Monitoring and controlling emissions in Europe

Implementing the EU's Industrial Emissions Directive calls for quality and consistency in technologies for monitoring and controlling emissions

STEPHEN HARRISON
Linde Gas

The European Commission's Industrial Emissions Directive (IED) will standardise the maximum emission levels across a very broad range of industries throughout the European Union (EU). The IED reorganised seven existing overlapping directives related to industrial emissions into a single, clear and coherent legislative instrument and its implications will be cascaded through national governments into local or provincial legislation of EU member countries and enforced by inspectors in their local authorities.

The seven existing directives that will coalesce into the IED are the Large Combustion Plant directive (LCPD); the Integrated Pollution Prevention and Control directive (IPPCD); the Waste Incineration directive (WID); the Solvent Emissions directive (SED) and the three existing directives on titanium dioxide on disposal (78/176/EEC), monitoring and surveillance (82/883/EEC) and programmes for the reduction of pollution (92/112/EEC).

Best available techniques

One of the main reasons for the recast of the directive was the inadequate and incoherent implementation of the application of best available techniques (BAT) to optimise all-round environmental performance across the EU. In addition, the fact that relevant provisions were spread across seven different legal instruments was deemed to place unnecessary administrative burdens on companies, particularly those with operations spanning several member states.

Many of the primary industrial sectors in the EU are already well regulated in terms of emissions, but the aim of the IED is to harmonise and standardise how they are regulated and how BAT is utilised across the entire region by setting minimum emissions benchmarks and improving the quality and consistency of implementation.

For companies already operating above and beyond this benchmark, there will be no change required to their operating protocols. For instance, Sweden and Denmark, where a tax on nitrous oxide (NOx) and sulphur oxides (SOx) is in place, very little additional impact is likely. In these countries industrial companies have already invested heavily in emissions reduction technologies to minimise paying these taxes. It is also predicted that there will be similar low impact in the Netherlands, a leading EU member state in terms of environmental policy, where very low legislated emissions levels are already in effect.

The Industrial Emissions Directive principally covers control of pollution to the air and to water

The impact of the IED is therefore more likely to be felt in countries like France, the UK and in certain member states in Eastern Europe, which have lagged behind the leading environmental legislation in Europe. It will address shortcomings in the newer member states, such as the Czech Republic, Bulgaria, Romania and Poland, as well as Turkey, a candidate member state, which has never before operated in this sphere of environmental regulation.

Better consistency

The IED will describe how measuring and monitoring should take place and will be driven by an increase in the use of BATs via revised BAT Reference (BREF) documents in order to obtain better consistency of implementation across the EU member states. The BAT approach is aimed at identifying and applying the best technology available worldwide and applying it as cost effectively as possible on an industrial scale to reduce emissions and achieve a high level of environmental protection. The BREF documents contain the maximum emissions values for industries outside of power generation, such as iron and steel, refining, glass, cement and chemicals.

The IED principally covers control of pollution to the air, land and water and focuses on 13 specific pollutants or polluting substances to air: sulphur dioxide (SO_2) and other sulphur compounds; NOx and other nitrogen compounds; carbon monoxide (CO); volatile organic compounds (VOCs); metals and their compounds; dust, including fine particulate matter; asbestos; chlorine (Cl) and its compounds;

fluorine (F) and its compounds; arsenic (As) and its compounds; cyanides; substances and mixtures that have been proved to possess carcinogenic or mutagenic properties, or properties that may affect reproduction via the air and polychlorinated dibenzodioxins and polychlorinated dibenzofurans. For many industries, much of the impact for emissions to air will be focused on four pollutants: SO_2, NOx, CO and VOCs.

The LCPD, one of the seven existing EU directives related to industrial emissions, has required member states to legislatively limit emissions from combustion plants with a thermal capacity of 50 MW or greater. The directive applies to large thermal plants, many of which are fossil-fuel power stations. IED will repeal and replace LCD as of 1 January 2016 and, through BREF notes, is set to strengthen and extend those provisions across a very broad range of industries, covering the operation of combustion plants beyond the power generation industry. Examples include the ferrometals (iron and steel) industry and coke production, since coke is an essential ingredient in the manufacture of iron and steel. Non-ferrous metal production, such as aluminium processing, will also come into scope, as will the chemical, glass and cement industries where huge kilns are needed.

Developments

The link between this legislation and technology is very clear. The roll-out of regional directives like the IED will serve to drive the development and raise the profile of new pollution control technologies around the world by defining and referring to BAT. The BREF documents which record these BATs will herald new, lower emissions limit values (ELV) that will necessitate investment in more advanced pollution control measures. This will require investment in advanced pollution control unit operations with new process control instrumentation and, very likely, will need new instrumentation, specialty gases and calibration gas mixtures. In some cases, like continuous emission monitoring (CEM), the composition and quality of these gases and calibration mixtures will be independently regulated and controlled by external auditors and is likely to be regulated through accredited schemes for measurement such as ISO17025. Some of these new pollution mitigation unit operations, such as selective catalytic reduction (SCR), will also require chemical additives like ammonia (NH_3), which would need to be measured as a potential pollutant if SCR does not work properly.

As often happens when legislation is updated in a specific country or region, other countries outside its range adopt certain principles as a blueprint or starting point for their own local legislation. This is why many of the changes taking place in environmental legislation in the EU reflect developments in the United

States, where authorities like the Environmental Protection Agency (EPA) are also striving to level the playing fields across industries.

For example, a trend that is likely to be taken up in the EU in the future is the move towards speciation analysis in the VOC arena. Speciation analysis is defined as the separation and quantification of different chemical forms of a particular element. Until recently, determining total element concentrations was thought to be sufficient for environmental considerations, but now it has been recognised that it is important to understand the toxicological properties of the sample's various components in order to manage environment risk more accurately.

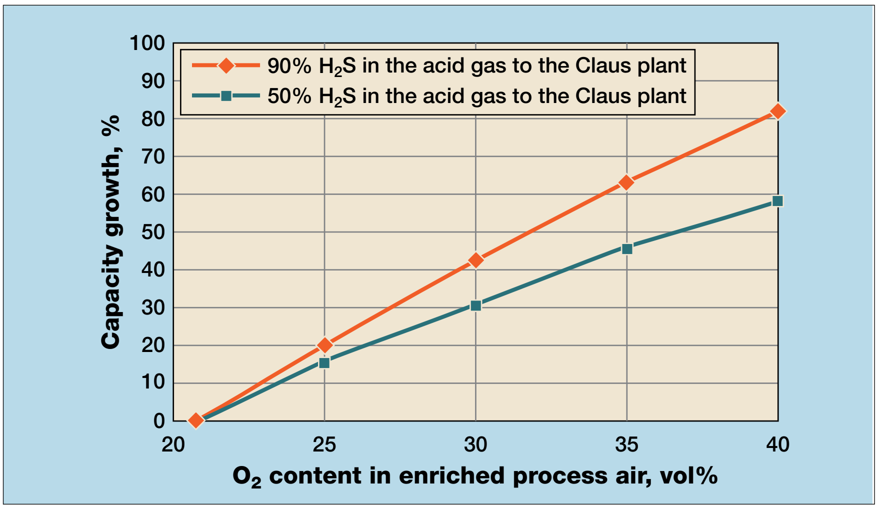

Figure 1 Oxygen enrichment in Claus plant

Controlling sulphur

Despite technological advances, controlling sulphur remains a technical challenge for the petrochemical industry as the sulphur content of the world's dwindling crude oil resources is increasing. For refiners, throughput can be limited by the speed at which plants can desulphurise crude. However, the more stringent the desulphurisation process becomes, increasing Claus plant loadings with hydrogen sulphide and ammonia, the more frequently bottlenecks in the production process also become. Claus plants operating in refineries process concentrated hydrogen sulphide fractions, converting them into elemental sulphur. The technology is also able to destroy pollutants, particularly ammonia. Although not new, enrichment technology has now come to the fore as a viable and cost-effective solution for significantly increasing a plant's sulphur handling capacity, as well as addressing problems associated with contaminants such as ammonia and hydrocarbons.

Oxygen enrichment of the combustion air significantly increases sulphur handling capacity. 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 around 150% (see **Figure 1**).

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.

Low level enrichment is achieved by injecting oxygen via a diffuser into the process air to the sulphur recovery unit. The maximum oxygen enrichment level which can be accommodated via this method is 28% and provides a capacity increase of approximately 30%, when processing acid gas rich in H_2S, as is the case in most oil refineries.

Despite technological advances, controlling sulphur remains a technical challenge for the petrochemical industry

Generally, the sulphur plant will require no equipment modification other than the provision of a tie-in point for oxygen injection into the combustion airline.

However, when even greater capacity is needed and increased levels of oxygen beyond 28% are required, it is necessary to introduce the oxygen into the reaction furnace separately from the air supply, as the combustion-air piping in conventional sulphur plants and air-only burners are unsuitable for use with highly oxygenated air.

Addressing this challenge, a new type of burner, SURE, developed by Linde Gases, has been specifically designed for this purpose – a self-cooled tip-mix burner with separate ports for acid gas, oxygen and air supply. The burner can be used in both end fired and tangential fired furnace designs. The burner achieves excellent mixing of hydrogen sulphide and oxygen enriched air over a wide load range.

The intensive mixing characteristics of these burners have been developed through extensive test work at Linde's own pilot plant — a commercial scale sulphur recovery unit — harnessing computational fluid dynamics (CFD) modelling to achieve excellent contaminant destruction and significantly increased tonnage output.

For operation with high levels of oxygen enrichment – greater than 45% – methods must be employed to mitigate high flame temperature in the reaction furnace. The SURE double combustion process provides full capability at up to 100% oxygen in an uncomplicated process that is easy to install, operate, and maintain.

Double combustion, as the name implies, splits the heat release into two separate reaction furnaces with cooling between. In the first reaction furnace, all amine gas, sour water stripper gas and, if required, air, are fed to the SURE burner together with the supplied oxygen, the level of which depends on plant throughput. The tip-mix burner allows for thorough mixing, giving excellent contaminant destruction efficiencies.

There is no sulphur condenser between the first waste heat boiler (WHB) and the second reaction furnace. Also, there is no burner in the second reaction furnace. By design, the gases exiting the first WHB and entering the second reaction furnace are substantially above the auto-ignition temperature of hydrogen sulphide and sulphur vapour, under all normal and turndown operation conditions. This system allows for low pressure drop, which is easy to control and easy to install.

The result of this type of control is a temperature profile ideally suited to the Claus process.

Operating temperatures in the first reaction furnace are high enough to destroy ammonia and hydrocarbons, but remain well below refractory limitations.

NOx control

A common approach to controlling NOx emissions is to modify the basic combustion process within the furnace. By using oxygen instead of air in the production process, which removes the nitrogen ballast, energy efficiency is not only increased, but one of the most important benefits is the very significant reduction of both direct and indirect greenhouse gas emissions, including CO_2 and NOx. CO_2 emissions can be reduced by up to 50% and, for NOx emissions, levels of below 50 mg/MJ can be reached. However, since emissions vary widely according to changes in temperature and air/fuel mixing, modifications to the combustion process impact not only the emissions, but very frequently also the efficiency and operability of the furnace. This renders NOx control a technically challenging undertaking that calls for understanding of complex issues around combustion chemistry and plant operations, as well as the economic issues related to plant fuel consumption and maintenance. NOx reduction by combustion modification is limited, typically in the 30-50% range, and must be implemented where it is effective and applicable without significant derating of the combustion furnace. Alternatively, replacement of the existing combustion equipment can be done but this is obviously capital intensive.

NOx can also be treated post-combustion and the most commonly specified technique for the removal of high levels of NOx

A common approach to controlling NOx emissions is to modify the basic combustion process within the furnace

is selective catalytic reduction (SCR), a technology designed to facilitate NOx reduction reactions in an oxidising atmosphere. It is called 'selective' because it reduces levels of NOx using ammonia as a reductant within a catalyst system. The reducing agent reacts with NOx to convert the pollutants into nitrogen and water. SCR has been adopted effectively in lowering NOx emissions from gas fired clean flue gas streams. However, treating dirty gas streams from industrial processes involving kilns, furnaces and combusting coal or oil with SCR carries a risk of the catalyst being compromised by chemical poisons in the flue gas, or blinded by the dust and particulate matter also resident in the flue gas.

SCR must be integrated into a high temperature region of the process, so if it is not included in the original design of the furnace, later installation will require a major rework of the process. The intermediate technology selective non-catalytic reduction (SNCR) is also applicable in the high temperature regions impacting the client's process. SNCR does not make use of a catalyst, but requires a highly defined temperature region to provide a reaction with ammonia. This technology is capable of achieving 50-60% NOx removal.

The effective temperature for reduction of NOx through a SCR catalyst is in the range 200-400°C, and for SNCR to be effective, the ammonia injection and reduction needs to be in the range 900-1100°C. Additionally, retrofitting NOx reduction solutions such as SCR or SNCR can often be disruptive to the industrial process and can have negative implications with respect to operations and costs.

Linde's LoTOx technology (low temperature oxidation) has been developed for the control of NOx emissions. LoTOx, which works on 'dirty' exhaust gas streams to oxidise and then capture NOx, is a selective, low temperature oxidation technology that uses ozone to oxidise NOx to water soluble and very reactive nitric pentoxide (N_2O_5). The LoTOx process is applied at a controlled temperature zone within the scrubbing system. LoTOx does not require additional scrubbers but can leverage those already installed to remove other criteria pollutants such as SOx. Dirty gas means gas with other criteria pollutants, typically particulate matters, SOx and other acid gases. Irrespective of NOx removal, for control of these pollutants, air pollution control devices such as wet and dry scrubbers are required to remove those pollutants. Integrating the LoTOx process within such air pollution control devices is relatively simple and truly results in a multi-pollutant removal system. Inside a wet or dry scrubber, N_2O_5 forms nitric acid that is subsequently scrubbed by aqueous spray and neutralised by the alkali reagent. The conversion of higher oxides of nitrogen into the aqueous phase in the scrubber is rapid and irreversible, allowing an almost complete removal of NOx, in the region of 90-95% – even as high as 98% – from flue gases. The low operating temperature allows stable and consistent control, regardless of variation in flow, load or NOx content, and acid gases or particulates have no adverse effect on the performance of the LoTOx process.

LoTOx is a versatile NOx removal process but particularly applies where the removal required is greater than 80% or where stack emissions must be below 20 ppm. The process offers flexibility in NOx removal. In most gases, simply increasing the amount of ozone injection may meet increasingly stringent regulations or limiting tiered NOx emissions. The benefits of this technology include increased capacity, greater flexibility in the choice of feeds, increased conversion rates and reduced emissions. Since it is a post-combustion solution that treats the flue gas at the end of the process, it does not interfere with the process in any way. The system does not utilise a fixed catalyst bed and does not impact system hydraulics, making it robust and reliable, capable of operating without maintenance for periods of two to three years between refinery shutdowns. It is also able to manage unit upsets without impacting overall reliability and mechanical availability.

The ozone required is produced from oxygen on site in response to the amount of NOx present in the flue gas generated by the combustion process and the final NOx emission required.

Additionally, for the recovery of carcinogenic VOC emissions, including benzene – for which the IED imposes a highly stringent 1mg per cubic metre – BATs include cryogenic condensation technologies employing liquid nitrogen.

Calibration mixtures

A further BAT development is the precise calibration gas mixtures and ultra high purity zero gases which are employed as critical components of the measurement process. When considering emissions control within the oil and gas industry, there are two main applications in which ultra high precision gases have become indispensable.

The first involves environmental emissions monitoring, which is heavily legislated, demanding accurate and precise measurements to ensure a refinery or hydrocarbon processing facility is operating within its consent levels. Since such monitoring is a legal requirement, emissions measurements could have an impact on the hours a refining facility is permitted to operate over the course of the year and therefore can have a significant financial implication to the corporate balance sheet.

The second application is emissions trading, which is a market-based approach used to control pollution by providing economic incentives for achieving reductions in the emissions of pollutants. Emissions trading is a common practice in the US today, where facilities such as petrochemical plants are able to sell part of their emissions quota that has not been emitted within an environmental consent level. It is also an emerging practice in Europe. This means there is a direct financial consequence attached to accurate measurement. The smallest variation in accuracy could have immediate financial implications. Today, greenhouse gases feature prominently in emissions trading schemes, notably carbon dioxide (CO_2) which represents the majority of traded greenhouse gas emissions, but also methane and nitrous oxide are of notable importance in this application.

Future technologies

The introduction of the IED is a major development in emissions control in the EU and it begs the question, "What will the next major development in this arena look like?"

Some speculate that the focus in the EU may extend at some future date to regulate the emission of metals such as mercury, as is already the case in the US. In the realm of VOCs, the trend towards speciation might lead to a closer focus on substances like benzene or toluene. Speciation might also take place in the area of oxides of nitrogen, since nitric oxide, nitrous oxide, and nitrogen dioxide each play a different role in the ambient air in terms of the pollution they cause.

NH_3 is also very likely to come into the measurement species, because it is added to a lot of raw combustion gas processing operations which use SCR or selective non-catalytic reduction (SNCR) technology to reduce NOx emissions. Measurement and control of NH_3 will ensure it is being added in an optimum quantity so that the NOx emissions are minimised, whilst the NH_3 is not being overdosed to the extent that it is emitted as a pollutant in its own right nor is it wasteful, with related cost implications. And it is now becoming common practice to measure ammonia 'slip' after the catalytic reaction at around 5 ppm ammonia. However, the accurate measurement of ammonia using on-line instrumentation in such a hot, wet emissions stream is a real technological challenge. The issues are not related to the instrumentation or the availability of high quality specialty gases calibration mixtures, but lie in the problems of sample conditioning and delivery. In fact, to enable the high precision measurement of ammonia in legislated environmental applications, Linde Gas became the first laboratory in Germany to offer ISO17025 accredited calibration gas mixtures in this range of ammonia concentrations. As an alternative to on-line ammonia measurement in the flue gas, some proxy measures are also used. For example, ammonia salts can be measured in fly ash samples. However, due to the intermittent sampling and batch analysis technique, this is a relatively slow feedback process control loop.

In line with the consistent trend towards lower emissions levels, it is clear that, as in the US, the scope of emissions legislation will extend ever wider to cover more factories that have not yet been greatly impacted by regulation. The existing LCPD legislation focuses on huge power plants that run the largest possible combustion units. The IED will stretch this scope a bit further, and there are already plans to introduce medium combustion plant legislation that will fill a gap not yet been addressed by the IED, to focus on slightly smaller combustion operations related to small scale heating and power generation. Ultimately, it is possible that within the next decade, the impact of EU emissions legislation will impact any operation burning material on an industrial scale.

In the petrochemical industry, in seeking to mitigate emissions related to the desulphurisation of petroleum products, speciation is also on the cards. Improved monitoring and control would be achieved by isolating and examining the various sulphur compounds most frequently encountered during these desulphurisation process steps. These compounds typically tend to be dimethyl disulphide and a range of mercaptans, as well as hydrogen sulphide.

In many combustion operations, speciation between SO_2 and sulphur trioxide (SO_3) will also come into focus. The distinction between SO_2 and SO_3 becomes vital if flue gas processing will subsequently involve electrostatic precipitation because SO_3 can have a very detrimental impact on this process.

It is possible that, within the next decade, the impact of EU emissions legislation will impact any operation burning material on an industrial scale

As international emissions legislation becomes more sophisticated, it is propelling the specialty gases and instrumentation sectors into completely new levels of technology, beyond traditional solutions where a calibration gas mixture could simply be hooked up to an analyser. A good example of this is analysis of the SO_3 molecule whose half life is too short to allow for the production of a calibration gas standard. This calls for the mixture to be produced on site using generator technology.

Advances in emissions legislation will therefore continue to challenge companies to be able to supply products that underpin its requirements. Legislators also need to ensure through BAT and BREF documents that the technology actually exists, or can be cost effectively applied, to any new legislative requirements.

Stephen Harrison leads Linde's global Specialty Gases & Specialty Equipment business from Munich, Germany. He holds a master's degree in chemical engineering from Imperial College, London, UK and is a British Chartered Engineer (MIChemE).