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COPE™ Ejector— Reliable High Level Oxygen Enrichment Technology

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Abstract

The COPE™ Process was first developed and commercially introduced in 1985 to permit increasing the capacity of Claus Sulfur Recovery Units (SRUs) by utilizing oxygen instead of air in the main reaction furnace burner. There are 21 COPE Process units in operation with over 180 train years of operating success. The patented COPE Ejector Process was introduced in 1998. There are two units in operation and two other units in the design and construction phase. The first unit was commissioned and has operated successfully since July 2000.

Historically, the COPE Phase II Process has successfully demonstrated the use of a blower to sustain recycle stream flow. The most recent innovation uses a steam driven ejector for recycling the process gas.

The COPE Ejector Process has proven to provide significant mechanical advantages and beneficial results on critical aspects of the overall process chemistry. These advantages have translated into high capacity and process reliability in a robust process with both capital expenditure and operating cost advantages. Furthermore, the ejector driven recycle stream has improved operations for irregular operating situations such as SRU start-ups, shutdowns and feed disturbance rejection.

The three years of process operating data at the Conoco Lake Charles Refinery supports the expected mechanical and cost benefits and has proven justification for retrofitting the COPE ejector process to the second train at the refinery.

Oxygen Enrichment Fundamentals

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 process flow rate 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.

For rich H₂S acid gas feeds, commercial application of oxygen enrichment has been limited by the maximum allowable operating temperature of the SRU reaction furnace refractory. Commercially available refractories 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 H₂S 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.

Historically, the COPE Phase II Process has successfully demonstrated the use of a blower to sustain recycle stream flow. The most recent innovation uses a steam driven ejector for recycling the process gas. The recycle gas and motive steam are utilized to maintain the furnace flame temperature within the limitations of the refractory material while satisfying the primary objective of increasing the SRU capacity.

THE COPE PROCESS

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 Conoco, Inc. installed it on two existing Claus SRUs at their refinery located in Lake Charles, Louisiana. The Conoco Refinery at Lake Charles also was the first to install a recycle ejector. It was initially installed in parallel with the recycle blower in one SRU train. The ejector was first started up in July 2000 and has performed very well. Due to the demonstrated success, the second train was commissioned and has operated successfully since December 2002.

There have been continuing developments and improvements in the COPE Process. Some of the developments include improved calculation methods for the reaction furnace temperature. The refinement is an empirical adjustment using operating data from the over 180 train years of operation. Also, the COPE Burner has been very reliable and durable. The original burners, including Conoco Lake Charles, are still in service on all COPE units. However, there have been several refinements to the burner that have further improved the reliability of the burner and reduce the burner cost. More recent COPE Phase II developments include experimental study by Alberta Sulphur Research Ltd. (ASRL) to quantify the beneficial results on critical aspects of the overall process chemistry. The Claus furnace chemistry is complex but ASRL has made significant progress in increasing the understanding of this chemistry.

The COPE Process uses a proprietary burner design in which oxygen is brought into the combustion chamber separately from the air and other gas streams. This allows for the safe and effective processing of a combination of separate feed streams, as they may be required. These include the combination of air, pure oxygen, acid gases, start-up fuel gas, TGTU recycle gas and when necessary, COPE recycle gas. The key 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.

Pure oxygen is injected at the tip of the burner gun directly into the combustion zone. The oxygen is injected separately into the center of the flame producing a short, localized, high

temperature zone that maximizes the dissociation of H₂S into hydrogen and sulfur. This highly endothermic cracking reaction reduces both the oxygen-enriched flame temperature and oxygen consumption.

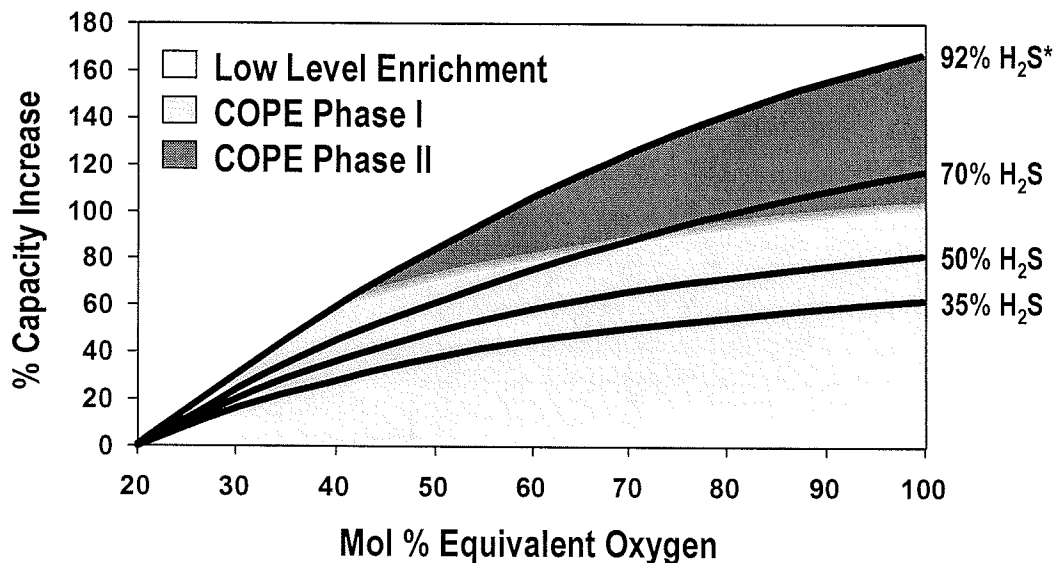
COPE Process – Staged Approach

Figure 1 below illustrates the capacity increases that can be obtained for given acid gas concentrations and varying oxygen enrichment levels. 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 1. COPE™ Capacity Expansions
for Claus Sulfur Recovery Units**



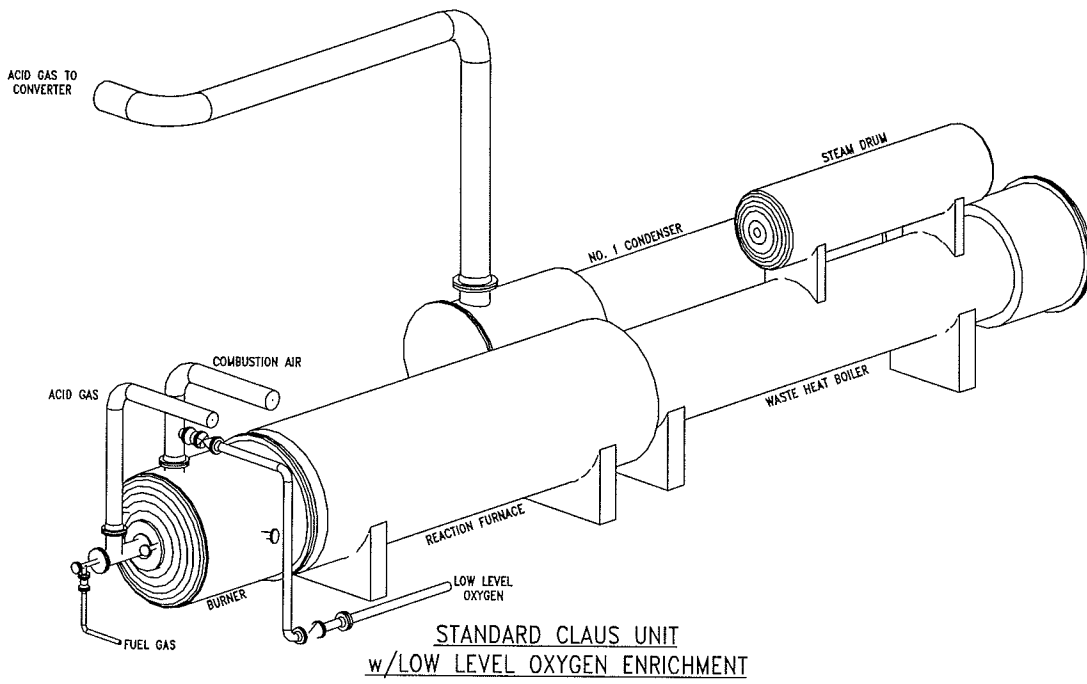
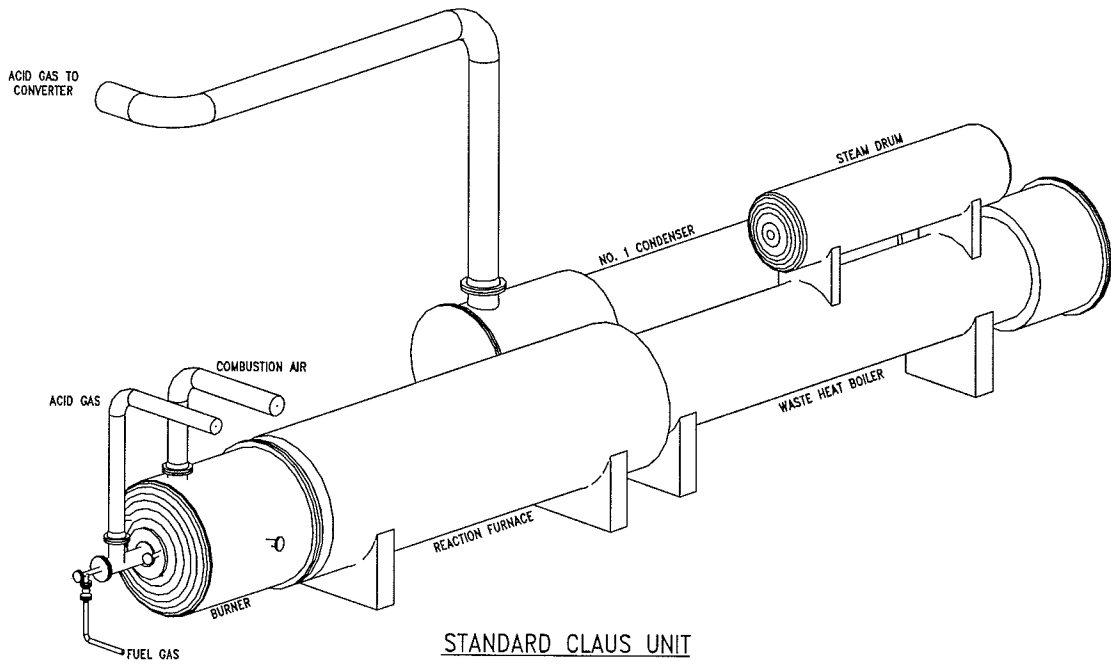
*Other Amine Acid Gas Components Are:
H₂O 7.0%, C₁ 0.5%, C₂ 0.5%, CO₂ Balance

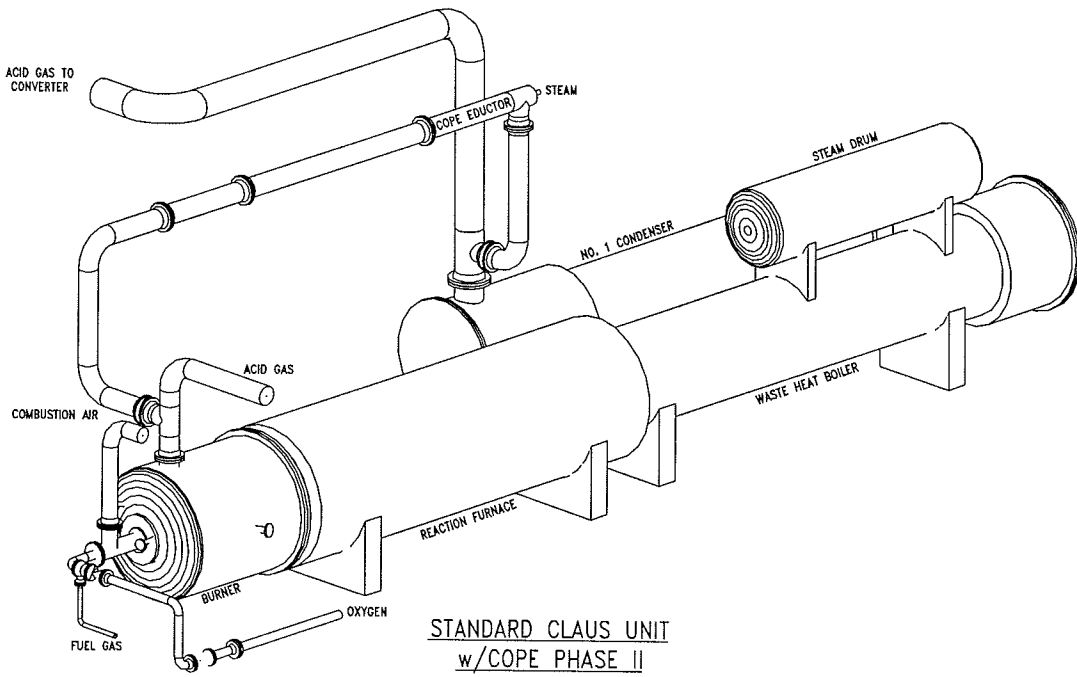
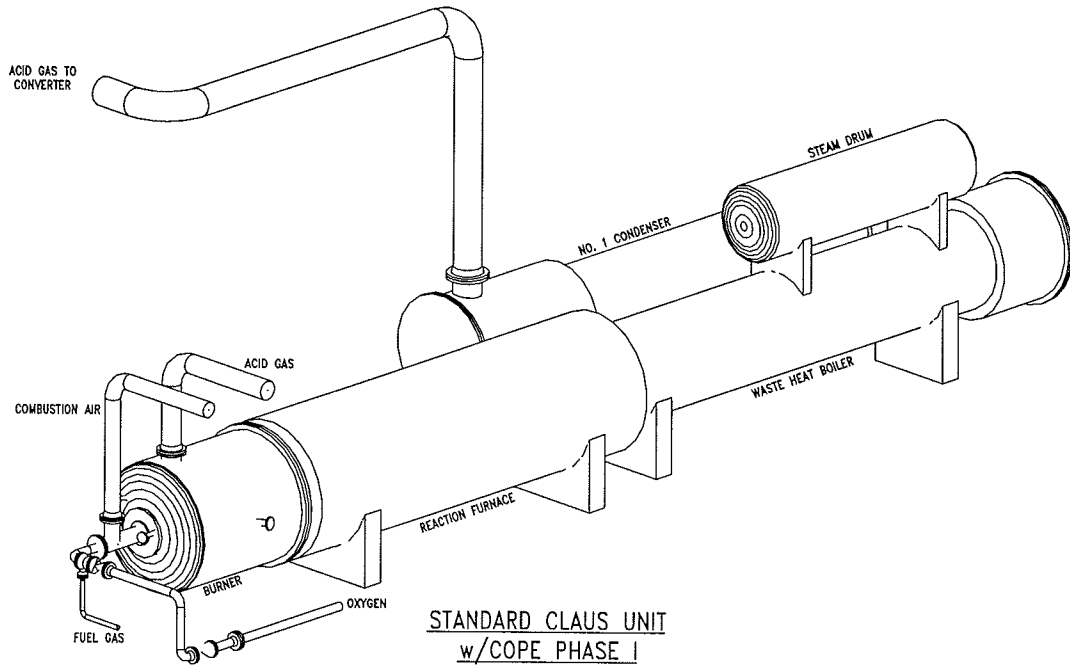
The second step, the COPE Phase I Process, introduces oxygen using the COPE burner and allows enrichment up to the temperature limit of the reaction furnace refractory, usually about 2800°F (1540°C). Enrichment levels of 40-50% oxygen (composition of the combustion "air" if the oxygen and air feeds are 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 2 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 (Table I). 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. Refer to Table II for the typical capacity increase and respective revamp costs for this staged approach.

Figure 2. Staged Approach of Oxygen-Enrichment. Standard Claus Unit through to COPE Phase II.





**Table I. COPE Process Retrofits ⁽¹⁾.
Required Equipment Replacements.**

Retrofit Type:	COPE Phase I	COPE Phase II
Units in Operation/Design	15	8
Furnaces	1	2

Waste Heat Boilers	4	2
Steam Drum (only)	3	0
No.1 Sulfur Condenser	0	2

Note 1. Of the 23 COPE Process units in operation/design, 20 are retrofits.

Table II. COPE Staged Installation. Capacity Increase and Costs			
Basis: 100 tpd Sulfur Plant			
Case	Low level	COPE Phase I	COPE Phase II
New S capacity, tpd	130	175	250
O ₂ Required, t/d	35	80	160
Total Capex, \$MM	0.2-0.4	1.0-1.5 (note 1)	1.5-2.5 (note 2)

Notes:

1. Installed cost includes new burner (if required), new oxygen piping and controls, increased size of acid gas piping and controls, additional TGTU quench system cooling (if applicable), engineering and license fee.
2. Installed cost includes items of Note 1 plus new WHB or No.1 Condenser (if required), burner modifications, ejector, ejector piping and controls, additional TGTU quench system cooling (if applicable), engineering and license fee.

COPE Ejector

The COPE Process was first implemented in 1985 when it was retrofitted by Conoco, Inc. on two existing Claus SRUs at their refinery located in Lake Charles, Louisiana. Using an oxygen-enrichment level of 55-65%, the capacity of each SRU was increased from air-based 108 LTPD to more than 200 LTPD. The patented COPE Ejector Process was introduced in 1998. The first unit was commissioned at one of the Conoco Lake Charles SRUs and has operated successfully since July 2000. Due to the demonstrated mechanical benefits, capital cost and operating cost benefits, Conoco commissioned the second train in December 2002.

COPE Ejector – Mechanical and Operating Benefits

Physical Layout

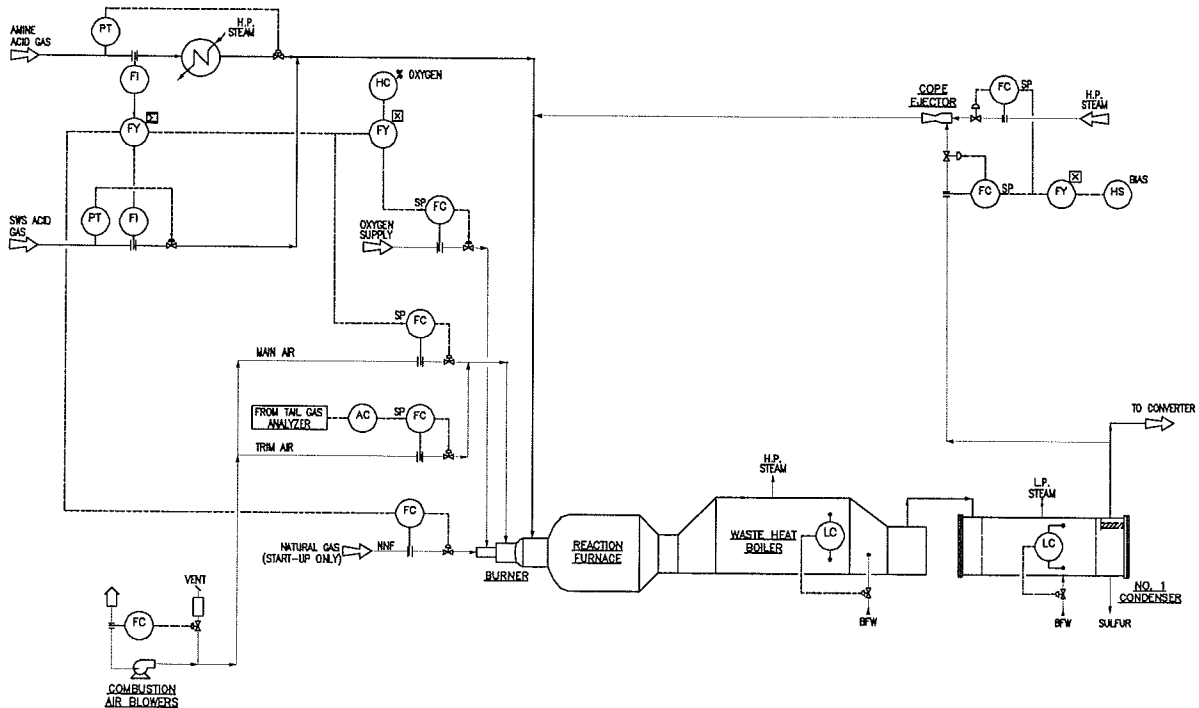
The recycle blowers at Conoco Lake Charles have worked well, but the ejector option offered reliability and operating cost benefits. The Conoco Refinery installed the first recycle ejector in parallel with the recycle blower in one train. The ejector first started up in July 2000 and has performed very well. The recycle blower is being dismantled, and an ejector is being installed on the second SRU.

The principal advantages of the steam ejector over the recycle blower are reduced capital cost, reduced operating cost, less plot requirement, and elimination of rotating equipment (the blower). 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 3).

Figure 3. COPE Phase II – Process Control



As illustrated, the COPE Ejector air/oxygen demand control scheme can use a typical SRU process control which is based on a combination of feedforward main air/oxygen ratio control and feedback trim air control. In this scheme all of the oxygen consuming feed streams (amine acid gas, sour water stripper acid gas, fuel gas) flow rates are measured and a factor is applied to provide approximately 90-95% of the total main air flow. The remaining 5-10% of the air flow is provided by the trim air loop that is controlled by the tail gas analyzer. Process schemes and variations of this type are common and effective for addressing feed flow and compositional disturbances. In this scheme the resulting furnace flame temperature depends only upon the feed stream composition and oxygen concentration, and therefore is not a degree of freedom.

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 process requirements allows for the simplicity of individual single loop process control or, if desired, the control system can easily be adapted to sophisticated advanced control schemes. The level of technical support usually dictates the level of control scheme sophistication. 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 Conoco Lake Charles 250 psig steam is generated in the WHB, but Conoco has chosen to utilize imported 350 psig steam as the motive steam for the ejector. At full design loads the ejector requires only 2280 lbs/hr of steam, this represents 7.9% 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.

Reduced Operating Costs

The savings in ejector operating costs are realized due to the mechanical design features and utility requirements.

The ejector has no moving parts. The material of construction is stainless steel, which is more resistant to erosion and corrosion than carbon steel. Relative to the maintenance cost of sustaining the blower, this has ejector operation has resulted in an annual savings in operating cost of \$50,000.

The efficiency of the ejector relative to the blower also reduces the power requirement and consequently reduces energy consumption. The power consumption of the blower indirectly

leads to CO₂ emissions. At this time this reduction in CO₂ may not have quantifiable benefits but it is anticipated that more stringent environmental regulations will make this an attractive feature.

The key process operating data and measured benefits of the Conoco Lake Charles SRUs are summarized in Table III.

Table III. Summary of Operating Data at Conoco Lake Charles		
Item	Data	Comment
Sulphur Capacity (LTPD)- maximum:		
Air-based	108	· original nameplate.
Oxygen-enriched	200	· demonstrated w/ blower and ejector units.
Sulphur Recovery (%)- calculated		
Recycle blower	97.6	
Recycle ejector	97.2	
Oxygen Levels (% O ₂)		
	21-70	· oxygen utilized as necessary and dictated by SRU load.
Tail Gas Flow (lbmol/hr)		
Recycle blower	880	
Recycle ejector	950	· 8% higher
Water content in tail gas (gpm)		
Recycle blower	23	
Recycle ejector	26	· 13% higher
HP PSIG Steam (lbs/hr):		
WHB Generated	28780	
Ejector use	2280	· 7.9% of total available HP steam.
Blower		
Design motor size (bhp)	109	
Ejector On-line factor		
	100	· on/off operating feature allows ejector to be utilized as necessary on demand.

Summary

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. The Conoco Refinery was the first to install a recycle ejector. It was initially installed on one train in parallel with the recycle blower. The ejector first started up in July 200 and has performed very well. Due to the demonstrated mechanical benefits, capital cost and operating cost benefits, Conoco commissioned the second train using the ejector in December 2002.

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 180 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.

Appendix A: Licensed COPE™ Process Units

Client	SRU Train	Location	Project Type	Air based Capacity, LTPD	COPE Capacity, LTPD	Start-up Date
COPE[□] Units in Operation						
Conoco Inc.	2	Lake Charles, LA	Phase II Revamp	108	190	March 1985
Conoco Inc.	1	Lake Charles, LA	Phase II Revamp	108	190	May 1985
CITGO (Champlin Refining Co.)	A	Corpus Christi, TX	Phase I Revamp	70	87	April 1986
CITGO (Champlin Refining Co.)	B	Corpus Christi, TX	Phase I Revamp	70	87	June 1986
Valero Energy Co. (Champlin)	1	Wilmington, CA	Phase I Revamp	58	90	Dec. 1987
Valero Energy Co. (Champlin)	2	Wilmington, CA	Phase I Revamp	58	90	Jan. 1988
Valero Energy Co. (TOTAL)	1	Ardmore, OK	Phase I Revamp	60	85	June 1994
Premcor Refining Group (Chevron USA)	A	Port Arthur, TX	Phase I Revamp	100	160	Nov. 1994
Premcor Refining Group (Chevron USA)	B	Port Arthur, TX	Phase I Revamp	100	160	Nov. 1994
Wabash River Energy (Dow/Destec)	1	Terre Haute, IN Coal Gas Facility	Phase I New Plant	---	120	Aug. 1995
Valero Energy Co. (Ultramar)	1	Wilmington, CA	Phase II Revamp	58	150	Sept. 1995
Valero Energy Co. (Ultramar)	2	Wilmington, CA	Phase II Revamp	58	150	Oct. 1995
Valero Energy Co. (Phibro Energy)	A	Texas City, TX	Phase I Revamp	206	330	May 1996
Valero Energy Co. (Phibro Energy)	B	Texas City, TX	Phase I Revamp	206	330	July 1996
Excel Paralubes, Inc. (Conoco/Pennzoil joint venture)	A	Lake Charles, LA	Phase II New Plant	90	180	Oct. 1996
Excel Paralubes, Inc. (Conoco/Pennzoil joint venture)	B	Lake Charles, LA	Phase II New Plant	90	180	Jan. 1997
ExxonMobil Mary Ann Gas Plant	--	Coden, AL	Phase I Revamp	280	470	June 1997
Chevron Canada	--	Burnaby, BC	Phase I Revamp	12	20	Mar. 1998
ExxonMobil (Pacific Offshore Pipeline Co.)	--	Goleta, CA	Phase I Revamp	30	60	April 1998
COPE™ Units in Engineering and Construction						
Conoco Limited	1	Grimsby, UK	Phase I Revamp	60	118	Oct. 2002
Conoco Limited	2	Grimsby, UK	Phase I Revamp	78	118	Oct. 2002
Motiva Enterprises	4	Convent, LA	Phase I Revamp	145	230	Mid 2003

Total COPE™ Trains 20
 Total Train-Operating Years > 160

NOTE: If a plant has been sold or changed names, the current owner/name is shown with the original licensee shown in parentheses.