



Stephen Harrison, Linde Gas, Germany, and Shivan Ahamparam, Linde Gas, USA, look at how industrial gases are helping to meet one of the biggest technological challenges of the decade, namely satiating the world's appetite for low sulfur content fuels.

**R**ecently, environmental authorities such as the US Environmental Protection Agency (EPA) have applied stringent regulations governing hazardous emissions from industries such as oil refineries. This in turn has placed a heavy emphasis on accurately measuring the sulfur content of emissions and in refining operations.

#### Measurement techniques

In refining process control, or for determination of incoming crude oil composition, sulfur is often measured quantitatively in percentages, guided by documented standards of measurement and recommended analytical methods, including various methods by the American Society for Testing and Materials (ASTM). Similar procedures are used to determine total sulfur content in incoming natural gas feedstocks. The analytical technique most commonly used for this purpose in modern refineries and LNG processing terminals involves chemiluminescence. These instruments use a two stage method where the sample is first pyrolysed in a flame of purified or synthetic air and high purity hydrogen under vacuum to generate sulfur monoxide. This is then transported by a carrier gas, typically argon or nitrogen at a purity of 99.999%, to a chamber where it reacts with ozone to generate sulfur dioxide and UV light. The light generated is measured by a photomultiplier tube to measure the total quantity of sulfur in the sample.



**Figure 1.** Identification of sulfur containing molecules like carbonyl sulfide, methyl mercaptan or ethyl mercaptan, is needed in order to understand where the various sulfur compounds originate from.

Another technique is atomic emissions spectroscopy (AES), a method of chemical analysis that uses the intensity of light emitted from a flame or plasma to determine the quantity of sulfur in the sample. The wavelength of the atomic spectral line identifies the element, while the intensity of the emitted light is proportional to the quantity of atoms present. AES is a sensitive technology, capable of measuring down to ppm levels and also of identifying actual molecules, therefore providing both qualitative and quantitative information at these low levels. It is suitable for measuring sulfur levels as part of process control, final product quality control and for environmental emissions monitoring applications.

AES can also be combined with inductively coupled plasma (ICP), a technique that is highly sensitive and can quantify concentrations in ppm or ppb ranges. This technique requires high purity argon. Alternatively, AES can be combined with gas chromatography (GC) in a technique labelled GC-AED. The chromatography would consume a carrier gas such as high purity helium, to drive the sample through the column and separate the various components to allow species identification in the atomic emission detector. The system would also require periodic calibration with appropriate calibration gas mixtures.

The benefit of these techniques is that they can identify some of the sulfur containing molecules (for example carbonyl sulfide, methyl mercaptan or ethyl mercaptan) in order to understand where the various sulfur compounds originate from. This is useful for crude oil refining and equally relevant to liquid natural gas processing.

## Emissions monitoring

In addition to these measurement techniques, refineries have installed continuous emission monitoring systems (CEMS) in the plant stacks to measure emissions from the exhaust streams on a continuous basis. To be able to trust the values of these analysers, very accurate calibration gas mixtures are required. Suppliers such as Linde provide traceable calibration mixtures for measuring sulfur compounds in petrochemical refinery stacks.

In 2010, the US EPA, in cooperation with the National Institute of Standards and Technology (NIST), conducted a blind audit of EPA protocol gases used to calibrate CEMS and the instruments used in EPA reference methods. These gases and the associated quality assurance/quality control checks help to ensure the quality of the emission data the EPA uses to assess achievement of emission reductions required under the Clean Air Act.

This verification programme evaluated gas companies in regard to how accurately their products measured SO<sub>2</sub>, nitrogen oxides and CO<sub>2</sub>. Linde's US production site at Alpha, New Jersey passed the audit with zero failures. Additionally, Linde was granted continued approval in 2011 to produce EPA protocol gas standards both at this site in the USA and an additional site near Toronto, Canada.

As in other parts of the world, the EU is introducing stricter limits on pollutant emissions from light road vehicles, particularly for emissions of nitrogen particulates and oxides. Since 2009, it has been mandatory to have ultra low sulfur petrol and diesel: that is, fuels containing less than 10 ppm of sulfur.

Analysis of sulfur compounds in fuels has therefore become a critical requirement. However, so has the need to measure for lower and lower levels of sulfur compounds. It is now vital to be able to detect extremely low levels of sulfur (down to ppb). In order to achieve this, a range of instrumentation techniques and detectors are required. One of the typical methods used for the determination of sulfur species in fuel samples is GC separation, followed by sulfur chemiluminescence detection (SCD).

## Desulfurising crude in the production process

SO<sub>2</sub> is formed when sulfur containing fuels, such as coal and oil, are burned. The primary sources of SO<sub>2</sub> emissions are power plants, refineries and smelting facilities. SO<sub>2</sub> is also found in the exhaust of diesel fuel and gasoline. Volcanoes and decaying organic matter also produce SO<sub>2</sub>. However, manmade emissions of SO<sub>2</sub> have been the cause of some of the worst air pollution episodes in the last century. Despite technological advances, controlling sulfur remains a technical challenge for the petrochemical industry as the sulfur content of the world's dwindling crude oil resources is increasing.

Crude oil is a mixture of liquid hydrocarbons, often found together with natural gas. It is normally described as sweet (low sulfur) or sour (high sulfur) and light or heavy, depending on its density. Sweet crude oil has a sulfur content of less than 0.5% and anything higher is dubbed sour. Sweet crude is therefore preferable to sour, since, like light crude, it is more suited to the production of the most valuable refined products. Heavier oils may also be described as medium and bitumen, which is so heavy that it is actually solid under ambient conditions.

## Environmental issues

As a primary source of sulfur emissions, the refining segment of the petrochemical industry has found itself juggling fears of energy insecurity with concerns about climate change. SO<sub>2</sub> is one of the major air pollutants that impacts the global climate and is a key focus for the UN and environmental activists. It can be harmful to health as it is a potent asthma trigger and can cause other potentially damaging respiratory health effects. When sulfur combines with oxygen to create SO<sub>2</sub>, it is defined as a critical air pollutant by the EPA and can form dangerous sulfates, which can be breathed deep into the lungs. Once oxidised by air, it also forms sulfuric acid, the major component of acid rain. Acid rain harms fish, damages forests and plants, and can erode buildings.

In addition to sulfuric acid as the key component of acid rain, other environmentally hazardous sulfur components produced as a result of crude oil processing include hydrogen sulfide and carbonyl sulfide, both highly corrosive and toxic chemical compounds.

Air and water pollution are particularly harmful as they can drift from the source to other areas with no wall or fence to contain them. As sulfur dioxide is the key component in acid rain, this substance may be carried to other countries and be precipitated there. Similarly, rivers flowing across borders often carry pollutants, discharging in lakes and seas. Some countries are exporters of acid rain and other pollutants, meaning that neighbouring countries are unable to stop such



**Figure 2.** As a primary source of sulfur emissions, the refining industry has found itself juggling fears around energy insecurity with concerns about climate change.

substances entering their territories. The cumulative impact of these factors is that increasingly rigorous regulations are being introduced by environmental authorities to minimise sulfur emissions at the point of generation.

### Refining challenges

Almost every oilfield produces crude with a unique mixture of characteristics, which presents distinct challenges to oil companies involved in separating crude into different products. In addition to sulfur content, refineries are being challenged to manage increased levels of acid gas or sour water stripper gas and the occasional lean acid gas feed.

For refiners, throughput can be limited by the speed at which plants can desulfurise crude. However, the more stringent the desulfurisation process becomes, increasing Claus plant loadings with hydrogen sulfide and ammonia, the more frequently bottlenecks in the production process also become. Claus plants operating in refineries process concentrated hydrogen sulfide fractions, converting them into elemental sulfur. The technology is also able to destroy pollutants, particularly ammonia.

Despite lacking novelty, oxygen enrichment technology has now come to the fore as a viable and a cost effective solution for significantly increasing a plant's sulfur handling capacity, as well as addressing problems associated with contaminants such as ammonia and hydrocarbons.

Oxygen enrichment of the combustion air significantly increases sulfur 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 the employment of 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 by extending 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 sulfur recovery unit. The maximum oxygen enrichment level that can be accommodated via this method is 28%, providing a capacity increase of approximately 30% when processing acid gas rich in  $H_2S$ , as is the case in most oil refineries. Generally, the sulfur plant will require no equipment modification other than the provision of a tie in point for oxygen injection into the combustion airline.<sup>1</sup>

### New technology

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. This is because the combustion air piping in conventional sulfur plants and air only burners are unsuitable for use with highly oxygenated air.

Linde Gas has developed a new type of burner specifically designed for this purpose. SURE™ is 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 sulfide and oxygen enriched air over a wide load range.

The intensive mixing characteristics of these burners have been developed through extensive test work, harnessing computational fluid dynamics (CFD) modelling to achieve 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 simple 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 air (if required) 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, offering efficient contaminant destruction.

There is no sulfur 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 sulfide and sulfur vapour, under all normal and turn down 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 specifically 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. KOA Oil in Japan has successfully harnessed Linde's double combustion process since 1990.

A novel approach has used the benefits of a multi pass WHB for plants with restricted footprint. The zone between the first and second passes of the boiler is utilised as the second reaction furnace of the double combustion process. In this situation, lances are installed in the channel head connecting the first and second pass of the WHB tube sheets (where the remaining oxygen can be added). For the optimum design and location of the SURE burner and oxygen lances, Linde uses a validated CFD model. This particular approach has been operational at API Falconara, Italy since 1996 and at Shell, Puget Sounds, and General Chemicals Anacortes.

The change out of the WHB can improve energy efficiency at a plant through the generation of valuable high pressure steam. Other energy efficiency benefits arise from the much reduced process gas flow through the plant. This reduces the converter reheat and incinerator fuel gas requirements to a minimum, and reduced energy requirements mean significantly reduced carbon dioxide emissions.  

### References

1. HEISEL, M; SCHREINER, B; adn DE LOURDES COUDE, M; 'Oxygen enrichment is an option to reduce loadings for Claus plants'; Hydrocarbon Processing, February 2007.