TIMOTHY D. LEBRECHT, AIR PRODUCTS, USA, RECOMMENDS OXYGEN ENRICHMENT TECHNOLOGY TO OPTIMISE THE OPERATING FLEXIBILITY IN REFINERIES AND MAXIMISE PROFITABILITY.

perations flexibility in refineries is a must today. To maximise profitability, refiners are tasked with optimising tight oil from shale, heavy oils from Canada, and variations of sour and other impurity laden crudes. Crude flexibility and operating flexibility can now differentiate refiners and enable them to maximise profitability in their refineries.

These operating changes have transformed the way oxygen enrichment in refineries is viewed. A number of years ago, as sulfur content continued to increase, sulfur recovery unit (SRU) oxygen enrichment was a common way to boost capacity at a relatively low cost. Today, this efficient method of increasing capacity also gives refiners the ability to process crude blends of various densities and sulfur content.

Typical operating philosophy

In today's refineries, SRU oxygen enrichment is typically used in one of three different ways:

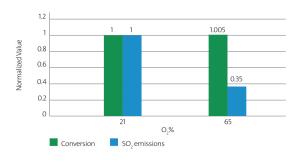
- As an insurance policy against the unplanned shutdown of an SRU (in facilities with more than one SRU).
- For short term sulfur or ammonia processing increases due to a shift in crude slate or increase in overall crude throughput.
- For long term overall refinery capacity increases.

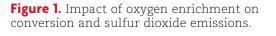
The 'insurance policy' approach is used when one of multiple SRUs in a refinery unexpectedly goes off line, causing the refinery to reduce rates. Should SRU capacity need to be increased quickly, an oxygen based system can turn on automatically to boost the flow rates of the remaining SRUs in operation. Consequently, flowrate reduction in the refinery is less significant. While oxygen runs only a few days a year, the cost of keeping the oxygen system operational is easily paid for by the added refinery capacity during an SRU upset.

For short term increases, SRU oxygen enrichment gives refiners the flexibility to run opportunity crudes that are high in several impurities, such as sulfur or nitrogen. This approach also enables the refinery to ramp up to higher rates when its products are most profitable or when inventory increases are requested.

For long term increases, the use of oxygen is an ideal alternative because it enables refiners to avoid capital investment. The oxygen based technology is established, and capacity increases can easily be handled through low, mid, or high level enrichment. The concept is simple; replacing the nitrogen in air with more oxygen not only increases the ability to process sulfur, but also decreases total flow through the SRU, which eliminates velocity issues.

Table 1. SRU oxygen enrichment economics (based on 100 tpd sulfur plant)				
Case	Low level	Mid level	High level	
New S capacity (tpd)	130	175	250	
O ₂ required (tpd)	35	80	160	
Total CAPEX (US\$ million)	0.2 - 0.4	1.0 - 1.5	1.5 - 3.0	





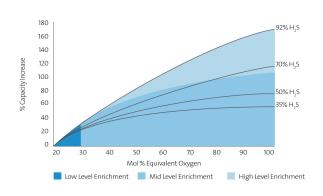


Figure 2. SRU capacity increase with oxygen enrichment.

Advantages of SRU oxygen enrichment

Incorporating oxygen enrichment into a normal operating plan builds upon the already known and understood benefits of the process change. These benefits and how they influence the operating plan are highlighted below.

Capacity increase

The most common driver for implementing SRU oxygen enrichment is to increase processing capacity. When an SRU is bottlenecked by hydraulic or residence time limitations, oxygen enrichment of the combustion air reduces the nitrogen flow through the SRU. This allows an increase in the acid gas and sour water stripper gas streams while staying within the existing pressure drop and/or residence time constraints.

Capital cost savings

There is no reason to incur a capital penalty associated with building an oversized SRU that is fully utilised just a few times a year. As the oxygen is often a variable cost with a relatively small fixed component, there is no financial penalty for operating below the maximum capacity. Depending on the enrichment technology, the cost of implementing SRU oxygen enrichment is only 5 - 25% of the cost to build a new SRU. Table 1 shows typical costs for SRU oxygen enrichment. Oxygen enrichment can also be economical for grassroots plants due to smaller equipment for the same capacity.

Quick implementation

SRU oxygen enrichment can be implemented quickly. No downtime is required for low level enrichment (up to 28% oxygen in air), as an oxygen diffuser can be hot tapped into the air main. For higher levels of oxygen enrichment, tie ins and modifications can be achieved within the timing of a normal turnaround.

Improved conversion and reduced emissions

The reduction of diluent nitrogen results in higher concentration of H_2S and SO_2 in the process stream, which leads to higher conversions in the SRU. In addition, the reduction in nitrogen entering the tail gas cleanup unit (TGCU) results in higher H_2S partial pressures in the amine absorber, which in turn results in better absorption and lower sulfur emissions. Figure 2 is a set of normalised commercial data that demonstrates the impact of oxygen enrichment on conversion and sulfur emissions, comparing an oxygen based operation with the projected air based case.

Hotter flame and better ammonia destruction

SRU oxygen enrichment results in higher reaction furnace (RF) temperatures, contributing to more complete destruction of ammonia and heavy hydrocarbons (BTX) in the RF. Incomplete destruction of ammonia due to RF temperatures lower than 2200 - 2300 °F can result in the formation of ammonium salts that could cause plugging and increased pressure drop in the cooler sections of the SRU. Furthermore, higher flame temperatures with oxygen enrichment can often eliminate the need for 'split flow' operation, where some of the acid gas is diverted to the rear of the RF to achieve higher temperatures.

Compact footprint

The space required to implement SRU oxygen enrichment is negligible when compared with the space needed for a new SRU. At refineries limited by available space near their amine unit, oxygen enrichment may turn out to be the only practical and economical solution. The oxygen storage or onsite generation plant can be conveniently sited where space is available, even at a considerable distance from the existing SRUs.

SRU oxygen enrichment theory

In the Claus process, one third of the H_2S is combusted with oxygen to produce SO_2 , which is then further reacted with the remaining H_2S to form elemental sulfur and water. For a typical refinery acid gas stream, 60 - 70% of the conversion to sulfur is achieved in the RF at temperatures typically between

Table 2. Choosing the right oxygen supply mode				
Supply features	Liquid oxygen	Onsite generation	Pipeline	
Flow range (tpd)	0 - 50	50 - 300+	100+	
Commitment	Low	High	Medium	
Time to implement (months)	1 - 2	10 - 18	6 - 8	
Location limitations	Yes	No	Yes	
Application best fit				
Flow	Low	Medium/high	High	
Use pattern	Variable	Steady	Variable/steady	

2100 - 2600 °F. The remaining equilibrium conversion of H₂S to sulfur takes place in a series of catalytic reactors at much lower temperatures. Representative reactions are summarised below:

Oxygen enrichment reduces the nitrogen content in the combustion air stream. This allows more acid gas to be processed while maintaining a constant total flowrate to the RF and lowering the flowrate downstream, thus providing dramatically higher throughputs within the hydraulic limits of the SRU. This is the underlying principle for the effectiveness of oxygen enrichment as a debottlenecking solution in the refining, chemical, and other process industries.

Oxygen enrichment technologies

Figure 2 illustrates the expected capacity increase for various acid gas stream concentrations and enrichment levels. The range of oxygen concentration can vary between 21 - 100%, and different technologies are required at various oxygen enrichment levels. Overlaid on Figure 2 are the three proven SRU oxygen enrichment technologies offered by Air Products and Goar, Allison & Associates (GAA).

Low level oxygen enrichment technology (LLE)

Oxygen is injected into the combustion air main through a custom designed diffuser, which provides good mixing and oxygen safety. Considerations related to oxygen compatibility and cleanliness of the air main and other components usually limit this technology to enrichment levels of approximately 28%. As this technology requires minimum capital investment and process modification, it is the easiest to implement and typically offers an incremental SRU capacity increase of 10 - 30%. This is the most common means of oxygen enrichment for creating operating flexibility.

Mid level oxygen enrichment technology

The Claus oxygen based process enhancement (COPE®1) process is an SRU oxygen enrichment technology jointly developed by Air Products and GAA. Oxygen enrichment levels exceeding 28% require the use of a special burner with discrete oxygen port(s) to safely handle oxygen. The air and oxygen are not premixed as in the LLE technology because of material compatibility concerns. The COPE burner can safely handle the incoming gas streams and has large turndown, high intensity mixing, and excellent ammonia destruction capability. COPE Phase I allows capacity increase of up to 70% at oxygen enrichment levels of up to 40 - 45% for typical refinery acid gas streams. The upper limit of this technology is set by the temperature limitations of the furnace refractory.

High level oxygen enrichment technology

Oxygen enrichment levels higher than 40 - 45% may cause the RF temperature to exceed the refractory temperature limit. COPE Phase II is a patented temperature moderation technology developed to allow even greater capacity increase beyond that achievable from mid level enrichment. This technology can be deployed at oxygen enrichment levels up to 100%, more than doubling the capacity of an existing SRU. COPE technology is most frequently used when long term capacity expansion is required. It provides an excellent low cost solution to a large increase in SRU capacity.

$H_2S + 1.5 O_2 \longrightarrow$ (Combustion)	$SO_2 + H_2O$
$2 H_2S + SO_2$ (Claus reaction)	3 S + 2 H ₂ O
$3 H_2S + 1.5 O_2 $	3 S + 3 H ₂ O

Implementation

Air Products works closely with refiners to help evaluate the technical and economic merits of oxygen enrichment of the SRU versus other capacity increase options. Once oxygen enrichment has been chosen as the preferred solution, Air Products can provide, on a case specific basis, the necessary equipment, technology, services, and know how for the timely installation and startup of the oxygen based solution:

- Calculating the expected oxygen requirement, using process simulation software and incorporating heat transfer and other limitations.
- Determining the best means of oxygen supply.
- Designing, procuring, and installing the appropriate equipment for the applicable oxygen enrichment technology, along with the oxygen storage and supply system. This includes design and fabrication of a flow control skid with the necessary interlocks for reliable operation and safe startup and shutdown.
- Consulting on oxygen material compatibility and cleaning procedures for piping within the refinery.
- Collaborating on hazard and operability studies (HAZOPs) and operator safety training for oxygen based operations prior to commissioning of oxygen enrichment.
- Assisting with the startup of the oxygen enrichment technology by trained engineers until the system has reached the desired operating rates.
- Ongoing technical support and equipment maintenance.

Oxygen supply alternatives

Oxygen for SRU oxygen enrichment can either be delivered to the refinery or generated onsite. The most common mode of supply for delivered oxygen is via on road liquid oxygen tankers from a central manufacturing facility. The oxygen is stored as a liquid at the refinery in an insulated tank and vaporised at the time of use. This is the most flexible mode of supply. Oxygen can also be generated onsite using cryogenic or adsorption technologies. At locations in the vicinity of an oxygen pipeline, supply via pipeline could be the most cost effective and flexible source of oxygen. Evaluating the optimal mode of supply requires the review of a host of factors, including:

- Size of the oxygen requirement (average and peak demand).
- Expected use pattern (continuous, seasonal, erratic).
- Need for coproduct nitrogen (for inerting, blanketing, etc.) in the refinery.
- Presence of other nearby oxygen consuming applications.
- Power availability and cost.
- Proximity of delivered oxygen source.

Table 2 provides rough guidance about the best mode of supply in the context of these parameters. From the early stages of the project, Air Products works closely with a refinery considering SRU enrichment to jointly determine the best mode of oxygen supply.

Conclusion

With its versatility and proven track record, oxygen enrichment is one of the best ways to optimise refinery onstream capacity and maximise refinery profitability. For many years, oxygen has safely increased throughput at refineries around the world. Now, refiners can further utilise the gas as a means of low cost flexibility. Once an SRU is set to run on oxygen, the refiner can choose to run with it or without it depending on the sulfur load. Transition time required to move to or from oxygen enrichment is minimal, creating the ability to increase rates to an SRU very quickly.

Air Products has positioned itself as a leader in the refining industry in process design, industrial safety, equipment supply, and applications expertise. The company's vast experience in oxygen enrichment allows it to now apply this core technology to traditional process challenges such as raw material variability. Air Products works with refiners to safely and quickly evaluate supply options and install equipment, matching unique gas specific requirements to the refiner's sulfur processing needs.

References

1. COPE is a registered trademark of Goar, Allison & Associates, LLC.

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