Improving the Fuel Properties of Soy Biodiesel

P. S. Wang, J. Thompson, T. E. Clemente, J. H. Van Gerpen

Abstract. *Certain undesirable characteristics are associated with the use of soy methyl esters as a direct replacement for petroleum diesel fuel. When compared to petroleum diesel, soy methyl esters have higher NOx emissions, poorer cold flow, and a shorter shelf life. This article investigates whether the careful choice of alcohol and triglyceride feedstocks can improve these fuel properties. Three different triglyceride feedstocks with three different levels of oleic acid were examined. It was determined that a high amount of oleic acid in the triglyceride feedstock eliminates the tradeoff between cold flow and oxidative stability. The study also examined the role of three different alkyl groups (methyl, ethyl, and isopropyl) on the high-oleic feedstock. In NOx emissions testing, no significant difference was found between the alkyl groups. Isopropyl esters had the best cold flow properties, while methyl esters had the poorest cold flow properties for the three different alkyl groups. The induction periods for the methyl and ethyl esters from the high-oleic feedstock were 14 and 26 h, respectively, according to the Rancimat method. These numbers are in close agreement with the oxidative stability index. Isopropyl esters from the high-oleic feedstock had an induction period of less than an hour, which was unexpected. Further investigation revealed that the high-oleic isopropyl esters had no vitamin E in the form of α-tocopherol, and it was speculated that the washing step in the manufacture of the fuel removed all vitamin E content.*

Keywords. *Biodiesel, Cold flow performance, Ethyl esters, Isopropyl esters, NOx emissions, Oleic acid, Soy methyl esters, Storage stability.*

Soy methyl esters, the predominant type of biodiesel fuel in the U.S., have higher NOx emissions, poorer cold flow, and shorter shelf life when compared to petroleum diesel. These shortcomings are partly due to the fatty acid profile of the soybean oil feedstock itself. The fatty acid profile and the alcohol moieties determine the characteristics of the fuel such as cetane number, cold flow, oxidative stability, lubricity, and viscosity (Knothe, 2005). This article examines the choice of feedstock and alcohol used in the transesterification reaction and its effects on fuel properties such as cold flow, NOx emissions, and shelf life (oxidative stability).

With the current ability to modify the fatty acid profile of oil-bearing crops, it is now possible to have a "designer" oil feedstock for biodiesel production. A feedstock that is mostly monounsaturated (i.e., oleate) helps balance the tradeoff between cold flow and oxidative stability. Polyunsaturation increases cold flow performance but reduces shelf life. Saturated feedstocks such as tallow or palm oil have better shelf life but tend to crystallize more rapidly in cold weather conditions.

This high-oleic (HO) soybean oil feedstock has greater oxidative stability because the polyunsaturated fatty acid content is reduced (from the suppression of the desaturase enzyme, which boosts the oleic acid content). It has been reported that methyl linoleate and methyl linolenate oxidized 12 and 25 times faster than methyl oleate (Gunstone and Hilditch, 1945). However, the effect of the alkyl group is still unclear. In a two-year storage study, the acid value, peroxide value, and density of methyl esters and ethyl esters from rapeseed were observed (Thompson et al., 1998). The methyl esters deteriorated at a faster rate than the ethyl esters. However, the units of acid value and peroxide value are based on the weight of the sample, and ethyl esters have a higher molecular weight than methyl esters, so part of the apparent improvement in stability is due to the way the results are presented. Isopropyl esters are even bulkier than the latter two esters, and the effect of the head groups should be decoupled from the oxidation activity.

McCormick et al. (2001) investigated the impact of feedstock oil on NOx emissions. The conclusions of their study were that unsaturation increases NOx emissions and replacing the methyl group with the ethyl group does not change the emissions significantly. So far, the only study performed on the emissions effects of fueling with isopropyl esters shows that the differences between methyl and isopropyl esters were not significantly different (Wang et al., 2005).

The reported cetane number for isopropyl oleate is 86.6 (Knothe et al., 2003), which is very high compared to conventional soy methyl esters with cetane numbers ranging from 45 to 55 (Mittelbach and Ramschmidt, 2004). The cetane number is a key parameter for fuels used in a diesel engine as it determines how readily the fuel self-ignites. The HO isopropyl esters were expected to have a cetane number of at least

The authors are **Paul S. Wang,** Senior Engineer, Caterpillar, Inc., Mossville, Illinois; **Joseph Thompson, ASABE Member Engineer,** Research Support Scientist, Department of Biological and Agricultural Engineering, University of Idaho, Moscow; **Thomas E. Clemente,** Associate Professor, Department of Agronomy and Horticulture, University of Nebraska, Lincoln, Nebraska; and **Jon H. Van Gerpen, ASABE Member Engineer,** Professor and Chair, Department of Biological and Agricultural Engineering, University of Idaho, Moscow. **Corresponding author:** Jon Van Gerpen, Department of Biological and Agricultural Engineering, P.O. Box 440904, 419 Engineering and Physics Building, University of Idaho, Moscow, ID 83844-0904; phone: 208-885-7891; fax: 208-885-7908; e-mail: jonvg@uidaho.edu.

70, if the effect of isopropyl oleate was proportional to the amount present. Higher cetane numbers have been shown to correlate with lower NOx emissions (Tat et al., 2007).

A survey of the literature showed that soy methyl esters have cloud points ranging from -2°C to 2°C and pour points ranging from -3°C to -1°C (Mittelbach and Ramschmidt, 2004). The cold flow properties for methyl, ethyl, and isopropyl esters of the HO soybean oil are characterized in this work as well.

This present work examines the impact of a high-oleic feedstock on the performance and emissions of a diesel engine by comparing it with two other feedstocks possessing differing levels of oleic acid. In addition, the role of the alkyl group is studied in relation to the high-oleic feedstock to determine if it plays a significant role in solving the problems described earlier. In summary, the fuel characteristics that are of interest from the changes to the alkyl and fatty acid type are: reduced NOx emissions, better cold flow, and oxidative stability when compared to normal soybean methyl esters as biodiesel fuel.

MATERIALS AND METHODS

This work was carried out in two parts. The initial work was carried out to compare common triglyceride (TG) as a feedstock to make quality methyl esters. Two common feedstocks for producing biodiesel are soybean oil in the U.S. and rapeseed oil in Europe. In North America, canola (a cultivar of rapeseed that is low in erucic acid) oil is an important cash crop. Thus, soybean oil and canola oil were the benchmarks used for a comparison with high-oleic soybean oil. This initial work focused on the effect of the fatty acids found in the TG feedstock and how they affect the fuel properties. The second part of the work studied the effects of different alkyl groups on the best TG candidate that was identified in the first phase of this work. The characteristics that are of importance in evaluating the fuels are the NOx emissions, cold flow properties, and oxidative stability.

FUEL PREPARATION AND CHARACTERIZATION

High-oleic soybeans were obtained from a breeding program at the Department of Agronomy and Horticulture of the University of Nebraska-Lincoln (Lincoln, Neb.). They were pressed at the University of Idaho (Moscow, Ida.) and transesterified to produce methyl esters (HOME), ethyl esters (HOEE), and isopropyl esters (HOiPrE). The HOME and HOEE were produced using an alkali-catalyzed process with a 6:1 alcohol-to-oil molar ratio and 5 g catalyst per kg HO soybean oil. The catalysts used were sodium methylate to make methyl esters, sodium ethylate to make ethyl esters, and potassium isopropylate to produce isopropyl esters. The sodium ethylate (21% in ethanol) was obtained from Degussa (Parsippany, N.J.), and the sodium methylate (25% in methanol) was obtained from Oxychem (Dallas, Tex.). The HO soy isopropyl esters were produced using a 20:1 isopropanol-to-triglyceride ratio and 0.5% (w/w) potassium isopropylate (19% in isopropanol) from BASF (Evans City, Pa.). The normal soy biodiesel was purchased from Air Energy (Creston, Wash.). Canola oil was donated by Seattle Biodiesel (Seattle, Wash.), and the canola oil was transesterified to methyl esters using the same chemicals and procedure as the HOME. Diesel fuel was obtained from a local commercial source. Properties of the test fuels are listed in table 1.

All biodiesel samples were analyzed using gas chromatography (GC) according to the ASTM D6584 method to ensure that the total glycerol mass fraction was below the specified limit of 0.24% as specified by the ASTM D6751 biodiesel standard. GC analyses were performed using an Agilent Technologies 6890N gas chromatograph with a 7683B series injector (Santa Clara, Cal.) and a flame ionization detector. The capillary column used was a custom Agilent DB-5HT (Folsom, Cal.) that was 15 m × 0.32 mm with a 0.1 μm film thickness. The column was fused with a guard column (5 m × 0.53 mm). Data were acquired with a Dell Dimension 4700 equipped with GC Chemstation software (Rev. B.01.01).

Kinematic viscosity at 40°C was measured following the ASTM D445 method. The appropriate Cannon-Fenske (State College, Pa.) viscometer was used bearing in mind that isopropyl esters are bulkier and more viscous than methyl and ethyl esters. The viscometer was set in a K-233 oil bath made by Koehler Instruments (Bohemia, N.Y.).

A gallon of each type of fuel was sent to Phoenix Laboratories (Chicago, Ill.) for determination of the heating value, cetane rating (ASTM D613), as well as the carbon and hydrogen content. The values for these fuel properties are listed in table 1, which will be discussed later.

Analysis of variance (ANOVA) and post-hoc tests (Tukey HSD) were performed using R, an open-source statistical software package (R developmental core team, 2005).

Property	Soy Methyl Esters (SME)	HO Soy Methyl Esters (HOME)	Canola Methyl Esters (CME)	HO Soy 2-Propyl Esters (HOiPrE)	Diesel
Lower heating value (MJ kg^{-1})	37.44	37.70	37.65	38.53[a]	43.07
Carbon (%)	77.2	77.0	77.3	77.7	86.83
Hydrogen (%)	11.9	12.2	12.0	12.4	12.80
Oxygen (%)	11.3	11.1	11.1	9.89	N.A.
Cetane No.	47.2	51.5	49.4	57.1	44.0
Specific gravity (corr. to 15.5°C)[a]	0.883	0.881	0.879	0.870	0.846
Cloud point[a] (°C)	-1	-5	-2	-10	-6
Pour point[a] (°C)	0	-9	-9	-18	-9
Total glycerol[a] (mass %)	0.097	0.068	0.004	0.08	NA
Free glycerol[a] (mass %)	0.017	0.006	NA	0.016	NA
Kinematic viscosity[a] (cSt @ 40°C)	4.012	4.780	4.783	5.907	2.686

[a] Measured at the University of Idaho (Moscow, Ida.). Other properties measured at Phoenix Chemical Laboratory, Inc. (Chicago, Ill.) unless stated otherwise. Elemental composition for biodiesel fuels determined from fatty acid profile.

FATTY ACID PROFILING

The chain length and degree of saturation were objective criteria for feedstock evaluation and were deduced from the fatty acid profile. Fatty acid (FA) profile analyses for the different feedstocks were done at the University of Idaho. The FA profiles were obtained using a Hewlett Packard 5890 Series II gas chromatograph (Wilmington, Del.) equipped with a J&W DB-23 column (0.25 mm × 30 m, 0.25 μm film thickness; Folsom, Cal.). Signals were produced by a flame ionization detector (FID), and the chromatograms produced by an HP 3396 Series II integrator.

Samples (1 μL) were injected by an HP 7673 autosampler at a temperature of 250°C with a split flow ratio of 100:1. The initial oven temperature of 215°C was held for 3 min, followed by a ramp of 3°C min^{-1} to a final temperature of 230°C. The final temperature was held for 1.5 min. Helium (1.0 mL min^{-1}) was the carrier flow gas in the column. The FID temperature was 300°C, and the flow rate of the nitrogen makeup gas was 30 mL min^{-1}.

EMISSIONS TESTING

The emissions tests were carried out with older engines that may not necessarily be representative of engines equipped with newer common-rail fuel systems with multiple injection strategies. Newer engine technologies may not be as sensitive to biodiesel fuels in terms of NOx production (Matheaus et al., 2000; McCormick et al., 2001). However, the information gleaned is applicable to older engines that are still in use today and also provides some insight into the fuel characteristics.

Initial Screening

The methyl esters derived from HO soy oil, soybean oil, and canola were evaluated initially at different steady-state operating conditions. A 1994 Dodge Ram 2500 with a 5.9 L Cummins diesel engine (B series) that had over 100,000 miles on biodiesel was used in this phase to evaluate the NOx emissions. The Bosch P7100 pump used with this engine is an inline-style fuel pump with no dynamic timing adjustment capability (i.e., injection timing is fixed).

All emissions tests were conducted at an engine speed of 1800 rpm at three different load conditions (brake mean effective pressure = 0.2, 0.4, and 1.0 MPa). For each fuel, three replications were conducted and the order of all runs in each block (four fuels) was randomized. The exhaust emissions were sampled on a dry basis, and NOx (ppm) and CO_2 (%) numbers were measured. Fuel consumption measurement was available on the current setup, but not air flow rate. Thus, the air-fuel ratio was estimated from the exhaust CO_2 measurements. A chassis dynamometer (SF 602, Superflow Corp., Colorado Springs, Colo.) was used to measure the power at the wheels, and the following gas analyzers were used for the steady-state emissions tests: a Rosemount Analytical, Inc., model 880A non-dispersive infrared CO_2 analyzer, and a Teco chemiluminescent NO/NOx analyzer.

Alkyl Group Effects

To investigate the effect of alkyl group, the NOx emissions from methyl esters and isopropyl esters of HO soybean oil were compared to diesel fuel. A John Deere 3150 tractor was connected to an M&W P4450 power take-off (PTO) dynamometer made by M&W Gear Company (Gibson City, Ill.). Steady-state tests were performed at an engine speed of 2000 rpm with a brake mean effective pressure of 0.67 MPa. For each fuel, three replications were conducted and the order of all runs in each block (three fuels) was randomized.

The exhaust emissions were sampled on a wet basis for NOx and on a dry basis for CO_2. Fuel consumption measurement was available, but not air flow rate. The air flow rate was estimated from the fuel flow rate and the exhaust CO_2 measurements. NOx measurement was done using an Eco Physics CLD 83 analyzer (Ann Arbor, Mich.) based on chemiluminescense detection. CO_2 measurement was performed using a Rosemount Analytical model 880A non-dispersive infrared CO_2 analyzer.

OXIDATIVE STABILITY AND COLD FLOW TESTS

The oxidative stability of the HOME, HOEE, and HOiPrE were compared using the oxidative stability index (AOCS Cd 12b-92) at 110°C and the Rancimat method (EN 14112). These tests were conducted at the USDA-ARS National Center for Agricultural Utilization Research (Peoria, Ill.). In addition, the peroxide values (AOCS Cd 8-53) were evaluated for the freshly produced fuels to determine the effects of different alkyl groups. All of these tests were done on fuels that were made at the same time from the same initial HO soybean oil feedstock to block out independent aging. The α-tocopherol content was analyzed at the University of Idaho by the Holm Center analytical laboratory.

The cold flow tests were done according to the ASTM D 2500 method for cloud point and the ASTM D 97 method for pour point. A Neslab LT-50 low-temperature bath circulator was used with ethanol as the cooling medium. Type-T thermocouples were used for temperature measurement, and data acquisition was performed using a Visual Basic program with an HP 3497A controller.

RESULTS AND DISCUSSION

Table 1 lists the test fuels for use in emissions testing. The HOiPrE had slightly higher energy content among the biodiesel fuels, which resulted in marginally improved brake specific fuel consumption (BSFC) when compared to the HOME. The BSFC using HOiPrE, HOME, and diesel fuel are 248.7, 253.0, and 228.9 g/kW-h, respectively. The HOEE fuel was not tested.

All of the test fuels in table 1 meet the ASTM D6751 requirements for viscosity as well as the total glycerol content. The HOiPrE had a viscosity of 5.907 centistokes (cSt) at 40°C, which barely meets the ASTM D6751 standard for viscosity, which is 6.0 cSt. The higher viscosity of isopropyl esters in comparison to methyl esters has been reported elsewhere (Wang et al., 2005; Choo et al., 2005a).

NOX EMISSIONS

The fatty acid profiles for the emission test fuels are shown in figure 1. The three TG feedstocks are differentiated by the amounts of oleic and linoleic acids present. From the fatty profile analysis, the oleic acid content for soybean oil, canola oil, and HO soybean oil are 23.7%, 61.6%, and 85.3%, respectively. The fatty acid profiles (mass %) for the fuels are shown in table 2.

The NOx emissions from HOME, CME, SME, and diesel fuel were measured and are shown in figure 2. The error bars reflect the standard deviations of the brake specific NOx
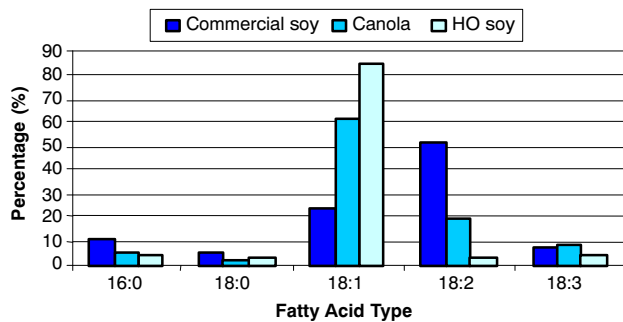
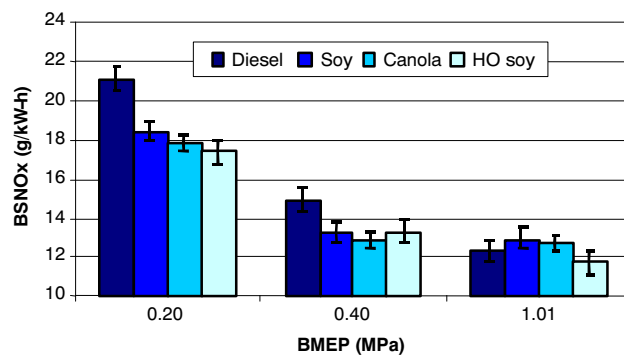**Figure 1. Fatty acid profile for fuels used in emissions testing.**

Figure 2. Evaluation of NOx emissions on basis of fatty acid composition. A 1994 Dodge Ram with a 5.9 L Cummins engine was loaded using a chassis dynamometer.

(BSNOx) emissions for each fuel. The brake specific basis is used as an indication of the amount of pollutants divided by the work produced by the engine, which is more meaningful than simply reporting the volumetric composition. The BSNOx emissions are the highest at low loads for all the fuels tested. An interesting trend from figure 2 is that the NOx emissions from diesel fuel are significantly higher than for the three different biodiesels at low loads. This phenomenon has been observed in the past where soybean biodiesel had a lower brake specific NOx emissions compared to diesel fuel at low loads (Tat et al., 2007).

The increased NOx emissions of diesel fuel at low loads when compared to biodiesel fuel can be explained through the operation of the engine at low loads and through the fuel properties. The Bosch P7100 pump has no dynamic timing adjustment capabilities, which is an advantageous feature for comparing the effects of different loads. For fixed injection timing, as the load decreases, the ignition delay increases (Stone, 1999). A longer ignition delay results in more pre-mixed burning, which leads to a higher peak temperature and increased NOx emissions. NOx emissions from diesel engines are primarily the result of the thermal (Zeldovich) mechanism, which is strongly affected by temperature (Heywood, 1988; Stone, 1999). Thus, it would be expected that NOx emissions would be highest at light loads when normalized by the engine work, which is associated with the amount of fuel burned.

To explain the higher NOx emissions of diesel fuel compared with the ester fuels, we need to look at the cetane number. The cetane number is an important fuel property that determines how readily the fuel autoignites. From table 1, the cetane numbers for the three biodiesels are higher than that of diesel fuel. Therefore, the longer ignition delay at low loads exacerbated by diesel fuel's lower cetane number is a plausible explanation for its increased NOx emissions.

At a BMEP of 1.0 MPa, the NOx emissions differences between the biodiesel fuels and diesel fuel are not as significant compared to the lower load conditions. While the high cetane number of the biodiesel fuels reduced its NOx emissions at low loads, it is not necessarily beneficial at high loads. The injection timing is advanced when using biodiesel because of the higher bulk modulus of biodiesel and its higher cetane

number (Tat et al., 2007). In general, advancing the timing leads to higher NOx emissions. Thus, the differences in NOx emissions between the biodiesel fuels and diesel fuel are reduced at the higher load when combustion timing is already advanced due to the shorter ignition delay caused by the high in-cylinder temperatures and pressures.

From figure 2, it is not apparent if there were any significant differences between the biodiesel fuels in terms of NOx emissions. Analysis of variance showed that there was a difference between at least two of the means ($p < 0.05$). There was a significant difference between the biodiesel fuels and the diesel fuel. At low load and high load conditions, higher NOx emissions from the biofuels followed the level of polyunsaturation: SME > CME > HOME. However, these differences were not statistically significant ($\alpha = 0.05$) after performing the Tukey post-hoc test.

The brake BSNOx emissions for comparing the alkyl groups are shown in figure 3. The three bars for each fuel are the three measurements for each fuel. The standard deviations for the BSNOx for diesel fuel, HOME, and HOiPrE are 0.25, 0.54, and 0.31 g/kW-h, respectively. Due to the limited amount of fuel available, only one load condition with a brake mean effective pressure of 0.67 MPa was studied. At this condition, the biodiesels generated higher NOx emissions than diesel fuel, which acted as the baseline. At this steady-state load, the increases in BSNOx for both HOME and HOiPrE relative to diesel fuel were 49% and 58%, respectively. This is quite significant, and the different fuel in-
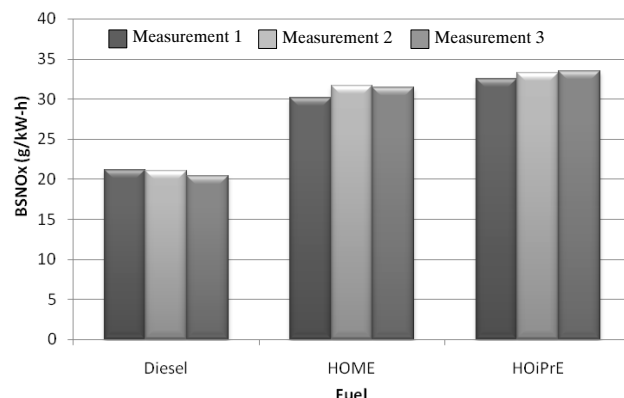

Figure 3. Evaluation of NOx emissions on basis of alkyl groups. A John Deere 3150 tractor was loaded using a PTO dynamometer.

Table 2. Fatty acid profile (mass %) for test fuels.

Fuel	C16:0 (%)	C18:0 (%)	C18:1 (%)	C18:2 (%)	C18:3 (%)	C20:1 (%)	C22:1 (%)
Soy	10.3	4.5	23.7	51.5	7.2	--	--
Canola	4.4	2.0	61.6	19.2	8.8	1.3	0.2
HO Soy	3.4	2.9	85.3	2.6	3.4	--	--

jection system on the naturally aspirated John Deere 6359 engine apparently exacerbated the NOx emissions. These engines are equipped with rotary-style fuel injection pumps that change the start of injection timing for different loads. There were statistically significant differences between the BSNOx means of the biodiesel fuels and diesel fuel ($p < 0.05$), but the difference in BSNOx emissions between HOME and HOiPrE was not statistically significant.

The HOiPrE, labeled as HO soy 2-propyl esters in table 1, showed an increase in cetane number, but the increase was below expectations. The cetane number of 57.1 for the HOiPrE did not decrease its BSNOx emissions when compared to the HOME. However, the bulkier isopropyl group also has several positive qualities, such as its higher energy content and improved cold flow.

OXIDATIVE STABILITY

To isolate the effects of the alkyl group on oxidative stability, the original HO soybean oil was characterized for peroxide value, acid value, and α-tocopherol before the transesterification reactions with the three different alcohols. The HO soybean oil had a peroxide value of 10.3 meq peroxide per kg sample, an acid value of 0.82 mg KOH per g sample, and 420 ppm of α-tocopherol. Prankl (2005) states that γ-tocopherol is the most effective agent for delaying the oxidation of unsaturated fatty acid compounds. However, α-tocopherol is the most stable form and should offer the best form of protection against oxidation.

The transesterification process resulted in alkyl esters with peroxide values that were lower than the peroxide value of the starting feedstock. The resulting esters had peroxide values of less than 2 meq peroxide per kg sample. The peroxide value is reported on a weight basis, and as such, higher molecular weight esters have better peroxide values even though the number of peroxide molecules may be the same. Figure 4 shows the initial peroxide values for HOME, HOEE, and HOiPrE. The error bars show the standard deviation in the measurements. Analysis of variance showed that at least two of the means were different. The Tukey post-hoc test showed that the difference in peroxide values for HOME and HOiPrE was statistically significant ($\alpha = 0.05$).

Since the HOiPrE has a lower initial peroxide value and the same number of double bonds as the other two esters, it was expected to have a longer induction period. Unexpectedly, the HOiPrE had a short induction period of less than an
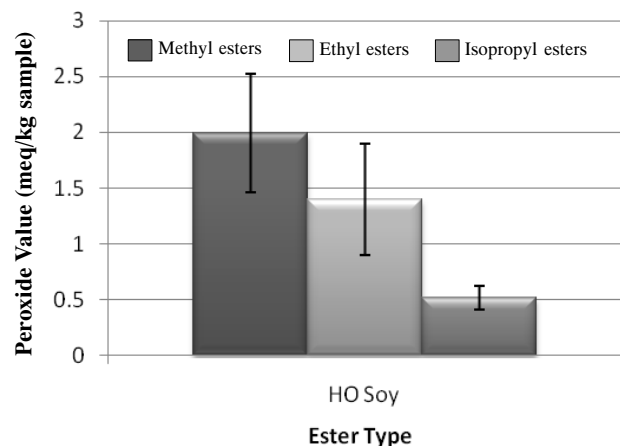
Figure 4. Initial peroxide values for three types of HO soy esters.

Table 3. Comparison of the stability between different alkyl groups

	Oxidative Stability Index (h)	Rancimat Method (h)
HO methyl esters	12.30 ±0.35	14.23 ±0.32
HO ethyl esters	21.92 ±0.33	26.03 ±0.20
HO isopropyl esters	0.82 ±0.06	0.69 ±0.02

hour. The induction periods as determined by the oxidative stability index (AOCS Cd 12b-92) at 110°C and the Rancimat method (EN 14112) are tabulated in table 3. Both these tests yielded results that were in good agreement with each other, where the induction periods were above 10 h for methyl esters, >20 h for the ethyl esters, and less than an hour for the isopropyl esters.

The HOME and HOEE had very good oxidative stability, and both exceeded the 6 h minimum (110°C) set by the European biodiesel standard (EN 14214). The HOME had an induction period of 12.3 h according to the OSI, which is twice the 6 h minimum. The HOEE had a longer induction period than the HOME, by at least 6 h. The short induction period for the HOiPrE warrants a closer look into the production process, and an alternative process for producing isopropyl esters may be needed.

The process for producing the isopropyl esters differs from the other two esters, notably in the amount of alcohol used (20:1 alcohol-to-oil molar ratio) and by the use of higher temperatures (~80°C) to drive the reaction toward the product side. This temperature is close to the boiling point of isopropanol of 82.3°C. The boiling points of methanol and ethanol are lower, at 64.7°C and 78.4°C, respectively. However, it is unlikely that vitamin E is destroyed at these temperatures since vitamin E extraction includes multi-stage vacuum distillation processes with temperatures as high as 200°C (Choo et al., 2005b).

Isopropanol is a particularly good solvent and can be used for various extraction processes, including vitamin E, which is a generic term for the various forms of tocopherols and tocotrienols. In preparing the isopropyl esters, there is no phase separation at the end of the process as is the case with methyl esters, where there is an ester layer on top of the glycerin layer. A phase separation is created by adding water to the isopropyl ester-isopropanol-glycerin mixture, and more wash water is needed than when washing methyl esters. Perhaps the low oxidative stability for the HOiPrE is due to the separation processes that might have reduced the vitamin E concentration in the HOiPrE itself. To confirm this suspicion, a sample of the HOiPrE was sent for vitamin E analysis, and vitamin E was not detected in the sample. This indicates that the vitamin E was extracted in the wash, where it may have had a higher affinity for the water-isopropanol solvent.

COLD FLOW PROPERTIES

The cold flow properties for the HO soybean oil esters show improvement over typical soy methyl esters. Table shows that soy methyl esters had a cloud point and a pour point of -1°C and 0°C, respectively. Due mainly to the lower level of palmitic acid in the HO soybean oil, the HOME had even better cold flow properties; with a cloud point and pour point of -5°C and -9°C, respectively. This performance is similar to the methyl esters of low-palmitic soy studied by Lee et al. (1995), which had a cloud and pour point of -7°C and -9°C, respectively. Overall, the HOME is a better fuel than low-palmitic soy because it has the added advantage of

Table 4. Effects of alkyl groups on cloud and pour points (˚C).[a]

	HO Soy		Normal Soy[b]		Low-Palmitate Soy[b]	
	CP	PP	CP	PP	CP	PP
Methyl	-5	-9	-2	-3	-7	-9
Ethyl	-7	-15	-2	-6	-8	-12
Isopropyl	-10	-18	-9	-12	-14	-21

[a] CP = cloud point; PP = pour point.
[b] Source: Lee et al. (1995).

high oxidative stability due to its low polyunsaturated content.

Previously, Lee et al. (1995) showed that by replacing the methyl group with isopropyl, the crystallization onset temperature can be reduced by as much as 11˚C. Their report also included the cold flow properties of ethyl esters derived from normal soybean oil and low-palmitate soybean oil. The trends for the different alkyl groups for esters of HO soy are in agreement with this previous work, which showed that the cold flow properties improve for the bulkier alkyl groups. The cloud and pour points for the HO soy esters tabulated in table 4 agree with the general trends from Lee et al. (1995) as well. The cold flow properties improve for a TG feedstock with the cloud points occurring in the following order: methyl > ethyl > isopropyl. The cloud points and pour points for HO soy esters (all three alkyl groups) are not very different from the low-palmitate soy, with differences of 4˚ or less. For example, the cloud point for ethyl esters made from HO soy and low-palmitate soy are -7˚ and -8˚C, respectively.

The cloud points and pour points of the esters from the HO soy fall in between the values reported for normal soybean oil and low-palmitate soy. The low-palmitate soy esters have lower cloud and pour points because of a higher level of polyunsaturation. The low-palmitate soybean oil had 3.8% palmitic acid and 62.0% linoleic acid. The induction period for methyl linoleate (1.2 h) is significantly shorter than that of methyl oleate (10.7 h) at 90˚C (Knothe and Dunn, 2003). There is a tradeoff between cold flow and shelf life, and the HO soybean oil esters balance these two competing demands well.

CONCLUSION

Despite the different engines for the emissions characterization, the outcomes are consistent in that the NOx emissions from the designed fuels were not significantly different from normal soybean methyl esters. The NOx emissions are not only influenced by the fuel's physical properties but also by engine hardware and the fuel injection system. In this study, for a Dodge truck with a Cummins B series engine, the biodiesel's NOx emissions were neutral or lower than diesel fuel, whereas the older John Deere engine showed a marked increased in NOx emissions for biodiesel fuels.

The clear effects from the use of an HO feedstock are improved cold flow properties and an increased shelf life. These effects are improved by using bulkier alkyl groups such as ethyl or isopropyl. The bulkier alkyl groups make it harder to crystallize at low temperatures and have a "diluting" effect on the concentration of double bonds present in the sample. When an ethyl group replaced the methyl group, the induction period was extended by more than 6 h, where 6 h is the minimum standard for any given fuel. This is quite remarkable given that the alkyl group is only a small portion of the fatty acid alkyl ester. Perhaps, there is another effect here.

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