A Simple Method for Measuring the Oxidation Potential of Fish Oil Biodiesels, with Observations.

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Abstract

One major issue with the use of biodiesel fuels is the propensity of these fuels to oxidize during storage and form lacquers, resulting in failure of fuel handling systems. During one season of testing of a fish oil biodiesel in Alaska, a total of six out of six engines failed, all caused by fuel system seizures from lacquer films from partially oxidized fish oil. In retrospect, the oxidation of the biodiesel was due to the lack of understanding by the test program participants of the need for anti-oxidant additives, and for the proper storage conditions and time.

This paper will present a simple monometer method for evaluating the oxidation potential of biodiesel fuels. This method can be used to test compare the differences in oxidation potential between different materials, including biofuels. This is of particular interest to establish the efficacy of fuel additives for anti-oxidation. Also noted is the difference in oxidation potential show by fuels from the same source, but stored in various containers, and exposed to different amounts of air.

Background

The benefits of using biofuels are many, perhaps most importantly the production of energy from a renewable resource, using technology developed and perfected for the use of fossil fuels. Much recent discussion has centered on the relative energy benefits of some of these fuels, particularly ethanol from corn, where the perceived benefits might well be larger than the real effects. [1]

Fish oil is a natural product produced by heating fish until the oil is rendered. The highest value use of this product is a human food supplement, as the omega 3 fatty acids have been shown to reduce cholesterol. [2] Fish oil gel tablets are sold in many health food stores at a price of about $75 per pound ($500 per gallon), but raw fish oil purchased from processors for this use is obtained at about $4.50 per gallon. Fish oil is also sold for animal feed at a price of about $3.50 per gallon.

However, in fishing communities in Alaska, more fish oil could be produced than the human or animal feed markets currently can sustain, and much fish processing byproduct is disposed without rendering the oil. The recent rise in the cost of diesel fuel has created interest in rendering this oil to replace diesel for the generation of electricity. Estimates are that approximately 30,000,000 gallons of fish oil could be produced in Alaska alone.

In 2004, an initial study was done to evaluate the use of B100 fish oil biodiesel (B100 refers to pure biodiesel without conventional diesel added) for both on road and off road vehicles, and for stationary power generation. The National Park Service was interested in the use of B100 as a possible fuel for use in environmentally sensitive areas. (Spills might attract bears, but not the attention of the EPA, since fish oil is a food and not considered toxic.)

Fuel for this study was created as follows: bulk fish oil was purchased from processors working in the North Pacific just off the Alaskan coast in 24000 liter lots (a full ISO shipping container). [3] This raw fish oil was then shipped to Hawaii for conversion to biodiesel, through the transesterification process by a commercial biodiesel plant. The biodiesel was then returned to the ISO containers for shipment to Alaska. The full containers were split into smaller lots in 300 gallon totes for shipment to the various testing sites.

Two batches of fish oil biodiesel were created: the first batch (one ISO container) from oil purchased in the fall of 2003, with the biodiesel conversion done in March of 2004, the second (two ISO containers) purchased in December 2004, converted to biodiesel in March 2005, and delivered to Anchorage in April, 2005. Oxidation of the fuel was not considered a problem. No anti-oxidants were added to the fuel, and no special attention was paid to preventing exposure to air.

In the summer of 2005, the fish oil biodiesel was tested in a total of six diesel engines. Initial results were encouraging, as it appeared that the fuel burned well with no apparent difference with conventional diesel fuel. However, by late summer, numerous problems began appearing. Some of these issues involved the production of smoke and an increase in the crankcase oil level of diesel generators after about a week of operation, but the failures were all in the fuel handling systems. One engine failed due to the seizure of the injectors, while the other engines had fuel pump failures. Visual examination of the injectors and fuel pumps revealed that an orange film similar to varnish covered all surfaces inside the fuel systems, and that failure had occurred when this film prevented the movement of close tolerance parts. These types of issues have been noted by other experimenters [4-7].

At one site, the failure coincided with a switch in the fuel supply. [8] The engine had been operating for approximately 40 hours on B100 with no apparent problems, but when the supply was changed from one storage container to another, the engine failed within minutes. When the fuel was inspected, it was noted that the fuel used when the failure occurred had a yellow cast as compared to the more orange color of the initial fuel. It was also noted that fuel stored in tightly sealed jars tended to retain the orange color, but that open containers became more yellow over time. Based on these observations, it appeared that the oxidation and resulting polymerization of the oils to form polymers was the cause of the engine failures.

The polymerization of vegetable oils has been observed for centuries, and is the basis of oil based paints. Boiled linseed oil is the carrier for these paints, which solidifies when the oxygen in the air reacts with the oils to form a solid polymer when the paint "dries". [9] Spontaneous combustion of oily rags is also a well known safety hazard, associated with the linseed oils in inks used in printing. Cooking oils also will react with oxygen to form gummy solids.

Fish oil biodiesel stored in closed air tight containers with air spaces were observed to have partial a partial vacuum, as exhibited by a partial collapse of the walls of the container or a strong sucking sound when a rigid container was opened. This is consistent with the depletion of oxygen from the air due to the oxidation of the oil. However, most of these containers had been allowed to sit for several months, and it was not clear how rapidly the oxidation took place. If the pressure changes inside the container could be measured, this would provide an indication of the rate at which the oxygen was being removed from the air.

Experimental Methods

This study began as a elementary school science fair project, with the intention to simply observe if fish oil would oxidize quickly enough to be observed within the time frame of the several weeks before the project was due.

One simple and direct way of measuring a small change in pressure is to use a water manometer, which consists of a tube partially filled with water. When there is no difference in pressure between the ends of the tube, the water level is the same in both legs of the tube. When different pressures are applied to the ends of the tube, a change in the relative levels is observed, with the difference proportional to the density of the fluid.

The manometers used in this experiment were constructed from readily available materials from the hardware store. (See Figure 1 Schematic of manometer. Sample is placed in canning jar, and changes in water level measure pressure changes within closed systems with respect to the atmosphere. The fluid reservoir was a one cup (236 ml) canning jar and lid, the manometer tube was 8 mm vinyl tubing cut to approximately 2 meter length. There was some concern about the seal between the canning jar lid and the vinyl tubing, so short pieces of plastic tubing with rounded ends were cut from tubes intended for toilet installation. The inner diameter formed a snug seal with the tubing, while the outside could easily be glued to the canning jar lid with 5 minute epoxy. Food coloring was added to the water so that the water levels could be more easily observed.

A drop of dish soap was also added to the water to reduce the surface tension of the water in the tubes. A total of 12 manometers were made, at a total cost of approximately $50.

The manometer tubes were fastened to a rigid foam board, and the twelve jars placed on a shelf approximately 5 feet (1.6 m) from the floor. Measurements were recorded on paper attached to the foam behind the manometer tubes. Colored pencils were used to reduce the confusion in reading the measurements. Readings were made at approximately 12 hour intervals throughout the test.

There are some obvious issues associated with the use of water manometers for measuring pressure inside a closed container. The first is that the atmospheric pressure is not constant, but varies with the weather. Furthermore, the relative humidity in the ambient air will vary and be less than 100%, while the closed jar will approach 100% due to the presence of the water surface inside the tube. The absolute humidity will vary if there are changes in the room temperature, and there will also be a direct change in pressure associated with temperature. Other problems include the possibility of leaks from the canning jar lid seals, or the epoxy holding the vinyl tubes. Any of these problems could lead to erroneous results, so care was taken to assure that these issues did not occur.

Some of the possible sources of error were addressed through the use of blanks. In the first run, two separate blanks were used—an air blank (closed jar contains only air), a water blank (closed jar contains 50 ml water plus air space). In the second run, a salt blank containing approximately 30 g of table salt to absorb water vapor was used to see a water vapor effect could be noted. (See Figure 2) However, all three blanks exhibited nearly the same behavior, so in the final analysis, the air blank was used to correct measurements for changes in atmospheric pressure. All data reported below are with the blank values subtracted from the measured values.

One issue in starting the experiments was heat transfer from handling the jars during the tightening of the lids. Once the jar was tightened, holding the jar would cause the pressure to rise due to the rising temperature. Also, the tightening of the threaded lid resulted in compression of the seal on the jar lid, and would usually result in a slight positive pressure inside the jar at the beginning of the run. These problems were addressed by marking the initial water levels, waiting about one hour for the system to come to equilibrium, and marking the water levels again. The one hour marks were used as the zero values, to eliminate the thermal differences due to handling.

Once the run was started, water level measurements were recorded twice a day, usually in the morning and then again in the late afternoon or evening. Each measurement was numbered, and the date and time of the measurement were written on the paper behind the manometers. Color pencils were used, to limit the confusion of multiple marks close together (a problem mostly on the blanks).

Each run was stopped when the majority of the active samples approached the limits of the manometer. However, some of the most active samples quickly reached the limits of the manometer, and it was discovered that the run could be continued by resetting the level by opening the jar after marking the position, then noting the zero position again. Surprisingly, this gave a satisfactory reading, as some samples were shown to have nearly uniform reaction rates over a total pressure range of eight times the length of the manometer.

Data was collected by measuring the difference between water levels as recorded on the paper. An increase in pressure inside the jar was considered positive, while a decrease in pressure was negative. Oxidation consumes molecules from the air sealed inside the jars, and thus results in a decreasing pressure. Measurements were transferred to a spreadsheet, and corrected for changes in atmospheric pressure using the air blank.

Three separate runs were conducted, with a variety of oils and treatments of fish oil biodiesels. The first run compared fish oil biodiesel with and without additives, common vegetable oils, and petroleum based oils. The second run used various concentrations of additives, and the third compared various fish oil biodiesels from different storage containers, representing various oxidation histories.

Results:

Results from the first screening run are shown in Figure 3. Several oils showed little propensity to oxidize, including motor oil, synthetic diesel fuel, and canola oil. It is not surprising that the petroleum based oils are relatively inert in air environments, but the canola oil sample is quite interesting, as this oil is frequently mentioned as a replacement for conventional diesel fuel. This canola oil was from a new sealed bottle of food grade oil purchased at a grocery store, with the only ingredient listed being canola oil. However, it is legal to add small quantities of additives to food products without listing them as ingredients, so it is possible that this canola oil had been stabilized in some way.

Three oils did show significant oxygen uptake: the fish oil biodiesel, the olive oil, and the linseed oil. The oxidation of linseed oil was expected, as linseed oil is an important component in oil based paints, and the “drying” of these paints occurs by the polymerization of the linseed oil as it oxidizes. The surprise was that the fish oil biodiesel reacted more quickly than the linseed oil, which was not expected. However, the linseed oil source was from a partially used can approximately 10 years old from the author’s garage, so a fresh can of linseed oil was purchased for the second run. The fresh linseed oil exhibited a much more aggressive uptake of oxygen, approximately ten times faster than the fish oil biodiesel.

Figure 4 shows the effect of two additives to the fish oil biodiesel. Both additives are commercially available, although only Ethoxyquin is sold as an anti-oxidant. The second additive was more of a general additive for fuels, but the exact composition of this substance or the mechanism for improved performance were never clearly stated. It is clear that adding approximately 1000 ppm (one drop in 50 ml of oil) of Ethoxyquin provided significant resistance to oxidation. The second additive had no measurable effect on the oxidation rate.

The results of run 1 indicated that approximately 1000 ppm Ethoxyquin provides significant oxidation protection, but it was not clear if this dosage was sufficient, although it was close to the 400 ppm recommended by the supplier. In run 2, the dose was varied from approximately 500 ppm (.5 drops in 50 ml) to 5000 ppm (5 drops in 50ml). Figure 6 shows the results, indicating that while there is some increased resistance to oxidation when the dose is increased from 500 to 2000 ppm, the major effect is seen even at the lower dose.

In planning the second run, several observations were made. As noted above, the old linseed oil was replaced with freshly purchased linseed oil. But more importantly, the condition of the fish oil biodiesel was also considered. There were a number of fish oil biodiesel samples in the laboratory, taken from different locations at different times. In run 2, these various samples were examined, and fish oil was selected based on the earliest date sampled (taken several weeks after the fuel was delivered to the test site), which also had the virtue of being filled nearly to the top before the lid was closed. This aliquot represented the minimal oxygen exposure of any fish oil biodiesel on hand in the laboratory.   When tested, this sample showed a much lower rate of oxidation: in run 1, the fish oil biodiesel had reached the limit of the manometer of approximately 30 inches after 84 hours, but the fish oil biodiesel in run 2 was at approximately 8 inches of water vacuum after the same 84 hours.

Based on the above differences, either the method is inconsistent, or significant differences in the chemistry of the various fish oil biodiesel samples have occurred due to the oxygen history of each individual sample. This became the basis for Run 4, when an attempt was made to measure the variability due to the method as compared to the variability of fish oil biodiesel samples from various storage locations. The results of this are seen in Figure 5. Sample jars 2,3 and 4 contained fish oil biodiesel from the same container as used in run 2, to serve as replicates. Sample jar 6 was from the same container as used in run 1. The other jars contained fish oil biodiesel from several other bulk fuel containers, except for jar 10, which contained raw fish oil. Two things are worth noting: the replicas are nearly identical, providing confidence in the method, while each of the other samples exhibits significant variations from the replicates, indicating a significant history effect.

As noted above, the fish oil biodiesel was made by taking raw fish oil and processing it though the transesterfication process, primarily to remove glycerin and acids from the oil, to make it suitable for use as a fuel in diesel engines. The raw fish oil sample in jar 10 of run 4 appeared darker and more viscous than any of the biodiesel samples. However, it also exhibited a much lower oxygen reaction rate than the biodiesels. Figure 7 shows a comparison between the oxidation rate of the raw fish oil as compared to fish oil biodiesels treated with Ethoxyquin, showing approximately equal resistance to oxidation.

A more rigorous analysis of the data is also possible by converting the pressure change into a molar rate of oxygen consumption. Given that the sample jars have a total volume of 236 ml, and that 50 ml of fluid are added, this gives a total air volume of 186 ml. The air tube has an inner radius of 0.16 cm, and approximately 50 cm of tube is filled with air on the closed container side. This gives a total air volume of approximately 190 ml. Dividing by the standard volume of 1 mole of gas of 22.4 means that there are .00843 moles of air in the jar. Of this, the oxygen content is 20.95%, for a total of 0.00177 moles. 1 standard atmosphere is equal to 407.18 inches of water, so a change in pressure of 1 inch of water is a change in .00245 atmospheres. Consuming all the oxygen in the closed sample should result in a change in pressure of 85.28 inches of water. Or a 1 inch water level change equals 9.95 E -05 moles of O2, or approximately 1 E -04 moles per inch of water.

We can also estimate the total number of moles of fish oil molecules by assuming that the fish oil biodiesel has approximately the same molecular weight as diesel fuel $C_{12}H_{26}$. The density of fish oil is approximately .8, so 50 ml contains 40 grams, or .235 moles of oil.

Conclusions

While biodiesel fuels have been proposed to replace fossil energy sources, there are some technical challenges that must be addressed. Petroleum based fuels exhibit very little spontaneous oxidation when in contact with air, but some bio oils exhibit fairly rapid oxidation in air. Linseed oil is known to oxidize rapidly in air, forming a natural polymer as a result. However, rapid oxidation is not a desirable attribute in fuels used for power generation, as the formation of polymer films can lead to rapid engine failure.

In this study, a simple method for measuring the oxidation rate of various oils was developed and used to study the oxidation of fish oil biodiesel. The following conclusions were reached:

1. Simple, inexpensive water manometers can be used to observe oxidation rates of fish oil biodiesels and other liquids.
2. Fish oil biodiesels oxidize when exposed to air, resulting in the formation of polymer layers, leading to fuel system and engine failures. The rate of oxidation is somewhat slower than that of linseed oil, but fast enough to be of major concern for users of biofuels. Canola oil did not exhibit rapid oxidation in this work.
3. Oxidation of fish oil biodiesels can be retarded through the use of Ethoxyquin, a commercially available food grade anti-oxidant.
4. Raw fish oils exhibit anti-oxidant behavior similar to that provided from the addition of Ethoxyquin. These natural anti-oxidants seem to be removed in the transesterfication process used to make bio-fuels
5. Use of fish oils as biodiesel requires attention to exposure to oxygen. Suggestions for minimizing exposure include: treatment with an anti-oxidant at the bio-diesel processing plant immediately after completion of the transesterifcation process, storing and shipping the fish oil bio-diesel in full, air-tight containers, and using the fish oil biodiesel as quickly as possible.

Acknowledgements

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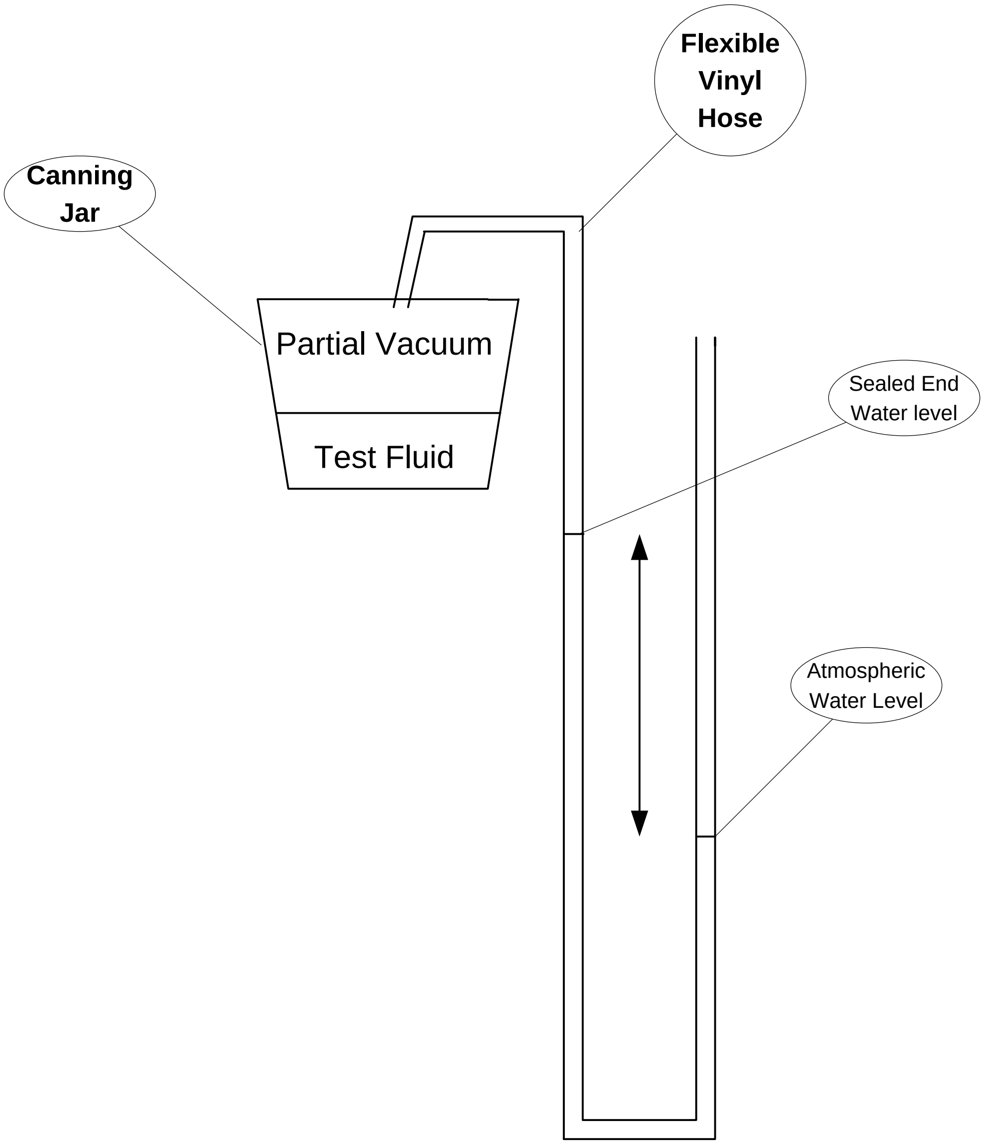

Figure 1 Schematic of manometer. Sample is placed in canning jar, and changes in water level measure pressure changes within closed systems with respect to the atmosphere.

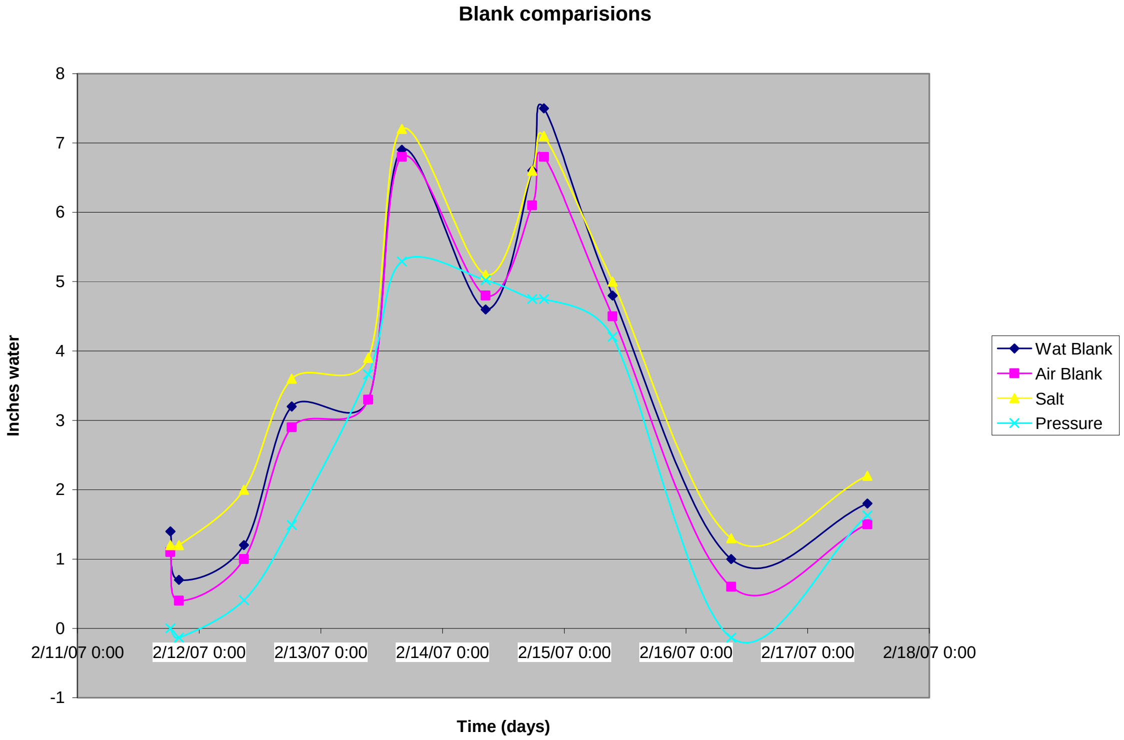

Figure 2 Comparison between air blank, water blank, salt blank, and pressure as reported by local weather service.

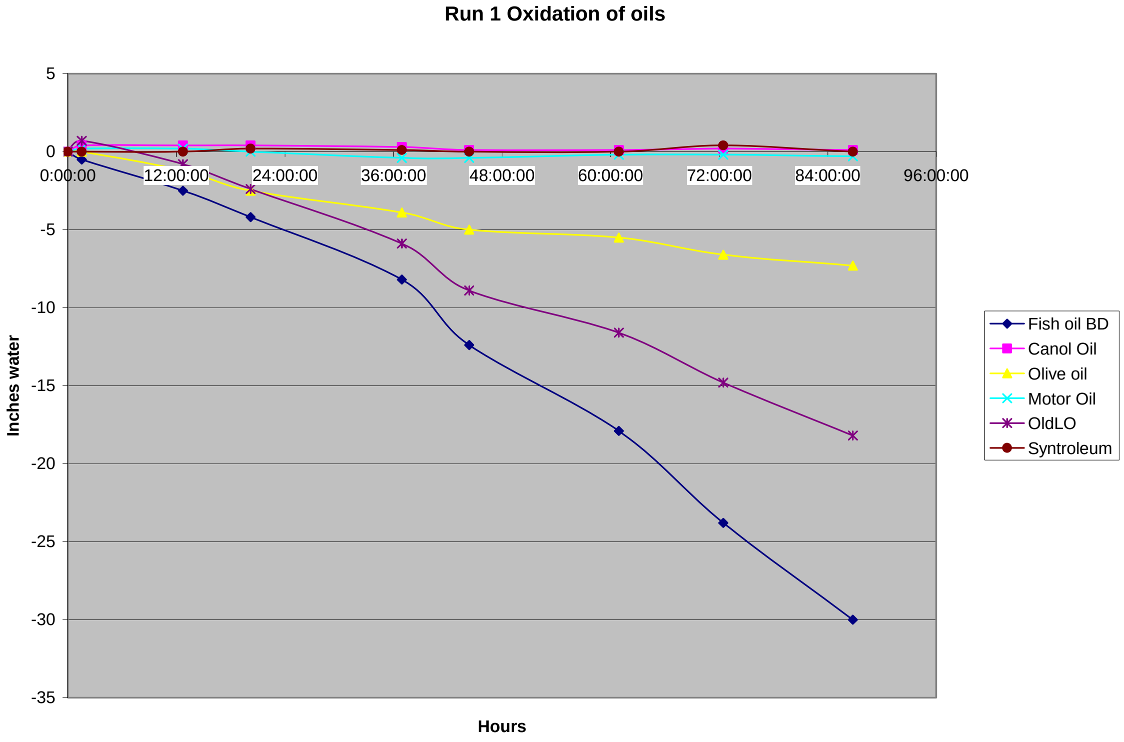

Figure 3 Oxidation of various oils in first run. Note Fish Oil Biodiesel oxidizes more rapidly than other oils. Canola oil is very stable with respect to oxidization. Syntroleum is a synthetic diesel fuel derived from natural gas.

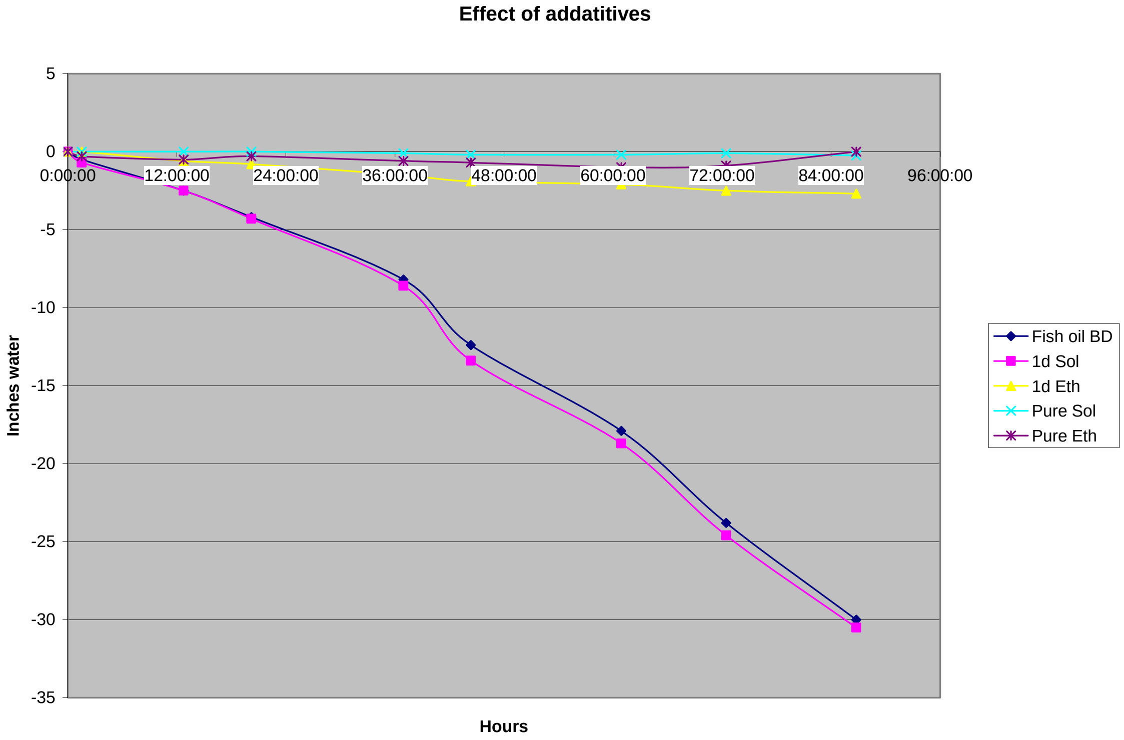

Figure 4 Effect of two additives. Ethoxyquin dramatically reduced the rate of oxidation, while the Soltron additive had no effect on oxidation rate. Pure Soltron and pure ethoxyquin were also tested, but they showed no direct oxidation.

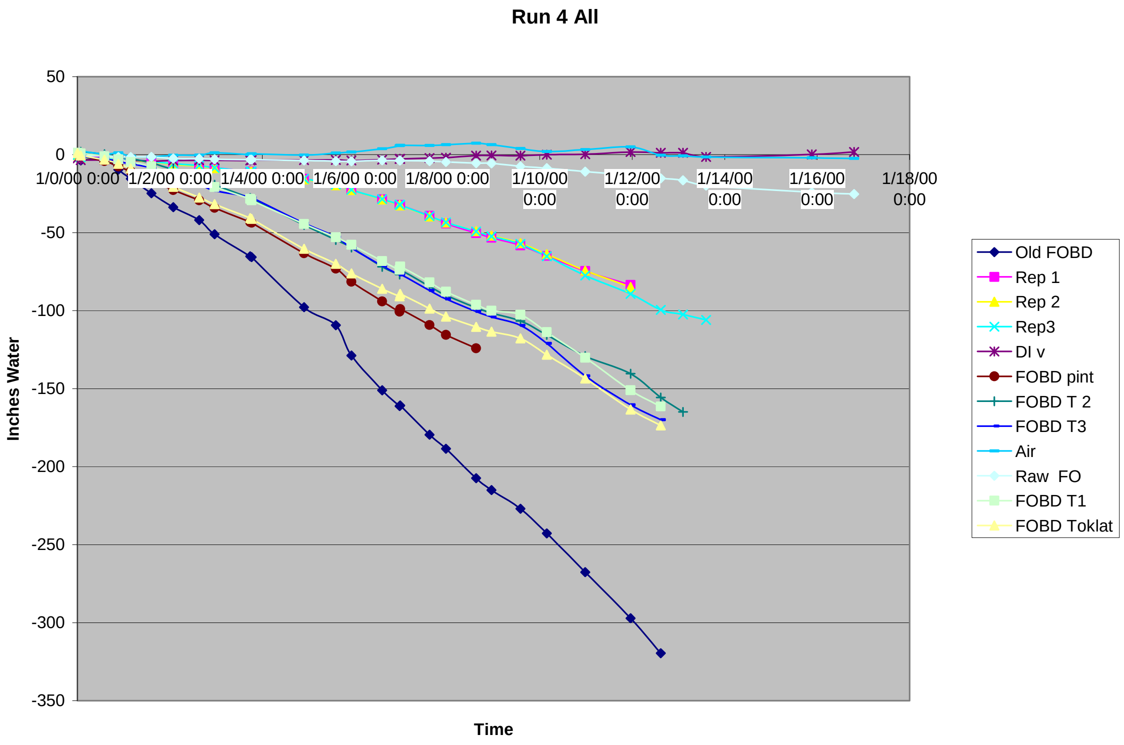

Figure 5 Comparison of various samples of fish oil biodiesel and raw fish oil, each with different sample oxidation histories. Note that the three replica samples provide identical oxidation rates, but other samples show higher oxidation rates.

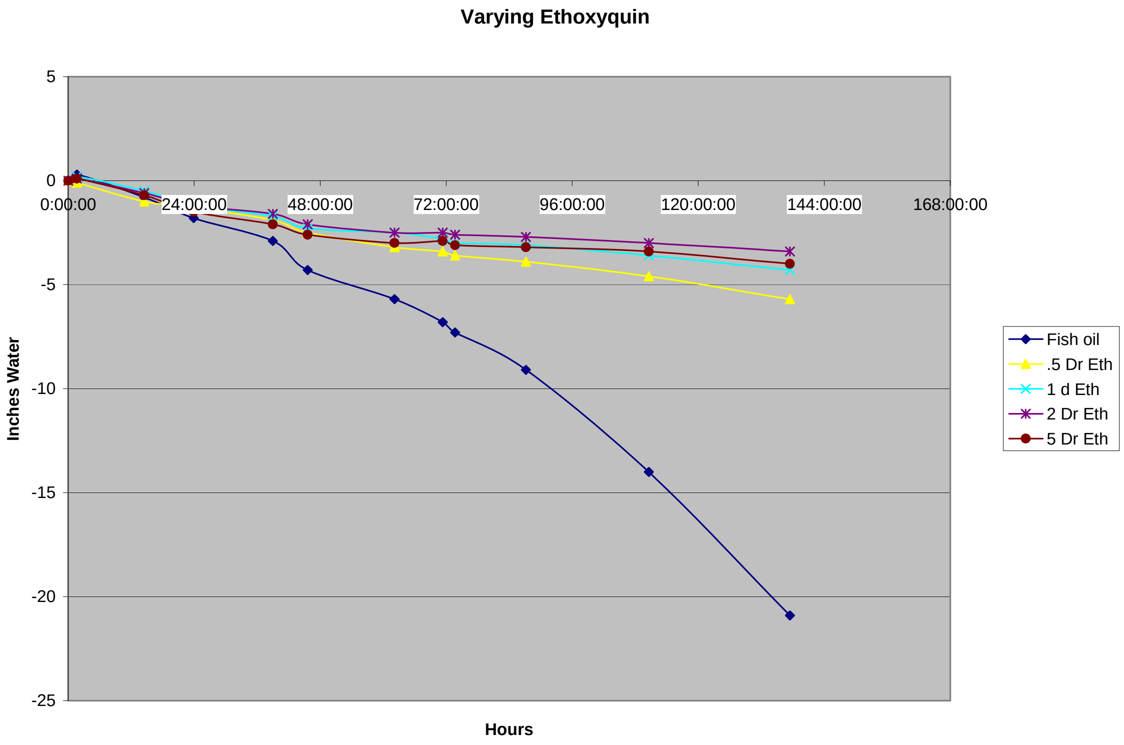

Figure 6 Effects of varying amounts of Ethoxyquin, in run 2. Recommended dosage of 400 ppm corresponds to approximately .5 drop in 50 ml. Note that increasing levels above this did not affect oxidation rates significantly.

Correlation between raw fish oil and fish oil biodiesel

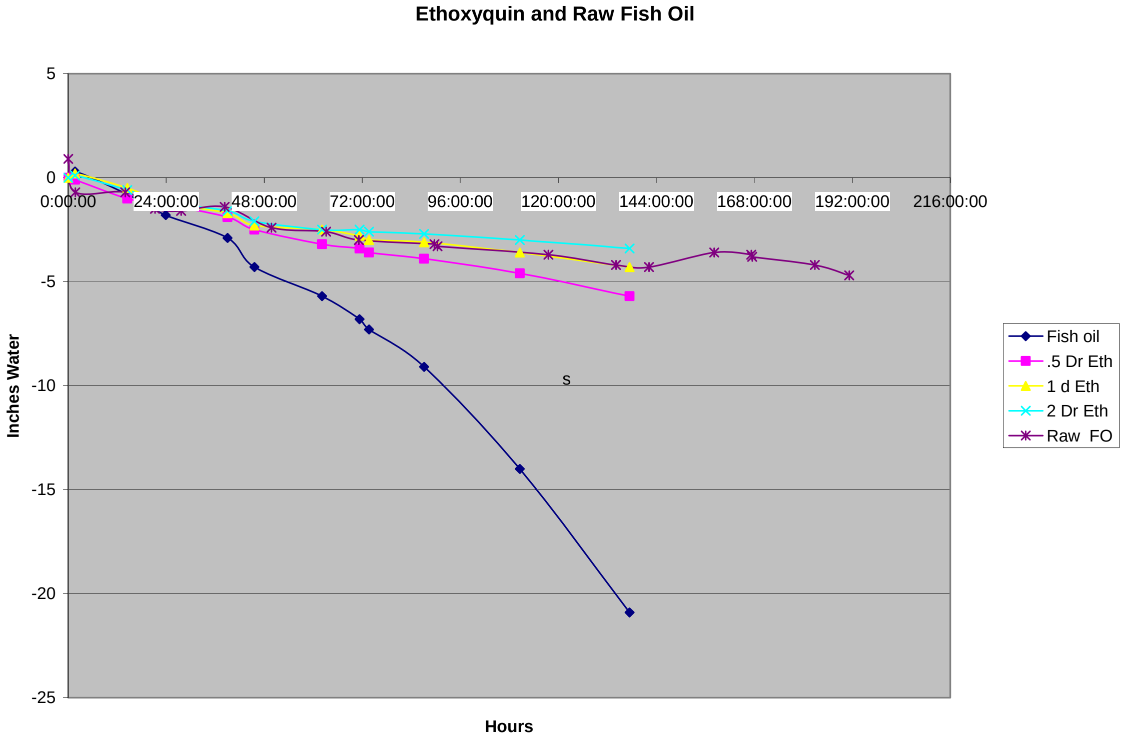

Figure 7 Comparison between raw fish oil and fish oil biodiesel treated with ethoxyquin. Note the apparent resistance of raw fish oil to oxidation, as compared to the fish oil biodiesel.

Jar #	Run 1 February 6-10, 2007	Days to Oxidation
1	Fish Oil Biodiesel	12.5
2	Fish Oil Biodiesel + 1000 ppm Additive 1	12.1
3	Fish Oil Biodiesel + 1000 ppm Ethoxyquin	119.0
4	Food grade Canola Oil	-1487.8
5	Water Blank	112.3
6	Food grade Olive oil	45.1
7	Motor Oil	1487.8
8	Old Linseed Oil	20.1
9	Air Blank	129.4
10	Pure Additive 1	2975.5
11	Pure Ethoxyquin	330.6
12	Synthetic Diesel Fuel	-743.9
	Run 2 February 11-17, 2007	
1	Fish Oil Biodiesel	43.1
2	Fish Oil Biodiesel+ 500 ppm Ethoxyquin	86.2
3	Fish Oil Biodiesel+ 1000 ppm Ethoxyquin	104.6
4	Fish Oil Biodiesel+ 2000 ppm Ethoxyquin	117.2
5	Wat Blank	-117.2
6	Fish Oil Biodiesel+ 5000 ppm Ethoxyquin	101.0
7	Pure Additive 2	-2929.6
8	Fish Oil Biodiesel+ 1000 ppm Additive 2	42.5
9	Air Blank	-58.6
10	Dry Table Salt	-732.4
11	Old Linseed oil	21.5
12	New Linseed oil	1.4
	Run 4 February 26-March 16, 2007	
1	Oxidized FO Biodiesel from Run 2	7.0
2	Fish Oil Biodiesel Replicate 1	40.6
3	Fish Oil Biodiesel Replicate 2	39.0
4	Fish Oil Biodiesel Replicate 3	41.8
5	Water Blank	81.2
6	Fish Oil Biodiesel from run 1	10.0
7	Fish Oil Biodiesel Tote 2	19.0
8	Fish Oil Biodiesel Tote 3	15.2
9	Air Blank	1461.4
10	Raw Fish oil	112.4
11	Fish Oil Biodiesel Tote 1	16.9
12	Fish Oil Biodiesel Toklat Day tank	10.6

Table 1. List of samples in each run. “Days to Oxidation” approximates the time necessary for 1 molecule of oil to react with