

Some key concepts about NO₂ and about its possible controls.
(Each of the following items can be documented in details)

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- 1 NO_x (nitrogen oxides) are a mixture of diverse compounds of nitrogen and oxygen. Most known members of the family, being present in engine exhausts, are NO (nitrogen oxide), NO₂ (nitrogen dioxide) and N₂O (laughing gas). Due to its high toxicity, NO₂ is the only member of the family which is mentioned in WHO global Air Quality Guidelines (6 October 2006). Other species are due to chemical reactions with other chemicals and sunlight in atmosphere. Hilarious gas is a real concern as a green house contributor
- 2 NO₂ exposure risk is not anymore only linked with atmosphere (at large), but has to be mainly associated with microenvironments (hotspots). For health risks assessment the traditional background air (with monitors placed far from emissions sources) is now insufficient and local air (street level or in-cabin monitoring) is more representative of the environment where huge population commute, walk, shop, live and work. Therefore primary emissions deserve a special interest and the complex atmospheric chemistry can not explain the changes of pollutant concentrations monitored in these limited areas and air volumes.
- 3 NO₂ is naturally produced by diesel combustion, but to limited extend (typically less than 5% for old combustion processes to 15% with most modern ones) and is also more and more generated by some catalytic exhaust control systems, but not by all of them. The capacity to produce NO₂ from NO in a catalytic process is function of the nature and the load of the catalytic phase and of the space velocity of the gases in the catalytic volume: Pt is the most active catalyst to transform NO to NO₂, while Pd is less active and base metals are not active at all.
- 4 Driving cycle is the key to estimate properly contribution of vehicle exhausts to air quality as it conditions the space velocity. There are evidence that FTP and NEDC underestimate by a factor of 2 to 5 actual emissions of NO_x and NO₂ when compared with specific bus or car urban driving such NYBC or ARTEMIS urban. It is therefore not a surprise that street levels air quality monitoring data are not predictable from emissions factors obtained in "legal" cycles used for certifications or verifications.
- 5 Measuring actual values of NO₂ in vehicles exhausts is also a tricky exercise as cooling or storing the gases in bags induces huge modification of the original equilibrium. According to specialists, only measurements on hot exhausts will give actual values and are more representative of the reality as the mixture is dispersed before cooling, when in CVS or in bags the mixture is cooled before dispersion. European Norm CEN/prEN14792 is a good approach.
- 6 In order to get a good evaluation of the NO_x and NO₂ impacts on the urban environment, it is absolutely necessary to proceed with embarked analysis (David Kittelson's truck) or with chase study (Morin's study). The known results are impressive and disturbing.
- 7 The only way to avoid high levels of NO₂ formation on highways, in tunnels, in urban environments, in traffic jams, in canyon streets ... is to limit to minimum and if possible zero level the use of Pt in DOC and CDPF technologies. Priority should be given to thermal regenerations strategies, eventually supported by FBC to reduce the energy demand and the CO₂ production.
- 8 Thermal regeneration can be considered as standard ones during trucks highway driving and FBC are not useful (and would be an unnecessary cost), as exhaust temperatures are high enough for "natural" regenerations. But when trucks are in urban areas, pure thermal regenerations would be difficult to be achieved; a very little concentration of FBC will make it possible. On-board dosing technologies exist which provide doped fuel only when necessary
- 9 NO₂ is an even more concerning problem in off-road applications, just because the machines are operating in a small environment volume, sometimes with a large number of machines. Additionally the dispersion effect, which is linked with displacement of on-road vehicles, does not occur with machines working without real movement and workers are operating in plumes of machines exhausts. Exposure risk associated with secondary emissions, especially NO₂, has been addressed within an exemplary approach by a consortium of occupational national insurances companies and environmental agencies in Austria, Germany and Switzerland under the leadership of Switzerland (VERT). In no other country exists a similarly ambitious program

Important differences between European and US risks associated with NO₂:

With the exception of off-road applications, domain where risks are quite similar, all concerns under urgent investigation in Europe are not similar in USA.

Europe is concerned by its large share of diesel passenger cars (most of them with DOC), high density of population in centres of cities with a lot of canyon streets and large fleets of diesel buses and diesel urban vehicles, more and more equipped with DPF. Within such a frame, exposure risk of huge populations is the core of the debate.

USA and specifically California are more concerned by the time that commuters spent in cars and schools buses (public transportation is not a real concern being exceptional). Some in-cabin exposure studies, made in California, have shown that any commuter get more than 55% of its daily exposure to pollutants such PM and NOx during only one hour driving time. Concerned population are also huge.

Europe has adopted WHO Air Quality Guideline with an annual mean value of 40µg/m³ (~20 ppb) and a 1-hour mean value of 200µg/m³ (~100ppb) [not to be exceeded more than 18 times year], applicable in 2010; while in USA the only known 1-hour exposure limit is in California with a 250 ppb (2.5 times the European limit) without exceedances consideration. Now that WHO has extended its guideline to global level, we can expect that USA and especially California will adjust their standards for good air quality at least to WHO guidelines.

Is it possible to control these emissions?

- 1 First and most effective way is avoiding producing NO₂ on purpose and to destroy NO₂ when generated by in-cylinder combustion, which is feasible with NOx control treatments close- coupled with engines (SCR or lean NOx traps)
- 2 All Pt-catalyzed DPFs are producing NO₂ on purpose: CRT patent claimed the essential role of NO₂ in soot burning but developers of such systems never tried (officially) to control the excess of NO₂ which is inevitably produced, as systems require a large excess of NOx over PM. Typically 50%+ of NOx are emitted as NO₂ in urban driving conditions, even more when the DPF itself is Pt-coated (such as in CCRT) technology. In fact there was no necessity to control NO₂ as there was no specific regulation.
- 3 Some industrial stakeholders claim that adding a SCR downstream of CRT (it is proposed as SCRT) will eliminate the NO₂ after the necessary portion being used to burn soot. It looks as an attractive option, even if it is a costly one. But the main remaining question is about its real possibility to work in the most concerning conditions: city driving and its typical creep period. SCR needs a minimum temperature of 200-220°C to work properly (complete decomposition of urea and NO₂ reduction by NH₃).
- 4 Results published on Paris trial by JM at 2005 SAE are not encouraging and the basic kinetics of NO, NO₂ and their mixtures let emerging some doubts about real efficiency regarding NO₂ itself, when NOx reduction efficiency looks good. Using vanadium or not is also important. Vanadium makes it possible to work with different ratios of NO₂/NOx, but at relatively low speed. High speed SCR, based on doped-zeoliths (avoiding vanadium attrition emissions) required a narrow NO₂/NOx ratio window of 50%, higher content of NO₂ being reduced but at a speed 10 times slower.

Conclusion

As a consequence of above concerns it is really preferable to recommend, as first option, all thermal regenerations approaches, which do not produce any additional NO₂ and to eliminate NO₂ produced in cylinder by a close-couple NOx control devices. It is the recommendation that a group of experts, working under contract for EU Commission, is going to remit soon to EU for urban area applications. Improvements of thermal approaches are required for reducing excessive energy consumption. Measuring NO₂ in addition of NOx will give a better appreciation of exposure risks.