The CONTACTOR™

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Differences between Simulators: Waste Heat Boiler Models

The Claus Waste Heat Boiler (WHB) is a critical equipment item in any sulfur recovery unit (SRU). WHB failures have become increasingly common as higher sulfur feedstocks have found greater use and placed more load on the SRU. Such failures are extremely costly when an out-of-service SRU either reduces refinery throughput or shuts off production altogether. WHB failure is often caused by high temperatures, fouling, and corrosion in the immediate vicinity of the protective ferrules at the tube-to-tubesheet joint, the most common failure point. Accurate temperature, heat flux, and fouling prediction can help keep WHBs well away from dangerous operating conditions.

This issue of The Contactor reports the results of a case study that compares actual measurements from an operating unit with the ProTreat® reaction kinetics-based model, and with three other commercial simulation models.

The ProTreat SRU simulator is based exclusively on the kinetics of the reactions that occur in the various units. Using chemistry and reaction kinetics rather than curve fits, empiricism and idealized approximations makes the model fully predictive. This fundamentals-based model provides quantitative insights into several aspects of the WHB that impact sulfur plant performance. In particular, the exothermic sulphur recombination reactions that occur at the front of the WHB, namely

$$2H_2 + S_2 \rightleftharpoons 2H_2S$$
$$2CO + S_2 \rightleftharpoons 2COS$$

not only influence sulfur recovery, air demand, and hydrogen production in the SRU, but also affect the heat flux and performance of the WHB. These reactions occur towards the front (inlet) side of the WHB and are exothermic. Together with radiative heat transfer, the "hidden" heat associated with these reactions tends to increase heat flux towards the critical tube-to-tubesheet joint. In addition, it is well known that the S_2 vapor allotrope is exothermally converted into the S_6 and S_8 forms as the gas is cooled:

$$3S_2 \rightleftharpoons S_6$$
$$4S_2 \rightleftharpoons S_8$$

Unlike in heat exchangers further downstream, radiation is also an important and often neglected heat transfer mechanism.

Approaches to Recombination Modeling

The recombination reactions can generate significant heat near the front of the WHB, i.e. close to the fragile tube-to-tubesheet joint area, so getting the simulated temperature there as correct as possible is important. Until very recently, the models used in all commercial SRU simulators handled recombination using one of these three approximations:

- Ignore local recombination and assume the reaction furnace (RF) is at equilibrium.
- Lump these reactions into the RF effluent.
- Freeze the reactions by assuming they reach equilibrium at a user-supplied quench temperature.

The only correct approach, however, is to model the reactions as they truly are:

- Use a fully reaction kinetics or rate basis.

The ProTreat Simulation Approach

ProTreat's first-principles, rate-based model incorporates the effects of reaction kinetics, rigorous heat transfer (with temperature, composition, and geometry-dependent radiation), and condensation calculations for liquid sulphur (including thermodynamic and physical property effects resulting from the varying distribution of sulphur allotropes.) The interdependency of physical properties, reaction rates with heats of reaction/redistribution, bulk heat transfer, and stream enthalpies (both latent and sensible) are solved together to provide a consistent and powerfully predictive modeling tool.

Briefly, the set of equations governing the WHB, including recombination and polymerization reactions, are numerically integrated along the boiler tube length. Adaptable segmentation is used to yield the highest precision results by placing more segments in the locations where properties are changing fastest and consequently higher numerical resolution is needed. The importance and relevance of these reactions is demonstrated in the following case study.

Case Study: An SRU on 30% Oxygen Enrichment

Confidentiality prohibits us from disclosing the particular unit used in this case study. However, pertinent data collected in air-only and oxygen-enriched operation can be reported. The SRU conformed to a standard SRU flowsheet configured for processing amine acid gas (AAG) and sour water acid gas (SWAG) with and without 30% oxygen enrichment. It included the reaction furnace and WHB followed by a first sulphur condenser, and then three catalytic converter stages.

Initially designed for approximately 100 LTPD sulfur on air operations, the plant was revamped to use low-level oxygen-enrichment (to 30% O_2) to process 25% more throughput. The AAG (90% H_2S, 0.5% C_1, balance CO_2, water saturated) and SWAG (55% NH_3, 45% H_2S, water saturated) are typical and had an AAG:SWAG flow ratio of 5.6:1 and resulted in nominally 6% NH_3 in the combined acid gas feeds.

Table 1 shows the important configuration data for the WHB. Failures above mass velocities of 5.0 lb/sec-ft^2 have been reported to be more common. At the time of the plant data collection, the unit was running at a mass velocity of approximately 2.0 lb/sec-ft^2.

Table 1: WHB Configuration & Parameters

Tube OD/ID, inches	2 / 1.783
Tube length, feet	32
Steam generation pressure, psig	350
BFW temperature, °F	280
Mass velocity, lb/ft^2·s	2
Inside tube wall emissivity	0.9
Fouling resistances, process / steam sides, hr·ft^2·°F/BTU	0.008 / 0.002
Steam side HTC, BTU/hr·ft^2·°F	150-1000

The effect of steam side heat transfer coefficient (HTC) and a comparison between air-only and oxygen enriched cases will be reported in a subsequent issue of The Contactor. The present issue focusses on simply comparing ProTreat simulator predictions with measure key performance parameters, and lining these plant measurements up against results from three other widely-used simulators: Simulator P (equilibrium reaction furnace), Simulator S1 (lumped reaction model), and Simulator S2 (freeze-quench model).

What do less rigorous models predict in the oxygen-enriched operation?" A sensitivity analysis was run using ProTreat on the 30% oxygen-enriched case. Table 2 summarizes the results.

Table 2: Key Process Prediction Differences using Less Rigorous Modeling Methods (30% Oxygen)

Parameter	Plant Data	Kinetic Model	Equil. Furnace (P)	Lump Rxn (S1)	Freeze-Quench (S2)
Enriched air flow, lbmol/hr	749.5	682.6	623.2	682.6	682.5
Furnace Temperature, °F	2300	2383	2304	2515	2383
WHB Outlet, °F	512	512	517	512	N/A
WHB Steam Production, lb/hr	32,000	30,337	27,526	30,322	30,332
Peak wall temperature, °F	N/A	622	606	626	N/A
Peak heat flux, Btu/hr-ft^2	N/A	25,800	23,600	26,200	N/A
H_2 in Quench OHD, mole%	5.13	5.84	11.4	5.63	5.85
Sulfur recovery, %	N/A	97.52	97.80	97.51	97.52

The equilibrium furnace (Model P) does quite well in reproducing the reported furnace temperature. However, it considerably underestimates the steam production from the WHB, grossly overestimates hydrogen production and is over-optimistic about sulfur recovery. Superficially, the extent of the overestimate of sulphur recovery (97.80 vs. 97.52) may appear quite small; however, in terms of unrecovered sulphur load on the TGU downstream, it can be quite a substantial underestimate.

Lumping the recombination reactions into the Reaction Furnace by model S1 causes the reaction furnace temperature to be over-estimated by more than 200°F. Any model that employs empirical thermal reaction kinetics relying on an improperly calculated furnace temperature is inherently flawed. Because the furnace temperature is wrong to begin with, the software developer is forced to concoct many different kinetic models to fit different operations (oxygen enriched, lean acid gas, ammonia destruction). The software user is then forced to choose the most appropriate operating mode. So what happens when multiple modes apply, for example, oxygen enriched ammonia destruction?

For both the lumped reaction and the freeze-quench methods, we knew the answer to begin with (from ProTreat's kinetics model). Trying to rate the Waste Heat Boiler using these techniques is not much more than guesswork. The recombination reactions have to be either ignored for the WHB rating, or applied to an arbitrarily fixed length of tubes. There is absolutely nothing predictive with either of these approaches.

One of the main advantages of a fundamental reaction kinetics based SRU model is its ***predictive*** power. Other models are based on either

- Gross simplifications which therefore produce unreliable estimates, or
- Regressions to measured plant performance data that all too often have wide margins of error or that may not cover the range of operating parameters necessary to obviate the extrapolation of problematic data.

A soundly-based SRU simulator is beneficial not just for design. It can also be an indispensable aid to troubleshooting and in SRU optimization to minimize the operating expenses associated with this significant cost center. Furthermore, the ability to integrate it into highly accurate rate-based models of upstream and downstream gas processing allows interactions between units to be very reliably assessed.

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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.