



The CONTACTOR™

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Claus Tail Gas Hydrogenation

The tail gas coming from the final sulfur condenser in a Claus-based SRU contains enough unconverted SO_2 and other sulfur species to present the plant with a significant challenge to meeting sulfur emissions regulations if discharged to the stack without further treatment (Weiland, Jones & Hatcher, *The Role of Tail Gas Treating Unit Quench Towers*, PTQ Gas, 2016). Conventional treatment involves its hydrogenation to convert the S_x , COS, CS_2 , and SO_2 content to H_2S so it can be removed and recycled by a downstream amine treating unit. A secondary function is CO conversion to CO_2 via the water-gas shift reaction, which provides additional hydrogen. CO discharge limits also exist in most jurisdictions. Hydrogenation (also called hydrodesulphurisation) is followed by a direct contact water quench step to cool the hydrogenated gas to a low enough temperature to make H_2S removal by an amine system feasible.

Catalysts

The hydrogenation catalyst is usually cobalt-molybdenum (or nickel-molybdenum) supported on γ -alumina. The industrial manufacture of hydrodesulphurization catalysts consists of four steps: carrier preparation, addition of active compounds, calcination, and sulphiding. Each step influences the activity and is well-discussed by W. Ripperger and W. Saum in *J. Less Common Metals*, 54 (2), 353 (1977) (<https://www.sciencedirect.com/science/article/pii/0378382079900316>, 13 Feb 2022). Much of the following general introduction is taken from that work. The usual starting material for the carrier is converted to $\gamma\text{-Al}_2\text{O}_3$ by heat treatment. The chemical and physical properties of the carrier are important in determining the way in which the metal oxides are incorporated into and onto the pores, hence the catalyst's chemical activity.

The pore size distribution also has to be adjusted to the particular hydrodesulphurization problem, i.e., to the size of the molecules being desulphurized. A precise prediction of the most favorable Co(Ni):Mo ratio is not possible. The ratio depends mainly on the properties of the support and the way in which the metal oxides are added. The most active catalysts are those prepared by impregnation of alumina with solutions of molybdate and cobalt (or nickel) salts. The activity of the Ni-Mo catalyst can, however, be increased by phosphoric acid.

The oxide catalyst is activated by pre-heating in an atmosphere of hydrogen and hydrogen sulphide.

Sulphiding begins at low temperatures (about 250°C) to avoid reduction of the oxides before their conversion to the sulphides or more likely to oxysulphides. A partial reduction to the metals before sulphiding results in a considerable loss of activity. Compared with Co-Mo catalysts, Ni-Mo catalysts possess a higher activity for the reduction of nitrogen compounds at a given level of hydrodesulphurization activity. Ni-Mo catalysts are also preferred for the hydrogenation of unsaturated compounds and particularly for the hydrogenation of aromatics.

A frequent question engineers ask is how well pre-sulphiding really works. SulphurPro's Tail Gas Hydrogenation Reactor model now allows that question to be answered.

Important Factors

Chemical and physical properties of the support are important in determining the way in which the metal oxides are incorporated, hence the chemical activity. The deposited metals are activated by sulphiding, so the sulphidation conditions can strongly influence catalyst activity.

The catalyst itself takes the form of pellets but most of the metallic catalyst is deposited, not on the exterior of the pellets, but on their interior surface, in particular within the macro and micro pores making up the internal structure of the catalyst pellet. Thus, important factors determining catalyst activity are catalyst porosity, pore size, pore size distribution, pellet diameter, pellet size, and pellet shape.

The hydrogenation reactor model in OGT | SulphurPro® results from having taken great pains to ensure that the model reflects as much as possible the detail of the catalysts themselves. Model accuracy is critically important because hydrogenation is such an important step in determining the final sulphur recovery and establishing sulphur emissions.

Reactions

A sizeable number of reactions occur in the hydrogenation reactor, including not just H_2S generation from SO_2 but also hydrogen production via the water-gas-shift reaction,

methyl mercaptan, and CS₂ and COS formation and destruction. An excellent summary was presented by P. D. Clarke, N. I. Dowling, and M. Huang at the 2015 Brimstone Sulfur Symposium, Vail, CO. These reactions are all included kinetically in the OGT | SulphurPro hydrogenation reactor module.

Model Parameters

The OGT | SulphurPro® simulator provides a tremendous wealth of information on the performance of multi-layered beds of spherical, cylindrical and trilobe catalyst particles including 11 reactions in horizontally and vertically aligned vessels, and bed heat loss, and the effect of catalyst aging and poisoning.

The interface shown in **Figure 1** allows for reactions to be turned on and off so they can be studied individually. The products of some reactions become reactants for others, so the reaction set must be solved simultaneously in a manner that is flexible so as to accommodate many potential user specifications. Reaction-level options include kinetic mode, equilibrium, conversion and specified by reaction.

The OGT | SulphurPro Hydrogenation Reactor uses a robust numerical solver that permits different layers of catalysts to be modelled in a kinetic rate-based manner inclusive of hydraulic calculations for accurate pressure drop predictions across the catalyst bed.

Rigorous handling of vessel geometries which incorporates mensurated cylinder and head volumes are included to permit accurate accommodation of the plant thermocouple locations, and catalyst volume variation with catalyst bed depth for both horizontal and vertical geometries (**Figure 2**).

Tail gas hydrogenation reactor calculations are extremely detailed and are on a rate basis (not equilibrium) which leads to exceptional reliability and predictive power. The composition of the gas feeding and leaving the TGTU accurately reflects reality with OGT | SulphurPro®.

		Mode
<input checked="" type="checkbox"/>	Water-Gas Shift	CO + H ₂ O <-> CO ₂ + H ₂
<input checked="" type="checkbox"/>	COS Hydrolysis	COS + H ₂ O <-> CO ₂ + H ₂ S
<input checked="" type="checkbox"/>	COS Hydrogenation	COS + H ₂ <-> CO + H ₂ S
<input checked="" type="checkbox"/>	CS ₂ Hydrolysis	CS ₂ + H ₂ O <-> COS + H ₂ S
<input checked="" type="checkbox"/>	CS ₂ Hydrogenation	CS ₂ + 3 H ₂ <-> CH ₃ SH + H ₂ S
<input checked="" type="checkbox"/>	CS ₂ to Sulphur	CS ₂ + SO ₂ <-> 3 S + CO ₂
<input checked="" type="checkbox"/>	CH ₃ SH Hydrogenation	CH ₃ SH + H ₂ <-> CH ₄ + H ₂ S
<input checked="" type="checkbox"/>	SO ₂ Hydrogenation	SO ₂ + 3 H ₂ <-> H ₂ S + 2 H ₂ O
<input checked="" type="checkbox"/>	Claus	SO ₂ + 2 H ₂ S <-> 3 S + 2 H ₂ O
<input checked="" type="checkbox"/>	Sulphur Hydrogenation	S + H ₂ <-> H ₂ S

Figure 1 Reaction Specification Interface

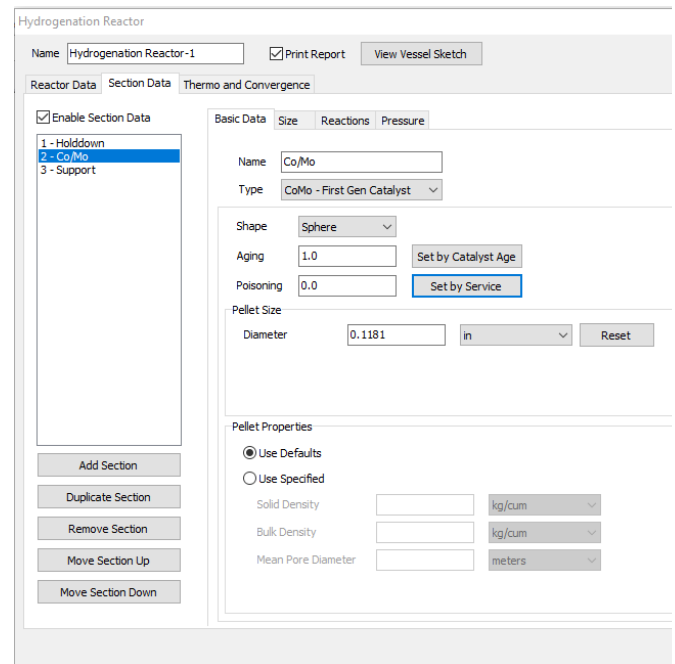


Figure 2 Layered Catalyst Specification Interface

Why a Detailed Hydrogenation Model Matters

That an accurate fundamentals-based hydrogenation reactor model matters is most easily demonstrated with a simple example. The case refers to a refinery SRU processing SWS gas through the first zone of a two-zone reaction furnace with amine acid gas (AAG) split between the two zones. (This approach allows the first zone to run hotter promoting ammonia destruction.) This is a two-converter-bed setup using alumina catalyst without oxygen enrichment.

When the unit is run with combustion air set to maintain a 2:1 H₂S:SO₂ ratio (defined to be zero excess air) the normal SO₂ level from the hydrogenation reactor is a quite acceptable. However, with even 2.5% excess air the SO₂ level in the hydrogenation reactor effluent is predicted to escalate to 400 ppmv. This can play havoc with the quench system and, if not mitigated, will cause a host of problems ranging from corrosion and plugging of the quench to the rapid loss of activity of the amine solvent in the TGTU. The solution is to cut back on combustion air, or add more hydrogen to the reactor feed. However, none of this may be immediately obvious to the operators without using OGT | SulphurPro® to simulate the system, and possibly OGT | ProBot™ to monitor the system online and give advance warning of impending trouble.

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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