SULFUR AND HYDROGEN SULFIDE RECOVERY

1. Introduction

The previous decade has seen a rapid shift in the mode of sulfur production with native sulfur recovery by the Frasch process being eliminated in the United States and in steep decline elsewhere (1). The increasing reliance on sour natural gas (CH_4, H_2S, and CO_2) throughout the World and the production of low sulfur fuels in refineries has resulted in nearly all of the World's elemental sulfur coming from conversion of H_2S. This trend will continue as very large reserves of oil with associated sour gas and new nonassociated sour natural gas reservoirs are developed in Kazakhstan and in the Middle East region (1). In addition, high sulfur-content bitumen recovered from Canada and Venezuela is expected to become a major source of synthetic crude oil. The accessible bitumen in Alberta, equivalent in volume to all crude oil reserves in Saudi Arabia, is upgraded to yield synthetic crude oil with associated production of large amounts of sulfur. By 2010, it is expected that production of 3 million bbl/day of synthetic crude oil in northern Alberta will yield 5 million tons of sulfur per annum (1). With these factors in mind, the bulk of this article will describe processes for removal of H_2S from large volume gas streams that originate from oil and sour natural gas recovery and refining.

2. H_2S Removal Using Aqueous Ethanolamines and Related Materials

2.1. General Comments. Removal of H_2S and CO_2 from industrial gas streams is practiced on a very large scale in the natural gas, refining, and hydrogen-production industries. Most processes are based on a closed recirculation system that includes absorption and chemical reaction to remove the H_2S and CO_2, then regeneration of the treating agent. Chemical solvents, eg, aqueous ethanolamines and a variety of physical and hybrid solvents, are used to perform this function (2). For chemical solvents, the key aspect of the technology (Fig. 1) is that H_2S and CO_2 are removed from high pressure gas streams in a contactor at moderate temperatures (15–35°C) and the chemistry is reversed at higher temperature (120°C) in a regenerator yielding low pressure acid gas, a mixture of H_2S and CO_2. As may be seen from the general scheme depicted in Figure 1, heat exchangers are used to heat the rich solvent and to cool the aqueous solvent to ambient temperatures such that residual levels of H_2S do not exceed 4 ppmv in the treated gas. The amount of CO_2 removal depends on the type of solvent used, operating conditions, and physical arrangement of the contactor. In some processes, selective separation of H_2S from CO_2 is achieved (3,4).

2.2. The Chemistry of H_2S and CO_2 Removal by Alkanolamines. All amines are weak bases and produce aqueous solutions with pH 10–12, the actual pH being dependent on the type of amine and the amount in solution (Fig. 2). Absorption of H_2S occurs by solubility and reaction with the free amine and the protonated amine to yield soluble hydrosulfide species (Fig. 2). The rates of these reactions are rapid with the result that removal of H_2S from a gas stream depends on mass transfer rates of the H_2S from the gas-to-liquid phases. Thus, the internal structure of an amine contactor is a critical design feature that along with countercurrent downflow of regenerated amine through the contactor, engenders highly efficient H_2S removal.

Absorption of CO_2 from a gas stream is more complicated as it involves two pathways, the bicarbonate and the carbamate mechanisms (Fig. 3). The bicarbonate pathway is minor under most circumstances as the first step, formation of carbonic acid (H_2CO_3), is equilibrium limited. The formation of the carbamate (Fig. 3) is rapid. As in the case of H_2S removal, the rate-limiting step is the mass transfer of CO_2 from the gas phase. Since at least one H atom must be bonded to the N atom of the amine for carbamate formation to occur, tertiary amines, eg, MDEA (Fig. 4) can be used for selective removal of H_2S due to the slow bicarbonate path kinetics, a desirable process for treating off-gas from reducing Claus plant tail gas units.

A large number of ethanolamines (Fig. 4) are now used in the industry with different blends and formulations for the various industrial gas mixtures under consideration (2). The choice of solvent depends on a number of factors related to treating pressure and temperature; energy requirements for regeneration; the need to leave CO_2 in the treated stream; degradation rates of the solvent due to irreversible reactions of H_2S, CO_2, and other trace impurities in the feed gas; and the potential for corrosion in a particular plant.

Key system design parameters are the amine solution strength, the rich amine loading, which sets circulation rate, the lean amine loading (required to attain 4 ppm H_2S in treated gas), and the regeneration energy required to the lean loading. Some typical parameters are given in Table 1.

Note that rich loading values are a function of pressure. Values given in Table 1 are good for absorber pressures $> 2700\,\text{kPa}$. Rich loading values should be checked against equilibrium values available in open literature.

2.3. Hybrid and Physical Solvents. As is implied by the name, physical solvents, eg, glycols and NFM (Fig. 5) remove H_2S and CO_2 from industrial gas streams without chemical reaction (5,6). Advantages of these solvents are they can accept higher amounts of H_2S and SO_2 per volume of solvent; less energy is required to regenerate the solvent; and these solvents possess increased efficiency over alkanolamines for removal of COS and mercaptans, two minor components sometimes present in industrial gases. A hybrid solvent, a mixture of an ethanolamine and a physical solvent, is used when a combination of the properties of two solvents is required (5). Overall, nearly all application needs can be met by integration of design and solvent choice.

One limitation of both amine and physical solvent processes is that the loaded solvent dissolves some CH_4 or other hydrocarbons. Thus, the regenerated acid gas contains H_2S, CO_2, and CH_4, and aromatic and larger aliphatic hydrocarbons if these materials are present in the raw gas. Usually, the hydrocarbon content of the acid gas does not exceed 1 vol.%, but even this small amount can have a significant impact on the operation of downstream sulfur recovery units. Physical solvents typically absorb significantly more hydrocarbons than chemical solvents.

3. Conversion of H_2S to Elemental Sulfur by the Claus Process

3.1. General Comments. The original Claus process envisaged direct oxidation of H_2S (2) using air in a catalytic unit, but the associated temperature rise could not be controlled when significant amounts of H_2S were present.

$$\mathrm{H_2S} + \frac{1}{2}\mathrm{O_2} \longrightarrow \frac{1}{8}\mathrm{S_8} + \mathrm{Heat}$$

This difficulty was overcome by designing a multistage process in which the heat could be removed sequentially in a number of units (Fig. 6). A modern Claus sulfur recovery plant (SRU) is a complex system consisting of a high temperature furnace stage, a series of catalytic converters operating at successively lower temperatures, possibly a tail gas unit for improved sulfur recovery, and an incinerator (7). Overall, the SRU system can be designed to achieve $> 99\%$ conversion of the SRUs inlet H_2S to sulfur. When state of the art tail gas units are applied, $> 99.8\%$ sulfur recovery is possible. Part of the complexity of the Claus process arises from the fact that elemental sulfur exists in two main forms: S_2 at temperatures $> 500°C$ and S_8 below that temperature. The two allotropes readily interconvert as the temperature crosses the $500°C$ threshold.

$$4\mathrm{S_2} \rightleftharpoons \mathrm{S_8} + \mathrm{Heat}$$

The bond-breaking process to form S_2 accounts for the unusual behavior for the equilibrium % sulfur recovery as a function of temperature (Fig. 7), as formation of sulfur at high temperature is endothermic. The overall enthalpy changes for both the furnace and catalytic steps of what is usually referred to as the modified-Claus process are given in Figure 8. Note that the furnace stage, despite producing S_2 in an endothermic process, is, overall, exothermic because of the formation of SO_2 and H_2O. Oxygen input, either via air or O_2 enriched air, can be adjusted to control the product gas H_2S/SO_2 ratio leaving the furnace. As Figure 8 shows, the furnace produces sulfur as well as SO_2 with the latter used to react with H_2S in the downstream catalytic stages in a 2:1 ratio. This ratio control is usually achieved by analysis of sulfur species in the tail gas, with feedback of that information to the air/O_2 flow control devices.

The catalytic stages are operated at successively lower temperatures to achieve increased conversion to sulfur (8) (Figs. 6 and 7), but within the dew point constraint that liquid sulfur must not be formed inside the pore structure of the catalyst to avoid mass transfer limitations. The simplified equation for production of sulfur in the catalytic converters is as follows:

$$2\,\mathrm{H_2S} + \mathrm{SO_2} \rightleftharpoons \frac{3}{8}\mathrm{S_8} + 2\,\mathrm{H_2O} + \mathrm{Heat}$$

The catalysts used in the converters are based on either alumina or titania, with many variations and composite materials now applied to achieve high efficiency and continuous operation over many years. The temperature regime used in the catalytic converters ($< 350^\circ$C) is such that S_8 is now formed by an exothermic process. For equilibrium processes, Le Chatelier's principle states that a system will move to oppose disturbances to the system. As such, if sulfur is removed between the catalytic stages by condensation, the system moves toward increasing conversion. The need for interstage condensation of liquid sulfur requires gas reheating to avoid subdew point operation in the converters (converters, condensers and re-heaters are designated conv., C and R in Fig. 7).

3.2. The Principles of the Claus Furnace. The furnace stage of the Claus process requires an alumina refractory lined reaction chamber and a waste heat boiler to remove the heat of reaction, generally by production of steam (Fig. 9). Steam or a heated fluid is produced in the WHB. This high pressure steam (typically 1050–4200 kPag) can be utilized in other parts of the plant for heat. This high pressure steam can be utilized in the amine plant to drive the regeneration units, to drive steam turbines in the STU, or may be exported. The configuration of the burner and internals of the furnace chamber are designed to control the shape of the flame, to avoid hot spots developing on the refractory lining, and to ensure good mixing of air and inlet acid gas. These factors are particularly important with use of oxygen-enriched air or pure O_2 supported combustion as flame temperatures can easily exceed the softening point of the alumina brick lining (1700–1800°C). The simplified chemistry given in Figure 9 does not adequately describe the very complex combustion system of the furnace as H_2, CO, CS_2, and COS are nearly always found in addition to the major products of sulfur, H_2O, SO_2, and unreacted H_2S. New work on Claus furnace chemistry, much of which is summarized in a review article (9), shows that H_2 may arise by a series of partial oxidation processes and dissociation of H_2S in the anoxic zone of the combustion chamber [Figs. 10 and 11]. The formation and retention of H_2 in the process gas, a matter related to the design of the WHB among other factors, is of considerable interest as H_2 is a necessary component for tail gas units that produce H_2S for recycle to the front end of the plant.

The formation of COS and CS_2 is related to the presence of CO_2 and CH_4 or other hydrocarbons in the acid gas fed to the main burner of the furnace (10,11). Carbon dioxide can be a major constituent of acid gas stream, along with CH_4 and other hydrocarbons that are present as a result of their solubility in rich amine systems. The highly reducing conditions of the anoxic region of the combustion chamber lead to the formation of COS and CO from CO_2, as follows:

$$\begin{aligned} CO_2 + H_2 &\longrightarrow CO + H_2O \\ CO_2 + H_2S &\longrightarrow COS + H_2O \\ 2\,CO + S_2 &\longrightarrow 2\,COS \\ 2\,CO_2 + S_2 &\longrightarrow CO + COS + SO_2 \end{aligned}$$

Each of these species presents significant challenge to the operator as COS must be eliminated in the catalytic converters and CO must be destroyed in the incinerator.

It has been shown that CS_2 arises only from hydrocarbons and not from CO_2 as had been assumed for many years (10). The solubility of CH_4 and other hydrocarbons in the loaded amine results in $\sim 0.5-1.0$ vol.% hydrocarbon leaving the amine regenerator with the acid gas. Thus, formation of CS_2 and even soot under unfavorable conditions is a perennial difficulty of Claus furnace operation (Fig. 12). If the acid gas is high in H_2S content, the overall temperature of the anoxic chamber may be high enough for complete destruction of COS and CS_2 as it is formed:

$$CS_2 + 2\,H_2O \longrightarrow 2\,H_2S + CO_2$$

$$COS + H_2O \longrightarrow H_2S + CO_2$$

$$CS_2 + SO_2 \longrightarrow CO_2 + 3/2\,S_2$$

$$2\,COS + SO_2 \longrightarrow 2\,CO_2 + 3/2\,S_2$$

But, the large quantity of CO_2 in the acid gas from natural gas operations results in too low a temperature for complete CS_2 and COS destruction. This situation may have to be rectified in the downstream catalytic stages to avoid low total sulfur recovery and excessive emissions.

Due to the presence of nitrogen compounds in nearly all crude oils, refinery Claus plants must be configured to deal with an NH_3-containing stream originating from the refinery hydrotreating units. In major conurbations, transport of ammonia is highly regulated and banned in some jurisdictions. Therefore, technology has been developed for conversion of the NH_3 to N_2 in the partially oxidizing regime of the Claus furnace typically with temperatures of $\sim 1200°C$ required. In most cases, specialized burners must be employed with injection of the NH_3-containing stream into the furnace chamber so as to avoid conversion to NO_x. The chemistry of this process (Figs. 13 and 14) has come under intense scrutiny in the last 10 years (12) with implementation of commercial strategies that take advantage of the rapid conversion of NH_3 to N_2 by reaction with SO_2 (Fig. 14).

Overall, the furnace stage can be responsible for 65–70% of the sulfur produced in the entire plant (Fig. 7). As is evident from the preceding discussion, the high temperature and anoxic conditions of the system lead to a very complex mixture of gases, in addition to sulfur, SO_2, and water. In a “classic” Claus plant, O_2 supply to the furnace is regulated to leave some H_2S in the product gas such that a 2:1 H_2S/SO_2 ratio is obtained for the catalytic stages. However, high sulfur recovery and elimination of sulfur-based emissions from the plants means, that in many cases, O_2 supply is regulated to produce an H_2S/SO_2 ratio of 4 or greater since many modern tail gas units work most efficiently under this condition.

A Claus SRU typically contains at least two catalytic reactors (converters) (Fig. 6) to further promote H_2S/SO_2 reaction to form sulfur and increase recovery to 95–97%. These reactors generate low pressure steam that can provide much of the amine regeneration energy.

3.3. The Principles of Claus Catalysis.

The principles of operation of a Claus converter are well known, but recently it has become clear that a detailed understanding of the chemistry of this process is helpful in practical operation of the units (13). A catalyst speeds up a chemical reaction by lowering the activation energy of the process. In the case of the Claus reaction, it is thought that adsorption of SO_2 onto the surface weakens the bonds in that molecule and activates it towards attack by H_2S (Fig. 15). One ramification of this adsorption is that a deficit of SO_2 may be observed in the period shortly after start-up of a new catalyst bed, resulting in the tail gas analyzer “overadjusting” air or O_2 supply to the main burner. It is generally accepted that the catalyst bed must be preheated to the operating temperature (300−340°C for the first converter) before introducing process gas to the catalyst. Preheat of process gas leaving the upstream sulfur condenser is achieved by either O_2-fired combustion systems, heat exchange units or by electric heaters, as previously described.

The equilibrium limitation of the Claus reaction is illustrated by the K_p values (Fig. 16) calculated for the 120−500°C range. The actual conversion to sulfur is dependent on the amount of water already in the process gas from the upstream amine unit and that produced in the furnace stage. Clearly, it would be very beneficial to configure a Claus process that includes both water removal and sulfur condensation after all stages but, as yet, no technology has been developed that would allow this improvement to be implemented. The fact that a catalyst has to be used at all illustrates that the gas-phase Claus reaction is too slow for practical purposes at 120−350°C. Moreover, as depicted in Figure 17, the practical operation of a Claus converter is actually an interplay between three factors: equilibrium limitations (Fig. 7); reaction kinetics; and sulfur dew-point control; with these last two factors being the overriding issues for commercial operation.

A valuable insight into the catalytic chemistry of the Claus process is obtained from the observation that sulfate and thiosulfate species can be found on alumina and titania that have been used in Claus service (14). Moreover, as a general rule of thumb, the amount of sulfate found on the catalyst increases as the temperature of operation decreases (Fig. 18). In the past, it was generally accepted that sulfate was an artifact of O_2 ingress into the system either as a result of poor combustion in the furnace stage or as a consequence of direct fired reheaters upstream of the converter. However, sulfate-contaminated alumina is found in plants in which the furnace operates efficiently and which use indirect (no O_2) reheat of the gas. Of course, unless the main burner is operating so inefficiently as to allow air/O_2 to stream through the furnace and the WHB, one may well ask the question as to how O_2 could possibly survive a 1200°C reaction chamber that always contains excess fuel (H_2S and S_2).

A mechanistic scheme for the reaction of H_2S and SO_2 (Fig. 19) reveals that sulfate forms as part of the catalytic cycle and should reach a steady-state concentration on the catalyst surface that is dependent on the temperature and the amount of H_2S in the process gas. Laboratory studies confirmed that sulfate was always produced during the Claus reaction on alumina and titania under conditions that rigorously excluded O_2.

4. Practical Implications of Sulfate Formation on Claus Catalysts

4.1. O_2 Carry-over. The most important implication of natural sulfate relevant to commercial operation of Claus converters is that the presence of sulfate is not justification alone for change out of the catalyst during a turnaround.

Key factors in making the decision to replace the catalyst are Claus reaction performance, hydrolysis reaction performance, catalyst surface area and available pore volume, and the carbon content (from carbon−sulfur polymer, carsul) of the catalyst.

Although direct-fired reheaters are becoming less common for a variety of reasons, a valid question is whether O_2 scavenging catalysts, designed to prevent sulfate formation, should be used in Claus converters. An O_2 scavenging catalyst is usually an iron oxide modified alumina that is designed to remove low levels of O_2 from the process gas that, most probably, works via the following chemical cycle:

$$2\,Fe^{II} + 2\,H^+ + 1/2\,O_2 \longrightarrow 2\,Fe^{III} + H_2O$$

$$2\,Fe^{III} + H_2S \longrightarrow 2\,Fe^{II} + 2\,H^+ + 1/8\,S_8$$

In addition to the natural sulfate formation discussed earlier in this article, it is known that O_2 will cause excessive and, perhaps, irreversible sulfate formation. Since iron oxide promoted alumina is an efficient Claus catalyst in addition to being an O_2 scavenger, many plants employing direct fired reheaters incorporate an O_2 scavenging catalyst as the top layer in each converter downstream of such a reheater.

4.2. Ratio Control, CS_2 and COS Conversion. The overall chemistry of the catalytic conversion of H_2S/SO_2 (Fig. 19) is a controlling factor in determining how much sulfate resides on a Claus catalyst. The amount of sulfate is important because it has been determined that although sulfate is an integral part of the Claus conversion chemistry because it produces thiosulfate ($S_2O_3{}^{2-}$), it also inhibits conversion of carbon disulfide (CS_2) and carbonyl sulfide (COS), species invariably found in Claus process gas. Since efficient catalytic conversion of CS_2 and COS is paramount to H_2S/SO_2 ratio control due to reformation of H_2S in the hydrolysis reactions below, understanding the factors that control sulfate amounts, hence catalytic activity for CS_2 conversion, are relevant to plant control.

$$CS_2 + 2\,H_2O \longrightarrow 2\,H_2S + CO_2$$

$$COS + H_2O \longrightarrow H_2S + CO_2$$

Interestingly, just as predicted by the mechanism illustrated in Figure 19, the amount of sulfate found on a catalyst is dependent on the H_2S/SO_2 ratio (and, indeed, H_2S quantity) in the process gas (Fig. 20**a**). Furthermore, there is a direct relationship between CS_2 conversion and ratio or, of course, sulfate amount (Fig. 20**b**). These observations have two very important ramifications to operation of Claus plants. The first is that plants operated at deliberately high H_2S/SO_2 ratios, as is the case for those with direct oxidation or reducing tail gas systems, will experience superior CS_2 conversions (usually $> 85\%$). Second, it would seem that the practice of catalyst rejuvenations for sulfate removal at high ratio for plants that normally operate at a standard 2:1 ratio has no merit since the sulfate level will simply readjust to its natural sulfate level almost immediately on reestablishment of the working H_2S/SO_2 ratio. This conclusion has been justified by observations in the laboratory (13) that reveal "normal" sulfate levels are reestablished within 2 h of restart of a converter at the new H_2S/SO_2 ratio. This comment should not be taken to infer that high ratio H_2S/SO_2 soaks are of no value as it has been shown that "carsul" can be removed by this process.

The level of CS_2 conversion is then determined by the H_2S/SO_2 ratio, the temperature of operation of the converter, and the type of catalyst. As already discussed, high ratio operation increases conversion of CS_2 and COS, but the converter must also be operated at appropriate temperatures and space velocities in order to achieve optimum CS_2 conversion. In practice, a high quality alumina will enable 90% CS_2 and total COS conversion at 330°C and a $1000\,h^{-1}$ space velocity. If CS_2 is anticipated to be a significant problem, the first converter could be designed to operate at a lower space velocity. The more usual strategy has been to utilize titania as all or part of the catalyst in the first converter as it is considerably more active than alumina for CS_2 conversion. Although titania is very efficient in catalyzing the hydrolytic conversion of CS_2 and COS, it has been established that it also promotes CS_2 conversion by reaction with SO_2. As may be seen from the data plotted in Figure 21, titania very effectively promotes the CS_2/SO_2 conversion reaction, but alumina is, in comparison, only a weak catalyst for this process (15). Most often, when titania is used as a composite catalyst bed with alumina, it is used as the lower layer of catalyst in order to protect the more expensive catalyst from particulate matter entering with the process gas.

4.3. Catalyst Degradation by BTX. The formation of sulfate as part of the Claus reaction catalytic cycle is also an important factor in controlling catalyst degradation by BTX. The abbreviation BTX is the acronym given to a collection of aromatic hydrocarbons that are sometimes found in Claus process gas (Fig. 22). These hydrocarbons may be present in the acid gas in refineries and in sour gas processing plants, although their presence tends to have a much greater consequence in the gas plants where CO_2 is present in high concentrations. In these cases, low furnace temperatures or some acid gas by-pass to the first converter results in some BTX entering the catalytic units. The overall problem of having BTX in the gas is that chemical interaction with sulfur results in polymeric carbon–sulfur junk (carsul) accumulating in the pore structure of the catalyst. Xylenes are, by far, the most troublesome aromatic, but toluene also results in significant degradation of the catalyst. The options of removing BTX from an acid gas or operating the reaction furnace at a high enough temperature to completely destroy these aromatics are technically difficult and expensive (16). Designers are advised to consider measures in the gas treating unit to reduce BTX pickup.

Sulfate on the catalyst appears to be the driving force for BTX degradation because the countercation to sulfate on the surface is a proton (H^+) (it could also be an aluminum cation) and this Brønsted acidity (Lewis acidity in the case of an aluminum cation) initiates reactions with the electron-rich aromatics, BTX (Fig. 23). Since the positively charged aromatic species are surrounded by a sea of sulfur, rapid $C — S$ bond formation proceeds with production of carsul that occludes the catalyst surface. Laboratory experiments confirmed that sulfate was a key player in this chemistry as it was seen that alumina catalyst that had not been exposed to Claus conditions (no sulfate) did not promote reaction with xylene or other aromatics (17). Thus, any oxide that forms a stable sulfate at Claus reactions conditions will promote both H_2S/SO_2 conversion and BTX degradation.

4.4. Tail Gas Processing. A standard Claus sulfur recovery system consists of a furnace and two or three catalytic converters, which, as is evident for the theoretical sulfur recovery (Fig. 7), limits total sulfur recovery to 95–98%. Environmental considerations have lead to legislated limits that stipulate >99% recovery in most regions of the World, although the total sulfur recovery required is often linked to the capacity of the plant. Many regions of the world now require a minimum 99.8% recovery of all sulfur contained in the SRU feed gas. The regulations have lead to the development of a variety of “tail gas” treatment options to achieve recoveries $> 99\%$ (2).

5. The Claus Reaction at Subdew Point Conditions

It is clear from Figure 7 that operation of a converter bed at 125°C would be advantageous as equilibrium limitations for conversion to sulfur are minimized at these temperatures. Contrary to regular Claus reactors, the subdew point reactors are operated at these low temperatures where sulfur will condense. As a result, subdew point systems require two or more catalyst beds in order that removal of the sulfur can be accomplished off-line for one of the beds. The basic features of the process are that the inlet H_2S/SO_2 ratio of 2 is maintained as closely as possible as any deviation from this value will decrease conversion to sulfur (Fig. 24). As discussed earlier, catalysts work by adsorption of materials on the surface, reaction of the adsorbed species, and desorption of the products, sulfur, and water in this case. Clearly, water will still be desorbed to the gas phase at 125°C, but sulfur will accumulate at the catalyst surface.

The catalyst bed is regenerated by introducing hot process gas (300–330°C) into the catalyst bed to evaporate the sulfur from the catalyst pore structure (Fig. 25). At the end of the uptake cycle, the amount of SO_2 and other materials adsorbed on the surface is a function of that temperature. Most probably, more SO_2 can be held on the catalyst surface at the lower temperatures employed in the uptake mode (125–130°C). Since the process gas used for regeneration is rerouted to the other converters and the subdew point beds in uptake mode, SO_2 is removed preferentially from the gas stream as the subdew points beds are switched from uptake to regeneration and vice versa. Indeed, from a practical viewpoint, a spike in emissions from the incinerator is observed during the switch-over period. Obviously, such emission spikes can be minimized with longer uptake/regeneration cycles.

6. Direct Oxidation of H_2S

Another major tail gas process for increasing the total sulfur recovery beyond 99% are technologies based on direct oxidation of H_2S using catalytic methods (Fig. 26) (18). It is very important to remove as much SO_2 as possible from the tail gas before the direct oxidation step as this species is not treated and, consequently, will contribute to emissions in the final incinerator step. As in the reducing tail gas technologies, the plant is operated to achieve a high H_2S/SO_2 ratio (4–8) before the tail gas enters the direct oxidation unit. This is accomplished by restricting the air supply to the main burner of the Claus furnace and, in an adaptation recently introduced to commercial operation, by placing a layer of hydrogenation catalyst at the bottom of the catalyst bed preceding the direct oxidation reactor. This new strategy then decreases the quantity of SO_2 entering the oxidation reactor, possibly allowing a lower amount of SO_2 leaving the converter in comparison to equilibrium prediction. The chemistry of the hydrogenation on the reducing catalyst in the second converter may be similar to that described for the low temperature reduction described in the previous section.

The direct oxidation catalyst is based on iron species deposited on silica although various modifiers are used to limit secondary reactions that result in SO_2 formation. Silica is chosen because it is an oxide that does not form a stable sulfate and, thus, cannot promote the Claus reaction. This facet of catalyst behavior is important because use of a Claus active support would result in reconversion of sulfur to H_2S and SO_2 by the reverse Claus reaction. The catalytic cycle of the direct oxidation reaction formally involves an $Fe^{(III)}/Fe^{(II)}$ couple that is cycled by reaction of $Fe^{(II)}$ species with O_2 added in controlled amounts upstream of the direct oxidation reactor. Apparently, the catalyst can only be kept in an active state if excess O_2 is present in the tail gas. However, this feature of the process imposes a small limitation on overall recovery as sulfur vapor produced in the direct oxidation reaction can be converted to SO_2 in homogeneous or surface-catalyzed chemistry. Overall, direct oxidation tail gas treatment can result in 98.8–99.5% total recovery dependent on the original acid gas under treatment.

7. Reduction of Tail Gas Sulfur Species to H_2S

Another popular tail gas process that enables $>99.8\%$ total sulfur recovery is reduction of all sulfur species to H_2S with recycle of H_2S to the front end of the plant. A key feature of the process is that the plant is controlled to result in a high H_2S/SO_2 ratio (4–8) to limit the amount of SO_2 entering the tail gas unit. This technology (Fig. 27) was introduced in the late 1960s at a time when there was little concern about CO_2 emissions. Operation of the reducing gas generator/reheating unit at the front end of the plant, handling sour water from the quench unit and recycle of the H_2S, utilizing an amine unit, all have associated energy demands that result in considerable CO_2 emission. Note that the amine unit, not shown in Figure 27, processes the gas from the top of the quench column. The alumina-CoS/MoS_2 catalyst employed in the hydrogenation unit converts all sulfur species to H_2S although in the case of CS_2 and COS, it is thought that conversion occurs via hydrolysis reactions (Fig. 28). In original versions of the process, the H_2 and CO produced in the Claus furnace was supplemented by operation of a partial combustion system (labeled reheater in Fig. 27) in which CH_4 is burnt with a restricted air supply. This unit also serves to reheat the gas to $\sim 340°C$, the temperature required for operation of the catalytic unit.

In a drive to make the process more efficient, low temperature catalysts have been introduced that operate at ~240°C (19). This innovation has the very important effect of replacement of the partial oxidation system with an indirect reheating unit as supplemental H_2 is not required in most plants. All versions of this tail gas process require the use of selective tertiary amine systems to reject CO_2 from the treated gas and so avoid build-up of CO_2 in the plant.

8. Tail Gas Treatment in an Organic Solvent

The Claus reaction of H_2S and SO_2 can be carried out in liquid solvent, eg, polyethylene glycols, when a basic catalyst in present is the medium (2). The only process currently in operation was introduced by Institute Francois Petrol and, although used quite widely in Europe, it has not become popular in North America or elsewhere. The chemistry of this technology is simply the Claus reaction, so overall efficiency depends on maintaining a 2:1 H_2S/SO_2 ratio throughout the system. The liquid sulfur separates at the bottom of the reactor and is drawn off from the solvent. Periodic cleaning of the solvent is required to remove inorganic salts that build up in the glycol solution. Given the ratio control constraints and vapor losses from liquid sulfur handling, total sulfur recovery from plants employing the IFP process is in the range of 99–99.5%.

9. Recovery of Sulfur Values as SO_2

Oxidation of Claus tail gas converts all sulfur compounds to SO_2. In many cases, this simply represents the tail gas incineration step before final release of the tail gas to the atmosphere, but it is possible to capture that SO_2 in various forms (2). Such technologies are not used widely, but may be applied more extensively in the future. One adaptation involves conversion of the SO_2 to useful inorganic derivative taking the SO_2 directly from the tail gas while another utilizes a diamine solvent to capture the SO_2 for recycle to the front end of the Claus plant. These technologies may be limited by the markets for the inorganic derivatives in the former case and by issues of economics and process consequences of returning large volumes of SO_2 to the furnace in the diamine technology.

10. Small Scale Recovery of H_2S and Sulfur

A growing number of processes are being introduced to handle gas streams that produce <10 ton/day of sulfur in response to increased environmental awareness (2). The only process applied on a wide scale is based on aqueous iron systems that hold iron in solution using a sophisticated array of chelating compounds. The iron species oxidize H_2S to elemental sulfur and the iron is reoxidized by using air in chemistry related to that described in previous sections for O_2 scavenging and the direct tail gas oxidation. Sulfur is usually produced as a water-wet filter cake and is disposed of in landfill sites. Newer methods based on gas phase or subdew point catalytic oxidation have been introduced in Canada.

This technology is similar to the direct oxidation tail gas process, but the catalyst does not require excess air for continuous operation. Both the aqueous and the catalytic processes can be applied to H_2S removal from natural gas streams as well as to acid gases separated from the hydrocarbon feed.

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P. D. CLARK
University of Calgary

Table 1. **Typical Alkanolamine Parameters**

Amine	Concentration, wt %	Maximum rich loading, mol AG/mol amine	Maximum lean loading, mol AG/mol amine	Regeneration energy, kJ/m^3
MEA	15	0.40	0.12	334,440
DEA	25	0.45	0.06	278,700
MDEA	45	0.50	0.01	250,830
DGA	50	0.45	0.05	362,310

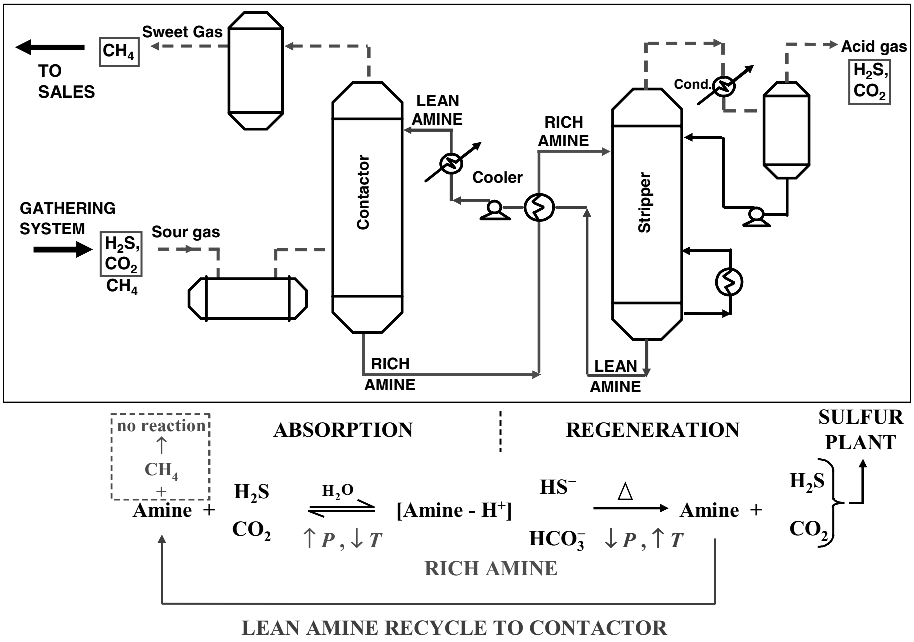


Fig. 1. Overview of amine sweetening process.

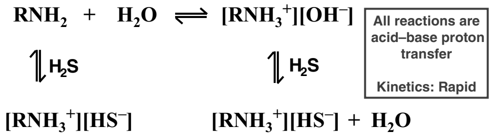


Fig. 2. The uptake of H_2S by aqueous amines. The efficiency of H_2S removal depends on the concentration of $[RNH_3{}^+][OH^-]$ (gas–liquid contact requires countercurrent flow of gas and liquids).

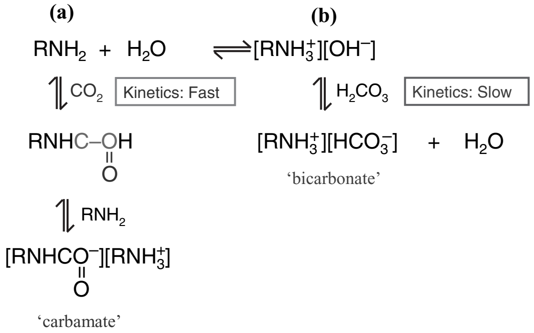


Fig. 3. The uptake of CO_2 by aqueous amines. The carbamate pathway is favored for primary and secondary amines only; tertiary amines take up CO_2 by bicarbonate route only.

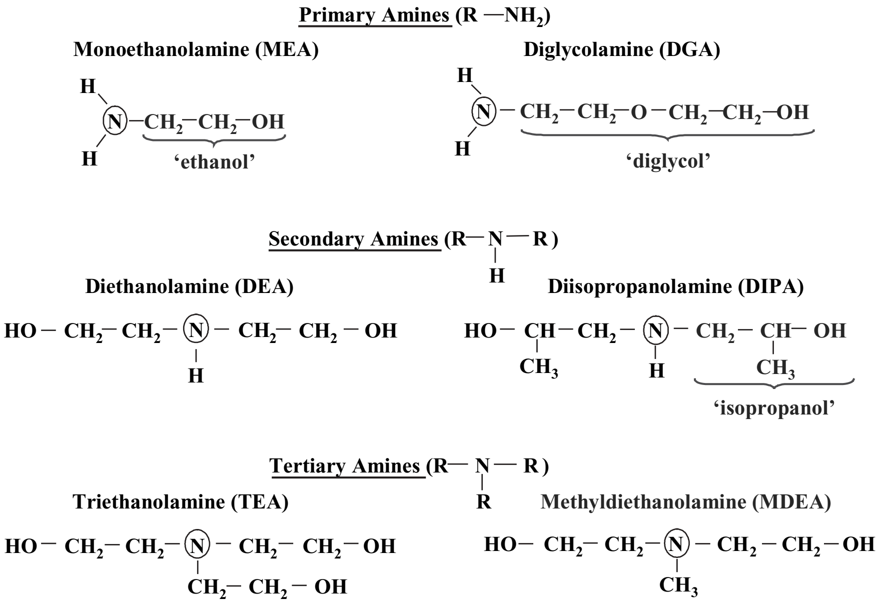


Fig. 4. Molecular structure of common gas treating amines.

Hybrid:

Sulfinol - Sulfolane / H_2O / amine (DIPA, MDEA)

Hybrisol - MeOH / H_2O / amine (DEA)

Physical:

Selexol - dimethylethers of polyethylene glycols
$CH_3O(CH_2CH_2O)_nCH_3$ ($n = 3 - 9$)

Morphysorb - *N*-formyl-morpholine ; *N*-acetyl-morpholine
(NFM) (NAM)

- **better removal of other S compounds (e.g., COS and RSH)**
- **higher coabsorption of hydrocarbons (than aqueous amine systems)**

Fig. 5. Representative physical sweetening solvent systems.

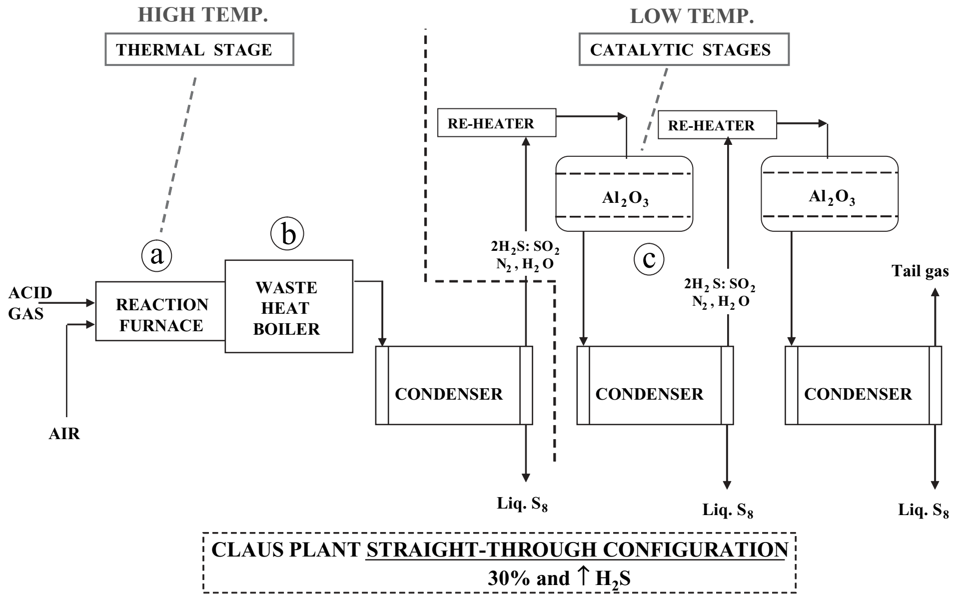


Fig. 6. Simplified process scheme for the modified-Claus sulfur recovery process.

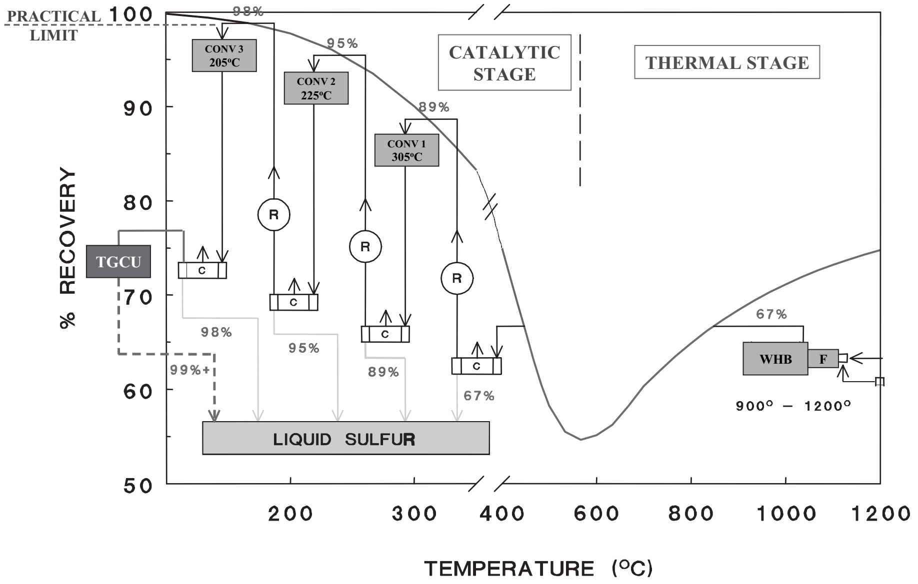


Fig. 7. Claus sulfur recovery.

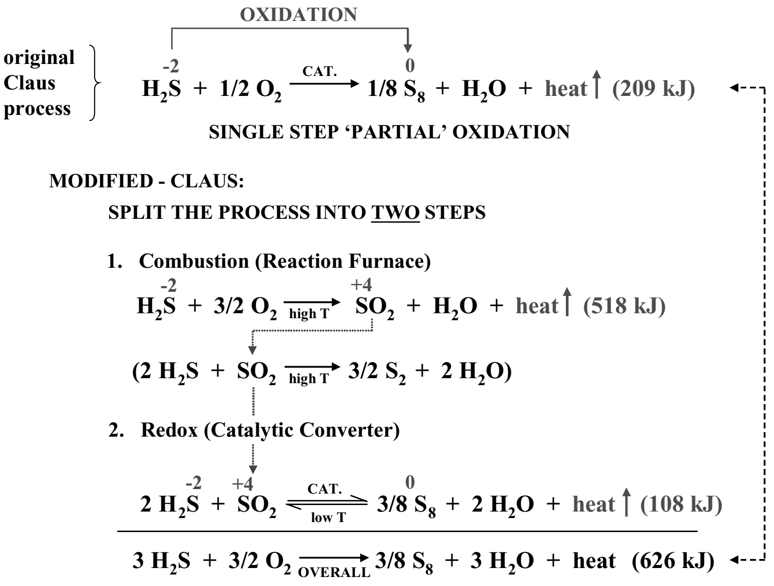


Fig. 8. Claus process overview.

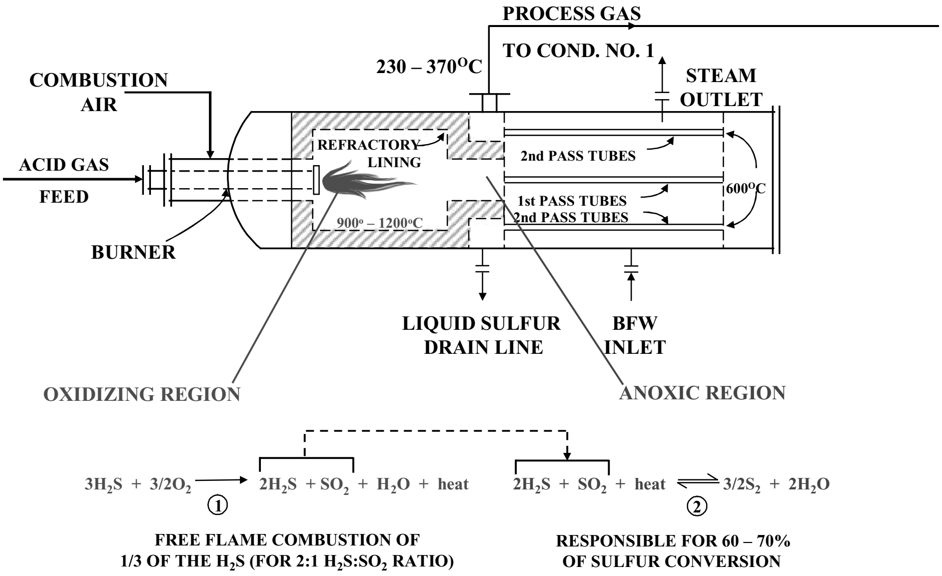


Fig. 9. Reaction furnace chemistry: Main reactions.

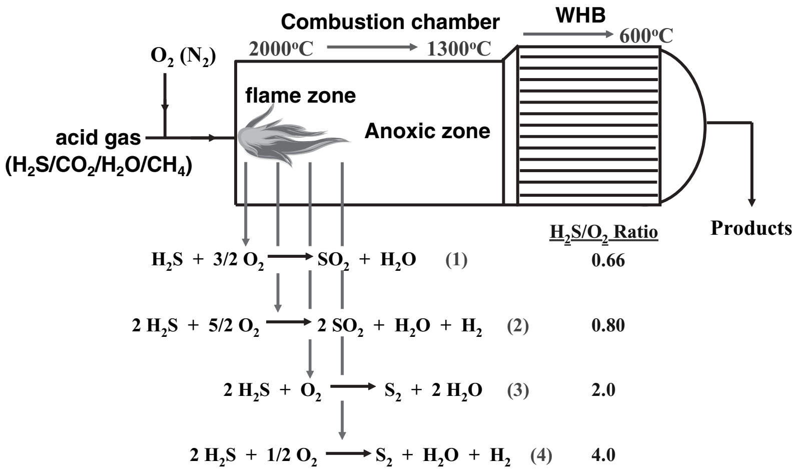


Fig. 10. Claus furnace: Primary combustion processes (fast).

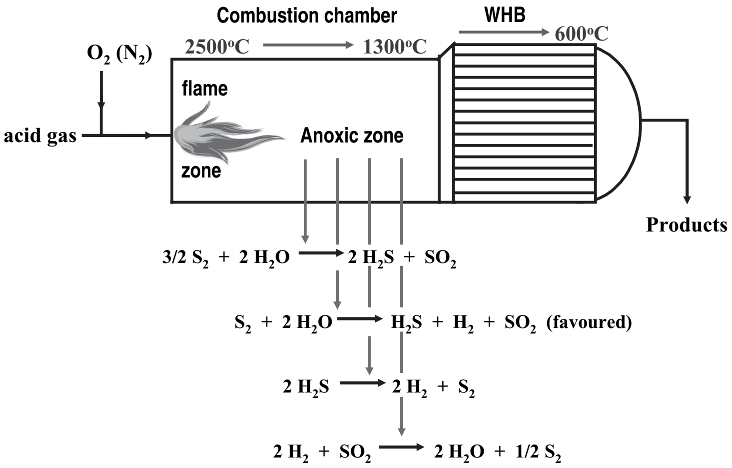


Fig. 11. Claus furnace: Anoxic, high *T* processes (sulfur species).

$$\left.\begin{array}{rl} CH_4 & \longrightarrow C + 2\ H_2 \\ C + H_2O & \longrightarrow CO + H_2 \\ CO + H_2O & \longrightarrow CO_2 + H_2 \\ \underline{\text{Overall}}\text{: } CH_4 + 2\ H_2O & \longrightarrow CO_2 + 4\ H_2 \end{array}\right\} \text{Endothermic reactions, a source of hydrogen}$$

$$\begin{array}{rl} \underline{\text{Also}}\text{: } CH_4 + 2\ S_2 & \longrightarrow CS_2 + 2\ H_2S \\ C + S_2 & \longrightarrow CS_2 \end{array}$$

<u>Note</u>: Other hydrocarbons also lead to CS_2

Fig. 12. Claus furnace: Anoxic, high *T* processes (hydrocarbons).

$$\left.\begin{aligned} 2\,NH_3 + 3/2\,O_2 &\longrightarrow N_2 + 3\,H_2O \\ 2\,NH_3 + O_2 &\longrightarrow N_2 + H_2 + 2\,H_2O \\ 2\,NH_3 + O_2 &\longrightarrow N_2 + 2\,H_2 + H_2O \end{aligned}\right\}\ \textbf{Exothermic}$$

$$\downarrow$$

$$\left.2\,NH_3 \longrightarrow N_2 + 3\,H_2\right\}\ \textbf{Endothermic}$$

➢ **More O_2 must be added to the combustion chamber**

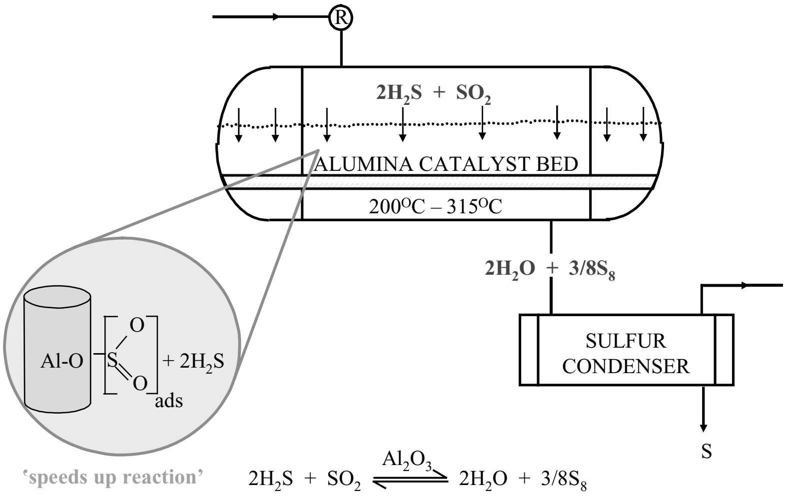
Fig. 13. Ammonia destruction in the Claus furnace.

Oxidation rates: $H_2S >> NH_3 \sim CH_4$

Consequences: $\underset{\text{(excess)}}{H_2S + 3/2\,O_2} \longrightarrow SO_2 + H_2O$

$$\left.\begin{aligned} 4\,NH_3 + 3\,SO_2 &\longrightarrow 2\,N_2 + 6\,H_2O + 3/2\,S_2 \\ 2\,NH_3 + SO_2 &\longrightarrow N_2 + 2\,H_2O + 1/2\,S_2 + H_2 \end{aligned}\right\}\ \text{Rapid reactions}$$

Fig. 14. Effect of rates of oxidation of ammonia destruction.



$$2H_2S + SO_2 \xrightleftharpoons{Al_2O_3} 2H_2O + 3/8S_8$$

RESPONSIBLE FOR REMAINING 1/3 SULFUR CONVERSION

Fig. 15. Claus converter chemistry: Main reaction.

The Claus Reaction

$$2\,H_2S + SO_2 \overset{K_{eq}}{\rightleftharpoons} 3/8\ S_8 + 2\,H_2O + \text{HEAT}$$

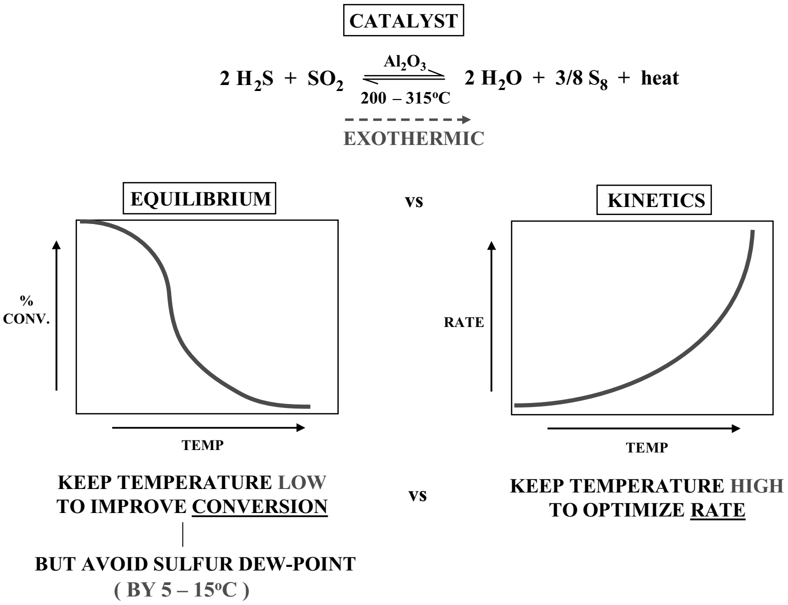
$$K_p = \frac{P_{S_8}^{3/8}\,P_{H_2O}^{2}}{P_{H_2S}^{2}\,P_{SO_2}}$$

K varies with temperature

Temperature	K_p
120°C	1.26×10^8
200°C	4.84×10^5
300°C	4.41×10^3
400°C	175
500°C	16.9

becomes larger at
lower temperatures
for exothermic rxns
—
Le Chatelier's principle

Fig. 16. Equilibrium position of a chemical reaction.



CATALYST

$$2\,H_2S + SO_2 \underset{200-315°C}{\overset{Al_2O_3}{\rightleftharpoons}} 2\,H_2O + 3/8\,S_8 + \text{heat}$$

EXOTHERMIC

EQUILIBRIUM vs KINETICS

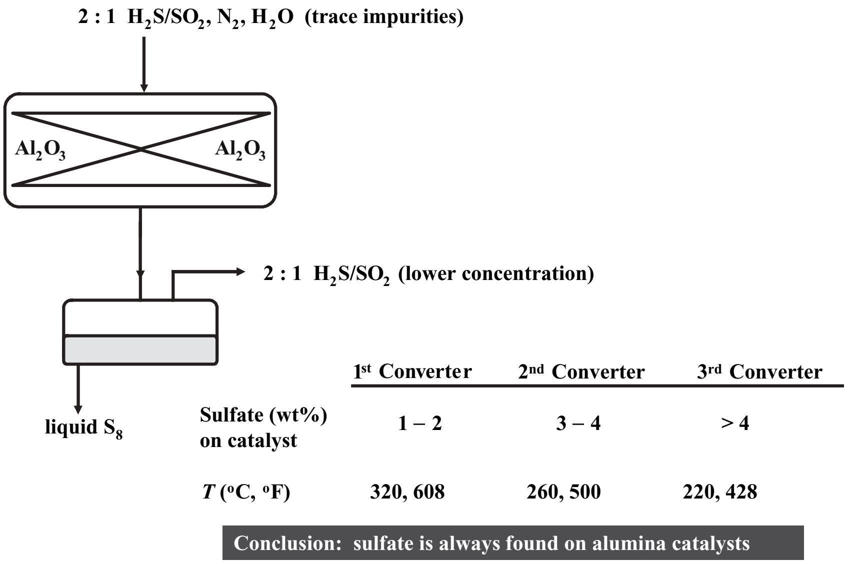
KEEP TEMPERATURE LOW
TO IMPROVE CONVERSION

vs

KEEP TEMPERATURE HIGH
TO OPTIMIZE RATE

BUT AVOID SULFUR DEW-POINT
(BY 5 – 15°C)

Fig. 17. Claus converter: Principles of operation.



	1st Converter	2nd Converter	3rd Converter
Sulfate (wt%) on catalyst	1 – 2	3 – 4	> 4
T (°C, °F)	320, 608	260, 500	220, 428

Conclusion: sulfate is always found on alumina catalysts

Fig. 18. Sulfate on Claus catalysts: Commercial observations.

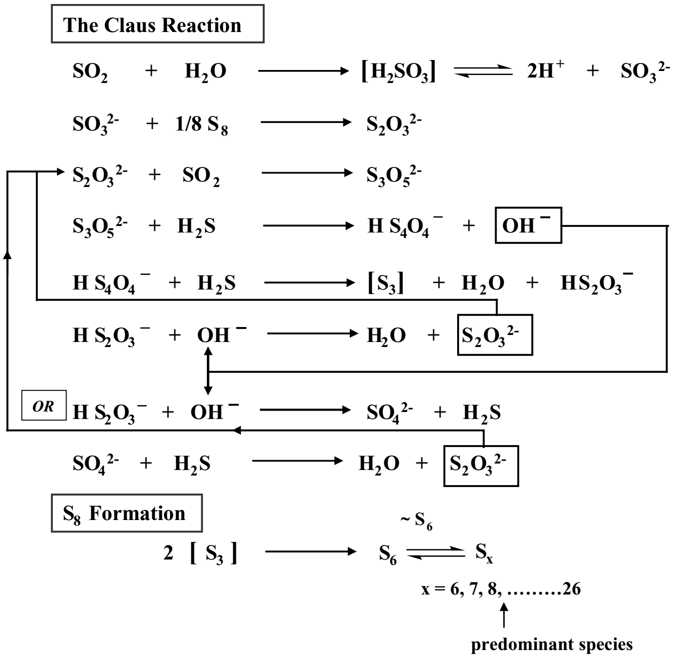


Fig. 19. How is sulfur formed on an Al_2O_3 Claus catalyst?

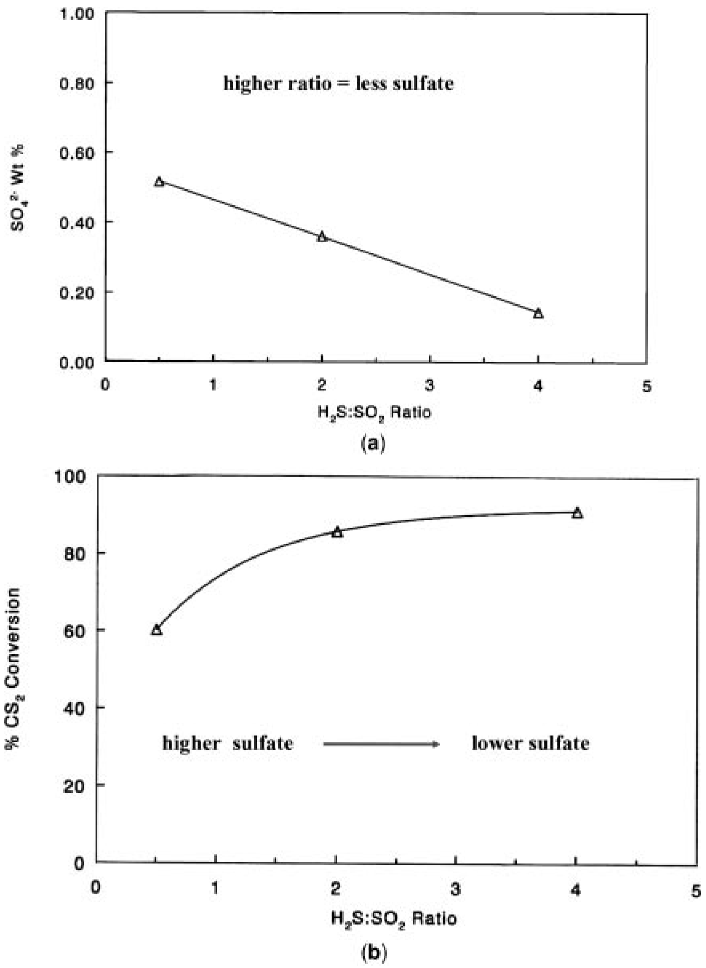


Fig. 20. (**a**) Average bed weight % SO_4^{2-} as a function of $H_2S:SO_2$ ratio in the sulfating environment at 320°C. (**b**) Steady-state CS_2 conversion as a function of $H_2S:SO_2$ ratio in the sulfating environment at 320°C.

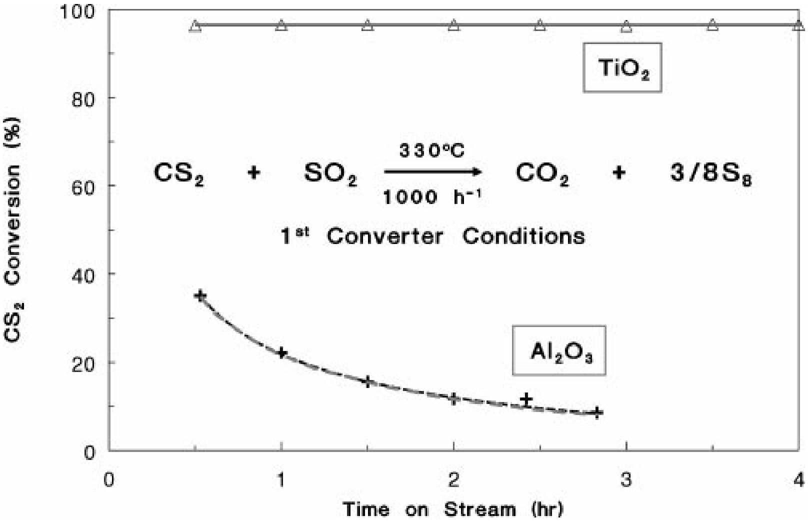


Fig. 21. The CS_2 conversion by direct SO_2 reaction. Titania more active than alumina.

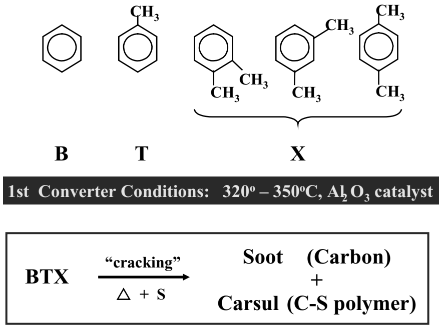


Fig. 22. Deactivation of Claus catalysts by aromatics.

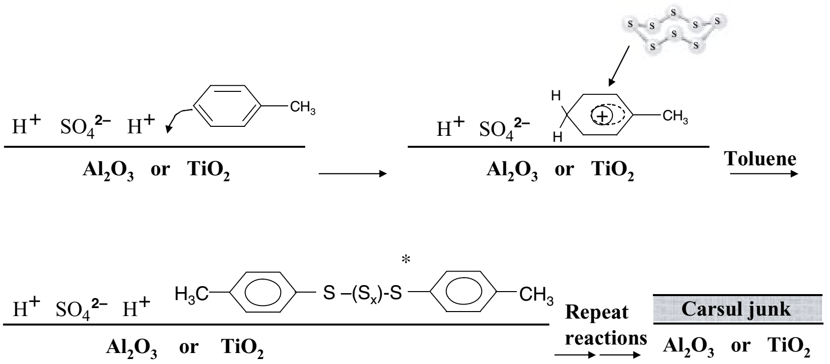
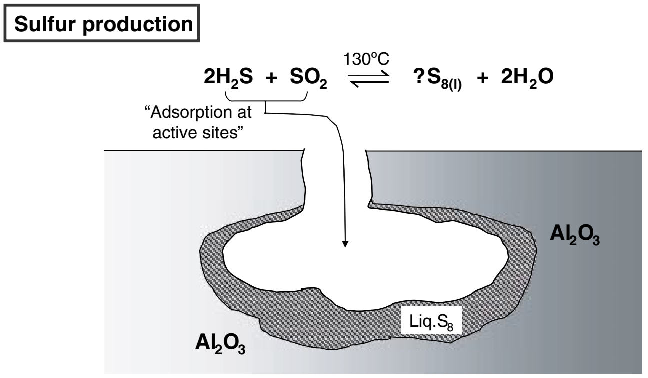
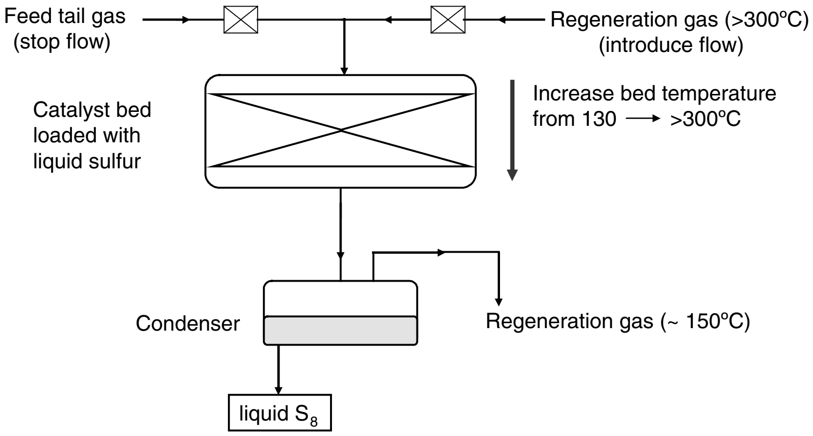


Fig. 23. A mechanism for catalyst degradation by BTX. *Immature carsul; substitution pattern changed for artistic convenience.



- Condensation of sulfur occurs in pore structure of catalyst
- Conversion to sulfur to equilibrium value until mass transfer effects prevents access of H_2S and SO_2 to active sites
- Sulfur production is controlled by the process temperature and control of ratio (2:1)

Fig. 24. The chemistry of subdew point Claus tail gas operation.



- Key point - exposes active alumina sites to SO_2 coverage at temperature of regeneration gas

Fig. 25. The principle of regeneration of a catalyst bed.

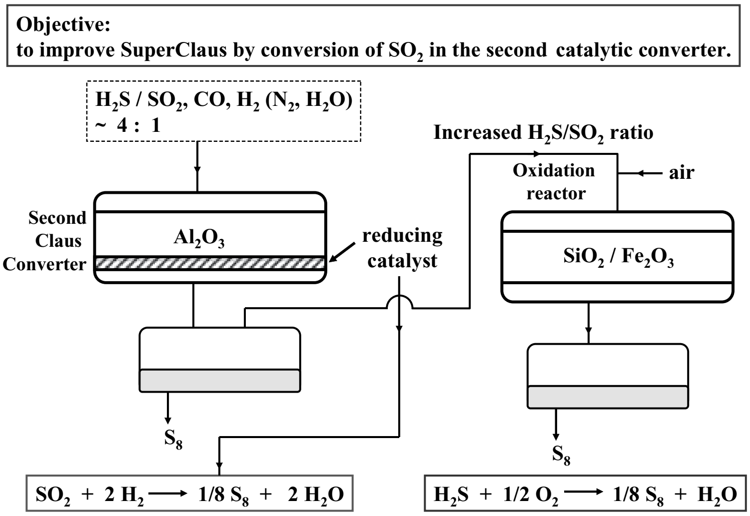
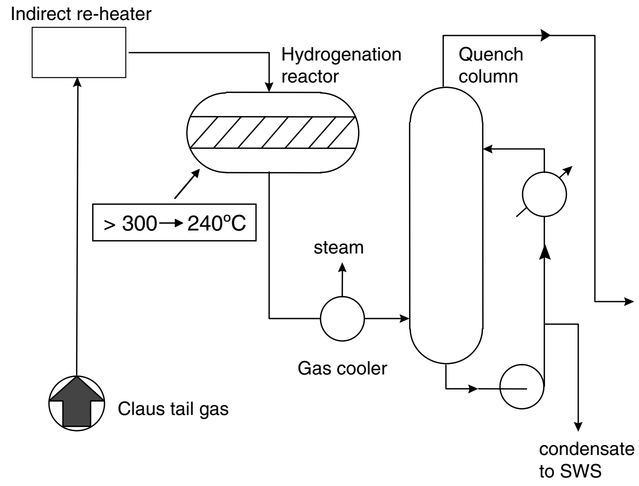
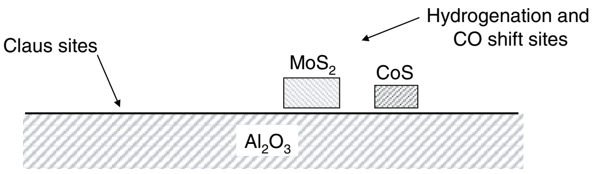


Fig. 26. Euro-Claus (Jacobs Nederland B.V.).



* Catalyst active at lower temperatures

Fig. 27. Low temperature tail gas reduction.



Claus chemistry (equilibrium favored at low temperatures)

$2\,H_2S + SO_2 \rightleftharpoons [S_3] + 2\,H_2O$

Hydrogenation chemistry

$S_3 + 3\,H_2 \longrightarrow 3\,H_2S$

$SO_2 + 3\,H_2 \longrightarrow H_2S + 2\,H_2O$

Shift chemistry

$CO + H_2O \longrightarrow CO_2 + H_2$

Hydrolysis chemistry

$CS_2 + 2\,H_2O \longrightarrow CO_2 + 2\,H_2S$

$COS + H_2O \longrightarrow CO_2 + H_2S$

Fig. 28. Low temperature reducing tail gas chemistry.