Aftertreatment for Low Emission Vehicles

A SELECTIVE REPORT FROM THE 1999 SAE ANNUAL CONGRESS

The 1999 annual congress of the Society of Automotive Engineers (SAE) took place in Detroit from 1st to 4th March with 46,309 delegates and 1104 companies exhibiting new products. Some 1120 papers were scheduled for presentation covering all the automotive technologies, although fire curtailed some sessions. Papers on exhaust gas aftertreatment focused on tighter emissions requirements from conventional gasoline, lean-burn gasoline and diesel engines. Some new legislation and a selection of papers are reviewed here, with SAE numbers being given.

New Legislation

In 1998 a number of new emissions levels were introduced or proposed. In the U.S.A. National, NLEV, standards were adopted in 49 states, and the Environmental Protection Agency (EPA) concluded that the more stringent Tier II standards were needed. California adopted a LEV II programme, stringent standards for hand-held engines, a three-way catalyst (TWC) based standard for off-road spark ignition (SI) engines less than 25 hp, tight standards for recreational marine engines, and higher requirements for some motorcycles. The EPA announced plans to establish a voluntary heavy-duty diesel engine retrofit programme. The revised LEV and ULEV standards involve major hydrocarbon (HC) and nitrogen oxides (NOx) reductions, and the SULEV standard has exceptionally demanding emission levels.

In Europe gasoline car emissions have been agreed for 2000 (Stage 3) and 2005 (Stage 4). A range of measures will be developed for on-board diagnostics (OBD), cold start and in-service compliance along with tax incentives allowed for early introduction of Stage 4 standards. Gasoline and diesel fuel sulfur levels will also be markedly reduced.

Conventional Gasoline Engines

Low emissions demand that aftertreatment systems operate immediately after starting the engine. High activity catalyst formulations have low temperature light-off, and when combined with effective heat - and mass transfer and low heat capacity, respond quickly. Mounting the catalyst close to the manifold (close-coupled) minimises the time the catalyst takes to reach working temperature.

In the U.S.A., SWRI and MECA (1999-01-0774) demonstrated that LEV II ULEV levels can be obtained by combining advanced catalysts on high cell-density substrates with insulated exhaust components. In examining systems for Europe – Elasis, Napoli University, Magneti Marelli and Fiat in Italy (1999-01-0775) concluded that a close-coupled starter catalyst and a main underfloor catalyst, or a closed-coupled main catalyst, are cost-effective solutions.

Thin Wall High Cell-Density Catalysts

These catalysts have high geometric surface area with lower heat capacity and backpressure than standard materials. BMW, NGK and Friedrich Boysen (1999-01-0767) developed a system with a relatively thin wall substrate (400 cpsi/4.3 mil, cells per square inch/thousandths of an inch) for a LEV/Stage 3 V8 engine. This had a close-coupled high palladium tri-metal catalyst on each air-gap insulated manifold, and an underfloor palladium/rhodium (Pd/Rh) catalyst. Corning, Johnson Matthey and DaimlerChrysler (1999-01-0273) compared physical durability of standard (400 cpsi/6.5 mil) and thin wall substrates (600 cpsi/4.3 mil and 400 cpsi/4.5 mil) coated with high temperature stable washcoats. Predicted and measured thermal shock parameters agreed, showing that the new catalysts have superior thermal shock resistance and are suitable for close-coupled positions.

Corning (1999-01-0269) confirmed improved thermal shock characteristics are due to a lower coefficient of expansion resulting from improved composition and manufacturing processes. Delphi, Corning, SWRI and ASEC (1999-01-0271) had benefits using 600 cpsi/3.5 mil substrate over standard 400 cpsi/6.5 mil material;

but 600 cpsi/4.3 mil had more backpressure, restricting acceleration, which was not the case with the 600 cpsi/3.5 mil substrate.

DaimlerChrysler, Degussa and NGK (1999-01-0272) reported a similar study for V6 and V8 engines for Stages 3 and 4. Their system used close-coupled (600 cpsi/3.5 mil) and two underfloor catalysts (400 cpsi/4.3 mil). Contributions from the washcoat thickness to the backpressure of high cell-density catalysts were noted. Mazda (1999-01-0307) varied the amount and ratio of platinum group metals (pgm), catalyst promoters, catalyst layering and cell-density. Both 600 cpsi/4 mil and 900 cpsi/2 mil substrates were examined, the latter giving 35 per cent lower tail-pipe HC emissions. Honda and NGK (1999-01-0268) compared 600 cpsi/4.3 mil and 1200 cpsi/2 mil catalysts. High conversion was obtained with the high cell-density catalyst, but mechanical strength was a concern.

Honda's (1999-01-0772) ZLEV system (one-tenth of the ULEV limits) had reduced engine emissions due to high swirl with variable valve timing and lift, and improved spark plugs with durable small-diameter iridium centre electrodes. They maintained high temperature and prevented quenching. Fuel control was optimised during start-up, and precise air:fuel control was maintained by controlling the air:fuel ratio in each cylinder. Retardation of the ignition gave fast heating of a close-coupled high cell-density Pd-only starter catalyst (1200 cpsi/2 mil), followed by TWCs and a two layered catalyst comprising a HC-trap with a top layer TWC. At low temperature HC is trapped, but is released as the system warms to 100°C, when the TWC layer converts part of the released HC.

Electrically Heated Catalysts

Trapping HCs when cold then releasing them onto a working catalyst has several variations. Other methods of treating HCs include Exhaust Gas Ignition (EGI) when air-diluted rich exhaust gas is combusted ahead of a TWC, and the use of a special catalyst which oxidises carbon monoxide (CO) at low temperature. Electrical pre-heating has been widely researched and Emitec (1999-01-0770) reviewed the advantages of Electrically Heated Catalysts in SULEV systems. Increasing the gas temperature by electrical heating can offset thermal mass effects and shorten the catalyst light-off time.

Platinum Group Metals in Catalysts

Originally TWCs were predominately platinum/rhodium (Pt/Rh) formulations. Legislation, particularly in the U.S.A., emphasised attaining low HC emissions, and Pd-containing catalysts can achieve high HC conversions. Using these catalysts resulted in a wider use of Pd at increasingly higher loadings. Three types of Pd-containing TWCs are available: Pd-only, Pd/Rh, and tri-metal (Pd/Rh/Pt). The amount of Pd used in autocatalysts now exceeds that of Pt and Rh, and greater flexibility in the metals used might help future supply/demand considerations.

Johnson Matthey examined (1999-01-0309) conditions favouring Pd/Rh compared with Pd-only catalysts for NOx control. At low temperature both perform similarly, but high temperatures accentuated differences which give advantages to Pd/Rh catalysts in NOx conversions. This is because sulfide poisoning becomes more significant at high temperature when the exhaust is rich (reducing), so actual catalyst choice depends on the vehicle. Johnson Matthey (1999-01-0308) showed that increasing the Rh:Pd ratio in a standard lower loaded Pd/Rh catalyst maintained acceptable performance, but new improved formulations have lower Pd content. The activity of a new low-loaded Pd/Rh catalyst is better than the standard with twice the amount of pgm. This will allow Pd load reductions or improved performance at standard loadings. Pt/Rh catalysts with higher activities than standard Pd/Rh formulations have also been developed, thus giving options for managing pgm demand.

Lean-Burn Gasoline Engines

Direct injection (DI) gasoline engines capable of lean operation offer reduced fuel consumption, but their NOx control is a challenge. One method is to store NOx and release it for reduction over a TWC. A NOx-trap combines these. Ricardo (1999-01-1281) had a fast light-off close-coupled catalyst and underfloor NOx-trap on a car with a stratified charge DI engine. With significant engine management modifications low tail-pipe emissions can be achieved, and effective NOx-traps allow engine calibration for fuel economy.

Control of operating parameters is critical for optimum performance and Ford (1999-01-1283) measured stored NOx from the quantity of fuel used in regeneration. Bosch (1999-01-1284) described a management system for DI gasoline engines, aftertreatment assumed a fast heated catalyst for early HC conversion, a NOx-trap with low oxygen storage (OSC) and a TWC with significant OSC. Temperature and oxygen sensors provided control inputs. Toyota (1999-01-1279) analysed NOx-trap sulfur poisoning, and suggested a hexagonal cell substrate of uniform washcoat thickness containing components which form hydrogen via steam reforming. While progress has been made, NOx-traps need low sulfur fuel, which should become increasingly available.

Diesel Aftertreatment

Diesel engines run lean with excellent fuel economy, but reduction of their NOx and particulate matter (PM) is difficult to achieve. Michael Walsh (1999-01-0107) reviewed diesel legislation and the tremendous progress in diesel combustion engineering, fuelling, and oxidation catalysts. A few modern diesel cars already meet Stage 3 emissions levels and a few small cars may meet Stage 4 requirements before 2005, but most vehicles will require effective NOx aftertreatment.

NOx Reduction and Soot Removal

Methods to remove NOx were discussed by the German FEV (1999-01-0108). Diesel exhaust contains only a small concentration of reducing species, limiting lean-NOx catalysts to about 15 per cent conversion. Injecting fuel, via the engine or directly into the exhaust, increases the available reductant and can increase NOx conversion to about 30 per cent. Degussa and ICT (1999-01-0109) showed how two Pt catalysts could be optimised. Unfortunately, such approaches will be insufficient in many situations, and methods able to provide high NOx conversions are needed, Selective Catalytic Reduction (SCR) being one. Ammonia, or a derivative such as urea, is injected into the exhaust before a SCR catalyst.This can give NOx conversions of 75 per cent, but there is no infrastructure for urea distribution and the weight and volume of an additional tank for refuelling must be considered. Another emerging technology is NOx-trap technology, similar to that for DI gasoline engines and operating at the lower temperatures of diesel exhaust. Sulfur tolerance, low temperature operation and obtaining regenerating conditions are concerns.

Soot (or PM) removal from diesel exhaust is necessary to meet future legislation. Major engine-based improvements have been successful, but more are needed. Hino (1999-01-0471) stated that with low sulfur fuel, high loaded Pt oxidation catalysts can remove some PM, but with high sulfur fuel sulfate forms over the catalyst and thus increases the PM. The Continuously Regenerating Trap (CRT™) uses a Pt catalyst to provide nitrogen dioxide which oxidises filtered PM at low temperature and prevents soot build-up in the filter and possible uncontrolled burning which can destroy filters. FEV described (1999-01-0108) a light truck fitted with a CRT™, cooled and filtered recycled exhaust gas, and fuelled by low sulfur fuel. The exhaust temperature of 200-500°C was suited to a CRT™ and is likely to be used more in future. FORTH/CPERI from Greece and Johnson Matthey (1999-01-0468) described design and selection criteria for sizing CRT™ filters. This employed a filter flow model that was validated by experimental measurement.

Conclusions

The Detroit SAE Congress has again been a focus for reviewing developments in emissions control technology; catalyst systems containing pgms clearly will still play a most crucial role in exhaust aftertreatment of low emission vehicles. SAE papers may be obtained from http://www.sae.org/products/sae99pap.htm or 400 Commonwealth Drive, Warrendale, PA 15096. M. V. TWIGG