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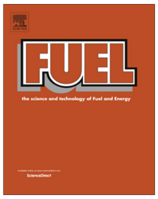

Influence of engine load and speed on regulated and unregulated emissions of a diesel engine fueled with diesel fuel blended with waste cooking oil biodiesel

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ABSTRACT

This study is focused on investigating the regulated and unregulated emissions of a 4-cyclinder natural-aspirated direct-injection diesel engine fueled with neat diesel fuel, B10 (diesel containing 10 vol.% of biodiesel), B20, B30 and neat biodiesel (B100). Experiments were conducted on the Japanese 13-mode test cycle for the diesel engine so that the influence of engine load and engine speed on the regulated and unregulated emissions can be identified. The 13-mode weighted results show that with an increase of biodiesel in the blended fuel, there are reductions of HC, CO and particulate mass concentrations but an increase in NO_x. For the unregulated emissions, formaldehyde and acetaldehyde emissions increase with increasing biodiesel content. The same trend can be observed for 1,3-butadiene, propene and ethene. For the aromatics emissions, biodiesel addition leads to an increase in benzene emission but reductions in toluene and xylene emissions. The results also show that all the emissions are affected by the engine operating modes, especially the engine load.

1. Introduction

The increasing energy demand and environmental deterioration are two major factors which drive for the search of alternative fuels for replacing the conventional petroleum fuels for motor vehicles. Among all the alternative fuels, biodiesel is one of the most widely investigated as a replacement for diesel fuel due to its renewability, potential of reducing greenhouse gas emissions, and inhibition of soot formation [1–3]. In addition, there is no need to modify the diesel engine when biodiesel is applied in either the neat form or in the blended form [4]. Therefore, extensive studies have been conducted on diesel engines fueled with biodiesel or biodiesel/diesel blends [5–8]. In general the use of biodiesel will lead to increase in fuel consumption, reductions in HC, CO, smoke and particulate emissions and a slight increase in NO_x emission. Furthermore, several theoretical and computer modeling studies provided insights into the biodiesel combustion and emission characteristics [9–11]. Mohamed Ismail et al. [10] conducted a computational fluid dynamics (CFD) simulation on biodiesel combustion, using a reduced methyl butanoate mechanism combined with a n-heptane mechanism. The simulated results show that the proposed mechanisms give reliable predictions of in-cylinder combustion and emission processes.

A number of investigations on the influence of biodiesel on the unregulated emissions of a diesel engine have been carried out. Sharp et al. [12] conducted investigations on three diesel engines using diesel fuel, B20 and B100. The biodiesel used was soybean oil biodiesel. They found reduced emissions of speciated vapor phase hydrocarbons in the C_1 to C_{12} range and reduction in aldehydes. USEPA [13] reported reductions in acetaldehyde, formaldehyde and xylene, but inconsistent results in benzene, 1-3-butadinene and toluene. McGill et al. [14] conducted tests on different engines and test cycles, using rapeseed biodiesel, soy bean biodiesel and used vegetable oil biodiesel. They concluded that the unregulated emissions of interest – aldehydes and 1,3-butadiene – did not seem to have much dependence on the fuel. Correa and Arbilla [15] investigated the influence of castor oil biodiesel on the carbonyl emissions of a six-cylinder heavy-duty diesel engine using B2, B5, B10 and B20. Experiments were conducted at three engine speeds but the engine load was not specified. They found increase in both formaldehyde and acetaldehyde emissions. Peng et al. [16] also investigated the aldehyde emissions of a 4-cylinder diesel engine under the US transient cycle protocol,

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using diesel fuel blended with 20% waste cooking oil biodiesel. The results show lower formaldehyde emission but higher acetaldehyde emission. Di et al. [17] conducted investigations on a 4-cylinder diesel engine using waste cooking oil biodiesel, with B20, B40, B60, B80 and B100 at an engine speed of 1800 rpm on five engine loads. They found decrease of formaldehyde, increase in acetaldehyde, reduction in 1,3-butadiene, increase in benzene and reductions in toluene and xylene. Cheung et al. [18] investigated on a 4-cylinder diesel engine using neat waste cooking oil biodiesel at an engine speed of 1800 rpm on five engine loads. They found increase of formaldehyde and acetaldehyde and reductions in 1,3-butadiene, benzene, toluene and xylene.

Besides investigations on the carbonyls and the aromatics, experimental work has also been conducted on other species. Karavalakis et al. [19] investigated 16 PAHs, 4 nitro-PAHs, 6 oxy-PAHs and other unregulated emissions of a 2.2 litre common-rail diesel engine with an oxidation catalyst on a chassis dynamometer over the New European Driving Cycle and the Artemis driving cycle. Lin et al. [20] used waste cooking oil biodiesel to investigate the trace species in the emissions of a diesel engine while Grigoratos et al. [21] investigated the effects of rapeseed biodiesel on the inorganic ions.

Lapuerta et al. [6] commented that the information given in the literature about the effects of biodiesel on the unregulated emissions is scarce. There is no conclusive trend regarding the emissions of oxygenated compounds, including the aldehydes. Xue et al. [4] reported that most research showed that the aromatic and polyaromatic emissions for biodiesel reduced with regard to diesel while for carbonyl emissions, there are discordant results despite it is widely accepted that biodiesel increases these emissions because of the higher oxygen content.

The above review shows that there is a need to further investigate on the unregulated emissions of a diesel engine when using waste cooking oil biodiesel and diesel/biodiesel blended fuel under different engine loads and engine speeds. To fill in this knowledge gap, in this study, the unregulated emissions of a diesel engine are investigated under the Japanese 13-mode test cycle for diesel engine which covers three engine speeds and different engine loads at each engine speed, using biodiesel derived from waste cooking oil, pure diesel and three diesel/biodiesel blends. The unregulated emissions investigated include formaldehyde, acetaldehyde, 1,3-butadiene, ethene, propene, benzene, toluene and xylene which are classified as air toxics by USEPA and the maximum incremental reactivity (MIR) of some of them are very high. For example, the MIR of formaldehyde, acetaldehyde, 1,3-butadiene, ethene, propene and xylene are higher than 6 [22], indicating their significant influence to ozone formation.

2. Experimental

The experiments were carried out on a 4-cyclinder natural-aspirated direct-injection diesel engine fueled with different mixed concentrations of biodiesel and diesel fuel, including pure diesel fuel, B10 (diesel containing 10 vol.% of biodiesel), B20, B30 and pure biodiesel. The blended fuel is limited to B30 because higher biodiesel/diesel blends are not in common use. Specifications of the engine are listed in Table 1 while the experimental setup is shown in Fig. 1. The engine was coupled with an eddy-current dynamometer and a control system (Ono Sokki system) was used to adjust the engine speed and torque. The diesel fuel used contains less than 10-ppm-wt of sulfur while the biodiesel used in present study was manufactured from waste cooking oil by Dynamic Progress Ltd., complying with EN14214. The composition of the biodiesel was analyzed and the results are shown in Table 2. The FAMEs were measured using the Agilent GC 7890A with FID and Supelco SP-2560 column, with each FAME calibrated against C11 signal which was complied with the gas chromatographic analysis as stated in the AOAC Official Method 996.06 [23]. The biodiesel contains mainly Methyl palmitate (11.46%), Methyl oleate (35.22%) and Methyl linoleate (39.73%), which is very close to the major FAMEs in the waste cooking oil biodiesel used in Lapuerta et al. [7] and in Armas et al. [24]. The major physical–chemical properties of the tested fuels are listed in Table 3 which are the same as the fuels used in Zhu et al. [25] and Man et al. [26].

Table 1
Engine specifications.

Model	Isuzu 4HF1
Type	In-line 4-cylinder
Maximum power	88 kW/3200 rev/min
Maximum torque	285 N m/1800 rev/min
Bore × stroke	112 mm × 110 mm
Displacement	4334/cc
Compression ratio	19.0:1
Fuel injecting timing (BTDC)	8°
Injection pump type	Bosch in-line type
Injection nozzle	5 × 0.3 mm × 130° (with 5 orifices)

The regulated gaseous emissions analyzed include unburned hydrocarbon (HC), nitrogen oxides (NO_x) and carbon monoxide (CO), using the following standard equipment: a heated flame ionization detector (HFID, CAI Inc.) for HC; a heated chemiluminescence analyzer (HCLA, CAI Inc.) for NO_x; and non-dispersive infra-red analyzers (NDIR, CAI Inc.) for CO and CO_2. To ensure the accuracy of the experimental data, each gas analyzer was calibrated with the corresponding standard gas and the zero gas in each experiment.

The unregulated emissions, including formaldehyde, acetaldehyde, 1,3-butadiene, propene, ethene and BTX, were measured with a V&F multi-components gas analyzer (V&F Airsense Net) which is an Ion Molecule Reaction (IMR) mass spectrometer capable of detecting concentrations at ppb level. According to the equipment supplier, the lower detection limit is 1 ppb for benzene in exhaust gas. The principle of operation can be found in Refs. [27–29]. Standard gases were also used to calibrate all the measured unregulated emissions before conducting each test.

The particulate mass concentration was measured with a tapered element oscillating microbalance (R&P TEOM 1105). A Dekati mini-diluter was used to dilute the exhaust gas before passing it to the TEOM. The dilution ratio was determined from the measured CO_2 concentrations of background air, undiluted exhaust gas and diluted exhaust gas and it varied from 5.5 to 8.5 depending on the actual engine operating conditions. The fuel consumption was measured with an electronic balance with sensitivity of 0.1 g (Shimadzu Balance, Model BX-32KH).

The Japanese 13-mode test cycle for diesel engine was adopted to evaluate the effect of the biodiesel on the regulated and unregulated emissions. The operating conditions of each mode are listed in Table 4. At each operating condition, after the engine has attained the steady state operating conditions, as indicated by the stabilized exhaust gas temperature, cooling water temperature and lubricating oil temperature, the experimental data were recorded for a period of five minutes and the average results over the 5-min period are presented in this paper. Furthermore, in order to assess the repeatability and experimental uncertainty of the experimental results, each experiment was repeated twice. The experimental results were found to agree with each other within the 95% confidence level. The experimental uncertainty (at 95% confidence level) and standard errors in the measurements as determined based on the method of Kline and McClintock [30] are shown in Table 5.

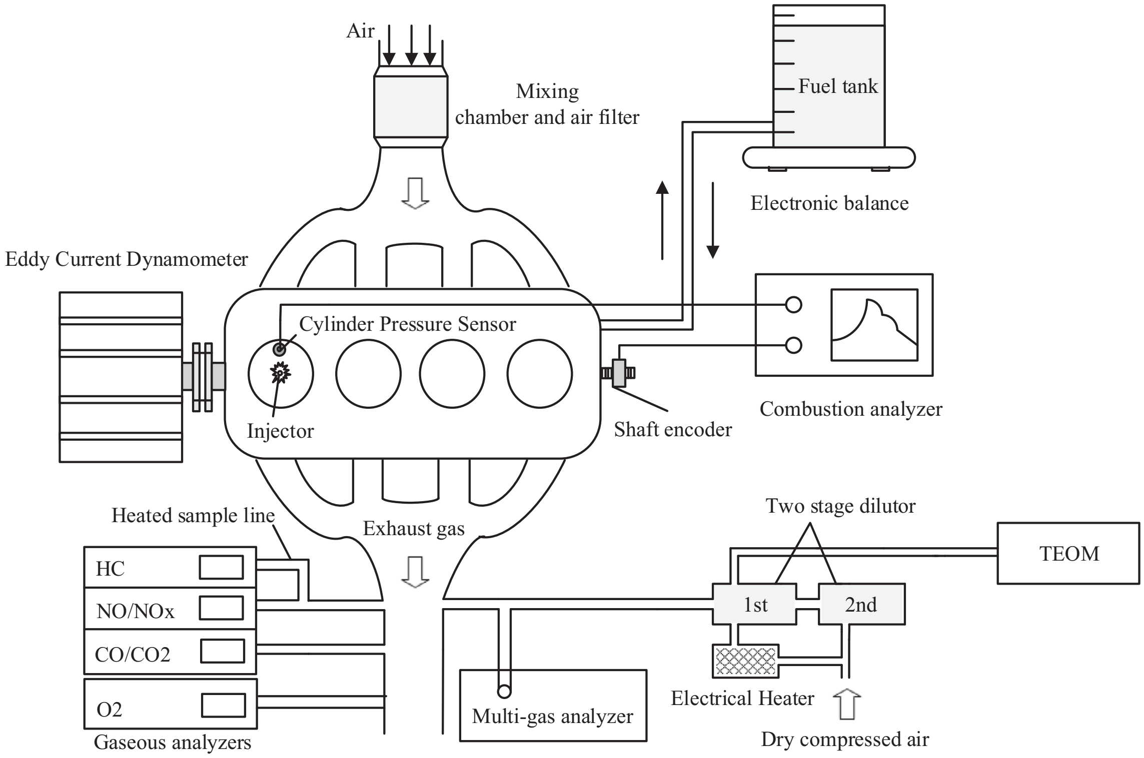

Fig. 1. Schematic diagram of the experimental setup.

Table 2
Composition of fatty acids in waste cooking oil biodiesel.

Fatty acid methyl esters		Weight (%)
c13	Tridecanoic acid	1.12
c14	Myristic acid	1.11
c16	Palmitic acid	11.46
c16:1	Palmitoleic acid	0.6
c18	Stearic acid	4.22
c18:1	Oleic acid	35.22
c18:2	Linoleic	39.73
c18:3	Linolenic acid	6.24
c24	Lignoceric acid	0.3

Table 3
Fuel properties.

Properties	ULSD	Biodiesel
Cetane number	52	51
Lower heating value (MJ/kg)	42.5	37.5
Density (kg/m^3) at 20 °C	840	871
Viscosity (mPa s) at 40 °C	2.4	4.6
Heat of evaporation (kJ/kg)	250–290	300
Carbon content (wt%)	86.6	77.1
Hydrogen content (wt%)	13.4	12.1
Oxygen content (wt%)	0	10.8
Sulfur content (mg/kg)	<10	<10

Table 4
Japanese 13-mode test cycle for diesel engine.

Mode number	Speed (rev/min)	Torque (%)	Weighting factor	Maximum in-cylinder temp.[a]([b]) (°C)	Exhaust temp.[a]([b]) (°C)
1	Idle	0	0.205	1073 (1072)	94 (94)
2	1280	20	0.037	1295 (1287)	176 (174)
3	1280	40	0.027	1482 (1482)	254 (250)
4	Idle	0	0.205	1066 (1083)	95 (95)
5	1920	20	0.029	1316 (1330)	232 (226)
6	1920	40	0.064	1508 (1529)	327 (317)
7	2560	40	0.041	1542 (1547)	412 (396)
8	2560	60	0.032	1720 (1724)	541 (522)
9	1920	60	0.077	1687 (1719)	439 (425)
10	1920	80	0.055	1898 (1918)	571 (556)
11	1920	95	0.049	1986 (1972)	667 (635)
12	2560	80	0.037	1936 (1935)	726 (691)
13	1920	5	0.142	1172 (1187)	168 (164)

[a] Diesel.
[b] Biodiesel.

3. Results and discussion

3.1. Engine performance

The fuel consumption rates, expressed in kg/h, for different test fuels are listed in Table 6. Based on the engine speed, engine torque and fuel consumption rate, the brake thermal efficiency (BTE) was calculated and the results are also shown in Table 6. In general, using biodiesel leads to an increase in fuel consumption, corresponding to an increase in the brake specific fuel consumption (BSFC), which is due to the lower calorific value of biodiesel in comparison with that of diesel fuel. In order to maintain the same output power, more fuel is required. Moreover, the results show that using biodiesel usually leads to a higher BTE than using diesel fuel. The higher BTE is due to the oxygen content in biodiesel which can improve the combustion and the higher lubricity of biodiesel which can reduce friction loss.

The engine operating conditions also affect the fuel consumption and BTE. Increasing the engine speed would lead to an increase in fuel consumption and a decrease in BTE. However, the BTE increases with increasing engine load, except that it drops slightly at the highest engine load tested. These general trends are the same for both diesel fuel and biodiesel.

Table 5
Experimental uncertainty.

Parameter	Standard error (%)	Uncertainty (%)	Parameter	Standard error (%)	Uncertainty (%)
HC	7.8	8.9	FC	1.3	1.9
CO	4.2	2.2	PM concentration	1.7	3.3
NO_x	1.9	0.53	Unregulated gas	<5.4	<5.1
CO_2	1.8	0.65	Exhaust temp.	1.0	1.2

Table 6
Fuel consumption (FC) and brake thermal efficiency (BTE) at each mode.

Mode	Diesel		B10		B20		B30		Biodiesel	
	FC (kg/h)	BTE (%)	FC (kg/h)	BTE (%)	FC (kg/h)	BTE (%)	FC (kg/h)	BTE (%)	FC (kg/h)	BTE (%)
1	0.74	–	0.75	–	0.76	–	0.77	–	0.89	–
2	2.31	26.5	2.34	26.6	2.35	26.8	2.36	26.9	2.53	27.4
3	3.50	35.0	3.53	35.1	3.57	35.2	3.61	35.2	3.86	36.0
4	0.75	–	0.75	–	0.76	–	0.76	–	0.87	–
5	3.88	24.6	3.91	24.7	3.95	24.7	4.00	24.7	4.33	25.0
6	5.81	32.8	5.87	32.9	5.93	33.0	5.99	33.0	6.45	33.5
7	8.49	28.9	8.56	29.0	8.67	29.0	8.79	29.0	9.45	29.4
8	11.58	31.8	11.67	31.9	11.82	31.9	11.93	32.0	12.80	32.6
9	8.08	35.4	8.16	35.5	8.23	35.6	8.32	35.7	8.83	36.7
10	10.27	37.1	10.38	37.2	10.50	37.2	10.62	37.3	11.42	37.9
11	11.82	36.0	11.98	36.0	12.15	35.9	12.31	35.9	13.21	36.5
12	15.55	31.5	15.66	31.7	15.87	31.7	16.00	31.8	17.21	32.3
13	2.36	10.1	2.48	9.7	2.53	9.7	2.58	9.6	2.76	9.8

3.2. Regulated gaseous emission

Regulated gaseous emissions including unburned hydrocarbon (HC), nitrogen oxides (NO_x) and carbon monoxide (CO) were measured. Detailed results are shown in Figs. 2–4 while the weighted 13-mode test results are shown in Table 7.

3.2.1. Hydrocarbon and carbon monoxide emissions

Fig. 2 shows that biodiesel addition leads to the decrease of HC emission in all test conditions and using pure biodiesel gives the lowest HC emission. This result can be attributed to the oxygen content in biodiesel, which enables more complete combustion [31,32], and the lower carbon content in biodiesel. Moreover, the HFID used for measuring HC emissions have a lower sensitivity in detecting oxygenated compounds, such as the ones that might be present in the exhaust gas when using biodiesel. Table 7 shows reductions of 2%, 7%, 10% and 23% weighted HC emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle.

With reference to the results at the engine speed of 1920 rpm, the HC emission profile has a peak value at medium engine load for both diesel fuel and biodiesel. It is also observed that at the two low engine loads at 1280 rpm, HC emission increases with increasing engine load; while at the three high engine loads at 2560 rpm, HC emission decreases with increasing engine load. Thus at both 1920 rpm and 1280 rpm, there is an increase in HC emission when the engine load is increased from 20% to 40%. It is because at these two engine loads, the in-cylinder gas temperatures are low and unfavorable for the oxidation of HC, the increase in fuel consumption leads to the increase in HC emission. At higher engine loads, the high in-cylinder gas temperature and the high exhaust gas temperature reduce the formation of unburned HC with increasing engine load. HC emission also decreases with increasing engine speed, due to the increase in in-cylinder gas temperature and exhaust gas temperature, as shown in Table 4, which enhance the oxidation of HC.

Table 7
Effect of biodiesel addition on regulated and unregulated emissions (calculated based on the weighting factors and the individual result in each mode).

	Diesel	B10	B20	B30	Biodiesel
Regulated emissions					
HC ($ppmC_1$)	183	177	171	165	141
CO (ppm)	315	293	279	275	237
NO_x (ppm)	199	203	212	218	236
PM (mg/m^3)	34.9	28.6	25.9	24.2	18.1
Unregulated emissions					
HCHO (ppm)	79.2	82.6	85.5	89.6	97.6
CH_3CHO (ppm)	6.2	6.7	7.4	8.2	9.8
1,3-C_4H_6 (ppm)	0.8	0.9	1.0	1.1	1.5
C_3H_6 (ppm)	6.8	7.4	7.9	8.7	10.4
C_2H_4 (ppm)	13.2	14.8	16.5	17.9	23.1
Total BTX (ppm)	2.62	2.62	2.50	2.48	2.43

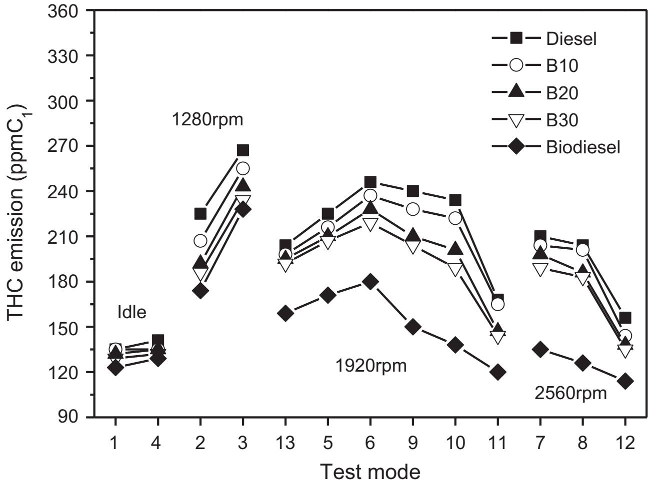

Fig. 2. Effect of biodiesel addition and engine modes on total hydrocarbon emission.

Similar to the HC emissions, there is reduction in CO emission with increase in biodiesel, as shown in Fig. 3. Table 7 shows reductions of 7%, 11%, 13% and 25% weighted CO emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle.

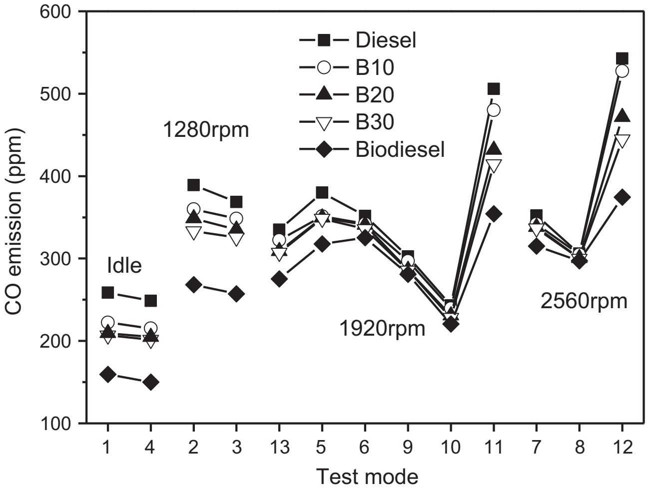

Fig. 3. Effect of biodiesel addition and engine modes on carbon monoxide emission.

With reference to the effect of engine load, there is an increase in CO emission at modes 11 and 12, both are due to the increase of fuel/air ratio at the very high engine loads. CO emission increases with increasing engine speed, due to the increase in fuel/air ratio associated with the reduction in volumetric efficiency and increase in fuel consumption associated with the increase in engine speed.

3.2.2. Nitrogen oxides emission

Fig. 4 shows that biodiesel addition leads to an increase in NO_x emissions. In a diesel engine, NO_x formation is dominated by the thermal mechanism [33]. Thus, NO_x formation is affected by the combustion temperature, the local oxygen concentration and the residence time. The higher bulk modulus of biodiesel which leads to earlier fuel injection, as well as the oxygen contents of biodiesel, favors NO_x formation [4,17]. Table 7 shows increments of 2%, 7%, 10% and 20% weighted NO_x emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle.

The engine operating mode affects the combustion temperature and combustion duration and thus they could promote or prohibit the NO_x formation. Buyukkaya et al. [34] reported that with increasing engine speed, the reaction time of each cycle was reduced so that the residence time of air–fuel mixture with high temperature in cylinder was shortened leading to a lower NO_x emission. Moreover, with constant static injection timing, the crank angle of fuel injection would be retarded at higher engine speed, leading to reduction in NO_x emissions as well. Under higher engine load, more injected fuel leads to higher combustion temperature and hence there is an increase in NO_x emission.

3.2.3. Particulate mass (PM) concentration

The variation of PM emission is shown in Fig. 5. Modes 3, 6, 7, 8 and 12 are chosen from the 13 modes to illustrate the effects of biodiesel addition or engine operating modes on PM emission. PM emission decreases with increasing biodiesel content in the blended fuel for modes 6, 7, 8 and 12. This reduction can be attributed to the following factors: (a) the absence of aromatic content in biodiesel; (b) the oxygen content in biodiesel could enhance soot oxidation; and (c) the advancement in combustion which increases the heat release rate in the stage of premixed combustion [35]. Similar trend can be obtained for the other operating modes and the trends are in line with those reported in Lapuerta et al. [6] and Haas et al. [36]. Table 7 shows reductions of 18%, 26%, 31% and 48% weighted PM emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle.

Furthermore, PM emission increases continuously with increasing engine load due to the increasing amount of fuel being consumed and hence an increase in the overall equivalence ratio. PM emission also increases with increasing engine speed due to the decreasing volumetric efficiency and the decreasing brake thermal efficiency. The decrease in volumetric efficiency leads to a higher fuel–air ratio which favors the formation of soot particles.

3.3. Unregulated gaseous emission

3.3.1. Carbonyl compounds

The variations of formaldehyde and acetaldehyde emissions with operating modes are shown in Fig. 6(a) and (b), respectively. It can be observed that both formaldehyde and acetaldehyde emissions increase with increasing biodiesel contents in the fuel. Correa and Arbilla [15] studied the carbonyl emissions of a diesel engine fueled with biodiesel blended with diesel fuel. They also observed a significant increase in formaldehyde and acetaldehyde as the biodiesel addition was increased. The possible reasons are as follows. Firstly, biodiesel from waste cooking oil contains ester molecules which could be a source of these carbonyls [15,37]. Secondly, the biodiesel used in this study was produced from waste cooking oil which might contain aldehydes formed during the frying or cooking process and the esterification process [16]. Thirdly, the short

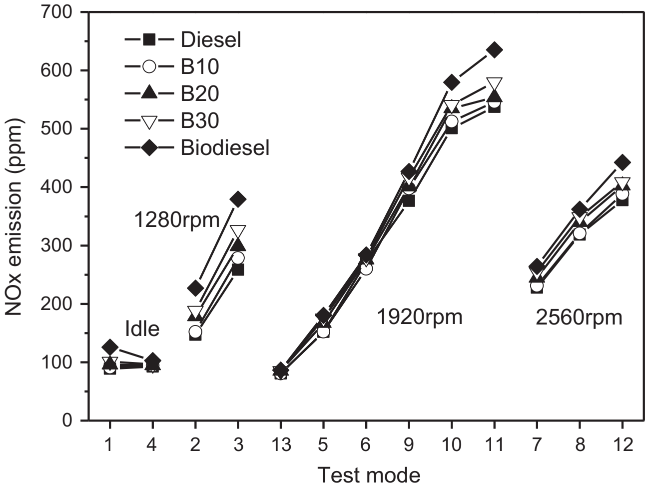

Fig. 4. Effect of biodiesel addition and engine modes on NO_x emission.

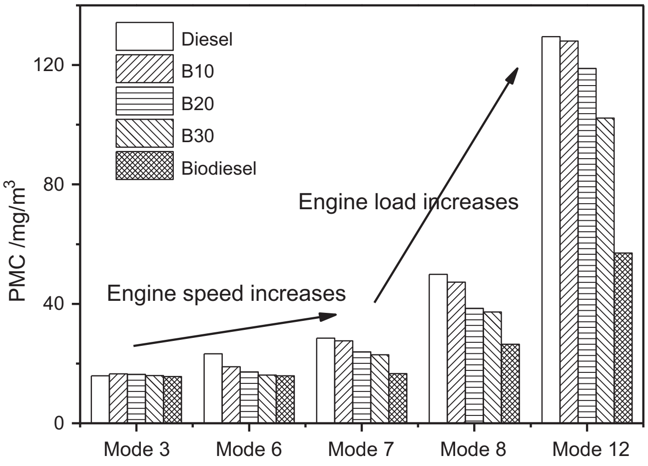

Fig. 5. Effect of biodiesel addition and engine modes on PM emission.

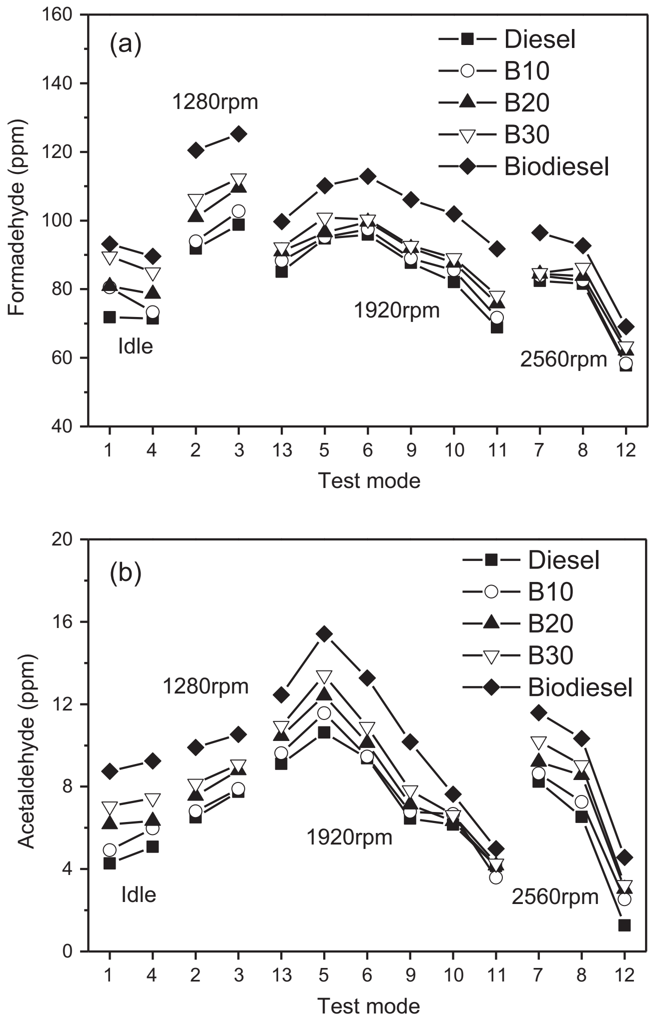

Fig. 6. Effect of biodiesel addition and engine modes on (a) formaldehyde and (b) acetaldehyde emissions.

chain chemicals in waste cooking oil biodiesel favor the formation of the shortest chain carbonyl (formaldehyde and acetaldehyde) during combustion [38]. However, Sharp et al. [12] found a substantial reduction in carbonyl emissions with pure biodiesel and a small reduction with B20. Peng et al. [16] also found an average reduction of 23% in formaldehyde and 17% increase in acetaldehyde, using 20% waste cooking oil biodiesel in diesel and under the US transient test cycle. The different results are associated with different kinds of biodiesel being used, different engines and different operating conditions. Table 7 shows increments of 4%, 8%, 13% and 23% weighted formaldehyde emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle, while the corresponding increments in acetaldehyde emissions are 8%, 19%, 32% and 58%.

Engine operating conditions have a remarkable effect on the formaldehyde and acetaldehyde emissions. Formaldehyde emission for all test fuels increases from low to medium engine load and decreases from medium to high engine load, as shown in Fig. 6(a), at the engine speed of 1920 rpm. Acetaldehyde emission has similar trend, as shown in Fig. 6(b). The increase in carbonyl emissions at relatively low engine load can be attributed to the increase in fuel consumption. The decrease at relatively high engine load can be attributed to the higher combustion temperature and exhaust gas temperature. Liu et al. [39] showed an increase in carbonyl emissions when the diesel engine was run on biodiesel and its blends at different engine loads. Zarante et al. [40] simulated the formation of formaldehyde and acetaldehyde. They suggested that formaldehyde and acetaldehyde are generated when the decomposition process of the unburnt fuel in the exhaust gas is stopped at an intermediate stage of the chemical reaction due to reduction of temperature and oxygen concentration.

In regard to the effects of engine speed, for formaldehyde, there is an obvious reduction with increasing engine speed. For acetaldehyde, it increases from 1280 to 1920 rpm at low engine loads but decreases from 1920 to 2560 rpm at high engine loads. With increasing engine speed, lower formaldehyde and acetaldehyde emissions are observed due to the increase of in-cylinder temperature, as shown in Table 4. From Table 4, it can also be found that the engine load plays a more important role in determining the in-cylinder temperature compared with engine speed. Therefore, at low load, despite a slightly higher in-cylinder temperature is found with increasing engine speed, the in-cylinder temperature remains at a low level so that subsequently higher acetaldehyde emission is observed due to the increase of fuel consumption at the higher engine speed.

3.3.2. Olefins

1,3-Butadiene (C_4H_6), propene (C_3H_6) and ethene (C_2H_4) are unsaturated alkenes formed through thermal pyrolysis of the fuel [41]. They can lead to the formation of PAHs that are soot precursors. Particularly, 1,3-butadiene is considered as one of the most toxic pollutants in the atmosphere due to its carcinogenic and mutagenic properties [42].

Fig. 7(a)–(c) shows that the concentrations of 1,3-butadiene, propene and ethene increase with increasing biodiesel in the fuel. Table 7 shows increments of 13%, 25%, 38% and 88% weighted 1,3-butadiene emissions for B10, B20, B30 and B100, respectively, over the 13-mode test cycle. The corresponding increments are 9%, 16%, 28% and 53% for propene and 12%, 25%, 36% and 75% for ethene.

The concentration of 1,3-butadine in engine exhaust is usually on the low side. Thus, McGill et al. [14] concluded that 1,3-butadiene emission did not seem to have much dependence on the fuel. Sharp et al. [12] conducted investigations on three diesel engines. With B20 and B100, they found reductions of ethene and propene and little change of 1,3-butadiene for two of the engines and increase of all the three pollutants for the third engine, compared with diesel fuel. Bermúdez et al. [43] investigated three biodiesel fuels. In comparison with diesel fuel, they found increase in ethene and propene for each biodiesel while the results on 1,3-butadiene was fuel dependent.

With increasing engine load, there is in general a decrease in the emissions of the three pollutants, but, their concentrations increase at modes 11 and 12. The effect of engine speed on these pollutants is not significant. The emissions of C_4H_6, C_3H_6 and C_2H_4 are strongly related to the combustion temperature and the air/fuel ratio. Higher engine load leads to a relatively higher combustion temperature that promotes the oxidation of the pyrolytic products but it also has a lower air/fuel ratio which favors the formation of the pyrolytic products. The increase of these three pollutants at the very high engine loads (modes 11 and 12) is mainly because the rate of pyrolysis of the fuel molecules is higher than the rate of oxidation of the pyrolytic products under the high combustion temperature and locally fuel rich environment.

According to Takada et al. [41], 1,3-butadiene is produced easily in regions with high air–fuel ratio. They found higher 1,3-butadiene emission at low load when both exhaust gas temperature and fuel–air ratio were low. Since the air fuel ratio of B100 is lower than that of diesel fuel, which could lead to an increase in 1,3-butadiene emission. With regard to the effect of engine load, our results are in general in line with those reported in Takeda

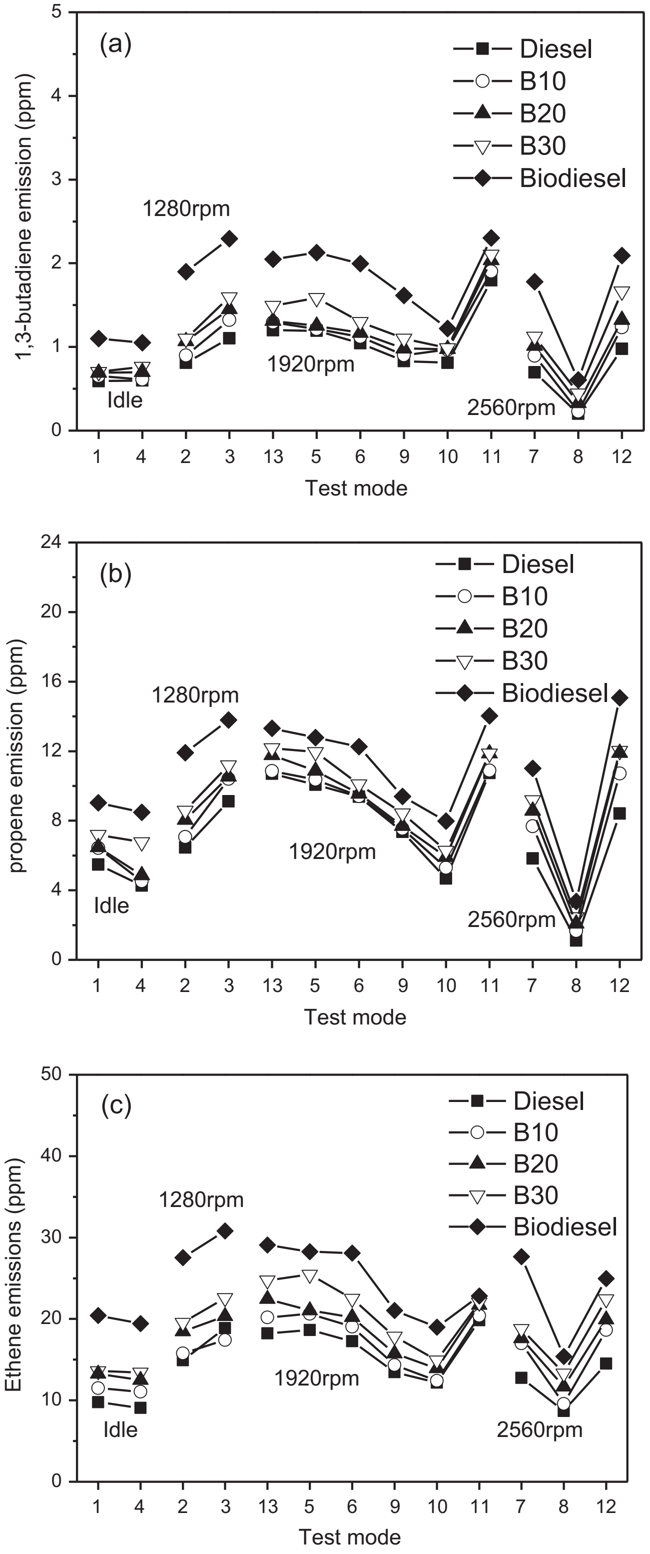

Fig. 7. Effect of biodiesel addition and engine modes on (a) 1,3-butadiene; (b) propene and (c) ethane emissions.

et al. [41], however, they reported increase of 1,3-butadiene emission with engine speed which is not obvious in our study.

Thus it can be concluded that the 1,3-butadiene emission is usually low and hence significantly affected by many factors which contributed to different results being obtained from different investigations. The same conclusion can also be extended to ethene and propene, despite these emissions are usually much higher in concentrations than that of 1,3-butadiene, because the three are similar thermal cracking products.

3.3.3. Benzene, toluene and xylene (BTX) emissions

The main source of BTX in engine exhaust is the unburned molecules from fuel, pyrosynthesis and structural modifications during combustion [44]. The effects of biodiesel addition on the brake specific emissions of benzene, toluene and xylene are given in Table 8, for the engine loads of 0.16, 0.33, and 0.65 MPa at the engine speed of 1920 rpm, corresponding to modes 5, 6 and 10 of the Japanese 13-mode test cycle, to illustrate the effects at low, medium and high engine loads. It can be seen that benzene emission increases with the increase of biodiesel addition in the fuel for each engine load. Turrio-Baldassari et al. [45] and Di et al. [17] also reported that using biodiesel has a higher benzene emission than using diesel fuel. Opposite results can be found in Cheung et al. [18] and Correa and Arbilla [44]; while USEPA [13] reported inconsistent results. Takada et al. [41] pointed out that more benzene was emitted under lower exhaust temperature conditions. Biodiesel addition would lead to a reduction of exhaust temperature, hence slowing down the oxidation of benzene. Moreover, biodiesel would enrich the oxygen concentration of the fuel, thus promoting the conversion of carbon atoms to carbon dioxide and leading to the decrease of benzene emission. Probably the influence of exhaust temperature overrides the influence of oxygen enrichment, leading to the increase of benzene emissions with increase in biodiesel. However, the toluene and xylene emissions show reduction with the increase of biodiesel. It can be inferred that the oxygen enrichment is more dominant for the reduction of these two pollutants. Di et al. [17], Cheung et al. [18], Correa and Arbilla [44] and Turrio-Baldassari et al. [45] all reported reduction in toluene and xylene with biodiesel. However, USEPA [13] reported decrease in xylene but increase in toluene emissions. Table 8 shows that the total BTX emissions do not vary significantly with biodiesel, because the increase in benzene emission is balanced by the reductions in toluene and xylene emissions.

The overall BTX emissions decrease with increasing engine load at the engine speed of 1920 rpm because the higher combustion temperature at higher engine load promotes the oxidation of the BTX emissions [41]. Similar results are obtained under the other two engine speeds (1280 rpm and 2560 rpm). However, the influence of engine speed on the BTX emissions is insignificant.

Table 8
Brake specific benzene, toluene and xylene emissions at various engine loads (at 1920 rev/min).

Load (MPa)	Fuel	C_6H_6 (mg/kW h)	C_7H_8 (mg/kW h)	C_8H_{10} (mg/kW h)	BTX (mg/kW h)
0.16	ULSD	80.9	10.1	37.0	128.0
	B10	86.9	8.8	29.7	125.5
	B20	88.7	7.6	27.4	123.7
	B30	92.6	7.0	23.8	123.3
	Biodiesel	102.3	4.8	8.5	115.6
0.33	ULSD	44.4	3.7	12.8	60.9
	B10	45.5	3.6	11.3	60.4
	B20	47.2	2.7	9.9	59.8
	B30	48.2	2.6	8.4	59.2
	Biodiesel	52.4	2.0	4.0	58.4
0.65	ULSD	22.4	1.9	5.4	29.6
	B10	23.7	1.9	4.1	29.6
	B20	23.3	1.6	3.6	28.4
	B30	23.6	1.5	3.3	28.5
	Biodiesel	26.2	1.1	1.7	29.0

4. Conclusions

This investigation focuses on the effects of a waste cooking oil biodiesel on the regulated emissions (including the unburned hydrocarbon, carbon monoxide, nitrogen oxides and particulate mass concentrations) and the unregulated emissions, including the two carbonyl compound (formaldehyde and acetaldehyde), three unsaturated hydrocarbons (1,3-butadiene, propene and ethene) and three aromatics (benzene, toluene and xylene). The experiments were carried out with the Japanese 13-mode test cycle for diesel engine to enable the effects of fuel, engine load and engine speed to be investigated.

For the regulated emissions, the 13-mode weighted results show that there is a reduction in HC and CO emissions but an increase in NO_x emission for all test conditions when compared to diesel fuel.

For the unregulated emissions, formaldehyde and acetaldehyde emissions increase with increasing biodiesel in the fuel. The same trend can be observed for 1,3-butadiene, propene and ethene. For the aromatics, biodiesel addition leads an increase in benzene emission but a reduction in toluene and xylene emissions. However, there is no significant change in the total BTX emissions because the increase in benzene is balanced by the decrease in toluene and xylene. The results also show that all the emissions are significantly affected by the engine operating modes, especially the engine load.

It can be concluded that despite biodiesel addition to diesel fuel can reduce the total hydrocarbon emissions, there could be increase in the emissions of certain air toxics, like formaldehyde, acetaldehyde, ethene, propene, 1,3-butadine and benzene.

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References

[1] Demirbas A. Progress and recent trends in biofuels. Prog Energy Combust Sci 2007;33:1–18.
[2] Demirbas A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. Energy Convers Manage 2008;49:2106–16.
[3] Basha SA, Gopal KR, Jebaraj S. A review on biodiesel production, combustion, emissions and performance. Renew Sustain Energy Rev 2009;13:1628–34.
[4] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. Renew Sustain Energy Rev 2011;15:1098–116.
[5] Choi CY, Bower G, Reitz R. Effects of biodiesel blended fuels and multiple injections on D. I. Diesel Engines. SAE Technical Paper; 1997.
[6] Lapuerta M, Armas O, Rodríguez-Fernández J. Effect of biodiesel fuels on diesel engine emissions. Prog Energy Combust Sci 2008;34:198–223.
[7] Lapuerta M, Herreros JM, Lyons LL, García-Contreras R, Briceño Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008;87:3161–9.
[8] Utlu Z, Koçak MS. The effect of biodiesel fuel obtained from waste frying oil on direct injection diesel engine performance and exhaust emissions. Renewable Energy 2008;33:1936–41.
[9] Westbrook CK, Pitz WJ, Curran HJ. Chemical kinetic modeling study of the effects of oxygenated hydrocarbons on soot emissions from diesel engines. J Phys Chem A 2006;110:6912–22.
[10] Mohamed Ismail H, Ng HK, Gan S, Lucchini T, Onorati A. Development of a reduced biodiesel combustion kinetics mechanism for CFD modelling of a light-duty diesel engine. Fuel 2013;106:388–400.
[11] Lai JYW, Lin KC, Violi A. Biodiesel combustion: advances in chemical kinetic modeling. Prog Energy Combust Sci 2011;37:1–14.
[12] Sharp CA, Howell SA, Jobe J. The effect of biodiesel fuels on transient emissions from modern diesel engines, part II unregulated emissions and chemical characterization. SAE 2001-01-1968; 2000.
[13] Agency. EP. A comprehensive analysis of biodiesel impacts on exhaust emissions. US Environmental Protection Agency, Washington, DC; 2002.
[14] Mcgill R, Storey J, Wagner R, Irick D, Aakko P, Westerholm M, et al. Emission performance of selected biodiesel fuels. SAE 2003-01-1866; 2003.
[15] Correa SM, Arbilla G. Carbonyl emissions in diesel and biodiesel exhaust. Atmos Environ 2008;42:769–75.
[16] Peng C-Y, Yang H-H, Lan C-H, Chien S-M. Effects of the biodiesel blend fuel on aldehyde emissions from diesel engine exhaust. Atmos Environ 2008;42:906–15.
[17] Di Y, Cheung CS, Huang Z. Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra-low sulfur diesel fuel blended with biodiesel from waste cooking oil. Sci Total Environ 2009;407:835–46.
[18] Cheung CS, Zhu L, Huang Z. Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. Atmos Environ 2009;43:4865–72.
[19] Karavalakis G, Stournas S, Fontaras G, Samaras Z, Dedes G, Bakeas E. The effect of biodiesel on PAHs, nitro-PAHs and oxy-PAHs emissions from a light vehicle operated over the European and the Artemis driving cycles. SAE Technical Paper; 2009.
[20] Lin Y-f, Wu Y-pG, Chang CT. Combustion characteristics of waste-oil produced biodiesel/diesel fuel blends. Fuel 2007;86:1772–80.
[21] Grigoratos T, Fontaras G, Kalogirou M, Samara C, Samaras Z, Rose K. Effect of rapeseed methylester blending on diesel passenger car emissions – Part 2: unregulated emissions and oxidation activity. Fuel 2014;128:260–7.
[22] Carter WP. Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. California Air Resources Board Contract 07-339; 2009.
[23] Latimer GW. Official methods of analysis of AOAC International. 19th ed. Maryland, USA: AOAC International; 2012.
[24] Armas O, Hernandez J, Cardenas M. Reduction of diesel smoke opacity from vegetable oil methyl esters during transient operation. Fuel 2006;85:2427–38.
[25] Zhu L, Cheung CS, Zhang WG, Huang Z. Emissions characteristics of a diesel engine operating on biodiesel and biodiesel blended with ethanol and methanol. Sci Total Environ 2010;408:914–21.
[26] Man XJ, Cheung CS, Ning Z, Yung KF. Effect of waste cooking oil biodiesel on the properties of particulate from a DI Diesel Engine. Aerosol Sci Technol 2015;49:199–209.
[27] Dearth MA. Evaluation of a commercial mass spectrometer for its potential to measure auto exhaust constituents in real time. Ind Eng Chem Res 1999;38:2203–9.
[28] Villinger J, Federer W, Resch R, Dornauer A, Lubich M, Sejkora W. SIMS 500-rapid low energy secondary ion mass spectrometer for in-line analysis of gaseous compounds-technology and applications in automotive emission testing. SAE Technical Paper; 1993.
[29] Villinger J, Federer W, Dornauer A, Weissnicht A, Hönig M, Mayr T. Dynamic monitoring of differentiated hydrocarbons in direct engine exhaust: a versatile tool in engine development. SAE Technical Paper; 1996.
[30] Kline SJ, McClintock F. Describing uncertainties in single-sample experiments. Mech Eng 1953;75:3–8.
[31] Zouaoui N, Brilhac J, Mechati F, Jeguirim M, Djellouli B, Gilot P. Study of experimental and theoretical procedures when using thermogravimetric analysis to determine kinetic parameters of carbon black oxidation. J Therm Anal Calorim 2010;102:837–49.
[32] Lujan J, Bermúdez V, Tormos B, Pla B. Comparative analysis of a DI diesel engine fuelled with biodiesel blends during the European MVEG-A cycle: performance and emissions (II). Biomass Bioenergy 2009;33:948–56.
[33] Fernando S, Hall C, Jha S. NOx reduction from biodiesel fuels. Energy Fuels 2006;20:376–82.
[34] Buyukkaya E. Effects of biodiesel on a DI diesel engine performance, emission and combustion characteristics. Fuel 2010;89:3099–105.
[35] Tsolakis A. Effects on particle size distribution from the diesel engine operating on RME-biodiesel with EGR. Energy Fuels 2006;20:1418–24.
[36] Haas MJ, Scott KM, Alleman TL, McCormick RL. Engine performance of biodiesel fuel prepared from soybean soapstock: a high quality renewable fuel produced from a waste feedstock. Energy Fuels 2001;15:1207–12.
[37] Cardone M, Prati MV, Rocco V, Seggiani M, Senatore A, Vitolo S. Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: engine performance and regulated and unregulated exhaust emissions. Environ Sci Technol 2002;36:4656–62.
[38] Guarieiro LLN, de Paula Pereira PA, Torres EA, da Rocha GO, de Andrade JB. Carbonyl compounds emitted by a diesel engine fuelled with diesel and biodiesel–diesel blends: sampling optimization and emissions profile. Atmos Environ 2008;42:8211–8.
[39] Liu Y-Y, Lin T-C, Wang Y-J, Ho W-L. Carbonyl compounds and toxicity assessments of emissions from a diesel engine running on biodiesels. J Air Waste Manage Assoc 2009;59:163–71.
[40] Zarante P, Costa T, Sodré J. Aldehyde emissions from an ethanol-fuelled spark ignition engine: simulation and FTIR measurements. Blucher Chem Eng Proc 2015;1:7738–45.
[41] Takada K, Yoshimura F, Ohga Y, Kusaka J, Daisho Y. Experimental study on unregulated emission characteristics of turbocharged DI diesel engine with common rail fuel injection system. SAE Technical Paper; 2003.
[42] Krahl J, Munack A, Schröder O, Stein H, Bünger J. Influence of biodiesel and different designed diesel fuels on the exhaust gas emissions and health effects. SAE Technical Paper; 2003.
[43] Bermúdez V, Lujan JM, Pla B, Linares WG. Comparative study of regulated and unregulated gaseous emissions during NEDC in a light-duty diesel engine

fuelled with Fischer Tropsch and biodiesel fuels. Biomass Bioenergy 2011;35:789–98.

[44] Corrêa SM, Arbilla G. Aromatic hydrocarbons emissions in diesel and biodiesel exhaust. Atmos Environ 2006;40:6821–6.

[45] Turrio-Baldassarri L, Battistelli CL, Conti L, Crebelli R, De Berardis B, Iamiceli AL, et al. Emission comparison of urban bus engine fueled with diesel oil and 'biodiesel' blend. Sci Total Environ 2004;327:147–62.