



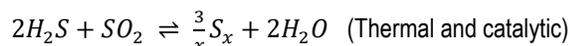
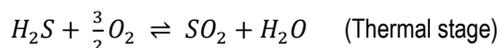
Using SulphurPro® to Simulate Hydrogenation in an SRU

Hydrogenation in an SRU is a reaction step done for the same purpose as hydrodesulfurization. It is carried out to convert all sulphur compounds such as SO₂, COS and mercaptans in the tail gas into H₂S for subsequent capture by the TGU amine system for recycling back to the front end of the SRU for conversion back into elemental sulphur. This issue of The Contactor™ describes the development of a reaction kinetic model for the TGU Hydrogenation Reactor that forms an important part of SulphurPro®. Two subsequent issues will deal with (a) a case study and (b) a more general description of catalyst deactivation.

Process Background

The sulfur recovery complex in a refinery or gas plant is part of the overall system for extracting H₂S, other acid gases and organic sulfur compounds from the process feed gas. The acid gas removal system is regenerative and produces an acid gas (and often sour water acid gas, SWAG) which is processed in the sulfur recovery unit (SRU), comprised of Claus, TGU, and Thermal Oxidizer. Sulfur compounds are either recovered as elemental sulfur or they are emitted to the atmosphere.

Fundamental Claus process chemistry converts H₂S to sulfur in two or three stages with about 95–97% overall recovery efficiency:



The tail gas unit recovers unconverted sulfur from the Claus unit as H₂S, and achieves the very high sulfur recovery required by today's environmental standards. A TGU is an independent process but is also an integral part of the SRU. Process chemistry involves the catalytic conversion of non-H₂S sulfur species to H₂S by hydrolysis and hydrogenation, continuation of Claus, and conversion of carbon monoxide to hydrogen and CO₂. Hydrogen aids hydrogenation reactions and in addition reduces CO emissions. Main reactions in the catalytic bed are:

- COS, CS₂ - hydrolysis on alumina
- SO₂, S_x, COS, CS₂ - hydrogenation on Co/Mo
- CO - water gas shift on Co/Mo

The process chemistry is more complex, with several parallel reactions as well as reactions between SO₂ and other reduced sulfur species. Figure 1 shows the overall TGU process. Claus unit off-gas is preheated and charged to the hydrogenation reactor where a cobalt-molybdenum catalyst converts sulfur compounds to H₂S. After quenching to remove water and heat of reaction, H₂S is recovered using an H₂S-selective amine. The off-gas is incinerated and vented to atmosphere. Amine regeneration recycles H₂S to the SRU reaction furnace. A high degree of sulfur recovery is achieved by substantial conversion of all species to H₂S. The TGU admits of low sulfur slip with overall SRU/TGU recovery performance of 99.9% or better.

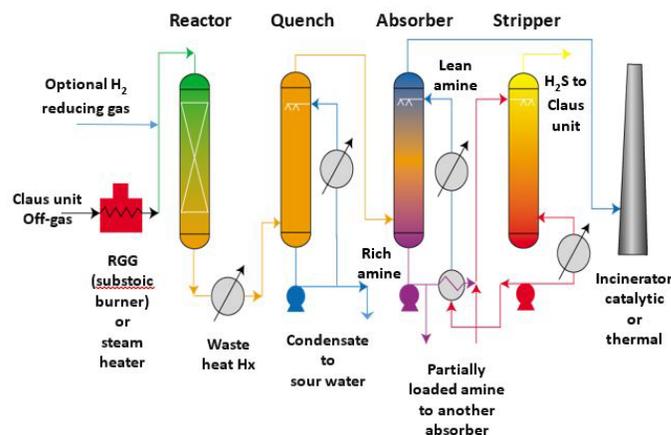


Figure 1 Tail Gas Treating Unit

The primary performance characteristic of a TGU catalyst is that SO₂ should be fully converted. If SO₂ enters the quench circuit, it will foul, corrode, potentially deactivate and subsequently degrade the amine. Secondly, a high degree of conversion is required for COS, CS₂ and mercaptan; otherwise, these components pass through the amine system are incinerated and discharged to atmosphere as SO₂. Finally, any elemental sulfur not converted will plug and corrode the quench circuit.

Historically, TGU design is based on fresh catalyst. The designer selects temperature and catalyst quantity needed to achieve high conversion of non-H₂S sulfur compounds and meet environmental performance requirements. The importance of compliance with permitted environmental emissions from start- to end-of-run means sufficient catalyst inventory must be provided such that even in an aged condition, the needed sulfur recovery is achieved.

Kinetic Framework and Model Development

The fundamental TGU reaction matrix is (1) hydrolysis on alumina, (2) hydrogenation, and (3) water gas shift on CoS/MoS₂. In the basic frame in Table 1, an expanded reaction set is invoked to quantify the multiple pathways involving SO₂, which are also Co/Mo catalyzed. These reac-

Table 1 Reaction Pathways

Reactant(s)	Products			
	Reverse	Hydrolysis	Hydrogenation	Shift / Exchange
COS	X	H ₂ S + CO ₂	--	H ₂ S + CO
CS ₂		H ₂ S + COS	H ₂ S + CH ₃ SH	--
SO ₂		--	H ₂ O + S (or H ₂ S)	
S		--	H ₂ S	
CO	X	--	--	H ₂ + CO ₂
CH ₃ SH			H ₂ S + CH ₄	
SO ₂ + CS ₂				CO ₂ + S
SO ₂ + CO				CO ₂ + S
Claus H ₂ S+SO ₂				S + H ₂ O

tions are parallel to the conventional ones, and address compositionally-dependent observations. Whereas, stoichiometry for the reaction is well known, reaction order and kinetics must be determined from reaction rate data and generally these do not follow stoichiometric coefficients.

The following steps were carried out in the development of the reaction kinetics model:

1. Collect published experimental data
2. Postulate a reaction set
3. Determine reaction order from published data
4. Assess of equilibrium influences, if > 10% outlet, include reverse reaction
5. Determination of kinetic rate temperature coefficients for Arrhenius expression from data
6. Identification and regression of compositional resistances to reaction rates
7. Refinement of the reaction set and rates with experimental and operational observations

The kinetic rate model has been fitted to published experimental data [1, 2]. An apparent kinetics approach was adopted which lumps the intrinsic active-site-based kinetics, k_{int} , with effectiveness factor, η , for resistances to reaction rate that result from mass transfer and diffusional effects within the pores of the catalyst pellet. This decision was made by considering

$$k_{app} = \eta k_{int} \quad \text{and} \quad k_{app} = A \exp(-E_a/RT) \quad \text{Arrhenius}$$

the magnitudes of Thiele modulus and effectiveness factors. The approach provided good representation of temperature-dependent kinetics using Arrhenius-based, experimentally-determined, rate coefficients.

The effect of adsorption resistances and compositional interaction with the reaction rate were modeled using either Langmuir-Hinshelwood type factors or a fractional-order rate expression. An example is the analysis of the interaction between *hydrogen, water and carbon dioxide in the water-gas shift reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$* . Water is usually in substantial excess (normally the reaction kinetics would be addressed as pseudo-first-order with water as zero-order) but competitive adsorption of water on active sites influences reaction rate. Additionally at lower water concentrations, reaction rate declines, exhibiting second-order behavior. The Langmuir/Hinshelwood relationship provides an effective form to represent this relationship.

$$rate = \frac{-[CO] * k_{eff} * K_w * [H_2O]}{(1 + K_w[H_2O]^{aw} + K_c[CO_2]^{ac} + K_h[H_2]^{ah})^d}$$

Hydrogen is a product of the reaction yet it has an influence beyond an equilibrium limitation expression because it is strongly adsorbed and as a leaving group it becomes rate limiting, restricting access to new reactants. The effect of hydrogen can be represented as a fractional order compositional dependency or with the adsorption mechanism: $rate = -k_{eff}[CO][H_2]^a[H_2O]^b[CO_2]^c$.

The hydrolysis reaction of COS and shift reactions of CO and COS share several components so these are parallel reaction pathways. Since the reaction system is not at equilibrium, kinetic parameters for all paths (including reverse reactions) must be defined. Additionally, COS is a product of CS₂ hydrolysis. The hydrolysis reaction of COS is reversible and equilibrium limited as are the shift reactions of CO and COS. All the other reactions have diminishingly small equilibrium values and are considered irreversible. When reversible, kinetics must respect equilibrium so forward and reverse rates comply with:

$$k_{forward}/k_{reverse} = K_p \quad \text{and} \quad k_{reverse} = k_{forward}/K_p.$$

where $K_p = [R]^r [S]^s / ([A]^a [B]^b)$. The hydrolysis reaction of COS and shift reactions of CO and COS share several components so these are parallel reaction pathways. Since the reaction system is not at equilibrium, kinetic parameters for all paths (including reverse reactions) must be defined. Additionally, COS is a product of CS₂ hydrolysis.

An interesting aspect of CS₂ hydrogenation is formation of methyl mercaptan which is further hydrogenated to methane and hydrogen sulfide. The extent of methyl mercaptan production is determined by the sum of mercaptan and methane, which then allows fitting for conversion of mercaptan to methane.

SO₂ has multiple roles in TGU reaction kinetics. A known effect of SO₂ is the moderation of hydrolysis of COS and CS₂ [3]. The more subtle role of SO₂, revealed with discretized finite element bed modeling, is providing an alternate conversion pathway for CS₂, moderating production of mercaptan and COS. Additionally, SO₂ provides a direct conversion of CO (vs. water gas shift/hydrogenation) acknowledging a substantial enhancement influence on CO conversion when present.

These rigorous reaction kinetics with added interference from pore diffusion limitations were ultimately implemented as a hydrogenation reactor model in SulphurPro®, thereby providing an essential ingredient in rate-based, plant-wide simulation of SRUs and TGUs. The reaction scheme comprised 11 individual reactions, and the reactor is represented by a series of small discrete segments. In each segment the progress of each reaction is represented by:

$$\frac{\Delta C_a}{\Delta x} = -C_a^n C_b^m k_{app} \Delta t,$$

where Δx = fractional depth in reactor (a segment) ; n, m = reaction order, Δt = residence time per segment = 3600 x catalyst volume / hourly gas rate. All reactions are solved in parallel in each reactor segment, with conversion is summed across all reactor segments.

The model presented here captures not just the detailed reaction kinetics, but also accounts for deactivation from aging (depending on temperature, humidity, and time) and poisoning (related to operational stresses, e.g., BTEX or O₂ in feed). Hydrothermal aging affects the relative activity of an entire bed, whereas poisoning impacts the bed along the flow path, starting at the inlet and moving toward the outlet. Poisoning accelerates performance decline, related to loss of conversion of sulfur species that slip through the TGU into the Thermal Oxidizer.

Conclusions

Sound technical tools, which represent kinetics of the TGU system and enable meaningful simulation, helps to reveal substantial effects on performance, allowing a potentially serious event to be identified and mitigated before it happens.

With kinetics and deactivation elements considered, one can use the model to analyze and predict the performance and useful life of a real reactor based on comparison of simulated vs. actual temperature profiles, especially over time. Designers using SulphurPro® now have a better tool to specify reactors, and operators are better able to quantify what is actually occurring instead of only simulating ideal operation.

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