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## Characterization of polycyclic aromatic hydrocarbon emissions from diesel engine retrofitted with selective catalytic reduction and continuously regenerating trap

Asad Naeem Shah<sup>1,2</sup>, Yunshan Ge<sup>1,\*</sup>, Jianwei Tan<sup>1</sup>, Zhihua Liu<sup>1</sup>, Chao He<sup>1</sup>, Tao Zeng<sup>1</sup>

1. National Lab of Auto Performance and Emission Test, School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, China. E-mail: [naeem.138@hotmail.com](mailto:naeem.138@hotmail.com)

2. Department of Mechanical Engineering, University of Engineering and Technology, Lahore 54000, Pakistan

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### Abstract

Two after treatment units, selective catalytic reduction (SCR) and continuously regenerating trap (CRT), were independently retrofitted to a diesel engine, with the objective to investigate their impact on the conversion/reduction (CR) of polycyclic aromatic hydrocarbons (PAHs). The experiments were conducted under the European steady state cycle (ESC) first without any retrofits to get baseline emissions, and then with SCR and CRT respectively, on the same engine. The particulate matter (PM)-phase PAHs were trapped in fiberglass filters, whereas gas-phase PAHs were collected in cartridges, and then analyzed using a gas chromatograph-mass spectrometer (GC-MS). Both PM-phase and gas-phase PAHs were greatly reduced with CRT showing respective CR of 90.7% and above 80%, whereas only gas-phase PAHs were abated in the case of SCR, with CR of above 75%. Lower molecular weight (LMW) PAHs were in abundance, while naphthalene exhibited a maximum relative contribution (RC) to LMW-PAHs for all three cases. Further, the CR of naphthalene and anthracene were increased with increasing catalyst temperature of SCR, most likely due to their conversion to solid particles. Moreover, the Benzo[a]Pyrene equivalent (BaP<sub>eq</sub>) of PAHs was greatly reduced with CRT, owing to substantial reduction of total PAHs.

**Key words:** diesel engine; continuously regenerating trap; urea-selective catalytic reduction; polycyclic aromatic hydrocarbons; unregulated emissions

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### Introduction

Among efficient and economical working machines, the diesel engine is deemed as one of the most reliable and durable. The power produced by a diesel engine is well suited not only to road transportation but also to stationary working machines. However, there has always been a challenge with this unmatched prime mover in the form of increasing emissions standards. In the past, different strategies including engine modification, fuel and/or lubrication alteration or the combination of both were used by researchers for the control of pollutants (Ferguson and Kirkpatrick, 2001; Park et al., 2004). Engine modifications comprise high pressure fuel injection, exhaust gas recirculation, homogenous charge compression ignition, and turbocharging/supercharging (Xiaoping and Shu, 1995; Zheng et al., 2004).

The ever tighter emission levels for diesel engines have compelled researchers to work not merely on engine tuning or modification but also on suitable advanced aftertreatment devices to meet the upcoming more stringent

standards. For instance, a number of aftertreatment devices such as active and passive DeNO<sub>x</sub> catalysts, Lean NO<sub>x</sub> Trap, SCR, diesel oxidation catalyst (DOC), and DPF technologies have been used with the prime objective to abate either oxides of nitrogen (NO<sub>x</sub>) or particulate matter (PM) emissions (Pouille et al., 1998; Gekas et al., 2002; Hoard et al., 2004). Depending on filter regeneration techniques, DPF systems have been further categorized as fuel-borne catalyst, catalyzed soot filter, and catalyst-DPF (Khair, 2003). Currently, SCR and DPF units are being used separately prior to the engine set-up or calibration first to abate either PM or NO<sub>x</sub>, and then to control the remaining category of pollutants through retrofitting (Liu et al., 2008). Work has also been reported on the integration of SCR and DPF units to reduce both pollutants simultaneously (Walker et al., 2004).

In urea-SCR technology, a solution comprising 32.5% urea (by wt.) and water referred to as AdBlue is introduced in the exhaust pipe after the engine turbocharger (Dieter et al., 2003). The urea-water solution is converted into isocyanic acid, and then into ammonia and carbon dioxide (Willand, 1998). Ammonia, serving as a reductant, reduces

\* Corresponding author. E-mail: [Geyunshan@bit.edu.cn](mailto:Geyunshan@bit.edu.cn)

the nitric oxide (NO) or nitrogen dioxide (NO<sub>2</sub>) through the oxidation process in the presence of oxygen. Urea-SCR technology has the potential to perform with higher sulfur contents and operate on a wider temperature range with lower fuel economy penalty and higher durability (Willand, 1998; Fritz et al., 1999). Various factors such as exhaust gas temperature, concentrations of pollutants and oxygen, catalyst temperature, space velocity (SV), and normalized stoichiometric ratio may affect the performance of a urea-SCR system (Calabrese et al., 2000).

In a catalyst-diesel particulate filter (DPF) commonly known as continuously regenerating trap (CRT) or CR-DPF, the functions of oxidation catalyst and DPF have chemically been integrated to achieve passive regeneration. NO<sub>2</sub> produced by the oxidation of NO in the catalyst zone of the unit is used to combust the trapped soot, and thus to regenerate the filter (Khair, 2003). The oxidation of NO is also accompanied by the oxidation of hydrocarbons (HC) and carbon monoxide (CO) yielding ideally carbon dioxide and water. In this way, CRT at the same time gives very good control of PM, CO and HC emissions (Liu et al., 2011). However, the performance of a CRT unit is a function of sulfur content, and thus decreases with increasing sulfur levels in the fuel (Walker et al., 2002).

A multitude of regulated (CO, HC, NO<sub>x</sub>, and PM) and unregulated (PAHs, carbonyls or aldehyde and ketones, number-size distribution of particles, volatile organic compounds etc.) emissions originating from diesel engines in the atmosphere depend on the type of engine, its tuning and maintenance, mode of operation, and fuel type. PAHs, however, have been selected for this study because of their harmful effects on human health. Some of these PAHs are considered to be carcinogenic and mutagenic, and hence are grouped into class 2A (probably carcinogenic to humans) by the International Agency for Research on Cancer (Chen et al., 2006). Some researchers are of the view that PAHs are immunosuppressive pollutants in the environment, and are involved in antiandrogenic and antiestrogenic activities (Kizu et al., 2000; Lin et al., 2006). Many studies focused on PAHs have revealed that benzo(a)pyrene, an important PAH component, injures the respiratory and immune system, and causes cell mutation and cancers (Lin et al., 2006). According to Ravindra et al. (2008), benzo[a]anthracene and chrysene consisting of four rings are actively involved in teratogenic and carcinogenic activities.

PAHs, being the most stable form of hydrocarbons and having low hydrogen-to-carbon ratios, do not exist as single compounds owing to their complicated structure (Ravindra et al., 2008). These pollutants constitute a class of semi-volatile organic species that consist of two to seven carbon rings. The lighter PAHs with two to three rings exist in the gas phase, while the heavier PAHs with five to seven rings are found adsorbed onto particles (Park et al., 2002). These are formed due to the incomplete combustion of fuel molecules, high temperature pyrosynthesis of organic material, and structural modifications leading to conversion of one PAH into another during the combustion process (Corrêa and Arbilla, 2006). Bartok and

Sarofim (1991) proposed that formation of PAHs during combustion takes place possibly in three distinct ways, i.e., rapid radical reactions, ionic reactions, and slow Diels-Alder condensations. It has also been reported that about 80% of benzo(a)pyrene in the exhaust is formed by the same molecules originally available in the fuel (Corrêa and Arbilla, 2006), leading to the fact that it can retain the same carbon skeleton or survive the combustion.

The objective of the current work is to identify, and hence quantify PAH concentrations from a common rail diesel engine exhaust without and with two different retrofits, i.e., vanadium-based urea SCR and CRT, and hence to compare the results with those of baseline measurements. Although many studies have successfully examined PAH emissions from diesel engine exhaust under different conditions, this field is still open for researchers owing to the limited data of PAHs available in cases of different engines, working cycles/working conditions, and retrofits. To best of the authors' knowledge, comparative study of the effect of vanadium-based SCR and CRT on PAHs has seldom been addressed. The primary objective of current CRT and SCR system studies has been to examine their impact on the control of regulated emissions from diesel engines (Shah et al., 2009; Liu et al., 2011). In the current study, however, the objective is extended to investigate their effect on PAH emissions due to the expected secondary reactions in the aftertreatment units.

## 1 Materials and methods

### 1.1 Engine, operating cycle and fuel

A 2.771-L, turbocharged, 4-cylinder, common rail diesel engine was used in the current study. The bore and stroke of the engine were 93 and 102 mm, respectively, while the compression ratio was 18.2:1. The rated power and maximum torque of the engine were 85 kW and 270 Nm respectively, whereas their corresponding speeds were 3600 and 1900 r/min. The engine was operated on an AC electrical dynamometer (Schenck HT350, Hori-ba, Germany) in accordance with the 13-mode European steady-state cycle (ESC), as shown in Fig. 1. The ESC test parameters are listed in Table 1. The weighting factor (WF) of pollutants during modes A25, A50, A75, C25, C50 and C75 was 5% for each case, while it was 8% during A100 and C100 modes. Further, WF was 9% during B100, and 10% during B25, B50 and B75 modes. The WF during the idle mode is 15% in this cycle.

The properties of the fuel used in this study are given in Table 2. The fuel flow rate, and coolant and engine oil temperatures were measured using a PLU4000 (Pierburg Inc., Germany) and temperature sensor (Pt-100), respectively. The air flow rate and exhaust temperature were measured using a Sensy flow P (ABB Inc., Switzerland) and a k-series thermocouple, respectively.

### 1.2 SCR and CRT systems

The urea-SCR system that was used in this study was designed and developed in the Beijing Institute of Tech-

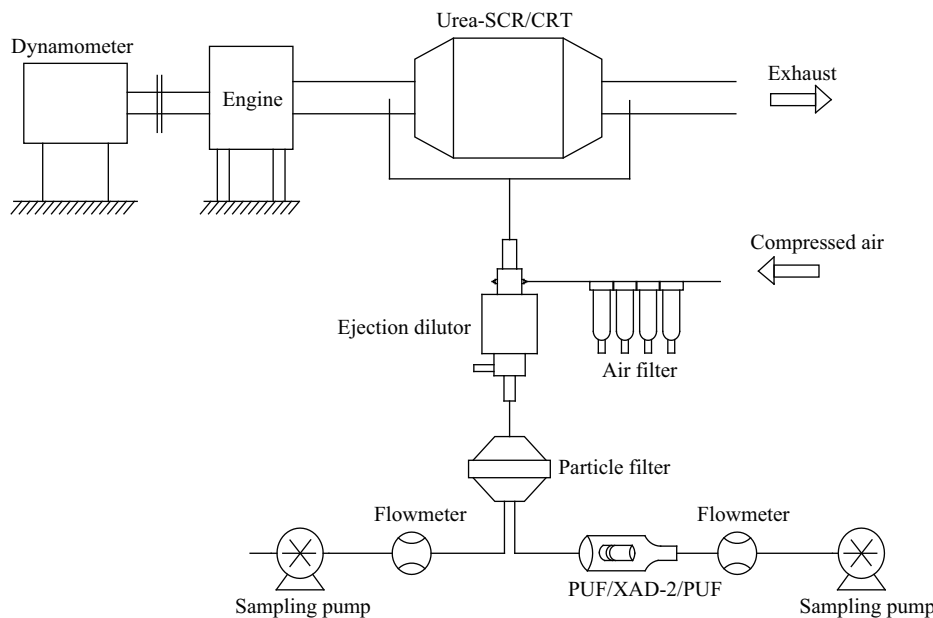


Fig. 1 Schematic of experimental setup.

Table 1 Specifications of the test engine

Parameter	Feature/Size
A*	64.3
B	75.2
C	84.4
50% $P_{max}$	42.5
70% $P_{max}$	60.2
$P_{max}$	84.9
Idle	0

\* A is the point between B and 50% of maximum power (50%  $P_{max}$ ), whereas B is the point between 50%  $P_{max}$  and 70% of the maximum power (70%  $P_{max}$ ), and C is the point between B and 70%  $P_{max}$ .

Table 2 Specifications of the test fuel

Properties	Diesel	Chinese standard
Sulfur content (ppm)	350	SH/T 0253-92
Density ( $\text{kg}/\text{m}^3$ )	841	SH/T 0604
Cetane number	52	GB/T 386-91
Lower heating value (MJ/kg)	42.8	GB/T 384
Viscosity ( $\text{mm}^2/\text{sec}$ ) at 20°C	4.0	GB/T 265
Carbon content (%)	87	SH/T 0656-98
Hydrogen content (%)	13	SH/T 0656-98
Oxygen content (%)	0	Elemental analysis

nology, so it was given the name BiTBlue-P (Shah et al., 2011). A urea tank, urea pump, injector, measuring unit, air assistant system, and catalyst are the major parts of this unit. The significant features of the pump are as follows: volume 20–1000 mL/min; 70 W; DC 24 V; and rated pressure 700 kPa. The injector specifications are as follows: No. of holes = 4; diameter of each hole = 0.5 mm; and injection angle = 90°. All the catalyzed honeycomb ceramic substrates of the catalyst are similar with a cell density of 62 cell/cm<sup>2</sup> (or 400 cells/in<sup>2</sup>). The diameter, length, and volume of the catalyst are 190 mm, 320 mm and 9.07 L, respectively. This SCR system has already been discussed by the authors in terms of its performance for the controlling of exhaust emissions such as NO<sub>x</sub>, CO, HC, number size distribution of particles, and carbonyls

(Shah et al., 2009), and volatile organic compounds (Shah et al., 2011), operating the engine under an 8-mode (ISO 8178 Type C1) steady-state test cycle (Shah et al., 2009).

In this study, a commercial CRT unit was used. The PM trapping efficiency of the unit and its effects on other regulated emissions such as CO, HC and NO<sub>x</sub> together with its impact on number-size distribution of particles, nuclei and accumulation mode particles, and the economy of the engine have already been addressed by the authors (Liu et al., 2011). The significant features/characteristics of the unit are given in Table 3.

### 1.3 Sampling and analysis of PAHs

The sampling process for PAHs was carried out for both particle and gas phases at a temperature below 52°C as per the sampling scheme shown in Fig. 1. The samples were drawn both upstream and downstream of the retrofits, and diluted using an ejection dilutor (Dekati, Finland). The diluted exhaust was taken using a battery-operated constant volume pump (Air Chek2000 SKC, USA) at a flow rate of 5 and 35 L/min for gas-phase and particle-phase PAHs respectively, with sampling time of 30 min. There was a flow meter downstream of the pump to control its flow rate.

In order to collect the gas-phase PAHs, a glass cartridge ‘PUF/XAD-2/PUF’ (Supelco, Orbo-1500, USA) was used, while a fiberglass filter was used for the collection

Table 3 Characteristics of continuously regenerating trap (CRT)

Parameter	Feature/Value
DPF substrate	Cordierite
DOC substrate	Cordierite
DPF Pt. content ( $\text{g}/\text{ft}^3$ )	35
DOC Pt. content ( $\text{g}/\text{ft}^3$ )	50
DPF cell density (cells/in <sup>2</sup> )	200
DOC cell density (cells/in <sup>2</sup> )	400
Diameter × Length (inch × inch)	8.5 × 14.0

DPF: diesel particulate filter; DOC: diesel oxidation catalyst.

of particle-phase PAHs. Prior to sampling, filters were cleaned in a muffle furnace at a temperature of 450°C for about 8 hr to prevent the presence of any organic material. The cleaned filters were pre-conditioned in a desiccator for 8 hr to remove any moisture content, and then weighed on an electronic digital balance (Mettler Toledo AT261, Switzerland). After sample collection, filters were placed again in a desiccator for 8 hr, and weighed to find out the net mass of the collected particles by the difference between the two weights. The sampled material was stored in a refrigerator at about -4°C till its subsequent extraction within 7 days.

A Soxhlet extractor was used for 24 hr to extract the sampled cartridge using dichloromethane (DCM), while an ultrasonic extractor was used three successive times (30 min each time) to extract the sampled filters. Both the gas-phase and particle-phase PAHs extracts were concentrated by a rotary evaporator (Kuderna-Danish). The concentrated sampled material was then cleaned up using a column chromatography procedure so that potential interferences would be removed before the analysis. For this, the sample was passed through a silica gel column at 2–3 mL/min speed. Finally, the re-concentration of the eluent was carried out again by (K-D) evaporator exactly to 1 mL, and then collected in a volumetric flask for the subsequent analysis.

The extracted liquid was placed in a 500 mL flask, then concentrated by a rotary evaporator (Kuderna-Danish evaporator) to 1 mL. The concentrated sample was cleaned up by passing it through a silica gel column at a speed of 2–3 mL/min as discussed earlier. The column which is connected to a solid-phase extraction (SPE) device was activated with 3 mL *n*-hexane. In order to wash PAHs retained on the silica gel column, a 15 mL mixture of *n*-hexane and DCM (volume ratio, 1:1) was added to the sample. Finally, the PAHs-washing liquid was concentrated by evaporator (K-D) exactly to 1 mL, and refrigerated until analysis.

PAHs were analyzed on the basis of EPA method TO-13A (1999), and determined by GC/MS (Agilent 6890N/5795C, USA). A capillary column HP-5MS with specifications (30 m × 0.25 mm × 0.25 μm) was used for the GC, while the oven temperature was programmed 80–160°C at 20°C/min, from 160–280°C at 5°C/min, and then kept at 280°C for about 10 min. The carrier gas was helium with a flow rate of 1 mL/min. For the MS, the ion source was electron impact (EI) at a temperature of 220°C, while the transfer line to MS was at 250°C. The acquisition/qualification mode of PAHs was selected ion monitoring (SIM). The curves were constructed under five-point calibration, with correlation coefficient of 0.999. Analysis of field blanks and recovery was carried out to guarantee the experiment reliability.

#### 1.4 Chemical analysis of PAHs

PAHs are grouped according to their number of rings as follows: Naphthalene (Nap) consists of 2-rings, while Acenaphthylene (AcPy), Anthracene (Ant) Fluorene (Flu), Acenaphthene (Acp), and Phenanthrene (PA)

carry 3-rings. Pyrene (Pyr), Fluoranthene (FL), Chrysene (CHR), and Benzo[a]anthracene (BaA) are composed of 4-rings, whereas Benzo[b]Fluoranthene (BbF), Benzo[a]Pyrene (BaP), Dibenzo[a,h]Anthracene (DBA), and Benzo[k]Fluoranthene (BkF) have 5-rings. Finally, Benzo[g,h,i]Perylene (BghiP) and Indeno[1,2,3-cd]Pyrene (IND) are made up of 6-rings. Furthermore, total PAHs can be divided into three groups depending on their molecular weight (MW), e.g., low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW). In this way, LMW species consist of 2–3 rings, MMW-PAHs have 4 rings, while HMW-PAHs are composed of 5–6 rings. Generally, the toxicity of PAHs increases with their molecular weights, which implies that gas-phase PAHs are less toxic as compared to PM-phase PAHs (He et al., 2010).

## 2 Results and discussion

In the current study, PAHs are discussed in terms of brake specific emissions (BSE), which is defined as the mass of pollutants emitted during one kilowatt power development of engine in one hour. The conversion/reduction (CR) of pollutants with SCR or CRT aftertreatment is given as follows:

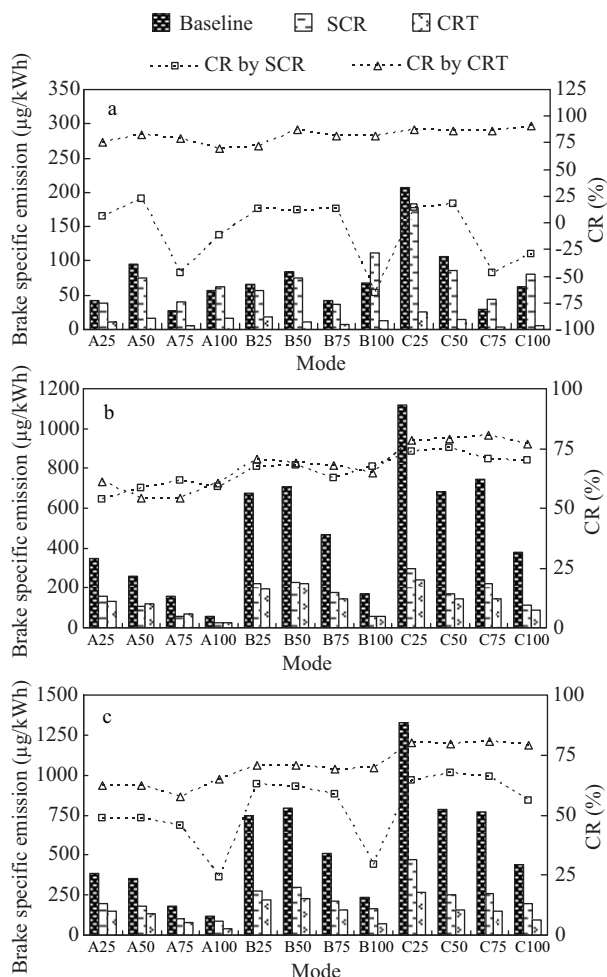
$$CR = \left( \frac{U_E - D_E}{U_E} \right) \times 100\% \quad (1)$$

where,  $U_E$  and  $D_E$  are upstream (baseline) and downstream (with aftertreatment) PAH emissions, respectively.

### 2.1 Phase-distributive analysis and conversion/reduction of PAHs

Figure 2a shows PM-phase PAH emissions and their respective CR at various modes in the ESC cycle. It is clear that CRT gave very good control of these emissions, and CR was from 71.8% to 90.7%. On the contrary, SCR remained unable to reveal any significant control of these emissions; even the CR was negative during most of the modes in the cycle. Particularly, at higher load modes SCR exhibited more negative conversion or reluctance to conversion, and thus CR was higher in terms of negative value. The decrease in PM-phase PAHs with CRT was an expected result owing to the filtration, and subsequent regeneration of the trap. The authors have already reported the remarkable reduction in PM mass and accumulation mode particles due to the removal of solid carbonaceous matter across CRDPF units (Liu et al., 2011). PM, basically, consists of four major substances such as elemental carbon, trace metals, inorganic ions and organic matter, and all of these compounds are decreased with CRT (Liu et al., 2008). The reluctance to conversion of PM-phase PAHs with SCR was probably due to the formation of ammonium sulfates at higher load modes, especially with the high sulfur fuel used in this study (Shah et al., 2011). Thus ammonium sulfate clogged the catalyst pores, and reduced the conversion of pollutants. Authors have also reported that urea-SCR has the potential to shift the number-size distribution of particles from smaller to larger sizes





**Fig. 2** PM-phase (a), gas-phase (b), and total PAHs (c) emissions before and after the retrofits along with their conversion/reduction (CR).

(Shah et al., 2009). Thus, larger size (accumulation mode) particles might be responsible for choking the catalyst. Further, it is probable that naphthalene and anthracene were converted to phthalic anhydride ( $C_6H_4(CO)_2O$ ) and anthraquinone ( $C_{14}H_8O_2$ ) solid particles respectively, particularly at higher loads where the catalyst temperature was conducive to their conversion on the  $V_2O_5$  catalyst. Phthalic anhydride and anthraquinone solid particles blocked the catalyst pores, and thus conversion of PAHs was adversely affected. However, it is not immediately clear whether conversion of naphthalene and anthracene are directly related with catalyst temperature. This issue will be undertaken separately, later in the current study.

Figure 2b presents gas-phase PAHs and their corresponding CR during various modes of the cycle. In this case, SCR and CRT both showed substantial reduction in pollutants, and CR was up to above 75% and 80%, respectively. The reduction in gaseous pollutants is attributed to the tendency of both catalysts of the retrofits to remove gaseous organic emissions prior to their adsorption on EC. In previous studies (Shah et al., 2009; Liu et al., 2011), authors have previously reported that gaseous hydrocarbons causing a major portion of gaseous PAHs are substantially reduced across CRT and SCR.

Figure 2c displays the total PAH emissions upstream and downstream of the retrofits. It is elucidative that total

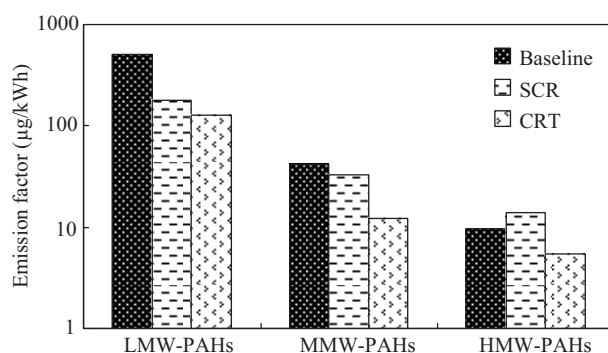
PAH emissions were greatly reduced across SCR and CRT, and CR varied from 24% to 67.5% and 57% to 80.7%, respectively. This overall appreciable reduction in total PAHs, especially with SCR, is ascribed to the substantial abatement of gas-phase PAHs, constituting a major portion of PAHs.

It is important to note that baseline PM-phase, gas-phase, and total PAHs were higher during low-load modes of the cycle. The trend was more uniform in the case of gas-phase PAHs, and hence in total PAH emissions. Furthermore, among the three speeds, i.e.,  $N_A$ ,  $N_B$  and  $N_C$  involved in the cycle, PAH emissions were, in general, higher at maximum speed modes. Higher PAHs at lower load modes are due to the higher HC emissions caused by higher values of the excess air-to-fuel ratio or lambda (Shah et al., 2009). Moreover, at low engine load the flame front is quenched in the clearance of the cylinder between top dead center and the piston top, which leads to an increase in PAH emissions (Collier et al., 1995). On the other hand, higher PAHs at higher speeds are most likely due to the adsorption of particles on the inorganic nuclei (such as sulfuric acid) formed by the oxides of sulfur and dilution air during the cooling process (Armas et al., 2008). Thus heterogeneous nucleation was promoted at higher exhaust temperatures caused by higher speed modes.

## 2.2 Molecular weight-based analysis of PAHs

Figure 3 presents the molecular weight-based analysis of PAHs. Total PAHs (PM and gas-phases) were calculated in accordance with weighting coefficients regulated by the ESC test (known as emission factors) for the baseline, SCR, and CRT retrofits. The emission factors of LMW-, MMW-, and HMW-PAHs in the case of the baseline engine were 502.2, 41.5 and 9.5 µg/(kWh), respectively. The respective emission factors with SCR were 178.6, 33.3 and 14 µg/(kWh), while with CRT they were 127.4, 12.1 and 5.4 µg/(kWh). In all the three cases, LMW-PAHs were predominant, while HMW-PAHs exhibited the minimum contribution to total PAHs. Since LMW-PAHs consist of 2–3 rings, while HMW-PAHs are made up of 5–6 rings, their respective maximum and minimum contributions to total PAHs are again expected results.

Due to their dominance, LMW-PAHs were further analyzed in terms of their RC within the same group. It is evident from Fig. 4 that naphthalene was the dominant



**Fig. 3** Total low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW)-PAH emissions.



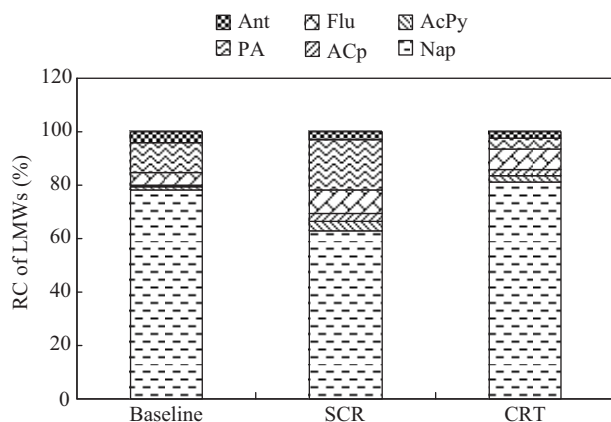


Fig. 4 Relative contributions (RC) of LMW-PAHs.

compound within the LMW-PAHs group with RC of 78.4%, 63.2%, and 81% in the case of baseline, SCR, and CRT, respectively. Since naphthalene has the lowest MW among LMW-PAHs, its highest RC was quite predictable. After naphthalene, phenanthrene was the next major contributor in the case of baseline and SCR showing respective RC of 11.2% and 18.6%, whereas fluorene was the subsequent major contributor in the case of CRT with RC of 7.5%. The next highest contributor was fluorene in the baseline and SCR cases with respective RC of 4.6% and 9.2%. The lowest contributor to LMW-PAHs were acenaphthene and then acenaphthylene for the baseline engine, while it was anthracene with both the retrofits. The variation in order of contribution of phenanthrene and fluorene with the two retrofits may be due to the difference in properties of the catalyst materials used in them, which leads to the variation in order of control. The lowest RC of anthracene, particularly with SCR, may be due to its conversion to anthraquinone, while the relatively higher RC of acenaphthene with both the retrofits is most likely due to the conversion of some other PAHs into these compounds.

### 2.3 Effect of catalyst temperature on naphthalene and anthracene

Figure 5a displays the effect of catalyst temperature on the conversion of naphthalene. It is evident that there was a strong correlation between catalyst temperature and naphthalene conversion rate. With increasing catalyst temperature, naphthalene conversion was increased and reached 50.2%, 59.4%, and 70% under the full load of the ESC test speeds  $N_A$ ,  $N_B$ , and  $N_C$  respectively, at which point the respective catalyst temperatures were at their peaks. Higher catalyst temperatures promoted the decomposition of naphthalene, thus leading to the higher conversion rate of naphthalene on the SCR catalyst.

Figure 5b presents the influence of catalyst temperature on the conversion of anthracene. Although the conversion rate was enhanced with increasing catalyst temperature, the increase was not significant. In fact, most of the cyclic modes revealed negative conversion or simply reluctance. Thus conversion fluctuated between -44.8% (Mode A25) to 30.7% (Mode C50) within the cycle. This maximum conversion at mode C50 is most likely due to the optimum

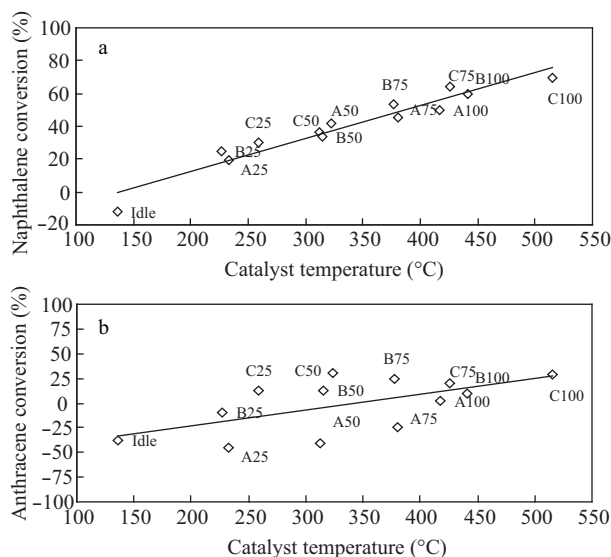


Fig. 5 Effect of catalyst temperature on naphthalene (a) and anthracene (b).

values of both catalyst temperature and space velocity because both the factors play a critical role in the conversion of pollutants.

From the above discussion, it is noteworthy that correlation of catalyst temperature with anthracene conversion is weaker than that of naphthalene. This leads to an important finding that the role of naphthalene in the deactivation of the SCR catalyst, particularly at higher load modes, is dominant as compared to anthracene. Thus our speculation made in Section 2.1 that naphthalene and anthracene were responsible for the fouling of catalysts owing to their conversion to solid particles seems to be valid, particularly in the case of naphthalene.

### 2.4 Toxicity analysis of PAHs

Table 4 presents the emission factors of various PAHs calculated on the basis of the weighting coefficients of

Table 4 Mean brake specific emission (BSE) of total PAHs with their corresponding TEF

PAHs	Mean BSE ( $\mu\text{g}/\text{kWh}$ )			TEF
	Baseline	SCR	CRDPF	
Naphthalene	414.643	129.223	107.627	0.001
Acenaphthylene	5.263	4.134	3.474	0.001
Acenaphthene	3.323	3.965	2.925	0.001
Fluorene	12.042	9.966	4.669	0.001
Phenanthrene	61.592	24.574	5.874	0.001
Anthracene	5.307	6.750	2.803	0.010
Fluoranthene	11.251	9.599	3.318	0.001
Pyrene	21.880	12.933	3.869	0.001
Benzo[a]anthracene	2.491	4.405	2.234	0.100
Chrysene	5.851	6.376	2.685	0.010
Benzo[b]fluoranthene	2.016	3.569	1.342	0.100
Benzo[k]fluoranthene	1.508	2.999	1.277	0.100
Benzo[a]pyrene	1.684	1.683	0.941	1.000
Indeno[123-cd]pyrene	0.950	1.358	0.457	0.100
Dibenzo [ah]anthracene	1.396	1.743	0.550	1.000
Benzo[ghi]perylene	2.388	2.659	0.869	0.010
$\Sigma$ Mean BSE	553.587	225.936	144.912	
Total BaP <sub>eq</sub>	4.442	5.011	2.217	

TEF: toxic equivalent factor.

the ESC cycle, and their corresponding toxic equivalent factors (TEFs). According to Nisbet and LaGoy (1992) and the US EPA (1993), TEFs are used to calculate the carcinogenic potency of all PAHs using the Benzo[a]Pyrene equivalent concentration (BaP<sub>eq</sub>). For this purpose, total BaP<sub>eq</sub> was evaluated as follows:

$$\text{BaP}_{\text{eq}} = \sum (E_i \times \text{TEF}_i) \quad (2)$$

where,  $E$  ( $\mu\text{g}/\text{kWh}$ ) is the emission factor of a certain PAH measured; and  $i = 1-16$ .

It is clear from Table 4 that the total emission factor of all the PAHs was greatly reduced with both the retrofits. The emission factor of BaP, the most carcinogenic PAH, was appreciably reduced with CRT, while it decreased marginally with SCR compared with the baseline engine. The CRT retrofit abated each individual PAH pollutant remarkably, whereas SCR could reduce only 2–3 ringed PAHs. The BaP<sub>eq</sub> emission factor followed the order of CRT < baseline < SCR. This leads to an important finding that the potential carcinogenicity of the compounds was outstandingly abated with the CRT unit. Although BaP and total emission factor were lower with SCR, BaP<sub>eq</sub> was higher compared with baseline engine. This is, no doubt, due to the increase in most of the MMW and HMW-PAHs with SCR, particularly those having higher TEFs. The reduction in total emission factor in the case of SCR is attributed to the considerable conversion of gas-phase PAHs across SCR. The reduction in BaP<sub>eq</sub> with CRT is due to its marked control of both PM-phase as well as gas-phase PAHs.

### 3 Conclusions

An SCR and CRT were independently retrofitted to a common rail diesel engine with an objective to characterize PAH emissions in all three cases, and hence to make a comparative analysis of them. Gas-phase pollutants were collected in 'PUF/XAD-2/PUF', while PM-phase PAHs were trapped in a fiberglass filter. A total of 16 PAHs were identified and quantified in the current study. The phase-distributive analysis, MW-based analysis, RC of LMW-PAHs, catalyst-temperature effect on some important PAH compounds, and finally BaP-based toxicity analysis of PAHs were addressed in the study.

Phase-distributive analysis of PAHs with CRT revealed an unmatched impact on the control of both PM-phase as well as gas-phase PAHs, thus CR varied between 71.8% and 90.7% for PM-phase and above 80% for gas-phase PAHs under the ESC test. On the contrary, urea-SCR was unable to serve the purpose of conversion/reduction of PM-phase PAHs. However, it exhibited a strong impact on the control of gas-phase PAHs. Relative to the baseline engine, the CR of total PAHs were 67.5% and above 81% with SCR and CRT, respectively. LMW-PAHs were predominant, whereas HMW compounds were lowest in all three cases. The emission factors of LMW-, MMW- and HMW-PAHs all decreased with CRT, while HMW-PAHs were higher in the case of SCR compared with the baseline engine. Naphthalene was the most abundant

compound in the LMW-PAHs of the baseline as well as the retrofitted engine, while acenaphthene and anthracene were the lowest contributors in the baseline and retrofit cases, respectively. Also, naphthalene exhibited a strong correlation with the catalyst temperature of SCR, and increased with increasing temperature. Furthermore, the BaP<sub>eq</sub> emission factor was greatly reduced with CRT, while it increased with SCR as compared to the baseline engine. Thus CRT demonstrated a marked control on the potential carcinogenicity of emissions.

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