Oxygen enrichment in desulphurisation

Oxygen enrichment technology is a viable and a cost-effective solution for significantly increasing sulphur treatment capacity

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As a primary source of sulphur emissions, the refining segment of the petrochemical industry has found itself juggling fears around energy insecurity with concerns about climate change. Sulphur dioxide (SO_2) is one of the major air pollutants that impact our climate and is a key focus for the United Nations 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 sulphur combines with oxygen to create SO_2, it is defined as a critical air pollutant by the US Environmental Protection Agency (EPA) and can form dangerous sulphates, which can be breathed deep into the lungs. Once oxidised by air, it also forms sulphuric acid, the major component of acid rain. Acid rain harms fish, damages forests and plants, and can erode buildings.

SO_2 is formed when sulphur-containing fuels, such as coal and oil, are burned. The primary sources of SO_2 emissions are power plants, refineries and smelting facilities. SO_2 is also found in the exhaust of diesel fuel and gasoline. 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.

Almost every oil field 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 sulphur 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 desulphurise crude. However, the more stringent the desulphurisation process becomes, increasing Claus plant loadings with hydrogen sulphide (H_2S) and ammonia, the more frequently bottlenecks in the production process also become. Claus plants operating in refineries process concentrated H_2S fractions, converting them into elemental sulphur. The technology is also able to destroy pollutants, particularly ammonia.

Increased capacity

Although not new, oxygen 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%.

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 that 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.

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.[1] 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 is unsuitable for use with highly oxygenated air.

Self-cooled burner

Addressing this challenge, a new type of burner, Sure, developed by Linde Gas, 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- and tangential-fired furnace designs. The burner achieves effective mixing of H_2S and oxygen-enriched air over a wide load range.

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

For operation with high levels of oxygen enrichment, greater than 45%, methods must be employed to mitigate a 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

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 effective 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 H_2S and sulphur vapour, under all normal and turndown operation conditions. This system allows for a low pressure drop, which is easy to control and easy to install.

Temperature profile

The result of this type of control is a temperature profile 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 a 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 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 Sound refinery and General Chemical's Anacortes site.

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.

Measuring sulphur levels

Inseparable from the crude oil refining process is the measurement of sulphur levels present in raw materials during the process, in finished products and being emitted to the atmosphere.

In refining process control, or for determination of incoming crude oil composition, sulphur is often measured quantitatively in percentages, guided by documented standards of measurement and recommended analytical methods such as various ASTM methods. Similar procedures are used to determine total sulphur 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 pyrolised in a flame of purified or synthetic air and high-purity hydrogen under vacuum to generate sulphur 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 SO_2 and UV light. The light generated is measured by a photomultiplier tube to determine the total quantity of sulphur in the sample.

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 sulphur 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 levels of parts per million (ppm) and also of identifying actual molecules, therefore providing both qualitative and quantitative information at these low levels. It is suitable for measuring sulphur 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 the range of parts per million, or even billion — which would require high-purity argon. Alternatively, AES can be combined with gas chromatography, where the technique would be referred to as 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.

Sulphur-containing molecules

The benefit of these techniques is that they can identify some of the sulphur-containing molecules, such as carbonyl sulphide, methyl mercaptan or ethyl mercaptan, in order to understand where the various sulphur compounds originate from. This is useful for crude oil refining and equally relevant to natural gas processing.

In addition to sulphuric acid as the key component of acid rain, other environmentally hazardous sulphur components produced as a result of crude oil processing include H_2S and carbonyl sulphide, both highly corrosive and toxic chemical compounds.

Environmental authorities such as the EPA have applied stringent regulations governing hazardous emissions from industries such as oil refineries and this, in turn, has placed a heavy emphasis on accurately measuring the sulphur content of emissions.

To this end, among other measurement techniques, refineries have installed continuous emission monitoring systems (CEMS) in plant stacks to measure emissions from exhaust streams on a continuous basis.

To be able to trust the values of these analysers, very accurate calibration gas mixtures are required. In this realm, Linde supplies traceable calibration mixtures for measuring sulphur compounds in petrochemical refinery stacks.

Verification programme

In 2010, the 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 Linde in regard to how accurately its products measured SO_2, nitrogen oxide and carbon dioxide. Linde's US production site, at Alpha New Jersey, passed the audit with zero failures and, in 2011, the company was granted continued approval to produce EPA protocol gas standards both at this site in the US and at an additional site near Toronto, Canada.

As in other parts of the world, the European Union 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-sulphur petrol and diesel; that is, fuels containing less than 10 ppm of sulphur.

Analysis of sulphur compounds in fuels has therefore not only become a critical requirement, but so has the need to measure for lower and lower levels of sulphur compounds. It is now vital to be able to detect extremely low levels of sulphur, down to parts per billion, and a range of instrumentation techniques and detectors are required to meet these requirements. One of the typical methods used for the determination of sulphur species in fuel samples is GC separation followed by sulphur chemiluminescence detection (SCD).

References

1 Heisel M, Schreiner B, De Lourdes Coude M, Oxygen enrichment is an option to reduce loadings for Claus plants, *Hydrocarbon Processing,* Feb 2007.

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