

Sulfur Recovery

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Abstract

This paper was written in motivation to understand vital processes that save millions of lives. It promotes great appreciation of industrial applications that prevent deadly chemicals from the atmosphere. The paper first breaks down the science and most common industrial practices used to break down and dispose of hydrogen sulfide. In doing such, challenges of such processes are recognized. Solutions are offered to some of these issues which in themselves must be optimized in consideration of drawbacks in other facets. This paper should demonstrate the author's understanding of design principles at an introductory level that many engineers implement into such processes as this. Additionally, understanding and recognition of safety hazards that a lot of processes like these are subjected should be shown.

Introduction

Energy sources have been a driving force of the modern economies across most established nations since the 1800's. During the 19th century before natural gas and oil were discovered, coal was the most readily available and reliable source of energy that was mined in large scale portions. Unfortunately, this substance has several toxic chemicals with lethal effects, most notably is hydrogen sulfide which is typically present in coal gas at concentrations of 100-1000 ppm (Yang). To put this in context, an adult male will suffer respiratory failure when exposed to concentrations of 10-500 ppm and death from concentrations over this range (Doujaiji). On top of the gaseous hazards that this chemical presents, it can also have deadly effects in its liquid form. Hydrogen sulfide produces sulfur trioxide when combined with oxygen through two reactions which in turn can produce sulfuric acid when contacted with water. Sulfuric acid is highly acidic so much that it can tear through human flesh. It has been a known hazard for quite some time and is unfortunately unavoidable because of modern day demands. Crude oil is extracted from various sources and contains small but significant amounts of crude oil that must be separated. Crude oil is extracted in mass quantities and so efforts to contain acid gas (H₂S) have been promptly developed. The origin of such research began from chemists such as Carl Friedrich Claus of Britain to develop a countermeasure like the "Claus Process" which is largely used today (Steudel). This process, designed in 1883, extracts pure sulfur from hydrogen sulfide by oxidizing it, the full mechanism is pictured below:

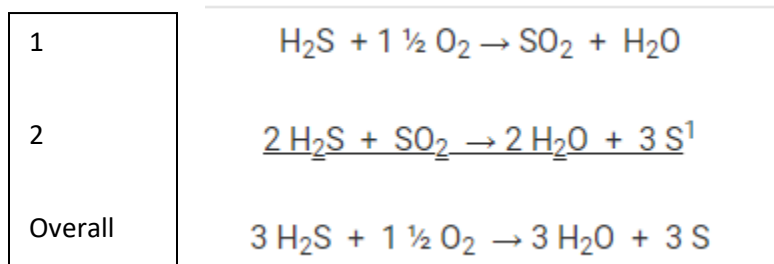


Figure 01: Claus Process Mechanism (Steudel)

A reactor furnace is required to combust the feed gas, hydrogen sulfide, into sulfur dioxide. This reaction furnace for reaction 1 must be operated at very high temperatures (>1700 F). Sulfur dioxide is used subsequently in reaction to produce elemental sulfur by reacting with the remaining acid gas. A combustion furnace is used to perform the first reaction and actually yields a good amount of the second reaction in the process. The reaction furnace is prone to a wide range of side reactions that produce species such as carbonyl sulfide, carbon disulfide, and hydrogen gas. Higher furnace temperatures and larger furnaces result in less production of these side products. A subsequent boiler is used to extract high pressure steam from this product and cool it enough so that it can be induced into a condenser. This condenser is used to extract the elemental sulfur and moves unreacted hydrogen sulfide and sulfur dioxide to the

catalytic stages in which only the second reaction is performed. Claus originally performed this first reaction in combustion conditions within a furnace which was not feasible as it produced a low yield (Goar). The second reaction pictured above is best performed at low temperatures where it is kinetically favorable. Both reactions are significantly exothermic and must be reacted within controlled environments. Equipment progressions have been noted from this time period to present which have significantly increased conversion. Modern-day catalyst stages of SRUs contain heaters, condensers, and reactor beds coupled in series. The reheaters are known to be powered by a wide variety of methods, one of which includes a utilizing the high-pressure steam produced from the thermal stage along with a generator to extract energy. The reactors used in these stages are fluidized beds as catalysts are induced upon the streams. These systems compose the catalytic stages of the SRU design and follow the reactor furnace in which the first reaction takes place. This reaction, that is the first reaction pictured in figure 01, is kinetically favorable at lower temperatures but must not be at a temperature lower than sulfur's dew point (Kohl). Dropping below the given dew point will result in catalyst deactivation as the liquid sulfur will interfere with the reaction (these reactions are homogenous) and stall conversion. Fortunately, the dew point decreases with decreasing sulfur content so this in turn means that catalytic reactors can be operated at lower temperatures as the process progresses. The conversion-temperature relationship is shown below in figure 02 and is indicative of how modern SRUs are designed.

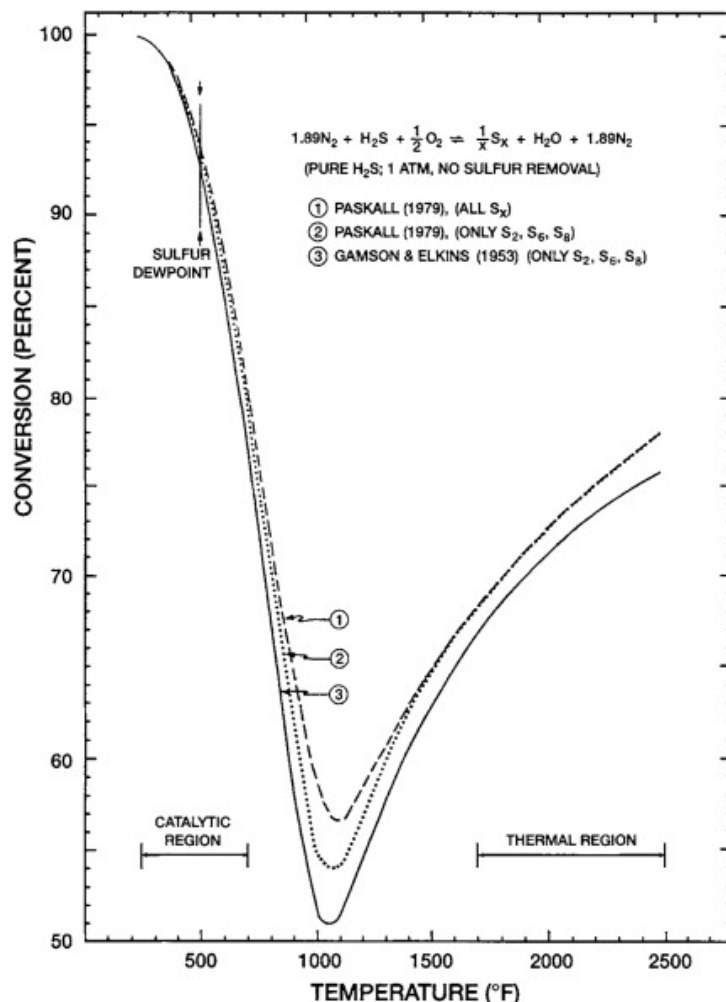


Figure 02: Equilibrium Conversion (Kohl)

Shown above are 3 different allotrope compositions as elemental sulfur is found primarily in the 3 listed configurations. Modern catalysts systems are listed to be about 90 percent efficient in themselves in terms of extracting sulfur from sulfur dioxide and are used within large scale refineries that extract hydrocarbon gasses from crude oil (Rezazadeh, Rezvantlab). So from the thermal stage consisting of the furnace, boiler, and condenser to the described catalytic units follows a tail gas treatment unit (TGTU) in which the hydrogen sulfide stream can be recycled, such as with the SCOT process, or terminated using a process such as the SUPER Claus process. Literature suggests multiple additional variants of the Claus SRU tail processes ranging from Sulfreen systems to Maxisulf systems but all will not be discussed for the sake of simplicity (AP-42). Each of these processes can be used with either or with both a split flow process or a straight through process.

Distinctions between Straight-through and split-flow methods are important for understanding SRU design as the two configurations are designed around some of the major problems encountered in SRU optimization. The most notable method of the Claus Process is the mentioned straight-through method which does not utilize a side-stream ahead of the combustion burner and reaction furnace. Straight through processes are preferred as a large amount (~60 percent) is collected in the thermal stage which is substantially higher than traditional split flow methods in which a large portion of the extraction occurs in the catalytic stages (Kohl). Straight-through methods are employed when the composition of hydrogen sulfide in the feed stream is greater than 50 mol percent. The split flow method is notable in that it redirects up to 2/3 of the acid gas feed stream away from the combustion chamber and the reaction furnace (Kohl). The portion of the stream that is subjected to the combustion/furnace process is then recombined with the redirected portion for a catalyzed reaction to remove the majority of the remaining sulfur from the un-heated stream. The general flow chart of this process looks something like the following...

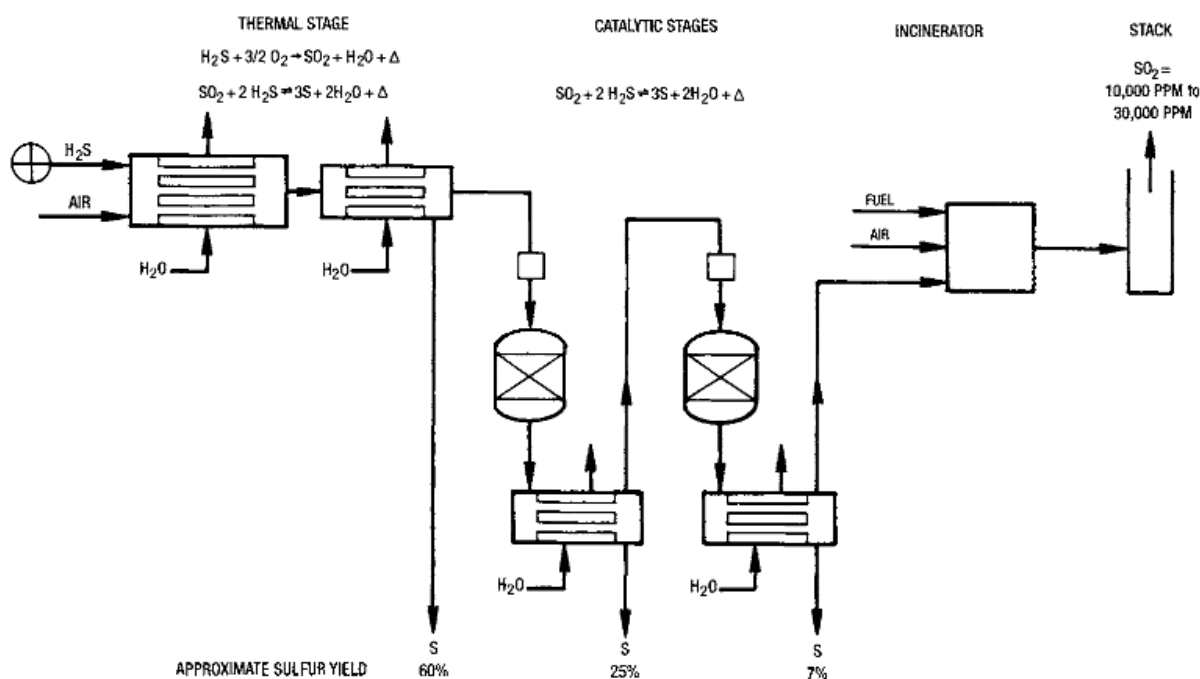


Figure 03: Claus Process Flow Diagram (Kohl, Nielson)

Tail Processes:

The largest component of an SRU is the Claus process that has been mentioned. Such as the case with many process designs, different processes can be combined to maximize performance (Cheremisinoff). To increase sulfur recovery from 95 percent to near 100 percent, tail gas treatment processes are added in subsequence to the Claus process of an SRU. There are several notable TGTUs used for industrial processes which can be classified under the following methods:

- Direct Oxidation to Sulfur
- Reduction to Hydrogen Sulfide with subsequent recovery
- Oxidation to Sulfur Dioxide with subsequent recovery
- Continuation of Claus Process

The most successful method as of now is the reduction of claus tail stream to hydrogen sulfide and then sulfur recovery from this reduced stream (Jafarinejad). More specifically, the SCOT process is the most widely used amongst this particular method. The SCOT (Shell Claus Off Gas Treating Process) process is a recycling method in which Hydrogen sulfide ultimately gets recycled back to the claus combustion chamber. The SCOT scrubbing process in which the claus tail stream is reduced to hydrogen sulfide using hydrogenation (addition of hydrogen in the presence of a catalyst) along with hydrolysis (addition of water). The reaction typically uses a cobalt-molybdenum catalyst and is operated at a temperature of around 300 Celsius. An absorber and regenerator are used so that the hydrogen sulfide can be extracted and recycled back to the original claus process.

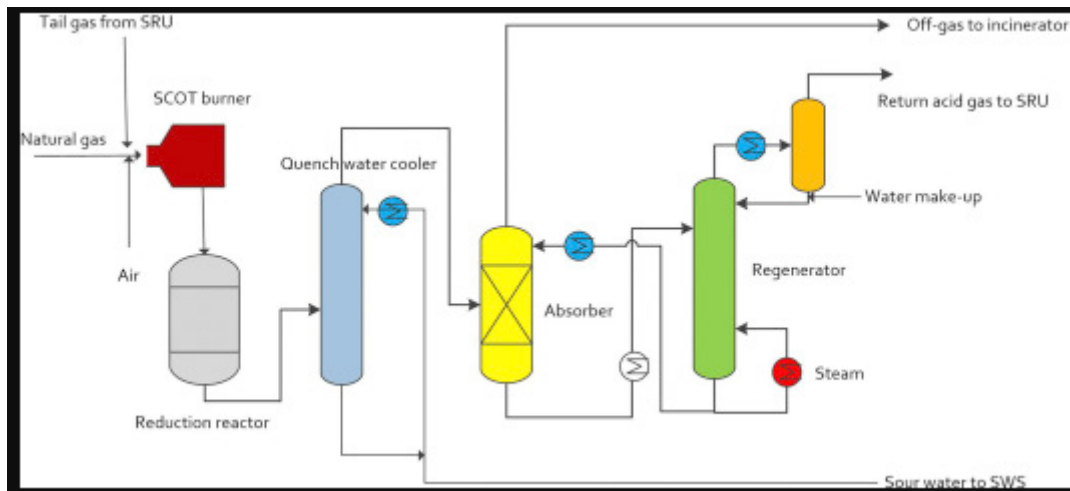


Figure 03: SCOT Process Flow Diagram (Jafarinejad)

Design Considerations:

Optimizing the design of a sulfur process is critical both for maintaining emissions standards but also making the process affordable. Literature (Zahid) suggests that 3 variables for optimization consideration are reactor size, oxygen flow rate, and reaction temperature. Other variables such as reaction pressure, feed flow rate, TGTU flow rate/composition can also be considered for optimization but these variables have less of an effect on the overall recovery of sulfur which is the purpose of this process. Overall optimization of SRU processes is measured through Gibbs free energy equation in which the change in Gibbs free energy is

equivalent to the change in enthalpy minus the product of temperature and ΔS (Kohl). This relationship explains that for exothermic processes (both of the mentioned reactions) the favorability of that particular reaction will depend on the entropy change occurring through the reaction. In simple terms, this can be visualized through the change in number of species present through the moles of the products and reactants. It is observed from Figure 01 that the first reaction sees a decrease in moles present and therefore a decrease in entropy. This, through the Gibbs free energy equation, reveals that this reaction will be more favorable, that is it is more spontaneous, at higher temperatures which is confirmed through the equilibrium data of figure 02. The opposite is true for the second reaction because of the increasing entropy as shown by the increasing number of moles from reactants to products.

Furnace Size

Since these reactors are plug flow reactors (Autoclave) they are measured and therefore optimized in terms of their diameter and length. Within this reactor turbulent flow is expected along with an appreciable degree of not slip to the sides. This condition results in a relatively large amount of dead volume for a given diameter so conversion (recovery) is predictably expected to increase with an increasing diameter. The length of the reactor is actually negligible after a shortened length because reaction behavior is relatively constant after the initial length. The majority of the deviation occurs in the axial direction of the reactor. Now is an appropriate time to mention the feed gas stream from refinery processes is not purely hydrogen sulfide as there are actually significant concentrations of ammonia present. This creates an issue of ammonia buildup within the reactor furnace which can be transferred to the catalytic reactors. Ammonia causes corrosion to these reactors if not cleaned out so this material is ideally limited as equipment is too expensive to replace every given duration. Also notable is that corrosion is a significant safety hazard (will be discussed) and so should be avoided. Both mentioned behaviors (Sulfur Recovery and Ammonia formation) increase but plateau after a given reactor volume (Zahid). This reactor should therefore be designed so that an optimal size is chosen with these variables in mind knowing that bigger reactors cost more money. From this section alone, it can be deduced that the main goal of reactor design, or any equipment design for that matter, is aimed to optimize production with cost while meeting the relevant safety constraints.

Oxygen Flow Rate

While equipment costs increase with size, the same principle applies to feed streams. Whether it be the cost of the equipment to capture material or the actual material itself, streams must be optimized in the same manner as equipment. In this reaction (line 3 of the reaction mechanism, figure 01), oxygen is the limiting reactant and therefore is the basis for sulfur conversion in terms of the reactants. The impact of this magnitude is much less than the reactor volume but is still significant considering sulfur regulations are critical up until the hundreds decimal place for sulfur recovery. For fixed conditions, sulfur recovery increased in decreasing manner against oxygen flowrate such that the behavior is described to plateau, meaning that there is an optimal flow rate of oxygen to apply to the reactor (Zahid).

Reactor Temperature

Reactor temperature is a key component to any reactor and it is no different in this case. As mentioned in previous sections, these reactions being performed are exothermic and so the temperature of the reactor increases with greater reaction rates. The problem in this case is that the increasing temperatures also increase the catalyst deactivation which in turn reduces

the reaction rate and therefore the conversion (Zahid). The optimization of this system is measured through this relation and applied to the determination of how much cooling equipment (heat exchangers) must be applied to these reactors to keep these reactors at a desirable temperature. This is an example of how one optimization relationship from one piece of equipment is the deciding factor towards the design of another piece of equipment.

Safety Considerations:

As mentioned in the previous section, ammonia is a major by-product that has serious implications towards safety due to its corrosive properties. From a molecular scale, its lone pair of electrons are vulnerable to bond with nearby metals and in this context that means the metal composites of the reactor itself. This occurrence over time will result in thinning of reactor walls and therefore leaks. Leaks can be catastrophic for exothermic reactors especially in the case of pure ammonia leakage (Bohme). Pure ammonia that is in its vapor form will act as a bond since it will violently expand when subjected to room temperature. Also resulting from this ammonia leakage is the likelihood that sulfur, whether elemental or compounded with hydrogen, will also release which defeats the whole purpose of this process.

Hydrogen Sulfide is an extremely deadly chemical that can induce lethal effects on a full adult in the matter of seconds. A recent incident from Odessa, Texas demonstrates this phenomenon and shows why plants are installed with numerous rounds of security against sulfur exposure.

Suggestion

One suggestion on behalf of the author to improve this process is to implement a purification system towards the feed air, whether this stream will be split or not. Air has a 4:1 ratio of nitrogen to oxygen and as shown by figure 01 oxygen is the only species that participates in the required reaction while nitrogen just acts as an inert. Having this inert in this great of volume inside of the combustion chamber decreases heat transfer dramatically as it acts as almost an insulator for the system. It has been shown that the system is kinetically favorable at higher temperatures for this combustion reaction so long as the exothermic release of energy is contained than this method should be seriously explored. Not only that, reduction of nitrogen within this system will require a lower starting temperature as the temperature will rise in the system much greater for the same combustion conversion as heat will spread significantly easier. It should also be noted that a reduction of nitrogen will require a proportionately smaller system throughout the clause process as through no point of the SRU is the nitrogen deposited. This will mean, for the same extraction rate of sulfur, smaller pipes, smaller reactors, smaller condensers, etc. Not only that, since water is used to cool/condense heated product, less water will have to be supplied as heat transfer, that is the cooling in this context, will be that much more efficient due to the absence of nitrogen.

The most likely implementation of this proposal would have to be through a bulk-gas adsorbed in which nitrogen is extracted from oxygen to purify the air stream. This process is relatively energy-relaxed in comparison to the energy costs of combustions as pressure swing absorbers are primarily used for such processes (Cen). While this subject will give a net increase in area for equipment required the initial diagnostic of energy savings from this implementation is substantial.

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