ISSN PRINT 2319 1775 Online 2320 7876
 UGC CARE Listed (Group -I) Journal Volume 11, Iss 12, 2022

IMPACT OF MICROALGAL BIODIESEL CHARACTERISTICS ON EXHAUST PARTICLE EMISSIONS AND OXIDATIVE POTENTIAL IN DIESEL ENGINES

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Abstract:

Microalgae are considered to be one of the most viable biodiesel feedstocks for the future due to their potential for providing economical, sustainable and cleaner alternatives to petroleum diesel. This study investigated the particle emissions from a commercially cultured microalgae and higher plant biodiesels at different blending ratios. With a high amount of long carbon chain lengths fatty acid methyl esters (C20 to C22), the microalgal biodiesel used had a vastly different average carbon chain length and level of unsaturation to conventional biodiesel, which significantly influenced particle emissions, leading to similar total particulate matter (TPM) emissions as petroleum diesel, especially at higher blending ratios. In contrast, blends of up to 10% showed slight reductions in PM emissions. However, based on measurements of reactive oxygen species (ROS), the oxidative potential of particles emitted from the microalgal biodiesel combustion were lower than that of regular diesel. Biodiesel oxygen content was less effective in suppressing TPM emissions for biodiesels containing a high amount of polyunsaturated C20-C22 fatty acid methyl esters and generated significantly increased nucleation mode particle emissions. The observed increase in nucleation mode particle emission is postulated to be caused by very low volatility, high boiling point and high density, viscosity and surface tension of the microalgal biodiesel tested here. Therefore, in order to preserve PM emission benefits attributed to the use of biodiesel, this study recommends that the target composition of future microalgal biodiesel should not include FAMEs with high amounts of polyunsaturated long-chain fatty acids (≥ C20).
Keywords: Microalgae biodiesel, particle emissions, blending ratios, reactive oxygen species, sustainable biofuels.

1. Introduction

Biodiesel presents a promising alternative for compression ignition (CI) diesel engines, offering compatibility without major modifications and contributing to reduced carbon emissions. Despite its environmental advantages as a carbon-neutral fuel derived from renewable sources, its widespread use faces challenges due to higher costs and potential conflicts with food production. To address these issues, exploration of alternative feedstocks is crucial, with microalgae emerging as a promising third-generation biofuel option. Microalgae offer higher yields, require less land, and can thrive in diverse environments, including non-arable land [1]. While there is extensive research on microalgae production and characterization, limited attention has been given to engine performance and emissions from microalgae biodiesel.

This study aims to bridge this gap by conducting comprehensive particle emission measurements for various blends of microalgal biodiesel. Building on previous engine performance analyses [2], this research specifically investigates particle emissions from a microalgal biodiesel rich in C20 and C22 polyunsaturated fatty acids (PUFAs) and compares it with B20 blends of vegetable biodiesels (cotton seed oil (CSO) and waste cooking oil (WCO)). The study extends earlier work, focusing on the influence of very long-chain polyunsaturated FAMEs on exhaust particle emissions.

2. Materials and Methods

Experimental measurements were conducted on a turbocharged common rail engine commonly found in passenger cars. Refer to Table.1 for detailed engine specifications. Emission measurements employed a two-stage dilution system, utilizing two connected ejector diluters (Dekati DI-1000). Sampling occurred post-exhaust manifold through a 0.5-meter stainless steel tube. A fraction of the exhaust was directed to gas analyzers via a copper tube fitted with a HEPA filter and water trap. The remaining gas underwent dilution before particle measurement. Raw CO2 and NOx measurements utilized a CAI 600 series CO2 analyzer and a CAI 600 series CLD NOx analyzer. Diluted exhaust CO2 concentrations were recorded by a SABLE CA-10. A DMS-500 (Cambustion Ltd) measured particle number size distribution without the heated sample line connected. PM mass was derived from DMS 500 data using a re-inversion tool in the DMS data analysis suite (version UIv 7.11), following the approach suggested by Jonathan et al. [3]. A TSI DustTrak 8530 also measured PM. The oxidative potential (OP) of PM (nmol of ROS per mg of PM) relied on the mass concentration of reactive oxygen species (ROS). Utilizing profluorescent nitroxides (PFN) as optical sensors, a BPEA (bis(phenylethynyl) anthracene-nitroxide) molecular probe measured OP, indicating PM's capacity to induce oxidative stress. ROS samples (n=2) were collected by bubbling the aerosol through an impinger with 20 mL of 4 µM BPEA solution, followed by fluorescence measurements using a spectrophotometer (Ocean Optics). The amount of BPEA reacting with combustion aerosol was determined from a standard curve plotting known concentrations of the methanesulfonamide adduct of BPEA (fluorescent) against fluorescence intensity at 485 nm.

Table 1: Test engine specifications

Model	Peugeot 308 2.0 HDi
Cylinders	4
Compression ratio	18
Capacity	2.0 (L)
Bore × Stroke	85 × 88 (mm)
Maximum power	100 kW @ 4000 rpm

Microalgal biodiesel, derived from the dinoflagellate Crypthecodinium cohnii (Martek, Singapore), underwent testing at three blending ratios: 10%, 20%, and 50% biodiesel to petroleum diesel (v/v), designated A10D90, A20D80, and A50D50, respectively. The diesel used, supplied by Caltex Australia, was consistent across all blends, created from a single batch. As additional points of comparison, neat diesel and a 20% blend of waste cooking oil (WCO) and cotton seed oil (CSO) biodiesel, labeled WCO20D80 and CSO20D80, were included. These reference fuels exhibited shorter carbon chain lengths and varied levels of saturation. All blends were precisely prepared in volumetric flasks and then introduced into a purpose-built engine fuel tank. Engine operation occurred at a maximum torque speed of 2000 rpm under four distinct loads: 25%, 50%, 75%, and 100%.

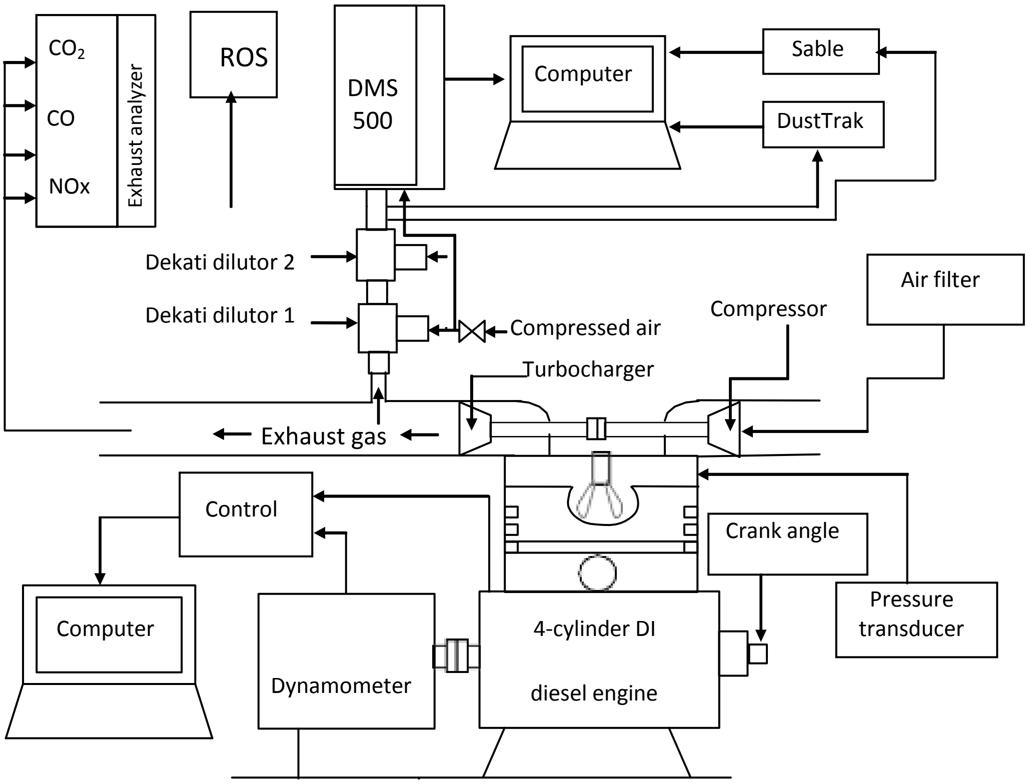

Figure 1: A diagram illustrating the experimental setup

Microalgal biodiesel, derived from Crypthecodinium cohnii, was tested at blending ratios of 10%, 20%, and 50% with petroleum diesel (A10D90, A20D80, A50D50). Compared to cotton seed oil (CSO) and waste cooking oil (WCO) biodiesels, microalgal biodiesel exhibited a longer average carbon chain (20.38) and higher unsaturation (3.46), with a predominant polyunsaturated fatty acid composition (~69%). Physical properties and elemental compositions of blends (Table. 2) were calculated following the Grunberg–Nissan mixing rule. Viscosity, density, and normal boiling point increased with biodiesel content, resulting in decreased higher heating value and cetane number. Microalgal blends showed higher viscosity, density, and normal boiling point than CSO and WCO at equivalent ratios, meeting ASTM 6751-12 or EN 14214 standards, although the cetane number of pure microalgal biodiesel slightly deviated.

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Table 2: The engine-tested biodiesel blends' elemental compositions and crucial physical characteristics were examined.

	A05D95	A10D90	A20D80	A50D50	CSO20	WCO20	Diesel
Elemental composition							
Carbon (wt%)	85.59239	85.18283	84.39271	82.027	84.17297	84.14255	86.62
Hydrogen (wt%)	13.04325	12.933531	12.71945	12.09869	12.90275	12.95212	13.25
Oxygen (wt%)	0.560253	1.117552	2.21853	5.425324	2.375328	2.365328	0
Relevant physical properties							
Viscosity(mm^2/s)	2.761	2.882	3.124	3.85	2.946	3.076	2.64
Density (Kg/l)	0.8436	0.8472	0.8544	0.876	0.848	0.846	0.84
HHV (MJ/kg)	45.62365	45.3203	44.7136	42.8935	44.4264	44.6924	45.927
NBP (^{o}C)	145.5	151	162	195	146	148	140
CN	50.3	50.1	49.7	48.5	57.8	52.12	50.5

HHV: Higher heating value, NBP: Normal boiling point, CN: cetane number

3. Results and Discussion

3.1 Particulate Matter (PM) Emissions

Figure.2 displays brake-specific total particulate matter (TPM) emissions for reference diesel and various biodiesel blends. Microalgal biodiesel blend-TPM emissions exhibited load-dependent trends, being lower than petroleum diesel at 25% load, comparable or higher at 50% and 75% load for A20:D80 and A50:D50 blends, and nearly as high for A50:D50 blends at 100% load (Figure 2). Generally, TPM emissions correlated positively with increased petroleum diesel in microalgae biodiesel blends. In contrast, WCO20D80 and CSO20D80 biodiesels consistently showed lower TPM emissions than the A20 blend, with CSO20D80 exhibiting a ≥50% reduction compared to WCO20D80, except at 25% engine load where the difference was less pronounced (Figure 2).

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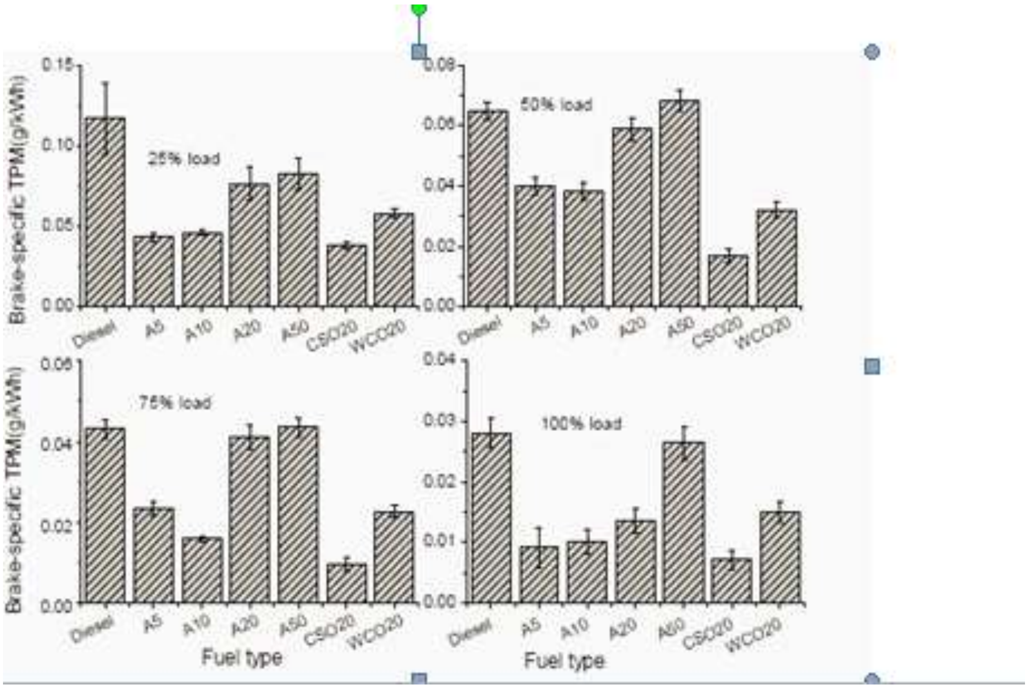

Figure 2 : illustrates the brake-specific total particulate matter (TPM) emissions of both diesel and biodiesel blends

Biodiesel literature [4] suggests a linear correlation between blend properties, pure biodiesel properties, and their blending ratio, a notion supported by studies on microalgae biodiesel [5]. Similar to pure microalgal biodiesel, the diesel-microalgal biodiesel blends tested had higher density, viscosity, boiling point, surface tension, and lower cetane number than the reference diesel and the other two biodiesels at the same blending ratio [6]. The average carbon chain length and unsaturation of microalgal biodiesel were also higher than those of the other two biodiesels, while the oxygen content was nearly the same. Consequently, based on our previous study [6], higher PM emissions were anticipated from microalgal biodiesel blends compared to CSO and WCO blends. Schönborn et al. [7] tested pure C22:0 FAME in their custom-made engine system and found PM emissions to be similar to diesel. In terms of carbon number, the microalgal biodiesel in this study was similar to that used in Schönborn et al. [7], except for its high amounts of C22:5 and C22:6. The impact of biodiesel poly-unsaturation on PM emissions remains unclear, with conflicting reports in the literature [6,8]. The observed decrease in PM emissions for lower blends of microalgae biodiesel (B5 and B10) might be attributed to their oxygen content, while changes in other properties such as viscosity and boiling point, typically linked to increased PM emissions, may have been insufficient to produce an effect at such low blend ratios.

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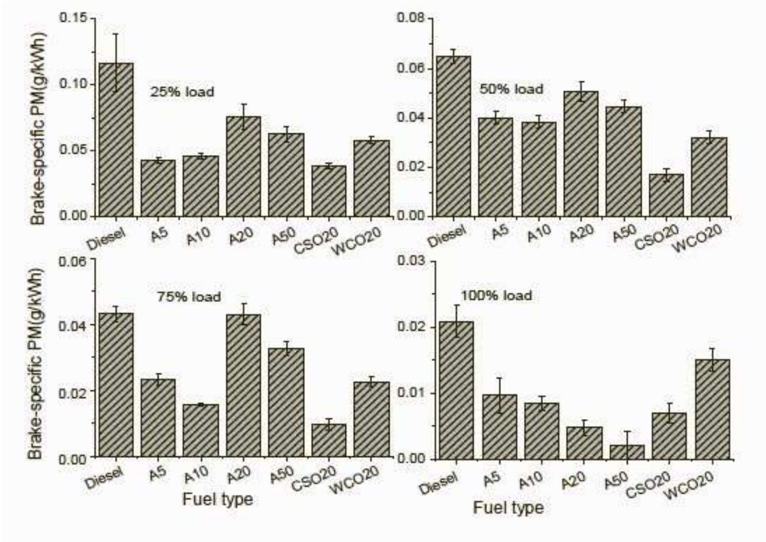

Figure 3: Brake-specific accumulation mode PM emissions of diesel and biodiesel blends

3.2 Particle Number (PN) Emission

The DMS 500's log-normal PSD spectra for nucleation and accumulation mode particles, integrated for total particle number concentration (TPN), presents challenges in the presence of a nucleation mode peak (Figure SI-2). Notably, the A50D50 blend showed a nearly 10-fold TPN increase, primarily driven by nucleation mode particles.

In Figure 4, the trend in accumulation mode PN emissions mirrors particle mass trends. Microalgal blend accumulation mode PN decreases for 5% and 10% blends, then increases for 20% and 50% blends, except at 100% engine load, where it consistently decreases with rising biodiesel content. Conversely, TPN from WCO and CSO blends slightly lags the reference diesel, aligning with TPM emission trends. This implies that WCO and CSO blends contribute less to nucleation mode particles than microalgal blends, likely due to variations in chemical composition and physical properties. The higher boiling point of microalgal biodiesel blends, influenced by elevated C22:5 and C22:6 levels, may allow unburned fuel to persist in the exhaust, potentially forming nucleation mode particles.

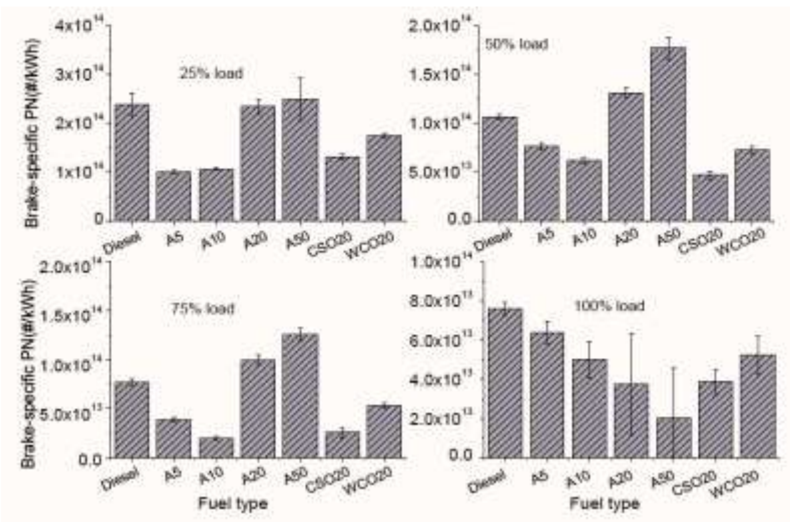

Figure 4: Brake-specific particle number emission (accumulation mode) for diesel and biodiesel blends

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Despite established positive effects of fuel-bound oxygen on particle emissions, studies on biodiesels with the same FAME content as those investigated here are lacking, challenging the widely accepted notion that biodiesel oxygen content primarily drives reduced TPM emissions, especially for biodiesels with a carbon number >22 in their FAME [7].

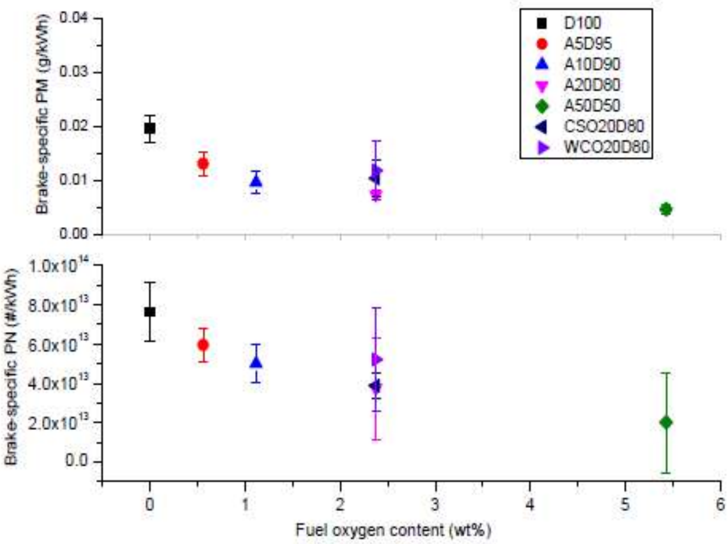

Figure 5: Relationship between accumulation mode PM and PN emissions with fuel oxygen content at 100% load for diesel and biodiesel blends

3.3 Oxidative Potential of Microalgal Biodiesel Blends

Comparing oxidative potential (OP), the tested microalgal biodiesel blends exhibited lower OP than diesel (Figure 6). Reactive oxygen species (ROS) concentrations were measured at idle and 50% load. Idle emissions typically result in higher ROS concentrations, consistent with prior observations [9].

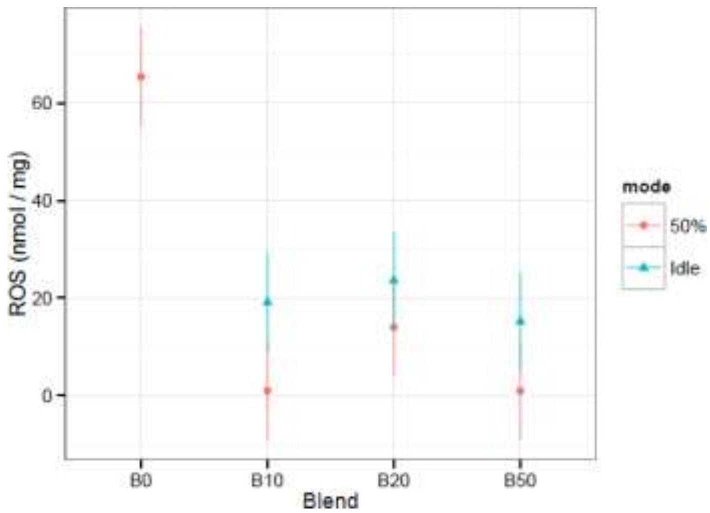

Figure 6: Oxidative potential of particles produced from diesel and microalgal biodiesel blend combustion

The contribution of combusted lubricating oil to overall OP could explain this outcome. Interestingly, the biodiesel content did not significantly influence OP, with

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B20 displaying the highest OP among the blends. This implies that blending with microalgal biodiesel has the potential to reduce OP and mitigate particle-associated toxicity.

4. Conclusion

This study delved into the particle emission characteristics of microalgal biodiesel blends, characterized by a high carbon chain length (20.38) and unsaturation (3.46) compared to traditional biodiesel feedstocks like WCO and CSO blends. The findings revealed that C22 fatty acid methyl esters (FAMEs) in biodiesel blends led to TPM emissions similar to diesel, with a slight reduction observed at lower blends (up to 10%). Notably, the 20% microalgae biodiesel blends exhibited significantly higher particle emissions than their WCO and CSO counterparts. Moreover, increased biodiesel oxygen content failed to effectively suppress TPM emissions, especially in blends with high percentages of FAMEs featuring a carbon number >22 and substantial polyunsaturation. While such biodiesel blends triggered a notable rise in nucleation mode particle emissions, they demonstrated lower oxidative potential and particle-associated toxicity compared to diesel, regardless of blend ratio. In contrast, biodiesel blends with a FAME carbon chain length <18 were less prone to generating nucleation mode particles, unless contaminated with impurities like glycerol. The study underscores the importance of avoiding FAMEs with >22 carbon atoms in future microalgal biodiesel blends to preserve the positive particulate matter emission benefits associated with biodiesel use. This can be achieved through species selection, genetic modification, or manipulation of microalgae growth conditions.

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