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Effect of methanol-containing additive on the emission of carbonyl compounds from a heavy-duty diesel engine

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Abstract

This study was aimed at determining the effect of methanol-containing additive (MCA) on the emission of carbonyl compounds (CBCs) generated from the diesel engine. For this experiment, a heavy-duty diesel engine was connected with a full flow critical flow venturi (CFV) type dilution tunnel, a Schenck GS-350 DC dynamometer, and a DC-IV control system in series. The operating conditions of the heavy-duty diesel engine for both cold-start and hot-start Transient Cycle tests and for both low-load and high-load steady-state tests were ascertained. The exhaust of CBCs collected from a 2,4-dinitrophenylhydrazine (2,4-DNPH)-coated cartridge were first converted to corresponding hydrazone derivatives, which were then solvent-eluted and analyzed by a High Performance Liquid Chromatograph (HPLC) with an ultraviolet–visible (UV) detector. When either 10% or 15% MCA was used, the emission factors of the CBCs acrolein and isovaleraldehyde increased by at least 91%. Accordingly, future studies must be done to cut down the emission of CBCs when MCA and methanol alternative fuels are used. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carbonyl compounds; Methanol-contained additive; Emission factor; Diesel; Engine

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1. Introduction

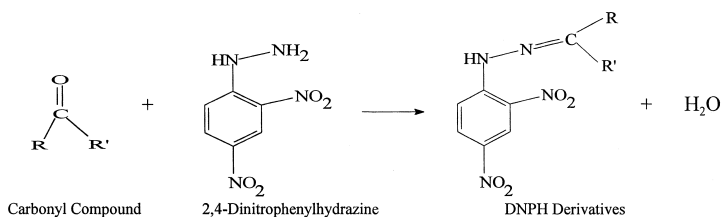
Human beings have been using diesel fuel and engines for over a century. During this long period of time, there have been several major improvements in diesel engines. They gradually evolved into modern internal combustion engines, which are now widely used on trucks and passenger cars. Although diesel engines provide power and convenience in our daily life, their emissions carry bad odors and contain many different types of air pollutants, such as hydrocarbons (HC), carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NO_x), sulphur oxides (SO_x), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and soot [1,2]. Most previous studies often focused on the emission of HC, CO, NO_x and PM which are regulated already [3–5]. Some types of compounds found in diesel exhaust, such as PAHs, aldehydes, VOCs and SVOCs, though not yet regulated, are always threatening public health due to their toxicity.

Diesel fuel additives are usually used to improve combustion efficiency, increase cetane number, reduce the formation of fuel deposits, avoid oxidation reactions and the contamination of fuel and filters blocked by rust, and inhibit potential explosions caused by changes in static electricity and delusions [1,6,7]. Methanol and ethanol as alternative fuels are environmentally more friendly because they emit less NO_x, PM and smoke than diesel fuel does [8,9].

Carbonyl compounds (CBCs), such as formaldehyde, acetaldehyde and acetone, play a major role in photochemical reactions in the troposphere. They exist in the atmosphere for a short period of time, and are easily converted into other secondary air pollutants. The major sources of atmospheric CBCs are exhaust from vehicles and chemical industries. CBCs are also emitted by natural sources, such as vegetation [10,11]. Anthropogenic CBCs are believed to come from incomplete combustion. In vehicular engines, the fuel was burned incompletely and it reacted with hydrocarbons via hydroxyl radical to form CBCs [12–14]. Notice that CBCs are the precursors of some photochemical oxidants, including peroxy-carboxylic acids, peroxyacyl nitrate and ozone frequently found in the troposphere [14,15].

To human, CBCs are irritating to the skin, eyes, and the nasal mucous membrane. They are well-known to be neurotoxic, mutagenic, or even carcinogenic, and thus are hazardous to human health [16–18]. Due to these reasons, CBCs were also listed as the regulated hazardous air pollutants in the Clean Air Act Amendments in the US in 1990 [19].

In recent years, most analysis methods for CBCs in the ambient air and automobile exhaust involve derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by HPLC analyses [20–25], which offers more speed and convenience compared to other approaches [26–29]. However, due to their shorter half-lives, CBCs need to be converted into other derivatives immediately after air samples are collected. The carbonyl compounds react with acidified dinitrophenylhydrazine (DNPH) to form the corresponding hydrazones, which can then be analyzed by HPLC with a UV detector.



In the past, the 2,4-DNPH impinger technique was commonly used to collect air samples from vehicular exhaust for subsequent determination of aldehydes. Lately, a new impinger method, involving derivatization with the reaction product of aldehydes and cystamine to form more stable derivatives (thiazolidines) has been developed for automobile exhaust [30].

To further facilitate the collection, sampling time, transportation, and analysis, the 2,4-DNPH impinger method was replaced with the 2,4-DNPH-cartridge methods. Each exhaust sample, once collected in a Tedlar bag, was immediately pumped through an absorbent tube which contained 2,4-DNPH coated silica. In the tube, CBCs react with 2,4-DNPH to form corresponding 2,4-dinitrophenylhydrazone and subsequent HPLC analyses are performed [31–33]. In the present study, the use of 5%, 8%, 10%, and 15% of MCA in diesel was investigated. A heavy-duty diesel engine was then operated for both cold-start and hot-start Transient Cycle tests, and for both low-load and high-load steady-state tests. Due to the facilitation of the collection, sampling time, transportation, and analysis, USEPA method 18 and 2,4-DNPH cartridge methods were chosen. Thus, the effect of methanol-containing additive (MCA) on the emission of CBCs was studied.

2. Experimental section

2.1. Engine and dynamometer

A heavy-duty, non-catalyst diesel-powered engine was used. The diesel engine is a product of Mitsubishi (model 6D 14) with six cylinders, four strokes, natural-aspirated, direct injection, fuel sequence (1–5–3–6–2–4), bore and stroke ($110 \times 115 \text{ mm}^2$), total displacement of 6557 ml, maximum horsepower of 107 kW at 2800 rpm and maximum torque of 570 N m at 2000 rpm. This engine was installed on a Schenck GS-350 DC dynamometer with a DC-IV control system. The DC dynamometer with an automatic control system supplies a maximum power of 350 kW and a maximum torque of 2000 N m. The DC dynamometer is also capable of switching promptly from negative to positive torque values and it can be operated in both Transient Cycle and steady-state modes. Each Transient Cycle test followed a standardized US Federal Test Procedure (FTP) to simulate designated driving conditions of diesel engines. To determine the effect of the engine-load on the emission of CBCs, both low-load and high-load modes

Table 1

Experimental parameters for diesel-powered engine at two different steady-state modes
NA: Not applicable.

Mode	Torque (N m)	Speed (rpm)	Power (kW)	Sampling temperature (°C)	Sampling time (min)
FTP	NA	^a	NA	< 50	20
Low load	90	2000	18.8	240–260	20
High load	270	2000	56.6	451–494	10

^aVarying according to FTP test.

were chosen for steady-state tests, as shown in Table 1. In each steady-state test, constant loads and speeds were maintained. A commercially available synthetic engine lubricating oil (API-SG/CE⁺, 15 W/40) was used, flushed out and replaced with a fresh batch before each run to avoid possible errors.

2.2. Fuel and additive

The MCA consisted of 65% methanol (v/v) and 35% ethanol (v/v). Four different diesel–MCA mixtures, 5%, 8%, 10%, and 15% (v/v) were prepared. The specification of base diesel fuel, MCA, and diesel–MCA mixtures are shown in Table 2. Prior to

Table 2

The specification of base diesel fuel and diesel–MCA mixed fuel

Fuel parameter	MCA	MCA + diesel	Diesel	Analytical method
Density, kg/l (15°C)	0.8095	0.8304	0.8338	ASTM D-1298
Flash point PM, °C	Ambient temperature	48	71	ASTM D-93
Pour point, °C	< -33	-15	-12	ASTM D-97
Viscosity, CST at 50°C	-	2.267	2.773	ASTM D-445
Water and Sediment, vol%	0.01	0.01	0.00	ASTM D-1796
Corrosion, Copper Strip	1b	1a	1a	ASTM D-130
Sulfur Content, wt. %	< 0.0006	0.05	0.11	ASTM D-4294
Ash, wt. %	0.00	0.00	0.00	ASTM D-482
Carbon residue on 10%	0.03	0.08	0.08	ASTM D-86
BTM, wt. %				
Distillation, °C				
I.B.P.	60.0	68.4	189.8	
5%	66.7	108.8	217.5	
10%	68.3	153.6	228.6	
20%	71.7	219.6	240.9	
50%	88.1	262.0	270.1	
90%	116.8	320.3	324.3	
95%	117.8	339.2	343.3	
FBP	122.8	354.3	353.5	
Residue, vol%	0.8	1.6	1.6	
Demulsifier test				
Interface	-	4	2	
Separation	-	3	3	ASTM D976-80
Centane index		52.8	53.4	

conducting each Transient Cycle test and steady-state test, the residual diesel–MCA mixture left in the combustion chamber in the earlier test was drained up. Following the drainage, the engine was then run at a high idling condition for more than 1 h.

2.3. Sampling and analyses of engine exhaust

The engine exhaust samples were collected in 10-l or 100-l Tedlar bags through a full flow critical flow venturi (CFV) type dilution tunnel 350 mm in diameter. Once passed through this tunnel, the exhaust was diluted with air simultaneously drawn into the tunnel and they were mixed with the exhaust completely by a Spencer blower. The volume of sampling air varied with different venturi sizes of the CFV system. All the engine exhaust was introduced into the dilution system through a solid insulated pipe with 10-cm in diameter and 7.5-m in length [34].

For the measurement of CBCs, the exhaust samples were collected from the combustion of the diesel engine according to US EPA Method 18 [35,36]. The sampling train was equipped with a 20-mm i.d. dilution pipe which was directly connected to the dilution system. The exhaust was then collected in a 10-l Tedlar bag (SKC-10L) placed inside a vacuum sampling box (SKC-40L). Air was pumped out of the vacuum box, thus causing the exhaust to be sucked into the Tedlar bag. Sampling was maintained at a rate less than 1 l/min and depending on the test modes (Table 1). The total sampling time for each run lasted for more than 10 min. After sampling, all Tedlar bags were stored in black opaque plastic bags to keep away the sunlight. The exhaust samples previously collected in the Tedlar bags were individually and immediately pumped through a 2,4-DNPH-coated cartridge (Sep-Pak cartridge, Supelco) at a flow rate of 150 ml/min (determined by the mass flow control) for 7 min. All CBCs were then captured within the cartridge and converted to corresponding hydrazone derivatives. After that, each cartridge was eluted with acetonitrile, and the eluted solutions were then analyzed by a High Performance Liquid Chromatograph (HPLC) with an ultraviolet–visible (UV) detector ($\lambda = 360$ nm).

2.4. Analyses of CBCs and carbon dioxide

The rapid sampling method described earlier allowed easy analyses of CBCs within 1 to 2 h. Eleven CBCs, including formaldehyde (Form.), acetaldehyde (Acet.), acetone, acrolein, propionaldehyde (Propion.), crotonaldehyde (Croton.), benzaldehyde (Benz.), butyraldehyde (Butyr.), isovaleraldehyde (Isovaler.), valeraldehyde (Valer.), and hexaldehyde (Hex.) were identified and quantified with a Hewlett Packard HP 1100 HPLC/UV [34]. The standard solutions of the 11 CBCs were purchased from Supelco.

To separate the aforesaid 11 CBCs, a column C₁₈ (3 μ m in film thickness, 4.6 mm i.d., and 150 mm in length) was used (Waters, USA). Meanwhile, either solvent A (water/acetonitrile/tetrahydrofuran mixture at 60:30:10 (v/v)) and/or solvent B (water/acetonitrile mixture at 40:60 (v/v)) were used as the mobile phase. The flow rate was maintained at 1.5 ml/min and the injection volume was 20 μ l. The concentra-

tion gradient of the two solvents A and B in the mobile phase was varied linearly from 100% A at the beginning to 100% B in 10 min.

For the blank tests in the measurement of the CBCs, ultra-pure nitrogen was introduced into a Tedlar bag. Thereafter, the content of the bag was analyzed for CBCs in exactly the same way described earlier. The amount of formaldehyde and acetaldehyde measured from the blank-test accounted for 0.52% and 0.97% of typical sample collected, respectively. On the other hand, field blank tests show that formaldehyde and acetaldehyde per cartridge were 0.02 and 0.04 μg , respectively.

For determining the instrument detection limit (IDL) of CBCs, seven measurements are made on a sample whose concentration is at or near the detection limit. The standard deviation and variance are calculated for the data set and used to calculate the IDL at the 99% confidence level. The IDL of 13 CBCs determined were between 0.074 and 3.88 ng. Some researchers reported that several dimers form when acrolein and crotonaldehyde are absorbed onto 2,4-DNPH cartridges. They found that acrolein exhibited poor recovery and stability because of the formation of dimer [29,37,38]. So far, the best recovery of acrolein is still less than 35% [29].

In this study, recovery efficiencies for CBCs were determined using the same procedures as described earlier for the blank tests, except that the bag was spiked with known amount of each individual aldehyde instead. The results showed that the recovery efficiency of CBCs varied from 71.6% to 103% and averaged 84.9%, except for acrolein (31.4–40.9%). The mean relative standard deviation (RSD) in recovery efficiencies was below 13.0%.

The breakthrough test was conducted by pumping collected exhaust in Tedlar bags out and through two 2,4-DNPH cartridges connected in series. The measured CBCs in the front cartridge was greater than 95%, while those for the back cartridge was less than 5%. To cope with the wide concentration ranges of CBCs emitted from the diesel engine exhaust, calibration curves for both high and low concentrations of CBCs were prepared during each sampling day.

2.5. Calculation of emission factors

In order to compare the emission for CBCs and CO between Transient Cycle tests and steady-state tests, the emission factors for CBCs and CO in the diesel exhaust were measured and expressed in mg/brake horse power per hour (BHP-h) and g/BHP-h, respectively. In the steady-state tests, the emission factors for CBCs and CO were calculated and measured using parameters shown in Table 2. In Transient Cycle tests, the emission factors for CBCs and CO were calculated according to FTP tests in the Code of Federal Regulation (the sum of [(1/7 cold) + (6/7 hot)]).

3. Results and discussion

3.1. Comparison of CBCs emissions between cold-start and hot-start tests

In Transient Cycle tests, the emission factors of CBCs for cold-start and hot-start of diesel engine are shown in Table 3. The results show that formaldehyde, acetaldehyde,

Table 3

The emission factors of carbonyl compounds at Transient Cycle mode

The weighted mean is 1/7 (cold start)+6/7 (hot start).

Compound	Cold start			Hot start			Weighted mean (mg/BHP-h)
	Range (mg/BHP-h)	Mean (mg/BHP-h)	RSD (%)	Range (mg/BHP-h)	Mean (mg/BHP-h)	RSD (%)	
Formaldehyde	72.5–97.7	85.1	10.7	60.0–78.4	65.9	11.2	68.6
Acetaldehyde	64.3–69.8	67.3	3.24	53.9–57.5	55.5	2.34	57.2
Acetone	42.6–140	86.5	41.5	80.6–90.7	83.9	4.94	84.3
Acrolein	3.29–19.3	9.49	64.0	7.19–8.54	7.73	6.55	7.98
Propionaldehyde	8.63–16.2	12.4	25.9	7.65–11.3	9.85	16.1	10.2
Crotonaldehyde	20.2–24.9	22.2	8.14	7.56–34.8	21.3	47.1	21.4
Butyraldehyde	6.15–38.9	22.0	53.4	9.45–23.9	16.3	38.0	17.1
Benzaldehyde	10.0–15.5	13.2	15.1	1.34–19.0	13.0	68.3	13.0
Isovaleraldehyde	3.89–8.12	5.15	33.6	0.78–7.36	4.55	60.1	4.64
Valeraldehyde	9.44–13.3	10.5	15.2	3.31–12.1	8.33	38.2	8.64
Hexaldehyde	8.77–14.8	10.3	25.10	6.66–14.0	9.09	32.2	9.26
Total CBCs	263–425	344	22.0	246–354	295	7.93	302

and acetone were the three major CBCs found in engine exhaust in both cold-start and hot-start runs. The mean emission factors of formaldehyde, acetaldehyde, and acetone calculated for the cold-start runs were 85.1, 67.3, and 86.5 mg/BHP-h, respectively; while those calculated for the hot-start runs were 65.9, 55.5, and 83.9 mg/BHP-h, respectively. In contrast, the calculated mean emission factors of acrolein and isovaleraldehyde, for cold-start runs were 9.49 and 5.15 mg/BHP-h, respectively; while those for hot-start runs were 7.73 and 4.55 mg/BHP-h, respectively. Moreover, the calculated mean emission factor of total CBCs for cold-start runs was 344 mg/BHP-h, which was 14.2% of magnitude higher than that for hot-start runs (295 mg/BHP-h). Also, the emission factors of the 11 individual CBCs calculated for cold-start runs were all higher than those for hot-start runs. Specifically, the calculated mean emission factors of butyraldehyde, formaldehyde, valeraldehyde, and propionaldehyde for cold-start runs were 34.0%, 29.1%, 26.1%, and 25.8% higher than those for hot-start runs. These data compare favorably with those reported by Lemaire and Khair [1], who indicated that cold-start mode contributed more amounts of nine individual CBCs than hot-start mode did in FTP Transient Cycle tests.

According to the Code of Federal Regulation set for the Transient Cycle tests, the weighted mean of emission factor of total CBCs is calculated by summing both the emission factors calculated for cold-start and hot-start runs at a weight ratio of 1:6. Thus, the emission factors of total CBCs obtained in this study is 302 mg/BHP-h, which is between those calculated for the cold-start and hot-start runs.

In Transient Cycle tests, the combustion temperatures of the diesel engine for cold-start runs were lower than that for hot-start runs. Therefore, more amounts of CBCs were detected from the exhaust.

3.2. Comparison of steady-state CBCs emissions between low-load and high-load tests

In steady-state tests, the emission factors for CBCs for low-load and high-load runs of the diesel engine are shown in Table 4. The results show that formaldehyde, acetaldehyde, and acetone were also the three major CBCs in the engine exhaust in both low-load and high-load runs. The mean emission factors of formaldehyde, acetaldehyde, and acetone calculated for low-load runs were 335, 72 and 141 mg/BHP-h, respectively; while those calculated for high-load runs were 29.7, 11.0 and 41.5 mg/BHP-h, respectively. In contrast, the emission factors of acrolein, isovaleraldehyde, and valeraldehyde, calculated for low-load runs were 3.42, 6.54 and 4.58 mg/BHP-h, respectively; while those calculated for high-load runs were 0.81, 0.31 and 0.89 mg/BHP-h, respectively. Moreover, the calculated mean emission factor of total CBCs for low-load runs was 703 mg/BHP-h, which was 6.2 times higher than that for high-load runs (113 mg/BHP-h). In addition, the emission factors of the 11 individual CBCs calculated for low-load runs were all higher than those calculated for high-load runs. In particular, the calculated mean emission factors of isovaleraldehyde, formaldehyde, acetaldehyde, and crotonaldehyde for low-load runs were 21.1, 11.3, 6.55, and 6.22 times significantly higher than those for high-load runs.

In steady-state tests, the mean exhaust temperatures of the diesel engine operated at low loads and high loads were 241°C and 452°C, respectively. At the same engine

Table 4

The emission factors of carbonyl compounds at low load and high load of steady-state mode

Compound	Low Load			High Load		
	Range (mg/BHP-h)	Mean (mg/BHP-h)	RSD (%)	Range (mg/BHP-h)	Mean (mg/BHP-h)	RSD (%)
Formaldehyde	306–368	335	9.73	21.4–42.8	29.7	34.6
Acetaldehyde	40–152	72	74.3	5.46–22.5	11.0	71.9
Acetone	123–175	141	16.9	38.9–44.3	41.5	7.06
Acrolein	0.70–7.23	3.42	81.1	0.44–1.25	0.81	41.1
Propionaldehyde	11.1–26.4	21.6	33.0	2.84–4.89	4.06	25.6
Crotonaldehyde	47.9–86.6	60.2	26.3	6.34–13.0	9.68	29.7
Butyraldehyde	27.4–48.1	34.6	28.2	3.05–10.4	6.65	49.9
Benzaldehyde	6.45–19.2	10.8	52.4	3.73–5.07	4.07	16.3
Isovaleraldehyde	3.01–13.7	6.54	74.5	0.07–0.62	0.31	75.3
Valeraldehyde	3.93–6.43	4.58	26.9	0.27–1.96	0.89	87.9
Hexaldehyde	6.21–8.79	7.33	12.4	4.13–4.78	4.66	22.6
Total CBCs	640–784	703	9.10	106–131	113	10.6

speeds, an increase in engine load would raise the combustion temperature, resulting in more complete decomposition of CBCs. Accordingly, engine load appears to be one of the most important controlling factors in the emission of CBCs.

3.3. Effect of MCA on CBCs emission

With each increase in percentage MCA (i.e., 5%, 8%, 10%, and 15%), the increment ratios of emission factors for individual CBCs are shown in Fig. 1. The increment ratio (R) is defined as:

$$\text{Increment Ratio } (R) = \frac{E_{f,A} - E_{f,N}}{E_{f,N}}$$

where $E_{f,N}$: The emission factor of CBCs when base diesel alone was used. $E_{f,A}$: The emission factor of CBCs when certain portion of MCA was used. Therefore, a positive R means increase in emission, while a negative R indicates decrease in emission.

In Transient Cycle runs, when 5% MCA was used, the increment ratios (R) were between -0.16 and 1.46 and averaged 0.20 . Among the 11 CBCs, isovaleraldehyde had the highest R value (1.46) (Fig. 1A). Acetaldehyde and crotonaldehyde were the only two CBCs with negative R values. With the use of 8%, 10%, and 15% MCA, the calculated mean R were 0.62 , 0.89 and 1.71 , respectively (Fig. 1). These results indicate that during Transient Cycle runs, the use of MCA did cause a pronounced increase in the emission of CBCs.

In the steady-state, low-load runs, when 5% of MCA was used, the calculated R values were between -0.88 and 3.82 and averaged 0.03 (Fig. 2A). When 8% of MCA

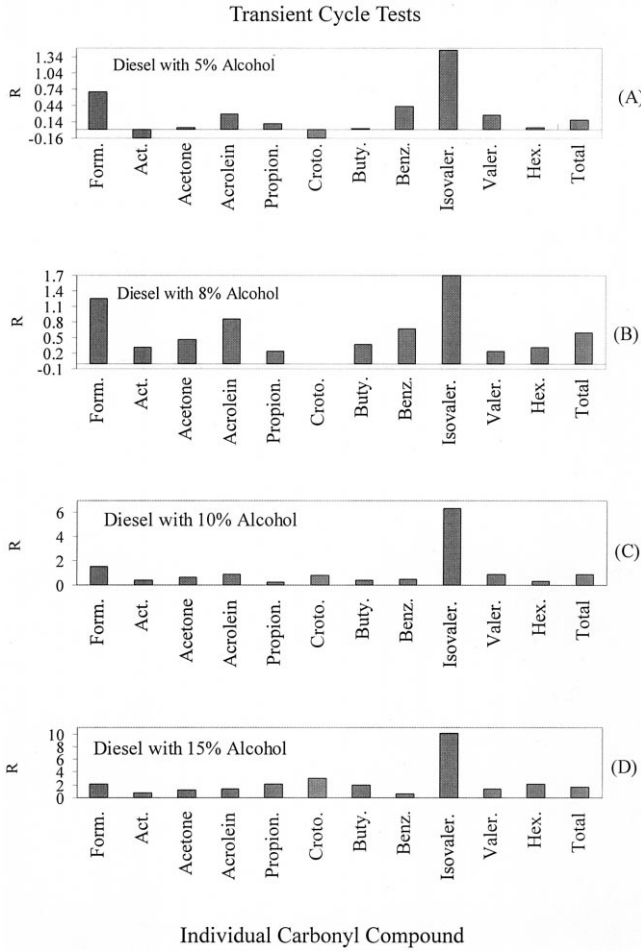


Fig. 1. The Increment Ratios of Individual Carbonyls were the use of MCA at Transient Cycle Tests.

was used, the R values ranged from -0.63 and 6.86 and averaged 0.17 (Fig. 2B). When 5% of MCA was used, propionaldehyde, crotonaldehyde and butyraldehyde had negative R values but acrolein and benzaldehyde had the highest R values (3.82 and 2.14 , respectively). When 8% of MCA was used, only propionaldehyde and crotonaldehyde had the negative R values and acrolein and isovaleraldehyde had the highest R values (4.00 and 6.86 , respectively). When 10% of MCA was used, the R values were between 0.12 and 8.11 and averaged 0.48 (Fig. 2C). When 15% of MCA was used, the R values ranged from 0.15 to 23.0 and averaged 1.20 (Fig. 2D). When 10% and 15% of MCA was used, all of the R values were positive, implying that the emission factors of the 11 CBCs were all increased. When 10% of MCA was used, both acrolein and isovaleraldehyde had the highest R values (5.61 and 8.11 , respectively). When 15% of MCA was

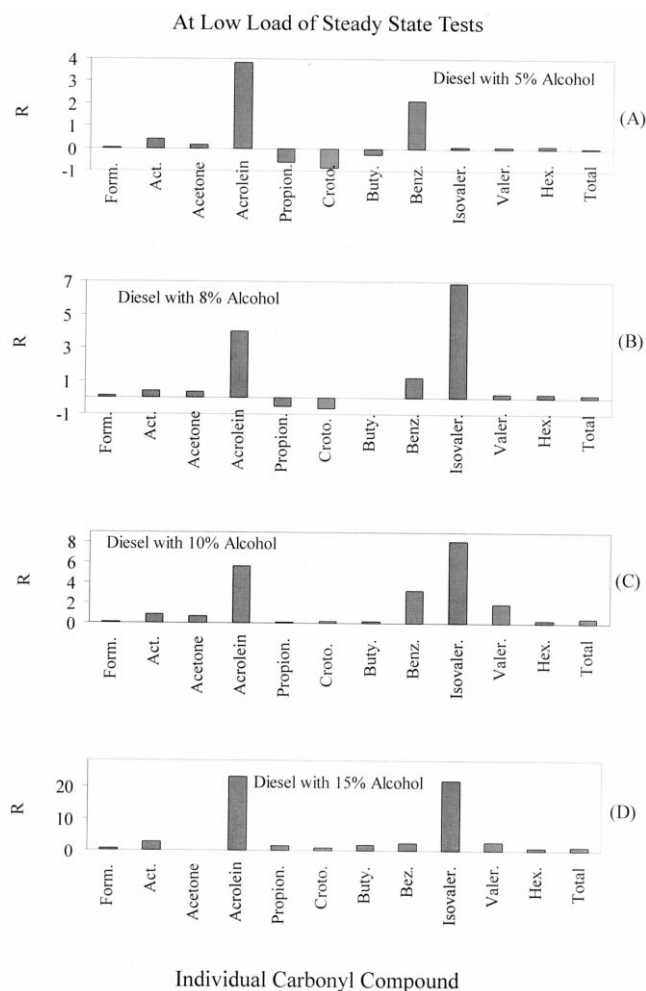


Fig. 2. The Increment Ratios of Individual Carbonyls were the use of MCA at Low Load of Steady State Tests.

used, the R values of the aforesaid two CBCs peaked at 23.0 and 21.8, respectively. If we arbitrarily define that an R value greater than one means a significant increase in the emission of CBCs, then the use of either 10% or 15% of MCA can cause significant increase in the emissions of acrolein, benzaldehyde, isovaleraldehyde, and valeraldehyde. The emission factors of the four CBCs with use of MCA were at least 1.90 times of magnitude higher than those without the use of MCA for the steady-state, low-load runs (Fig. 2).

The effects of percentage MCA (5%, 8%, 10%, and 15%) on the increment ratios (R) in steady-state, high-load runs are shown in Fig. 3. The obtained results are similar to those shown in Fig. 2. Fig. 3(A)–(D) show that isovaleraldehyde and acrolein had the

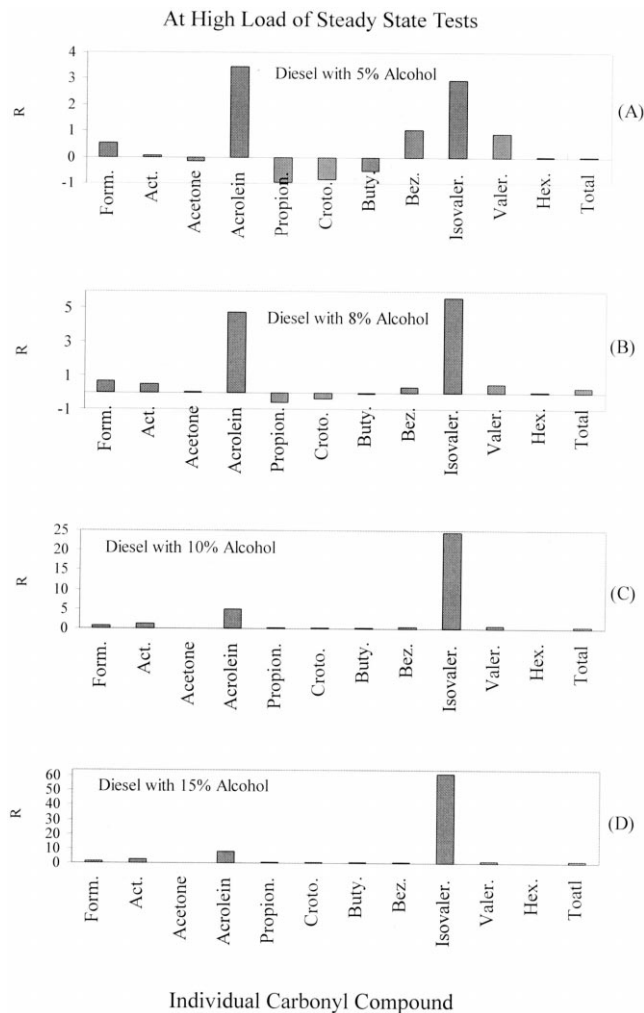


Fig. 3. The Increment Ratios of Individual Carbonyls were the use of MCA at High Load of Steady State Tests.

highest R values. Similarly to low-load runs, acetone, propionaldehyde, crotonaldehyde, and butyraldehyde had negative R values when 5% of MCA was used (Fig. 3(A)). When 8% of MCA was used, the R values of propionaldehyde, crotonaldehyde, and butyraldehyde were negative (Fig. 3(B)). Nonetheless, the use of 10% or 15% of MCA did not result in negative R values of the three aforesaid CBCs (Fig. 3C and D). Fig. 3(A)–(D) also show that the R values of isovaleraldehyde (i.e. 2.93–61.6) were clearly higher than those of the rest of the 10 CBCs (i.e. -0.88 –23.0).

It is clear that the use of MCA significantly increase the R values of CBCs, especially for acrolein, benzaldehyde, and isovaleraldehyde. Accordingly, if the diesel

and gasoline fuels are expected to be replaced by methanol as an alternative fuel in the future, the increased emissions in CBCs will be a major environmental concern.

3.4. Correlation between the emission factors of CO and total-CBCs

There is a fairly good correlation ($R^2 = 0.9319$ with 72 data points) between the emission factors of CO and total-CBCs, as shown in Fig. 4. This finding is not unexpected since both CO and CBCs are incomplete combustion by-products from the diesel engine. In the future, any measure taken to cut down CBCs emissions will quite possibly have the parallel benefit in CO reduction.

3.5. Effect of MCA on toxic CBCs emission

Among the 11 CBCs investigated, three CBCs, formaldehyde, acrolein, and crotonaldehyde, are especially singled out for their emission factors because of their lower LD_{50} (oral rat) and LC_{50} (inhalation rat) values and their higher toxicity [39]. Toxicity of these three toxic CBCs, formaldehyde, crotonaldehyde, and acrolein, are 100, 240, and 26 mg/kg of LD_{50} values (oral rat), respectively [39]. The calculated mean emission factors for the three toxic CBCs are shown in Fig. 5. The results show that formaldehyde is the major toxic aldehyde found in the engine exhaust. In contrast, the amounts of acrolein and crotonaldehyde emitted are much smaller for Transient Cycle tests (Fig. 5(A)). Similarly, in both low-load and high-load runs formaldehyde is abundant, while acrolein and crotonaldehyde are only minor products for the steady-state tests (Fig. 5(B) and (C)).

Although acrolein was the most toxic pollutant among these 11 CBCs, its calculated mean emission factors are lower than those of formaldehyde. Considering the concentration of toxicity from all CBCs, formaldehyde in the diesel exhaust appears to have a tremendous impact on the environment. Due to their low LD_{50} values and very high

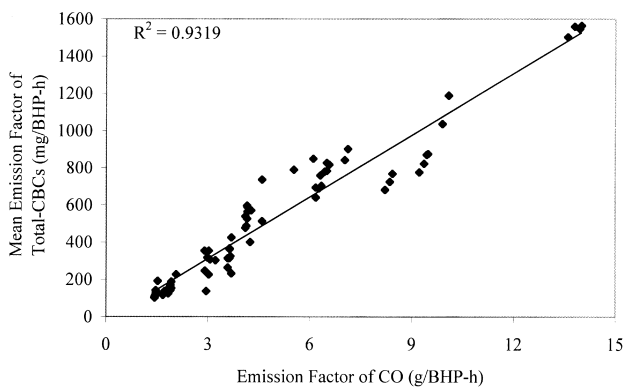


Fig. 4. Correlation between the emission factors of CO and Total-Carbonyl Compounds.

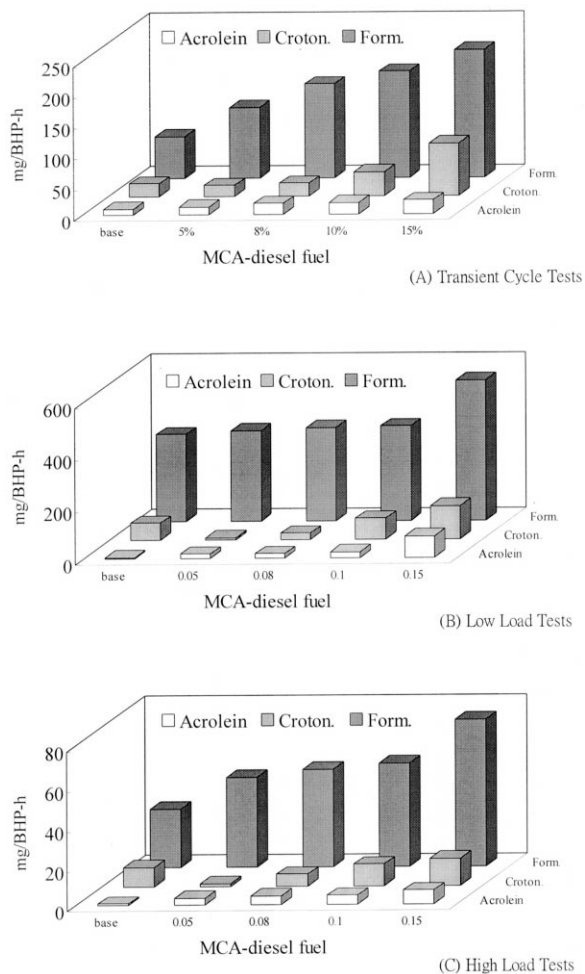


Fig. 5. Emission Factors for the Three Most Toxic CBCs in Diesel Exhaust in Transient Cycle Tests and in both Low-Load and High-Load Steady State Tests.

emission factors, formaldehyde, acrolein, and crotonaldehyde in diesel exhaust are a potential threat to the public health.

4. Conclusions

Results from both cold-start and hot-start runs in Transient Cycle tests show that the calculated mean of the emission factors of a total of 11 carbonyl compounds (CBCs) for cold-start runs was only 12% higher compared to those for hot-start runs. Also, all emission factors of the 11 CBCs for cold-start runs were higher than that for hot-start runs. The results also indicate that formaldehyde, acetaldehyde, and acetone are the three

major CBCs found in the diesel engine exhaust. According to the Code of Federal Regulation, the calculated weighted mean of the emission factors of formaldehyde, acetaldehyde, and acetone are 68.6, 57.2, and 84.3 mg/BHP-p, respectively; while the calculated weighted mean of the emission factor of total CBCs was 302 mg/BHP-h. It is noted that the calculated mean emission factors of butyraldehyde, formaldehyde, valeraldehyde, and propionaldehyde for cold-start runs are 34.0%, 29.1%, 26.1%, and 25.8% of magnitude higher than those for hot-start runs.

In contrast, for steady-state tests, the calculated emission factors of the 11 CBCs for low-load runs are found drastically higher than those for high-load runs. Specifically, the mean emission factors of isovaleraldehyde, formaldehyde, acetaldehyde, and crotonaldehyde for low-load runs are 21.1, 11.3, 6.55, and 6.22 times of magnitude higher than those for high-load runs. This can be explained by the fact that at higher engine load, an increase in the engine load the combustion temperature is raised, which in turn results in better decomposition of CBCs.

In either Transient Cycle tests or steady-state tests, the use of either 10% or 15% of MCA can cause a significant increase in the emissions of acrolein, benzaldehyde, isovaleraldehyde, and valeraldehyde. The emission factors for these four CBCs with the use of MCA are at least 1.90 times of magnitude higher than for those without the use of MCA. The emission factors for both CO and total CBCs, both of which are incomplete combustion by-products in diesel exhaust, correlate very well with each other ($R^2 = 0.9319$). It is quite clear that the use of MCA will significantly increase the increment ratios (R) of CBCs, particularly acrolein, benzaldehyde, and isovaleraldehyde.

Among the 11 CBCs investigated, three CBCs, formaldehyde, acrolein, and crotonaldehyde, are especially singled out for their emission factors because of their lower LD_{50} (oral rat) and LC_{50} (inhalation rat) values. Considering the concentration of toxicity from all CBCs, formaldehyde in the diesel exhaust appears to have a tremendous impact on the environment. However, depending on their low LD_{50} values and very high emission factors, formaldehyde, acrolein, and crotonaldehyde in diesel exhaust are a potential threat to the public health. Accordingly, if the diesel and gasoline fuels are to be replaced by methanol as an alternative fuel in the future, the problem of increased emissions in CBCs need to be solved first.

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