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Particle emissions from biodiesels with different physical properties and chemical composition

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HIGHLIGHTS

16 • Four biodiesels were used to investigate their influence on particle emissions.

17 • Particle emission increased with the increase of biodiesel carbon chain length.

18 • Particle emissions reduced consistently with fuel oxygen content. 19

• Particle median size found dependent on the type of fuel used.

20 Biodiesel chemical composition found more important than physical properties.

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ABSTRACT

Biodiesels produced from different feedstocks usually have wide variations in their fatty acid methyl ester (FAME) so that their physical properties and chemical composition are also different. The aim of this study is to investigate the effect of the physical properties and chemical composition of biodiesels on engine exhaust particle emissions. Alongside with neat diesel, four biodiesels with variations in carbon chain length and degree of unsaturation have been used at three blending ratio (B100, B50, B20) in a common rail engine. It is found that particle emission increased with the increase of carbon chain length. However, for similar carbon chain length, particle emissions from biodiesel having relatively high average unsaturation are found to be slightly less than that of low average unsaturation. Particle size is also found to be dependent on fuel type. The fuel or fuel mix responsible for higher PM and PN emissions is also found responsible for larger particle median size. Particle emissions reduced consistently with fuel oxygen content regardless of the proportion of biodiesel in the blends, whereas it increased with fuel viscosity and surface tension only for higher diesel-biodiesel blend percentages (B100, B50). However, since fuel oxygen content increases with the decreasing carbon chain length, it is not clear which of these factors drives the lower particle emission. Overall, it is evident from the results presented here that chemical composition of biodiesel is more important than its physical properties in controlling exhaust particle emissions.

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1. Introduction 56

57 Compression Ignition (CI) engines are increasing in popularity due to their higher thermal efficiency. They power a wide range 58 of land and sea transport as well as provide electrical power, used 59 in farming, construction and industrial applications. Tail pipe 60

http://dx.doi.org/10.1016/j.fuel.2014.05.053 0016-2361/© 2014 Elsevier Ltd. All rights reserved. emissions of diesel engines, especially particulate matter (PM) are still a matter of concern due to its harmful effects both on human health and the environment [1,2]. Exposure to diesel particulate matter (DPM) can cause pulmonary diseases such as asthma, bronchitis and lung cancer [1] and because of these adverse effects, the International Agency for Research on Cancer (IARC) included DPM as carcinogenic to human health.

The harmful effects caused by DPM are related to both the physical properties and chemical composition of the particles. The physical properties that influence respiratory health include parti-

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M.M. Rahman et al./Fuel xxx (2014) xxx-xxx

71 cle mass, surface area, mixing status of particles, number and size 72 distribution [3]. The particles deposit in different parts of the lung 73 depending on their size. The smaller the particles the higher the 74 deposition efficiency [4] and the greater the chance of them pene-75 trating deep into the lung. The smaller particles stay suspended in 76 the atmosphere for longer thus have a higher probability of being 77 inhaled and consequently deposited deep in the alveolar region 78 of the lung. Particle number governs the ability of particles to grow 79 larger in size by coagulation while particle surface area determines the ability of the particles to carry toxic substances. Recent studies 80 reveal that DPM surface area and organic compounds play a signif-81 82 icant role in initiating various cellular and chemical processes 83 responsible for respiratory disease [3,5]. In addition to this, a large fraction of DPM is black carbon, which is considered the second 84 85 most potential green house warming agent after carbon dioxide 86 [2]. After treatment devices (ATD) like diesel particulate filters 87 (DPF) and diesel oxidation catalysts (DOC) aid in reducing DPM 88 [6]. Alternative fuels are another potential emission reducing 89 source [7]. Of these fuels, biodiesel is considered one of the more 90 promising for diesel engines [8,9] as it produces less PM and other 91 gaseous emissions [9-11]. Biodiesel in diesel engines also has the 92 potential to neutralize carbon emissions as it comes from a renew-93 able source of energy.

94 Biodiesel is a mixture of fatty acid esters with physicochemical 95 properties that mostly depend on the structure of the ester mole-96 cule. They can be produced from a variety of feedstock sources 97 such as vegetable oil, animal fat, municipal and industrial waste 98 and some even from insects [12-15]. The vast majority of feedstocks actually used now days are derived from vegetable oils 99 100 and animal fats. An extensive range of fatty acid profiles exist 101 among these feedstocks [16], with fatty acid profiles being even different within the same feedstocks. If plant sources are used, 102 103 these variations can be controlled by manipulating stock growing 104 conditions. Physical properties and chemical composition of bio-105 diesel varies among different feedstocks, which can have a notice-106 able influence on engine performance and emissions [17]. 107 McCormick et al. [18] reported constant PM emissions from differ-108 ent biodiesel feedstocks when the density was less than 0.89 g/cm^3 109 or cetane number was greater than about 45, but increase of NOx 110 emissions with the increase of biodiesel density and iodine num-111 ber. In contradiction to these findings, a difference in particle emissions from biodiesel from different feedstocks has also been 112 reported [19,20]. Lapuerta et al. [10] reported a 10% increase of 113 114 NOx and 20% decrease of particle emissions by unsaturated biodiesel. Benjumea et al. [21] found that the degree of unsaturation in 115 116 biodiesel does not significantly affect the engine performance but 117 increases smoke opacity and THC emissions. Karavalakis et al. 118 [22] reported noticeable influence of biodiesel origin on particle 119 emissions, especially particle associated PAH and carbonyl emis-120 sions. Very recently Salamanca et al. [23] reported increased PM 121 and HC emissions from biodiesel that contains more unsaturated compounds that favor soot precursor formation. There is no dis-122 tinction however in the literature, which indicates whether chem-123 ical composition of biodiesel, physical properties or a combination 124 of these is responsible for this variation in engine performance and 125 126 emissions. This study therefore, aims to investigate the effect of biodiesel physical properties and chemical composition on engine 127 exhaust particle emissions. It is an extension of the previous study 128 129 [24] where results from the same experiments were presented for 130 the engine performance characteristics and emission of pollutants 131 including some preliminary results for the particle emission, par-132 ticularly for pure biodiesel. It should be noted that the results for 133 B100 are reproduced here for comparison purposes. Furthermore, 134 the paper elaborates on these findings and presents new analysis 135 in terms of the physical properties chemical composition of the 136 fuels and their blends.

2. Materials and methods 137

2.1. Engine and fuel specification

This experimental study was performed in a heavy duty 6 liters, 139 six cylinders, turbocharged after cooled, common rail diesel engine 140 typically used in medium size trucks. Test engine is the same as 141 used in Pham at el. [24]. Table 1 shows specification of the test 142 engine. The engine was coupled to a water brake dynamometer, 143 and both of them are connected to an electronic control unit 144 (ECU). Engine was operated at 1500 rpm (maximum torque speed) 145 and at 2000 rpm (intermediate speed), and four different loads 146 including 25%, 50%, 75%, and 100% for each engine speed. Maxi-147 mum load at any particular engine speed depends upon the type 148 of fuel used. Therefore, for each fuel maximum load was measured 149 at first when engine was in full throttle for a particular speed. This 150 measured load is then considered as 100% load for that speed and 151 other load conditions were determined based upon measured 100% 152 load. Although PM emissions can be quiet different for transient 153 testing, we had to conduct steady state tests as most of our mea-154 surement techniques required steady emission over longer sam-155 pling time. 156

An ultra low sulfur diesel (sulfur content 2.5 mg/kg) and four 157 biodiesels with different physical properties and chemical compo-158 sition were used to run the engine. All four biodiesels originated 159 from palm oil that was then fractionated to separate its fatty acid 160 ester components with specific composition. Since all of them have 161 originated from the same feedstock, the given code names (C810, 162 C1214, etc.) are to indicate the carbon chain length of the most 163 abundant FAME. For example C810 means biodiesel that is mainly 164 composed of FAME's with 8–10 carbon atoms. All four biodiesels 165 were used at three blending ratios i.e. 100% biodiesel (B100), 166 blends of 50% diesel and 50% biodiesel (B50), and blends of 80% 167 diesel and 20% biodiesel (B20). Table 2 shows the fatty acid profile 168 of used biodiesels as found using gas chromatography mass spec-169 trometry (GCMS) analysis. Biodiesel samples were analyzed using 170 Perkin Elmer clarus 580GC-MS equipped with Elite 5MS 171 $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$ column with a flow rate of 1 mL/min. 172 Before analysing, each biodiesel was diluted with *n*-hexane 173 (1:100 v/v). Initial temperature was 120 $^\circ C$ for 0.5 min, then raised 174 to 310 °C for 2 min at 10 °C/min and kept at 310 °C for 2 min. The 175 mass selective detector was optimized using calibrating standards 176 with reference masses at m/z (40–350). Among four biodiesels, 177 C810 is fully saturated and composed of 52% and 46% caprylic acid 178 and capric acid ester respectively. C1214 is also dominated by sat-179 urated compounds but has comparatively longer carbon chain 180 length fatty acid ester i.e. 48% lauric, 19% myristic, 10% palmitic 181 and 18% oleic acid ester. On the other hand both C1618 and 182 C1822 are dominated by long chain unsaturated fatty acid esters. 183 C1618 is composed of 21% palmitic, 9% stearic, 58% cis-oleic and 184 10% linoleic acid ester where C1822 has 10% more oleic and linoleic 185

Tabl	e 1	
Test	engine	specification,

Model	Cummins ISBe220 31
Cylinders	6 in-line
Capacity (L)	5.9
Bore \times Stroke (mm)	102×120
Maximum power (kW/rpm)	162/2500
Maximum torque (Nm/rpm)	820/1500
Compression ratio	17.3
Aspiration	Turbocharged & after cooled
Fuel injection	Common rail
After treatment systems	None
Emissions certification	Euro III

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