

# **The Impact of Contaminants on Biodiesel Quality**

**Jon H. Van Gerpen, Abdul Monyem, and Mustafa Canakci**  
Department of Mechanical Engineering

**Earl G. Hammond and Liangping Yu**  
Department of Food Science and Human Nutrition

**Iowa State University**  
**Ames, Iowa**

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## ABSTRACT

The methyl esters of vegetable oils and animal fats, known as biodiesel, are receiving increasing attention as an alternative fuel for diesel engines. Although the production of biodiesel involves a relatively simple chemical process, there is potential for various contaminants to be present in the fuel. These contaminants include water, free glycerin, bound glycerin, alcohol, free fatty acids, soaps, catalyst, unsaponifiable matter and the products of oxidation. The objective of this paper is to present data showing the effect of contaminants on biodiesel quality. Small amounts of these various contaminants were added to biodiesel and their impact on the properties and performance of the biodiesel was measured. Samples of biodiesel were also oxidized to varying degrees to study its effect on biodiesel. The study identifies water contamination, bound glycerin, and oxidation as three areas of concern. Biodiesel can absorb up to 40 times more water than conventional diesel fuel. High levels of bound glycerin can cause crystallization and increased viscosity. Oxidation can produce chemical compounds that improve cetane number but also increase the acidity and viscosity of the fuel.

## INTRODUCTION

*Biodiesel*, as used in this paper, is defined to be the alkyl monoesters of vegetable oils or animal fats. It is attracting interest as a renewable alternative fuel for diesel engines. It is produced by chemically reacting the oil or fat with an alcohol in the presence of a catalyst. One of the products of this reaction is biodiesel. In the United States, soybean oil is the most common feedstock, but in Europe, rapeseed oil is used. Because of its low cost, methanol is the most common alcohol but ethanol is used in some cases. All of the work presented in this paper uses biodiesel produced from methanol and soybean oil. This particular form of biodiesel is often called *methyl soyate*.

The American Society for Testing and Materials (ASTM) is currently developing a specification for biodiesel. Although this specification is still in draft form, it will almost certainly contain limits on the amounts of contaminants such as water, alcohol, and glycerin. The limits on these properties are set as compromises between the desire of the engine manufacturer to have no contaminants and the desire of the fuel supplier to have levels that will be easy and inexpensive to meet.

A related problem is that different researchers, running the same standardized tests on biodiesel, have obtained very different results. For example, measured values of the cetane number for methyl soyate have varied between 48 and 60. This difference is well beyond measurement error and is probably attributable to fuel contamination. Thus, in addition to the need to control fuel quality to protect the engine, there is also the need to understand the general relationship between contaminants and fuel properties. This paper describes the current status of a project to determine the effect of contaminants on biodiesel quality.

## RESULTS

This section presents the results of investigations into the allowable values of contaminant concentrations in biodiesel to be used as an engine fuel. The contaminants considered are: unsaponifiable matter, water, free glycerin, bound glycerin, alcohol, free fatty acids, soaps, residual catalyst, and oxidation products.

### Unsaponifiable matter

Typical crude soybean oil contains as much as 1.6% *unsaponifiable matter*, which consists of plant sterols, tocopherols, and hydrocarbons as major components, with very small quantities of pigments and minerals. The unsaponifiable matter is not affected by ester preparation, so it is likely to be present at similar levels in biodiesel. The unsaponifiable matter probably has no harmful effect on engine performance except possibly for a change in the crystallization onset temperature caused by polar sterols. Therefore, the effect of the unsaponifiable matter on the crystallization properties of neat esters and 20% esters/80% diesel fuel blends was studied. All blends of esters and diesel fuel described in this paper were prepared on a volume basis unless otherwise noted.

Simulated unsaponifiable matter that resembles that found in crude soybean oil was formulated with 70%  $\beta$ -sitosterol, 14%  $\alpha$ -tocopherol, 8% squalane, and 8% squalene. Distilled methyl soyate (purchased from Interchem Environmental of Kansas City, MO) was prepared with various unsaponifiable levels (0%, 1%, 2%, and 3%). A 20% blend of methyl soyate in 80% No. 1 diesel fuel was prepared with the same percentages of unsaponifiables in the blended fuel. Two separate samples were prepared for each unsaponifiable level, and two measurements were made for each sample. Unsaponifiable matter was measured by the AOCS Official Method Ca 6a-40. Crystallization properties were characterized by the cloud point (ASTM Standard Method D2500), pour point (ASTM Standard Method D97) and the crystallization onset temperature ( $T_{co}$ ) as determined by differential scanning calorimeter (DSC) analysis. The  $T_{co}$  was determined as the end point (where the tangent of the peak meets the baseline) of the highest melting transition peak, that is, the lowest temperature at which the sample was completely liquid.

The amounts of unsaponifiable matter measured in several samples of soybean oil and the methyl esters produced from those samples were all between 0.4 to 0.5%, which is on the low end of the expected range. The amounts of unsaponifiable matter in both crude and RBD (refined, bleached, and deodorized) oils, were not significantly changed (at  $\alpha=0.05$ ) during the preparation, transesterification, and washing of the methyl soyates.

The effect of unsaponifiable matter on the crystallization properties of biodiesel and its blend with No. 1 diesel fuel is shown in Table 1. Unsaponifiable matter up to 2% caused no adverse effect on  $T_{co}$  in the neat esters. The  $T_{co}$  of ester samples containing small amounts (<2%) of unsaponifiables was even slightly less than the neat esters. This was probably due to a melting point depression effect of such "impurities." At the 3% unsaponifiable matter level in the neat esters, the  $T_{co}$  was significantly increased. However, in the 20% esters/No. 1 diesel fuel blends, there was no significant effect on  $T_{co}$  up to 3% unsaponifiable matter. Results of cloud and pour point measurements agreed with those from DSC. Only the sample with 3% unsaponifiables in neat esters had higher cloud and pour points and no difference was found in the 20% blends with No. 1 diesel fuel. It appears that at normally expected levels of unsaponifiable matter, there should be no deleterious effect on the cold flow properties.

**Table 1. The effect of unsaponifiable matter on crystallization properties of neat methyl esters and 20% esters-kerosene blends**

Samples	% Unsaps	$T_{co}$ (°C)	Cloud Point (°C)	Pour Point (°C)
Neat esters	0% (control)	4.7 <sup>a</sup>	-5	-3
	1%	3.8 <sup>b</sup>	-5	-3
	2%	3.8 <sup>b</sup>	-5	-3
	3%	19.1 <sup>c</sup>	8	-3
20% esters w/ 80% #1D	0% (control)	-14.7 <sup>d</sup>	-28	<-36
	1%	-14.9 <sup>d</sup>	-28	<-36
	2%	-14.2 <sup>d</sup>	-28	<-36
	3%	-14.6 <sup>d</sup>	-28	<-36

Values with different superscript in the same row are significantly different at  $\alpha=0.05$

## Water

Water is a major source of fuel contamination. While fuel leaving a production facility may be virtually water-free, once it enters the existing distribution and storage network, it will come into contact with water. Water in the fuel generally causes two problems. It can cause corrosion of engine fuel system components, and it can contribute to microbial growth which produces sludges and slimes that can cause filter plugging [1].

Water will be present in the fuel in two basic forms. It will be dissolved in the fuel or as free water collected at the bottom of the tank. To investigate the problem of water contamination, the solubility of water in methyl esters was measured and compared with diesel fuel. Specifically, the solubility of water in neat methyl esters, a 20% esters/80% No. 2 diesel fuel blend, and No. 2 diesel fuel were compared. The effect of oxidation level of the methyl esters on the solubility of water was also determined. Fuel oxidation was included as a variable since the polar nature of the hydroperoxides formed during oxidation might cause the oxidized fuel to have different solubility properties than the unoxidized fuel.

At 25°C, the solubility of water in diesel fuel is only about 60 ppm [2]. This is quite low and probably results in no adverse effects. ASTM standard D975 for No. 2 diesel fuel allows up to 0.05% water (500 ppm) which includes both dissolved and free water. With No. 2 diesel fuel, most of the water will be present as free water.

Four fuel samples, highly-oxidized Interchem methyl esters with a peroxide value (PV) of 124, freshly made methyl esters with a PV of 20, a 20% blend of methyl ester in 80% No. 2 diesel fuel, and No. 2 diesel fuel, were vigorously mixed with an equal volume of water. The water content in the fuel phase was then determined by Karl Fischer titration after 0, 1, 3, 18, 24, and 120 hours of mixing.

Table 2 summarizes the results from the water solubility tests. The data shown for zero hours was the baseline case before water was added. Karl Fischer titration values were zero or negative when samples of highly-oxidized Interchem methyl soyate were titrated. This result may have been caused by re-oxidation of the iodine ion, formed during blank titration of the solvent methanol, by the peroxides in the highly oxidized methyl soyate (PV=124). Slight signs of the re-oxidation were observed during the titration of freshly-prepared methyl soyate (PV=20), however, positive titrations were obtained with this sample. The freshly-prepared esters, vacuum-dried after washing with water, had a fairly low water content of about 40 ppm, which was almost as low as that of No. 2 diesel fuel. When mixed vigorously with water, the methyl soyate was saturated with water in one hour, and the water level in the esters did not increase after 5 days of mixing. There was no change in the peroxide value of the ester samples during the mixing. The saturation level of water in methyl soyate was about 40 times greater than that of diesel fuel and was close to the 1500 ppm level, which had been observed for water-washed esters before vacuum drying. The diesel fuel had a very low water content at the start of the test, about 28 ppm, and no increase was observed after 18 hr of vigorous mixing. The values reported for the solubility of water in diesel fuel, 28 ppm, 81 ppm, and 30 ppm are very low and their differences are not statistically significant. Their average is close to the value mentioned above for No. 2 diesel fuel. The 20% blend of methyl soyate in 80% diesel fuel had a water

**Table 2. Water contents (ppm) in various methyl soyates, No. 2 diesel fuel and 20% esters-diesel fuel blend after vigorous mixing with water for various periods at 25°C.\***

	0	1 HR	3 HR	18HR	1 D	5 D
Methyl soyate (PV=124)	0	0	0	0	-	-
Methyl soyate (PV=20)	37 <sup>c</sup>	1460 <sup>a</sup>	1595 <sup>a</sup>	-	1255 <sup>b</sup>	1225 <sup>b</sup>
20% Blend (PV=20)	40 <sup>a</sup>	37 <sup>a</sup>	38 <sup>a</sup>	-	33 <sup>a</sup>	45 <sup>a</sup>
Diesel fuel (No.2)	28 <sup>a</sup>	-	81 <sup>a</sup>	30 <sup>a</sup>	-	-

\*The values are the average of duplicate measurements.

Values with different superscript in the same row are significantly different at  $\alpha=0.05$

**Table 3. The solubility of glycerin in methyl esters**

Mixing time	4 hr	24 hr	48 hr
% free glycerin in ester	0.072	0.082	0.144

content similar to diesel fuel, and there was no increase in water content after an extended period of vigorous mixing. These results suggest a possible separation of free water if water-saturated esters are blended with diesel fuel.

The conclusion of this study of water contamination is that water is a much more significant issue for biodiesel than for diesel fuel. Methyl soyate can contain up to 40 times more dissolved water than diesel fuel. In fact, if methyl soyate comes into contact with free water during transport and storage, which is a virtual certainty if the existing infrastructure is used, it will absorb 1200-1500 ppm of this water. This is well above the 500 ppm level allowed by the current specification. The greater solubility of water in methyl soyate will require that either biodiesel be transported and stored with special procedures or the acceptable level of water be raised to 1500 ppm. It is unclear whether the higher solubility of water in pure biodiesel would have any adverse impact on engine operation.

### Free Glycerin

Free glycerin, a product from the transesterification reactions, is not present when esters are washed thoroughly with water. However, glycerin may be present in biodiesel as a result of inappropriate processing, such as insufficient separation of the glycerin phase or insufficient washing by water after separation. Glycerin will also be present when distillation is used as the primary mechanism for its removal. Free glycerin in the fuel is suspected to contribute to deposit formation in the engine.

Distilled methyl esters purchased from Interchem (Kansas City, MO) were mixed with pure glycerin, and the free glycerin content of the ester phase was measured by the AOCS Official Method Cc 17-79 after 4 hr, 24 hr, and 48 hr of vigorous mixing. To determine the effect of water on the solubility of glycerin in methyl esters, distilled methyl esters were mixed with a 1:1 (v/v) mixture of pure glycerin and distilled water. The free glycerin content in the ester-phase was measured by the AOCS Official Method Cc 17-79 after 4 hr, 8 hr, 48 hr, and 72 hr of vigorous mixing.

The results are presented in Table 3. The solubility of glycerin in methyl esters was quite low. Even after 48 hr of mixing, the free glycerin content shown in Table 3 was less than 0.15%.

### Bound Glycerin

At the end of the transesterification reaction to produce biodiesel, a portion of the original triglyceride (TG) from the soybean oil will remain unreacted. Another portion will be partially reacted to monoglyceride (MG) and diglyceride (DG). Collectively, these compounds will be referred to as *bound glycerin*. When 100% excess alcohol is used (2.0 times theoretical) the amount of unreacted TGs should be essentially zero [3]. However, some MGs and DGs may be present. Due to their polarity, these partially reacted glycerides should be preferentially attracted to the glycerin phase and mostly removed when the phases are separated.

The current specification level of total glycerin in the National Biodiesel Board (NBB) specification is 0.24%, which includes the bound glycerin and free glycerin. For soybean oil, this translates into 0.92% MG if all the glycerin is present as MG, and 1.59% DG if all the glycerin is present as DG.

There are two reasons for keeping the amount of bound glycerin low. First, if the bound glycerin is in solution and is injected into the engine, there is suspicion that it will cause carbon deposits on the fuel injector tips and piston rings. This suspicion is apparently based on historical experience with trying to use vegetable oils as diesel fuel extenders in the 1970s [4]. The second reason for controlling the amount of bound glycerin is that the partially reacted glycerides, particularly the saturated MGs, have very low solubility in methyl esters and require high temperatures to keep them from crystallizing. Evaluation of the deposit formation tendency of bound glycerin requires extensive engine testing and is beyond the scope of the current study. This study will focus on the effect of bound glycerin on the crystallization properties of biodiesel. Some limited data will be presented on the effect of

**Table 4. Composition of material removed from plugged fuel filter.**

Isolates	% in Fuel Filter Sample	Fatty acid composition, %				
		16:0	18:0	18:1	18:2	18:3
MG	14%	60.8	35.9	1.7	1.37	0.15
DG	11%	14.9	6.3	29.6	44.5	4.68

bound glycerin on the *carbon residue*, a rough indicator of a fuel's tendency to form deposits. Data published elsewhere [5] was also collected to determine the impact of bound glycerin on fuel viscosity. These tests showed the effect to be small as long as crystals are not formed.

Table 4 shows the analysis of a creamy paste-like material that was extracted from a plugged fuel filter that had been used with a mixture of 20% biodiesel in 80% No. 1 diesel fuel. The plugged fuel filter was a final filter located immediately before the fuel fill nozzle at a bus refueling station in Ames, Iowa. The paste consisted of about 25% MGs and DGs. The MGs are over 95% saturated, as would be expected since the saturated MGs crystallize at higher temperatures than the unsaturated MGs. There were two surprising results associated with this analysis. First, that the DGs were present in almost as large an amount as the MGs. This was unexpected since the DGs have lower crystallization temperatures than the MGs. Second, that the DG composition is not skewed toward the saturated species but rather approximates the fatty acid composition of the original soybean oil. At the start of this project it was expected that the principal compounds to be involved with crystallization would be saturated MGs. However, based on the data presented in Table 4, the study was expanded to include DGs.

**Crystallization of Pure Monoglycerides and Diglycerides** - Monoglycerides and diglycerides should be present in methyl soyate in very small amounts when transesterification is properly executed. However, as noted above, both MGs and DGs were found in large amounts on plugged fuel filters. Due to their high melting points and polar characteristics, MGs and DGs, especially saturated MGs and DGs, may cause crystallization problems in fuels.

Samples of pure MGs and DGs in methyl ester were prepared by dissolving three MGs (monopalmitin, monostearin, and monoolein) and one DG (dipalmitin) in heated methyl esters. The esters were distilled esters (from Interchem Environmental) that had been found to have very low levels of MG and DG.

The effects of the pure MGs and DG on the crystallization of methyl esters are presented in Table 5. In addition to the crystallization onset temperature,  $T_{CO}$ , measured by Differential Scanning Calorimetry (DSC), the pour point (PP), by ASTM standard method D97, and the cloud point (CP), by ASTM standard method D2500, were measured also. The values in the table are the average of duplicate measurements. The presence of the MGs and DG, up to 1%, did not change the pour point of the esters samples. However, the cloud point of the samples increased with increasing amounts of the saturated MGs or DG, and even the sample with 0.05% saturated MG had a CP significantly higher than that of the control. Dipalmitin had a similar effect on the crystallization properties of the methyl esters as was found for monopalmitin. This was surprising because the DGs generally have higher crystallization temperatures. Monoolein (up to 2%), as expected, had no effect on the CP and PP of the esters. This confirmed observations made about the fatty acid composition of MGs that were collected from the plugged fuel filter. About 95% of the MGs in the plugged filter sample were saturated MGs. Unsaturated MGs seemed not to contribute to the crystallization of the fuels at low temperature. Determination of  $T_{CO}$  from DSC thermograms was difficult (thus, not very reproducible) for the samples with less than 0.5% MG because the melting-transition peaks of the MGs were very flat on the baseline in this range. This was especially true for monostearin. For the same reason, the DSC analysis for  $T_{CO}$  was not very useful for 20% ester blends with less than 1% MG. However, distinctive MG peaks were not observed with the samples with less than 0.25% monopalmitin and with less than 0.20% monostearin. Apparently, the cloud of crystals that was observed in measuring the CP of the samples has a very low melting enthalpy so the melting of the crystals was not detected as a distinctive peak in the DSC thermograms. For this reason, the trends of the CP and  $T_{CO}$  data did not agree well.

**Table 5. Crystallization properties of neat methyl esters with various amounts of pure monoglyceride or diglyceride.**

% MG or DG in esters	l-monopalmitin			l-monostearin			monoolein		dipalmitin	
	T <sub>co</sub> (°C)	CP (°C)	PP (°C)	T <sub>co</sub> (°C)	CP (°C)	PP (°C)	CP (°C)	PP (°C)	CP (°C)	PP (°C)
2.0	57.5	-	-	56.5	-	-	-6	-3	29	0
1.0	47.4	22	-3	51.6	26	-3	-6	-3	21	-3
0.75	-	19	-3	-	26	-3	-	-	-	-
0.6	-	-	-	-	-	-3	-6	-3	14	-3
0.5	17.7	10	-3	55.3	22	-3	-	-	11	-3
0.4	15.0	8	-3	54.8	11	-3	-6	-3	5	-3
0.3	11.7	1	-3	50.0	9	-3	-	-	1	-3
0.25	4.4	5	-3	18.2	7	-3	-	-	-	-
0.2	-	1	-3	3.8	7	-3	-6	-3	-3	-3
0.1	-	-3	-3	-	-1	-3	-	-	-4	-3
0.05	-	-4	-3	-	-4	-3	-	-	-	-
0 (control)	4.7	-6	-3	4.7	-6	-3	-6	-3	-6	-3

**Effect of Bound Glycerin on the Carbon Residue** - The carbon residue is sometimes used as an indicator of a fuel's tendency to produce in-cylinder deposits. Varying amounts of MG and TG were added to a commercially available biodiesel (NOPEC Corp., Lakeland, FL) to vary its total glycerin level. The total glycerin was calculated by taking the fraction of the MG, DG, or TG times the ratio of the molecular weight of glycerin to the molecular weight of the glyceride. The total glycerin is 26.2% of the MG concentration and 10.6% of the TG concentration.

Figure 1 shows the Ramsbottom Carbon Residue (ASTM D 524) for different levels of total glycerin in the biodiesel. The test was conducted on 100% of the sample rather than the normal 10% distillation residue. This is due to the difficulty of obtaining a 10% distillation residue for biodiesel without cracking. Figure 1 shows that while the carbon residue increases when TGs are added to raise the total glycerin, the carbon residue is not affected when the increase in total glycerin comes from MG. The baseline biodiesel used for this test had a total glycerin level of 0.15% and a carbon residue of 0.08%. When this biodiesel was filtered through a packed bed of silica gel to remove the bound glycerin, the carbon residue was 0.06%.

**Discussion of the Bound Glycerin Specification** - If all of the 0.24% bound glycerin allowed by the NBB specification were present as MGs, then this would correspond to 0.92% MGs. However, in soybean oil-based biodiesel, only about 15% of the MGs are saturated. The crystallization onset temperature data presented in Table 5 indicated that saturated MGs amounts over 0.25% for monopalmitin and 0.20% for monostearin would begin to crystallize. The cloud point indicates that crystals will form even at saturated MGs concentrations as low as 0.05%. If all of the bound glycerin is present as MGs, and the MGs composition is the same as for soybean oil, the amount of monopalmitin and monostearin should be about 0.10% and 0.04%, respectively. This should raise the cloud point of the fuel by 2-3°C.

### Alcohol

Methyl alcohol is the most common alcohol used for producing biodiesel although ethanol is used in some cases. When the tranesterification of soybean oil is conducted with 100% excess methanol, about half of the excess methanol is in solution with the ester phase and half is with the glycerin phase. If the biodiesel is washed with water when the tranesterification reaction is complete, there should be very little alcohol left since the alcohol is more soluble in the water than in the biodiesel. Further, if the biodiesel is vacuum dried to remove the residual water from the washing operation, any remaining methanol should also be removed.

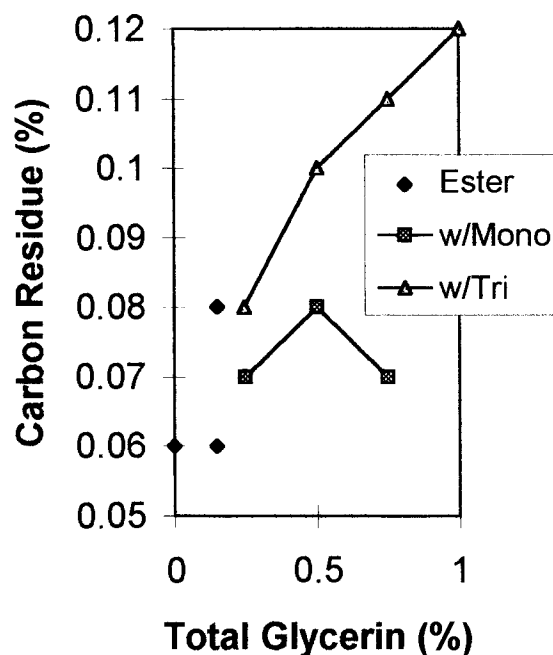


Figure 1. The Effect of Total Glycerin on the Carbon Residue

High concentrations (>5%) of methanol could have an impact on fuel lubricity and cetane number but low concentrations (<1%) should have no measurable effect. The only fuel or engine parameter likely to be affected by the residual alcohol is the flash point. Figure 2 shows the flash point of biodiesel with varying amounts of methanol and ethanol. If 100°C is set as the minimum allowable flashpoint for biodiesel, this will be exceeded by a methanol fraction between 0.18 and 0.22%. The allowable limit for ethanol is slightly higher at 0.26%. Since there is no known deleterious effect associated with these small concentrations of methanol, there does not seem to be any reason to place restrictions on alcohol except as dictated by the flashpoint restriction.

### Free fatty acids, soap, and catalyst

Free fatty acids, soap, and catalyst are treated together because they are related compounds. Most biodiesel is produced using alkaline catalysts such as sodium methoxide, sodium hydroxide, or potassium hydroxide. Any free fatty acids that are present will react with the alkaline catalyst to form soaps. These soaps are then removed during the washing process. The washing process also removes any residual catalyst.

The primary problem associated with these contaminants is that when the fuel burns in the engine, the metal remaining from the soap or catalyst will be converted to ash. The current specification for the ash content of biodiesel is 0.02% and the value given by ASTM D 975, the standard for No. 2 diesel fuel is 0.01%. The current specification for biodiesel uses the Sulfated Ash (ASTM D 874) rather than the Oxidative Ash used for petroleum-based diesel fuel (ASTM D 482). The method was changed due to the ability of the sulfated ash to better measure ash resulting from sodium or potassium hydroxide, the two major catalysts used in biodiesel production. The limit for biodiesel is set slightly higher than for diesel fuel due to the heavier weight of the sulfate portion of the ash.

To investigate the amount of residual catalyst and soap formed during the transesterification reaction, an experiment was conducted to determine the effectiveness of water washing. A batch of methyl soyate was produced from a food-grade soybean oil using potassium hydroxide as the catalyst. The methyl soyate was separated from the mixture of methyl soyate, soap, and catalyst by washing with distilled water. The washing process consisted of vigorously mixing 100 cc of distilled water with 200 cc of raw methyl soyate and then, after waiting about 15 minutes, the water and ester phases were separated. This process was repeated seven times and a fresh batch of distilled water was used each time.

The amount of soap and residual catalyst in the methyl soyate was determined by adding a sample of the wash water to a larger quantity of ethanol and titrating with 0.01N HCl using a phenolphthalein indicator solution.



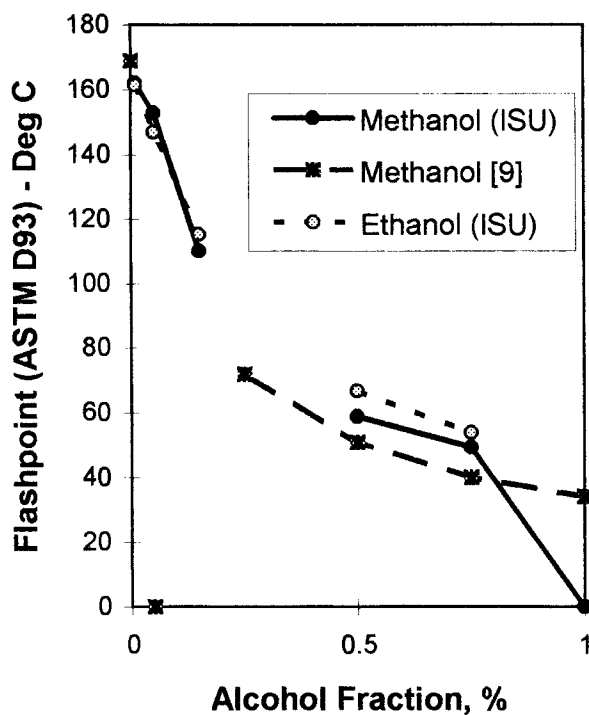


Figure 2. The effect of alcohol on the flashpoint of biodiesel

For the soap measurement, 4-5 drops of bromophenol blue indicator solution was added and the titration continued to the yellow end point.

The percentage of soap and catalyst in the unwashed methyl soyate, wash water, and glycerin are shown in Table 6. The unwashed methyl soyate was found to have 0.149% soap content and no measurable catalyst. When this methyl soyate was washed, the first batch of wash water contained most of the soap and a trace of catalyst was found. The second and third batches of wash water contain less soap and no measurable catalyst. The other batches of wash water contain essentially no soap or catalyst. The level of soap indicated is equal to that measured on the distilled water used for washing and is attributed to a bias caused by the phenolphthalein solution. For the calculations described later, the soap shown for distilled water was subtracted from the other quantities. Table 6 also shows that most of the soap and catalyst are present in the glycerin phase.

Table 6. Percentage of soap and catalyst in wash water, unwashed methyl soyate and glycerin.

Sample	% Soap	% Catalyst
Unwashed methyl soyate	0.149	0
1st washing	0.249	0.015
2nd washing	0.038	0
3rd washing	0.018	0
4th washing	0.015	0
5th washing	0.015	0
6th washing	0.015	0
7th washing	0.015	0
distilled water	0.015	0
glycerin phase	6.058	7.173

As mentioned earlier, the ash standard for diesel fuel is 0.01%. If this standard is applied to biodiesel, then it is necessary to get the residual catalyst below 0.015% since potassium makes up only about 70% of the catalyst mass. The measurements presented here indicate that this level is achievable by 1-2 water washes.

### **Oxidation of Biodiesel**

Methyl soyate is more prone to oxidation than esters from more saturated feedstocks and metals that can catalyze oxidation reactions are frequently present in fuel storage tanks. Upon oxidation, the chemical compositions of methyl esters will be changed, and this can alter the properties of biodiesel. When this process occurs at ordinary temperatures, the initial products are hydroperoxides formed by the addition of oxygen to a carbon atom adjacent to a carbon-carbon double bond [7]. Generally, at this step, the double bond is left intact. The extent of this level of oxidation can be characterized by the *peroxide value*. As oxidation proceeds, the peroxides may split and form aldehydes and short chain acids.

When esters are used as fuel, an important consequence of oxidation is that the hydroperoxides are very unstable and tend to attack elastomers. In addition, the hydroperoxides can induce polymerization of the esters and form insoluble gums and sediments. Sediment and gum formation can be a problem with diesel fuel also, although the unsaturated nature of soybean-based biodiesel may aggravate the problem. Recent engine durability testing with soybean-based biodiesel has shown that oxidized biodiesel may be subject to fuel filter plugging problems caused by sediment and gum formation [8]. The final stage of the oxidation process produces acids that cause corrosion in the engine fuel system.

One objective of this project was to determine whether oxidation could be responsible for some of the differences that have been observed in the cetane number of biodiesel. In particular, biodiesel that has been distilled is generally observed to have a higher cetane number than undistilled fuel.

If biodiesel has been distilled to remove the high boiling point materials such as monoglycerides and glycerin, the natural antioxidants such as tocopherol are also removed. To investigate the effect of removing the natural antioxidants, methyl esters freshly prepared from refined vegetable oil were distilled under vacuum. The distillates were collected from 120°C-150°C at less than 0.05 torr. Peroxide value (PV) and fatty acid composition of the esters were measured before and after distillation and were found to be very similar.

The freshly prepared and distilled methyl esters were oxidized under fluorescent light with continuous stirring at room temperature. The peroxide value was measured every two days by the AOCS Official Method Cd 8-53. The oxidation curve for distilled and nondistilled methyl esters is presented in Figure 3. The peroxide value of the freshly prepared, nondistilled esters increased almost linearly with increasing time during the oxidation period. It took 24 days for these esters to reach a peroxide value of 80. However, the distilled methyl esters oxidized much faster. It took only 6 days to reach a peroxide value of 96. Distillation apparently removes the naturally occurring antioxidants without changing the fatty acid composition of the esters.

It was suspected that changing the oxidation level of the biodiesel would have an impact on the cetane number since peroxide compounds have been proposed as cetane improvers [9]. Table 7 shows the results of cetane number measurements on the samples described in Figure 3, before and after oxidation.

As can be seen in the table, when the freshly prepared esters were oxidized to a peroxide value of 81, the cetane number increased from 47.8 to 54.6. A soybean oil with a peroxide value of 81 would generally be considered to be rancid. However, methyl soyate with a high peroxide value does not always have the unpleasant smell usually associated with rancidity. The cetane testing of the distilled esters showed that when the cetane number was determined before oxidation occurred, the cetane number was the same as before distillation. The decrease from 47.8 to 46.8 is not considered to be significant. However, as with the undistilled esters, there was a large increase in cetane number as the esters were oxidized, from 46.8 to 55.4. While the reason for the cetane number increase is not entirely certain, it is likely that the hydroperoxides formed during the oxidation of the esters are responsible. Dialkylperoxides have been shown to be strong cetane enhancers [9] and hydroperoxides are likely to increase the cetane number also.

To further investigate the effect of oxidation on the cetane number of biodiesel, samples of methyl soyate at six different PV levels were prepared. To produce these samples, freshly prepared, undistilled methyl soyate was mixed in varying amounts with highly oxidized, distilled methyl soyate. Since the previous testing had established that distillation did not affect the cetane number, any changes in cetane number between these samples were

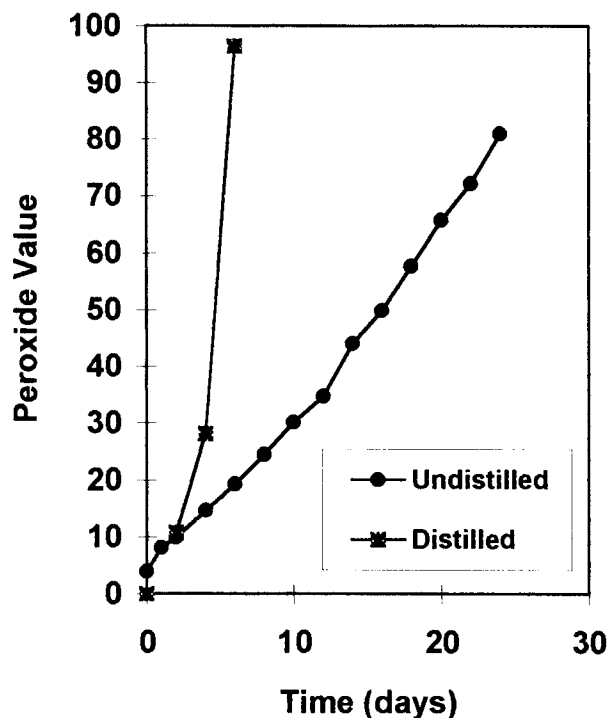


Figure 3. Rate of increase of peroxide value for distilled and undistilled esters.

assumed to be due to the difference in oxidation. Each of the six samples was split into three parts and the 18 test specimens were submitted as blind samples to a commercial laboratory for cetane testing. The results of this testing are shown in Figure 4. In spite of the experimental variation, the trend toward increasing cetane number with increasing peroxide value is clear.

Recent work on the effect of oxidation on biodiesel properties is shown in Figure 5. Figure 5 shows the increase in peroxide value (PV) for a sample of biodiesel that was heated to 60°C in the presence of air. The PV increases from about 85 to over 300 in six hours. The viscosity increased from 4.49 cS to 4.92 cS in the same interval.

Figure 6 shows a sample of biodiesel that was already highly oxidized (PV > 400) as it is heated to 80°C in the presence of air. The PV does not continue to increase. It actually decreases after about 3 hours. However, the biodiesel viscosity goes from 6.8 cS to over 8 cS. While these temperatures are well above any that would be expected in fuel storage containers, they are within the expected range for fuel returned from a diesel engine to the

Table 7. Effect of oxidation and distillation on cetane number.

Sample	Rep 1	Rep 2	Average
Freshly prepared methyl esters (PV=6)	46.8	48.7	47.8
Oxidized methyl esters (PV=81)	54.6	54.5	54.6
Distilled methyl esters (PV=0)	46.5	47.2	46.8
Distilled and oxidized methyl esters (PV=82)	55.5	55.2	55.4

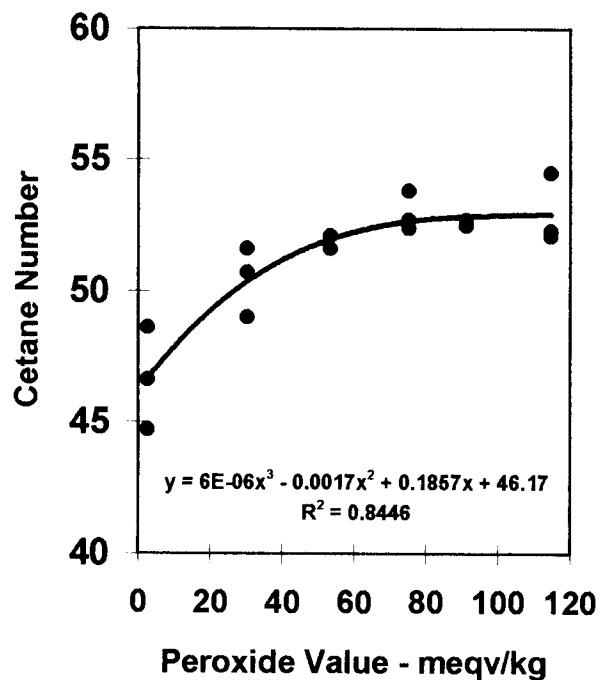


Figure 4. The effect of peroxide value on cetane number.

fuel tank. Current work is focusing on measuring the oxidation rate and the impact of temperature, contact with metals, and concentration of diesel fuel.

### Conclusions

The following conclusions can be drawn from the work performed in this project:

1. No specification value is needed for the amount of unsaponifiable matter in biodiesel as long as the level of unsaponifiable matter is no higher than is present in the original feedstock.
2. The current specification for water content in the NBB specification is not compatible with the existing diesel fuel distribution and storage network. Pure biodiesel that is transported or stored in this system will be in frequent contact with water and will eventually become saturated. When saturated, biodiesel can absorb about three times the amount of water allowed by the current standards for both biodiesel and No. 2 diesel fuel. If biodiesel is to be used in pure form, the standard should be raised (probably to 1500 ppm) or biodiesel will need to be transported and stored in special, water-free systems that are separate from those used for diesel fuel.
3. The current specification for free glycerin is well below the solubility limit of glycerin in methyl soyate.
4. The amount of alcohol in biodiesel is controlled by the specification on the flashpoint. The current flashpoint limit of 100°C is well above the limits for No. 1 and No. 2 diesel fuels which are 38°C and 52°C, respectively.
5. The crystallization properties of pure monoglycerides suggest that the specification value for bound glycerin is at the limit to prevent crystal formation.
6. The amounts of free fatty acids, soap, and residual catalyst are not currently included in the National Biodiesel Board specification. The specification on ash content will keep these contaminants at a low level and is acceptable as long as an alkaline catalyst is used and the biodiesel is water-washed.

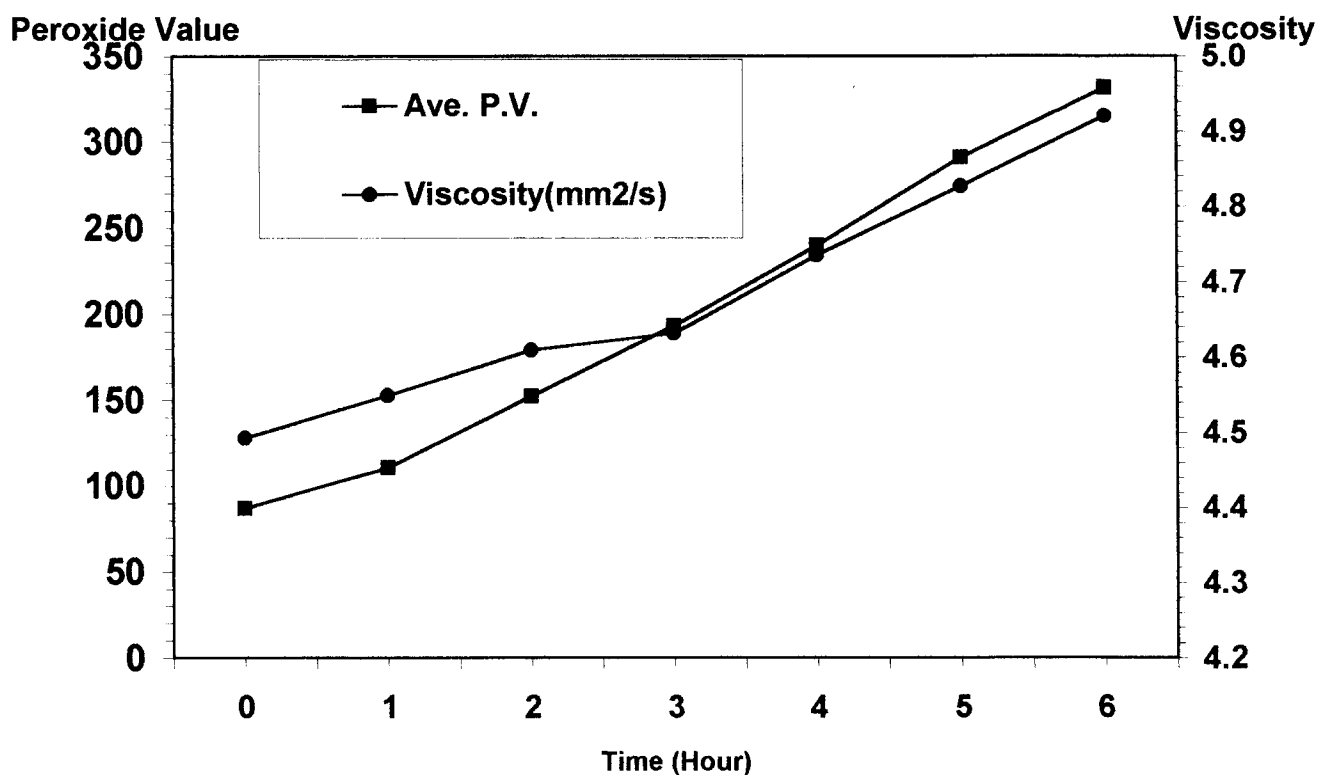


Figure 5. Oxidation of biodiesel in air at 60°

7. The specification for biodiesel should include a limit on the tendency of the fuel to oxidize and a limit on the maximum degree of oxidation allowable for use of the fuel in diesel engines. More research is needed to determine the appropriate tests and limiting values for these properties.

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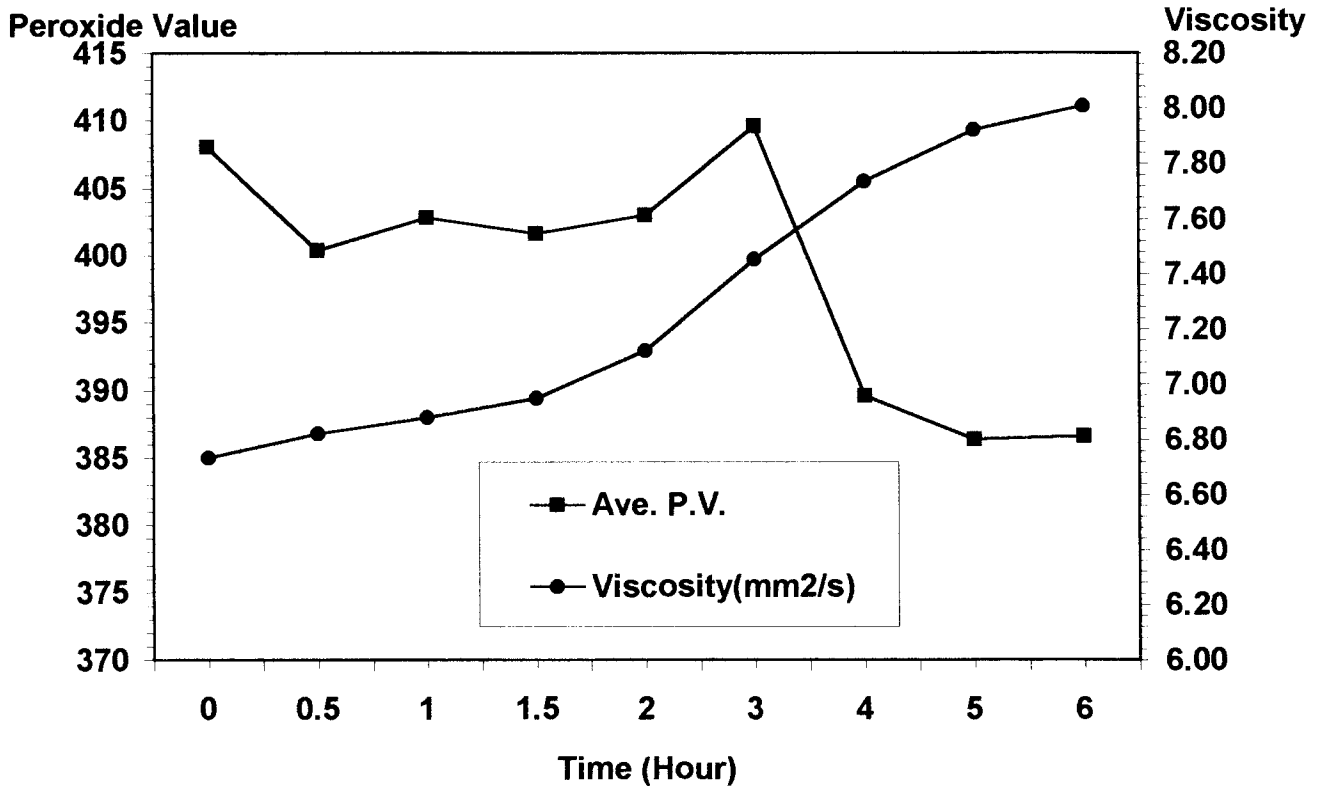


Figure 6. Oxidation of previously aged biodiesel in air at 80°C

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