Effects of Biodiesel Blending on Particulate and Polycyclic Aromatic Hydrocarbon Emissions in Nano/Ultrafine/Fine/Coarse Ranges from Diesel Engine

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Abstract

The influences of different blending percentages of biodiesel on the size distributions of particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) are not well known. In this study, commercial pure petroleum-based diesel (D100) and three biodiesel blends of 20% (B20), 60% (B60), and 100% (B100) were tested in an engine operated on a dynamometer following the US transient-cycle test procedure. PM size distributions were measured with micro-orifice uniform deposit impactor (MOUDI) and Nano-MOUDI of 0.01-10 μm aerodynamic diameter. The collected samples were extracted then analyzed for PAHs by GC/MS. The results revealed that PM emissions decrease apparently as the blending percentages of biodiesel increase. For D100, B20, B60 and B100, PAH emission factors were 3704, 2720, 1709 and 1514 μg/Hph (horsepower per hour), respectively. Increasing the biodiesel blending percentage reduces the emission of both PAHs and PM. As the blending fractions of biodiesel increased, the PM emissions for the four size ranges decreased. The reductions were significant especially for ultrafine (41.3%) and fine (44.8%) PM. The PAH mass was 32.5%, 32.6%, 34.5%, 30.0% in the ultra-fine size range and 23.8%, 24.3%, 29.2%, 34.5% in the nano size range for D100, B20, B60 and B100, respectively. The addition of biodiesel would cause higher percentages of ultra-fine and nano particulates in exhaust gas. For most biodiesel blending mixtures in the four size ranges, the percentages of PAH emission reduction were higher than those of PM emission. The reduction percentages reached 45.1% and 63.7% for B60, 66.5% and 68.3% for B100, respectively in ultrafine and fine size ranges. The BaPeq emission factors for B100 were 27.2,

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49.5, 74.2 and 13.0 μg/Hph in nano, ultrafine, fine and coarse size ranges. Biodiesel can reduce both PAH emission factors and the PAH corresponding carcinogenic potency in the full size ranges.

**Keywords:** Size distribution; Diesel engine; Engine dynamometer; Emission factor; PAH corresponding carcinogenicity.

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**INTRODUCTION**

In recent years, due to increasing fuel prices and diminishing petroleum reserves, considerable concern has been raised over diesel-powered vehicles using biodiesel as fuel in many countries. Biodiesel, a fuel that can be made from renewable biological sources, such as vegetable oils, animal fats and waste cooking oils, may have the potential to reduce the reliance on imported oil and reduce air pollutant emissions from diesel engines (Wang *et al.*, 2000; Durán *et al.*, 2005). Many studies on air pollutant emissions with biodiesel have been carried out worldwide. Most studies have shown that emissions of carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) are reduced by using biodiesel instead of diesel (e.g. McCormick *et al.*, 2001; Ramadhas *et al.*, 2004; Rakopoulos *et al.*, 2008).

It has been shown that vehicles are important contributor of air pollution in urban areas (Srivastava *et al.*, 2008; Tsang *et al.*, 2008; Zhang *et al.*, 2008). PM emissions from diesel-powered vehicles are typically 10-100 times higher than those from gasoline-powered vehicles (Kittelson, 1998). Previous studies have shown that diesel-powered vehicles are the major contributors of PM in urban areas (Fushimi *et al.*, 2008; Takahashi *et al.*, 2008). The size of PM is an important factor affecting human health, because it determines the deposition position in the respiratory tract. Fine particulates are especially important in regard to adverse health outcomes, such as increased cardiovascular, respiratory morbidity and mortality rates, due to their larger active surface and the higher likelihood of deposition in the alveolar region of the lungs (Schwartz *et al.*, 2002; Hartog *et al.*, 2003).

The influence of biodiesel used in diesel engines on PM size distribution has been investigated. Bagley *et al.* (1998) found that 65% of submicron (0.01-0.1 μm) PM was reduced when using soybean-oil biodiesel in an indirect injection diesel engine. Turrio-Baldassri *et al.* (2004) blended 20% rapeseed-oil with diesel and used it as fuel for buses. The results indicated that most of the emitted PM was in the size range of 0.06-0.3 μm. Jung *et al.* (2006) used pure rapeseed-oil biodiesel as fuel and found a 38% PM reduction. The mean diameter was reduced from 0.08 m with diesel to 0.062 m with rapeseed-oil diesel. Lin *et al.* (2007)
used a palm-biodiesel/diesel blend as fuel. Their results indicated mass median diameters of 0.439, 0.380 and 0.465 m for diesel, B20 (20% biodiesel + 80% diesel) and pure biodiesel, respectively. Fine particulates were found to cause a stronger toxic effect than coarse particulates at the same mass level (Donaldson et al., 1998; Obersdörster et al., 2001). Hence, researchers have paid increasing attention to ultrafine and nano particulates (Hitchins et al., 2000; Shi et al., 2001; Kittelson et al., 2004). Although several studies have been performed on the effects of biodiesel blending on PM size distribution, investigation on PM in nano size range is still lacking.

Diesel-powered vehicle is also an important source of PAHs. Some PAHs have been proven to be carcinogenic (IARC, 1987). Most PAHs are found to be associated with particulate, predominately fine or nano particulate (Kahandawala et al., 2004; Westerdahl et al., 2005). The understanding of the emission characteristics of PM and associated PAHs in a broad size range (from nano to coarse) is useful for assessing the impacts of biodiesel on atmospheric environment and human health. In this study, petrol-diesel, biodiesel transformed from waste cooking oil and blended mixtures of diesel and biodiesel, were tested. The PM and the associated PAHs in diluted exhaust were collected by a MOUDI (micro-orifice uniform deposit impactor) and a Nano-MOUDI. The PM emissions and associated PAHs in nano/ultrafine/fine/coarse ranges were measured and the influences of biodiesel blending on the emission characteristics of PM and PAHs were investigated.

EXPERIMENTAL SECTION

Fuels

Commercial pure petroleum-based diesel (D100) and three different blending mixtures of diesel and biodiesel, i.e. volume percentages of biodiesel 20% (B20), 60% (B60), 100% (B100), were tested in this study. The biodiesel was obtained from esterification of waste cooking oil. The diesel was supplied by the Chinese Petroleum Company and the biodiesel was supplied by Taiwan NJC (New Japan Chemical) Corp. The fuel properties of D100 and B100 were measured and are listed in Table 1. Before each test, the engine was run for 20 min with the test fuel to avoid possible memory effects from the previous run.

Engine, Dynamometer and Driving Cycle

The experiments were carried out with a modern diesel engine (Mitsubishi, type 6M60-1AT2): six cylinders, turbocharged with indirect fuel injection, bore and stroke of 95 mm × 100 mm, total displacement volume of 7545 c.c., maximum torque of 217.6 Nm at 2000 rpm, and maximum horsepower of 80.9 kW at 3700 rpm. The engine was mounted and operated on a Schenck DyNAS 335 dynamometer with a...
Table 1. Fuel properties of D100 and B100.

<table>
<thead>
<tr>
<th>Fuel properties</th>
<th>D100</th>
<th>B100</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubricity (μm)</td>
<td>376</td>
<td>153</td>
<td>HFRR-Diesel lubricity test</td>
</tr>
<tr>
<td>Micro carbon residue test (wt%)</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>ASTM D4530</td>
</tr>
<tr>
<td>Density (g/mL at 15.56°C)</td>
<td>0.8338</td>
<td>0.8794</td>
<td>ASTM D4052</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>ASTM D482</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-9</td>
<td>6</td>
<td>ASTM D97</td>
</tr>
<tr>
<td>Kinetic viscosity at 40°C (cSt)</td>
<td>3.158</td>
<td>4.422</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>81</td>
<td>165</td>
<td>ASTM D93</td>
</tr>
<tr>
<td>Net heat of combustion (cal/g)</td>
<td>10273</td>
<td>8819</td>
<td>ASTM D240</td>
</tr>
<tr>
<td>Water and residue (vol%)</td>
<td>&lt; 0.0005</td>
<td>0.0005</td>
<td>ASTM D2709</td>
</tr>
<tr>
<td>Sulfur (ppmw)</td>
<td>28.2</td>
<td>2.1</td>
<td>ASTM D-5453</td>
</tr>
<tr>
<td>Heat value (cal/g)</td>
<td>10957</td>
<td>9440</td>
<td>ASTM D240(gross)</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>85.06</td>
<td>76.35</td>
<td>ASTM D-5291</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>13.50</td>
<td>12.26</td>
<td>ASTM D-5291</td>
</tr>
</tbody>
</table>

DC-IV control system. The DC-current dynamometer with a fully automatic control system is capable of supplying maximum power and torque at 335 kW and 800 Nm, respectively.

The driving cycle was in accordance with the U.S. Code of Federal Regulations 40, Part 86, Subpart N (U.S. transient cycle). The U.S. transient cycle includes a wide variety of speeds and loads sequenced to simulate real-traffic on an expressway in congested and uncongested urban driving. The details of the driving cycle are described elsewhere (Yang et al., 2007).

**Dilution Tunnel and Sampling System**

The emission measurement system was operated on the constant volume principle, and a dilution tunnel was used to collect particulate Fig. 1. The dilution tunnel, 9175 mm in length and 610 mm in diameter, is used to dilute the exhaust gas with filtered air. It had a constant dilution air/sample flow ratio of 25:1 and a total of 30 m³/min, mixed with the dilution air to ensure good mixing. These settings were chosen in order to maintain the temperature below the U.S. EPA specification of 52°C at the sampling point.

After dilution, PM (the bound PAHs, as well) was size-separated and collected with a MOUDI and a Nano-MOUDI (model 100 and 115, respectively; MSP Co.) equipped with aluminum foil with a diameter of 47 mm. The sampling flow rates for the MOUDI and Nano-MOUDI were 30 and 10 L/min, respectively. The impactors separated the PM into 13 size ranges with the following equivalent cutoff diameters (dp, at 50% efficiency): 0.010-0.018, 0.018-0.032, 0.032-0.056, 0.056-0.1, 0.1-0.18, 0.18-0.32, 0.32-0.56, 0.56-1.0, 1.0-1.8, 1.8-3.2, 3.2-5.6,
5.6-10, and 10-18 μm. The collected PM was combined and classified into four size groups in this study: nano (0.01 μm < dp < 0.056 μm), ultrafine (0.056 μm < dp < 0.32 μm), fine (0.32 μm < dp < 1.8 μm) and coarse (1.8 μm < dp < 10 μm). The combined filters were extracted together for PAH analysis. Combining the 13 filters into the 4 groups was done to increase the PAH analysis sensitivity.

**Analysis of PM and PAHs**

Before and after sampling, the filters were stored for 24 h in a desiccator at 25°C in 45% relative humidity. They were then weighed on an electronic balance (Sartorius CP225D) with a resolution of 1.00 μg. The emission factor of PM was determined by dividing the mass emitted by the horsepower-per-hour of that driving test. After weighing, the combined filter samples were Soxhlet-extracted with a mixed solvent (n-hexane 125 mL and dichloromethane 125 mL) for 24 h. The extract was then concentrated by purging with ultra-pure nitrogen to 2 mL for the cleanup procedure and then reconcentrated to 0.5 mL with ultra-pure nitrogen. The concentrations of the following PAHs were determined: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, cyclopenta[c,d]pyrene, benz[a]anthracene, chrysene, benzo[b]-fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3,cd]pyrene, dibenz[a,h]-anthracene, benzo[b]chrysene, benzo[ghi]-perylene and coronene.

A gas chromatograph (GC) (Agilent 6890) with a mass selective detector (MS) (Agilent 5973N) and a computer workstation was used for the PAH analysis. This GC/MS was
equipped with an Agilent capillary column (Agilent Ultra 2 - 50 m × 0.32 mm × 0.17 μm), an Agilent 7673A automatic sampler, with an injection volume of 1 μL, splitless injection at 310°C, ion source temperature at 310°C, oven, from 50°C to 100°C at 20°C /min; 100°C to 290°C at 3°C /min; hold at 290°C for 40 min. The masses of primary and secondary ions of PAHs were determined by using the scan mode for pure PAH standards. Qualification of PAHs was performed by using the selected ion monitoring (SIM) mode. The analysis of PAHs is described in detail in our previous study (Yang et al., 2005). In this study, two internal standards (phenanthrene-d10 and perylene-d12) were used to check the response factors and the recovery efficiencies for PAH analysis. The recovery efficiencies of 16 individual PAHs and these two internal standards were determined by processing a solution containing known PAH concentrations through the same experimental procedure used for the samples. The recovery efficiencies of two internal standards were between 83.0% and 88.0%, and were fairly constant.

RESULTS AND DISCUSSION

PM Emissions and Size Distributions

The weights of particulates collected on the 13 stage filters of the MOUDI and nano-MOUDI were recorded and added together as total PM emission. The emission factors (mass emitted per horsepower hour) of PM with the four fuels are listed in Table 2. PM emission factors were 0.052, 0.044, 0.041 and 0.037 g/Hph for D100, B20, B60 and B100, respectively. PM emissions decrease as the blending percentages of biodiesel increase. This result agrees with those of the previous studies (Haas et al., 2001; Lapuerta et al., 2008). Reduction of PM emission for biodiesel can be attributed to the fact that biodiesel contains no aromatic constituent and much less sulfur in comparison to diesel (Wang et al., 2000; Dorado et al., 2006).

The PM size distributions (df/dlog dp versus dp: f is the mass fraction of PM in a certain size interval) from 0.0018 to 10 μm for the test fuels are shown in Fig. 3. Of the four size ranges (i.e. nano, ultra-fine, fine and coarse) adopted in this study, approximately 80% of PM is smaller than 1.0 m for all the four fuels, which indicates that the particulates emitted from diesel engine are primarily inhalable particulates. There is no significant difference for the PM size distribution between D100 and B20. As the biodiesel blending percentage increases to 60% (B60), the ultra-fine and nano particulates increase. While pure biodiesel (B100) was used, nano particulates predominated in the size distribution. The calculated mass median diameters (MMDs) of PM shown in Fig. 2 are 0.146, 0.144, 0.134 and 0.124 μm for D100, B20, B60 and B100, respectively. The results show that as the blending percentage of biodiesel increase, the emitted particulates shift to ultrafine size range. The results also show that the PM size distribution of the biodiesel
Table 2. Emission factors of PM and PAHs.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>D100</th>
<th>B20</th>
<th>B60</th>
<th>B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM (g/Hph)</td>
<td>0.052</td>
<td>0.044</td>
<td>0.041</td>
<td>0.037</td>
</tr>
<tr>
<td>PAHs (µg/Hph)</td>
<td>3704</td>
<td>2720</td>
<td>1709</td>
<td>1514</td>
</tr>
</tbody>
</table>

Fig. 2. PM size distributions for the four size ranges.

blending fractions is similar to those of the previous studies (Bagley et al., 1998; Jung et al., 2006).

**PAH Emissions and Size Distributions**

Emission factors of the 16 PAHs for the test fuels are listed in Table 2. For D100, B20, B60 and B100, PAH emission factors are 3704, 2720, 1709 and 1514 µg/Hph, respectively. Increasing the biodiesel blending percentage reduces PAH emission, which agrees with the results of PM. In comparison with D100, the reduction of PAH emissions for B20, B60 and B100 are 11.7%, 53.9%, 56.4%, respectively. The results also agree with previous studies (Corrèa and Arbilla, 2006). Reduced PAH emission was caused by the fact that PAHs are derived from unburned fuel and from lubricating oil of physical and/or chemical condensation (Tancell et al., 1995; Miguel et al., 1998). The nil or very little aromatic
content of biodiesel fuel could contribute to reducing particulate-phase PAHs; but more importantly biodiesel’s oxygen content most likely enables more complete combustion than diesel fuel, causing a decrease in PAH emissions. This phenomenon is especially true in this study because only particulate-phase PAHs are analyzed. Since PM emissions are reduced for the biodiesel blending mixtures, the particulate-associated PAHs would be reduced as well.

PAH size distributions are shown in Fig. 3. The size distributions of PAHs for the four fuels are quite similar with those of PM (Fig. 2); i.e. the size distribution of PAHs shift to ultrafine and nano size ranges as the biodiesel blending fractions increase. These results are expected since particulate phase PAHs are bound with PM. Particle-bound PAH emissions are closely related to PM emissions. The PAH mass are 32.5%, 32.6%, 34.5%, 30.0% in ultra-fine size range and are 23.8%, 24.3%, 29.2%, 34.5% in nano size range for D100, B20, B60 and B100, respectively. The addition of biodiesel would cause a higher percentage of ultra-fine and nano particulates in exhaust gas.

**Influences of Biodiesel Blending on PM and PAH Emissions**

The influences of biodiesel blending on
PM and PAH emissions are assessed by comparing the effects of the various ratios of blended biodiesel fuels with D100. These reduction percentages (\( \eta \), %) were calculated using the formula:

\[
\eta (\%) = \left[ \frac{\text{Emission With D100} - \text{Emission With biodiesel blend}}{\text{Emission with D100}} \right] \times 100
\]

(1)

This means that the emissions are reduced by biodiesel blending mixtures if the reduction percentages are positive. The reduction percentages of PM and PAH emissions by using B20, B60 and B100 instead of D100 in nano, ultrafine, fine and coarse size ranges are shown in Fig. 4. The results show that PM and the associated PAH emissions for the four size ranges were all reduced with B20, B60 and B100 in comparison with D100. For B20, reduction percentages for PM emissions were 11.2%, 14.9%, 19.8% and 10.6% for nano, ultrafine, fine and coarse size ranges, respectively. As the blend ratio of biodiesel increased, the PM emissions for the four size ranges were reduced. The reductions were significant especially for ultrafine and fine PM. The reduction percentages were 21.8% and 35.4% for B60, 41.3% and 44.8% for B100, respectively in ultrafine and fine size ranges.

The influences of biodiesel blending on

Fig. 4. Reduction percentages of (a) PM and (b) PAH emissions by biodiesel blending mixtures compared with D100.
PAH emissions were similar to PM; i.e., the reduction percentages for PAH emissions increased as the biodiesel blending ratio increased. The percentages of PAH emission reduction were actually higher than that of PM emissions for most biodiesel blending mixtures in the four size ranges. The reduction percentages reached 45.1% and 63.7% for B60, 66.5% and 68.3% for B100, respectively in ultrafine and fine size ranges. Biodiesel contains much lower PAH content, which is the main reason why PAH emissions were reduced (Agarwal, 2007). It is worth noting that for pure biodiesel (B100), PAHs were still emitted. Previous studies have proposed that PAH emissions can arise from fuel PAH surviving and synthesizing during the combustion process (Tancell et al., 1995; Rhead and Hardy, 2003). The results indicate that thermal synthesis plays an important role for PAH generation in the process of diesel/biodiesel combustion.

**PAH Corresponding Carcinogenity**

In this study, toxic equivalency factors (TEFs) were applied for the 16 analyzed PAHs to assess the carcinogenic potencies of nano, ultrafine, fine and coarse particulates for the four fuels. The TEFs have been devised as a way of comparing the carcinogenic potency of the individual PAHs with the carcinogenicity of BaP (Nisbet and LaGoy, 1992). The TEFs are expressed in terms of their BaP emission equivalent (BaPeq). The BaPeq factor for each individual PAH was calculated by multiplying the emission factor with corresponding TEF values. Fig. 5 shows the BaPeq emission factors for the four size ranges with the four test fuels. For D100 as well as the three biodiesel fuels, the fine particulate has the highest BaPeq emissions, followed by ultrafine particulates. The results indicate that fine size particulates emitted from diesel engine have the strongest PAH-related carcinogenic

![Fig. 5. BaPeq emission factors for the four size ranges with four test fuels.](image)
potencies. The results also show that D100 has the highest BaPeq emissions in all size ranges compared with the three biodiesel mixtures. The BaPeq emission factors for D100 are 114, 128, 202 and 128 μg/Hph for nano, ultrafine, fine and coarse particulates, respectively. As the biodiesel blending ratios increase, the BaPeq emissions decrease gradually. The BaPeq emission factors for B100 are 27.2, 49.5, 74.2 and 13.0 μg/Hph in nano, ultrafine, fine and coarse size ranges. The results indicate that biodiesel can reduce both PAH emission factors and the PAH corresponding carcinogenic potency in the full size ranges.

CONCLUSIONS

In this study, the effects of the three different blending mixtures of biodiesel fuel (B20, B60, B100) on particulate, particulate PAH size distributions, and their carcinogenic potencies are examined and compared with those of diesel fuel (D100). Approximately 80% of PM is smaller than 1.0 μm for all the four fuels, which indicates that the particulates emitted from diesel engine are primarily inhalable particulates. As the biodiesel blending percentage increased to 60% (B60), the ultrafine and nano particulates increased. The MMDs of PM are 0.146, 0.144, 0.134 and 0.124 μm for D100, B20, B60 and B100, respectively. The results show that as the blending percentage of biodiesel increased, the emitted particulates shifted to ultrafine and nano size ranges. The size distributions of PAHs for the four fuels were quite similar with those of PM; i.e. the size distribution of PAHs shifted to ultrafine and nano size ranges as the biodiesel blending fractions increased. Particle-bound PAH emissions were highly related to PM emissions. The PAH mass was 32.5%, 32.6%, 34.5%, 30.0% in ultra-fine size range, and 23.8%, 24.3%, 29.2%, 34.5% in nano size range for D100, B20, B60 and B100, respectively. As the blending ratio of biodiesel increased, PM emissions for the four size ranges were reduced. The reductions were significant especially for ultrafine and fine PM. The reduction percentages were 21.8% and 35.4% for B60, 41.3% and 44.8% for B100, respectively in ultrafine and fine size ranges. For most biodiesel blending mixtures in the four size ranges, the percentages of PAH emission reduction were higher than those of PM emission. The reduction percentages reached 45.1% and 63.7% for B60, 66.5% and 68.3% for B100, respectively in ultrafine and fine size ranges. Biodiesel is more lower in PAH content, which is the main reason for the reduction in PAH emissions. Biodiesel can reduce not only PAH emission factors, but also the PAH corresponding carcinogenic potency.

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