NOx Emissions Control for Euro 6

The control of oxides of nitrogen (NOx) emissions to meet more stringent motor vehicle emission legislation has been enabled by the development of various exhaust gas aftertreatment technologies, notably those that employ platinum group metals (pgms).

Technology Developments
For gasoline engines the most common aftertreatment for the control of NOx, as well as the other major regulated pollutants, carbon monoxide (CO) and unburnt hydrocarbons (HCs), is the three-way catalyst (TWC). This technology was developed in the late 1970s (1). It allows the oxidation of CO and HC over platinum-palladium or just palladium during lean (excess oxygen) conditions to form carbon dioxide and water, while rhodium performs the reduction of NOx to N2 under rich (oxygen depleted) conditions. This technology relies on the engine operating around the stoichiometric point (air:fuel ratio of 14.7:1) where maximum simultaneous reduction of NOx and oxidation of CO and HCs can take place. Emissions standards for European gasoline vehicles which have been in force since 2009 (2) specify NOx emissions must not exceed 0.06 g km⁻¹ (Table I), a limit that is met by TWC technology.

For diesel engines, which operate under lean conditions, NOx is harder to deal with. Previous diesel vehicles used advanced engine technologies to significantly lower NOx emissions. For example, exhaust gas recirculation (EGR) is used to recirculate a proportion of the exhaust gas back into the engine cylinders to reduce the cylinder temperature during combustion and thereby reduce formation of NOx. A disadvantage of this method is that it increases emissions of particulate matter (PM). Tighter PM limits have now been enforced across many jurisdictions and are met by using a pgm-coated diesel particulate filter (also known as a catalysed soot filter (CSF)).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Date</th>
<th>NOx, g km⁻¹</th>
<th>Particulate mass, g km⁻¹</th>
<th>Number of particles, km⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compression Ignition (Diesel)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 5a</td>
<td>2009.09ᵃ</td>
<td>0.18</td>
<td>0.005ᵈ</td>
<td>–</td>
</tr>
<tr>
<td>Euro 5b</td>
<td>2011.09ᵇ</td>
<td>0.18</td>
<td>0.005ᵈ</td>
<td>6.0 × 10¹¹</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>0.08</td>
<td>0.005ᵈ</td>
<td>6.0 × 10¹¹</td>
</tr>
<tr>
<td><strong>Positive Ignition (Gasoline)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 5</td>
<td>2009.09ᵃ</td>
<td>0.06</td>
<td>0.005ᶜ,ᵈ</td>
<td>–</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>0.06</td>
<td>0.005ᶜ,ᵈ</td>
<td>6.0 × 10¹¹ᶜ,ᵉ</td>
</tr>
</tbody>
</table>

ᵃ 2011.01 for all models
ᵇ 2013.01 for all models
c Applicable only to vehicles using direct injection engines
d 0.0045 g km⁻¹ using the particulate measurement procedure
e 6.0 × 10¹² km⁻¹ within first three years from Euro 6 effective dates
New Legislation Challenges

New legislation in force for European heavy-duty diesel vehicles from 2013, light-duty diesels from 2014 and some non-road diesel engines from 2014 requires a further reduction of NOx emissions. As shown in Table I, NOx emissions for light-duty diesel passenger cars reduce from the current Euro 5 limit of 0.18 g km\(^{-1}\) to the Euro 6 limit of 0.08 g km\(^{-1}\) from 2014. PM emissions are already regulated to the extremely low level of 0.005 g km\(^{-1}\) by the current Euro 5 legislation. The development of fuel efficient lean-burn gasoline engines also presents new challenges – NOx levels typically generated in the engine cylinder, whilst lower than conventional gasoline engines, are nevertheless still well above the Euro 6 limits and therefore some form of catalytic aftertreatment is required.

The two leading catalyst technologies used to remove NOx in a lean-burn engine to meet the above legislation are lean NOx trap (LNT) or selective catalytic reduction (SCR). LNT catalysts remove NOx from a lean exhaust stream by oxidation of NO to NO\(_2\) over a platinum catalyst, followed by adsorption of NO\(_2\) onto the catalyst surface and further oxidation and reaction with metal species incorporated in the catalyst, for example barium, to form a solid nitrate phase. Once the catalyst is filled with the solid nitrate phase, the engine is then run rich for a short period to release the NOx from its adsorbed state. The released NOx is then converted during the rich period to N\(_2\) over a rhodium catalyst. SCR systems use a platinum-based diesel oxidation catalyst (DOC) or a combination of a DOC and a platinum-based CSF to oxidise a proportion of the NOx into NO\(_2\) and remove HC/CO. A NOx reductant, usually in the form of aqueous urea, is then injected into the exhaust gas after the oxidation catalyst and the NO/NO\(_2\) mixture is then selectively reduced over the downstream SCR catalyst.

The decision whether to use LNT or SCR on a vehicle involves many factors. SCR requires space on the vehicle to fit the urea tank and dosing system, which is less of a constraint on heavy-duty and larger light-duty vehicles. Furthermore, the need to run the engine rich for LNT systems is more technically demanding for larger engines so LNT systems are more suited to smaller light-duty vehicles. SCR systems are impractical for use on gasoline vehicles as their NOx output is significantly higher than from diesel, and hence unfeasibly large urea tanks would be required.

The Future

NOx and other pollutant levels emitted from vehicles are assessed by use of a standardised driving cycle for Europe. The current driving cycle which is used to measure emissions from light-duty vehicles may be changed in the future to include an even wider range of driving conditions, for example further extended low speed driving conditions such as common in congested city driving or much higher speed driving conditions than used in the current drive cycle.

For diesel LNTs the future challenge is to maximise NOx conversion at low speed driving conditions as well as providing high NOx conversion during high speed driving. For diesel SCR systems, the future challenge is also to boost NOx conversion when the engine is operating at very low speeds. This low speed challenge may be helped by moving the SCR closer to the engine where it can benefit from higher temperatures, but there are space and system layout considerations. There is currently a good deal of research ongoing into diesel powertrain optimisation for a wide range of driving scenarios.

The proposed enforcement of a particulate number limit (3) for gasoline engines in Europe also presents challenges by requiring control of PM to extremely low levels in addition to keeping emissions of other pollutants at minimal levels. One possibility is to use a filter coated with similar material to a TWC as part of the overall aftertreatment system.

For gasoline engines, new on-board diagnostic limits that come into force at Euro 6 part 2 in 2017 (3) reduce by 70% the threshold amount of NOx emitted before the driver is notified of a problem with the catalyst. Some manufacturers are therefore looking at ways of further improving the durability of catalysts, including by increasing the relative loadings of rhodium. Due to the excellent NOx reduction capability of rhodium, it may be possible to substitute palladium with small quantities of rhodium to give a cost- and performance-optimised system.

Conclusions

There remains a good deal that can be done on controlling NOx emissions from vehicles using pgms. As regulations tighten, cover more vehicle types and are adopted by more jurisdictions around the world, greater
use of pgm-containing emissions control systems can be anticipated. Good progress has been made on the control of NOx from gasoline engines and developments are being made on lowering NOx emissions from diesels to meet upcoming emissions limits.

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References

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