Station” was conducted by Bluewater

Network collaborating with Red and White Fleet and Orange Diesel of Berkeley to operate the Harbor Queen on B20 in San Francisco in June 2005 (Bluewater Network, 2006). In the week-long trial period, the project demonstrated that no technical or supply hurdles exist that would prevent a ferry operator to run on biodiesel; cost and distribution remain the primary issues.

Case 3: National Oceanic and Atmospheric Administration (NOAA) Green Ship Initiative on the Great Lakes

The NOAA Great Lakes Environmental Research Laboratory (GLERL)'Green Ship' initiative has run a six year trial using B100 in three vessels. We have contacted Dennis Donahue of GLERL to request any documentation on this trial. There is no technical report currently available.

Case 4: "A Feasibility Study for the Use of Bio-diesel Type Fuels" by the U.S. Navy

The US Navy prohibits the use of biodiesel fuel for tactical applications and does not support tactical fleet demonstrations until all technical related concerns are resolved through this study. Concerns associated with biodiesel application in a marine environment include in order of priority, fuel stability, formation of emulsified gel layers, and long-term engine durability. The technical concerns are listed below:

- Significantly more susceptible to storage instability (oxidation) than petroleum-based fuel;
- Biodiesel instability is accelerated by high temperature conditions;
- Poor cold weather properties;
- Biodiesel is highly hydroscopic in nature. In the presence of water, a heavy milky emulsion could be formed, which causes hydrolysis of the ester, subsequently forming acids. These acids will lead to increased corrosion and increased maintenance needs in fuel systems containing steel, zinc, and aluminum. In addition, biodiesel, due to its affinity for water, is an excellent medium for the promotion of microbial growth;
- Biodiesel may interact adversely with certain elastomers and plastics;
- Biodiesel may have a "solvency" effect in cleaning existing fuel system deposits; and
- Intermittent use of biodiesel may cause an increase in required filter replacements.
- The use of additives to control stability, microbes and cold flow has not been fully understood during application of biodiesel fuels.

- Biodiesel fuel is an excellent medium for microbial growth which is more prevalent in biodiesel fuels than in petroleum-based fuel. Water needs to be controlled since microorganisms usually grow at the fuel-water interface. However, water control is a problem in marine applications as fuel tanks are vented to the atmosphere.

Case 5: Biodiesel Marine Marketing Opportunities: Successes and Challenges in the Chesapeake

Another early trial program on biodiesel use in recreational vessels also showed very encouraging results [10]. Boaters have shown interest in using biodiesel in their diesel powered vessels because of the benefits it has brought to the boating experience. Many boaters indicated that safety, lack of smoke, and the dramatic change in exhaust odor as reasons to use biodiesel or biodiesel blends. In addition, the use of biodiesel did not require any engine modifications. No difficulties and/or concerns regarding biodiesel quality were reported. The trail was conducted mainly in warm weather.

4.2 Land-based application including fuel quality, challenges and solutions

Several road tests have been performed in land-based applications. The results of these tests, in particular for filter clogging problems, are summarized below.

Case 1: "100,000-mile evaluation of transit buses operated on biodiesel blends (B20)" in 2006, Boulder, Colorado, USA

The objective of this study was to compare transit buses (nine 40-ft. vehicles), five buses operating on with B20, and four buses operating as a control group on petroleum diesel, as to engine performance, fuel economy, maintenance, and emissions. All buses ran about 100,000 miles over two years.

There were only occasional fuel filter plugging events for the B20-fueled buses. Two buses reported engine misfiring and stalling caused by plugging fuel filters. A brown "grease-like" material was found in the filter pleats. In order to understand the cause of this plugging problem, five samples of the fuel were taken from the fuel tank and tested for several parameters, such as percentage of biodiesel, water content, microbial contamination, etc. The results indicated that none of the samples exhibited excessively high levels of biodiesel (15.0 % - 20.3 %). The water content in the samples was 72 ppm to 97 ppm, which were higher levels than typical diesel fuel, but not excessively high. In addition, the microbial growth test did not indicate microbial contamination. Tests were also conducted on the gelatinous residue on the filter. GC-MS analysis detected plant sterols present in the residue sample, suggesting that high levels of plant sterols may have caused the filter plugging in this trial. However, due to the fact that only one sample was taken for such an analysis it cannot draw a conclusion as to the plugging problem. Therefore the exact cause could not be conclusively determined although the plugging problem was likely caused by out-of-spec biodiesel due to the sterols.

In the 100,000-mile evaluation of the buses operated on B20 and petrodiesel, there was no significant difference between the average fuel economies of the two groups. Engine and fuel system related maintenance costs were nearly the same.

Case 2: "Long range on road test with twenty percent rapeseed biodiesel" in 1999, Moscow, Idaho, USA.

Rapeseed Biodiesel (B20) was tested in an on-the-road pickup truck operated for 100,000 miles. It was reported that rust was formed in the biodiesel tank and was transferred to the fuel filter during the first 19,800 miles. The filters were replaced approximately every 3,000 miles due to filter plugging problems. The solution to the filter plugging was that the mild steel tank and combining chamber were replaced with a stainless steel tank, and the diesel fuel supplier was changed. After that, the filter plugging problem was solved.

4.3 Biodiesel and the blend tests in engines

Tests in engines using biodiesel and the blends are summarized below.

Case 1: "Study of using JP-8 aviation fuel and biodiesel in CI engines" in 2003

In this study, the stationary Petter engine (model AV1-LAB with single cylinder, indirect injection) was employed to test emission and consumption measurements. The engine was fueled with two different fuels containing biodiesel at various ratios. The fuels were JP-8 aviation fuel and blends of the JP-8 containing 13, 30 and 50% biodiesel from sunflower oil and olive oil. It was reported that the two types of biodiesel tested performed in a similar way, and the biodiesel addition in the JP-8 fuel improved the emissions of particulate matter (PM).

Case 2: "The engine tests of biodiesel from used frying oil" in 2004.

The objective of this study was to evaluate engine performance and emissions using pure biodiesel from frying oil in comparison with no. 2 diesel fuel in Turkey. The tests were in a Fiat Doblo 1.9 DS, four-cylinder, four-stroke, 46 kW diesel engine. It was concluded that the biodiesel was a more environmentally friendly fuel than no. 2 diesel, with a CO emission reduction of 8.59%, HC reduction of 30.66%, and particulate matter reduction of 63.6%. In addition, the biodiesel consumption was 2.43% less than that of no. 2 diesel.

Case 3: "Biodiesel development and characterization for use as fuel in compression ignition engines" in 2001.

A typical engine used in the agricultural sector of India, with a single cylinder, direct injection, water-cooled, portable diesel 4 kW rating, with an alternator coupled to it, was investigated in this study. The engine was provided with a centrifugal governor at the rated speed of 1,500 rpm. This test was aimed at optimizing the concentrations of biodiesel from linseed oil to be used for long term engine operation. Several blends ranged from 0 (neat diesel) to B100 (neat biodiesel), were tested, including B5, B10, B15, B20, B25, B30, B40, B50, and B75. These blends were then subjected to performance and emission tests on the engine. Based on these tests, it was concluded that biodiesel fuel can be used in existing conventional diesel engines without any major modifications required in the system, as proved by long term endurance tests. The results indicated B20 gave the best performance among all the blends tested, improving the thermal efficiency of the engine by 2.5 %, and reducing the exhaust emissions and the brake specific energy consumption.

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5. Effects of Environmental Conditions on Fuel Quality

5.1. Biodiesel cold flow issues

Cold flow properties are important in biodiesel utilization. Due to the nature of its origin, biodiesel starts to crystallize (become “cloudy”) or gel (or “solidify”) at higher temperatures than petrol-diesel. When biodiesel becomes cloudy at low temperatures, the crystals formed would likely clog fuel filters. When temperatures are even lower, biodiesel starts to show jelly-like behavior and cannot be pumped. Scientifically, three parameters are used to evaluate biodiesel’s cold flow properties: cloud point, pour point, and cold filter plugging point.

Cloud point (CP) is defined as the temperature at which crystals of organic matter in the biodiesel are visualized when measured by lowering its temperature according to the procedures described by ASTM D2500.

Pour point (PP) is the temperature at which biodiesel turns to a jelly-like semi-solid. The actual test of PP involves cooling the fuel sample and checking the temperature every 3 degrees C.

When a temperature is found where the fluid does not move when the container is turned on its side, then 3 degrees is added to this temperature to get the pour point (the lowest temperature at which the fuel can be poured). For fuels (like some biodiesel fuels) that gel quickly, the pour point can actually come out to be equal to or higher than the cloud point.

Cold filter plugging point (CFPP) is the temperature at which the crystals formed after reaching CP have accumulated enough on the fuel filter so that the flow through the filter has been significantly restricted. CFPP is affected by many variables and conditions, for example, it will vary, for the same fuel, depending on how fast the temperature drops. Although CFPP is a practical parameter, it is not easily measured in laboratories. CFPP has been shown to be well correlated with CP. Since CP and PP are relatively easy to measure, they are commonly used to characterize the cold flow operability of biodiesel fuels.

Cold flow properties of biodiesel are determined by many factors, including the types of feedstock, which determines the chemical profiles the feedstock contains, the impurities in the biodiesel, addition of cold flow property enhancers, etc. Specifically, biodiesel cloud point is highly related to the fatty acid composition of biodiesel. High percentages of saturated fatty acids of long- and linear- chains are responsible for high cloud points. In using biodiesel under cold weather conditions, a general guideline for storing B100 biodiesel is that the storage temperatures should be at least 5°F to 10°F higher than the cloud point of the biodiesel (Biodiesel Handling and Use Guideline. U.S. DOE, 2006). The practice of blending biodiesel and petro-diesel varies and different methodologies are developed especially under cold weather conditions (e.g., Copeland et al., *US Patent Application,* 2006). A study on cold weather blending (Cold Flow Blending Consortium, 2005) revealed that circulating diesel or biodiesel fuels through a pump does not match up with real world rack blending systems and the practice may have provided additional shearing and mixing that helped to eliminate crystallization. Successful B2 blends were prepared when biodiesel was 10°F above its **CP**, however, no further tests were reported on blends of biodiesel levels higher than B2.

Extensive research has been conducted on cold flow properties of biodiesel from various feedstocks. Some of the key findings in published literature are briefly discussed below.

Dunn (2005) has summarized the cold flow properties of methyl and ethyl esters of biodiesel derived from several feedstocks from various resources. The properties of CP, PP, and CFPP of these biodiesels vary quite widely and obvious differences in CP and PP between biodiesel and petro-diesel exist (note that the CP and PP for regular #2 petro-diesel are -16°C and -27°C, respectively).

Table 2. Cold flow properties of biodiesel derived from different feedstocks (Dunn, 2005).

	Oil or fat	**Alkyl group**	**CP (°C)**	**PP (°C)**	**CFPP (°C)**
1	Babassu	Methyl	4		
2	Canola	Methyl	1	-9	
3	Canola	Ethyl	-1	-6	
4	Coconut	Ethyl	5	-3	
5	Cottonseed	Methyl	-4		
6	Linseed	Methyl	0	-9	
7	Linseed	Ethyl	-2	-6	
8	Mustard seed	Ethyl	1	-15	
9	Olive	Methyl	-2	-3	-6
10	Palm	Methyl	13	16	
11	Palm	Ethyl	8	6	
12	Peanut	Methyl	5		
13	Rapeseed	Methyl	-2	-9	-8
14	Rapeseed	Ethyl	-2	-15	
15	Safflower	Methyl	-6		
16	Safflower	Ethyl	-6	-6	
17	Soybean	Methyl	0	-2	-2
18	Soybean	Ethyl	1	-4	
19	Sunflower seed	Methyl	2	-3	-2
20	Sunflower seed	Ethyl	-1	-5	
21	HO Sunflower seed	Methyl	-12		
22	Tallow	Methyl	17	15	9
23	Tallow	Ethyl	15	12	8
24	Used hydrogenated Soybean	Ethyl	7	6	
25	Waste cooking	Methyl	-1		
26	Waste grease	Ethyl	9	-3	0
27	Waste olive	Methyl	-2	-6	-9

Table 3. Cold flow properties of biodiesel/petro-diesel blends (Dunn, 2005).

	Oil or Fat	Alkyl group	Diesel grade	Blend ratio	CP (°C)	PP (°C)	CFPP (°C)
1	(Petro-diesel)	-	D-1	B0	-31	-46	-42
2	Soybean	Methyl	D-1	B10	-22	-42	
3	Soybean	Methyl	D-1	B20	-17	-30	-27
4	Soybean	Methyl	D-1	B30	-14	-25	-20
5	Soybean/tallow	Methyl	D-1	B20	-21	-29	-21
6	Soybean/tallow	Methyl	D-1	B30	-13	-24	-18
7	(Petro-diesel)	-	D-2	B0	-16	-27	-18
8	Coconut	Ethyl	D-2	B20	-7	-15	
9	Rapeseed	Ethyl	D-2	B20	-13	-15	
10	Soybean	Methyl	D-2	B20	-14	-21	-14
11	Soybean	Methyl	D-2	B30	-10	-17	-12
12	HO sunflower seed	Methyl	D-2	B30		-12	
13	Tallow	Methyl	D-2	B20	-5	-9	-8
14	Tallow	Ethyl	D-2	B20	-3	-12	-10
15	Soybean/tallow	Methyl	D-2	B20	-12	-20	-13
16	Soybean/tallow	Methyl	D-2	B30	-10	-12	-11
17	Used hydrogenated soybean	Ethyl	D-2	B20	-9	-9	
18	Waste grease	Ethyl	D-2	B20	-12	-21	-12

Fuel additives are used to improve the cold flow properties of petro-diesel. Similar products are claimed effective for use in biodiesels to reduce the pour point temperatures. In general, these additives act by distorting the wax crystal shape and size to inhibit crystal growth and thereby reducing PP temperatures. The additives usually contain copolymers of ethylene and vinyl acetate or other olefin-ester copolymers. A study was conducted at the University of Idaho to evaluate the performance of different biodiesel additives on reducing PP and CP of soy biodiesel and its blends with #2 diesel (Shrestha et al., 2007). It was found that the reductions in CP were about 0°C to 1.3 ºC and a maximum reduction in cloud point of 1.8°C was observed with one additive on B20. Most of the differences between the additives were not statistically significant. In reducing the PP of the B5 blend, all of the fuel additives tested were equally effective into reducing B5 PP to -36°C or lower (note that #2 diesel has a CP of -17°C and PP of -22°C). For B20, three of the four fuel additives reduced the PP to -36°C or lower. It is to be mentioned, however, that the additives had almost no significant effects on the PP for B100 according to statistical analysis. It is concluded that the fuel additives were more effective in petro-diesel fuel than in the soy biodiesel. The observed reduction in PP at the B5 and B20 may primarily be due to the PP depression of the petro-diesel. Even though the fuel additives were recommended for use in biodiesel, none of them has shown effectiveness in reducing CP and PP for B100.

The above findings are in agreement with the conclusions drawn by Dunn et al. in 1996 on other types of cold flow improvers for petro-diesel fuels (Table 3), although other researchers have indicated that the additives were more effective in their studies (e.g., Çetinkaya et al., 2005).

Table 4. Cold flow properties of biodiesel and biodiesel/petro-diesel blends treated with cold flow improver additives (Dunn et al., 1996).

	Biodiesel	**Diesel**	**Blend ratio**	**Additive**	**Loading** (ppm)	**CP** (°C)	**PP** (°C)
1	SME	-	B100	DFI-100	1000	-2	-6
2	SME	-	B100	DFI-200	1000	-1	-8
3	SME	-	B100	Hitec 672	1000	-2	-6
4	SME	-	B100	OS110050	1000	-1	-7
5	SME	-	B100	Paramins	1000	0	-5
6	SME	-	B100	Winterflow	1000	0	-5
7	SME	D-1	B30	DFI-l00	1000	-14	-49
8	SME	D-1	B30	DFI-200	1000	-21	-45
9	SME	D-1	B30	Hitech 672	1000	-13	-44
10	SME	D-1	B30	SO110050	1000	-17	-46
11	SME	D-1	B30	Paramins	1000	-14	-29
12	SME	D-1	B30	Winterflow	1000	-19	-39
13	SME	D-2	B20	DFI-l00	1000	-14	-26
14	SME	D-2	B20	OFI-200	1000	-14	-32
15	SME	D-2	B20	Hitech672	1000	-14	-27
16	SME	D-2	B20	OS110050	1000	-15	-18
17	SME	D-2	8B20	Paramins	1000	-14	-27
18	SME	D-2	B20	Winterflow	1000	-13	-39

Selvidge (2006) has patented a method for improving cold weather performance of biodiesel fuels by inhibiting filter deposits due to water content at low temperature. He claimed that biodiesel fuels can include chemical additives such as glycol ethers to prevent or inhibit low temperature filter deposits when used in low temperature conditions. Selvidge stated in the patent that water rich phase will precipitate, freeze, and form a problematic solid phase in the diesel fuel-biodiesel mixture. The circumstance could be true; however, it is unlikely under typical low temperature conditions.

Esters of branched-chain alcohols have the tendency to reduce biodiesel crystallization temperature. Isopropyl and 2- butyl esters of soybean oil crystallized at 7-l1 and 12-14°C lower, respectively, than the corresponding methyl esters. The benefit of the branched-chain esters in lowering crystallization temperatures increased when the esters were blended with diesel fuel (Lee et al., 1995). This effect can be clearly seen by comparing the esters made of C3 and C4 alcohols, and with methyl and ethyl esters (table 5).

Table 5. Cold flow properties of selected mono-alkyl esters (Dunn, 2005).

	Oil or Fat	**Alkyl group**	**CP (°C)**	**PP (°C)**	**CFPP (°C)**
1	Canola	Isopropyl (C3)	7	-12	
2	Canola	n-Butyl (C4)	-6	-16	
3	Linseed	Isopropyl (C3)	3	-12	
4	Linseed	n-Butyl (C4)	-10	-13	
5	Soybean	Isopropyl (C3)	-9	-12	
6	Soybean	n-Butyl (C4)	-3	-7	
7	Soybean	2-Butyl (C4)	-12	-15	
8	Tallow	n-Propyl (C3)	12	9	7
9	Tallow	Isopropyl (C3)	8	0	7
10	Tallow	n-Butyl (C4)	9	6	3
11	Tallow	Isobutyl (C4)	8	3	8
12	Tallow	2-Butyl (C4)	9	0	4

Winterization has been shown to be an effective way to decrease CFPP values. When methyl esters of waste cooking oil were winterized at 1, 0, -1, and -2°C, the saturate FFA esters were decreased by 1.5-6% and the CFPPs were reduced by 2-4°C (Gomez et al., 2002). These results are in agreement with the research on methyl esters of soybean oil by Lee et al. (1996).

To have better cold temperature behaviors, the use of biodiesel prepared from animal fats needs to be carefully formulated. A research on methyl esters of vegetable oils and animal fats has shown that mixtures with CFPP values of -5°C and lower may contain up to 25% of pork lard methyl esters. Only 5% of biodiesel from animal fats can be used in winter time in cold climate conditions such as in Europe (Kazancev et al., 2006).

Biodiesel cold flow properties can also be altered by chemically modifying the molecular structures of biodiesel constituents. Yori et al. (2006) reported that the cloud point decreases by 4~6.5°C were achieved on a soybean oil based biodiesel, which has an initial cloud point of 5.2°C, through an isomerization (or branching) under medium-level of temperatures (125-200°C) and a solid acid catalyst (Yori et al., 2006). However, the application of this technique to bulk biodiesel processing is questionable due to its obviously related cost issues.

5.2. Engine and winter road test performances of biodiesel

Studies on engine performance using biodiesel as an alternative diesel fuel have been widely conducted (e.g., Marshall et al., 1995; Peterson and Reece, 1996; Peterson et al., 1996; Haas et al., 2001; Arnal et al., 2002; Arnal et al., 2003; Canakci and Van Gerpen, 2003; Ramadhas et al., 2005; Lin and Lin, 2006). General conclusions that are agreed on by most researchers include more efficient combustion, less torque and power output, much lowered emissions, and contradictorily higher NOx emissions. For example, Çetinkaya et al. has conducted a project to investigate the engine and road performance of a vehicle fueled with biodiesel originated from used cooking oil (Çetinkaya et al., 2005). One of the tests was on a vehicle with a four-stroke, four-cylinder, 75 kW Renault Mégane Diesel engine in winter conditions. The tests included 7500 km road tests in urban and long distance traffic. The results showed that carbonization of the injectors was observed with biodiesel usage as a result of winter conditions and insufficient combustion in the initial test; the injectors were observed to be cleaner. This statement seems contradictory. In the second stage test, no carbonization was observed on the surface of the cylinders and piston heads. Despite other minor concerns, such as lower torque and power output, biodiesel originated from used cooking oil was recommended as a diesel fuel alternative for winter conditions. Due to the consideration that engine test and performance are not the focus of this review, as an example of such tests, the studies conducted at the University of Idaho are summarized below.

Multiple engine and road tests have been conducted at the University of Idaho (UI) (Lowe et al., 1998; Peterson and Thompson, 1998; Peterson et al., 1999; Chase et al., 2000). The UI worked with four diesel-powered pickups in the biodiesel tests. Engines were not modified, but modifications have been made to the pickups for testing convenience. Total of four vehicles were used: a 1992 Dodge pickup on B20, a Ford pickup on 20% raw rapeseed oil and 80% D2, a 1994 Dodge pickup on B100 REE, and a 1995 Dodge Truck on B100. The goal was to operate each vehicle about 25,000 miles per year, and to reach 100,000 miles in about four years.

All vehicles were tested on a chassis dynamometer every 10,000 to 15,000 miles to obtain information on horsepower to the wheels, torque, fuel consumption, fuel temperature, inlet air temperature, coolant temperature, exhaust temperature, engine blow by, engine rpm, and turbo boost pressure. Oil samples were taken at each oil change, which was every 3,000 to 4,000 miles, and analyzed for wear metals and physical tests for antifreeze, fuel dilution, water and viscosity. An infrared analysis of the oil checks for soot, sulfur, nitration, and oxidation. The tank heating system performed well during the cold winter months keeping the biodiesel at 50°F.

As of January 1995, the on-road vehicle tests were progressing very well. No major mechanical difficulties had occurred. The two 1992 on-road vehicles, one fueled with B20 and one 20% raw rapeseed oil have reached 55,400 miles and 46,500 miles respectively. Reduced fuel filter life had been a problem in the B20 RME blend fueled vehicle. Continuous improvements to the onboard mixing system have been made in order to obtain a more accurate mixture.

At the 16,000 mile dynamometer test, the 1994 pickup fueled with the B100 had a 7.8% reduction in horsepower compared to D2; the 1992 pickup, at the 50,000 mile dynamometer test, had horsepower changes of -1.5 and-2.9% when fueled with B20 blend and B100 RME, respectively. The injectors and compression were tested at each dynamometer inspection. Injector valve opening pressures (VOP) varied as much as 100 psi. No differences were noted between the cylinder compression tests.

In summer 1994, personnel from UI drove the 1994 Dodge 2500 pickup 8,742 miles at an average of 18.7 mpg, fueled only with B100 ethyl ester of rapeseed oil in a coast-to-coast trip. All of the B100 REE fuel was carried onboard.

The UI, along with the Montana Department of Environmental Quality, Wyoming Department of Commerce, Dodge Truck, and J.R. Simplot Company explored the market for biodiesel in the tourism industry and other environmentally sensitive applications. The Dodge Truck Division of Chrysler Corporation supplied a 1995 diesel pickup, fueled with B100 REE and operated by the National Park Service in Yellowstone National Park through 1996. This “Biodiesel in the Park” program has been a great success and now the biodiesel uses are applied to all tour buses in the Yellowstone National Park (U.S. Department of the Interior National Park Service, 2005).

5.3. Effect of marine conditions on biodiesel quality

Two common circumstances have to be considered when biodiesel is considered for use in marine conditions. The first is the relatively low but constant sea water temperature year around. The sea water temperatures in the Puget Sound region are in the range of 46-56°F (7.8-13.3°C) at Seattle ports (National Oceanographic Data Center, 2007). This temperature range is above most of the biodiesel CPs except biodiesel from palm oil, tallow, and hydrogenated waste cooking oil (see Table 1), and is not a negative factor that dramatically affects biodiesel uses in marine vessels, especially when used as petro- and bio-diesel blends. Therefore, careful selection of the proper types of biodiesel and/or use of proper level of blends would take care of this concern.

The second circumstance is the high moisture environment where the biodiesel is to be used. Due to its tendency to absorb moisture, fuel properties can be adversely affected. This can lead to fuel delivery problems, which are a common challenge in the use of biodiesel on marine vessels.

Biodiesel has the characteristics of absorbing more moisture than fossil diesel. High water solubility in biodiesel may cause problems in handling, transportation and storage. Generally, high moisture content in biodiesel is often caused by improper treatment after water washing or by the absorption of moisture from the atmosphere during storage. Condensation and precipitation may occur if the moisture content in biodiesel is beyond its saturation point as its storage temperature decreases. Microbial growth, storage container corrosion, and fuel contamination are examples of the consequences of high fuel moisture content.

Experiments were conducted at the University of Idaho to explore moisture absorption of biodiesel of different origins (He et al., 2007). Results have shown that the moisture absorbency at given temperatures has no significant differences regardless the origins of the vegetable oils or alcohols used. As a clear contrast, biodiesel absorbed 1,000 to 1,700 ppm (or 0.1%wt to 0.17%wt) moisture from 4 to 35°C, which was 15~25 times higher than that of petro-diesel in the same temperature range. The level of moisture content in biodiesel had a strong linear relationship with its temperature. Moisture absorption into biodiesel is a very fast process. The moisture content in biodiesel will reach equilibrium levels under constant relative humidity within 24 hours. The moisture absorption rate in biodiesel was much faster than in petro-diesel. As temperature increased, biodiesel had a 22.2 ppm/°C moisture absorbing rate which is more than 9 times higher than that of petro-diesel. This may lead to the phenomenon that high moisture was absorbed by stored biodiesel at high temperature and water would precipitate out due to the low solubility once the temperatures drops.

Results also showed that in biodiesel and petro-diesel blends, both the temperature and the level of blending affected the moisture absorbance linearly. The combination effects of individual parameters and their interactions affected the moisture content at varying levels. It was observed that the moisture contents of petro- and bio-diesel blends were not a simple addition of the two moisture contents of biodiesel and petro-diesel. Blending did create a mixture that tended to decrease absorbing moisture into the blends, which may lead to water precipitation to the bottom of storage containers.

A text of Marine Biodiesel In Recreational Boats was written by von Wedel, where general information about biodiesel, such as its production, environmental advantages, low impact on marine environment, engine performance, etc. were described (von Wedel, 1999). No specific technical information on biodiesel uses in marine environment or test trial data was provided. However, a survey conducted by his project group revealed that most boaters were happy with the use of biodiesel in their boats on the San Francisco Bay (Survey of 100 Recreational Boaters Using Biodiesel 1994-1997. CytoCulture, 1997). Eighty seven of the 100 surveys responded with “no problem”. Among the boaters who experienced problems, four (4) had “fuel filter clogging” problem and six (6) had “fuel tank sediment” problem. “To avoid condensation of the moist sea air inside a cold fuel tank” is one of the suggestions the author recommended for preventing the problem from happening.

The effects of environmental conditions on biodiesel quality are mainly the cold flow properties. Compared to petro-diesel, biodiesel has relatively higher cloud point and pour pint which limits its application as a pure fuel (i.e., B100) in low temperature conditions. Proper procedures should be taken in biodiesel fuel transportation, storage, blending, and utilization to avoid fuel filter clogging problems. Although some existing fuel improving additives can lower biodiesel PP, they generally do not work well for improving biodiesel CP. Considering that the temperatures of sea water are 46-56°F year around in Seattle ports, blended fuels such as B20 may be more appropriate than B100 for use in marine applications including the WSF fleet.

Biodiesel has a comparatively strong affinity for moisture as compared with petro-diesel. Due to the high humidity conditions on marine vessels, there is significant risk of moisture being absorbed into the fuel which can adversely effect fuel properties and lead to a host of onboard problems, including filter clogging. If possible, measures should be taken to minimize this risk. In spite of the challenges many biodiesel applications in marine environment have been successful and proven that the environmental issues can be resolved and/or prevented if proper biodiesel handling procedures are established and followed.

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6. Fuel Storage, Stability, Transport, and Blending

6.1. Biodiesel fuel storage and stability

After its production, biodiesel fuel typically is held in a storage tank. Long term storage can lead to fuel deterioration, including gum formation. Biodiesel stability refers to two issues: (1) oxidative stability related to long term storage, and (2) thermal stability related to aging at elevated temperatures and/or pressures as fuel is circulated through an engine's fuel system. Biodiesel oxidation and aging can lead to high acid numbers, high viscosity, and the formation of gums and sediments that may clog fuel filters.

Some studies have been performed on the relationship between storage and stability. Two-year storage in two types of containers, steel and glass, was investigated with methyl and ethyl esters of rapeseed [1]. This study focused on gum formations due to oxidative polymerization. Significant changes were found in the values of five measured parameters during storage. The peroxide, acid values, density, and viscosity tended to increase, while the heat of combustion decreased over the storage time. The results also showed that no significant effect was found based on container type.

Another study was conducted on biodiesel stability under commercial storage conditions for one year [2]. Eleven different feedstock samples, such as rapeseed, sunflower, a mix of both, etc., were collected to test the fuel quality. The results demonstrated that all samples met the specification limits at the end of the one-year storage period, with the exception of Rancimat Induction Period (RIP) testing for oxidation stability. Oxidation stability was the most significant change based on the Rancimat test method. The RIP decreased with time, and the rate of this decrease depends on the fuel quality and storage conditions.

The National Renewable Energy Laboratory conducted a survey of the quality and stability of biodiesel fuel and biodiesel blends in the United States in 2004 [3]. 27 B100 samples and 50 B20 samples were collected from distributors nationwide. 85% of the B100 samples met all the requirements of ASTM D 6751. The B20 samples showed high levels of peroxides, indicating the formation of peroxides as the initial step in fuel oxidation.

Biodiesel degradation characterization was also investigated under different storage conditions [4]. Twelve biodiesel samples were divided into three groups and stored at different temperatures and environments over a period of 52 weeks. It was concluded that temperature and air exposure are two important factors in biodiesel degradation. The degradation rate is greatly increased if the biodiesel is stored at a high temperature (e.g., 40 ^{o}C) and exposed to ambient air. However, the temperature or air exposure alone had little influence on the biodiesel degradation. In addition, high levels of water in the biodiesel enhanced the biodiesel degradation due to its hydrolysis, but its effect is much less than the temperature and air exposure factors.
Recently, thermal and oxidation degradation of castor oil biodiesel was reported [5]. This study was performed on the degradation process of biodiesel at different high temperatures and exposure times. Results showed that the biodiesel was thermally stable up to 150 ^{o}C, but that gum formation occurred at 210 ^{o}C after 48 hours, suggesting the oxidative polymerization of biodiesel was completed.

6.2. Biodiesel fuel transport

It is noted that biodiesel transportation containers must not be contaminated. The following procedures are recommended for biodiesel distributors and transporters [6].

- Trucks and railcars are made of aluminum, carbon steel or stainless steel.
- Proper inspection and/or washout for certification.
- Check for previous load carried and residuals. Some residuals may not be acceptable, such as food products or raw vegetable oils, gasoline, or lubricants.
- No residual water.
- Clean hoses and seals.
- Proper insulation or heating methods may be needed if transporting during cold weather.

When shipping in cold weather, biodiesel should be transported in one of the following ways:

- Temperature under 130 ^{o}F to 80 ^{o}F in tanker trucks for immediate delivery;
- Temperature under 120 ^{o}F to 130 ^{o}F in railcars for delivery within 7 – 8 days;
- Frozen in railcars equipped with external steam coils in order that the fuel in the railcars is liquid at the final destination;
- A blend of biodiesel and winter diesel fuel in either railcars or tanker trucks.

It is important that B100 and its blends be stored and handled at temperatures above their cloud point.

6.3. Biodiesel blending with diesel

The most popular biodiesel blend is B20. Biodiesel is blended into diesel fuel via three different methods commonly used in practice.

(1) Splash Blending

Splash blending is loading both biodiesel and diesel into a vessel separately with relatively little preliminary mixing. The vessel is typically an individual vehicle tank or fuel delivery truck, or a drum or a tote. Once both the diesel and biodiesel are loaded into the vessel, the fuels are sufficiently mixed by agitation of the vessel contents during driving.

(2) In-Tank Blending

This process also typically loads the biodiesel and diesel separately. In some cases, however, in-tank blending loads fuels at the same time through different incoming sources, but at a high fill rate. This is similar to splash blending but without the required agitation of the vessel contents by driving. In-tank blending is usually sufficient to get a homogenous blend since the biodiesel and diesel mix readily.

(3) In-Line Blending

In-line blending is when the biodiesel is added to a stream of diesel as it travels through a pipe or hose. The biodiesel and diesel become thoroughly mixed by the turbulent movement through the pipe. The biodiesel is added slowly and continuously to the moving stream of diesel. This is similar to the way other additives are blended into diesel, and is most commonly used at pipeline terminals and racks.

Blending can be a concern in cold weather when the temperature is below the cloud point of B100, because crystals may form during blending. Blending properties of biodiesel were studied under low temperatures in order to define operating parameters [7]. Splash blending tests were performed in making B20. Results indicated that the biodiesel must be kept at least 10 ^{o}F above its cloud point to ensure successful blending. The target temperature for blending should be determined on an individual basis because of the various fuel properties.

It is also a good idea to filter biodiesel blends in northern (colder) climates because the crystallized saturated fatty acid methyl esters formed may cause filter clogging.

6.4. References

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7. Effects of Biodiesel Production on its Quality

The most critical fuel quality parameter for biodiesel production is the total glycerin. In the original vegetable oil or fat, the glycerin composes approximately 10.5% of the molecules. This must be reduced to 0.24% or less by the fuel production process. The residual glycerin might be in the form of free glycerin, or as bound glycerin consisting of the triglycerides from the original oil or partially reacted mono- and diglycerides. Elevated levels of total glycerin can increase the tendency of the fuel to form solid precipitates in the engine's fuel system which may plug the fuel filter (Van Gerpen et al., 1997). The monoglycerides of saturated fatty acids have very high melting points (e.g., 77°C for monopalmitin) and have low solubility in the biodiesel (Yu et al., 1998). High total glycerin levels can also raise the carbon residue of the fuel, causing it to fail to meet another specification within the ASTM standard (Van Gerpen et al., 1997).

Another set of important quality parameters for the fuel are the levels of trace elements such as sulfur, phosphorus, sodium, potassium, calcium and magnesium. Vegetable oils are typically very low in sulfur but animal fats can contain 30-60 ppm of sulfur. Phosphorus originates in phospholipid compounds extracted from the plant during the oil extraction process (Erickson, 1995). These compounds are usually removed during oil processing in an operation called *degumming*, but the desire to reduce feedstock costs has caused some producers to use oil that has only been partially degummed. Some producers have seen high phosphorus levels in the fuel produced from these partially degummed oils (Van Gerpen, 2005). Other metallic contaminants such as sodium and potassium from the catalyst or calcium and magnesium from the wash water may cause high ash deposits in the engine. All of these contaminants may cause deactivation of the exhaust after treatment devices that are required on on-highway diesel engines in 2007 and after. It also does not apply to the engines on WSF ferries which are not outfitted with exhaust after-treatment.

7.1. Effect of Residual Alcohol on Fuel Quality

Production of biodiesel generally uses 100% excess methanol (Van Gerpen, 2005). This excess methanol must be recovered both for cost reasons and to minimize emissions. Small amounts of methanol left in the biodiesel will lower the flashpoint of the fuel.

Figure 1 shows that as little as 0.1% residual methanol can lower the flashpoint below the 130°C level required by the ASTM specification (ASTM, 2007). Reducing the methanol to this level or below requires heating the fuel to sufficient temperature (usually 70°C or higher) so that the methanol vaporizes and leaves the less volatile methyl esters behind. This is an energy intensive process and some processors, as a result of attempting to reduce energy costs, have used methanol recovery processes that do not remove sufficient methanol to meet the ASTM specification.

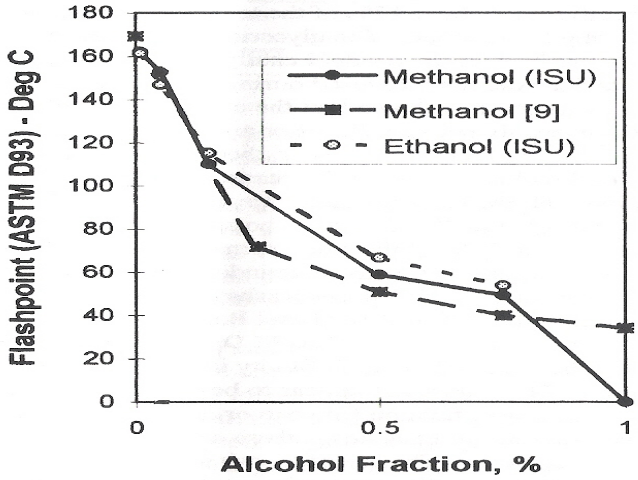

Figure 1. Biodiesel Flashpoint for Varying Alcohol levels (Van Gerpen et al., 1997)

7.2. Crude Glycerol and Fuel Quality

Glycerol has a very low solubility in biodiesel (Van Gerpen et al., 1997), so if a portion of the glycerol produced by the transesterification reaction is left in the fuel, it is likely to be in the form of small droplets. Over time these droplets will settle to the bottom of a storage tank and collect as a pool of glycerin. The glycerin may attract water and monoglycerides from the fuel (Van Gerpen et al., 1997). If the glycerin is drawn into the engine it is too viscous to pass through the engine’s fuel filter and the engine will usually cease to run until the filter can be changed.

Fuel quality is absolutely essential for trouble-free operation of engines on biodiesel. Most operational problems associated with fuel quality will result in fuel filter plugging and potentially stop the engine until the filter is changed. Other issues, such as the flash point, relate to safety and fuel that does not meet the specification present a serious safety concern. Other specifications are included to protect ancillary equipment such as the particulate filters and catalytic converters that are required on new diesel engines. This is an on-road requirement, not yet applicable to the marine sector. EPA has not yet finalized marine tier 3 and tier 4 standards for diesel engines. However, it is likely that tier 4 standards will only be possible by the use of exhaust after-treatment devices. But since this is not the case with the engines on these vessels, it is not relevant to the discussion and may only confuse the issue.

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8. Other Biodiesel Related Research

This section describes additional research on improvements in current production techniques, alternative feedstocks for biodiesel production, and biodiesel production through other techniques.

8.1. Improvements in current production techniques

Biodiesel is produced commonly by transesterification of a catalyzed reaction. Several factors, including the type of catalyst, molar ratio of alcohol to vegetable oil, temperature, water content, and free fatty acid content, have an influence on the transesterification reaction [1, 2]. The following are some examples of approaches to biodiesel production research.

One of approached on improvements of biodiesel production is to use new reactors. The optimization of transesterification of canola oil was investigated using a continuous-flow reactive distillation (RD) system [3]. Six process variables, including the feed methanol to triglycerides molar ratio, reaction time, temperature, catalyst concentration, methanol circulation mode, and catalyst formation, were optimized. Results showed that the optimum product yields ranged from 96.8 % to 98.6 % with the productivity ranging from7.2 m^3/m^3. h to 18.5 m^3/m^3. h. A two-phase membrane reactor was developed to enhance mass transfer of canola oil in methanol in the early stages of transesterification [4]. It was reported that this reactor enabled the separation of reaction products (biodiesel/glycerol in methanol) from original canola oil feed. One of the advantages in using this reactor is to yield high purity biodiesel and shift the reaction equilibrium to the product side.

Another improvement in biodiesel production was attempted based on the application of ultrasound [5]. It is claimed that the application of ultrasound improves the efficiency of biodiesel production from materials not typically used for this purpose, such as seed cake. Advantages of this technique include elimination of saponification, low reaction times, milder reaction conditions, and higher biodiesel yields.

The biodiesel production by supercritical alcohol, such as methanol, ethanol, propanol and butanol, has proved to be one of most promising process [6]. This supercritical method allows a simple process and high yield because of the simultaneous transesterification of triacylglycerols and methyl esterification of fatty acids. It was reported that the conversion yield was raised 50 – 95 % for a short first 10 minutes in the supercritical alcohol transesterification [6]. In addition, the presence of water positively affected the formation of methyl esters in the supercritical method. However, the presence of water has negative effects on the yields of methyl esters in the current alkali-catalyzed method because water can cause soap formation, as well as consumes catalysis and reduces catalyst effectiveness. Furthermore, it has been reported that supercritical methanol combined with CO_2 is superior to the common supercritical methanol method on lower reaction temperature and lower pressure required [7]. These relatively mild reaction conditions led to less energy and resulted in lower production cost.

8.2 Alternative feedstocks for biodiesel production

The majority of current biodiesel production cost (60 – 90%) arises from the cost of feedstock oil. Thus the use of cheap feedstocks, including waste frying oil, should greatly reduce the cost of biodiesel production. The two-stage transesterification process was developed using waste frying oil [8]. The biodiesel produced using waste frying oil has similar properties to No. 2 diesel. Therefore, the use of waste frying oil is an effective way to reduce the raw material cost.

Another potential type of feedstock may be microalgae oil, because microalgae use light to produce oils. Oil productivity from some microalgae exceeds the oil productivity of the producing oil crop, although the process cost for biodiesel production using microalgae may be not economically competitive with petrodiesel [9]. There are technical limitations to producing microalgae biodiesel. It is noted that improvements to algal biology are required for producing low-cost microalgae biodiesel [9]. Unlike commonly phototrophic microalgal oil utilizing sunlight, heterotrophic microalgal oil using a photobioreactor has been suggested to produce biodiesel [10]. Heterotrophic growth of some microalgae has been proved to efficiently produce biomass and lipids in high densities, potentially reducing the cost of microalgal oil.

8.3. Biodiesel production through other techniques

The catalyst is one of the most important factors for biodiesel production. Unlike commonly used alkali-catalyzed transesterification for biodiesel production, acid-catalyzed transesterification (such as by using sulfonic and sulfuric acids) has not been developed because of its slower reaction rate [6]. However, the acid-catalyzed process offers benefits due to its independence from free acid content, which in turn favors raw materials containing high free fatty acids such as waste cooking oils.

Another approach to biodiesel production is to use a new heterogeneous catalyst including solid superacid catalysts of metal oxides [6, 11]. For instance, a superacid catalyst consists of a mixed oxide of zinc and aluminum promoting the transesterification reaction without catalyst loss. It is claimed that such a process can provide simple purification of products, very high yields of methyl esters (e.g., 98 %), high purity of glycerin (>98%), and the absence of special chemical requirements as well as waste streams [11].

Enzymes as catalysts are also proposed in the production of biodiesel. It is important to note that glycerol can be easily recovered without any complex process, free fatty acids in the oils can be converted into methyl esters, and subsequent wastewater treatment may not be required [12]. Lipases are typical enzymes that can be used for biodiesel production. It should be noted, however, that enzymes are expensive and the reaction yields as well as the reaction times are still unfavorable compared to the alkali-catalyzed systems.

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