Titania Catalyst Placement in a Claus SRU Convertor

High COS and CS₂ in the process gas can make Titania catalyst almost essential in some Claus SRUs. But to understand why these components are a problem, it’s useful first to understand where they come from and how to deal with them in the most efficient manner possible.

Simply stated, COS and CS₂ are byproducts from combusting hydrocarbons in the presence of sulphur in the Thermal Reactor. In rare cases, COS will be present in the acid gas feed itself. COS and CS₂ formation are just two of several undesirable side reactions that often occur in the Thermal Reactor, including:

\[ CH_4 \rightarrow 2H_2 + C \]
\[ C + S_2 \rightarrow CS_2 \]
\[ H_2S + CO_2 + HEAT \rightarrow H_2O + COS \]

This issue of The Contactor™ focusses on the byproducts formed from the last two reactions. However, the appearance of elemental carbon, “C”, represents soot formation, and this spells a host of other problems for the Claus Converters. This is discussed in depth in previous issues of The Contactor and will not be repeated here. So, why does all this matter?

The COS and CS₂ components are important simply because they do not participate in the main Claus reaction where H₂S and SO₂ convert to elemental sulphur and water. Consequently, if there are no other means to destroy them, they will end up contributing to the overall sulphur emissions from the Stack, and they could potentially push a facility over its environmentally-regulated emission limits.

With an understanding now of the source of these components and of the problems they can cause, how can we take care of them? There are realistically two places where COS and CS₂ can be dealt with: (1) In the Claus Converter beds through the use of strategic operation or auxiliary catalyst (Titania), and (2) In the TGU Hydrogenation Reactor. Ideally, the Hydrogenation Reactor would take care of any residual COS and CS₂ after bulk destruction has already occurred in the Claus Converter beds. The first method for COS and CS₂ destruction in the Converter is to operate the bed at an elevated temperature. Unlike the Claus reaction, COS and CS₂ have better kinetics for destruction the higher the temperature as seen in Figure 1, representing fresh Alumina.

![Figure 1 COS and CS₂ Destruction vs. Temperature](image)

An unfortunate side effect of running the Converter hot is that the Claus conversion is lowered because high temperatures do not favor equilibrium conversion of H₂S and SO₂ to sulphur. The practice of elevating the operating temperature of the converter bed to enhance the COS and CS₂ kinetics is conventionally done in the first converter with the second and (if present) the third bed operating as close to the sulphur dew point as possible to maximize the extent of the Claus reaction.

Case Study: Setup

To examine how Titania performs, as well as determine the best placement for it, a case study was set up using a typical three-bed Claus unit processing acid gas from a refinery’s amine and sour water stripper systems (Figure 2). Simulations were run in OGT | SulphurPro®.

![Figure 2 Three Bed Claus Unit](image)
To understand better the role of Titania catalyst, a study was performed looking at the placement of Titania catalyst in beds 1, 2, and 3, all one at a time (not simultaneously). In all cases, Titania replaced approximately 1/3rd of the overall alumina catalyst volume. In the first converter bed, the effects of Titania placement at the top and bottom of the converter bed were examined. To get a baseline for all comparisons, the base-case was run first with Alumina catalyst alone.

Case Study: Results

The results of the fifteen simulations are tabulated as shown in Figures 3 and 4. The first bar cluster in both graphs is the base case. The first group in Figure 3 for the base case refers specifically to Converter 1 with no Titania. The second and third groups in both Figures 3 and 4 represent Converter 1 with Titania placement in the top and placement in the bottom of the first Converter’s bed. The fourth and fifth bar clusters represent adding Titania to converters 2 and 3, respectively. Figure 4 specifically shows the overall destruction of COS and CS2 across the entire Claus catalytic section (all beds). The general operating strategy for an SRU dealing with COS and CS2 is to operate Converter 1 at an elevated outlet temperature (typically 550–650°F). This enhances the COS and CS2 kinetics but sacrifices Claus equilibrium conversion. Equilibrium conversion is then enhanced by operating Converters 2 and 3 at as low an outlet temperature as safely possible while still keeping it at least 25–30°F above the sulphur dew point. This allows the greatest possible conversion of H2S to sulphur.

Case Study: Discussion

From Figure 3, adding Titania to Converter 1, regardless of whether we add it at the top or bottom of the converter bed, causes the COS and CS2 conversion to improve dramatically. Figure 4 shows the same thing. Overall destruction of COS and CS2 appears to show no appreciable difference with Titania placement, although there seems to be a very slight increase in conversion when placed in the top versus the bottom of the 1st Converter bed. This raises the question; why is Titania not added to Converter 2 or, if present, Converter 3 rather than just to Converter 1? The results in both Figures 3 and 4 show that although there is some benefit over not using Titania at all, the increase is insufficient to justify having Titania in Converters 2 or 3 rather than in Converter 1 (where both temperature and reactant concentrations are the highest). The main reason Titania is placed in the bottom of the first converter bed rather than in later in the process relates to operating temperature. Although some Titania in the second or third bed is better than none at all, there is evidently not enough benefit from having Titania in these beds to justify the cost of such an expensive catalyst simply because temperatures aren’t high enough in those beds to provide sufficiently enhanced COS and CS2 destruction.

To learn more about this and other aspects of gas treating and sulphur recovery, plan to attend one of our training seminars. Visit www.protreat.com/seminars for details.

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