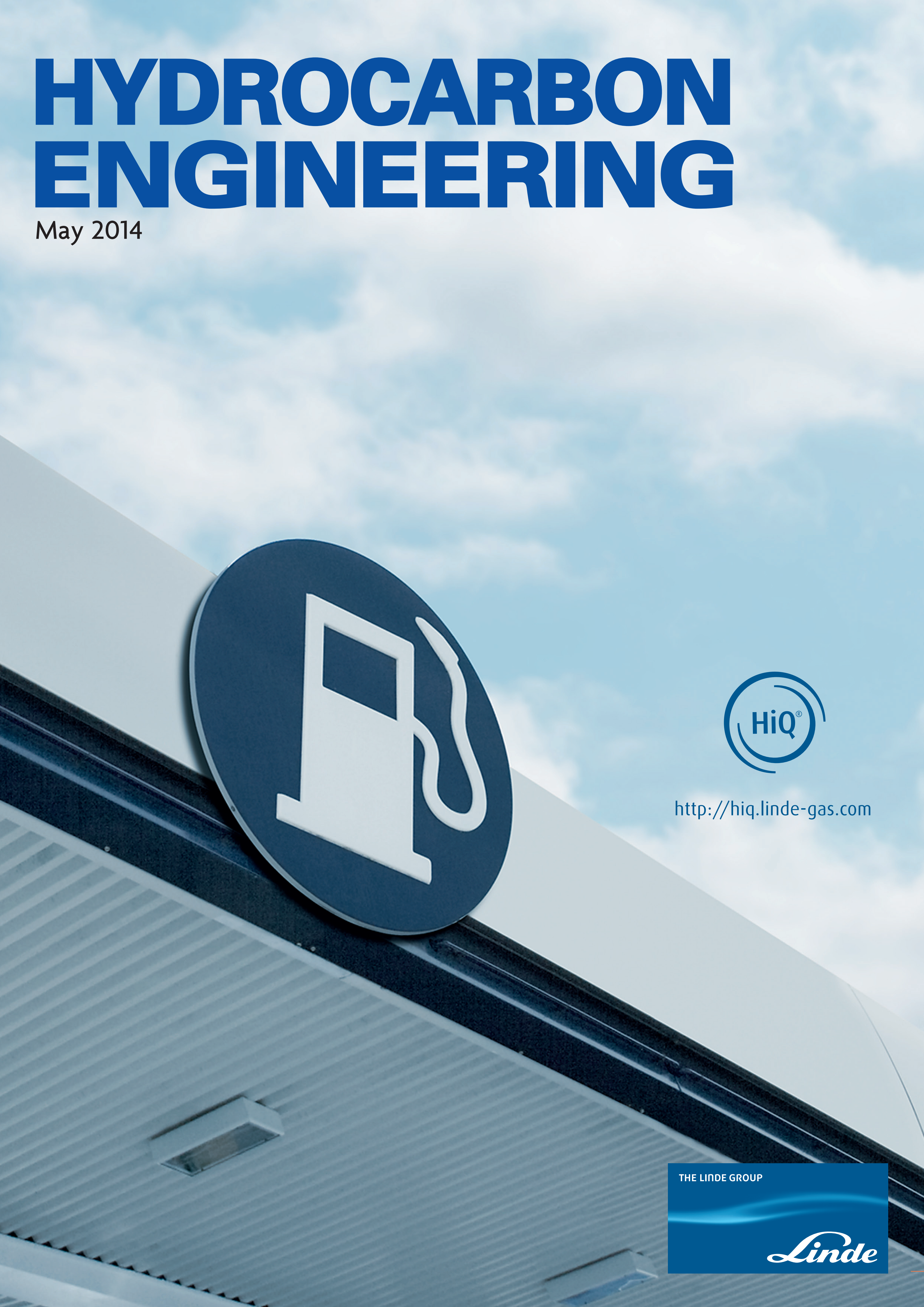
HYDROCARBON ENGINEERING

May 2014



COVER FEATURE

DRIVING REFINING CHANGE: PART 1

Stephen Harrison, Linde, USA, takes a look at how automotive emissions legislation and the drive for energy sustainability are impacting the refining industry.

The EU designated 2013 as 'The Year of Air', with issues around clean air taking centre stage during environmental policy discussions throughout the year. That the European Commission is collaborating with the World Health Organisation (WHO) on this matter is a strong message that air quality is a major concern in Europe and globally.

Both recent and upcoming legislation on automobile emissions has become the major change agent within this environmental arena. As with all legislation, regulation around emissions levels the playing field for all stakeholders in the automotive industry, effectively ensuring a competitive business climate. All participants must adjust their operations to comply with the latest regulations, leaving none at a competitive disadvantage.

Legislation also has the purpose of setting common targets within geographic economic zones such as the US and the EU, aligning the many diverse organisations involved in automotive research and development (R&D) and the production supply chain through common goals and objectives. This ensures that consistent standards are set for the industry and that change applies across the board, with all players being measured by the same performance yardstick.

In this industry, R&D to improve the environmental performance of vehicles demands substantial investment. A high level of technical complexity is involved, with great reliance on first and second tier suppliers, who are among a vast number of partners in the automotive value chain. Therefore, when all these technology partners work towards a clear and common target, such as limiting the amount of CO_2 or nitric oxide emitted from a car, the fragmented value chain aligns all its resources to achieve this common objective.

Another common benefit of legislation is that it creates an enabling environment for cost effective transfer of technology, by broadly communicating best practice to achieve the required changes, for example, offering guidance on the latest analytical measurement instrumentation.

An excellent example of technology transfer is the Euro IV, V and VI emission standards developed for European markets that have been adopted elsewhere in the world, for example South Korea and China. Europe has successfully prescribed targets and adopted relevant and useful technology to achieve targets, and this effective approach is being replicated elsewhere.

Today there are three main global legislation groups related to automotive emissions coming out of Europe, the USA and Japan.

Figure 1. Both global automotive emissions legislation and the drive for energy sustainability are having an impact on refinery end products.

European legislation is already progressing towards Euro VII, while in the USA, the Environmental Protection Agency (EPA) takes a leading role. The USA also has federal environmental legislation, as well as certain state specific regulations and one of the most common terms, ultra low emissions vehicle (ULEV), in fact, derives from California state legislation. There is also a formidable legislative movement in Japan, since a large number of automotive producers originate in that country. China, however, which also has a substantial automotive industry in terms of the number of production centres, tends to take its cue from European legislation.

So, what are the common goals of all this disparate geographical legislation? Firstly, legislation seeks to drive fuel economy by developing more economical ways to move people and goods from A to B, in order to conserve the world's dwindling fossil fuel resources for future generations. There are also economic benefits associated with the issue of fuel economy, as the more economic it is to move people and goods, the more competitive a market will be. The other key goal of legislation is to mitigate the effects of damaging automotive emissions, such as carbon dioxide, on climate change. This is also closely linked to the goal of fuel economy, as the less fuel we burn, the fewer emissions are released into the atmosphere.

Environmental impact

In terms of climate change the industry also looks at other greenhouse gases with global warming potential (GWP). An example is nitrous oxide, which has a much higher GWP than CO_2, but because it exists in relatively low quantities in the atmosphere, it attracts less headline press. Other issues exist around particulate matter and soot and there is a more recent focus on minimising the emission of any substance that has stratospheric ozone depleting potential, since stratospheric ozone's role is to absorb potentially harmful ultraviolet rays from the sun.

For the first time, greenhouse gases such as CO_2 and nitrous oxide are being included into US EPA protocol gases. Not that long ago, these greenhouse gases were introduced in addition to what was previously referred to as the criteria pollutants, the six most common air pollutants of concern: ozone, carbon monoxide, nitrogen dioxide, sulfur oxides, particulate matter and lead. This is a significant step forward that could even be described as a fundamental evolution in legislation, not only towards controlling toxic gases, but also those which contribute to global warming.

Automotive emissions such as nitrogen dioxide and sulfur dioxide must also be controlled to protect our physical environment. These emissions can react with rainwater and create acid rain that damages forests and buildings, since it reacts with limestone and concrete to corrode structures. Ground water contamination is another concern, since the chemicals benzene and methyl tertiary butyl ether (MTBE), added to improve engine combustion, are also damaging when they are washed down in rainfall.

Public health

With a strong historic US EPA focus on so called criteria pollutants, much automotive legislation has been structured around public health issues, resulting in tightening emission targets. It is noticeable that there has been a tangible move from purely monitoring automotive emissions, to monitoring the ambient environment, including detecting the presence of chemicals in the air that the public is breathing. A significant section of legislation is moving into prescribing exactly what should be measured in the ambient environment, how often it should be measured and in which locations. And there is more data transparency around these findings than ever before, giving the public real time access to this important information.

Improving public health by controlling air quality is a key focus of automotive legislation. Air quality must be maintained at a level that ensures it does not cause disease. With this in mind, there is a contemporary focus on minimising ground level ozone that has the potential to damage the human respiratory tract and is produced principally by a reaction between nitric oxide and volatile organic compounds (VOCs).

Carbon monoxide is a prevalent gas in automotive exhaust systems that, in enough quantity, can damage the nervous system, while formaldehyde gas is categorised as a 'probable carcinogen' and, like ozone, has the potential to cause respiratory problems. Benzene is a VOC that not only contributes to the ground level ozone problem, but is a toxic chemical and pollutant in its own right. It is a known carcinogen that can be inhaled from the atmosphere or absorbed into the human body by eating contaminated fish and crops. Nitrogen dioxide, ammonia and sulfur dioxide are other examples of gases that can cause health problems by weakening the respiratory system and rendering humans more susceptible to illness. Chemicals like this must be reduced or completely eliminated from automotive emissions.

Cohesion of the issues

Any legislation framework must address these problems effectively, but how do these issues all cohere in a matrix? On the issue of fuel economy, the USA has two sets, or 'tiers', of emission standards for light duty vehicles, defined as a result of the Clean Air Act Amendments of 1990. Within the Tier II ranking, there is a subranking ranging from BIN 1 – 10, with 1 being the cleanest (zero emission vehicle) and 10 being the dirtiest. These standards specifically restrict emissions of carbon monoxide, oxides of nitrogen, particulate matter, formaldehyde and non-methane organic gases (non-methane hydrocarbons).

President Barack Obama has recently called for America's fleet of trucks, lorries and cars to be elevated into the next category of environmental cleanliness and fuel economy, BIN 4. This target cascades down to automotive producers to incentivise them to make sure that the average vehicle being sold is moving to a progressively more fuel efficient future.

The changing legislative environment relating to fuel economy is enabling the introduction of new generation fuel types in a safe and consumer friendly manner. In the US all eyes are on E15, fuel with a 15% ethanol blend, which will soon be commercially introduced to that market. This could herald in a new era, enabling the production and sale of a new generation of environmentally friendly fuels.

Many years ago it was decided to transition to unleaded fuels, a decision principally taken to protect the catalysers installed in cars for the enablement of nitric oxide, nitrogen dioxide and carbon monoxide emissions reduction. With catalysers becoming prevalent, legislation was needed to facilitate the introduction of unleaded. And, to limit the sulfur dioxide emissions that react with rain to create acid rain, ultra low sulfur diesel was introduced.

However, legislation always needs to look ahead holistically to possible consequences, so that the totality and end result of changes is truly beneficial. This is because, inevitably, as one problem is solved, there are consequences of changes and in some cases it might even become a case of 'out of the frying pan and into the fire'. Legislation would not be effective if it had this effect on automotive producers. Therefore in seeking to create change in a particular area, it is essential to look at any secondary implications the change is likely to create and to simultaneously mitigate secondary outcomes.

An example is the ambition to reduce nitrous oxide emissions from car engines by converting oxides of nitrogen simply into nitrogen itself. One way to achieve this is to harness a technology called selective catalytic reduction (SCR) that converts nitrogen oxides back to harmless nitrogen gas, using ammonia in the catalysers. However, in trying to resolve the problem of nitrogen oxide emissions, urea is being added to create ammonia in the catalyser and this could potentially lead to the secondary negative impact of ammonia as an automotive emission gas. Ammonia must now also be added to the list of emissions that must be monitored.

Another secondary impact of emission legislation involves carbon monoxide. The principle reduction of carbon monoxide is achieved through catalytic converters to oxidise it to CO_2, which is potentially a problem in its own right in terms of global warming, but is considered preferable to emitting carbon monoxide. These catalytic converters in turn reduce the overall fuel economy of the engine, so there a compensating increase in overall engine efficiency is needed to ensure that the introduction of the catalytic converter is having an overall beneficial effect.

It is evident that this is a complex legislative area that highlights the delicate balance at play. Well intentioned legislation may be able to solve one problem, but could also introduce an unanticipated secondary risk that needs to be compensated for. Legislators must find a way to arrive at a careful balance by trading off one chemical consequence against another.

Recent or imminent legislative changes

In addition to greenhouse gases now being included in the US EPA protocol, for the first time protocol standards for formaldehyde and ammonia have now been introduced. Ammonia is being included at an emissions level of 10 ppm in the Euro VI legislation that will come into force in 2014 in Europe, with the automotive industry already aligning itself to those requirements, elevating the subject of ammonia emissions from diesel engines. Another impact of Euro VI will be the reduction of oxides of nitrogen emissions, bringing diesel oxides of nitrogen emissions more closely in line with petrol engine emission standards.

An interesting change is the move from, in UK terminology, 'miles/gal.', to 'grams of CO_2 emitted/km travelled' as an emissions standard. Miles per gallon refers to the amount of fuel required to travel a certain distance, regardless of fuel type and the amount of CO_2 emitted by that fuel. With the move to grams of CO_2 emitted/km, there is a clear signal that CO_2 is becoming the ultimate goal of measurement. It also recognises that hybrid vehicles running on electricity, and therefore emitting no CO_2, can also fit into these legislative measures.

Another significant development with regard to Euro VI legislation refers to a trend called 'speciation' that focuses on the various chemical species present in the automotive emissions. An example of this is the split of total hydrocarbons (THC) into methane, which is a hydrocarbon, and non-methane total hydrocarbons (NMTHC). Historically, emissions were measured in terms of total hydrocarbons, but in future we will increasingly see a split between methane and NMTHC and this recognises that methane has its own issues with regard to GWP. However, it is the NMTHC that relates to public health issues and this intensified focus will allow for better control of such emissions.

Chinese legislation is moving forward very rapidly in this major market for auto producers and consumers alike. Here the changes include a nationwide move from Euro IV for diesel engines in 2011 a move to Euro IV for combustion engines in 2013. Similar to the USA, legislation in China exists both at a national level and a more specific, geographically targeted level, and in Beijing the legislation will move to Euro V in 2013.

Analytical techniques

Euro VI legislation specifies that ammonia must be measured at a maximum level of 10 ppm in diesel and petrol engine emissions and this effectively requires the measurement of a new molecule in our exhaust emissions. Legislation is only as good as its enforcement and this enforcement relies on effectively applying analytical techniques to measure automotive emissions. One of the hidden benefits of this legislation is that it points the industry in the direction of the most suitable technology to accomplish this task.

Legislative requirements to measure new emission molecules must bring with them a requirement for reliable, repeatable technology to conduct these measurements. Legislation also explains to the industry how to perform this measurement in a consistent and dependable way, for example, providing two types of technology deemed to be suitable for ammonia measurement in exhaust emissions.

Both these technologies are described in detail in Euro VI legislation. The first technology uses laser light tuned to a certain light frequency designed to be absorbed by ammonia and other exhaust chemicals. In other words, a laser light is shone through an exhaust emission to measure the chemical levels present. The other type of technology for measuring ammonia in exhaust emissions is Fourier transform infrared (FTIR) spectroscopy, based on the principle of shining infrared light through the exhaust gas mixture and determining at which frequencies light is being absorbed in order to assess which chemicals are present and at what concentration they occur. The principle is the same for both technologies, absorption of light by chemicals.

Legislation also prescribes the types, traceability and degree of accuracy of calibration gas mixtures needed to calibrate instruments used for these measurements. This clarifies for suppliers of calibration mixtures, such as Linde Gases Division, which mixtures they should be developing for this particular market. Detailed specifications for pure gases which are used for gas chromatography or to zero instruments and for fuel and oxidant gases which are used for flame based analytical detection methods are also prescribed in the Euro VI legislation.

The other area of legislative change is the reduction in nitrogen oxide levels, also prescribed in Euro VI. The technology referred to in this regard is chemiluminescence, an analytical technique based on the emission of light spectra by the chemical molecules. The industry is now seeing the reduction of nitrogen oxide levels in diesel to a similar level that exists for petrol engines. It could therefore be argued from an analytical techniques perspective, that this technology shift is not all that onerous, since it is simply bringing diesel engines in line with the measurements currently required for petrol engines.

The future

Against this background of robust legislative change, it is interesting to speculate what the future might hold by examining past trends and extrapolating them to determine future legislative direction.

For the first time in the USA, the EPA protocol has issued standards for zero air. This is important, because when setting up an analyser, a calibration gas is needed to calibrate at the high end of the scale, as well as a zero gas to determine the zero of that instrument. Both these gases are equally critical in setting up the instrument. For many years, the EPA protocol has regulated on the calibration gas mixture required for the high end of the scale, but this is the first time that standards for zero air have been set. At present, the requirement to use this zero air standard is voluntary, but industry stakeholders can speculate that it will become mandatory in the near future.

On the issue of speciation, with the increasing concern about nitrogen dioxide, nitrous oxide and nitric oxide emissions it is very likely that future legislation might mandate measurement and control for each one, instead of for the total oxides of nitrogen that is in place at the moment. With more speciation taking place within the total hydrocarbons, there is likely to be further speciation within the total hydrocarbons element, looking specifically for molecules such as ethanol and formaldehyde, the new potential pollutants arising from the move towards biofuels and LNG. The industry could therefore also be moving towards a requirement to measure particular chemical species within automotive emissions going in the direction of ethanol, formaldehyde and specific oxides of nitrogen.

Exhaust after treatment is perhaps one of the most dynamic parts of the auto industry right now. The companies involved in producing the catalysers and the overall after treatment systems are facing an enormous technological challenge to keep up with the pace of change. Here, in addition to SCR, exhaust gas recycling (EGR) is coming to the fore, representing two very fundamental changes in exhaust gas treatment technology to reduce harmful emissions from the engine.

The other area of considerable change is the sophistication of engine management systems (EMS) or on board diagnostic systems (OBD). Emissions are now being controlled by these micro computers which rely on multiple engine sensors responsible for ensuring the engine is working at optimum fuel efficiency and releasing minimum emissions. In this regard the industry is seeing a whole new suite of regulations being targeted to ensure these systems are stable and that they function correctly.

Finally, the increasing use within the industry of gases that comply with US EPA protocols, or relevant ISO standards relating to the traceability and accuracy of calibration gas mixtures, such as ISO17025 will be of great consequence to companies like Linde, which support measurement technology with accurate and consistent calibration gas mixtures across the EU and other legislative groups. Applicable worldwide, these standards will make sure that international automotive producers and environmental agencies working in this arena are working from a uniform base.