

HC Traps for Gasoline and Ethanol Applications

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ABSTRACT

In-line hydrocarbon (HC) traps are not widely used to reduce HC emissions due to their limited durability, high platinum group metal (PGM) concentrations, complicated processing, and insufficient hydrocarbon (HC) retention temperatures required for efficient conversion by the three-way catalyst component. New trapping materials and system architectures were developed utilizing an engine dynamometer test equipped with dual Fourier Transform Infrared (FTIR) spectrometers for tracking the adsorption and desorption of various HC species during the light-off period. Parallel laboratory reactor studies were conducted which show that the new HC trap formulations extend the traditional adsorption processes (i.e., based on physisorption and/or adsorption at acid sites) to chemical reaction mechanisms resulting in oligomerized, dehydro-cyclization, and partial coke formation. This results in the initially adsorbed hydrocarbons being retained in the HC trap to sufficiently high temperatures for effective combustion via the three-way-catalyst (TWC) over-layer. Vehicle testing using a 2008 SULEV Ford Focus with E85 fuel and a 2007 BIN-8 1.6L GTDI Mini Cooper with gasoline confirmed an improved design. Additional vehicle work also showed that the HC trap performance may be enhanced with air/fuel calibration during the HC desorption phase. These new trap formulations not only improve HC storage and conversion efficiency, but substantially decrease the PGM requirement compared to previous designs.

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INTRODUCTION

Increasingly stringent transportation biofuel requirements and tailpipe emission standards for hydrocarbons and carbon dioxide (CO₂) demand new technologies on automobiles to enable combinations of flexible fuel capability, Partial Zero Emission Vehicle (PZEV) certification and turbocharged engines. Conventional three-way catalyst (TWC) converter technologies currently do not enable PZEV tailpipe emission certification on E85 fuel since the excess fuel that provides equivalent starting performance to gasoline is delivered before the TWC is warmed-up and active [1]. Turbochargers will help auto manufactures meet federal fuel economy mandates, but are placed at the outlet of the engine, which further delays the warm up of the TWC required to eliminate regulated emissions [2]. Currently, less than 20% of a manufacturer fleet average must meet tailpipe emissions of NMOG (non-methane organic gases at 0.01 wt. g/mile and

NO_x (oxides of nitrogen) at 0.02 wt. g/mile, but LEV-III mandates 100% fleet NMOG + NO_x at 0.03 wt. g/mile by the 2025 model year [3]. In addition a flexible fueled vehicle certified to the PZEV level must meet the tailpipe emissions standard with both E85 and gasoline fuels [3]. Therefore, trapping of HC emissions may be required for automobile manufacturers to produce flexible fuelled and turbocharged vehicles, while meeting LEV-III mandates.

A catalyzed HC trap combines a conventional TWC washcoat (WC) layer over a HC adsorbant material, such as a zeolite WC layer on a cordierite honeycomb monolith as shown in [Figure 1](#). Ideally, cold-start HC emissions are retained by a combination of physical and chemical interactions in the channels and/or cages of the zeolite structure and then as the exhaust gas warms-up the WC layer, the stored HC emissions are passively released out of the zeolite and through a hot TWC over-layer where they are oxidized to CO₂ and water.



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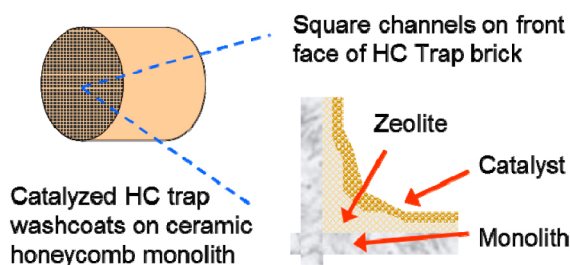


Figure 1. Example of a Catalyzed HC Trap

Catalyzed HC trap technologies have been evaluated at automotive companies such as Ford Motor [1] and Hitachi [4], while others went further and put them on production vehicles such as the Nissan Sentra CA [5] and the Toyota Camry PZEV [6]. The structure of a HC trap zeolite is known to degrade from exposure to steam above 800°C [5]. Therefore HC traps are placed far from the engine at the second converter assembly, or underbody location, where they are limited to a temperature of 750°C at the inlet [5] during dynamometer durability aging to accumulate an equivalent use of 150,000 miles (241,402 km) according to the PZEV certification mandate.

Solving the challenge of HC storage efficiency and effective HC release temperature requires careful selection of the zeolite with high temperature aging resistance. This involves selection between zeolite types having different primary and secondary building units, pore mouth diameters, pore structure in terms of 1-dimensional, 2-dimensional and 3-dimensional pores and pore volume. The silica to alumina ratio (SAR) also impacts thermal stability as well as Brønsted acidity. Molecules that are small enough to enter the pores are physically stored and may chemically interact with Brønsted acid sites ($\text{Al}^+-\text{OH}^+-\text{Si}$) which are formed at the trivalent alumina sites due to the need for electrical neutrality within the structure and the presence of strong electric fields in the vicinity of the OH groups. These Brønsted acid sites are known to donate protons to adsorbed HC molecules such as alkenes and alcohols. This can result in the dehydration of alcohols such as ethanol to alkenes which can further oligomerize to higher molecular weight hydrocarbons via a carbenium ion mechanism. Gasoline PZEV cold start hydrocarbon exhaust contains significant amounts of propene and toluene [8], and these molecules are commonly used to probe the range of effectiveness of a zeolite as a HC trap [1, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14].

Solving the challenge of stored HC oxidation in a gasoline vehicle exhaust environment requires oxygen to be available when the HC desorbs from the zeolite. Oxygen storage (OS) materials in TWC WCs provide oxygen to the catalyst during rich exhaust perturbations (deficient oxygen) for HC oxidation; then are replenished during lean exhaust perturbations (excess oxygen) and effectively dampen the inlet air/fuel fluctuations [9, 15]. The second converter assembly receives the residual oxygen and operates at or just

below the stoichiometric level. In addition, the availability of stored oxygen as a function of temperature is not well aligned for the release of stored HC from the zeolite. For typical aged OS materials redox activity associated with the reduction of Ce^{4+} to Ce^{3+} falls in the temperature range of 350 - 600°C which is higher than the desorption temperature of the hydrocarbons. However, in the presence of the PGMs such as platinum (Pt), palladium (Pd) and rhodium (Rh) the OS function can be strongly promoted with redox activity now shifted to temperatures as low as 150 - 350°C [16, 17]. Typical Pd catalyst on ceria-zirconia has shown oxygen release at 300°C and above after aging [16, 17], while HC release data has shown that the majority of the HC desorbed from a typical zeolite below 300°C after aging [4].

Recent HC trap evaluation studies disclosed the TWC layer PGM content in the range of 80-100g/ft³ [1, 18]. The first production catalyzed HC trap was from Nissan in 1999 [5]. Nissan HC trap technology at that time used a total Pd and Rh loading of 320 g/ft³ (Pd/Rh of 11/1) [19]. High content of precious metal enables a costly method of low temperature oxidation of stored HC in the zeolite. Other, less costly methods to improve catalyzed HC trap operation could be used such as changes to the zeolite layer and TWC WC OS content.

This work will demonstrate significant advancements in HC trap material sets. Durability has been extended beyond 800°C. The performance has been further enhanced by optimizing their architecture. This results in improved HC trap performance at significantly lower PGM loadings with the proper vehicle calibration.

HC TRAP FORMULATIONS

The HC trap formulations consisted of two basic architectures. The first architecture consisted of the HC trap layer by itself. The second architecture applies a conventional TWC layer over a HC adsorber layer, c.f. Figure 1. For the Base reference technology the trap layer had a silica binder consisting of 12 wt% of the trap layer with the remainder of the WC consisting of a medium pore size zeolite, in this case a beta zeolite. In the current study the Base technology was always evaluated with the TWC layer present. The higher PGM loaded baseline trap was designed similar in PGM load to those used by Nissan over ten years ago [19]. On the other hand the lower PGM loaded baseline HC trap was similar to HC traps described in reference [1] based on WC and PGM loading. Two generations of prototype HC traps were developed to improve upon the baseline formulation for vehicle applications with E85 fuel. Gen 1, Gen 1a, Gen 2 and Gen 2a technologies consisted of medium to large pore zeolites where acidity was controlled using different ion exchange and processing conditions before coating. Gen 1/Gen 2 differs from the corresponding Gen 1a/Gen 2a technologies by washcoat loading (WCL) only to reduce thermal mass during light-off. The Gen 2 trap was similar to Gen 1, but with a different kind of acidic zeolite. The TWC

overcoat for these later technologies was different than the Base technology and consisted of a more advanced TWC layer where all three PGMs (Pt, Pd and Rh) were included in the same layer. Coating of the traps was achieved by preparing slurries of appropriate solids and then flooding and clearing the support substrate channels using techniques well known in the art [21]. The trap layer was dried and calcined at 550°C before application of the TWC layer. The supports used for the dynamometer studies consisted of ceramic monolith substrates having a nominal cell geometry of 62 cells/cm² (400 cpsi), 150 µm wall thickness (6.5 mil) and dimensions of 10.16 cm × 10.16 cm × 15.24 cm (4" × 4" × 6") giving a total volume of 1.23L or 75.4 in³. The sample descriptions are summarized in Table 1 below.

Table 1. Sample Information

Sample	TWC Layer			Zeolite Layer	
	WCL	PGM Load	Pt/Pd/Rh Ratio	WCL	Acidity
Base	High	300g/ft ³	20:278:2	High	Low
Base	High	135g/ft ³	6:127:2	High	Low
Gen 1	Low	135g/ft ³	6:127:2	Low	High #1
Gen 1a	Low	100g/ft ³	4:94:2	High	High #1
Gen 2	Low	135g/ft ³	6:127:2	Low	High #2
Gen 2a	Low	100g/ft ³	4:94:2	High	High #2

EXPERIMENTAL METHODS

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 dynablender and flow controllers to 3 L/min. Most of the stainless steel tubing was wrapped with heating tape (red lines) and maintained at 150°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 one inch long HC trap sample core was placed towards one end of the quartz reactor tube as shown in Figure 2. The inlet face of the core was positioned near the oven outlet to primarily heat 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 direct the gases either to the sample or to the bypass line. Flow leaving the downstream solenoid was evenly split off to two sets of analyzer benches. One stream was diluted with 2 L/min of nitrogen, mixed in a 4ft long × ¾ inch OD heated tube and sent to an MKS Fourier Transform Infra-Red (FTIR) analyzer. The other stream was diluted with

11 L/min of nitrogen, mixed in a 4ft long × 5/8 inch OD tube and a sample was pumped to the FID/O₂ gas analyzer bench with the rest going to vent. Instrument signals from the various analyzers were acquired at a 1 Hz rate. The MKS FTIR recipe (calibration) included the following HC species: methane, formaldehyde (methanal), ethene (ethylene), ethane, ethanol, ethanal (acetaldehyde), acetylene, propene (propylene), iso-butene (2-methyl propene), 1,3-butadiene, iso-pentane (2-methyl butane), cyclohexane, benzene and toluene (methyl benzene).

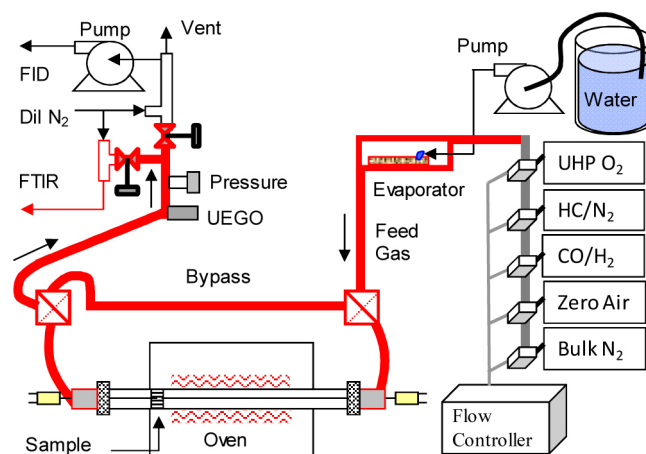


Figure 2. Ford Lab Flow Reactor Schematic

The feed stream used for the flow reactor adsorption experiments consisted of a 0.18% HC blend, 0.25% CO, 0.08% H₂, 10% H₂O vapor and balance air at 3 L/min. The HC blend contained 500 ppm ethanol (C₂H₅OH), 90 ppm ethanal (C₂H₄O), 706 ppm propene, 282 ppm iso-pentane, and 212 ppm toluene. This gas composition was chosen to be roughly between gasoline and E85. Initially a baseline feed was established by running in bypass mode. 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 directed to the bypass mode. The flow reactor feed stream was adjusted to one of two types while maintaining the reactor feed at 3 L/min. The feed stream used for the flow reactor inert temperature programmed desorption (TPD) experiments consisted of 100 ppm CO, 40 ppm H₂, 10% H₂O vapor and balance N₂ at 3 L/min. This inert feed gas stream was used to determine the temperatures of unconverted HC desorption. The feed stream used for the flow reactor stored HC oxidation TPD experiments consisted of 500 ppm CO, 200 ppm H₂, 700 ppm O₂, 10% H₂O vapor and balance N₂ at 3 L/min. This oxidation feed gas stream was used to determine the efficiency of stored HC conversion through the TWC overlayer. The reactor feed was directed to the sample as the oven began the TPD phase at 85°C/min up to 650°C inlet/550°C outlet. At the end of the temperature ramp, a burn-out procedure was performed where the water pump was shut off, the bulk gas was switched to air and the sample tube was

moved so that the entire sample was inside the oven. Once the outlet temperature reached 650°C, the oven temperature was cooled to 500°C. The bulk gas was then switched to a rich preconditioning feed of 0.25% CO, 0.08% H₂ in N₂. Once the UEGO signal reached 0.99λ, the CO/H₂ flow controller was shut off and the sample was cooled back down to 30°C in N₂. At least three tests of each TPD evaluation type were run per sample.

The samples evaluated on the flow reactor were aged downstream of a sample furnace fed with pulse combusted isooctane with 0.0 ppm sulfur, as shown in Figure 3. The full useful life (FUL) 4-mode aging procedure is identical to one described in another paper [20] for a “Conditioning TWC” sample located one inch behind the secondary oxygen injection point. To mimic an underbody aging, the desired HC trap sample was located 85mm behind the conditioning TWC and was cyclically heated between 740°C during the rich mode 2 ($\lambda = 0.92$) and 840°C during the lean exothermic mode 4 ($\lambda = 1.3$) for an exponentially weighted average temperature of about 760°C over 50 hours. This HC trap aging protocol has been correlated to 150,000 miles of accumulated deterioration on a vehicle underbody HC trap.

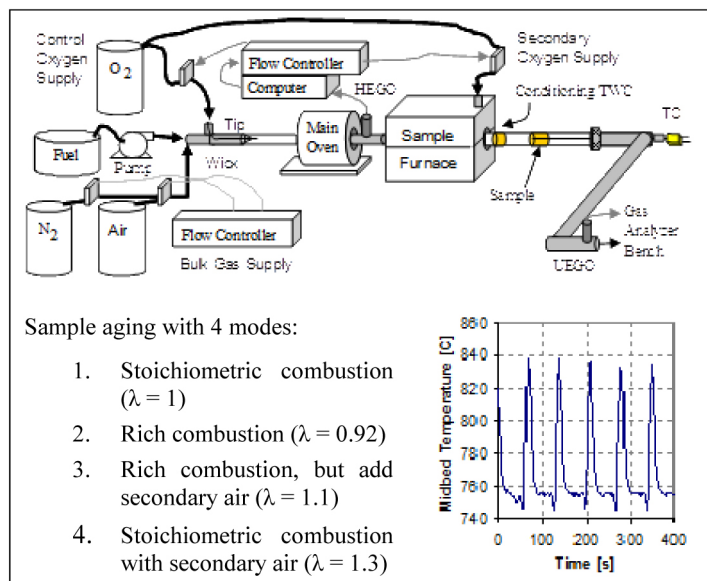


Figure 3. Ford Lab Pulse Flame Combustor Schematic

Engine Dynamometer Evaluation

Engine dynamometer testing was carried out using a Ford 4.6 L, V-8 engine with multi point fuel injection (MPFI). Wide-range oxygen sensors on each exhaust manifold allowed for tight fuel control on each exhaust bank. The intake air for the engine was controlled for temperature and humidity in order to provide a stable and repeatable exhaust environment. The intake air flow rate was measured with a mass air flow meter (MAF) and controlled by adjusting the throttle position. Engine RPM was controlled by adjusting the

dynamometer loading. The exhaust from only one bank was used for the evaluation.

Two types of fuel were used for the catalyzed trap evaluations. The primary fuel is EPA Tier II EEE. This fuel is not adjusted seasonally so the hydrogen-to-carbon ratio is very consistent year round. The second fuel is a mix with a target of 15% EPA Tier II EEE and 85% ethanol. There were no changes made to the fuel delivery system on the engine for the different fuel types. Table 2 shows a typical analysis for each of the fuel types.

Table 2. Engine Dynamometer Evaluation Test Fuel

	EPA Tier II EEE	EPA Tier II EEE w/ 85% Ethanol
Density, kg/l	0.743	0.783
Carbon, wt %	86.18	56.29
Hydrogen, wt %	13.37	13.14
Oxygen, wt %	0.00	30.60
Sulfur, wt ppm	23	3
Ethanol, vol %	0	85±1
Gasoline, vol %	100	15±1

Two emission benches were used to measure exhaust gas constituents entering and leaving the HC trap. Each bench consisted of an FTIR, a heated flame ionization detector (HFID) for THC, and a paramagnetic O₂ analyzer. The FTIR provided volumetric concentrations of CO, CO₂, NO, NO₂, N₂O, NH₃, and various HC species.

At the beginning of the test, before the engine was started, compressed air was introduced into the exhaust system at the outlet of the HC trap (HCA). As illustrated in Figure 4, the air flows through the HC trap and the TWC thus preventing the exhaust from contacting the parts being tested. To initiate a test the engine is started and allowed to reach a stabilized operating temperature. The air intake flow rate is controlled at 20 g/s and the engine speed at 1000 RPM. Fueling is controlled to maintain lambda at 1.00 with a very small modulation. Only half of the engine exhaust is utilized for the evaluation of the HC trap samples.

When the engine has reached a stabilized operating temperature and the HCA In TC measures below 35°C, the HC storage phase begins. The cooling air is turned off, the bypass valve is closed, and the valve downstream of the HC trap is opened, forcing the exhaust through the TWC and then through the HC trap. This is illustrated in Figure 5. As the TWC heats up, hydrocarbons are adsorbed and stored in the HC Trap, and then released as the trap heats up. HCs entering and leaving the trap, as well as temperature data are collected at 1 HZ. These conditions are maintained until the HCA In TC reaches 400°C.

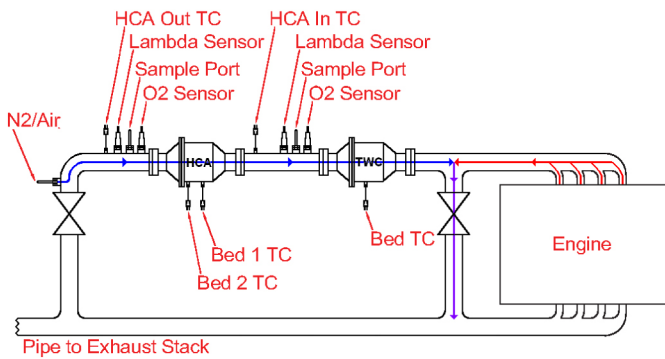


Figure 4. Exhaust flow during engine warm-up and HC Trap cool-down

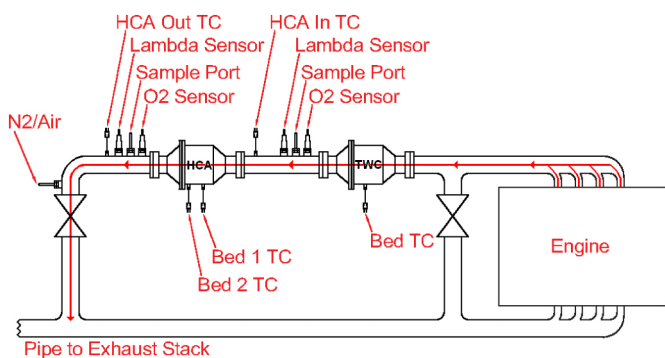


Figure 5. Exhaust flow during HC Storage, HC Release, and Lean Purge

At this point, the engine conditions are adjusted to provide a hot, lean environment. This step ensures that the HC trap is purged of all hydrocarbons. The air intake is increased to 30 g/s while fueling is adjusted to lambda 1.02. This condition is maintained for 10 minutes.

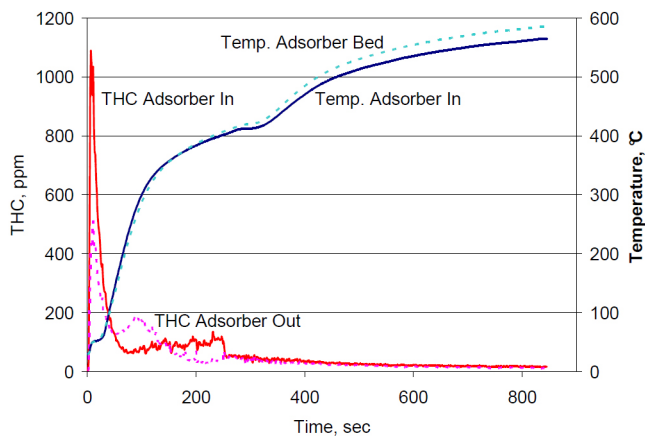


Figure 6. THC Concentrations and Temperatures during a Typical Cycle using EPA Tier II EEE Fuel

The flow is then set to the bypass configuration as at the beginning of the test using N₂ to cool the HC trap until the *HCA In TC* reaches 150°C. Then, the N₂ is replaced with compressed air until the *HCA In TC* reaches 35°C. The process is repeated two additional times for a total of three HC storage and release cycles. The first cycle acts as a conditioning cycle and the data from cycles two and three was either averaged or the 3rd cycle was used for reporting the storage and release data. A typical cycle is shown in Figure 6.

Vehicle Emission Evaluation

The test cell evaluation facility consisted of a 48 inch single roll dynamometer, a constant volume sampler (CVS), a three-probe modal emission sampler, a remote mix tee (RMT) dilution system and a data acquisition unit for electronic signals. The test cell was maintained at a temperature between 70°F and 80°F (21°C and 27°C). The dynamometer simulated road conditions that allowed the test vehicle to run at the correct speed, torque and load during the test. Tailpipe emissions were collected in a bag during each phase using a procedure that was consistent with the methods used by the EPA. THC, CO, NO_x, CO₂, Methane (CH₄), non-methane hydrocarbon (NMHC), ethanol (C₂H₅OH), ethanal (C₂H₄O) and methanal (CHOH) emissions were measured using Horiba MEXA 9000 and fourier transform infra red (FTIR) analyzers at a 1 Hz data collection rate. Gas chromatography (GC) was used to analyze the bag 1 HC emissions. Wet chemistry impingers and cartridges were used to collect alcohols, aldehydes and ketones from the tailpipe exhaust to calculate NMOG emissions.

Engine Dynamometer Aging

Engine Dynamometer aging was carried out using an 8.1 L V-8 engine with MPFI. Up to four exhaust systems could be aged in parallel, one per channel. The 4-mode engine operation used during aging is similar to the one described in Figure 3.

CALCULATIONS

The calculation method employed to determine the HC trap performance metrics in the plug flow reactor are shown in Figure 7. 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 (A1) and the adsorbed HC desorbed value (A2). 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. C₂H₄O, CO₂, etc.) were calculated by the area under the desorption curve divided by the sum of the adsorbed HC converted on a C1 hydrocarbon basis. The temperature was recorded at which 50% and 80% of each HC component desorbed out of the trap unconverted. 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 hydrocarbon basis. The total species integrated desorption area (A1) was divided by the integrated adsorption area (A0) for the five HC species and the results for each trap were 100% +/- 4%.

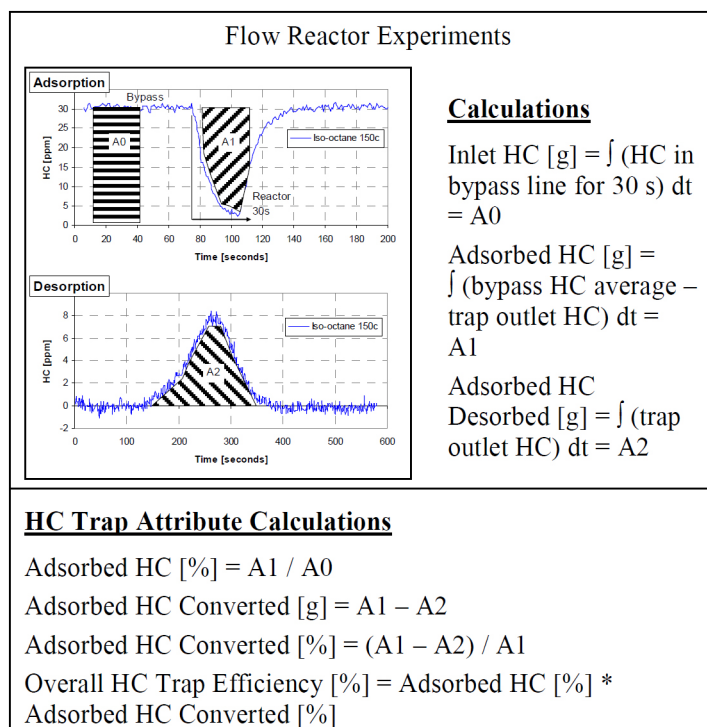


Figure 7. Calculations for HC Trap Efficiency

RESULTS

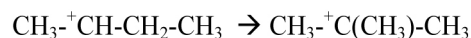
Laboratory Plug Flow Reactor

Appendix 1 shows the results of the aged samples described in Table 3 with a pulse of the 5-part HC blend for 30 seconds at 30°C. The inlet HC species were adsorbed with about 95% efficiency, except for propene. Propene adsorption efficiency varied among the samples. The Gen 1 and Base 135 g/ft³ sample propene efficiencies were 63% followed by the Gen 1a at 69%, Base 300 g/ft³ at 75% then the Gen 2a sample at 81%. Propene may have chemisorbed on the abundant Pd metal sites considering the performance

difference with the Base HC trap at the two TWC PGM loadings. Thus, the inherent adsorption features of the trap may be convoluted by adsorption of propene by the higher Pd loading of the TWC layer of the Base 300 g/ft³ sample.

Appendix 2 shows the results of the aged samples preloaded with the 5-part HC blend and subjected to a TPD in the inert feed gas stream. Several HC species were observed that were not fed to the zeolite in the adsorption step yet desorbed at high temperatures during the TPD. The main desorption products at the higher temperatures consisted of 2-methyl butane, toluene, methane, and ethanol and to a lesser extent ethene and 2-methyl propene. Our MKS FTIR recipe categorized 2-methyl butane and 2-methyl propene as surrogate species for all medium and large chain alkane and alkenes, respectively. CO and CO₂ formation was also observed with much higher formation of CO and CO₂ at lower temperatures for the temperature programmed desorption under oxidizing conditions.

The presence of the main hydrocarbons during the desorption process can be accounted for based on the expected chemistry for alkenes and alcohols adsorbed onto acidic silica-aluminas and zeolites as described in other papers [22, 23, 24, 25, 26, 27, 28, 29] and references therein. These types of supports are known to adsorb alkenes strongly and promote oligomerization to higher hydrocarbons [22, 29]. Ethanol can easily be adsorbed into zeolites through an ethoxy or carbenium ion formation at the Brønsted acid site, which can then desorb as ethene and water with no other desorption products observed [30]. The oligomerization reactions are expected to proceed via carbenium ion formation and the reaction products should depend on the relative stability of the formed carbenium ions in the order: tertiary > secondary >> primary. Protonation of ethene by a Brønsted acid site will lead to a primary carbenium ion ZO⁻...⁺CH₂CH₃ and oligomerization using ethene as reactant will always require initial primary carbenium ion formation. The expected initial products from oligomerization of ethene are 1-butene, 2-butene and isohexene [24, 25]. The formation of 2-methyl propene can be accounted for by the fact that the secondary butene carbenium ion can rearrange on the surface to give the more stable tertiary carbenium ion which is then desorbed:



The fact that very little 2-methyl propene was observed to desorb from the high acidic zeolites in Appendix 2 indicates that oligomerization of ethene was not favored in the current system. However, later for dynamometer testing using E-85 fuel, large quantities of the branched C6 hydrocarbon methyl pentane (iso-hexane) will be observed consistent with oligomerization of ethene. Here, the large excess of ethene produced from ethanol dehydration coupled with strong Brønsted acidity can account for this observation.

A C1 hydrocarbon mass balance of the desorbing species in Appendix 2 revealed the amount of 2-methyl propene