Exhaust emissions and fuel properties of partially hydrogenated soybean oil methyl esters blended with ultra low sulfur diesel fuel

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Important fuel properties and emission characteristics of blends (20 vol.%) of soybean oil methyl esters (SME) and partially hydrogenated SME (PHSME) in ultra low sulfur diesel fuel (ULSD) were determined and compared with neat ULSD. The following changes were observed for B20 blends of SME and PHSME versus neat ULSD: improved lubricity, higher kinematic viscosity and cetane number, lower sulfur content, and inferior low-temperature properties and oxidative stability. With respect to exhaust emissions, B20 blends of PHSME and SME exhibited lower PM and CO emissions in comparison to those of neat ULSD. The PHSME blend also showed a significant reduction in THC emissions. Both SME and PHSME B20 blends yielded small increases in NOx emissions. The reduction in double bond content of PHSME did not result in a statistically significant difference in NOx emissions versus SME at the B20 blend level. The test engine consumed a greater amount of fuel operating on the SME and PHSME blends than on neat ULSD, but the increase was smaller for the PHSME blend.

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1. Introduction

Biodiesel, an alternative fuel composed of mono-alkyl esters of long-chain fatty acids prepared from renewable vegetable oils or animal fats, has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). Biodiesel possesses significant technical advantages over petrodiesel, such as derivation from a renewable and domestic feedstock, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, and superior flash point and biodegradability, as well as reductions in most exhaust emissions. Important disadvantages of biodiesel include inferior oxidative and storage stability and low-temperature operability, lower volumetric energy content, and, in some cases, higher oxides of nitrogen (NOx) exhaust emissions [1–5]. Although biodiesel can be used in modern unmodified compression-ignition (diesel) engines in neat form, it is more commonly encountered as a blend component in petrodiesel, such as B20 (20% biodiesel by volume in petrodiesel). Currently, blends of up to B5 are allowed by ASTM D975 [4], the U.S. diesel fuel standard (Table 1). In addition, a new ASTM standard, ASTM D7467 [5] (Table 1), was recently adopted for blends from B6 to B20 in petrodiesel. Biodiesel must be certified as acceptable according to ASTM D6751 [6], the B100 standard (Table 1), before it can be used as a blend component in petrodiesel per either ASTM D975 or D7467.

Exhaust emissions regulated by title 40, part 86 of the U.S. Code of Federal Regulations include NOx, particulate matter (PM), total hydrocarbons (THC), and carbon monoxide (CO). Previous studies have confirmed that combustion of B100 in diesel engines results in an average increase in NOx exhaust emissions of 12% and decreases in PM, THC, and CO emissions of 48, 77, and 48%, respectively, versus petrodiesel [7–12]. For B20 soybean oil methyl ester (SME) blends, NOx emissions are increased by 0–4% in comparison to petrodiesel, but PM, THC, and CO emissions are reduced by 10, 20, and 11%, respectively [11,12]. This increase in NOx emissions is of particular concern for environmentally sensitive locations such as national parks and places prone to high levels of air pollution such as urban areas. For biodiesel to be universally accepted, it is desirable to reduce smog-forming NOx exhaust emissions to levels equal to or lower than those observed for petrodiesel.

The Zeldovich (thermal) and Fenimore (prompt) mechanisms are two potential pathways by which NOx may be produced during combustion of fuels [10,13–15]. Thermal NOx is formed at high temperatures when molecular oxygen (O2) combines with molecular nitrogen (N2). Prompt NOx is produced by a complex pathway whereby hydrocarbon radicals react with N2 to form species that subsequently react with O2 to form NOx. However, a previous study concluded that there is negligible NOx production by the prompt mechanism during combustion of petrodiesel [16]. Consequently, the

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important fuel properties, such as low-temperature operability, cetane number, sulfur content, oxidative stability, lubricity, acid value, and kinematic viscosity. The PHSME was of interest because it is derived from a plentiful vegetable oil feedstock; soybean oil ranked second in annual worldwide production in 2008 according to the U.S. Department of Agriculture [31]. In addition, PHSME is satisfactory according to the European biodiesel standard, EN 14214 [30], with regard to IV (≤120) and oxidative stability (≥6 h, according to EN 14112 [32]) whereas untreated SME cannot satisfy the IV requirement. Also, because of the higher level of allylic methylene positions in SME, it is less stable to oxidation than PHSME according to the Rancimat (EN 14112) method [29].

2. Experimental section

2.1. Reagents and materials

The baseline diesel fuel was a 2007 Certification ULSD supplied by Haltermann Products (Channelview, Texas, USA) that was used for baseline comparison as well as the petrodiesel blend stock for the biodiesel blends. Soybean oil methyl esters (IV 134; measured according to American Oil Chemists’ Society (AOCS) official method Cd 1c-85) were supplied by Agland, Inc. (Eaton, Colorado, USA). Partially hydrogenated soybean oil (PHSBO, IV 116) was donated by the Oils & Fats division of Archer Daniels Midland Company (Decatur, Illinois, USA). All other chemicals and reagents were obtained from Aldrich Chemical Company (Milwaukee, Wisconsin, USA) and used as received. The SME and PHSME (their preparation is described in Section 2.2) were blended at 20% by volume into the baseline 2007 Certification ULSD fuel.

2.2. Methanolysis of partially hydrogenated soybean oil

Methanolysis of PHSBO was accomplished as described in a previous work [29] with a sodium methoxide catalyst (0.5 wt.% with respect to PHSBO). 6:1 molar ratio of methanol to PHSBO, 60 °C internal reaction temperature, and 1.5 h reaction time. After the glycerol was removed by gravity separation, the crude methyl esters were washed with distilled water until a neutral pH was obtained. The ester phase was then dried by treatment with anhydrous magnesium sulfate (MgSO4) to afford PHSME, which was independently verified as satisfactory according to ASTM D6751 by Magellan Midstream Partners, L.P. (Kansas City, Kansas, USA).

2.3. Fuel properties of ULSD and B20 samples

All measurements were made in triplicate except where indicated and mean values are reported (Table 2). Cloud (CP, °C) and pour points (PP, °C) were measured in accordance to ASTM D5773 and D5949, respectively, using a model PSA-705 Phase Technology Analyzer (Richmond, B.C., Canada). CP and PP were rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>ULSD</th>
<th>B20 SME</th>
<th>B20 PHSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP, °C</td>
<td>−20 ± 1</td>
<td>−15 ± 1</td>
<td>−14 ± 1</td>
</tr>
<tr>
<td>PP, °C</td>
<td>−24 ± 1</td>
<td>−22 ± 1</td>
<td>−19 ± 1</td>
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<td>−17 ± 1</td>
</tr>
<tr>
<td>IP, 110 °C, h</td>
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<td>3.2 ± 0.2</td>
<td>9.0 ± 0.1</td>
</tr>
<tr>
<td>v, 40 °C, mm²/s</td>
<td>2.67 ± 0.01</td>
<td>2.84 ± 0.01</td>
<td>2.94 ± 0.01</td>
</tr>
<tr>
<td>Lub, 60 °C, μm</td>
<td>538 ± 5</td>
<td>182 ± 3</td>
<td>197 ± 3</td>
</tr>
<tr>
<td>DCN</td>
<td>41.4</td>
<td>45.1</td>
<td>47.3</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>10</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>AV, mg KOH/g</td>
<td>0.00</td>
<td>0.08 ± 0.03</td>
<td>0.05 ± 0.03</td>
</tr>
</tbody>
</table>

* Derived cetane number.
were made with a resolution of 1 °C instead of the specified 3 °C increment. Cold filter plugging point (CFPP, °C) was determined following ASTM D6371 utilizing an ISL Automatic CFPP Analyzer model FPP 5Gs (Houston, Texas, USA). Kinematic viscosity (ν; mm²/s) was measured with a Cannon-Fenske viscometer (Cannon Instrument Co., State College, Pennsylvania, USA) at 40 °C according to ASTM D445. Lubricity (Lub, µm) determinations (duplicate) were performed at 60 °C (± 1 °C) according to ASTM standard D6079 using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, England) via Lazar Scientific (Granger, IN). Reported wear scar (µm) values were the result of measuring the maximum lengths of the x- and y-axes of each wear scar with a Prior Scientific (Rockland, Massachusetts, USA) Epimat model M4000 microscope, followed by calculating the average of these maximum values.

The induction period (IP, h) was measured following EN 14112[32] utilizing a Metrohm USA, Inc. (Riverview, FL) model 743 Rancimat instrument. The chemical compositions of PHSME and SME are known to have higher melting points than the corresponding cis-unsaturated isomers. For instance, the melting points of B20 SME displayed a slightly lower PP value in comparison to B20 PHSME (– 22 versus – 19 °C). The chemical compositions of PHSME and SME may explain the difference in PP observed for the resultant blends: saturated and trans FAME, which PHSME has in greater abundance, are known to have higher melting points than the corresponding cis-unsaturated isomers. For instance, the melting points of the methyl esters of linolenic (methyl 9Z,12Z,15Z-octadecatrienoate; all cis double bonds), linoleic (methyl 9Z,12Z-octadecadienoate; all cis double bonds) and oleic (methyl 9Z-octadecenoate; cis and trans) FAME are 18, 22 and 32 °C respectively. Derived CN (DCN) was determined (single determination) by Southwest Research Institute (San Antonio, TX) utilizing an Ignition Quality Tester™ (IQT) in accordance to ASTM D6890. Sulfur (S, ppm) content was measured (single determination) by Magellan Midstream Partners, L.P. using ultraviolet fluorescence spectroscopy according to the ASTM standard D5453.

2.4. Engine testing

Testing of ULSD, B20 SME, and B20 PHSME was conducted using a 2002 model year Cummins 5.9 L, 300 hp compression–ignition engine operated over a custom 8-mode test cycle which captures a wide range of engine operating conditions. The engine employed cooled high-pressure exhaust gas recirculation (EGR), a variable geometry turbocharger, electronic control, and high-pressure common rail direct fuel injection, designed and calibrated to meet the 2004 U.S. heavy-duty emission standards. Properties of the test engine are shown in Table 3. The eight test modes are shown in Fig. 1. Three consecutive hot start repeats were conducted for each fuel. Measurements of NOx, PM, THC and CO exhaust emissions were collected, as well as fuel consumption. Results are shown in Tables 4 and 5 and in Fig. 2.

2.5. Detection of emission species

Regulated emission measurements were performed using procedures consistent with title 40, part 86, subpart N of the U.S. Code of Federal Regulations [33]. Total hydrocarbons were determined by a continuous flame ionization detector, NOx by chemiluminescence and CO by nondispersive IR. Gas standards, supplied by Scott Specialty Gases (Brighton, Colorado, USA), were not changed during the test program. All gas mass emissions, which were background and humidity corrected, were determined by flow compensated integration of the instantaneous mass rates. Particulate matter was collected on Pall (Pall Corp., East Hills, NY) R2PJ047 47 mm 2.0 µm filters of a common lot. Particle filter handling and weighing were conducted in an environmental chamber/clean room with constant humidity, barometric pressure and temperature control.

3. Results and discussion

3.1. Fuel properties of B20 blends of SME and PHSME and comparison with ULSD

The baseline certification ULSD fuel exhibited superior low-temperature operability relative to B20 blends of PHSME and SME, as indicated by lower CP, PP, and CFPP values (Table 2). Although B20 SME and PHSME were nearly indistinguishable with regard to CP and CFPP, B20 SME displayed a slightly lower PP value in comparison to B20 PHSME (– 22 versus – 19 °C). The chemical compositions of PHSME and SME may explain the difference in PP observed for the resultant blends: saturated and trans FAME, which PHSME has in greater abundance, are known to have higher melting points than the corresponding cis-unsaturated isomers. For instance, the melting points of the methyl esters of linolenic (methyl 9Z,12Z,15Z-octadecatrienoate; all cis double bonds), linoleic (methyl 9Z,12Z-octadecadienoate; all cis
double bonds), oleic (methyl 9Z-octadecenoate; cis double bond), elaidic (methyl 9E-octadecenoate; trans double bond) and stearic (methyl octadecanoate) acids are −57, −35, −20, 13 and 39 °C, respectively [34]. The percentage of polyunsaturated FAME contained in SME was 60%, compared to 45% for PHSME [29]. Furthermore, trans-containing FAME constituted 8% of PHSME, whereas SME was free of these constituents [29].

Biodiesel is susceptible to autoxidation, which is initiated at sites allylic to double bonds along the fatty acid backbones of unsaturated FAME. Hydrodesulfurization of petroleum to reduce sulfur content to acceptable limits (<15 ppm S) also eliminates the double bond content of ULSD, which results in a fuel with excellent oxidative stability, especially in comparison to biodiesel. In the neat form, the SME exhibited an IP value of less than 3 h, whereas PHSME yielded a value in excess of 6 h [29]. In contrast, ULSD in the current study displayed excellent stability to oxidation, as evidenced by an IP value of 28.9 h (Table 2). Blends of PHSME and SME in ULSD exhibited considerably lower IP values (9.0 and 3.2 h, respectively) than did neat ULSD, and the difference was attributed to the progressively greater polyunsaturated FAME content of the blends investigated, as previously mentioned. Polyunsaturated materials are particularly vulnerable to autoxidation, as indicated by the relative rates of oxidation of the unsaturates: 1 for ethyl oleate, 41 for ethyl linoleate, and 98 for ethyl linolenate [35]. The low IP value of our B20 SME (3.2 h) was not satisfactory according to the minimum limit prescribed in ASTM D7467 (>6.0 h, Table 1), so antioxidant additives would be necessary to obtain an acceptable value. In contrast, the IP of B20 PHSME (9.0 h) satisfied the limit.

The kinematic viscosity (40 °C) of ULSD (2.67 mm²/s) was lower than that obtained for B20 blends of SME (2.84 mm²/s) and PHSME (2.94 mm²/s) (Table 2). Both blends were satisfactory according to the range specified in ASTM D7467 (1.9–4.1 mm²/s, Table 1). This trend is not surprising, as biodiesel fuels in neat form generally have kinematic viscosities in excess of 4.0 mm²/s [22,25,29,36,37]. Furthermore, PHSME (5.0 mm²/s) in the neat form was more viscous than SME (4.1 mm²/s), which was attributed to the presence of trans constituents in PHSME and fewer polyunsaturated FAME [29]. Trans FAME are more viscous than the corresponding cis isomers. For instance, the kinematic viscosities of the methyl esters of linolenic, linoleic, oleic, elaidic, and stearic acids were 3.14, 3.65, 4.51, 5.86, and 5.85 mm²/s, respectively [36].

Not only does hydrodesulfurization lower sulfur content, but it negatively impacts lubricity by reducing the oxygen, nitrogen, aromatic, and olefinic content of petrodiesel [38]. Consequently, the petroleum industry adds proprietary additives to petrodiesel to satisfy ASTM D975 [4] with respect to lubricity (520 μm maximum wear scar length according to ASTM D6079, Table 1). In the present study, the certification baseline ULSD fuel was unsatisfactory according to the ASTM D975 standard, exhibiting a wear scar length of 538 μm (Table 2); the result is most likely because this is a specialty fuel for emissions testing that is typically supplied without additives. The use of biodiesel blends as opposed to neat ULSD negates the need for lubricity enhancing additives, as biodiesel dramatically improves the lubricity of ULSD even at relatively low blend levels [37]. This finding was confirmed in the present study, as evidenced by the wear scar data for SME and PHSME blends in ULSD (182 and 197 μm, respectively, Table 2), which were satisfactory according to ASTM D7467 (maximum limit of 520 μm, Table 1). The small difference in lubricity between the blends may be a result of the difference in polyunsaturated FAME content between SME and PHSME, as lubricity is positively impacted by unsaturation [39]. For instance, the wear scar data (ASTM D6079) for methyl linolenate, linoleate, oleate, and stearate were found to be 183, 236, 290, and 322 μm [39].

The sulfur content of the certification baseline ULSD fuel (10 ppm; Table 2) was satisfactory according to the maximum limit specified in ASTM D975 (<15 ppm S; Table 1). Because biodiesel normally does not contain sulfur, a 20% reduction in sulfur content was found for the B20 SME and PHSME blends (8 ppm each; Table 2). The petrodiesel–biodiesel blend standard (ASTM D7467; Table 1) limits sulfur content to a maximum of 15 ppm as well.

As mentioned previously, hydrodesulfurization removes oxygen from petroleum products, thus eliminating any carboxylic acids from the resultant fuel. Consequently, ULSD displayed a negligible AV (Table 1). Both of the SME and PHSME blends exhibited very low AV as well (0.08 and 0.05 mg KOH/g, respectively), and these were satisfactory according to ASTM D7467 (maximum limit of 0.30 mg KOH/g, Table 1).

3.2. NOx exhaust emissions and cetane number

Regulated NOx exhaust emissions for the baseline certification ULSD fuel were 3.17 g/bhp h (Table 4). Note that the test cycle used was not the heavy-duty (HD) transient cycle component of the heavy-duty federal test procedure, but a more highly loaded cycle; therefore NOx was higher than is normally seen with this engine. This engine produced about 2.2 g/bhp h NOx from B20 SME on the HD transient cycle [40]. In agreement with previous studies [6–15,22–2739–45], an increase in NOx emissions of 4.8% (Fig. 2) was noticed in the case of B20 SME. An increase of 4.8% was detected with B20 PHSME, which was not statistically different from the result for B20 SME.

The certification ULSD exhibited a derived CN (DCN) value of 41.4 (Table 2), which was satisfactory according to the minimum limit in ASTM D975 (>40; Table 1). The DCN of B20 blends of SME (45.1) and PHSME (47.3) was higher than neat petrodiesel and above the minimum ASTM D7467 specification (>40; Table 1). This result is in agreement with prior studies that indicated that biodiesel [46] and blends [45] of biodiesel in petrodiesel had both higher CN and NOx emissions than neat petrodiesel. It is important to point out that NOx emissions from fuels of significantly different chemical compositions (petrodiesel versus blends) are influenced by factors other than CN, such as changes in bulk modulus, energy content, fuel density, and

![Fig. 2. Change (%) in NOx, THC, CO, and PM exhaust emissions, along with fuel consumption (FC) and work, relative to the certification ULSD baseline fuel.](image-url)
In the current study, PM emissions of the 2007 certification ULSD fuel were 0.107 g/bhp h (Table 4). Reductions in PM emissions of 27.9 and 22.5% were noticed for B20 SME and PHSME, respectively (Fig. 2). This result is in agreement with the aforementioned trend relating PM to NOx exhaust emissions. Oxygenated fuels, such as biodiesel, are known to exhibit lower PM emissions because fuel combustion is more complete [7,8,22,41]. Furthermore, previous studies demonstrated that larger reductions in PM emissions can be achieved with greater chemically-bound fuel oxygen content [7,42]. It is speculated that since neat ULSD is devoid of oxygenation, it had higher PM emissions than biodiesel and blends thereof. Despite the benefits of oxygenation on PM emissions, oxygen content was found to be an important factor in the formation of NOx because of higher local peak temperatures during fuel combustion, which result in increased thermal NOx formation [8,11,43]. While the inverse relationship between NOx and PM is generally a result of changes in engine operating conditions, (e.g., EGR or injection timing), fuel-born oxygen may partially explain the NOx–PM emissions tradeoff observed in these tests.

3.5. Other exhaust emissions

Several factors may affect CO production, including the air to fuel equivalence ratio, fuel type and composition, combustion chamber design, atomization rate, start of injection timing, engine load, and speed [44]. Hydrocarbon emissions during biodiesel combustion under high load conditions are typically very low, perhaps two orders of magnitude lower than CO emissions, and thus are more difficult to quantify precisely. Biodiesel has a shorter ignition delay time (high CN) than petrodiesel, so it exhibits lower THC emissions [19,45–50]. Fuels with long ignition delay times (low CN), such as petrodiesel, allow extra time for mixing and thus usually have higher THC emissions. As mentioned previously, oxygenation results in more complete combustion of fuels. Therefore, one would expect that increased oxidation of combustion intermediates due to chemically-bound oxygen present in biodiesel blends would result in a decrease in CO and THC emissions. In the present study, CO and THC emissions of the baseline ULSD fuel were 1.38 and 0.023 g/bhp h, respectively. Combustion of B20 SME and PHSME resulted in a reduction of 11.3 and 11.1% (Fig. 2), respectively, in emissions of CO in comparison to neat ULSD; these findings were in agreement with those of previous studies [7,8,22,25–27,44,51–52]. With respect to THC emissions, B20 SME resulted in a negligible increase (0.6%) in comparison to ULSD, but B20 PHSME yielded a THC emission reduction of 19.8% (Fig. 2). Although there appears to be a dramatic difference in THC emissions between B20 SME and B20 PHSME, these results are not considered significant because the measured emissions of these fuels (0.024 ± 0.002 and 0.019 ± 0.002 g/bhp h, respectively) fell within the standard deviation reported for the THC emissions of the 2007 certification ULSD fuel (0.023 ± 0.010 g/bhp h, Table 4). However, previous studies [7,8,22,25,26,44,46,51] have indicated that the combustion of biodiesel resulted in a reduction in THC exhaust emissions. Given the very low levels of THC emissions from this engine, the main conclusion to be drawn is that biodiesel blends had little measurable effect in comparison to the 2007 certification ULSD fuel on the already very low levels of these emissions.

3.5. Other factors

Although not measured directly in the current study, several previous reports have confirmed that biodiesel and B20 blends possess lower energy content than neat petrodiesel [45–48,53]. For example, in a recent study the heats of combustion of petrodiesel, B20 SME, and neat SME were found to be 46.7, 43.8 and 38.1 MJ/kg, respectively [53]. As the biodiesel component in the fuel was increased from 0 to 100%, a concomitant decrease in energy content was observed. The same result was indirectly obtained in the present study, as measured by fuel consumption (Table 5). Because of the lower energy content of biodiesel, more fuel was required in the case of the B20 blends to accomplish the same amount of work (72.9 bhp h, Table 5) as ULSD. Consequently, 3.8 and 3.1% more fuel on a mass basis was consumed in the case of B20 SME and PHSME, respectively, in comparison to neat ULSD (Fig. 2).

As seen in Table 6, although a number of FAME exhibit higher heats of combustion when measured on a MJ/mol basis than typical components of ULSD, the trend is reversed when compared in units of MJ/kg, which is due to the generally greater molecular weights of FAME versus hydrogen constituents of ULSD. For instance, methyl palmitate (MW 270.45 g/mol) and hexadecane (MW 226.44 g/mol) have similar molar heats of combustion (10.67 and 10.70 MJ/mol), but when they are compared in MJ/kg units, hexadecane (47.12 MJ/kg) has considerably more energy content than methyl palmitate (39.45 MJ/kg, Table 6). The difference is even more striking in the case of methyl palmitate and dodecane (MW 170.33), the latter of which has a lower molar heat of combustion (8.09 MJ/mol) but a higher value when compared in units of MJ/kg (47.48 MJ/kg). Since fuel consumption, production, and usage is measured in terms of volume (or mass), the molar heat of combustion data (MJ/mol) are less applicable and predictive of performance than values reported in MJ/kg.

Factors that influence the energy content of FAME include the oxygen content and carbon-to-hydrogen ratio. Generally, as the oxygen content of FAME is increased (as measured by the lower C/O ratios shown in Table 6), a corresponding reduction in energy content is observed. For example, methyl stearate (C/O ratio of 9.5:1) possesses greater energy content (11.96 MJ/mol or 40.07 MJ/kg) than methyl laurate (C/O ratio of 6.5:1: 8.14 MJ/mol or 37.97 MJ/kg), which has greater energy content than methyl caprylate (C/O ratio of 4.5:1: 5.52 MJ/mol or 34.91 MJ/kg). Therefore, the energy content of FAME is directly proportional to chain length [54], since longer-chain FAME contain more carbons but a similar number of oxygens. Another important factor is the CH ratio. Generally, FAME with similar C/O but lower C/H ratios (i.e., more hydrogen) exhibit greater energy content. For instance, FAME with a C/O ratio of 9.5:1 in Table 6 include methyl stearate (C/H ratio of 1:2), oleate (C/H ratio of 1:1.90), linoleate (C/H ratio of 1:1.79) and linolenate (C/H ratio of 1:1.68). As seen in Table 6, methyl stearate possesses the highest energy content and methyl linolenate the lowest, as measured by heat of combustion. The result of this trend is that lower energy content is obtained from progressively greater levels of unsaturation of FAME of similar chain length. This observation is manifested in the current study by the greater amount of fuel consumed in the case of B20 SME (3.8% more than ULSD, Fig. 2) than B20 PHSME (3.1% more than ULSD, Fig. 2). As mentioned previously, SME contained more polyunsaturated FAME than PHSME, which resulted in lower energy content and greater fuel consumption. Components of ULSD generally have greater energy content [15,18–20]. Consequently, it is speculated that the well established trend discussed previously of lower NOx emissions with higher CN was not obeyed in the current study as a result of the significant change in chemical composition between petrodiesel and biodiesel blends. The higher DCN of the PHSME blend versus the SME blend may be a result of the lower unsaturated FAME content of B20 PHSME, as increasing levels of unsaturation are known to decrease CN [21]. It is speculated that the difference in DCN between B20 PHSME and SME was not substantial enough to yield a statistically significant reduction in NOx exhaust emissions.
content than FAME in part because they do not contain oxygen. Since combustion is an oxidative process, FAME are in effect initially more oxidized than hydrocarbons as a result of the presence of chemically-bound oxygen, which results in lower heats of combustion (MJ/kg).

4. Conclusions

Blending SME and PHSME with ULSD resulted in the following changes in physical properties in comparison to those of neat ULSD: improved lubricity, higher kinematic viscosity and cetane number, lower oxidative stability and sulfur content, and reduced low-temperature operability. With respect to exhaust emissions, B20 blends of PHSME and SME exhibited reduced PM and CO emissions in comparison to ULSD. Furthermore, the PHSME blend also resulted in a significant reduction in THC emissions. Both SME and PHSME B20 blends resulted in a similar increase in NO\textsubscript{x} emissions. The reduction in double bond content of PHSME was not substantial enough to result in a statistically significant difference in NO\textsubscript{x} emissions in comparison to SME at the B20 blend level. Finally, it was believed that the test engine consumed a greater amount of fuel operating in SME and PHSME blends than neat ULSD as a result of the lower energy content of biodiesel blends versus petrodiesel [45–48,53]. However, the increase in fuel consumption was smaller for B20 PHSME. The PHSME blend displayed superior oxidative stability and similar CP, CFPP, and AV when compared to B20 SME. The SME blend exhibited superior kinematic viscosity and lubricity versus B20 PHSME, although both blends were acceptable with regard to these properties. The difference in chemical composition between PHSME and SME was in part responsible for the differences in fuel properties and exhaust emissions observed in this study.

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U.S. Code of Federal Regulations, Title 40 (Protection of the Environment; Clean Air Act), Section 86 (Control of Emissions from New and in-Use Highway Vehicles and Engines, Subpart N (Emissions Regulations for New Otto-Cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures), 1999.


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