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COPE™ with Your Clean Fuels Sulfur

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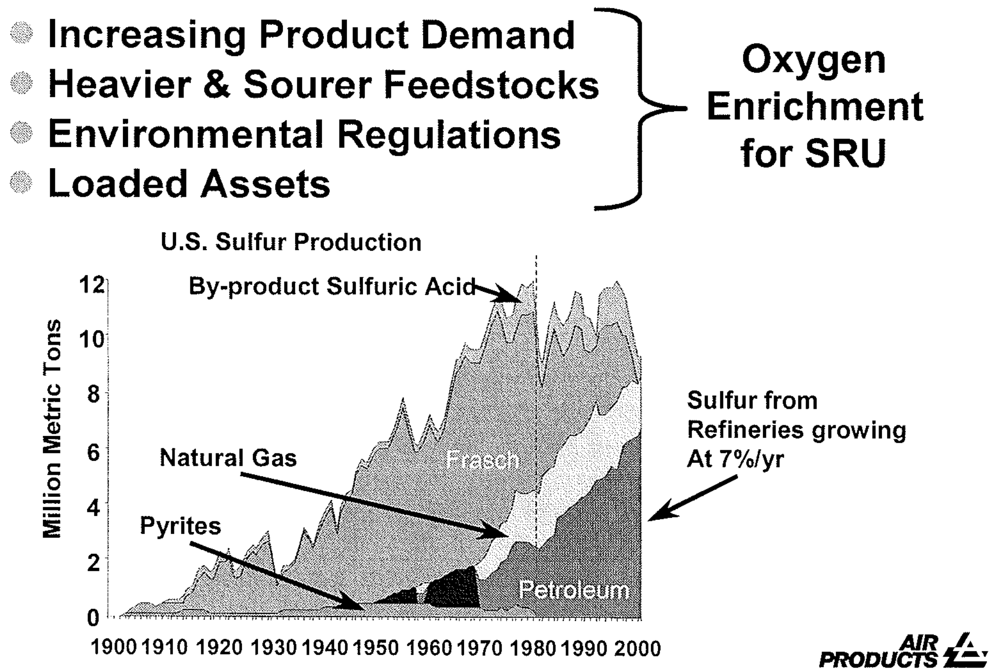
Oxygen Enrichment Fundamentals

Current trends in the characteristics of crude oil supply, petroleum product demand, and tightening environmental regulations require continuous change in the worldwide refining industry. Refiners are confronted with more stringent specifications on motor transportation fuels, greater demand for light transportation fuels, and increasing dependence on heavy, sour crude oil feedstock. Environmental regulations in Europe, North America and Asia all require progressively cleaner motor transportation fuels. Product demand is away from heavy bottom of the barrel products toward light transportation fuels. Simultaneously, an overall lighter product mix must be produced from a heavier crude slate.

These developments have led to reconfiguring refinery processes with greater use of hydroprocessing to upgrade crude oil into light transportation fuels and to improve fuel quality. More hydrotreating and increased processing severity is required for removing sulfur and nitrogen compounds from fuels to meet future environmental regulations. The resulting increase in production of hydrogen sulfide (H_2S) and ammonia (NH_3) has placed new demands on the processing capability of refinery sulfur recovery units (SRU's).

A good example of the challenge can clearly be seen in the graph of US sulfur production (Figure 1). The growth in sulfur from oil refining is particularly noticeable, growing at 7% / year, a rate which is expected to continue. Refiners need to find the most economic way to handle these increases. In many cases, oxygen enrichment has proved to be the best solution to boost SRU capacity.

Figure 1. U.S. Sulfur Production Forecasts for Oil Refineries



Oxygen enrichment of the combustion air to the reaction furnace is a proven means of increasing SRU capacity, and of improving the SRU's ability to handle contaminants. Expanding SRU capacity with oxygen enrichment is gaining acceptance as a proven measure to handle extra acid gas loading at significantly reduced capital expense. Oxygen enrichment is also finding application as the answer to requirements for SRU redundancy and improved sulfur recovery.

The concept of increasing SRU capacity with oxygen enrichment has been of interest for at least thirty years, and has been applied on a commercial scale since 1985 (Refer to COPE Reference Table - Appendix A). The typical SRU reaches its ultimate sulfur production capacity when the maximum allowable front-end pressure prevents further increase in feed rate. Oxygen enrichment reduces the flow of process gases by reducing the quantity of nitrogen that enters with the combustion air. This reduction in process flow rate allows a corresponding increase in SRU acid gas feed rate and subsequent increase in sulfur production. The ultimate objective of utilizing high levels of oxygen enrichment is to increase SRU capacity and to improve feed contaminant destruction.

Commercial application of oxygen enrichment with acid gas feeds rich in H_2S has been limited by the maximum allowable operating temperature of the SRU reaction furnace refractory. Commercially available refractory have demonstrated reliability at process temperatures of up to about 2800 °F (1540 °C). Some companies prefer to conservatively limit process operating temperatures to a range as low as 2500-2600 °F (1370-1430 °C). Of course, the choice of maximum allowable furnace operating temperature has a bearing on the SRU throughput that can be achieved without special temperature moderating techniques.

The COPE Processes can address these refractory limitations. The COPE Phase I Process utilizes the approach of a "shaped" burning technique to achieve a high degree of H_2S dissociation in the flame high temperature zones. If and when necessary, the COPE Phase II Process can be used to introduce a process recycle stream to act as a heat sink for controlling the temperature of combustion products in the reaction furnace.

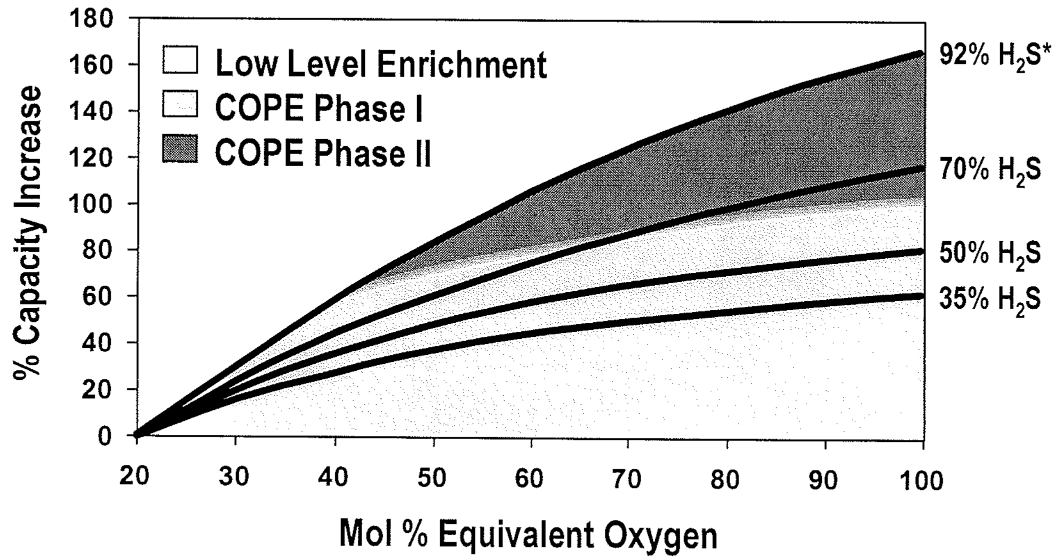
COPE Process – Staged Approach

Figure 2 below illustrates the capacity increases that can be obtained for given acid gas concentrations and varying oxygen enrichment levels. The limitations incorporated in Figure 1 include piping and burner metallurgy and the maximum allowable operating temperature of refractory materials used to line the burner, furnace and WHB inlet tubesheet. If necessary, oxygen enrichment by the COPE Process can be implemented in a staged approach that can be implemented in up to three steps. The three levels of oxygen enrichment are:

1. Low-level enrichment,
2. COPE Phase I, and
3. COPE Phase II utilizing an ejector.

The first step is low-level enrichment (LLE), in which the oxygen is injected through a diffuser directly into the combustion air stream. Due to oxygen handling issues, this method is limited to about 28% oxygen content in the air mixture, and typically yields up to 25% increased sulfur plant capacity.

Figure 2. COPE Capacity Expansions for Claus Sulfur Recovery Units



*Other Amine Acid Gas Components Are:
H_2O 7.0%, C_1 0.5%, C_2 0.5%, CO_2 Balance

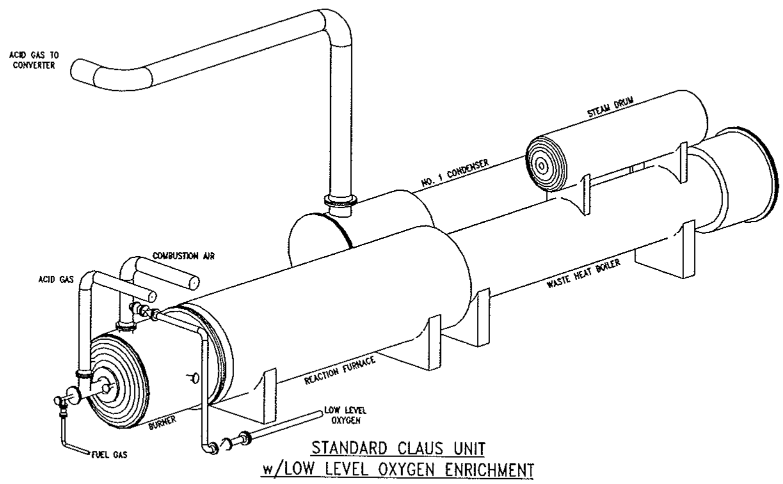
The second step, the COPE Phase I Process, introduces oxygen using the COPE burner and allows enrichment up to the temperature limit of the reaction furnace refractory, usually about 2800^{O}F (1540^{O}C). Enrichment levels of 40-50% oxygen (composition of the combustion "air" if the oxygen and air feeds are theoretically combined) and capacity increases of 60-75% are typical for rich feeds, depending upon the exact feed composition and the specific design of the SRU.

The third step, the COPE Phase II Process, uses a recycle stream to moderate the reaction furnace temperature so that, as more oxygen is added, the temperature does not rise above the limit of the refractory. The recycle is taken from the outlet of the first sulfur condenser. The flow of recycle gas is controlled to maintain the desired temperature in the reaction furnace. A mechanical blower or steam driven ejector is used to provide the necessary head so that the recycle flows back to the burner.

Figure 3 illustrates the staged approach, evolving from low-level enrichment through COPE Phase I to COPE Phase II. With oxygen enrichment there is a large increase in heat duty for the waste heat boiler and No. 1 condenser for large increases in SRU capacity. These equipment items must be checked but are frequently of adequate size. The key feature of the COPE Process is that once a proper burner has been installed, capacity can be increased stepwise with relatively minor plant modifications on an as needed basis. A plant operating on LLE with a proper burner can be expanded to COPE Phase I by replacing the conventional firing assembly with a COPE burner gun; thus permitting oxygen enrichment to the limit of the refractory operating temperature. If necessary, additional capacity can be obtained by expanding to the COPE Phase II

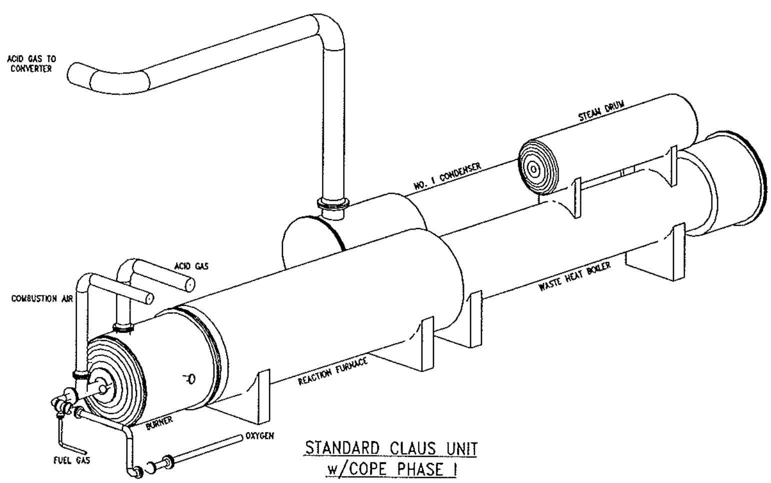
Process, by installing a steam driven ejector with the necessary process recycle piping and instrumentation.

Figure 3. Staged Approach of Oxygen-Enrichment. Incremental steps from Low Level Oxygen-enrichment through to COPE Phase II.



Low Level Oxygen Enrichment:

- Oxygen stream introduced to air stream.
- Limited to 28% oxygen.
- Typically yields 25% capacity increase.



COPE Phase I:

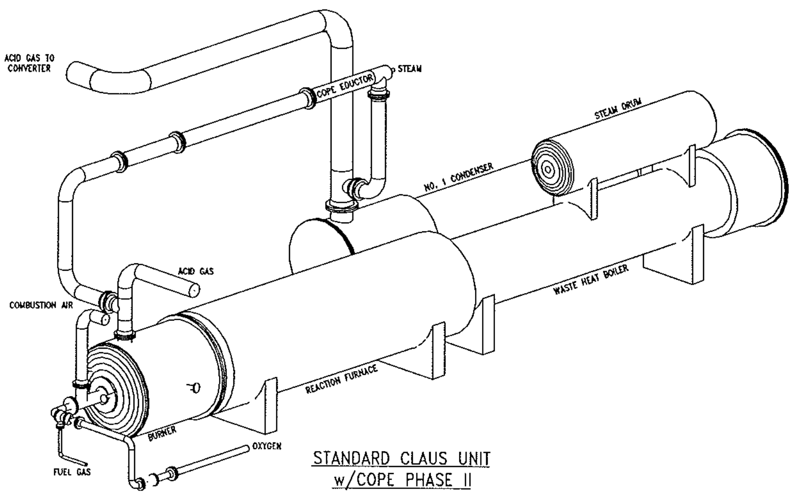
- Oxygen stream introduced to burner.
- Limited by working temperature of the refractory.

Lean Feed

- Enrichment up to 100% oxygen.
- Potentially yields up to 90% capacity increase.

Rich Feed

- Enrichment up to 40 to 50% oxygen.
- Potentially yields up to 60 to 75% capacity increase.



COPE Phase II:

- Recycle stream added to moderate flame temperature to a desired set point; no limitation on oxygen-enrichment regardless of acid gas feed composition.
- Enrichment up to 100% oxygen.
- Potentially yields up to 150% capacity increase.
- Easy upgrade from COPE Phase I.

Process Considerations

Combustion and Enhanced Dissociation in the COPE Burner

The injection of high purity oxygen takes place at the tip of the burner gun directly into the combustion zone. Introducing the oxygen directly into the center of the flame produces a short, localized, high temperature zone that maximizes the dissociation of H_2S into hydrogen and sulfur. Operating experience with the COPE burner has verified that this direct injection of oxygen enhances H_2S and NH_3 dissociation. These highly endothermic reactions provide dual benefits by reducing the flame temperature and also reducing the consumption of oxygen for a fixed amount of acid gas feed.

The destruction of ammonia in a sulfur recovery unit is always of major concern. At the very hot furnace conditions of the COPE Process, ammonia is removed to a negligible concentration, so that the potential for downstream problems are eliminated. The high operating temperature in the furnace also minimizes the formation of soot from hydrocarbons that may be present in the acid gas feed, and destroys any CS_2 that may be formed from the hydrocarbons.

Improved SRU Recovery

One of the unexpected results of oxygen enrichment is that the overall sulfur recovery of the SRU is increased by as much as 0.5%. This happens because removal of nitrogen from the process gas increases the H_2S and SO_2 concentrations in the Claus converters and leads to higher equilibrium conversion. Another consequence of the removal of nitrogen is a greater temperature rise across the Claus converters. Since the converters are usually designed for a particular outlet temperature, the inlet temperature can be reduced. This decreases the amount of energy required to reheat the gas to each converter.

Effects on Tail Gas Cleanup Unit and Incinerator

The SRU tail gas flow to the TGCU when operating the COPE Process is equal to or less than the flow with air-only operation. Operation of the hydrogenation portion of the TGCU is relatively unchanged. This is not true of the quench section, where the condensing load on the quench tower and cooler increases more or less in direct proportion to the increase in sulfur throughput. Usually this section will have to be debottlenecked if the increase in SRU capacity is more than a modest amount. After the quench section, where the water formed in the Claus reaction is condensed and removed, the flow of tail gas is greatly reduced compared to air-based operation. The amine absorber will have a lower feed gas flow and a higher partial pressure of H_2S, resulting in a lower quantity of H_2S in the absorber vent gas. Thus, there is less incineration fuel consumed, reducing operating cost as well as CO_2 emissions.

COPE Ejector – Mechanical and Operating Benefits

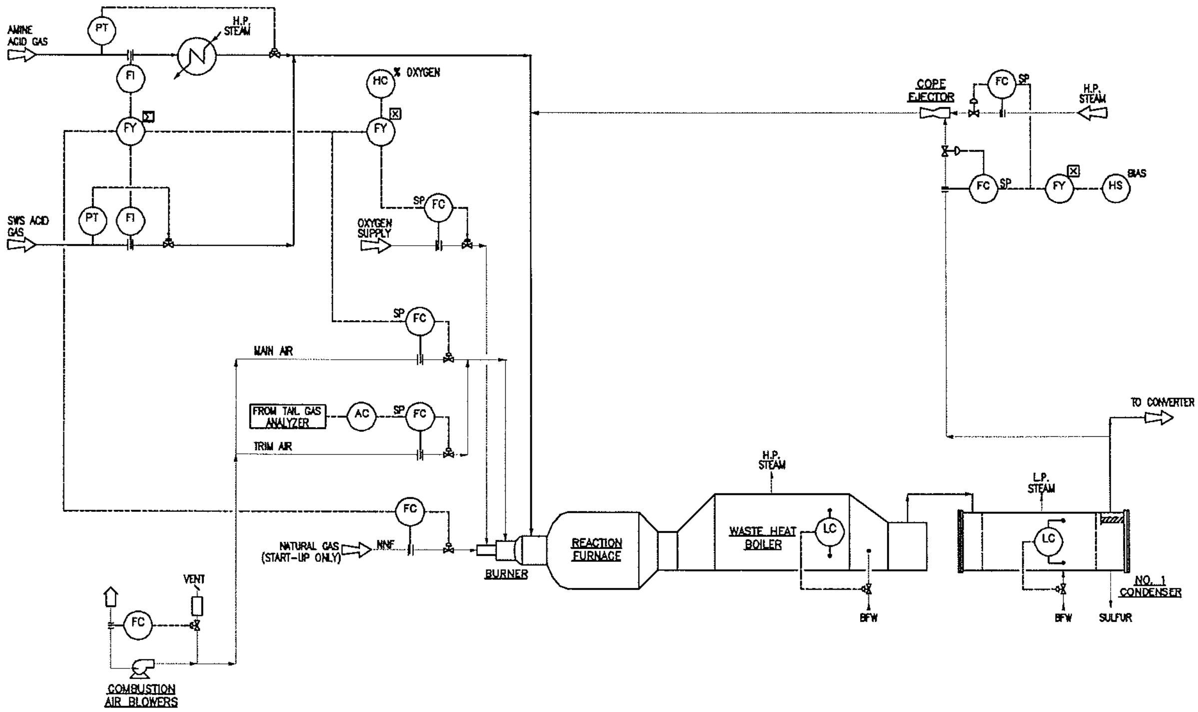
Physical Layout

The ejector is located at an elevation above the first condenser and reaction furnace to allow all the ejector piping to be self-draining. It is also very easy to install a spare ejector if desired.

Simple Process Control

The key process control feature is that the total flow of all feed components is fed to one burner location. There are no manifolds or split flows of the feed stream components - this includes the acid gases (amine and sour water), combustion air (if any), pure oxygen, fuel gas (when necessary) and recycle gas (when necessary). All SRU feed streams are fed to only one burner that generates only one flame. Furthermore, the air/oxygen control scheme is independent and decoupled from the flame moderation recycle stream (Refer to Figure 4).

Figure 4. COPE Phase II – Process Control



The recycle is a simple, but powerful tool for independently controlling the furnace temperature to a desired setpoint. The recycle is utilized only as necessary for the required flame moderation and additional operating flexibility. During upset or abnormal operation, the availability of the on-line recycle can be beneficial for maintaining a high on-stream factor by protecting the reaction furnace and waste heat boiler from temperature excursions. The mechanical features of the ejector and the associated steam jacketed piping system allow for on/off or continuous operation on demand.

The key feature is the simplicity of the process scheme, the associated control loops and thus, the ability for operating personnel to ensure a safe, reliable and optimized operation.

Safe start-ups and shutdowns

Start-ups and shutdowns of SRUs, whether scheduled or unscheduled, often present the most hazard to both personnel and equipment. Fuel gas firing the main burner is frequently the most difficult step due to concerns with high flame temperature and turndown operation that may result in oxygen-breakthrough or soot formation due to metering difficulties and/or burner limitations. Traditionally nitrogen or steam is used for the fuel gas flame temperature moderation. The steam driven ejector stream has proven to provide several benefits for start-ups and shutdowns that include:

- The recycle stream is indigenous to the process that includes permanent process piping, pressure and flow measurement and control valves. This minimizes the risk associated with introducing a moderating stream, such as steam or nitrogen, which is used on an irregular basis.
- High volumes of recycle gas can be utilized thus allowing the main burner to operate closer to design conditions. This ensures better mixing in the burner and thus reduces the risk of oxygen breakthrough or soot formation often associated with turndown fuel gas fired operation.
- The mechanical features of the ejector and the associated steam jacketed piping system allow for on/off or continuous operation on demand. This would include full availability for fuel gas fired temperature moderation for unscheduled shutdowns.

Reliability

The ejector can utilize the high pressure steam that is generated within the Claus Plant. At full design loads the ejector requires only approximately 5 to 10% of the total of the steam that is generated in the WHB. Thus, the ejector scheme can be supported by the SRU plant and does not require electricity as an external utility. This self-supporting feature along with the simplicity of the ejector system results in high on-stream factors. The small space requirement, simplicity of installation, and low capital cost make fully or partially spared configurations an attractive option to further enhance ejector reliability.

Summary

The growth in sulfur from oil refining is growing at rapid rate. Refiners need to find the most economic way to handle these increases and in many cases, oxygen enrichment has proved to be the best solution to boost SRU capacity.

The COPE Process is an oxygen-enrichment technology that has been successfully applied to SRU's in replacing air with up to 100% oxygen. The COPE Process was first implemented in 1985 when it was installed by Conoco, Inc. on two existing Claus SRUs at their refinery located in Lake Charles, Louisiana.

For high levels of oxygen-enrichment, the COPE Ejector Process offers several advantages. The key features of the process include:

- Proven technology with demonstrated operation of high level of oxygen-enrichment in 21 COPE trains with over 210 train years of operating success;
- Simple process equipment layout and straightforward process control;
- High level of reliability and flexibility. The COPE Ejector process provides the benefit of on-line recycling for normal high level oxygen-enrichment

operation, but also for irregular operations such as start-ups, shutdowns and feed disturbance rejection;

- Complete self-draining system requiring minimal plot space;
- Increasing sulfur production by the COPE Process can be implemented in a cost-effective staged approach that can be implemented in up to three steps.