

Treatment of Vehicle Emissions from the Combustion of E85 and Gasoline with Catalyzed Hydrocarbon Traps

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ABSTRACT

Ethanol has been gaining attention as a partial substitute in North American pump gasoline in amounts up to 85% ethanol and 15% gasoline, or what is commonly known as "E85". The problems with E85 fuel for cold start emissions relative to gasoline fuel are the lower energy density and vapor pressure for combustion. Each contributes to excess E85 fuel injected during cold start for comparable combustion quality and drivability to gasoline. The excess emissions occur before the first three-way catalyst (TWC) converter is warmed-up and active for engine-out exhaust conversion. The treatment of non-methane organic gas (NMOG) emissions from the combustion of E85 and gasoline was evaluated using several different zeolite based hydrocarbon (HC) traps coated with different precious metal loadings and ratios. These catalyzed HC traps were evaluated in a flow reactor and also on a gasoline Partial Zero Emissions Vehicle (PZEV) with experimental flexible fuel capability. Fourier Transform Infra Red (FTIR) spectroscopy and other methods were used to analyze the alcohols, aldehydes and ketones necessary to quantify NMOG emissions. HC trap performance was quantified through measurement of adsorption and desorption of specific hydrocarbon species, and formation of CO₂ and partial combustion products. Temperature data was used to quantify where specific hydrocarbon species desorbed in relation to catalyst activation. The traps evaluated in the lab reactor all showed similar adsorption efficiencies, and the traps with platinum catalyst generated the most CO₂, but also the most acetaldehyde. The HC traps evaluated on the vehicle with E85 improved the weighted tailpipe emissions of NMOG from the base

TWC results of 0.016 grams/mile down to 0.013 grams/mile. The results illustrate the challenges of adsorbing NMOG emissions, retaining it for conversion and achieving complete oxidation, with the overall system efficiency reflecting the combination of these efficiencies.

INTRODUCTION

Reducing cold start vehicle tailpipe emissions, where about 90% of hydrocarbon emissions occur, is a major challenge in complying with PZEV emission regulations. Operation of the vehicle and catalytic converter begins at ambient conditions, and the catalyst is not active for significant emission reduction until the raw combustion exhaust that passes through the brick channels warms the precious metal sites above 200°C. One way to improve overall HC conversion efficiency during the cold start period is to adsorb or trap the HC species. A catalyzed HC trap is similar to a conventional TWC except that a HC adsorbing zeolite has been added under a TWC washcoat that will adsorb HC species from the engine-out exhaust when the zeolite is cold. Once the catalyzed HC trap begins to heat up, the trapped HC molecules then desorb from the zeolite and are converted ideally to carbon dioxide and water on the active catalytic oxidation sites contained in the TWC washcoat.

Results from a previous study in our laboratory using a Flame Ionization Detection (FID) analyzer have shown that catalyzed HC traps work well for reducing

tailpipe non-methane hydrocarbon (NMHC) mass with E85 fuel [1]. HC mass not observed to desorb from the trap with the FID was assumed to all be converted to CO₂. However, the previous work did not investigate the relative adsorption and reaction efficiencies of the full complement of NMOG emissions. In this study, FTIR spectroscopy and other methods were used to analyze the alcohols, aldehydes and ketones necessary to quantify NMOG emissions. The present study also highlights an important HC trap design feature – selectivity for converting adsorbed ethanol to CO₂ (NMOG benefit) versus partial oxidation to acetaldehyde (no NMOG benefit).

EXPERIMENTAL PREPARATION

TEST VEHICLE – A test vehicle with a 2.3L four cylinder, naturally aspirated, port fuel injected engine was fitted with an experimental exhaust system designed for PZEV emissions as shown in Figure 1. The close-coupled Catalyst A was 41 in³ (0.7 L) with a cell density of 900 cells/in² and a wall thickness of 2.5 mil. The close-coupled Catalyst B was 30 in³ (0.5 L) with a cell density of 400 cells/in² and a wall thickness of 6.5 mil. Both were coated with the same proprietary TWC washcoat layer and the same total precious metal loading of palladium and rhodium at 200g/ft³. The Catalyst C and Catalyst D underbody bricks were each 55 in³ (0.9 L) with a cell density of 400 cells/in² and a wall thickness of 6.5 mil. Both were coated with a proprietary TWC washcoat layer and had a total precious metal loading of palladium and rhodium at about 100 g/ft³. For each catalyst, the distance between its front face and the exhaust manifold inlet flange was: 7.1 inches (18.1 cm) for Catalyst A, 13.1 inches (33.2 cm) for Catalyst B, 45.4 inches (115.2 cm) for Catalyst C, and 49.3 inches (125.2 cm) for Catalyst D. The feedgas emission probe was located upstream of Catalyst A. The midbed 1 emission probe was located upstream of Catalyst C. The midbed 2 emission probe was located between Catalysts C and D. The tailpipe emission probe was located downstream of Catalyst D. All exhaust system components were aged to a Full-Useful Life (FUL) condition simulating 150,000 miles on the standard Ford Motor Company 4-Mode proprietary air/fuel cycle with a Catalyst A inlet temperature of 850°C for 168 hours. All underbody bricks (TWCs and HC traps) used for vehicle testing in this paper experienced maximum temperatures between 830-860°C at 1 inch after the front face during aging. Thermocouples were then inserted 1 inch before the front face, 1 inch after the front face and one inch after the rear face of each converter assembly.

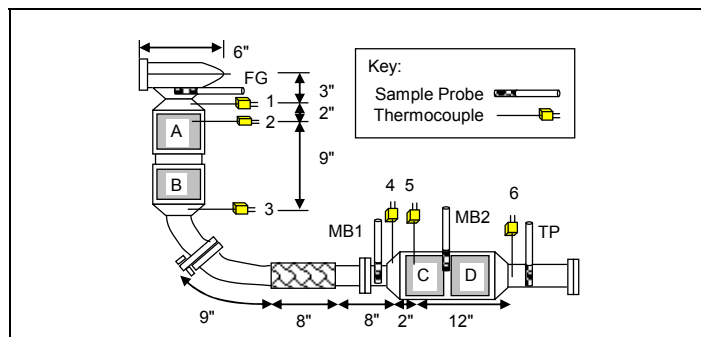


Figure 1: Test Vehicle Experimental Exhaust System

PLUG FLOW REACTOR – A plug flow reactor laboratory setup was used to evaluate catalyzed HC trap samples and is shown in Figure 2. The gas feed was controlled with a Matheson dynablander and flow controllers to 3 L/min. The stainless steel tubing was wrapped with heating tape and maintained at 100°C to prevent condensation of water. The reaction chamber was a ¾ inch ID quartz tube that was placed inside a Lindberg Furnace with heating element control to provide the desired temperature ramp. A 1 inch long HC trap sample core was placed towards one end of the quartz reactor tube and the inlet face of the core was positioned near the oven outlet to primarily heat only the feed gas. The resulting gas space velocity through the sample was 25000 hr⁻¹. Two K-type thermocouples were installed, one through the center of the sample up to the front face, the other up to the rear face. Solenoids were placed before and after the reaction chamber to send the gases either to the sample or to the bypass line. Flow leaving the downstream solenoid was split off to two sets of analyzer benches and the rest was sent to the lab vent. The raw feed was sent to the MKS Fourier Transform Infra Red (FTIR) analyzer and the other feed was diluted with 21 L/min of nitrogen, mixed in a long tube and a sample was pumped to the FID/O₂ gas analyzer bench. Signals from each analyzer were acquired at a 1 Hz rate.

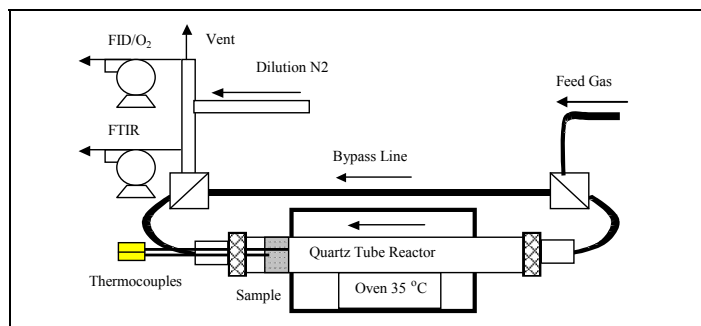


Figure 2: Flow Reactor Schematic

HC TRAP SAMPLES – The HC trap technologies obtained from Ford Motor Company catalyst suppliers are listed below in Table 1. The zeolites were designed primarily for adsorption of either ethanol or gasoline exhaust emissions. The precious metal loadings for each sample were selected to be comparable to the baseline underbody TWC loading of palladium and rhodium. Platinum metal was added for trap samples 2 and 4 to create tri-metal formulations. Samples evaluated in the flow reactor as sample cores measured 11/16 inch diameter by 1 inch long. Samples evaluated in the vehicle underbody assembly as full sized bricks were 55 in³ (0.9 L). All samples and bricks were individually aged to equivalent FUL conditions in pulse flame combustion reactor exhaust. The HC trap bricks were exchanged into the Catalyst C and Catalyst D locations after the baseline testing was complete.

Table 1: List of Samples Evaluated		
Sample #	Intended HC in Zeolite Design	PGM Ratio
1	Ethanol	Pd:Rh
2	Ethanol	tri-metal
3	Gasoline	Pd:Rh
4	Gasoline	tri-metal

EXPERIMENTAL PROCEDURE

TEST VEHICLE EVALUATION – The Vehicle Emission Research Laboratory (VERL) facility at Ford Motor Company was used to evaluate the emissions performance of the test vehicle. Evaluations were conducted using the Cold/Hot Start Emissions Test (FTP4) with certification grade gasoline fuel and E85 fuel (15% cert. fuel + 85% ethanol). The 48 inch single roll dynamometer simulated road conditions that allowed the test vehicle to run at the correct road engine speed, torque and load during the test. The test cell was maintained at a temperature between 21°C and 27°C during testing. The three bench modal emission sampler allowed for emissions to be measured across each catalytic converter can assembly at a 1 Hz data collection rate. Tailpipe exhaust from the first bag of the FTP4 was analyzed by Gas Chromatography (GC). There were nearly 200 different HC molecules specifically detected in the exhaust, with a limited amount of the HC molecules falling into the uncalibrated range. The known HC molecules were classified by the number of carbon atoms in the chain as Methane (C₁), small (C₂–C₃), medium (C₄–C₅) or large (C₆₊). Cartridges and impingers were plumbed to the CVS/RMT or Tunnel during vehicle testing for alcohol and/or aldehyde and ketone determination. These oxygenated species are added to the NMHC mass to give the NMOG mass. At least six vehicle test repeats were run at each different

configuration of fuel (E0 or E85) and underbody technology (TWC or HC trap).

TEST VEHICLE PREPARATION – Our test vehicle had a 150,000-mile, full useful life (FUL), aged PZEV exhaust system, but no flex-fuel vehicle (FFV) hardware upgrades such as improved fuel injectors and fuel pump. Vehicle emission testing was done with alternating the tank fuel week to week. The engine calibration was also alternated each week for gasoline or E85 to account for the differences in cold start fuel schedule, fuel stoichiometric point, transient fuel and closed loop fuel bias needed for optimal emissions and drivability. The calibration parameters that controlled cold start spark timing and engine speed were held at the gasoline calibration values when running with E85.

PLUG FLOW REACTOR –The feed stream used for the flow reactor adsorption experiments consisted of 0.15% HC, 0.1% CO, 0.1% O₂, 10% H₂O vapor and balance N₂ at 3 L/min. The HC feed ranged from a gasoline-like blend ("E0") that contained: 18% Toluene (C₇H₈), 24% IsoPentane (C₅H₁₂) and 58% Propylene (C₃H₆), to one containing just pure Ethanol ("E100") to observe the chemistry mechanisms over the precious metal during the oven temperature programmed desorption (TPD). The intermediate HC feed ("E85") contained almost an even split of the E0 and E100 feeds with 10% Toluene, 13% IsoPentane, 31% Propylene, 7% Acetaldehyde and 40% Ethanol. This composition was chosen to be roughly representative of the exhaust gas composition presented to the HC traps during bag 1 of the FTP4 cycle. Initially a baseline feed was established by running in bypass. The reactor feed was then sent to the sample for a 30 second adsorption phase. The sample was maintained at 30°C–40°C during HC adsorption. The feed was then put in bypass. The flow reactor feed stream was adjusted by removing the HC and CO components and adding more N₂ to maintain the reactor feed at 3 L/min. The reactor feed was sent to the sample as the oven began the TPD phase at 85°C/min up to 630°C. At the end of the temperature ramp, the oxygen level was increased to 2% until observed CO₂ went to zero. Three of these Adsorption/Desorption tests were run per sample, with one or more tests without O₂ to determine the unconverted HC desorption temperatures.

CALCULATIONS

TEST VEHICLE – Figure 3 shows the calculations used for HC trap efficiency on the vehicle experiments. The inlet trace represents the NMHC emissions upstream of the underbody assembly, while the outlet trace represents the NMHC emissions downstream of the underbody assembly. The inlet HC value for the vehicle adsorption phase was the measured levels from the inlet

NMHC emissions integrated over the length of the adsorption phase (A0). The adsorbed HC value was determined by integrating the area where the inlet NMHC mass was greater than the outlet NMHC mass (A1). The adsorbed HC efficiency of the HC trap was the adsorbed HC mass divided by the inlet HC mass. The adsorbed HC desorbed value was determined by integrating the area after the point where the outlet HC mass was greater than the inlet HC mass (A2). The adsorbed HC converted value was calculated by taking the difference between the adsorbed HC value and the adsorbed HC desorbed value. The converted HC efficiency of the HC trap was the adsorbed HC converted value divided by the adsorbed HC value. The overall HC trap efficiency was the product of the adsorbed HC efficiency and the converted HC efficiency.

PLUG FLOW REACTOR – The calculation method employed to determine the HC trap performance metrics are shown in Figure 3. The lab reactor experiment could measure only outlet emissions at the analyzer bench. The inlet HC value for the lab reactor adsorption phase was the measured hydrocarbon emissions from the feed gas through the bypass line integrated over the length of the adsorption phase (A0). The adsorbed HC value was determined by integrating the area where the hydrocarbon emissions from the HC trap sample were below the hydrocarbon emissions level through the bypass line (A1). The adsorbed HC efficiency of the HC trap was the adsorbed HC value divided by the inlet HC value. The adsorbed HC desorbed value was determined by integrating the area where the outlet HC level was above zero (A2). The adsorbed HC converted value was calculated by taking the difference between the adsorbed HC value and the adsorbed HC desorbed value. The converted HC efficiency of the HC trap was the adsorbed HC converted value divided by the adsorbed HC value. Emissions generated during the temperature ramp from stored HC emissions in the trap (i.e. C_2H_4O , CO_2 , etc.) were calculated by the area under the desorption curve divided by the sum of the adsorbed HC converted to a C1 basis. The temperature was recorded at which 50% and 80% of each HC component desorbed out of the trap unconverted. CO_2 emissions generated during the temperature ramp from stored HC emissions in the trap were calculated by the area of the desorption curve divided by the sum of the adsorbed HC converted to a C1 basis.

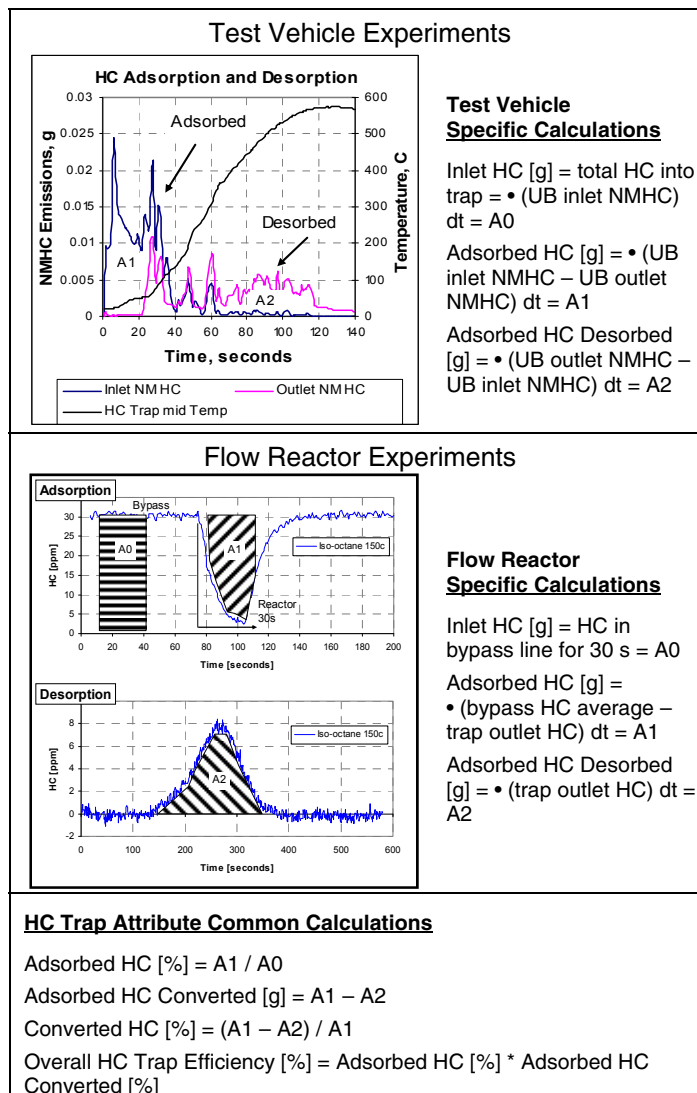


Figure 3: Calculations for HC Trap Efficiency

WEIGHTED FTP4 NMOG – The FTP4 drive cycle is separated into four phases and the tailpipe emissions from each phase are collected into a bag for analysis. The calculations used to determine the weighted emission levels from the FTP4 drive cycle are shown below in Figure 4. According to the California Air Resources Board (CARB), vehicles operating on fuels containing ethanol must correct total HC mass, determined by the integrated FID reading, by subtracting out the mass of methane and ethanol, and then adding in the measured mass of alcohols and carbonyls to get the NMOG emission value [2]. The test cell FID analyzer provided NMHC emission values to use in the mass equation. The impingers and cartridges were sent to Ford Central Labs for analysis to get the total amounts of carbonyls and alcohols, of which the ones of any significant amount were ethanol, acetaldehyde, formaldehyde and acetone. Therefore the NMOG emission equation in Figure 4 reflects only the significant compounds measured.