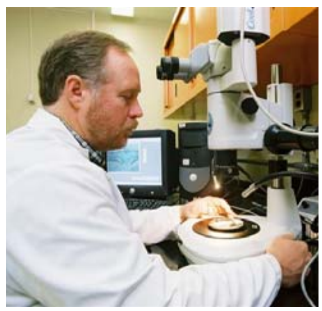
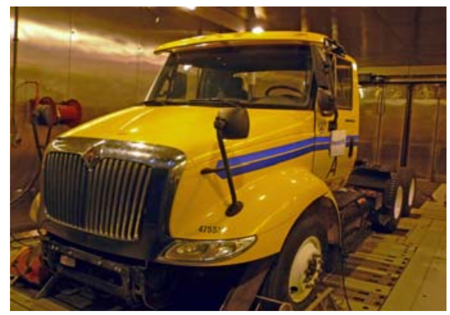
Biodiesel Research Project Final Report Summary

Funded by
Imperial Oil, Canadian Petroleum Products Institute and
Natural Resources Canada under National Renewable Diesel Demonstration Initiative (NRDDI)

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Canadian Oil Heat Association
Canadian Renewable Fuels Association
Canadian Trucking Alliance

Disclaimer

This report is produced with financial support from Natural Resources Canada. Its contents do not necessarily reflect the opinions of the Government of Canada.

1. Summary

In December 2006, the Government of Canada announced its intention to develop a regulation requiring an average 2% renewable fuel content in diesel fuel and heating oil no later than 2012, upon successful demonstration of renewable diesel fuel use under the range of Canadian conditions. During consultations, Canadian industry sectors and end-users have raised questions related to the large-scale integration of renewable diesel into existing distribution networks. The National Renewable Diesel Demonstration Initiative (NRDDI) aims to address these questions in advance of the proposed regulations coming into effect.

Imperial Oil and the Canadian Petroleum Products Institute (CPPI) have a vested interest in ensuring a successful transition to renewable diesel in Canada. In the opinion of Imperial Oil and CPPI, the two main areas of concern for industry and end-users that need to be tested/demonstrated in advance of the proposed regulation are: 1) cold flow performance of finished fuel (filterability/operability above cloud point, vehicle operability); and 2) stability (long term storage particularly at low temperatures, high temperature deposit formation in engines and furnaces). A proposal to conduct four tests at the Imperial Oil Sarnia Research Centre as the best approach for addressing these concerns about renewable diesel in Canada was accepted for NRDDI funding.

The research program was designed to enhance stakeholder understanding of the technical issues related to renewable diesel use via first hand experience, to provide guidance for decision-makers on the appropriate applications for renewable diesel, and appropriate regional and/or seasonal distribution of renewable diesel blends, and to provide information to direct future renewable diesel blending formulation and for standard-setting bodies to set specifications that will ensure "fit for service" fuel products. Imperial Oil, the prime lead on the Project, was supported by a Technical/Advisory Committee for a technical peer review. Membership on the Committee included the federal government, CPPI, the Canadian Oil Heat Association, The Canadian Renewable Fuels Association and the Canadian Trucking Alliance. The project utilized existing facilities and expertise leveraged by ongoing work in industry such as the performance of renewable diesel in light duty engines (Europe), a study on optimum additives (cold flow and oxidation control) use with renewable diesel blends, a study of the low temperature operability of soybean methyl ester in on-road heavy-duty engines (US industry), a study of the long term operability of B2 & B5 diesel in on-road heavy-duty engines (Alberta Renewable Diesel Demonstration), and finally, studies of test method development/appropriateness (ASTM International, National Renewable Energy Laboratory, Comité europeen de normalisation etc) for assessing renewable diesel blends.

The key technical outcomes from this research work are: 1) long-term furnace operation and performance was negligibly impacted by fuel up to B10: 2) the deleterious impact of saturated mono-glycerides in renewable diesel on the low temperature operability of filters in fuel handling systems was further confirmed underscoring the need to limit their content to prevent potential field issues: and 3) the long-term storage

stability of renewable diesel fuel can be assured via the use of commercially available oxidation control additives.

CPPI member companies are using the information generated to develop renewable diesel formulations that will help to ensure "fit for service" fuel products. The results of this work were shared with the Middle Distillate committee of the Canadian General Standards Board and may be used to set renewable fuel specifications.

The Project was executed as four tests or tasks, the results of which are summarized below:

2. Bio-Furnace Fuel Test Program

The use of renewable fuels, such as bio-diesel, is expected to grow in North America as a result of government mandates, both federal and state/provincial. Bio-diesel or B100 obtained from trans-esterification of fat and vegetable oils with methanol are composed of fatty acid methyl esters (FAME). Although bio-diesel has been promoted mostly as a fuel for diesel-powered vehicles, bio-diesel is suited as a blending component in furnace fuel oil. Several studies on the use of bio-diesel fuels in space heating equipment and residential furnaces have been reported in the literature. These studies showed that 5 percent bio-diesel blends appeared to be compatible with standard flame sensors for the burner-boiler tests that were conducted. Blend ratios as low as B20, however, could cause the flame sensing and control system to shut the burner down at mid to high excess air settings that are commonly observed in the field. In addition, there has not been an evaluation of the long-term performance of residential furnaces using bio-furnace fuel reported in the literature.

A test program was carried out to evaluate the long term performance of late-model furnaces using bio-furnace fuel and to gain a better understanding of the above mentioned concerns. The test facility was equipped with three Kerr furnaces. Each test consisted of 3 X 40 day cycles to simulate spring/fall, moderate severity and winter cold snap operations using furnace fuel blended with Canola Methyl Ester (CME), Soybean Methyl Ester (SME) and Tallow Methyl Ester (TME). The CME, SME and TME samples (B100) met the ASTM D6751 Standard. The base furnace fuel as well as B5, B10 and B20 bio-furnace fuels was tested. Although there is no bio-furnace fuel Standards at this time, the properties were compared with the CAN/CGSB-3.2 Standard. All bio-furnace fuels met the CAN/CGSB-3.2 Standard. Furnace operating parameters such as furnace efficiency, excess air, flue gas composition and temperature, smoke number, breech draft and breech temperature, cad cell resistance, pump and nozzle temperature were monitored weekly during the test. Inspection of systems (filters, burners, pumps, burner nozzles, and heat exchangers) was performed after each test. The furnace inspection, the tuning and maintenance was performed by an independent, qualified furnace technician who was unaware of the composition of the fuels being tested.

The results from the test program showed that there was negligible impact on furnace operation and performance with furnace fuel up to B10. The bio-furnace fuel should not exceed a B10 blend in order to be compatible with the existing seals in the fuel pump. Saturated monoglycerides were found to have deposited in the drain lines of two fuel tanks during the test that was carried out during the coldest period. This observation underscores the need to limit the level of saturated monoglycerides in the FAME to prevent potential field issues.

3. Low Temperature Storage Test Program

Biodiesel is a fuel component made from plant or animal feedstocks through an esterification process. The resulting fatty acid methyl esters (FAME) have a large variation in cloud point from -5° C to +15° C, depending upon the source. In Canada where a large geographic area experiences a cold climate, the poor low temperature properties of FAME and blends containing same (wax, gelling, and phase separation above the Cloud Point) must be well understood to avoid operability issues. The need for this understanding is underscored by reports of field issues that have occurred in the United States and Europe. Investigations of these issues have implicated saturated mono-glycerides (SMG) in the FAME as the cause of filter plugging.

To gain a better understanding of the saturated mono-glyceride issue, the low temperature storage stability of fifty seven bio-diesel fuels comprising essentially B5 and B20 made with canola, soybean, tallow and palm methyl esters was examined. The laboratory program was designed to address the phase separation of the FAME impurities above the cloud point of the blended fuel. The storage stability was assessed using the filter blocking tendency test (ASTM D2068-08). The deposits from selected B20 blends were analyzed by Gas Chromatography/ Mass Spectrometry (GC-MS) to identify the problem species.

The study showed that precipitates form in the fuel after ten days of storage at 2 - 4 °C above its Cloud Point or at 1°C. Analyses of the selected precipitates by GC/MS show them to be enriched in SMG content. The filter blocking tendency (FBT) test correlates fairly well ($R^2 = 0.71$) with the SMG content of the fuel. The correlation can be used to indicate the level of SMG in the renewable diesel that would result in a FBT value of <1.4 similar to conventional diesel fuels. Additional work to improve the correlation between SMG and FBT as well as a fundamental study of the kinetics of SMG precipitation and re-dissolution, including the impact of base fuel aromatic content, would be very valuable.

The results of this study further confirm the previous reports in the literature regarding the deleterious impact of saturated mono-glycerides in FAME on the low temperature operability of filters in fuel handling systems. This is a very important consideration when formulating renewable diesel fuels for a Canadian climate.

4. Low Temperature Operability Test Program

The Biodiesel is a fuel component made from plant or animal feedstocks through an esterification process. The resulting fatty acid methyl esters (FAME) have a large variation in cloud point from -5° C to +15° C, depending upon the source. In Canada where a large geographic area experiences a cold climate, the poor low temperature properties of FAME and blends containing same (wax, gelling, and phase separation above the Cloud Point) must be well understood to avoid operability issues. The need for this understanding is underscored by reports of field issues that have occurred in the United States and Europe. Investigations of these issues have implicated saturated mono-glycerides (SMG) in the FAME as the cause of filter plugging.

To gain a better understanding of these concerns, the low temperature operability, above the cloud point, of a B5 CME bio-diesel fuel spiked with three levels of saturated monoglycerides (SMG) was examined in 2004/2005 model year heavy-duty trucks in an All Weather Chassis Dynamometer. The levels of SMG were selected to give a Filter Blocking Tendency (ASTM D2068) range of ~1 to 6 based on the results of the previous low temperature storage study.

The study showed that the performance of the fuel delivery systems associated with the heavy duty diesel trucks tested was negatively impacted by the phase separation of spiked SMG from the renewable diesel fuel at -16°C well above its -26°C cloud point. A spiked SMG content of 250 mg/L resulted in an operability failure; 200 mg/L resulted in a high fuel filter pressure drop and restricted fuel re-circulation; 150 mg/L caused high fuel filter pressure drop without causing fuel re-circulation problems. The SMG on the fuel filter did not re-dissolve in the fuel as it warmed up, either via fuel re-circulation or by letting the truck warm up to ambient conditions. This is due to the high melting point (71 to 81°C) of individual SMG components. The performance of the fuel systems associated with the heavy duty diesel trucks tested correlated reasonably well with the FBT of the spiked fuel post a low temperature pre-soak. The data suggests that the renewable diesel blend should have a FBT in the 1 to 1.4 range similar to conventional diesel fuels. Future work to determine whether the SMG spiking procedure/level adversely affected the way precipitates form in renewable diesel fuels would be valuable.

The results of this study further confirm the previous reports in the literature regarding the deleterious impact of saturated monoglycerides in FAME on the low temperature operability of filters in fuel handling systems. This is a very important consideration when formulating renewable diesel fuels for a Canadian climate.

5. Thermal/Oxidative Storage Stability Test Program

Bio-diesel is a fuel component made from plant or animal feed stocks through an esterification process. Because of its chemical structure, bio-diesel namely fatty acid methyl esters (FAME) can be very sensitive to oxidation and thermal degradation. Depending on the feedstock, some bio-diesels may contain naturally occurring antioxidants. The oxidation stability properties of bio-diesel can also be improved through the use of commercially available antioxidant or stability additives. Oxidation of bio-diesel can lead to the formation of corrosive acids and deposits that could increase wear in engine fuel pumps and fuel injectors.

To gain a better understanding on the oxidation stability of bio-diesel fuel blends, the 12-weeks storage stability of fifty four bio-diesel fuels comprising essentially B5 and B20 made with canola methyl ester (CME), soybean methyl ester (SME) and tallow methyl ester (TME) was examined with and without an antioxidant. Two commercially available antioxidants chemistries (tert-butylhydroquinone and hindered phenols/amine mixture) were used in this study. The laboratory program was designed to address the formation of insoluble oxidation products produced in the bio-diesel fuel blends during long-term storage. The oxidation stability was assessed by performing the Rancimat oxidation stability test (prEN 15751-08) before and after the long-term storage as well as the total insolubles (ASTM D4625-04) and filter blocking tendency test (ASTM D2068-08) on the samples after the long-term storage.

The study showed that the use of antioxidant additives improved the long term storage stability of B5 and B20 CME, SME and TME bio-diesel fuel blends as measured by Total Insolubles (ASTM D4625), Rancimat Oxidation Stability (prEN 15751) and Filter Blocking Tendency (ASTM D2068) test methods. Both of the antioxidant chemistries (tert-butylhydroquinone and amine/hindered phenol mixture) tested were able to provide adequate long term storage stability performance. No attempt was made to optimize the treat rate of the antioxidant additive. The 50 vppm treat rate worked very well for the B5 fuels. The B20 fuels may require a treat rate >50 vppm.

The results of this study confirm that antioxidant use will assure the long term storage stability of bio-diesel fuels. This is a very important consideration when formulating renewable diesel fuels to prevent thermal degradation and sediment formation during long term storage. To maximize the benefit of the antioxidant, the additive should be added to the B100 during the manufacturing process after the trans-esterification and purification steps per industry best practice.