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PERFORMANCE EVALUATION OF CONTINUOUSLY REGENERATING TRAPS FOR CONTROLLING THE CARBONYL EMISSIONS FROM A TURBOCHARGED COMPRESSION IGNITION ENGINE*

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Abstract– Two continuously regenerating traps CRT-A and CRT-B were evaluated under the controlled carbonyl emissions from a turbocharged diesel engine run on an AC electrical dynamometer. The gas-phase carbonyls were taken in silica gel cartridges coated with 2,4-dinitrophenylhydrazine both upstream (baseline) and downstream of the traps, and a total of fourteen carbonyls were identified and then quantified using the high performance liquid chromatography (HPLC) with ultraviolet (UV) detector. Carbonyls were predominant during higher load modes as well as at maximum speed modes. The conversion/reduction rate (CR) of carbonyls was directly affected by the physical characteristics of the traps. The CR revealed a strong correlation with NO_2/NO_x ratios of CRT units, and the performance of retrofits was adversely affected by the increasing upstream back pressure (P) due to the clogging phenomenon. Carbonyls such as formaldehyde, acetaldehyde, acrolein + acetone and propionaldehyde were in abundance, and abated up to 75.4, 83, 60, and 69.3% respectively with CRT-A, and 81.2, 81.5, 57.3, and 65.2% respectively with CRT-B. Nevertheless, formaldehyde and propionaldehyde exhibited reluctance to CR during lower load modes, which was higher with CRT-B relative to CRT-A due to the different features of the traps. A positive correlation was observed between the conversion of acetaldehyde and propionaldehyde within the cycle, and between the mean relative contributions of formaldehyde and acetaldehyde within the CRT units. Moreover, total carbonyls including aromatic aldehydes, and their specific reactivity (SR) both were reduced with CRT technologies showing the order of magnitude as Baseline > CRT-A > CRT-B.

Keywords– Diesel engine, exhaust emissions, carbonyls, unregulated emissions, continuously regenerating trap

1. INTRODUCTION

The scientific community is of the view that forthcoming emission levels associated with compression ignition (CI) engines will no longer be satisfied merely by changes in fuel composition and engine hardware. Some extraordinary efforts in the form of post treatment technologies such as diesel oxidation catalyst (DOC), particle oxidation catalyst (POC), selective catalytic reduction (SCR), and continuously regenerating trap (CRT), etc. are therefore being made for the survival of such an efficient, economical, robust, reliable and powerful machine against the stringent emission standards.

A CRT unit consists of a DOC and a trapping or filtering chamber. The DOC section of the unit plays a significant role not only in the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) which will later be used for the combustion of trapped soot (regeneration), but also in the oxidation of carbon monoxide (CO) and total hydrocarbons (THC) ideally into carbon dioxide (CO_2) and water (H_2O). In this way, a CRT provides very good control, both on particulate matter (PM) as well as on gaseous CO and THC

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emissions [1, 2, 3]. The PM filtration efficiency of a CRT is associated with diffusion and interception processes followed by other forces known as electrophoresis and thermophoresis [4]. Higher efficiency means a larger accumulation of PM mass on the filter which is achieved at the cost of restrained gas flowing through it. This leads to the inhibition in the engine performance such as fuel economy and power [4].

In a CRT unit, the regeneration process which takes place at about 250°C is continuous. This targeted temperature can easily be achieved during the normal operating conditions of a heavy duty CI engine which in turn enables the engine to maintain an acceptable low P [2]. Nevertheless, the regeneration of a CRT depends on sulfur content of the fuel, and thus reduces with the increase in sulfur amount in the fuel [5]. In addition to this, NO_2 contribution to total nitrogen oxides (NO_X) is increased up to one-third or even 40–50% with CRT [6, 7]. In 2004, Carslaw and Beevers [8] reported that NO_2 is more toxic than NO because of its involvement in the photochemical ozone production.

Carbonyls – a subset of volatile organic compounds (VOCs) are caused mainly by the motor vehicle exhaust and the oxidation products of other VOCs available in the atmosphere [9, 10]. They are affected by the changes in fuel composition and emission control technologies [11]. Many of the carbonyls are important precursors of ozone and peroxyacylnitrates (PAN), and actively participate in the formation of photochemical smog and other air pollutants owing to their higher reactivity [12]. Some of them are considered as mutagenic, toxic, and are even suspected to be carcinogenic to human health [13]. Aldehydes constituting an important class of carbonyls are responsible for the contribution of diesel exhaust odor [11].

The main objective of the current paper is to evaluate the effectiveness/performance of two commercial CRT units on controlling carbonyls or aldehyde and ketone emissions. Although such after treatment systems are basically designed with the aim to control the PM emissions from the diesel engine exhaust, the objective is extended here to investigate their potential to abate the unregulated emissions as well. Authors have already reported in their previous study [3] that CRT technologies give a good control on polycyclic aromatic hydrocarbon (PAH) pollutants which are an important class of unregulated emissions.

Carbonyls are considered an other important class of unregulated emissions. However, there have been a limited number of papers with discordant findings in the literature addressing the characterization of carbonyl emissions from CI engines retrofitted with CRT systems [6, 14]. In particular, the carbonyl emissions from engines fuelled with higher sulfur content (350 ppm) diesel and run on 8 mode steady state cycles have seldom been addressed. Moreover, the comparative analysis of the effectiveness of two or more CRT units (with different physical features) regarding the control over the same kind of species such as carbonyls has not been addressed comprehensively. It is important to note that carbonyls emitted from a CI engine equipped with CRT are fundamentally different from those emitted from an un-equipped CI engine, both in quantity and species. The evaluation or gauging of the effects of two retrofits with different specifications on carbonyl species is therefore deemed to contribute to the international scientific community. It is expected that each individual physical separation system with distinct features will yield the different secondary reactions in the presence of catalyst and other features. Consequently, the distinct results are expected from this study which would be helpful to gauge the overall performance or effectiveness of each of the units.

Moreover, the goals of the current work also include the investigation and detailed understanding of the ozone forming potential of these carbonyls in terms of SR evaluated both upstream and downstream of these post treatment technologies. The higher NO_2/NO_x ratios associated with CRT technologies are considered the potential threats to ground level ozone and urban air quality, as higher NO_2 concentration may oxidize the organic compounds to some potent pollutants [6, 15]. It is therefore necessary to gain deep insight into the ozone formation potential of such post treatment units. Some research work related to the SR of carbonyls has been reported previously [16, 17], but that is confined only to alternative fuels. In this study, however, an attempt has been made to address the effects of CRT units on the carbonyl components and their associated SR. To the best of author's knowledge, no detailed work on SR related to CRT is available in the literature yet.

2. MATERIALS AND METHODS

a) Test Engine, fuel and operating cycle

In the current study a turbocharged intercooled direct injection (DI) CI engine with 2771 cc capacity was coupled with an electrical AC dynamometer (Dynas$_3$ HT350, Schenck) on a test bed as depicted in schematic diagram Fig. 1. The other common features of the engine are as follows: Type = 4-stroke, 4-cylinder, high pressure, common rail, inline category; stroke = 102 mm; bore = 93 mm; compression ratio = 18.2:1; Maximum Torque = 270 N-m at 1900 rpm; Maximum Power = 85 kW at 3600 rpm; valves = 2 valves per cylinder.

The rates of fuel and air flows were measured through PLU4000 (Pierburg Inc., Germany) and Sensyflow P (ABB Inc., Switzerland), respectively. The engine exhaust temperature was known through thermocouple (k-series), while the engine oil temperature and coolant temperature both were measured with the help of sensors Pt-100.

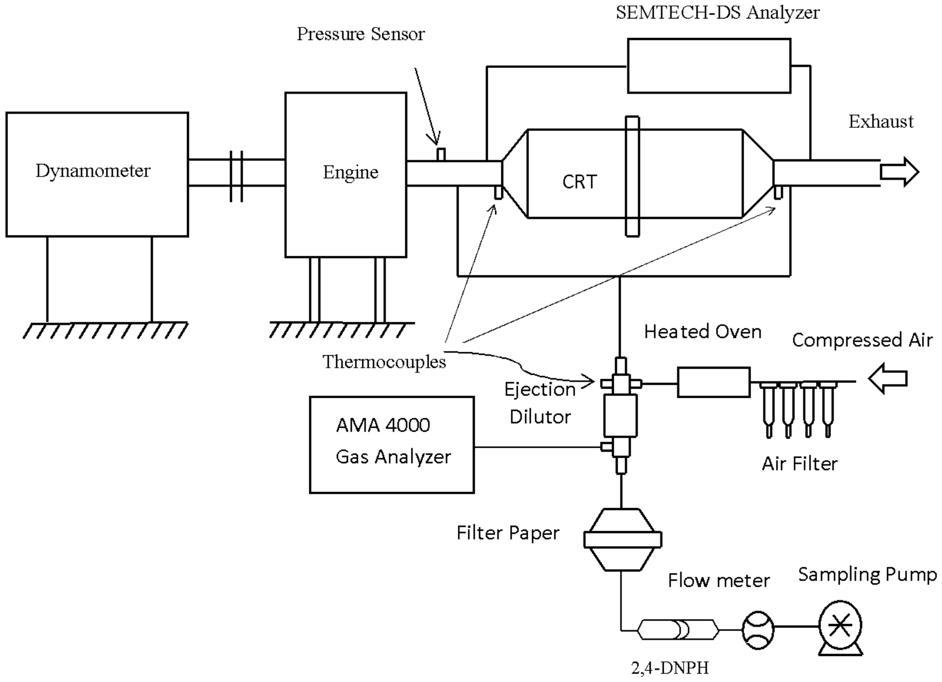

Fig. 1. Schematic of test bed

The engine was run on locally available petroleum diesel being sold in Beijing city. The properties and corresponding standards of the fuel are listed in Table 1. The engine operating cycle consisted of 8 steady-state modes, known as ISO 8178 Type C1 [16, 17]. According to this cycle, the first four modes of the cycle are devised at 3600 rpm speed at 100%, 75%, 50%, and 10% of full load, while the next three modes are planned at a speed of 1900 rpm at 100%, 75%, and 50% of full load known as Modes 5, 6, and 7 respectively. The 8th mode of the cycle is excogitated at a speed of 800 rpm which is known as an idle mode.

Table 1. Properties and standards of fuel

Properties	Diesel	Standard[a]
Cetane number	52	GB/T 386-91
Sulfur content (ppm)	350	SH/T 0253-92
Density (kg/m^3)	841	SH/T 0604
Viscosity (mm^2/s) at 20 ºC	4	GB/T 265
Lower heating value (MJ/kg)	42.8	GB/T 384
Oxygen content (%)	0	Element analysis
Carbon content (%)	87	SH/T 0656-98
Hydrogen content (%)	13	SH/T 0656-98

[a] Chinese standard

b) CRT technologies and their specifications

Two post treatment technologies (commercial packages) known as CRT-A and CRT-B were retrofitted to the same engine one by one. The former after treatment system is South Korean made, whereas the latter one is a Chinese made unit. The detailed specifications of both the units along with their construction and working have been discussed by authors elsewhere [2, 3], however parameters are listed in Table 2 for the interest of the readers. The trap or filter substrates of both units are of ceramic material made in porous cordierite ($2MgO. 2Al_2O_3. 5SiO_2$). The DOC washcoat consists of a thin layer of γ-alumina (Al_2O_3) impregnated with platinum (Pt) catalyst. Principally, the exhaust is led first through the DOC chamber where the oxidation of NO to NO_2 takes place, then through the filtration portion of the unit in which PM pollutants get trapped.

Table 2. Specifications of the CRT units

Parameter	CRT-A	CRT-B
Trap substrate	Cordierite	Cordierite
Structure	Porous, wall-flow monoliths	Porous, wall-flow monolith
Trap Pt. content (g/ft^3)	35	35
Trap cell density ($cells/in^2$)	200	100
Diameter × Length (inch × inch)	8.5 × 14	8.5 × 14
DOC substrate	Cordierite	Metal
Structure	honeycomb	honeycomb
DOC Pt. content (g/ft^3)	50	50
DOC cell density ($cells/in^2$)	400	600
Diameter × Length (inch × inch)	8.5 × 3.5	8.5 × 3.5

c) Sampling, analysis and measuring of pollutants

The regulated gaseous pollutants NO_x were measured using gas analyzer AMA 4000 (Pierburg GmbH, Germany), while nitric oxide (NO) and nitrogen dioxide (NO_2) were individually measured with the help of SEMTECH-DS (Sensor, USA) as per sampling scheme Fig. 1. The engine exhaust was taken in silica gel cartridges (Supelco, USA) coated with 2,4-dinitrophenylhydrazine (DNPH) by employing an ejector-dilutor before and after the CRT. The dilution ratio of the preceding dilutor was about 8, which was calibrated with two concentrations of CO_2 measured in front as well as behind the dilutor prior to starting the experiments. The sample was then led through a filter for its purification from the particulates, and thus trapped in the cartridge. For this purpose, a battery operated constant volume sampling pump Air Chek2000 (SKC, USA) having a flow rate of 500 mL/min was used for an interval of 10 min at each mode. The trapped carbonyl species reacted with the DNPH material and formed the corresponding stable dinitrophenylhydrazone derivatives. The task of sample collection was accomplished at a temperature < 60°C, which is far behind the melting temperatures of DNPH materials. The sampled cartridges were then sealed and kept in a refrigerator at about -10°C.

The trapped carbonyl material was extracted by placing the cartridges on solid phase extractor (Supelco Inc., USA), and thus collected material was eluted with the help of 3 mL acetonitrile (Fisher Company, USA) through washing. After the filtration, the eluted carbonyl material was poured into a flask with a volumetric capacity of 5 mL as discussed by authors elsewhere [17].

Carbonyls were analyzed in accordance with a standard method TO-11A proposed by the environment protection agency (EPA) [18]. An HPLC system (1200LC Agilent, USA) provided with an automatic injector was employed to detect the carbonyls at 360 nm of UV detector. A C-18 XDB column with specifications (4.6 mm × 150 mm × 5 µm) was utilized for the eluting of the derivatives of carbonyls-DNPH. Acetonitrile and water with a volumetric ratio of (60 : 40) were used as mobile phases. An aliquot of volume 25 µL was injected at a flow rate of 1.0 mL/min and the temperature gradient of 25°C. In this way a total of 14 carbonyl compounds such as formaldehyde (FOR), acetaldehyde (ACE), acetone (ATE), acrolein (ACR), crotonaldehyde (CRO), propionaldehyde (PRO), methacrolein (MET), methyl ethyl ketone (MEK), benzaldehyyde (BEN), butyraldehyde (BUT), tolualdehyde (TOL), valeraldehyde (VAL), hexanaldehyde (HEX), and cyclohexanone (CYC) were in a position to be identified and quantified.

For identification of the carbonyls, their HPLC retention times were matched with those of authentic standards (Supelco, USA). Moreover, their chromatographic-peaks retention times were matched with those of standard solutions. For the quantification of carbonyls, their linear standard curves with correlation coefficient > 0.999 were made using external standard method. The purchased standard solution was taken in six different concentrations such as 0.5 µL, 1 µL, 2 µL, 5 µL, 10 µL, and 20 µL employing micro-sampler. The pollutants were analyzed under their respective chromatographic conditions. Thus target compounds were quantified through their peak areas by applying the regression method [17]. In the current study, acetone and acrolein were quantified together owing to their same retention time, and the complexity of same chromatographic peaks.

The data given in the present study has subtracted the interference of the filter from a field blank test. Field blanks levels at the sampling site were less than 5%. Further to this, quality control and quality assurance (QC/QA) were also maintained through recovery rate and duplicate analyses.

3. RESULTS AND DISCUSSION

In this study, carbonyls are discussed in terms of their mass flow rate (mg/h) rather than in brake specific emissions (BSE) in which pollutants are expressed in terms of their mass per unit power developed. So it was not possible to consider an important mode of the cycle known as an idle or zero load mode (Mode 8) if the emissions were to be discussed in terms of BSE. The conversion/reduction of carbonyls with CRT units is expressed as follows:

$$CR = \left(\frac{U_S - D_S}{U_S} \right) \times 100 \tag{1}$$

where U_S and D_S stand for upstream (or baseline) and downstream carbonyl emissions, respectively.

a) Effect of engine operating conditions on carbonyls

Figure 2 presents the carbonyl emissions both upstream and downstream of CRT technologies. It is obvious that pollutants are, in general, higher at higher load modes as compared to lower load modes, and decrease as the load is decreased. Nevertheless, the upstream carbonyls are lower at Modes 2 and 6 (75% load modes), relative to Modes 3 and 7 (50% load modes). Also, the emissions are higher during idle mode i.e., Mode 8. Moreover, carbonyls are predominant at maximum speed modes as compared to lower speed modes. This finding is consistent with previous studies that a positive correlation exists between carbonyls and engine speed [13, 16].

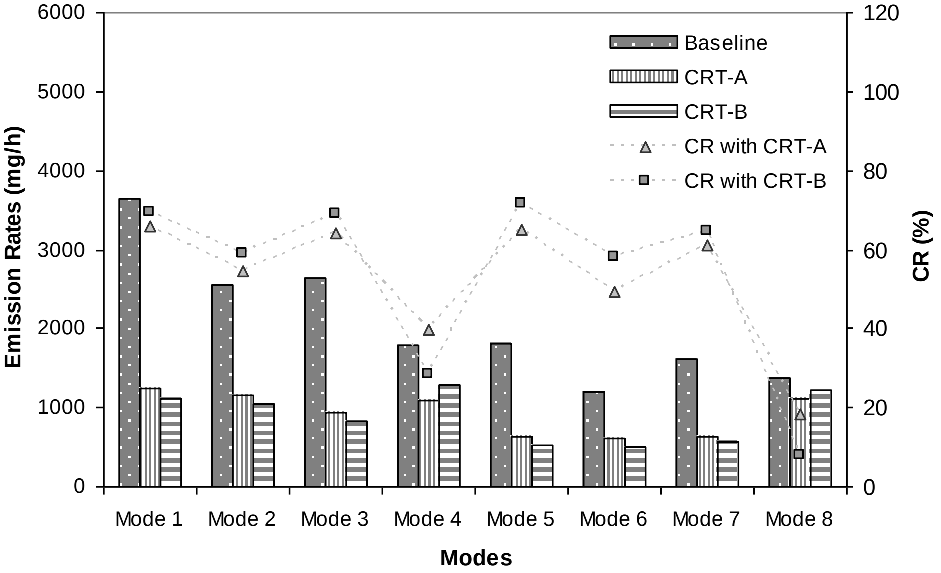

Fig. 2. Carbonyl emissions and their CR with CRT units

Elevated carbonyl emissions at higher loads are due to the rich mixture formed in the combustion chamber of the engine, but higher carbonyl compounds at Mode 8 (an idle mode) are attributed to relatively lean mixture formation. It has been reported in the literature that the over lean mixture in the combustion chamber is responsible to retard the flame propagation speed and the reaction rate with the consequent incomplete combustion products [2]. The lower upstream emission rates at 75% load modes relative to 50%, however, are most likely due to the load levels that are more prone to decomposition of THC including carbonyls, since carbonyls are partly oxidized species of THC [19]. It is well known that neither fuel nor air contain carbonyls [16], they actually originated from the combustion chamber of the engine on account of incomplete or partial oxidation of THC. Carbonyls were thus mitigated by virtue of overall control on the THC emissions caused by the DOC section of retrofits. It has been demonstrated that a combination of DOC and diesel particulate filter gives a very good control on THC as well as on particulate emissions even in complying with the Bharat Stage 5 (BS5) emission norms [20].

The increased carbonyl emissions on maximum speed modes, on the other hand, are attributed again to rich mixture area during the maximum speed modes relative to lower speed modes. The rich mixture area suppresses the oxidation process of the fuel, and thus causes more unburned compounds in the form of carbonyls. In addition to this, some authors are of the view that time duration for the combustion process is short at higher engine speeds which leads to incomplete combustion of carbonyl compounds [16].

b) Effect of CRT-parameters on carbonyls

The percentage conversion/reduction of carbonyl compounds or CR at various modes is also shown in Fig. 2. The downstream carbonyls are decreased by 40–66% and 37–71.6% with CRT-A and CRT-B, respectively. Although both the CRT units give a good control on carbonyls, the CR values are relatively higher with CRT-B as compared to CRT-A. The results show that CR values are directly dependent on the physical characteristics of the units.

As a CRT unit comprises a DOC as well as a filtration chamber, there is a physical separation for each individual system. The CRT-B unit consists of a DOC section with metallic monolith, while the CRT-A is incorporated with a DOC section of ceramic monolith. The DOC cell density of CRT-B is higher relative to that of CRT-A as shown in Table 2. The metallic monolith is responsible for higher oxidation of pollutants as well as higher oxidation rates of NO to NO_2. Moreover, the thermal conductivity of metallic monolith is 15–20 times higher than that of ceramic monolith, while backpressure is 10–15% lower with metallic monolith compared with ceramic monolith, resulting in faster warm up and hence better conversion of pollutants [21]. In addition to this, metallic monoliths have higher flow area on account of lower cell wall thickness, and thus exhibit smaller pressure drop [21, 22]. Normally, the higher back pressure of a CRT unit or a back pressure beyond the certain designed limit means a greater risk of clogging the unit [15], and thus higher probability of suppression of the oxidation rates.

In order to support the above discussion and to justify the results, the auxiliary data in terms of upstream back pressure, downstream temperature and NO_2/NO_x ratios is also provided in Table 3 for the interest of the readers. The CRT-B unit, in general, exhibits higher CR due to higher downstream NO_2/NO_x ratios, relative to CRT-A. These higher NO_2/NO_x ratios reflect the higher combustion rates of soot and other PM pollutants through the CRT-B units, relative to its counterpart CRT-A. It has been reported in previous studies that NO_2 is a stronger oxidant of pollutants as compared to oxygen (O_2) within the temperature window of 200–500°C [15, 23]. Thus higher values of NO_2 followed by the higher downstream temperatures with CRT-B as compared to CRT-A as shown in Table 3 are responsible for the higher CR values.

Table 3. Upstream back pressures, and downstream temperatures and NO_2/NO_x ratios of two CRT units

	Mode 1		**Mode 2**		**Mode 3**		**Mode 4**	
	CRT-A	CRT-B	CRT-A	CRT-B	CRT-A	CRT-B	CRT-A	CRT-B
P (kPa)	9.24	9.05	8.84	8.35	8.55	8.18	6.48	6.49
T (°C)	352.7	371.5	345.4	354.8	298.5	303.4	300.5	296.3
NO_2/NO_x (%)	26.65	28.45	24.83	26.54	19.12	21.88	15.02	14.86
	Mode 5		**Mode 6**		**Mode 7**		**Mode 8**	
	CRT-A	CRT-B	CRT-A	CRT-B	CRT-A	CRT-B	CRT-A	CRT-B
P (kPa)	5.37	5.12	4.71	4.43	3.82	3.74	1.70	1.72
T (°C)	284.8	305.8	277.5	309.6	275.6	280.2	161.3	153.5
NO_2/NO_x (%)	30.27	33.76	20.35	24.65	17.46	18.74	15.24	14.53

However, the higher CR values with CRT-A relative to CRT-B during the lower load modes (Modes 4 and 8) are attributed again to downstream NO_2/NO_x ratios which are higher this time with CRT-A, compared with CRT-B. This is due to the lower combustion temperature and relatively higher upstream back pressure caused by the choking of filter, with the consequent decrease in NO_2/NO_x ratios in case of CRT-B, relative to CRT-A. The variations in the back pressure drop of the units are actually ascribed to both physical structure of the DOC section as well as operating conditions (i.e. load and speed in this case) of the engine. Moreover, it is probable that the conditions for sulfur trioxide (SO_3), formation in the engine exhaust due to higher sulfur content (350 ppm) in the fuel, are more conducive at such lower load levels for the deactivation of catalyst in case of CRT-B, relative to CRT-A. The sulfur content in a fuel plays a key role in the conversion of NO to NO_2 on the oxidation catalyst, which in turn affects the performance of CRT [24].

c) Effect of CRT units on CR of some selected carbonyls

The CR of formaldehyde, acetaldehyde, propionaldehyde, and acrolein + acetone has further been considered here for individual discussion owing to their potential threats to the environment. The scientific community is of the view that formaldehyde and acetaldehyde are suspected carcinogens as per declaration by the European Union (EU) and National Institute for Occupational Safety and Health (NIOSH), whereas acrolein has been found as a possible human carcinogen by the EPA [25].

It is clear from Fig. 3 that both post treatment units give good control on formaldehyde, acetaldehyde, acrolein + acetone and propionaldehyde during all the cyclic modes except the idle mode (Mode 8) at which formaldehydes reflect negative CR, and Mode 4 and Mode 8 during which propionaldehydes reveal negative CR. However, these negative CR trends are deeper with CRT-B, relative to CRT-A. The CR of formaldehydes varies by 46–75.4% and 37.3–81.2% with CRT-A and CRT-B respectively, and that of acetaldehydes by 40.2–83% and 18–81.5% with CRT-A and CRT-B respectively. Meanwhile, acrolein + acetone components exhibit 5–60% and 8.6–57.3%, while propionaldehydes show 4–69.3% and 32–65.2% CR with CRT-A and CRT-B, respectively.

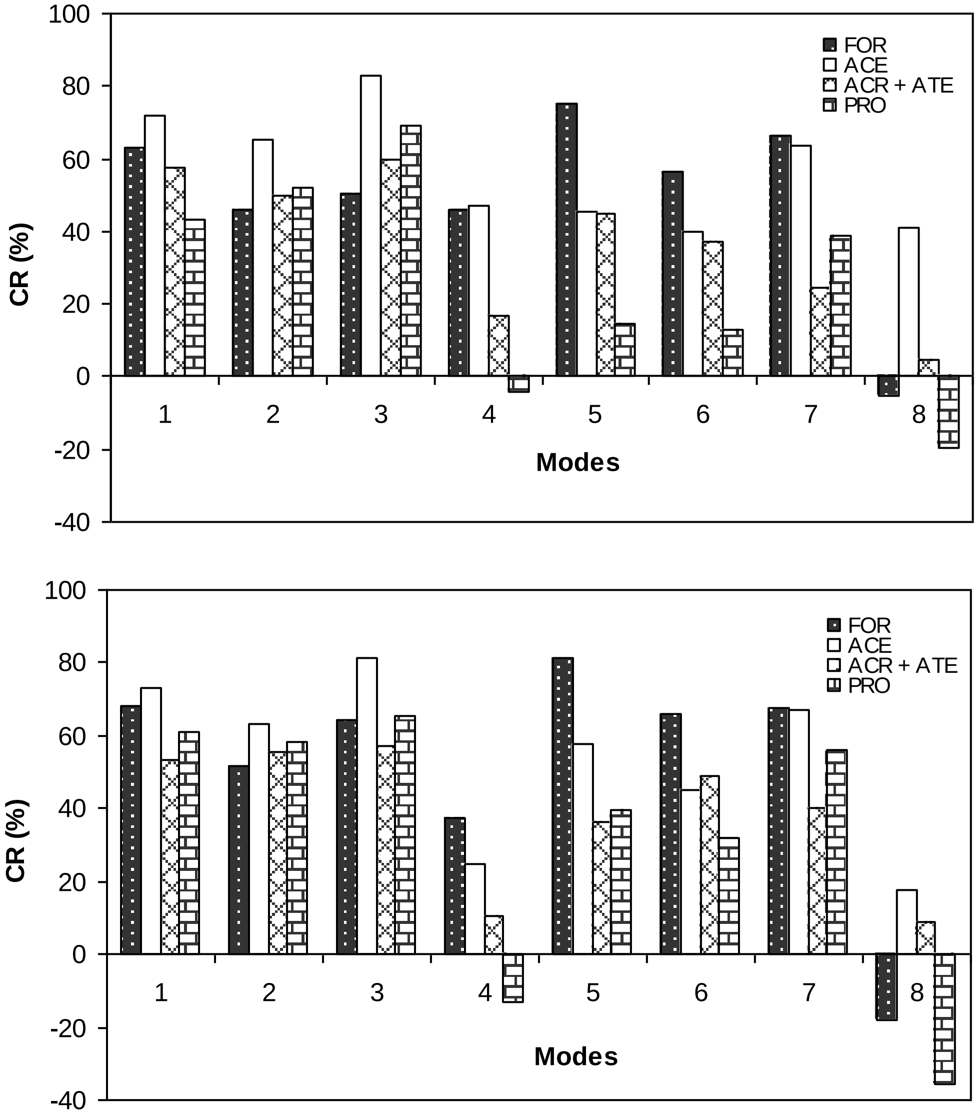

Fig. 3. The CR of some abundant carbonyls with (a) CRT-A, and (b) CRT-B

The substantial abatements with higher CR of the above discussed components are attributed, obviously, to better oxidation rates of THC with CRT retrofits containing Pt catalysts. Authors have already demonstrated in their previous study [2] that CRT technologies have the potential to decrease the THC emissions above 91%. The negative CR or reluctance to conversion of formaldehydes during idle mode and that of propionaldehydes during lower load modes (0–10%) with both units, however, may be ascribed to the choking of filters as discussed in preceding section b, and also to reduction in NO_2/NO_x ratios as shown in Table 3. Further, it is speculated that this is the load range during which temperature and physical parameters of the units are conducive to convert some other species such as aldehydes, ketones or dicarbonyls and some other VOC components into these carbonyls.

Moreover, a direct correlation is found between the CR of propionaldehyde and acetaldehyde emissions during the entire cycle in general, and at the lower load modes including idle in particular, with both after treatment units. As the CR of acetaldehydes decreases, the CR of propionaldehydes decreases too and vice versa. Thus the higher the decrease in CR of acetaldehydes or alternatively the higher the reluctance to conversion of acetaldehydes, the deeper the negative CR trends of propionaldehydes as shown at lower load modes (Mode 4 and Mode 8) in Fig. 3.

d) Mean relative contribution of carbonyls

Some significant carbonyls such as formaldehyde, acetaldehyde, propionaldehyde, and acrolein + acetone have been selected again here for their mean relative contribution (MRC) based on mean or average values taken during the entire cycle. These carbonyl components have contributed the most throughout the cycle modes in this study, and thus are declared here as major components. It is evident from Fig. 4 that formaldehyde and acetaldehyde are the most abundant components with their respective MRC labeled therein. After them, the third and fourth larger contributions to the total carbonyls are made by acrolein + acetone and propionaldehyde species, respectively. Only 9.4, 6.6, and 5.7% of MRC is shared by all the remaining 9 components of carbonyls in case of upstream, downstream of CRT-A, and downstream of CRT-B, respectively. In other words, the MRC values in three cases are of the order 90.6, 93.4, and 94.3%, respectively. Above findings are in line with those of previous studies that 90% of carbonyls are shared among formaldehyde, acetaldehyde, propionaldehyde, and acrolein components [17, 26].

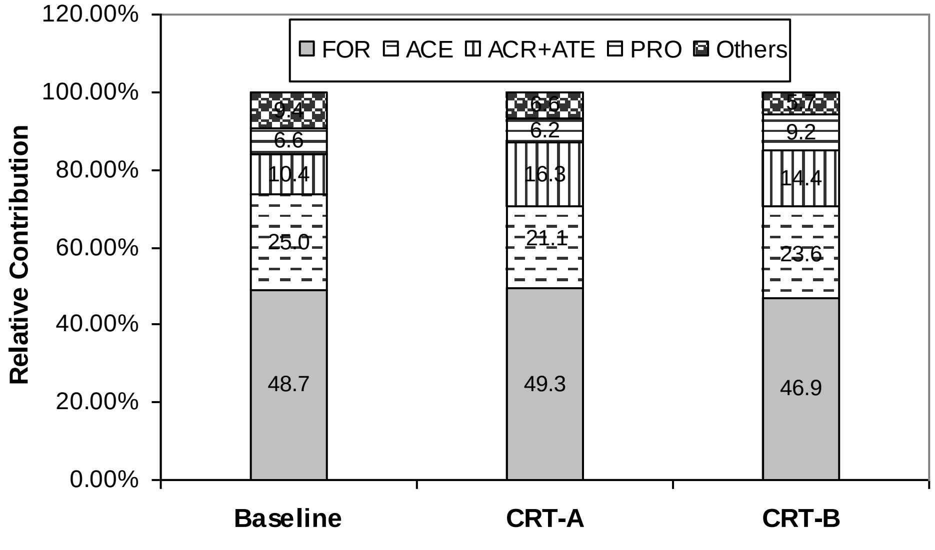

Fig. 4. Relative contribution of major carbonyls upstream and downstream of CRT units

It is interesting to note that MRC of formaldehyde follows the order of magnitude as CRT-A > CRT-B, while that of acetaldehyde is in the sequence of CRT-B > CRT-A. This phenomenon of higher MRC of formaldehyde followed by lower MRC of acetaldehyde with CRT-A or the lower MRC of formaldehyde accompanied by higher MRC of acetaldehyde with CRT-B shows that oxidation of these components are directly affected by DOC cell density rather than by catalyst content. The catalyst contents in both units are the same, but the cell densities are different as shown in Table 2.

The CRT-A with lower DOC cell density exhibits lower oxidation rates of formaldehydes and a majority of other components (to be discussed later in this study) relative to its counterpart. However, it gives better control over acetaldehyde as well as on a couple of other components. Contrary to CRT-A, CRT-B gives better oxidation rates of formaldehydes and a majority of other carbonyl species due to higher cell density as well as metallic monolith of its DOC section. Thus pollutants are exposed to more surface area and become abated in this case. It is established that the higher the cell density of a unit, the greater the geometric surface area with increased catalyst activity under the same volume of substrates [21].

Although the trap structure of both units consists of porous, wall-flow monoliths with the same content of Pt (g/ft^3) as shown in Table 2, the cell density is different in each case. The CRT-A unit with trap cell density equal to double that of the CRT-B gives better filtration of acetaldehydes relative to its counter part. It is thus concluded from this section that CRT-B with relatively higher DOC-cell density is more effective for the control of formaldehydes as well as the majority of other carbonyls. The CRT-A, on the other hand, with higher trap-cell density is more effective in the abatement of acetaldehydes.

e) Specific reactivity of carbonyls

In 1990, Carter and Lowi [27] examined the air modeling on the basis of ozone forming potential of pollutant species depending on their maximum incremental reactivity (MIR) factors taken as indices for ozone formation. These indices indicate the maximum increase in ozone formation of the pollutants under discussion, and thus help in the formulation of specific reactivity of all the components. The SR is defined as algebraic sum of the product of individual NMOG mass flow rate (mg/h) and the corresponding MIR value to the algebraic sum of mass flow rates of all the NMOG species. Mathematically, the SR is given as follows:

$$SR = \frac{\sum\left(NMOG_i \times MIR_i\right)}{\sum NMOG_i} \tag{2}$$

where the subscript *i* stands for a certain carbonyl component, whereas NMOG is the abbreviation of non-methane organic gas such as carbonyls or aldehydes and ketones. The California Air Resources Board (CARB) has given the MIR values of carbonyls as listed in Table 4, and the method to determine their SR [16].

Table 4. Mean ER of carbonyls along with their corresponding MIR values

Component	Emission Rate (mg/h)			MIR
	Baseline	CRT-A	CRT-B	
Formaldehyde	1011.57 ± 451.22	456.97 ± 169.88	415.32 ± 161.70	7.15
Acetaldehyde	519.79 ± 249.97	195.77 ± 55.62	209.62 ±79.61	5.52
Acrolein+Acetone	215.14 ± 68.31	130.11 ± 43.04	128.11 ± 48.50	6.77*, 0.56**
Propionaldehyde	136.35 ± 135.87	83.35 ± 74.40	81.77 ± 78.36	6.53
Crotonaldehyde	37.36 ± 35.19	11.32 ± 6.88	11.71 ± 8.33	5.41
Methyl ethyl ketone	85.29 ± 38.28	15.42 ± 3.01	16.77 ± 4.59	1.18
Methacrolein	22.89 ± 24.26	12.06 ± 16.69	10.09 ± 15.81	6.77
Butyraldehyde	4.66 ± 3.53	3.90 ± 4.10	2.63 ± 2.82	5.26
Benzeldehyde	7.72 ± 4.95	2.14 ± 0.78	0.81 ± 0.71	-0.56
Valeraldehyde	8.83 ± 4.40	5.10 ± 4.19	1.15 ± 1.43	4.41
Tolualdehyde	10.26 ± 11.16	4.84 ± 4.88	3.00 ± 3.57	-0.56
Cyclohexanone	8.80 ± 8.29	3.29 ± 1.96	2.86 ± 1.73	6.53
hexanaldehyde	9.54 ± 13.10	2.74 ± 2.69	2.07 ± 1.16	3.79
Total ER	*2078.19 ± 813.35*	*927.02 ± 264.47*	*885.90 ± 325.48*	
SR	**5.64 ± 0.34**	**5.58 ± 0.30**	**5.52 ± 0.24**	

6.77* for Acrolein and 0.56** for Acetone

Table 4 shows the carbonyl emissions taken upstream and downstream of CRT units. It is clear that total ER and the SR of carbonyls follow the orders of magnitude as Baseline > CRT-A > CRT-B. Further, aromatic aldehydes such as benzeldehyde and tolualdehyde are profoundly reduced showing respective CR of 72.3 and 53%, and 89.5 and 70.8% with CRT-A and CRT-B, respectively. This means CRT-B provides better control not only on total ER but also on aromatic aldehyde emissions due to better physical characteristics leading to better oxidation rates, relative to CRT-A.

Generally, it is good to view the data listed in Table 4 that both post treatment units exhibit better performance with reduced carbonyl emissions and SR. The lower SR means the reduction in ozone formation in the lower atmosphere leading to decreased respiratory problems. Nevertheless, the demand for more NO_2 necessary for the higher particle removing efficiency of CRT units may increase the risk of NO_2 exposure to the atmosphere, and thus may cause the increase in ground level ozone.

4. CONCLUSION

This study evaluates the performance of two after treatment units CRT-A and CRT-B of different specifications on the basis of controlled carbonyl emissions from a turbocharged CI engine operating on an AC electrical dynamometer. The engine was run first with CRT-A, and then with CRT-B under the auspices of an 8-mode steady-state cycle to obtain upstream (baseline) and downstream measurements. The diluted exhaust of gas-phase carbonyls was trapped in 2,4-DNPH coated silica gel cartridges, and thus carbonyls were analyzed through HPLC with UV detector. According to the experimental results:

- Carbonyls were higher during higher and idle load modes due to rich and lean mixtures respectively. Also, they were predominant at maximum speed modes of the cycle owing to again rich mixture formation.
- The CR of carbonyls was directly affected by the physical characteristics of the retrofits, and remained elevated with the DOC section of metallic monolith and higher cell density, relative to DOC of ceramic monolith with lower cell density. Moreover, the CR revealed a strong correlation with downstream NO_2/NO_x ratios of CRT units, and thus increased with increasing NO_2/NO_x ratios due to higher oxidation rates of pollutants.
- The performance of CRT systems was adversely affected by the increase in P on account of choking or blocking of the units.
- Carbonyls such as formaldehyde, acetaldehyde, propionaldehyde, and acrolein + acetone were highly abated with respective maximum CR of 75.4, 83, 60, and 69.3% with CRT-A, while that of 81.2, 81.5, 57.3, and 65.2% with CRT-B.
- However, formaldehyde and propionaldehyde revealed reluctance to conversion or negative CR during lower load modes, which were deeper in case of CRT-B compared with CRT-A due to different physical characteristics of the two units.
- A positive correlation is found between acetaldehyde and propionaldehyde showing that the CR of propionaldehydes increases as the CR of acetaldehydes is increased and vice versa.
- MRC of formaldehydes was higher, while that of acetaldehydes lower with CRT-A. However, there were opposite results in case of CRT-B, relative to its counterpart which means the former unit gives better control over formaldehyde, while the latter is more effective for the controlling of acetaldehydes.
- Formaldehyde, acetaldehyde, propionaldehyde, and acrolein + acetone were the most abundant components with the same order of magnitude showing MRC of above 90, 93, and 94% of total carbonyls in case of baseline, CRT-A, and CRT-B respectively.

- Total carbonyl components including aromatic aldehydes, and their SR were decreased with CRT technologies, and the SR was in the order of magnitude as Baseline > CRT-A > CRT-B.

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