Kinetic model for TGU hydrogenation reactors: Part 1 – model development

Development of rigorous model for reaction kinetics and catalyst deactivation mechanisms capable of predicting SRU and TGU performance is presented

Michael A Huffmaster **Independent Consultant**
Prashanth Chandran, Nathan A Hatcher, Daryl R Jensen and Ralph H Weiland **Optimized Gas Treating, Inc.**

The most widely applied tail gas unit (TGU) is the SCOT-type with a hydrogenation reactor to reduce all sulphur species to H_2S and subsequently recover and recycle H_2S to the Claus thermal reactor. World Bank standards now require a minimal TGU level of performance for all but the smallest sulphur recovery units (SRUs). Across 50+ years of TGU application, many improvements have been made, increasing process efficiency, raising sulphur recovery, and reducing capital cost. Contributions include more effective process design, improved catalyst performance, enhanced solvent selectivity, and the development of increasingly sophisticated process simulation tools.

Included in a rigorous model for reaction kinetics and catalyst deactivation mechanisms capable of predicting SRU and TGU performance are molecular reaction pathways and reaction rates for chemical species that are encountered in tail gas hydrogenation reactors as functions of temperature and residence time. The resulting model has been implemented as a fixed bed hydrogenation reactor in OGT | SulphurPro, a rate-based process simulator widely used in modelling sulphur recovery and tail gas treating units (TGTUs).*

Since catalyst activity declines, provisions must be made to include sufficient catalyst to achieve environmental performance at EOR when catalyst can be replaced

Engineering analysis must ensure environmental performance standards are achieved from start-of-run (SOR) conditions right through to end-of-run (EOR). Quantifying expected performance across time is necessary, too. Catalysts age with exposure to process conditions and are poisoned by process contaminants. Because catalyst activity declines, provisions must be made to include sufficient catalyst (or operational flexibility) to achieve environmental performance at EOR when catalyst can be replaced. The model, whose development is discussed in more detail, provides the means to address ageing and poisoning effects, which will help engineers optimise designs, forecast performance, and troubleshoot operations using the analysis of operating data against model predictions.

Process background

The sulphur recovery complex in a refinery or gas plant can be viewed as part of the overall system for extracting H_2S, other acid gases, and organic sulphur compounds from the process. The acid gas removal system is regenerated and produces an acid gas (and often sour water acid gas, SWAG) which is processed in the SRU, comprised of Claus, TGU, and thermal oxidiser. Sulphur compounds are recovered as elemental sulphur or emitted to atmosphere.

Fundamental Claus process chemistry converts H_2S to sulphur in two to three stages with about 95-97% overall recovery efficiency:

$$H_2S + \frac{3}{2} O_2 \rightleftharpoons SO_2 + H_2O \qquad \text{(Thermal stage)}$$

$$2H_2S + SO_2 \rightleftharpoons \frac{3}{x} S_x + 2H_2O \qquad \text{(Thermal and catalytic)}$$

The TGU recovers unconverted sulphur from the Claus unit as H_2S, achieving the very high sulphur recovery required by today's environmental standards. Although an independent process, a TGU is an integral part of the SRU. Process chemistry involves the catalytic conversion of non-H_2S sulphur species to H_2S by hydrolysis and hydrogenation, continuation of Claus, and conversion of carbon monoxide to hydrogen and CO_2. Hydrogen aids hydrogenation reactions and, in addition, CO emissions are reduced. The main reactions in the catalyst bed are:

COS, CS_2	- hydrolysis on alumina
SO_2, S_x, COS, CS_2	- 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 SO_2 and other reduced sulphur species. A more comprehensive discussion of reaction pathways is deferred until later. **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 sulphur compounds to H_2S. After quenching to remove water and heat of reaction, H_2S is recovered using an amine selective for H_2S. The off-gas is

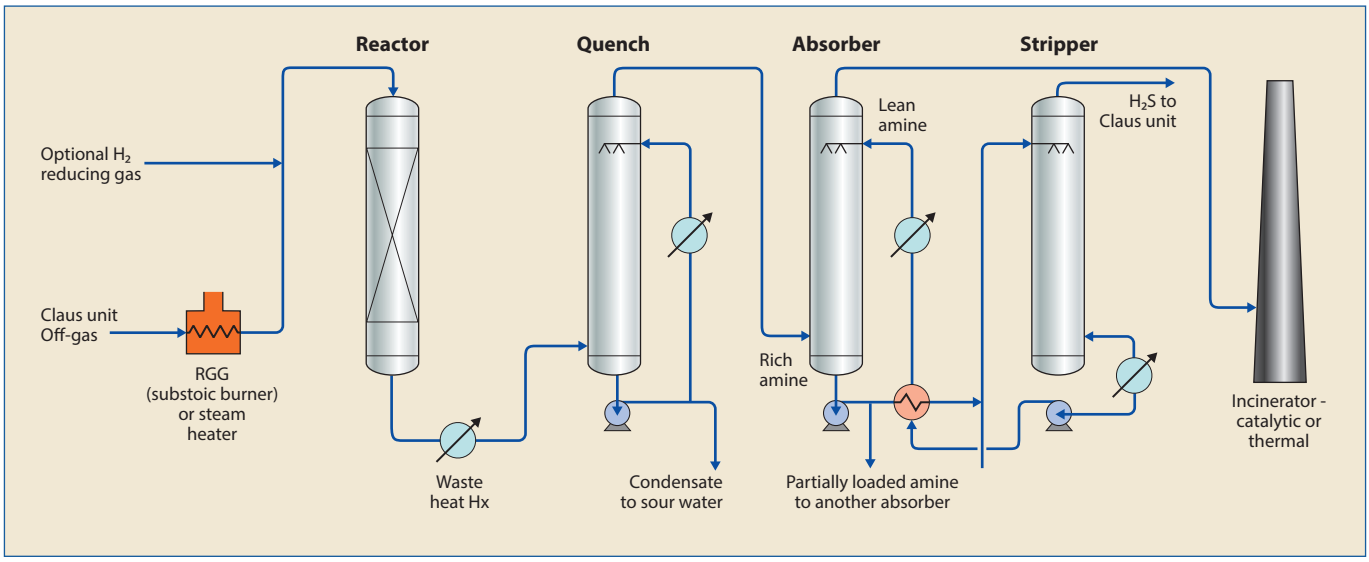

Figure 1 Tail gas treating unit (TGTU)

incinerated and vented to atmosphere. Amine regeneration recycles H_2S to the SRU reaction furnace. A high degree of sulphur recovery is achieved by substantial conversion of all species to H_2S. The TGU admits a low sulphur slip with an overall SRU/TGU recovery performance of 99.9% or better.

The primary performance characteristic of a TGU catalyst is that SO_2 should be fully converted. If SO_2 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, CS_2, and mercaptan; otherwise, these components pass through the amine system, are incinerated and discharged to atmosphere as SO_2. Finally, any elemental sulphur not converted will plug and corrode the quench circuit.

Historically, TGU design is based on fresh catalyst. The designer selects the temperature and catalyst quantity needed to achieve high conversion of non-H_2S sulphur compounds and meet environmental performance requirements. The importance of compliance with permitted environmental emissions from SOR to EOR means sufficient catalyst inventory must be provided such that even in an aged condition, the needed sulphur recovery is achieved.

A temperature profile of the TGU reactor is commonly used to provide insight into catalyst performance and health. The adiabatic reactor experiences a temperature rise from the exothermic reactions associated with the conversion of various sulphur species to H_2S and shift of carbon monoxide to hydrogen. **Figure 2** shows three approximately equal segments of the bed, with the percentage contribution of each bed to the overall temperature rise across the entire bed: top zone is green and shows 70% of DT, middle zone is blue with 30% DT, and bottom zone is red with negligible DT. The fresh catalyst is achieving almost complete conversion in the first two zones.

The overall temperature rise across the bed is virtually constant across time (not shown), reflecting that even with sulphur slip as outlet concentrations of non-H_2S species increase, there is still a high percentage conversion. The magnitude of temperature rise is related primarily to the concentration of sulphur dioxide, carbon monoxide, and elemental sulphur in the feed. The relative amount of temperature rise in each zone reflects the degree of conversion in each zone.

Mid-life activity distribution shifts to a 20% rise in the top zone, 70% in the middle zone, and 5% in the bottom, eventually moving lower into the middle and bottom zones as the top and middle zones deactivate. Incidentally, the temperature profile chart reflects declining activity, which results from deactivation by ageing and poisoning. The significance of shifting reactor bed temperature profile and its implications for ageing, poisoning and potential bed life and the new modelling tool is the subject of the commentary here and in Part 2 of this article.

Reaction pathways

Reactant(s)	Products			
	Reverse	Hydrolysis	Hydrogenation	Shift / Exchange
COS	X	$H_2S + CO_2$	--	$H_2S + CO$
CS_2		$H_2S + COS$	$H_2S + CH_3SH$	-
SO_2		-	$H_2O + S$ (or H_2S)	
S		-	H_2S	
CO	X	-	-	$H_2 + CO_2$
CH_3SH				$H_2S + CH_4$
$SO_2 + CS_2$				$CO_2 + S$
$SO_2 + CO$				$CO_2 + S$
Claus $H_2S + SO_2$				$S + H_2O$

Table 1

Kinetic framework and model development

The fundamental TGU reaction matrix is (1) hydrolysis on alumina, (2) hydrogenation, and (3) water gas shift on CoS/MoS_2. In the basic frame in **Table 1**, an expanded reaction set is invoked to quantify the multiple pathways

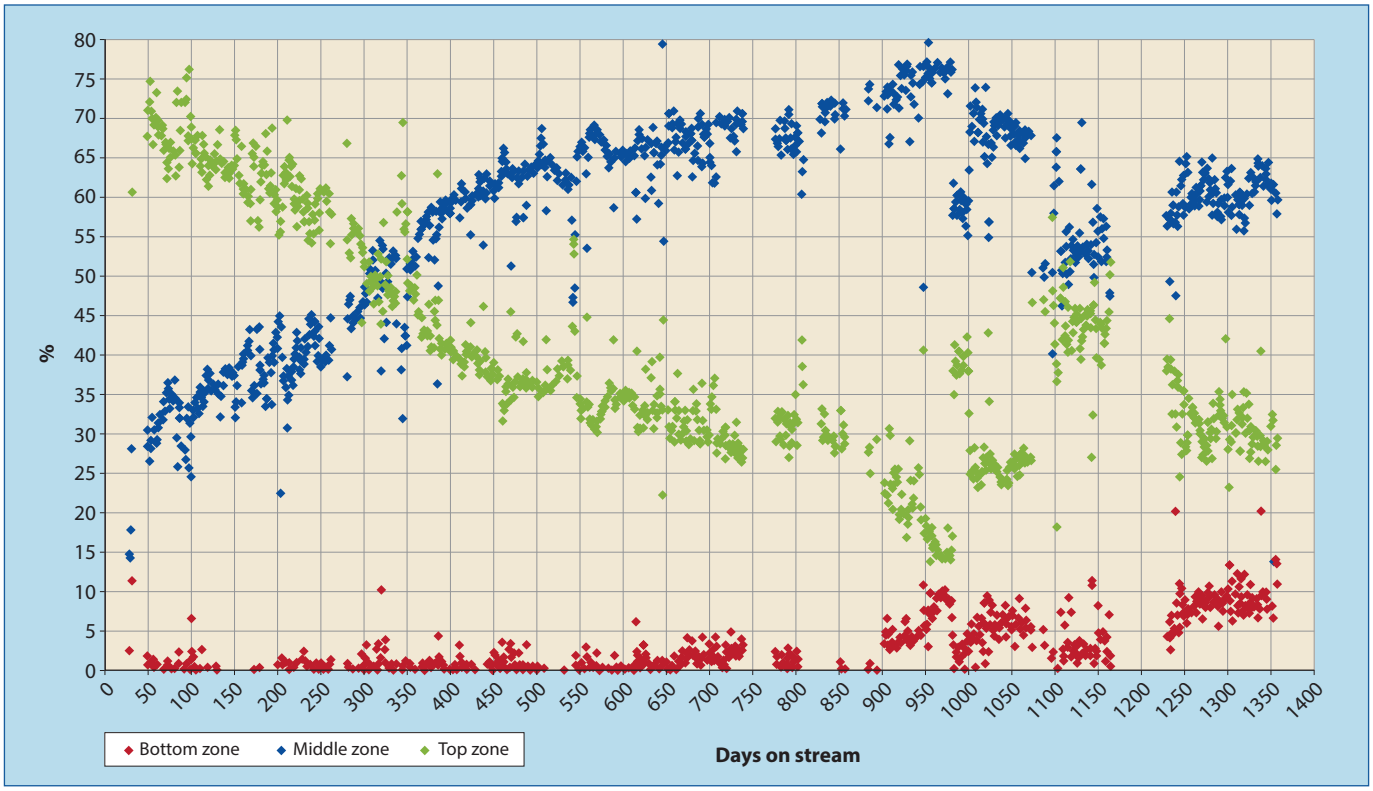

Figure 2 Temperature profile operating data of a typical refinery over days

involving SO_2, which are also Co/Mo catalysed. These reactions 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:

❶ Collection of published experimental data
❷ Postulation of a reaction set
❸ Determination of reaction order from published data
❹ Assessment of equilibrium influences, if >10% outlet, including reverse reaction
❺ Determination of kinetic rate temperature coefficients for Arrhenius expression from data
❻ Identification and regression of compositional resistances to reaction rates
❼ Refinement of the reaction set and rates with experimental and operational observations.

The kinetic rate model was 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

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

the magnitudes of Thiele modulus and effectiveness factors. Experimentally determined effectiveness factors were 0.7 or greater (although this excludes sulphur dioxide and elemental sulphur reactions). These reactions are generally first or second order, so there is concern of confounding kinetics if mass transfer presents controlling resistance. The approach provided a good representation of temperature-dependent kinetics using Arrhenius-based rate coefficients determined from the experimental data. The operational domain for fluid dynamics in commercial applications has sufficient velocity that stagnation/backflow areas do not have a significant influence on bed fluid dynamics and reactor efficiency.

The effect of adsorption resistances and compositional interaction with the reaction rate were modelled using either Langmuir-Hinshelwood type factors or a fractional-order rate expression. An example of this application 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 present in substantial excess (normally the reaction kinetics would be addressed as pseudo-first order with water as zero order), but competitive water adsorption on active sites influences the reaction rate. Additionally, at lower water concentrations, the reaction rate declines, exhibiting second-order behaviour. The Langmuir/Hinshelwood relationship provides an effective form to represent this relationship:

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

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, becomes

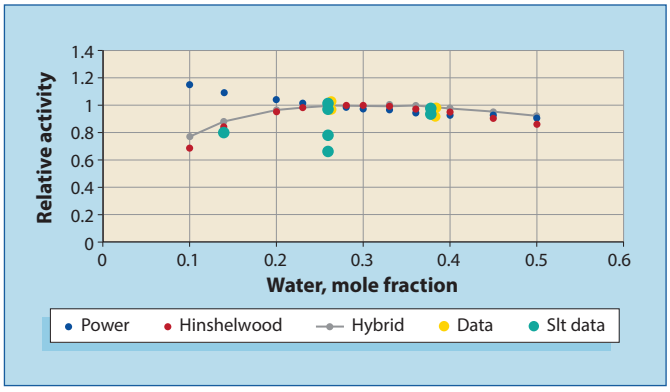

Figure 3 Water gas shift reaction – resistance from water

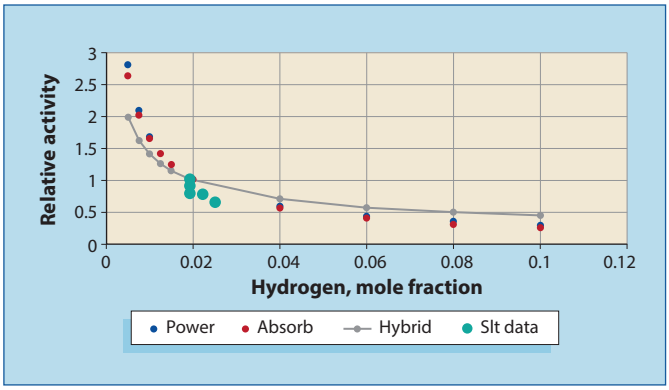

Figure 4 Water gas shift reaction – resistance from hydrogen

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:

$$\text{rate} = -k_{eff}\,[CO]\,[H_2]^a\,[H_2O]^b\,[CO_2]^c$$

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 comply with:

$$k_{forward}/k_{reverse} = K_p \text{ and } k_{reverse} = k_{forward}/K_p. \text{ where } K_p = [R]^r\,[S]^s / ([A]^a\,[B]^b)$$

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 CS_2 hydrolysis.

An interesting aspect of CS_2 hydrogenation is the formation of methyl mercaptan, which is further hydrogenated to methane and hydrogen sulphide. The extent of the first reaction, the production of methyl mercaptan, is determined by the sum of mercaptan and methane, which then allows fitting for the conversion of mercaptan to methane.

SO_2 has multiple roles in TGU reaction kinetics. A known effect of SO_2 is the moderation of hydrolysis of COS and CS_2.[3] The more subtle role of SO_2, revealed with discretised finite element bed modelling, is providing an alternate conversion pathway for CS_2, moderating the production of mercaptan and COS. Additionally, SO_2 provides a direct conversion of CO (versus water gas shift/hydrogenation), acknowledging a substantial enhancement influence on CO conversion when present.

Figure 5 compares reactor outlet concentrations measured from experimental data versus model predictions for CO, COS, mercaptan, and methane. The parity plots show a good fit of data across the operation range of temperature from 260°C to 335°C and actual gas hourly space velocity from 1,500 to 6,000 hr^{-1}. Composition of the feed was: H_2 = 2%; CO_2 = 7%, 14%, 21%; H_2S = 0.8%; CO = 1%; COS = 0.025%, 0.05%; SO_2 = 0.4%, 0.2%, 0%; CS_2 = 0%, 0.025%; H_2O = 13%, 26%, 39%; N_2 = balance.

This rigorous reaction kinetics model was ultimately implemented as a hydrogenation reactor model in the proprietary SulphurPro, providing an essential cog in rate-based, plant-wide simulation of SRUs and TGUs. The reaction scheme comprised 11 individual reactions, and the

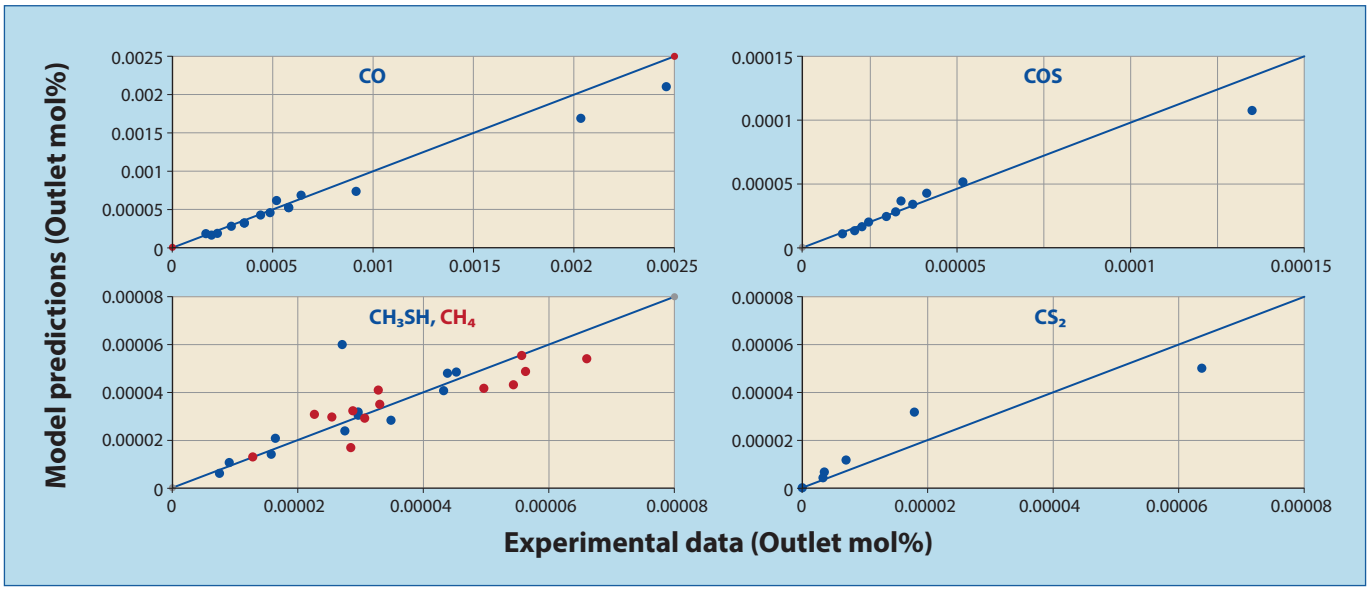

Figure 5 Parity plots comparing outlet gas concentration from experimental data to model predictions

reactor is represented by a series of small discrete segments. In each segment, the progress of each reaction is represented by.km,m:

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

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, and overall conversion is summed across all reactor segments. **Figure 6** shows the user interface.

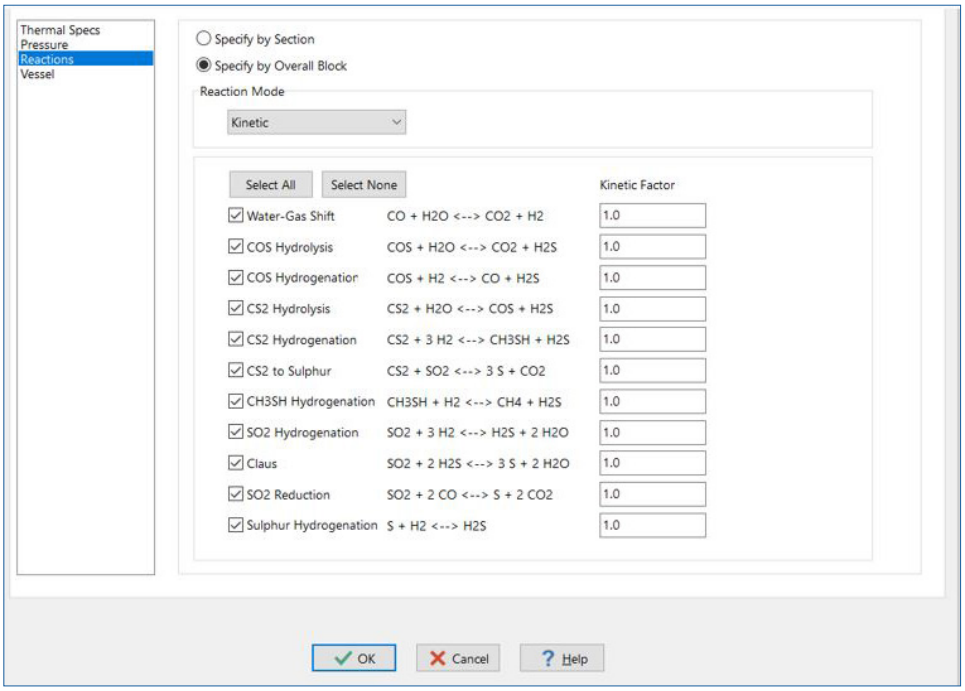

Figure 6 Hydrogenation reactor model interface in OGT SulphurPro

The model presented here captures not only the detailed reaction kinetics but also accounts for deactivation from ageing (depending on temperature, humidity, and time) and poisoning (related to operational stresses, such as BTEX or O_2 in feed). Hydrothermal ageing 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 sulphur species that slip through the TGU into the thermal oxidiser.

Sound technical tools, which represent the kinetics of the TGU system and enable meaningful simulation, help to reveal substantial effects on performance

Conclusions

Sound technical tools, which represent the kinetics of the TGU system and enable meaningful simulation, help 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 analyse and predict the performance and useful life of a real reactor based on a comparison of simulated versus actual temperature profiles, especially over time. Designers will have a tool to better specify reactors, and operators will be able to better quantify what is actually occurring instead of only simulating ideal operation. Improved operation and better designs can reduce sulphur emissions, improving the quality of life on our planet.

References

1 Huffmaster M, Maldonado F, *Time and Temperature Effects on Tail Gas Catalyst Performance*, Brimstone 2013, Sulphur 2014.

2 Maldonado F, Krueger K, Huffmaster M, *Low Temperature Tail Gas: kinetic functions – what they are – really*, Brimstone 2016.

3 Lavery C B, Sui R, Loftali-Kazemi M, Marriott R A, *Kinetic Studies for the Hydrolysis of CS_2 and COS across the Claus Catalytic Converters*, Alberta Sulphur Research Ltd, Brimstone, 2019.

SulphurPro is a mark of Optimized Gas Treating, Inc.

Michael A Huffmaster consults to industry on sulphur recovery, treating, gas processing, advanced control, and CO_2 capture, and has contributed to numerous publications and presentations on these topics. His career includes 17 years as a consultant after 36 years with Shell. He holds a BSc degree in chemical engineering, and is a registered P.E. in Texas.

Prashanth Chandran is Software Development Team Lead at Optimized Gas Treating, Inc. He holds a B.Tech in chemical engineering from Anna University, India and a MS in chemical engineering from Oklahoma State University.

Nathan A Hatcher served as Vice-President, Technology Development for OGT from 2009. For most of his career, he has been involved with some facet of gas treating and sulphur recovery. He holds a BS in chemical engineering from the University of Kansas, is a registered professional engineer in the state of Kansas, and currently a member of the industry Amine Best Practices Group.

Daryl Jensen is a Development Engineer at OGT, experienced in design/development, simulation, basic engineering design package project execution, process control design, and on-site start-up/troubleshooting. He holds BS and MS degrees in electrical engineering from New Mexico State University and is a registered professional engineer in Texas.

Ralph H Welland formed Optimized Gas Treating in 1992. He was OGT's original President and now serves as Chairman. He holds BASc, MASc, and PhD degrees in chemical engineering from the University of Toronto, and was a post-doctoral fellow in applied mathematics at the University of Western Australia.