Particulate Emissions and Biodiesel: A review

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Abstract
The current mode of transport using fuel cannot be characterized as harmless to human health or as sustainable. The whole process of extracting, processing and using of petroleum products can be seen as the raw material cycle in nature. This cycle also cause serious damage to the environment and human health. Many studies on air pollutant emissions with biodiesel have been carried out worldwide. Studies have shown that diesel-powered vehicles are the major contributors of PM emissions. PM 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. Hence, it is overwhelming argument that the use of biodiesel instead of diesel causes reduce of PM emissions. Of course, this reduction will become smaller with the reduction of biodiesel proportion in the blended fuel. The trend with which PM emissions of biodiesel will be reduced, is due to lower aromatic and sulfur compounds and higher cetane number for biodiesel, but the more important factor is the higher oxygen content.

Keywords: biodiesel, emission, exhaust, human health, particulate matter, reduction

1. Introduction

The aim of study is to give an overview of particular emissions for biodiesel application. Following this aspect we focused our attention on the literary knowledge of fuel development new trend in relation to human health and environment, particular emissions and human health, and particular emissions and biodiesel.

New trend fuel development in relation to human health and environment
The whole process of extracting, processing and using of petroleum products can be seen as the raw material cycle in nature. The problem is that the cycle is closed. The time that was required for mineralization of fossil organic matter is much longer than the time that humanity needs to usage of these resources. This cycle is also causing serious damage to the environment and human health. Using alternative fuels is conditional on a many of aspects. In addition to legislative measure is necessary to fulfill the technical and economic requirements. Also important are the effects on the engine, production of the emissions and fuel consumption, which affect the economics of their using. New types of fuel must fulfill strict environmental requirements and must correspond to technical standards.

Table 1. The concept of the development of alternative fuels in the European Union by 2020 [1]

<table>
<thead>
<tr>
<th>Year</th>
<th>biodiesel (%)</th>
<th>Natural gas (%)</th>
<th>Hydrogen (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>2010</td>
<td>6</td>
<td>2</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>2015</td>
<td>7</td>
<td>5</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>2020</td>
<td>8</td>
<td>10</td>
<td>5</td>
<td>23</td>
</tr>
</tbody>
</table>

Source: European Commission, DG Tren (TREN)

The European Air Quality Directive 2008/EC/50 (EC, 2008) includes the requirement that the daily average PM10 concentration of 50 μg per m³

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should not be exceeded on more than 35 days each year. Despite a generally declining trend in the number of days on which PM10 concentrations exceeded $50 \, \mu g\, m^{-3}$, many cities are still not in compliance with the European Air Quality Directive in particular at traffic locations [2]. In addition to measures addressing residential and industrial emissions to reduce the urban background, further traffic measures would therefore seem to be required. PM10 is the statutory indicator for evaluating the effectiveness of such measures. Potential candidates in this regard are particle number concentration, PM2.5. In this section, EC, PM2.5 and PM10 are compared as indicators of PM emissions by road traffic. This comparison is based on results from a study by Putaud et al. [3] into the chemical composition of PM across Europe. The data for EC has been expanded by measurements taken in the context of “TRANSPHORM” (www.transphorm.eu) a current European research project into transport-related PM.

**Particular emissions and human health**

Many studies on air pollutant emissions with biodiesel have been carried out worldwide. Most studies have shown that emissions of particulate matter (PM) are reduced by using biodiesel instead of diesel [4-6]. Studies have shown that diesel-powered vehicles are the major contributors of PM in urban areas [7, 8]. 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 [9, 10]. Direct evidence via a controlled inhalation study is lacking [11] and the potentially harmful effects of emissions may not be suitably predicted by studies using cells or healthy animals. The association between exposure to urban PM and cardiovascular disease is well established and pose a serious problem [12-15]. Therefore, technologies that alter PM and co-pollutants require testing in models of cardiovascular disease. Diesel exhaust is a complex mixture of organic and inorganic compounds and gas, liquid, and solid phase materials. Diesel particulates consist of an elemental carbon core with several organic compounds (soluble and insoluble in organic solvents), sulfates, nitrogen oxides, heavy metals, trace elements and irritants (such as acrolein, ammonia, acids, fuel vapors, unburned lubricating oils, moisture) adsorbed to its surface. The organic or hydrocarbon compounds are made up of a continuous gradation of carbon-containing compounds that change from a hydrogen to carbon ratio of 2:1 to eventually a ratio of 0:1 [16]. They include various classes of compounds such as aldehydes, alkanes and alkenes, (both straight and branched chain), and aromatic compounds (single rings, substituted, and poly-nuclear). Any of these species may also contain functional groups such as carbonyl (C=O), hydroxyl (OH) and nitro (NO$_2$). These organic compounds originate primarily from the unburned fuel and the lubricating oil, although some may be formed during the combustion process and/or reaction with catalysts. The inorganic species include sulfur, oxygen, carbon, and nitrogen-containing compounds such as sulphate (SO$_4$), carbon monoxide (CO), elemental carbon, and oxides of nitrogen (NOx). Some of these compounds may also have their origin from the fuel, especially those containing sulfur and carbon [17]. About 90% of diesel particulates encompass a size range from 7.5 nm to 1.0 m [18] and are therefore important in terms of potential health impacts due to the ability of tiny particles to be inhaled and eventually get trapped in the bronchial passages and alveoli of the lungs. The carcinogenic effects related to diesel exhaust particles is now considered to have at least two components, one related to the inorganic “carbon core” or solid or insoluble portion and the other due to the adsorbed organics or soluble organic fraction portion. Studies on the health effects of diesel exhaust have until recently focused primarily on cancer outcomes [19]. However, in recent years, attention has begun to focus on understanding the non-cancer respiratory effects of diesel exhaust and their possible role in the acute or chronic health effects of airborne PM. There is emerging experimental evidence of irritants and/or immunologic effects of diesel exhaust on the respiratory system. In addition, recent epidemiological studies have demonstrated association between residential proximity to traffic sources and adverse respiratory outcomes, including asthma hospitalization among children, increased respiratory symptoms, and diminished
lung function [20-22]. Fine particulates were found to cause a stronger toxic effect than coarse particulates at the same mass level [23, 24]. Use of waste cooking oil derived biodiesel as an alternative fuel in diesel engines has increased significantly in recent years. The effect of waste cooking oil derived biodiesel on particulate emissions from diesel engines needs to be investigated thoroughly. This study was conducted to make a comparative evaluation and size-differentiated speciation of the particulate bound elements from ultra-low sulfur diesel and waste cooking oil derived biodiesel and a blend of both of the fuels (B50). Particle mass and their elemental size distributions ranging from 0.01-5.6 μm were measured. It was observed that more ultrafine particles (<100 nm) were emitted when the engine was fueled with waste cooking oil derived biodiesel. Fifteen particulate-bound elements such as K, Al, Mg, Co, Cr, Cu, Fe, Mn, Cd, Ni, As, Ba, Pb, Zn and Sr were investigated and reported in this study. Potential health risk associated with these particulate bound elements upon inhalation was also evaluated based on dose-response assessments for both adults and children. The findings indicate that the exposure to PM of the B100 exhaust is relatively more hazardous and may pose adverse health effects compared to that of ultra-low sulfur diesel. Also, investigations on human health risk due to exposure to more ultrafine particles indicate that more ultrafine particles contribute a major fraction (>70%) of the total estimated health risk [25].

**Particular emissions and biodiesel**

Hence, it is overwhelming argument that the use of biodiesel instead of diesel causes reduce in PM emissions [26-39]. Wu et al. [40] investigated the emission performance for five pure biodiesels on a Cummins ISBe6 DI engine with turbocharger and intercooler, and found different biodiesels reduced PM emission by 53–69% on average compared with the diesel fuel. Lin et al. [30] also observed that there was significant reduction (ranging from 50% to 72.73%) in the smoke emission for 8 kinds of vegetable oil methyl ester fuels compared with petroleum diesel fuel. In addition, it was reported in [27, 41-44] that the decreased PM value were over 50% for biodiesel in regard with diesel. A small portion of authors found that there was no difference in PM emissions for biodiesel relative to diesel [45], or even there was a bit increase [46-48]. Most of the authors contributed these phenomena to higher viscosity of biodiesel which causes fuel atomization worse and combustion quality deterioration [45, 46, 48]. But Armas et al. [47] considered that the increased PM was due to the unburned or partially burned hydrocarbon emissions. This hydrocarbon will condense and be absorbed on the PM surface, thus result in the increase of soluble organic fraction which is the main component of PM. The contrast experiments were implemented with different contents of biodiesel blends, including 2 kinds blends compared in [32, 37, 49, 50], 3 kinds in [26, 43, 44, 51], and 4 or above 4 kinds in [4, 52, 53, 54]. Generally, PM emissions decrease remarkably with increasing in biodiesel content in blends. Sahoo et al. [44] compared the effect of the blending ratio of 20%, 50% and 100% for 3 kinds of jatropha, karanja and polanga based biodiesel on smoke emissions, and found the use of KB20, KB50 and KB100 caused a reduction in smoke in the range of 28.96%, 44.15% and 68.83% with respect to diesel at a rated speed, respectively. Similarly, decrease in smoke for JB20, JB50, JB100, PB20, PB50 and PB100 are 28.57%, 40.9%, 64.28%, 29.22%, 44.15% and 69.48% was observed at the rated speed, respectively. Luján et al. [43] showed a reduction in PM emissions of 32.3%, 42.9% and 53% for B30, B50 and B100 respectively, which is obtained from after-treatment on a high speed direct injection 4-cylinder, 1.6 L, turbo diesel engine. Additionally, Canakci [55] showed that the smoke numbers of no. 2 diesel fuel, no. 1 diesel fuel, SME20 (20% soybean oil methyl ester), and SME100 (100% soybean oil methyl ester) were 1.09, 1.06, 0.89, and 0.42, respectively. Haas et al. [56] found that PM emissions reduced by 20% and 50% for 20% blends and 100% biodiesel, respectively. PM reduction [57] which was gained with biodiesel blends (B35), is significant. B35 normally reduces PM emissions by 25% in the same unaltered trucks. When comparing CO and PM emissions, we note that CO emissions correlate with PM emissions very well, which coincides with the test results of Choi et al. [58]. B35 PM the reductions can be attributed to two factors. First, SME has no aromatic content and much lower sulfur content than no. 2 diesel. Aromatic content is widely known to contribute to PM formation. Diluting the sulfur in no. 2 diesel lowers the amount of sulfate
and its bonded water, reducing particulate emissions. B35 reduced aromatic content to less than 20%, from 30% in no. 2 diesel. However, the more important factor is most likely biodiesel’s oxygen content. Soot formation, caused by high temperature decomposition, mainly takes place in the fuel rich zone at high temperatures and pressures, specifically within the core region of each fuel spray. If fuel is partially oxygenated, it could reduce locally fuel-rich regions and limit soot formation, thus reducing PM emissions. Because of its low volatility, any unburned ester will condense on the filter and be measured as soluble organic fraction. Some studies have shown that neat soybean oil methyl ester increased volatile organic diesel particulate matter but greatly reduced nonvolatile diesel particulate matter with a net decrease in total diesel particulate matter. Because of the high volatile particulate matter content in exhaust, benefits may be realized through using an oxidation catalyst. Aydin and Bayindir [46] found that the higher content of biodiesel in the blends caused the more PM emissions and contributed the reason to the higher density and the higher viscosity which deteriorates the fuel atomization. Lapuerta et al. [51] obtained that, there were higher reduce in PM for the 25% biodiesel blends than that of 50%, 70% and 100% biodiesel content. Many authors contributed the reduce in PM emissions to the higher oxygen content in biodiesel, which causes combustion more complete, and further promote the oxidation of soot. Particularly, Frijters and Baert [59] tested 14 biodiesel blends with oxygenates and found that it had a good relationship between PM emissions and fuel oxygen content. The lack of aromatic and sulphur compounds further contribute to reduction in PM emissions [43, 52, 60].

Korres et al. [53] reported that biodiesel addition to JP-5 reduced PM emissions as compared to the JP-5 alone and this was attributed to the higher cetane number of biodiesel from soybean oil compared to the reference diesel and improved combustion efficiency. This argument was approved in [52]. Higher density and viscosity of biodiesel could affect the volatilization and atomization processes, and further deteriorate combustion in chamber. This viewpoint was applied to the explanation of the increased PM emissions for B75 and B100 fuels in [46], which also appeared in [52]. Advance in combustion for biodiesel, as a result of the higher cetane number [32], and advance of start of injection of biodiesel due to the higher density and viscosity and the lower compressibility [27], prolong the residence time of soot particle in the high temperature environment, and thus further promote the oxidation in the presence of oxygen [61]. Although biodiesel has a higher distillation temperature, the lower boiling point of biodiesel enhances the probability of the lower soot or tar formed from the heavy hydrocarbon emission compounds [51]. Some authors [30, 40, 44] investigated the effect of biodiesel feedstock on PM emissions. Of course, a few authors found no relationship between PM emissions and biodiesel feedstock. Haas et al. [56] tested biodiesels with different saturation levels on a 6-cylinder direct Injection engine. The PM emissions reduced by 50% for all biodiesel, and had nothing to do with their saturation levels. However, they all concluded that the main factors affecting PM formation is the oxygen content of biodiesel. Emissions also depend on biodiesel chemical composition, and are thus feedstock-dependent. Determination of the emissions profile is a key step in assessing the acceptability of a biodiesel fuel produced from a new feedstock [62]. Other authors took a similar position in their studies on research of emissions in this field, too [63-68].

2. Conclusion

Based on analysis above, the following conclusions are available:

(a) Biofuels are easily available from common biomass sources, they are represent a carbon dioxide-cycle in combustion, biofuels have a considerable environmentally friendly potential, there are many benefits the environment, economy and consumers in using biofuels, and they are biodegradable and contribute to sustainability.

(b) It is dominating argument that PM emissions of biodiesel are significantly reduced compared to diesel. Of course, this reduction will become smaller with the reduction of biodiesel proportion in the blended fuel, and abnormal variation may appear in the case of a certain content of biodiesel.

(c) The trend which PM emissions of biodiesel will be reduced is due to lower aromatic and sulfur compounds and higher cetane number for biodiesel, but the more important factor is the higher oxygen content.
(d) The feature of injection advance of biodiesel is inappropriate to the diesel engine in optimal state, it is necessary to further study the matching characteristics of biodiesel and/or its blends with engine.

(e) The use of EGR might deteriorate PM emissions of biodiesel, although PM emissions level is still very low relative to diesel. But PM emissions of biodiesel compared to diesel will increase abnormally in the case of low temperature condition. This trend is worthwhile to further study.

(f) Emissions also depend on biodiesel chemical composition, and are thus feedstock-dependent. Determination of the emissions profile is a key step in assessing the acceptability of a biodiesel fuel produced from a new feedstock.

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