Pak. J. Sci. Ind. Res. 2009 **52**(3) 158-166

Experimental Investigation of VOCs Emitted from a DI-CI Engine Fuelled with Biodiesel, Diesel and Biodiesel-Diesel Blend

Asad Naeem Shah[ab]*, G. E. Yun-shan[a], Tan Jian-wei[a] and Liu Zhi-hua[a]
[a]School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China
[b]Department of Mechanical Engineering, University of Engineering and Technology, Lahore 54000, Pakistan

(received November 6, 2008; revised March 25, 2009; accepted March 28, 2009)

Abstract: Experimental investigation of volatile organic compounds (VOCs) emitted by a turbocharged direct injection compression ignition (DI-CI) engine, alternatively fuelled with biodiesel and its 20% blend with diesel, revealed dominancy of diesel and biodiesel in aromatic hydrocarbons, esters other oxides, respectively, in total volatile organic compounds (TVOCs). The overall brake specific emission of VOCs increased at rated speed compared to maximum torque speed. The VOCs exhibited their maxima at low load, and minima at medium load for diesel and B100. Engines with a speed of 2300 r/min and 100% load showed a reduction in BTX emissions from B20 and B100, as compared to diesel. The sum of VOC-components of B20 and B100 reduced as compared to that of the diesel, for all the engine conditions. The mean BSE of BTX-components taken from all the engine conditions decreased with B20 and B100, relative to fossil diesel.

Keywords: compression ignition engine, biodiesel, unregulated emissions, volatile organic compounds

Introduction

In the face of depleting reservoirs of conventional fossil fuels and stringent emission regulations for compression ignition (CI) engines, biofuels are promising alternative fuels, which could resolve not only the energy security problems but the environmental pollution issues as well.

Biodiesel (methyl esters of animal and plant origin) as an alternative fuel has already been investigated for performance, combustion, injection and emission in diesel engines. Many studies regarding regulated emissions have reported that biodiesel reduces the particulate matter (PM), carbon monoxide (CO), hydrocarbons (HC) and oxides of sulfur (SO_x) (Sinha and Agarwal, 2005; Senda *et al.*, 2004; Turrio-Baldassarry 2004; Monyem and Gerpen, 2001). Unregulated emissions comprise a wide range of pollutants such as individual non-methane hydrocarbons (NMHC), polycyclic aromatic hydrocarbons (PAHs), medium diameter of the PM (D_m), soluble organic fraction (SOF) of the PM, and volatile organic compounds (VOCs) (Ballesteros *et al.*, 2008). Some studies, focused on unregulated emissions, have revealed that biodiesel and its blends reduce the polycyclic aromatic hydrocarbons (PAHs) (Shah *et al.*, 2009a; Lin *et al.*, 2006). It has also been reported that mutagenicity of biodiesel particulate emissions is much lower than that of petroleum-based diesel fuel (McDonald *et al.*, 1995). Although some work on VOCs has been reported on the exhaust of diesel engines, however, biodiesel and its blends with diesel fuel still need to be addressed comprehensively. This should be done particularly for VOC-emissions at maximum torque speed and rated speed for varying loads, particularly when engine is unmodified. In this work, it has been attempted to determine the VOC-components emitted from a direct injection compression ignition engine fuelled with diesel, biodiesel and 20% biodiesel-diesel blend. Results are drawn on comparison in terms of brake specific emissions (BSE) for different engine conditions (loads and speeds).

The VOC-components are an important class of unregulated emissions from the exhaust of diesel engines. The World Health Organization (WHO) has defined the VOCs as organic compounds that has boiling point with in the ranges of 50-100 °C and 240-260 °C. There are two major reasons to select VOCs for the current study. In the first place, some volatile organic compounds are toxic and thus directly influence the human health. According to international chemical safety cards published by The National Institute for Occupational Safety and Health (NIOSH), U.S.A., benzene is carcinogenic to humans and may affect the blood forming organs, liver and immune system; toluene may affect the central nervous system, resulting in decrease in learning ability and psychological disorders; *p*,*m*-xylene may affect the central nervous system and human reproduction; and *o*-xylene may cause damage to central nervous and hearing systems (Haupt *et al.*, 2004). Furthermore, it has also been reported that among the non-methane volatile organic compounds (NMVOCs), the aromatic

---

*Author for correspondence; E-mail: naeem138@hotmail.com & anaeems@uet.edu.pk; [a]Present address

compounds like benzene, toluene and xylene isomers are suspected carcinogens and their prolonged exposure may lead to leukemia (US EPA, 1990).

Secondly, VOCs contain reactive compounds which are capable of participating in the formation of photochemical smog or ozone (Schulz, 1999), and thus pose a serious air pollution problem under direct sunlight. Xylene isomers, the important components of VOCs, have been blamed for converting significant amounts of NO to NO_2 (Simpson, 1995).

Materials and Methods

Test engine, fuels, and working conditions. The engine used in this study is a heavy duty, turbocharged, direct injection, intercooled, with 4 cylinders (China made 4CK series), which was run on an electric dynamometer (SCHENCK HT 350) as shown in Fig. 1. No modification or alteration was made in the engine. Its specifications (Shah *et al.*, 2009a) are listed in Table 1.

Three fuels were used in the study namely commercial diesel (D), biodiesel (B100) and its 20% blend by volume with diesel (B20) using commercial diesel as a reference fuel. Biodiesel was obtained from waste cooking oil, provided by Zhenghe Bioenergy Co., Ltd., Hainan, China, (Shah *et al.*, 2009a,b). Main properties of the test fuels are given in Table 2. The experiments were performed in accordance with the engine conditions given in Table 3. The maximum torque speed at full load and maximum power speed (rated speed) at 10%, 50%, and 100% loads were selected for the study. The engine load (torque) was measured by torque flange and was read, along with engine speed, directly on monitor supported by software “Automation system STARS Rev. 1.5” in the control room. Fuel flow rate was measured by PLU-V2 (Pier Berg); crank angle was found with the help of a sensor (2613A) by Kistler Corporation and Dewetron (DEWE-5000); instantaneous pressure in the cylinder was determined using Piezo-electric sensor (Kistler 6125B) and combustion analyzer (Dewetron, DEWE-5000); ignition delay was estimated using the needle lift curve, traced by needle lift transducer (sensor) and cylinder pressure curve (Shah *et al.*, 2009b). Engine oil and coolant temperatures were measured using Pt-100 (sensor) and exhaust temperature was measured using thermocouple (K-series).

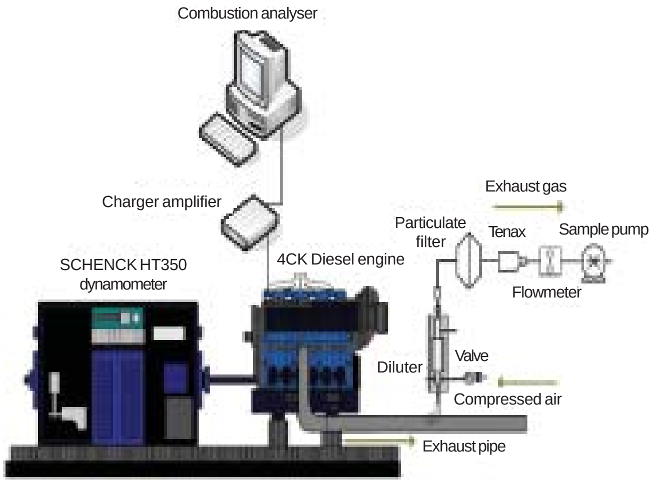


Fig. 1. Experimental setup

Table 1. Engine specifications.

Number of cylinders	4
Bore (mm)	110
Stroke (mm)	125
Displacement (litre)	4.752
Compression ratio	16.8
Rated power (kW@ r/min)	117/2300
Maximum torque (N.m@ r/min)	580/1400
Nozzle hole diameter (mm)	0.23
Number of nozzle holes	6

Sampling methodology. An ejector diluter is used in order to get emissions directly from the exhaust pipe, (Dekati Ltd. Finland). Its J-shaped stainless-steel sampler probe was inserted into the exhaust pipe as shown in Fig. 1. The specifications of the ejector-diluter (Shah *et al.*, 2009a), in brief, are as follows. It consists of a set of filters, a dryer, a temperature controller, a pressurized air heater and two diluters. The dry, particle-free and pressurized air was introduced into the primary diluter and was heated up to the exhaust gaseous

Table 2. Properties of fuels.

Properties	B100	B20	D	Standards
Density (kg/m^3)	886.4	845.1	834.8	SH/T 0604
Viscosity (mm^2/s) at 20 ºC	8.067	4.020	3.393	GB/T 265
Lower heating value (MJ/kg)	37.3	41.57	42.8	GB/T 384
Sulfur content (mg/L)	25	n/a	264	SH/T 0253-92
Cetane number	60.1	n/a	51.1	GB/T 386-91
Carbon content (%)	76.83	n/a	86.92	SH/T 0656-98
Hydrogen content (%)	11.91	n/a	13.08	SH/T 0656-98
Oxygen content (%)	11.33	n/a	0	Element analysis

Table 3. Engine conditions.

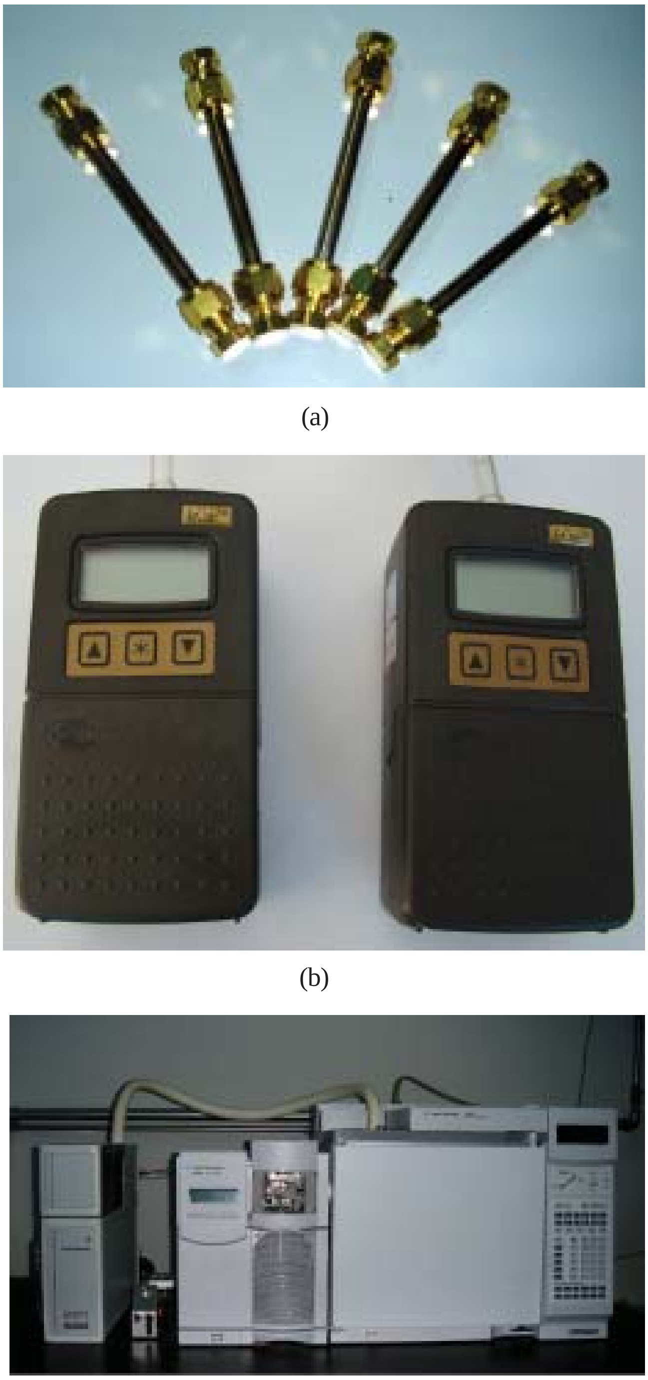
	Speed (r/min)	Load (%)
Engine condition 1	1400	100
Engine condition 2	2300	10
Engine condition 3	2300	50
Engine condition 4	2300	100

temperature. The diluted sample was then introduced into the secondary diluter for further dilution. The dilution ratio of the primary and the secondary diluters was 8, so the over all dilution ratio of the instrument was about 64. Before sampling, the calibration was made by using two concentrations of CO_2 which were measured before and after the dilution. Total residence time was about 0.1s for primary and secondary diluters as discussed by Dekati Ltd. The exhaust gas, filtered from the fiber glass filter, was taken in sampling tubes Tenax TA® (Markes U.K.) shown in Fig. 2a, and all the samples were collected at a temperature less than 58 °C. Sampling pumps used are constant volume pumps (SKC USA, Air Chek 2000), (Fig. 2b). Sampling volume was 220 ml and it took 10 minutes to sample at every mode. After sampling the Tenax tubes were sealed with aluminum foil and were refrigerated at -10 °C.

Extraction of sampled material and analysis of VOC-components. After sampling, tubes were analyzed in the laboratory for VOCs according to the Environment Protection Agency (EPA) standard method TO-17 (US EPA, 1999). For thermal desorption, automatic thermal desorber (TD), UNITY (Markes UK) was used. Tenax tubes were first blown by dry inert gases and then heated. The desorbed compounds were cryogenically focused in a cold trap at -10 °C. After focusing, the trap underwent rapid heating to 280 °C to volatilize the compounds into the gas chromatograph (GC) (Agilent 6890N/ 5975) capillary column (HP-5MS, 30m × 0.25 mm × 0.25 μm) through a fused silica line heated at 280 °C. The temperature programme was 35 °C (10 min)-5° C/min–280 °C. The equipment and its specifications are given in Fig. 2c and Table 4, respectively.

Materials used for the identification and quantification of the compounds were purchased from Sino-Japan Friendship Center for Environment Protection. Six different concentrations of the standard solution were used for the calibration curve. In this way benzene, toluene, butyl acetate, ethyl benzene, *p,m*-xylene, styrene, *o*-xylene, and undecane were identified by comparing retention times of chromatographic peaks of emission samples with those from standard mixtures and by comparing mass spectra with those contained in U.S. National Institute of Standards and Technology (NIST) library (the grade of similarity was more than 85%).

After identification, the compounds were quantified by using external standard method to make the linear standard curve. The purchased standard liquids were measured in quantities 1, 2, 4, 10, 20 and 40 μl, using micro- sampler. The standard gas from the gas carrier was injected into the Tenax tube and then material was put into GC/MS for analysis to get the target compounds (Table 5) by the regression method of their peak areas. In this case, peak areas of the relative standard deviation (RSD) of each compound were recorded.


(a)

(b)

(c)

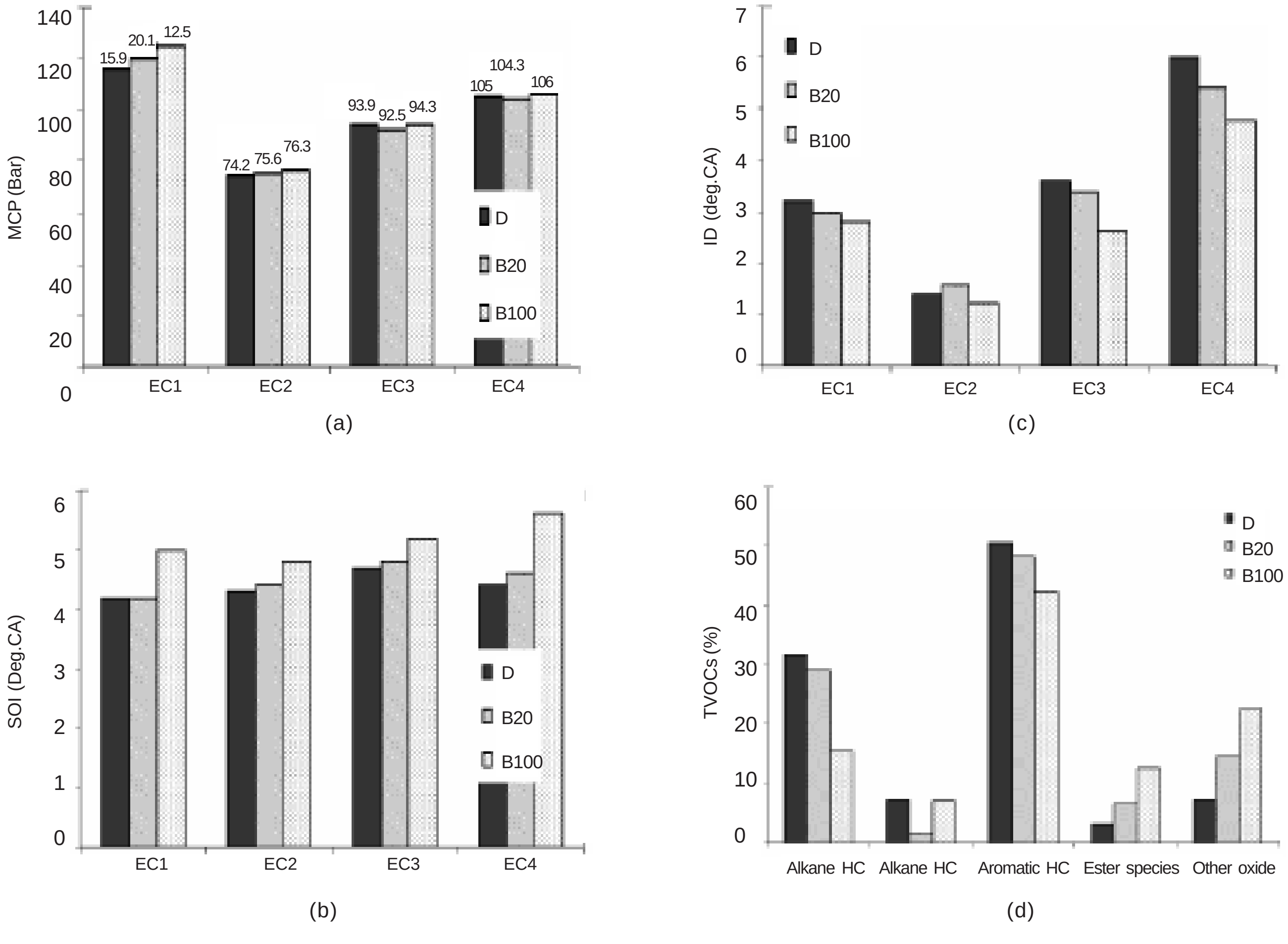
Fig. 2a-c. (a) Tenax TA sampling tubes, (b) constant volume sampling pumps and (c) TD-GC/MS.

Results and Discussion

Combustion parameters. Even though it is not the purpose of this study to discuss combustion parameters of the engine at different engine conditions (ECs) for different fuels because authors have already studied them for their performance and combustion (Shah *et al.*, 2009b), some basic data is mentioned for the discussed engine conditions in order to provide a background for the study. As presented in Fig. 3a, maximum combustion pressure (MCP) is higher compared with fossil diesel in the cases of B20 and B100. This is due to the difference in physio-chemical properties of the test fuels as illustrated in Table 2. Properties like higher cetane number, faster flame propagation speed, better fuel atomization and simple chemical structure of the biodiesel and its blends advance the combustion process when they burn in an unmodified diesel engine. Moreover, biodiesel is an alkyl ester containing internal oxygen atoms which promote the burning of the impurities under the same condition of use (Kegl, 2008).

As shown in Fig. 3b, B20 and B100 have larger start of injection (SOI) angle relative to diesel for all the engine conditions. This is attributed to different densities and bulk modulus or compressibility of the test fuels. Biodiesel is less compressible than fossil diesel, so, faster pressure develops in the fuel injection system; consequently, the propagation of pressure wave is faster in biodiesel than diesel fuel even at the same nominal pump timing, resulting in earlier injection of biodiesel with higher pressure and rate. Moreover, higher viscosity of biodiesel and its blends is helpful in reducing the fuel losses during the injection process as compared to lower viscosity of diesel. The reduction in fuel losses results in quicker development of pressure which ultimately improves the injection timing (Shah *et al.*, 2009b).

From Fig. 3c, it is clear that biodiesel has shorter ignition delay (ID) as compared to the commercial diesel. This shorter ID angle of biodiesel is ascribed to the difference in cetane numbers of the test fuels. Relative to fossil diesel fuel, biodiesel has larger cetane number, hence resulting in earlier start of combustion in the combustion chamber of the engine. Furthermore, shorter ignition delay results in complete



(a) (c)

(b) (d)

Fig. 3a-d. (a) Maximum combustion pressure, (b) angle of start of injection, (c) ignition delay, and (d) Percentage distribution of total volatile organic compounds of the test fuels volatilization and hence clean burning of the fuel with the reduction of pollutants (Sureshkumara *et al.*, 2008).

Total volatile organic compounds. Total volatile organic compounds (TVOCs), based on the mean of the four values taken at four working conditions, have been discussed in term of percentage distribution of the detected species including alkanes, alkenes, aromatics, esters and some other species containing oxygen, as shown in the Fig. 3d. Among the detected species, aromatics and alkanes are more prominent in their percentage for all the test fuels. Aromatic hydrocarbons in diesel, B20 and B100 are 50.6%, 48.3% and 42.2%, respectively, and alkanes are 31.6%, 29.1% and 15.5%, respectively. Esters and other oxides show their dominancy in B100 and B20 as compared to diesel, however, alkenes of diesel and biodiesel are almost equal in their percentage distribution. Relative to B20 and B100, higher percentage of aromatic species in commercial diesel is quite understandable and is due to the aromatic content inherently possessed by the diesel fuel. The possible reason for higher percentage of esters and other oxides in B20 and B100, compared with diesel fuel is the higher oxygen content possessed by them; since biodiesel has been produced by the esterification of the waste cooking oil, so it is inherently oxygen enriched. Considering their maximum contribution to TVOCs and health hazards, especially associated with benzene, toluene, *p,m*-xylene, and *o*-xylene (BTX), aromatic species commonly known as VOCs have been selected for this study.

Effect of engine conditions on VOCs. The VOC-components have been discussed in term of their brake specific emissions (BSE), defined as the mass of the pollutants emitted per kilo-watt power developed in the engine in 1 h. Fig. 4 shows emissions of the eight confirmed aromatic compounds, designated as VOCs, for four different engine conditions. Experimental results show that overall BSE of VOCs increase at engine condition 4 (rated speed) relative to the condition 1 (maximum torque speed). This increase is 67%, and varies from 16% to 90% for different species. The increase in BSE at condition 4 relative to condition 1 is attributed to the decrease in combustion temperature and the increase in ignition delay caused by the increase in engine speed, as illustrated in Fig. 3, since engine speed can affect the swirl characteristics, injection timing and combustion temperature of the engine (Shah *et al.*, 2009a). At higher speed (2300 r/min), turbulence in the combustion chamber increases which increases the heat loss to the combustion chamber walls hence decreases the combustion temperature (Gill *et al.*, 1959). Higher temperature is prone to decomposition of VOC-components, especially the BTX compounds which decrease in amount at higher temperatures (Di *et al.*, 2009; Cheung *et al.*, 2008).

A positive correlation has been found between engine load and VOC-components for all the test fuels. The VOCs show their maxima at low load (10%), and minima at medium load (50%) for the diesel and B100 fuels; however, B20 exhibits its minima at full load (100%). This anomaly may be attributed to different stoichiometric air/ fuel ratios of the test fuels.

The reason for maximum VOCs pollutants at low load is the large excessive air/fuel ratio and increase in over-lean mixture area, which results in incomplete combustion of the fuels, and hence high VOC emissions. Furthermore, low engine load gives rise to emissions by quenching of the flame front in the clearance between the piston top and the cylinder head near top dead center (Shah *et al.*, 2009a). This argument is further strengthened by the statement of Kittelson (1998) that volatile particles originate from unburned or partly combusted fuel, oil fumes, water etc. Minimum VOC emissions of diesel and B100 at medium load indicates the load level at which optimum air/fuel ratio develops in the combustion chamber, and thus both of the fuels combust completely with minimum emissions. The increase in VOC emissions of diesel and B100 at full load (condition 4) relative to medium load (condition 3) may be due to their incomplete combustion or due to decrease in higher air/fuel ratio, resulting in rich mixture formation thus reducing the oxidation rate of the fuels.

When VOC-components are treated individually, results show that emissions of benzene, toluene, butyl acetate, ethyl benzene, *p,m*-xylene, *o*-xylene and undecane decrease for all the test fuels at engine condition 4, relative to condition 2; styrene on the other hand, shows an opposite trend. BTX-components, the most carcinogenic in the VOCs, decrease appreciably at engine condition 4 (high load) compared to engine conditions 2 and 3, particularly in cases of B20 and B100. In the case of B20, the decrease in benzene, toluene, and *o*-xylene at condition 4 is 66% and 80%, 20% and 23%, and 39% and 81%, respectively, for the engine conditions 2 and 3, respectively. In case of B100, the decrease in benzene, toluene, and *o*-xylene at condition 4 is 38% and 100%, 14% and 100%, and 0% and 13%, respectively, compared with conditions 2 and 3.

Although it is difficult to explain the exact behaviour of individual species at different load conditions because VOCs emitted from a diesel engine are complex mixtures (Ballesteros *et al.*, 2008), the reduction in BTX-components of B20 and B100 at condition 4 relative to conditions 2 and 3 is, however, attributed to the development of comparatively higher combustion temperature because of rich mixture formation. This is further enhanced in the presence of B20 and B100 due to their oxygen enrichment, and hence decomposes the

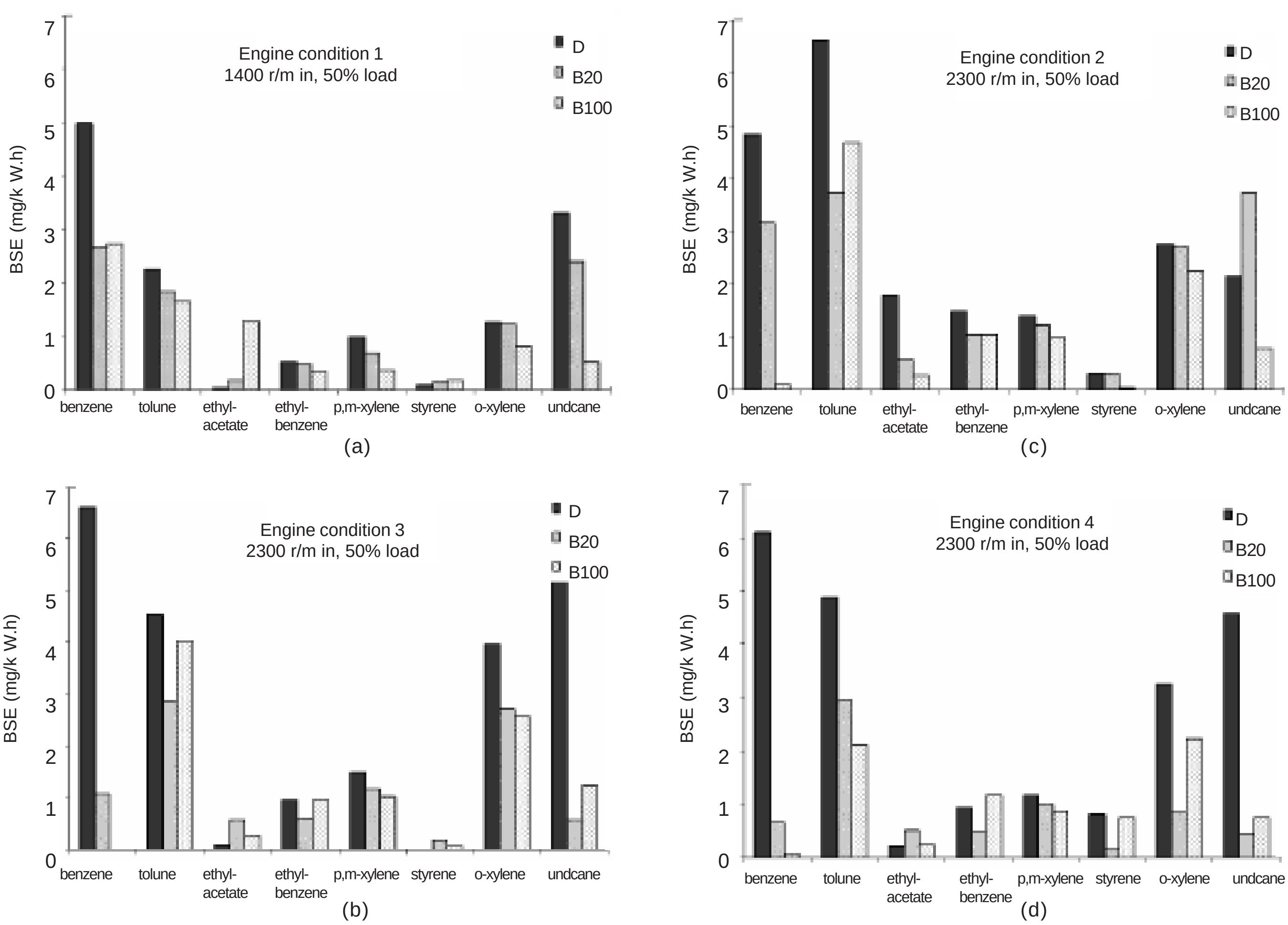


Fig. 4a-d. Brake specific emission of VOCs at different engine conditions.

BTX-components. This finding is in good agreement with that of Di *et al.* (2009) that BTX reduction efficiency is higher at higher engine load because of the higher combustion temperature and exhaust gas temperature.

Effect of biodiesel on the VOC-components. Relative to B20 and B100, diesel VOCs are all high at all the engine conditions discussed in this study when VOCs are treated collectively. In case of B20, the reduction in VOCs emission relative to diesel is 26.9%, 14.5%, 48.1%, and 73.9% for engine condition 1, 2, 3 and 4, respectively. Similarly, relative to diesel, B100 shows a reduction of 41.7%, 45.8%, 57%, and 39.6% in VOC-components for engine condition 1, 2, 3 and 4, respectively. The reduction in VOC-components in cases of B20 and B100 relative to diesel fuel is ascribed to oxygen enrichment, maximum cylinder pressure and temperature, shorter ignition delay, higher flash point, earlier fuel injection, higher cetane number, higher viscosity and faster flame propagation speed, as discussed above regarding combustion parameters.

Table 4. TD- GC/MS specifications.

Thermal desorber (TD)	Tube: 280 °C (5 min); purge: 1 min; column pressure: 8.5 psi; split ratio: (75:1); cryotrap: from -10 °C at 40 °C/s to 280 °C (3 min)
Gas chromatograph (GC)	Capillary column: HP-5MS (30m × 0.25 mm × 0.25 µm); column flux: 1 ml/min; carrier gas: helium (99.999%); oven temperature program: from 35 ºC (10 min) at 5 ºC/min to 280 ºC
Mass spectrometer (MS)	Transfer line to MS: 250 ºC; ion source: electron impact (EI) 70 eV; ion source temperature: 200 ºC; solvent cut time: 2.5 min; acquisition mode: SCAN; range of scan: 35-450 amu; electron multiplier voltage: 1.0 kV; NIST05 library

Table 5. Compounds with their equations of standardization curve, correlation coefficients and RSD.

Compound	Quantitative ion	Reference ion	Standard curve	Correlation coefficient	RSD (%)
Benzene	78	77, 52	y =3413356x	0.9952	2.93
Toluene	91	92, 65	y =4234547x	0.9873	3.04
Butyl acetate	43	56, 73	y =4137719x	0.9933	4.32
Ethyl benzene	91	106, 51	y =5453847x	0.9918	2.08
p,m-Xylene	91	106, 105	y =10143114x	0.9919	2.08
Styrene	91	78, 104	y =3129981x	0.9995	5.44
o-Xylene	91	106, 105	y =5397768x	0.9996	1.62
Undecane	57	43, 71	y =2813398x	0.9996	4.81

The most important parameter which is deemed to be responsible for the reduction of emissions, particularly VOC-components in case of biodiesel is its simple chemical structure, compared with diesel fuel. Fossil diesel consists of straight chain alkanes which have to be converted into carbon dioxide and water during the combustion process. This conversion of diesel to CO_2 and water is not direct, rather through a series of processes from alcohols, to carbonyl compounds, to carboxylic acids, to esters and finally to CO_2 (Guarieiro *et al.*, 2008). But, for the burning of biodiesel and its blends, conditions are more favourable for conversion of the esters directly to CO_2, particularly when biodiesel is obtained from waste cooking oil. Waste cooking oil, normally, comes from soybean oil which has already undergone repeated thermal oxidative process before using it for the biodiesel production. So, this residual oil consists, mainly, of minor short-chain compounds originating from the breakdown of unsaturated fatty acids during cooking (Peng *et al.*, 2006). This is the major reason for better oxidation, complete combustion, and hence reduced VOC emissions in cases of B20 and B100, compared with commercial diesel.

In order to discuss the effect of biodiesel on the individual species of VOCs, components having serious impact on human life and environment have been considered in terms of their mean values taken from four different engine conditions. The results show that the mean BSE of benzene, toluene, *p,m*-xylene, and *o*-xylene decreases by 68.8% and 87%, 42.7% and 4.1%, 28.8% and 33.5%, and 14.1% and 30.1%, respectively, for B20 and B100 respectively, compared with diesel fuel. This decrease in BTX emissions is consistent with the previous studies (Di *et al.*, 2009; Correa and Arbilla, 2006; Turrio-Baldassarri *et al.*, 2004). The important point to consider from this discussion is the reduction of mean BSE of benzene, toluene and xylene isomers in cases of B20 and B100, which indicates the superiority of biodiesel and its blends over diesel in terms of toxic emissions.

Conclusion

The VOC-components emitted from biodiesel, diesel, and 20% biodiesel-diesel blend have been investigated in this study. Followings are the significant findings:

- In the total volatile organic compounds, diesel, B20 and B100 contribute 50.6%, 48.3% and 42.2%, respectively to aromatic hydrocarbons, and 31.6%, 29.1% and 15.5%, respectively, to alkanes. Relative to diesel, B20 and B100 show their dominancy in esters and other oxides, however, alkenes of diesel and biodiesel are almost equal in their percentage distribution.
- The overall BSE of VOCs is 67% higher at engine condition 4, relative to condition 1. The VOCs show their maxima at low load, and minima at medium load for diesel and B100, however, B20 reflects its minima at full load.
- Benzene, toluene, butyl acetate, ethyl benzene, xylene isomers, and undecane decrease for all the test fuels at engine condition 4, relative to condition 2; however, styrene shows an opposite trend.
- In case of B20, the decrease in benzene, toluene, and *o*-xylene at condition 4 is 66% and 80%, 20% and 23%, and 39% and 81%, respectively, compared with the engine conditions 2 and 3, respectively. In case of B100, the decrease in benzene, toluene, and *o*-xylene at condition 4 is 38% and 100%, 14% and 100%, and 0% and 13%, respectively, compared with conditions 2 and 3, respectively.
- In case of B20, the reduction in VOC emissions relative to diesel is 26.9%, 14.5%, 48.1%, and 73.9% for engine condition 1, 2, 3, and 4, respectively. Relative to diesel, B100 shows a reduction of 41.7%, 45.8%, 57%, and 39.6% in VOC-components for engine condition 1, 2, 3, and 4, respectively.
- Mean BSE of benzene, toluene, *p,m*-xylene, and *o*-xylene decreases by 68.8% and 87%, 42.7% and 4.1%, 28.8% and 33.5%, and 14.1% and 30.1%, respectively, for B20 and B100, respectively, compared with diesel fuel.

Acknowledgements

The authors gratefully acknowledge the technical guideline provided by the laboratory staff and the financial support of National Laboratory of Auto Performance and Emission Test, Beijing Institute of Technology (BIT), Beijing, P. R. China through National Natural Science Foundation Project No. 50576063.

References

Ballesteros, R., Hernandez, J.J., Lyons, L.L., Cabanas, B., Tapia, A. 2008. Speciation of the semi volatile hydrocarbon engine emissions from sunflower biodiesel. *Fuel* **87:** 1835-1843.

Cheung, C.S., Di, Y., Huang, Z. 2008. Experimental investigation of regulated and unregulated emissions from a diesel engine fueled with ultralow-sulfur diesel fuel blended with ethanol and dodecanol. *Atmospheric Environment* **42:** 8843-8851.

Correa, S.M., Arbilla, G. 2006. Aromatic hydrocarbon emissions in diesel and biodiesel exhaust. *Atmospheric Environment* **40:** 6821-6826.

Di, Y.G., Cheung, C.S., Huang, Z.H. 2009. 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. *Science of the Total Environment* **407:** 835-846.

Gill, P.W., Smith, J.H., Ziurys, E.J. 1959. *Fundamentals of Internal Combustion Engines*, 4th Revised Edition, Oxford & IBH Publishing Co. Pvt. Ltd., India.

Guarieiro, L.L.N., Pereira, P.A.P., Torres, E.A., da Rocha, G.O., de Andrade, J.B. 2008. Carbonyl compounds emitted by a diesel engine fuelled with diesel and biodiesel-diesel blends: Sampling optimization and emissions profiles. *Atmospheric Environment* **42:** 8211-8218.

Haupt, D., Nord, K., Egeback, E.K., Ahlvik, P. 2004. Hydrocarbons and aldehydes from a diesel engine running on ethanol and equipped with EGR, catalyst and DPF. *Society of Automotive Engineering (SAE) Technical Paper Series. No.* 2004-01-1882.

Kegl, B. 2008. Effects of biodiesel on emissions of a bus diesel engine. *Bioresource Technology* **99:** 863-873.

Kittleson, D.B. 1998. Engine and nanoparticles: a review. *Journal of Aerosol Science* **29:** 575-588.

Lin, Y.C., Lee, W.J., Wu, T.S., Wang, C.T. 2006. Comparison of PAH and regulated harmful matter emissions from biodiesel blends and paraffinic fuel blends on engine accumulated mileage test. *Fuel*. **85:** 2516-2523.

McDonald, J.F., Purcell, D.L., McClure, B.T., Kittleson, D.B. 1995. Emission characteristics of soy methyl ester fuels in an IDI compression ignition engine. *Society of Auto motive Engineering (SAE) Technical Paper Series*. No. 950400.

Monyem, A., Van Gerpen, J.H. 2001. The effect of biodiesel oxidation on engine performance and emissions. *Biomass and Bioenergy* **20:** 317-325.

Peng, C.Y., Lan, C.H., Dai, Y.T. 2006. Speciation and quantification of vapor phases in soy biodiesel and waste cooking oil biodiesel. *Chemosphere* **65:** 2054-2062.

Schulz, H., De Melo, G.B., Ousmanov, F. 1999. Volatile organic compounds and particulates as components of diesel engine exhaust gas. *Combustion and Flame* **118:** 179-190.

Senda, J., Okui, N., Tsukamoto, T., Fujimoto, H. 2004. On board measurement of engine performance and emissions in diesel vehicle operated with biodiesel fuel. *Society of Auto motive Engineering (SAE) Technical Paper Series. No.* 2004-01-0083.

Shah, A.N., Yun-shan, G., Jian-wei, T., Zhi-hua, L. 2009a. An experimental investigation of PAH emissions from a heavy duty diesel engine fuelled with biodiesel and its blend. *Pakistan Journal of Scientific and Industrial Research* **51:** 293-300.

Shah, A.N., Yun-shan, G., Chao, H., Baluch, A.H. 2009b. Effect of Biodiesel on the Performance and Combustion Parameters of a Turbocharged Compression Ignition Engine. *Pakistan Journal of Enggineering and Applied Sciences* **4:** 6169.

Simpson, D. 1995. Hydrocarbon reactivity and ozone formation in Europe. *Journal of Atmospheric Chemistry* **20:** 163-177.

Sinha, S., Agar wal, A.K. 2005. Performance evaluation of a biodiesel (rice bran oil methyl ester) fuelled transport diesel engine. *Society of Automotive Engineering (SAE) Technical Paper Series. No.* 2005-01-1730.

Sureshkumar, K., Velrajb, R., Ganesan, R. 2008. Performance and exhaust emission characteristics of a CI engine fueled with *Pongamia pinnata* methyl ester (PPME) and its blends with diesel. *Renewal Energy* **33:** 2294-2302.

Turrio-Baldassarry, L. 2004. Emission comparison of urban bus engine fueled with diesel oil and biodiesel blend. *Science of the Total Environment*. **327:** 147-162.

US EPA. 1999. *Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes*, 2nd edition, US Environment Protection Agency, Washington, USA.

US EPA. 1990. *Cancer Risk from Outdoor Air Toxics*, vol. I, United States Environmental Protection Agency, Washington, USA.