

Kinetic model for TGU hydrogenation reactors: Part 2 Catalyst model validation

A rigorous high-fidelity kinetic model can help designers and operators forecast the life expectancy of reactor catalyst beds

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Part 1 of this article, published in *PTQ*'s Q1 2023 issue, involved the development of a model for the reactions occurring in the hydrogenation reactor of a sulphur recovery unit (SRU). The model addressed 11 different reactions and alluded to the catalyst ageing and poisoning that inevitably occurs over the life of the catalyst. Part 2 takes a deeper look at catalyst deactivation from a modelling standpoint and quantifies how deactivation can be included in the reaction kinetics model. Part 3 will detail catalyst deactivation and poisoning mechanisms. The model is validated with a case study.

Catalyst ageing and poisoning model

Ultimately, catalyst activity sets the sulphur recovery performance of the tail gas unit (TGU). Deactivation of heterogeneous catalysts, such as the ones used in the TGU hydrogenation reactor, occurs by ageing and poisoning; this is a ubiquitous problem that causes gradual loss of catalytic rate. For a comprehensive TGU design, catalyst deactivation over the life of the catalyst charges and its effect on meeting sulphur emission requirements must be addressed.

When fresh catalyst is loaded into the TGU reactor and activated, it has maximum surface area and activity. On start-up, the catalyst is immediately exposed to several possible deactivation stresses, most causing irreversible damage. Mechanisms that alter catalyst activity do so by affecting the dispersed, active, metal-sulphide phases of cobalt and molybdenum and the high surface area alumina support. Alumina (and titania) are often used in the process industry as supports for many heterogeneous catalysts, as well as for the Claus process, so one can draw on this larger body of knowledge and on sulphur recovery industry experience.

The activity of these catalysts is strongly related to the γ -alumina (or mixed phase alumina) surface area of the base, alumina crystallites and their microporous structure that facilitates accessibility to the reactants. The alumina matrix has hydroxyl ions on the catalyst surface that serve as weak Brønsted-Lowry acid sites, promoting hydrolysis and Claus reaction. Their extensive surface area both supports and interacts with the active cobalt and molybdenum metals.

Activity declines as a function of time, and exposure to

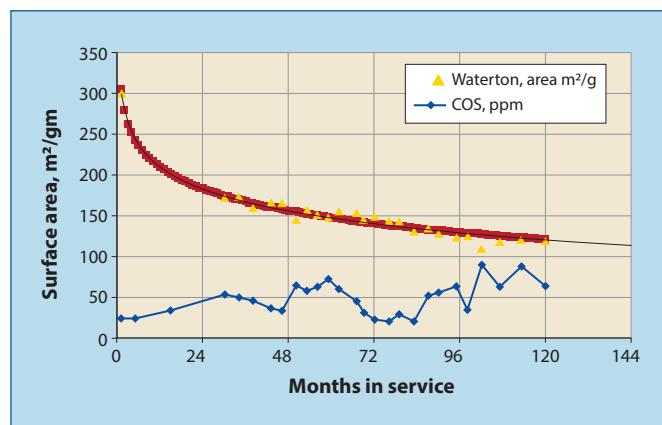


Figure 1 Puget Sound Refinery, sulphur-plant samples from SCOT reactor, lab data¹

normal process conditions is treated as ageing and related to loss of surface area and active sites. The remaining fraction active surface area can be represented by an ageing factor, AF. Ageing tends to occur uniformly throughout the catalyst bed, with catalytic activity or conversion of reactive species declining rapidly at first and then slowly over the catalyst's life. Spent catalyst activity approaches about 50% of fresh activity, and the model is fitted to this operating data for ageing, as observed in the measurements of the sulphur-plant data shown in Figure 1.¹

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Assays of used TGU catalysts report surface area, crush strength, carbon, and sulphate.² Typically, when the surface area reaches 120 m²/g, they are considered spent. Other 'spent' criteria are carbon-on-catalyst as seen at levels approaching 1% and crush strength declining to half the fresh value. Sulphate is not always observed, but about 1% is not unusual (although spent catalyst may have substantial

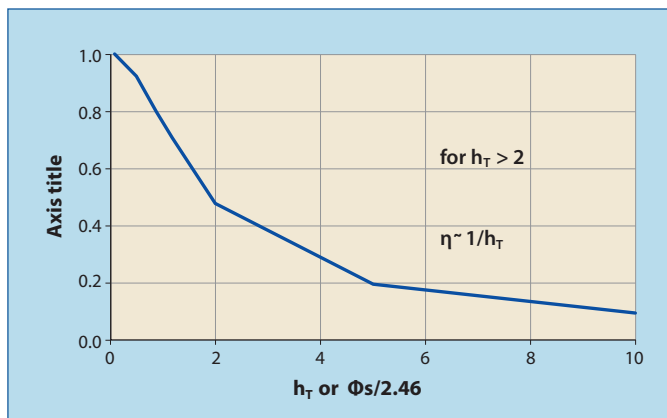


Figure 2 Effectiveness factor vs Thiele modulus

sulphate). Activity testing reported on abused catalyst (due to exposure to extreme temperatures) in spent conditions expresses about 50% of fresh activity, with carbon typically 0.1 or 0.2%.

Catalyst deactivation and poisoning is a vast and fascinating subject in its own right, and it deserves much more than a cursory treatment. Part 3 will take a deeper plunge into the subject so, for now, the discussion of mechanisms and causes of deactivation is deferred. Suffice it to mention that hydrothermal ageing, sooting, chemisorption of poisons (especially of oxygen) and, by sulphation, coking and sintering are all causes of deactivation. Ultimately, the loss of specific surface area directly affects catalyst performance as the number of active Al-OH surface sites falls.

Quantification of poisoning

Generally, fresh alumina catalyst has a specific surface area of 300-350 m²/g; with initial ageing, surface area declines to 240-260 m²/g and then stays relatively stable, declining only slowly over several years until 'spent', at approximately 120 m²/g. Hydrothermal ageing tends to occur uniformly throughout the catalyst bed, approaching about 50% of fresh activity when spent.

Poisoning is treated as activity loss related to any of several contaminants in the feed. Certain streams that wind up

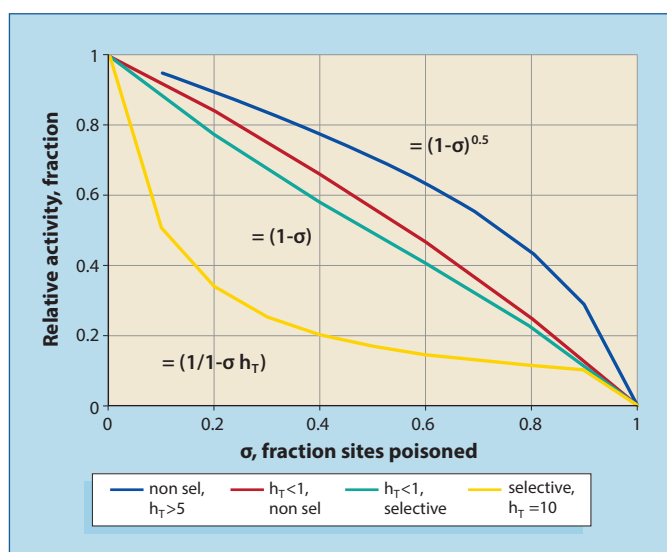


Figure 3 Relative activity vs fraction sites poisoned

at the TGU are known to contribute to poisoning. Although not ideal for an SRU, this method of disposal is sometimes taken as the one with least consequences. SRUs that process BTEX-containing acid gas can pass those species on to the TGU, especially in lean acid gas situations. The effect of BTEX is thought to be reduced at temperatures below 240°C, as discussed elsewhere.³

Deactivation is connected with catalyst pore and active site distribution.⁴ Catalytic activity is conveniently defined in terms of the observed external rate constant k_{obs} , which is equal to the product of the catalyst active site-based intrinsic rate constant k_{intr} , the effectiveness factor η , and the active site surface number density, σ (number of sites per area of surface), and an ageing factor, AF:

$$k_{obs} = k_{intr} \eta \sigma AF$$

Poisoning corresponds to a loss of active sites, i.e., $\sigma = \sigma(1 - \alpha)$, where α is the fraction of sites poisoned. The effect on activity is a combination of site number density, poison selectivity, mass transfer resistance, and loss of surface area. Deactivation directly affects:

- Selectivity: how quickly the poison interacts with the catalyst active sites; selective poisoning preferentially affects sites near the pore mouth and slowly progresses along the pore, vs non-selective, which progresses more or less uniformly along the entire length of the pore.
- η : effectiveness factor, i.e., reaction rate with mass transfer resistance/intrinsic reaction rates without mass transfer resistance.
- h_T : Thiele modulus, i.e., the ratio of kinetic rate to mass transfer (diffusion) rate.

The activity response to poisoning depends on the combination of selectivity and Thiele modulus. The approximate order is as follows:

- Half-order for non-selective, large h_T
- First-order for small h_T (<2)
- Reciprocal function ($1/(1+\sigma h_T)$) (selective with large h_T).

Catalysts used in TGU service have enhanced pore structures with macro-, meso- and micropores. These facilitate good transport of reactants into the interior surface and active Co/Mo sites with moderate diffusional resistance. Classic particle geometry estimation of characteristic pore radius, pore length, and tortuosity gives a rather low value for Thiele modulus and an overly conservative estimate of effectiveness factor. Comparison between experimentally determined whole and crushed catalyst activity coefficients is the best way to determine effectiveness factors because finely crushing the catalyst eliminates pore diffusion.

The effect of poisoning on overall activity depends on the product of effectiveness factor and the fraction of sites poisoned (see **Figure 2**). Selective poisoning can have a dramatic effect when the Thiele modulus is large ($h_T \gg 1$). A linear relationship represents both selective and non-selective poisoning when $h_T \leq 1$ (see **Figure 3**). This was selected for the model. Poisoning is seen to occur at the inlet section of the reactor bed, caused by the presence of contaminants and SO₂, with the poison moving through the bed.

The effect of poisoning on TGU reactor performance

is cumulative but dependent on the level of poison in the feed. Because poisoning rates depend on concentration, it should be apparent at the inlet in a short reaction zone and slowly progress through the bed.

A way to forecast performance across the lifetime of a catalyst charge is provided in OGT's proprietary SulphurPro simulator. Examples will illustrate application to field observations to interpret operating system temperature profiles. Primary causes of deactivation and considerations for its mitigation are discussed further in Part 3.

All ageing and poisoning mechanisms are implemented in SulphurPro as function declines, requiring the user to input service run-time and exposure to poisoning stresses. Different user-configurable poisoning factors include options to specify the use of a reducing gas generator (RGG) burner, refinery gas, and reformer hydrogen as fuel sources. There is also an option to specify whether the unit processes off-gas from acid gas recovery units. In addition, the interface allows for specifying conditions such as the percentage of excess air and the level of BTEX in the feed gas. Taken together, these options allow the construction of a poisoning factor that is built into the mathematical framework of the catalyst bed. The SulphurPro user interface for specifying the ageing and poisoning level is shown in Figure 4.

Model case study

To study the usability of the model, a case study was done by running the hydrogenation reactor model on a typical tail gas reactor feed at various levels of catalyst ageing and poisoning. Figure 5 shows the temperature profiles in the bed as a function of catalyst age under various poisoning conditions. The x-axis denotes the time online in months,

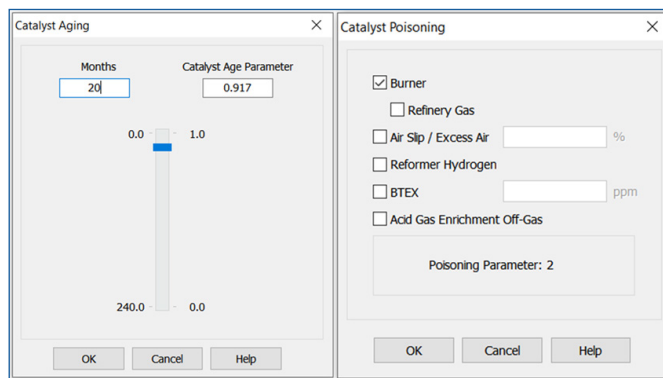


Figure 4 OGT SulphurPro interface for specifying catalyst age and poisoning level

the primary y-axis shows the percentage temperature rise that occurs in each quarter of the bed, and the secondary y-axis gives the total temperature rise across the entire catalyst bed. Each plot refers to a different poisoning mechanism. Note: these profiles show four zones, but the bottom zone (lower bed-to-outlet) in most operating units is disregarded because heat losses accrue here, and DT is often negative.

The poisoning situations that were studied include an idealised operating scenario, which has no poisoning sources, including the expected poisoning of a gas plant and a refinery operating with a clean source of hydrogen; units with an inline RGG burner; reformer hydrogen and a TGU processing the off-gas from an acid gas enrichment (AGE) unit. Figure 6 shows the outlet concentration of various sulphur species for the same runs. The Figure 6 curves represent the different poisoning cases, and each sulphur-bearing species is shown in the individual plots.

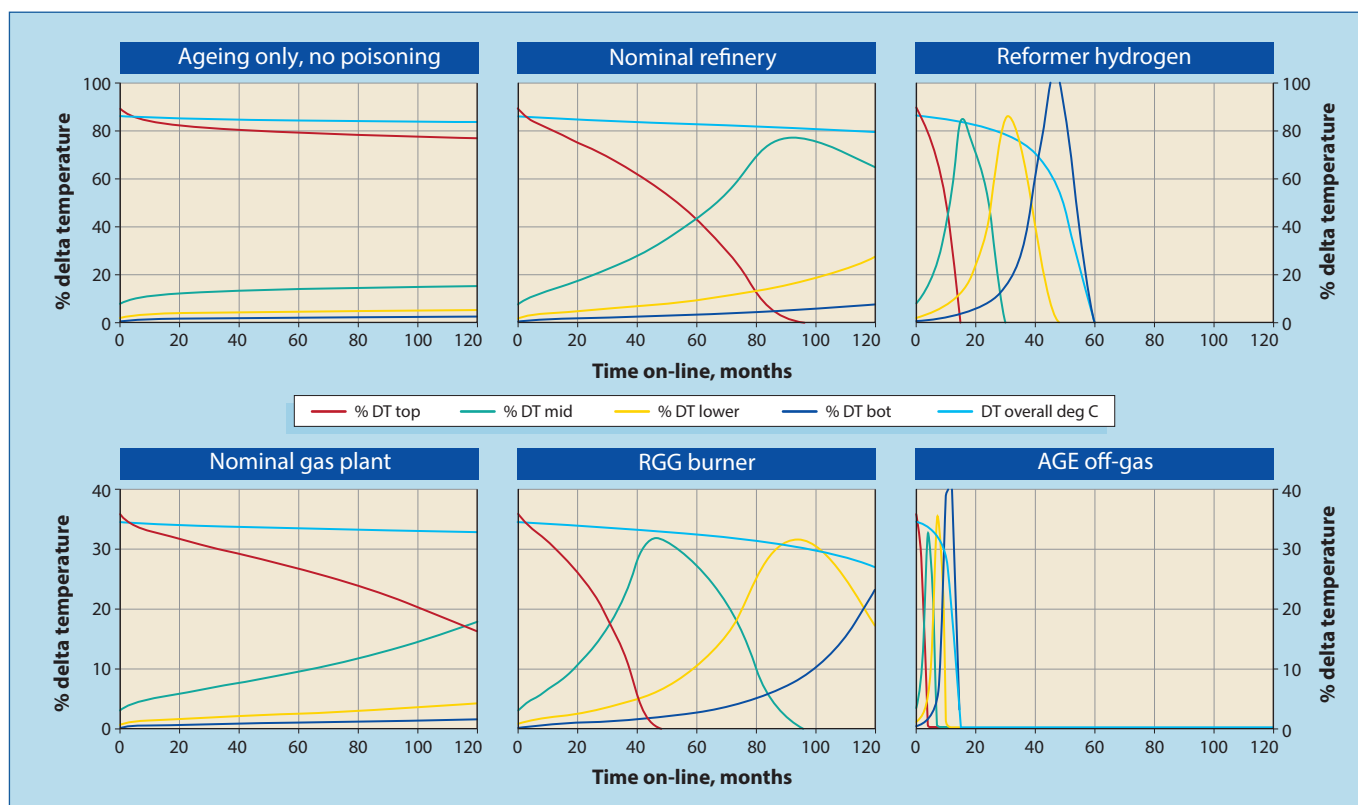


Figure 5 Reactor temperature profile as a function of catalyst age at various poisoning levels

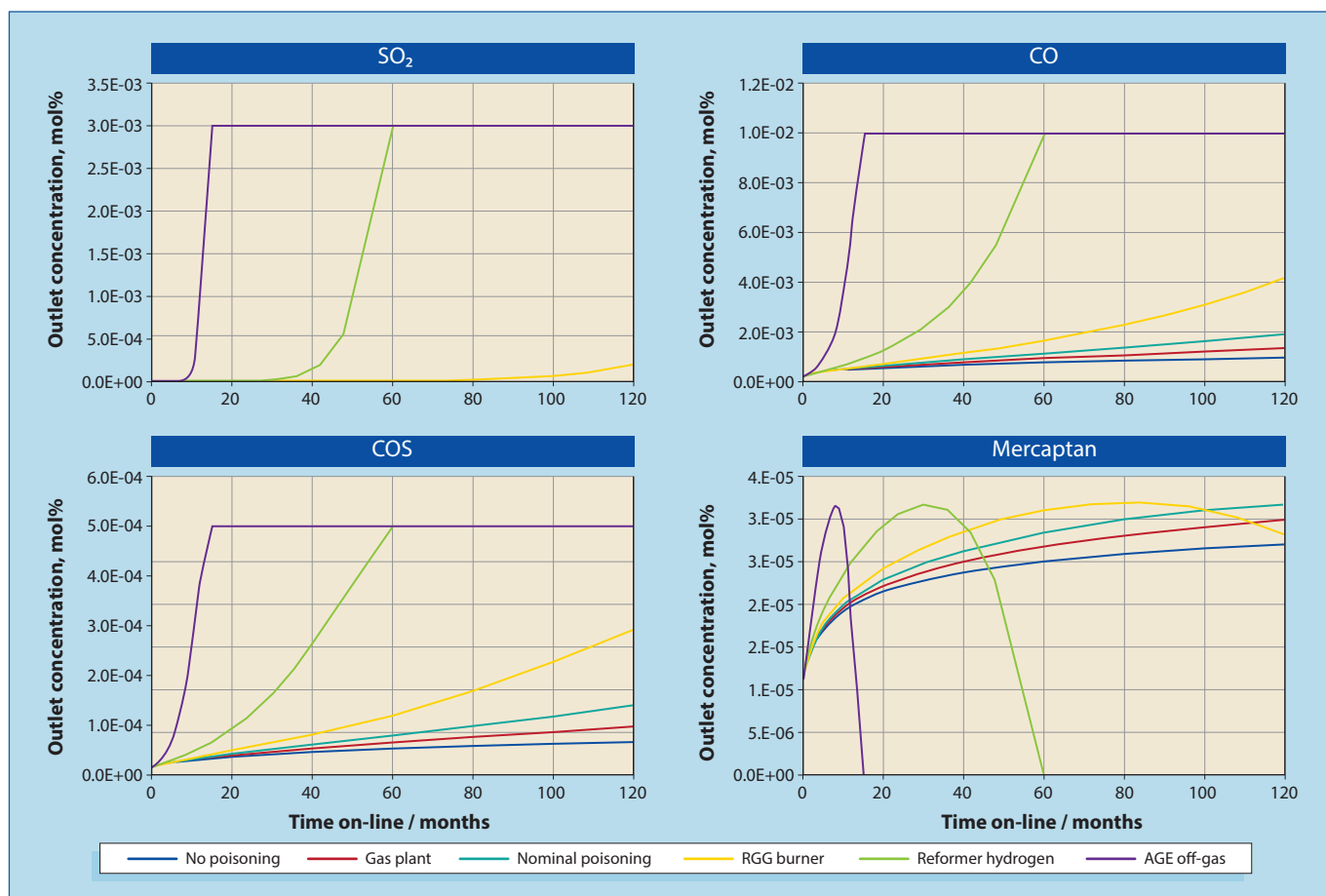


Figure 6 Reactor outlet gas concentrations as a function of catalyst age at various poisoning levels

It is noteworthy that for the idealised case without poisoning, almost all the exotherm still occurs in the top quarter of the bed, even for fully aged catalyst. Slip of non-H₂S sulphur compounds increases from 25 ppm for fresh to 100 ppm for fully aged catalyst because catalyst activity is reduced to the expected spent half-fresh level, with conversion decreasing for all reactions. The exotherm shift typically observed in operations reflects poisoning in the top of the bed, effectively reducing the amount of catalyst and the conversion, which further increases sulphur slip.

Exposure to mild levels of contaminants, as encountered in a gas plant or refinery, and moderate levels (as expected) with a unit operating on an RGG burner causes catalyst deactivation at the inlet, moving the exotherm away from the top of the bed. At shorter operating periods, a less deactivated catalyst offsets the effect of poisoning and moderates sulphur slip. In the latter two cases, the model predicts that the first quarter of the bed is completely deactivated after about 100 months and 40 months, respectively. These poisoning contributions leave very little room for other plant upsets and shorten the operating life. In the most severe cases, such as reformer hydrogen or AGE off-gas, even meeting typical turnaround objectives of 3-5 years (36-60 months) is precluded.

Figure 6 shows that in the case of reformer hydrogen and AGE off-gas, the bed activity declines rapidly compared to the other cases owing to the significant levels of contaminants in the feed. Catalyst is exhausted by 60 and 20 months, respectively, with an even shorter useful operating

life. Outlet concentration plots also indicate the onset of trace sulphur slippage as COS and mercaptans in addition to carbon monoxide. All these compounds typically escape the TGU amine loop and reach the thermal oxidiser, thus increasing sulphur emissions.

With severe poisoning, SO₂ slip also occurs early in the life cycle. Even minute levels of SO₂ slip can lead to its gradual accumulation in the quench system and TGU amine loops downstream. SO₂, being a relatively strong acid (compared to the reduced sulphur compounds), can severely reduce the amine solvent's ability to remove other acid gases, in turn increasing overall emissions. Furthermore, the build-up of SO₂ can lead to severe fouling and corrosion in the quench system. This rigorous high-fidelity kinetic model can help designers and operators forecast the life expectancy of the catalyst bed.

Figure 7 shows composition profiles along the reactor bed for various species. These would otherwise not be available from normal operating data. For fresh catalyst, all the SO₂ is converted in just the first 20% of the bed. This increases to 40% at 48 months without poisoning and 60% with an RGG burner for a 48-month-old catalyst. The significance of the water-gas shift reaction as a source of hydrogen can be inferred from the minima in the H₂ concentration profile. The sudden initial drop can be attributed to the fast reduction of SO₂ to H₂S, which stoichiometrically consumes 3 moles of hydrogen per mole of SO₂ converted. The hydrogen concentration then gradually starts increasing through the conversion of carbon monoxide by the

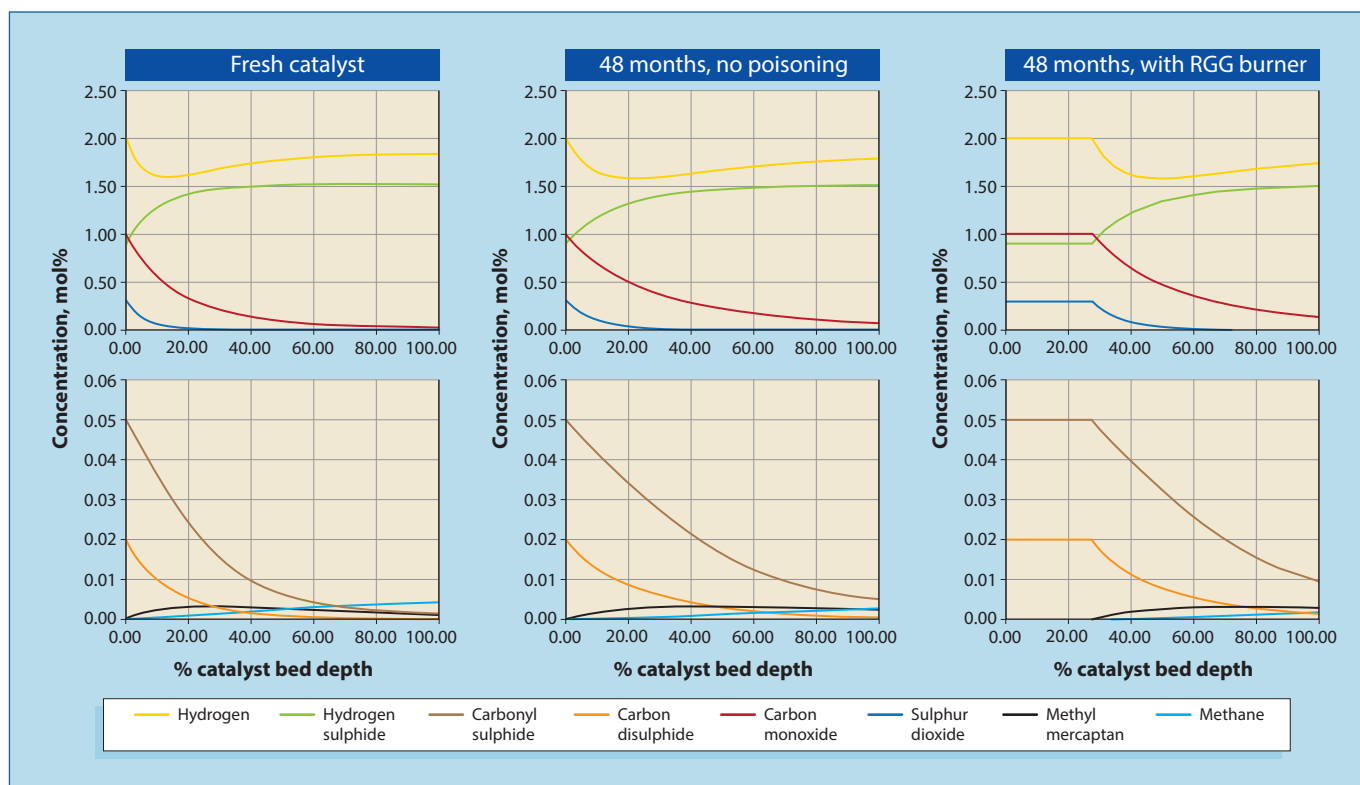


Figure 7 Reactor composition profiles

water-gas shift reaction. In addition to providing a hydrogen source for the reduction of trace sulphur species, this ensures carbon monoxide emissions are reduced.

The mercaptan concentration initially increases with depth into the bed because it is an intermediate product in the CS₂ reaction. However, it is later hydrogenated, driving down the outlet concentration. However, as activity decreases from ageing and poisoning, mercaptan concentration increases as it is still formed from CS₂ (which is still almost completely converted), but the degree of intermediate RSH destruction declines as the active portion of the

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bed shrinks. Total sulphur slippage (represented by the total of all sulphur atoms in COS, CS₂x2, and RSH) typically slips past the amine system into thermal oxidiser. Both ageing and poisoning affect sulphur slip, as seen for fresh and 48-month conditions:

- Fresh ~26 ppmv
- Ageing only at 48 months ~83 ppmv
- Refinery + RGG at 48 months ~153 ppmv

Note that this analysis does not consider additional plant-specific factors. Firstly, the analysis is limited to a

typical TGU feed with first-generation Co/Mo hydrogenation catalyst. Improved catalysts may be available at some sites. Secondly, a robust TGU design will allow operators to increase the reactor inlet temperature to compensate for some slower reactions. The penalties for this flexibility are incremental fuel or energy usage (cost) and increased baseline hydrothermal ageing of the catalyst. Both factors can be studied with the use of the OGT SulphurPro model.

Conclusions

A hydrogenation reactor that accounts only for ageing shows most of the temperature rise in the top zone even at the end of catalyst life. Some degree of poisoning is indicated for most units as they exhibit operating temperature profiles shifting into middle and bottom zones across the life cycle.

The temperature profile in a TGU hydrogenation reactor provides useful insight into performance and catalyst health. Catalyst deactivation is caused by ageing and poisoning – it is inevitable and generally irreversible. Deactivation and poisoning lower conversion and increase slip of non-H₂S compounds; in severe cases, SO₂ may slip, causing corrosion, fouling, and equipment damage.

The kinetic model presented here captures the detailed reaction kinetics and accounts for deactivation from ageing (depending on temperature, humidity, and time) and poisoning (related to operational stresses, such as BTEX or O₂ in the feed). Hydrothermal ageing affects the relative activity of the entire bed, whereas poisoning affects 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 sulphur species that slip through the TGU into the thermal oxidiser.

All operators aspire to achieve longevity of catalyst service. With this information, it is possible, through analysis of the operation, to recognise an acceptable decline in catalyst activity vs a more severe decline. Modelling with appropriate ageing and poisoning factors provides the opportunity to use the knowledge presented by the model to decide whether to remove the poison or plan for catalyst replacement.

With all elements considered, the model lends itself to analysing and predicting the performance and useful life of a reactor based on comparison between simulated and actual temperature profiles, especially over time. Designers now have a tool to specify reactors better, and operators can better quantify what is occurring instead of only simulating ideal operations.

Improved operation and designs can reduce sulphur emissions, improving quality of life.

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