

# A Coordinated, Holistic Approach to SRU & TGTU Catalyst Selection

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*“There is a slow but increasing awareness of the interrelatedness of things. We are becoming less prone to accept an immediate solution without questioning its larger implications.”*

-Arthur Erikson, architect and community planner  
from “Address to the Institute of Canadian Bankers”, 1972

*“There may be no such thing as a two-person relationship.”*

-Edwin Friedman, family therapist, consultant, and rabbi  
from “A Failure of Nerve”, 2007

## Introduction

Catalyst selection for sulfur recovery facilities is typically approached as the purchase of unique, unrelated entities. Alumina catalyst must be replaced; titania catalyst must be replaced; tail gas catalyst must be replaced. In contrast, the implications of interrelatedness have become filters through which we see societal, economic, environmental, and relational issues over recent decades.

In this paper, we advocate for an approach to selection of sulfur recovery catalysts which considers the interrelatedness of these catalysts within the unit itself, as well as with processes outside the sulfur recovery unit boundary.

## Fundamentals of sulfur recovery catalysts

### Sulfur recovery processes

The sulfur recovery processes employed today at most refinery facilities are similar. A combination of amine and sour water stripper acid gases is fed to a modified-Claus sulfur recovery unit (SRU), consisting of a thermal stage and between one and three Claus catalytic stages. In the modified-Claus unit, elemental sulfur is formed as a product of the Claus reaction, condensed to a liquid, and separated for collection. The remaining process gas consisting primarily of nitrogen and water vapor, contains some small amount of residual sulfur species.

To reduce air emissions which would result from combustion or release of these residual sulfur species, the remaining process gas (called “tail gas”) is treated in an amine-based\* Tail Gas Treating Unit (TGTU†). This provides a high degree of separation of the sulfur species from the remaining process gas. These sulfur species are then recycled back to the modified-Claus unit. This recycle scheme results in a very high level of overall (that is, SRU combined with TGTU) sulfur recovery efficiency, often exceeding 99.5%.

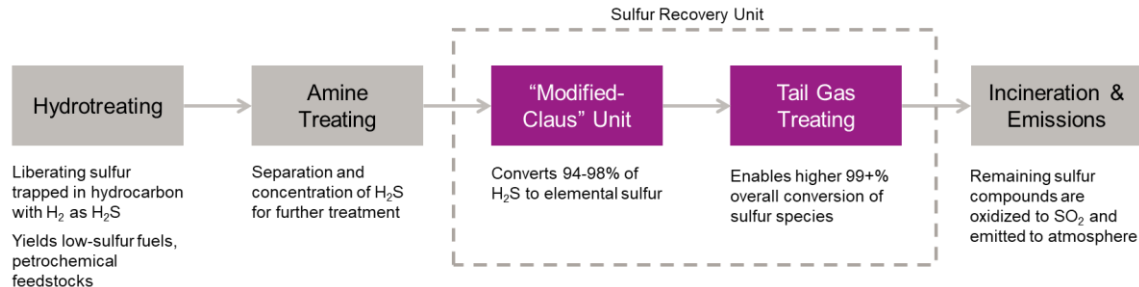


Figure 1. Block flow diagram of typical sulfur recovery process in a refinery.

\* Some tail gas treating processes are not amine-based. For example, selective oxidation and/or caustic treating may be employed instead of an amine-based process scheme.

† Tail gas treating units are often given a name based on the technology licensor's specific design. For example, the TGTU in a particular facility may be referred to as a Tail Gas Treater (TGT), HCR, Resulf, BSR-Amine, SCOT, RAR, etc. The role of the tail gas catalyst in each of these processes is essentially the same. Accordingly, the statements made in this paper are intended to be broadly applicable to reduction- and hydrogenation-type tail gas treating processes, not specific to one licensor configuration.

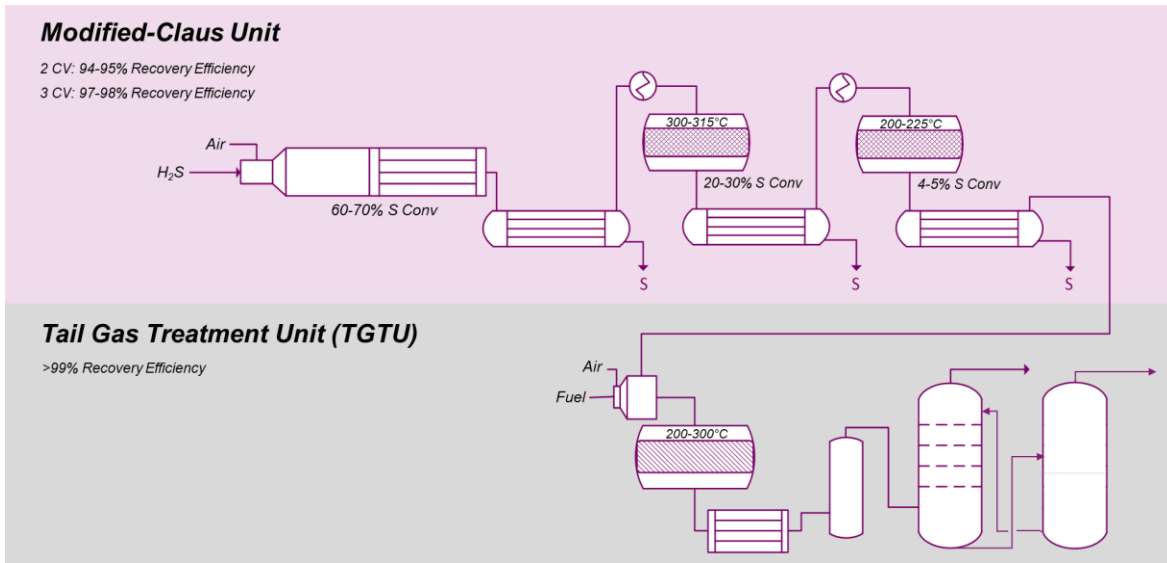
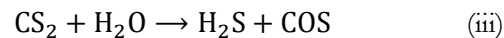
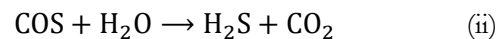
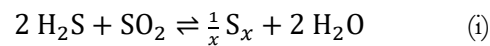


Figure 2. Schematic of typical SRU & TGTU

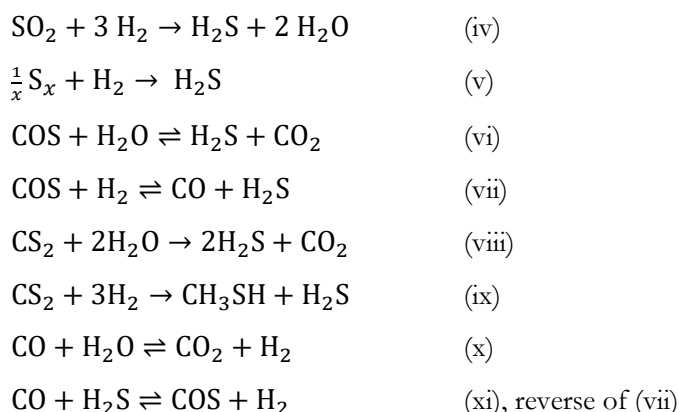
Catalysts are employed in both the SRU and TGTU processes to increase the rate of the desired reactions in each process step. In the SRU, catalysts affect the rate of the Claus reaction, as well as the rate of conversion of COS and CS<sub>2</sub> by hydrolysis. These carbon-sulfur compounds are byproducts formed in the upstream thermal reactor which, if left unconverted, can significantly affect the overall sulfur recovery efficiency [1]. The relevant reactions for SRU catalysts are shown below.



Reaction (i), called the Claus reaction, is an exothermic equilibrium-limited reaction. This has two important implications on how sulfur recovery unit Claus reactors are operated. First, this explains why subsequent reactors are optimally operated at successively lower temperatures – to achieve successively higher equilibrium conversion of the reactants. Also, this explains why sulfur condensers are implemented between each catalytic conversion stage. The elemental sulfur formed as part of the Claus reaction, denoted as S<sub>x</sub> in reaction (i) above, must be condensed and separated from the process, in order that the Claus reaction may proceed further in the second (and later) Claus catalytic stages.

Reactions (ii) and (iii) are not significantly limited by equilibrium. The activity of a Claus catalyst can drive these reactions towards completion and thus maximize overall sulfur recovery efficiency.

In the TGTU, a different set of reactions is desired. Broadly speaking, the aim of the TGTU reactor is to convert all remaining sulfur-containing compounds to H<sub>2</sub>S. This H<sub>2</sub>S may then be separated from the remaining process gas by absorption in an amine solvent, and in turn recycled to the SRU. These reactions are summarized below.



Several of the reactions which are desired in the TGTU reactor are limited by equilibrium and intertwined with other reactions. For example, increasing the concentration of CO<sub>2</sub> in the tail gas reactor feed will limit the equilibrium extent of COS hydrolysis conversion (vi) and of CO conversion via water-gas shift reaction (x). This in turn will produce less additional hydrogen, which is needed for the reduction reactions (iv), (v), (vii), and (ix). Successful modeling of TGTU reactors has been achieved by others [2] based on significant laboratory and field testing.

### Catalysts for sulfur recovery processes

The catalysts employed today for sulfur recovery processes stand on the foundation of substantial research and development spanning more than thirty years. Over this time, various formulations of catalyst have made their entrance into and subsequent exit from the sulfur recovery stage. We will focus on those types of catalyst used most today.

#### *Alumina catalyst*

The most common type of catalyst used in the SRU is activated alumina (aluminum oxide, Al<sub>2</sub>O<sub>3</sub>, commonly referred to as “alumina”). Similar materials are used across a wide variety of applications, for example, chloride adsorption in catalytic reforming units; propylene purification

in propylene recovery units; fluoride adsorption in HF alkylation units; dehydration in numerous applications. The activated alumina spheres used in SRUs are unique from those used in these other applications. First, the pore structure of this formed catalyst is highly macroporous, that is, the catalyst has a relatively “open” pore structure. This high macroporosity yields increased activity toward the desired reactions (i), (ii), and (iii), among other benefits [3]. Furthermore, these catalysts are different from other activated alumina-based materials because they are not manufactured with an additive or “promoter”. The performance of an activated alumina adsorbent in some applications is enhanced by incorporation of chemicals containing calcium, sodium, magnesium, etc. However, the result is opposite for SRUs; these chemicals do not improve or can even inhibit catalytic activity.

This spherical catalyst is manufactured by forming and calcining aluminum trihydrate. The aluminum trihydrate powder is first reduced to an appropriate particle size, then rapidly dehydrated, yielding a very hygroscopic powder. This hygroscopic powder is formed into spheres by a nodulizer, aided by the addition of water. Nodulizers can take various shapes, sizes, and forms, but the intent is always to begin to form spheres by rolling the particles across a hard surface as they accumulate mass. The catalyst particles are formed to a specified size in the same way that a snowball gathers mass and increases in size as it is rolled across a snowy field. The desired properties of the particle (pore structure, density, crushing strength, etc.) may be achieved by tuning certain operating parameters of the nodulizer. Once the particles are formed, they are passed through a moderate temperature activating dryer (similar to calcining, but at much lower temperature). This removes excess moisture from the particle and fixes the pore structure in place.

Activated alumina catalyst may be considered the starting point for SRU catalyst beds configuration. This catalyst provides high activity for the Claus reaction (i), achieving equilibrium conversion over a lifetime of many years in most applications. Some facilities have used Maxcel 727 activated alumina catalyst for more than twenty years without a single catalyst replacement while maintaining sufficient activity! Activated alumina catalyst also provides good conversion of COS and CS<sub>2</sub> by reactions (ii) and (iii), respectively. If the concentration of these contaminants is not too high, activated alumina catalyst may be sufficient to provide the required level of overall sulfur recovery efficiency in an SRU. If the concentration of these contaminants is higher, then the catalyst bed designer will incorporate top- or bottom-bed layers to increase conversion.

Activated alumina catalyst is robust, but process upsets can cause rapid deactivation. The most common cause of deactivation of an activated alumina catalyst in SRU applications is hydrothermal aging. As the name suggests, high temperatures (especially in upsets > 500°C /

1000°F) and the presence of water (which is always present in the SRU) are required. These conditions result in rapid loss of active surface area of the catalyst. A second common deactivation mode for activated alumina catalyst in SRU applications is sulfation, the formation of a high concentration of stable sulfate ( $\text{SO}_4^{2-}$ ) ions on the catalyst surface active sites. Sulfation occurs when molecular oxygen ( $\text{O}_2$ ) is allowed to enter the reactor feed stream. This is often associated with poor mixing in an upstream fired reheater or burner. Sulfation prevents the affected surface active sites from participating in useful reactions, and thus presents as deactivation. A final cause of deactivation worth mentioning is contamination. Contamination of the activated alumina catalyst in the SRU can occur especially in cases of hydrocarbon ingress. This contamination causes fouling or coking on the catalyst. Refinery fuel gas-fired reheaters are a common source of such contaminants.

### ***Titania catalyst***

In cases where activated alumina catalyst does not provide sufficiently high catalytic activity, titanium dioxide ( $\text{TiO}_2$ , commonly referred to as “titania”) catalyst is employed. There are similar materials employed across a wide range of applications (photocatalysis, pigments) but the materials used for sulfur recovery catalysis are unique because of the phase or polymorph of  $\text{TiO}_2$  which is used. In applications such as pigments, rutile titania may be preferred. In the Claus catalysis application, anatase titania is required because rutile displays very low activity.

Unlike spherical alumina catalyst, titania catalyst is typically formed as an extrudate. The anatase titanium dioxide powder is combined with other feed components and mixed thoroughly. This mixture is then extruded through a die which determines the particle’s shape. For example, a cylindrical shape or multi-lobe shape may be chosen. The physical properties of the resulting catalyst particle may be optimized by adjusting the operating parameters of the extruder. After extrusion, the particle is dried at a moderate temperature to remove excess moisture and set the particle properties and pore structure.

Titania catalyst delivers a boost in reaction rates for conversion of COS and  $\text{CS}_2$  by hydrolysis. According to research by others [4], this is attributable to the surface structure of titania catalyst in the SRU environment. The unique combination of oxidation states on the titania surface (which alumina catalyst does not display) provide fast reaction for these carbon-sulfur compounds.

When titania catalyst is incorporated into a SRU catalyst bed design, it is typically installed first in the lower section of the first Claus reactor catalyst bed. Rather than installing the titania catalyst in the top of the first reactor bed, this location is selected for the reasons of temperature, contamination, and replacement. The temperature of the Claus reactor will be highest at the

bottom of the bed under normal circumstances because reactions (i), (ii), and (iii) are all exothermic. When we place the titania catalyst at the bottom of the bed, we leverage this catalyst's activity by ensuring it is at the part of the reactor with the highest temperature. Also, placing the titania catalyst at the bottom section of the catalyst bed helps prevent its contamination in case of a process upset. This leads to the third reason: replacement. In case of a process upset and the need for replacement ("skimming") of the top of the catalyst bed, the deactivated alumina catalyst can be easily removed by vacuum, while the titania catalyst remains in place.

It has been shown that titania catalysts are quite susceptible to deactivation by BTEX (benzene, toluene, ethylbenzene, xylene) [5]. These aromatic compounds are typically not present in the sulfur recovery unit because they are not present in the feed or are eliminated by conversion in the thermal reactor. However, in certain facilities, BTEX may persist past the thermal reactor, and rapid catalyst deactivation is observed in these units.

#### ***Cobalt-molybdenum tail gas catalysts***

Tail gas treating unit catalysts are commonly composed of cobalt sulfide and molybdenum sulfide active phases on an alumina substrate. These catalysts are commercially available in various sizes and shapes including spheres, cylinders, and multi-lobed extrudates. Two common methods for tail gas catalyst manufacturing are discussed here.

The first common method of tail gas catalyst manufacturing is forming a product from a mixture of raw materials in a single step. The most common embodiment is extrusion of a mixture. A mixture of materials containing (typically) aluminum oxide, cobalt, and molybdenum, is passed through an extruder to form a particle. This particle may be cylindrical or multi-lobed in shape and can be made in a variety of diameters.



*Figure 3. An extruded tail gas catalyst*

After extrusion, the catalyst particle is heated to remove moisture, set the internal structure (catalytic surface area and pore structure), facilitate phase change of the alumina carrier, and convert the active metals from their precursor form to oxidic form. After heating, the catalyst is in the metal-oxide form and is ready for use in the tail gas treating unit. As described further below, a post-treatment activation process may be employed to convert the metal-oxide catalyst to its active, metal-sulfide state.

The second common method of tail gas catalyst manufacturing is impregnation of a substrate. The substrate, typically composed of either activated alumina or gamma alumina, is made first. This particle (which can be spherical or extruded) is formed, then heated to reduce water content and to achieve the required pore structure and surface area. Cobalt and molybdenum salt solutions are then used to impregnate the substrate with the active metal compounds. This process distributes the cobalt and molybdenum throughout the catalyst pore structure on the surface of the carrier. After impregnation, the catalyst must again be heated to remove solvents and to convert the active metals from precursor form to oxidic form. Finally, the catalyst in its metal-oxide form may be submitted to a post-treatment activation process as discussed below.



*Figure 4. A spherical tail gas catalyst*

The methods for manufacturing tail gas catalyst which are described above are not the only ones. Recent developments have led to breakthroughs in catalyst reuse technology for hydroprocessing catalysts. These developments [6] extend the benefits of catalyst reuse (lower cost, smaller carbon footprint) to the TGTU, with the added benefit of delivering even higher activity than traditional tail gas catalysts in some cases. This may be accomplished by qualification and reuse of a regenerated or rejuvenated spent hydroprocessing catalyst itself, or by the recovery of cobalt and molybdenum metals from the spent catalyst for subsequent formulation of a fresh catalyst.



Unlike SRU catalysts, TGTU catalysts must be converted to an active phase before they are ready for the intended application. SRU catalysts are manufactured in their metal-oxide state (that is, aluminum oxide or titanium dioxide) and this state is suitable for facilitating the desired reactions. TGTU catalysts are manufactured in the metal-oxide form ( $\text{CoO}$  and  $\text{MoO}_3$ ) and must be converted to their metal-sulfide form ( $\text{Co}_9\text{S}_8$  and  $\text{MoS}_2$ ) to be active toward the desired hydrogenation and shift reactions ((vi) through (xi)). This conversion, called sulfiding, can take place once the catalyst is installed in the reactor (*in situ*), or prior to installation at a separate catalyst treatment facility (*ex situ*). Several methods exist for both in situ and ex situ activation.

A refinery can choose whether to buy an already sulfided (i.e. activated and ready-to-use) catalyst for direct deployment in the TGTU reactor. The drawback is the more demanding handling of such a pre-sulfided catalyst, which must be stored and managed under exclusion of oxygen. If instead an easy-to-handle un-activated catalyst in metal-oxide form is filled into the TGTU reactor, the refinery must manage the sometimes-critical sulfiding agents and a difficult activation procedure inside the reactor. A compromise is to use a pre-sulfurized catalyst, which is a catalyst that contains the metals in oxide form plus the sulfiding agents. It can be easily handled under air, and only needs to undergo activation in the reactor.

The list of reactions which a tail gas catalyst is intended to facilitate (refer (iv) through (xi) above) is longer and more inter-related than the relevant reactions for Claus catalysts. Accordingly, there can be great variety between catalysts' performance, across these reactions. The most critical reactions are certainly the conversion of both  $\text{SO}_2$  and elemental sulfur back to  $\text{H}_2\text{S}$  (by reactions (iv) and (v)). Without successful completion of these two reactions, downstream process problems will rapidly ensue. Breakthrough of  $\text{SO}_2$  into the downstream quench column will cause rapid corrosion, and subsequent breakthrough to the amine system will result in rapid amine degradation by formation of heat-stable salts. If any elemental sulfur is left unconverted, the quench column can quickly become plugged with solids. Facilitating conversion of  $\text{SO}_2$  and elemental sulfur is therefore a must-have qualification of any tail gas catalyst. Where tail gas catalysts differ is primarily in activity toward conversion of  $\text{COS}$ ,  $\text{CS}_2$ , and  $\text{CO}$  (refer (vi) through (xi) above).

The activity of a tail gas catalyst toward conversion of  $\text{COS}$  and  $\text{CS}_2$  can reduce  $\text{SO}_2$  emissions from the SRU/TGU. The tail gas reactor is followed by an aqueous quench column (equivalently, direct-contact condenser), which cools the process gas from the reactor effluent and allows condensation of most of the water present in the gas stream. The remaining process gas is treated with a solvent, for example MDEA or a physical solvent. In most cases, these solvents will absorb  $\text{H}_2\text{S}$  (preferentially) and some  $\text{CO}_2$  but will not absorb  $\text{COS}$  or  $\text{CS}_2$ .  $\text{COS}$  and  $\text{CS}_2$  will pass

through the absorber column in the vapor phase, and on to the final step of the sulfur recovery unit, a thermal oxidizer. In the thermal oxidizer these compounds will be converted to SO<sub>2</sub> (1 mol/mol COS, 2 mol/mol CS<sub>2</sub>) and contribute to the refinery's emissions. For this reason, it is important to ensure that tail gas catalysts have sufficient activity toward conversion of COS and CS<sub>2</sub>.

Carbon monoxide (CO) plays a surprising role in the tail gas reactor. Despite it having no sulfur atoms, CO can be a key contributor to the overall temperature rise in the tail gas reactor *and* source of additional H<sub>2</sub> by means of the water gas shift reaction (x). In a typical refinery tail gas treating reactor, conversion of CO contributes approximately half of the overall heat release, as shown in Figure 5. This conversion results in the production of hydrogen in a one-to-one molar ratio to CO. This can increase the amount of H<sub>2</sub> (critical for reactions (iv) and (v), and others) by about 50% from what is contained in the SRU tail gas alone.

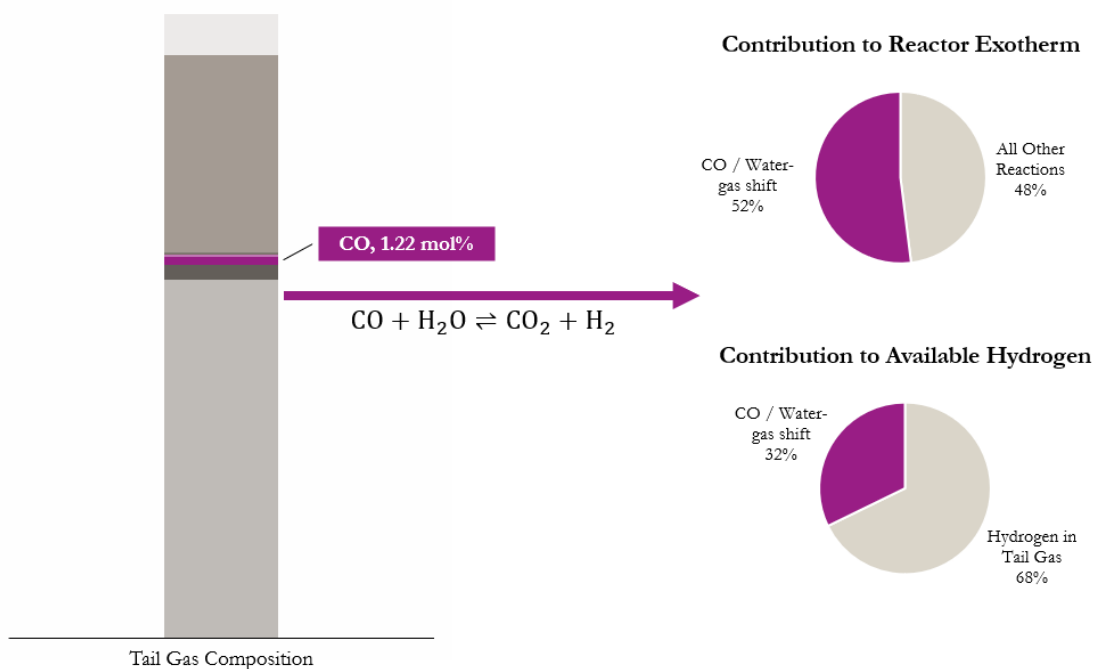


Figure 5. The importance of the water-gas shift reaction in TGTU reactor operation

Tail gas catalysts are typically quite robust, which is fortunate because these reactors are the second-to-last line-of-defense in the refinery's control of SO<sub>2</sub> emissions. There are three important deactivation mechanisms to be aware of: oxidation, reduction, and contamination.

Tail gas catalysts in their metal-sulfide state may be oxidized back to their inactive metal-oxide state. This will occur if metal-sulfide tail gas catalysts are exposed to oxygen in the absence of H<sub>2</sub>S

for a prolonged time. This oxidation reaction is very exothermic, and if temperatures are allowed to increase in the reactor the oxidation can complete for the whole reactor within a matter of hours. Fortunately, this deactivation is reversible. In the same way that a tail gas catalyst in its metal-oxide state from the manufacturer may be sulfided in situ, a tail gas catalyst which has undergone deactivation by oxidation can be “re-sulfided” in situ. In fact, some operating companies have leveraged this reaction as a method for shutting down tail gas reactors, converting the catalyst to the oxide state in a safe and controlled manner (keeping temperatures closely controlled) prior to turnaround.

Tail gas catalysts may also be reduced<sup>‡</sup>. Reduction of a tail gas catalyst occurs when the catalyst is subjected to hydrogen or another reducing gas, in the absence of H<sub>2</sub>S, for a prolonged time. Similar types of catalysts in other refinery processes, e.g. high-pressure diesel hydrotreating, have been shown to undergo deactivation by reduction in a matter of hours of being exposed to these conditions. However, field experience has shown that this reaction proceeds very slowly in tail gas reactor conditions. This is attributable to the significantly lower partial pressure of hydrogen in tail gas reactors compared to other refinery units. Table 1 summarizes oxidation and reduction of tail gas catalysts.

*Table 1. Summary of tail gas catalyst deactivation by oxidation and reduction.*

Deactivation Mode	H <sub>2</sub> S	H <sub>2</sub>	O <sub>2</sub>	Speed	Reversible
Oxidation	No	Either	Yes, in excess <sup>§</sup>	Fast	Yes
Reduction	No	Yes	No	Slow	No

Like alumina and titania catalysts, tail gas catalysts are also susceptible to deactivation by contamination. Contamination of tail gas catalyst typically occurs when C<sub>6+</sub> hydrocarbon compounds, especially those with olefinic qualities, are fed to the tail gas reactor. For example, some facilities source their supplemental hydrogen stream to the tail gas reactor feed from a nearby reformer’s excess hydrogen. A process upset in the reformer causing poor quality excess hydrogen can allow reformat-type hydrocarbons to find their way into the excess hydrogen stream, and in turn onto the tail gas catalyst. Deactivation quickly ensues. Another possible source

<sup>‡</sup> The terms *reduced* and *reduction* are used in this section in the chemical reaction sense of “gaining electrons”, not in the physical sense of “becoming lesser or smaller”.

<sup>§</sup> If H<sub>2</sub>S and/or H<sub>2</sub> are present, oxidation of the catalyst would require oxygen present in excess of that consumed in reaction of H<sub>2</sub>S and H<sub>2</sub>.

of deactivation is BTEX, which may be found remaining in the SRU tail gas under unusual conditions.

## Common catalyst selection approaches

Most refineries will replace SRU and TGTU catalysts during a planned turnaround, every four to eight years. The frequency of replacement is commonly selected to coincide with other refinery unit downtime (hydroprocessing units, cokers, fluidized catalytic crackers, etc.). The refinery process engineer, procurement representative, and management personnel must select replacement catalysts prior to these turnarounds, and this selection is prone to pitfalls.

The first common method to select replacement catalyst is to select identical type, shape, size, and quantity of catalyst which was installed last time. An even more dramatic example of this is the tendency for some operating facilities to purchase the catalyst(s) which were specifically named in the original licensor documents, which are sometimes dated decades in the past! The obvious shortfall of this approach is its failure to appreciate that both catalyst technologies and (more importantly) unit process conditions change over time. Whether the change is a natural gas processing plant operating with a sweeter mix of wells, or a refinery beginning to incorporate renewable feedstocks in the crude slate, a failure to evaluate alternative catalyst options (a failure to plan) is planning to fail.

The second common approach to catalyst selection is to request proposals from SRU catalyst vendors for SRU catalyst and request separate proposals from TGTU catalyst vendors for TGTU catalysts. This approach addresses many of the shortfalls of the first but fails to appreciate the interaction of SRU catalysts with TGTU catalysts – that is, to consider the sulfur recovery unit's catalysts as a system. After all, there is no storage tank or holding volume for the SRU tail gas before it enters the TGTU, nor for the TGTU recycle stream before it enters the SRU.

The following examples describe how these approaches might be followed in real-world scenarios.

### Example 1: A new feed stream causes increased emissions

Renewable fuels have gained traction in the global oil refining market over recent years as technologies to co-process these feedstocks have become more widely demonstrated and available. While the contribution of renewable fuels and feedstocks to total diesel production is still quite small (notably in the United States, as shown in Figure 6), further development of these technologies holds the promise of energy use in transportation and industry with lesser total greenhouse gas emissions.

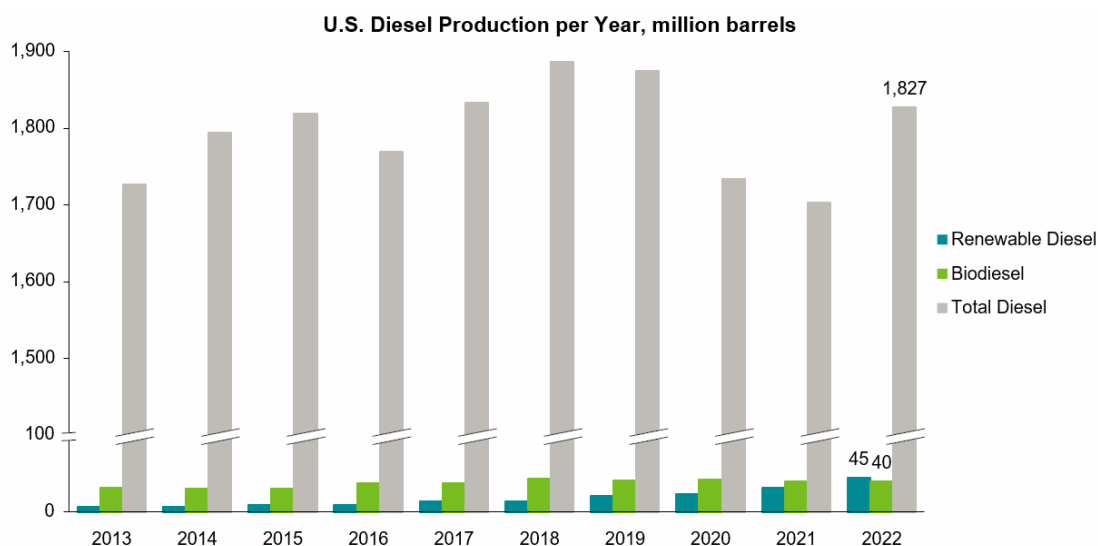


Figure 6. Contribution of renewables and biodiesel to total U.S. diesel production [7] [8] [9]

Co-processing of a renewable feedstock in a refinery hydroprocessing system is a complex matter, impacting the hydroprocessing units themselves, amine treating, sour water processing, sulfur recovery, intermediate and finished product tankage, and blending of fuels. Such discussion is beyond the scope of this paper. In summary, the net impact on the feed to the sulfur recovery unit is increased  $\text{CO}_2$  and  $\text{NH}_3$ , and decreased  $\text{H}_2\text{S}$ . This results in significant changes for the sulfur recovery unit itself, which may not be addressed by either of the two catalyst selection approaches mentioned above.

Consider a refinery which is implementing renewable feedstock co-processing at 10% of the original crude throughput capacity. This example refinery operates a 500 LTPD sulfur recovery unit (containing both a SRU and TGTU). The co-processing of renewable feedstock results in impacts to their sulfur recovery unit feed streams as summarized in Table 2. The impacts indicated here are adapted from a detailed study by others [10].

Table 2. Summary of impacts of renewable feedstock co-processing on feed streams to sulfur recovery unit

Feed Stream	Flow rate	[H <sub>2</sub> S]	[CO <sub>2</sub> ]	[NH <sub>3</sub> ]
Amine Acid Gas	Similar	Decrease	Increase	No Change
Sour Water Stripper Gas	Increase	Decrease	Increase	Increase
TGTU Recycle	Increase	Decrease	Increase	No Change

As the feed streams to the sulfur recovery unit change, so too do the process streams through the unit. One notable change is that more COS and CS<sub>2</sub> remains unconverted in the SRU tail gas. This is caused by the increase in carbon compounds entering the net feed to sulfur recovery unit (more CO<sub>2</sub>), as well as the increased flow rate and CO<sub>2</sub> content of the recycle stream from the TGTU. The total net feed molar flow has been kept equal between these two cases for simplicity.

A refinery which selects their catalysts based on what has been used in the past may find that their sulfur recovery unit does not perform up to requirements after the transition to renewables feed co-processing. Figure 7 shows a visual comparison of the tail gas molar flow rates of the sulfur species between the two cases.

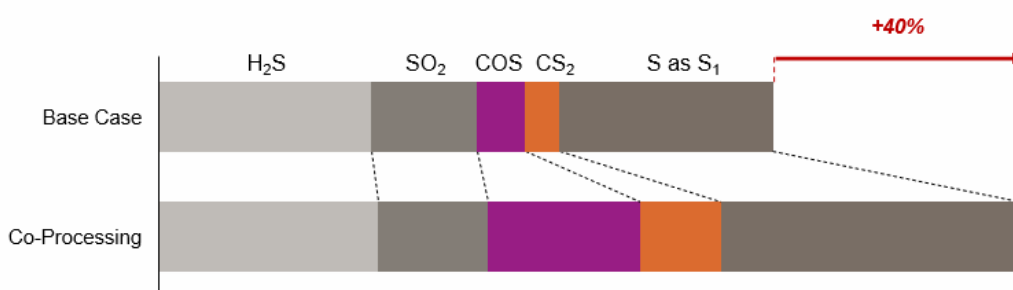


Figure 7. Comparison of SRU tail gas composition (molar flow rates)

It is certainly important to consider not only the concentration of key sulfur species, but also their total flow rate. In this case, the predicted increase of >200% in COS feed rate to the tail gas reactor along with >125% increase in CS<sub>2</sub> feed rate to the tail gas reactor could put a tail gas unit reactor or amine system beyond its capabilities, resulting in higher emissions or ultimately a reduction in refinery throughput capacity. If we assume that in both cases the tail gas catalyst achieves conversion efficiency of 90% for both COS and CS<sub>2</sub>, this new co-processing operation can yield an increase of hundreds of tons per year in SO<sub>2</sub> emissions in this 500 LTPD unit design.

### Example 2: Switching to low temperature TGTU operation and catalyst leaves more sulfur compounds unconverted

A common improvement project executed at refineries today is the conversion of a conventional-temperature TGTU to a low temperature TGTU. This change can reduce energy consumption and even simplify equipment configurations. But if the refinery approaches this modification as a change to the TGTU only, it could have a negative impact on overall sulfur recovery efficiency.

Low temperature tail gas catalysts are so named because of their ability to provide the necessary levels of conversion at lower temperature than so-called conventional temperature tail gas catalysts. Such catalysts can offer sufficient activity for low temperature operation at facilities with relatively low space velocity in the TGTU reactor and/or little COS and CS<sub>2</sub> conversion requirements in the TGTU reactor. These catalysts have higher activity than conventional temperature catalysts, which require operation at higher temperatures to achieve sufficient SO<sub>2</sub> and S<sub>x</sub> conversion. But this increase in activity is not so straightforward as “a shift to the left” on a chart of activity versus temperature. In most cases, low temperature catalysts display differences in relative conversion of each sulfur species. Some low temperature tail gas catalysts may provide excellent COS conversion but mediocre CS<sub>2</sub> conversion, for example. Other low temperature tail gas catalysts only provide high SO<sub>2</sub> and S<sub>x</sub> conversion at the desired low reactor temperatures. This can leave a shortcoming in the conversion of the other sulfur compounds.

We consider the same refinery sulfur recovery unit as in Example 1, but instead of incorporating the modified feed composition for renewables co-processing, we change only the tail gas catalyst to an “intermediate temperature” tail gas catalyst. This catalyst selection enables the refinery to operate the tail gas reactor at a lower temperature and maintain 100% SO<sub>2</sub> and S<sub>x</sub> conversion in the tail gas reactor. The refinery may have chosen to pursue this change to realize fuel/energy savings at the Reducing Gas Generator (RGG, the feed heater for the tail gas reactor). The savings in fuel consumption is deemed to more than offset the slight increase in catalyst cost. This intermediate temperature catalyst delivers excellent SO<sub>2</sub> and S<sub>x</sub> conversion, but shortcomings in conversion of COS and CS<sub>2</sub> leave a dramatic impact on overall efficiency, as shown in Table 3.

Table 3. Switching to LT TGTU conditions without considering the SRU catalyst

Parameter	Base Case	LT TGTU Conditions
SRU Catalyst Type	Alumina only	Alumina only
TGTU Catalyst Type	Conventional Temp.	Intermediate Temp.
CV1 COS Conversion Efficiency	79%	79%
CV1 CS <sub>2</sub> Conversion Efficiency	47%	47%
SRU Cumulative Recovery Efficiency	96.4%	96.4%
TGTU SO <sub>2</sub> Conversion	100%	100%
TGTU S <sub>x</sub> Conversion	100%	100%
TGTU COS Conversion	94.7%	87.9%
TGTU CS <sub>2</sub> Conversion	99.4%	91.2%
TGTU CO Conversion	84.6%	85.3%
Treated Tail Gas COS Concentration	74	160
Treated Tail Gas CS <sub>2</sub> Concentration	5	79
Lost Efficiency from COS and CS <sub>2</sub>	0.05%	0.19%

As shown in the bottom row of the table, the overall sulfur recovery efficiency of the unit has decreased from 99.95% to about 99.80%. And this is of course the simulated operation under steady state; actual refinery operation and variability could result in a further deviation downward from 99.80%.

### Example 3: Too many options between SRU and TGTU catalysts?

One can imagine various reasons for which a refinery might choose to increase COS and CS<sub>2</sub> conversion in the sulfur recovery unit (SRU and TGTU). Perhaps there is a desire to improve the unit's capability to handle upsets by increasing the “buffer” between normal operation and exceeding SO<sub>2</sub> emissions limits. Because COS and CS<sub>2</sub> contribute to emissions, their elimination upstream (in either the SRU or TGTU) represents a real increase in the “buffer”. Or refinery management may desire a longer catalyst life. This also might be achieved by increasing activity toward COS and CS<sub>2</sub> conversion, since activity for these reactions tends to drop off earlier than that for the Claus reaction (in SRU catalysts) or SO<sub>2</sub> and S<sub>x</sub> reactions (in TGTU catalysts).

The possible combinations of catalyst configurations can be overwhelming. As shown in Example 1, titania catalyst can be incorporated, but determining the optimal amount (or is it necessary to use all titania catalyst in all SRU reactors?) is a particular challenge. Different tail gas catalysts offer different activity toward each of the relevant reactions. One tail gas catalyst



manufacturer offers four different tail gas catalysts. How many should be evaluated? If a refinery is approaching this change with existing equipment (in contrast to a licensor/EPC approach), the size of the existing reactors can also be a limiting factor in the evaluation. In addition to the conversion aspects, the refinery management may be particularly interested in the economics and sustainability aspects of the decision.

## **A coordinated, holistic approach**

The correct way to approach selection of sulfur recovery unit (SRU & TGTU) catalysts is by evaluating them in conjunction. After all, these are not separate units whose operation is buffered by a product storage or feed storage tank. Tail gas from the SRU flows directly and continuously to the TGTU. Lagging performance in the SRU “spills over” into the TGTU. A process upset in the TGTU does not initiate temporary shutdown of the SRU alone while the TGTU issues are resolved. Like two train cars pulled by the same engine, the SRU and TGTU are closely coupled. Catalyst bed designs and catalyst selections must take this into account.

By evaluating the SRU and TGTU catalyst bed configurations together, a refinery positions itself for optimization across catalyst activity, reaching the desired level of performance, and controlling overall cost. This approach may be applied to each of the previous examples, and clear benefits are shown for each.

### **Solution 1: Anticipating impacts of feed stream changes when choosing replacement catalysts**

In the earlier section of Example 1, a case was presented where renewable feedstock co-processing at a refinery resulted in changes to the feed streams to the SRU thermal reactor. This change caused surprisingly high levels of COS and CS<sub>2</sub> remaining in the feed to the TGTU, as well as higher CO<sub>2</sub> content of the SRU tail gas and the TGTU recycle stream back to the front-end of the SRU.

Facilities anticipating a change in SRU feed gas composition should evaluate the available options for catalyst bed designs. The increased concentration of CS<sub>2</sub> and (especially) COS in the SRU tail gas suggest that a different Claus catalyst configuration could help to alleviate the conversion load on the tail gas catalyst. The impact on the SRU tail gas composition of different catalyst bed configurations is shown in Figure 8 and Figure 9 below.

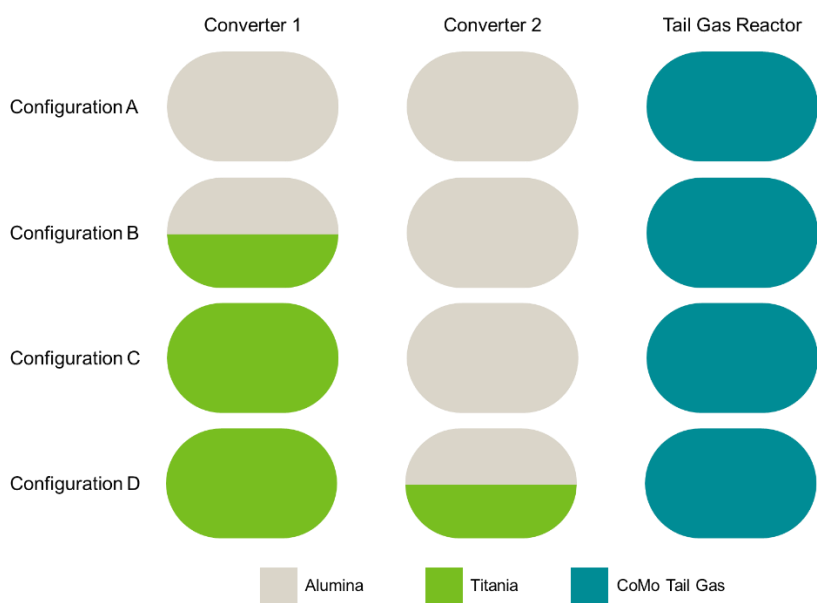


Figure 8. Catalyst configurations considered for Example 1 (other options also exist).

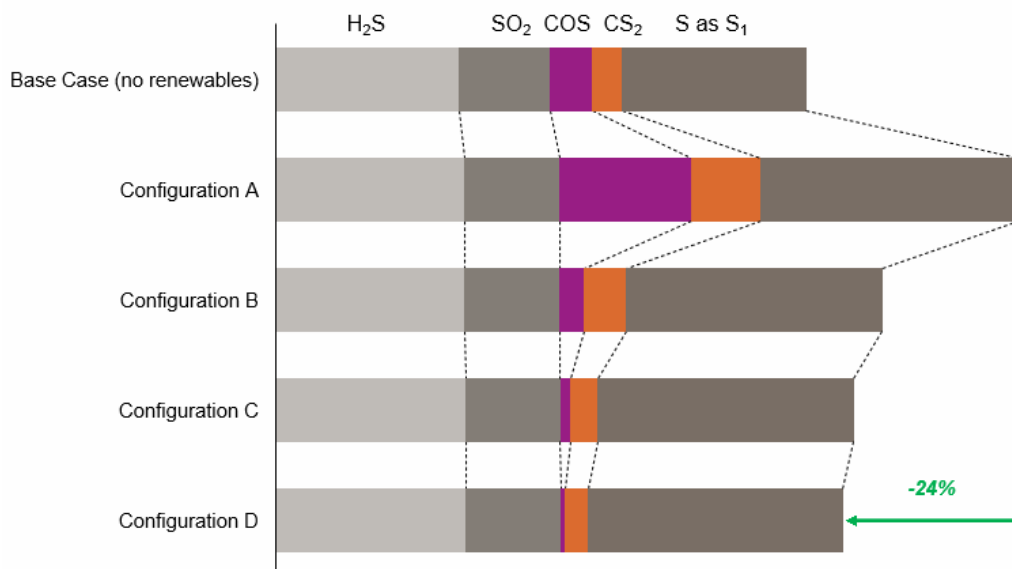


Figure 9. Comparison of SRU tail gas composition with different SRU catalyst configurations (molar flow rates)

The improvement in COS and CS<sub>2</sub> conversion over titania catalyst (superior to alumina catalyst in this regard) provides a marked reduction in the flow rates of these two compounds to

the tail gas reactor. A refinery may elect to “include titania”, and this might be implemented in the bottom 50% of the first converter, as is the typical case. This is represented in Configuration B. However, a further elimination of COS and CS<sub>2</sub> is possible incorporating a greater amount of titania, as shown in Configuration C and Configuration D. In some facilities, this further maximization of COS and CS<sub>2</sub> conversion may be necessary to adjust the load on the tail gas treating unit and ultimately reduce SO<sub>2</sub> emissions.

Although only four configurations are considered here, one can imagine (and should examine) additional configurations considering, for example, different activity levels of the tail gas catalyst, and their respective impact on the remaining COS and CS<sub>2</sub> downstream of the tail gas reactor. Differences in tail gas catalyst activity can have an impact on the types of SRU catalysts required, as described further in Example 3 below.

### **Solution 2: Adjusting SRU catalyst configuration supports new LT TGTU operation**

A change of tail gas catalyst to a catalyst with higher activity and reduction in temperature of the tail gas feed heater may not be enough to make the transition to low-temperature TGTU operation, as shown in Example 2 above. Instead of focusing attention exclusively on the TGTU reactor, the upstream SRU reactors should be included in the consideration.

The primary shortcoming indicated in the earlier section of Example 2 was the breakthrough of COS and CS<sub>2</sub> through the tail gas reactor. One solution to this issue is to further boost tail gas catalyst activity, as discussed in the following section on Example 3. Here in Table 4, it is demonstrated that the impact of the change on the unit could be resolved by increasing COS and CS<sub>2</sub> conversion in the SRU.

Table 4. Improving overall recovery efficiency by considering the SRU catalyst while switching to LT TGTU conditions

Parameter	Base Case	LT TGTU Conditions	Improved Configuration
SRU Catalyst Type	Alumina only	Alumina only	50% Titania**
TGTU Catalyst Type	Conventional Temp.	Intermediate Temp.	Intermediate Temp.
CV1 COS Conversion Efficiency	79%	79%	99% ↑
CV1 CS <sub>2</sub> Conversion Efficiency	47%	47%	78% ↑
SRU Cumulative Recovery Efficiency	96.4%	96.4%	97.1% ↑
TGTU SO <sub>2</sub> Conversion	100%	100%	100%
TGTU S <sub>x</sub> Conversion	100%	100%	100%
TGTU COS Conversion	94.7%	87.9%	87.7%
TGTU CS <sub>2</sub> Conversion	99.4%	91.2%	91.2%
TGTU CO Conversion	84.6%	85.3%	85.3%
Treated Tail Gas COS Concentration	74	160	12 ↓
Treated Tail Gas CS <sub>2</sub> Concentration	5	79	31 ↓
Lost Efficiency from COS and CS <sub>2</sub>	0.05%	0.19%	0.05%

### Solution 3: Optimizing the SRU and TGTU catalyst configuration together

Approaching the challenge of optimizing the catalyst configuration in a sulfur recovery unit (SRU & TGTU) requires knowledge of Claus alumina catalysts, Claus titania catalysts, and the various types and activity levels of tail gas catalysts. Evonik has been active in the industry of sulfur recovery catalysts for many decades†† and currently leads sulfur recovery catalyst technology in several key areas.

We consider again the sulfur recovery unit from the previous example. In the base case, we incorporated an intermediate-temperature tail gas catalyst. One such catalyst is Maxcel TGE-01 from Evonik, a 3.5-mm trilobe extruded CoMo tail gas catalyst. These catalysts are often selected because of their relatively low cost to fill and good catalytic activity. However, as demonstrated in Example 2, this level of activity is not sufficient to enable low temperature operation at this

\*\* For the sake of simplicity, no other operational parameters were adjusted besides the catalyst configuration between these three cases. However, some further optimization could be possible with each catalyst configuration.

†† Porocel began manufacturing and supplying Claus activated alumina catalysts to the sulfur recovery industry in 1998. Twenty-two years later, Porocel was acquired by Evonik. Today, Evonik maintains the emphasis and expertise on sulfur recovery catalysts as part of the Catalysts business line.

facility<sup>‡</sup> due to levels of COS and CS<sub>2</sub> which remain in the SRU tail gas, that is, in the feed to the TGTU reactor.

One approach to resolving this issue is to install a tail gas catalyst with even higher activity. This can be done with true low-temperature tail gas catalysts, such as Maxcel TGS-02. These catalysts can deliver the required activity with reactor inlet temperatures at 465°F / 240°C or lower. Alternatively, we might adjust the amount of titania catalyst (Maxcel 777) in the SRU reactors. As demonstrated earlier, this approach will reduce the amount of COS and CS<sub>2</sub> in the tail gas reactor feed, and therefore also reduce the amount of these components which contribute to SO<sub>2</sub> emissions. A final approach to consider here is one which achieves the required conversion and minimizes catalyst spend, while also delivering a reduced carbon footprint. The oil and energy industry continues to implement goals and strategies to reduce carbon footprint of their operation; catalyst selection can be key factor in this. In this approach, we would implement a tail gas catalyst which delivers even higher COS and CS<sub>2</sub> conversion, Evonik's EcoMax TG catalyst. This catalyst is unique in the industry in delivering high activity combined with sustainability benefits. Table 5 summarizes the results of these four approaches.

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<sup>‡</sup> As stated above, some facilities operate without issue using intermediate-temperature tail gas catalyst at low temperature conditions. Whether or not this can be done depends on the space velocity, component conversion requirements, etc.

Table 5. Examples of optimizing SRU and TGTU catalysts together

Case Description		Base Case	Boost TG Catalyst Activity	Incorporate Titania	Improve performance, increase conversion, reduce footprint
SRU Catalyst Config		Alumina only	Alumina only	50% Titania in CV1	50% Titania in CV1
TG Catalyst Config.		Intermediate Temp. (Maxcel TGE-01)	Low Temp. (Maxcel TGS-02)	Intermediate Temp. (Maxcel TGE-01)	Sustainable TG Catalyst (EcoMax TG)
Thermal Stage Recovery Eff.	%	65.9	65.9	65.8	65.9
CV1 COS Conv	%	78.9	78.9	<b>99</b>	<b>99</b>
CV1 CS <sub>2</sub> Conv	%	46.9	46.9	<b>78.2</b>	<b>78.2</b>
CV1 Cumulative Recovery Eff.	%	92	89.7	92.5	92.5
CV2 Cumulative Recovery Eff.	%	96.8	96.4	97.5	97.5
RGG Effluent Temp <sup>§</sup>		450	450	450	450
TGTU Effluent COS	ppm	<b>317</b>	<b>102</b>	<b>17</b>	<b>8</b>
TGTU Effluent CS <sub>2</sub>	ppm	<b>120</b>	<b>1</b>	<b>84</b>	<b>0</b>
Relative Total Catalyst Cost	(vs. Base Case)	1.00	<b>1.62</b>	<b>1.54</b>	<b>1.41</b>
Total Catalyst Footprint***	ton CO <sub>2</sub> e	430	<b>526</b>	<b>517</b>	<b>432</b>

<sup>§</sup> TGTU reactor inlet temperature (RGG Effluent Temperature) intentionally kept unchanged between cases for the sake of comparison.

\*\*\* Note: Catalyst Footprint calculated as global warming potential (CO<sub>2</sub> equivalents, CO<sub>2</sub>e) according to ISO 14041. Footprint for cobalt-molybdenum TGTU catalyst determined as part of certified Life Cycle Assessment completed by Evonik, September 2022. Footprint for alumina SRU catalyst and titania SRU catalyst estimated according to Evonik internal information.

Certainly, there are other configurations which could be analyzed. For example, we might increase the amount of titania catalyst in the first converter, simultaneously reducing the reactor temperature. This would realize energy savings (not commonly a priority for sulfur recovery units, considering the quantity of high-pressure steam produced from the thermal stage waste heat exchanger) in the SRU while also increasing  $\text{H}_2\text{S}$  and  $\text{SO}_2$  conversion by shifting Claus reaction equilibrium. By reducing the amount of  $\text{SO}_2$  as well as COS and  $\text{CS}_2$  in the feed to the tail gas reactor by this approach, further optimization could be done by reducing TGTU reactor inlet temperatures, saving further energy.

## Conclusion

Selection of catalysts for the sulfur recovery unit (including both SRU and TGTU, together) is an exercise which is best approached as a system, not as separate processes. While these two processes may be called different “units”, they act in concert with one another. The activity and performance of the catalyst in the SRU affects the TGTU by influencing the amount of COS and  $\text{CS}_2$  which must be converted in the TGTU. Efforts at optimization of one reactor require knowledge of the other’s performance. In addition, aspects such as cost of installation and carbon footprint of the catalyst should be considered when selecting catalysts. Ultimately, optimum economic and technical performance can only be ensured if catalyst and processes are considered, evaluated, and selected holistically.

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