EXPECTATIONS FROM SIMULATION: PART TWO – CASE STUDIES

As a follow-up to part one of this article, Prashanth Chandran, Nathan Hatcher and Ralph Weiland, Optimized Gas Treating, Inc., USA, present a series of case studies whereby simulators have been used across a range of treating applications.

Part one of this article, which featured in the February 2023 issue of *Hydrocarbon Engineering*, examined factors that make some simulators more reliable than others. It also explained how detailed a simulator should be; how to choose the right simulator for the task at hand; how simulators should be benchmarked; and what comprises benchmarking data.[1]

The case studies presented in this article feature a range of treating applications, namely treating gas typical of a refinery; the effect of heat stable salts (HSSs) and

tower internals on hydrogen sulfide (H_2S) removal from fuel gas using MDEA; and selective H_2S removal using structured packing in a tail gas treating unit (TGTU).

Hellenic Petroleum refinery revamp

This refinery, located in Thessaloniki on the Aegean Sea in far northern Greece, was the subject of a large-scale revamp. Siirtec Nigi was engaged to investigate the impact of the revamping project on the amine system and the downstream sulfur recovery unit (SRU). The results of the study were reported at the Vienna 2014 Brimstone Sulfur Symposium, and the information provided in this article is taken from the conference proceedings.[2]

As a consequence of the upgrading project, the feedstock to the amine absorbers changed. The total amount of H_2S produced from the crude oil increased, as well as many sour gas stream flow rates.

Siirtec Nigi proposed the replacement of the old monoethanolamine (MEA) solvent with methyldiethanolamine (MDEA) in the refinery amine system, and the implementation of an oxygen-enriched Claus process for the SRU. In 2012, the refinery completed the first part of the amine system revamp. The overall comparison between the actual plant performance and the expected plant behaviour based on the process simulation results presented in the Brimstone paper is of interest here.

To provide context, the revamp project consisted of increasing the refinery crude processing capacity from 70 000 bpsd to 100 000 bpsd. Consequently, the amine treating system and the downstream SRU capacities had to be increased, too. In addition to this, as part of the project, the crude types and blends were changed and the refining operations modified. As a result, the gas and liquid streams to be treated in the amine absorbers changed in composition (mainly the H_2S concentration). This led to significant modification of the amine system configuration.

The feeds to the amine scrubbers after revamping are shown in Table 1, together with the solvent flows and the types of tower internals. Towers T-170 and T-1902 are both high-pressure columns; the others are low-pressure. There is also a mix of trayed and packed absorbers, with T-407 having been repacked with Pall Rings as part of the revamp. What is important here is the fact that field data is available against which to benchmark the simulator.

With the exception of T-170 for which no performance data is available, the simulator matches the field data quite well. It must be pointed out that the simulations were not adjusted to match the data; the simulations are pure out-of-the-box predictions.

Table 1. Amine treater performance data

Scrubber	T-407	T-170	T-410	T-1902
Internals	Pall rings	Trays	Packing	Trays
Gas conditions				
Temperature (°C)	46	43	43	49
Pressure (kg/cm^{2}g)	18.6	42	4.1	53
Mass flow (kg/hr)	1036	6700	3119	8458
Composition (mol%)				
Hydrogen	71.8	68.7	51.2	88.2
Methane	14.4	22.5	16.5	6.3
Ethane	7.6	4.8	8.3	1.4
Propane	2.5	1.7	5.8	0.6
n-butane	0.4	0	3.5	0.3
i-butane	0.1	0.5	1.0	0
n-pentane	0.2	0	2.1	0
i-pentane	0.1	0.2	1.2	0
C6+	0.6	0.2	2.5	0.3
H_2S	1.9	1.2	6.1	2.6
Water	0.5	0.2	1.8	0.3
Solvent				
Flow rate (m^3/hr)	6	8	8	10
Treated gas				
Measured H_2S (ppmv)	25	N/A	70	10
ProTreat H_2S (ppmv)	26	8	60	8

Table 2. Fuel gas treater: solvent analysis

MDEA (wt%)	38
CO_2 (loading)	0.00014
H_2S (loading)	0.0009
Acetate (ppmw)	2580
Formate (ppmw)	14 305
Sulfate (ppmw)	230
Thiocyanate (ppmw)	3225
Chloride (ppmw)	1675

Conclusion 9

Continuing the numbering of conclusions from part one of this article[1], the mass transfer rate-based simulations predict the performance data quite well. Because this is actual measured data, one can have considerable confidence in the validation.

Treating a refinery fuel gas

This case study involves H_2S removal in one of two fuel gas treaters in a refinery on the west coast of the US. To take advantage of the lower regeneration energy required by MDEA, the refinery had switched out the DEA solvent to 38 wt% generic MDEA. At the same time, trays were replaced with packing in both treaters. The treater of interest here was 2.5 ft dia., and its

original 17 valve trays were replaced with 25 ft of rings. The gas to the treater was 0.2 mol% carbon dioxide (CO_2) and 0.5 mol% H_2S at 200 psig, with the balance two-thirds hydrogen with 17% methane, and minor amounts of C1 – C5 hydrocarbons.

Performance after the revamp was disappointing. Despite the low, acid gas, lean loadings (0.0009 for H_2S and 0.008 for CO_2), the H_2S leak from the absorber was measured at 26 ppmv, whereas a value closer to 3 or 4 ppmv was expected. Simulation indicated that the H_2S in the treated gas should have been less than 1 ppmv, in disagreement with actual measured data. A consultant tasked by the refiner to determine the cause for the larger-than-expected H_2S leak suggested that the residence time on the packing was too short to achieve good treating, and he recommended the refinery return to using trays. However, after reinstalling the 17 trays, the H_2S leak remained stubbornly at 25 – 26 ppmv. The costly shutdown and revamp back to trays produced no benefit.

As part of a new, independent investigation, Optimized Gas Treating, Inc. (OGT) ran ProTreat against the data, but this too predicted less than 1 ppmv H_2S in the treated fuel gas. Then, OGT asked for a solvent analysis (see Table 2). When the real solvent composition was used in the simulation, the predicted H_2S leak rose to 22 ppmv when the absorber was packed, and 26 ppmv when it was trayed. It is worth noting that the predicted H_2S leak and the measured value from the trayed absorber are virtually identical. Incidentally, the presence of HSSs led to several percent more CO_2 slip for both trays and packing.

Without a proper solvent analysis, the wrong results are generated. Predicted treating without HSSs is very optimistic because HSSs effectively create higher acid gas vapour pressures (back pressure) in the absorber than HSS-free solvent would. Naturally, they also create higher back pressures in the regenerator and this assists solvent regeneration, hence the relatively low lean loadings, even for MDEA. But the reduced lean loadings are not enough to compensate for increased equilibrium backpressures in the absorber.

Any simulation based on ideal stages fails to reveal the existence of pinches because it treats the column as a black box – virtually an empty shell. What is inside the tower makes a huge difference to real treating performance; 4 in. Raschig rings perform completely differently from a small or medium crimp structured packing, both perform differently from trays, and what type of tray and the physical features affect performance too. It is unrealistic to expect to be able to diagnose internals problems using ideal stage simulation (with or without efficiencies) because such simulations are blind to what is actually in the tower.

Table 3. Solvent analysis: HSSs

MDEA (wt%)	33.374
DEA (wt%)	0.338
Thiosulfate (ppmw)	5930
Oxalate (ppmw)	220
Acetate (ppmw)	1150
Formate (ppmw)	815

Conclusion 10

Failure to account for HSS contamination of the solvent can lead to completely erroneous simulation results and expensive but unsuccessful revamps to cure a problem whose cause lies in the solvent, not the tower internals.

Conclusion 11

A column that is lean-end pinched cannot have its performance altered by changing or modifying the internals. Pinch conditions are only revealed by mass transfer rate-based simulation which, in the present case, points unmistakably to the correct solution to poor performance – a cleaner solvent.

Conclusion 12

If a small change in a variable causes a huge change in a simulated performance parameter, a simulator may not have gone crazy, but rather it may be saying something important. Only mass transfer rate-based simulation is capable of revealing bulge pinches, for example. Such cases deserve close scrutiny.

Tail gas treating

The final case study is a Texas Gulf coast refinery's 6 ft dia. TGTU containing 20 ft of structured packing and treating 3 million ft^3/d of 1 psig gas containing 3.4 mol% CO_2 and 1.7 mol% H_2S. The refinery claims that the gas to the thermal oxidiser was only 3 ppmv H_2S until the solvent was cleaned. Treating was not successful, and the refinery's sulfur emissions went up against the permitted limit.

The original solvent was 34 wt% MDEA (see analysis in Table 3). There were over 8000 ppmw HSSs in the solvent. After cleaning, there were virtually none.

Using the as-reported solvent analysis, ProTreat simulation predicted that the treated gas should contain 3.8 ppmv H_2S – very close to the refinery's claim of 3 ppmv (the H_2S lean loading was predicted to be 0.00008). Again, this is an out-of-the-box prediction with absolutely no adjustments or fitting of any kind. This is plant performance data and is therefore a valid point of reference against which to benchmark a simulator.

Beyond stating that the treating was unsuccessful after solvent cleaning, the refinery did not provide actual data on H_2S leakage from the TGTU. However, simulation with the HSSs removed from the solvent but with all other conditions the same predicted that there should be 80 ppmv H_2S in the treated gas (the predicted H_2S lean loading was now 0.009). Treating is certainly 'unsuccessful' compared with the

HSS-contaminated solvent, and provides at least anecdotal evidence of the effect of HSSs. The HSSs can greatly reduce lean loading, which is responsible for better treating in this application. But, depending upon the specific system and operating conditions, this may not always be the case.

Conclusion 13

The performance of structured packing was very successfully simulated in a TGTU application, and the observed H_2S leak was predicted to within better than 1 ppmv.

Conclusion 14

Modest concentrations of HSSs in an MDEA treating solvent can have quite a beneficial effect on TGTU performance.

Concluding remarks

Relevant conclusions have been scattered throughout part one and two of this article. In summary:

- Simulators cannot be validated by comparison with other simulators. Doing so assumes one of them is correct when, in fact, both may be wrong. Comparing three simulators and assuming the two closest to each other are the best ones is tantamount to taking the foolish position that correctness can be established by democratic vote.
- Simulators cannot be validated against 'supplier data'. Solvent and process suppliers provide solvent and process performance guarantees. This is not data; this represents how far the supplier is willing to stick out its neck.
- Simulators can be validated only against real plant performance data measured in the field. One is not permitted to adjust or fit the simulation to the measured data and then claim an accurate prediction. Using adjustments, the best one can say is that one has achieved an accurate fit, but to call it a prediction is disingenuous.
- An achievable expectation from simulation is that one should be able to predict the performance of existing plants as measured in the field, without simulator adjustments. Experience and rules-of-thumb are valuable adjuncts to simulation, but they are not reliably predictive, especially in new circumstances. If they are needed to provide input information to the simulator then the simulation is not nearly as reliable as imagined.

References

1. CHANDRAN, P., HATCHER, N., and WEILAND, R., 'Expectations from simulation: part one – realistic and reliable', *Hydrocarbon Engineering*, (February 2023).
2. ROSSETTI, T., PEREGO, G.C., SKANDILAS, A., and LERAS, E., 'Refinery Upgrading Project – Amine and Claus Units Revamping', Brimstone 2nd Vienna Sulfur Symposium, Vienna, Austria, (19 – 23 May 2014).