Sādhanā Vol. 34, Part 3, June 2009, pp. 467–481. © Printed in India

Development and test of a new catalytic converter for natural gas fuelled engine

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MS received 18 October 2007; revised 25 January 2009

Abstract. This paper presents characteristics of a new catalytic converter (catco) to be used for natural gas fuelled engine. The catco were developed based on catalyst materials consisting of metal oxides such as titanium dioxide (TiO_2) and cobalt oxide (CoO) with wire mesh substrate. Both of the catalyst materials (such as TiO_2 and CoO) are inexpensive in comparison with conventional catalysts (noble metals) such as palladium or platinum. In addition, the noble metals such as platinum group metals are now identified as human health risk due to their rapid emissions in the environment from various resources like conventional catalytic converter, jewelers and other medical usages. It can be mentioned that the TiO_2/CoO based catalytic converter and a new natural gas engine such as compressed natural gas (CNG) direct injection (DI) engine were developed under a research collaboration program. The original engine manufacture catalytic conveter (OEM catco) was tested for comparison purposes. The OEM catco was based on noble metal catalyst with honeycomb ceramic substrate. It is experimentally found that the conversion efficiencies of TiO_2/CoO based catalytic converter are 93%, 89% and 82% for NO_x, CO and HC emissions respectively. It is calculated that the TiO_2/CoO based catalytic converter reduces 24%, 41% and 40% higher NO_x, CO and HC emissions in comparison to OEM catco respectively. The objective of this paper is to develop a low-cost three way catalytic converter to be used with the newly developed CNG-DI engine. Detailed review on catalytic converter, low-cost catalytic converter development characteristics and CNGDI engine test results have been presented with discussions.

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Keywords. Catalyst; emissions; CNG-DI engine; OEM catco; TiO_2/CoO.

1. Introduction

Conventional natural gas engines are facing problem with in-cylinder combustion as they produce higher unburned hydrocarbon (HC) and carbon monoxide (CO) emissions. The NO_x emission either increases or decreases, as it strongly associated with in cylinder fuel combustion temperature characteristics that depend on air–fuel ratio and fuel injection system (Scott *et al* 2004). However, the gaseous pollutants from engine exhaust can be reduced either by thermal or catalytic system. In order to oxidise HC and CO gases using thermal system, a residence time of greater than 50 ms and temperature excess of 600°C to 700°C are required (Heywood 1989). Temperature high enough for some homogeneous thermal oxidation can be obtained by spark retarded (with some loss in efficiency) and insulation of the exhaust ports and manifold. The residence time can be increased by increasing the exhaust manifold volume to form a thermal reactor. However, this approach has limited application (Heywood 1989). Hence, the catalytic converter will be the easiest way to reduce exhaust pollutants.

A catalytic converter is a device used to reduce the exhaust pollutant gases from an internal combustion engine. The catalytic converter is placed between engine manifold and exhaust tailpipe. Pollutant gases flowing out of the engine pass through it and undergo chemical processes by which they are converted into relatively harmless gases. Gas flows through the passages and reacts with catalyst within the porous washcoat. It can be said that a catalytic converter consists of steel cover plate or steel box, monolithic substrate (used to make tubular walls), washcoat (as binder) usually alumina on which catalyst materials like Pt, Rh, Pd, TiO_2/CoO are dispersed with various ratio(s). Apart from catalyst materials, CeO_2, or CeO_2-ZrO_2 mixed oxides are also added in the washcoat of three way catalytic (TWC) converter for improved oxygen storage capacity and thermal stability of alumina (Osawa 1998; Kaspar *et al* 1999).

Continuous exposition of the catalytic converter to high temperature may cause an alteration on its components that lead gradually to its deactivation (Poulopoulos & Philippopoulos 2004). The thermal aging of the catalytic converter may have an undesirable impact on both catalyst substrate and noble metal load in various ways. For operation temperatures of the catalytic converter above 600°C, Rh_2O_3 reacts with alumina to form inactive $Rh_2Al_2O_4$ (Forzatti & Lietti 1999), while above 700°C, Pt sintering occurs. For temperatures higher than 900°C, sintering of γ-Al_2O_3 and alloying of the noble metals may occur. At even higher temperatures, severe sintering of γ-Al_2O_3 undergoes as a result of its crystalline phase, transformation into another as δ-Al_2O_3 or α-Al_2O_3, with a decrease in the alumina surface area. The formation of α-Al_2O_3 is accompanied by mechanical tensions which may cause substrate fragments and noble metal losses. Thermal deactivation is normally irreversible, although redispersion of the sintered metal surface is possible (Angelidis & Papadakis 1997).

The conventional catalyst materials are mainly noble metals or platinum group metals (PGMs). The PGMs comprise the rare metals such as platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). All these materials have the common properties like inert as regards biological reactions or less chemical reactions; and to be immobile. However, the recent studies show that the application of these materials have been extensively increased in vehicle exhaust catalyst, industry, jewelerys, anticancer drug, in dentistry as alloy that cause their anthropogenic emission and spread in the environment. Platinum content of road dusts can be soluble and consequently it enters the waters, sediments, soil and finally the food chain. In addition, PGMs have also been associated with asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis and other serious health problems in humans (Kielhorn *et al* 2002; Merget & Rosner 2001; Ravindra *et al* 2004; Whitely & Murray 2003).

In this investigation, a new type of catalytic converter based on CoO/TiO_2 materials has been developed with wire metal substrate to oxidize/reduction emissions from CNGDI engine. The advantages of this catalytic converter are stated as low-cost, domestically available and higher substrate area which is efficient to oxidize/reduction emission as compared to conventional catalytic converter.

2. Catalyst and substrate preparation

2.1 *Material selection for catalyst*

In this study, several stock solutions with different aqueous molar ratios and weight ratios were used. Titanium dioxide and cobalt oxide were used as a metal oxide catalyst. The pure cobalt oxide is used as the reducing agent and titanium dioxide is the oxidizing agent. Its inertness to sulphate formation and surface properties makes it preferred carrier in selective catalytic reduction of NO_x from the stationary pollution sources.

2.2 *Catalyst slurry preparation*

Sodium silicate solution and sodium metabisulphate were used in wash coat material to increase the coating strength to surface of woven stainless steel substrate. Ninety grams of sodium silicate solution was added into 10·0 gm TiO_2 to get 10% TiO_2 slurry. The slurry was then stirred at 500 rpm for two hours. Two grams of CoO and 1·0 gm of sodium metabisulphate were gradually added. To ensure homogenization, it was milled for around 6·0 hours by using ball mill at 1400 rpm and then dried frozen at temperature 23°C for 24 hours. Slurry reactor preparation was done as suggested by (Nijhuis *et al* 2001) and compared with monolithic reactor as described in (Avila *et al* 2005) and (Heber 1991). The figure 1(a) shows the prepared catalyst slurry.

2.3 *Material selection for substrate*

The substrate material is stainless steel, as it is widely used in the automotive exhaust system not only due to its advantages in mechanical and physical properties but also low-cost (Bode *et al* 1996). The stainless steel wire mesh was cut to a circular shape with a diameter of 7·0 cm prior to catalyst coating. Figure 1(b) shows the wire mesh substrates.

2.4 *Treatment of wire mesh substrate*

The wire mesh substrates were immersed into a preparation of 10% HCl solution for 30 minutes to remove all the impurities. It was then rinsed in distilled water before being dried in an oven at temperature of 100°C. The drying process takes about 1·0 h before coating it with catalyst.

2.5 *Wash coat material*

Titanium dioxide, TiO_2 served dual functions: a reduction catalyst and a titanium substance for the wash coat. Rutile form of TiO_2 was chosen because of its thermal stability from 500°C and high durability. This property is suitable for catalyst embedment or catalyst as described in (Alois 1995).

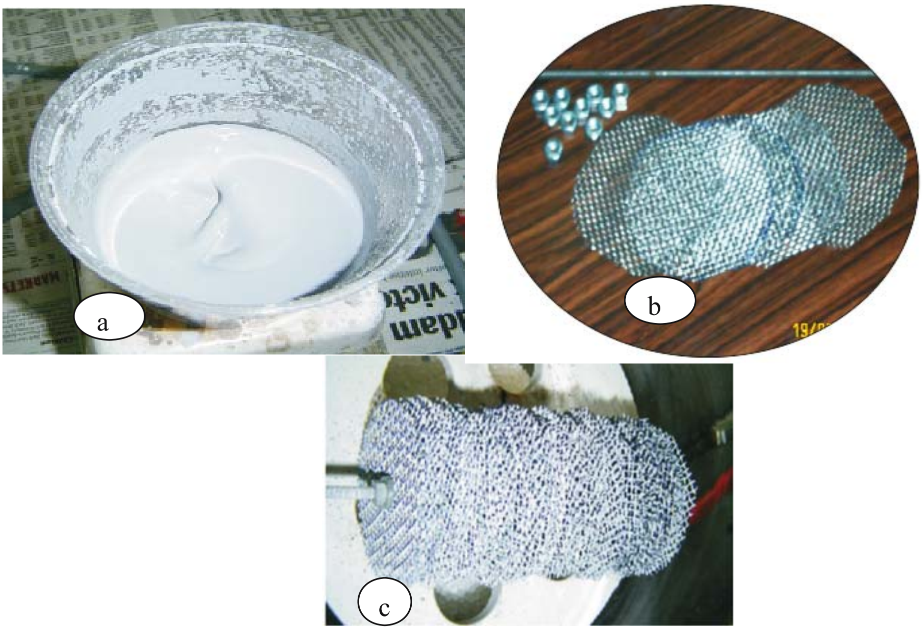

Figure 1. **(a)** Finished mixture of metal catalyst and wash coat slurry, **(b)** wire mesh substrates are cut in circular shape, **(c)** arranged calcined wire mesh substrate.

2.6 *Substrate coating*

The stainless steel wire mesh was then coated with the metal catalyst via dipping technique. Figure 1(c) shows coated wire meshes that are calcined. In this process stainless steel wire mesh was immersed into prepared catalyst slurry for the duration of 5·0 minutes. Then the coated wire mesh was removed from catalyst slurry to be blowered using air at the speed of 1·0 l/min until the unwanted residual catalyst was evaded from the surface of the stainless steel wire mesh. After blowered process, coated stainless steel wire mesh was dried in an oven at temperature 120°C for 12·0 h before being calcined in a muffle furnace. Calcination is a process in which a material is heated to a high temperature without fusing, so that hydrates, carbonates, or other compounds are decomposed and the volatile material is expelled. Calcinations take 6·0 hours at a temperature of 550°C with temperature ramping upon 10·0°C/min and holding time of a 300 minutes. After the calcinations process the stainless steel wire mesh were arranged into straight bar to become a substrate for use as a catalytic converter.

3. Catalytic converter fabrication

3.1 *Catalytic converter (catco) chamber*

The fabrication of catalytic converter consist of few components, namely the converter chamber, substrate and insulator. The catalytic converter casing and chamber remain as same as originally installed into the vehicle system. The same outer dimensions were purposely fixed in order to avoid redesign of the existing exhaust system, which then required further thermal optimization and design validation studies.

Figure 2. **(a)** Wire mesh substrate configurations, **(b)** wire mesh substrate in catalytic converter casing.

3.1a *Substrate:* The stainless steel wire mesh pieces were then coated with metal catalyst before arranged onto a straight bar. The length of stainless steel wire mesh arrangement was around 10·0 cm. The gap between the each pieces of stainless steel wire mesh was around 0·1 cm each that was created by using the stainless steel washer. Size of the washer used in this study was 1·0 cm in diameter and 0·6 cm of hollow diameter with thickness around 0·1 cm. Stainless steel bars which was used as a wire mesh support which was a screw type bar with a diameter of 0·4 cm and 14·0 cm length. A total of 50 pieces were used in an arrangement for 10·0 cm length. The stainless steel wire mesh substrate configurations are shown as in figures 2(a) and (b). The original Proton honeycomb ceramic substrate and casing are shown in figures 3(a) and (b).

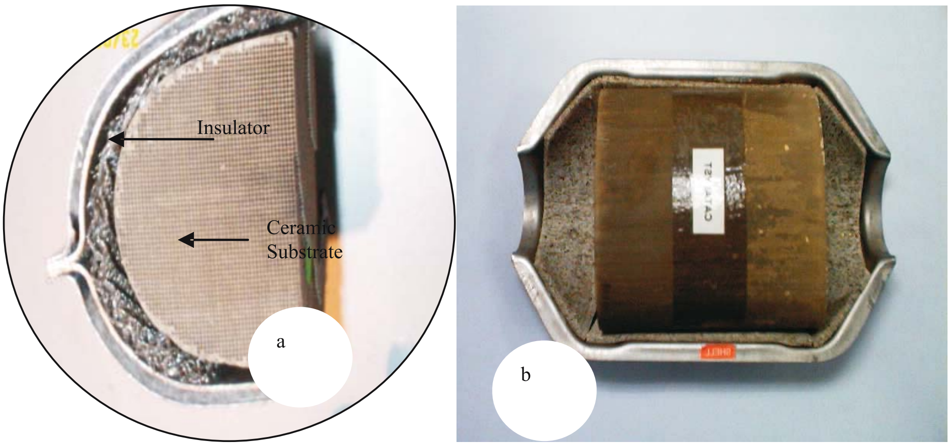

Figure 3. **(a)** Original proton honeycomb ceramic substrate and **(b)** casing for honeycomb ceramic substrate.

Figure 4. Modified and original catalytic converters.

3.1b *Insulation layer:* Beside the catalytic converter chamber and substrate, mat (An aluminum net wrap layers of glass wool called as mat) also plays an important part in catalytic converter. The mat is rolled with press machine to reduce the thickness as required. The width of the mat was made to cover whole wire mesh stainless steel substrate inside catalytic converter body as insulation for vibration. Figure 4 shows modified and original catalytic converters.

Table 1 shows summary of the TiO_2/CoO based catalytic converter and original OEM catalytic converter specifications. It can seen that the catalyst volume for both catalytic converters were 1·6 litre but the specific area of TiO_2/CoO based catalytic converter was 25 times higher than original catalytic converter. Figure 5 shows the summary of catalyst into substrate preparation.

4. Catalytic converter characterization study

The TiO_2/CoO catalyst characterization study was conducted with the following equipments –

(i) The oxidation and reduction study were carried out using the equipment of Thermo-Finnigan TPO/TRO system. The details procedure of oxidation/reduction activity can

Table 1. Summary of the catalytic converter specifications.

Specification	New catalytic converter (Wire mesh catco)	Original catalytic converter (OEM catco)
Substrate material	SUS 304 Wire mesh	Cordierite-ceramic
Specific surface area, cm^2	7560	300
Wash coat	TiO_2, Titania	Al_2O_3, Alumina
Catalyst	CoO/TiO_2	Pt/Pd/Rh
Catalyst loading (g/cu.ft)	$10 + 2$, $TiO_2 + CoO$	1·13 Pt/Rh
Catalyst volume (liter)	1·6	1·6

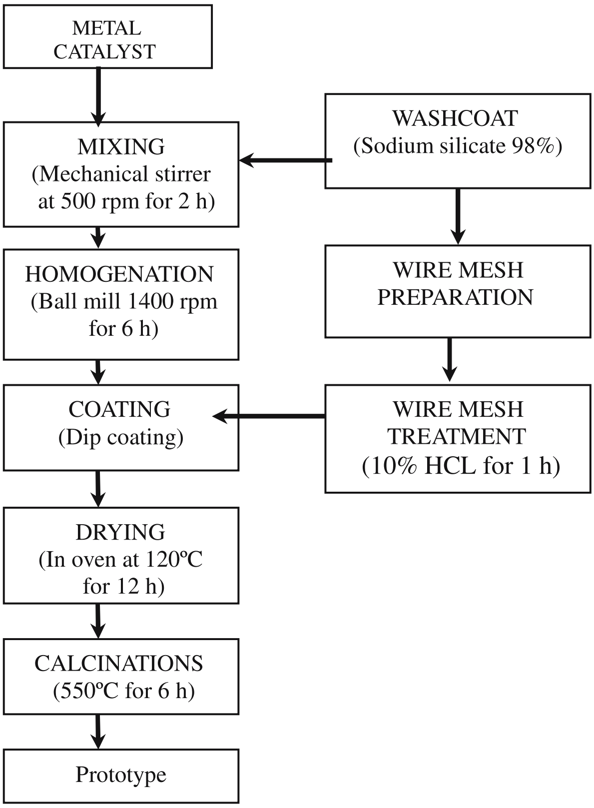

Figure 5. Summary of catalyst and substrate preparation.

be found elsewhere (Akula & Mike 2004; Eric *et al* 1996; Umit *et al* 1998; Fuad 2006).

(ii) Catalyst crystalline phase was identified using a X-Ray diffractometer (Siesens D500). The detailed procedure can be found in (Ettireddy & Rajender 2004).

(iii) Catalyst surface such as topography, morphology and composition were determined using a scanning electron microscope (SEM) (Hitachi S2700).

(iv) Catalyst weight loss was measured using a Thermo gravimetric analyzer (TGA).

(v) A test was conducted (Fuad 2006) to determine the pressure loss across the woven stainless steel wire mesh substrate. The minimal pressure loss could indicate its capability to store oxygen from random gas flow within the substrate in comparison to flow through original cordierite ceramic substrate. It was found that the maximum pressure loss difference only 0·07 psi at the maximum flow rate of 5 l/min with open throttle condition.

4.1 *Reaction in catalytic converter*

Gases from exhaust port entered into TWC is referred to as feed gases such as HC, CO, NO_X, CO_2. In the catalytic converter two chemical processes are occurred such as catalytic reduction and catalytic oxidation.

In the catalytic reduction process, nitrogen oxide gives up its oxygen to form pure nitrogen. Then the free oxygen reacts with CO to form CO_2 emission. In the oxidation process,

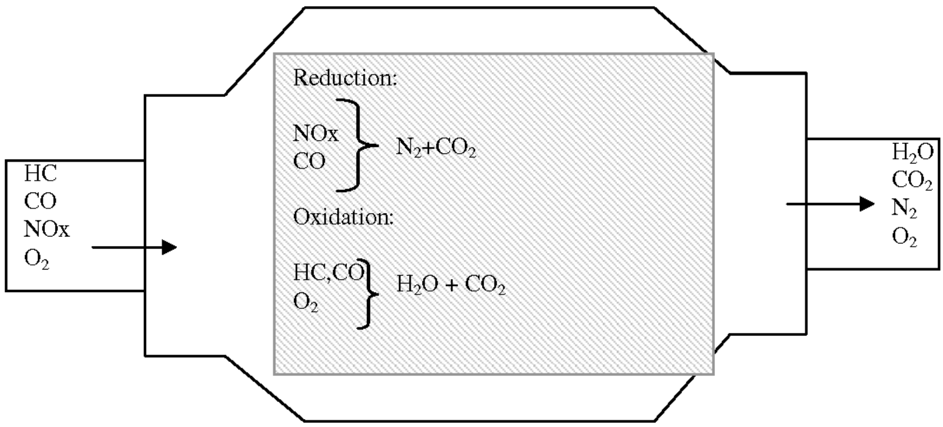

Figure 6. Oxidation and reduction process into catalytic converter.

hydrocarbons and carbon monoxide continue to burn. This occurs only if there is a sufficient amount of oxygen available for the hydrocarbons and carbon monoxide to form with. This chemical reaction results in oxidation of hydrocarbons and carbon monoxide to form water (H_2O) and carbon dioxide (CO_2). Detailed of catalytic reduction and oxidation phenomena can be seen in figure 6.

5. Catalytic converter test on a CNG–DI engine

Both of the catalytic converters such as conventional catalytic converter based on Pt/Rh and new catalytic converter based on CoO/TiO_2 catalyst were tested at Engine and Fuel Testing Laboratory, Department of Mechanical Engineering, University of Malaya. The catalytic converter fabrication was done at University Technology of Mara, Malaysia. The test engine was a multi-cylinder compressed direct injection compressed natural gas engine. It can be mentioned that both the catalytic converter and CNG-DI engine were developed under a research collaboration program. The CNG-DI engine has been developed from modification of a gasoline engine. The major modifications of the engine are: (a) changing compression ratio from 10 to 14, (b) changing gasoline fuel injection to direct injection compressed natural gas system, (c) high energy spark plug instead of normal spark plug. The displacement of the engine is 1597 cm^3. The bore and stroke are 76 mm and 88 mm respectively. The maximum brake power of the engine was achieved as 73 kW at 6000 rpm. The details specification of the engine can be seen in (Kalam 2007).

Horiba exhaust gas analyzer was used to measure the exhaust pollutants concentration. The engine was tested at wide open throttle (WOT) from speed range from 1500 rpm to 6000 rpm. However, the test were also conducted for 50% throttle and 50 Nm load conditions. The engine was operated at the maximum best torque (MBT) optimization which was achieved at the lambda value of 0·83. It can be stated that conventional carburetor or port injection engine with gas conversion kit losses brake power about 15% to 20% as compared to original gasoline fuelled engine. Hence, it was developed a new direct injection engine to recover the power. To achieve the maximum best torque (MBT) the engine requires a lambda value of 0·83 which is rich mixture. Even it is rich mixture, the fuel does not contain sulfur, lead and

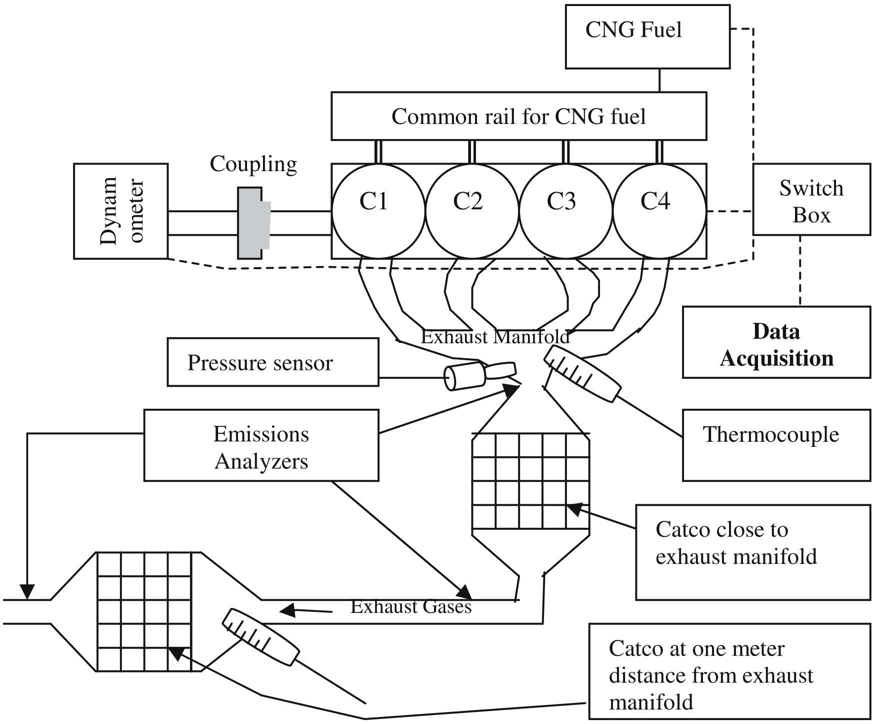

Figure 7. Schematic diagram of catco(s) on the engine exhaust pipe.

phosporhous (in lube oil), so that at rich mixture CO will react with NO_x at high temperature to reduce NO_x to N_2 (as well as O_2). In the later case at Catco 2 (1 meter far from manifold) CO and O_2 will react HC to convert into CO_2 and H_2O. Hence, Oxide catalyst can be used for rich mixture and at higher exhaust temperature (Richard Stone 1999). The engine was tested without catalytic converter (without catco), with conventional catalytic converter or original engine manufacture catalytic converter (OEM catco) and new CoO/TiO_2 based catalytic converter (which can be stated as wire mesh catco). It can be mentioned that the wire mesh catco consists of two parts such as wire mesh catco A and wire mesh catco B. The wire mesh catco A was placed close to exhaust manifold and the wire mesh catco B was placed at one meter distance from engine exhaust manifold. Figure 7 shows the schematic diagram of catco on engine exhaust pipe. Figures 8, 9, 10, 11 and 12 show the wire mesh catco results when both parts are installed on exhaust pipe and data collected from the exit of wire mesh catco B.

6. Results and discussion

Table 2 shows the legend description used in the various figures. Figure 8 shows NO_x emission versus engine speed from 1500 rpm to 6000 rpm with and without catalytic converters. The test was conducted at wide open throttle (WOT). It is found that wire mesh catalytic converter produces lower level of NO_x emission with an average of 57 ppm all over the engine speed range followed by OEM catalytic converter (average 255 ppm). Without catalytic converter, the natural gas engine produces average 813 ppm NO_x all over the engine speed range. It can

Table 2. Legend description.

Legend	Emission characteristics	Figure(s)
Without Catco	Present emission results when no catalytic converter was fitted on the exhaust system.	8, 9, 10, 11, 12.
OEM Catco	Present emission results when the OEM catco was fitted on the exhaust system at close to engine exhaust manifold.	8, 9, 10, 11, 12.
Wire mesh catco	Present emission results when both the wire mesh catco A and Wire mesh catco B were fitted on the exhaust system, and the data were collected from the exit/entrance of wire mesh catco B.	8, 9, 10, 11, 12.

be calculated that the conversion efficiency of wire mesh and OEM catalytic converter(s) are 93% and 69% respectively. The wire mesh catalytic converter reduces 24% higher NO_x emission than OEM catalytic converter. This is mainly due to the effect of metal oxide(s) such as TiO_2 with the higher wire mesh substrate area. The rutile phase of TiO_2 is very stable at high temperature to catalyse the decomposition of NO to N_2 and O_2. Similar results were achieved using TiO_2 as catalyst in (Matsubara 2007; Morita *et al* 2007; Masakazu 2000). In addition, the lowest period to reach the light off temperature obtained by the TiO_2/CoO catalyst leads to increase the efficiency. It was found that the TiO_2/CoO catalyst achieved light off temperature at 30 sec faster than OEM catalyst (Fuad 2006).

Figure 9 shows CO emission versus engine speed from 1500 rpm to 6000 rpm with and without catalytic converters. The test was conducted at wide open throttle. It is found that wire mesh catalytic converter produces lower level of CO emission as an average of 0·22% all

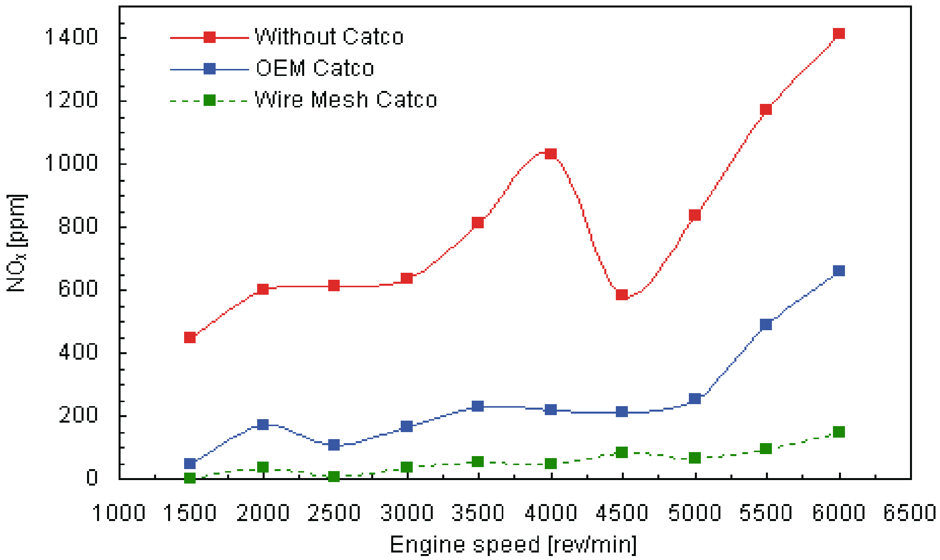

Figure 8. NO_x emission versus engine speed (with and without catalytic converter) at WOT.

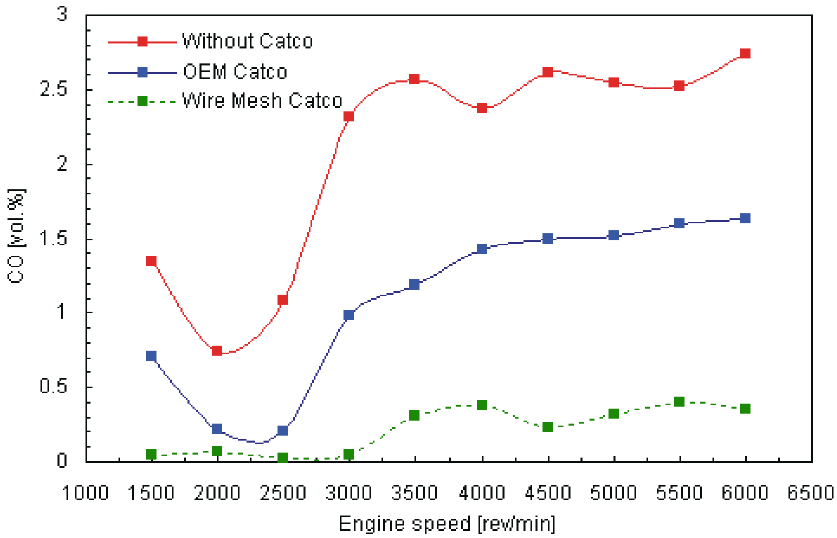

Figure 9. CO emission versus engine speed (with and without catalytic converter) at WOT.

over the engine speed range followed by OEM catalytic converter (average 1·09%). Without catalytic converter, the natural gas engine produces average 2·08% CO emission all over the engine speed range.

It can be calculated that the conversion efficiency of wire mesh and OEM catalytic converter(s) are 89% and 48% respectively. The wire mesh catalytic converter reduces 41% higher CO emission than OEM catalytic converter. It can be explained that the higher specific surface area of the wire mesh substrate when compared with the monolith substrate is beneficial at higher operating temperature. Conversion efficiency of monolith type substrates at

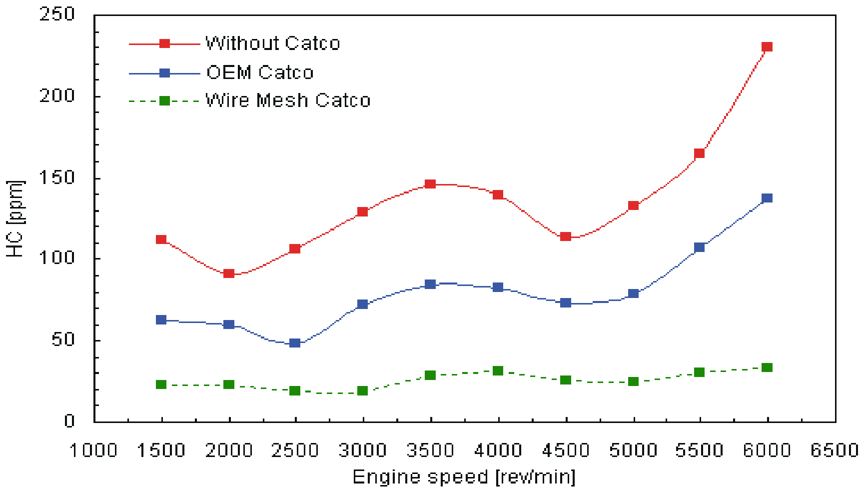

Figure 10. HC emission versus engine speed (with and without catalytic converter) at WOT.

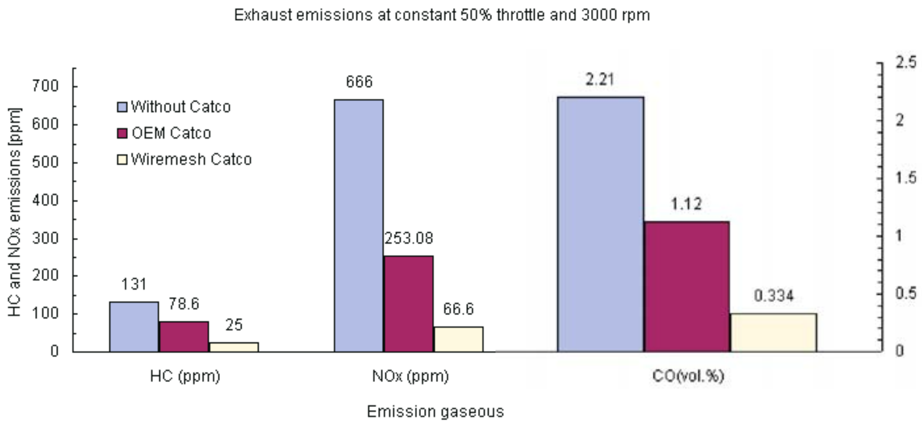

Figure 11. HC, CO and NO_x emissions at constant 50% throttle and 3000 rpm.

high operating temperatures and space velocities depends strongly on the external mass transfer process. Thus the observed higher conversion efficiency for wire mesh substrate can be attributed to external mass transfer limitations rather than to kinetic limitations. In addition, it is due to the effect of metal oxide(s) CoO with the higher wire mesh substrate area. The CoO containing catalysts calcined at high temperature (between 350 and 700°C) exhibited catalytic activity in CO oxidation (US Patent 2007).

Figure 10 shows HC emission versus engine speed from 1500 rpm to 6000 rpm with and without catalytic converters at wide open throttle condition. It is found that wire mesh catalytic converter produces lower level of HC emission as an average of 25 ppm all over the engine speed range followed by OEM catalytic converter (average 80 ppm). Without catalytic converter, the natural gas engine produces average 137 ppm HC all over the engine speed range. It can be calculated that the conversion efficiency of wire mesh and OEM catalytic converter(s) are 82% and 42% respectively. The wire mesh catalytic converter reduces 42% higher HC emission than OEM catalytic converter. This is mainly due to the effect of metal

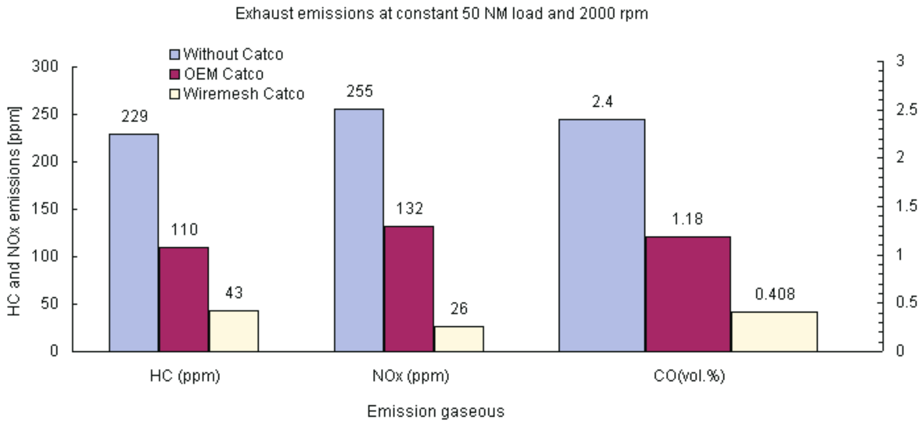

Figure 12. HC, CO and NO_x emissions at constant 50 Nm load and 2000 rpm.

oxide(s) such as TiO_2/CoO with the higher wire mesh substrate area. The CoO is the key catalyst to oxides HC emissions from CNG fuel (Joy Industries 2007). The CoO/TiO_2 catalyst materials are 75% cheaper than noble metals in Malaysia.

Figures 11 and 12 show HC, CO and NO_x emissions for different engine operating conditions other than WOT. Figure 11 shows exhaust emissions for all the catalytic converters at engine operating condition with constant 50% throttle and 3000 rpm. It is found that HC reduces from 131 ppm to 78·6 ppm and 25 ppm by OEM Catco and Wire mesh Catco respectively. Similar reductions of NO_x and CO emissions are found by OEM and Wire mesh Catco(s).The results for other engine speeds (rather than 3000 rpm) showed similar reduction as trend in figure 11.

Figure 12 shows HC, CO and NO_x emissions with constant brake pressure 50 Nm load and 2000 rpm. It is found that HC reduces from 229 ppm to 110 ppm and 43 ppm by OEM and Wire mesh Catco(s). Similar reductions are found for NO_x and CO emissions.

7. Conclusions

The following conclusions may be drawn from the present study.

- CoO/TiO_2 catalyst and wire mesh based substrate based catalytic converter has been successfully developed. The surface area of wire mesh substrate is about 25 times higher than ceramic substrate.
- The NO_x conversion efficiency of OEM and wire mesh catalytic converters are 69% and 93% respectively. Wire mesh reduces 24% higher than OEM catalytic converter.
- The CO conversion efficiency of OEM and wire mesh catalytic converters are 48% and 89% respectively. Wire mesh reduces 41% higher than OEM catalytic converter.
- The HC conversion efficiency of OEM and wire mesh catalytic converters are 42% and 82% respectively. Wire mesh reduces 40% higher than OEM catalytic converter.
- Similar reductions (as WOT) of HC, CO and NO_x are found at 50% throttle and 50 Nm load conditions.
- The wire mesh catco reduces average 3·48% brake power as compared to without catco (table A1 in Appendix A).
- Light off temperature for OEM and Wire mesh Catco(s) are 220°C to 280°C) and 270°C to 360°C respectively (figure A1 in Appendix A).

Hence, TiO_2/CoO oxide-based catalytic converter is effective for natural gas direct injection engine.

The authors would like to thank Ministry of Science, Technology and Innovation (MOSTI), Malaysia for financial support for this investigation. The authors also thank University of Malaya (UM), Proton Car Manufacture Company, University of Technology Mara (UiTM), University of Putra Malaysia (UPM), University of Kebangsaan Malaysia (UKM) for producing this work through collaborative research program.

Appendix A

Detailed summary of the experimental results for this investigation is shown in table A1.

Table A1. Average test results all over the test cycle such as engine speed from 1500 rpm to 6000 rpm at WOT.

Parameters	Without catco	OEM Catco	Wire mesh Catco A	Wire mesh Catco B	Wire mesh Catco (A + B)
Brake power (kW)	45·37	44·78	45·15	44·73	43·79
Exhaust gas pressure (Kpa)	2·12	−1·18	−1·27	−1·19	1·99
Inlet manifold pressure (Kpa)	−3·29	−3·12	−3·14	−3·23	−3·10
Exhaust gas temperature at exhaust manifold (deg.C)	697·23	632·94	662·37	663·66	671·87
Temperature at the entrance of catco	–	405·43	374·49	326·69	387·82
CO emission (% vol.)	2·08	1·10	0·52	0·37	0·23
HC emission (ppm)	136·50	80·35	69·99	41·83	26·73
NO_x emission (ppm)	812·50	254·65	356·01	116·52	66·15

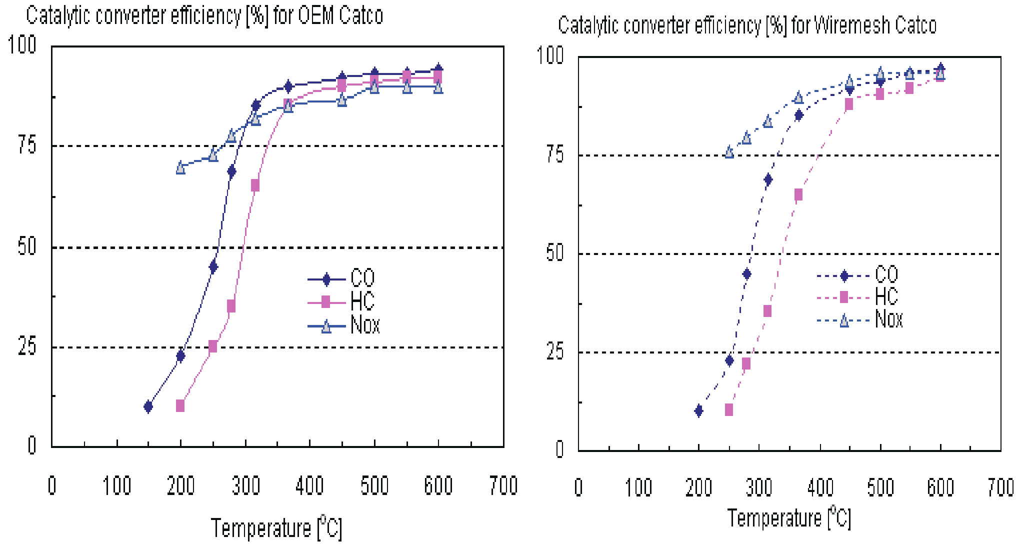

Figure A1. Catalytic converter efficiency versus temperature at 50% throttle condition.

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