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Full Length Article

# Physical and chemical properties of RME biodiesel exhaust particles without engine modifications

Robin Nyström [a], Ioannis Sadiktsis [b], Trifa M. Ahmed [b], Roger Westerholm [b], Johannes H. Koegler [c], Anders Blomberg [d], Thomas Sandström [d], Christoffer Boman [a,*]

[a] Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University, SE-901 87 Umeå, Sweden
[b] Department of Environmental Science and Analytical Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden
[c] Volvo Group Trucks Technology, Advanced Technology & Research, Chalmers Teknikpark, SE-412 88 Gothenburg, Sweden
[d] Department of Public Health and Clinical Medicine, Division of Medicine/Respiratory Medicine, Umeå University, SE-901 87 Umeå, Sweden

## HIGHLIGHTS

- Halved PM emissions for biodiesel compared to petro diesel.
- Smaller particles for biodiesel, higher fraction of organic compounds and less soot.
- Considerable lower PAH and Oxy-PAH emissions with biodiesel.

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## ABSTRACT

A major contributor to ambient particulate air pollution is exhaust from diesel engines and other vehicles, which can be linked to different adverse health effects. During the last decades, a global drive towards finding sustainable and clean bio-based alternative fuels for the transport sector has taken place and biodiesel is one of the most established alternatives today. To better assess the overall effects on a public health level when introducing biodiesel and other renewable fuels, a better understanding of the detailed exhaust particle properties, is needed. In this work, the physical and chemical properties of biodiesel exhaust particles were studied in comparison to standard diesel exhaust emissions, in an existing engine without modifications, focusing on particulate carbonaceous matter and PAH/Oxy-PAH as well as fine particle size distribution. An older off-road engine, produced between 1996 and 2004, was used with three different fuels/fuel blends; (1) 100 wt% low-sulfur standard petro diesel (SD), (2) 100 wt% rapeseed methyl ester biodiesel (B100) and (3) a blended fuel – B30 consisting of 30 wt% RME and 70 wt% SD. The study focused mainly on emissions from transient engine operation, but includes also idling conditions. The gaseous emissions measured for the biodiesel fuel were in general in accordance with previous reported data in the literature, and compared to the standard petro diesel the emissions of CO was lower while $NO_x$ emissions increased. The particulate mass concentration during transient operation was almost halved compared to when petro diesel was used and this was associated with a decrease in average particle size. The shift in particle mass and size was associated with a higher fraction of organic matter in general, considerable less PAH's but a relative higher fraction of Oxy-PAH's, when shifting from petro diesel to biodiesel.



## 1. Introduction

The European Union has estimated that air pollution is responsible for approximately 350 000 excess deaths/year in the members states [1], which is twice the number of deaths caused by traffic accidents [2]. Air pollution, in particular ambient particulate matter (PM), can be linked to a variety of different health effects e.g., increased; risk of cardiovascular diseases, airway inflammation, and the severity of asthma [3,4]. The toxicity of the PM may depend on several diverse properties such as particle mass, particle size, surface area, chemical composition and oxidative potential [5]. A major contributor to air pollution is exhaust from diesel engines and other vehicles. In numerous epidemiological, chemical and

* Corresponding author.
*E-mail address:* christoffer.boman@umu.se (C. Boman).

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toxicological studies, exposure to traffic-related PM has been associated with both cardiovascular [6] and respiratory effects [7].

Diesel engine exhaust emissions are a complex mixture consisting of inorganic and organic components both in gaseous and particulate phase. The major part of the diesel PM mass consists of fine particles (Diameter (D) < 1.0 μm) with the highest number concentration in the ultrafine range (D < 0.1 μm). A general conceptual model for diesel exhaust PM formation and characteristics has been developed as described by Mariqc [8]. It has been shown that diesel PM consists of agglomerates of primary carbon particles, traces of metallic ash coated with condensed heavier end organic compounds and sulfates, and nucleation particles composed of condensed hydrocarbons and sulfates that is characteristically bimodal with different properties that indicates different origin - nucleation and soot [8].

During the last decades, a global drive towards finding sustainable and clean bio-based alternative fuels for the transport sector has taken place. The EU directive 2009/28/EC sets a goal for a minimum of 10% biofuels for the transport sector in every EU member state by 2020. Furthermore, the US Environmental Protection Agency's Renewable Fuel Standard contains targets to quadruple the use of biofuels in the US transport sector by 2022 [9]. In light of this, considerable R&D effort has been undertaken during the last decade and some alternative fuels have already been introduced to the market. One of the most established biofuels on today's international market is biodiesel. In Europe during 2011, biodiesel accounted for 82% of the total biofuel production [10]. Biodiesel is an ester-based fuel obtained through transesterification of fatty acids from different plant and animal fats. They are primarily adapted to be used in blends with standard fossil-based diesel directly in unmodified diesel engines. Some advantages that have been discussed when using biodiesel as fuel, except being produced from renewable resources, are for example that it is virtually free from sulfur and aromatic compounds, and it is non-toxic and much more biodegradable than fossil diesel [11]. Today, the major part of the produced biodiesel in Europe is rapeseed methyl ester (RME), while in US the most common assortment is produced by soy bean ester.

There is considerable variation in emission data reported, which preferably is explained by the fact that the emissions are strongly linked to engine technology, operating conditions [12] as well as the origin and quality of the biodiesel [13]. In a recent review, however, it was concluded that most studies on biodiesel exhaust have reported an increase in $NO_x$ emissions and a reduction in PM emissions, as well as a decrease in the emissions of CO, total (gaseous) hydrocarbons and polycyclic aromatic hydrocarbons (PAH) [12]. However, emission data of oxygenated PAHs (Oxy-PAH) from biodiesel combustion are scarce but have been reported to increase in comparison to petro diesel, as shown by Karavalakis and co-workers [14]. Both PAH and Oxy-PAHs have been shown to be important compound classes that correlate with oxidative stress *in vitro* [15,16].

It has been discussed that PM originating from biodiesel combustion, compared to petro diesel, can have a stronger mutagenic effect [17]. Furthermore, increased pro-inflammatory responses but decreased oxidative potential from biodiesel PM have been observed [18]. In addition, in a review based on available *in vitro* and *in vivo* animal studies, it was concluded that biodiesel PM showed an increased cytotoxicity and stronger irritant effects, while the mutagenic effects were more variable [19]. In a recent unique human exposure study it was shown that exhaust from RME biodiesel induced acute adverse cardiovascular effects on par with those seen following exposure to petrodiesel exhaust, despite almost a 50% reduction of the PM mass concentration and differences in physical and chemical exhaust particle characteristics [20].

Thus, whilst there is a positive climate-related impact of replacing fossil fuels with biofuels, it has been emphasized that there is still a need for dedicated studies focusing on the detailed exhaust particle properties from biodiesel and other biofuels, especially related to toxicity and adverse health effects during exposure [21]. The aim of this work was therefore to determine the physical and chemical properties of biodiesel exhaust particles in comparison to standard diesel exhaust emissions, from an off-road engine without modifications. The focus was to study the effect on the particle emissions when introducing biodiesel in an existing older engine originally operated on petro diesel, with focus on the characteristics of particulate carbonaceous matter and PAH/Oxy-PAH as well as fine particle size distribution.

## 2. Material and methods

### *2.1. Engine and operating conditions*

The experimental setup consisted of an engine produced between 1996 and 2004, meeting the particle emission class EU Stage I and Tier 1 for non-road engines (0.54 g/kW h PM). It has a flat power curve at 74.6 kW, 2200 rpm and 4 cylinders and 4 L displacement with mechanical distributor pump and direct injection. This older type of engine is not fitted with a diesel particulate filter and, thus, this study aimed at to simulate the introduction of biodiesel into this type of engine without modifications.

The engine was connected to an engine dynamometer, controlled by a computer program, and operated at the European Transient Cycle (ETC) or at constant idling mode. The ETC cycle is a standardized running protocol used to test engines and vehicles during transient conditions, mimicking real life running situations. It is based on recordings of accelerations and retardations, with variations in engine load and speed. It contains frequent starts, stops and idling running and a maximum speed of 50 km/h. In combination with the European Stationary Cycle, the ETC cycle is used for emission certification of heavy-duty diesel engines in Europe. The ETC protocol originally includes three different sections, i.e. urban, rural and motorway conditions. In this study, only the urban part of the ETC cycle was used and therefore is hereby referred to as modified ETC cycle.

In this study the focus was on exhaust particle characterization during the modified ETC running cycle, applying both online and offline measurements. In addition, online characterization was also performed during idling engine conditions for evaluation of particle size distributions when introducing biodiesel.

### *2.2. Fuels*

Three different fuels/fuel blends were used; (1) 100 wt% low-sulfur standard petro diesel (SD) meeting EN 590 specifications for diesel fuels sold in the EU (used as reference fuel). (2) 100 wt% rapeseed methyl ester biodiesel (B100) that meet the requirements for EN 14214 specifications for biodiesel fuels. (3) A blended fuel – B30 consisting of 30 wt% RME and 70 wt% SD. Both the B100 and the SD were delivered by Preem AB, Sweden. The RME used here contained a fuel additive ACP (Active Cleaning Power) to improve combustion and decrease engine corrosion. The composition of the ACP additive is, however, not known to the authors, since it is confidential. A complete list of fuel properties is given in Table S1 in the Supplementary Information.

### *2.3. Dilution of exhaust*

To sample the particulate emissions, dilution of the exhaust gases was needed. During this study a virtual dilution tunnel