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explain why next generation fuels demand a new take on environmental control.

THE NEXT GENERATION

A spectrum of new generation fuels has emerged onto the international automotive scene in response to the call for fuels to emit fewer harmful pollutants into the environment, to diversify fuel sources or to enable sustainable transportation with renewable fuels. In terms of their overall environmental impact, their introduction has the challenging effect of shifting the onus of emissions control all the way back down the production chain to the source and through the various manufacturing processes. Today, the environmental implications of fuel production are therefore being viewed from a broad perspective that goes well beyond the automotive and wider transportation industry to include the fuel production industry in its entirety.

The drive for cleaner fuels is being driven from both national regulatory bodies, who continue to regulate emissions of both transport and production machinery through ever tightening legislation, and end users, who have a desire to be more environmentally responsible. The recently enacted Euro VI automotive emissions legislation is the most stringent to date in the EU, while in the USA, strict Environmental Protection Agency (EPA) emissions standards have also been in play for many years. Other regions in the world tend to follow these legislation blocks, or have similar local laws in place.

From the perspective of fuel processors, producers and distributors, the new generation fuels have brought with them significant shifts in technological options and in the business models associated with producing them. However, among the many variables confronting these organisations, one fixed requirement remains sound environmental management.

Beyond the traditionally predominant liquid fuels (petrol and diesel) of two decades ago, newer generations fuels, such as

Figure 1. Ethanol can also be produced from algae, a faster and more environmentally friendly production alternative to arable crops.

Figure 2. Hydrogen fuel for passenger cars is regarded as an environmentally attractive option as it produces water vapour rather than harmful emissions.

Figure 3. LNG releases significantly less CO_2 per unit of energy than coal or some other liquid fuels.

hydrogen, LPG/propane, compressed natural gas (CNG) and LNG, ultra low sulfur diesel (ULSD) and low sulfur diesel (LSD), ethanol and biodiesel, are increasingly being used, while the development of electrically powered cars and fuel/battery hybrids is also gaining ground.

Biofuels are also being introduced to conventional fuels as additives, or in other applications, and can be used as 100% biodiesel from rapeseed oil or other plant sources.

In mitigating pollution from diesel engines in general, whether biodiesel or conventional diesel, a urea solution is often added under the brand AdBlue®. The objective is to convert oxides of nitrogen simply to nitrogen itself. One way to achieve this is to harness selective catalytic reduction (SCR) that converts nitrogen oxides back to harmless nitrogen gas, using ammonia from the urea in the catalysers. However, in trying to resolve the problem of nitrogen oxide emissions, the urea being added to create ammonia in the catalyser could potentially lead to the secondary negative impact of an ammonia emission gas. Ammonia must now also be added to the list of automotive emissions that must be monitored and the environmental responsibility also extends to the urea production chemicals facility. European emissions from such facilities will soon be controlled by legislation such as the European Commission's Industrial Emissions Directive (IED), which harmonises the maximum emission levels across a broad range of chemicals production industries throughout the EU. So, with the intention to minimise automotive NO_X emissions, additional monitoring requirements are required in the overall chemicals supply chain to ensure a positive environmental impact overall.

Ethanol

Ethanol is now a common additive to petrol, especially in countries that favour petrol engines over diesel engines and in locations where sub tropical climates favour high starchy crop yields with year round harvesting potential. Ethanol has the same implication for refineries as biodiesel, in that it reduces the volume of fossil fuel the refinery needs to process. The properties of ethanol as a fuel for transportation are quite similar to the properties of the regular petrol currently used in today's vehicles, and in comparison to diesel, it has the advantage of being a relatively particulate free burning fuel source.

Ethanol can be derived from crops such as sweetcorn, which is converted to ethanol by fermenting it in a similar process to producing beer and wine. The process removes sugars from the sweetcorn and converts them through a process of biological fermentation to produce a mixture of water and ethanol. This mixture is then distilled to yield ethanol, which can be added to petrol.

One of the main environmental implications of introducing ethanol into fuels derives from this fermentation and distillation phase between agriculture and adding the ethanol to the fuel, as it consumes vast quantities of energy to convert the water/ethanol mixture into pure ethanol. Therefore, while there are emissions benefits from using ethanol over petrol, the environmental impact shifts to agriculture in terms of land usage and fertiliser production and usage, as well as the highly energy intensive fermentation and distillation process, that also creates emissions typical of any combustion process. A clean combustion process calls for efficient burner technology, perhaps using oxygen or oxygen enrichment, and good process control using speciality gases and calibration mixtures. Emissions monitoring, requiring regular validation from calibration gas mixtures to ensure emissions are within prescribed legal levels, is also important for overall environmental impact control. An upcoming and highly environmentally friendly alternative to making ethanol from arable crops is the use of algae. Algae are extraordinarily fast at using photosynthesis to convert CO_2, salt water and sunshine into sugars to ferment into ethanol, approximately 50 times faster than the arable plants.

In terms of ethanol usage in car engines, fuel with higher ethanol content is more volatile and has the potential to vapourise at petrol stations and from car engines, and this requires accurate measurement and control of volatile organic compounds (VOCs) with high accuracy VOC calibration gas mixtures for mitigation and control. Ethanol also burns very differently in the car engine to conventional fossil fuels and has a different footprint of emission molecules, including methanol and formaldehyde, a dangerous chemical. In effect, formaldehyde has gained entry into recent US environmental legislation as a 'new' pollutant as a consequence of trying to introduce more environmentally friendly fuels. Emissions from large scale ethanol production facilities will be controlled through the IED in Europe and often through other similar legislation worldwide. To ensure that the overall environmental impact of this fuel change is controlled and mitigated, the use of accurate calibration gas mixtures for precise calibration of analysis instrumentation to measure formaldehyde and VOC emissions will be critical.

These are significant changes to the conventional fossil fuels industry and are forcing many refineries to rethink their business models. An implication of the increasing use of biofuels is that less crude oil will be processed, so requiring the refining facilities to be adjusted in order to accommodate the storage and blending of these quite different fuels. For example, as increasing numbers of ethanol fermentation/distillation plants are needed, some fuel producers may elect to integrate such facilities into their own production value chain, rather than them remaining as part of the agricultural industry or becoming independent entities.

All this begs the question: why switch to ethanol if there are so many additional issues to be addressed in producing and using this biofuel? The answer is that beyond environmental concerns, the quest for energy diversity is also being driven by geopolitics. Security of oil supply is a growing concern among countries who import massive quantities of oil for transportation fuel. A desire to establish a sustainable economic strategy or minimise foreign currency requirements by reducing expenditure on oil imports is another factor in play. So while major fuel consuming countries like China will continue to import oil from leading suppliers in Middle East, Venezuela and Brazil, there is an unprecedented trend aimed at achieving greater geopolitical self sufficiency through the development of local biofuel production capabilities based on plant science. This trend recognises that fuel sources which harness the continuous energy of the sun to produce crops are both sustainable and cost efficient.

Figure 4. Linde has built a showcase plant for LNG production 600 km north of the Arctic Circle.

Hydrogen powered fuel cells

Hydrogen fuel for passenger cars and buses is regarded as an environmentally attractive option because it produces no harmful emissions, only water vapour. Currently, however, the environmental impact cannot be avoided entirely as it takes place further back in the supply chain; for example, in terms of consumption of a fossil fuel (natural gas) to make the hydrogen. In addition, steam reformer technology consumes large amounts of energy to operate. An alternative is to use electrolysis to produce the hydrogen, which in turn puts the focus on the environmental impact of the electrical power generation.

In terms of environmental impact and climate protection, hydrogen powered transportation makes most sense when hydrogen is produced using regenerative energy sources. Linde has set itself the long term goal of producing green hydrogen from regenerative energy sources such as sun and wind, as well as from renewable raw materials and biological waste. The list of possible production chains is long and includes, for example, sourcing hydrogen from glycerine, a byproduct of biodiesel production. Linde is also one of the partners involved in the development of the world's largest green hydrogen plant, which has recently seen commencement of production in Mainz, Germany. The energy park is the result of a joint collaboration between several partners, including Siemens and RheinMain University of Applied Sciences, and has been designed to produce hydrogen using electricity from environmentally sound sources of energy such as neighbouring wind parks.

LPG/propane

Liquefied petroleum gas (LPG) is a fossil fuel rich in propane, which is a popular alternative fuel in the automotive sector, widely regarded as a cost effective, clean and safe. Lower

Figure 5. Natural gas is the cleanest fossil fuel with the lowest CO_2 emissions.

Figure 6. A pilot plant in Munich undertaking the biotechnological process of anaerobic digestion to create biofuel.

maintenance costs are another reason behind propane's popularity for those who are driving long distances.

Propane's high octane level combined with its low carbon and low oil contamination characteristics have resulted in improved engine life compared to conventional gasoline engines. As the fuel's mixture of propane and air is completely gaseous, cold start problems associated with liquid fuels can be reduced as well.

LPG is a byproduct of natural gas processing and crude oil refining with almost equal amounts of production derived from each of these sources. LPG components include ethane, methane, propane, and butane, as well as heavier hydrocarbons. Burning LPG releases carbon dioxide, a greenhouse gas.[1] The reaction also produces some carbon monoxide. LPG does, however, release less CO_2 per unit of energy than does coal or some other liquid fuels. It emits 81% of the CO_2/kWh produced by oil, 70% of that of coal, and less than 50% of that emitted by coal generated electricity distributed via the grid.[2] So, a switch to propane can result in substantial reductions of hydrocarbon, carbon monoxide, oxides of nitrogen, and greenhouse gas emissions. LPG also has a virtual absence of sulfur, leading to cleaner burning. With these superior features, it finds many different applications from transportation, cooking, heating and powering up the barbeque.

CNG/LNG

CNG and LNG are comprised of the same molecule: methane. The difference between them lies in the fact that CNG is supplied in a compressed phase and LNG in a liquid phase. Natural gas, a mixture of gases containing primarily hydrocarbon gases, is colourless and odourless and is the cleanest fossil fuel with the lowest carbon dioxide emissions. LNG is used as a transport fuel and is in the early stages of becoming a mainstream fuel for a diverse range of transportation needs. It is already popular for marine propulsion as an alternative to diesel fuels and very commonly used in buses and garbage trucks that have a slow start/stop operation in urban driving cycles. Another benefit in this application is that it effectively reduces vehicle noise, which is also regarded as an environmental impact. However, the combustion process also produces formaldehyde, which might need to be monitored and measured in line with contemporary legislation.

The main reason for LNG becoming more popular in the marine industry over recent years is the lower sulfur and NO_X emission limit values being brought in by MARPOL legislation. In order to comply with the ever tightening emission regulations, shipping operators might choose to adopt an integrated approach that considers the use of lower sulfur content fuel, the use of wet gas scrubbing for SO_2 removal, the use of SCR for NO_X reduction, or a conversion to LNG. With LNG now being used as an alternative marine fuel, Linde has already developed the necessary technology to supply the maritime industry with this efficient and environmentally friendly replacement for sulfur rich bunker oil. The use of LNG allows for a significant reduction in SO_X, NO_X, PM and CO_2 emissions, offering ship owners and operators a sustainable solution to meet existing and future emission standards. LNG can also be combined with other fuels in a dual fuel engine.

As well as being an important fuel source, methane from natural gas is a major feedstock for fertilisers and petrochemicals. As a raw material, it is almost as versatile as crude oil. Methane is extracted from natural gas fields and the emergence of fracking has represented a recent significant transition and expansion in natural gas production, particularly in the US. Fracking is able to release natural gas from sources that would be uneconomical to drill using conventional technologies. In Europe, fracking is still a sensitive and highly debated issue, owing to the potential risk of groundwater pollution. At the moment, the current falling fuel prices are having an impact on this debate, rendering the economics of fracking temporarily marginal for many new projects.

The other huge emerging source of natural gas production is biomethane. This industry looks to agriculture to be part of the solution, effectively harnessing energy from the sun to produce crops such as grass and maize, which are digested in a biotechnological process similar to fermentation called an anaerobic sludge digester. The methane produced this way can be compressed, liquefied or introduced into the natural gas supply chain. Alternatively, it can be burnt onsite to generate electrical power for introduction into the distribution grid. For total environmental impact control, the combustion emissions from these small scale generators would also require analysis leading to monitoring and control.

Another common way to produce biomethane is by digestion of human wastewater. Unfortunately, operators of this type of plant have no control over the kind of waste going into the sludge digesters, which poses an environmental issue. Municipal plants are known for having a broad spectrum environmental footprint, owing to new chemicals being added to hygiene products. For example, shampoos and conditioners contain silicone oils which, after the process, manifest as silicone containing pollutant molecules, a totally new environmental emissions footprint that requires analysis, monitoring and potentially additional mitigation steps.

As biomethane becomes more important in the alternative fuels arena, high tech solutions will be required in coming years to prevent environmental pollution in the gaseous phase emerging from the biogas reactors. The gas emissions analysis instrumentation will require a broad range of calibration gas mixtures and high purity speciality gases for operation and certification, and the Linde HiQ range of products is innovating to meet this emerging need. Europe leads the way in biogas production, which is still regarded as emerging technology. Germany leads the region with more than 100 sludge digesters in the country, followed by the Netherlands with more than 10 digesters. A key attraction of this technology is that it is a strategy that achieves fuel diversity to minimise and mitigate the risk of being a fossil fuel importer.

From the perspective of refineries or hydrocarbon processing operators, biomethane production could have similar effects to ethanol production, in that there is an alternative source for the fossil fuels they have historically processed on the refinery. They are now being confronted with the option to change their business models in order to become involved in non-traditional areas of fuel production, or watch their overall share of the energy market fall.

ULSD and LSD

ULSD and LSD have been refined to make them significantly cleaner than historical highway use diesel fuels. This focus on lowering sulfur levels in diesel to reduce vehicle emissions from vehicles has brought the issue of desulfurisation to the fore. Desulfurisation in refineries has been a challenge for many years and is becoming ever more important as the natural crude oils remaining in the earth are becoming heavier and dirtier, with higher sulfur content. For the hydrocarbon processing industry, overall refinery throughput is often determined by the speed at which plants can desulfurise the crude, yet the more stringent desulfurisation process is increasing Claus plant loadings with hydrogen sulfide and ammonia, frequently causing bottlenecks in the production process. The increasing amount of sulfur to be removed impacts the amount of fuel a refinery is able to produce and therefore its revenue and profit generation potential.

Whilst the combustion of low sulfur diesel in the vehicle reduces sulfur oxide emissions on the roads, it transfers the environmental burden to the refinery. Operation of the desulfurisation plant requires energy, which ultimately results in CO_2 emissions and requires hydrogen, which itself will have been produced using additional energy and/or fossil fuel resources. So, control and mitigation of the environmental impact at the refinery using, for example, best available technology (BAT), as outlined in the BREF notes associated with the new EU IED legislation, will potentially be required. The IED also calls for CEMS in the refinery stacks with the associated need for specialty gases calibration mixtures and high precision gas distribution equipment.

As an example of BAT, oxygen enrichment in the Claus process is a viable and cost effective solution for significantly increasing a refinery's sulfur handling capacity, as well as addressing problems associated with contaminants such as ammonia and hydrocarbons. Associated benefits include increased productivity achieved without changing the pressure drop, more effective treatment of ammonia containing feeds and less effort required for tail gas purification (reduced nitrogen flow). Oxygen enrichment is also a highly customisable approach to improving Claus plant yield with options varying from low level oxygen enrichment to employing advanced proprietary technology to bring about capacity increases of up to approximately 150%. In practical terms, this means that refineries can delay new Claus investment decisions as they can extend their existing Claus plant capacity. This is a particular advantage to those refineries whose plant footprints cannot accommodate the introduction of additional Claus plants. As an example of this oxygen enrichment technology, Linde has implemented its SURE burner technology and supplies the oxygen required to refineries in many continents around the globe.

Complex environmental implications

The rapid changes in the fuels arena in the pursuit of reduced automotive emissions have clearly brought with them complex environmental and operational implications. While automotive vehicle emissions have certainly become less harmful, more robust environmental management is being demanded at the production source and across the production chain to avoid simply moving the problem to another location.

New emissions legislation is intensifying this requirement, calling for a spectrum of process solutions and emissions monitoring gases, underpinned by more accurate calibration gas mixtures. Not only must these new gases and mixtures meet higher purity and accuracy standards, they must often also be certified and fully traceable with a scheme of accreditation, such as ISO17025, to prove that.

Linde is involved in every one of the new fuel arenas, whether it be fuel production, fuel extraction in terms of LNG storage or processing, pollution reduction or calibration mixtures for environmental monitoring, and has long followed a strategy of creating and developing products that are tailor made to meet the latest legislation requirements. This takes the pressure off customers to spend time searching for calibration mixtures and pure gases for process control that meet these standards.

References

1. *http://www.afdc.energy.gov/fuels/propane_production.html.*
2. *Sources: EPA 2009, GREET 1.8c.*