

Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Oxidation Catalyst Test Protocol

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SUMMARY

Catalyst testing protocols are being developed to address the need for consistent and realistic metrics for aftertreatment catalyst evaluation. Catalyst testing protocols will consist of a set of standardized requirements and test procedures that sufficiently capture catalyst technology's performance capability and are adaptable in various laboratories. This document represents the first step in this effort, an oxidation catalyst testing protocol.

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BACKGROUND

Catalyst based vehicle aftertreatment development and characterization efforts are becoming multi-organizational partnerships exploiting the wide breadths of expertise from the various partners involved. These multi-partnership efforts have highlighted the need for standardized testing and characterization efforts to increase the consistency of data reporting. This initiative would also address a U.S. DOE and USDRIIVE effort to improve evaluation and management of solicited projects. Therefore, to satisfy both requirements, the development of a series of standardized aftertreatment test protocols has been undertaken by the ACEC group of USDRIIVE, the first of which is presented in this document.

Catalytic aftertreatment can include various single functionalities, including oxidation, reduction, adsorption, desorption, and physical filtration. However, current and future aftertreatment strategies often integrate multiple functionalities. Thus, “device” is the term used to describe an aftertreatment system and strategy that may employ one or multiple functionalities. With this in mind, test protocols will likely take unique forms depending on multiple factors, including (i) the research activity the protocol is supporting, (ii) the nature and complexity of the aftertreatment strategy (e.g. conversion versus passive adsorption, singular versus multi-functionality), and (iii) the combustion platform of interest (e.g. diesel vs. gasoline, lean burn vs. stoichiometric combustion).

The activity the protocol is supporting can be broadly characterized as performance screening, reaction engineering, or development to achieve a performance target. Performance-based protocols for screening catalyst reactions are global in nature, providing only the overall conversion efficiency of the species of interest; they must be simple to execute in a timely manner, as it is desirable to maximize the pace of catalyst development. This is in contrast to more detailed protocols intended to probe individual reaction steps of a global process (e.g., for supporting reaction engineering of predictive simulation efforts). In these instances, the focus is placed on isolating and characterizing each contributing reaction that supports the overall reaction scheme. This dictates that these protocols will be more complex and will likely place additional demands on the testing requirements needed.

The relative complexity of the aftertreatment process under investigation is expected to affect the form of the protocol employed. Specifically, the level of sophistication is primarily determined by the focus of the protocol being either a singular functionality or overall system performance characterization. In some cases, functionality and device performance are synonymous. Oxidation catalysis is a representative example of this case and is more straight-forward to probe. However, in many instances, multiple functionalities facilitate overall device performance, e.g. NO_x storage-reduction (NSR) catalysts. In this instance, NSR test protocols would require additional steps to adequately characterize performance. Therefore, the method of characterization will often differ as a function of the relative complexity required to adequately quantify performance. With respect to test procedures under consideration here, conversion-based processes are typically characterized by quantifying a single reaction or class of reactions, whereas, adsorption-based processes are more complex and require the characterization of both capacity and response time (i.e. adsorption and desorption rates). Adsorption-

based functionalities, therefore, are inherently more difficult to characterize and require more complex strategies.

In order to begin the process of effectively comparing catalyst technologies developed at various organizations, a performance-based protocol for evaluating conversion processes is envisioned as a logical first step due to its relative simplicity. The first protocol will focus on oxidation, since it represents both a singular functionality as well as overall device functionality. By modifying the simulated exhaust gas composition to include appropriate reactant species, the protocol is expected to have application to all conversion-based processes associated with advanced engine combustion technologies.

OVERVIEW

This protocol is developed as a guide for conducting continuous flow reactor studies for evaluating and comparing performance of candidate aftertreatment catalyst technologies. The goal is to efficiently characterize steady state (or pseudo-steady state) conversion performance of applicable catalysts. Specifically, this protocol will address the performance evaluation of oxidation catalysts for low temperature aftertreatment systems intended for advanced combustion strategies. Description of the protocol provided below is separated into five (5) sections: (i) reactor description and best practices, (ii) exhaust simulation, (iii) protocol execution, (iv) de-greening and aging, and (v) reporting.

REACTOR DESCRIPTION AND BEST PRACTICES

A reactor description is provided as a set of minimum instrumentation, sample, and reactor performance requirements for execution of the protocol. Design best practices, derived from industry, university, and national laboratory reactor experience, are provided as a guide to achieve accurate and reproducible results that can be easily shared throughout the aftertreatment R&D community.

Instrumentation Requirements

A minimum of two (2) thermocouples should be employed in the reactor configuration: (i) an inlet thermocouple intended to measure the temperature of the simulated exhaust stream entering the catalyst, and (ii) a catalyst thermocouple intended to measure the temperature of exhaust within the catalyst sample. The inlet thermocouple should be located less than ½-inch upstream of the catalyst bed (or the upstream-face of the core) but not in contact with the catalyst. The catalyst thermocouple should be embedded within the powder catalyst sample, preferably at or downstream axially of mid-bed and radially close to centerline from the exit face of the catalyst. In a core sample, the catalyst thermocouple should be inserted into a monolith channel near the radial centerline. Maximum thermocouple diameter should be 0.032 inch (~0.8 mm) to minimize adverse effects of the thermocouple on catalyst powder flow dynamics, or to avoid channel plugging as a result of thermocouple insertion in monoliths. For core testing, it is best practice to place an inert monolith core just upstream of the catalyst, with the inlet thermocouple embedded within the inert core. This serves two functions: it provides a higher confidence in accuracy of the inlet temperature measurement, and it insures the inlet thermocouple is located radially close to centerline and not in contact with the reactor wall.

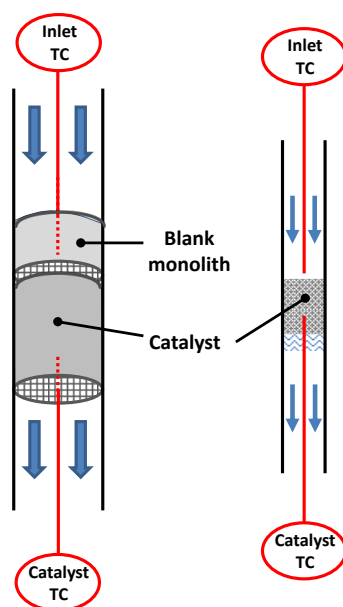


Figure 1 – Inlet and catalyst thermocouple (TC) placement

Chemical analysis capability should include, at a minimum, quantitative analysis of total hydrocarbon (HC), CO, NO, NO₂, N₂O, NH₃, and CO₂. It is preferable to have quantitative analysis of each HC species employed as well as CH₄, but this is not required. For stoichiometric combustion applications, it is preferable to have quantitative analysis of O₂, but this is not required. Analytical capability less than the minimum stated here will limit use and applicability of results. It is important to note that not all analytical methods provide the necessary measurement or resolution for emissions analysis. The level of reproducible detection must be equal or greater to the relative conversion reported, e.g. reporting of 95% conversion of a component at 100 ppm feed dictates that reproducible detection of 5ppm is feasible for that component. Please note that the preferable resolution of an emission measurement is ≤2% of feed concentration, and capability less than this will limit the use and applicability of results.

For tests employing temperature ramping, two important considerations include frequency of sample analysis and rate of response. The frequency of sample measurements will be dictated by the required resolution of the data, which is set at a minimum of 2°C/measurement. In most instances this is easily achieved. However, in situations where the sample measurement rate is slow (e.g. chromatography-based analysis) the thermal ramp of the test can be slowed to facilitate the necessary data resolution. Regarding rate of response, sufficiently fast sampling is necessary to insure measured performance is accurately attributed to the actual catalyst temperature. This can be characterized by the rate of response to a step-change in feed composition: a response time of ≤ 15 seconds is required to reach 90% of steady-state concentration following a step-change in feed composition.

Catalyst Sample Requirements

Powder

- Bed diameter (i.e. reactor ID) > 3 mm and < 13 mm
- Catalyst particle size ≤ 0.25 mm (60 mesh)

- Catalyst bed aspect ratio (length/diameter) ≥ 1

Monolith Core

- Core diameter > 12 mm, preferably > 19 mm
- Cordierite core substrate
- 400 CPSI or as appropriate to the application
- Catalyst bed aspect ratio (length/diameter) ≥ 1

Reactor Performance Requirements

For protocol testing, it is best practice to try to minimize any thermal gradients within the catalyst sample. Therefore, in nitrogen-only flow the allowable temperature gradient measured between the inlet thermocouple and catalyst thermocouple is $\leq 5^{\circ}\text{C}$ at 100°C feed and $\leq 20^{\circ}\text{C}$ at 500°C feed. If a dedicated pre-heating furnace is employed (in addition to a catalyst furnace), this is generally accomplished. However if only a single catalyst furnace is employed, it is best practice to place the catalyst immediately downstream of the actively heated zone.

In order to accurately assign the oxidation conversion efficiency to the catalyst under test, the reactor test protocol must first be run without a catalyst in place. This step is required to insure that the reported performance is solely attributed to catalyst behavior and does not contain artifacts originating from the apparatus. This reactor “base-lining” is to be performed once per specific application and per unique apparatus configuration. It should be repeated following any significant hardware repair, replacement, or reconfiguration. Reactor base-lining is conducted by executing the full protocol with an empty reactor tube or inert sample. The recovery of reactants over the entire temperature ramp of the protocol should be $\geq 95\%$.

Additional Reactor Configuration and Operation Requirements and Recommendations

- System leak checked daily and following each sample change or any hardware re-configuration.
- Analyzer calibration at least once daily (e.g. zero gases and span gases)
- Inlet gas composition characterized each experiment.
- Passivated stainless steel tubing for gas transport to and from the reactor (recommended).
- All reactor gas transport tubing heated to $\geq 190^{\circ}\text{C}$ to prevent condensation or absorption.
- If employing dedicated pre-heating, suggested pre-heating of inert species only (e.g. air, N_2 , H_2O , CO_2). Care should be taken with regard to particularly difficult reactants, e.g. low boiling point (high MW) HCs, NH_3 , and NO_2 . These should be added to pre-heated exhaust as close to the catalyst as possible, while allowing for adequate mixing (recommended).
- Calibrate mass flow controllers at least once per year or according to manufacturer guidelines (recommended).

EXHAUST SIMULATION

This protocol is intended to characterize the oxidation performance of catalysts for a specific combustion mode by using a suitable gas composition for the simulated exhaust. The recommended gas compositions are detailed in Table 1 for stoichiometric GDI (S-GDI, diluted with EGR), clean diesel

combustion (CDC), low temperature combustion of diesel (LTC-D), low temperature combustion of gasoline (LTC-G), and lean gasoline direct injection (L-GDI). The difference between measured and targeted gas concentrations (from Table 1) should be $\leq 10\%$. If the user does not have a targeted application for their development efforts, it is suggested that they employ CDC conditions as a default.

The protocol requires a number of operating parameters to be held constant, including O_2 , H_2O , CO_2 , and H_2 content, HC make-up (i.e., HC surrogates employed and relative fractions), space velocity (SV), and catalyst aged state. The variable components include CO, NO, and HC (as C_1) concentration. However, each of these species are to be held constant during a single test (excluding pre-treatment), with the dependence of catalyst performance on any of these parameters measured by repeating all or a portion of the protocol following modification of the parameter(s) of interest.

The exact HC surrogate blend will be based on the engine combustion mode; recommendations for starting points have been provided in Table 1. The HC blend will consist of one or more of the following species:

- ethylene (C_2H_4)
- propylene (C_3H_6)
- propane (C_3H_8)
- 2,2,4-trimethylpentane (i- C_8H_{18} , i.e. isooctane) for catalysts intended for gasoline applications
- dodecane (n- $C_{12}H_{26}$) for catalysts intended for diesel applications.

Isooctane and dodecane are low boiling-point liquid fuels intended to represent unburned fuel-type species in the exhaust of gasoline and diesel applications, respectively. Each will require liquid vaporization hardware for inclusion in the simulated exhaust, e.g. liquid injectors or diffusers. Their employment is strongly encouraged. However, the researcher is provided the choice to omit the liquid HC component and employ a gas-phase only feed. If the user chooses to omit the liquid HC component, then the HC C_1 concentrations in parenthesis in Table 1 should be used. Please note that the inclusion of the liquid HCs will improve the use and applicability of results. For the stoichiometric case, if HC concentration is altered for any reason, O_2 should also be adjusted to maintain stoichiometry.

The standard space velocity to be employed is $30,000 \text{ hr}^{-1}$ for monolith catalysts and 200 L/g-hr for powder catalysts across all combustion modes. Optionally, a higher $60,000 \text{ hr}^{-1}$ space velocity for monolith catalysts and 400 L/g-hr for powder catalysts, across all combustion modes, is encouraged if more appropriate for the application.

The gas concentrations shown in Table 1 were selected by a team of experts in the field to reflect the actual exhaust compositions for the various combustion strategies listed. Therefore, it is important that these gas compositions as well as the testing conditions described above are followed when evaluating new catalyst materials. Omitting or significantly altering the components and concentrations identified in Table 1, or employing a smaller space velocity than what is identified above, will cast significant doubt on the ability of the catalyst to perform analogously to the data presented when evaluated on actual engines.

Table 1 – Simulated exhaust parameters: oxidation catalysis*

Constant components	S-GDI	CDC		L-GDI	LTC-G	LTC-D
[O ₂]	0.74%	12%		9%	12%	12%
[H ₂ O]	13%	6%		8%	6%	6%
[CO ₂]	13%	6%		8%	6%	6%
[H ₂]	1670 ppm	100 ppm		670 ppm	670 ppm	400 ppm
Variable components	all in [ppm]					
[CO]	5000	500		2000	2000	2000
[NO]	1000	200		500	100	100
	Hydrocarbon – [ppm] on C ₁ basis**					
Total [HC]	3000	1400		3000	3000	3000
[C ₂ H ₄]	700 (1050)	500 (778)		700 (1050)	700 (1050)	500 (1667)
[C ₃ H ₆]	1000 (1500)	300 (467)		1000 (1500)	1000 (1500)	300 (1000)
[C ₃ H ₈]	300 (450)	100 (155)		300 (450)	300 (450)	100 (333)
[i-C ₈ H ₁₈]	1000 (0)	-		1000 (0)	1000 (0)	-
[n-C ₁₂ H ₂₆]	-	500 (0)		-	-	2100 (0)

* Balance N₂

** The HC C₁ concentrations in parenthesis to be used if the user chooses to omit the liquid HC species

PROTOCOL EXECUTION

The protocol should only be executed on a catalyst that has been, at a minimum, fully calcined and de-greened [see section (iv)]. Protocol execution consists of an initial pre-treatment step followed by test section. The pre-treatment step is employed to insure that common conditions prevail prior to activity characterization. During the test section, a slow thermal ramp is employed where catalytic activity is characterized in pseudo-steady state fashion. The rate of temperature ramping employed is intended to reach a compromise between timely execution of the test and insuring steady state conditions prevail during activity characterization. The temperatures referenced below, as well as the temperature of the catalyst accompanying the activity data, should reflect the catalyst inlet temperature and not the catalyst bed temperature due to potential presence of catalyst-derived exotherms and/or endotherms.

The protocol test strategy is shown in Table 2 and Figure 2. The pre-treatment section of the protocol consists of heating the catalyst to 600°C and holding for 20 minutes prior to cooling to 100°C. This is performed in the presence of O₂, H₂O and CO₂ (balance N₂) for CDC, LTC-D, LTC-G, and L-GDI; for S-GDI, this is performed in the presence of H₂O and CO₂ only (balance N₂). The concentrations of species are given in Table 1 for the applicable mode of combustion. Only a single pre-treatment should be performed per test. The test section of the protocol is 3.5 hours in duration and employs the full simulated exhaust detailed in Table 1 for the targeted combustion mode; it consists of an isothermal hold at 100°C for 10 minutes followed by a 2°C/minute ramp from 100°C to 500°C. Investigating the sensitivity of catalyst performance to one or more test parameters would consist of repeating the applicable pre-treatment step at 600°C, cooling down to 100°C, and repeating the protocol test following modification of the protocol parameter(s) of interest.

Table 2 – Protocol test strategy

Pre-treatment – CDC, LTC-D, LTC-G, L-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1-1	Hold 20 min @ 600°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	20 min
LTP-1-2	Cool 600°C – 100°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	-**
Pre-treatment – S-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1-1S	Hold 20 min @ 600°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	20 min
LTP-1-2S	Cool 600°C – 100°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	-**
Test Section – all modes									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1-3	Hold 100°C for 10 min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	10 min
LTP-1-4	Ramp 100-500°C @ 2°C/min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	200 min

* Bracketed concentration values are combustion-mode dependent and found in Table 1.

** Cool down time varies depending on apparatus configuration; no limitations are placed on rate of cool-down.

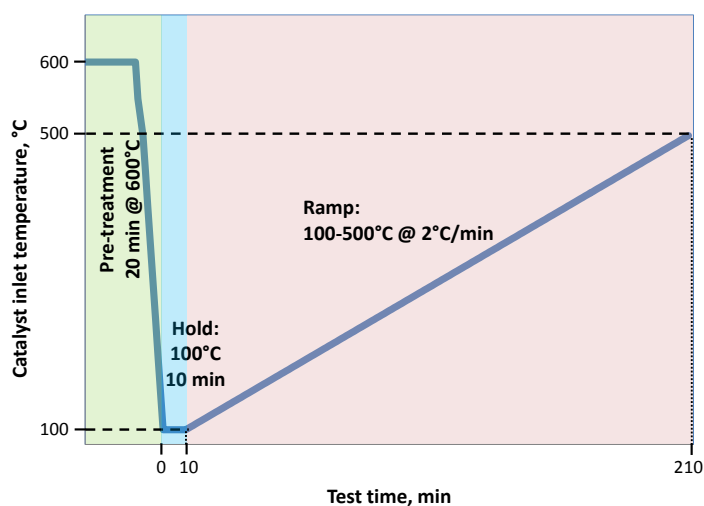


Figure 2 – Protocol temperature control (excluding hysteresis)

Hysteresis and Repeated Tests

Catalyst performance may not be solely a function of its current environment, but may have also resulted from previously encountered conditions. Thus, it is suggested that the user investigate hysteresis when characterizing catalytic performance. Characterizing hysteresis is facilitated by employing a testing strategy that includes temperature ramping both in the downwards and upwards directions. If hysteresis is to be investigated, the full-simulated exhaust flow should be employed during cool down following pre-treatment with the rate of cooling actively controlled. It is important to note that the ability to adequately control the rate of temperature ramping downward (i.e., when cooling) is dependent on the user's hardware. Caution should be taken to ensure that catalytic performance is not

affected by radial or axial temperature gradients incurred from cooling. It is left to the user's discretion to insure this is the case. However it is best practice to characterize the maximum rate of cooling feasible with the user's specific test apparatus and then "back off" this rate significantly to insure pseudo-steady state conditions prevail. It may be necessary for the user to employ a comparatively lower rate of cooling (versus heating) to insure pseudo-steady state conditions prevail. However, assuming analogous rates of cooling and heating are achieved, the testing portion of the protocol would be 7 hours in duration, with details provided in Table 3 and Figure 3.

Table 3 – Protocol test strategy including hysteresis

Pre-treatment – CDC, LTC-D, LTC-G, L-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1H-1	Hold 20 min @ 600°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	20 min
LTP-1H-2	Cool 600°C – 500°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	-**
Pre-treatment – S-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1H-1S	Hold 20 min @ 600°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	20 min
LTP-1H-2S	Cool 600°C – 500°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	-**
Activity Characterization – all modes									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							Time
LTP-1H-3	Hold 500°C for 10 min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	10 min
LTP-1H-4	Ramp 500-100°C @ 2°C/min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	200 min
LTP-1H-5	Hold 100°C for 10 min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	10 min
LTP-1H-6	Ramp 100-500°C @ 2°C/min	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	200 min

* Bracketed concentration values are combustion-mode dependent and found in Table 1.

** Cool down time varies depending on apparatus configuration; no limitations are placed on rate of cool-down.

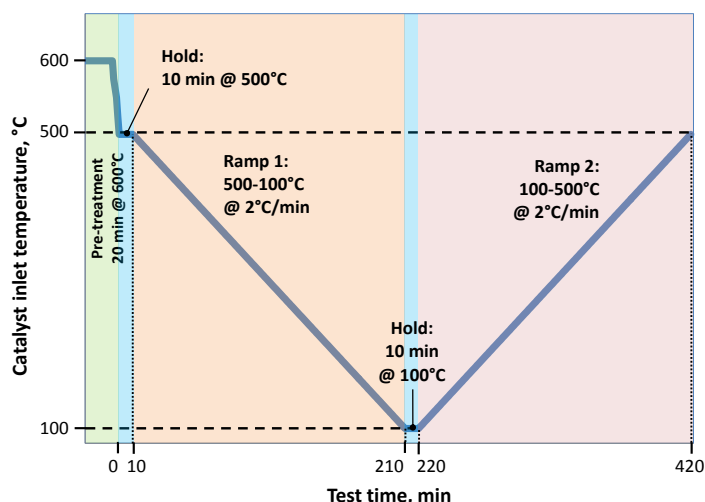


Figure 3 – Protocol temperature control (including hysteresis)

DE-GREENING AND AGING

At a minimum, fresh catalysts should be “de-greened” prior to initial catalyst testing to insure a common and stabilized initial state of performance. Catalyst de-greening is not included as part of the protocol test strategy, but should be done prior to activity characterization. It is important to note that the pre-treatment portion of the protocol is not intended to replace adequate de-greening.

The catalyst aged state is considered a constant parameter in the protocol. Procedures for providing a realistic and representative aged state are described in this section. If it is the user’s intent to characterize activity of an aged catalyst, then the procedures for providing the aged state should take place in completion prior to the test protocol. Catalyst aging consists of both thermal aging and chemical poisoning. It is suggested that the user first characterize activity of the de-greened catalyst, followed by thermal aging and chemical poisoning in sequential fashion, with the test protocol conducted following each treatment.

Please note that low temperature combustion of gasoline (LTC-G) is de-greened and aged analogous to gasoline GDI SI combustion strategies, as it is currently expected that LTC-G combustion strategies will require the employment of SI strategies under certain situations. This dictates that de-greening and aging must defer to SI conditions (LTP-1DG-G and LTP-1A-G-1 to -3, respectively). If the user’s application intends to employ LTC-G combustion strategies over the entire engine cycle, then lean combustion conditions (LTP-1DG-D and LTP-1A-D-1, respectively) can be used for de-greening and aging. However, this will limit the use and applicability of results to solely that condition.

Catalyst De-greening

De-greening is not intended to replace full and complete catalyst calcination; all catalysts should be fully calcined prior to de-greening. The de-greening conditions are shown in Table 4, and consist of neutral conditions (10% CO₂, 10% H₂O, balance N₂) for all gasoline applications (S-GDI, L-GDI, LTC-G), and lean conditions (10% O₂, 5% CO₂, 5% H₂O, balance N₂) for all diesel applications (CDC, LTC-D). The de-greening procedure consists of exposing the catalyst to the most applicable mixture for the application (Table 4), ramping from room temperature to 700°C and holding for 4 hours. The user should perform only a single de-greening per catalyst sample. The temperatures noted above for catalyst de-greening refer to the catalyst inlet temperature.

Table 4 – Catalyst de-greening parameters

S-GDI, L-GDI, LTC-G					
Step No.	Mode	Condition	Exhaust make-up (balance N ₂)		
			[O ₂]	[CO ₂]	[H ₂ O]
LTP-1DG-G	Neutral	700°C/4 hours	-	10%	10%
CDC, LTC-D					
Step No.	Mode	Condition	Exhaust make-up (balance N ₂)		
			[O ₂]	[CO ₂]	[H ₂ O]
LTP-1DG-D	Lean	700°C/4 hours	10%	5%	5%

Catalyst Thermal Aging

Thermal aging representative of anticipated in-use durability requirements is to consist of 50 hours continuous operation at 800°C inlet temperature, with the gas composition dependent on the combustion mode which the aftertreatment technology will address. As detailed in Table 5 and Figure 4, gasoline applications will employ a 1-minute cycle consisting of 40 seconds neutral, 10 seconds rich, and 10 seconds lean operation conducted in continuous sequential fashion for the 50 hours at 800°C. Diesel applications will employ continuous lean operation over the entire 50 hours. Users should conduct only a single 50-hour aging cycle per catalyst. As with de-greening, the temperatures noted above for thermal aging refer to the catalyst inlet temperature.

Table 5 – Catalyst aging cycle parameters

S-GDI, L-GDI, LTC-G							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N ₂)				
		1-minute cycle	[O ₂]	[CO ₂]	[H ₂ O]	[CO]	[H ₂]
LTP-1A-G-1	Neutral	40 seconds	-	10%	10%	-	-
LTP-1A-G-2	Rich	10 seconds	-	10%	10%	3%	1%
LTP-1A-G-3	Lean	10 seconds	5%	10%	10%	-	-
CDC, LTC-D							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N ₂)				
			[O ₂]	[CO ₂]	[H ₂ O]	[CO]	[H ₂]
LTP-1A-D-1	Lean	Continuous	10%	5%	5%	-	-

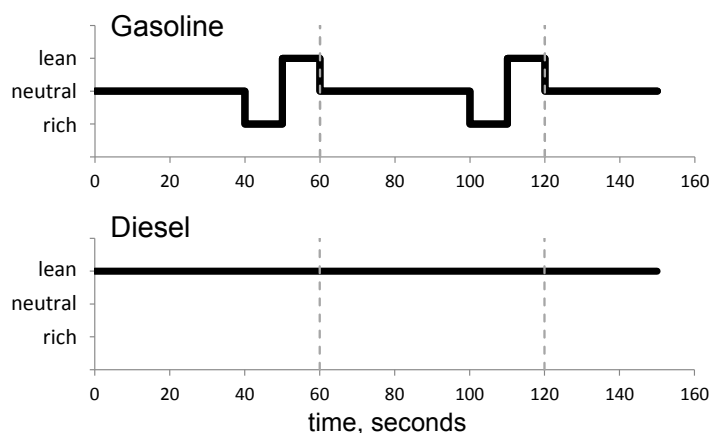


Figure 4 – Catalyst aging cycles

For diesel applications, the presence of an LNT will require periodic rich operation for desulfurization. This is particularly stressful for aftertreatment catalysts and must be addressed separately for aging. To be considered for deployment together with an LNT, the catalyst must be thermally aged an additional 10 hours at 800°C as described in Table 6 and Figure 5; this is in addition to the 50-hour thermal aging cycle for all diesel applications from Table 5 (LTP-1A-D-1). The LNT aging is a 1-hour cycle consisting of 45 minutes lean and 15 minutes rich operation conducted 10 times in continuous sequential fashion for a total of 10 hours at 800°C. For diesel LNT applications, the user should characterize catalyst performance following the initial 50-hour lean thermal aging cycle, and then a second time following the 10-hour LNT thermal aging cycle.

Table 6 – Diesel with LNT catalyst aging cycle parameters

CDC, LTC-D							
Step No.	Cycle mode	Duration	Exhaust make-up (balance N ₂)				
		1-hour cycle	[O ₂]	[CO ₂]	[H ₂ O]	[CO]	[H ₂]
LTP-1A-D-LNT-1	Lean	45 minutes	10%	5%	5%	-	-
LTP-1A-D-LNT-2	Rich	15 minutes	-	5%	5%	3%	1%

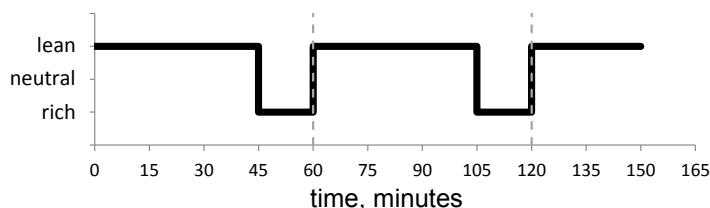


Figure 5 – Diesel with LNT catalyst aging cycle

Temperature Control during Thermal Aging

Physical and chemical changes of a catalyst due to thermal exposure are generally expected to follow an exponential increase with temperature described by an Arrhenius type relationship. As such, deviations in aging temperature between successive tests run for comparison or quality purposes can exhibit different results if the temperature is not controlled adequately. An example of the relationship between equivalent aging hours and temperature is shown in Figure 6. For this reason, it is recommended that temperature control for catalyst aging be held to $\pm 2^\circ\text{C}$ of the desired temperature in reference to the catalyst inlet temperature. Additionally, exotherms experienced during rich-lean thermal aging also accelerate damage accumulation due to the elevated temperature experienced during the exotherm. Thus, accurate and repeatable temperature and methodology control during catalyst aging procedures is important, especially when sequential tests will be used to compare different catalyst formulations or designs. This also emphasizes the importance of controlling off of catalyst inlet temperature.

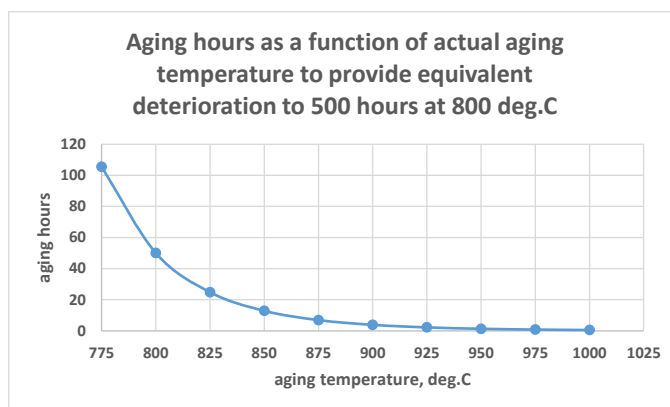


Figure 6 – Aging equivalent hours with temperature differing from 800°C set point

Chemical Poisoning

Chemical poisoning will initially focus only on transitory poisons in the form of sulfur derived from in-use fuels. A total exposure level of approximately 1 g sulfur per liter of catalyst (for core samples) is to be achieved by exposing the catalyst to 5 ppm SO₂ added to the full simulated exhaust at 30,000 hr⁻¹ SV and 300°C catalyst inlet temperature for 5 hours. As shown in Table 7, poisoning is to occur following the applicable pre-treatment for the combustion mode of interest. For powder samples, this is to be performed at 200 L/g-hr under the same conditions, resulting in approximately 7 mg sulfur exposure per gram of catalyst. After sulfur exposure, SO₂ is to be removed from the feed and the sample cooled to 100°C at which point the protocol is to be executed. The pre-treatment and cooling steps are to be performed in the presence of O₂, H₂O and CO₂ (balance N₂) for CDC, LTC-D, LTC-G, and L-GDI. For S-GDI, the pre-treatment and cooling steps are to be performed in the presence of H₂O and CO₂ only (balance N₂).

Table 7 – Catalyst poisoning parameters*

CDC, LTC-D, LTC-G, L-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							
LTP-1P-1	Pretreat 20 min @ 600°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	-
LTP-1P-2	Cool 600°C – 300°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	-
LTP-1P-3	Poison 5 hrs @ 300°C	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	5 ppm SO ₂
LTP-1P-4	Cool 300°C – 100°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	-
S-GDI									
Step No.	Temperature	Exhaust make-up (balance N ₂)*							
LTP-1P-1S	Pretreat 20 min @ 600°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	-
LTP-1P-2S	Cool 600°C – 300°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	-
LTP-1P-3S	Poison 5 hrs @ 300°C	[NO]	[CO]	[H ₂]	[HC]	[O ₂]	[H ₂ O]	[CO ₂]	5 ppm SO ₂
LTP-1P-4S	Cool 300°C – 100°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	-

* Bracketed concentration values are combustion-mode dependent and found in Table 1.

REPORTING

When reporting on catalyst performance, it is important to ensure that all applicable details of the catalyst sample, reactor configuration, and test conditions are adequately reported along with the catalyst performance data.

Catalyst Sample

For monolith core samples, details that should accompany catalyst test results include:

- Core length and diameter
- Cell density, i.e., cells per square inch (CPSI)
- Substrate wall thickness
- Substrate composition, e.g., cordierite, aluminum titanate
- Washcoat loading density, e.g., grams/in³

For powder samples, details that should accompany catalyst test results include:

- Mass of the catalyst sample tested
- Catalyst bed dimensions, i.e., bed length and diameter
- If possible, catalyst particle size range, i.e., mesh-size

For all catalyst samples (monolith and powder), general information is required regarding the catalyst composition to assess the manufacturability and cost of the catalyst.

Reactor Configuration

A minimum level of reactor and test configuration detail should accompany catalyst test results. This includes:

- Reactor tube (e.g., catalyst housing) description and dimensions
- Catalyst heating method (e.g., furnace description and configuration, pre-heater description)
- Location and orientation of catalyst sample within the heating apparatus
- Thermocouple description and location
- Chemical analysis technique(s) and instrumentation used (e.g., Nicolet 6700 FTIR with 190°C heated gas cell)
- Pertinent chemical analysis sampling details, such as temperature of sampling lines and any sample conditioning performed
- Water vaporization hardware for wetting the simulated exhaust
- Liquid hydrocarbon vaporization hardware and technique, if used, for inclusion of liquid hydrocarbons (i.e., iso-octane or dodecane) in the simulated exhaust

Test Conditions

Full details of the conditions employed for testing catalyst performance should accompany the reported results, including, at a minimum, the items listed below.

- The intended engine application/combustion strategy
- The procedures used for de-greening and/or aging the catalyst(s) prior to activity characterization, including gas composition, flowrate, temperature, and hold times, if they are

different than those specified in Tables 4 through 6. If they are not, then referencing the applicable table(s) and engine application (i.e., combustion strategy) is sufficient

- The procedures used for pre-treating or poisoning the catalyst(s) and measuring performance, including gas compositions, flowrate, temperatures, hold times, and ramp rates, if they are different than those specified in Tables 1, 2 or 3, and 7. Again, if they are not, then referencing the applicable tables and engine application is sufficient

Test Results/Performance Data

The catalyst performance data should include the following items for each test:

- Measured inlet and outlet concentrations of each reactive species (i.e., variable components from Table 1) and outlet concentrations of NO₂, N₂O, and NH₃, along with the associated catalyst inlet and catalyst bed (or monolith) temperatures. At a minimum total HC should be reported, however it is preferred to have the measured concentrations of each HC species. It is also preferred to have measured concentrations of CH₄ and O₂ (for stoichiometric combustion applications) but not required.
- Conversion efficiency as a function of catalyst inlet temperature, preferably in graphical format (e.g., see Appendix B).
- T50 and T90 determination, referencing inlet catalyst temperature, for each reactive species (e.g., see Appendix B).

If a carbon balance is being conducted, then inlet and outlet measurements should include CO₂ as well. If any outlet concentrations are presented as a fractional conversion and/or selectivity, then the method (i.e., equation) used to calculate each of these values should be presented.

APPENDIX A: PROTOCOL FLOW CHART

It is suggested that the user conduct catalyst testing in the order as it appears in Figure A1 below. An appropriate application should be selected based on the engine type (diesel vs. gasoline) and combustion mode (CDC vs. LTC-D, or LTC-G vs. L-GDI vs. S-GDI) that the catalyst is expected to support. If multiple engine types are to be investigated, they should be done so with separate samples. If the user wishes to test aged catalysts only, then aging can be conducted without requiring an initial de-greening.

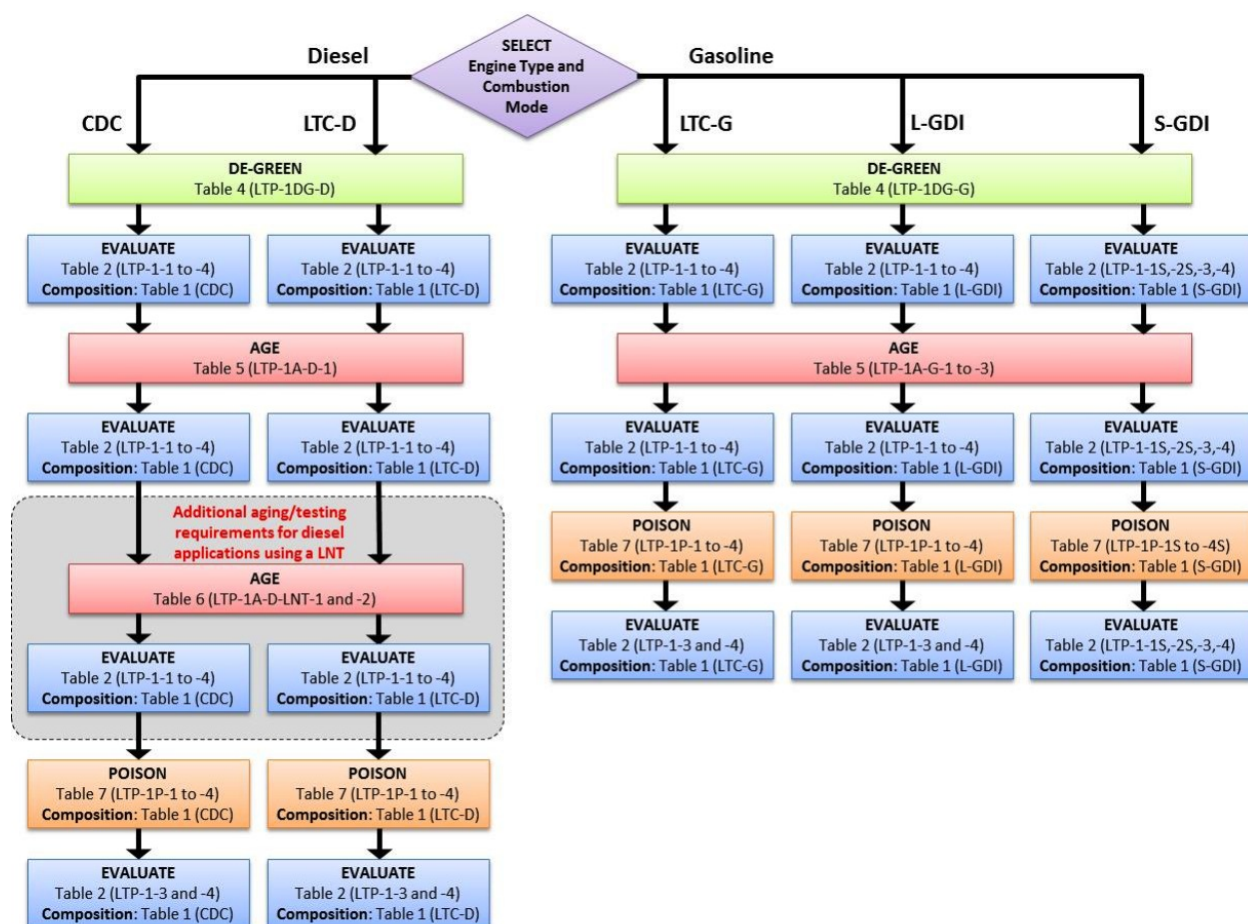


Figure A1 – Test strategy flow chart for oxidation catalyst test protocol

APPENDIX B: PERFORMANCE DATA

The test portion of the protocol is intended to generate a set of CONVERSION versus TEMPERATURE data analogous to Figure B1 below (illustrative only). Comparing the results of multiple protocol tests (e.g. investigating catalyst performance sensitivity to test parameters, or comparing the results of multiple catalysts) is most easily accomplished by extracting T50 and T90 data (temperature at which a component reaches 50% and 10% of its feed concentration, respectively) and presenting in column format. This is shown in Figure B2 below (illustrative only) for an example of four (4) successive protocol tests.

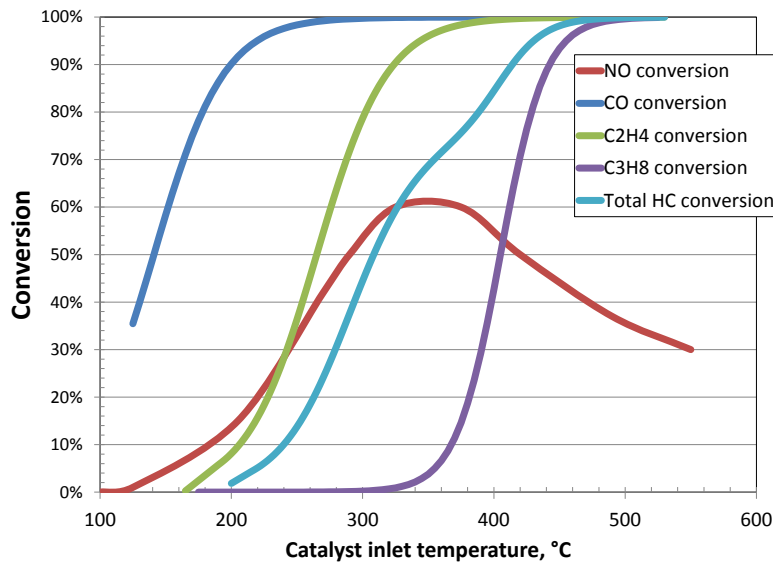


Figure B1 – Illustrative example of conversion versus temperature data

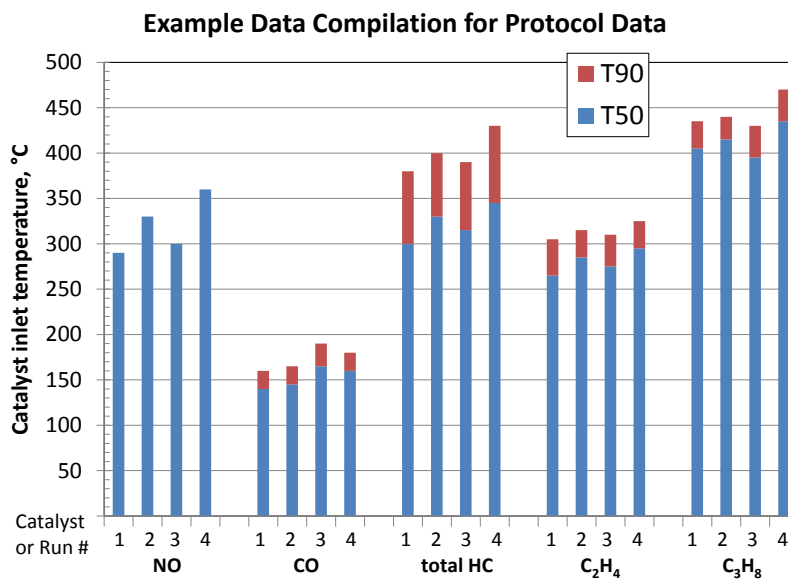


Figure B2 – Illustrative example of T50 & T90 data

APPENDIX C: POTENTIAL MODIFICATIONS

Analytical Challenges

With certain analytical techniques, it may be necessary to make modifications to exhaust gas composition in order to achieve necessary analytical capability. An example of this is the employment of mass spectroscopy for exhaust gas composition, where resolution of CO from N₂ and resolution of N₂O from CO₂ are prohibitively challenging. In the former case, the user may choose to replace N₂ with an alternative inert diluent (e.g. Ar) to allow accurate CO detection; alternatively, the user may choose to omit CO₂ from the simulated exhaust feed to allow accurate CO₂ detection at [ppm] level in the catalyst effluent as a strategy for indirectly quantifying CO oxidation. In the latter case, the situation is more complex. For oxidation applications, resolution of N₂O from CO₂ with mass spectrometry is not readily feasible. This requires the user to replace N₂ with an alternative diluent to allow accurate N₂ detection at the [ppm] level; the discrepancy in the N-balance could then be attributed to N₂O. However, employment of this strategy would preclude the inclusion of CO in the test matrix due to the interfering effect on N₂ analysis.

With the above strategies, it is important to consider the validity of the aftertreatment process as being representative in the presence of the proposed exhaust modification. For this reason, it is best practice for the user to conduct sensitivity studies comparing catalyst performance in the presence and absence of the proposed simulated exhaust modification to insure catalyst insensitivity to the modification.

Selectivity

In its most simplistic form, the protocol defines conversion as the disappearance of a component. However, selectivity is a potential contributing factor. It is a safe assumption that the fate of CO oxidation is entirely CO₂, and thus the disappearance of CO and the oxidation of CO to CO₂ are synonymous. However, during oxidation catalysis, certain conditions will lead to NO being partially or completely reduced through HC-SCR type reactions to N₂O or N₂, respectively; in this situation the disappearance of NO and the oxidation of NO to NO₂ will see a divergence. Thus, this highlights the importance of N₂O measurement either directly or indirectly via N-balance (as described above).

The fate of HC conversion (i.e. HC selectivity) is more complex. Under certain conditions, HC can undergo partial conversion (e.g. partial oxidation, cracking) as opposed to complete oxidation to CO₂ and H₂O. In this situation, the disappearance of HC in the feed and the oxidation of HC to CO₂ would see a divergence. Characterizing all potential partial-conversion products is not practical, which leads to potential modification of the protocol to include carbon balancing. Carbon balancing characterizes partial conversion products as a lump total, and is most efficiently conducted by omitting CO₂ from the simulated exhaust feed. Omitting CO₂ from the feed allows the user to measure CO₂ at the [ppm] level in the effluent; the discrepancy in the C₁-balance can then be attributed to products of partial conversion as a lump sum.