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Performance of a Non-Catalytic Syngas Generator for LNT and DPF Regeneration

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ABSTRACT

Previous research has shown that hydrogen and carbon monoxide are superior agents for the regeneration and de-sulfation of Lean NO_X Traps (LNT). It has also been proposed that a syngas stream could be useful for active regeneration of Diesel Particulate Filters (DPF). The challenge of supplying syngas on-board a vehicle has always been the design and control of an inexpensive and simplistic fuel processor. This technical paper presents the operating results for a non-catalytic, auto-thermal syngas generator, that converts diesel fuel and a small portion of an engine's exhaust stream, into a syngas stream. Also described, is the general control scheme used to operate the syngas generator.

INTRODUCTION

While the diesel engine industry continues to work on developing in-cylinder methods to reduce tailpipe emissions, the industry as a whole has recognized that exhaust after-treatment is required if the evermore stringent emission regulations are to be met. Particulate Matter (PM) will be reduced using filtration systems that are now being commercialized. The industry will reduce tailpipe emissions of oxides of nitrogen (NO_X) by chemically reducing these compounds into H_2O and N_2. There are various systems and operating methods being proposed to reduce tailpipe NO_X concentration. The two elements that the various systems and methods have in common are the use of catalysts to promote the reduction reaction, and the use of a chemical reducing agent to be reacted with the NO_X over the catalysts.

One proposed NO_X reduction system uses aqueous urea that decomposes into ammonia. The ammonia then selectively reacts with the NO_X to produce H_2O and N_2. This type of system is called UREA Selective Catalytic Reduction (UREA-SCR) and is presently the strategy that is in the forefront of development activity [1]. While aspects of UREA-SCR have been proven, there are still some significant concerns about commercializing UREA-SCR for use on mobile applications. The major concerns are that an aqueous urea distribution and sales infrastructure that delivers the urea widely enough and for a low enough price can not be developed, and that vehicle operators will not comply by simply not filling the vehicle's urea tank [2].

A path to remove the infrastructure and compliance problems is to use a reducing agent that already exists on the vehicle. The diesel fuel already present on-board, can be used with Hydrocarbon Selective Catalytic Reduction (HC-SCR) systems. The NOx conversion rate has been relatively low (approximately 30%) for these HC-SCR systems. LNT systems have been developed to increase the NO_X conversion, and diesel fuel can also be used as the reducing agent. Numerous previous papers have described this type of work [3, 4, 5, 6 and 7].

Engine manufacturers, OEM's, and Tier 1 system suppliers find a syngas solution beneficial because on-board syngas can be used for various different applications. These applications include LNT regeneration [8, 9, 10, 11] and de-sulfation [12], active regeneration of DPF's [13], use of syngas to supply fuel cell auxiliary power units [14], and the use of syngas to assist Homogeneous Charge Compression Ignition (HCCI) [15, 16] engine control. While some of these solutions do have a long timeline to adoption there is a logical product path for syngas technology. UREA-SCR technology is only useful for the task of NO_X reduction.

Syngas generator development to date has generally involved reactors that use catalysts to promote reactions that result in the desired reducing agents of H_2 and CO [17]. The reactors also often have various subsystems associated with them to supply air or steam to the reactor resulting in an expensive system. This technical paper describes work that has been done and results collected to date as part of a program to develop a non-catalytic, autothermal syngas generator that uses on-board diesel fuel and engine exhaust as the reactant feeds.

LEAN NOX TRAP REACTIONS

While it is not the intent of this paper to study chemical reactions in the LNT it is helpful to understand the reactions that define the quantity of syngas that must be produced for a given NOx reduction rate.

Lean NOx trap operation is a multiple step process [18]. The first part consists of oxidizing NO over a platinum catalyst producing NO_2 in a lean air fuel ratio during typical diesel engine operation.

$NO + ½ O_2 \rightarrow NO_2$ (over Pt catalyst) (R1)

This in turn is chemically adsorbed by a barium oxide adsorbent in the following process.

$BaO + 2NO_2 + ½ O_2 \rightarrow Ba(NO_3)_2$ (R2)

When the desired adsorption capacity has been reached the barium oxide adsorbent will need to be regenerated. This is accomplished in an oxygen depleted environment. This will facilitate the release of the trapped NOx in the following R3 and R4 reactions

This environment can be created through post injection of diesel fuel into a hot cylinder which will consume excess oxygen in the exhaust stream. Alternatively, the exhaust flow can be diverted around the LNT being regenerated thus creating an oxygen depleted environment. .

$Ba(NO_3)_2 \rightarrow BaO + 2NO + 1½ O_2$ (R3)

or

$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½ O_2$ (R4)

With this, reactions R5 through R10 occur essentially simultaneously. It is believed R5 and R6 may happen preferentially.

$H2 + ½ O_2 \rightarrow H2O$ (over Rh or Pt) (R5)
$CO + ½ O_2 \rightarrow CO_2$ (over Rh or Pt) (R6)

$NO + H_2 \rightarrow ½ N_2 + H_2O$ (over Rh or Pt) (R7)
$NO + CO \rightarrow ½ N_2 + CO_2$ (over Rh or Pt) (R8)

or

$NO_2 + 2 H_2 \rightarrow ½ N_2 + 2 H_2O$ (over Rh or Pt) (R9)
$NO_2 + 2 CO \rightarrow ½ N_2 + 2 CO_2$ (over Rh or Pt) (R10)

In summary, 2.5 moles of H_2+CO are required to trap and chemically reduce every mole of NO throughout a complete LNT working cycle as described above. The stoichiometric H_2+CO consumption becomes (2.5-x) mol of H_2+CO throughout a complete LNT cycle, x being the molar fraction of NO_2 in total NOx.

Considering non-ideal flow distribution, mass transfer limitations, possible presence of oxygen storage materials in the catalyst washcoat, and other factors require that excess H_2 and CO be provided to achieve a desired NOx reduction target. The practical (H_2+CO)/NOx molar ratio usually varies between 3.0 and 5.0.

LNT SYSTEM CONFIGURATIONS

The configuration of the LNT(s) also affects the production of syngas desired. It is possible to configure an exhaust after-treatment such that the entire engine exhausts gas passes through a single LNT. The NO_X trapping time and regeneration time can be independently varied to achieve the desired NO_X reduction and minimizing fuel penalty. This variation affects the required instantaneous syngas production rates.

It is also possible to configure the LNTs in multiple paths where all or a portion of the engine exhaust flow is diverted from an LNT if it is being regenerated. The number of LNT paths and the time devoted to trapping and regeneration will affect the required instantaneous syngas flow rate.

SYNGAS GENERATOR

The syngas generator tested has both endothermic and exothermic reactions taking place in the same reaction volume. The endothermic reactions use the heat released from the exothermic reactions. Such a reactor is typically referred to as an autothermal reformer.

The syngas generator tested contained no catalysts. A non-catalytic syngas generator differs from a catalytic syngas generator in two primary ways. A catalytic unit operates at lower temperatures because it utilizes a catalyst to decrease the activation energy of the various reactions taking place. Lower temperature means less mechanical design challenges. The advantage of a non-catalytic reactor is that there is no catalyst, whose performance could be degraded due to sulfur poisoning, carbon masking of catalytic sites, or decreased durability due to thermal damage.

Plasma or arc assisted reformers require a significant amount of external electrical energy input in addition to the fuel [19]. The breakdown of the fuel is caused by heat generated through an electrical arc.

The syngas generator or Device Under Test (DUT) from which the results were obtained is shown in Figure 1. The direction of flow is from left to right. Dimensions are in millimeters. There are numerous temperature and gas sampling points along the length of the DUT. There are three different points where ignition sources can be placed. There are six points at which the exterior wall temperature is measured.

To facilitate access to internal syngas generator components, a clamp was used to allow inspection and change-out of reactor internals. Total DUT internal reaction volume is less than 2 liters.

In general, the syngas generator consisted of a stainless steel vessel with an exhaust gas inlet, diesel fuel injection entry point, premixing chamber, reaction chamber, and syngas outlet. Due to the proprietary nature of this technology, no further internal description is possible.

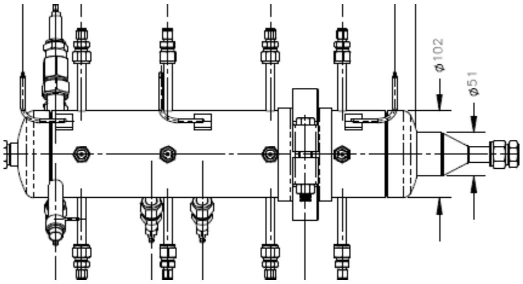

Figure 1 – Device Under Test

TEST EQUIPMENT AND SET UP

SYNGAS TEST STAND

The syngas generator test stand consisted of a diesel fuel supply, simulated exhaust gas supply module, fixture for the DUT, gas analyzers, a system controller, and a data acquisition system as shown in Figure 2 and schematic in Figure 3.

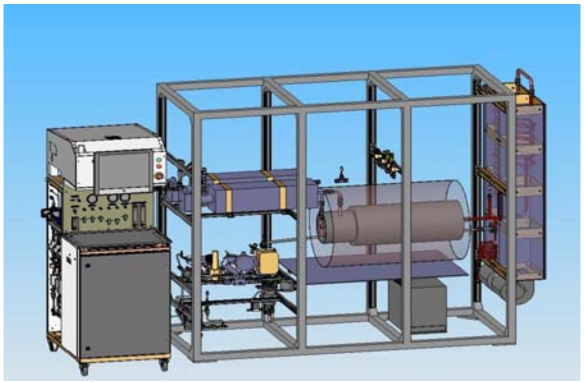

Figure 2 – Syngas Generator Test Stand

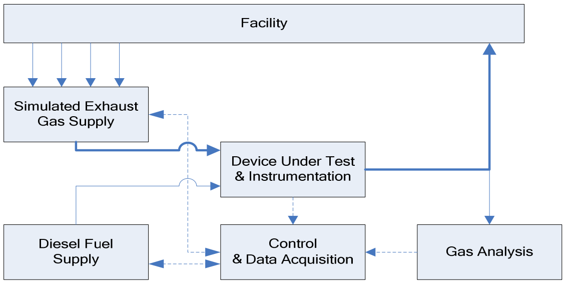

Figure 3 – Block Diagram of Syngas Generator Test Stand

The parameters of the simulated exhaust stream included carbon, hydrogen, nitrogen and sulfur. All of which can be adjusted within the ranges described in Table 1.

Sim Exhaust Parameter	Unit	Nominal Minimum	Nominal Maximum
Mass Flow	kg/hr	1.5	10
Temperature	°C	100	700
Pressure	kPa (g)	15	200
O2	vol %	5	20
CO2	vol %	2	8
H2O	vol %	2	15
N2	vol %	91	57

Table 1 – Simulated Exhaust Gas Parameters

TEST FUEL

The test station also contained a diesel fuel storage tank and distribution system that could supply diesel fuel at a rate of between 0.05 kg/hr and 1.0 kg/hr. Ultra Low Sulfur Diesel (ULSD) was used for all tests. The ULSD was measured by a third party lab using ASTM tests and was found to have the characteristics as show in Table 2.

Fuel Parameter	ASTM Test	Unit	Value
Density	D4052	kg/m^3	851.8
H/C ratio	D5291	-	1.81
Heating value	D240	kJ/kg	45,345
Carbon	D5291	mass %	86.81
Hydrogen	D5291	mass %	13.20
Nitrogen	D4629	mg/L	9.52
Sulfur	D5453	ppm wt	5.34

Table 2 – Test Fuel Analysis

GAS ANALYZERS

The syngas generator’s product stream was analyzed using two different technologies. A gas chromatograph, SRI 8610C Serial Chassis with a Thermal Conductivity Detector and three columns, including a mol sieve 5A packed column, a mol sieve 13X packed column, and a HayesSep D packed column was used to measure H_2, CO, CO_2, O_2, CH_4, and C_2H_6. The following ranges were calibrated with certified standard calibration gases using a minimum of 3 calibration points, see Table 3.

Gas	Unit	Range
CH_4:	vol %	0.1 – 4
C_2H_6:	ppmv	200 – 9800
CO:	vol%	3 – 25
CO_2:	vol%	4 – 16
H_2:	vol%	1 – 22
N_2:	vol%	53 – 96
O_2:	vol%	6 – 18

Table 3 – Gas Analyzer Calibration Range

Also used were on-line analyzers to measure H_2, O_2, CO_2 and CO. An ADC MGA 3000 was used to measure CO, CO_2 and O_2, and a Nova Model 430RM analyzer was used to measure H_2 which was corrected for CO_2. The measurement principle and calibration ranges were as follows, see Table 4.

Gas	Calibration	Vol %
CO	NDIR	0 - 25
CO_2	NDIR	0 - 20
O_2	Paramagnetic	0 - 25
H_2	Thermal conductivity	0 - 25

Table 4 – Gas Analyzer Measurement Parameters

TEST PLAN

The test plan consisted of operating the syngas generator to simulate several operating points of the ESC 13 mode test [20] while controlling test inputs and measuring hydrogen and carbon monoxide production from the syngas generator.

CONTROL OF TEST INPUTS

The Device Under Test is designed to be supplied with an engine exhaust stream and diesel fuel. The engine exhaust stream is passively taken from the exhaust manifold. Therefore the mass flow of engine exhaust into the syngas generator will change as the engine's exhaust temperature, pressure, and composition change with engine load. The test stand adjusted the simulated engine exhaust parameters appropriately to represent the actual conditions that would be expected.

The diesel fuel mass flow rate was controlled such that there was appropriate oxygen to carbon ratio in the reactant mixture. If there is too much oxygen, the H_2 and CO production will be low, and if the oxygen is too low, there will be large amounts of soot and coke produced.

TEST PROCEDURE

Steady state tests were performed at five different operating points. These operating points correlated with modes of the ESC 13 mode test protocol. For each of the test points the temperature, pressure and composition of the simulated engine exhaust was adjusted based on measurements that had previously been taken on a 2004 heavy duty, 15 liter, turbo-charged engine with EGR. Table 5 details the reactant feeds to the syngas generator at the primary test points.

	Units	**Test Points (ESC Modes)**				
Mode	**-**	1	9	13	12	10
Duty	**-**	-	22	50	75	100
Fuel	kg/hr	0.42	0.36	0.39	0.42	0.45
Simulated Exhaust To DUT						
Flow	kg/hr	3.70	4.34	5.69	6.81	7.87
O_2	vol%	18.6	12.1	10.4	9.08	7.72
H_2O	vol%	2.59	6.57	7.59	8.43	9.26
CO_2	vol%	1.27	5.34	6.36	7.21	8.06
Temp	°C	119	407	558	627	685
Press	kPa(g)	17.8	52.2	105	148	198
Syngas Flow From DUT						
Temp	°C	910	865	905	921	922
Press	kPa(g)	3.7	4.7	6.4	8.5	9.5
Mass	kg/hr	4.12	4.7	6.08	7.23	8.31

Table 5 – Syngas Generator Process Streams

RESULTS

Syngas production rates over the engine's duty range are shown in Figure 4. The syngas production rates reflect the fact that the syngas generator was designed to passively accept an engine exhaust stream from a diesel engine's exhaust manifold.

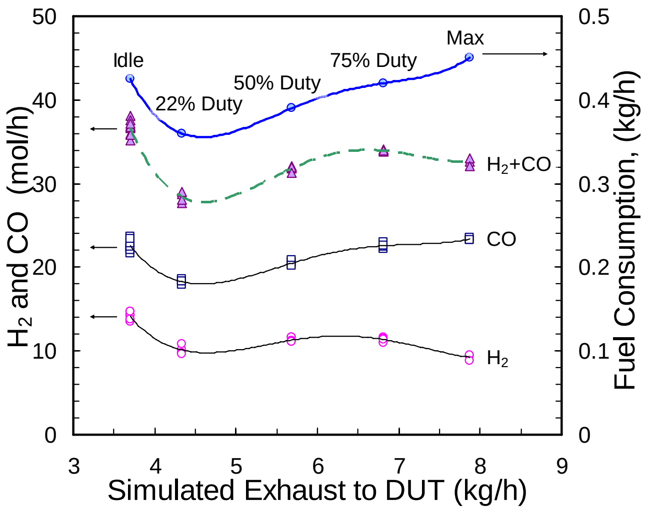

Figure 4 – Syngas Production

The syngas production concentrations of H_2 and CO are shown in Figure 5. The deviation from chemical equilibrium can be appreciated by comparing the measured data to the line that represents chemical equilibrium.

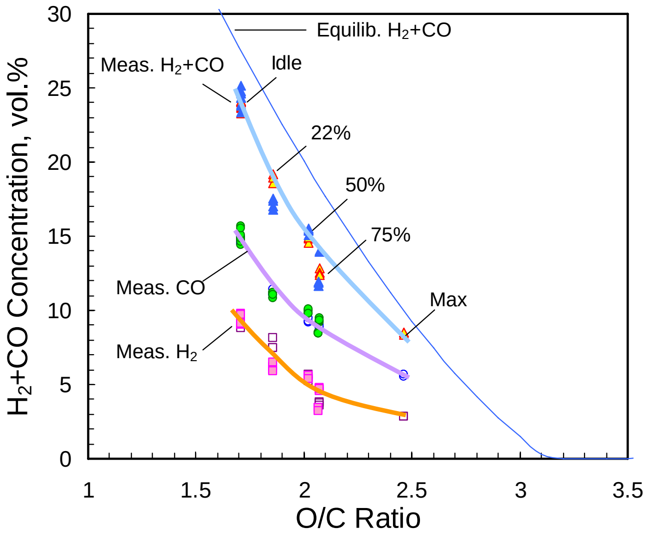

Figure 5 – Measured Concentration vs. Equilibrium Concentration

DISCUSSION

SYNGAS GENERATION

The results indicate that the syngas generation rate is relatively constant over the duty range of a diesel engine. Therefore, the LNT and associated trapping and regeneration controls would be designed to best take advantage of this stable syngas flow rate. The data presented can be used to size a syngas generator that will produce a syngas flow rate required by a specific system design. The use of the syngas could be for LNT or DPF regeneration.

To date the basic work on DPF regeneration has been performed by the team. The work that has been performed has shown that when syngas is mixed with engine exhaust prior to a catalyzed DPF the temperature increase of the exhaust gas across the DPF can be predicted. This ability allows understanding of the engine's operating domain where active regeneration is possible with a specific amount of syngas.

SYNGAS NOX FORMATION

NO_X produced by the syngas generator in theory is negligible. Production of NO_X is not considered a concern by the authors because of a number of reasons.

First, formation of thermal NO_X from air-borne nitrogen through the Zeldovich mechanism requires high temperature, excess oxygen, and long residence time in the high-temperature zone. None of these three conditions are satisfied in the syngas generator operation.

Second, according to fuel analysis data, ULSD fuel contains only 9.52 mg/L of fuel-nitrogen. Even if all the fuel-bound nitrogen is converted, the additional fuel-NOx production from syngas generator is only 20-25 mg/h,

Thirdly, the syngas generator is operated in a fuel rich mode. Under these conditions NOx will be consumed.

CARBON FORMATION

Another possible by-product of the syngas generation process is carbon formation. Any carbon formed in the syngas generator is captured internally and given sufficient residence time and exposure to the reactant gases that it is gasified or oxidized.

The syngas generator's control strategy adjusts the O/C ratio to ensure a negative net production of carbon in the syngas generator. This in turn will limit any possibility of it entering the exhaust stream. Quantitative measurements of this expectation will be verified during the next stage of development testing.

CARBON ANALYSIS

External labs were utilized to characterize carbon compounds found in the DUT after it had been opened after a shut-down.   Table 5 shows the composition of carbon material found in the DUT after both a lean shut-down and a rich shut-down. ASTM Test Method D3176 was used.

		Composition	
Parameter	**Unit**	**Lean**	**Rich**
Carbon	mass %	2.93	83.8
Hydrogen	mass %	0.01	0.28

Sulfur	mass %	0.03	0.0004
Nitrogen	mass %		0.56
Oxygen	mass %		6.51
Ash	mass %	97.03	8.84
Calorific Value	kJ/kg.	1,516	27,467

Table 5 – Residual Carbon Content Analysis in DUT

FUEL USAGE DURING SYNGAS GENERATION

As shown previously in Figure 4, fuel consumption by the syngas generator at the maximum duty ESC mode was 0.45 kg/hr.

The fuel-specific H_2+CO production achieved on the DUT was 70-90 mol/kg-fuel. The H_2 and CO produced from 1 kg diesel fuel can support reduction of 18-23 mol of engine-out NOx using LNT, assuming a (H_2+CO)/NOx molar ratio of 4. The actual (H_2+CO)/NOx molar ratio required will depend on many system and component factors.

SYNGAS CONSTITUENT ANALYSIS

Small amounts of methane (CH4) and ethane (C2H6) were also produced during the syngas generation as shown in Figure 6. The concentrations of these hydrocarbons increased with decreasing gas residence time (increasing load).

These species are found to be best correlated to the O_2 equivalence ratio in the feed since it is primarily a partial oxidation process for the feed composition considered. These species all vanishes when the O_2 equivalence ratio is larger than 0.6.

Although increased levels of methane and ethane are produced at higher engine duty cycles, this will occur with corresponding higher exhaust temperatures. The higher exhaust temperatures will also facilitate the reduction of these secondary gases over a rhodium or platinum catalyst. The extent of this reduction will be studied further in subsequent analyses.

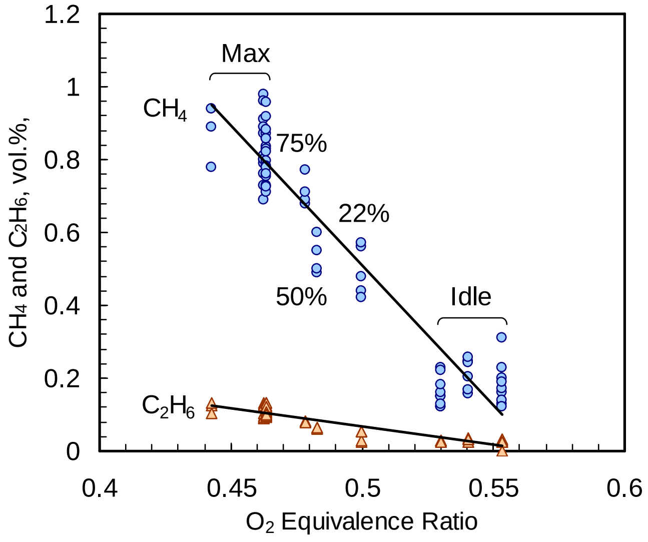

Figure 6 – Hydrocarbon to O2 Equivalence Ratio

CONTROL STRATEGY AND TRANSIENT OPERATION

Due to on-going intellectual property filings, only a general description of the syngas generator's control strategy is given at this time. This description will be expanded in upcoming presentations and papers. To minimize costs and control complexity engine exhaust is directed from the engine's exhaust manifold to the syngas generator with a passive control device. The diesel fuel supplied to the syngas generator is set to ensure an appropriate reactant mixture that will produce hydrogen and carbon monoxide.

To maintain the appropriate reactant mixture through transients the control system senses or predicts the change in exhaust flow to the syngas generator and adjusts the diesel flow in a timely manner. The broader the range of reactant mixtures can be, the more robust the syngas generator's operation will be through transients.

CONCLUSIONS

The production of syngas from diesel fuel and engine exhaust without the use of a catalyst is practical.

The use of syngas and hydrogen supplementation is beneficial and feasible for LNT and DPF regeneration, engine combustion, and as an alternate fuel source for APU's.

Subsequent NOx and carbon formation is negligible and poses no risk to increased emissions or component durability.

FUTURE WORK

With the syngas generation process demonstrated, the next steps will be to perform testing with single and multi-path LNT and DPF system (as earlier described) to verify the NOx and PM reduction efficiency.

In addition, continued study of reformate constituents will be undertaken to further understand the composition of syngas products.

With prototype components developed, the next steps will also be to perform endurance and durability testing to ensure component reliability.

Lastly, controller development will be needed to allow the optimization of system size and syngas requirements for the various applications.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

Autothermal Reforming: Process in which a fuel (such as diesel) is reduced by endothermic and exothermic reactions taking place in the same reaction volume.

Auxiliary Power Unit (APU): A device that provides power to vehicle sub-systems which would normally be supplied by the primary engine system.

De-sulfation: The process of removing the accumulation of sulfur on catalytic substrates through the use of high temperature decomposition.

Diesel Particulate Filter: A metallic or ceramic substrate design to contain carbonaceous material from an exhaust stream, that will be either physically removed (during periodic maintenance) or thermally decomposed during engine and vehicle operation.

ESC 13: European Stationary Cycle used on engines for the evaluation of emissions. The cycle consists of 13 separate operation parameters with which torque and engine speed are varied.

Lean NOx Trap: A catalytic bed that adsorbs NOx during lean operation and reduces the adsorbed NOx to N2 during rich operation.

Particulate Matter: The carbonaceous material produced by an engine during the combustion process.

Syngas: A generic term for a gaseous stream containing carbon monoxide and hydrogen.