

Hydrogen in Diesel Exhaust: Effect on Diesel Oxidation Catalyst Flow Reactor Experiments and Model Predictions

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ABSTRACT

Engine operating strategies typically geared towards higher fuel economy and lower NO_x widely affect exhaust composition and temperature. These exhaust variables critically drive the performance of After Treatment (AT) components, and hence should guide their screening and selection. Towards this end, the effect of H₂ level in diesel exhaust on the performance of a Diesel Oxidation Catalyst (DOC) was studied using flow reactor experiments, vehicle emission measurements and mathematical models. Vehicle chassis dynamometer data showed that exhaust from light-duty and heavy-duty diesel trucks contained very little to almost no H₂ (FTP average CO/H₂ ~ 40 to 70) as compared to that of a gasoline car exhaust (FTP average CO/H₂ ~ 3). Two identical flow reactor experiments, one with H₂ (at CO/H₂ ~ 3) and another with no H₂ in the feed were designed to screen DOCs under simulated feed gas conditions that mimicked these two extremes in the exhaust H₂ levels. The results from these experiments showed that at moderate space velocities when H₂ was present in the feed, DOC light-off temperature was 20°C lower as compared to when H₂ was not present in the feed. This large difference in light-off temperature suggested that DOCs should be screened using feed gas conditions that more closely represent actual vehicle exhaust H₂ level (which is typically not measured). A DOC model was calibrated using the light-off data from the two flow reactor experiments. The model based on the calibration that included H₂ in the feedgas resulted in predictions of light-duty diesel vehicle CO and HC conversions that were up to 32% higher than the actual measured conversions, further confirming the importance of using realistic engine exhaust conditions on AT design and model development.

INTRODUCTION

Exacting North American NO_x emission standards continue to be a challenging factor in the wide spread commercialization of Light-Duty (LD) diesel vehicles even though they deliver higher fuel efficiency and more power compared to gasoline counterparts. An example of a diesel AfterTreatment (AT) system which might be used to achieve these difficult standards consists of a Diesel Oxidation Catalyst (DOC), a Selective Catalytic Reduction (SCR) catalyst and a Diesel Particulate Filter (DPF) (Lambert *et al.*, 2005). The SCR used ammonia obtained by the thermal hydrolysis of externally supplied urea to reduce NO_x. The DPF was used for Particulate Matter (PM) trapping. While the primary function of the DOC (Farrauto & Voss, 1996) is to oxidize Carbon Monoxide (CO) and Hydro-Carbons (HCs) in the engine exhaust, it can also be used to help improve the performance of the downstream SCR and DPF components. For example, by burning CO, HC and, if necessary, extra fuel injected upstream of the DOC, an exotherm can be generated to raise the temperature and thereby improve the performance of the SCR catalyst. The DOC may also be required to periodically burn injected fuel to raise the temperature of the downstream DPF to initiate burning of the soot collected on the DPF. DOC can produce NO₂ via NO oxidation at low reductant levels and this may help enhance NO_x reduction performance of certain types of SCR, eg. iron-based. In summary, the performance of individual AT components and the system as a whole is driven by DOC performance and outlet temperature which in turn is a key offshoot of catalytic reactions and chemical composition of the engine exhaust.

Engine emissions are a strong function of engine calibration and operating conditions. Significant

differences between diesel and gasoline exhaust exist, and are due largely to the fact that diesel is run under fuel lean conditions whereas gasoline operation is predominantly in the close-to-stoichiometric regime. Diesel engines themselves are operated differently to get the best fuel economy (FE) at an optimized NO_x-PM trade-off level, and this can impact exhaust composition as well. Typical engine control parameters used to alter the NO_x-PM level in the exhaust include fuel injection timing, the quantity of fuel injected, and exhaust gas recirculation (EGR). Techniques such as pre-mixed compression ignition (Akihama *et al.*, 2001) to optimally maneuver the NO_x-PM trade-off curve could result in higher CO and HC emissions compared to a "typical" compression ignition diesel engine operation. Moreover engine emissions could vary widely due to non-uniform operation of engine cylinders (Heywood, 1988), and other techniques such as the use of a variable geometry turbo-charger, low temperature EGR, etc.

Catalyst design, screening and optimization need to consider engine calibration and operating conditions to ensure that the catalyst performance is aligned with engine emissions. A particular catalyst formulation or a set of catalyst formulations that work under certain exhaust conditions may not be optimal for even a slightly different engine strategy. This report explores how differences in the engine exhaust H₂ concentration affect flow reactor catalyst screening results and the impact on catalyst models which utilize this flow reactor data to predict vehicle performance.

This paper is organized as follows. Section 2 describes the experimental details including the setup, catalyst properties, feed conditions and emission measurement devices for the chassis dynamometer and the flow reactor experiments. Chassis dynamometer engine-out CO and H₂ measurements from a LD diesel vehicle and a gasoline vehicle, and flow reactor light-off data are also presented and analyzed in Section 2. The DOC model calibration using flow reactor light-off data and prediction of vehicle tailpipe CO and HC are presented in Section 3. The final section summarizes and discusses the key results.

EXPERIMENTAL

CHASSIS DYNAMAMOMETER EXPERIMENTS - The chassis dynamometer at the Ford Motor Company Vehicle Emission Research Laboratory (VERL) was used for emission measurements. Engine-out CO and H₂ levels were measured from a (1) LD diesel, (2) Heavy-Duty (HD) diesel, and (3) a gasoline vehicle over a standard Federal Test Procedure (FTP) drive cycle. Vehicles were operated on a 48" (1.22 m), single-roll, AC electric dynamometer (Shah *et al.*, 2007). Thermocouples (1/16") were used to record temperature near the emission sampling points. As shown in Table 1, CO and O₂ were measured using a Horiba Mexa 7000 series Non-dispersive Infra Red (NDIR) analyzer and a Horiba Mexa 7000 series Magneto-Pneumatic Analyzer

(MPA) respectively. A Horiba Mexa 7000 series heated Flame Ionization Detector (FID) was used to detect the total HCs, and NO and NO₂ were measured using a Horiba 4000FT Fourier Transformed Infra Red (FTIR) analyzer. An H-sense mass-spectrometer was used to measure H₂ in the exhaust.

A DOC was located downstream of the engine-out sampling point on the LD diesel vehicle, and a second sampling point was used to collect DOC-out CO and HC emissions over an FTP drive cycle. Key characteristics of the commercial DOCs used in this study are as shown in Table 2. The DOC was hydrothermally aged in an oven to simulate 120,000 miles of vehicle aging.

Table 1: Emission measurement systems

Species	Chassis dynamometer	Flow reactor
CO, CO ₂	Horiba Mexa 7000 series Non-dispersive Infra Red analyzer (NDIR)	Midac Fourier Transformed Infra Red analyzer (FTIR)
HC	Horiba Mexa 7000 series heated Flame Ionization Detector (FID)	Horiba FID
H ₂	H-sense Mass spectrometer	-
NO, NO ₂	Horiba 4000FT FTIR / Horiba Mexa 7000 series Chemi-luminescent detector	Midac FTIR
O ₂	Horiba Mexa 7000 series Magneto-Pneumatic (MPA)	Horiba MPA

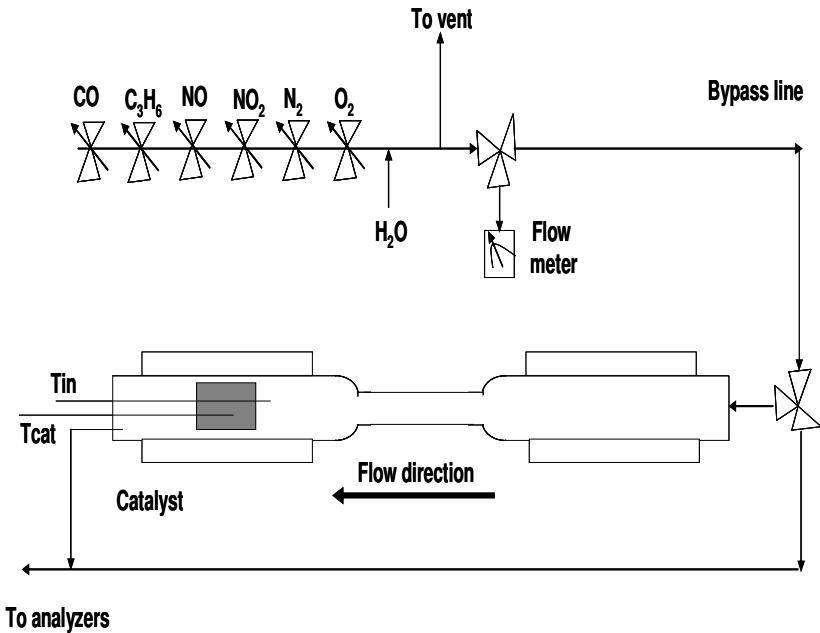


Figure 1: Flow reactor setup

FLOW REACTOR SETUP - The flow reactor setup for DOC screening and evaluation is shown in Figure 1. The reactor system consisted of a quartz tube placed inside two temperature controlled furnaces. The first section of tube was primarily used for enabling homogeneous mixing of gases. Mass flow controllers were used to meter gas flow rates into the reactor. The gases used to simulate the surrogate engine exhaust included CO, propylene (for HCs), NO, N₂ and O₂. Water was sourced through a peristaltic pump and was fed to a wick placed in a heated chamber. Nitrogen and CO₂ were then passed over the wick to sweep the evaporated water into the reactor. Gas flow could be directed through the reactor or switched to bypass the reactor and flow directly to the analyzers to enable steady state feed measurements.

A typical flow rate of 6.4 standard liters per minute was maintained. With a catalyst of 1" diameter x 1" long, this resulted in a space velocity of 30,000 1/h. Two type K thermocouples of 1/16" dimensions were used to measure the DOC-inlet (Tin) and DOC-midbed (Tcat) temperatures. The thermocouple measuring the DOC-inlet temperature was placed 1/4" upstream of the front face of the catalyst and the thermocouple measuring the catalyst midbed temperature was placed 1/2" into the catalyst roughly along the centerline of the catalyst. The gas flow from the reactor was diluted before being sent to the analyzers. As shown in Table 1, an FTIR was used to measure CO, CO₂, NO and NO₂. Hydrocarbon was measured using a FID and O₂ using a Magneto-Pneumatic Analyzer (MPA). The properties of the DOC used in the flow reactor test are as shown in Table 2. The DOC was aged in a pulsator to simulate 120,000 miles vehicle aging. Further details of the formulation and aging cycles are proprietary.

Table 2: Properties of the DOCs

Properties	Chassis dynamometer (LD diesel)	Flow reactor
Formulation	A	B
Size	4.66" D x 4"	1" D x 1"
Cell count (cells/in ²)	400	400
Wall thickness (inch x 10 ³)	4.5	4.5
Washcoat loading (g/in ³)	1.25	1.75
Zeolite	No	Yes
Aging (120k miles equivalent)	Oven aged	Pulsator aged

A temperature ramp of 5 °C/min was used to explore the light-off and light-out characteristics of the DOC. A typical feed gas (Table 3) consisted of 750 ppm CO, 1200 ppm C₁ propylene, 5% O₂, 100 ppm NO, 3.5% H₂O and 6% CO₂. A CO/H₂ molar ratio of 3 was used when H₂ was included in the feed. The remainder of the gas was made up of N₂.

Table 3: Feed gas composition for flow reactor experiments (ppm and % on molar basis)

Species	Experiment without H ₂	Experiment with H ₂
CO (ppm)	750	770
H ₂ (ppm)	0	257
C ₃ H ₆ (ppm C ₁)	1200	1480
O ₂ (ppm)	5%	6%
NO (ppm)	100	100
NO ₂ (ppm)	0	0
H ₂ O (%)	3.5%	3.6%
CO ₂ (%)	6%	5.8%

DATA AND ANALYSES - Engine-out CO and H₂ were measured from the LD and HD diesel vehicles over an FTP cycle on the chassis dynamometer. The sampling port was ~1" upstream of the DOC. The choice of the location was primarily driven by the objective of the study – which was to use this FTP data to design realistic feed conditions for the flow reactor experiments. Maximum values of CO and H₂ were 0.5% and 0.07% respectively. Figure 2 shows the second-by-second molar ratio of engine-out CO to H₂ from the LD diesel vehicle (solid thick line to the left axis) over the first bag of the FTP test. The average CO/H₂ over the first bag of the FTP test (from two different tests) for this diesel vehicle was 46. The calibration (developed independent of this study) of the HD diesel vehicle was such that the engine was run 50% leaner (15% engine-out O₂ at the 150s idle point of the FTP test) as compared to that of the LD diesel vehicle (10% engine-out O₂ at the same time point). This resulted in the HD vehicle exhaust containing 85% lower FTP bag 1 average CO and 91% lower FTP bag 1 average H₂ (compared to the LD diesel vehicle) with the average CO/H₂ (over two FTPs) being 65. The CO/H₂ curve from the HD vehicle is not shown in Figure 2 for clarity. Thus data from the LD and HD diesel vehicles show that DOC-inlet H₂ concentration, on an average, is negligible especially compared to that of CO.

In order to compare the H₂ in the diesel exhaust to that of H₂ levels from a gasoline vehicle, engine-out CO and H₂ were measured over an FTP test from a gasoline vehicle. The emissions were sampled ~1" upstream of the Three-Way Catalyst (TWC) inlet. Second-by-second molar ratio of CO/H₂ is shown as the dotted lines (to the right axis) in Figure 2. The maximum values of CO and H₂ in the exhaust were 4% and 2% respectively with an average CO/H₂ ~ 3. The ratio agrees well with the steady state CO and H₂ measurements from a spark-ignition engine (Heywood, 1988). Comparing this to the diesel CO/H₂, it was clear that gasoline exhaust contains much more H₂. Intuitively this could be because of the lean exhaust of diesel, which gives more opportunity for H₂ in diesel exhaust to be oxidized and consumed. The fact that emissions have been sampled close to the DOC inlet and not close to engine-out could also result in further reduction in H₂ levels along the lines from the engine-out to the DOC-inlet.