

ACCELERATED OXIDATION PROCESSES IN BIODIESEL

M. Canakci, A. Monyem, J. Van Gerpen

ABSTRACT. Biodiesel is an alternative fuel for diesel engines that can be produced from renewable feedstocks such as vegetable oil and animal fats. These feedstocks are reacted with an alcohol to produce alkyl monoesters that can be used in conventional diesel engines with little or no modification. Biodiesel, especially if produced from highly unsaturated oils, oxidizes more rapidly than diesel fuel. This article reports the results of experiments to track the chemical and physical changes that occur in biodiesel as it oxidizes. These results show the impact of time, oxygen flow rate, temperature, metals, and feedstock type on the rate of oxidation. Blending with diesel fuel and the addition of antioxidants are explored also. The data indicate that without antioxidants, biodiesel will oxidize very quickly at temperatures typical of diesel engines. This oxidation results in increases in peroxide value, acid value, and viscosity. While the peroxide value generally reaches a plateau of about 350 meq/kg ester, the acid value and viscosity increase monotonically as oxidation proceeds.

Keywords. Diesel, Energy, Engines, Fuel, Oil, Oilseed, Soybean oil.

Biodiesel has come to be recognized as the alkyl monoesters of fatty acids from vegetable oils or animal fats. It is an alternative fuel for diesel engines that can be used neat or in blends with diesel. One drawback of biodiesel is that there is an inverse relationship between biodiesel's oxidative stability and its cold flow properties. Saturated compounds are less prone to oxidation than unsaturated compounds but they raise the cloud point of the fuel. Biodiesel from soybean oil is highly unsaturated. It is very prone to oxidation and its cloud point is about 0°C. The impact of this oxidation on an engine's performance and emissions is not currently understood. The oxidation process produces hydroperoxides, aldehydes, ketones, and acids that change the fuel's properties. Hydroperoxides are the initial products of oxidation at ordinary temperatures. They are very unstable and have a tendency to attack elastomers.

As it oxidizes, biodiesel becomes more viscous. The hydroperoxides can induce polymerization of the esters and form insoluble gums and sediments. Recent research has shown that the oxidation products, sediment and gum, can cause fuel filter plugging (System Lab Services, 1997; Tao, 1995). However, no research has yet been conducted to determine the maximum degree of oxidation allowable for the fuel to be used in diesel engines.

Other fuel properties are also affected by oxidation. A recent study (Van Gerpen et al., 1997) showed that the cetane number of biodiesel increased as the biodiesel

oxidized up to a peroxide value of 80 meq/kg ester. Higher cetane number means that the fuel autoignites more easily in the engine cylinder.

This study was part of a larger effort to relate the chemical and physical processes associated with biodiesel oxidation to the conditions that affect fuel system performance. A companion article to this work describes testing under simulated in-use conditions to determine the impact of oxidized biodiesel on an engine's fuel system (Monyem et al., 1999).

There are a number of existing oxidation test procedures. ASTM D2274, probably the most well accepted measure of stability for diesel fuels, was found to be inappropriate for use with biodiesel (Monyem et al., 1999). The prescribed solvents and filter washing procedures that allow gums and sediments to be separated from diesel fuel are ineffective for biodiesel. An oxidation stability test for lipids, known as AOCS (American Oil Chemists' Society) Cd 12b-92, Oil Stability Index, can be used for biodiesel and has the advantage of being implemented in a commercial instrument. However, the test temperature, 110°C, is quite high. The data presented later indicate that oxidation at high temperatures may induce reactions that would not occur during actual use of biodiesel. The experiments described below held the biodiesel at 60°C which, from the author's experience, is a reasonable estimate for a fuel tank temperature with normal fuel return rates. This test also used oxygen bubbling through the fuel to simulate the aeration that occurs in fuel tanks. The availability of O₂ for oxidation is greater for this case than for actual diesel applications. However, this was found to have no effect on the reaction paths.

The inability of ASTM D2274 to characterize the oxidative stability of biodiesel means that a new procedure is needed. This article presents data to quantify the chemical and physical processes that occur in oxidizing biodiesel. These data should provide the basis for the development of an oxidative stability test for biodiesel.

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This article describes an extensive set of oxidation tests where variables such as temperature, water, and blend level with diesel fuel were investigated. In many cases, the extent of oxidation was carried beyond the level that would likely be encountered in practice. This was done to more clearly identify the trends that are associated with the different test parameters. The tests were intended to assess the impact of the parameters under conditions the fuel can be expected to encounter after it has been supplied to a diesel-powered vehicle and may not be relevant to storage in stationary fuel tanks.

EXPERIMENTAL METHODS

To gain an understanding of the processes that occur during biodiesel oxidation, an accelerated method for measuring oxidation stability was developed. A 1000-mL glass container was filled with 500 to 900 mL of biodiesel. The long-term tests used up to 1800 mL of biodiesel in a 2-L glass container. The particular type of biodiesel used for most of the tests was soybean oil methyl ester (SME) purchased from a commercial supplier (NOPEC Corporation, Lakeland, Fla.). Oxygen (99.6% pure) was supplied through a glass tube with a fritted glass tip so the gas passed through the SME as very fine bubbles. The entire container was submerged in an oil bath held at a constant 60°C. Changing the pressure on the upstream side of a fixed orifice valve varied the O₂ flow rate. These conditions were designed to follow ASTM D-2274 which also uses oxygen bubbling through heated fuel. However, the temperature used for most of the work reported in this study (60°C) was lower than that used by D-2274 (95°C) and a range of oxygen flow rates were used. The range of flow rates studied (0.26×10^{-6} kg/s to 1.85×10^{-6} kg/s) included the prescribed flow rate for D-2274 (1.07×10^{-6} kg/s).

Samples of approximately 50 mL of SME were removed from the glass container at regular intervals and the peroxide value, acid value, and viscosity of the methyl soyate were measured throughout the test. The following methods were used to measure these quantities: AOCs Official method Cd 3a-63 for acid value, Cd 8-53 for peroxide value, and ASTM D-445-88 for kinematic viscosity.

To investigate the metal effect on the rate of oxidation of the SME, two kinds of metals, steel and copper, were immersed in glass containers of SME. A third container of SME was used as a control. The steel (ASTM 1020) and copper strips used were 75 × 20 × 0.5 mm. The strips were polished with fine sandpaper and cleaned with acetone before starting the test. The test conditions were selected to be 12 h at 60°C and the 1.85×10^{-6} kg/s O₂ flow rate. During the test period, a sample was taken every hour to analyze the SME's peroxide value, acid value, and viscosity.

To investigate the effect of chemical structure, methyl esters were prepared from five kinds of vegetable oil. These oils were canola oil, corn oil, safflower oil, sunflower oil, and soybean oil. After purchasing the oils from a local food store, their methyl esters (MEs) were prepared under laboratory conditions. The oxidation test duration was selected to be 240 h at 60°C with the highest (1.85×10^{-6} kg/s) O₂ flow rate.

To measure the influence of temperature on the oxidation of SME, three different temperature levels, 60°C,

80°C, and 97.8°C, were selected for a 12-h test period. The same O₂ flow rate, 1.85×10^{-6} kg/s, was used for all three temperatures. Samples were taken every hour for peroxide value, acid value, and viscosity.

RESULTS AND DISCUSSION

The effect of time, oxygen flow rate, temperature, metals, feedstock type, and antioxidant were tested using the apparatus described in the experimental methods section. Most of these variables were tested individually as deviations from a standard test condition of 60°C and 1.85×10^{-6} kg/s O₂ flow rate.

EFFECT OF O₂ FLOW RATE ON PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

Previous studies (Johnson and Kummerow, 1957; Raghuvver and Hammond, 1967) have shown that the chemical structures of fats, oils, and fatty acid esters change during oxidation. These studies have shown that the peroxide value, acid value, and viscosity increase during oxidation. The availability of air or oxygen is a major factor affecting oxidation. Johnson and Kummerow (1957) found that the peroxide value and viscosity of corn oil at 200°C increased proportionally with the rate of aeration during 24 h of reaction.

Romano (1982) investigated the effect of accelerated oxidation on soybean oil and its methyl ester by aerating the samples (30 L/h) at 140°C for 100 h. He noted that the viscosity of the methyl ester increased 46% and the viscosity of the soybean oil increased 2820%. However, the acid value of the ester increased more rapidly than for the soybean oil.

The influence of the O₂ flow rate on the peroxide value, acid value, and viscosity during a 6-h test conducted for this project, are plotted in figures 1, 2, and 3, respectively. Although the dissolved oxygen concentration was not measured directly in this test, the response to higher O₂ flow rates strongly indicates that the oxygen concentration increased as the O₂ flow rate increased. During the 6-h test period, the greatest increase in the peroxide value, acid value and viscosity of the SME corresponded to the highest O₂ flow rate. The peroxide value, acid value, and viscosity at zero O₂ flow rate did not change during the test period. However, as the O₂ flow rate increased, the rate of increase in the peroxide value, acid value, and viscosity rose also.

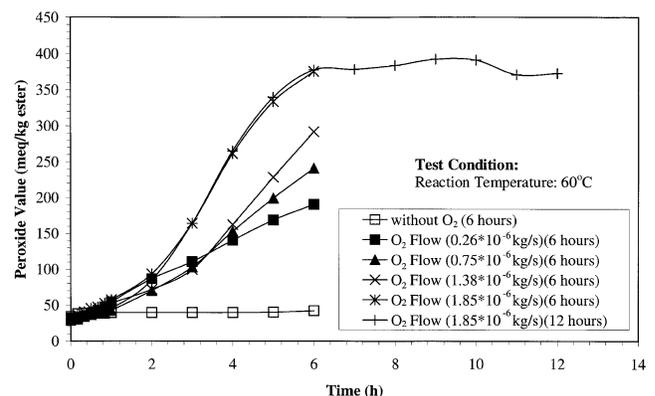


Figure 1—Effect of O₂ flow rate on the peroxide value of SME.

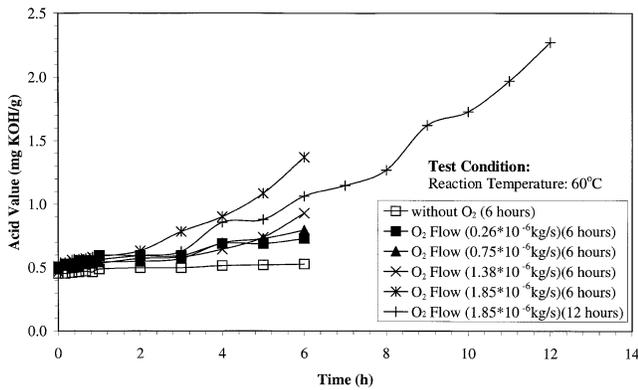


Figure 2—Effect of O₂ flow rate on the acid value of SME.

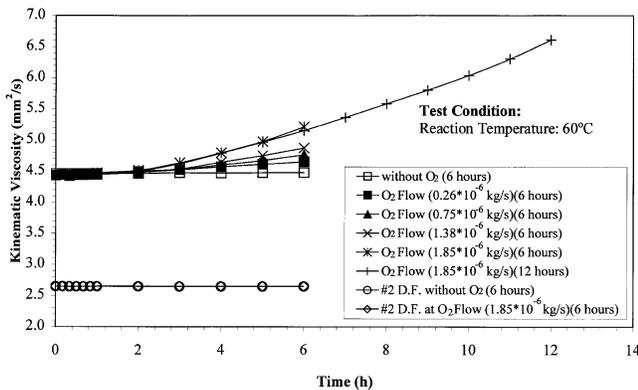


Figure 3—Effect of O₂ flow rate on the kinematic viscosity of SME.

When an additional test was run for 12 h at the highest O₂ flow rate, there was very little change in the peroxide values of the SME between 6 and 12 sample hours.

The data presented on these figures correspond to single measurements, so the uncertainty cannot be determined. However, for the cases when the test condition was repeated for a longer time period, the data show excellent repeatability for the peroxide value and viscosity. The repeatability of the acid value was not as good but was still acceptable. The data show that the peroxide value reaches a plateau at about 375 meq/kg ester and does not increase further. The acid value and viscosity of the SME continuously increased. At the end of the 12-h test period for the highest O₂ flow condition, the acid value and viscosity reached 2.27 mg KOH/g and 6.61 mm²/s, respectively. The strong effect of O₂ flow rate shown by these data indicate that the methyl soyate was not saturated with dissolved oxygen and that the rate of O₂ consumption by oxidation is limited by the availability of O₂.

As a comparison, the viscosities of no. 2 diesel fuel for the 6 h test are also shown in figure 3. The viscosity, peroxide value, and acid value of the diesel fuel did not change after 6 h for either the case of no O₂ flow or with the maximum O₂ flow. When no. 2 diesel fuel was tested for a 6-h test period without O₂ and at the maximum O₂ flow, the peroxide and acid values of no. 2 diesel fuel were zero at the end of both tests.

Figure 4 shows the viscosity plotted as a function of the peroxide value for the different O₂ flow rates. It is clear that the relationship between these two parameters was

identical for all the O₂ flow conditions over the range where data are available. The oxidation reactions that occur in the biodiesel are complex and not well understood but they are known to involve multiple pathways (Chan, 1987). The peroxide value, acid value, and viscosity are indicators of the levels of some of the intermediate products that are formed by these reactions. If the relationship between these indicators stays the same when a variable such as the O₂ flow rate is varied, this is an indication that the oxidation reactions may be following the same pathways, even though the reaction rates may be different. This is an important requirement of any accelerated test. For example, an accelerated test that produced a large viscosity increase without corresponding increases in acid value and peroxide value would be difficult to compare to actual practice. The similarity of the peroxide value-viscosity curves in figure 4 provides part of the justification for using higher O₂ flow as a means to accelerate the oxidation process. While the higher O₂ flow rates caused faster reactions, the manner in which the peroxide value and viscosity increase does not change. Although not shown, plots of the peroxide value versus acid value and acid value versus viscosity also show coincident lines for the various O₂ flow rates.

EFFECT OF EXTENDED TIME ON PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

Du Plessis et al. (1985) studied the oxidative stability of methyl and ethyl esters produced from sunflower oil under various experimental conditions for a test period of 90 days. During the test period, the peroxide value, acid value, and viscosity of the methyl esters increased monotonically with time at temperatures under 30°C, but at 50°C, the peroxide value of the methyl ester started to decrease after about 60 days. The tests of Du Plessis were conducted without bubbling O₂ through the esters. This is reflected in the much longer oxidation times in their test. The tests described here used O₂ addition to accelerate the oxidation process. Some stirring and aeration would be expected to occur in the fuel tank of an operating diesel vehicle but the O₂ level used here is likely to be well beyond what would be encountered in practice. As explained earlier, the O₂ addition is intended to accelerate the oxidation process without changing the reactions.

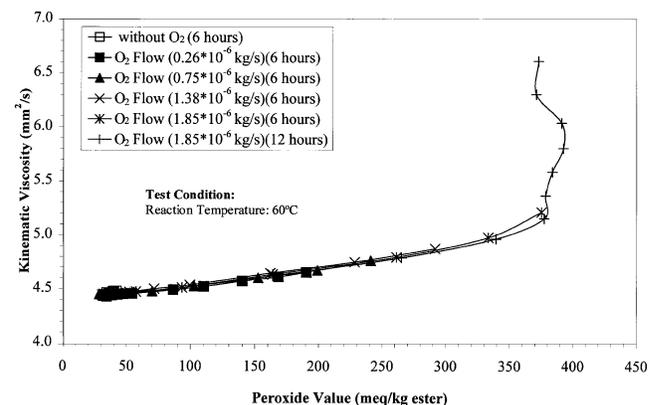


Figure 4—Relationship between peroxide value and kinematic viscosity of SME.

To see whether the drop in peroxide value observed by Du Plessis would occur in the accelerated tests described here, the test duration was extended for a few selected conditions. Besides the 6-h tests and the 12-h test at the 1.85×10^{-6} kg/s O_2 flow described above, a 16-h test at 0.75×10^{-6} kg/s O_2 flow, and a 48-h test at 1.85×10^{-6} kg/s O_2 flow were conducted on SME. Figures 5, 6, and 7 show the changes in the peroxide value, acid value, and viscosity of the SME at extended times. The earlier data are shown for comparison. As mentioned in the previous section for the 6-h tests, the higher O_2 flow rates cause the peroxide value, acid value, and viscosity of the SME to increase more rapidly. When the time was extended to 12 h and 48 h at the highest O_2 flow (1.85×10^{-6} kg/s), the

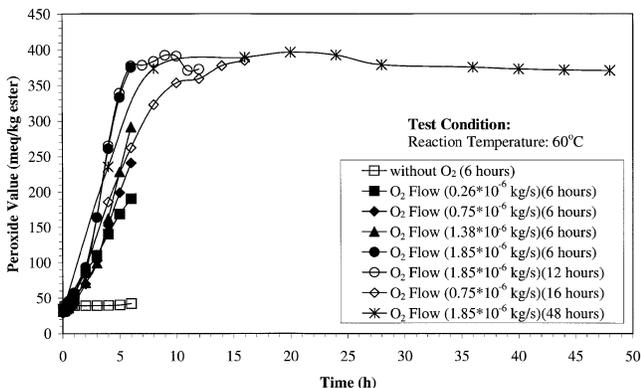


Figure 5–Effect of extended time on the peroxide value of SME.

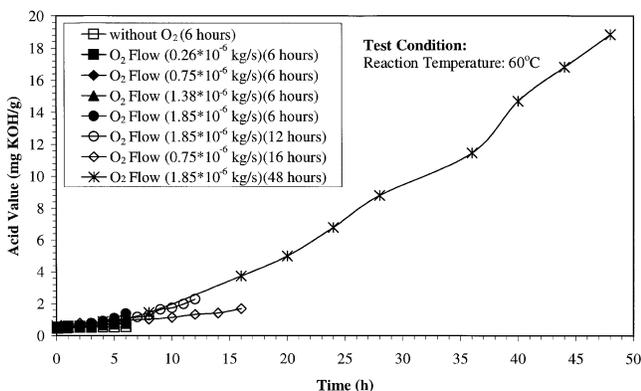


Figure 6–Effect of extended time on the acid value of SME.

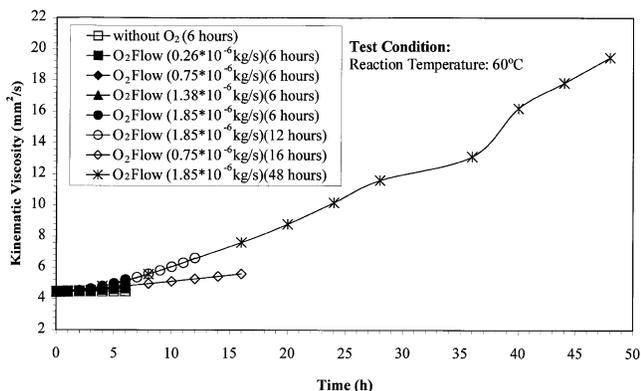


Figure 7–Effect of extended time on the kinematic viscosity of SME.

peroxide value reached the maximum value achieved at the end of the 6-h test, and then stayed almost constant. When the time was extended to 16-h for the 0.75×10^{-6} kg/s O_2 flow rate case, the peroxide value reached the same maximum value noted earlier and appeared to be leveling off. The acid value and viscosity continued to increase.

The trends described here are somewhat different than were observed in the simulated in-use testing of biodiesel mentioned earlier (Monyem et al., 1999). During that testing the peroxide value of the biodiesel rose rapidly to a level between 300 and 400 meq/kg ester as was seen here, but then immediately dropped off again to a low value, in some cases below 30 meq/kg ester. That testing, which was conducted by circulating biodiesel through fuel filters, did not involve deliberate aeration. The rapid formation of peroxides may have exhausted the dissolved oxygen in the fuel which slowed the formation of new peroxides. Existing peroxides would be converted to aldehydes, ketones, and acids causing the peroxide concentration to drop. The progress of the entire oxidation process is believed to be controlled by the rate at which oxygen from the air can diffuse into the biodiesel of the storage tank (Monyem et al., 1999). The highly efficient aeration performed in the current study apparently kept the dissolved oxygen at a level that replenished the peroxides that converted to aldehydes, ketones, and acids, and this kept the peroxide value from declining as rapidly.

EFFECT OF BLENDING WITH DIESEL FUEL ON THE PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

To investigate the influence of diesel fuel blend levels on the oxidation of the SME, two blend levels, 20% and 50%, were selected. The test periods were determined to be 60 h and 240 h for the 20% blend and 12 h, 48 h, and 240 h for the 50% blend. During the tests the temperature was 60°C and the O_2 flow rate was 1.85×10^{-6} kg/s. After analyzing the properties of the blends, the results were compared with 100% SME, which was tested at the same test conditions for 48 h.

The peroxide values, acid values, and viscosities of the different blend levels and the 100% SME are plotted in figures 8, 9, and 10, respectively. For both the 20% and 50% blends, the repeatability of the values can be assessed by the duplicated values at earlier times. After the peroxide value of the 50% blend reached its maximum, it remained almost constant, and then started to decrease, as can be seen in figure 8. For the 20% blend level, the peroxide

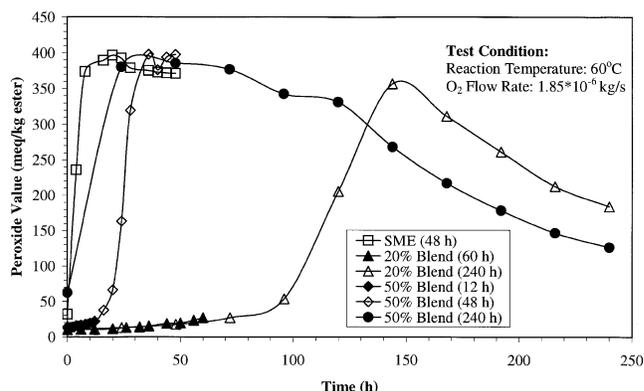


Figure 8–Effect of blend level on peroxide value.

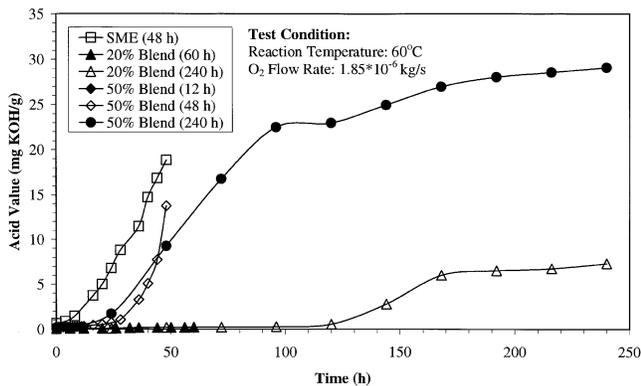


Figure 9–Effect of blend level on acid value.

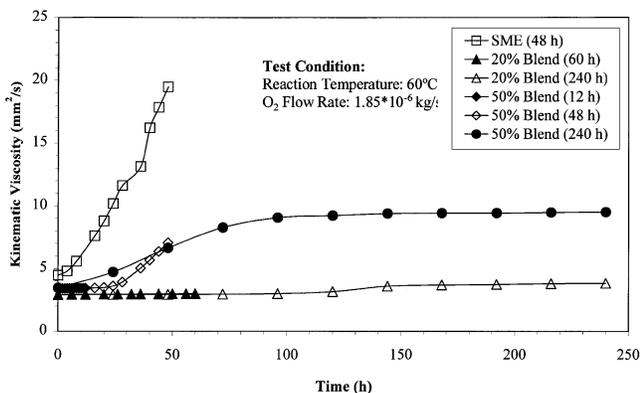


Figure 10–Effect of blend level on the kinematic viscosity.

value took longer to reach its maximum due to the lower concentration of SME, but then it also immediately started to decrease. This behavior is similar to that observed in the simulated in-use testing described earlier. The induction period also varied with the different blend levels. The induction period is a time early in the oxidation process where reactions are slow either due to the need to develop a necessary concentration of reaction intermediates or due to the presence of an antioxidant. The longest induction period as indicated by the rise in peroxide value, acid value, and viscosity was evaluated for the 20% blend level, and the shortest one was for pure SME.

EFFECT OF METALS ON BIODIESEL OXIDATION

The metals used in fuel storage tanks and fuel supply systems in the engine may catalyze the oxidation of the SME. Klopfenstein and Walker (1985) stored soybean methyl ester in steel and plastic containers for 20 months. They found that the samples stored in steel containers had higher peroxide values (80 meq/kg ester) than samples stored in plastic containers (about 60 meq/kg ester). In a similar study by Thompson et al. (1998), steel and glass containers were compared and no differences in the rate of oxidation were found.

Bondioli et al. (1995) found that at 20°C, the peroxide value of biodiesel in an iron container did not increase as much as that of biodiesel in a glass container. At 40°C, the peroxide value of biodiesel in an iron container decreased while the peroxide value of biodiesel in a glass container increased.

The results for the peroxide values of the SME with steel and copper measured for the current study are plotted in figure 11. The increase in peroxide value of SME with steel is very similar to that of the SME without metal, but the increase in peroxide value of the SME with copper occurred more rapidly. There was no significant difference between the final peroxide value reached by the SME under the conditions of this test.

Although the results are not shown here, the acid value and the viscosity also increased more rapidly when copper was present compared with the steel strip and the SME with no metal present, which were about the same.

EFFECT OF TBHQ ON PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

To evaluate the effect of an antioxidant on the oxidation of SME, tertiary-butylhydroquinone (TBHQ) from Aldrich Chemical Supply was used. This is an antioxidant that has been used in several previous studies on biodiesel oxidation (Du Plessis et al., 1985; Klopfenstein and Walker, 1985; Asap and Augustin, 1986; Akoh, 1994). The results of these studies showed that TBHQ can improve the oxidative stability of vegetable oils, esters, and fatty acids.

Du Plessis et al. (1985) investigated the influence of TBHQ on the oxidative stability of methyl and ethyl esters produced from sunflower oil for a test period of 90 days. They reported that TBHQ at a 0.04% concentration was effective in controlling peroxide value increase at 20°C. However, at 30°C and especially at 50°C, the TBHQ was ineffective. They also showed that the viscosity increase could be controlled with TBHQ addition at 20°C and 30°C, but it failed at 50°C.

Three different TBHQ concentrations, 0.4%, 0.04%, and 0.004% (by weight), were tested for this project. The test was run for a 6-h period at the 1.85×10^{-6} kg/s O_2 flow condition and 60°C. As can be seen in figure 12, at 0.004% the TBHQ was able to slow but not stop the oxidation. The higher concentrations of TBHQ, 0.4% and 0.04%, appear to have been effective at eliminating oxidation for the 6 h duration of the test. This was confirmed by the acid value and viscosity measurements. These results are in contrast to Du Plessis (1985) who found TBHQ to be ineffective at elevated temperatures. The reason for this is not clear but is probably related to the fact that Du Plessis conducted long term tests without acceleration as was done here by making oxygen more available.

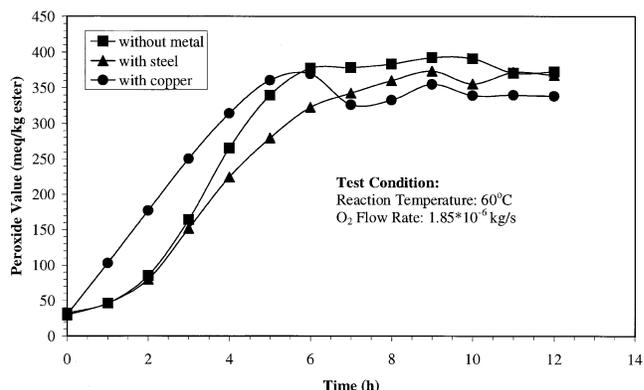


Figure 11–Effect of metals on peroxide value of SME.

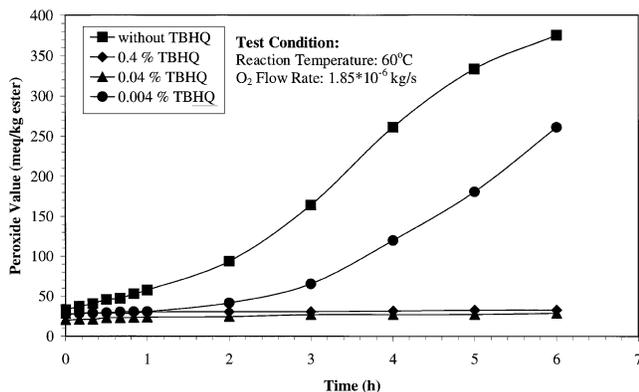


Figure 12—Effect of TBHQ on peroxide value of SME.

EFFECT OF FEEDSTOCK ON PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

The chemical structure of the vegetable oil is an important factor in the oxidation reaction. In previous studies (Raghuvier and Hammond, 1967; Neff et al., 1992), it was shown that the fatty acid composition of a triglyceride has an effect on oxidation. Vegetable oils rich in polyunsaturated fatty acids are much more susceptible to oxidation than vegetable oils rich in saturated or monounsaturated fatty acids (Romano, 1982). Considine (1974) reported that fatty acids with one double bond have oxidation rates about 10 times slower than those with two double bonds and about 15 times slower than those with three double bonds at temperatures in the range of 20°C to 100°C.

The current study investigated methyl esters (MEs) produced from five different vegetable oil feedstocks. The results for peroxide values of the MEs during the test period are plotted in figure 13. After the peroxide value reached its maximum, it stayed almost constant. The MEs oxidized at different rates but appeared to reach a single maximum peroxide value of 300 to 350 meq/kg ester. The corn oil methyl ester might also follow this pattern but the test duration of 240 h was reached before the corn oil had oxidized to this level.

The results for the different rates of oxidation are close to what would be expected. The methyl esters of oils that are less saturated tend to have higher rates of oxidation. One surprising result was that the resistance to oxidation of the soybean oil methyl ester was greater than the sunflower

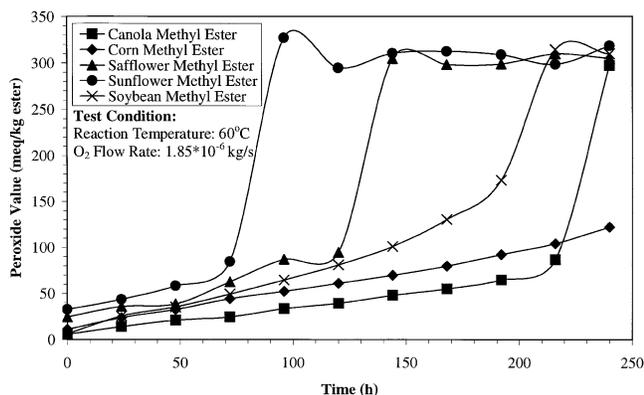


Figure 13—Effect of feedstock on peroxide value.

oil even though their levels of saturation are close. It can also be seen that the increase in the peroxide value for the SME shown in figure 13 is much slower than for the SME shown in figure 5. The SME shown in figure 13 was produced from soybean oil purchased at a food store. The SME shown in figure 5 was purchased as biodiesel from a commercial supplier. To investigate the reason for the difference in oxidation rates for these two samples, the tocopherol (Vitamin E) contents of these two samples of SME were analyzed. These data are shown in table 1. The reason for the slower oxidation of the food store soybean oil methyl ester is clear. The tocopherol levels of the food store oil and its methyl ester were much higher than either of two successive batches of commercial biodiesel. The antioxidant effect of tocopherol will slow the oxidation in a similar manner to the TBHQ discussed earlier. It is not known why the tocopherol level of the commercial biodiesel was so low. It may have been deliberately removed or it may have been consumed by oxidation reactions during storage. Bondioli and Folegatti (1996) have shown that prior storage history of the biodiesel has a strong effect on its oxidative stability.

EFFECT OF TEMPERATURE ON PEROXIDE VALUE, ACID VALUE, AND VISCOSITY

Johnson and Kummerow (1957) investigated the effect of temperature on the oxidative stability of corn oil. They thermally oxidized the oil, which was aerated at 150 mL/min-kg of oil, for 24 h at 120°C, 160°C, and 200°C. Their study showed that the peroxides were not heat-stable, that is, their concentration decreased at higher temperatures even though oxidation was continuing.

Du Plessis et al. (1985) reported the effect of temperature on the peroxide value, acid value, and viscosity of the methyl ester produced from sunflower oil for a test period of 90 days at three different temperatures, 20°C, 30°C, and 50°C. They found that the peroxide value, acid value, and viscosity increased more rapidly with increasing temperature.

The effect of temperature was also investigated for the current study. Three different temperature levels, 60°C, 80°C, and 97.8°C were used. The changes in the peroxide value, acid value, and viscosity of the SME during the 12-h test period are plotted in figures 14, 15, and 16, respectively. As found by Du Plessis, the peroxide value of the SME increases much more rapidly at higher temperatures. Figure 14 shows that at a temperature level of 60°C, the peroxide value reached a plateau in peroxide value after about 6 h. At 80°C, the peroxide value rises much more quickly than at 60°C and reaches the same plateau after about 4 h. For the temperature level of 97.8°C, the peroxide value levels off at about the same time as at 80°C and at about the same peroxide value. As

Table 1. Tocopherol content of soybean oil and SME

	Total Tocopherols* (ppm)
Soybean oil from food store	385.00
Methyl esters of soybean oil from food store	302.00
Commercial methyl esters sold as biodiesel, 1st batch	5.90
Commercial methyl esters sold as biodiesel, 2nd batch	31.00

* Measured by Woodson-Tenent Laboratories, Des Moines, Iowa, using gas chromatography.

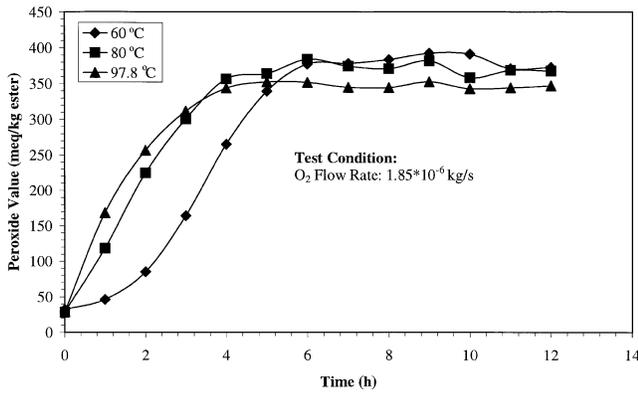


Figure 14—Effect of temperature on the peroxide value of SME.

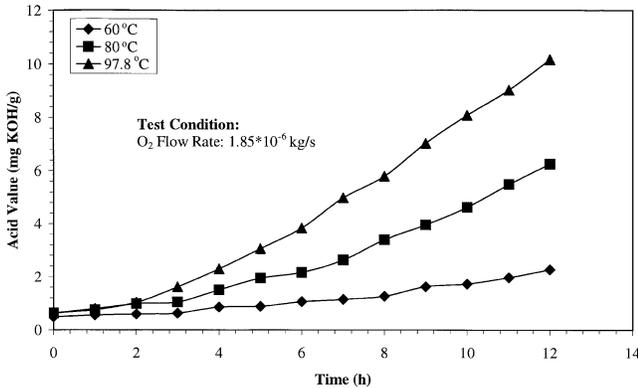


Figure 15—Effect of temperature on the acid value of SME.

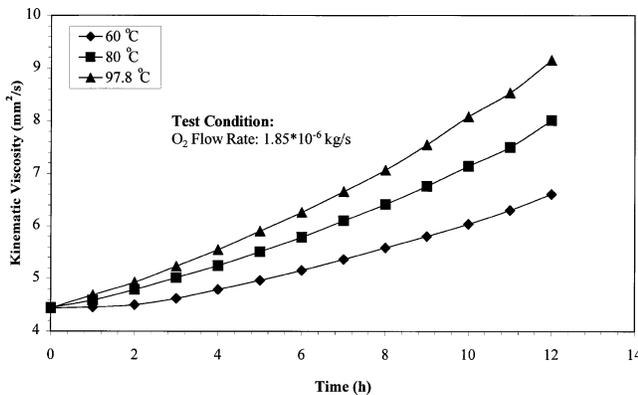


Figure 16—Effect of temperature on the kinematic viscosity of SME.

can be seen in the figures, the higher temperature level also caused the acid value and viscosity of the SME to increase more rapidly.

Figure 17 shows the viscosity of the SME plotted as a function of the peroxide value for each of the three reaction temperatures. While the relationship between these two properties is similar for the three temperatures, the lines appear to be different at higher peroxide values. This indicates that there may be different reaction pathways as the SME oxidizes at the different temperatures. This supports the earlier concern expressed about accelerated oxidation tests that use high temperatures. High temperature tests may not duplicate the phenomena that will occur in practice at lower temperatures. This issue

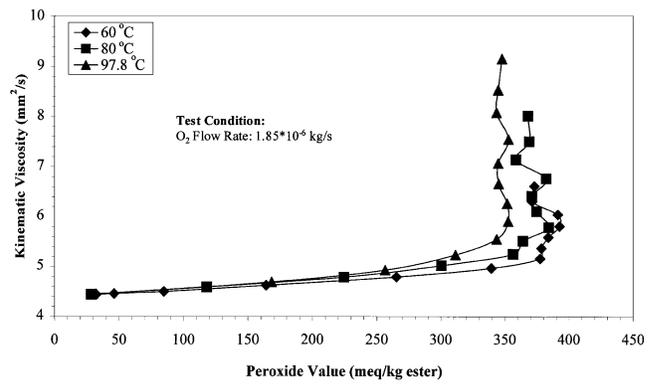


Figure 17—Effect of temperature on the relationship between peroxide value and kinematic viscosity.

merits further investigation, possibly at lower O_2 flow rates, to more clearly identify any differences in the oxidation processes at higher temperatures.

CONCLUSIONS

This project focused on understanding the changes that occur in the fuel when it oxidizes. The following conclusions can be drawn about the oxidation process of biodiesel.

The SME oxidized much more rapidly than no. 2 diesel fuel. The oxidation rate of biodiesel increases with increasing availability of oxygen. The relationship between peroxide value, acid value, and viscosity is the same as the O_2 flow rate is varied. This indicates that accelerating the reactions by increasing the availability of oxygen does not change the reaction pathways.

The maximum peroxide value for all samples was between 300 to 400 meq/kg ester. Initially, the peroxide value rose to the maximum level (300-400 meq/kg ester) and then dropped off.

When biodiesel was mixed with diesel fuel the induction period varied with different blend levels. The shortest period was measured for pure SME and the longest one at the 20% blend level.

Copper has some catalytic effect on the oxidation of the SME, but the effect of steel was found to be minimal.

The antioxidant TBHQ controls the oxidation of the SME at concentrations above 0.04%. The natural concentration of tocopherols also has an antioxidant effect.

The induction periods for methyl esters of different feedstocks were different. This is likely due to a combination of the level of saturation and the amount of natural antioxidants in the feedstock oil.

The oxidation of SME occurs more rapidly at higher temperatures. Changes in the relationship between peroxide value, acid value, and viscosity were observed which indicates that the oxidation reaction pathways may change as the temperature varies.

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