Hydrogen is an essential component for hydrotreating and hydrocracking (image courtesy of Air Liquide).

SPECIAL SOLUTIONS

Andy Shurtleff and Brandon D. Sumners, Airgas, an Air Liquide company, explain the role of industrial and specialty gases in reducing sulfur emissions.

The reduction of sulfur emissions in crude refining operations has been a foremost environmental initiative over the past 25 years. Rules and standards focused on lowering emissions relate to both direct crude refining operations and to the fuels they produce. This initiative continues to gain momentum with new sulfur-related fuel regulations, including regulatory changes in the US, China and India and through worldwide organisations such as the International Maritime Organization (IMO), which will start decreasing allowable sulfur content in bunker fuels used as fuel for ships in January 2020.

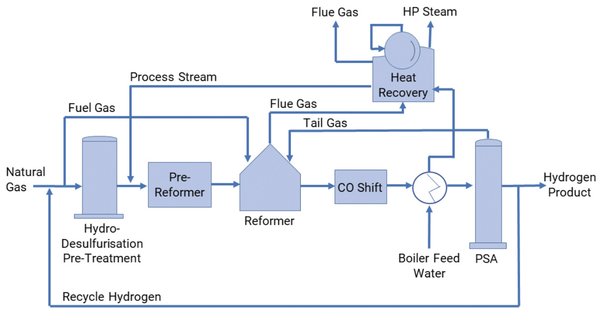

Figure 1. Steam methane reformers (SMRs) are a primary production supply mode alternative to pipelines.

Figure 2. Processing capacity for sulfur recovery units (SRUs) may be increased through the addition of oxygen.

Maintaining production levels while complying with sulfur content reduction (along with emissions monitoring) requirements creates significant pressure for refining operations.

Industrial and specialty gases play a major role in helping crude refining operations meet new demands by:

- Enabling production capabilities to reduce sulfur content and increase throughput.
- Removing bottlenecks and expanding sulfur processing operation capacity.
- Ensuring accurate emissions monitoring at plants and sulfur content in end use products.

This article explores a few of the contributions made by industrial gases in each of the above areas.

Hydrogen

Implementation of new regulations limiting sulfur content in gasoline, diesel and bunker fuel will continue to increase worldwide hydrogen demand.

The first step in petroleum refining is distillation, where heated crude oil is run through distillation units and separated into various components. These components will be additionally treated to produce fuel gases and liquids along with heavier oils and byproducts. Following distillation, fuel products are run through hydrotreater systems that include desulfurisation among other processes. Hydrotreater units rely on high temperatures and pressure along with catalytic reactions and hydrogen to separate sulfur from hydrocarbons. Sulfur removal is necessary for products to meet compliance requirements and to prevent potential corrosion of refinery equipment and poisoning of downstream catalysts that are used to further process hydrocarbon fractions into finished products.

Hydrogen utilised in hydrotreating is sometimes referred to as a sulfur scavenger as, in this process, sulfur molecules are separated from hydrocarbon chains and replaced with hydrogen to produce stable molecules. Freed sulfurs are scavenged through attachment to additional hydrogen molecules forming hydrogen sulfide (H_2S) to be removed in later processes. The volume of hydrogen needed at this process stage is proportional to the amount of sulfur to be removed.

Hydrogen is also used in the operation of delayed coker units (DCUs), hydrocrackers and other critical process systems. In turn, volume requirements are typically high enough in refineries that supply is provided either through pipelines tied to major local or regional production systems or through steam methane reformer systems (SMRs) located either at or near refinery sites. These SMRs utilise a combination of natural gas, steam and catalyst to produce hydrogen, carbon monoxide (CO) and carbon dioxide (CO_2), which, in combination, are commonly referred to as 'syngas'. The syngas CO component can be steam shifted to a secondary reactor to produce additional hydrogen plus CO_2. Pressure swing adsorption (PSA) purification can then be used to separate the hydrogen for use in the hydrotreaters and other processes outlined above.

Crude refining plant systems and flows can vary significantly and incorporate multiple hydrotreating systems at various points in the process stream.

Oxygen

To increase production capacity, refineries regularly employ oxygen enhancement of sulfur recovery systems.

The sulfur molecules that were freed from crude oil in the hydrotreating process and converted to H_2S – along with other gases produced from atmospheric distillation and hydrotreater systems – are run through amine treating systems to separate the H_2S. Isolated H_2S is then run to a sulfur recovery unit (SRU) where it is either reduced to elemental sulfur through a Claus process system or converted to sulfuric acid, which is typically accomplished through a wet process system. Claus-produced elemental sulfur is either shipped out as liquid or dried and shipped as a familiar yellow powder, while sulfuric acid is shipped as a liquid. Recovered sulfur and sulfuric acid are primarily utilised in the manufacture of fertilizer products, with most of the balance consumed as additive material in other chemical processes.

All process systems have finite production throughput capacities that limit the total volume of sulfur material they can process in a given time period. SRU system outages, along with requirements, to produce atypically high sulfur crude feedstocks can result in system bottlenecks that have the potential to severely reduce refinery production.

The financial implications of system downtime and reduced capacity have led many refining operations to increase overall sulfur recovery capacity, through oxygen enhancement or the addition of redundant standby or rotating systems. Adding oxygen to the feed gas systems can increase the capacity of an existing system substantially. It can also be utilised selectively when demand requires.

Both Claus and sulfuric acid systems rely heavily on heat generated by combustion processes as a major component of the recovery process.

Claus systems have the option of injecting oxygen either in the primary air feed line or at the burner nozzle. Direct air feed line injection can be accomplished quite easily, providing a quicker impact with greater ease and lower capital costs than when injected at the burner nozzle.

When installed in the primary air feed line, total oxygen concentration is typically limited to 23.5% by US regulations, but with certain precautions and system design it may be increased to the refining industry norm of 28%. This oxygen addition can result in increased capacity of up to approximately 25%. Capacity can be increased even more (up to 40% increased production with 35% oxygen enrichment) through the use of advanced, homogenous oxygen injection methods that provide better gas blending and even distribution of oxygen into the stream. These advanced methods are necessary to prevent oxygen ignition and fire in carbon steel piping systems.

Oxygen enhancement for wet sulfuric processing is similar to that of Claus systems as it is primarily based on increasing the burner efficiency of the sulfuric systems. Sulfuric system enhancements are most effective when combined with specially engineered feed and distribution systems. The combination can result in increased processing rates, increased sulfur dioxide conversion and reduced emissions from the convertors.

Adding oxygen provides the most financially appealing solution to sulfur recovery operations due to the ease and relatively low cost to add it to existing systems. As with hydrogen, worldwide oxygen demand in refining operations will continue to grow relative to the pace of sulfur removal requirements.

Specialty gases

Specialty gases play an important role as calibration and validation gases to ensure analyser accuracy and confirm regulatory compliance regarding sulfur emissions.

In the world of emissions monitoring, it is clear that trust follows verification, but only to the extent that the latest reports validate system performance. For example, the implementation of the US Environmental Protection Agency (EPA) 49CFR Part 65 Subpart Ja, which went into effect in November 2015, provides clear guidelines for monitoring and quantification of sulfur emissions from refinery flares. This rule not only required installation of special analysers for quantification of sulfur content in emissions, but also outlined requirements for flow monitoring to measure the total volume of emissions.

Previous US regulations were largely focused on 162 ppmv daily average limits and, in turn, EPA protocol gases had long been available for calibration and validation of analysers used to measure emissions. Subpart Ja raised the bar on verification with requirements to monitor emissions, even at high percentage levels where EPA protocol gas calibration standards did not previously exist, and are not expected to exist in the future, due to a lack of NIST traceable standards required for protocol production.

The need to monitor sulfur emissions at high percentage levels created challenges for refineries who were confronted by short shelf lives for highly reactive H_2S and other sulfur standard specialty gas mixes, along with relatively ambiguous guidelines on standards certification.

Specialty gas solutions have since been developed to address both short shelf lives and enhanced certification of calibration standards, up to and including dual-certified and interlocked standards.

Additionally, numerous US refineries have recognised the hazards of use, storage and exchange of high concentration sulfur standard gas mixes. Several have now worked with analyser manufacturers and their environmental teams to secure EPA approval for alternative monitoring procedures (AMPs), citing analyser linearity as a basis for lowering the total concentration of H_2S and other sulfur calibration standards needed for regular system validation.

Another facet to emissions monitoring relates to engine testing, to ensure that automatic and other internal combustion systems are meeting emissions requirements. New testing regimens and requirements are increasingly stringent. It can be difficult to produce repeatable, stable calibration standards when employing highly reactive sulfur components.

Manufacturers must meet individual country and regional guidelines as a price of market entry and governmental regulatory agencies are clearly on the side of verifying before trusting.

Conclusion

Regulations are tightening allowable sulfur level standards to reduce atmospheric sulfur levels worldwide. The crude refining market sector is under greater pressure from multiple fronts to limit sulfur from both their direct plant emissions and the products they manufacture. Consequently, industrial and specialty gases will play an even greater role in efforts to reduce and accurately validate sulfur content in hydrocarbon products and emissions.