EMISSIONS CONTROL TECHNOLOGIES TO MEET CURRENT AND FUTURE EUROPEAN VEHICLE EMISSIONS LEGISLATION

Cécile Favre, Joachim Demuynck, Dirk Bosteels

Association for Emissions Control by Catalyst (AECC) AISBL
Diamant Building, 80 boulevard Auguste Reyers, 1030 Brussels, Belgium
info@aecc.eu, tel: +32 2 706 8160, website: www.aecc.eu

ABSTRACT

The paper reviews the technologies available to meet the most recent exhaust emissions regulations for passenger cars, light-duty and heavy-duty vehicles, non-road mobile machinery and motorcycles adopted by the European Union. This includes fast light-off catalysts, more thermally durable catalysts, improved substrate technology, diesel and gasoline particulate filters, selective catalytic reduction catalysts, NOx adsorbers and lean DeNOx catalysts.

1. INTRODUCTION

AECC is an international association of European companies engaged in the development, production and testing of catalyst and filter-based technologies for engine exhaust emissions control. This includes the development, testing and manufacture of autocatalysts, ceramic substrates, filters and catalyst-based technologies to control gasoline and diesel engine emissions and specialty materials incorporated into the catalytic converters and filters.

Catalyst-equipped cars were first introduced in the USA in 1974 and appeared on European roads in 1985. It was 1993 before the European Union set new car emission standards that effectively mandated the installation of emission control catalysts on gasoline fuelled cars.

Nowadays, AECC members' technologies are incorporated in the exhaust emission control systems on all new cars, commercial vehicles, buses, and on an increasing number of non-road mobile machineries and motorcycles in Europe. They are used as part of an integrated approach to emissions control which includes the combustion system, fuel quality and electronic control systems.

2. EUROPEAN EMISSIONS LEGISLATION

The European Union (EU) emissions limits for passenger cars and heavy-duty vehicles have continuously been lowered since 1993 with the Euro 1 to 6 consecutive stages (1) and the Euro I to Euro VI stages (2) respectively. Not only have HC, CO, NOx and PM limits been dramatically reduced but also cold starts, particle number and CO_2 measurement have been added into emissions driving cycles. For engines intended for heavy-duty vehicles and non-road mobile machinery (NRMM), transient operation has also been added. The Euro 6/VI norms have also introduced requirements that ensure emissions are not only controlled on the regulatory test cycle but also in real world. Motorcycles and non-road mobile machinery have lagged behind but their environmental performance keeps improving nevertheless with Euro 1 to 5 stages for motorcycles (3) and Stages I to V for NRMM (4).

3. THE IMPORTANCE OF FUEL QUALITY

Fuel and lubricant quality affects the performance of emissions control systems either by preventing the use of a technology unless the fuel quality is improved (the improved fuel is 'enabling' the use of that technology) or by 'enhancing' the performance of emissions control systems. In this case both the existing fleet and new vehicle registrations benefit. The motor industry has published information on the effects of fuel quality, with recommendations, in the 'Worldwide Fuel Charter' (5).

Examples of enabling fuels are unleaded petrol that allows three-way catalysts to be used and ultra-low sulfur fuels required so that NOx adsorbers can be used and which ease the use of catalyst-based Diesel Particulate Filters (DPF). Lead has long been recognized as a catalyst poison as well as having impacts on human health, and is no longer permitted in European fuels. The ban on the sale of leaded petrol in EU and elsewhere, provides an example to influence other regions.

Examples of enhancing fuels are the further reductions in the levels of lead, phosphorus and alkali metals that improve the performance and life of three-way catalysts and the introduction of ultra-low sulfur gasoline and diesel fuels. Reducing sulfur levels all the way down to near-zero delivers improved performance of catalysts.

The negative impact on catalyst performance of sulfur in gasoline and diesel fuels has been reported by AECC as part of the stakeholders input to the European Commission's review on fuel quality. A technical summary on EU fuel quality is available on the AECC website (6).

The sulfate storage and release process was minimized by the introduction of the <10 ppm sulfur diesel fuel being progressively introduce across the EU since 2005. This fuel quality is necessary for the full potential of emissions control systems to be realized. Ultra-low sulfur fuels became mandatory in the EU in 2011 for passenger cars, heavy-duty applications and Non-Road Mobile Machinery.

Also, there are concerns over the use of some metallic additives, with suggestions that their use in gasoline fuel may, under some driving conditions, lead to deposits on exhaust system components such as the oxygen sensor and catalyst. Metallic or other ash-forming materials in diesel fuel will also add to the amount of ash captured by particulate filters and may require the system to be designed so as to allow for the additional ash. Detergent additives, on the other hand, offer positive benefits. Their use helps keep the fuel injection system and combustion system clean, so helping to prolong optimum operating conditions for the emissions control technology.

4. EXHAUST EMISSIONS FROM INTERNAL COMBUSTION ENGINES

Exhaust emissions can be lowered by reducing engine-out emissions through improvements to the combustion process and fuel management, or by changes to the type of fuel or its composition.
Emissions control systems – autocatalysts, adsorbers and particulate filters – in combination with good quality fuel (low-sulfur content) and enhanced engine management reduce emissions to very low levels, not only on regulatory test cycles but also in real-driving conditions.

Emissions control systems can also be applied in retrofit applications to good effect on heavy-duty vehicles and non-road machines.

5. CATALYST TECHNOLOGIES FOR EMISSIONS CONTROL

5.1 Substrate and Coating Technologies

The technology of the substrates, on which the active catalyst is supported, has seen great progress. In 1974, ceramic substrates had a cell density of 200 cells per square inch (cpsi) of cross section (31 cells/cm²) and a wall thickness of 0.012 inch or 12 mil (0.305 mm). By the end of the 70's the cell density had increased through 300 to 400 cpsi and wall thickness had been reduced by 50% to 6 mil. Now 400, 600 and 900 and even 1200 cpsi substrates are available and wall thickness can be reduced to 2 mil - almost 0.05 mm (7), (8), (9), (10) and (11).

Figure 1: Ceramic substrates

In parallel, in the late 1970's, substrates derived from ultra-thin foils of corrosion-resistant steels came on to the market. From the beginning, the foils could be made from material only 0.05 mm thick allowing high cell densities to be achieved. Complex internal structures can now be developed; 800 and 1000 cpsi metallic substrates are available and their wall thickness is down to 0.025 mm (12) and (13).

This progress in ceramic and metal substrate technology has major benefits. A larger catalyst surface area can be incorporated into a given converter volume and this allows better conversion efficiency and durability. The thin walls reduce thermal capacity and limit pressure losses. Alternatively, the same performance can be incorporated into a smaller converter volume, making the catalyst easier to fit close to the engine as cars are made more compact.

Optimized systems incorporating these new technologies are in production. The use of additional catalytic converters close to the exhaust manifold reduces the time to light-off in the cold start and, therefore, the total emissions. Light-off times have been reduced from as long as one to two minutes to a few seconds (14). Improved substrate technology, combined with highly thermally stable catalysts and oxygen storage components, allows the close-coupled catalyst approach to meet the Euro 4, 5 and 6 standards.

In the original automotive catalyst it was only possible to apply the active coating to the whole substrate. Precision coating technologies now allow different active material compositions to be applied to different areas of the substrate to optimize the performance or, in some cases, to allow different functions. This includes, for instance, coating the inlet end of a particulate filter to act as an oxidation catalyst or the outlet of a Selective Catalytic Reduction system with an ammonia slip catalyst.

A further option that can be used for some types of catalyst is to incorporate the active materials directly into the ceramic substrate, so that the extruded ceramic matrix provides catalytic activity without further coating. Such ‘homogeneous’ catalysts are primarily used in the Selective Catalytic Reduction of NOx emissions.

5.2 Three-Way Catalysts (TWC)

Three-Way Catalysts are the main autocatalyst technology used to control emissions from gasoline engines. The catalyst uses a ceramic or metallic substrate with an active coating incorporating alumina, ceria and other oxides and combinations of the precious metals - platinum, palladium and rhodium. Three-way catalysts operate in a closed-loop system including a lambda or oxygen sensor to regulate the air-to-fuel ratio on gasoline engines. The catalyst can then simultaneously oxidize CO and HC to CO_2 and water while reducing NOx to nitrogen.

Fast light-off catalysts allow the catalytic converter to work sooner after cold-start by decreasing the exhaust temperature required for operation. Untreated exhaust emitted at the start of the legislated emissions test and on short journeys in the real world is curtailed. Changes to the thermal capacity of substrates and type and composition of the active precious metal catalyst have together resulted in big improvements (15).

More thermally durable catalysts with increased stability at high temperature allow the catalytic converter to be mounted closer to the engine and increase the life of the catalyst, particularly during demanding driving conditions (16). Precious metal catalysts with stabilized crystallites and washcoat materials that maintain high surface area at temperatures around 1000°C are needed for this. Improved oxygen storage components stabilize the surface area of the washcoat, maximize the air-to-fuel 'window' for three-way operation and help the oxygen sensors to indicate the 'health' of the catalyst for On Board Diagnostic (OBD) systems. “Close-coupled” catalysts mounted immediately after the engine exhaust manifold allow the catalyst to start working within seconds (17).

5.3 Oxidation Catalysts

Oxidation catalysts are the original type of autocatalysts and were used from the mid-1970's for gasoline cars until superseded by three-way catalysts. They look much the same as three-way catalysts and their construction and composition is similar but slightly less complex. Oxidation catalysts convert carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide (CO_2) and water but have little effect on nitrogen oxides (NOx). They are now rarely used on gasoline cars in Europe because of the advantages of three-way catalysts, but they are still used in some parts of the world where emissions legislation is less stringent. They may also be used on some buses running on Compressed Natural Gas (CNG), motorcycles and for applications such as small gasoline engines for hand-held equipment such as strimmers and recreational boats.

Diesel Oxidation Catalysts (DOC) remain a key technology for diesel engines where the high oxygen content of the exhaust precludes the use of three-way catalysts. DOCs convert CO and HC but also decrease the mass of diesel particulate emissions by oxidizing some of the hydrocarbons that are adsorbed onto the carbon particles (18). All new diesel engines mounted in passenger cars, light-duty and heavy-duty trucks and buses are now equipped with DOCs.

DOCs may also be used in conjunction with NOx adsorbers, DPFs or SCR catalysts to increase the NO_2:NOx ratio or to minimize any residual injected reductant used for NOx reduction (hydrocarbons or ammonia).

5.4 Control Technologies for Particulate Matter

Particulate filters have first been introduced on diesel engines to remove diesel particulate matter (PM), but can be used with other types of engine/fuel combinations.

5.4.1 Diesel Particulate Filter (DPF)

Diesel Particulate Filters (DPFs) have been applied to production vehicles since 2000 and have become standard equipment on all new diesel cars in Europe since the introduction of the Euro 5 norm.

Some buses and trucks meeting the Euro IV, V and EEV (Enhanced Environmentally-friendly Vehicle) emissions standards were equipped with DPFs and now all Euro VI heavy-duty vehicles are equipped with them so as to meet the PM mass and particle number emissions requirements.

There is, as a result, quite an active field of development in regeneration optimization, substrates materials and catalyst improvements plus developments in related On-Board Diagnostics.

In wall-flow filters, particulate matter is removed from the exhaust by physical filtration using a honeycomb structure similar to a catalyst substrate but with the channels blocked at alternate ends. The exhaust gas is thus forced to flow through the walls between the channels and the particulate matter is deposited as a soot cake on the walls. Such filters are made of ceramic (cordierite (19), silicon carbide (20) or aluminium titanate (21)) honeycomb materials.

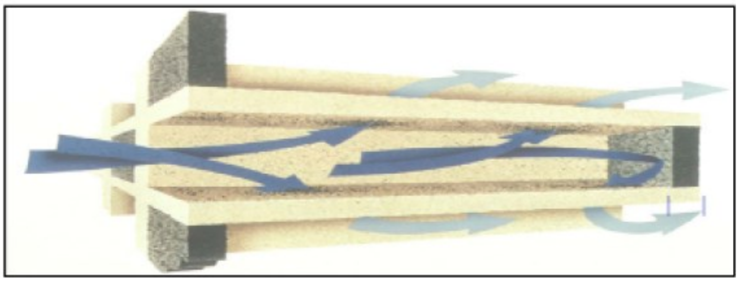

Figure 2: Exhaust gas flow through a wall-flow filter channel

Ceramic wall-flow filters remove almost completely the carbonaceous and metallic particulates, including fine particulates of less than 100 nanometers (nm) diameter with an efficiency of >95% in mass and >99% in number of particles over a wide range of engine operating conditions (22). The latest European emissions limit values (i.e. Euro 5, 6, VI and Stage V) are set on the basis of both mass and number counts to ensure control of the ultrafine particles, which are thought to be more critical indicators of health impact.

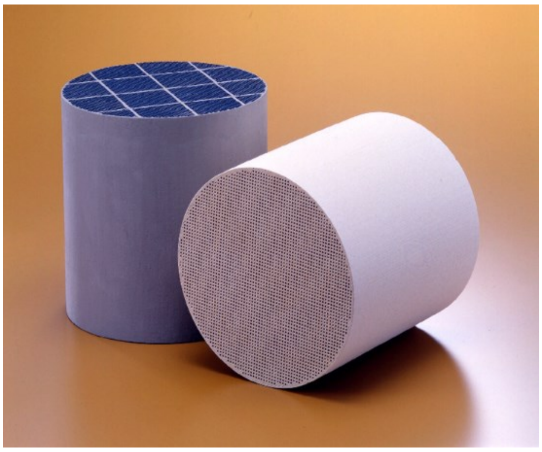

Figure 3: Wall-flow Diesel Particulate Filters (DPF)

Since the continuous flow of soot into the filter would eventually block it, it is necessary to 'regenerate' the filtration properties of the filter by burning-off the collected particulate on a regular basis. The most successful methods to achieve regeneration include:

- Incorporating an oxidation catalyst upstream of the filter that, as well as operating as a conventional oxidation catalyst, also increases the ratio of NO_2 to NO in the exhaust (23). NO_2 provides a more effective oxidant than oxygen and so provides optimum passive regeneration efficiency.
- Incorporating a catalytic coating on the filter to lower the temperature at which particulate burns. New formulations and process development intend to lower backpressure (24) and to substitute platinum by

palladium where ultra-low sulfur fuels are available. In (25), Pt/Pd formulations at a 3:1 ratio had lower light-off temperature (the temperature at which the catalyst starts to work) than Pt-only catalysts (240°C vs. 295°C) in the aged state, generated as much NO_2 for passive soot oxidation, and were resistant to sulfur contamination. In one investigation (26), platinum was completely substituted for palladium with use of a base metal catalyst. New formulations are using ceria or zirconia to make the soot react directly with oxygen at the catalyst-soot interface. One paper (27) shows a new zirconia-based soot catalyst that transfers oxygen from the gas to the soot-catalyst interface for 70% faster soot oxidation rates at 75°C lower temperatures. Enhanced versions based on ceria are showing potential to oxidize soot at temperatures as low as 260°C with very little precious metal (28).

- Using very small quantities of Fuel-Borne Catalyst (FBC), such as ceria (29) or iron additive compounds added to the fuel using an on-board dosing system. The FBC, when collected on the filter as an intimate mixture with the particulate, allows the particulate to burn at lower exhaust temperatures (around 350°C instead of 650°C) and increases the combustion kinetics (typically 2-3 minutes) while the solid residues of the catalyst are retained in the filter as ashes. The third generation of FBC (30) is based on 3 ppm iron allowing a 1.7 litre tank to last the life of the vehicle (240 000 km) and requiring no process for ash cleaning.

Figure 4: Fuel-borne catalyst dosing unit

- Fuel injector placed in the exhaust line upstream of the DPF (31). This provides a source of hydrocarbons to initiate the temperature rise for regeneration.
- Electrical heating of the trap either on or off the vehicle (32) and (33).

Trapped particulates burn off at normal exhaust temperatures using the powerful oxidative properties of NO_2 and can burn in oxygen when the temperature of the exhaust gas is periodically increased through post-combustion. Maximum exothermic temperatures must be controlled, especially in worst-case ‘drop-to-idle’ conditions when the soot combustion starts at high temperature and flow and then the engine drops to idle (34).

One study suggests that a Diesel Oxidation Catalyst is needed to get higher temperatures at the inlet face of DPF to assist the first centimetres to regenerate (35).

As the understanding of DPF fundamentals has moved forward, a porous membrane can now be added to the inlet wall so that soot is kept out of the wall (36). This improves filtration efficiency and back-pressure, as well as the correlation between back-pressure and soot loading. This correlation can be used for OBD purpose and for example, soot models using wall permeability algorithms have been developed (37). Soot sensors may also be needed in the future. Sensor concepts are being tested and compared (38). Concepts include using charge transfer by soot from one charged plate to another and using PM film electrical property measurement.

5.4.2 Gasoline Particulate Filter (GPF)

The European CO_2 legislation promotes the uptake of fuel-efficient Gasoline Direct Injection (GDI) cars in the EU. However for these GDI vehicles particle number emissions can be substantially higher on the road than on the regulatory test cycle (39), (40). Stemming from the success of the DPF for diesel vehicles, a new technology – the Gasoline Particulate Filter (GPF) – offers a durable solution to control ultrafine particles emissions from GDI cars in all driving conditions, even in highly dynamic driving (41), (42), (43), (44).

As stated by the Joint Research Centre (JRC) of the European Commission (45), the preferred solution is a relatively small GPF close-coupled to the engine. This configuration will enable passive regeneration under most operating conditions due to the relatively high exhaust temperatures of GDI engines. The main challenge in this case is to minimize any delay in the catalyst light-off imposed by the thermal mass of the GPF. Alternatively, the GPF can also be installed in an underfloor position in which case there might be some need for active regeneration under urban and repeated start-stop operating conditions. In both cases, active regeneration will most probably be achieved through retarded spark timing and split fuel injection for engines running stoichiometric and by post fuel injection for engines running lean, approaches already employed to heat up the catalyst under cold start. The ultimate target is to replace conventional Three Way Catalysts (TWC) with coated GPF systems, using the same precious metal content (46).

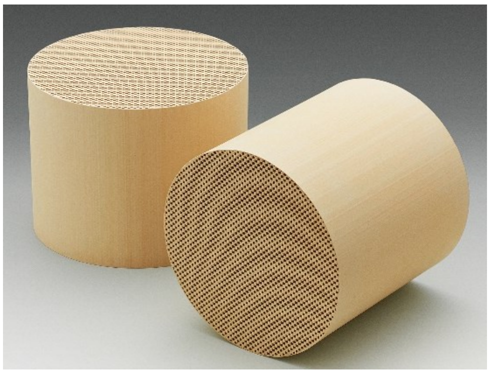

Figure 5: Gasoline Particulate Filters (GPF)

5.5 NOx Control Technologies

Lean burn systems limit CO_2 emissions and reduce fuel consumption and so are key technologies for mitigating climate change. With the increased use of diesel engines in passenger cars and the development of lean burn direct injection gasoline engines, there is an increasing need for the control of nitrogen oxide (NOx) emissions in lean combustion systems.

5.5.1 Selective Catalytic Reduction (SCR)

SCR was originally developed and used to reduce NOx emissions from coal, oil and gas fired power stations, marine vessels and stationary diesel engines. SCR technology permits the NOx reduction reaction to take place in an oxidizing atmosphere. It is called “selective” because the catalytic reduction of NOx with ammonia (NH_3) as a reductant occurs preferentially to the oxidation of NH_3 with oxygen.

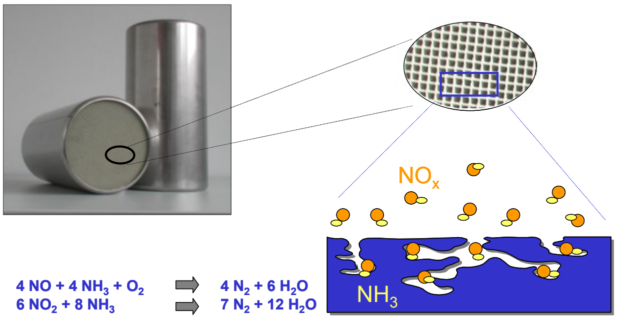

Figure 6: Selective Catalytic Reduction

In Europe SCR technology is now fitted to most new heavy-duty diesel vehicles (i.e. truck and bus) and non-road mobile machinery such as construction equipment. A growing number of diesel light-duty vehicles and passenger cars are also equipped with SCR systems. The efficiency of SCR for NOx reduction also offers a benefit for fuel consumption. It allows diesel engine developers to take advantage of the trade-off between NOx, PM and fuel consumption and calibrate the engine in a lower area of fuel consumption than if they had to reduce NOx by engine measures alone. Particulate emissions are also lowered and SCR catalytic converters can be used alone or in combination with a particulate filter.

Once the exhaust system is warm enough, SCR provides high levels of NOx reduction, when appropriate amounts of ammonia reductant are injected into the exhaust stream. For mobile source applications ammonia is used as a selective reductant, in the presence of excess oxygen, to convert over 70% (up to 95%) of NO and NO_2 to nitrogen over a special catalyst system. Different precursors of ammonia can be used; but for vehicles the most common option is a solution of urea in water (e.g. AdBlue®) carefully metered from a separate tank and sprayed into the exhaust system where it hydrolyses into ammonia ahead of the SCR catalyst. AdBlue® is a stable, non-flammable, colourless, and odourless solution containing 32.5% urea which is not classified as hazardous to health and does not require any special handling precautions. It is made to internationally-recognized standards. Urea is used as an artificial fertilizer and is found in products such as cosmetics.

The consumption of AdBlue® for a Euro 6b vehicle strongly depends on the car manufacturer product strategy, vehicle application, driving style, load, and road conditions and the urea tank needs to be topped up periodically.

For heavy-duty vehicles, the consumption of AdBlue® is typically 5-7% of fuel consumption for a Euro V engine, and 2.5-6% for a Euro VI engine, depending on driving, load and road conditions. A truck can have an AdBlue® tank which will hold enough urea solution to last for up to 10 000 km. On-board systems alert the driver when it is time to fill up the urea tank. An AdBlue® infrastructure was put in place over Europe and a dedicated website www.findadblue.com is available to show heavy-duty vehicle drivers facilities where AdBlue® is available.

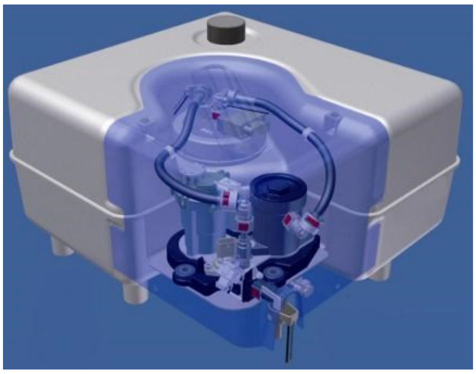

Figure 7: Urea dosing system

Development of SCR technology is very dynamic and improvements are being made in low temperature performance, urea delivery systems, system design, exhaust flow mixing devices, urea dosing strategy, and providing alternatives to liquid urea. Indeed, SCR has been introduced in the light-duty and passenger car sector with the Euro 6 standard and Real-Driving Emissions (RDE) requirements and further NOx reductions are also desired in the heavy-duty sector in urban driving or other low load conditions.

Urea injection quality and mixing are complex and critically important. A study shows (47) that the urea droplet quality from various nozzle designs can impact the deNOx system efficiency by up to 10% while the urea distribution across the catalyst can result in efficiency variations from 60 to 95%.

Modelling studies to improve urea injection and mixing using a variety of devices are numerous (48), (49) and (50). About 10-20% deNOx efficiency improvements can come from good injection practice, with nominally 5-10% coming from using a variety of mixers. Ammonia storage models also help with cold start deNOx (51).

Airless injectors (52), without a urea return line, simplify the urea delivery system and allow accurate delivery of lower volumes. The injector cooling is performed by raising off the exhaust pipe and using convection air and fins cooling rather than by using an excess of urea. Also, upon shut-off, the urea line drains to eliminate freezing issues and the need for line heaters.

Figure 8: Urea injector, mixing device and SCR catalyst

Several types of catalysts can be used in SCR systems, the choice of which is determined by the temperature of the exhaust environment. Originally SCR catalysts were based on vanadium which can be used where tolerance to sulfur is required, provided temperatures are below 600°C (mainly for heavy-duty diesel applications). If DPFs are used in combination with SCR systems, zeolites are preferred due to the better high temperature durability needed when exothermic reactions associated with DPF regeneration can expose SCR catalysts to temperatures up to 800°C. Currently copper-zeolites have the best low temperature performance and iron-zeolites have the best high temperature performance.

Optimized operation of SCR catalysts depends on control of adsorbed ammonia and use of oxidation catalysts to deliver the appropriate NO_2/NOx ratio. In fact, the 'fast SCR reaction' uses both NO and NO_2 at an optimum ratio of 1:1 and this is critical for good performance below 200°C. However, excess NO may be needed to oxidize ammonium nitrate (NH_4NO_3) which can condense and block catalytic sites. The reduction mechanism for the SCR reactions over zeolite catalysts are described in (53). It shows that with NOx present only as NO, the oxidation to NO_2 to promote the 'fast SCR reaction' is the limiting step.

Copper and iron can be used together for a balanced performance over a broad range of temperatures (54), (55). Vanadium is cheaper and more tolerant to sulfur, but deteriorates at temperatures greater than 600°C whereas zeolites are very little affected with long exposure at 800°C (56). Like vanadium, Fe-zeolites are quite tolerant to sulfur but Cu-zeolite performance deteriorates and can be restored with a desulfation cycle (57). New zeolite are being developed for low temperature conversion without copper (55) and new catalyst families based on acidic zirconia are also emerging (58).

On-Board Diagnostic (OBD) and closed loop SCR control are using either the reputable NOx sensors (59) or a new ammonia sensor (60) which has a ± 5 ppm ammonia detection accuracy up to about 30 ppm ammonia, and has negligible interference from NOx, HC and CO.

Finally, alternative SCR reductants are being developed as solid urea (61) and magnesium dichloride ammonia storage media (62). Both have three times more ammonia per litre than liquid urea.

5.5.2 NOx adsorbers or Lean NOx Traps (LNT)

Lean NOx traps adsorb and store NOx under lean conditions. The function of the NOx storage element is fulfilled by materials that are able to form sufficiently stable nitrates within the temperature range determined by lean operating engine points. Thus especially alkaline earth and to a certain extent also rare-earth compounds can be used to store NOx over a broad temperature range.

When this storage media reaches its capacity, it must be regenerated. This is accomplished in a NOx regeneration step. In such a regeneration, the stored NOx is released by creating a rich atmosphere. The rich running portion is of very short duration and can be accomplished in a number of ways, but usually includes some combination of intake air throttling, Exhaust Gas Recirculation (EGR), late ignition timing, fuel injection in upstream LNT position, and post-combustion fuel injection.

The released NOx is quickly reduced to N_2 by reaction with CO on a precious metal that is incorporated into this unique single catalyst architecture.

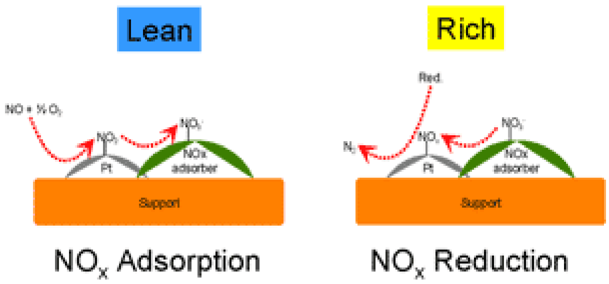

Figure 9: NOx adsorber system

As alkaline earth compounds have a strong affinity for sulfation, a regular desulfation (deSOx) strategy is implemented in all LNT applications to minimize this effect. Under oxygen rich conditions, the thermal dissociation of the alkaline earth sulfates would require temperatures above 1000°C. Such temperatures cannot be achieved under realistic driving conditions. However, it has been demonstrated in various publications (63), (64) and (65) that it is in principle possible to decompose the corresponding alkaline earth sulfate under reducing exhaust gas conditions at elevated temperatures. In this way, the NOx storage capacity can be restored.

Besides the deNOx functionality of an LNT, excellent low temperature conversions of CO and HC are beneficial to comply with Euro 6 limits. LNT can also be combined with the Diesel Particulate Filter or the NOx storage function can be combined with the DOC to simplify the global exhaust line integration. As with SCR, LNT technology is developing at high speed with improvements in the operation window, stability, and low and high temperature performance.

For instance, improved NOx adsorber formulations with greatly improved precious metal dispersion, result in less PGM usage for better performance (66).

LNT and SCR technologies can also be combined to ensure a proper control of NOx and CO_2 emissions in all driving modes including those outside of the NEDC or WLTC regulatory test cycles (67). In view of the introduction of Real-Driving Emissions (RDE) requirements in Europe, LNT and SCR combined systems start to be introduced on some Euro 6 passenger cars (68).

5.5.3 Lean deNOx Catalysts

Lean De-NOx catalysts, also known as hydrocarbon-SCR systems use advanced structural properties in the catalytic coating to create a rich 'microclimate' where hydrocarbons from the exhaust can reduce the nitrogen oxides to nitrogen, while the overall exhaust remains lean. The hydrocarbon may be that occurring in the exhaust gas (‘native’) or may be added to the exhaust gas through injection of a small amount of additional fuel. This has the advantage that no additional reductant source (i.e. urea) needs to be carried but these systems do not, at present, offer the same performance as ammonia-SCR systems and are therefore not considered as mainstream deNOx technology.

A study (69) evaluated the influence of diesel fuel sulfur content on the performance of a passive deNOx catalyst. The program used two specially prepared fuels with different sulfur contents, but with other fuel parameters unchanged. The NOx conversion efficiency of the deNOx catalyst increased from 14 to 26% over the European test cycle when the sulfur content was reduced from 49 to 6 ppm.

Developments on HC-SCR using hydrocarbons from the fuel are reported in the literature (70), (71) and a patent (72) specifies very low precious metal loadings (0.7 g/l) but the system needs temperature greater than 300°C to perform well.

A concept is reported (73) to combine an HC-trap and LNT, wherein the zeolite HC-adsorber is applied first on to the honeycomb substrate and the LNT material is placed on top. The HC-adsorber helps reducing cold start HC emissions and adsorbs HC during the lean periods. Upon release during the hotter rich periods, hydrogen and CO are formed to help LNT regeneration.

5.6 Combined PM and NOx Control Technologies

Thanks to the development of Diesel Particulate Filter substrates with a higher porosity (74), systems can now incorporate the Selective Catalytic Reduction catalyst onto the DPF substrate (75) and (76). Such SCR on DPF combined systems in close-coupled position, sometimes in association with a downstream SCR catalyst, are reaching vehicle application and give significant improvement in the NOx conversion efficiency compared to separate components (77), (78), due to the higher temperature level in the close-coupled position especially under low load conditions typical for urban driving. SCR on DPF systems are expected to be used more and more to meet light-duty Euro 6, heavy-duty Euro VI emissions and NRMM Stage V requirements.

6. AECC DEMONSTRATION PROGRAMS

Throughout several test programmes run over the last decades, AECC has consistently demonstrated technical feasibility of future and more stringent emissions limits, including durability aspects. Test programs results were published on passenger cars (79), (80), heavy-duty engine (81), (82), (83) and (22), non-road mobile machinery engine (84) and (85), and motorcycles (86) and (87).

More recently, AECC conducted a number of test programmes on passenger car that demonstrated the feasibility of low Real-Driving Emissions (RDE) Conformity Factors, be it for diesel NOx (88), (89), (90), (91), (92), (93) or Gasoline Direct Injection PN (43).

7. CONCLUSIONS

Technologies exist for control of CO, HC, NOx, PM and PN, for stoichiometric and lean-burn gasoline engines and diesel engines. They are used and proven in many different applications. Continuous improvement in substrate and coating technologies, as part of an integrated system comprising electronic control and fuel quality, allows meeting more and more stringent combustion engines emissions legislations under a wide range of engine operating conditions.

8. REFERENCES / LITERATURE

1. Directives 93/59/EEC, 96/69/EC, 98/69/EC, 2003/76/EC and Regulation (EC) 715/2007.
2. Directives 88/77/EEC, 91/542/EEC, 96/1/EEC, 1999/96/EC, 2001/27/EC, 2005/55/EC, 2005/78/EC, 2006/51/EC and Regulation (EC) 595/2009.
3. Directives 97/24/EC, 2003/77/EC, 2005/30/EC, 2006/27/EC, 2006/72/EC and Regulation (EU) 168/2013.
4. Directives 1997/68/EC, 2004/26/EC and European Commission proposal for a Regulation COM(2014) 581 final.
5. *Fifth Edition Worldwide Fuel Charter.* ACEA, Alliance, EMA and JAMA. September 2013. www.acea.be/uploads/publications/Worldwide_Fuel_Charter_5ed_2013.pdf.
6. *Technical summary: Quality of European gasoline and diesel fuels.* AECC. 2003. www.aecc.eu/content/pdf/QUALITY%20OF%20GASOLINE%20AND%20DIESEL%20FUEL%20rev%20080703.pdf.
7. *Thin wall ceramic catalyst supports.* Gulati, S. SAE 1999-01-0269.
8. *The impact of high cell density ceramic substrates and washcoat properties on the catalytic activity of Three Way Catalysts.* Schmidt, J., et al. SAE 1999-01-0272.
9. *Technology for reducing exhaust gas emissions in Zero-Level Emission Vehicles (Zlev).* Kishi, N., et al. SAE 1999-01-0772.
10. *Design considerations for advanced ceramic catalytic supports.* Gulati, S. SAE 2000-01-0493.
11. *New technologies targeting zero emissions for gasoline engines.* Nishizawa, K., et al. SAE 2000-01-0890.
12. *The necessity of optimizing the interactions of advanced post-treatment components in order to obtain compliance with SULEV legislation.* Brück, R., Maus, W. and Hirth, P. SAE 1999-01-0770.
13. *Zukünftige Abgasnachbehandlungstechnologien für Otto-Motoren; die nächste Generation Niedrigstemissionsfahrzeuge.* Maus, W., Brück, R. and Holy, G. Graz : AVL Congress, September 1999.

14. *Emission systems optimization to meet future European legislation.* Favre, C. and Zidat, S. SAE 2004-01-0138.
15. *The use of palladium in advanced catalysts.* Brisley, R., et al. SAE 950259.
16. *(Ce,Zr)O_2 solide solutions for Three-Way Catalysts.* Cuif, J-P., et al. SAE 970463.
17. *Utilization of advanced Pt/Rh TWC technologies for advanced gasoline applications with different cold start strategies.* Schmidt, J., et al. SAE 2001-01-0927.
18. *The effects of flow-through type oxidation catalysts on the particulate reduction of 1990s diesel engines.* Horiuchi, M., Saito, K. and Ichihara, S. SAE 900600.
19. *New Cordierite Diesel Particulate Filter Material for the Diesel Particulate - NOx Reduction System.* Kasai, Y., et al. SAE 2004-03-08.
20. *New Materials for Particulate Filters in Passenger Cars.* Schäfer-Sindlinger, Adolf, et al. 5, s.l. : Materials AutoTechnology, September 2003, Vol. 3.
21. *Performance evaluations of aluminum titanate Diesel Particulate Filters.* Ingram-Ogunwumi, R., et al. SAE 2007-01-0656.
22. *Heavy-duty engine particulate emissions: application of PMP methodology to measure particle number and particulate mass.* May, J., et al. SAE 2008-01-1179. www.aecc.eu/content/pdf/Heavy-duty%20Engine%20Particulate%20Emissions%20Application%20of%20PMP%20Methodology%20to%20measure%20Particle%20Number%20and%20Particulate%20Mass%20SAE%202008-01-1176.pdf.
23. *Effect of a continuously regenerating Diesel Particulate Filter on non-regulated emissions and particle size distribution.* Stommel, P., et al. SAE 980189.
24. *Catalyzed particulate filters for mobile diesel applications.* Maunula, T., et al. SAE 2007-01-0041.
25. *New platinum/palladium based catalyzed filter technologies for future passenger car applications.* Pfeifer, M., et al. SAE 2007-01-0234.
26. *Novel base metal-palladium catalytic diesel filter coating with NO_2 reducing properties.* Johansen, K., et al. SAE 2007-01-1921.
27. *Development of high performance catalyzed DPF with new soot burning mechanism.* Koichiro, H., et al. Berlin : Fisita Conference, September 2008.
28. *An investigation into the NO_2-mediated decoupling of catalyst to soot contact and its implications for catalysed DPF performance.* Southward, B. and Basso, S. SAE 2008-01-0481.
29. *Towards securing the particulate trap regeneration: a system combining a sintered metal filter and cerium fuel additive.* Zelenka, P., et al. SAE 982598.
30. *Latest development and registration of Fuel Borne Catalyst for DPF regeneration.* Rohart, E. SAE 2008-01-0331.
31. *Exhaust fuel injection system for efficient DPF regeneartions.* Fasolo, B., Hardy, J-P. and Leroy, K. s.l. : MTZ, 07-08 2009, Vol. 70.
32. *Electric heating regeneration of large wall-flow type DPF.* Kitagawa, J., Hijikata, T. and Yamada, S. SAE 910136.
33. *Active regenerative DPF using a plasma assisted burner.* Lee, D-H., et al. SAE 2009-01-1926.
34. *Regeneration strategies for an enhanced thermal management of oxide Diesel Particulate Filters.* Boger, T. SAE 2008-01-0328.
35. *Diesel Particulate Filter system - effect of critical variables on the regeneration strategy development & optimization.* Suresh, A., et al. SAE 2008-01-0329.
36. *Study on wall pore structure for next generation Diesel Particulate Filter.* Mizuno, Y., et al. SAE 2008-01-0618.
37. *A methodology to estimate the mass of Particulate Matter retained in a catalyzed particulate filter as applied to active regeneration and On-board Diagnostics to detect filter failures.* Dabhoiwala, R., et al. SAE 2008-01-0764.
38. *Partikelsensoren zur Überwachung der DPF-Funktion - Ergebnisse der Felderprobung an Off-Road Maschinen.* Sandig, R., Lindner, R. and Zikoridse, G. Dresden : FAD Conference, November 2008.
39. Andersson, J., et al. *Particle Measurment Programme (PMP) Light-duty Inter-Laboratory Correlation Exercise (ILCE_LD) Final Report.* s.l. : JRC, 2007.
40. Köhler, F. *Testing of particulate emissions from positive ignition vehicles with direct fuel injection systems.* s.l. : TÜV Nord, 2013.
41. *Novel GPF concepts with integrated catalyst for low backpressure and low CO_2 emissions.* Thier, D., et al. s.l. : 23rd Aachen Colloquium, 2014.
42. *Comprehensive gasoline exhaust gas aftertreatment, an effective measure to minimize the contribution of modern Direct Injection engines to fine dust and soot emissions?* Kern, B., Spiess, S. and Richter, J. SAE 2014-01-1513.
43. *Real-Driving Emissions of a GPF-equipped production car.* Bosteels, D. IQPC 3rd International Conference RDE, 2015, www.aecc.eu/content/pdf/151027%20IQPC%20RDE%20-%20AECC%20RDE%20of%20a%20GPF-equipped%20production%20car_final.pdf.

44. *Black Carbon Emissions in Gasoline Exhaust and a Reduction Alternative with a Gasoline Particulate Filter.* Chan, T., et al. 10, s.l. : Environ. Sci. Technol., 2014, Vol. 48.
45. Mamakos, A., et al. *Feasibility of introducing particulate filters on Gasoline Direct Injection vehicles.* s.l. : JRC, 2011.
46. *Platinum Group Metal and Washcoat Chemistry Effects on Coated Gasoline Particulate Filter Design.* Morgan, C. Johnson Matthey Technol. Rev., 2015, Vol. 59 (3), pp. 188-192.
47. *Urea preparation in exhaust systems of commercial vehicles.* Gorbach, A. Nürtingen : CTI Emission Control Forum, January 2009.
48. *Chemical challenges in the development of urea-SCR systems.* Kaiser, R. Karlsruhe : Car Training Institute SCR Forum, May 2007.
49. *Possibilities of optimizing SCR systems through improved urea preparation.* Calvo, S., et al. Karlsruhe : Car Training Institute SCR Forum, May 2007.
50. *Design of compact AdBlue evaporation and homogenization zones.* Gruenwald, J., et al. Berlin : IAV MinNOx Conference, February 2007.
51. *Concept development of an SCR demonstrator vehicle: meeting future European emission limits with low fuel consumption.* Grumbrecht, F. and al., et. Berlin : IAV MinNOx Conference, February 2007.
52. *Emission optimization of diesel engines with direct injection.* Krueger, M. Berlin : IAV MinNOx Conference, February 2007.
53. *New challenges for urea-SCR systems: from vanadia-based to zeolite-based SCR catalysts.* Kroecher, O. Berlin : IAV MinNOx Conference, February 2007.
54. *Combined Fe-Cu SCR systems with optimized ammonia to NOx ratio for diesel NOx control.* Girard, J., et al. SAE 2008-01-1185.
55. *Two catalyst formulations- one solution for NOx aftertreatment systems.* Iretskaya, S., et al. Detroit : US Dept. of Energy DEER, August 2008.
56. *Enhanced durability of a Cu-zeolite based SCR catalyst.* Cavataio, G., et al. SAE 2008-01-1025.
57. *SCR catalysts for low-emitting diesels.* Anderson, P. Detroit : US Dept. of Energy DEER, August 2008.
58. *Acidic zirconia materials for durable NH_3-SCR deNOx catalysts.* Rohart, E. SAE 2008-01-1022.
59. *Smart NOx-sensor - Application in Diesel systems.* Walde, T. et al. Nuertingen, Germany : Car Training Institute Exhaust Systems Forum, January 2007.
60. *Delphi NH_3 ammonia sensors.* Weisgerber, V. Nuertingen, Germany : Car Training Institute Exhaust Systems Forum, January 2007.
61. *Solid urea-SCR - An alternative.* Mueller, W. Karlsruhe, Germany : Car Training Institute SCR Forum, May 2007.
62. *Ammonia storage and delivery systems for automotive SCR-deNOx.* Johanssen, T. Karlsruhe, Germany : Car Training Institute SCR Forum, May 2007.
63. *New developments in lean NOx catalysis for gasoline fuelled passenger cars in Europe.* Strehlau, W., et al. SAE 962047.
64. *Evaluation of NOx storage catalysts as an effective system for NOx removal from the exhaust gas of lean-burn gasoline engines.* Brogan, M., et al. SAE 952490.
65. *Moderne NOx-adsorber-technologien, Grundlagen, Voraussetzungen, Erfahrungen.* Göbel, U., Kreuzer, T. and Lox, E. Frankfurt : Proceedings of VDA conference, 1999.
66. *Development of advanced NOx storage and reduction system for cleaner diesel aftertreatment.* Inoue, M. Berlin : IAV MinNOx Conference, June 2008.
67. *Emission Control for Diesel Passenger Cars to Meet Euro 6c.* Harth, K., et al. 35th International Vienna Motor Symposium, 2014.
68. *NSC/SDPF System as Sustainable Solution for EU 6b and Up-coming Legislation.* Mussmann, L., et al. s.l. : 23rd Aachen Colloquium, 2014.
69. *Vehicle study on the impact of diesel fuel sulfur content on the performance of deNOx catalysts and the influence of deNOx catalysts on particle size and number.* Searles, R., et al. SAE 2000-01-1877.
70. *HC-SCR lean NOx catalysis for automotive applications.* Blint, R. Detroit : CTI deNOx forum, December 2008.
71. *Control strategy for the removal of NOx from diesel engine exhaust using hydrocarbon Selective Catalytic Reduction.* Schmieg, S., Blint, R. and Deng, L. SAE 2008-01-2486.
72. *Catalyst to reduce NOx in an exhaust gas stream and methods of preparation.* Catellano, C., et al. March 20, 2008. US Patent US2008/0070778.
73. *Development of a diesel emission catalyst system for meeting US-SULEV standards.* Onodera, H., et al. SAE 2008-01-0449.
74. *Development of New High Porosity Diesel Particulate Filter for Integrated SCR Technology/Catalyst.* Jin, Y., et al. SAE 2015-01-1017.
75. *Evaluation of Cu-based SCR/DPF technology for diesel exhaust emission control.* Lee, J.H., Paratore, M. and Brown, D. 2008-01-0072.

76. *Simplification of diesel emission control system packaging using SCR coated on DPF.* Oladipo, B., et al. Detroit : US Dept. of Energy DEER, August 2008.
77. *Emission Optimization of Diesel Passenger Cars to Fulfill "Real Driving Emission (RDE)" Requirements.* Krüger, M., et al. s.l. : 24th Aachen Colloquium, 2015.
78. *The new generation of the Audi V6 TDI engine 25 years of Technology – Dynamics – Innovation.* Knirsch, S., et al. s.l. : 35th International Vienna Motor Symposium, 2014.
79. *'Regulated' and 'Non-regulated' Emissions from Modern European Passenger Cars.* Bosteels, D., et al. SAE 2006-01-1516. www.aecc.eu/content/pdf/SAE%202006-01-1516.pdf.
80. *160 000 km Emissions Durability of a Diesel passenger Car with Particulate Filter.* Bosteels, D., et al. Dresden : 3. Emission Control Conference, 2006. www.aecc.eu/content/pdf/AECC%20AVL-MTC%20paper%20Dresden%20emission%20control%20conference%20180506.pdf.
81. *Particle Emissions From a EU 3 Heavy-duty Diesel Engine with Catalyst-based Diesel Particle Filter and Selective Catalytic Reduction System: Size, Number, Mass & Chemistry.* Andersson, J., et al. 2002, 11. Aachener Kolloquium Fahrzeug- und Motorentechnik. www.aecc.eu/content/pdf/Ricardo%20AECC%20Paper%20Aachen%202002%20final.pdf.
82. *Investigation of the feasibility of achieving Euro V Heavy-duty emissions limits with advanced emissions control systems.* Searles, R. A., et al. Fisita World Congress, Helsinki, 2002. www.aecc.eu/content/pdf/FISITA%20F02E310-PAPER.pdf. F02E310.
83. *The Application of Emissions Control Technologies to a Low-Emissions Engine to Evaluate the Capabilities of Future Systems for European and World-Harmonised Regulations.* May, J., et al. 2007, 16. Aachener Kolloquium Fahrzeug- und Motorentechnik. www.aecc.eu/content/pdf/AECC_PAPER_for_Aachen_Final_20070716.pdf.
84. *AECC Heavy-duty NRMM test programme: particle measurement and characterisation.* May, J., et al. 2010, 14th ETH-Conference on Combustion Generated Nanoparticles. www.aecc.eu/content/pdf/ETH%20Extended%20Abstract_AECC%20NRMM%20Test%20Program_particles%20190810.pdf.
85. *Measured emissions from a dedicated NRMM engine fitted with particulate and NOx emissions controls.* Bosteels, D., et al. Göteborg, 2010, Heavy-duty Diesel Emissions Symposium. www.aecc.eu/content/pdf/100921%20AECC%20NRMM%20Test%20Program%20SAE%20HDD%20Gothenburg.pdf.
86. *An investigation into the challenges of achieving future legislative limits over Euro III and WMTC drive cycles for current state-of-the-art motorcycle technologies.* Bosteels, D., et al. SAE 2005-01-2156. www.aecc.eu/content/pdf/SAE%20paper%202005-01-2156.pdf.
87. *An emissions performance evaluation of state-of-the-art motorcycles over Euro 3 and WMTC drive cycles.* Favre, C., et al. SAE 2009-01-1841. www.aecc.eu/content/pdf/SAE%202009-01-1841.pdf.
88. *An Assessment of Emissions from Light-Duty Vehicles using PEMS and Chassis Dynamometer Testing.* May, J., Bosteels, D. and Favre, C. SAE 2014-01-1581, www.aecc.eu/content/pdf/2014-01-1581.pdf.
89. *A comparison of light-duty vehicle emissions over different test cycles and in real-driving conditions.* May, J., Bosteels, D. and Favre, C. Fisita 2014, www.aecc.eu/content/pdf/2014%20Fisita%20AECC_Comparisons%20of%20LD%20emissions%20tests.pdf.
90. *On-road testing and PEMS data analysis for two Euro 6 diesel vehicles.* May, J., et al. TAP Conference, 2014, www.aecc.eu/content/pdf/140918%20AECC%20paper%20on%20RDE%20-%20TAP%20Conference%20Graz.pdf.
91. *On-Road and Chassis Dynamometer Evaluations of Emissions from two Euro 6 diesel vehicles.* Andersson, J., et al. SAE 2014-01-2826, www.aecc.eu/content/pdf/SAE%202014-01-2826%20On-road%20and%20chassis%20dynamometer%20evaluations%20of%20emissions%20from%20two%20Euro%206%20Diesel%20vehicles.pdf
92. *Potential for Euro 6 Passenger Cars with SCR to meet RDE Requirements.* Holderbaum, B., et al. 36th International Vienna Motor Symposium, 2015, www.aecc.eu/content/pdf/150507%20FEV-AECC%20paper%20Potential%20for%20Euro%206%20Passenger%20Cars%20with%20SCR%20to%20meet%20RDE.pdf.
93. *New results from a 2015 PEMS testing campaign on a Diesel Euro 6b vehicle.* Favre, C., et al. 11th Integer Emissions Summit Europe, 2015, www.aecc.eu/content/pdf/150618%20Integer%20conf%20AECC%20RDE%20Program%20presentation%20final.pdf.

April 2016