GOAR, ALLISON & ASSOCIATES, INC.

The COPE™ Process— Continued Development of a Proven Technology

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Abstract

The COPE™ Process was developed to permit increasing the capacity of Claus Sulfur Recovery Units (SRU's) by utilizing oxygen instead of air in the main reaction furnace burner. The COPE Process was commercially introduced in 1985. There are currently 17 trains in operation which have a combined operating time in excess of 100 train-years. The COPE Process is a time proven technology that has been applied to a wide range of acid gas feeds and oxygen enrichment levels in refining, gas plant and coal gasification applications.

Of the 17 trains in operation, 11 trains are COPE Phase I units, which do not use recycle for moderating the flame temperature in the furnace. The remaining 6 trains are COPE Phase II units, which moderate flame temperature by using a motor driven blower to recycle an indigenous process stream back to the burner.

Application of the COPE Process in many varied situations has provided valuable experience in determining practical increases in Claus sulfur plant capacity, and has led to improvements in the COPE Process. The most recent innovation uses an ejector in place of a blower for sustaining recycle flow in the COPE Phase II system. Goar, Allison & Associate and Air Products & Chemicals, Inc. have filed for a patent on this new variation of the COPE Process. The ejector method of recycle offers several process, mechanical and economic advantages.

Fundamentals

The concept of increasing SRU capacity with oxygen enrichment has been of interest for at least twenty-five years, and has been applied on a commercial scale since 1985. The typical SRU reaches its ultimate capacity when maximum allowable front-end pressure prevents further increase in feed rate. The front-end pressure of an SRU is usually limited by either process seal leg depth, combustion air blower discharge pressure or the operating pressure of an upstream amine unit regenerator. Oxygen enrichment reduces 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 feed rate.

Technically, commercial application of oxygen enrichment has been limited by one major obstacle - the maximum allowable operating temperature of the SRU reaction furnace and inlet to the waste heat boiler. Commercially available refractories have demonstrated reliability at process temperatures of up to about 2800°F. However, traditional combustion chemistry indicates oxygen enrichment will exceed this temperature, in some cases at enrichment levels as low as 30 % oxygen in equivalent combustion air.

This problem has been addressed with various processing techniques to reduce furnace operating temperature. Innovations known to the authors include three different approaches: 1) "shaped" burning to achieve a high degree of H_2S dissociation in high temperature zone(s) within the overall combustion chamber, 2) recycle of an indigenous process steam to reduce temperature through dilution, and 3) staged combustion with intermediate cooling to limit maximum temperature by distributing the heat release. Furthermore, the increase in furnace temperature is to some degree self moderating, since higher temperature increases H_2S dissociation, which is an endothermic reaction. COPE Phase I relies exclusively on above item 1 for moderation of flame temperature. COPE Phase II depends on both items 1 and 2 to achieve high level oxygen enrichment, without exceeding the temperature limitations of commercially available refractories.

Background

The COPE Process is an oxygen-enrichment technology which has been successfully applied to SRU's in replacing air with up to 100% oxygen. The main feature of the COPE Process is the proprietary LD Duiker COPE® Burner. The specially designed COPE Burner allows for the safe and effective processing of separate feed streams: air, pure oxygen, acid gases, startup fuel gas and when necessary, recycle gas. The COPE Burner is a high intensity, swirl vane burner that includes a small combustion chamber designed to produce a short highly turbulent flame. The swirling combustion air is injected at right angles into the high velocity swirling mixed acid gases. The multiple vortices created by expanding gases from the burner nozzle produce high intensity burning and rapid mixing to utilize the full volume of the furnace for the desired reactions to destroy ammonia, consume hydrocarbons and form sulfur. Also, this eliminates nonuniform heating and hot spots in the burner/furnace area.

Pure oxygen is injected at the tip of the burner gun directly into the combustion zone. The oxygen injected separately into the center of the flame produces a short, localized, high temperature zone which maximizes the dissociation of H_2S into hydrogen and sulfur. As verified through the substantial operating experience with the COPE Burner, this direct injection of oxygen produces benefits of enhanced H_2S, and NH_3 dissociation and hydrocarbon cracking. These highly endothermic cracking reactions reduce both the oxygen-enriched flame temperature and oxygen consumption.

In addition to achieving significant increases in sulfur processing capacity, the oxygen-enriched COPE Process achieves much better destruction of ammonia and hydrocarbon impurities which are often present in SRU acid gas feeds. The overall sulfur recovery for oxygen-enriched operation typically increases by 0.5-1.0%. Even at greatly increased SRU capacity, the existing downstream tail gas cleanup units can process the SRU tail gas with little modification. The SRU tail gas flow rate relative to acid gas feed rate is progressively reduced as the level of oxygen enrichment is increased.

The COPE Phase I Process (Figure 1) utilizes oxygen enrichment to increase sulfur processing capacity up to the reaction furnace refractory temperature limit, typically 2700 to 2800°F. For rich acid gas feeds and those SRU's processing sour water stripper gas, capacity increases of 50% or more are typical. For lean acid gas feeds, increases of up to 100% may be possible. In many cases the only major equipment required for implementation of the COPE Phase I Process is the proprietary COPE Burner.

The COPE Phase II Process (Figure 2) moderates the combustion temperature by recycling a portion of the process gas from the outlet of the first sulfur condenser to the burner. The recycle gas rate is controlled to limit the reaction furnace temperature. The recycle flow is sustained with a mechanical blower in all COPE Phase II units now in operation.

The new modification of the COPE Phase II Process (Figure 3) utilizes an ejector in place of the mechanical blower. The recycle stream consists of a stream indigenous to the process (SRU process gas) and the ejector motive stream. The motive stream can be steam, compressed air, compressed nitrogen, compressed carbon dioxide, compressed sulfur dioxide or similar gases; high pressure steam is the preferred motive stream. Utilizing an ejector in place of a mechanical blower offers several process, mechanical and economic advantages.

Recycle Advantage

Recycle is a simple, but powerful tool for controlling furnace temperature when other methods become inadequate or cumbersome. During normal and continuous operation the recycle stream, where necessary, moderates the combustion temperature. 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 or stoichiometric variations. The option to moderate the recycle flow can be beneficial for dealing with commonly occurring operating problems such as:

- instantaneous SRU feed composition changes, and
- sudden changes in SRU feed flow rates.

Over the years the COPE Phase II operating units have demonstrated these recycle advantages. The new version of the COPE Phase II Process, utilizing an ejector, maintains the advantage of recycle with added process, mechanical and economic advantages.

COPE Phase II with an Ejector

The use of recycle blowers have been demonstrated in sulfur recovery units since 1981 (Sid Richardson Recycle Selectox). The first COPE Phase II process utilizing a recycle blower in oxygen enriched Claus plant was commissioned in 1985. Use of an ejector in place of a recycle blower for the service of recycling sulfur recovery process gas has not been practiced. The primary purpose of oxygen enrichment is to increase plant capacity by reducing the flow rate of the main process stream for a given quantity of acid gas feed. The process flow rate is reduced due to a decrease in the quantity of nitrogen entering with the combustion air, thus allowing an increase in the acid gas feed to the plant. Replacing a mechanical blower with a steam motivated ejector does more than change the means of sustaining recycle, since the motive stream introduces an additional feed to the sulfur recovery unit.

Process Advantages

Furnace flame moderation and chemical reactions enhanced by the presence of ejector motive steam.

The purpose of the recycle stream in a Claus sulfur plant using oxygen enrichment is to moderate the flame temperature to acceptable working levels of the furnace refractory material, without interfering with the primary intent of increasing plant capacity. At a given heat load, the recycle stream from a blower and from a steam driven ejector are of essentially equal molar flows and of nearly identical composition on a dry basis; however, on the actual wet basis the water content, as expected, for the ejector recycle stream is 25% higher. The increased water content is beneficial for (1) improved heat absorption (flame moderation) through infrared activity1), (2) flame moderation due to endothermic reactions of water vapor with hydrocarbons, and (3) importantly, the improved hydrocarbon contaminant conversion due to direct chemical reaction of the water vapor with the hydrocarbon in sulfur plant feed2),3).

Nonsymmetrical species such as H_2O absorb heat by radiation but symmetrical species such as N_2 and H_2 have no or very little radiant capabilities. The radiant absorption of heat assists in moderation of the flame temperature. As summarized in Table I, the ejector recycle stream has 10% more nonsymmetrical species, and only 67% of the symmetrical species, contained in the blower recycle stream. The improved ratio of nonsymmetrical to symmetrical species is solely a result of the ejector steam motive stream.

The water vapor reacts with the hydrocarbons in the following endothermic reactions (Note: For purpose of example, only the reaction of methane is shown but the gases in a Claus sulfur plant feed contain other hydrocarbon species):

$$CH_4 + H_2O = CO + 3H_2 \quad (-)\ 88{,}000\ \text{Btu/lbmol}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \quad (-)\ 47{,}000\ \text{Btu/lbmol}$$

Thus, as indicated by the above reactions, the water vapor assists in the conversion (destruction) of undesirable hydrocarbons and the reactions are endothermic, thus further enhancing the desired flame moderation. Destruction of hydrocarbons is desirable and necessary for efficient and reliable sulfur plant operation.

These substantial flame moderation and furnace chemical reaction benefits for a Claus sulfur plant using oxygen enrichment are promoted by the use of a steam driven ejector.

Improved radiant heat transfer in the Waste Heat Boiler.

High levels of oxygen enrichment significantly increases the heat load on the waste heat boiler. To minimize downtime and capital cost in applying the process to existing plants, reuse of the waste heat boiler on existing sulfur plants is desirable. To afford this desirable reuse, the heat transfer rate must improve over the original air-based sulfur plant operation. There are several mechanisms for heat transfer in a Claus sulfur plant waste heat boiler; a mechanism of significant importance is radiant heat transfer. Some gases such as N_2, H_2 and others of nonpolar symmetrical molecular structure, are essentially transparent, while polar, nonsymmetrical gases such as H_2O radiate to an appreciable extent 4)5). The reaction furnace outlet stream for a blower, as compared to a steam driven ejector, is of equal molar flow and nearly identical composition on a dry basis. However, on the actual wet basis the water content of the furnace outlet, as expected, is 7% higher in the ejector-driver system (Refer to Table II).

"The degree of emissivity of a gas is a function of the degree of lack of molecular mass symmetry or the mass ratio. In this case, a greater mass ratio denotes greater emissive ability at any temperature. Mass ratios are based on atomic weights. In H_2O, the ratio is $16/2 = 8$ for greatest emissive ability of all the components of the reaction furnace stream".6)

The improved radiant heat transfer benefit, while still achieving the desired capacity improvement in a Claus sulfur plant using oxygen enrichment, is enhanced with a steam driven ejector.

Improved balance of flows within and downstream of the recycle loop.

As documented in Table I, the molar recycle flows for the ejector and blower are essentially equal, however the ejector mass flow is 12% lower because of the lower molecular weight due to the increased steam concentration. Thus, the pressure drop for the ejector recycle loop is also 12% lower than the blower recycle. Therefore, the ejector oxygen based pressure drop is 2.5 psi as compared to the original air-based 1.9 psi, only a 31% increase. The ejector operation results in a lower hydraulic load than the blower in the critical furnace stage.

Downstream of the recycle stream, oxygen-enrichment significantly unloads the catalytic stages. The net forward flow downstream of the recycle loop is reduced to 1.9 psi ΔP for the debottlenecked enriched air operation versus 5.1 psi ΔP for the base case air operation. The ejector operation results in 2.5 psi ΔP, and as documented below, the higher pressure drop for the ejector scheme has significant heat transfer benefits without adversely affecting plant capacity.

In summary, the ejector operation, relative to the blower operation, (1) hydraulically unloads the recycle section, and (2) increases net forward flow in the catalytic stages, thus improving heat transfer in exchangers. The redistribution of mass flow in the ejector operation provides overall pressure drop and heat transfer benefits.

Improved overall heat transfer coefficients

Sulfur condensers are exclusively shell and tube heat exchangers with the process gas on the tubeside; heat load is predominantly sensible heat. In modern Claus plants, the reheaters are predominantly shell and tube heat exchangers with the process gas on either the shellside or tubeside. Reheater heat load is exclusively sensible heat transfer. Thus, both Claus plant condensers and reheaters are sensible-heat exchangers. Heat transfer rates in sensible heat exchangers are directly related to velocities7).

Due to oxygen enrichment, the net forward flow downstream of the recycle loop is reduced to 1.9 psi ΔP for the debottlenecked enriched air operation versus 5.1 psi ΔP for the base case air operation. In essence the Claus plant downstream of the recycle is "unloaded" or "in turndown". "When major turndown is expected in the process gas stream, minimum tube side mass velocity of 2.5 lb/sec/ft^2 should never be exceeded. To maintain a tube side velocity above the recommended minimum velocity, install a blank segment (loose fitting) at the inlet end of the tube bundle."8) Low tube mass velocities result in sulfur fogging because condensing takes place in the gas stream instead of on the tube surface. The sulfur fog cannot be recovered and results in fouling of the catalyst in the converters and a loss in sulfur recovery. Thus, in order for the Claus plant to operate efficiently in oxygen-enriched mode, it may be necessary to install blanking plates in the exchangers. However, blanking plates reduce the original air-based Claus plant capacity.

In contrast, recycle driven by an ejector yields an improved balance between flow rate within and downstream of the recycle loop. While beneficially decreasing the mass flow within the recycle loop, the motive steam flow to the ejector increases the net forward flow downstream of the recycle loop, where increased flow is needed. As shown in Table III, the net forward flow for the ejector scheme is 109% of flow for the blower scheme. Thus, with concern with low flow rates downstream of the recycle loop, and the possible need for blanking plates, the original Claus plant air-based capacity is maintained.

Mechanical Advantages

High resistance to erosive/corrosive wear.

The materials in contact with the recycle process gas are exposed to hot corrosive gases that typically contain small quantities of liquid sulfur, and possible fine solids such as iron scale and refractory material. A standard material of construction for the entire ejector is stainless steel. Stainless steel is more resistant to erosion and corrosion than carbon steel. The ejector has no moving parts and the high velocity steam nozzle is exposed to clean and non-corrosive steam.

Motive Source from within the Claus Plant

A Claus plant produces two valuable products; sulfur and steam. Steam is a useful utility product that is typically used within the Claus plant for preheating, reheating, and steam tracing. Typically, only 60 to 70% of the high pressure steam generated in the Claus plant is utilized within the Claus plant . The ejector motive stream only requires 2 to 4% of the high pressure steam that is generated by the Claus plant. Thus, the ejector scheme can be supported by the Claus plant and does not require an external utility, such as electricity. This self-supporting feature along with the simplicity of the ejector system is beneficial for the on-stream factor.

Piping and Installation

The ejector is located at an elevation above the first condenser and reaction furnace to allow all sloped self draining piping from the condenser, thus eliminating the need for an additional sulfur seal and drain.

Redundancy

The small space requirement, simplicity of installation and low cost of ejectors make fully or partially spared configurations an attractive option. Two 100% units would be used for all but the largest SRU's, where three 50% units might be used.

Economic Advantages

The advantages of the recycle stream utilizing an ejector can be achieved with:

- low capital cost,
- low installation cost,
- low operating cost, and
- where space limitation is an issue, the ejector requires no ground space.

Summary

The COPE Process is a time proven technology for the use of oxygen enrichment in sulfur recovery units. Oxygen enrichment with the COPE Process offers several advantages such as increased sulfur processing capacity, improved sulfur recovery, and improved destruction of feed contaminants.

The availability of a recycle stream allows moderation of the flame temperature for high levels of oxygen enrichment with rich acid gas feeds, and also provides an indigenous process stream for disturbance mitigation and rejection. The recycle stream can help minimize the effects of sudden changes of acid gas flow rate and compositional changes. This reduces potential equipment damage and contributes to high on-line full flow SRU operation.

A recycle stream utilizing an ejector provides the advantages of the recycle stream with minimal capital cost, operating cost and operating complexity. The process advantages of utilizing a stream driven ejector include improved flame moderation, improved waste heat boiler radiant heat transfer, and improved convective heat transfer in condensers and reheaters. Mechanical advantages of utilizing a steam driven ejector include ease of installation with the option for ejector redundancy, high resistance to erosive/corrosive wear and a self-draining piping system.

Table I. Comparison of Ejector and Blower Recycle streams.

Basis:

- 300 LTPD SRU.
- Oxygen enrichment level: 65% O_2.

Component	**Recycle Stream** **Blower** (lbmol/hr)	**Ejector** (lbmol/hr)	**Percent Ejector vs. Blower** (%)
Flow(lbmol/hr):			
Symmetric species			
N_2, H_2, S, CO	96.89	64.67	67
Nonsymmetric species			
H_2O, H_2S, SO_2, CO_2	313.13	345.74	110
Total	410.02	410.42	100
Mass Flow (lb/hr):	10206	9099	89

Table II. Comparison of Ejector and Blower Reaction Furnace Streams.

Basis:

- 300 LTPD SRU.
- Oxygen enrichment level: 65% O_2.

Component	**Reaction Furnace Stream** **Blower** (lbmol/hr)	**Ejector** (lbmol/hr)	**Percent Ejector vs. Blower** (%)
H_2O (lbmol/hr)	868.54	926.76	107
Total Flow (lbmol/hr)	1655.55	1655.41	100
Molecular weight	28.05	27.55	
Mass Flow (lb/hr):	46438	45607	98

Table III. Comparison of Net Forward Claus Plant Flow Downstream of the Recycle.

Basis:

- 300 LTPD SRU
- Oxygen enrichment level: 65% O_2.

Component	**Reaction Furnace Stream**		**Percent Ejector vs. Blower** (%)
	Blower (lbmol/hr)	**Ejector** (lbmol/hr)	
CD#1 Net Forward			
Stream:	27593	29409	107
Total Flow (lb/hr)	1108.59	1208.77	109
Total Flow (lbmol/hr)	634.04	734.04	116
H_2O Flow (lbmol/hr)	57	61	106
H_2O Composition (%)			

References

1. "Furnace Operations", Robert D. Reed, Gulf Publishing Company, Houston, TX 1976, pp. 65.
2. "Furnace Operations", Robert D. Reed, Gulf Publishing Company, Houston, TX, 1976, pp. 162-164.
3. "Capability of the Modified - Claus Process", Harold G. Paskall, Western Research, Calgary, AB, 1990, pp.47-54.
4. "Heat Transfer", J.P. Holman, McGraw-Hill Book Company, New York, NY, 1981, pp. 341-351.
5. "Perry's Chemical Engineering Handbook, 6th Edition", Robert Perry and Don Green, McGraw-Hill Book Company, New York, NY, 1984, pp. 10-60 to 10-62.
6. "Furnace Operations", Robert D. Reed, Gulf Publishing Company, Houston, TX, 1976, pp. 65-66.
7. "Process Heat Exchangers", J.P. Fanaritis and J.W. Bevevino, McGraw-Hill, 1976, pp.13.
8. "Improve Sulfur Condensers", W.P. Knight, Hydrogen Processing, 57 (1978), pp. 239-41.

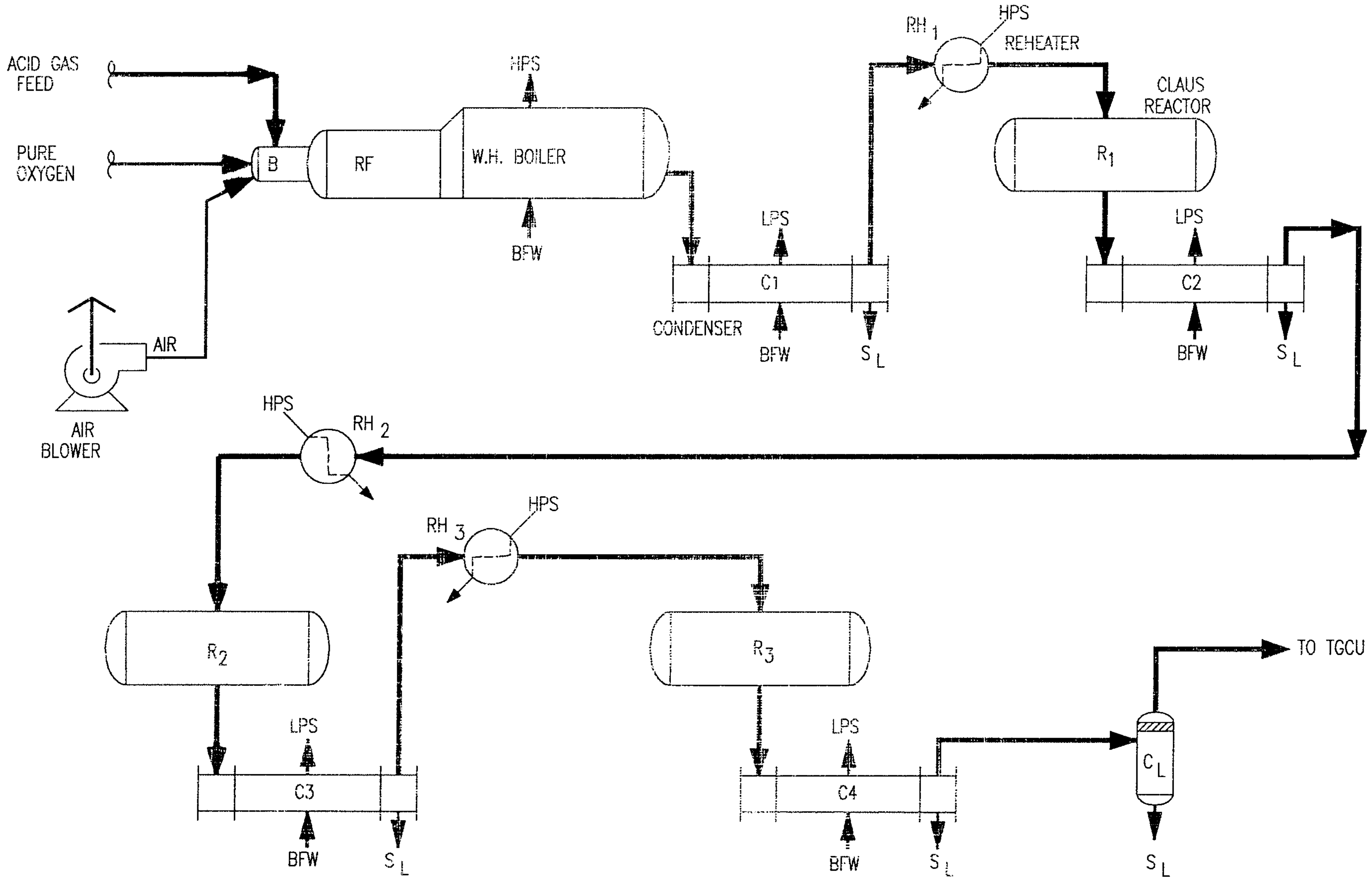

FIGURE 1
CLAUS SULFUR RECOVERY UNIT,
WITH MEDIUM-LEVEL O_2-ENRICHMENT
COPE™ PHASE I PROCESS

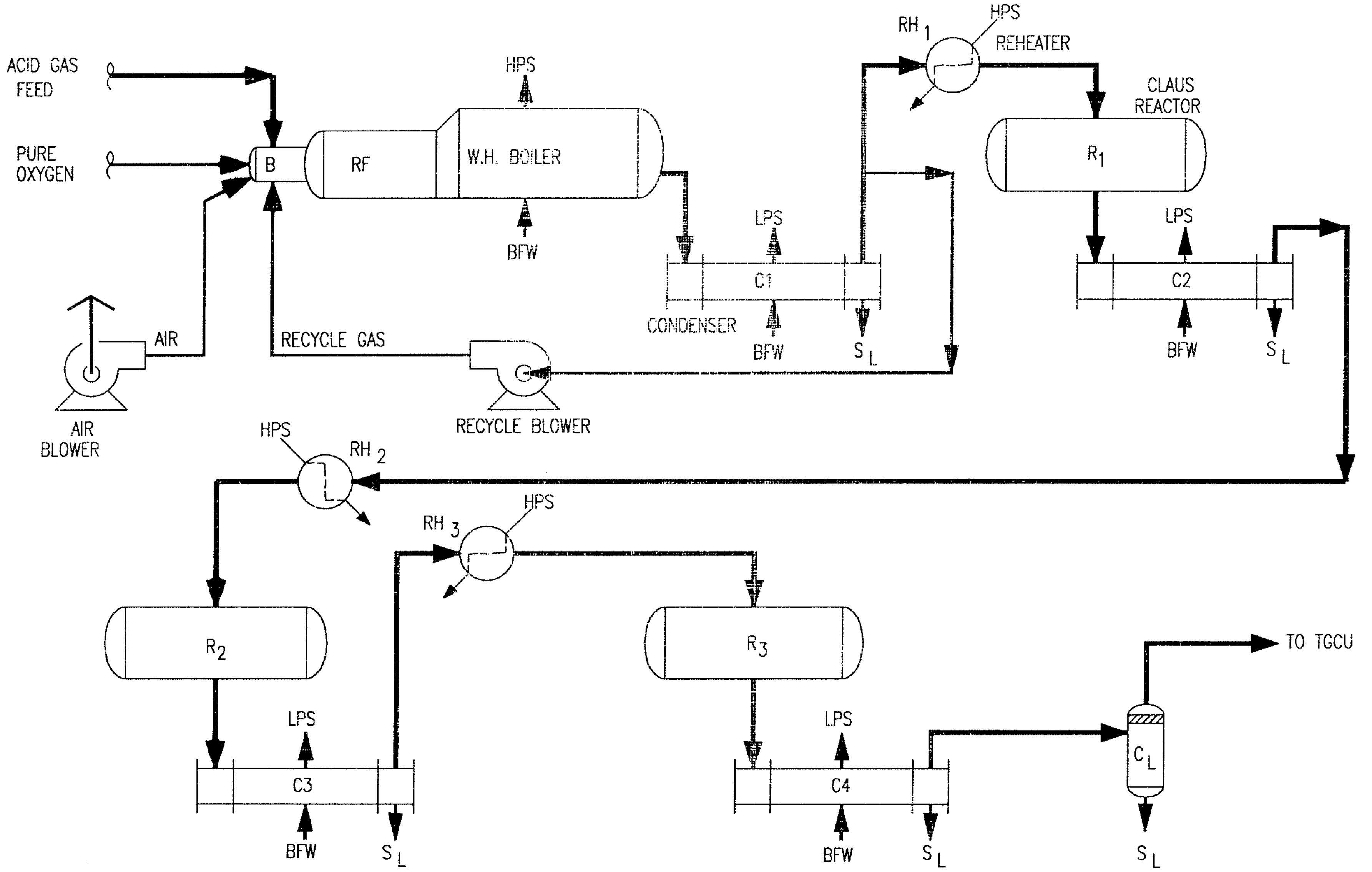

FIGURE 2

CLAUS SULFUR RECOVERY UNIT, WITH HIGH-LEVEL O_2-ENRICHMENT COPE™ PHASE II PROCESS

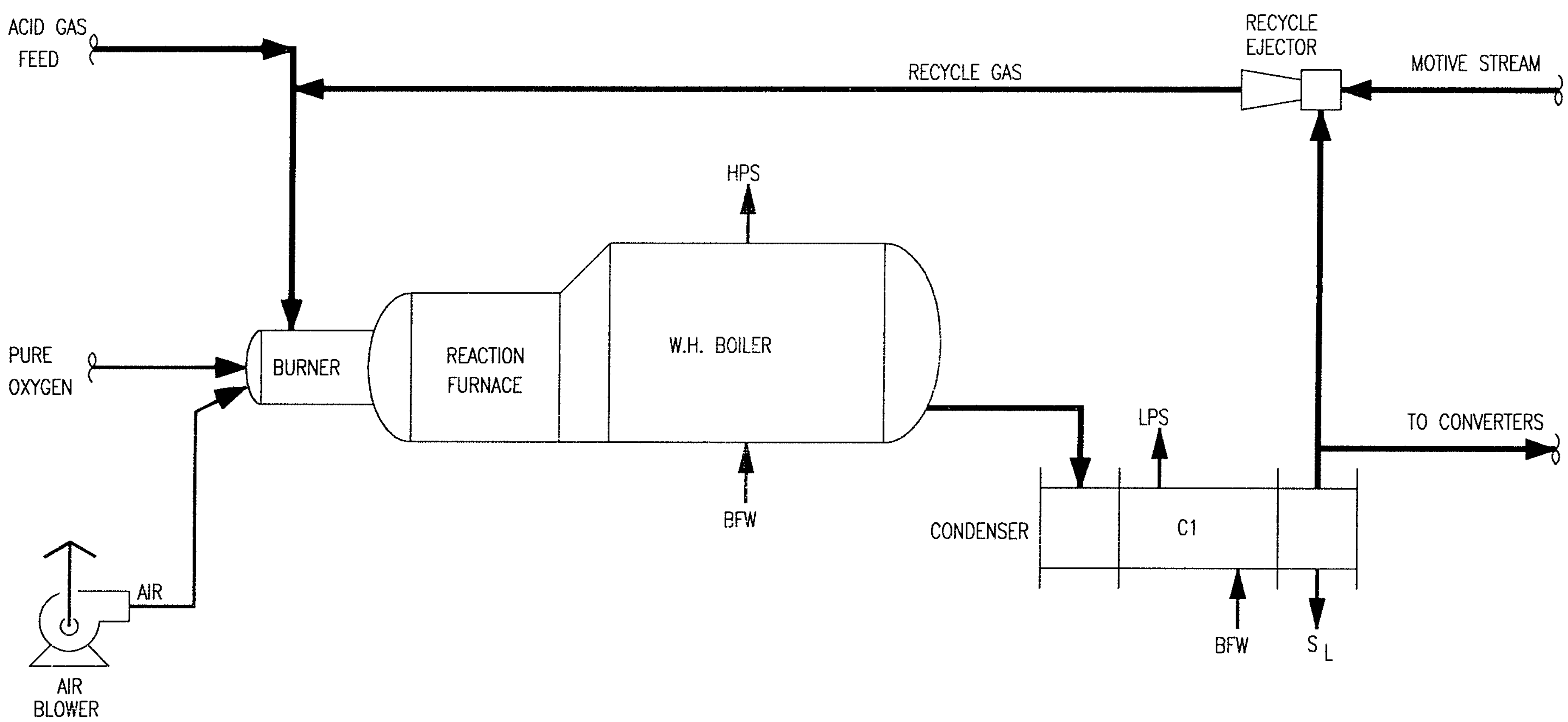

FIGURE 3

CLAUS SULFUR RECOVERY UNIT,
WITH HIGH-LEVEL O_2-ENRICHMENT
COPE™ PHASE II PROCESS
UTILIZING AN EJECTOR