Vegetable Oil as Fuel
By Joe Beatty

Introduction

Although much information can be found on the journey Vegetable Oil undertakes from the time of extraction to the time is discarded from the fryer, little information is available after this point due to the fact that it has generally been regarded as having ended it's serviceable life at this point.

However, with the every increasing interest in the use of this waste oil as fuel, an investigation was undertaken to better understand the changes that occur during use as an alternative fuel for compression ignition engines..

Specifically this research focuses on three reactions that take place in vegetable oils; soap formation, hydrolysis, and oxidation.

Soap Formation

Soap Formation, also known as saponification, is the reaction between a free fatty acid and an alkali of either Sodium or Magnesium to produce a soap plus a molecule of water:

$$RCOOH + NaOH \rightarrow RCOONa + H2O$$

Soaps are implicated in 3 reactions; first they are a necessary component in the hydrolysis reaction by acting as an emulsifier which allows water to more easily react with the oil. Second they can reduce the surface tension of the oil which allows Oxygen to more easily attack the oil in the oxidation reaction. Finally, again acting as an emulsifier at the oil and "free water" interface at the bottom of storage tanks, they can promote bacteriological growth.

Hydrolysis

Hydrolysis is a high-energy reaction that takes place between water, in the form of steam, released from food in a fryer operating between 325 and 375 degrees Fahrenheit. In this reaction the water vapor, in the presence of a surfactant, splits off a Free Fatty Acid in the following reaction:

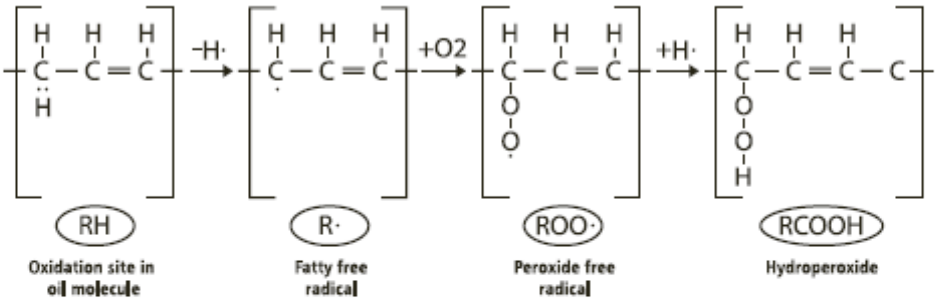
Triglyceride + H20 $\xrightarrow{\text{soap}}$ Free Fatty Acid(FFA) + Diglyceride

Free Fatty Acids are weak organic acid that can attack metals surfaces to release metallic ions.

Diglycerides are very hydrophilic and therefore strong emulsifiers.

Oxidation

Oxidation (Auto-oxidation) is a reaction in which Oxygen attacks an unsaturated fatty acid at the Carbon molecule immediately adjacent to the unsaturated site(where a Carbon has a double bond with another Carbon).



Initiation $RH \xrightarrow{\text{Energy Catalyst}} R^{\bullet} + {}^{\bullet}H$

Propagation $R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$

$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$

Termination $R^{\bullet} + R^{\bullet} \longrightarrow RR$

$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O$

$ROO^{\bullet} + {}^{\bullet}R \longrightarrow ROOR$

$ROO^{\bullet} + R_1OO^{\bullet} \longrightarrow ROOR_1 + O_2$

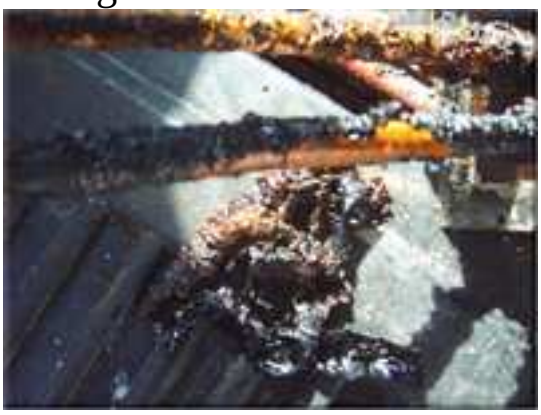
Several factors have been identified as promoting this reaction, they are in order of declining importance:

1. Availability of Oxygen- fuel storage tanks provide an ample supply of oxygen for the reaction.
2. Heat- A rule of thumb in chemistry is that the rate of a reaction doubles with ever 10 deg C increase in temperature, however it has been suggested that the oxidation reaction may even triple with every 10 deg C. (2)
3. Presence of Pro-Oxidants-Some Pro-Oxidants found in Veg Oil systems in order of decreasing activity, Copper, Mild Steel, Zinc, Aluminum.
4. Light- Ultraviolet light can act as a pro-oxidant.
5. Time- Longer exposures increase the degree of oxidation.

Now, tying all of these reactions together, free fatty acids, even thou only sparingly soluble, are carried in any water present and can therefore attack any metals they encounter. These metal ions can then catalyze the oxidation reaction. Given enough oxygen,

enough heat, the right metal catalyst, this oxidation can be quite rapid.

The problem with this rapid oxidation in vegetable oils is that the peroxide free radicals produced can and do also react with unsaturated sites to form long chain, cross-linked polymers, converting a triglyceride with a molecular weight in the 100's to a polymer with a molecular weight in the millions. The effect of these polymers can range from the major inconvenience of tank fouling:



To damage of vital engine components:

Or even possible fouling of injectors, deposits on cylinder walls, ring lands coking, and contamination of lubricating oil.

Background and Testing Os Submitted Samples

As a starting place for this study, samples were obtained from members of the vegetable oil community. Two samples were requested, one of the normal feedstock which they were collecting, after it had been processed for water and sediment removal and a second sample taken from their fuel tanks.

Samples were analyzed for the following components:

Peroxide Value- A measurement of the amount of oxidation, also called autoxidation, that has occurred in the sample. The results are expressed mEq/l, milliequivalents Peroxide per liter.

FOS- Food Oil Sensor- An instrument which measures capacitance of the sample. Pure vegetable oils are non-polar and would therefore be expected to give a reading of zero. Oxidative products and free fatty acids are polar and will elevate the readings. Results are expressed as FOS units which do exhibit a linear relationship with total polar compounds.

FFA's – Free Fatty Acids- Measures the products of the hyrolysis reaction in which fatty acids are broken away from the tryglycerides. Results are expressed as % FFA.

Water- A measurement of total water content of the sample As measured by Karl Fisher Coulemetric Titration. Results are expressed as ppm water, parts per million water.

NaCl A measurement of the total amount of salt, NaCl, as measured by Chloridometer. Results are expressed as ppm NaCl, parts per million salt.

		Food Oil Sensor	PV (7/5/06)	FFA %	H2O/PPM	NaCl/PPM
Cgoodwin	WVO	2.65	4.00	1.36	777	54
	Tank	N/A	10.50	0.8		
Carimbo	WVO	3.45	11.00	0.66	592	36
	Tank	3.16	11.50	0.64		
Scrawny	WVO	2.79	4.00	0.61	554	36
	Tank	2.26	11.75	0.58		
Veggie Ranger	WVO	3.67	2.20	0.71	559	39
	Tank	3.64	4.80	0.54		
SVO Supply	WVO	3.49	2.2	1.02	1140	34
	Tank	4.02	7.6	0.94		
Chinese Restaurant		3.38	3	4	460	40
Fresh Oil		2.12	0.3	0.015	125	28

Note-The Chinese Restaurant sample was used for the WVO studies that follow.

Oil is generally discarded at a certain color level or a set time interval, but the underlying reason is objectionable flavor in the foods being fried. This can be a result of either products of the oxidation reaction or the free fatty acid reaction. High peroxide values are generally an indication of poor fryer maintenance; high free fatty acids are an indication of excessive moisture introduced into the fryer in the food being fried. Of these test samples only the

Carimbo sample showed excessively high peroxide levels and only the Chinese Restaurant showed a high FFA.

The Food Oil Sensor is an instrument used by some restaurants and the suggested level for discarding is between 3.0 and 3.2. No samples were particularly high.

The moisture levels were all somewhat higher than the fresh oil but did not appear to be excessive. It is interesting to note that the cgoodwin sample did pass the "Crackle Test". This may be due to the fact that the limits of accuracy of the test are stated to be 1% or 10,000 ppm. (1)

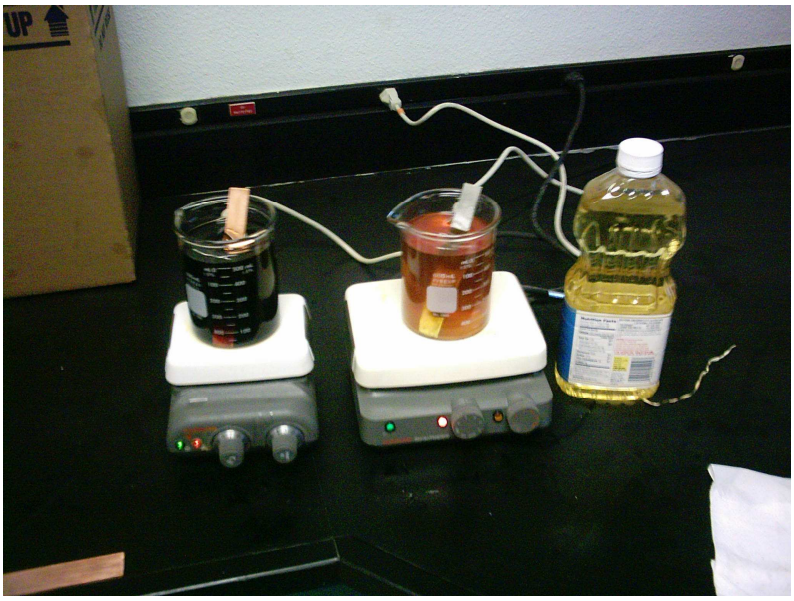
The NaCl levels were all quite low (Distilled water measured 20 ppm). Therefore, for these samples, it does not appear that significant quantities of salt are being contributed by the food being fried.

The most interesting result of this testing was the increases in Peroxide Values between the Waste Oil Feedstock and the "in Tank" samples indicating that further oxidation was taking place in the tank.

Oxidation and Pro-Oxidants

In an attempt to access the relative effect of various metals that can be found in fuel systems on these peroxide increases, the following experiment was developed,

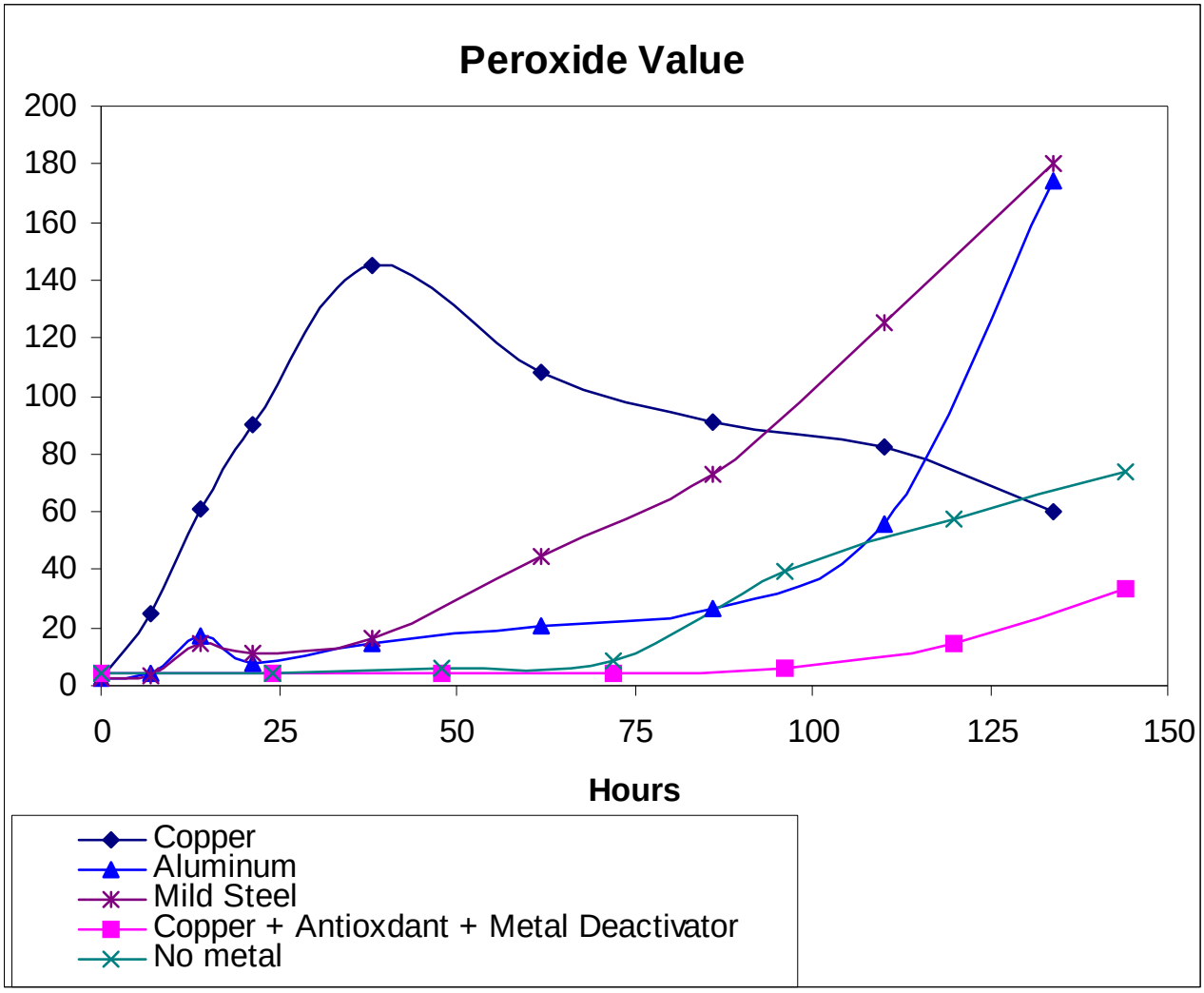
Samples of 400 mls of waste oil were placed in a 600ml beaker. The beaker was then heated to 70 deg C on a heating/ magnetic stirrer. To these, one of three different bars was added, copper, mild steel, or aluminum.



An interesting note here: both beakers started out the same color. The beaker on the right shows the dramatic bleaching effect of elevated peroxides. Two of the samples submitted by the test group exhibited “this phenomena” in the tank sample. (Cgoodwin, fpmbstca)

fpmbstca WVO Tank

The graph below illustrates peroxide value versus time for the three different metals, copper plus antioxidants/metal deactivator, WVO no metal bar.



Note the Copper reached a peak of 145 Meq/l at about 40 hours at which point the rate of the degradation of the peroxides began to exceed their productions. Degradation products of peroxides and hyperperoxides include aldehydes, ketones, dimers, trimers, and polymers.

A comparison of the five different samples representing the number of hours required for each to reach a peroxide value of 50 mEq/l.

Copper	12 hours
Mild Steel	60 hours
Aluminum	110 hours
No Metal	132 hours
Copper plus antioxidant/metal deactivator	192 hours

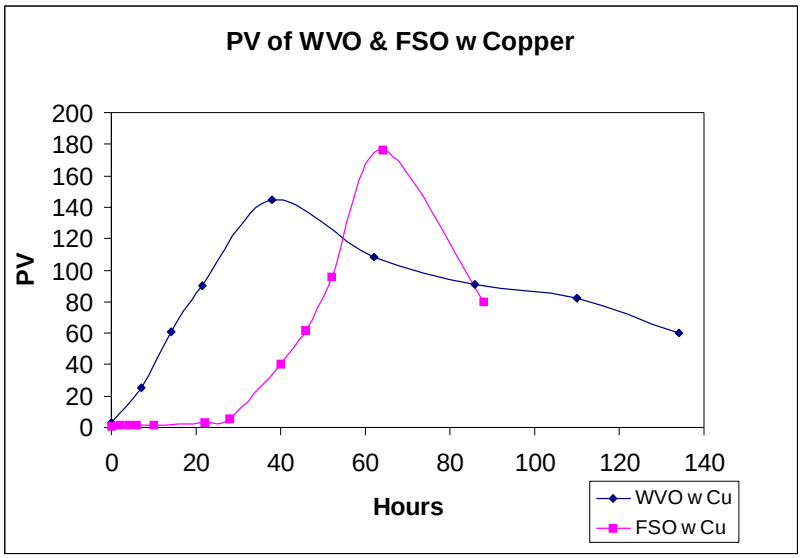
It is important to note here that no correlation is suggested between the times required to initiate rapid oxidation reported in this study and “real life” operating conditions nor is it felt that any such relationship can be formulated. These test conditions rapidly accelerate oxidation by agitation, which greatly increases the exposure of the oil to oxygen. The only conclusions that may be drawn are then relative differences between different pro-oxidants, no pro-oxidant, and copper pro-oxidant with antioxidants and metal deactivator.

Indeed the “real life” mechanism is believed to be that of a thin film of oil constantly spashed on tank surfaces followed by a classic drying reaction. As the level in the tank is drawn down, more surface area is exposed. Then, when the tank is refilled, some of the breakdown products of the drying reactions are swept back into the oil and act as catalyst to further accelerate the oxidative process. The rate of these reactions would again be governed by the factors previously mentioned, oxygen availability, heat, pro-oxidants, light, and time.

Free Fatty Acids And Oxidation

In this next experiment, which will most certainly become the most controversial of this investigation, two samples were once again exposed to the Copper bar at 70 degrees C with constant agitation. The first sample was WVO from the Chinese Restaurant as before, the second sample was fresh Vegetable oil of particularly good analysis.

	Fresh Oil	Chinese Restaurant
FFA	.015 %	3.0 %
Peroxide Value	.3 mEq/l	4.0 mEq/l
Moisture	125 ppm	460 ppm

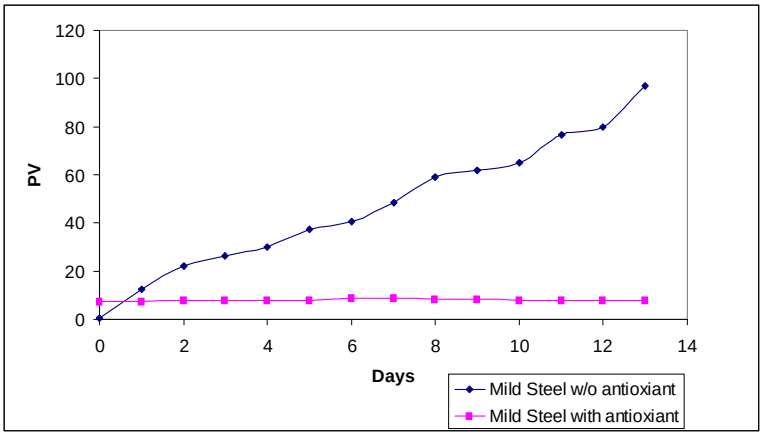


What this experiment demonstrates is that, after the initial delay in the induction period, most likely due to protection offered by the residual natural tocopherol present if fresh oil, the oxidative reaction proceeds quite rapidly. (4) (7) The implication of this finding is that the influence of elevated FFA's or excessive moisture levels as contributing factors to the speed of this reaction is probably quite limited. This is most likely due to the fact that very small quantities of Copper, perhaps on the order of 5 parts per billion, are sufficient to initiate the reaction and once started, it becomes self-sustaining. Therefore, contrary to popular belief, selection of low FFA oil and rigorous de-watering offer little protection from oxidation. The mechanism previously described of FFA's, carried in the water phase, leaching ions which act as pro-oxidants to catalyze the oxidation is still believed to be correct, however very small concentrations of FAA's and water appear to be sufficient to initiate the reaction.

In this next test the bar experiment was preformed once more with Biodiesel of particularly good analysis:

Peroxide Value	.4 mEq/l
FFA	.08 %
Moisture	364 ppm

The conditions of this test were a 400ml sample held at ambient temperature and exposed to a mild steel bar.



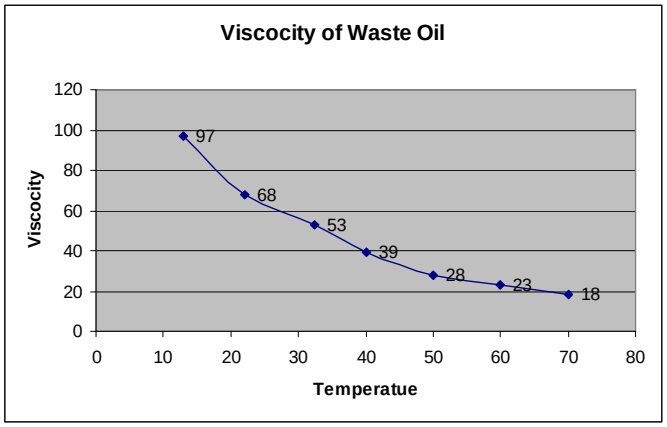
This reaction proceeded rather quickly notwithstanding the fact that it was preformed at room temperature in the presence of mild steel rather than Copper. This was most likely due to the fact that the surface tension of the Biodiesel was considerably less than that of WVO and therefore allowed better absorption of the Oxygen. This may explain why some industrial biodiesel manufacturers are experiencing problems with long term storage of biodiesel.

Oxidation and Polymerization

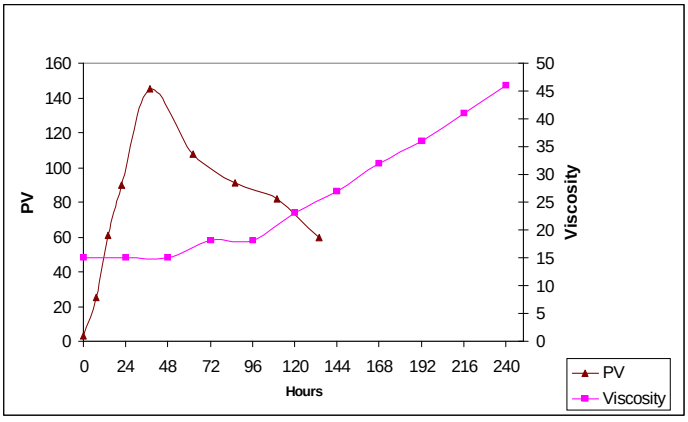
The focus of this next set of experiments was to attempt to demonstrate the link between the oxidation reaction as measured by peroxide value and actual polymer production.

First the copper bar experiments did produce polymers at the oil/air interface:

Secondly, there has been much discussion about the possible increases in viscosity in WVO as the oil polymerizes. This was examined with a Brookfield Viscometer fitted a LV1 spindle. For this experiment once again 400 mls of WVO was placed on the magnetic stirrer/hotplate and viscosity measured as the sample was slowly heated. When the sample reached 70 deg C , it was stabilized at that temperature and the Copper bar added. Peroxide and viscosity were then measured over time.



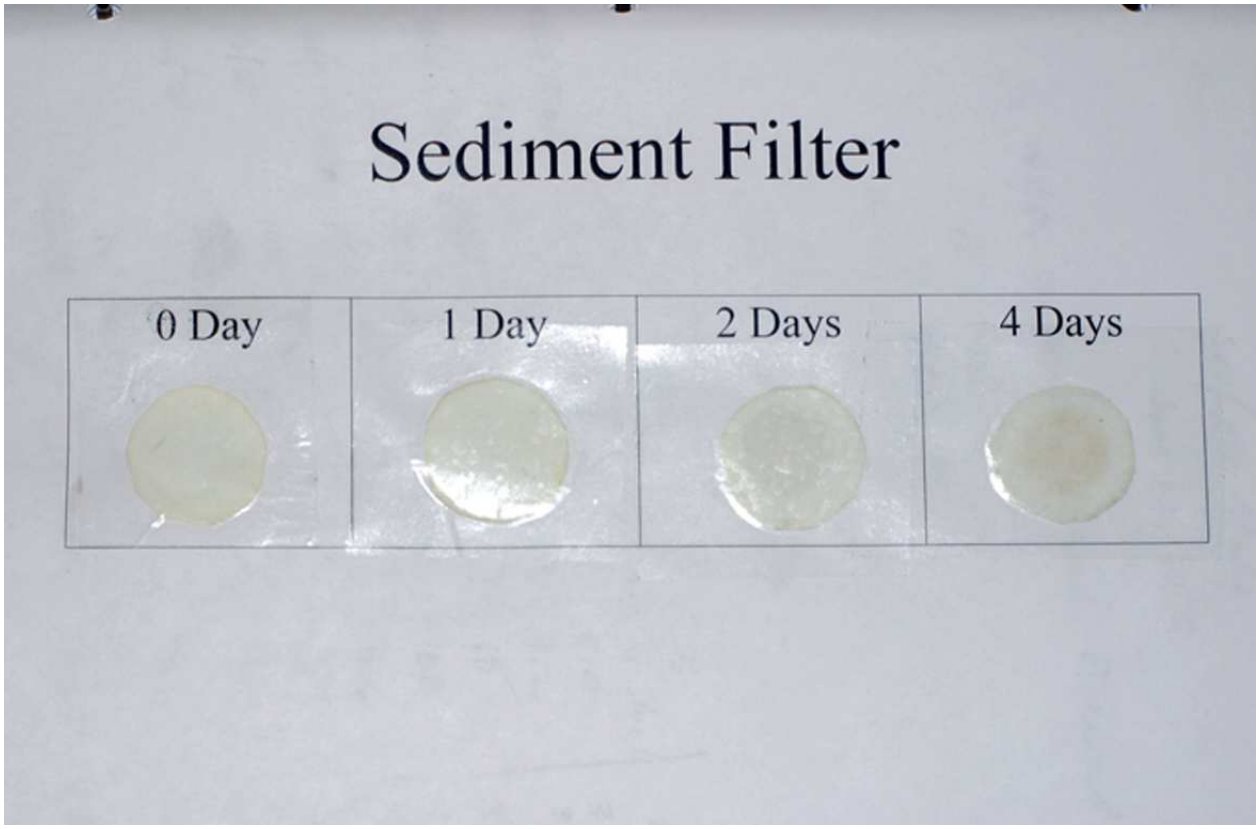
Viscosity versus Temperature



Peroxide and Viscosity (CP) versus Time

It is important to note here that the viscosity increases did not begin until late in the oxidation cycle and therefore might not be of concern in real life conditions. However the test does confirm that viscosity does indeed increase rather dramatically as the oil oxidizes suggesting the accumulation of high molecular weight polymers.

In one final test for polymers, WVO was filtered to .5 microns by vacuum filtration. The oil was then oxidized in the copper bar procedure. The graphic below is of filter pads taken over time.



Although somewhat difficult to see here, there was a definite increase in filterable material over time.

Therefore evidence of polymerization can be demonstrated in a laboratory environment, indications that a problem might exist in a real life setting are as follows:

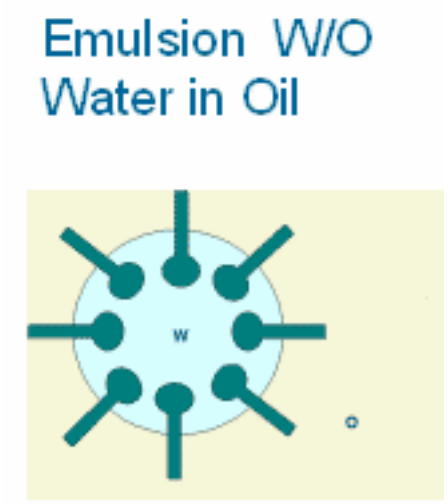
1. Visible evidence of a light brown, “waxy” textured substance, or a dark, reddish brown, harder substance. Note: often mistaken for mold or bacterial contamination, however since vegetable oils contain very little water, such contamination is highly unlikely.
2. “Bleaching” or decolorizing of the oil is strong evidence of the presents of Peroxide Free Radicals, a precursor of Polymerization.
3. The smell of the oil. A strong turpentine odor is a sign of advanced oxidation. This will not be a subtle odor at all, if the oil is highly oxidized the smell will be the unmistakable odor of paint. This powerful odor was observed in the tank sample submitted by cgoodwin.
4. Probably the best indicator is the need for more frequent filter changes. It is interesting to note this summer, during a very hot two-week period, many contributors on several forums noted that they were having to change filters more frequently than they were accustomed to. As stated before, temperature is a major contributor and the 10 to 15 deg C increase such as was experienced during this time would definitely be expected to have an effect.

Hydrolysis and Emulsification

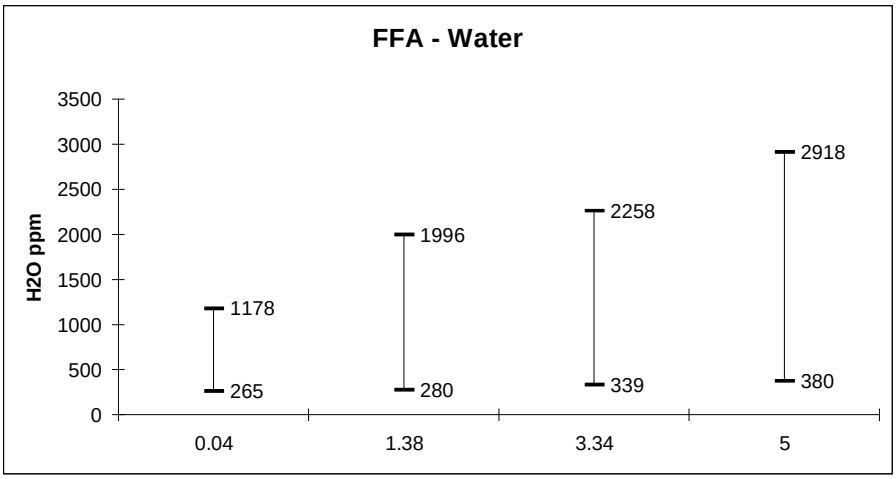
Finally in this next section the hydrolysis reaction was examined. Much discussion can be found regarding acceptable levels of FFA’s in WVO. The general consensus seems to be that, since FFA’s appear to be capable of complete combustion, they do not represent a particular threat. It is suggested however that this may be a case of interrogating the wrong suspect. If we look back at the hydrolysis reaction:

$$\text{Triglyceride} + H_2O \xrightarrow{\text{soap}} \text{Free Fatty Acid (FFA)} + \text{Diglyceride}$$

The reaction produces both a FFA and a Diglyceride. Diglycerides are extremely powerful emulsifiers and are sold commercially for that purpose. They have the ability to strongly bind water in oil with a molecular bond that is not easily broken.



The following experiment was preformed to demonstrate this point. Four samples of Vegetable Oil of varying FFA content were heated to 70 deg C. Then 25 mls of distilled water was added to each and the samples stirred for one hour. The samples were then placed in separatory funnels over night. The oil was separated from the water and then centrifuged for 45 minutes. The data below is of moisture levels before and after the water addition:



What this demonstrates is that high FFA oils are capable of emulsifying large quantities of water. This may be of concern if large quantities of water are available such as would be the case for those who water wash their WVO. However it is unclear if water so tightly bound at the molecular level would present the problems usually associated with high water content oil, such as cavitation. Further research needs to be done in this area.

Recommendations

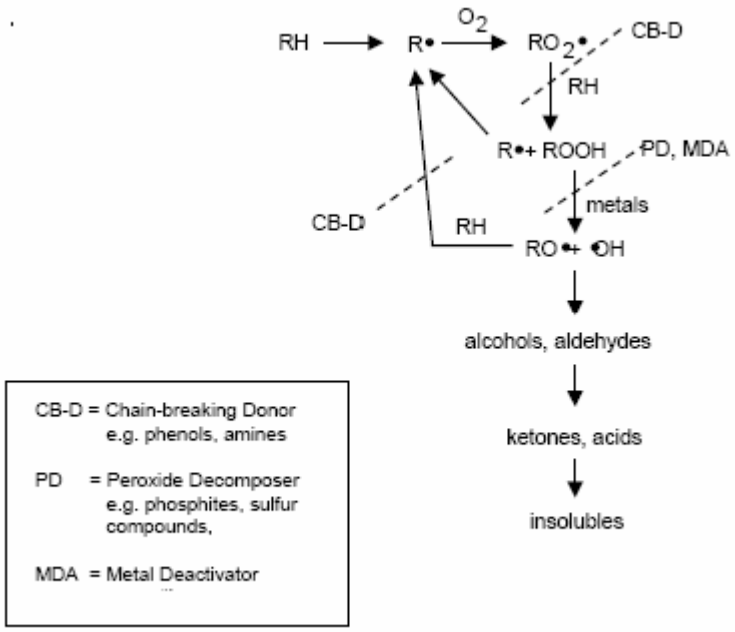
1. Do not allow Copper to come in contact with WVO. This is not revolutionary, many references in the literature site less than 5 parts per billion as the only safe level for copper in vegetable oil. (2) (3) (5) (6)

2. Coat your steel tank.
3. Don't insulate your Veg fuel tank unless absolutely necessary for you local climatic conditions. Heated oil says hot long after the engine is turned off.
4. If a heated fuel pickup is sufficient, use this rather than a heating coil. Keep in mind heat is number 2 on the list of contributors to auto-oxidation.
5. Loop your return. This serves two functions, heat from the remainder of the fuel system is not returned to the tank and secondly, any metallic ions scavenged in the fuel delivery system are not returned to the tank.
6. Don't use diesel fuel additives. One study finds that a dimer acid corrosion inhibitor found in virtually all diesel fuel additives and some diesel fuels greatly destabilizes vegetable oils in concentrations as low as 20 ppm. (3)

7. Do use an antioxidant/ metal deactivator. In conversations with three different commercial antioxidant manufacturers, all made the same, admittedly self-serving, statement that they would not consider the use of vegetable oil as fuel without antioxidant protection. This due to the fact that vegetable oils are, on average, 85% unsaturated and therefore very susceptible to oxidation. One of the three companies proved very helpful and sent several samples to evaluate. They stated that these antioxidants are routinely added to jet fuel and gasoline due to the presence of waxes and other oxidatable products. Interestingly they stated that additives had traditionally not been added to diesel due to the presence of sulfur in diesel that acts as a peroxide decomposer. However, with the ULSD , they were beginning to note evidence of oxidation problems in diesel fuels as well. Testing on food grade additives such as BHT, BHA, TBHQ, and Tocopherol were largely unsuccessful even at five times the FDA maximum allowable addition rate for

vegetable oils of 200 ppm. Testing of a blend of two of the commercial antioxidants with a metal deactivator was very effective and was the basis for the results graphically represented previously in the oxidation studies. An additional benefit of these chemicals is the fact that they are available in very concentrated form making it possible for one ounce of treatment to be sufficient for ten gallons of WVO if no copper or mild steel is present and two ounces per ten gallons if copper and mild steel are present.

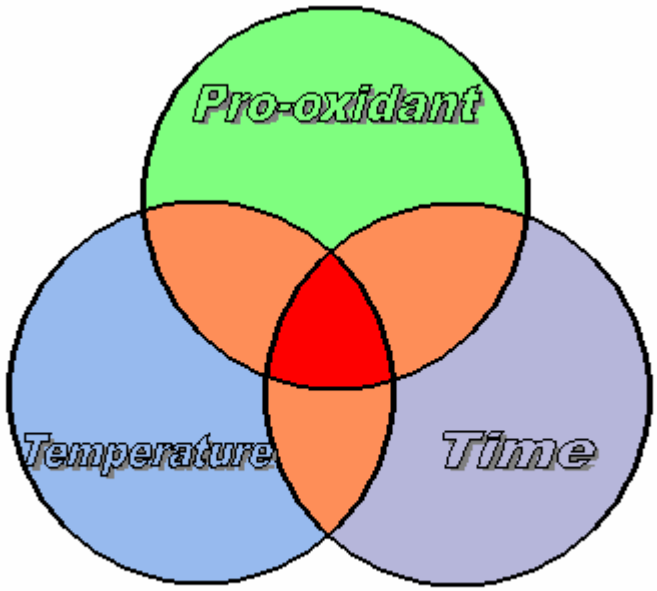
The following is the mechanism by which these additives interrupt the oxidation cycle:



Plans are underway to make this product available if there is interest in the vegetable oil community.

Conclusion

Diesel engines are expected to have a service life of perhaps 300,000 miles or more. Therefore the most fundamental tenet of any vegetable oil conversion should be " do no harm". It is felt that oxidation represents a substantial risk to this longevity. However, understanding and management of the three contributors listed below can greatly minimize this risk The addition of antioxidants and metal deactivators could also be quite helpful in minimizing this risk.



More research needs to be done as to acceptable levels of water in fuel. Toward this end the Karl Fisher unit used in this study can be made available if someone would wish to pursue this further.

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