Journal of Material Science and Mechanical Engineering (JMSME)
p-ISSN: 2393-9095; e-ISSN: 2393-9109; Volume 6, Issue 2; April-June, 2019 pp. 103-108

http://www.krishisanskriti.org/Publication.html

Study of the Effects of Diesel Oxidation Catalyst (DOC) on Emission Control in Diesel Engine - A Review

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Abstract—*Diesel engines are considered as one of the biggest contributors to environmental pollution and these are responsible for various health problems. Emission regulations are becoming more and more stringent for new vehicles but the issue of pollution from the older vehicles still needs to be addressed. In order to achieve the newer emission regulations by reducing the particulate matter, carbon monoxide(CO), hydrocarbon(HC) and nitrogen oxides (NO_x) emissions, the retrofitting of after-treatment devices in old vehicles has become necessary. This review article discusses about after treatment technologies with special focus on diesel oxidation catalyst (DOC) for the control of emissions in diesel engines.*
The results obtained from the study show that the DOC + (Diesel particulate filter) DPF + (Selective catalytic reduction) SCR retrofitting almost had no adverse effect on the performance of engine and fuel consumption. The use of DPF after DOC reduces the Particulate number (PN) and Particulate mass (PM) by an average of 91.6% and 90.9%, respectively. The DOC also increases the NO_2/NO_x ratio about to 40% which further increase the efficiency of DPF and SCR. When exhaust gases were passed through the SCR after DOC and DPF, significant decrease in NO_x emission was observed up to 85%. DOC reduces the CO and HC emissions by converting these emissions into CO_2 and H_2O by using oxidizing catalyst Platinum(Pt) and Palladium(Pd). Along with various benefits, a major problem is also associated with these oxidation catalysts. The sulphur content of fuel gets oxidized and converts into SO_2 to SO_3. Further, it reacts with water and forms harmful sulphates and sulphuric acid. So by using ultra low sulphur diesel(ULSD) the effectiveness of oxidation catalyst can be increased avoiding problems associated with its use. Thus, it is concluded that the use of DOC along with DPF and SCR will result in significant reduction in emissions.

Keywords: *Retrofitting, Diesel oxidation catalyst, Emission, Diesel engine*

Nomenclature:
DOC- Diesel oxidation catalyst
DPF- Diesel particulate filter
SCR- Selective catalytic reduction
HC- Hydrocarbon,
CO- Carbon monoxide
NO_x- Oxides of nitrogen
PM- Particulate Mass
PN - Particulate Number

1. Introduction:

Heavy-duty diesel vehicles have been widely used for their higher thermal efficiency, superior power capability and better economic performance throughout the world. But their abundant particulate matter (PM) and nitrogen oxide (NO_x) do harm to the environment as well as human health [1]. Particles, especially the fine ones accounting for most of typical particulate emissions generated by diesel engines, can be breathed into the alveolar region in human lungs and cause respiratory diseases [2]. NO_x, the main nitrogen-containing compound emitted by diesel engines, is mainly composed of NO and NO_2 [3]. Among them, the high concentration NO has adverse effect on human nerve center system, meanwhile the nitrite produced by NO is easy to be combined with haemoglobin and causes tissue hypoxia. [4].

In ideal case complete combustion of fossil fuel and air which results in emission of CO_2 and H_2O, which is rarely occurs in real, so in heavy duty diesel (HDD) engines, and other internal combustion engines as complete combustion can not takes place which leads to the formation of un-burnt hydrocarbons (HC), CO and also particulate matter such as soot in addition to CO_2 and H_2O.

The current European emission standard for HDD, which regulates emissions of CO, HC, NO_x, and particulate matter, is called Euro VI and was introduced in 2013. Neither date nor details of the next upcoming European emission standard are yet defined but the new limitations will with certainty further increase the need for the understanding of the after-treatment system. Therefore, the emission regulations have forced to install after-treatment devices includes DOC, DPF and SCR for Diesel engines to reduce CO, HC, NO_x, and particulate matter.

DOC is commonly used to oxidize carbon monoxide (CO) and Hydrocarbon (HC) Emissions as well as oxidize NO to NO_2, is employ to oxidize the particulate matter in Diesel particulate filter. The DPF is a cylindrical Ceramic structure which have thousands small channels, which is treated as efficient way to trap PM emissions in diesel engines [6].

Worldwide, Research scholars are done a many researches and reported that the integration of DOC and DPF would reduce to a greater extent of 90% the particulate emissions and change the particle size dispensation at the same time [7]. The upstream DOC is so important for the efficiency of downstream DPF, because DOC can increase the NO_2 proportion which could oxidize the particulate matter at higher rate [8]. DOC has a capability of reducing diesel particulate emissions by 20-65% by oxidize the soluble organic fraction(SOF), so that DOC have a better effect on decreasing SOF but had only a minor or no effect on soot [9]. By using a integration of DOC and DPF, not only the CO, HC but also reduce the emissions of PN and PM. As a reported that DOC+DPF system can reduce more than 45% of CO, 80% of HC and 90% of soot emissions from the test Diesel engine [10]. On the other hand, as many research scholars published that, while the application of SCR reduced NO_x emissions efficiently.

Although the DOC+DPF+SCR has proved to be an efficient after treatment system to decrease the particulate matter emissions and NO_x simultaneously, and it will be standard configuration for EURO VI emission standard diesel vehicles. However, there are large number of vehicles running on the road without after treatment devices in developing countries. On one hand, these vehicles are so important for development and construction so it is not easy to eliminated in short term. On the other hand, these vehicles emits emissions heavily specially NO_x and PM, so there is need to save the environment there is need of the apply of after-treatment devices in exhaust of diesel engine. Worse, there are so limited reports available of retrofit in-use diesel engine at present time.

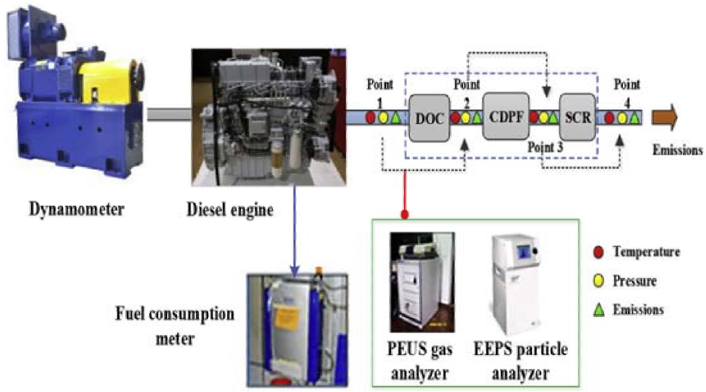

Fig.1: Schematic diagram of experimental system.[11]

Table 1 shows the Euro standards for M1, M2 and N1, N2 vehicles as defined in directive 70/156/EC with reference mass ≤ 2610 kg. There limit are defined as mass per energy (g/kWh). Regulations in Euro standards has been become more precise in the next future years. Comparison of Euro I to Euro VI standard as shown in table, there is clear fact that the standard for emissions like CO, HC, NO_X and PM has been decreased respectively 66, 76, 95 and 98%. The implementation date of Euro VI standard for heavy-duty vehicles was 1st of September 2014.

Table 1 Euro standards of European Union for heavy-duty vehicles [12]

	HC (g/kWh)	CO (g/kWh)	PM (g/kWh)	NO_X (g/kWh)
Euro I	1.1	4.5	0.61	8.0
Euro II	1.1	4	0.15	7.0
Euro III	0.66	2.1	0.13	5.0
Euro IV	0.46	1.5	0.02	3.5
Euro V	0.46	1.5	0.02	2.0
Euro VI	0.13	1.5	0.01	0.4

2. The role of DOC in the after-treatment system:

The diesel oxidation catalyst (DOC) is a satisfactory erected technology to decrease CO and HC emissions from diesel engine that has been in use since the 1960s. The Higher emission standards have made the importance of the DOC even greater in recent years since it has become an indispensible component for enhancing the performance of diesel particulate filters (DPF) and selective catalytic reduction (SCR) catalysts by utilization of oxidation of NO to NO_2.

Three reactions are desirable in the DOC; the oxidation of CO to CO_2, the oxidation of HC to CO_2 and the oxidation of NO to NO_2. In other words, the DOC does not remove NO_x but adjusts the NO_2/ NO_x ratio which is important later in the after-treatment system [13].

$CO + 1/2\ O_2 \rightarrow CO_2$.. (1)

$NO + 1/2\ O_2 \rightarrow NO_2$.. (2)

$C_3H_6 + 9/2\ O_2 \rightarrow 3CO_2 + 3H_2O$.............................(3)

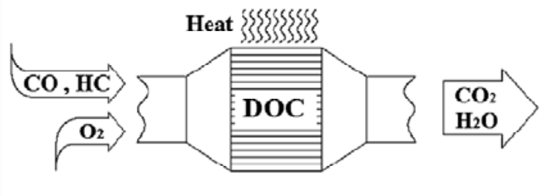

Fig. 2: Flow Diagram of Diesel oxidation catalyst[14]

Figure 3 shows a simple layout of an after-treatment system used for heavy duty diesel vehicles supported urea-SCR for controlling NO_x emissions. The fully oxidation of HC and CO emissions takes place When the DOC works at its ideal conditions and the pollutants left are NO_x and particulate matter (PM) and particulate number. The working of DPF is that it trapped the PM which is depending on that it is passively or actively regenerated(PM oxidation) the DOC plays different roles. The Temperature was periodically increases, if active DPF regeneration is takes place so that PM can be reduced by O_2 [15]. In this case the DOC is used to combust the temporarily increased HC content which increases the temperature. If passive DPF regeneration is used, on the other hand, the DOC have be needed to provide NO_2 that enables PM oxidation at lower temperatures.[15] For better fuel efficiency the passive generation DPF is preferable.

As shown in fig.3 In the SCR, by the decomposition of injected urea with NH_3 , NO_x will be reduced to N_2. The reaction occurred here is the so called fast SCR reaction where consumption of NO and NO_2 takes place in equal amounts [16]. The above reactions in the SCR will be dependent on the NO_2/ NO_x fraction out from the DOC. As shown in fig.3 the final component in after treatment system is the ammonia slip catalyst (ASC). In the ASC reduction of NH_3 in to N_2 takes place which is not consumed in the SCR and also NO_x where N_2 is the preferred product.

In the future some legislations also include CO_2 limits in emission standards [17]. This may make a necessary of more complete combustion in the engine which will increases the production of NO_x further and thereby increase the demand for NO_x reduction in the after treatment system.

DOCs are used not only in heavy-duty vehicles but also used in light-duty vehicles as a emission control systems, in many countries such as USA, Europe, and Japan. The oxidation catalysts containing Platinum and Palladium are the most prominent catalysts in world market.

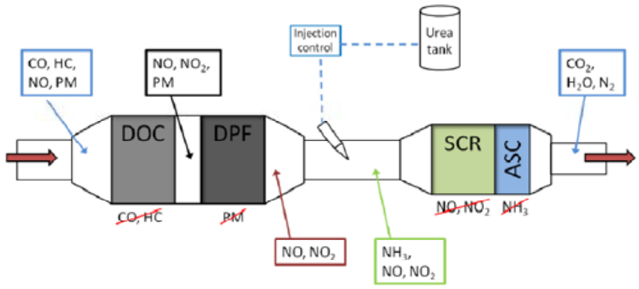

Fig.3: Typical layout of an after-treatment system used for heavy duty diesel vehicles[18]

One of the biggest problems of these valued catalysts is that they carried reaction of SO_2 to SO_3 which consequently react with water and produces forms of sulphates and sulphuric acid. These forms have quite harmful effects like damaging the after-treatment emission control systems along with create several environmental and health problems. There is no technology to keep from happening and eliminate these forms. Even Though Ultra low sulfur diesel (ULSD) is used in many countries worldwide, the problem could not be solved completely. Using alternative fuels as biodiesel, alcohol etc., can completely reduce or remove this pollutant. In addition, it should be possible to increase the conversion efficiency of DOC using of alternative fuels [19].

To conclude the DOC is an integral part of the after-treatment system today and will with certainty continue to be so in the future.

3. Effect of DOC on performance & emission characteristics:

Yunhua Zhang et al. investigate an experiment on 6 cylinder diesel engine by using with and without of DOC+CDPF+SCR and finding some results of performance and emission characteristics which is shown below:

4.1 Power and fuel consumption characteristics: Fig.4 shows that the torque of engine with and without of DOC+CDPF+SCR under a different load of 2300 RPM. As shown in Fig. 5, the engine torque increased with the increase of load. And due to the installation of DOC+CDPF+SCR led to a decrease of 1.75% on average for the engine torque, which conclude that the retrofit has a little bit negative effect on the engine power performance.

Fig. 6 reflects the fuel consumption of the engine under different loads at 2300 rpm with and without the installation of DOC+CDPF +SCR. The retrofit caused a slight increase of the fuel consumption by 1.58% on average under different loads, which could be negligible.

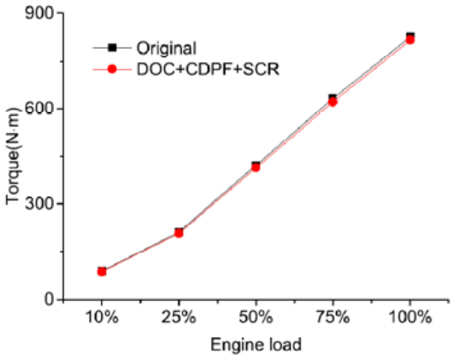

Fig.4: Torque under different loads.[11]

4.2 Particulate emission characteristics:

4.2.1 ***PN emissions*****:** As shown in fig.6 the filtration efficiency and PN emissions under different loads. As increase the load the PN emissions increased from 4.45 x 10^{12} to 1.15 x 10^{13}. As the load increases the quantity of fuel is increased, so that air-fuel ratio is decreased. Due to decrease of air fuel ratio, the degree of incomplete combustion is increased, so that concentrations of PN emissions increased [20].

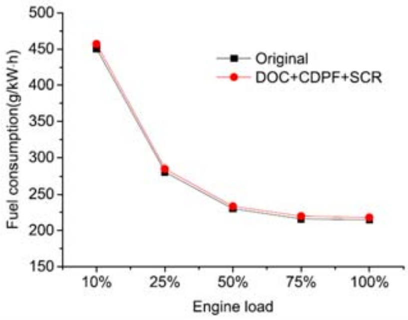

Fig.5: Fuel consumption under different loads.[11]

After the engine was retrofitted with DOC+CDPF+SCR, the PN concentrations are reduced significantly from 1 to 2 orders of magnitude. The upstream DOC should bring a 40–60% decrease of the PN emissions, which had been increased with the increase of the load.

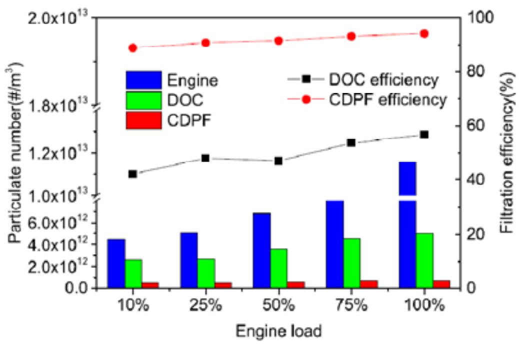

Fig.6: PN emissions and filtration efficiencies[11]

The filtration efficiency of CDPF is more than 90% except the load of 10% at which filtration efficiency is 88%. It was observed that the trapping efficiency increased with the load and attained a 91.6% reduction of the PN on average with different loads. The higher filtration efficiency is obtained due to the fact that the upstream DOC has a strength of oxidizing SOF in particulate matter and the downstream wall-flow CDPF shows the best trapping performance for the PN [21]. The ability of the DOC to oxidize SOF is dependent on the exhaust temperature, as well as the catalytic activity of the CDPF [22].

4.2.2. PM emissions: As shown in fig.7 the filtration efficiency and PM emissions under different loads. Similar to PN trend, As increase the load the PN emissions increased from 0.35 mg/m^3 at 10% load to 1.06 mg/ m^3 at 100% load. As the load increases the quantity of fuel is increased, so that air-fuel ratio is decreased. Due to decrease of air fuel ratio, the degree of incomplete combustion is increased, so that concentrations of PN emissions increased. When the engine retrofitted with DOC+CDPF+SCR, the PM decreased significantly. The filtration efficiency of the DOC on PM increased with the load from 14.5% at 10% load to 40.9% at 100% load and the average efficiency was 31.4%. In the downstream of the CDPF, the PM decreased more than 90% except 10% load with a drop of 87.7%. The filtration efficiency increased with the load due to higher oxidation activity of the DOC and CDPF induced by increasing exhaust gas temperature.

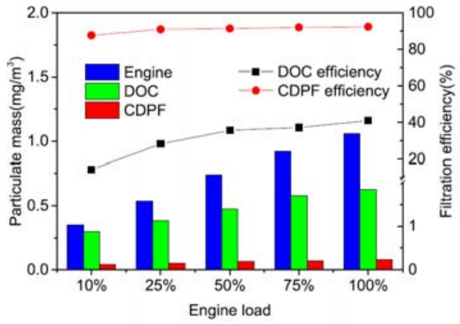

Fig.7: PM emissions and filtration efficiencies[11]

4.3 Nitrogenous compounds emission characteristics:

4.3.1 ***NO_x emission:*** The NO_x emissions under different loads is shown in Fig.8. It was shows that the NO_x emission is increased with the load from 487.22 ppm at 10% load to 1657.53 ppm at 100% load. The reason behind that is to increasing the in-cylinder temperature of the engine. Compared this results with the downstream of DOC and CDPF there is slightly decreased in the NO_x but follows the same trend with the Load. This happen due to fact that the porous structure of catalyst coating adsorbed some part of NO_x and stored them in form of nitrates and nitrites [23]. The NO_x emission of downstream SCR decreased significantly and kept below 160 ppm. The reduction of emissions happen due to the following two reactions [24]:

$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$............................. (3)
$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$.............................(4)

4.4 CO and HC emissions: Mitsuru Hosoya et al. investigates an experiment on a Turbo Charged Diesel engine using with or without of different types of catalyst with different loading of Pt and Pd.

Catalyst C : Palladium (Pd):14.2 g/ft^3

Catalyst D : Platinum (Pt): 2.8 g/ft^3

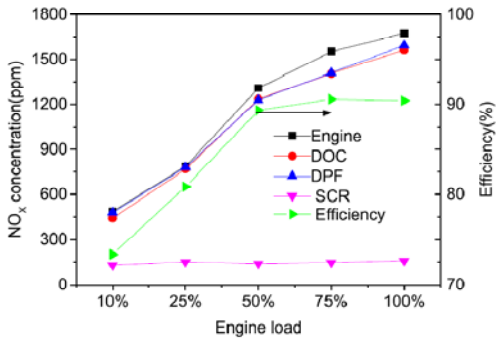

Fig.8: NO_x emission under different loads.[11]

The effects of different catalyst loading shown in Fig.9. Catalyst C and catalyst D were evaluated on the 6.5-l TC-engine using low sulphur fuel (sulphur content: 0.04 wt.-%). The results are shown in Fig. 10. Particulate reductions were very high, catalyst C at 21% and catalyst D at 19%. HC reduction was 45% for catalyst C and 65% for Catalyst D. CO reduction was 28% for catalyst C and and 57% for catalyst D [25].

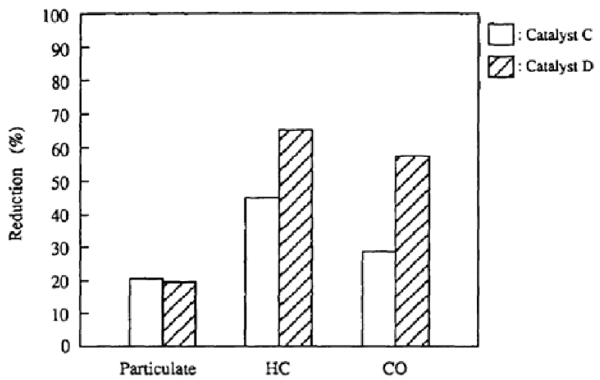

Fig.9: The effects of oxidation catalyst C and oxidation catalyst D for a TC-engine.[25]

5.CONCLUSIONS:

To reduce the pollutions in-use engines, this review paper projected a retrofit of DOC along with DPF and SCR, and their look into the fuel economy, torque and emission characteristics of a heavy-duty in-use diesel engine. The following emissions PM, PN, NO_x and CO, HC emissions are analyzed by using of DOC+DPF+SCR and compare with original enigne without Retrofitting. The conclusions are as follows:

- Diesel emissions from heavy-duty in-use diesel engine have embossed the health and welfare worries, but using a number of retrofit technologies exists or being developed that can greatly reduce the emissions from diesel-powered vehicles.
- Diesel oxidation catalysts can decrease PM emissions from 20 to 50 percent, CO and HC (including toxic emissions) greater than 90 percent, and substantially reduce smoke and odour from diesel engines. Fuel sulphur levels should below 500 ppm (0.05% wt) are recommended. Low level of sulphur improve the emission control performance of an oxidation catalyst.
- DOCs are used not only to reduce CO and HC emissions, but also to impact a significant effect on the performance of DPF and SCR after using with DOC.
- After retrofit the results was obtained by researchers that the power is decreases by 1.75% and the fuel consumption increases by 1.58%, which shows that fuel economy and power was not so much influenced by retrofit.
- The use of DPF after DOC reduces the Particulate number (PN) and Particulate mass (PM) by an average of 91.6% and 90.9%, respectively. The DOC also increases the NO_2/NO_x ratio about to 40% which further increase the efficiency of DPF and SCR. When exhaust gases passed through the SCR after DOC and DPF decreases NO_x emissions to about 85%.
- One of the biggest problems of these valued catalysts is that they carried reaction of SO_2 to SO_3 which consequently react with water and produces forms of sulphates and sulphuric acid. These forms have quite harmful effects like damaging the after-treatment emission control systems along with create several environmental and health problems. Even Though Ultra low sulphur diesel (ULSD) is used in many countries worldwide, the problem could not be solved completely.

Acknowledgements:

We are thankful to all the researcher who performed experiments that is the base of this review paper, also grateful to Mr. Pushpendra Kumar Sharma, Sumit Sharma and Digambar Singh, Deepak Jain, research fellow MNIT jaipur for english proofreading.

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