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Reducing Cold-Start Emissions by Catalytic Converter Thermal Management

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ABSTRACT

Vacuum insulation and phase-change thermal storage have been used to enhance the heat retention of a prototype catalytic converter. Storing heat in the converter between trips allows exhaust gases to be converted more quickly, significantly reducing cold-start emissions. Using a small metal hydride, the thermal conductance of the vacuum insulation can be varied continuously between 0.49 and 27 W/m^{2}K (R-12 to R-0.2 insulation) to prevent overheating of the catalyst. A prototype was installed in a Dodge Neon with a 2.0-liter engine. Following a standard preconditioning and a 23-hour cold soak, an FTP (Federal Test Procedure) emissions test was performed. Although exhaust temperatures during the preconditioning were not hot enough to melt the phase-change material, the vacuum insulation performed well, resulting in a converter temperature of 146°C after the 23-hour cold soak at 27°C. Compared to the same converter at ambient conditions, overall emissions of CO and HC were reduced by 52% and 29%, to 0.27 and 0.037 g/mile, respectively. The maximum converter temperature during the FTP cycle was 720°C. This limited testing was performed with a nearly-fresh palladium-only catalyst, but demonstrates the potential of this vacuum insulation approach for emissions reduction and thermal control. Further testing is ongoing. An initial assessment of several production issues is made, including high-volume fabrication challenges, durability, and cost.

BACKGROUND

Concern over air pollution is growing steadily. Vehicle emissions contribute between one-third and one-half of the total U.S. atmospheric burden of carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbon compounds (HC). Their impact is even greater in many U.S. urban areas [U.S. DOE, 1992]. Increased vehicle mileage is one reason this issue persists despite significant engine and catalyst progress.

Today's converters eliminate up to 97% of CO and HC emissions. Unfortunately, a catalyst is not fully effective at temperatures below approximately 250°C for CO and 250°–340°C for HC emissions. Auto manufacturers indicate that more than 60% of all HC emissions during an FTP cycle can occur during "cold-start" periods when the catalyst is at temperatures below its "lightoff" temperature [Laing, 1994]. Consequently, the U.S. Environmental Protection Agency (EPA) is conducting driver studies and re-evaluating the FTP driving cycle [U.S. EPA, 1993]. Several changes are being considered to make the FTP more accurately reflect typical urban driving conditions. One proposed change is to add moderate-length engine-off periods, which could further increase measured emissions caused by a cool catalyst ("cool-start" emissions).

The concern over cold-start and cool-start emissions has led to significant activity by auto manufacturers and suppliers to develop new emissions treatment techniques. Leading approaches include heating the converter electrically [Laing, 1994; Socha et al., 1994] or with a catalyzed fuel-burner [Oser et al., 1994]. Electrically heated systems typically require 1 to 2 kW for 20 to 40 seconds to reduce the cold-start emissions. This 10 to 20 W-h of electric energy may be supplied by the alternator or battery, requiring at least twice this fuel energy to be consumed. Durability issues with this approach include added stress to the alternator, battery, heating element, and connectors.

Fuel-burner systems can deliver significantly more power (10 to 20 kW) resulting in very rapid lightoff. However, these systems can be fairly complex and may expose the converter to severe thermal gradients. It is anticipated that these gradients may lead to a reduction in system durability. Durability is a key issue to auto manufacturers due to upcoming extensions in the warranties for emissions control systems.

Moving the converter closer to the engine manifold has been used to reach lightoff temperatures more quickly. However, in many autos this introduces additional unwanted heat into the engine compartment,

where thermal degradation of engine components is already a significant problem. Also, the catalyst is more susceptible to exhaust temperature excursions.

Work has also been reported by General Motors [Moore and Mondt, 1993] and Ford [Hartsock et al., 1994] using insulated converters located well downstream of the engine. This can involve double-walled insulating pipe leading from the manifold to the converter, as well as high-temperature refractory insulation around the converter itself. Sufficient insulation around the converter can help the converter maintain its temperature above lightoff for several hours after the engine is shut off. A trip initiated within this time would start with much lower emissions. Some vehicles may require air-injection to fully catalyze the fuel-rich mixture typically present in the first few seconds of engine operation.

Unfortunately, to provide sufficient thermal insulation for holding heat for more than about 3 hours, conventional refractory insulation must be extremely bulky and heavy. Also, during steady-state operation of the engine, this insulation may allow the catalyst temperature to exceed safe limits (approximately 1000°C), resulting in thermal degradation and loss of emission conversion efficiency.

A better approach to the thermal management of a converter would be to use a compact insulation that could be continuously varied in thermal conductance, providing the very low conductivity needed to retain heat between trips, but providing much higher conductivity for heat rejection from the converter during engine operation. This approach is being developed at the National Renewable Energy Laboratory (NREL). The thermal results of the first two prototypes were reported in an earlier SAE paper [Burch et al., 1994] and are summarized in the following section.

INITIAL PROTOTYPE DEVELOPMENT

During the past 10 years, NREL, a U.S. Department of Energy national laboratory, has been investigating vacuum insulation for a variety of energy conservation and thermal management applications such as energy-efficient refrigerator side-walls, window glazings, and electric vehicle high-temperature battery enclosures. Conductances as low as 0.15 W/m^{2}K have been measured through the 15-mm-thick walls of 350°C hot-battery enclosures being developed at NREL. Common non-vacuum refractory insulation would have to be more than 500 mm thick for equivalent thermal resistance.

Recently, NREL has studied ways to vary the thermal conductance in vacuum insulation [Benson et al., 1994; Benson and Potter, 1994]. One approach involves introducing a very small amount of hydrogen gas into the vacuum insulation. This can be accomplished by mounting a small metal hydride with an electric resistance heater to the cold side of the vacuum insulation. The pressure of the hydrogen is a predictable function of the hydride temperature, and the gas is readily reabsorbed whenever the hydride is allowed to cool. By controlling the temperature of the hydride, the thermal conductance of the insulation can be continuously adjusted between a minimum value determined by the construction of the insulation and a maximum value bounded roughly by the thermal conductance of the hydrogen gas.

This variable-conductance insulation (VCI) was applied to automotive catalytic converter thermal management. The first two catalytic converter test articles (TA-CC1 and TA-CC2) contained cordierite converter monoliths without precious-metal loading and were used only to verify thermal performance modeling. A standard laboratory heat-retention test involved heating the converter to 650°C with an electric air-heater and monitoring the converter cooldown. The time to reach a conservative lightoff temperature of 350°C was used to evaluate heat-retention performance. Based on EPA converter cooldown data [EPA, 1993], a baseline converter was defined to have a thermal conductance of 30 W/m^{2}K (R-0.19 ft^{2}h°F/Btu insulation) at 500°C, resulting in a cooldown from 650°C to 350°C in 25 minutes (in 27°C still air). The vacuum insulation of TA-CC1 reduced converter thermal conductance to 1.1 W/m^{2}K (R-5.2) and increased the time above 350°C to 90 minutes.

Phase-change material (PCM) was added to the design to increase heat storage. For the second test article (TA-CC2), aluminum (2.2 kg) was sealed in stainless steel between the outer surface of the converter monolith and the vacuum insulation. The additional latent and sensible energy storage of this PCM tripled the heat storage capacity of the converter system.

Thermal modeling and infra-red thermography indicated that half of the remaining heat loss was occurring at the converter inlet and outlet. In an attempt to reduce the radiation and natural convection in these regions, porous ceramic inserts were added. The combination of the PCM heat storage and the porous ceramic inserts resulted in a measured thermal conductance of 0.54 W/m^{2}K (R-11) and a cooldown from 650°C to 350°C in 10 hours.

DESIGN AND THERMAL TESTING OF TA-CC3

The design of the third test article (TA-CC3) is shown in Figure 1. Two cordierite monoliths with palladium-only precious-metal loading were used (see Table 1).

Table 1 - Converter Properties of TA-CC3

Diameter	90 mm	3.5 in.
Length*	152 mm	6.0 in.
Cell Density	62 cells/cm^2	400 cells/in^2
Mass*	0.73 kg	1.6 lb
Loading	10.6 g/L	300 g/ft^3
Catalyst Ratio	0/0/1 Pt/Rh/Pd	

*For each of two monoliths.

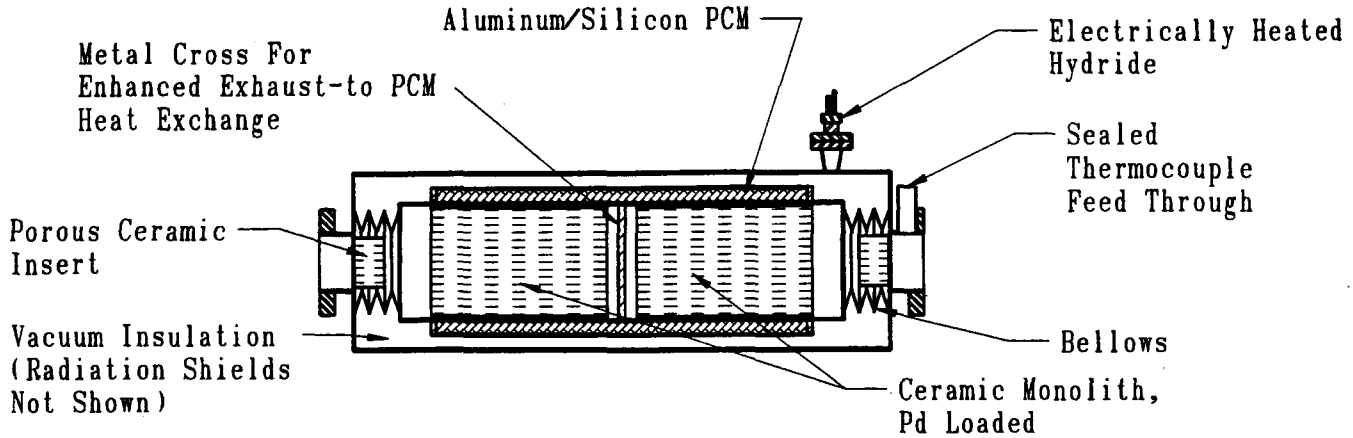

Figure 1 - Sectional View of TA-CC3

These monoliths were secured in a 102-mm-diameter stainless-steel pipe with a standard vermiculite intumescent mat. Sealed between this and a 125 mm-diameter pipe was 2.3 kg of an aluminum/silicon PCM. This eutectic alloy has 30% higher specific latent energy than pure aluminum and a lower melting point (575°C versus 620°C).

The 127-mm-diameter pipe was wrapped with 20 layers of copper-foil thermal radiation shielding and placed inside a 152-mm-diameter, 457-mm-long stainless-steel pipe. Circular radiation-shield end-caps were used to reduce heat leakage from the edges of the shields. A vacuum-capable space was formed between the outer two pipes by welding a flanged metal bellows at each end. Two 47-mm-diameter stainless-steel pipes were welded onto each bellows flange to serve as the exhaust gas inlet and outlet. The metal bellows not only reduced heat conduction from the hot inner pipe to the outer pipe, but also from the interior to the inlet and outlet pipes. Porous ceramic inserts, 25 mm long, were used in the inlet and outlet to reduce radiant and convective heat loss at the ends.

The vacuum insulation section of the test article was actively pumped down to a pressure of 9 x10^{-5} torr during a 550°C bakeout. A pinch-off seal was then made, and the hydride was heated for 10 minutes to increase its ability to getter any residual out gassing.

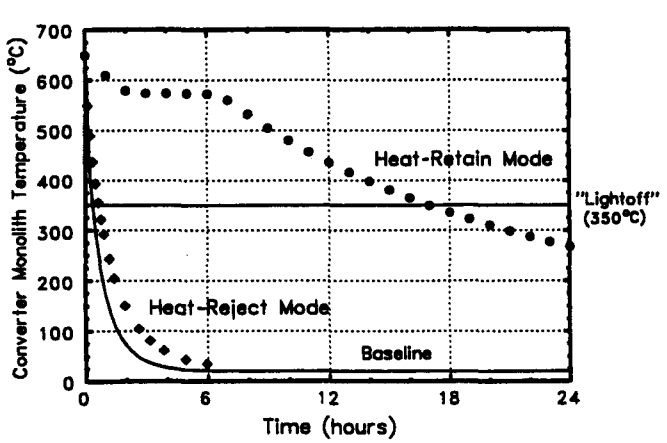

Figure 2 - Measured Converter Cooldown of TA-CC3

The cooldown test used to evaluate heat retention for TA-CC1 and TA-CC2 was repeated for TA-CC3. The results are shown in Figure 2 and Table 2. With the enhanced PCM thermal storage and vacuum insulation, the converter cooldown time from 650°C to 350°C was increased from 10 hours to 17 hours. After 48 hours, the catalyst was 135°C.

A second cooldown test was run to demonstrate the variable conductance potential of the vacuum insulation. With the converter hot, 13 kPa (100 torr) of hydrogen was introduced into the vacuum space. The converter cooldown of this heat-reject case is also shown in Figure 2. By introducing this small amount of hydrogen, the overall converter thermal conductance was increased from 0.49 W/m^{2}K (R-12) to 27 W/m^{2}K (R-0.21). This 55:1 ratio in thermal conductances would provide excellent converter heat retention between trips, yet allow heat rejection similar to standard converters when needed.

Table 2 - Thermal Performance of TA-CC3

	HRT*	HRJ*	BL*
Thermal conductance (W/m^{2}K)	0.49	27.0	30.0
650° - 350°C cooldown time (hr)	17	0.50	0.42
Vacuum pressure (torr)	10^{-4}	10^{2}	NA
Exterior temp. (650°C interior)	50°C	320°C	350°C

*HRT: TA-CC3 in heat-retain mode; HRJ: TA-CC3 in heat-reject mode; BL: baseline catalytic converter.

INITIAL FTP EMISSIONS TESTING

TA-CC3 was delivered to Chrysler for FTP emissions testing. A Dodge Neon with a 2.0-liter, 4-cylinder engine was used as the test vehicle. The standard catalytic converter was removed, and TA-CC3 was mounted in its place (about 0.8 m downstream of the exhaust manifold). No supplemental air pump was used on this vehicle. An initial FTP cycle was run. This first test served several purposes. It was an initial qualification of the test setup and instrumentation, including six thermocouples mounted within the test

article. It also served as a baseline for emissions of the vehicle/test-article combination at ambient (27°C) conditions. Finally, it provided some catalyst aging. Prior to this test, the only aging had been the vacuum bakeout (48 hours at 550°C) and 10 hours of exposure to 700°C air during thermal testing of TA-CC3.

Total measured FTP cycle emissions of HC, CO, and NO_x are shown in Table 3 (FTP1). The converter temperature during the cycle, measured at the center of the upstream monolith, briefly reached a maximum of 720°C. A control strategy had been developed to activate (heat) the hydride when the maximum temperature exceeded 850°C. The resulting release of hydrogen would increase the VCI thermal conductance and protect the catalyst. For these FTP tests, however, this protection was not needed.

After completing the FTP cycle, temperatures within the test article were monitored as the vehicle soaked in a 27°C ambient environment. At the beginning of the cold soak, the converter monolith was about 515°C, indicating that the aluminum/silicon PCM (melting point of 575°C) had not been melted. At the end of a 23-hour soak, the converter monolith was 146°C. These temperatures confirmed the low thermal conductance (0.5 W/m^2K at 500°C) and heat-retention capability observed during the previous laboratory thermal tests.

The vehicle was again pushed onto the chassis dynamometer and a second complete FTP cycle was run (FTP2). It was anticipated that the first pulses of exhaust gas might initially cool the monolith. A second-by-second log of monolith temperature, however, showed no signs of quenching. Instead, a steady and rapid temperature rise to lightoff was seen. Because of the heat retained in the converter, significantly lower CO and HC emissions were observed (see Table 3).

Following FTP2, the vehicle was put through a highway fuel-economy cycle plus an additional 12 minutes at 89 km/h in an attempt to fully melt the PCM. Maximum monolith and interior wall temperatures were 816°C and 657°C, respectively. This was sufficient to partially melt the PCM. Unfortunately, the higher wall temperatures caused outgassing from the fibrous ceramic material used to separate the radiation shields. This outgassing raised the pressure in the vacuum insulation above 10 mtorr and increased the thermal conductance to about 4 W/m^2K (versus 0.5 W/m^2K for a full vacuum). A problem with the hydride heater prevented reactivation of the hydride surface for gettering this residual gas. Because of the increase in the vacuum insulation conductance, the converter temperature was only 40°C after a 23-hour cold soak. To avoid this in future tests, a higher temperature bakeout will be used (750°C instead of 550°C).

A third FTP cycle was run (FTP3) with the catalyst at 40°C. HC and NO_x values were similar between the first and third FTP runs (FTP1 and FTP3). Comparing the average values for the two ambient converter tests (FTP1 and FTP3) with the warm-converter test (FTP2), Table 3 shows that total CO emissions were decreased by 52% and HC emissions were decreased by 29%.

No pressure drop or gas flow rate measurements were taken during these tests. Measurements of the test vehicle fuel economy and air/fuel ratios were compared to baseline Neon values and found to be very similar.

Table 3 - Preliminary Emissions Results of TA-CC3 (in g/mile)

Total Cycle

	FTP1	FTP2	FTP3	Ave.1&3	%Decr
HC	0.052	0.037	0.052	0.052	29%
CO	0.48	0.27	0.64	0.56	52%
NO_x	0.18	0.16	0.15	0.17	3%

Bag 1 Only

	FTP1	FTP2	FTP3	Ave.1&3	%Decr
HC	0.235	0.170	0.237	0.236	28%
CO	2.29	1.25	3.02	2.66	53%
NO_x	0.09	0.08	0.09	0.09	11%

MANUFACTURABILITY, DURABILITY, AND COST

A key question for any such new technology is whether it can be manufactured reliably and practically. Of particular interest with the variable-conductance insulation is the adequacy of standard manufacturing methods to produce a vacuum container that will survive underfloor exhaust-system conditions for 100,000 miles or more.

In the design and construction of these test articles, production catalytic converter materials have been used wherever possible (i.e. converter monolith and loading materials, stainless-steel thickness and grade, vermiculite intumescent mat). The primary components unique to this design are the vacuum insulation (hermetic welds, radiation shields, metal bellows closeouts), the variable-conductance feature (currently an electrically heated metal hydride), and the phase-change material used for heat storage.

Automated welding of clean, close-fitting parts now achieves the necessary hermeticity for production of vacuum parts in many other industries. In the automotive industry, vacuum containers with a similar size and pressure ($< 10^{-4}$ torr) have recently been introduced by Volkswagen. The item, an engine "heat battery" [Schatz et al., 1992], uses a phase-change material within a vacuum-insulated stainless-steel cylinder to store heat from the engine coolant for faster engine warmup.

On-line quality control, necessary to assure a hermetic container for the vacuum insulation, could be assured by introducing only pre-tested double-shells enclosing a vacuum to the assembly process. By treating the vacuum sub-assembly as a separately developed component, extremely high reliability will be maintained. Real-time helium leak-checking while the components are being assembled for final integration is

also a possibility. Maintaining the vacuum over the life of the vehicle will involve assuring weld durability and minimal outgassing of internal materials. An extensive durability study simulating the extreme thermal, vibrational, and corrosion environment of the vehicle is planned to address these issues. The effect of outgassing can be minimized through proper bakeout of the radiation shields and inclusion of getter material within the vacuum. The metal hydride used to vary the thermal conductance also behaves as a permanent getter for gases other than hydrogen.

The metal hydride mechanism has proven repeatable, with over 25,000 hydrogen expulsion-absorption cycles demonstrated at NREL. Its durability in underbody conditions needs verification. One area of concern is the increased permeability of many metals to hydrogen at the temperatures that can be reached in many catalytic converters. Surface treatments may be required to retain the hydrogen gas for 100,000 miles. Two alternatives to the externally mounted, electrically heated hydride would be an internally mounted hydride that would be passively heated by the catalytic converter, and a solid-conduction approach. The bimetallic solid-conduction method is well characterized in electrical switch applications in the automotive and other industries. Bimetal contacts used to rapidly and reliably carry heat to the outside shell may be adequate to protect the catalyst from extreme temperatures.

For TA-CC3, a eutectic aluminum/silicon alloy is used as a phase-change material to increase heat storage. It is sealed in the same uncoated 1.6-mm-thick 304 stainless steel used for the rest of the catalytic converter. Although there has been no sign of corrosion or leakage, a long-term, high-temperature durability study should be conducted to verify material compatibility. If needed, coatings or surface treatments would be developed.

Concerning the durability of the converter monolith and loading, this vacuum-insulation thermal management system has the potential for significantly greater protection against thermal degradation. As discussed in the previous section, extreme converter temperatures tend to be avoided with this system. In addition, cold-start emission reductions are achieved without the large thermal gradients experienced with electrically heated or fuel-fired pre-converters.

It is difficult to accurately assess the high-volume cost of this emissions reduction approach in this early stage of development. Initial estimates fall between $90 and $150 above a standard production converter. Less expensive designs have been developed that do not include the externally heated metal hydride.

WORK IN PROGRESS

These preliminary emissions results are being followed up with more extensive testing. The catalyst will be put through a full aging cycle, then FTP tests will be run using a broad range of cold-soak periods. Pressure-drop versus exhaust-flow measurements with and without the porous ceramic inserts will also be obtained.

Additional studies and test articles are planned to investigate the benefits of this approach for treating exhausts from alternative-fuel vehicles and hybrid vehicles. Engines using methanol and ethanol as fuel generally produce exhaust having much lower temperature, further delaying lightoff. Under some extended-idle and deceleration driving schedules, the converter can actually cool off and "unlight" while the engine is on. This situation is also possible with hybrid vehicle auxiliary power units (APUs). Both "series" and "parallel" hybrid vehicles can have drivetrain control systems that cause the APU to cycle on and off. Without thermal management of the converter, these cycles could produce cold-start (or at least "cool-start") emissions.

Another potential benefit of quicker catalyst lightoff might be more rapid use of exhaust heat downstream of the converter for supplemental winter heating of the passenger compartment. This additional heat source becomes increasingly important for automobiles with small, efficient engines such as those used in hybrid vehicles.

CONCLUSIONS

Based on thermal analysis and computer modeling, variable-conductance vacuum-insulated automotive catalytic converters with phase change material thermal storage were designed, built, and tested. Thermal tests demonstrated the ability of VCI and 2.3 kg of PCM to maintain the converter temperature above a lightoff temperature of 350°C for 17 hours (compared to 25 minutes with conventional converters). An electrically heated metal hydride source of hydrogen was used to increase the thermal conductance of the test article by 5500% and reject heat at a rate comparable to conventional converters.

Although limited FTP emission testing failed to fully melt the PCM, heat-retention performance of the vacuum insulation was verified. FTP-cycle CO and HC emissions were reduced by 52% and 29%following a 23-hour cold-soak at 27°C with a nearly-fresh palladium catalyst. This emission-reduction method offers several possible advantages over electrically heated or fuel-fired preheat converters including simplicity, lower cost, and reduced thermal strains.

Further development is needed to maximize performance and verify manufacturability, durability, and cost-effectiveness.

ACKNOWLEDGMENTS

This work was performed by the National Renewable Energy Laboratory under Contract No. DE-AC02-83CH10093 with the U.S. Department of Energy. The authors gratefully acknowledge the time, expertise, and resources contributed by Chrysler Corporation for the emissions testing and the reviewing of this paper.

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