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Carbonyls Emission Comparison of a Turbocharged Diesel Engine Fuelled with Diesel, Biodiesel, and Biodiesel-Diesel Blend

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Abstract

In order to characterize the carbonyls emissions from a turbocharged, direct injection, and intercooled compression ignition engine, an experimental study was conducted using diesel, biodiesel, and 20% biodiesel-diesel blend as test fuels. Fourteen carbonyls were identified and quantified from the engine exhaust at four different engine conditions. Experimental results show that formaldehyde and total carbonyls from the test fuels exhibit maximum BSE at low load, which decreases with the increase in load. Carbonyls such as formaldehyde, acetaldehyde, acrolein + acetone, propionaldehyde, crotonaldehyde, and methyl ethyl ketone show higher, but aromatic aldehydes (benzaldehyde and tolualdehyde) reflect lower BSE from B20 and B100 as compared to diesel fuel. Total carbonyls emissions from B20 and B100 are 8% and 32% higher respectively than those from diesel fuel. Formaldehyde is the most abundant carbonyl of the test fuels with 56.5%, 53.9%, and 52.7% contribution to total carbonyls in case of diesel, B20, and B100 respectively. Specific reactivity of carbonyls from the test fuels follow the order as B20 < D < B100.

Keywords: Turbocharged Engine; Direct Injection; Biodiesel; Unregulated Emissions; Carbonyls

NOMENCLATURE

CC	carbonyl compound or carbonyls
SR	specific reactivity
MIR	maximum incremental reactivity
BSE	brake specific emission
NO_x	oxides of nitrogen
SO_x	oxides of sulfur
CO	carbon monoxide
THC	total hydrocarbons
PM	particulate matter
CO_2	carbon dioxide
EPA	environment protection agency

1. Introduction

Internal combustion engines (both compression ignition and spark ignition) at the present time are facing the dual challenges of exhausting fossil fuels and ever-tighter emission standards. Because of their superiority in fuel economy, output power, and lower emissions of hydrocarbons (HC) and carbon- monoxide (CO), diesel engines rule over the fields of commercial transportation, construction, and agriculture. However, diesel engines are responsible for higher amount of particulate matter (PM), oxides of nitrogen (NO_x), carbon dioxide (CO_2), and oxides of sulphur (SO_x) which cause acid rain [1]. In this menace, biodiesel has not only resolved the issue of energy security but also proved its friendliness to the environment.

When a new fuel is introduced into the market, a prerequisite is that emissions are not to be more toxic than the emissions obtained when running on the standard market fuel [2]. Biodiesel, derived from vegetable oils or animal fats, consists of alkyl monoesters of fatty acids; and has received great attention as a substitute fuel in many countries because of its potential to reduce air pollutants like PM, THC, CO and SO_x [3-5]. It is well established that blends of biodiesel with conventional fossil fuel can be used in an unmodified diesel engine [6-7]. Biodiesel also reduces the polycyclic aromatic hydrocarbons (PAHs) and carcinogenicity [8], mutagenicity [9]; and has less adverse effect on human health as compared to diesel [10]. The performance of the engine remains unaffected when the biodiesel and diesel are compared on the basis of relative equivalence ratio [11]. Some studies have revealed an increase in rated power or torque when using biodiesel [12-13]. It has also been proved that biodiesel can reduce the extent of damage, coefficient of friction, wear of engine, and it improves the life of its vital moving parts [14].

In urban, atmospheric carbonyl compounds are mainly emitted from vehicular exhaust; and are an important class of vehicular total hydrocarbon (THC) emissions [15]. They are well known to participate in photochemical smog formation; and are important precursors of ozone and other

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hazardous substances such as peroxylacylnitrate (PAN) [16]. Some carbonyls such as formaldehyde, acetaldehyde, acrolein, and methyl ethyl ketone are toxic, mutagenic, and even carcinogenic to human body [17].

Although a lot of studies have been carried out on biodiesel for regulated and unregulated emissions, a limited and discordant literature is available on carbonyl compounds (CC). Literature data for carbonyls are somewhat conflicting due to biodiesel origin, engine type, engine conditions, and modes of operation [18]. In this study, an effort has been made to investigate the carbonyls, to analyze their behavior to different engine loads, and to make their comparison on the basis of used test fuels. In the end, ozone forming potential of these pollutants has been discussed in term of their specific reactivity (SR).

2. Material and Methods

2.1. Engine, Test Fuels and Experimental Conditions

The experiments were performed on a 4CK Diesel Engine (4-cylinder, turbocharged, direct injection, and intercooled). An electrical dynamometer (SCHENCK HT 350) was coupled to the engine to measure its power. No modification or alteration was made in the engine, and it was warmed up before starting the experiments. The schematic diagram of the experimental setup is given in figure 1, and the parameters of the engine are listed in Table 1. The engine was operated at constant speed (2300 r/min) for varying loads (10%, 20%, 50% and 100%).

The main properties of commercial diesel (D), biodiesel (B100), and its 20% blend (by volume) with diesel (B20) used in this study are given in Table 2. A 20% biodiesel-diesel blend (B20) has been taken in this study because B20 has become the most popular biodiesel fuel blend used, and this blend level has been studied in different countries [19, and references therein]. Biodiesel was produced from waste cooking oil.

Table.1 Engine specifications.

Items	Value
Number of cylinders	4
Bore (mm)	110
Stroke (mm)	125
Displacement (Liter)	4.752
Compression Ratio	16.8
Rated Power (kW@ r/min)	117/2300
Maximum Torque (Nm@ r/min)	580/1400
Nozzle hole diameter (mm)	0.23
Number of nozzle holes	6

2.2. Sampling Methodology

The sampling scheme is shown in figure 1. An ejector-diluter (Dekati Ltd. Finland) was used to obtain the emission directly from the exhaust pipe by inserting a J-shaped stainless- steel sample probe into the exhaust pipe as shown in figure 1. The exhaust gas from the engine was diluted by using dilution ratio of about 8. The real dilution ratio was determined by using the two concentrations of CO_2 which were measured before and after the dilution instrument. In order to get constant flow, a calibrated constant volume sampling (CVS) pumps (SKC USA, AirChek2000) shown in figure 2 (b), were used. The sampling rate was 260 ml/min, and it took 30 minutes to sample at every mode. Three samples of each diesel, B20, and B100 were taken for the four modes of operation. Carbonyls were sampled using 2, 4-dinitrophenylhydrazine (DNPH) coated silica gel cartridges (Accustandard® Inc) at 1 m away from the outlet of exhaust emission of the engine. The cartridges are shown in figure 2 (a). The DNPH inside the cartridges trapped the carbonyls to react with them and to form the corresponding stable 2, 4-dinitrophenylhydrazone derivatives. All the samples were collected at a temperature less than 60˚C, which is well below the melting points of the DNPH and DNPH-hydrazones. After sampling, the cartridges were sealed with aluminum foil and were refrigerated at -10˚C for the next process.

2.3. Sample Extraction

For the extraction of samples, solid phase extraction (SPE) was used. It is a column chromatography separation process in which 2, 4-DNPH sampling cartridges were placed on solid phase extractor (USA Supelco Inc.) and sampled material was eluted from the cartridges by washing it with 3 ml acetonitrile (USA Fisher Company). The extract was collected in a small test tube; and was filtered through a micro-pore filter of 0.45 μm membrane. The filtered elute was then poured into a 5 ml volumetric flask to get a constant volume solution with acetonitrile. Air bubbles were removed from the sample using ultrasonic degasser for 3 to 5 minutes, and final sample was then refrigerated in labeled sampling tube for the analysis within seven days.

2.4. Qualitative and Quantitative Analysis of Carbonyls

After the sampling and extracting, the sampled material was analyzed in the laboratory for the carbonyl compounds according to the environment protection agency (EPA) standard method TO-11A [20], using high performance liquid chromatography (HPLC) (USA Agilent 1200LC) system with an automatic injector and an ultraviolet detector. The radiant point of ultraviolet detector is a deuterium arc discharge lamp capable of launching wavelength of 190 nm to 600 nm ultraviolet. The HPLC system is shown in the figure 2 (c). A C18 column (Agilent Eclipse XDB-C18, 4.6 mm x 150 mm, 5μm) was used to elute the formed carbonyls-DNPH derivatives. Acetonitrile and distilled water were used as mobile phases according to a volume ratio of 60% acetonitrile/40% water (v/v). The flow rate and injection volume were 1.0 mL/min and 25 μL respectively, the temperature gradient was 25˚C, and carbonyl-DNPHs were detected at 360 nm.

Compounds were identified by matching the HPLC retention time with those of authentic standards (USA Supelco). The purchased standard solution was containing 14 kinds of carbonyl derivatives such as formaldehyde,

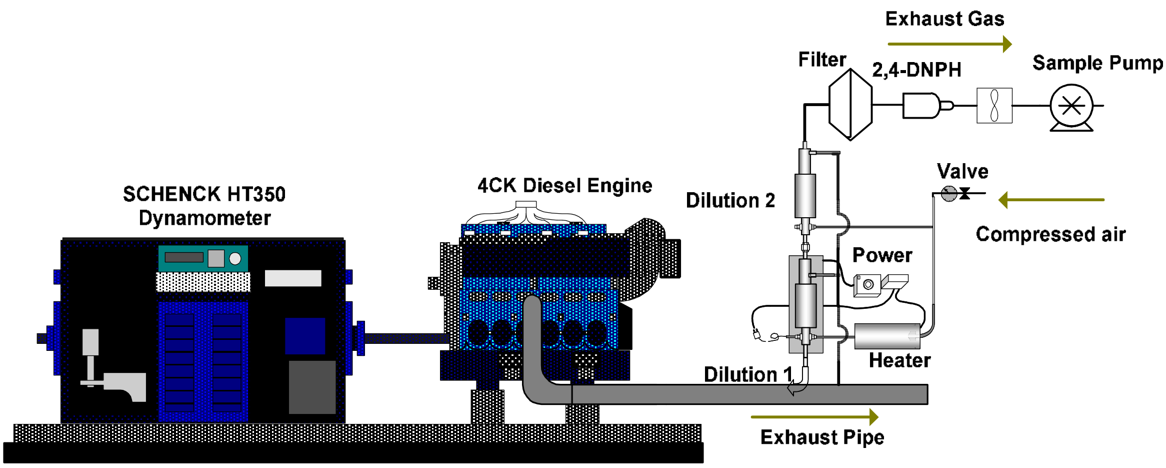

Figure 1. Experimental setup.

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 (wt %)	76.83	n/a	86.92	SH/T 0656-98
Hydrogen content (wt %)	11.91	n/a	13.08	SH/T 0656-98
Oxygen content (wt %)	11.33	n/a	0	Element analysis

acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methyl ethyl ketone, methacrolein, butyraldehyde, benzeldehyde, valeraldehyde,tolualdehyde, cyclohexanone, and hexanal. Because of their same retention time (almost same), it was difficult to separate acrolein and acetone in the column.

After the qualitative analysis, compounds were quantified using the external standard method to make the linear standard curves. The purchased standard solution was taken in 0.5 µL, 1µL, 2 µL, 5 µL, 10 µL, and 20 µL respectively with the help of micro- sampler. They were analyzed under a given chromatographic conditions, and the peak areas were recorded. According to these standard curves, the target compounds were quantified by the regression method of their peak areas. The curve equation, the correlation coefficient, and relative standard deviation (RSD) of each compound are given in Table 3.

3. Results and Discussion

3.1. Effect of Load on Brake Specific Emission of Major Carbonyls

Brake specific emission (BSE) is defined as the mass of the pollutants emitted per kilo-watt power developed in the engine in one hour. From Table 4, it is clear that there is a positive correlation between load and brake specific emission (BSE) of total carbonyl compounds (CC) and between load and BSE of formaldehyde and acetaldehyde which are two major carbonyls from the test fuels. At low load (10%), total CC show maximum BSE for all the test fuels. The BSE of total CC decreases as the load increases. This trend is more uniform for B100. However, both B20 and diesel show an increase in BSE at full load (100%) with their minimum BSE at 75% load. This anomaly may be ascribed to the different stoichiometric air/fuel ratio of biodiesel (12.6) and fossil diesel (14.6) [21]. The possible reason for maximum BSE of total CC at low load may be the incomplete combustion of the fuels due to the large excessive air/fuel ratio and increase in over-lean mixture area, which results in high carbonyl compounds and other pollutants. The reason for the increase in BSE of diesel and B20 at full load may again be the incomplete combustion, but this time is due to the decrease in excessive air/fuel ratio resulting in rich mixture formation in the combustion chamber, and hence reducing the oxidation rate. It has also been reported that load level (air/fuel ratio) of engine significantly affects the carbonyl compounds [22]. The minimum BSE of carbonyls at 75% load in the cases of diesel and B20 indicate that at this load level optimum air/fuel ratio occurs, so both of the fuels combust completely with minimum carbonyls emissions.

The BSE of formaldehyde shows maximum value at 10% load, and then decreases with the increase in load for all the test fuels. However, it displays its minimum value at full load for diesel and B100, and at 75% load for B20.

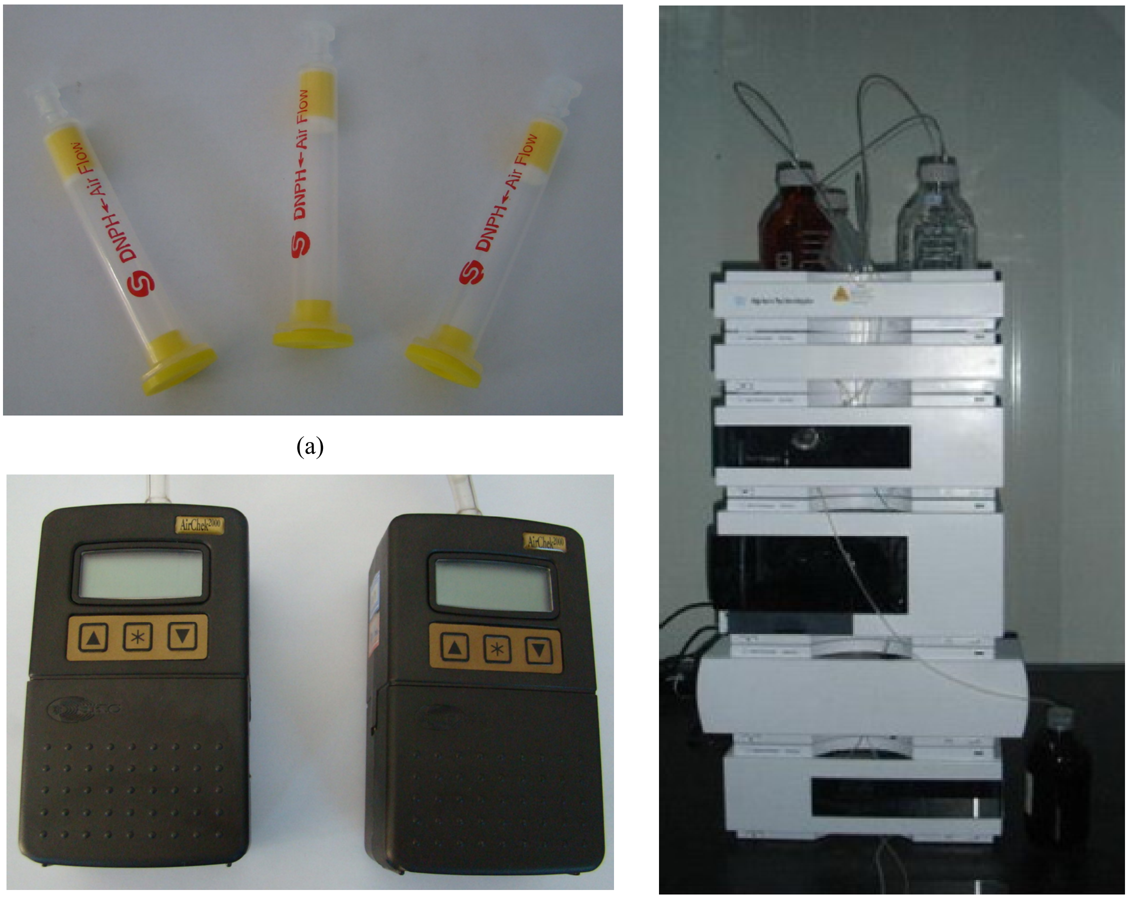

Figure 2. **(a).** 2, 4-DNPH sampling cartridges **(b).** CVS pumps **(c)**. High-performance liquid chromatographic (HPLC) system.

Table 3. Curve equations, correlation coefficients, and RSD of carbonyl compound (n=5; where n is number of replicates).

Carbonyls	Standard curve	Correlation coefficient	RSD (%)
Formaldehyde	Y=39.5831554x+0.0945798	0.9999	0.31%
Acetaldehyde	Y=29.4118202x+0.311986	0.9999	0.27%
Acrolein+Acetone	Y=50.5652502x-0.1692096	0.9999	0.22%
Propionaldehyde	Y=23.0412714x-0.2702525	0.9999	0.23%
Crotonaldehyde	Y=20.9908197x+0.1257449	0.9999	0.19%
Methyl ethyl ketone	Y=22.2728907x-2.2690313	0.9991	0.28%
Methacrolein	Y=16.895953x+1.4477462	0.9995	0.29%
Butyraldehyde	Y=18.9919747x+0.6199411	0.9999	0.84%
Benzeldehyde	Y=13.3801106x-0.1091313	0.9999	0.14%
Valeraldehyde	Y=35.8235502x-0.0072466	0.9999	0.19%
Tolualdehyde	Y=12.9693126x-0.2582609	0.9999	0.31%
Cyclohexanone	Y=4.86750669x-0.0144752	0.9998	0.26%
hexanal	Y=13.1505299x-0.0447244	0.9999	0.16%

This discrepancy may be attributed to the different physiochemical properties of the test fuels. Above finding is consistent with that of Takada et al. [23] who reported the higher formaldehyde emissions at lower engine loads.

Although acetaldehyde shows a positive correlation with load in case of biodiesel and exhibits a decreasing trend with the increase in load, B20 and diesel on the other hand do not show a clear trend of brake specific emission of acetaldehyde. However, BSE of acetaldehyde shows maximum value at low load for all the test fuels. Above

Table 4. BSE of carbonyls from test fuels at different loads.

Carbonyles	D				B20				B100			
	Load (%)											
	10	50	75	100	10	50	75	100	10	50	75	100
Formaldehyde	48.36	41.53	34.14	28.18	59.15	38.99	27.66	30.73	62.21	48.36	40.72	35.94
Acetaldehyde	26.61	9.06	5.43	14.30	20.26	5.38	11.90	19.24	27.18	18.00	10.83	9.04
Acrolein+Acetone	6.93	8.64	2.51	4.53	10.42	4.15	5.70	3.31	1.22	6.16	12.63	10.11
Propionaldehyde	1.94	3.50	2.21	1.99	4.04	1.11	1.23	3.38	9.15	6.08	8.71	12.06
Crotonaldehyde	0.79	0.92	0.29	0.85	0.19	0.37	0.13	2.39	2.54	0.01	0.06	1.04
Methyl ethyl ketone	2.07	1.77	0.94	0.93	1.27	2.30	0.00	2.40	0.12	3.39	4.01	2.02
Methacrolein	1.70	1.20	1.65	0.31	0.05	0.02	0.08	0.38	4.69	3.05	3.00	5.06
Butyraldehyde	0.02	1.70	0.06	1.26	9.01	6.46	8.02	5.53	2.29	1.76	3.04	0.02
Benzeldehyde	0.41	0.70	0.61	0.40	0.00	0.20	0.01	0.99	0.16	0.00	0.00	0.01
Valeraldehyde	0.54	1.26	0.11	1.02	0.93	0.72	0.58	0.86	0.01	0.01	0.06	0.00
Tolualdehyde	1.34	0.80	0.29	0.45	0.03	0.00	0.01	0.00	0.00	0.08	0.00	0.04
Cyclohexanone	1.20	0.91	1.01	1.23	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
hexanal	0.00	0.58	0.00	0.35	0.14	0.32	0.12	0.41	0.03	0.44	0.15	0.06
Total	91.91	72.57	49.25	55.80	105.49	60.02	55.44	69.64	109.60	86.90	83.21	75.40
∑ Total	269.53				290.59				355.11			

finding is similar to that of Cheung et al. [24] who showed that acetaldehyde emissions were more at low load as compared to high loads. Similar kind of result was also reported by Pang et al. [17].

3.2. Effect of Biodiesel on BSE of Carbonyls

As listed in Tables 4 and 5, the BSE of formaldehyde, acetaldehyde, (acrolein + acetone), propionaldehyde, crotonaldehyde, Methyl ethyl ketone, and total carbonyls exhibit a strong correlation with the biodiesel content; and increase in the cases of B20 and B100. These results are not surprising and were expected because of the two main reasons. First, biodiesel used in the tests was produced from waste cooking oil; and was expected to contain appreciable amount of carbonyls because of oxidation during the frying of the meats. Second, biodiesel inheriting oxygen atoms is basically an ester mixture of saturated and non-saturated fatty acids which may include secondary oxidation products such as volatile and non-volatile carbonyl compounds, cyclic fatty acid monomers, and polymerization products [16].

The increase in formaldehyde and acetaldehyde is 2.8% and 2.5% respectively in case of B20, and 23% and 17% respectively in case of B100 as compared to commercial diesel. The increase in acetaldehyde from B20 compared with diesel is also supported by other literature [25-26]. Similarly, it has also been reported that formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde increase from B20, compared with diesel [4]. The increase in BSE of acrolein + acetone may be attributed to acrolein, which has mostly been produced by the oxidation of glycerol residues and other fatty acid residues present in the biodiesel, so its BSE increases in the cases of B100 and B20 as compared to diesel [16]. The BSE of total carbonyls from B20 and B100 is 8% and 32 % higher respectively than that of diesel fuel. This result is in good agreement with that of previous study [15].

The BSE of aromatic aldehydes (benzaldehyde and tolualdehyde) decreases in the cases of B100 and B20 as compared to diesel as shown in Tables 4 and 5 which is understandable because aromatic content in biodiesel is less than that of diesel. Corrêa and Arbilla [25] have also reported the decrease in benzaldehyde from biodiesel-diesel blend, compared with diesel.

3.3. Comparative Analysis of Different Carbonyls from Test Fuels

According to the experimental results listed in Tables 4 and 5, formaldehyde is the most abundant carbonyl of the test fuels. The BSE of the formaldehyde is 56.5%, 53.9%, and 52.7% in case of diesel, B20, and B100 respectively. After formaldehyde, the second largest percentage contributor to the total carbonyls is acetaldehyde with 20.6%, 19.5%, and 18.3% in case of diesel, B20, and B100 respectively. This finding is in consistent with that of previous study that formaldehyde and acetaldehyde are two major aldehydes species in the exhaust from vehicles [27].

It is interesting to note that BSE of formaldehyde and acetaldehyde are more from B20 and B100 compared with diesel as discussed earlier in section 3.2, however their percentage contribution to the total CC from the test fuels follow the order as D > B20 > B100. This enigma comes to an end very soon when brake specific emissions of total Mean carbonyls of the test fuels are viewed from their respective columns in the table 5, which are following the order as D < B20 < B100.

Acrolein+Acetone and propionaldehyde are the next major contributors to the total carbonyls, each of them contributing less than 10% of the total carbonyls. Other carbonyls are minor contributors to the total carbonyls, and each of them is accounted for less than 4% in total carbonyls from the test fuels. Formaldehyde, acetaldehyde, acrolein + acetone, and propionaldehyde contribute 89%, 85%, and 89.6% of total carbonyls in case of diesel, B20, and B100 respectively. This result is similar to those of previous studies that 90% of aldehydes and ketones are made up of formaldehyde, acetaldehyde, acrolein, and propionaldehyde [4]. According to Grosjean et al. [27] formaldehyde, acetaldehyde, propionaldehyde, and acetone are the four largest emission factors of carbonyl emissions from vehicles.

3.4. Specific Reactivity of Carbonyls

Specific reactivity (SR) is defined as the milligram (mg) ozone potential per milligram non-methane organic gases (NMOG) emanated from the exhaust and can be evaluated as under [28]:

$$SR = \sum (NMOG_k \bullet MIR_k) / \sum NMOG_k \qquad (1)$$

The subscript k represents the certain carbonyl specie; NMOG is the sum of non-methane hydrocarbons and oxygenates, including aldehydes; and MIR is the maximum incremental reactivity. Carter and Lowi [28] examined air modeling based on ozone forming reactivates of species and proposed the MIR factor as an index for ozone formation. This index indicates the maximum increase in ozone formation.

Table 5. Mean BSE of carbonyls from test fuels with their corresponding MIR values.

Carbonyls	Mean Brake Specific Emission (mg/kW•h)			MIR
	D	B20	B100	
Formaldehyde	38.05	39.13	46.81	7.15
Acetaldehyde	13.85	14.20	16.26	5.52
Acrolein+Acetone	5.65	5.90	7.53	6.77*, 0.56**
Propionaldehyde	2.41	2.44	9.00	6.53
Crotonaldehyde	0.71	0.77	0.91	5.41
Methyl ethyl ketone	1.43	1.49	2.39	1.18
Methacrolein	1.22	0.13	3.95	6.77
Butyraldehyde	0.76	7.26	1.78	5.26
Benzeldehyde	0.53	0.30	0.04	-0.56
Valeraldehyde	0.73	0.77	0.02	4.41
Tolualdehyde	0.72	0.01	0.03	-0.56
Cyclohexanone	1.09	0.01	0.00	6.53
hexanal	0.23	0.25	0.17	3.79
Total Mean BSE	*67.38*	*72.65*	*88.89*	
SR	6.39	6.38	6.51	

6.77* for Acrolein and 0.56** for Acetone

Table 5 shows the mean BSE of carbonyls from the three test fuels with their corresponding MIR values. It is elucidated from the table that the specific reactivity of carbonyls from the test fuels follow the order as B20 < D < B100. This result advocates the use of B20 as a promising alternative fuel in an unmodified diesel engine because its use reduces the ozone formation in the lower atmosphere. This reduction in ozone formation in the lower atmosphere is beneficial in reducing the respiratory problems. However, further research is required to fully understand the behavior of neat biodiesel for photochemical smog formation, especially when engine is unmodified.

4. Conclusions

The brake specific emissions of carbonyl compounds from diesel, neat biodiesel, and 20% biodiesel-diesel blend have been investigated in the present work. The followings are the main findings:

- At low load, formaldehyde and total carbonyls show maximum BSE from all the test fuels. This BSE decreases as the load increases. The BSE of acetaldehyde shows maximum value at low load for all the test fuels.
- The BSE of formaldehyde, acetaldehyde, acrolein + acetone, propionaldehyde, crotonaldehyde, Methyl ethyl ketone, and total carbonyls increase from B20 and B100, compared with diesel fuel. However, the BSE of aromatic aldehydes decreases in the cases of B100 and B20 as compared to commercial diesel.
- Formaldehyde is the most abundant carbonyl among the test fuels followed by acetaldehyde, Acrolein+Acetone, and propionaldehyde in the same order of magnitude and their sum contributes 89%, 85%, and 89.6% of the total carbonyls in the case of diesel, B20, and B100 respectively.
- Specific reactivity of carbonyl compounds from the test fuels follow the order B20 < D < B100.

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References

[1] M.A. Kalam, M. Husnawan, H.H. Masjuki, "Exhaust emission and combustion evaluation of coconut oil-powered indirect injection diesel engine". Renewable Energy, Vol. 28, No. 15, 2003, 2405-2415.

[2] D. Haupt, K. Nord, K. Egeback, P. Ahlvic, "Hydrocarbons and aldehydes from a diesel engine running on ethanol and equipped with EGR, catalyst and DPF". Society of Auto motive Engineering (SAE) Technical Paper Series No. 2004-01-1882, 2004.

[3] J. Senda, N. Okui, T. Tsukamoto, H. Fujimoto, "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, 2004.

[4] L. Turrio-Baldassarri, C.L. Battistelli, L. Conti, R. Crebelli, B.D. Beradis, A.L. Iamiceli, M. Gambino, S. Iannaccone, "Emission comparison of urban bus engine fueled with diesel oil and biodiesel blend". Science of the Total Environment, Vol. 327, 2004, 147–162.

[5] A. Monyem, J.H. Gerpen, "The effect of biodiesel oxidation on engine performance and emission. Biomass Energy, Vol. 20, 2001, 317–325.

[6] L.C. Meher, D.V. Sagar, S.N. Naik, "Technical aspects of biodiesel production by transesterification -a review". Renewable and Sustainable Energy Reviews, Vol. 10, No. 3, 2006, 248–268.

[7] A.S. Ramadhas, S. Jayaraj, C. Muraleedharan, "Characterization and effect of using rubber seed oil as fuel in the compression ignition engines". Renewable Energy, Vol. 30, 2005, 795-803.

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

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

[10] O. Schroder, J. Krahl, A. Munack, J. Bunger, "Environmental and health effects caused by the use of biodiesel". Society of Auto motive Engineering (SAE) Technical Paper Series No. 1999-1901-3561, 1999.

[11] A. Senatore, M. Cardone, V. Rocco, M.V. Prati, "A comparative analysis of combustion process in D.I. diesel engine fuelled with biodiesel and diesel fuel". Society of Auto motive Engineering (SAE) Technical Paper Series No. 2000-01-0691, 2000.

[12] D. Altiparmak, A. Deskin, A. Koca, M. Guru, "Alternative fuel properties of tall oil fatty acid methyl ester-diesel fuel blends". Bioresource Technology, Vol. 98, 2007, 241–246.

[13] N. Usta, "An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester". Energy Conversion and Management, Vol. 46, 2005, 2373–2386.

[14] H. Chao, G. Yunashan, T. Jianwei, H. Xiukun, "Spray properties of alternative fuels: A comparative analysis of biodiesel and diesel". International Journal of Energy Research, Vol. 32, 2008, 1329-1338.

[15] X. Pang, Y. Mu, J. Yuan, H. He, "Carbonyls emission from ethanol-diesel used in engines". Atmospheric Environment, Vol. 42, 2008, 1349-1358.

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

[17] X. Pang, X. Shi, Y. Mu, H. He, S. Shuai, H. Chen, R. Li, "Characteristics of carbonyl compounds emission from a diesel-engine using biodiesel-ethanol-diesel as fuel". Atmospheric Environment, Vol. 40, 2006, 7057-7065.

[18] [Y. Di, C.S. Cheung, Z. Huang, "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, Vol. 407, 2009, 835-846.

[19] X. Shi, X. Pang, Y. Mu, H. He, S. Shuai, J. Wang, H. Chen, R. Li, "Emission reduction potential of using ethanol-biodiesel-diesel fuel blend on a heavy duty diesel engine". Atmospheric Environment, Vol. 40, 2006, 2567-2574.

[20] US. Environment Protection Agency (US EPA), "Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC)". Compendium method TO-11A, 1999.

[21] M. Cardone, M.V. Prati, V. Rocco, M. Seggiani, A. Senatore, S. Vitolo, "Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: engine performance and regulated and unregulated exhaust emissions". Environmental Science and Technology, Vol. 36, 2002, 4656-4662.

[22] R. Magnusson, C. Nilsson, B. Andersson, "Emissions of aldehydes and ketones from a two stroke engine using ethanol and ethanol-blended gasoline as fuel". Environmental Science and Technology, Vol. 36, 2002, 1656-1664.

[23] K. Takada, F. Yoshimura, Y. Ohga, J. Kusaka, Y. Daisho, "Experimental study on unregulated emission characteristics of turbocharged DI diesel engine with common rail fuel injection system". Society of Auto motive Engineering (SAE) Technical Paper Series No. 2003-01-3158, 2003.

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

[25] S.M. Corrêa, G. Arbilla, "Carbonyl emissions in diesel and biodiesel exhaust". Atmospheric Environment, Vol. 42, 2008, 769-775.

[26] N. Arapaki, E. Bakeas, G. Karavalakis, E. Tzirakis, S. Stournas, F. Zannikos, "Regulated and unregulated emissions characteristics of a diesel vehicle operating with diesel/biodiesel blends". Society of Auto motive Engineering (SAE) Technical Paper Series No. 2007-01-0071, 2007.

[27] D. Grosjean, E. Grosjean, A.W. Gertler, "On-road emissions of carbonyls from light-duty and heavy-duty vehicles". Environmental Science and Technology, Vol. 35, 2001, 45-53.

[28] W.P.L. Carte, A. Lowi, "A Method for Evaluating the Atmospheric Ozone Impact of Actual Vehicle Emissions". Society of Auto motive Engineering (SAE) Technical Paper Series No. 900710, 1990.