SO_2Clean for SRU Expansion

Jeff Hammerstrom
Calabrian Corp
jhammerstrom@calabriancorp.com

Ron Schendel
Process Consultant
Ron@RSchendel.com

Brimstone Sulfur Symposium

Vienna, Austria

May 27 - 31, 2013

Introduction

The push to produce cleaner, low sulfur fuels from higher sulfur crude has resulted in a need for increased capacity to recover sulfur. Historically, refiners wishing to increase capacity have added SRUs or debottlenecked existing units through oxygen enrichment. Adding SRUs requires major reengineering/reconstruction projects. High levels of oxygen enrichment require process changes, and additional equipment, to limit reaction furnace temperature. However, there is another way to limit temperature in the reaction furnace...direct injection of high purity sulfur dioxide (SO_2) into the SRU.

The benefits of using pure SO_2 to expand Claus capacity has been investigated in the past. However, the use of SO_2 has not realized commercial acceptance because of supply chain complexities and the reluctance of refiners to build and operate a sulfur dioxide plant.

Calabrian, the developer of the SO_2Clean Technology is seeking to meet this market need by supplying SO_2 analogous to the current practice of supplying other industrial gases (e.g. hydrogen, oxygen, nitrogen). Calabrian will build/operate a fence-line plant that manufactures SO_2 utilizing their proprietary SO_2Clean Technology and deliver it via pipeline to a refinery's SRU.

SO_2Clean is a proven, commercial, and proprietary technology to produce high purity SO_2 by burning sulfur with pure oxygen instead of air. Burning sulfur with oxygen offers significant advantages – nitrogen and other inerts are not present which significantly reduces downstream equipment size/costs. SO_2Clean eliminates gas separation/operational complexities and most importantly, the process is safe and environmentally friendly. There Are No Emissions, It's a Closed System.

This paper will describe the technology in further detail - both the use of SO_2 and oxygen in the Claus sulfur recovery unit, and the submerged combustion process used to produce SO_2. It will also discuss Calabrian Corporation's experience in the production of SO_2 and over the fence supply.

Discussion

How the direct addition SO_2 can double an SRU's capacity:

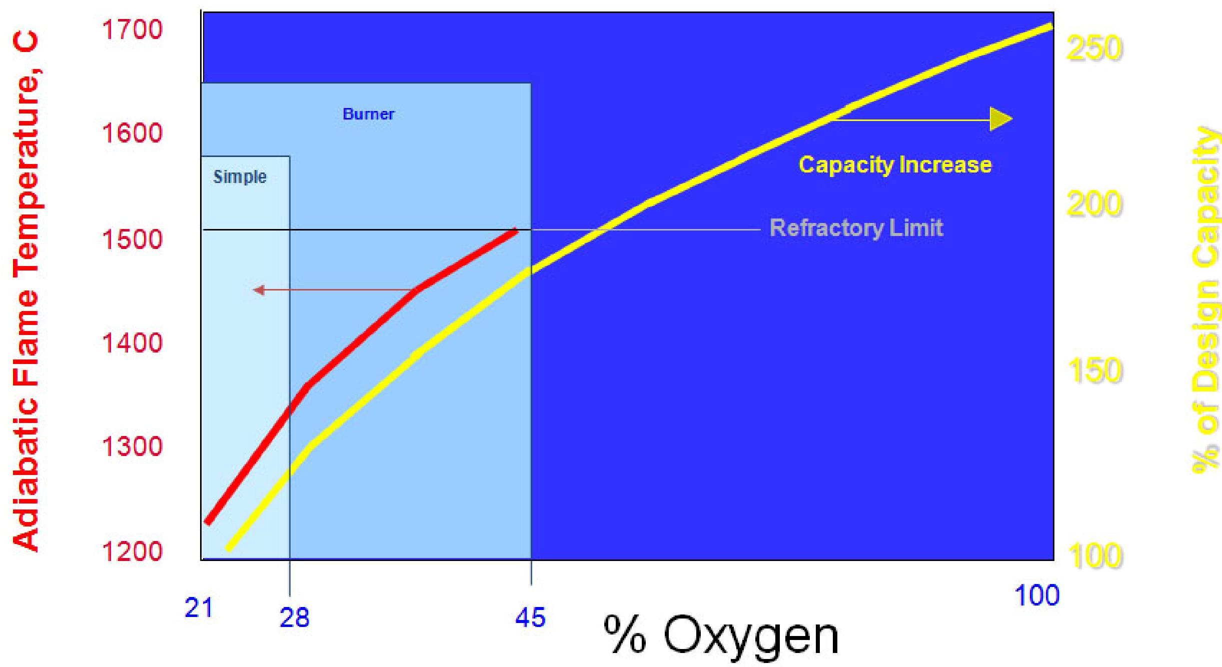
In a conventional Claus sulfur recovery unit, acid gas (H_2S) feed is combined with air in the reaction furnace, where the oxygen contained in the air reacts with hydrogen sulfide to produce sulfur dioxide. The sulfur dioxide then reacts with the remaining hydrogen sulfide to produce sulfur and water vapor.

$$\mathbf{H_2S + O_2 = H_2O + SO_2 + Heat}$$

$$\mathbf{H_2S + SO_2 = H_2O + S\ (Claus\ Reaction)}$$

The combustion of hydrogen sulfide to produce sulfur dioxide is highly exothermic.

Pure oxygen is often used to increase the capacity of sulfur plants. By replacing air containing oxygen with pure O_2, inert gases in air are removed. The result is more volumetric capacity available for processing acid gas. However, the combined effect of more acid gas processing (heat) and the removal of "heat absorbing" inerts results in furnace temperatures that limit the amount of O_2 that can be used. This limits the capacity increase that is available by use of oxygen alone.



On the other hand, the Claus reaction of sulfur dioxide and hydrogen sulfide to produce sulfur can be either exothermic or endothermic depending on the temperature and the prevalent form of sulfur produced. In either case the temperature effects are not significant when compared to the combustion of hydrogen sulfide to produce sulfur dioxide.

If sulfur dioxide is produced external to the SRU's reaction furnace and is instead introduced as a feed stream, the heat of formation is removed in the production process.

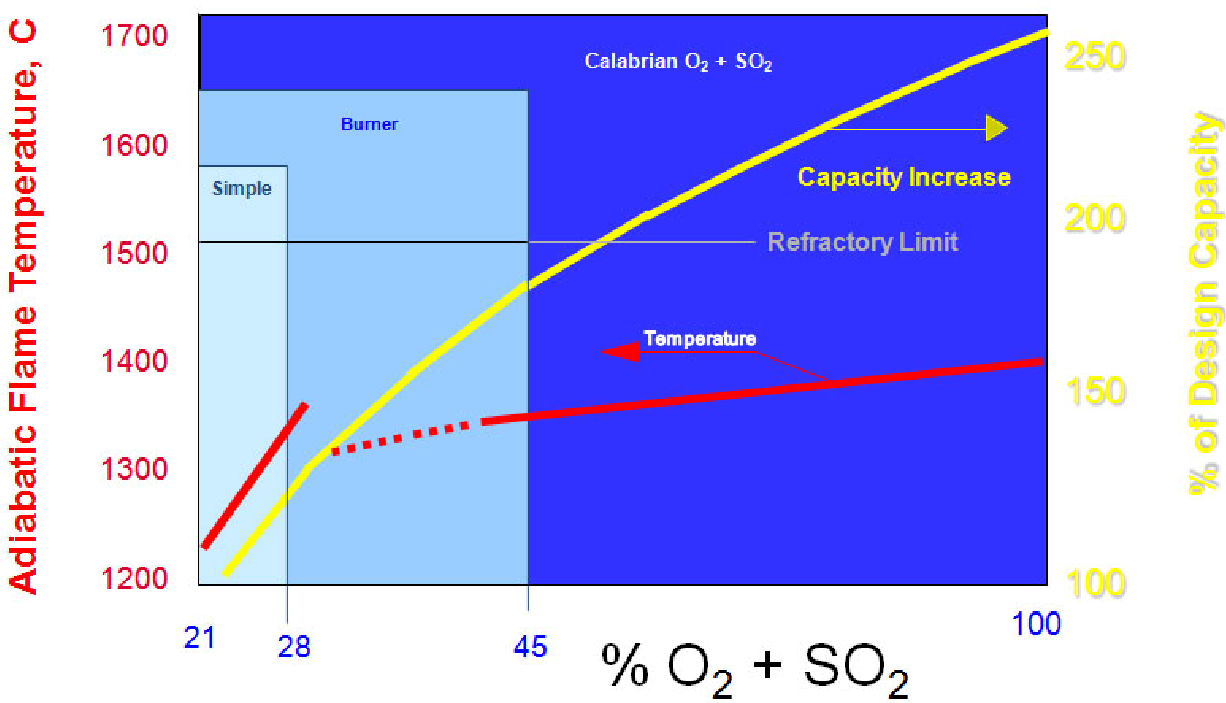
$S + O_2 = SO_2$ + Heat (Outside RF)

Therefore, if no air were added to the SRU feed gas and only the stoichiometric requirement of sulfur dioxide provided, the reaction would operate at very moderate temperatures and inert gases would be absent. The result…a significant increase in the ability to process acid gas.

The production of sulfur is not the only function of a typical sulfur recovery unit. Destruction of ammonia and hydrocarbons is also required. Therefore, operation of a reaction furnace with air or oxygen to react with these contaminants at a sufficiently high temperature to ensure complete destruction is necessary.

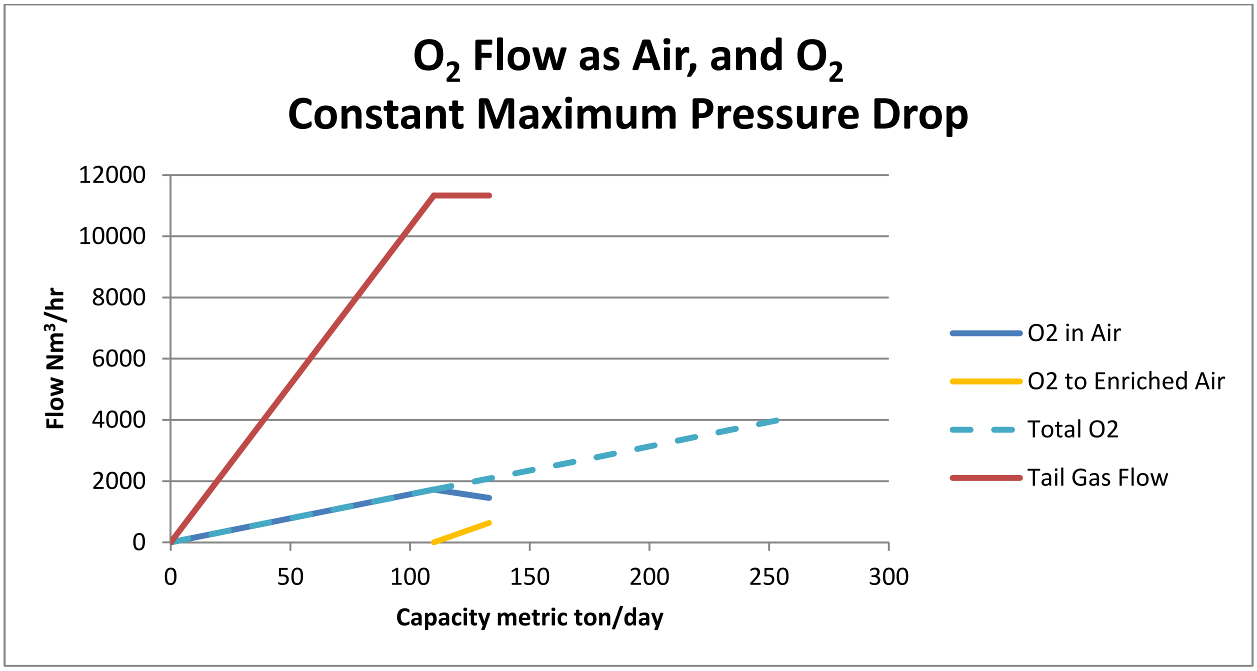
One solution to increasing capacity and limiting temperature in the reaction furnace, is to continue producing most of the sulfur dioxide required for the Claus reaction by combustion of hydrogen sulfide with a mixture of air and oxygen in the reaction furnace, but produce the remaining sulfur dioxide required external to the reaction furnace.

Controlling the relative amounts of oxygen and sulfur dioxide entering the reaction furnace provides the desired effect of controlling furnace temperature and achieving the desired capacity increase.

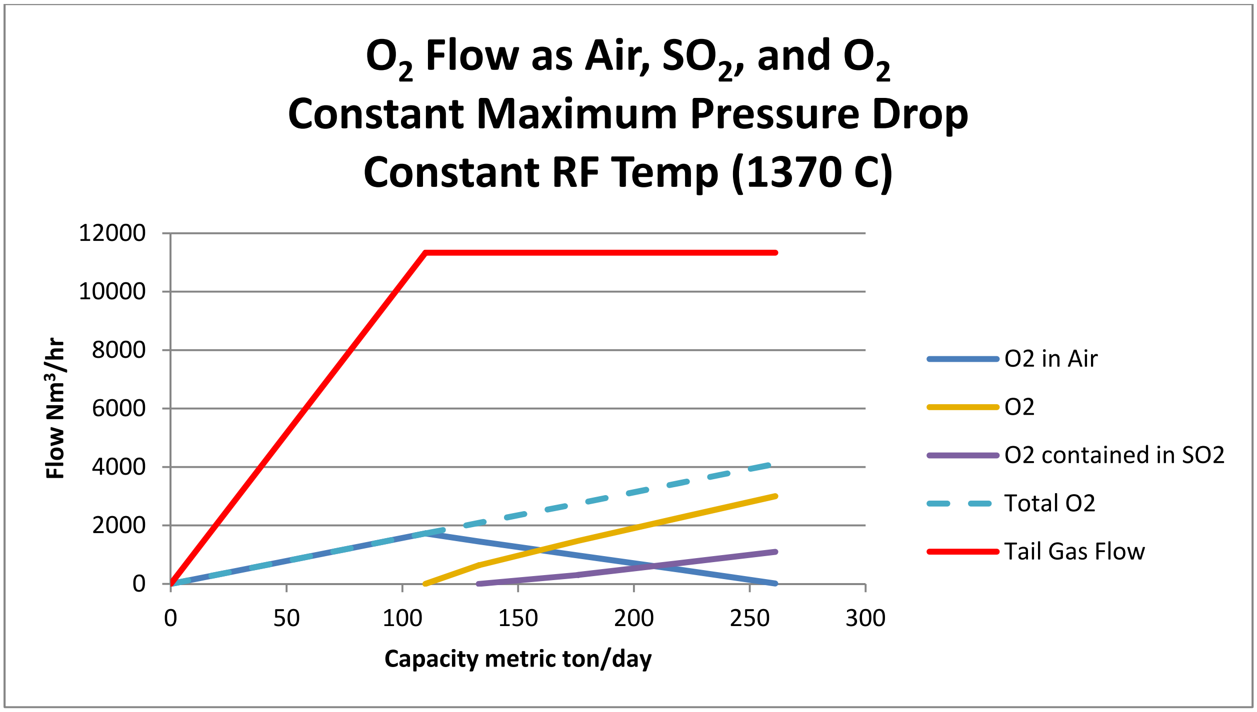


O_2 Demand:

At maximum air based capacity of a sulfur recovery unit, pressure drop is the limitation. Oxygen is used to increase capacity basically as a means to remove nitrogen, which is a major component of the gas flowing through the plant, and major contributor to pressure drop.



As oxygen is added to the system and air is removed, the temperature inside the reaction furnace increases. A limited amount of oxygen can be added before reaction furnace refractory limitations are reached. To add more oxygen (and remove more air) the temperature rise must be controlled. This is done by adding a mix of sulfur dioxide and oxygen rather than just oxygen.



The amount of oxygen required to convert H_2S to sulfur and water vapor is the same regardless of whether the oxygen comes from combustion air, supplemental oxygen, or oxygen already combined as sulfur dioxide. (Ignoring possible minor effects of dissociation of H_2S at higher temperature).

The amount of air relative to oxygen, or sulfur dioxide determines the capacity increase available. (Essentially the amount of nitrogen removed from the system).

The amount of sulfur dioxide relative to oxygen determines the resulting furnace temperature.

SO_2 Demand:

The amount of oxygen (and/or sulfur dioxide) required for any given system is determined by the capacity increase required and allowable pressure drop. For a typical refinery type feed, the rule of thumb is about 1 ton O_2/ ton of INCREASE in sulfur capacity. In North America O_2 is usually measured in short tons and sulfur is usually measured in long tons. Therefore, the rule of thumb can be stated as approximately 1.1 short ton of O_2 / long ton of Sx. In Europe, both are measured in metric tons and 1 mt O_2/ mt increase in sulfur capacity is valid.

To ensure complete destruction of ammonia and hydrocarbons, a reaction furnace temperature greater than 2350 F (1290 C) is desirable. To avoid refractory damage a reaction furnace temperature less than 2800 F (1540 C), or perhaps even 2700 F (1480 C) is desirable.

For a typical refinery with rich amine acid gas (~90% H_2S) processing sour water stripper gas, to maintain an optimal reaction furnace temperature of 2,500 F (1370 C) requires between 1/4 and 1/3 of the oxygen added to meet capacity (molar or volume basis) to be supplied as sulfur dioxide,

For example, to increase the capacity of a 100 metric ton/day (mt/d) Claus SRU to 200 mt/d (100 mt/d increase) requires approximately 1 x 100 or 100 mt/d of oxygen.

The maximum SO_2 required is 1/3 x 100 = 33 mt/d of oxygen supplied as sulfur dioxide. This leaves 67 mt/d of oxygen still supplied as oxygen. Since the MW of SO_2 is twice the MW of O_2, (64/32=2) the amount of SO_2 required on a weight basis is 2 x 33 = 66 metric ton of SO_2 per 67 metric ton of O_2, or approximately 1 ton SO_2 / ton O_2.

Normally, the SO_2 required is closer to 1/4 x 100 or 25 mt/d of oxygen supplied as SO_2. This leaves 75 mt/d of oxygen still supplied as oxygen. The amount of SO_2 required on a weight basis is 25 x 2 = 50 mt/d of SO_2/75 mt/d of O_2, or approximately 0.67 ton SO_2/ton O_2.

The furnace temperature is easily controlled at the desired set point by varying the relative amounts of O_2 and SO_2.

Calabrian provides high purity SO_2 via pipeline

SO_2 produced using Calabrian's SO_2Clean proprietary technology:-

By utilizing the unique properties of sulfur, oxygen is introduced into a pool of molten sulfur where it will immediately react to form sulfur dioxide. The heat of reaction will cause the pool of sulfur to boil, and the temperature of the system is limited to the boiling point of sulfur at the operating pressure of the reactor. The amount of sulfur vaporized is such that the heat of vaporization is exactly equal to the heat of reaction.

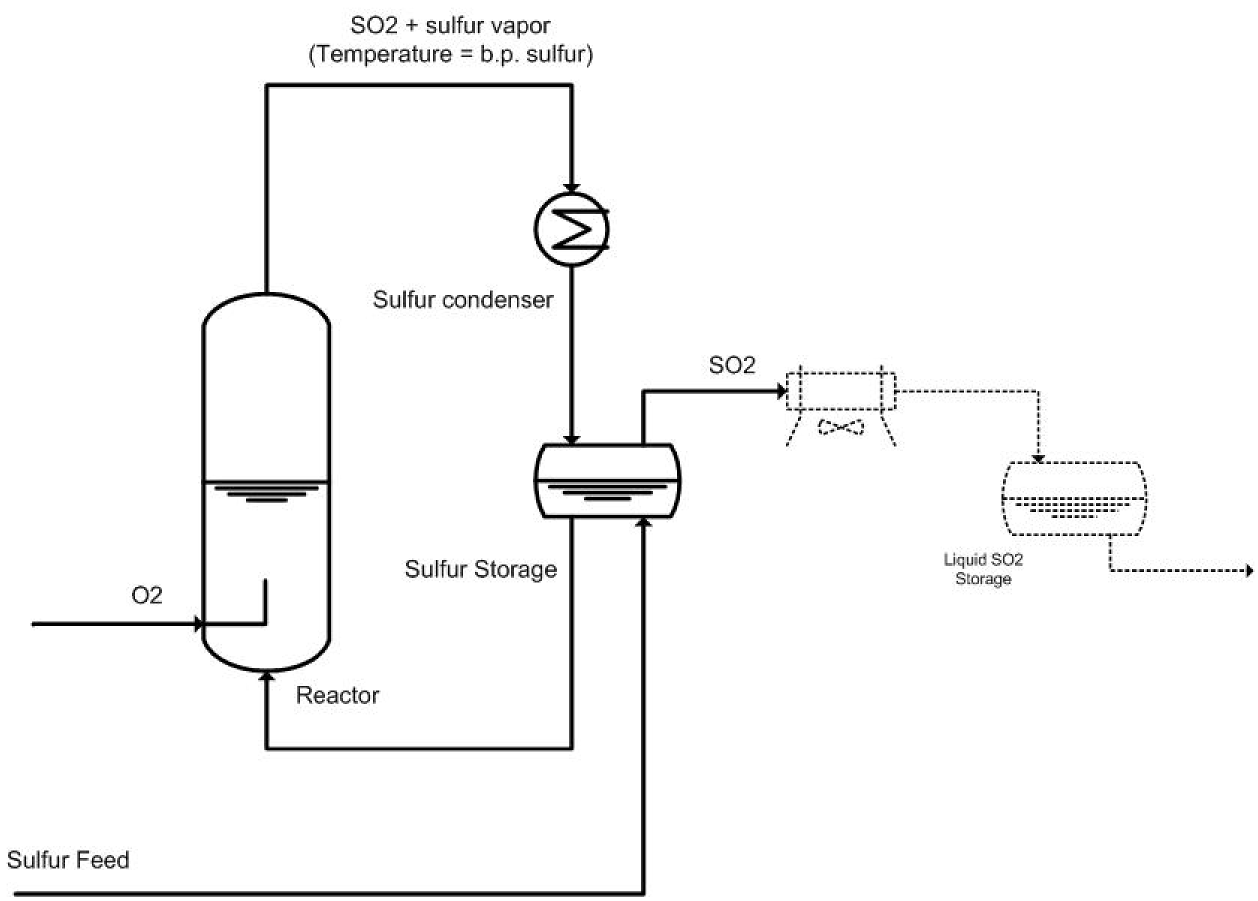
Even at atmospheric pressure the boiling point of sulfur (832 F (445 C)), is well above the auto ignition temperature. (Auto ignition of sulfur in air is 470 F (243 C)). This ensures immediate and complete reaction of the oxygen with sulfur as it enters the reactor.

Also, because oxygen is always the deficient reactant there is no possibility of forming sulfur trioxide. Even if SO_3 were somehow introduced, it would react with sulfur to immediately form sulfur dioxide.

The gaseous effluent from the reactor is a mixture of sulfur dioxide and sulfur vapor. Condensing the sulfur leaves the desired high purity sulfur dioxide product. The condensed liquid sulfur is returned to the reactor along with makeup sulfur.

Because there is no nitrogen or other inerts mixed with the oxygen (as there would be with air) the only remaining vapor after condensing out gaseous sulfur and returning it to the feed tank, is pure SO_2. The SO_2Clean process is a closed system…there are no emissions. Notably, there is no NOX.

If desired the SO_2 vapor can be condensed and stored as a liquid.



Benefits of Calabrian's SO_2Clean technology

SO_2Clean is uniquely suited to Claus sulfur plant expansion. The process is highly reliable, very safe, environmentally friendly and commercially tested.

- 98^{+}% documented on-stream time
- There are no gas emissions coming from the sulfur dioxide plant.
- There is no SO_3 or NO_X generated because the sulfur dioxide is produced in an excess of sulfur and deficient in oxygen.
- The plant's footprint is small, approximately 30 ft. wide by 100 ft. long for 100 tons of SO_2 production per day. While the plant would normally be located outside the refiner's fence, locating the plant is easier with the small footprint.
- Specific to the SRU expansion application, the reactants are readily available.
  - Oxygen is required for expansion whether in combination with sulfur dioxide or by other means. <u>The total amount of oxygen required is the same, whether the oxygen goes directly to the Claus plant or a portion of the same total is diverted to the sulfur dioxide plant.</u>
  - The liquid sulfur required (borrowed and returned as SO_2) is also available as it is the primary product of the Claus SRU. There is no net consumption of sulfur.

Benefits of SO_2 Injection vs. Oxygen Enrichment Technologies

Minimum Modifications to SRU

Typical modifications required are burner modification or replacement, and increase in quench tower cooling. These modifications are common to all O_2 enrichment projects (beyond simple enrichment).

No Additional Plot Space Inside Refinery Gate Required

Because the sulfur dioxide is produced outside the refinery gate, there is no additional plot space required inside the refinery. This can be a significant advantage in many refineries where space is severely limited.

Carbon Steel Supply Line Requires No Insulation or Special Preparation

Dry sulfur dioxide is non corrosive being typically stored and transported in carbon steel.

Significant Additional Benefit with Multiple Trains

For the expansion of a single train SRU, the economics may favor one of the alternative technologies available. However, in most refineries there are multiple units, and particularly in the case of providing redundancy it is desirable to increase the capacity of more than one unit. Alternative technologies require modification to each of the units requiring additional capacity. With the SO_2 plus O_2 approach, a single sulfur dioxide plant outside the refiner's gate can feed multiple units.

Experience

Submerged Combustion Production of Sulfur Dioxide

Calabrian Corporation is the largest North American producer of on-purpose sulfur dioxide and sulfur derivatives. Calabrian employs the SO_2Clean Technology at its plant in Port Neches, Texas to manufacture the highest quality sulfur dioxide in the industry. This product is sold to merchant SO_2 customers as well as consumed internally for production of sulfur derivatives.

Below is a photo of the Calabrian Corporation sulfur dioxide plant at Port Neches, TX. It consists of two parallel 50 ton/day trains. The Port Neches, Texas plant has been operating for over 20 years.

Over the Fence Supply of Sulfur Dioxide

Calabrian Corporation has been supplying sulfur dioxide via pipeline over the fence to a major chemical manufacturer for over 10 years.

SO_2 recycled to an SRU

SO_2 is currently recycled from tail gas treating units to the SRU in several refineries, and has been for many years.

Summary of Experience:

All the pieces have been demonstrated. What is new is over the fence supply to refiners. (Even over the fence supply has been proven, just not to refiners).

Conclusions

Increasing sulfur recovery capacity has become more important with the economic benefits derived from utilizing higher sulfur crude. Calabrian Corporation will build/operate a fence-line plant that manufactures SO_2 utilizing their proprietary commercially proven SO_2Clean Technology and deliver it via pipeline to a refinery's SRU burner-tip economically and safely, with no fugitive gas emissions, enabling refiners to inject high purity SO_2 to increase sulfur recovery capacity with no reduction in saleable sulfur.