LIQUID SULPHUR DEGASSING: FUNDAMENTALS AND NEW TECHNOLOGY DEVELOPMENT IN SULPHUR RECOVERY

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Abstract

Liquid sulphur degassing remains an important component of a Claus sulphur recovery system as a result of the need to produce high purity liquid and solid sulphur (< 10 ppmw residual H_2S). Importantly, this process must be accomplished without increasing plant emissions. At present, several effective technologies exist for sulphur degassing, mostly based on air sparge of the liquid in a variety of contraptions. These processes produce large volumes of air contaminated with sulphur vapour, H_2O, H_2S and SO_2 which, if compressed back into the air supply systems, cause plugging and corrosion problems. Formerly, the contaminated air was flowed to the incinerator but this practice is calculated to lower total sulphur recovery by as much as 0.1 %.
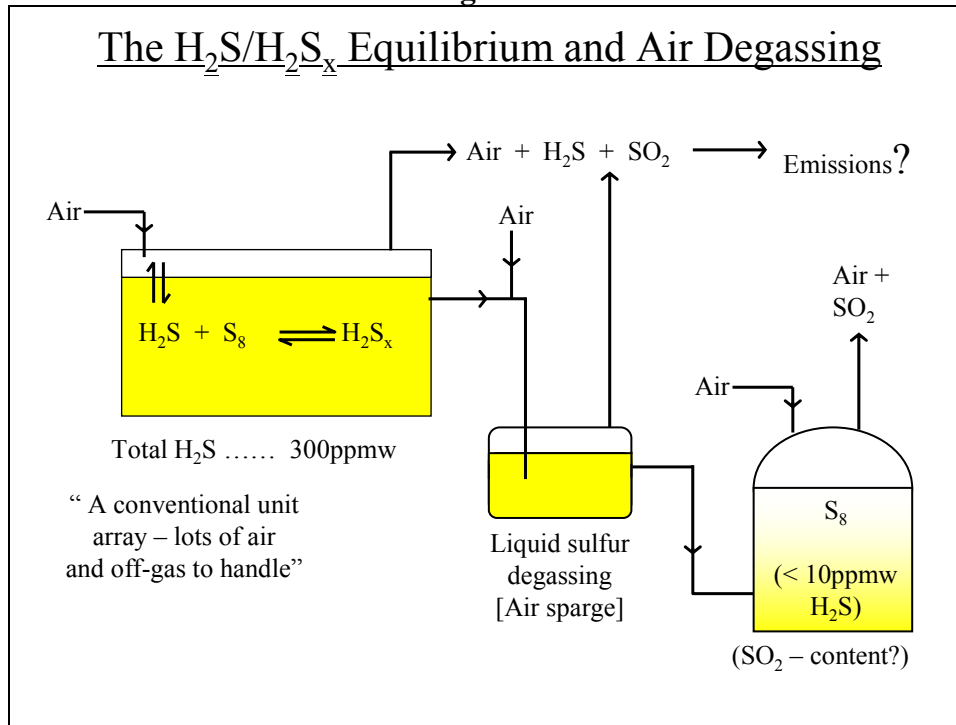
One objective of this paper is to review the fundamentals of sulphur degassing with air explaining how H_2S_x is decomposed and why SO_2 is always produced when air is used. Secondly, new data on liquid sulphur degassing with solid catalysts will be discussed, and it will be explained how this information could be applied to liquid sulphur degassing both upstream and downstream of the sulphur locks. These adaptations will avoid use of air and should improve overall sulphur recovery as well as achieve sulphur degassing.

Lastly, it will be shown that modifications to sulphur condensers throughout the plant may allow simultaneous degassing and, possibly, an increase in overall sulphur recovery.

Introduction

Liquid sulphur produced by the Claus process contains residual H_2S in both chemically combined and physically dissolved forms (Figure 1). The total residual H_2S in the liquid (200 – 400 ppmw) depends on numerous operational factors but its presence poses a considerable safety risk as degassing to headspaces in containers and even from solid formed from the liquid can lead to lethal gas phase concentrations. Without adequate draft in storage systems, concentrations may exceed the lower explosive limit for H_2S in air.

Figure 1

The H_2S/H_2S_x Equilibrium and Air Degassing

Air + H_2S + SO_2 ⟶ Emissions?

Air

Air

Air + SO_2

Air

H_2S + S_8 ⇌ H_2S_x

Total H_2S …… 300ppmw

" A conventional unit array – lots of air and off-gas to handle"

Liquid sulfur degassing [Air sparge]

S_8

(< 10ppmw H_2S)

(SO_2 – content?)

Commercial liquid sulphur degassing systems fall into three basic categories: air degassing, technologies which use a basic liquid catalyst with a gas sparge and methods which employ solid catalysts, also in combination with gas sparge. Air is the most common sparge gas as the off gases, contaminated with H_2S, SO_2 and sulphur vapour, can be combined with the air supply for the incinerator or the main Claus burner. Steam has also been used, typically in combination with liquid amine catalysts, but this sparge gas has become less popular as there is really no option but to pipe this steam to the incinerator, so increasing the overall sulphur emissions from the plant. It has been estimated that piping the degasser off-gases to the incinerator causes an overall loss of plant sulphur recovery efficiency of 0.1 %.

The first objective of this paper is to describe the chemistry of air degassing, alone and in combination with liquid catalysts, to explain the role of O_2 in decomposition of the polymeric form of H_2S (H_2S_x) and why SO_2 is always found in the off-gas. Indeed, the chemical mechanism of air degassing shows why attempts to use air degassing to achieve < 5 ppmw residual H_2S in sulphur lead to a product that can be highly contaminated with SO_2. Secondly, advances in solid catalyst degassing will be discussed explaining how Claus tail gas can be used as the sparge gas, a methodology which, possibly, presents new directions for improving overall sulphur recovery.
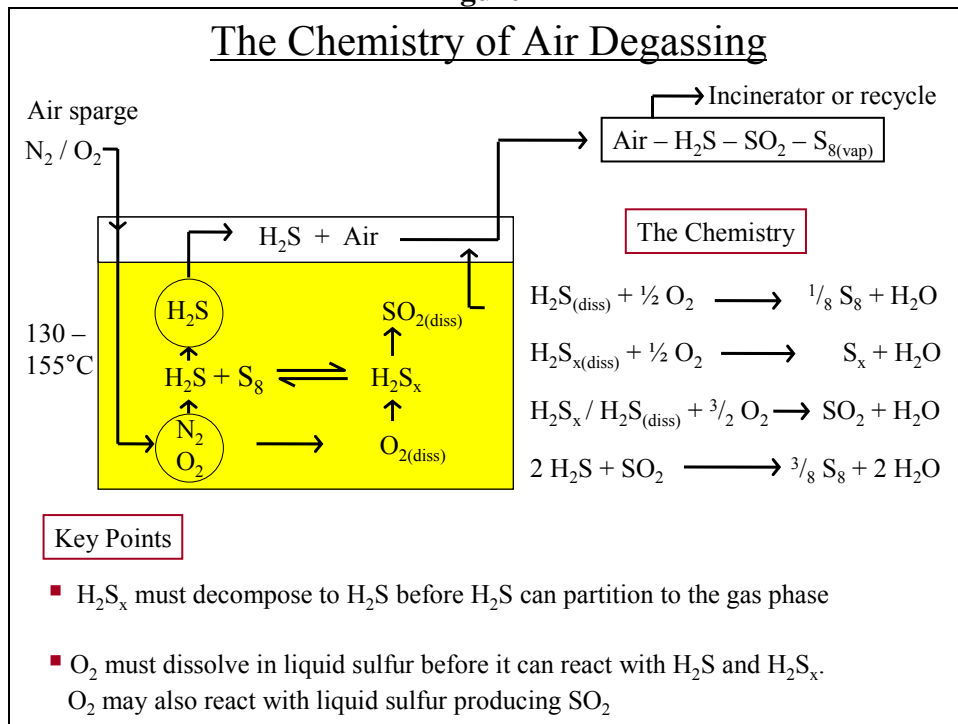
The Chemistry of Air Degassing

One mechanism for reduction in total residual H_2S content is that air bubbles simply aid the removal of physically dissolved H_2S so displacing the equilibrium governing decomposition of H_2S_x (Figure 2). If this was the only mechanism in play, no SO_2 would
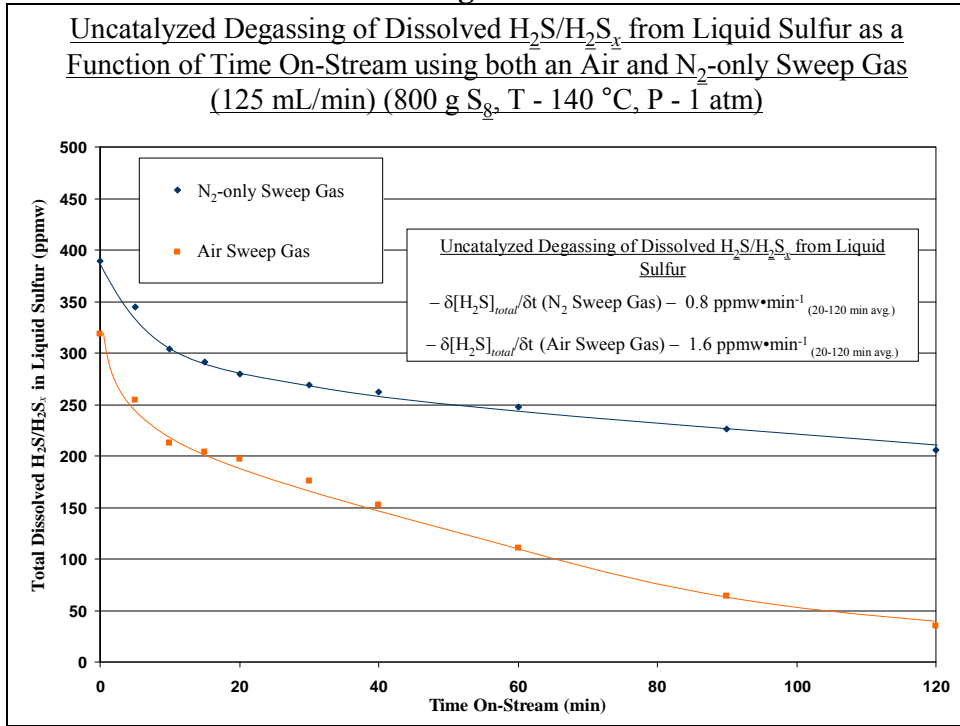
be formed. Moreover, if air simply removed physically dissolved H_2S by mass transfer to gas bubbles, nitrogen would work as well as air, but air is much more effective (Figure 3). As is suggested by the general equations in Figure 2, SO_2 can be formed by oxidation of either H_2S or H_2S_x. Also, SO_2 can be formed by reaction of O_2 with liquid sulphur (Figure 4), but this reaction is slow and would not explain the amount of SO_2 observed in commercial air degassing systems. The precise mechanism of air degassing likely involves specific reactions of the polysulphides with dissolved molecular oxygen. O_2 may initiate decomposition of H_2S_x by abstraction of an H-atom, a mechanism which automatically leads to production of SO_2 and H_2O (Figure 5). Thus, air degassing always results in both H_2S and SO_2 in the off-gas, most of the H_2S probably arising by sparging of physically dissolved species. If air degassing systems are designed for "deep" degassing (< 5 ppmw), typically by increasing the air flow, additional sulphur emissions occur due to liquid sulphur oxidation (Figure 4) and increased sulphur vapour losses. Since water is also a product of air degassing chemistry, degasser off-gases must be handled carefully to avoid corrosion by either elemental sulphur or via SO_2 (Figure 6).

Overall, air degassing occurs through a combination of mass transfer of H_2S to gas bubbles and through decomposition of H_2S_x, a process initiated by O_2. An adequate sparge gas flow and transport to and from the liquid is important because not only do these factors control removal of H_2S, they also control solution of O_2 in the liquid, a key factor in H_2S_x decomposition.

Figure 2

The Chemistry of Air Degassing

The Chemistry

$$H_2S_{(diss)} + \tfrac{1}{2} O_2 \longrightarrow \tfrac{1}{8} S_8 + H_2O$$

$$H_2S_{x(diss)} + \tfrac{1}{2} O_2 \longrightarrow S_x + H_2O$$

$$H_2S_x / H_2S_{(diss)} + \tfrac{3}{2} O_2 \longrightarrow SO_2 + H_2O$$

$$2 H_2S + SO_2 \longrightarrow \tfrac{3}{8} S_8 + 2 H_2O$$

Key Points

- H_2S_x must decompose to H_2S before H_2S can partition to the gas phase

- O_2 must dissolve in liquid sulfur before it can react with H_2S and H_2S_x.
  O_2 may also react with liquid sulfur producing SO_2

Figure 3

Uncatalyzed Degassing of Dissolved H_2S/H_2S_x from Liquid Sulfur as a Function of Time On-Stream using both an Air and N_2-only Sweep Gas (125 mL/min) (800 g S_8, T - 140 °C, P - 1 atm)

Total Dissolved H_2S/H_2S_x in Liquid Sulfur (ppmw)

- ♦ N_2-only Sweep Gas
- ■ Air Sweep Gas

Uncatalyzed Degassing of Dissolved H_2S/H_2S_x from Liquid Sulfur

$- \delta[H_2S]_{total}/\delta t$ (N_2 Sweep Gas) $- 0.8$ ppmw•min^{-1} (20-120 min avg.)

$- \delta[H_2S]_{total}/\delta t$ (Air Sweep Gas) $- 1.6$ ppmw•min^{-1} (20-120 min avg.)

Time On-Stream (min)

Figure 4

Mechanism of SO_2 Formation in Liquid Sulfur

$S_8 + O_2 \longrightarrow SO_2$

Headspace

O_2

SO_2

S_8 / Air Interface

$SO_2 \longleftarrow S_8 + O_2$

Liquid Phase

S_8

Liquid Sulfur

■ O_2 dissolves in liquid sulfur and reacts with sulfur di-radicals ($^{\bullet}S_x^{\bullet}$)

Figure 5

Simplified Reaction Mechanisms for Decomposition of H_2S_X with O_2

$H_2S_{x(soln)} \rightleftharpoons H_2S_{(soln)} + S_{8(l)}$

$\downarrow O_{2(soln)}$ (H-abstraction)

$H-S-S-S-S-S-S-S-S-S^{\bullet} + HO_2^{\bullet}$

$\downarrow$ (Cyclization)

$S_8 + HS^{\bullet} \xrightarrow{HO_2^{\bullet}} H-S-O-O-H$

$\downarrow$

$SO_{2(soln)} \xleftarrow{O_{2(soln)}} H-S-O^{\bullet} + {}^{\bullet}O-H$

$\downarrow$

$SO_{2(g)}$ ... $\downarrow H_2S_x$

$H_2O(g) \longleftarrow H_2O_{(soln)} + {}^{\bullet}S_xH$

Repeat Sequence of Reactions

l = liquid phase

g = gas phase

soln = dissolved in liquid sulfur

Figure 6

Potential Corrosion Processes From Air Degasser Off - Gases

Gas Phase

$S_{8(vap)}$ N_2 O_2 H_2O H_2S SO_2

T-reduction ⎰ Condensation

S_8 ... $H_2 S_x O_y$

Fe (carbon steel)   Fe

Sulfur Corrosion

$Fe + \frac{1}{8} S_8 \xrightarrow{H_2O} FeS$

Acid Corrosion

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

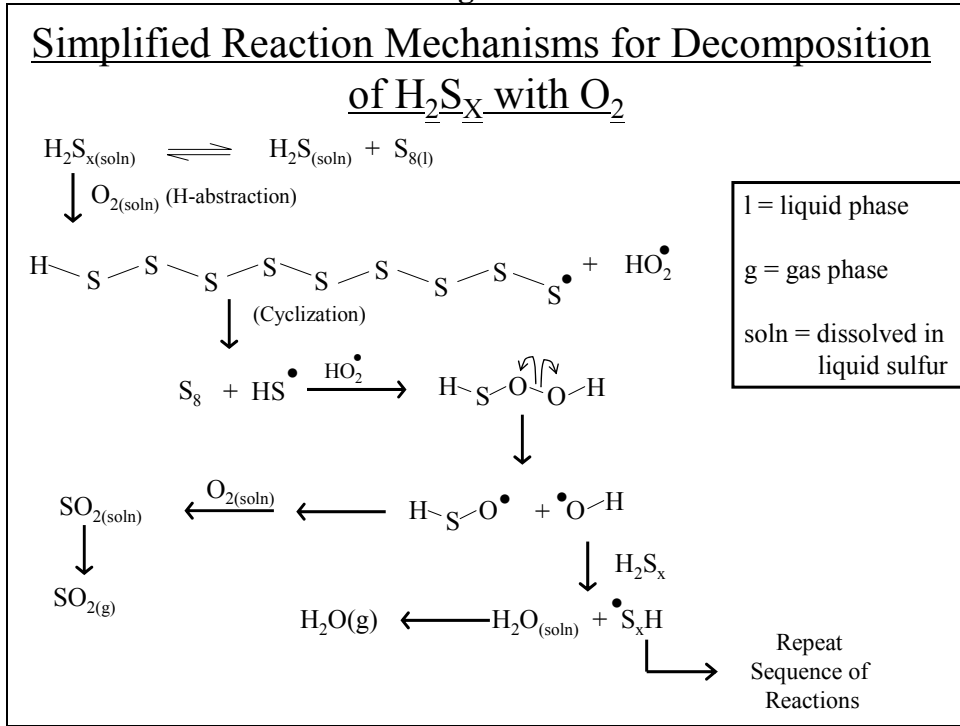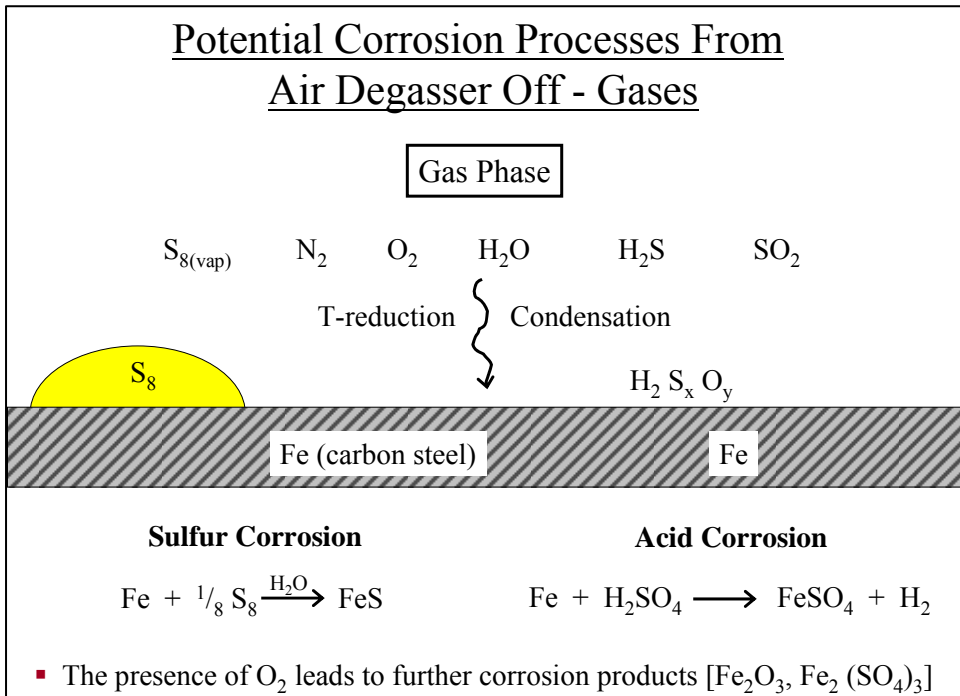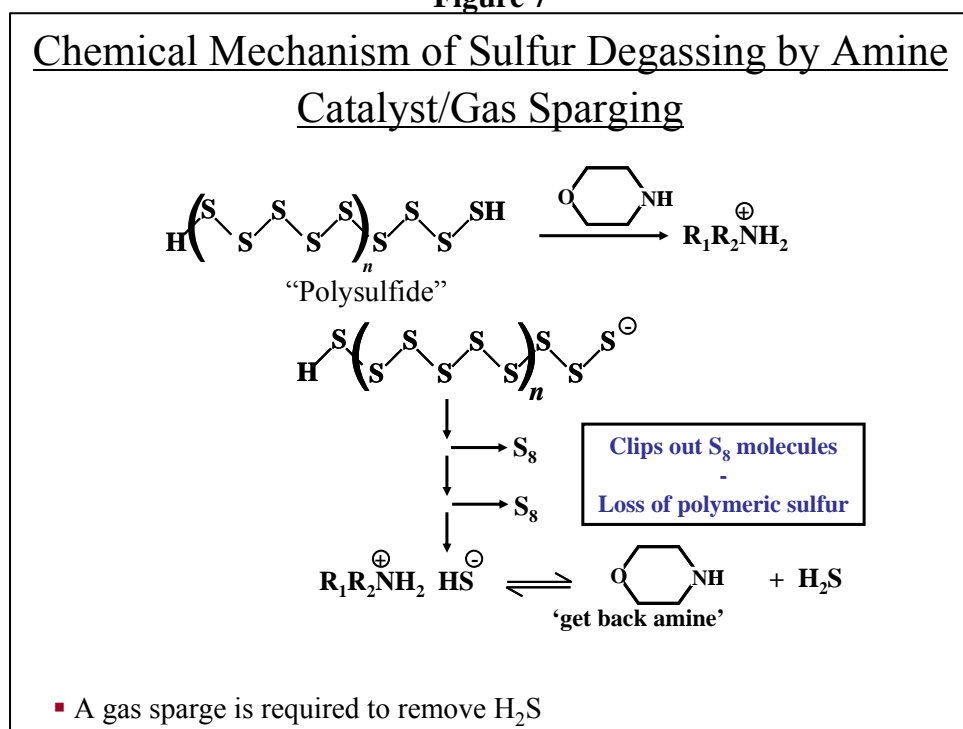- The presence of O_2 leads to further corrosion products [Fe_2O_3, $Fe_2(SO_4)_3$]
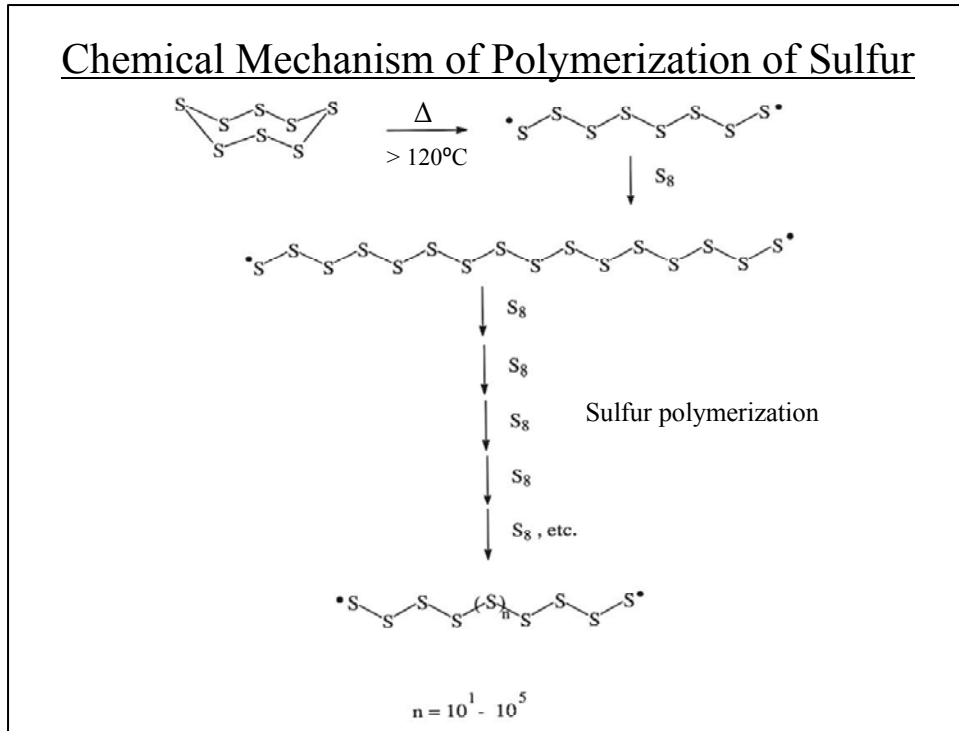
The Chemistry of Amine Catalyst Degassing

Basic materials such as morpholine (Figure 7) decompose H_2S_x by abstraction of a proton, a process which leads to unzipping of this polymeric molecule. By itself, this reaction would not degas liquid sulphur as the formation of H_2S_x would also be catalyzed by the amine but application of a sparge gas removes the H_2S so driving the system to a degassed state. One advantage of liquid catalyst degassing is that an amine can be chosen which readily dissolves in sulphur and sparge gases, other than air, can be used if the off gas can be handled within the plant. Indeed, if dry nitrogen or CO_2 were to be used, the off gas would contain only H_2S and sulphur vapour and, so, be relatively non-corrosive. Overall, the amine degassing is much more rapid than air degassing having a rate at least 10 times faster when used in combination with an air sparge [1, 2].

Figure 7

Chemical Mechanism of Sulfur Degassing by Amine Catalyst/Gas Sparging

- A gas sparge is required to remove H_2S

One objection to amine degassing has been that the unzipping of the polysulfide results in loss of sulphur polymer and a lower mechanical strength of solid produced from amine degassed liquid. However, this objection is unfounded as polymeric sulphur quickly re-establishes normal concentrations in degassed sulphur (Figure 8) [3, 4, 5]. Even if some amine remains within the liquid sulphur, the chemistry depicted in Figure 8 leads to polymer formation and the polysulphide decomposition chemistry (Figure 7) ceases because H_2S_x, now in low concentration, is required for the polysulphide decomposition to occur.

Figure 8

Chemical Mechanism of Polymerization of Sulfur

$$\xrightarrow[> 120^{\circ}C]{\Delta}$$

S_8

S_8

S_8

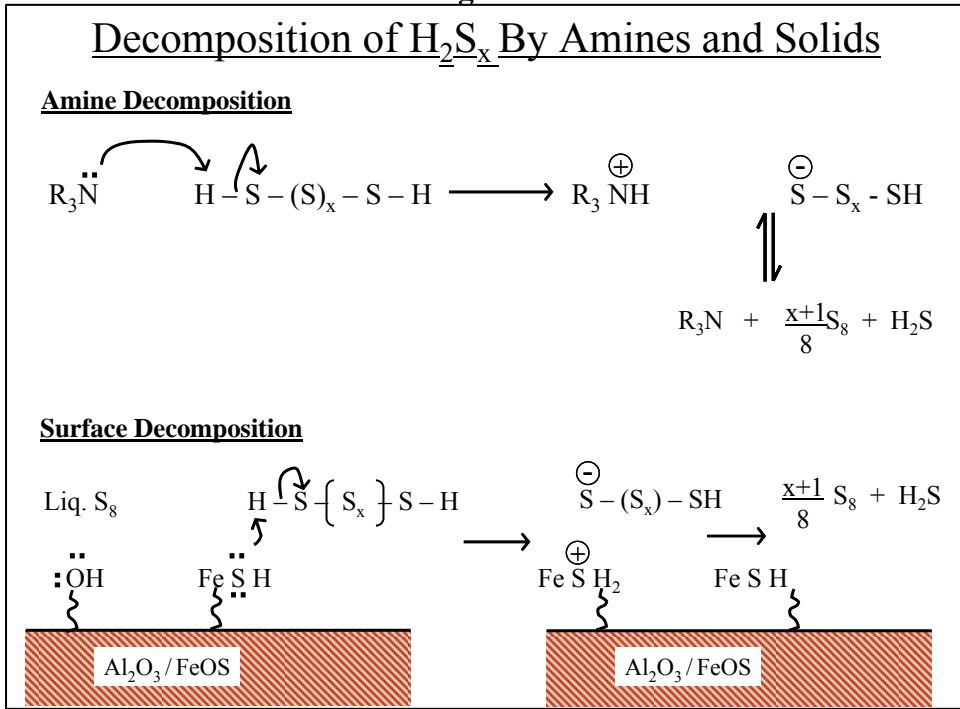S_8 Sulfur polymerization

S_8

S_8 , etc.

$n = 10^1 - 10^5$

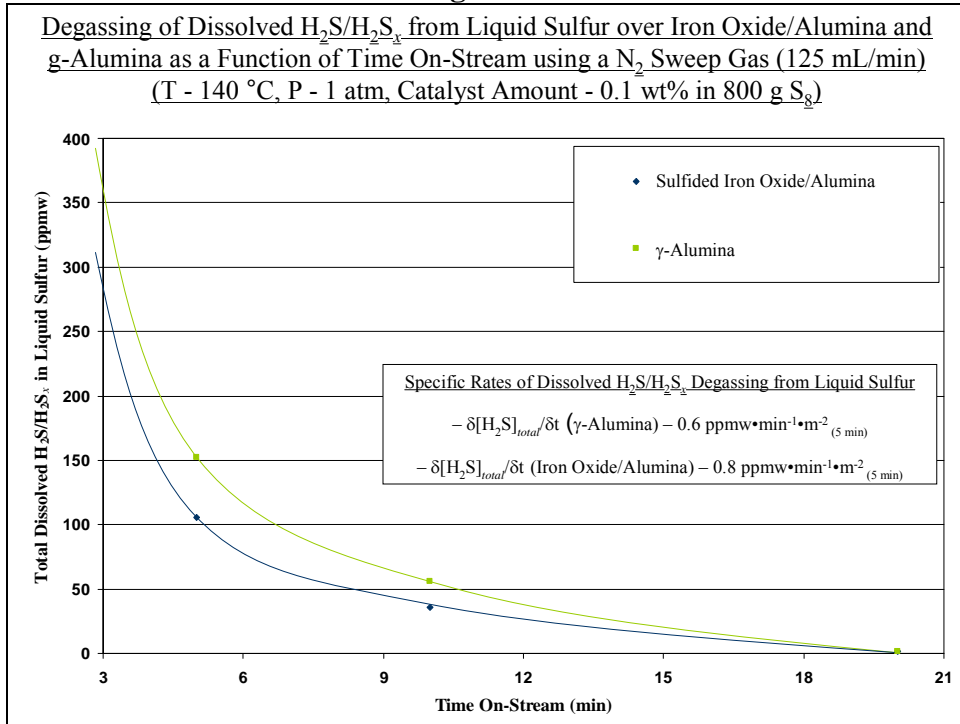Liquid Sulphur Degassing with Solid Catalysts

This technology involves flowing liquid sulphur and a sparge gas through an alumina catalyst bed using catalyst pellets that have been constituted to withstand the mechanical stresses caused by turbulent fluid flow. The process was first introduced by Amoco USA and is used effectively in several plants using air sparge. Although Amoco did not discuss the chemistry of this process, work in our laboratories has shown that the alumina surface provides basic sites which initiate polysulphide decomposition in a similar fashion as is the case with amines (Figure 9). As with amine catalysts, the basic sites on the alumina can catalyze both polysulphide formation as well as decomposition so a sparge gas is necessary to remove H_2S from the system. Clearly, any solid that can provide basic sites similar to those on alumina should promote sulphur degassing and any sparge gas should work as O_2 is not a necessary component of the process. These suggestions have been confirmed by our recent studies (Figure 10) with silica, alumina, promoted alumina and alumino-silicates in combination with air, steam and N_2 all being effective combinations.

Claus tail gas may be an effective sparge gas despite containing H_2S since if the gas flow rate is sufficient, mass transfer limitations for re-dissolving the degassed H_2S back into the sulphur should allow the polysulphide decomposition reaction to dominate over the formation reaction. This suggestion was confirmed by experiments using sparge gas containing H_2S at various concentrations (1, 50 and 100%) (Figure 11). As would be predicted, no degassing occurs with 100 % H_2S but significant degassing was observed with 50% H_2S in N_2. Claus tail gas was as effective as 100 % N_2 (Figure 12).

Figure 9

Decomposition of H_2S_x By Amines and Solids

Amine Decomposition

$$R_3\ddot{N} \quad H-S-(S)_x-S-H \longrightarrow R_3\overset{\oplus}{N}H \qquad \overset{\ominus}{S}-S_x\text{-}SH$$

$$R_3N \;+\; \frac{x+1}{8}S_8 \;+\; H_2S$$

Surface Decomposition

Liq. S_8 $\qquad H-\overset{\frown}{S}\left\{S_x\right\}S-H \qquad \overset{\ominus}{S}-(S_x)-SH \qquad \frac{x+1}{8}\,S_8 \;+\; H_2S$

$:\ddot{O}H \qquad Fe\,\ddot{S}\,H \qquad\qquad Fe\,\overset{\oplus}{S}\,H_2 \qquad Fe\,S\,H$

$Al_2O_3\,/\,FeOS$ $\qquad\qquad\qquad Al_2O_3\,/\,FeOS$

Figure 10

Degassing of Dissolved H_2S/H_2S_x from Liquid Sulfur over Iron Oxide/Alumina and g-Alumina as a Function of Time On-Stream using a N_2 Sweep Gas (125 mL/min) (T - 140 °C, P - 1 atm, Catalyst Amount - 0.1 wt% in 800 g S_8)

Legend:
- ◆ Sulfided Iron Oxide/Alumina
- ■ γ-Alumina

Specific Rates of Dissolved H_2S/H_2S_x Degassing from Liquid Sulfur

$- \delta[H_2S]_{total}/\delta t\; (\gamma\text{-Alumina}) - 0.6$ ppmw•min^{-1}•m^{-2} $_{(5\,min)}$

$- \delta[H_2S]_{total}/\delta t\; (\text{Iron Oxide/Alumina}) - 0.8$ ppmw•min^{-1}•m^{-2} $_{(5\,min)}$

Y-axis: Total Dissolved H_2S/H_2S_x in Liquid Sulfur (ppmw)

X-axis: Time On-Stream (min)

Figure 11

Catalyzed H$_2$S$_x$ Removal from Liquid Sulfur over γ-Al$_2$O$_3$ as a Function of Sweep Gas Composition

Pressure – 1 atm **Catalyst Loading – 0.1 wt%**

Gas Flow Rate – 125 mL/min **Stirring – 1000 rpm**

Figure 12

H$_2$S$_x$ Removal from Liquid Sulfur using a Claus Tail Gas

Temperature – 140 °C **Pressure – 1 atm**

Stirring – 1000 rpm **Gas Flow Rate – 125 mL/min**

Tail Gas Composition - ~ 1.20% H$_2$S: 0.60% SO$_2$: 30% H$_2$O: balance N$_2$
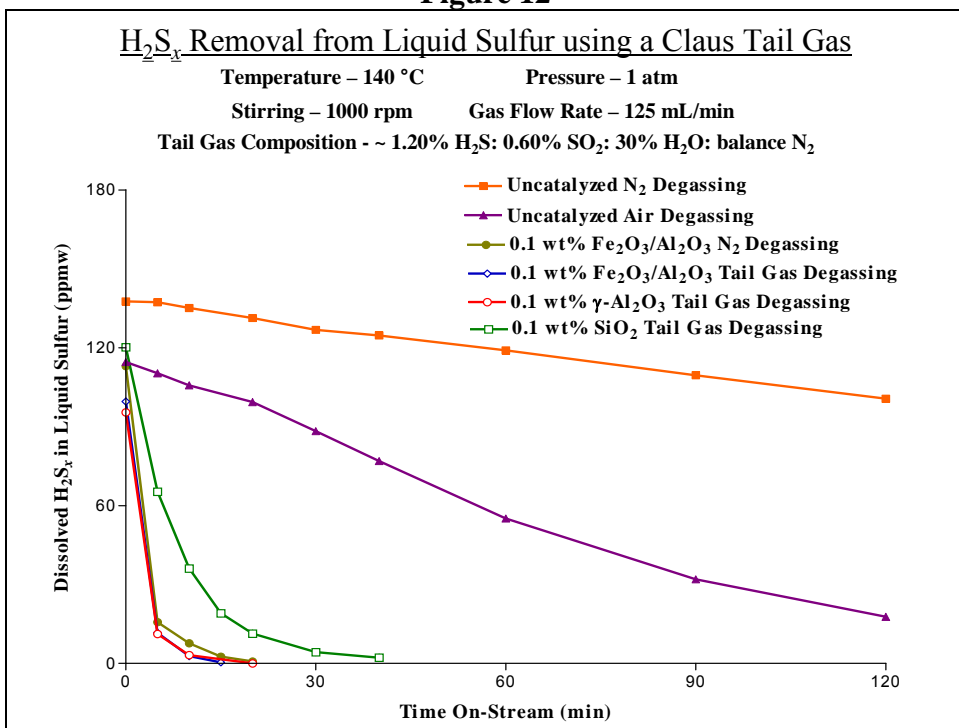
Overview of Liquid Sulphur Degassing Mechanisms

Air degassing is a relatively slow process involving mass transfer of O_2 to liquid sulphur, then chemical reaction of the polysulphide with the dissolved O_2 and mass transfer of the liberated H_2S to the gas bubbles. SO_2 is a co-product of the oxygen chemistry. Both soluble amine and solid catalysts decompose H_2S_x by proton abstraction but a sparge gas is still required to remove dissolved H_2S from the liquid. Since O_2 is not required for the polysulphide decomposition using either amines or solids, use of an inert sparge gas (e.g. N_2) would prevent SO_2 formation.

Subsequent sections of this paper will describe application of Claus tail gas as the sparge gas for degassing and possible use of condensers as combined degassing – sub-dew point reactors.

Degassing with Solid Catalysts and Claus Tail Gas

One way in which liquid sulphur could be degassed would be to flow it through a suitable reactor with a slip-stream of the tail gas such that all H_2S liberated in the degassing is collected in the tail gas. This gas stream would then be compressed back into the main Claus tail gas flow upstream of the tail gas unit. Since the extra H_2S would increase the H_2S/SO_2 ratio, this adaptation would be particularly suited to tail gas units operating at high ratio.
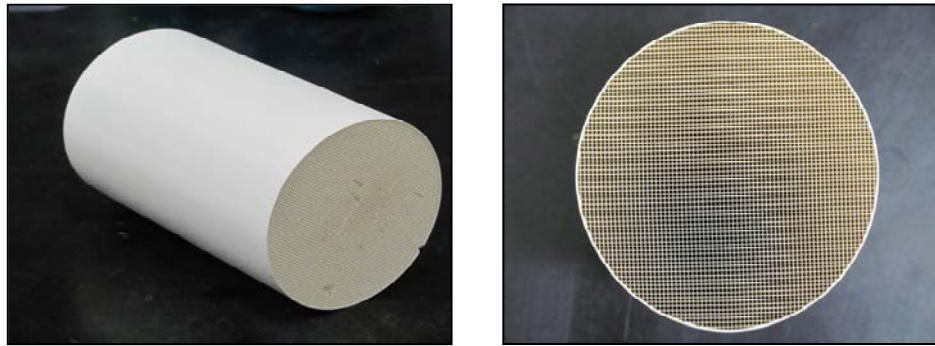
Cordierite or mullite-based monoliths, with appropriate channel sizes (Figure 13) could be used as these systems are mechanically and thermally stable, have basic chemical sites and have undergone extensive commercial application as auto converter catalyst supports. However, as is illustrated by the data presented in Figure 14, a large unit may be required because the low surface area of cordierite limits the effectiveness of this material as a catalyst for degassing. Interestingly, as can be seen for the specific rates for polysulphide decomposition, cordierite is a very active degassing catalyst with a higher specific rate than alumina-based materials (Figure 15). The low surface area problem of cordierite is simply overcome by using an alumina wash-coated cordierite (Figures 16, 17) prepared by calcining a layer of gamma alumina onto the cordierite monolith. This wash-coating technology is very well understood and is used in the auto-converter catalyst manufacturing process. It should be possible to obtain such systems from monolith manufacturers as off-the-shelf components.

A very interesting facet of the experiments with the alumina catalyzed degassing experiments using Claus tail gas is that about 60 % conversion of the H_2S and SO_2 in the tail gas sparge is converted to sulphur (Figure 18). This observation is not unexpected as it is well known that the Claus reaction occurs in liquid sulphur – alumina systems but the overall conversion is rate limited because of slow mass transfer of H_2S and SO_2 from the gas phase to the liquid and migration of these species to the catalyst surface. In the process design suggested in Figure 19, overall conversion of H_2S and SO_2 would be limited because only a slip-stream of the tail gas would be needed for degassing. Thus the question becomes as how to configure the system such that all of the tail gas is used in the degassing process. The obvious solution is to degas the sulphur as it liquefies in

the condenser since such a system could engender concomitant Claus conversion (Figure 20).

Figure 13

Use of Monoliths in Liquid Sulfur Degassing?

- Manufactured on a large scale for the auto-industry (catalytic converter).
- Channel size can be varied to accommodate desired pressure drop.
- Liquid sulfur and a sparge gas would be flowed through the monolith.

Figure 14

Catalyzed H_2S/H_2S_x Degassing from Liquid Sulfur using a N_2 Sparge

Temperature – 140 °C   Pressure – 1 atm
Sparge Gas – 125 mL/min N_2 Flow   Catalyst Content – 0.1 wt%

Surface Area (Cordierite) – 2.8 m²/g

Surface Area (γ-Al₂O₃) – 282 m²/g

Surface Area (Fe₂O₃/Al₂O₃) – 278 m²/g

Catalyst
- Uncatalyzed
- Uncoated Cordierite
- γ-Al₂O₃
- Fe₂O₃/Al₂O₃

Total Dissolved H_2S/H_2S_x in Liquid Sulfur (ppmw)

Time On-Stream (min)

Figure 15

Catalyzed H$_2$S/H$_2$S$_x$ Degassing from Liquid Sulfur using a N$_2$ Sparge

Temperature – 140 °C **Pressure – 1 atm**
Sparge Gas – 125 mL/min N$_2$ Flow **Catalyst Content – 0.1 and 0.5 wt%**

Catalyst
- ■ Uncoated Cordierite (0.5 wt%)
- ▲ γ-Al$_2$O$_3$ (0.1 wt%)
- ● Fe$_2$O$_3$/Al$_2$O$_3$ (0.1 wt%)

Specific Activity (Cordierite) – 0.19 ppmw·min^{-1}·m^{-2}

Specific Activity (γ-Al$_2$O$_3$) – 0.18 ppmw·min^{-1}·m^{-2}

Specific Activity (Fe$_2$O$_3$/Al$_2$O$_3$) – 0.15 ppmw·min^{-1}·m^{-2}

Y-axis: **Total Dissolved H$_2$S/H$_2$S$_x$ in Liquid Sulfur (ppmw)**
X-axis: **Time On-Stream (min)**

Figure 16

Catalyzed H$_2$S/H$_2$S$_x$ Degassing from Liquid Sulfur using N$_2$ and Air Sparge

Temperature – 140 °C **Pressure – 1 atm**
Sparge Gas Flow – 125 mL/min **Catalyst Content – 0.1 wt%**

γ-Al$_2$O$_3$ Washcoat

Sparge Gas (Catalyst)
- ◆ N$_2$ (Uncoated Cordierite)
- ■ N$_2$ (γ-Al$_2$O$_3$ Wash-Coated Cordierite)
- ▲ N$_2$ (Automotive Catalytic Converter)
- ◇ Air (Uncoated Cordierite)
- □ Air (γ-Al$_2$O$_3$ Wash-Coated Cordierite)
- △ Air (Automotive Catalytic Converter)

Y-axis: **Total Dissolved H$_2$S/H$_2$S$_x$ in Liquid Sulfur (ppmw)**
X-axis: **Time On-Stream (min)**

Figure 17

Catalyzed H₂S/H₂Sₓ Degassing from Liquid Sulfur using a Tail Gas Sparge

Temperature – 140 °C	**Pressure – 1 atm**
Tail Gas Flow – 125 mL/min	**Catalyst Content – 0.1 and 2.5 wt%**

Tail Gas Composition - ~ 1.20% H_2S: 0.60% SO_2: 30% H_2O: balance N_2

Catalyst

- ◆ **Uncoated Cordierite (0.1 wt%)**
- ■ **Uncoated Cordierite (2.5 wt%)**
- ▲ **γ-Al_2O_3 Wash-Coated Cordierite (0.1 wt%)**
- ● **Automotive Catalytic Converter (0.1 wt%)**

Figure 18

Off-Gas H₂S and SO₂ following Catalyzed H₂S/H₂Sₓ Degassing of Liquid Sulfur using a Claus Tail Gas

Temperature – 140 °C	**Pressure – 1 atm**
Stirring – 1000 rpm	**Gas Flow Rate – 125 mL/min**

Tail Gas Composition - ~ 1.20% H_2S: 0.60% SO_2: 30% H_2O: balance N_2

H_2S/SO_2 Conversion (SiO₂) ~ 4 %

H_2S/SO_2 Conversion (γ-Al₂O₃ and Fe₂O₃/Al₂O₃) ~ 60 %

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Figure 19

Catalyzed H_2S/H_2S_x Degassing of Liquid Sulfur using a Claus Tail Gas Sparge

Hydrogen Polysulfide Decomposition

$$H_2S_{x(d)} \xrightarrow{Fe_2O_3/Al_2O_3/SiO_2} H_2S_{(d)} + S_{x-1(l)}$$

Modified Tail Gas Stream (100%)
> 1% H_2S: 0.5% SO_2 (balance H_2O and N_2)

Tail Gas Conversion Unit

H_2S Removal from the Sulfur

$$H_2S_{(d)} \xrightarrow{Gas\ Sparge} H_2S_{(g)}$$

Reactor Off-Gas (10%)
>>> 1% H_2S: 0.5% SO_2 (balance H_2O and N_2)

Degassed Liquid Sulfur Free of Dissolved H_2S/H_2S_x

Main Tail Gas Stream (90%)
~ 1.0% H_2S: 0.5% SO_2: 30% H_2O (balance N_2)

Compressor

Slip Tail Gas Stream (10 %)

Pump

Liquid Sulfur Flow ($H_2S/H_2S_{x\ (soln)}$)

Condensers

Liquid Sulfur containing $H_2S/H_2S_{x\ (soln)}$

Figure 20

The Degassing/Sub-dewpoint Reactor-Condenser

Process Gas
2 H_2S: 1 SO_2
(balance S_8, H_2O and N_2)

Steam

Process Gas
2 H_2S: 1 SO_2
(balance H_2O and N_2)

Top View of Condenser Tube

T – 130°C

metal oxide tube

steel

$H_2O_{(l)}$

$S_{8(l)}$

• **Oxide layer function as a degassing catalyst (e.g. γ-Al_2O_3, Fe_2O_3, SiO_2)**

$$• \ H_2S_{x(soln)} \longrightarrow H_2S_{(soln)} + S_{x-1(l)} \longrightarrow H_2S_{(g)}$$

• **Oxide layer is a Claus active material**

$$• \ 2H_2S_{(ads)} + SO_{2(ads)} \underset{}{\overset{\sim\ 130°C}{\rightleftharpoons}} \ ^3/_8 \ S_{8(l)} + 2\ H_2O_{(g)} + Heat$$

• **Heat removal in the condenser tube drives the Claus equilibrium**

Sulphur Degassing and Enhanced Sulphur Recovery in Sulphur Condensers

Is it possible to achieve simultaneous liquid sulphur degassing and Claus conversion of H_2S and SO_2 in the process gas in a modified sulphur condenser? To answer this question, it is necessary to consider the mechanism for formation of H_2S_x in sulphur in a Claus system as well as the factors which would control the Claus reaction in liquid sulphur. When a degassing experiment with solid catalyst is to be conducted, a supply of liquid sulphur containing dissolved H_2S and H_2S_x is needed. One way to prepare H_2S/H_2S_x in liquid sulphur would be to contact the liquid containing the catalyst with some H_2S for some period of time. However, when this experiment is attempted with 10 % H_2S in N_2 at 140°C over 16 h, very little H_2S_x (ca. 10 ppmw) is produced. However, if the experiment is repeated without the catalyst, H_2S_x is produced to the anticipated equilibrium value (ca. 100 ppmw).

So, why is H_2S_x found in the run-down of the condenser from the catalytic converters? Most likely, H_2S_x is not present as the sulphur desorbs from the catalyst surface, but forms during condensation of sulphur from the gas phase in the condensers (Figure 21). The quantity of H_2S_x observed is generally well above the equilibrium amount for the final condenser temperature because the residence time in the system (ca. 5 s) is too low to allow the lower temperature equilibrium value to be established. Such a mechanism explains why very high H_2S_x amounts are seen in the liquid sulphur run-down from the furnace condenser because the temperatures before and during condensation are much higher, so favouring H_2S_x formation (Figure 21).

If this discussion is correct, then it can be concluded that the only reason H_2S_x is present in Claus liquid sulphur is because of high temperature reactions between sulphur and H_2S (say ca. 200°C) which occur in the gas phase and, most probably, as the sulphur condenses from the gas phase.

Figure 21

Formation of H_2S_x in Claus Process Gas

H_2S / SO_2 → 300°C → $H_2O_{(g)} + S_{8(g)}$ ⇌ $^{\bullet}S_{8\,(g)}^{\bullet}$

↘ S_8 / H_2O

Al$_2$O$_3$

Claus catalyst surface
(1st converter)

$\uparrow\downarrow$ H_2S, S_8

$H_2S_{x(g)} + H_2S_{x(l)}$

$\uparrow\downarrow$ Condensation

$S_{8(l)} + H_2S_{x(l)}$

Hypothesis

- When S_8 desorbs from the catalyst surface, no H_2S_x is present.

- H_2S_x forms in the gas and during sulfur condensation because S_x diradicals ($^{\bullet}S_x^{\bullet}$) are present in the sulfur.

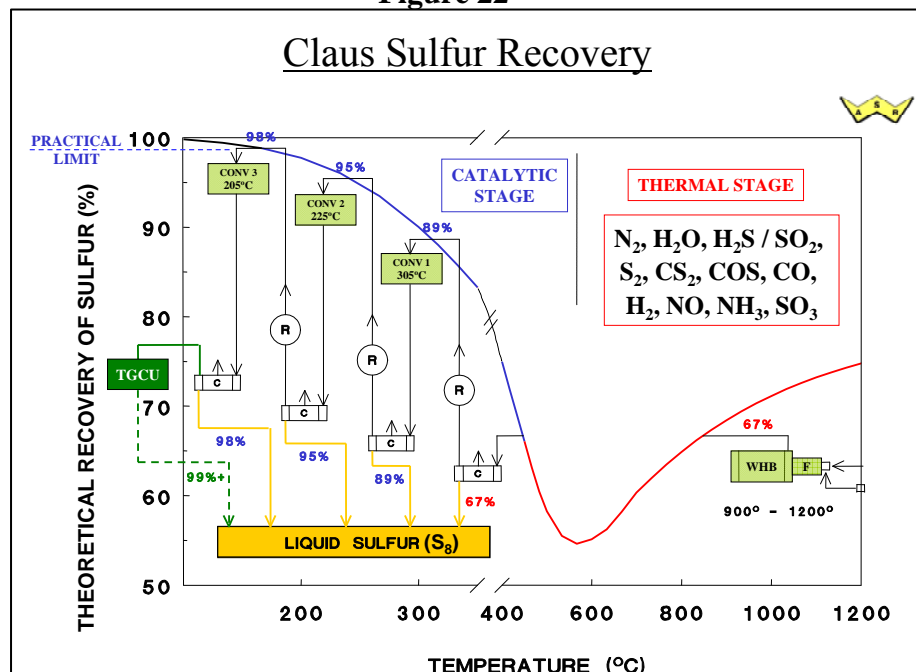- The amount of H_2S_x in the liquid at condenser temperature (155°C) exceeds equilibrium because it is formed at much higher temperatures.

Liquid sulphur degassing might then be accomplished in a condenser tube at ~ 150°C which is lined with cordierite on which Claus alumina is deposited (Figure 20). As liquid sulphur condenses on the alumina surface, the basic sites will cause decomposition of the H_2S_x and the process gas, although containing some H_2S, will act as the sparge gas so driving the liquid sulphur to a degassed state. It is thought that sulphur flows from horizontal condenser tubes by virtue of the process gas flow pushing the liquid through the tubes and out of the condenser. Thus, a relatively thin sulphur film, estimated to be 0.65 mm, 0.25 mm and 0.10 mm (average thickness around the tube circumference) for the condensers after the furnace, first and second converters should allow some, or perhaps, complete degassing of the condensed sulphur. Since the heat of reaction for polysulphide decomposition will be negligible for a few hundred ppmw concentration, this process should not affect the heat duty for the condenser.

Since alumina is part of the degassing catalyst it is interesting to consider whether Claus conversion also occurs in the catalytic degassing condensers. Clearly, further Claus reaction in these condensers could be useful as it would be occurring at ca. 150°C, a temperature which allows much higher equilibrium conversion (Figure 22). Obviously, such a system would be working at sub-dew point conditions so some insight into the potential operation of a catalytic degassing condenser can be gained by considering how conventional sub-dew point tail gas catalysts work. The generally accepted picture of a sub-dew point catalyst is that the bare catalyst surface initially functions by adsorption of reacting species from the gas phase and the system operates to give equilibrium conversion to sulphur until the liquid film builds up on the catalyst surface to a point where limited mass transfer becomes the controlling kinetic factor. However, it may be that when the sulphur film develops to a certain thickness, it also impedes bulk gas flow to the inner regions of the catalyst pellet (external mass transfer). Thus, a catalyst layer such as depicted in Figure 20 may be more efficient for sub-dew point conversion than a catalyst pellet since bulk mass transfer may be improved.

Figure 22

This possibility was examined by conducting experiments with alumina coated cordierite and comparing these data with data obtained using standard alumina pellets, keeping the alumina quantity constant for both experiments. Both catalytic systems were examined at sub-dew point conditions using a space velocity of 10,000 h^{-1}, in step with the 0.25 s residence time for a typical condenser but much higher than is usually employed for a typical sub-dew point reactor (500 – 1000 h^{-1}). It should be noted that these experiments were conducted as packed catalyst beds, so not really duplicating the situation depicted in Figure 20. Interestingly, and perhaps, not unexpectedly, the alumina coated cordierite was more effective enabling twice the conversion to sulphur over 20 h (Figure 23) although this catalyst did not enable equilibrium conversion beyond the time recorded for the alumina pellet experiments. However, these results suggest that it may be possible to design a condenser system in which liquid sulphur is removed mid-condenser so reducing the sulphur film thickness in later catalyst coated tubes. Clearly, development of monolith coated catalysts to enhance SO_2 adsorption, the primary step in the Claus reaction would also be beneficial to enhance overall sulphur formation in a catalytic condenser. So although these data show that some Claus reaction can be expected in a catalytic condenser, further developments are required to produce a useful system.

Figure 23

Sub-dewpoint Claus Conversion over Uncoated and γ-Al$_2$O$_3$ Coated Cordierite

Temperature – 130 °C   Pressure – 1 atm

Space Velocity – 10,000 h^{-1} Catalyst Packing Volume – 70 mL

Feed Gas Composition - ~ 1.02% H$_2$S: 0.52% SO$_2$: 30% H$_2$O: balance N$_2$

Aspects of Heat and Mass Transfer in a Catalytic Condenser

The thermal conductivity of the cordierite catalyst is approximately 3 W/mK, so a thin layer of catalyst lining in the condenser tubes will not have a significant effect on heat transfer. The thermal expansion of the cordierite is approximately 1.7 10^{-6}/C, which is about 10% of the thermal expansion of stainless steel. This will require consideration in the condenser design.

As previously mentioned, the heat of reaction for the degassing will be negligible and will not require an increase in surface area of the condenser. The Claus heat of reaction is more significant and may require a surface area increase of approximately 15% to 30% compared to a conventional condenser.

Possible Applications of the Catalytic Degassing and Catalytic /Converter Condensers

Firstly, it would seem that it should be possible to design a monolith/alumina tube reactor which uses tail gas as the sparge gas (Figure 19). If only a slip stream of the tail gas is used, the additional sulphur recovery obtained by conversion of H_2S and SO_2 in the tail gas will be minimal. However, such a system would have the advantage of allowing treatment of the degasser off-gas in the tail gas unit.

The viability of coating the condenser tubes with a combined degassing – Claus catalyst is interesting because any degassing or Claus conversion is, essentially, a bonus at the expense of lining the condenser tubes with the catalyst. Quite possibly, sulphur film thicknesses, especially for the condenser handling the furnace product gases, may impede degassing such that a stand-alone degasser may be required as a polishing unit. If all condenser tubes are treated in this manner some intriguing possibilities arise.

Assuming that some of the tubes in the first condenser can be kept relatively sulphur free, by removing some of the sulphur flow upstream of these tubes, significant Claus conversion may occur in these tubes. Thus, the downstream catalytic converter can be operated at lower temperature allowing higher conversion to sulphur. If CS_2 conversion is a vital function of the first catalyst unit, TiO_2 should be used in that reactor.

The question also arises as to whether a tail gas unit would be required for some plants as a 3 catalytic converter plant with use of alternating catalytic condensers after the third catalytic unit should give an overall recovery approaching 99.9 % (Figure 24, only 2 standard converters are shown). Another possibility is that catalytic sub-dew point condensers could be used either upstream or downstream of direct oxidation tail gas units. Furthermore, use of catalytic condensers upstream of either direct oxidation or reducing type tail gas systems could be employed to increase the H_2S/SO_2 ratio since even minimal steady state sub-dew point conversion in the catalytic condenser will reduce the SO_2 levels entering these units.

Figure 24

High Efficiency Sulfur Recovery using Catalytic Condensers and Direct Oxidation
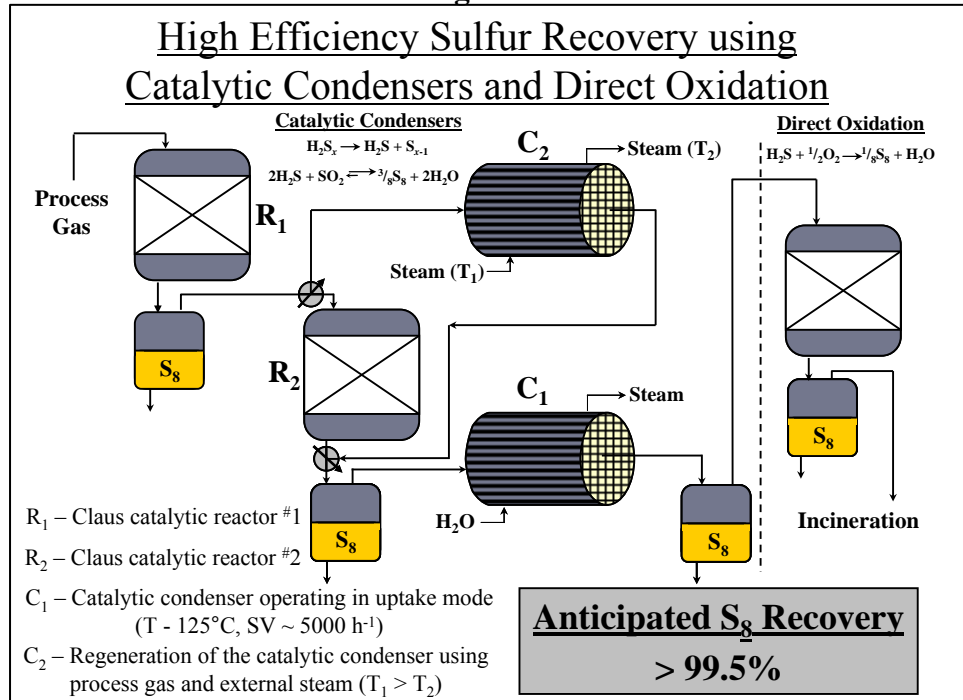
Concluding Comments

Liquid sulphur degassing is a complex interplay of chemical and mass transport phenomena. Use of air sparge, although almost an industry standard, may create as many problems as it solves, particularly with respect to handling the off-gases. Amine catalyst degassing is very effective but requires a constant input of chemical as well as systems to handle whatever sparge gas is chosen.

Research into catalyst degassing shows that almost any inorganic solid will work but a sparge gas is still required. Cordierite - alumina based devices may be very useful because their low thermal expansion and high mechanical strength make them suitable for commercial use. Claus tail gas is a suitable gas sparge if the degasser off-gases can be readily compressed back into the Claus system. Importantly, consideration of the low but significant Claus conversion observed in the laboratory when employing Claus tail gas leads to a number of interesting possibilities for improving the operation of Claus plants.

Acknowledgments

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