The Effect of Long-Term Cold Storage on Biodiesel Blends

Final Report

Daniel N. Pope Department of Mechanical and Industrial Engineering
University of Minnesota Duluth

November 26, 2007

University of Minnesota Duluth
Department of Mechanical and Industrial Engineering
105 Voss-Kovach Hall
1305 Ordean Court
Duluth, MN 55812-3042

Research funded in part by the Great Lakes Maritime Research Institute.
This study was supported by the U.S. Maritime Administration
Grant # DTMA1-G-06-005

Acknowledgements

I would like to extend a special thank you to the following people who were instrumental in the completion of this project:

- Sandy Winek, Residual Fuel Sales Representative, Murphy Oil USA Inc., and John B. Peterson, Chemist, Superior Refinery, Murphy Oil USA Inc. for providing the no. 2 diesel and biodiesel used in the testing, and for conducting the viscosity and flash point tests.
- Ed Priem, Director, Marine Logistics & Energy Resources, Mormac Marine Group, Inc. for participating in several discussions regarding the project and organizing a tour of the M/V Mesabi Miner.
- David Guay, Chief Engineer, M/V Mesabi Miner, The Interlake Steamship Company for taking the time to explain the diesel-powered systems aboard the Mesabi Miner.
- Richard (Doug) Ricketts, Research Associate, Large Lakes Observatory, UMD, and Michael B. King, Captain, R/V Blue Heron, Large Lakes Observatory, UMD for discussions regarding this and future projects, and for access to the Blue Heron.

Table of Contents

List of Tables

List of Figures

Executive Summary

The current project consists of two parts; the identification of the potential issues involved with the shipboard use of biodiesel blends, and the development of a long-term cold storage test and subsequent testing of biodiesel blends. The two parts of the project were conducted concurrently and in collaboration with fuel suppliers and carriers.

A review of typical diesel-powered ship systems was performed. In general, long-term cold storage of biodiesel blends is a concern in the following shipboard systems.

- Hatch/Deck Crane – This system has a low fuel turnover rate and is exposed to the external environment.
- Lifeboat Power Pack – This system has a low fuel turnover rate and is exposed to the external environment.
- Fuel Bunker and Main Engines – Even if heavy fuel oil (IF 280) is used as the primary fuel in the main engines, one fuel bunker is generally filled with no. 2 diesel near the end of the shipping season. Test results indicate that particulates may form in the fuel if a high percentage biodiesel blend (greater than B20) is used during winter lay up.

A long-term cold storage test was developed and results were presented for two different temperature ranges (23-25°F and 30-32°F). The test covered a period of four weeks and included a storage tank test for density variation via hydrometer testing of top and bottom tank samples, and the use of small samples to visually check for preferential gelling of the biodiesel component. The results of the long-term cold storage test indicate the following.

- The hydrometer tests indicated no measureable density difference between the top and bottom tank samples and thus no separation of the biodiesel component. This result was consistent for both temperature ranges.
- Particulate formation and settling was observed for a B50 blend in both the small sample and the bottom tank sample. This result was consistent for both temperature ranges.
- Blends up to B20 exhibited good cold storage characteristics for both temperature ranges.
- The flash point and viscosity of the small samples in the 23-25°F cold storage test were determined at the end of the test. All of the samples met the required fuel specifications.

An additional test to determine the effect of a common cold flow additive on biodiesel blends was also conducted. The test utilized small samples of no. 2 diesel, B5, B10, B20, B50, and B100 both with and without the additive. Sample temperatures were varied from 45°F to -9°F in 3°F increments. The samples were kept at each new temperature for a minimum of 24 hours to achieve thermal equilibrium. Visual inspection of the small samples and a review of the results established the following.

- The additive had a noticeable effect on the temperature at which a given biodiesel blend begins to gel. This was particularly evident for the B100 sample.
- The relatively simple procedure employed for this test yielded results for the B10, B5, and no. 2 diesel samples that appear to be inconsistent with the average cloud point of no. 2 diesel (3°F).
- Additional testing of a more quantitative nature could be undertaken to identify the appropriate mixture fraction of additive for each biodiesel blend.

There were several observations made during the tests that merit further investigation. The following additional work is therefore recommended to provide more detailed information.

- The chemical composition of the particulates formed in the B50 sample during the cold storage test should be determined.
- A filtration test using the samples from the cold storage test should be performed to check for particulates that could potentially plug fuel filters.
- A quantitative test to determine the appropriate mixture fraction of cold flow additive for each biodiesel blend should be performed. The test would consist of measuring the cloud point, pour point, and cold filter plugging point of biodiesel blends with varying mixture fraction of additive.

1. Introduction

The shipboard use of biodiesel blends presents some unique challenges due to the wide range of operating environments experienced by diesel-powered ship systems. Legislative and industrial efforts point to the use of up to 20% biodiesel blends for both on-road and off-road applications in the near future. These efforts are primarily driven by the advantages associated with the use of biodiesel. However, biodiesel also has some undesirable properties that can lead to operational problems. A majority of the potential problems are associated with the increase in cold flow properties associated with the use of biodiesel. Ship systems that utilize biodiesel blends instead of straight diesel fuel are more susceptible to fuel gelling when exposed to cold weather environments. Of particular concern is the long-term cold storage of fuel during the two-month winter layup period when fuel turnover is low and preferential gelling and separation of the biodiesel component in a blend is possible. The goals of this project were to identify potential problems associated with the use of biodiesel blends in diesel-powered ship systems, and to develop a long-term cold storage test for biodiesel blends.

The properties of, and testing procedures for, pure biodiesel (B100) are described in the international standard ASTM D 6751 [1]. B100 may be used as the primary fuel, or as part of a blend (e.g. B20, a blend of 20% biodiesel and 80% distillate fuel). There are several advantages associated with the use of biodiesel:

- Biodiesel is a renewable energy source, and its use reduces our dependence on foreign oil.
- Biodiesel can be used in current diesel engines with little to no change in performance. Biodiesel and no. 2 diesel have similar density and kinematic viscosity, resulting in comparable fuel delivery characteristics. In addition, the energy content of B100 is only slightly less than that for no. 2 diesel. Thus the use of biodiesel has little impact on engine torque, power, and fuel economy.
- Biodiesel has better lubricity than diesel fuel which reduces wear on fuel system parts such as injectors and pump bearings. Biodiesel could be used as an additive to ultra low sulfur diesel which suffers from low lubricity.
- Biodiesel combustion produces fewer harmful emissions than no. 2 diesel. A summary of “average” emissions results [2, 3] shows that the use of biodiesel and biodiesel blends reduces most regulated emissions. Total unburned hydrocarbons (THC), carbon monoxide (CO), and particulate matter (PM) emissions decrease significantly with biodiesel usage, while oxides of nitrogen (NOx) emissions increase moderately.
- Biodiesel is nontoxic and biodegrades faster than diesel fuel, reducing fuel handling requirements.

The increase in cold flow properties (tendency to gel) associated with biodiesel is quantified using cold filter plugging point, cloud point, and pour point tests. The cloud point, which is the temperature at which solid crystals first appear, has an average value of 3°F for no. 2 diesel and 32 to 40°F for B100. Therefore, B100 is not suited for use in cold climates if fuel system components are exposed to the environment. However, tests have shown that the cloud point for a B20 blend with no. 2 diesel is approximately 7°F. Thus, blends as high as B20 can be used as a direct replacement for no. 2 diesel under most conditions. Even if a low percentage blend such as B20 is employed, more frequent checking and cleaning of the fuel filters should initially be performed.

A complete review of diesel-powered ship systems is beyond the scope of the present work since these systems vary from ship to ship. Tours of the M/V Mesabi Miner, operated by Interlake Steamship Co., and the R/V Blue Heron, operated by UMD's Large Lakes Observatory, were undertaken to determine "typical" systems that utilize diesel fuel. Fuel turnover is rapid during the shipping season; however, during the two-month winter lay up period there is a long-term cold storage concern for systems exposed to the external environment. In general, if a high percentage biodiesel blend is used in any of the systems, the fuel system components should be checked to make sure that they are compatible with B100. Typical diesel-powered ship systems that were identified include the main engines, diesel generator sets, boilers, emergency generators, hatch/deck crane, and the lifeboat power pack.

Larger vessels utilize heavy fuel oil (IF 280) or no. 2 diesel as the primary fuel for the main engines which are supplied by fuel bunkers via a heated day tank. Even when heavy fuel oil is the primary fuel, one fuel bunker is filled with no. 2 diesel near the end of the shipping season. The main engines are then run on no. 2 diesel at the end of the season, and also at the start of the next shipping season. Thus, at least one fuel bunker contains no. 2 diesel during the winter lay up period. Since portions of the fuel bunker are in contact with the external environment, either above or below the waterline, long-term cold storage becomes a potential concern if a biodiesel blend is used. Other systems that are exposed to the external environment and that have a low fuel turnover rate during winter lay up include the hatch/deck crane, and the lifeboat power pack.

The potential problems associated with the long-term stability of biodiesel blends in cold weather have not been addressed in the literature. Current stability tests address both the thermal [4] and oxidation [5, 6] stability. These tests use a slightly elevated temperature to simulate long-term storage (greater than 4 to 6 months). This is unlikely to be a problem with vessels on the Great Lakes, which refuel often. The exception to frequent refueling occurs during the winter lay up period (2 months), when the portions of the main fuel tank below the waterline are at approximately 0°C and portions above the waterline may be at temperatures slightly below freezing. Auxiliary systems may also have components exposed to below freezing temperatures. The available stability tests do not address this potential cold weather problem.

1.1 Project Description

The current project consisted of two parts; the identification of the potential issues involved with the shipboard use of biodiesel blends, and the development of a long-term cold storage test and subsequent testing of biodiesel blends. The two parts of the project were conducted concurrently and in collaboration with fuel suppliers and carriers. The issues involved with the shipboard use of biodiesel blends was addressed earlier in the Introduction.

The development of the current long-term cold storage test was based in part on a test for stratification discussed in the 2004 Biodiesel Handling and Use Guidelines [7]. The characteristics of the testing procedure given in the original proposal were as follows.

- The test would check for density variation and preferential gelling of biodiesel in blends.

- Density variation would be determined via hydrometer measurements of samples from the top, middle, and bottom of a tank in cold storage.
- Blends tested would vary from 0% to 20% biodiesel.
- Gelling of the biodiesel component would be determined via visual inspection.
- The duration of the test would be approximately 2 months.
- The storage temperature used in the test would be between the cloud point of no. 2 diesel (approximately 3°F) and the cloud point of pure biodiesel (approximately 32°F to 40°F).

The following changes to the proposed test were made based on initial test results.

- Density variation was determined via hydrometer measurements of samples from the top and bottom of a tank in cold storage.
- B5, B10, B20, and B50 blends were tested. Some additional tests using no. 2 diesel and B100 were also performed.
- In addition to the storage tanks, small glass sample bottles were used in the cold storage test to visually check for gelling of the biodiesel component.
- The duration of the test was 4 weeks. The original two month time frame was deemed unnecessary, as the results did not change between the second and fourth week of the test.
- Two temperature ranges were used for the long-term cold storage test: 23-25°F and 30-32°F. Ranges were used instead of exact temperatures due to the nature of the cold storage test apparatus that was constructed.

Some additional tests were also conducted that went beyond the scope of the original proposal. These included viscosity and flash point tests of cold storage samples, and a cold flow additive test. A detailed discussion of the equipment, procedure, and results, for the long-term cold storage test and the additional tests that were performed is provided in the remaining sections of the report.

There are no direct economic impacts associated with the experimental work presented in this project. However, the expected increase in the shipboard usage of biodiesel blends that has motivated this research does have a potentially large impact as discussed in a previous report co-authored by the current PI [8]. The previous report [8] indicates that increased biodiesel usage, which includes maritime usage, could provide a large boost to local economies through the construction of biodiesel plants. An increase in biodiesel usage would also extend to agricultural markets since soybean oil is generally used in the production process. In addition, proactively identifying potential problems with biodiesel usage may contribute to reduced maintenance costs if higher percentage biodiesel blends are mandated in the future.

Portions of the results presented in this report were incorporated in two separate presentations, one given at a meeting of the Northeast Clean Energy Resource Team (CERT) held at UMD on March 23rd, 2007, and one given at the GLMRI University Affiliates Meeting held in Duluth, MN on September 28th, 2007. A seminar for the faculty and students in the Department of Mechanical and Industrial Engineering at the University of Minnesota Duluth is also planned for December 10th, 2007.

2. Long-Term Cold Storage Test

A long-term cold storage test was designed and tests were conducted for two different temperature ranges. Initial testing was geared toward simulating the two month winter lay up period, with samples held at a reduced temperature over an extended time period. There were no changes in the test results between the second and fourth week, thus, the final length of the test was set at four weeks. Each cold storage test included both a storage tank test and a small sample test with biodiesel blends of B5, B10, B20, and B50. An additional small sample test to determine the effect of a common cold flow additive was also conducted.

2.1 Cold Storage Test Apparatus

The various tests presented in the present work required the construction of a test apparatus to maintain the samples within a specified temperature range over extended periods of time. The apparatus consisted of a freezer with an external temperature controller. Figure 1 shows the Kenmore model #16082, 19.9 cubic foot capacity freezer used in the tests. The internal control system for the freezer has a temperature range of -10 to 10°F. An external temperature controller was constructed to extend the range of the controllable temperatures.

Figure 1: Freezer used in cold storage test apparatus.

Figure 2 shows the external temperature control unit. The unit consists of an AutomationDirect TC33-2010-AC temperature controller, an AutomationDirect QL2N1-A120 electro-mechanical relay, an AutomationDirect SQL08D relay socket, an Omega 5TC-TT-J-24-36 “J” type thermocouple, a Radio Shack model 274-670 8-position, dual row terminal strip, a six ft. AC power cord, an electrical outlet and wiring box, and associated wiring. The thermocouple input to the temperature controller sensed the temperature in the interior of the freezer, and the temperature controller energized the outlet that provided power to the freezer. On/off control with a 2°F hysteresis was used to avoid excessive cycling of the freezer’s compressor. The assembled apparatus is capable of providing a controlled temperature environment within 2°F ranging from room temperature to -10°F.

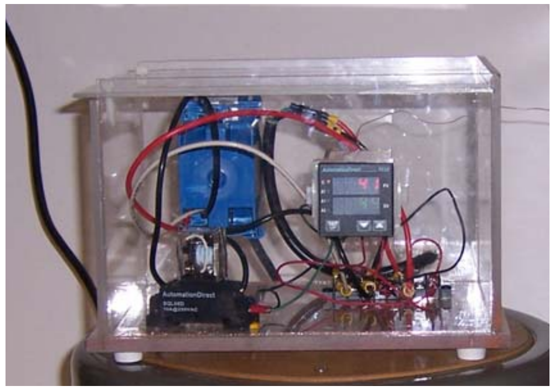

Figure 2: Temperature controller unit.

2.2 Cold Storage Test

Each cold storage test was conducted over a period of four weeks, and consisted of both a storage tank test and a small sample test. The storage tank tests were used to check for separation and gelling of the biodiesel component in B5, B10, B20, and B50 blends. Any separation of the biodiesel component would result in a density difference between the top and bottom of the storage tank. Top and bottom samples of the storage tanks were taken in two week intervals, and a hydrometer test was performed to check for density variations. A visual inspection for crystallization (cloudiness) of the fuel was performed using the small samples. The general procedure for the test is as follows.

1. Set the desired temperature for the cold storage test on the cold storage test apparatus. Ensure that the apparatus has reached the desired temperature prior to the start of the test.
2. Prepare the storage tank blends.
    a. Extract small samples of the diesel fuel and the B100 used to prepare the blends.
    b. Perform hydrometer tests on the diesel fuel and the B100 small samples.
3. Extract an initial representative sample and a small sample from the storage tanks prior to the start of the test.
    a. Perform hydrometer tests on the initial representative samples of B5, B10, B20, and B50.
4. Place the storage tanks and small samples in the cold storage test apparatus (freezer).
5. After two weeks of cold storage:
    a. Visually inspect the small samples for crystallization.
    b. Extract top and bottom samples from the B5, B10, B20, and B50 storage tanks.
    c. Allow samples to reach room temperature and perform hydrometer tests on the top and bottom samples.
6. After four weeks of cold storage:
    a. Visually inspect the small samples for crystallization.
    b. Extract top and bottom samples from the B5, B10, B20, and B50 storage tanks.
    c. Allow samples to reach room temperature and perform hydrometer tests on the top and bottom samples

Individual aspects of the general procedure are addressed in more detail below.

2.2.1 Tanks and Sample Preparation

The storage tanks used in the test consisted of 6+ gallon (23.2 L) self-venting gas cans. Each blend (B5, B10, B20, and B50) was mixed in 22 L batches and placed in a storage tank. Table 1 shows the volume fractions used in the preparation of each storage tank. A 1000±10 ml graduated cylinder was used to measure the fuel volumes. Thorough mixing was ensured via manual agitation (shaking) of each tank for a period of three minutes. The storage tanks were placed in the test apparatus as shown in Figure 3.

Sample	Vol. B100 (L)	Vol. #2 Diesel (L)
B5	1.1	20.9
B10	2.2	19.8
B20	4.4	17.6
B50	11.0	11.0

Table 1: Storage tank sample preparation.

Figure 3: Storage tank placement in test apparatus.

Step 3 in the general testing procedure calls for extracting a small sample from the storage tank prior to the start of the test. Each small sample consists of 400 to 450 ml of biodiesel blend placed in a 16 oz. glass sample bottle. Figure 4 shows the placement of a B5, B10, B20, B50, and B100 small sample in the test apparatus.

Figure 4: Small sample placement in test apparatus.

2.2.2 Bi-Weekly Tank Samples

Top and bottom samples are taken from each of the storage tanks at two weeks and four weeks after the start of the test. The top sample is taken first, in accordance with the guidance set forth in ASTM D 4057 [9], in order to avoid cross contamination of the samples. Samples volumes were 400 to 450 ml and were stored in 16 oz. glass sample bottles. The samples were extracted from the storage tanks using the hand-operated, stainless steel drum pump (Cole-Parmer model number EW-07079-20) shown in Figure 5.

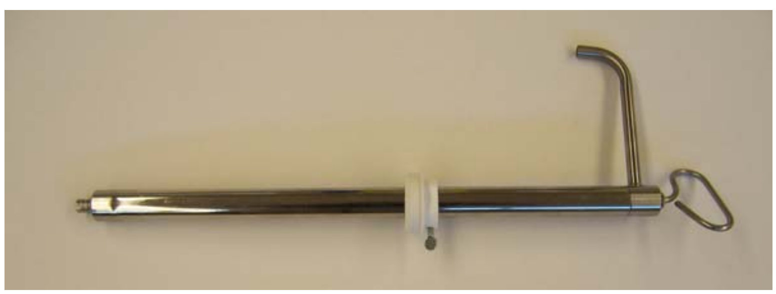

Figure 5: Stainless-steel drum pump.

2.2.3 Hydrometer Test

The specific gravity of the initial representative samples, the B100 and diesel fuel used in the sample preparation, and the bi-weekly tank samples was measured using a hydrometer in accordance with ASTM D 1298 [10]. An SG 60/60°F hydrometer with a range of 0.800 to 0.910 and divisions of 0.001 was used to measure the specific gravity of each sample. The samples were allowed to reach room temperature and were manually agitated prior to the hydrometer test. Figure 6 shows a B100 sample, the hydrometer cylinder, and the hydrometer. Initial and final sample temperatures were taken during the hydrometer test, and the resulting specific gravity was corrected to 60°F.

Figure 6: Hydrometer, cylinder, and B100 sample.

2.3 Test Results

The storage tank and small sample tests were conducted for two temperature ranges 23 – 25°F and 30 – 32°F. These temperatures were selected based on expected winter lay up operating conditions and average fuel properties. The higher temperature range is based on a fuel bunker in contact with the waterline which should exhibit minimum temperatures near freezing during winter lay up. The lower temperature range represents a conservative temperature that is slightly above the average cloud point of B50. High sulfur no. 2 diesel and soy-based biodiesel were used to prepare the sample blends. Some additional tests were also performed on a limited number of samples by an outside testing facility. The raw data and corrected hydrometer readings for the two temperature ranges are included in the appendices.

2.3.1 Results: 23 – 25°F

The hydrometer tests showed no measureable density variation between the top and bottom tank samples (see Appendix A for data). The specific gravity of a particular blend was also within the readability (0.001) of the hydrometer for all of the samples tested over the four week test period.

A small amount of particulate matter was observed in the B50 bottom samples taken at both the two week and four week point. The exact nature of the particulate matter formed is not known at this time, but it appears to be consistent with the formation of wax crystals described in ASTM D 2500 [11]. Additional tests to determine the chemical composition would be required to classify the particulate matter.

Visible cloudiness was observed in the B10, B20, and B50 small samples at both the two week and four week point. The cloudiness in the B10 and B20 samples disappeared when the samples were allowed to reach room temperature at the end of the test. Particulate matter was observed in the B50 small sample, which is consistent with the results obtained from the B50 storage tank bottom sample. The B100 small sample included in this test was completely solid since the temperature is well below the cloud point of biodiesel (32 to 40°F).

Two additional tests were conducted on the small samples at the conclusion of the cold storage test. The kinematic viscosity and flash point of the samples were determined in accordance with ASTM D 445 [12] and ASTM D 93 [13], respectively. The tests were performed by personnel at the Superior Refinery of Murphy Oil USA, Inc using a Koehler K23400 constant temperature viscosity bath and a Herzog HFP 360 Pensky-Martens closed cup flash point tester. Allowable ranges for these fuel properties are given in ASTM D 6751 [1] for B100, and ASTM D 975 [14] for no. 2 diesel. B100 has an allowable range for kinematic viscosity (at 40°C) of between 1.9 and 6.0 mm^2/s and a minimum flash point of 130°C. No. 2 diesel has an allowable range for kinematic viscosity (at 40°C) of between 1.9 and 4.1 mm^2/s and a minimum flash point of 52°C. Table 2 shows the test results. All of the samples met the required fuel specifications.

Sample	Viscosity (mm^2/s)	Flash Point (°C)
B100	4.031	138
B50	2.927	78
B20	2.425	72
B10	2.264	73
B5	2.200	68
#2 Diesel	2.132	65

Table 2: Kinematic viscosity and flash point results.

2.3.2 Results: 30 – 32°F

The test results at this higher temperature range were similar to the results obtained at the lower temperature range. Hydrometer tests showed no density variation between the top and bottom samples and particular blends showed no measureable density differences over the period of the test (see Appendix B for data). The B10 and B20 small samples did not exhibit cloudiness at this higher temperature. However, the presence of particulates in the B50 storage tank bottom sample and the B50 small sample was once again noted.

3. Cold Flow Additive Test

A test to determine the effect of a common cold flow additive (Polar Power manufactured by FPPF Chemical Co. Inc.) on biodiesel blends was also conducted. Small samples (450 ml) of no. 2 diesel, B5, B10, B20, B50 and B100 both with and without the additive were placed in the cold storage test apparatus. The manufacturer's recommended amount of 1 part additive to 1000 parts fuel by volume was used in the samples that included the additive. The manufacturer claims that this fraction of additive will lower the cold-filter plugging point of diesel by 10°F. The starting temperature for the test was 45°F, the temperature was decreased by 3°F per day, and the ending temperature was -9°F. Recall that the cold storage test apparatus uses a 2°F hysteresis loop, thus a setting of 45°F corresponds to a temperature range of 43-45°F. A visual inspection of the samples was performed each day and the following observations were made.

- At 36°F
    - A small amount of particulates were present in the B100 samples both with and without the additive
- At 33°F
    - The B100 sample without the additive exhibited significant gelling throughout the sample
    - The B100 sample with the additive exhibited some gelling at the base of the sample container
    - A small amount of particulate was present in the B50 samples both with and without the additive
- At 30°F
    - The B100 sample without the additive was almost completely gelled
    - The B100 sample with the additive exhibited significant gelling at the base of the sample container
- At 27°F
    - The B100 sample without the additive was completely gelled (solid)
    - The B100 sample with the additive exhibited significant gelling in the lower half of the sample container
    - The B50 sample without the additive had a small amount of particulate at the bottom of the sample and appeared cloudy throughout the sample
    - The B20, B10, and B5 samples both with and without the additive exhibited some cloudiness at the bottom of the samples
- At 9°F
    - The B50 sample without the additive had a slush-like appearance and was almost completely gelled
    - The B50 sample with the additive had a significant increase in particulates at the bottom of the sample
- At -3°F
    - The B20 sample without the additive had crystal-like formations dispersed throughout the sample
- At -6°F
    - The B20 sample without the additive had a slush-like appearance throughout the sample

    - The B20 sample with the additive exhibited some crystal-like formations in the bottom of the sample
- At -9°F
    - The B20 sample with the additive had a slush-like appearance in the bottom third of the sample

A review of the above observations shows that the additive had a noticeable effect on the temperature at which a given biodiesel blend begins to solidify. This was particularly evident for the B100 sample that contained the additive which exhibited no additional solidification when the temperature was lowered from 27°F to -9°F. There may be a more appropriate mixture fraction of additive to use for each biodiesel blend than the one suggested by the manufacturer.

An unexpected result was obtained for B10, B5, and no. 2 diesel samples at low temperatures. As noted above, the B10 and B5 samples began to exhibit cloudiness near the sample bottom at a temperature of 27°F. The cloudiness in the B10 and B5 samples did not appear to increase as the temperature was further decreased. This was not expected since the cloud point of no. 2 diesel has an average value of 3°F. One would expect that the B10, B5, and no. 2 diesel samples would exhibit significant cloudiness and/or gelling at the lowest temperature of -9°F. This unexpected result may reflect the limitations of the testing method employed in this section; the method is inexact since it relies solely on visual observation. Additional testing to determine the cloud point [11], pour point [15], and cold filter plugging point [16] could be done to quantify the appropriate additive mixture fraction for each blend.

4. Conclusions and Recommendations

The potential issues involved with the shipboard use of biodiesel blends were identified. Typical diesel-powered ship systems include the main engines, diesel generator sets, boilers, emergency generators, hatch/deck crane, and the lifeboat power pack. Long-term cold storage of fuel is a potential concern in the hatch/deck crane and the lifeboat power pack due to their low fuel turnover rate and exposure to the external environment. In addition, storage of high percentage biodiesel blends (greater than B20) in one or more fuel bunkers during the winter lay up period may lead to particulate formation within the fuel.

A cold storage test apparatus was constructed and the procedure for a long-term cold storage test was developed. The test consisted of maintaining tanks and small samples of B5, B10, B20, and B50 blends within a specified temperature range for a period of four weeks. Top and bottom samples were taken from the tanks at bi-weekly intervals and a hydrometer test was performed to check for density variation. A visual inspection of the small samples was also performed bi-weekly to check for gelling of the fuel. Test results were obtained for two different temperature ranges (23-25°F and 30-32°F). The hydrometer test results showed no measurable difference between the density of the top and bottom samples. However, there was some particulate formation observed in the B50 bottom tank sample and small sample. In general, blends of up to B20 exhibited good cold storage characteristics. The flash point and viscosity of the blends at the conclusion of the cold storage test were within the required fuel specifications.

The effect of a common cold flow additive on biodiesel blends was also investigated. Small samples of no. 2 diesel, B5, B10, B20, B50, and B100 both with and without the additive were placed in the cold storage test apparatus and the temperature of the samples was slowly decreased from 45°F to -9°F in 3°F increments. Visual inspection of the small samples showed that the additive lowered the temperature at which a given biodiesel blend started to gel. The presence of the additive kept the B100 sample from completely gelling, even at the lowest temperature. There was no observable gelling of the B10, B5, and no. 2 diesel samples, which is inconsistent with average cloud point of no. 2 diesel (3°F). The dependence of the test on visual observation, as opposed to quantifiable measurement, may be the cause of these unexpected results.

In light of the current observations and test results, the following additional testing is recommended. The characteristics of the particulates formed in the B50 sample are presently unknown. A test to determine the chemical composition of these particulates should be performed. Samples from the cold storage test should also be filtered to check for the formation of small particulates that could potentially plug fuel filters. Finally, the appropriate mixture fraction of cold flow additive for each biodiesel blend should be determined using quantifiable tests such as the cloud point, pour point, and cold filter plugging point.

References

[1] ASTM D 6751, "Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels", ASTM International.

[2] National Biodiesel Board (Internet), *Biodiesel Emissions*, *September 2006* (cited October 2007), http://www.biodiesel.org/pdf_files/fuelfactsheets/emissions.pdf

[3] "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions", U.S. Environmental Protection Agency, (EPA Technical Report, EPA420-P-02-001, October 2002, http://www.epa.gov/otaq/models/biodsl.htm).

[4] ASTM D 6468, "Standard Test Method for High Temperature Stability of Distillate Fuels", ASTM International.

[5] ASTM D 2274, "Standard Test Method for Distillate Fuel Storage Stability (Accelerated Method)", ASTM International.

[6] ASTM D 4625, "Standard Test Method for Distillate Fuel Storage Stability at 43°C (110°F)", ASTM International.

[7] "2004 Biodiesel Handling and Use Guidelines", U.S. Department of Energy, Energy Efficiency and Renewable Energy, (DOE/GO-102004-1999, October, 2004, http://www1.eere.energy.gov/biomass/pdfs/36182.pdf).

[8] Hasan, A. R., Pope, D., and Skurla, J. A., "Alternatives to Petroleum Based Fuel for Maritime Vessels", in Great Lakes Maritime Research Institute: Grant Completion Report, Report No. GLMRI-2006-0001, November, 2006.

[9] ASTM D 4057, "Standard Practice for Manual Sampling of Petroleum and Petroleum Products", ASTM International.

[10] ASTM D 1298, "Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method", ASTM International.

[11] ASTM D 2500, "Standard Test Method for Cloud Point of Petroleum Products", ASTM International.

[12] ASTM D 445, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity", ASTM International.

[13] ASTM D 93, "Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester", ASTM International.

[14] ASTM D 975, "Standard Specification for Diesel Fuel Oils", ASTM International.

[15] ASTM D 97, "Standard Test Method for Pour Point of Petroleum Products", ASTM International.

[16] ASTM D 6371, "Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels", ASTM International.

Appendix A

Results for Cold Storage Test
Temperature Range: 23 to 25°F

Date 6/26/07
Initial Representative Sample Hydrometer Tests
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B100	71.0	0.880	71.5	0.881
B50	73.0	0.857	73.0	0.858
B20	73.0	0.845	73.0	0.846
B10	72.0	0.841	72.0	0.842
B5	71.0	0.839	71.0	0.840
#2 Diesel	71.0	0.838	71.0	0.839

Date Samples Taken 7/10/07
Date of Hydrometer Test 7/17/07
Hydrometer Tests after 2 weeks cooling
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Sample	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B50	Top	76.0	0.857	76.0	0.858
	Bottom	76.5	0.857	76.5	0.858
B20	Top	76.5	0.844	76.5	0.845
	Bottom	76.5	0.844	76.5	0.845
B10	Top	76.0	0.840	76.0	0.841
	Bottom	76.0	0.840	76.0	0.841
B5	Top	76.5	0.838	76.5	0.839
	Bottom	76.5	0.838	76.5	0.839

Date Samples Taken 7/24/07
Date of Hydrometer Test 8/3/07
Hydrometer Tests after 4 weeks cooling
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Sample	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B50	Top	80.5	0.855	80.5	0.857
	Bottom	80.5	0.855	80.5	0.857
B20	Top	80.5	0.843	80.5	0.845
	Bottom	80.5	0.843	80.5	0.845
B10	Top	80.5	0.839	80.5	0.841
	Bottom	80.5	0.839	80.5	0.841
B5	Top	80.5	0.837	80.5	0.839
	Bottom	80.5	0.837	80.5	0.839

Appendix B

Results for Cold Storage Test
Temperature Range: 30 to 32°F

Date 8/14/07
Initial Representative Sample Hydrometer Tests
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B100	71.5	0.880	71.5	0.881
B50	71.5	0.866	71.5	0.867
B20	71.5	0.859	71.5	0.860
B10	71.5	0.857	71.5	0.858
B5	71.5	0.850	71.5	0.851
#2 Diesel	71.0	0.839	71.0	0.840

Date Samples Taken 8/28/07
Date of Hydrometer Test 9/4/07
Hydrometer Tests after 2 weeks cooling
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Sample	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B50	Top	76.0	0.866	76.0	0.867
	Bottom	76.0	0.866	76.0	0.867
B20	Top	76.0	0.859	76.0	0.860
	Bottom	76.0	0.859	76.0	0.860
B10	Top	76.0	0.857	76.0	0.858
	Bottom	76.0	0.857	76.0	0.858
B5	Top	76.0	0.851	76.0	0.852
	Bottom	76.0	0.851	76.0	0.852

Date Samples Taken 9/11/07
Date of Hydrometer Test 9/17/07
Hydrometer Tests after 4 weeks cooling
SG 60/60°F Hydrometer
Scale: 0.800 to 0.910

Fluid	Sample	Starting Temperature (°F)	Hydrometer Reading	Ending Temperature (°F)	Corrected Hydrometer Reading
B50	Top	72.0	0.867	72.0	0.868
	Bottom	72.0	0.867	72.0	0.868
B20	Top	72.0	0.860	72.0	0.861
	Bottom	72.0	0.860	72.0	0.861
B10	Top	72.0	0.858	72.0	0.859
	Bottom	72.0	0.858	72.0	0.859
B5	Top	72.0	0.851	72.0	0.852
	Bottom	72.0	0.851	72.0	0.852