PERFORMANCE INVESTIGATIONS OF A DIESEL ENGINE USING ETHYL LEVULINATE-DIESEL BLENDS

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Ethyl levulinate (EL) can be produced from bio-based levulinic acid (LA) and ethanol. Experimental investigations were conducted to evaluate and compare the performances and exhaust emission levels of ethyl levulinate as an additive to conventional diesel fuel, with EL percentages of 5%, 10%, 15% (with 2% n-butanol), and 20% (with 5% n-butanol), in a horizontal single-cylinder four stroke diesel engine. Brake-specific fuel consumptions of the EL-diesel blends were about 10% higher than for pure diesel because of the lower heating value of EL. NOx and CO2 emissions increased with engine power with greater fuel injections, but varied with changing EL content of the blends. CO emissions were similar for all of the fuel formulations. Smoke emissions decreased with increasing EL content.

Keywords: Ethyl levulinate; Diesel; Performance; Emissions

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INTRODUCTION

As global automobile production and the population increase every year, fuel supplies are under pressure and environmental pollution is becoming worse. Automobile companies worldwide have worked to develop diesel engines with high thermal efficiency and specific power output, always trying to keep inside the limits of the imposed emission regulations that are becoming increasingly more stringent (Rakopoulos et al. 2009). However, diesel engines have an intrinsic drawback of producing high levels of emissions. The need for diversification of energy sources and reduction of various emissions including CO2 emission in diesel engine can be met with alternative diesel fuels such as biodiesel blends (Moon et al. 2010). The use of reformed exhaust gas recirculation, along with new ultra-clean designed fuels and a selective catalytic reduction catalyst as an aftertreatment device may result in around 90% reduction of overall NOx emissions in a wide range of engine operation conditions (Rodriguez-Fernandez et al. 2009).

Ethyl levulinate (EL), one of levulinate esters, can be produced from levulinic acid (LA) and ethanol. Various bioresources, including wood, starch, cane sugar, grain sorghum, and agricultural wastes, have been used to produce LA (Lange et al. 2009; Fang and Hanna 2002; Chang et al. 2007) and ethanol (Wang and Zhu 2010; Millati et al. 2008). Thus, the production of EL is sustainable (Sen et al. 2012).
Compared with a gasoline engine, a diesel engine generally has higher efficiency, longer working lifetime, and less carbon monoxide (CO) emissions; however, a diesel engine has higher soot and NO\textsubscript{x} emissions, which can negatively impact the environment (Windom \textit{et al.} 2011). Many studies have focused on solutions to these problems, and one of the most important methods is to add oxygenated components to the fossil fuel. The addition of oxygenated compounds to fossil fuels has been shown to provide completely smoke-free combustion when 38\% (by mass) of oxygen is incorporated into the diesel fuel (Miyamoto \textit{et al.} 1998). The main oxygenated organic compounds are biodiesel, alcohols, and ethers. The most common method to produce biodiesel is transesterification of vegetable oil, waste animal fats, or restaurant greases (yellow grease) with a short-chain alcohol (Balat 2011; Yusuf \textit{et al.} 2011). Trans-esterified biodiesel differs from fossil diesel, which consists of paraffin and aryl hydrocarbons, in its chemical characteristics. Biodiesel also exhibits different physical properties than fossil diesel, such as higher cetane number, lower heating value, higher viscosity, and higher flash-point. The different properties may in turn affect the combustion and emissions in a diesel engine (Kousoulidou \textit{et al.} 2010).

Barabás \textit{et al.} (2010) showed that performance of a compression-ignition engine was worse when fuelled with diesel–biodiesel–bioethanol blends than with fossil diesel. This was because of the lower heating value of the biofuels compared with that of diesel fuel, especially at low engine loads. CO and unburned hydrocarbon (HC) emissions decreased, especially at medium and low loads, but CO\textsubscript{2} and NO\textsubscript{x} emissions increased. Buyukkaya’s (2010) investigation indicated that using rapeseed oil decreased smoke opacity, lowered CO emissions, and increased brake-specific fuel consumption (BSFC) compared with fossil diesel fuel, while the combustion behaviors of rapeseed oil and blends with diesel closely followed those of standard diesel.

Rakopoulos \textit{et al.} (2008) compared the performance and exhaust emission levels when ethanol was used as a supplement to conventional diesel fuel. They reported that the smoke density and NO\textsubscript{x} and CO emissions were equal or slightly reduced, while the HC emissions were higher. Concerning engine performance, slightly increased BSFCs have been observed with increasing ethanol content for blends with a corresponding very slight increase in brake thermal efficiency (BTE). Rakopoulos \textit{et al.} (2010) later reported the effects of butanol added to diesel fuel; the result showed that with the use of the butanol-diesel fuel blends, the smoke density, NO\textsubscript{x}, and CO emissions were reduced, but the HC emissions and BSFC were increased relative to those of the neat diesel fuel. Luján \textit{et al.} (2009) found that biodiesel could be safely used at small blending ratios with normal diesel fuel in a diesel engine. In that study, biodiesel consumption was higher than that of diesel fuel at the same engine efficiency, and particulate matter (PM), and CO, HC, and NO\textsubscript{x} emissions were also higher. Huang \textit{et al.} (2009) reported that the BTEs were comparable when ethanol–butanol–diesel blends were combusted in a diesel engine; while BSFCs increased, smoke opacity decreased, CO and HC emissions decreased under some conditions, and NO\textsubscript{x} emissions varied with different engine speeds, loads, and blends. Çelikten \textit{et al.} (2010) compared the performances and emissions of a diesel engine fuelled with fossil diesel or with blends of rapeseed oil and soybean oil methyl esters. They established that biodiesel could be used as an alternative diesel fuel without any modification to the diesel engine. However, the authors reported that these biodiesel fuels performed worse than normal diesel fuel; the poorer engine performance was attributed to the lower calorific values and higher viscosities of the biodiesel fuels.
Comparison of three different fuels showed that rapeseed and soybean biodiesel fuels generated less CO and smoke levels than diesel fuel, but had higher NO\textsubscript{x} emissions at all injection pressures. Sayin (2010) reported that BSFC and NO\textsubscript{x} emissions increased, while BTE, smoke opacity, and CO and HC emissions decreased with methanol–diesel and ethanol–diesel fuel blends. Qi \textit{et al.} (2011) found that adding fuels having higher oxygen contents and higher volatilities, such as diethyl ether and ethanol, was a promising technique for using biodiesel/diesel blends efficiently in diesel engines without requiring any modifications to the engine. A biodiesel blended fuel was shown to have reduced aldehyde emissions from diesel engine exhaust (Demirbas 2009a).

Significant barriers remain to using ethanol as a fuel for diesel engines. Compared with conventional diesel fuel, ethanol has a lower density and lower viscosity, which makes it difficult to mix with diesel fuel without the assistance of other additives. Biofuels from vegetable oil and animal fat have poor low-temperature properties; most have cloud points between 2 and 15 °C. Additionally, they have viscosities that can rise to much higher levels than most fossil diesel fuels, which can increase pump stress. The high cloud point makes using biodiesel fuel challenging in colder climates (Demirbas, 2009b).

A new processing technique was recently developed that converts the carbohydrates found in plant biomass into ethyl-levulinate (EL) (Mascal and Nikitin 2009). EL has properties making it an attractive oxygenation additive for diesel fuel. The Biofine process can convert approximately 50% of the mass of the six-carbon sugars to levulinic acid (LA), with 20% being converted to formic acid and 30% to tars (Fitzpatrick 1990, 1997). This process can make EL available at lower production costs. EL has an oxygen content of 33%. Hayes (2009) reported that a blend of 20% EL with 79% petroleum diesel and 1% co-additive had 6.9% oxygen content, and was significantly cleaner-burning. The fuel had high lubricity and low sulfur content, and met all the diesel fuel specifications required by ASTM D-975. Recently, Windom \textit{et al.} (2011) analyzed the distillation curve of blends of EL–diesel and fatty acid–levulinate ester biodiesel, and Joshi \textit{et al.} (2011) investigated the cloud points (CP), pour points (PP), and cold-filter-plugging points (CFPP) of biodiesels prepared from cottonseed oil and poultry fat with EL contents of 2.5, 5.0, 10.0, and 20.0 vol%.

To the best of our knowledge, there have not been any investigations of the effects of EL when it is blended with diesel fuel on engine performance and emissions. The present paper compares the characteristics of EL–diesel fuel blends having EL contents of 5, 10, 15 (with 2% \textit{n}-butanol), and 20 (with 5% \textit{n}-butanol) vol% with pure diesel fuel.

**EXPERIMENTS**

**Experimental Apparatus**

Engine performance was measured with an eddy current dynamometer (DW25, Chengbang, China) with 120 N•m torque and 25 kW of measurement capacity (accuracy of ±0.5 N•m torque). Engine speed and fuel consumption were measured by a tachometer (accuracy of ±1 rpm) and a digital intelligent fuel consumption meter (ET2500, accuracy of ±8 g·h\textsuperscript{-1}). During the tests, all measured performance data and control parameters were exchanged between the test apparatus and the computer by an ET2000 intelligent controller.
measurement and control system (Chengbang, China). Engine exhaust gas components (HC, CO\textsubscript{2}, and NO\textsubscript{x}) were measured with an exhaust gas analyzer (Testo360, Germany), CO was measured with an exhaust gas analyzer (FGA-4100, China), and light absorption coefficient (k) were measured with a smoke opacity analyzer (FTY-100, China). The emission test range and accuracies were as follows: NO\textsubscript{x}: 0 to 1000 ppm, ±3.8%; CO: 0 to 9.99%, ±0.06%; CO\textsubscript{2}: 0 to 20%, ±1.5%; k: 0 to 16 m\textsuperscript{-1}, ±2.0%.

The apparatus used for fuel performances and emissions tests is shown in Fig. 1. A horizontal, single cylinder, four stroke diesel engine was used, and its specifics are listed in Table 1.

![Fig. 1. Schematics of fuel test engine and set-up](image)

**Table 1. Specifics of the Tested Diesel Engine**

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Horizontal Four-Stroke, Single Cylinder</td>
</tr>
<tr>
<td>Combustion System</td>
<td>Direct Injection</td>
</tr>
<tr>
<td>Bore × Stroke (mm)</td>
<td>110 × 115</td>
</tr>
<tr>
<td>Displacement (L)</td>
<td>1.093</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>17:1</td>
</tr>
<tr>
<td>Max Power (kW)</td>
<td>14.7</td>
</tr>
<tr>
<td>Max Speed (rpm)</td>
<td>2200</td>
</tr>
<tr>
<td>Cooling Method</td>
<td>Water Cooling System</td>
</tr>
<tr>
<td>Lubrication Method</td>
<td>Combined Pressure &amp; Splashing</td>
</tr>
</tbody>
</table>

The system was warmed up for at least 30 minutes before each test; the warm-up time was increased to 3 hours if the fuel was changed to ensure that the fuel in the lines and engine had been completely replaced. The maximum speed and power of the engine were 2200 rpm and 14.7 kW, respectively. Based on preliminary noise and system stability testing with pure diesel over the full engine speed range (800 to 2200 rpm), 1200 rpm was set as the speed for each test. Then the torque was changed from 3.0 to
57.0 Nm at 3.0 Nm intervals; the system achieved the imposed conditions by automatically adjusting the load and throttle. The average engine power, fuel consumption, and emission data were read and recorded simultaneously by the computer once the system became steady.

**Tested Fuels**

Diesel fuel was obtained from China Petroleum and Chemical Corporation (Henan Branch), EL (>99.9 wt%) was obtained from Shanghai Zhuorui Chemical Industry Co., Ltd., and n-butanol (>99.9 wt%) was obtained from Tianjin Fuyu Fine Chemical Industry Co., Ltd. The performances and emissions of the engine fueled with pure 0# diesel were measured as the control (denoted as EL-0). Then subsequent tests were conducted when the engine was fueled with EL-diesel blends with EL of 5%, 10%, 15%, and 20% in volume (labeled as EL-5, EL-10, EL-15 and EL-20, respectively). It should be noted that the phase separation was observed when the EL volume percent in EL-diesel blend was ≥15% at room temperature (25 °C); the co-additive n-butanol was mixed in EL-15 and EL-20 at 2% and 5% (by volume), respectively, to improve the solubility of the EL in diesel. EL-5, EL-10, EL-15, and EL-20 were enclosed in reagent bottles, and the phase separation was not observed for more than one month at 4 °C, 10 °C, 15 °C, 20 °C, and 25 °C. The properties of the blends fuels are listed in Table 2.

**Table 2. Properties of the Blends Fuels**

<table>
<thead>
<tr>
<th>Properties</th>
<th>EL-0</th>
<th>EL-5</th>
<th>EL-10</th>
<th>EL-15</th>
<th>EL-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition/(vol%)</td>
<td>100%diesel</td>
<td>95%diesel +5%EL</td>
<td>90%diesel +10%EL</td>
<td>83%diesel +15%EL +2% n-butanol</td>
<td>75%diesel +20%EL +5% n-butanol</td>
</tr>
<tr>
<td>Cold Filter Plugging Point/(°C)</td>
<td>-2</td>
<td>-2</td>
<td>-3</td>
<td>-4</td>
<td>-3</td>
</tr>
<tr>
<td>Density(20 °C)/( g·cm⁻³)</td>
<td>0.836</td>
<td>0.845</td>
<td>0.853</td>
<td>0.862</td>
<td>0.870</td>
</tr>
<tr>
<td>Kinematic Viscosity (40 °C)/(mm²·s⁻¹)</td>
<td>2.83</td>
<td>2.68</td>
<td>2.63</td>
<td>2.56</td>
<td>2.25</td>
</tr>
<tr>
<td>Closed-cup Flash Point/(°C)</td>
<td>61</td>
<td>62</td>
<td>63</td>
<td>50</td>
<td>48</td>
</tr>
<tr>
<td>Oxygen Content/(wt%)</td>
<td>0</td>
<td>1.98</td>
<td>3.92</td>
<td>6.23</td>
<td>8.71</td>
</tr>
<tr>
<td>Low Heating Value/(MJ·kg⁻¹)</td>
<td>42.5</td>
<td>41.9</td>
<td>40.8</td>
<td>39.6</td>
<td>38.3</td>
</tr>
</tbody>
</table>

Note: Data was calculated on the base of (Zhang et al. 2010).

**EXPERIMENTAL RESULTS**

**Brake Specific Fuel Consumption**

The BSFC values for different fuel formulas at different engine powers are shown in Fig. 2. The inset has enlarged scales for convenient comparison. The BSFC is defined such that the fuel consumption is normalized with respect to the engine power. It was significantly higher at lower engine powers and showed a minimum at about 5.3 kW, corresponding to the highest engine efficiency at 1200 rpm. The BSFCs of the EL–diesel blends were about 10% higher than those for pure diesel and increased with EL content. The probable reason for this behavior was the lower heating value of EL (about 24 MJkg⁻¹ compared with 43 MJkg⁻¹ for standard 0# diesel (Hayes et al. 2008)).
lower BSFC for EL-20 compared with EL-15 was attributed to the higher heating value of \( n \)-butanol (about 33 MJkg\(^{-1} \)) compared with EL. The \( n \)-butanol was added to keep the 20% EL from separating in the EL-20 diesel blend.

**Emissions**

Figure 3 shows the variation in NO\(_x\) emissions for the different fuel formulas as a function of engine power. The NO\(_x\) emissions for the blends were not constant, but varied slightly. At lower powers (less than 3 kW), the NO\(_x\) emissions of EL-0 were lower than all the other blends. The NO\(_x\) emissions of EL-5 and EL-10 decreased at higher powers. EL-15 and EL-20 always had higher NO\(_x\) emissions than EL-0.

There are three primary sources of NO\(_x\) in the combustion process: thermal NO\(_x\), fuel NO\(_x\), and prompt NO\(_x\). Thermal NO\(_x\) formation is recognized as the most relevant source from engine combustion. At lower engine powers, the amount of injected fuel is relatively small for the lower torque and load. With the higher oxygen content of the blended fuels, carbon and hydrogen can combust more efficiently than in pure diesel fuel.
Hence, the combustion temperature may be higher. Additionally, the lower cetane number for the blends leads to longer ignition delays. These factors tended to increase the formation of NO\(_x\). As the engine power increased, the effect of the lower oxygen content in the fuel injections became less notable, and the blends having higher oxygen contents (EL-15 and EL-20) led to higher NO\(_x\) emissions. At lower engine powers, the NO\(_x\) emissions for EL-20 were lower than those for EL-15; this was attributed to the higher percentage of \(n\)-butanol present.

The varying NO\(_x\) emissions were probably caused by a competition between the temperature-lowering effect of the additive (because of the lower calorific value and higher heat of evaporation) and the opposing effect of the lower cetane number (and thus longer ignition delay) of the additive (leading possibly to higher temperatures during the premixing part of combustion). This delicate balance can shift one way or the other depending on the specific engine and its operating conditions (Corkwell et al. 2003).

Figure 4 shows the CO exhaust emissions for the pure diesel fuel and blends having various percentages of EL. Significant differences among the fuel formulas were observed only at the highest engine power, when the emitted CO by the blends was higher by about 30% compared to pure diesel. This was the limiting condition of the tested diesel engine at 1200 rpm: the engine efficiency was low and large amounts of injected fuel could not combust effectively. Such running conditions should be avoided in practical applications.

![Graph showing CO emissions vs engine power for different fuel formulas](image)

**Fig. 4.** Variations of CO emissions of different fuel formulas with engine power (constant speed: 1200 rpm, varying torque)

Figure 5 shows CO\(_2\) exhaust emissions for the pure diesel fuel and the various percentages of the EL in its blends. The trends were somewhat similar to those of NO\(_x\), with the higher oxygenation levels resulting in higher CO\(_2\) emission, while lower oxygenation levels resulted in lower emissions, and the pure diesel achieved intermediate results. With the oxygen content increasing in the overall fuels, carbon and hydrogen content must decrease, assuming all blend fuel combust completely, and CO\(_2\) emission should increase with increasing of oxygen content. As mentioned above, CO emissions were not significant among different fuel formulas, so the CO\(_2\) emission trends should be analyzed systematically with HC emissions. Unfortunately, the present work did not measure the HC emissions.
The formation of unburned hydrocarbons originates from various sources in the engine cylinder. But this process is poorly understood: increasing and decreasing HC emissions have both been reported for diesel fuel containing alcohols (Rakopoulos et al. 2008, 2010; Huang et al. 2009; Sayin 2010). Smaller EL addition levels may increase the formation of unburned HC, resulting in reduced CO₂ emissions; when the level of the added oxygenation compound is sufficiently high, fuel combustion will be more complete, resulting in higher CO₂ emissions.

Smoke emission data, represented by the light absorbing coefficient $k$, are shown in Fig. 6. Generally, the smoke opacity decreased with increasing EL oxygenation level. The smoke was generated in fuel-rich areas of the combustion chamber, especially in the...
fuel-spray core (liquid phase) of the pulverized jet. Oxidant from the additive ensures more complete combustion of the injected fuels and reduces the emission of smoke.

Because the highest engine efficiency was at 1200 rpm and about 5.3 kW, the BSFCs and emissions of the EL–diesel fuel blends were measured under these test conditions (Table 3).

Table 3. Test Results for Different Fuel Formulas

<table>
<thead>
<tr>
<th>Fuel Formula</th>
<th>BSFC (g·kW⁻¹·h⁻¹)</th>
<th>NOₓ (ppm)</th>
<th>CO (%)</th>
<th>CO₂ (%)</th>
<th>Opacity (m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL-0</td>
<td>247.2</td>
<td>272</td>
<td>0.085</td>
<td>5.30</td>
<td>0.489</td>
</tr>
<tr>
<td>EL-5</td>
<td>277.7</td>
<td>242</td>
<td>0.081</td>
<td>4.35</td>
<td>0.446</td>
</tr>
<tr>
<td>EL-10</td>
<td>277.6</td>
<td>264</td>
<td>0.092</td>
<td>4.70</td>
<td>0.351</td>
</tr>
<tr>
<td>EL-15 (2% n-butanol)</td>
<td>282.9</td>
<td>289</td>
<td>0.106</td>
<td>5.51</td>
<td>0.263</td>
</tr>
<tr>
<td>EL-20 (5% n-butanol)</td>
<td>282.2</td>
<td>321</td>
<td>0.085</td>
<td>5.55</td>
<td>0.071</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Experimental investigations have been conducted to evaluate and compare the performances and exhaust emission levels of EL as an additive to conventional diesel fuel, with EL percentages of 5%, 10%, 15% (with 2% n-butanol), and 20% (with 5% n-butanol), in a horizontal single cylinder four stroke diesel engine. The following conclusions were drawn:

1. The present commercial diesel engine can work normally when fuelled with EL-diesel blends with EL percentage up to 20%, without any modification to the engine.
2. BSFC of EL-diesel blends were higher than pure diesel by 10%, due to the relatively lower heating value of EL.
3. Generally, the emissions of NOₓ and CO₂ increased with engine power, in accordance with greater injection of fuels, while they were not stable with the increasing of EL percentage in EL-diesel blends. Emissions of CO were similar for all of the fuel formulas. Smoke emissions were reduced with increasing percentage of EL (Figs. 3 to 6).
4. There were no phase separations observed in the EL-diesel blends stored for more than one month at 4 °C, 10 °C, 15 °C, 20 °C, and 25 °C. The EL-10 (10% EL and 90% diesel fuel) blend is recommended for its efficiency and moderate emissions. Notably, it is stable without any other co-additive (Table 3).

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