Detailed speciation of emissions from a diesel engine fuelled with canola methyl ester

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Abstract. Although the effects of biodiesel combustion on emissions of regulated toxic components have been widely studied, the issue of specific hydrocarbon species production has not yet been comprehensively understood. This study compares detailed exhaust emissions from a compression ignition engine fuelled with canola methyl ester and mineral diesel, as a reference fuel. Additionally, blends of these two fuels were examined. The experiments were performed on a 4-cylinder diesel engine, where fuel was injected in a single dose. The experimental matrix included two engine load sweeps at rotational speeds corresponding to maximum torque and maximum power. Detailed exhaust composition was measured with the use of a Fourier transform infra-red analytical system. To enable unbiased evaluation of the effect of different fuels on hydrocarbons emissions fuel carbon conversion into species carbon was considered. The results showed that there is not a monotonic effect of the content of biodiesel fuel on particular hydrocarbon species. In the case of some hydrocarbon species, the lowest emissions were recorded for mixture of the two fuels.

1 Introduction

Global trends in energy sources diversification heavily rely on the increasing share of renewable transportation biofuels. Additionally, the use of biofuels has significant pro-environmental aspect. The biofuel carbon footprint is nearly zero, making these energy carriers completely neutral in terms of CO₂ emissions. Utilization of biofuels in diesel engines does not require any large scale hardware modifications. Thus, there is no additional energy and materials consumption associated with introduction of biofuels.

In the relevant literature, a great number of studies have been dedicated to research into the effects of biofuels on combustion, emissions of toxic compounds and energy consumption [1-14]. Evaluation of the performance and durability of engines is also of the great importance [2, 3]. From the point of view of the environmental impact, there is a common opinion that the use of bio-diesel decreases engines performance, but reduces all toxic exhaust gas compounds, except nitrogen oxides [2-5]. Duda et al. [6] demonstrated that both, plant and animal-originated biofuels combustion reduce gaseous components and smoke emissions in comparison to mineral diesel fuel. Nevertheless, despite the origin of the biofuel, reduction in brake specific efficiency by approximately 2% was noted. When analysing the results of studies concerning the effects of the use of renewable components on exhaust gas emissions attention is drawn to the small number of studies on the emissions of specific hydrocarbon components. In other words, the authors usually compare the so-called regulated toxic compounds. However, there are dozens of different hydrocarbon species having

different effects on living organisms. For example Claxton [7] indicated that 1,3-butadiene deserves special consideration because of its carcinogenic potential. It is considered to be one of the most harmful compounds among all toxic compounds emitted by motor vehicles. For gasoline fuel Zervas et al. [8] studied the effects of fuel composition on particular hydrocarbon species emissions from spark ignition engine. The authors determined the pathways of creation of specific hydrocarbons depending on combustion conditions. Hunicz and Krzaczek [9] demonstrated the effects of pre-combustion reactions on exhaust hydrocarbon compositions in low-temperature combustion system. Gupta and Agarwal [1] utilized FTIR exhaust gas analytical system to study the effects of non-edible vegetable oil on emissions of particular hydrocarbons. They concluded that addition of biofuel to mineral diesel reduces the content of the most harmful hydrocarbons in exhaust gases. It should be noted that some hydrocarbons pose a challenge in terms of catalytic oxidation, because at low loads diesel exhaust temperature is far below their light-off threshold [10]. Hunicz and Medina [11] demonstrated the effects of exhaust hydrocarbon compositions on oxidation catalyst efficiency. Despite a confirmation of slow oxidation properties of methane they demonstrated inhibiting effects of acetylene on oxidation of other hydrocarbons.

In this paper the results of measurements of the concentration of regulated and non-regulated exhaust components from a diesel engine fuelled with mineral diesel fuel, bio-diesel and their blend are presented. The effect of fuel and engine operation conditions on shares of particular hydrocarbons to total hydrocarbon is discussed.

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2 Measurements

The research was conducted on an engine test stand equipped with eddy-current dynamometer (AVL-Zollner Alpha 240), fuel consumption meter (AVL Dynamic Fuel Balance) and other instrumentation necessary for proper engine operation and control its basic parameters. The tests were performed on a 4-cylinder diesel engine with swept volume of 2.4 dm³, maximum torque of 146 Nm at 2500 rpm and rated power of 51.5 kW at 4200 rpm, according to the engine specification. The fuel was injected in one dose by an in-line injection pump.

AVL SESAM FTIR (Fourier Transform Infrared) multi-component gas analytical system was used to measure the concentrations of 23 compounds in exhaust gases. The system allowed for simultaneous measurement of the content of specific hydrocarbons, nitrogen oxides and other chemical compounds. The measured compounds are listed in Table 1. Exhaust gases flew from the engine to the FTIR analyser through a heated line. The sampling rate of the analyser was around 1 s. The time-averaged value of the 30 s measurement period was taken as a result of a single reading.

Table 1. Exhaust compounds measured.

Name of compound	Symbol
Methane	CH ₄
Acetylene	C ₂ H ₂
Ethylene	C ₂ H ₄
Ethane	C ₂ H ₆
Propylene	C ₃ H ₆
Propane	C ₃ H ₈
1,3 butadiene	C ₄ H ₆
N-octane	NC ₈
Aromatic hydrocarbons (toluene)	AHC
Formaldehyde	HCHO
Acetaldehyde	CH ₃ CHO
Formic acid	HCOOH
Isocyanic acid	HNCO
Hydrogen cyanide	HCN
Ammonia	NH ₃
Nitrogen monoxide	NO
Nitrogen dioxide	NO ₂
Nitrous oxide	N ₂ O
Carbon monoxide	CO
Carbon dioxide	CO ₂
Sulphur dioxide	SO ₂
Carbonyl sulphide	COS
Water	H ₂ O

Concentrations of particular exhaust components were measured for engine fuelled with regular diesel oil (D 100%), bio-diesel based on canola methyl ester (CME 100%) and their blend with 50% mass fractions. The basic parameters of the studied fuels are presented in Table 2.

The measurements were done at two engine rotational speeds: 2500 rpm (speed at which the engine achieved the maximum torque) and 3800 rpm (speed at which the engine actually achieved maximum power). At each selected rotational speed an engine load was changed

from 0 to 100% of torque attainable at the given speed. Before each single measurement the engine worked at steady-state conditions for minimum 2 minutes to assure also steady thermal conditions. During measurements relative air-fuel ratio calculated from carbon balance equation varied from 7.2 at idling to 1.3 and 1.4 at full load at 2500 and 3800 rpm, respectively.

Table 2. Parameters of the studied fuels.

Parameter	Unit	CME 100%	D 100%
Content of fatty acid methyl esters	% (m/m)	97,3	
Density at 15°C	kg/m ³	883	839
Kinematic viscosity at 40°C	mm ² /s	4,47	2,74
Sulphur content	mg/kg	4,7	6,3
Water content	mg/kg	117	76
Total impurities	mg/kg	17	11
Cetane number	–	51	51,6
Flash-point	°C	130	65
Temperature of cold fuel filter blockage	°C	-23	-32

3 Results and discussion

Figures 1-9 show the raw species concentration measurement results for all studied conditions. The concentration of carbon monoxide in the exhaust gases of engine fuelled with CME based fuel was smaller by 25% in comparison to that in engine fuelled with mineral diesel. For the blend of CME and mineral fuel that concentration was smaller by 13%. The content of CO decreased with the increase in engine load in the range of small and medium loads, despite the fuel used. However, for the highest loads CO production increased. This increase was especially rapid at the rotational speed of the maximum torque, as shown in Fig. 1. It should be noted that the increase of biofuel content reduced CO emissions considerably because of the oxygen content of the fuel. Thus, the global excess air ratio for biofuel was higher and combustion more complete.

A similar effect of the fuel was observed in the case of sulphur dioxide. On average, the content of SO₂ in exhausts was by 27% smaller for CME fuel, and by 15% for the blend in comparison to mineral diesel (Fig. 1). These differences were comparable to the differences in the sulphur content in the fuels (Table 2). The concentrations of SO₂ strongly increased with the increase in engine load, which was related to increase in fuel content in the combustion mixture.

In the case of nitrogen oxide the results were not that clear, although on average the concentration for CME fuel was 3% higher, and for blend 5% lower than for mineral diesel. For all tested fuels the content of nitrogen oxide increased with the increase in the engine load (Fig. 2).

The content of nitrogen dioxide in exhaust of engine fuelled with CME fuel was much higher than in the engine fuelled with mineral fuel – by 32% on average (Fig. 2). For the blend of fuels emission it was also slightly higher – by 4%. Contrary to NO, the concentrations of NO₂ decreased with the increase in the engine load, especially for 2500 rpm, where the content at full load was about

10 times higher than at idling. Although the concentration of NO₂ to NO_x is several times smaller than the concentration of NO, that big difference caused the concentration of NO_x for CME fuel to be on average by 6% bigger. For the blend it was on average by 4% smaller than for mineral diesel. The changes in the content of NO_x as function of load were similar to the content of NO – they increased together with the increase of load (Fig. 3). A total concentration of NO_x was determined by NO, NO₂ species, although the N₂O compound was also considered. Nevertheless, the N₂O contributed to the total NO_x emissions solely in a small extent.

Fig. 1. Concentrations of carbon monoxide and sulphur dioxide.

Fig. 2. Concentrations of nitrogen monoxide and nitrogen dioxide.

Fig. 3. Concentrations of total hydrocarbons and nitrogen oxides.

Concentrations of both determined aldehydes were increased by 11% for CME based fuel. However, the smallest concentrations were for the blend: 15% lower for formaldehyde and 11% lower for acetaldehyde in comparison to mineral diesel. The content of both formaldehydes decreased with the increase in engine load (Fig. 4).

Also concentrations of isocyanic acid were by 20% higher for CME fuel and by 14% smaller for the blend in comparison to mineral fuel (Fig. 5). Concentrations of strongly toxic hydrogen cyanide were very low and comparable for all tested fuels (Fig. 5).

Fig. 4. Concentrations of formaldehyde and acetaldehyde.

Fig. 5. Concentrations of isocyanic acid and hydrogen cyanide.

A concentration of total hydrocarbon related to one carbon atom (THC) was calculated as a sum of the concentration of particular hydrocarbons (the first 9 compounds in Table 1) taking into account the number of atoms of carbon in a specific hydrocarbon. The content of THC in exhausts of engine fuelled with CME fuel was lower, on average, by 8% than in the engine fuelled with mineral diesel. However, the lowest THC content was for the engine fuelled with the blend (13% lower than for diesel). These differences were particularly noticeable at small engine loads (Fig. 3). Concentrations of THC decreased with the increase in engine load for all fuels.

Concentrations of specific hydrocarbons in the exhaust gases of the engine operated on different fuels are presented in Figs. 6-9. Considering the mineral diesel as a baseline, the following average decreases of concentrations for CME fuel were recorded for particular

hydrocarbon species: C₂H₆ by 50%, AHC by 37%, C₃H₈ by 19%, C₄H₆ by 17%, and NC₈ by 9%. In contrast, average concentrations were higher for: CH₄ by 12% and C₂H₄ by 11%. The lowest concentrations of almost all determined hydrocarbons were manifested by the blend of the two basic fuels. For the mixture, especially significant drop was noted in the case of N-octane (by 24% in comparison to mineral fuel), which had the largest concentration to THC. In the case of C₂H₂ and C₃H₆ no distinction could be made between the fuels.

Regarding the effect of load on hydrocarbons content in the exhaust gases, the results showed that concentrations of CH₄, C₃H₈, NC₈ and AHC decreased together with the increase in engine load. In the case of C₂H₆, C₃H₆ and C₂H₄ moderate increases were observed, and finally, in the case of C₄H₆, the concentration was not affected by the load.

Fig. 10 shows the cumulative content of hydrocarbon species expressed as C₁ for all studied conditions. In other words, the graphs show the distribution of the conversion of fuel carbon into different hydrocarbon species. Without any detailed analysis it can be noted that despite different fuel compositions the trends in fuel conversion into unburned hydrocarbon species were similar. N-octane had the biggest concentration to THC. In the range of small loads this concentration even exceeded 60% and dropped with the increase in engine load to 20% at maximum load. The concentration of propane also slightly decreased with the load. On the other hand, the concentrations of ethylene, ethane, propylene, 1,3-butadiene and acetylene increased with the load.

Considering the effect of fuel it can be stated that despite the different fuels the composition of hydrocarbons in the exhaust gases did not changed significantly. Only concentrations of ethane, 1,3 butadiene, which is the most toxic hydrocarbon compound emitted by motor vehicles [7], and aromatic hydrocarbons were slightly smaller for CME fuel. In the case of other hydrocarbon species there was no clear influence of the fuel on specific hydrocarbons concentration into the total hydrocarbon.

4 Summary

In this work the concentrations of regulated and non-regulated components in the exhaust gases of a compression ignition engine fuelled with canola methyl ester, mineral diesel, as a reference fuel, and a blend of these two fuels were examined. The experiments were performed in an engine test bench on the engine operated in steady-state conditions at two rotational speeds corresponding to maximum torque and maximum power, and loads changed in a full range: from idling to maximum torque attainable at the given rotational speed. Detailed exhaust composition was measured with the use of a Fourier transform infra-red analytical system.

Combustion of biofuel reduced concentrations of CO and SO₂, and increased concentrations of NO_x for all studied conditions. Both trends are related to the molecular structure of the fuels. Namely, biofuels contain less sulphur and more oxygen than mineral fuels. For the

Fig. 6. Concentrations of methane and acetylene in exhausts of the engine fuelled with studied fuels.

Fig. 7. Concentrations of ethane and propylene in exhausts of the engine fuelled with studied fuels.

Fig. 8. Concentrations of propane and 1,3-butadiene in exhausts of the engine fuelled with studied fuels.

Fig. 9. Concentrations of ethylene, N-octane and aromatic hydrocarbons in exhausts of the engine fuelled with studied fuels.

Fig. 10. Cumulative content of particular hydrocarbon species in total hydrocarbon expressed as C1 for all studied fuels and conditions of engine operation.

same reason the combustion of biofuels increased the concentrations of aldehydes. For all studied conditions biofuel combustion reduced the concentrations of total hydrocarbon (THC). However, it is worth noting that this trend was not monotonic. The lowest THC production was recorded for the blend of fuels. This peculiar effect was already observed at high load regime at whole rotational speed range of the engine [15]. It can be attributed to the balance between auto-ignition and diffusion properties of the tested fuels [16].

Regardless of the fuel used, the increase in the engine load resulted in reduction of the long-chained saturated alkanes. A plausible reason of this reduction is more intense cracking of heavy fuel hydrocarbon species at higher combustion temperatures appearing at the higher engine loads. This effect is most evident for diesel fuel at the highest load. 1,3 butadiene (C₄H₆) also deserves comment, as it is the most toxic hydrocarbon compound emitted by motor vehicles. Combustion of fuel based on canola methyl ester reduced the production of this compound. Combustion of this fuel also slightly reduced the production of ethane and aromatic hydrocarbons. In the case of other hydrocarbon species there was no clear influence of the fuel on specific hydrocarbons emissions.

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