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Impact of Biodiesel Blends on Fuel System Component Durability

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ABSTRACT

An ultra-low sulfur diesel (ULSD) fuel was blended with three different biodiesel samples at 5 and 20 volume percent. The biodiesel fuels were derived from rapeseed and soybean oils, and in addition, a highly oxidized biodiesel was prepared from the soy biodiesel by oxidation under controlled conditions. A set of five elastomers commonly used in automotive fuel systems were examined before and after immersion in the six test blends and base fuel at 60°C for 1000 hours. The elastomers were evaluated for hardness, tensile strength, volume change and compression. Injector wear tests were also conducted on the base petrodiesel fuel and the biodiesel blends using a 500-hour test method developed for this study. Bosch VE (in-line) rotary pumps were evaluated for wear after testing for 500 hours on the base fuel, B5 and B20 test fuels. Additionally, a test procedure was developed to accelerate wear on common rail pumps over 500 hours. This procedure was used to evaluate Bosch pumps from tests conducted on the base fuel, B5, and B20 fuels. B5 blends, even with highly oxidized biodiesel, appeared compatible with the materials and components tested. B20 blends from non-oxidized biodiesel also appeared to be compatible with these materials and components. Test results for B20 prepared from highly oxidized biodiesel suggest the potential for significant problems with oxidized fuels, highlighting the need to prevent biodiesel oxidation. However, due to a lack of real-world field oxidized biodiesel samples for comparison, verifying the severity of the oxidization level of the biodiesel used in this study is not possible. There is some potential that the highly oxidized biodiesel sample used in the study represents an extreme condition that consumers may not encounter in the field; therefore, additional work is needed.

INTRODUCTION

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils, waste cooking oil, or animal fats. Biodiesel contains almost no sulfur and no aromatics. This material is increasingly being applied as either a replacement for, or a blending component with petroleum diesel. There is great potential for significant variation in product quality and products generically described as biodiesel. Research has shown that there are fuel quality, handling, storage, and vehicle operability requirements, which need to be addressed when biodiesel is used automotive diesel vehicles [1, 2]. This has led to numerous initiatives by fuel producers, original equipment manufacturers (OEMs), and their industry associations to publicize these issues. Also, standard-setting organizations have developed initiatives that include a number of parameters in regional biodiesel specifications.

In the United States, these initiatives have led to the development of a specification for biodiesel, ASTM D6751-03a. This standard is intended to address the quality of pure biodiesel (termed B100) when used as a blend stock of 20% and lower. No separate ASTM quality specifications currently exist for biodiesel when blended with fossil-derived fuels. The ASTM D6751 standard specifies biodiesel as long chain fatty acid esters from vegetable or animal fats containing only one alcohol molecule on one ester linkage. This effectively excludes raw or unrefined vegetable oils which contain three ester linkages. Within the United States, soybean oil is the leading predominant biodiesel feedstock.

Within the European Union, rapeseed oil is the most widely available biodiesel feedstock. The European Committee for Standardisation developed a uniform standard, EN14214. Modifications have been made to the European diesel specification (EN590), which allows for the use of up to 5% of an EN14214-compliant biodiesel as long as the finished blend meets the cold flow properties specified for the geographic area where the fuel is to be used. It is worth noting that EN 14214 generally excludes pure soybean methyl esters as fuel due to the high natural iodine value of this product. This requirement is intended to help insure the oxidation stability of the product, but seems misguided given that iodine value has been shown to be unrelated to oxidation stability [3].

Efforts to produce low and ultra-low sulfur fuels by hydrotreating have resulted in the removal of polar sulfur, nitrogen, and oxygen compounds; and have potentially reduced the lubricity of resulting diesel fuel. Several investigations have reported that biodiesel can significantly improve the lubricity of low sulfur diesel fuel at relatively low concentrations [4, 5]. However, it has also been reported that the formation of corrosive materials (such as organic acids, water, and methanol), polymers, gums, thermal and oxidative instability, and water separation may give rise to vehicle operability problems [2]. The current state of knowledge regarding biodiesel stability has been recently reviewed [6].

Potential vehicle operability problems for use of biodiesel blends have been identified as the following:

- Corrosion of fuel injection equipment components
- Elastomeric seal failures
- Low-pressure fuel system blockage
- Fuel injector spray hole blockage and excessive fuel injector wear
- Increased dilution and polymerization of engine oil
- Pump seizures due to high fuel viscosity at low temperatures
- Excessive injection pressure and pump wear.

While the various biodiesel quality standards are intended to prevent these problems, there are little data available to support the specific limits in the quality standards. As a consequence, OEMs and industry associations have been cautious in their acceptance of biodiesel and biodiesel blends. This study is designed to provide additional information on several of the issues that may occur for biodiesel blends, specifically the impact on fuel system elastomers, and wear of injectors and two different types of fuel pump. In specification soy and rapeseed biodiesels were employed, as well as a highly oxidized sample of soy biodiesel. These were blended with a ULSD fuel at 5% and 20%.

EXPERIMENTAL

FUELS AND FUEL PROPERTIES

Base fuel

A quantity of 2-D grade ULSD known as BP15 was used throughout the study as the base fuel and for blending. This fuel was produced in a commercial refinery unit, but cracked stocks were excluded from the feed. Future ULSD production will likely employ more advanced processing to allow the inclusion of cracked stocks. The roll out of ULSD in the United States is slated for September 15, 2006, and commercial fuel may be different from the fuel used in this study. Analysis of the base fuel was conducted to ensure the quality of the fuel according to the standard method, ASTM D975 and results are listed in Appendix 1. All fuels were stored in 200-liter, mild steel drums that were stoppered and inverted to prevent ingress of water.

Soy-based biodiesel

The soybean oil derived biodiesel was obtained from Peter Cremer, NA and labeled NEXSOL BD-0100. The shipment consisted of two lots of slightly differing product quality. To avoid doubt about the contribution of the different physical properties of the two lots, the batches were blended together to form a single sample.

Half of this combined sample of soy biodiesel was treated shortly after receipt with a commercially available antioxidant additive, tert-butyl hydroquinone (TBHQ) at 200 ppm. The objective of this was to inhibit oxidation of the fuel for the life of the study. Laboratory analysis on this now stabilized soy biodiesel was conducted according to the ASTM D6751 standard. In addition, tests for iodine value, peroxide value, and oxidative stability were performed. This fuel is now referred to as stabilized soy biodiesel, and characterization results are reported in Appendix 2. This stabilized material was used to prepare all B5 and B20 blends requiring soybean oil methyl ester (SME).

Oxidized soy biodiesel

One 200-liter drum of soy-based biodiesel was taken from the remaining (unstabilized) lot and prepared so as to achieve an acid number of at least 3.5 mg/KOH/g. The sample was heated to an average temperature of 57°C using an electric belt heater around the outside of the drum and sparged with BTCA 178 grade air (British Technical Council for the Motor and Petroleum Industries Fuels Committee) from a gas cylinder at a flow rate of approximately 4 liters/min. This sparging technique was considered to provide adequate mixing, without causing the sample to foam and to prevent a temperature gradient between the top to the bottom of the drum. Bottled air was used to ensure that the dew point was not compromised and that hydrocarbons were not introduced into the sample from site air compressors. The temperature of the sample was monitored throughout the oxidation treatment using an electronic digital thermometer. Acid number was measured daily using method ASTM D664 until it exceeded the required 3.5 mg/KOH/g. In fact, an initial acid number of 4.013 mg/KOH/g was achieved after 29 days, at which point heating and sparging was stopped. Acid number, however, decreased during the following days (3.818 mg/KOH/g), stabilizing at around 3.605 mg/KOH/g. The stabilized value is taken as the final value for this report. It is thought that erroneous results might have been caused by high levels of dissolved carbon dioxide, introduced through agitation and sparging.

This sample was labeled as 'Batch 1' and used to prepare all subsequent B5 blends, which required oxidized soy-based biodiesel.

To fulfill the testing requirements of the project, a second 200 liter sample of oxidized soy biodiesel was prepared. An acid number of 5.1mg/KOH/g was achieved in much less time than the previous batch. This was accomplished due to the use of a large diffuser, providing small air bubbles with relatively large surface area, thus making better gas to liquid contact. This sample was labeled as 'Batch 2' and used to prepare all B20 test blends which required oxidized soy-based biodiesel.

Laboratory analysis of the oxidized soy biodiesel batches was conducted to the ASTM D6751 standard. Tests for iodine value, peroxide value, and oxidative stability were also carried out. Characterization results for both batches of oxidized soy and results are also shown in Appendix 2.

Rapeseed biodiesel

A quantity of European, additive-free rapeseed methyl ester meeting the EN14214 specification was obtained for this study. It was considered prudent to stabilize the rapeseed biodiesel for the duration of the study, and so the fuel was treated with 200 ppm of TBHQ in the same manner as the soy biodiesel.

The rapeseed biodiesel was tested to the ASTM D6751 standard. Tests for iodine value, peroxide value, and oxidative stability were also conducted, as shown in Appendix 2. This stabilized rapeseed biodiesel was used to prepare all B5 and B20 test blends requiring the addition of rapeseed oil methyl ester (RME).

Biodiesel blends

A total of seven fuel blends containing 5%v/v (B5) and 20%v/v (B20) biodiesel in BP15 base fuel were prepared for the study:

- B5 RME – Sample ID 2031510
- B5 SME – Sample ID 2031511
- B5 Oxidized SME (Batch 1) – Sample ID 2031512
- B20 RME – Sample ID 2031513
- B20 SME – Sample – ID 2031514
- B20 Oxidized SME (Batch 2) – Sample ID 2031942
- B20 Oxidized SME (Batch 1) – Sample ID 2050822.

Each blend was assigned a unique sample number which identified the sample throughout its test life. The untreated ultra-low sulfur base fuel (BP15) was assigned sample number 2031163. Product quality analysis was conducted on each test fuel as directed by the ASTM D975 standard, with results reported in Appendix 3.

It has been noted that Batch 2 oxidized soy biodiesel (acid number of 5.1mg/KOH/g) was more extensively oxidized than Batch 1 (acid number 3.605 mg/KOH/g). One additional test fuel was subsequently blended to determine the behavior and pump wear effects of a B20 blend prepared from a less highly oxidized soy biodiesel. This B20 blend was prepared from Batch 1 oxidized soy biodiesel, the balance being the BP15 ULSD. Limited product quality analysis was conducted on this additional biodiesel fuel blend.

ELASTOMER TESTING

Five candidate elastomer types typically used in automotive fuel systems were selected for this study and are described in Table 1. The selection was based on the recommendations of a leading specialist supplier of automotive elastomers. 'O' ring test samples were specially molded for the study to ensure consistency of material dimensions and production batch.

Table 1. Fuel system elastomers tested in this study.

Elastomer Code	Description
NO674-70	Sulfur-cured acrylonitrile butadiene nitrile rubber Medium acrylonitrile content of 30-35%.
NB104-75	Peroxide- cured acrylonitrile butadiene nitrile rubber. Higher acrylonitrile content.
KB162-80	Hydrogenated nitrile polymer.
VB153-75	Fluorocarbon polymer, 67% fluorine content.
V1164-75	Fluorocarbon polymer, 66% fluorine content.

The physical properties of the test specimens prior to and after ageing in each of the test fuels were measured. Samples were immersed in candidate fuels at 60°C for 1000 hours. Control samples were conditioned in air at 23°C plus or minus 2°C for the same period. Test measurements were taken as required by the standard test methods listed in Table 2. The standard test methods prescribe procedures and defined conditions for measuring changes to physical properties such as volume swell, hardness, dimensional changes, and compression and tensile properties.

Table 2. Test methods applied to elastomer samples.

Test Method	Method Title
ASTM D1414	Standard Test Methods for Rubber O-Rings
ASTM D471	Standard Test Method for Rubber Property—Effect of Liquids
ASTM D395	Standard Test Methods for Rubber Property-Compressions Set

INJECTOR WEAR TEST

Injector wear testing was conducted on the base fuel and three B20 blends. The main operational conditions of the test procedure were as follows:

- The rig was operated at a constant speed of 1440 rpm ± 25 rpm for a period of 500 hours ± 10 hours.
- Fuel is used in 40 liter lots and at the completion of 100 hours ± 10 hours the fuel is drained and exchanged for fresh fuel.
- The injector block was heated to 150°C ± 10 °C to simulate normal operating conditions of the injectors.
- The bulk fuel temperature was controlled to 40°C ± 5 °C. It was permissible for the bulk fuel temperature to be outside these limits for the first 3 hours after start up and following a fuel change.
- Lucas injector nozzles, part number RDNOSD6754, were selected for the study. They feature an indirect injection design with corresponding nozzles. The injectors were checked for spray pattern, leaks, and opening pressure at the start of each test. The opening pressures were set to 130 ±5 bar absolute.

The test rig consisted of an in-line diesel injection pump running at a constant speed of 1440 rpm. The fuel control rack was mechanically locked to ensure a consistent injection of fuel across all tests. The injection pump cam and followers were lubricated by a separate source and so were independent of the test fuel for lubrication. This ensured consistency of testing across all candidate fuels.

A set of four injector nozzles was tested on each fuel. Test injector nozzle needles were dimensionally profiled. By determining the mean and standard deviation for a large number of measurements on new injector components, it was possible to produce information relating to the new or manufacturers' acceptable 'out of roundness'. For the injectors used in this project, there were 4 sets of 4 injectors and each injector needle was assessed for 'out of roundness' at 5 different axial locations. This provided a set of 80 measurements, on new components, as the base line 'acceptable' level of 'out of roundness.'

It was then possible to compare the post-test 'out of roundness' measurements (for each fuel tested) with this pre-test distribution to assess whether the fuel was acceptable or not; i.e., were the post-test results inside or outside the acceptable distribution at the 95% confidence level.

ROTARY PUMP TEST

The rotary pump test method was developed from the CEC F-32-X-99 test method for diesel pump lubricity, but employs a 500-hour test duration rather than 1000 hours. This test was performed on the base fuel and six biodiesel blends. For each test, a totally new Bosch VE pump, model number 0460 494 168, was used. Care was taken to ensure that the purchased pumps were not rebuilt, reconditioned, or overhauled. It is normal practice in this instance not to conduct a pre-test rating of the test components. Experience has shown that this is not necessary as the quality control of the new components and assembly by the manufacturer are very good.

The test cycle is outlined in Table 3. The test cycle was originally developed by the pump manufacturer, Robert Bosch GmbH, and was designed to accelerate the wear of the pump components in the following manner:

- The fuel control lever is locked in the maximum fuel position so as to increase the load on the pumping element components as well as increasing the duration of injection.
- Fuel is used in 40 liter lots and at the completion of 100 hours ± 10 hours the fuel is drained and exchanged for fresh fuel.
- The stop/start cycle repeatedly removes the hydrodynamic lubrication film between the moving components and so accelerates wear. This also provides a more realistic test cycle as fuel pumps in normal use would undergo many thousand starts, from a static condition, during their lifetime.
- The test cycle includes an over-speed section to exercise the components of the mechanical governor mechanism. The controlled fuel temperature and pressure have been chosen to simulate real-life operating conditions. At start of test and after every fuel exchange the fuel temperature must reach its set value of 60 ± 5 °C after a maximum of 3 hours running time.

At the end of each test, the test pump was carefully dismantled for visual rating. This rating was conducted by raters who had attended training sessions by Bosch and also participated in comparative rating exercises with other companies undertaking this type of test work. This ensures some consistency of rating across all companies involved.

Table 3. Pump operating cycle for rotary pump wear tests.

Phase	Acc. Running Time [s]	Pump Speed [% of rated speed]
1	0	0
2	5	110%
3	7	110%
4	9	100%
5	118	100%
6	120	80%
7	170	80%
8	175	0
9	180	0

COMMON RAIL PUMP TEST

The common rail test rig consisted of a common rail fuel pump (the test pump) operating at a speed representative of the more arduous conditions. The common rail fuel pump selected for the study was a Bosch common rail pump, part number 0445 010 010. The test cycle was based on the pump rig test cycle used by Bosch but limited to a 500-hour test duration. The key test conditions are as follows:

- The running speed chosen was approximately 2000 rpm which represented 4000 rpm engine crankshaft speed if we assume a 2:1 pump to engine speed ratio. Note that for common rail systems this ratio can vary widely and will not always be 2:1. The actual speed range was between 1950 and 2000 rpm.
- The pump was operated through a test cycle consisting of 3 minutes running at this test speed and 5 seconds stationary. The stationary portion of the test cycle was designed to accelerate the wear and better represent the stop/start nature of real life conditions.
- The pump was arranged to operate at a target pressure of 1350 bar, which is typical of many vehicle applications. Throughout the test, the operating pressure was arranged to be between 1200 bar and 1400 bar gauge.
- The test fuel was supplied to the pump at a flow rate and feed pressure matching the specifications of the vehicle system. This was arranged to be between 2.0 and 3.0 bar gauge.
- The fuel inlet temperature was controlled at 40°C ± 5°C. Fuel heating and cooling units were employed to meet this condition.
- The high-pressure outlet of the pump was connected to a fuel rail and electronic injector, as it would have been in the vehicle application. The injector was supplied with electrical signals in order to operate it at a fixed frequency and fixed open/close time periods (mark/space ratio). The injector was supplied with electrical pulses of 5 ms duration.

Common rail wear tests were conducted on the base fuel and B5 and B20 biodiesel test blends. One additional common rail test was also conducted to further investigate the behavior of a B20 oxidized soy biodiesel prepared from Batch 1.

At the end of a test, each test pump was dismantled and the critical components visually rated. The pump rating examines surface abrasion, fretting, and corrosion as well as polishing and wear.

RESULTS AND DISCUSSION

ELASTOMER TESTING

Most elastomer materials will undergo a physical or chemical change when in contact with fuel. The degree of change depends upon the tendency of the material to absorb a fuel or on compounds being dissolved or extracted by the fuel. This can lead to a number of changes in the physical characteristic of the material including swelling, shrinkage, embrittlement and changes in tensile properties. Natarajan et al. have studied the corrosivity, elastomer compatibility, toxicity, and biodegradability of several oxygenated diesel fuels [8]; and have shown a wide range of effects for different oxygenate chemistry.

The limit of a permissible physical change varies with the application and some degree of change can usually be tolerated. For example, a material that swells in a fuel or suffers a decrease in hardness may well continue to be fit for purpose for a long time as a static seal. However, in dynamic applications, swelling may result in increased friction and wear, and so a lower degree of volume change can be tolerated. For example, significant volume shrinkage can result in 'O' ring leakage whether the mechanical application is static or dynamic. However, a compound—which swells or is subject to elongation or changes to hardness or tensile strength—may remain serviceable as a static seal despite unfavorable conditions. Many material combinations do not fall neatly into a single category and some engineering interpretation is necessary.

Results for volume swell, hardness, dimensional changes, compression set, and tensile properties are shown in Appendices 4 through 8.

Volume Swell

The test data shows that the fluorocarbon 'O' ring materials, VB153-75 and V1164-75 exhibit the best overall chemical resistance in the fuel combinations tested, in terms of volume change. The maximum measured volume change of 6.8 % is acceptable for both dynamic and static applications.

Both the B5 and B20 blends of oxidized soy biodiesels have significant effect on the N0674-70, NB104-75 and KB162-80 test samples. In the B20 oxidized SME blend, all three materials present measurements which exceed

30% volume swell. Values of between 15.1% and 20.8% volume swell were measured in contact with the B5 oxidized SME blends. These elastomers might be subject to deterioration of mechanical properties in oxidized fuels especially in terms of extrusion resistance.

Test sample KB162-80 demonstrates poor swell resistance (24.3% volume swell) in contact with the B20 soy biodiesel blend, which might be considered unacceptable for dynamic uses. With the exceptions noted here, volume change for these materials in other fuels examined is within acceptable limits.

Hardness Properties

Hardness measurements conducted before and after fluid immersion show the nitrile rubber samples to exhibit most overall reduction in hardness in all test fluids. The sulfur-cured NBR material (NO674-70) exhibited most hardness change in the B5 and B20 oxidized soy biodiesel, giving 9 and 14 point reductions respectively when compared to the un-aged samples. The hydrogenated nitrile polymer (KB162-80) was most significantly affected by the B20 soy biodiesel blend with a reduction in hardness of 16 points. Test sample NB104-75 performed well in all fuels, exhibiting most hardness change, only 7 points, in the B20 oxidized blend.

The fluorocarbon materials (VB153-75 and V1164-75) exhibited the least decrease in hardness with maximum measurements of 5 points in all candidate fuels. These candidate test samples showed the best performance under the prescribed test conditions. However, it should be noted that all the materials tested are within what might be considered acceptable limits.

Dimensional Changes

All materials showed a positive change in overall dimension measurements with greatest dimensional changes occurring following immersion in the B20 and B5 oxidized soy blends. In general, shrinkage of a material is considered to be the more usual cause of seal failure.

Fluorocarbon materials, V1164-75 and VB153-75, demonstrated the best overall resistance to dimensional change (1.3% maximum change) in all fuels tested. Test sample NB104-75 was the most significantly affected across the range of fuels with between 6.6% and 9.9% dimensional change occurring in the B5 and B20 oxidized fuels. Similarly, test samples NO674-70 and KB162-80 showed greatest dimensional change (5.0% to 9.0%) in the oxidized fuels.

Compression Set Properties

This is generally reported as percentage change by elastomer manufacturers rather than percentage change in compression set relative to the original material deflection as required by ASTM D395. It is a measurement of how the elastomer recovers after a fixed time under specified conditions of temperature and 'squeeze' (compression). Zero percent indicates that no relaxation of the material has taken place, whereas 100% indicates total relaxation. A seal may subsequently contact mating surfaces but may not exert sufficient force against those surfaces. As with all the physical properties of elastomers, a good balance is generally required. For example, swelling of an elastomer may compensate for a poor compression set. A high compression set and dimensional shrinkage can lead to early seal failure except under conditions of high mechanical squeeze.

Overall, fluorocarbon test sample V1164-75 exhibited the best compression set characteristics for all material tested across the range of fuels (maximum 10 % change). Fluorocarbon material, VB153-75 did not perform well under this test (24.5-57.4 % change) even in base fuel. However, it should be noted that the test sample which was air conditioned at standard temperature and humidity also yielded relatively high compression set measurements (29.3 % change).

Sample NB104-75 exhibited acceptable overall compression set in all fuels, with values ranging from -9.3% to 8.5% change. However, 32.4 % change was measured in contact with the base fuel. Test samples NO674-70 and KB162-80 demonstrated acceptable overall performance in all test fuels giving values of between -3.1 to 19.7 % change.

Tensile Properties

The data demonstrate that the tensile properties of the two fluorocarbon materials (VB153-75 and V1164-75) were not significantly affected by any of the test blends. A maximum value of 19.6 % change in tensile strength was measured in contact with the B20 oxidized fuel. The nitrile 'O' ring seals (KB104-75) were most substantially affected overall with up -85.3% change in tensile strength and -79.7% elongation at break in contact with the two oxidized soy biodiesel blends. Test samples NO674-70 and KB162-80 gave acceptable results of around 50% or less for changes in tensile strength and elongation at break in all candidate fuels.

INJECTOR WEAR TEST

Injector wear tests were conducted on the base fuel and three B20 biodiesel blends. The injector wear test on the B20 oxidized soy biodiesel was terminated after only 12 hours of running following separation of the test fuel. Injectors from the tests on B20 oxidized soy biodiesel (sample 2031942) were examined following the brief running period. No evidence of gum formation was observed but significant needle sticking was noted.

Although the injector wear test is designed to examine the wear of internal injector components, not deposits on the exterior surfaces, each injector was examined for any obvious sign of material deposition. With the exception of one injector set, all injectors were found to be free from obvious deposits or 'lacquering.' For the B20 soy biodiesel (sample number 2031514), which had been stabilized with antioxidant, some deposition was evident on the outside of the injector nozzles. However, this material is not thought to be lacquer, which is defined as a hard, dry, and generally lustrous, oil insoluble deposit, as it was easily removed on washing.

The test injectors were checked for opening pressures, spray pattern, and leakage before and after each injector wear test. Some small increases in the 'leak back' measurements after testing are thought to be due to the seating of the needle in the nozzle during the test operation. There is no evidence that the fuel caused appreciable wear of the fuel inlet passage in the injector nozzles. In addition, post test fuel delivery measurements were similar across all test fuels and measurements were repeatable across the individual injectors.

The major parameter of concern when dealing with diesel fuel injector components is the quality of the surface finish of the high-pressure mating components. It is important to determine if these have deteriorated from the original surface finish when the components were manufactured. For cylindrical components, the surface finish may be evaluated by the 'out of roundness' measurement. The post-test 'out of roundness' mean and standard deviation measurements for each fuel test are compared with these pre-test acceptable values to identify any which potentially fall outside the acceptable range, and results are summarized in Table 4 (additional detail on the methodology and data analysis can be found in reference 7). All of the post-test measurements lie within the 95% confidence interval of the pre-test data. Therefore it may be concluded that the lubricity values of the fuels tested are adequate for the protection of the diesel injector components running under conditions similar to this test method.

Caution must be exercised in relation to fuel 2031942 (B20 oxidized soy biodiesel) as other fuel performance factors prevented this test being operated to completion. It must also be noted that no correlation work has been conducted to demonstrate how this injector test might relate to real-life operating conditions.

ROTARY PUMP TEST

The tests conducted are based on the Bosch VE four cylinder rotary diesel injection pump with mechanical governor. The test protocol had a duration of 500 hours and included a stop/start regime. A total of seven fuels were tested on Bosch VE rotary pumps. At the end of each test a wear rating assessment was conducted on each test. Pump components examined for wear or damage are shown in Figure 1.

The rating scale is based on a scale of 1 to 10. Ratings up to 3 indicate normal wear levels, which would be expected, and show no signs of damage, which would lead to premature failure of the pump. A rating of 3.5 is the absolute limit of the 'normal' wear and is generally taken as the pass/fail border line. Ratings between 4 and 6 are given when there is some evidence indicating a reduced service life of the pump. This may be large amounts of wear, scuffing, or fretting of the rated components. Ratings of 7 and above indicate major problems and likely catastrophic failure of the pump. Most pump tests conducted produce ratings below 6. Very poor lubricity fuels tend to cause seizure of the pump after only a few hours of running. However, tests which fail to reach their full duration would receive an automatic 'fail', whatever the condition of the components.

Table 4. Out-of-roundness results from injector wear tests.

	Pre test Distribution ALL	**Base Fuel**	**B20 RME**	**B20 SME**	**B20 SME Oxidized**
Maximum	0.92	0.55	0.59	0.73	0.80
Minimum	0.10	0.30	0.31	0.34	0.34
Average	0.48	0.40	0.44	0.48	0.54
σ	0.22	0.09	0.09	0.13	0.15
Mean + 2 σ	0.92	0.58	0.62	0.74	0.83
Mean – 2 σ	0.05	0.22	0.26	0.22	0.25

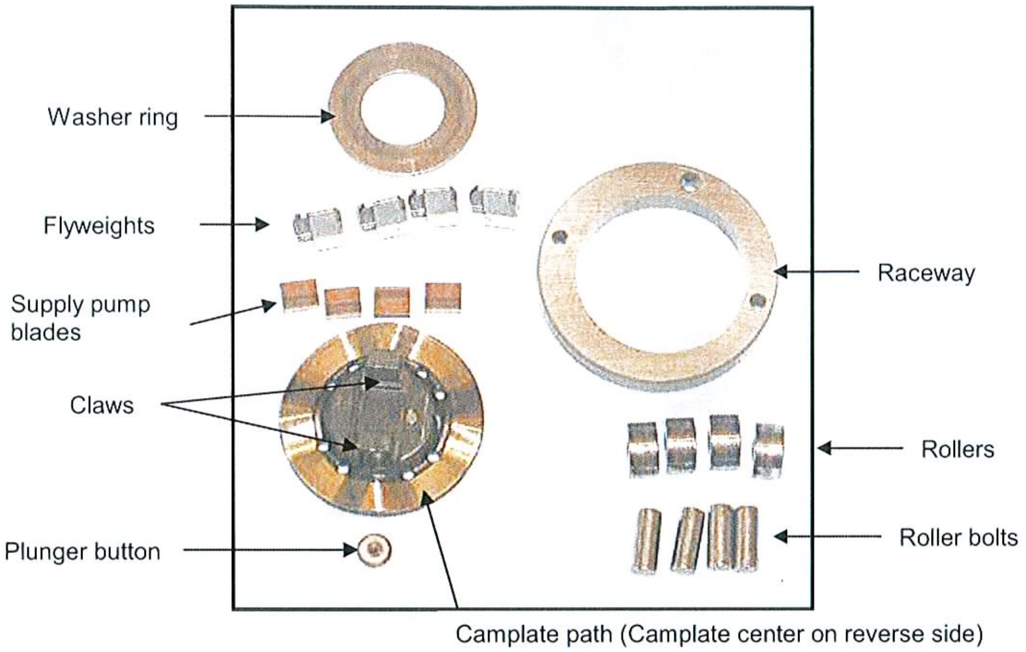

Figure 1. Bosch VE rotary pump components for wear rating.

The rotary pump test conducted on the B20 oxidized soy biodiesel blend failed to reach full duration, stopping after 66 hours. Examination of the data log showed that the computer control system had registered low pressure of the fuel supply system feeding the rotary pump. The cause was found to be blockage of the fuel filter. Closer inspection of the test fuel showed that it had separated into two distinct phases; the bottom phase being significantly more viscous and darker than the top phase. This was similar to our experience of the same fuel during the injector wear test and it would seem reasonable to conclude that the fuel had undergone decomposition during testing. It should be noted that the B5 oxidized soy biodiesel blend reached the full 500-hour test duration, and excessive wear was not evident on examination and rating of the corresponding fuel pump. Overall ratings are summarized in Table 5.

The ratings produced from the pump lubricity tests conducted indicate that all the fuels are within the range normally expected for commercial automotive diesel fuels. The amount of wear and consequently the ratings may have been slightly higher if the tests had continued to 1000 hours, but there is no evidence from the test components to suggest that the wear would have been outside the 'normal' range.

Table 5. Summary of wear rating assessments of Bosch VE rotary pumps.

Test Fuel/Blend	Overall Rating
Base fuel	2.5
B5 RME	2.5
B5 SME	2.5
B5 Oxidized SME (Batch 1)	3
B20 RME	3
B20 SME	3
B20 Oxidized SME (Batch 2)	Fail (2.5)

COMMON RAIL PUMP TEST

An in-house test method was developed to determine common rail pump wear using a 500-hour test procedure. Common rail wear tests were conducted on the base fuel, and B5 and B20 biodiesel test blends. At the end of the study, an additional common rail test was conducted to further investigate the behavior of a B20 oxidized soy biodiesel fuel prepared with Batch 2 of the oxidized soy biodiesel.

The pumps from these tests were dismantled and visually assessed for surface abrasion, fretting, and corrosion as well as polishing and wear steps. Pump components examined for wear or damage are shown in Figure 2. An overall rating was determined from the common rail pump wear tests, and these are summarized in Table 6.

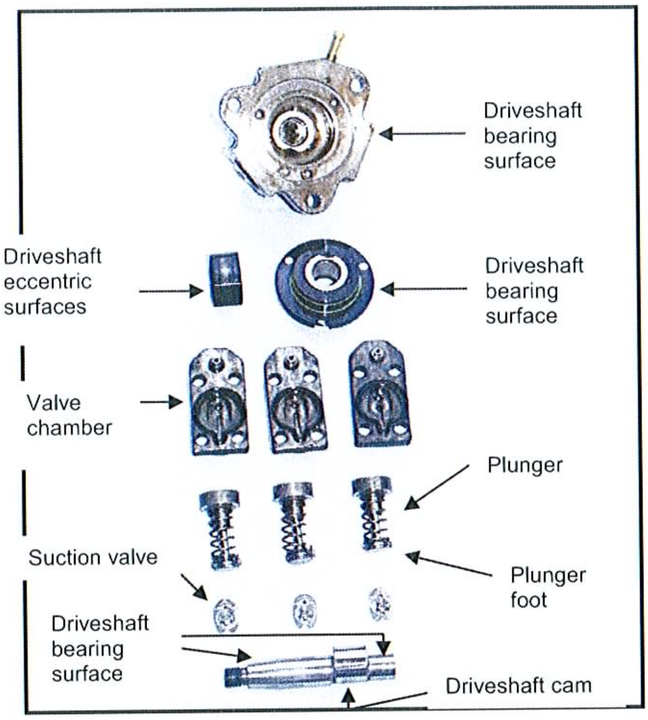

Figure 2. Dismantled Bosch common rail test pump showing components assessed for wear.

Table 6. Summary of wear rating assessments of Bosch Common Rail Test Pumps

Test Fuel/Blend	Overall Rating
Base fuel	2.0
B5 Rapeseed Methyl Ester	1.5
B5 Soy Biodiesel	1.5
B5 Oxidized Soy Biodiesel	2
B20 Rapeseed Methyl Ester	2
B20 Soy Biodiesel	2.5
B20 Oxidized SME (Batch 2)	1.5
B20 Oxidized SME (Batch 1)	1.5

All of the candidate test fuels completed the 500-hour test procedure. Overall, none of the fuel blends tested showed any adverse effects on the wear ratings of the common rail fuel pumps. With the exception of the B20 fuel blend (2031942) prepared from Batch 2 of the oxidized SME, there was no evidence of unusual deposits, gums, or lacquers on the pumps or any rated parts.

Examination of the fuel pump used to test the highly oxidized B20 fuel (2031942) revealed a thin lacquer coating on the shaft bearing surface. The lacquer was hard and dry with a lustrous appearance, oil insoluble and not removed on washing. In addition, there was evidence of seal swelling on dismantling the pump. Photographs of the lacquered component and the elastomer seal in the valve chamber which had become swollen are provided in Figures 3 and 4.

This test fuel consisted of 20% by volume of the highly oxidized soy biodiesel and had earlier resulted in failure of the Bosch VE rotary pump test and the injector test. Although the common rail test on this candidate fuel was completed without incident, a significant volume of a dark, viscous material was present in the bottom of the fuel tank when the fuel was changed after each scheduled 100 hours test run. Care had been taken to ensure that all test fuels were not subject to extremes of temperature in storage, and that representative and mixed samples were offered up for testing. Inspection of the test fuel revealed that two-phase separation had taken place: the bottom phase being significantly heavier and more viscous than the top phase. This was comparable to our experience of the same fuel during the injector wear test, and it would seem reasonable to conclude that the fuel had undergone decomposition during testing.

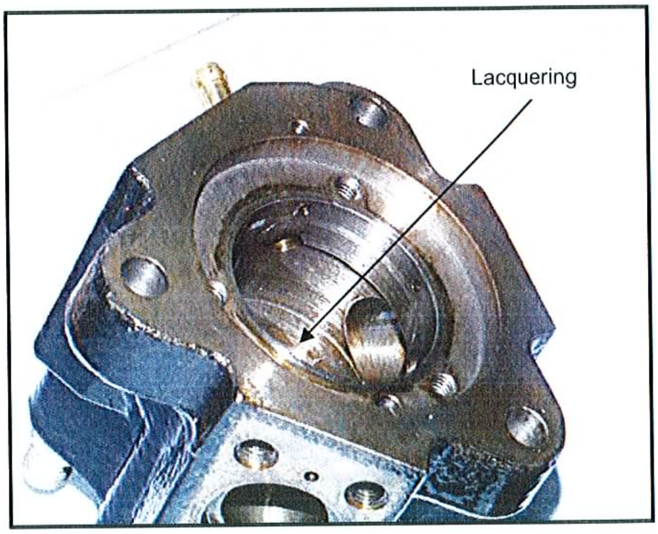

Figure 3. Lacquering on common rail test pump component.

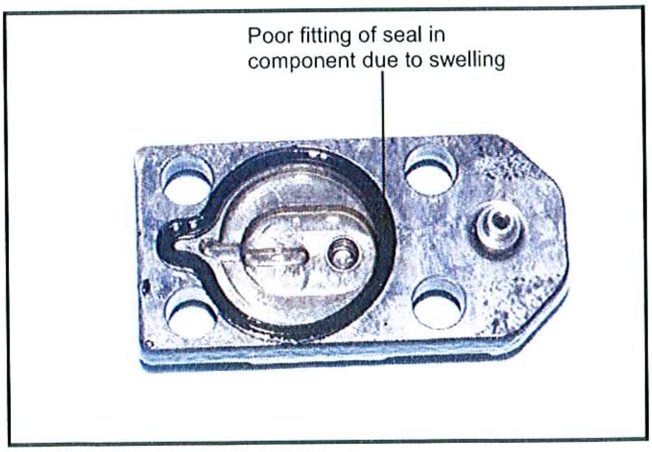

Figure 4. Common rail test pump component showing seal swell.

It is thought that filter blockage observed on the rotary pump rig did not occur on the common rail test rig due to the much higher feed pressures used: a 2.5 bar compared with 0.4 bar. In addition, the common rail test rig has a greater volume flow rate of fuel circulating via a by-pass system, and the outlet from the common rail test pump is higher (5 -10°C) than the VE pump. The fuel is also forced ('squeezed') through the filter which may prevent filter blockage.

The B20 fuel prepared from the less oxidized batch of soy biodiesel (sample number 2050822) completed the 500 hours of testing on the common rail test rig. Careful inspection of the fuel before testing provided no evidence of fuel separation, and heavier, more viscous fuel components were not evident in the fuel tank after completion of the test. However, there was clear evidence of seal swelling of the valve chamber seals on dismantling the pump. It has been established that fuel pump manufacturers typically employ 'O' ring seals prepared from hydrogenated nitrile polymers similar to test material KB162-80. From the results of the elastomer compatibility testing, this material exhibited significant volume swell (24.3%) and softening (16-point reduction in hardness) in the B20 oxidized SME fuel. Given these two physical changes, this might permit the extrusion of 'O' ring seals in certain applications such as in high pressure systems. However, it should be noted that the biodiesel used to produce both of the B20 test fuels discussed was oxidized and untypical of fuels meeting national specifications.

It is clear that the less oxidized B20 fuel (sample number 2050822) does not behave in the same way as the highly oxidized B20 fuel under the conditions of the test, i.e., significant phase separation does not take place. The test fuel was prepared immediately prior to testing and so was not subject to long periods of storage. Water and sediment content of 1% by volume was measured in the finished blend by the ASTM D2709 test method, well above the allowable limit in diesel fuel quality specifications. Acid value measured on Batch 1 oxidized SME at the end of the study showed that this parameter had not changed significantly on storage.

The available evidence indicates that phase separation did not occur in either of the B20 oxidized fuel blends on storage. Exposure to conditions occurring during the pump durability tests probably accelerated fuel separation in the more highly oxidized B20 test fuel. Phase separation did not occur during or after testing of the less oxidized B20 fuel. The B20 fuel prepared from less oxidized biodiesel contained lower amounts of water and sediment compared to the more highly oxidized B20 fuel. This indicates that the concentration of the oxidized component in the blend (the biodiesel) is not the main factor which determines fuel separation. The different behavior of the oxidized fuels is likely to be due to the extent of oxidation of the biodiesel component in the fuel.

CONCLUSION

- The highly oxidized B100 biodiesel and biodiesel blends prepared for this study have significantly different physical and chemical characteristics to non-oxidized biodiesel and biodiesel blends. The B20 test blend containing highly oxidized biodiesel may have been more highly oxidized than is likely to occur in the real world.
- Fuel filter blocking and fuel separation was observed during testing of the highly oxidized B20 test fuel in this study. Products of oxidation in the test fuel and decomposition reactions occurring under the conditions of test probably accelerated fuel separation in the fuel blend.
- Phase separation and filter blockage did not occur during testing of B5 and B20 blends prepared from biodiesel which had been less extensively oxidized and which contained lower water and sediment contents. The tests indicate the behavior of oxidized fuels under conditions of test are not dependant on the concentration of oxidized component and may be due to the extent of oxidation of the biodiesel component.
- B5 fuel prepared from oxidized biodiesel did not cause abnormal wear in either the injector or pump wear tests conducted in this study. Fuel filter blocking and fuel separation was not encountered during testing of this fuel.
- The results produced from injector wear tests indicate that the lubricity of the test fuels are adequate for the protection of diesel injector components running under similar conditions. The injector component wear test on the highly oxidized B20 blend failed to reach completion due to fuel filter blockage.
- The ratings produced from pump lubricity tests indicate that all test fuels are within the range normally expected for commercially available automotive diesel fuel running under the test conditions selected for this 500-hour test procedure. The rotary pump wear test on the highly oxidized B20 blend failed to reach completion due to fuel filter blockage.
- None of the candidate test fuel blends tested showed any adverse effects on the wear ratings of the common rail fuel pumps using a novel 500-hour test procedure. The test results indicate that the lubricity of the test fuels is adequate for the protection of common rail pumps running under similar conditions.
- Material compatibility testing of candidate elastomers has shown that fluorocarbon elastomers of medium to high fluorine content are most compatible with the test fuels under the specified conditions at concentrations of 20% or below. The results show that other candidate materials tested exhibited good resistance to changes in physical properties but exceeded the typically acceptable levels of degradation in one or more tests. These materials may be less compatible with biodiesel blends under certain applications.

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REFERENCES

1. U.S. Department of Energy, "Biodiesel Handling and Use Guidelines" DOE/GO-102006-2288, Second Edition, March 2006.
2. McCormick, R.L.; Alleman, T.L.; Ratcliff, M.; Moens, L.; Lawrence, R. "Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004" NREL/TP-540-38836, October 2005.
3. Kinast, J.A. "Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends" NREL/SR-510-31460, March 2003.
4. Knothe, G. "Structure Indices in FA Chemistry". Journal of the American Oil Chemists Society 79 (9) 847 (2002).
5. Knothe, G.; Steidley, J.R. "Lubricity of Components of Biodiesel and Petrodiesel. The Origin of Biodiesel Lubricity" Energy and Fuels 19 1193 (2005).
6. Waynick, J.A. "Characterization of Biodiesel Oxidation and Oxidation Products" CRC Project No. AVFL-2b Task 1 Results, August 2005 available from http://www.crcao.com/reports/recentstudies2005/AVFL-b%20Task%201%20Final%20rev%203.pdf.
7. Terry, B. "Technical Report CRC Project No. AVFL-2a: Impact of Biodiesel on Fuel System Component Durability" September 2005 available from http://www.crcao.com/reports/recentstudies2005/AVFL-2a%20Final%20Report.pdf
8. Natarajan, M. et al. "Oxygenates for advanced petroleum based fuels: Part 1. Screening and selection methodology for the oxygenates" Society of Automotive Engineers 2001-01-3631 (2001).

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

2-D: No. 2 diesel fuel

ASTM: American Society of Testing and Materials International

Bxx: Blend containing xx percent biodiesel, a 20% biodiesel blend is B20

HC: Hydrocarbons

NBR: Nitrile butadiene rubber

OEM: Original equipment manufacturer

RME: Rapeseed oil methyl ester

SME: Soybean oil methyl ester

TBHQ: tert-butyl hydroquinone

ULSD: Ultra-low sulfur diesel

APPENDIX 1: BASE DIESEL FUEL ANALYSIS

Property	**ASTM Method or Equivalent**	**Limits**	**BP- 15 2031163**
Flash Point	IP 34 (D93)	52°C min	57.5
Water & Sediment	D2709	0.050% vol.max	0.000
Kinematic Viscosity, 40°C	IP 71 (D445)	1.9-4.1mm^2/sec.	2.499
Sulphur	D3120	0.05% mass max	16µg/g
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a
Cetane Number	D613	40 min	49.3
Cloud Point	D5772	Report to customer	-11°C
Ash	D482	0.01% mass max	0.0
Carbon Residue,100% sample	D524	0.35% mass max.	-
Distillation, temp., 90% vol recovered	IP 123 (D86)	282-338°C max	322
Calculated Cetane Index	D976	-	50.3
HFRR wsd 1.4	CEC F-06-A-96	460µm	584

APPENDIX 2: BIODIESEL ANALYSIS

Property	Test Method	Limits	Rapeseed Biodiesel 2031040	Soy Biodiesel (Stabilized) 2031034	Batch 1 Soy Biodiesel (Oxidized) 2031382	Batch 2 Soy Biodiesel (Oxidized) 2031870
Flash Point	IP 34 (D93)	130°C min	>130	>130	>120	113.5
Water & Sediment	D2709	0.050% vol.max	0.000	0.000	0.000	0.000
Kinematic Viscosity,40°C	IP 71 (D445)	1.9-6.0 mm^2/sec.	4.686	3.972	7.276	9.837
Sulphated Ash	D874	0.020% mass max.	0.003	>0.001	0.004	0.003
Sulphur	D3120	0.05% mass max	<1.0μg/g	<1.0μg/g	<0.2μg/g	N/A
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a	1a	1a	1a
Cetane Number	D613	47 min.	50.9	50.4	59.1	* Note 1
Cloud Point	D2500	Report	-6	0	3	6
Oxidation Stability	D2274	-	1.52mg/100 ml	1.15mg/100ml	8.28mg/100 ml	8.38mg/100ml
Iodine Value	D1510	-	115	131	106	94
Peroxide Value	Cd 8b-90	-	14.18 meq/kg	34.62 meq/kg	381.11 meq/kg	662.43 meq/kg
Carbon Residue,100% sample	D189	0.050% mass max.	0.23	0.019	6.24	9.4
Acid Number	D664	0.80mg KOH/g max.	0.492 *Note 2 0.490 *Note 3	0.036	3.605*Note 2 3.370 *Note 3	5.101*Note 2 4.55 *Note 3
Free Glycerine	D6584	0.020% mass max.	<0.01	<0.01	<0.01	<0.01
Total Glycerine	D6584	0.240% mass max.	0.21	<0.01	0.03	<0.01
Phosphorus	D4951	0.001% mass max.	<10mg/kg	<10mg/kg	<10mg/kg	N/A
Distillation, atmospheric equiv. temp., 90% recovered	D1160	360°C max	179	175	301	463 *See Note 4

Note 1: Unable to rate fuel. Result exceeds T22 secondary reference fuel, 74.8 cetane number
Note 2: Acid value measured immediately after oxidation
Note 3: Acid value measured after approximately six months storage
Note 4: 90% recovery not attained. Cracking temperature reported. Recovery at cracking temperature: 88.0% vol.

APPENDIX 3: BIODIESEL BLEND ANALYSIS

Property	ASTM Method	Limits (D975 limits for 2-D)	B5 RME Biodiesel	B5 Soy Biodiesel	B5 Soy Biodiesel (oxidized – Batch 1)	B20 RME Biodiesel	B20 Soy Biodiesel	B20 Soy Biodiesel (oxidized – Batch 2)	B20 Soy Biodiesel (oxidized – Batch 1)
Sample No.			2031510	2031511	2031512	2031513	2031514	2031942	2050822
Flash Point	IP 34 (D93)	52°C min	64	66	61	59	66	60.5	60.5
Water & Sediment	D2709	0.050% vol.max	0.000	0.000	0.000	0.000	0.000	0.007	1.0
Kinematic Viscosity,40°C	IP 71 (D445)	1.9-4.1mm^2/sec.	2.544	2.561	2.619	2.833	2.705	3.068	3.036
Sulphur	D3120	0.05% mass max	11µg/g	10µg/g	10µg/g	9µg/g	8µg/g	N/A	N/A
Copper Strip Corrosion	IP 154 (D130)	No.3 max	1a	1a	1a	1a	1a	1a	1a
Cetane Number	D613	40 min	48.2	48.6	52.7	49.2	49.2	60.8	N/A
Cloud Point	D2500	Report to customer	-15°C	-14°C	-10°C	-8°C	-9°C	-10°C	N/A
Ash	D482	0.01%mass max	0.007	0.006	0.002	0.004	0.009	0.00	N/A
Cetane Index	D976	40 min	50.2	49.5	51.2	50.1	51.4	47.5	N/A
Carbon Residue,100% sample	D524	0.35% mass max.	0.04	0.07	0.12	0.07	0.06	0.89	N/A
Distillation, equiv. temp.,90% vol recovered	IP 123 (D86)	282-338°C max	325.5	325.5	325.0	334.0	332.5	336.5	N/A
HFRR wsd 1.4	CEC F-06-A-96	460µm	188	355	234	178	399	167	272

APPENDIX 4: ELASTOMER VOLUME SWELL RESULTS

Material	Volume Swell (%)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	0.0	12.2	12.7	15.1	30.6	11.0	11.3	11.2
NB104-75	-0.1	16.1	15.6	20.8	33.7	12.1	13.8	15.1
KB162-80	0.9	24.3	14.3	20.8	30.9	12.5	15.5	13.8
VB153-75	0.3	6.8	6.2	4.3	2.7	1.1	2.4	3.4
V1164-75	-0.2	5.0	4.5	2.0	4.4	1.2	1.3	1.7

APPENDIX 5: ELASTOMER HARDNESS RESULTS

Material	Micro Hardness (IRDH)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	64	59	59	55	50	60	59	60
NB104-75	65	62	59	64	58	60	60	63
KB162-80	75	59	68	70	72	69	71	68
VB153-75	68	63	63	64	63	65	64	64
V1164-75	76	73	72	71	72	74	73	72

APPENDIX 6: ELASTOMER DIMENSIONAL CHANGE RESULTS

Material	Dimensional Change (%)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	0.2	4.0	3.9	5.0	9.0	3.7	3.6	3.5
NB104-75	-0.3	5.1	6.1	6.6	9.9	4.1	4.4	4.7
KB162-80	-0.4	4.5	4.2	5.6	8.6	3.8	4.6	3.6
VB153-75	-0.3	0.5	0.7	0.9	1.2	0.6	0.7	0.5
V1164-75	-0.4	0.5	0.4	0.9	1.3	0.8	0.6	0.9

APPENDIX 7: ELASTOMER COMPRESSION SET RESULTS

Material	Compression Set (% change)							
	Un-Aged	Fluid 1 B20 Soy Blend	Fluid 2 B20 RME Blend	Fluid 3 B5 Oxidized Soy Blend	Fluid 4 B20 Oxidized Soy Blend	Fluid 5 Base Fuel	Fluid 6 B5 RME Blend	Fluid 7 B5 Soy Blend
NO674-70	8.7	14.3	15.2	2.6	16.0	10.2	12.1	19.7
NB104-75	8.5	-2.6	-1.9	-2.2	-9.3	32.4	3.0	-0.4
KB162-80	9.4	3.4	12.2	4.5	-3.1	3.4	5.2	-3.8
VB153-75	29.3	44.7	32.2	57.4	24.5	31.4	40.6	31.7
V1164-75	13.9	9.5	10.0	8.1	9.0	4.7	10.0	9.3

APPENDIX 8: ELASTOMER TENSILE PROPERTIES

Material	Tensile Properties							
	Un-Aged		Fluid 1 B20 Soy Blend		Fluid 2 B20 RME Blend		Fluid 3 B5 Oxidized Soy Blend	
	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
NO674-70	17.2	605	14.0	380	14.4	405	13.3	385
NB104-75	15.6	395	3.1	120	4.6	170	2.3	80
KB162-80	21.8	255	14.8	160	12.8	160	16.7	175
VB153-75	10.2	340	9.9	300	9.8	290	8.9	280
V1164-75	11.2	270	11.2	270	11.5	280	11.8	290

Material	Tensile Properties							
	Fluid 4 B20 Oxidized Soy Blend		Fluid 5 Base Fuel		Fluid 6 B5 RME Blend		Fluid 7 B5 Soy Blend	
	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
NO674-70	9.7	300	15.2	400	11.3	265	12.0	280
NB104-75	3.7	135	10.6	275	10.7	270	2.6	100
KB162-80	14.8	175	19.3	200	15.6	165	11.9	145
VB153-75	8.2	265	11.1	310	9.4	280	10.0	300
V1164-75	11.1	270	11.6	265	10.5	250	11.5	275