BREAKING BOUNDARIES IN LIQUID TREATER MODELING – VALIDATION AND SIMULATION STUDY WITH A NEW RATE-BASED MODEL

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Prashanth Chandran
Optimized Gas Treating, Inc.
212 Cimarron Park Loop, Buda, TX 78610
prashanth.chandran@ogtrt.com

Ralph Weiland
Optimized Gas Treating, Inc.
212 Cimarron Park Loop, Buda, TX 78610
ralph.weiland@ogtrt.com

ABSTRACT

Liquid extraction in the refining and natural gas industries is widely used for aromatics removal from reformates and pyrolysis gasolines in refineries, aromatics removal from engine lubricating oils in lube-oil plants, and removal of sulfur compounds, mainly H2S, COS, and mercaptans from LPGs and NGLs. Regardless of the application, however, there has never been a truly satisfactory way to confidently design such units. The best possible approach has been an ideal-stage calculation, augmented with anecdotal, experience-based estimates for tray efficiencies and HETP values. But the situation is more dire than this because such an approach takes no account of how the treater's actual internals, dispersed phase selection, the flowrates it handles, or the composition and temperatures of the streams feeding it affect its performance.

Apart from stationary trays vs. packing, there is a whole raft of trayed internals including rotating disc contactors (RDCs), Scheibel, Rushton, Graesser raining buckets (RTL), Kuhni, Wirz, and centrifugal types. Vertically reciprocating devices include Karr and pulsed columns. This, and the fact that sieve hole size and tray spacing make a significant difference even to stationary tray efficiency, makes assignment of efficiency an almost impossible task. Packing type, size, and material (steel vs. ceramic) can also be expected to make a potentially large difference to treater performance.

Sieve-tray efficiencies for H2S removal are typically in the range of 5–25% and HETPs are 5–15 feet. With performance parameters in these ranges, it is easy to understand the difficulty in coming up with performance estimates that are even remotely reliable. It also suggests the inappropriate-ness of ideal stage calculations in the first place. Nevertheless,

ideal stages augmented by unreliable rules-of-thumb are all engineers have ever been able to call upon, until now.

This contribution reports on the game-changing development of a mass transfer rate-based simulator for amine treatment of LPG and NGLs. The complete lack of commercial models was the motivation for leveraging our rate-based gas treatment model as the basis for developing a liquid treater model. The starting point is rigorous, accurate electrolyte thermodynamics for amine treating; a well-established, accurate and time-tested rate model for gas treating, carbon capture and sulfur recovery; and a flexible flowsheeting environment within existing software.

We begin with a brief historical perspective, followed by the development and validation of the model in ProTreat®, OGT's proprietary simulation software. A total of 15 sets of performance data from commercial, measured, LPG Treater in various refineries using MEA, DEA, MDEA, and a 3-amine blend were used for the validation. Finally, we present the results of a series of case studies concerning how sieve tray properties, packing size, extract and raffinate flow rates, temperatures, and compositions, and amine type and strength affect treater performance in sulfur removal.

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Introduction

A well-founded rate-based model for gas treatment is an excellent jumping-off point for understanding and developing a similar model for liquid treating. But what can a mass transfer rate model for liquid treating provide? In and of itself, column design is not necessarily of great concern because the fallback position of adding a few more trays or packed depth to a design can always be used. The real potential benefits of a rate model are the ability to troubleshoot existing equipment and predict the results of efforts to improve capacity or achieve a better separation, without incurring the expense and uncertainty of experimenting with commercial scale equipment.

A rate-based model provides a solid framework for what-if studies and for understanding the likely consequences of various equipment deficiencies, changes in feed composition and flowrates, and the effect of solvent selection on treating. Ideal stage calculations augmented with efficiencies and HETP values lack the certainty provided by rate-based modeling.

When tray efficiencies are 5 or 10% (Chandran and Weiland, 2025), the effect of even a small misjudgment of efficiency can lead to wildly different performance predictions. Furthermore, a single efficiency value for H_2S and CO_2 is bound to be quite erroneous — these components can differ in efficiency by a factor of 5 or more. It hardly needs to be stated that efficiencies in single digits bring into question the very significance of an ideal stage in this context.

Model Description

The ‘two-film’ theory of mass transfer was adopted for model development. Important factors are liquid–liquid equilibria, physical and transport properties of phases, including density, viscosity, and interfacial tension between the two liquids, and the mass transfer characteristics of the extraction column internals. Furthermore, it is critical to note that LPG treating using aqueous alkali such as alkanolamine solutions and caustic soda is a reactive process. The resulting concentration gradients lie within a reaction film that enhances the driving force available for mass transfer. Different solutes react at varying rates, and in turn, affect the mass transfer resistance of the solutes to different extents. This effect is quantified by an Enhancement Factor, which is the ratio of mass transfer rate into the extract phase compared with the rate without reaction. Enhancement Factors are not

freely assignable parameters like efficiencies — they are determined mathematically by solving the equations of diffusional mass transfer with chemical reaction. This involves reaction kinetics, reaction stoichiometry, component diffusion, phase viscosities, thermal properties of the phases being contacted, and all the nuances of phase equilibrium in highly nonideal systems. The reactions play a central role in determining mass transfer rates. For anyone interested in delving into the details of mass transfer rate modeling, Kooijman and Taylor (2025) and Weiland et al. (2003), in the contexts of non-reactive distillation and reactive acid gas removal, respectively, are good sources of information.

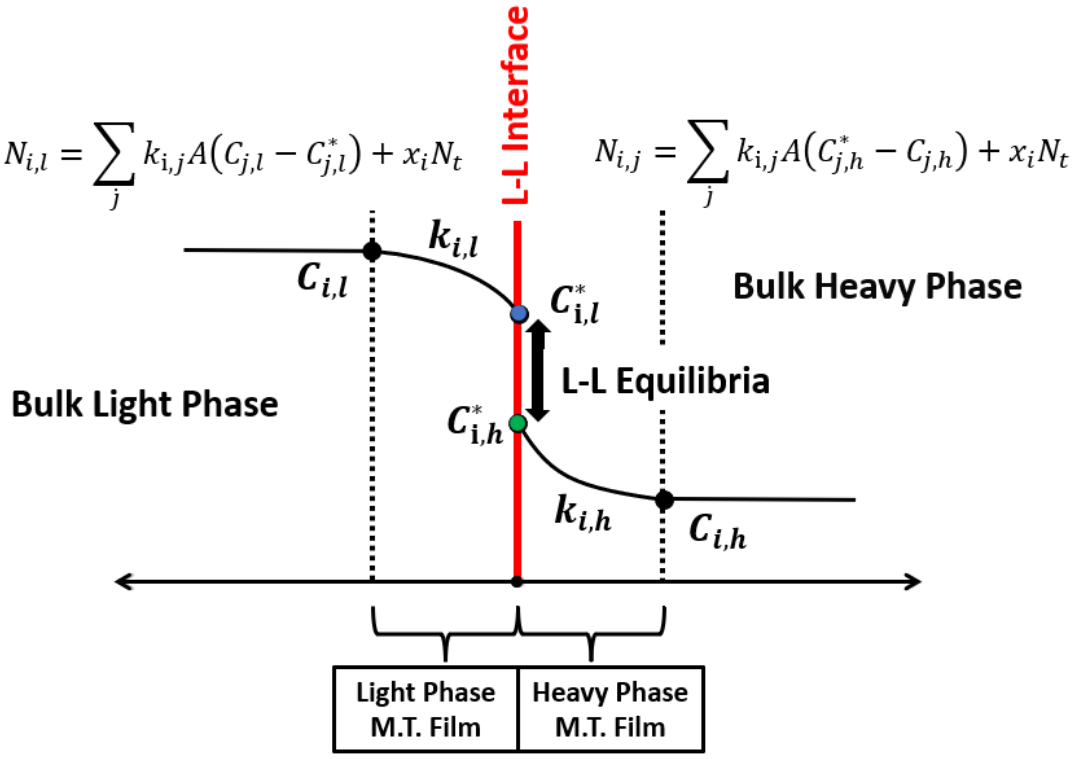

Figure 1 Schematic of the solute concentration profiles in the extract and raffinate phases across the liquid-liquid interface

Figure 1 shows schematically the solute composition in the immediate vicinity of the liquid-liquid interface where mass transfer rates are determined. Phase equilibrium exists only at the interface itself. It is purely physical (non-reactive) and mass transfer rates between the phases are directly related to solute concentration gradients at the interface. Reaction affects concentration gradients, not just phase equilibrium. In the ideal stage model, on the other hand, equilibrium exists between the bulk extract and raffinate phases and does not separate the effect of chemical reaction. Mass transfer rates are determined subjectively by the engineer's estimate of overall tray or packing efficiency.

Separation performance is determined by mass transfer coefficients for the transferring components in the light (hydrocarbon) and heavy (aqueous) phases ($k_{L,i}$ and $k_{H,i}$) in Figure 1, interfacial area, and concentration driving forces for diffusion. Mass transfer coefficients depend on relative velocity between dispersed (droplet) and continuous phases

which itself depends on relative density, liquid viscosities and drop size. Interfacial areas depend on Sauter mean drop size, sieve hole size and fractional open area of the trays. Transport of solute through the phases is governed by the Maxwell-Stefan equations describing diffusion together with kinetics of the reactions between solute and the active component(s) of the solvent. Thus, system performance depends on all the physical and transport properties of the various components, the detailed geometry of the column internals, and phase flowrates. It is all encompassing.

Model Validation

Before using the simulator to assess the effect of system chemical and equipment parameters on treater performance, it would be more convincing first to validate the model against observed plant performance test results over a range of conditions. The validation is against the measured performance of seven LPG treaters using sieve trays, and eight treaters containing various depths of random packing. The sour liquids contained 0–2.25 mol% H_2S, with one or more of C_1–C_4 mercaptans and COS ranging from 6 to 4,500 molar ppm. Solvents included MEA (one case), DEA (10 cases), MDEA (4 cases) and one case of a DEA-DGA-MDEA mixture. Treater diameters were in the range 0.675–2.90m and contained between 10 and 22 sieve trays (1/4-inch hole diameter on 2-ft spacing) or 20 to 40 feet of 2-in ceramic Raschig rings (8 cases) including one case each of 1-in Raschig Rings, and Intalox Ultra® packing. In three cases the packing size was unspecified, so 2-in rings were assumed. In all cases involving trays, the number and type were always specified in the original data but hole size and tray spacing were sometimes omitted. Where such specifications were missing, 1/4-in holes and 2-ft spacing were assumed.

All the treaters discussed here were embedded in much larger flowsheets, each containing between eight and 12 columns and treaters, so measured data for the lean amine feeding the liquid treaters themselves were not always available. Therefore, simulated lean loadings as calculated via whole flowsheet simulation had to be assumed correct, along with the lean solvent's mercaptan and COS content. All the plants these flowsheets represent were handling significant percentages of H_2S in various gas streams, but the liquid treaters usually had only a few 1000s of ppmv H_2S in the sour liquid. When residual H_2S in the treated raffinate was detected at a measurable level, it was invariably found to be < 1 ppmw. Simulated values were 0.3 – 2 ppmw which is very satisfactory agreement — H_2S removal was not performance limiting.

The most direct way to validate simulation against plant measurements is on a parity basis. Figures 2 and 3 compare measured and simulated mercaptans and COS levels in the treated liquid from trayed and packed columns, respectively. Given the approximations and estimates that had to be made to fill in the missing data from sometimes sketchily documented equipment and operating conditions, the extent to which simulations reproduce performance metrics is remarkable. It should be emphasized that the simulated results shown here are in every sense pure *prediction*. They certainly lend credence to the efficacy of the fundamental model used as the basis for the simulator. It seems that most of

the treater details germane to tray and packing performance in sour, liquid-hydrocarbon service have been correctly quantified.

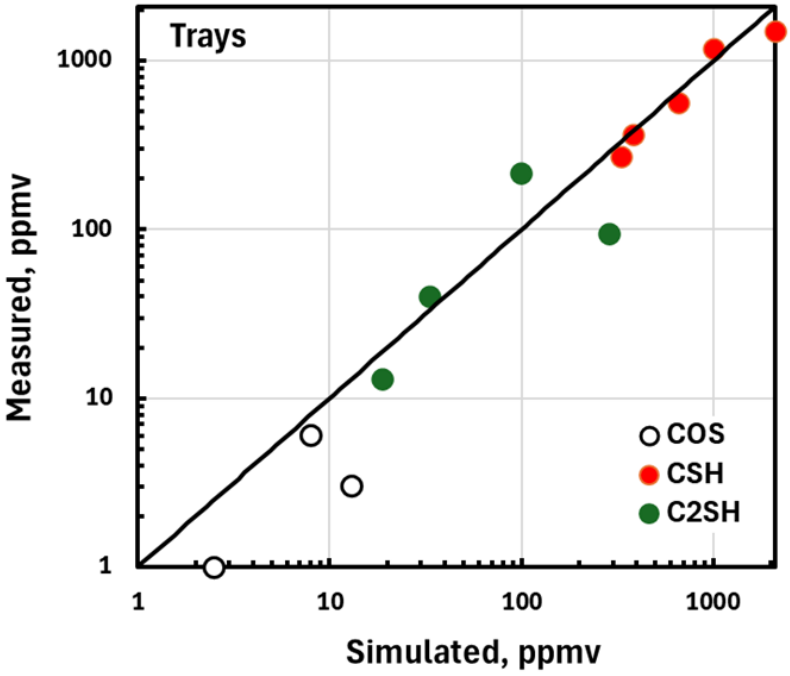

Figure 2	Validation of Trayed, Liquid-Treater Simulation

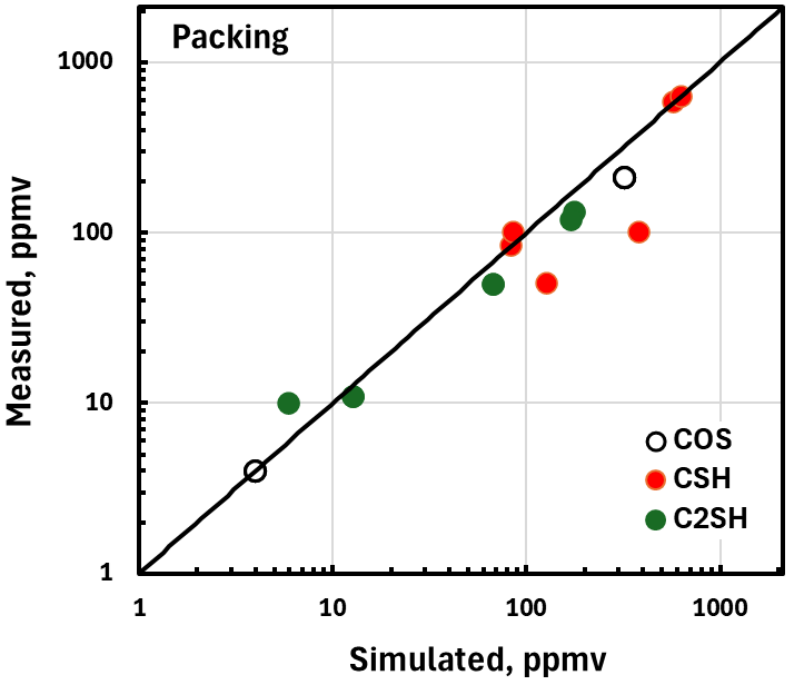

Figure 3	Validation of Packed Liquid-Treater Simulation

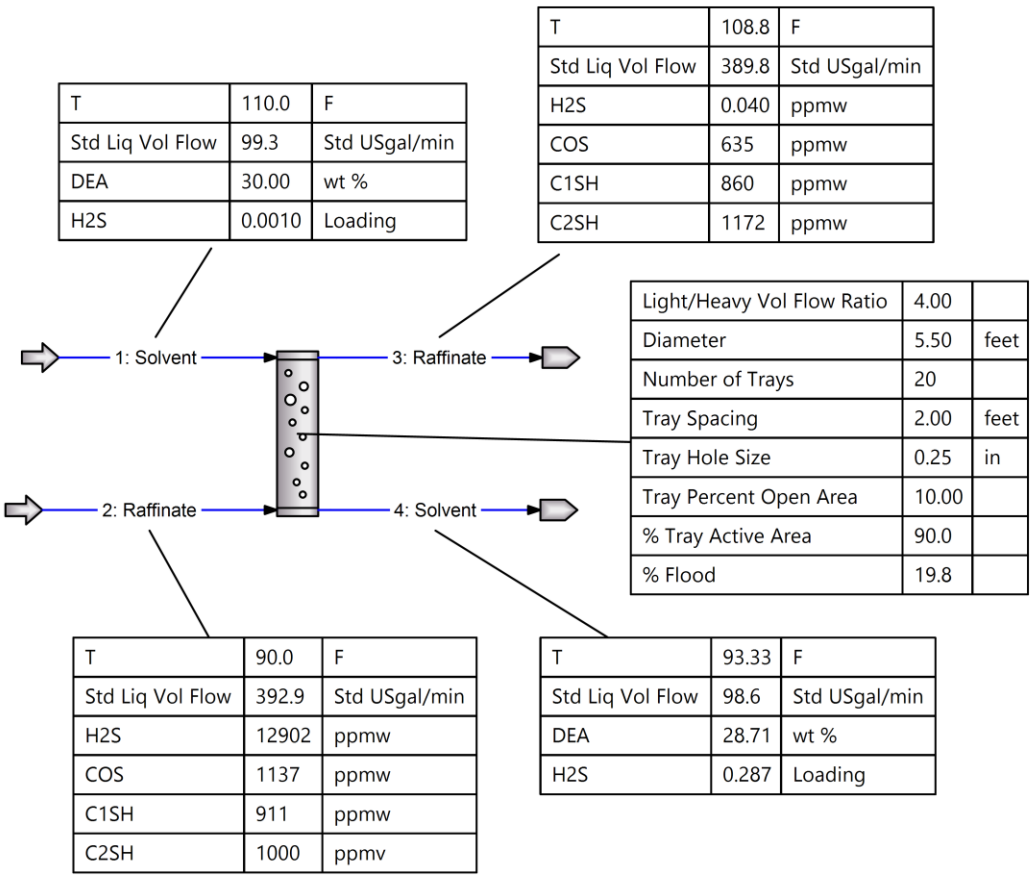

Figure 4 Base Case Parameter Values Used in Case Studies.

Simulation Study

The parametric study uses a base case that was close to a real operating unit. Figure 4 provides details about this unit and the streams entering and leaving it. Note that the specified volumetric liquid flows are at the standard temperature used in the simulation (25°C) but the light-to-heavy volume flow ratio uses actual flows at the tower average internal temperature. The column contains 20 sieve trays with 10% total downcomer area having ¼-inch holes with 10% open area.

Effect of Solvent Selection

The results of this parametric study are summarized in Figures 5–7 which show the treating response to solvent choice between 30 wt% MEA, DEA, MMEA, and DGA, 40 wt% MDEA, 40 wt% MDEA with 5 wt% piperazine, and 10 wt% caustic soda. If one is interested in knowing the solvent flow needed to treat LPG to 10 ppm (molar) H_2S, all these solvents are pretty much equivalent. Because the principal reaction of H_2S with the solvent is H2S dissociation into H+ and HS– ions, only hydrogen ions are involved. These

reactions are instantaneous and occur at the interface — H_2S doesn't have to diffuse into the bulk solvent; instead, it disappears instantly by dissociating. The remaining diffusional resistance is in the Raffinate (LPG) phase. This phase, therefore, dominates the H_2S removal process. Treating for H_2S removal is only weakly solvent dependent and to an extent that is related to solvent capacity through solvent pH and molar amine concentration. Mercaptans present a different picture as shown in Figures 6.

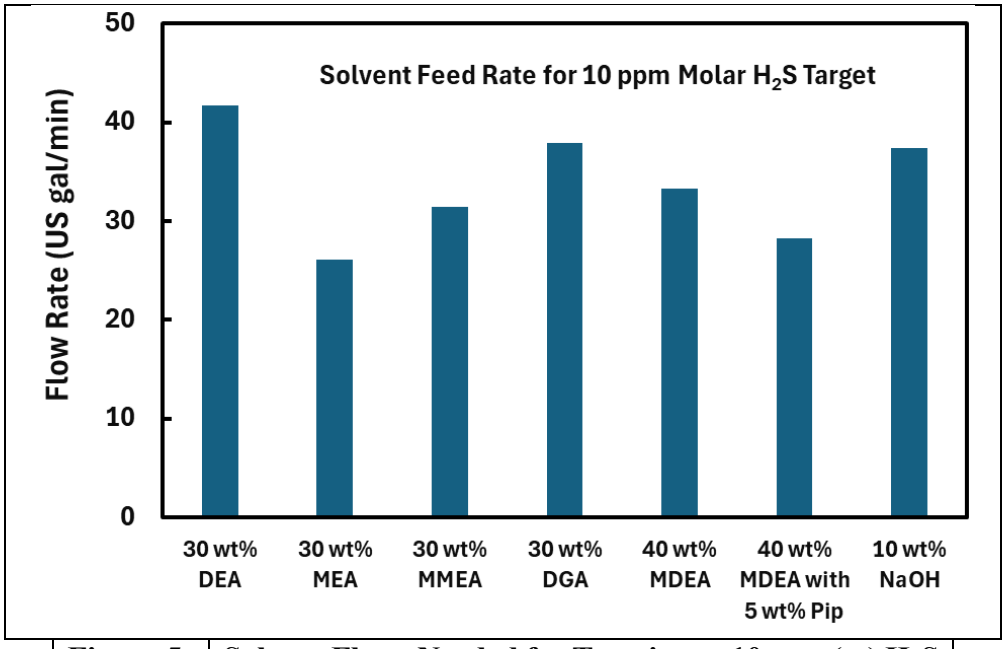

Figure 5 | **Solvent Flows Needed for Treating to 10 ppm(m) H_2S**

It is well established that amines are generally not very suitable for removing mercaptans to low concentrations from liquid (and gaseous) hydrocarbons, especially if there is much more than a trace of H_2S present in the LNG feed. The simulation results in Figure 6 support that contention. Methyl mercaptan removal ranges from 0.84% to 2.4% and ethyl mercaptan is even lower: 0.2% – 0.4%. However, caustic soda is virtually 100% effective. These observations are consistent with refinery practice where H_2S (and CO_2) are removed first with an amine, and the resulting raffinate is further treated with caustic to remove mercaptans.

The reason that using amines for mercaptans removal is so unsuccessful is the disparity in pH between mercaptans and H_2S, the latter being relatively a much stronger acid. The solvent picks up mercaptans at the top of the treating tower because the solvent is almost free from H_2S. However, as the solvent moves down the column it picks up more H_2S because it is a relatively stronger acid — the increasing acidity of the solvent forces already extracted mercaptans out of that phase and back into the raffinate. This results in a mercaptans "bubble" recirculating through much of the treating column; see Figure 10 below. Figure 7 shows a typical example (see Chandran and Weiland, 2025, for details). The concentration of both mercaptans in the raffinate throughout most of the column is higher than in the raw LPG. Only across the uppermost one or two trays do the mercaptans concentrations in the LPG fall below feed values. The COS picture is different still.

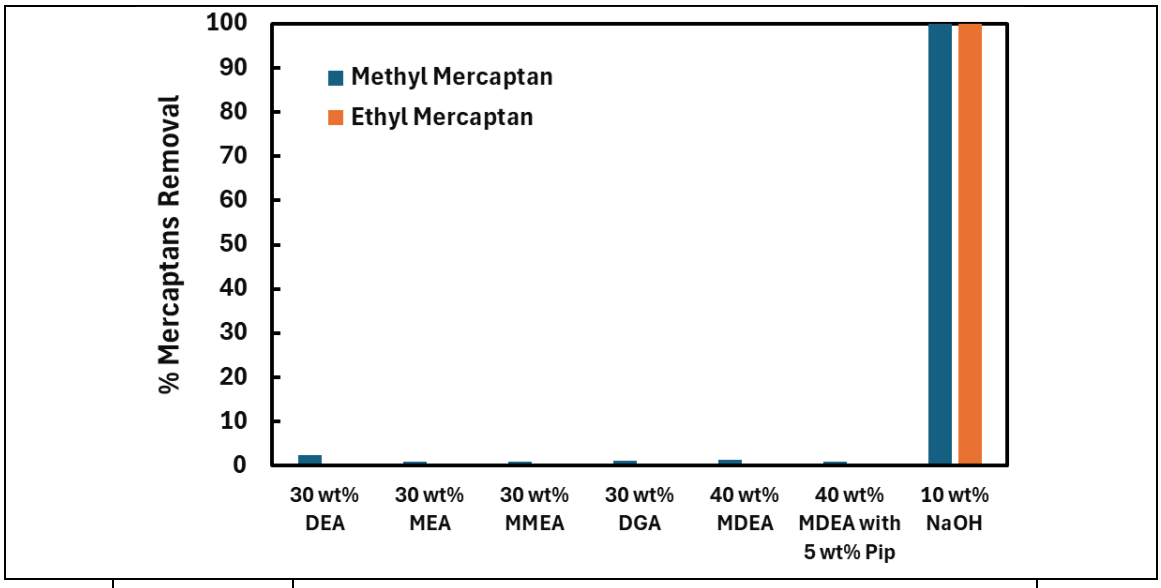

Figure 6 | **Effect of Solvent Selection on Mercaptans Removal**

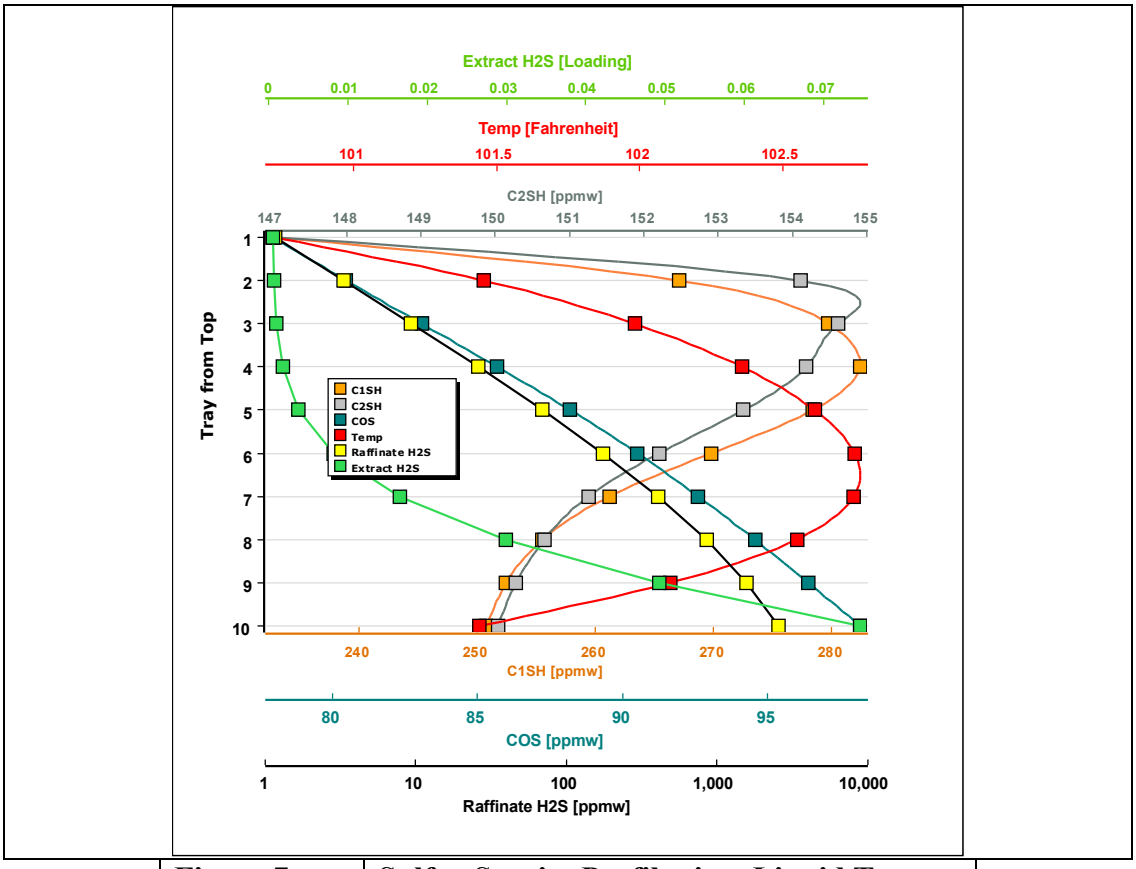

Figure 7 | **Sulfur Species Profiles in a Liquid Treater**

Figure 8 shows the simulated effect of solvent choice on COS removal. Unlike mercaptans with their very weak acidity, COS is removed to a surprisingly significant extent by all the amines except MDEA, and to 99.6% with caustic soda. Why is that? COS is a weak acid, too, so how does its behavior differ so radically from the mercaptans?

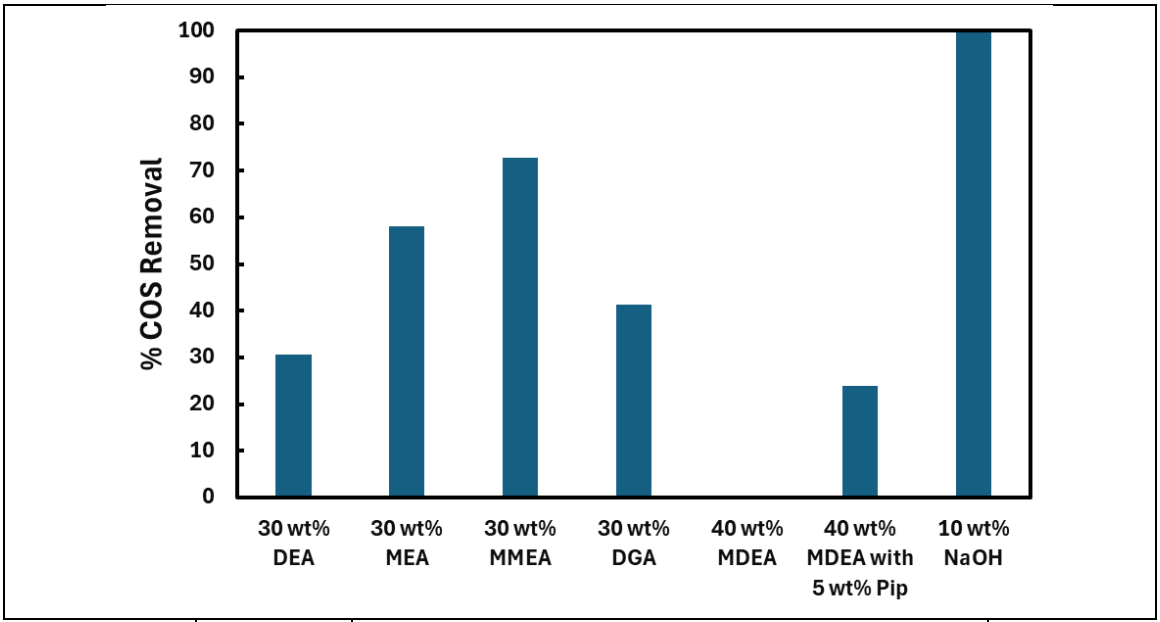

Figure 8 | **Effect of Solvent Selection on COS Removal**

The reactions of H_2S and CO_2 in aqueous amines are well known. RSH merely dissociates in aqueous media according to Reaction (1). But to describe the decomposition of COS in aqueous solution just by the reaction $COS + H_2O \rightarrow CO_2 + H_2S$ is deceptively oversimplified. The reaction mechanisms and kinetics of COS in amines are more complex than that, and although well-described in the literature (Vaidya and Kenig, 2009), they bear repeating.

As discussed by Chandran et al. (2023), in the context of gas treatment, COS reacts in aqueous solutions first to form thiocarbonate (Reaction 2). This further hydrolyses to bicarbonate and bisulfide (Reaction 3):

$$RSH \rightleftharpoons H^+ + RS^- \quad (1)$$

$$COS + H_2O \rightleftharpoons H^+ + HCO_2S^- \quad (2)$$

$$HCO_2S^- + H_2O \rightarrow H^+ + HCO_3^- + HS^- \quad (3)$$

The combined form of Reactions (2) and (3) along with other speciation reactions of CO_2 and H_2S is equivalent to the overall simplified hydrolysis of COS to CO_2 and H_2S. Reactions (2) and (3) are very slow *unless there is a base in the solution to catalyse them*. In the presence of amines, it is postulated that COS reacts by a base-catalysed mechanism according to:

$$COS + Am + H_2O \rightleftharpoons AmH^+ + HCO_2S^- \quad (4)$$

$$HCO_2S^- + Am + H_2O \rightarrow AmH^+ + HCO_3^- + HS^- \quad (5)$$

In addition to these reactions, COS forms thiocarbamate with ***primary*** and ***secondary*** amines (e.g., DEA) via a zwitterion mechanism:

$$COS + Am + H_2O \rightleftharpoons AmH^+COS^- + OH^- \quad (6)$$

$$AmH^+COS^- + B \rightarrow AmCOS^-(thiocarbamate) + BH^+ \quad (7)$$

Reaction (6) represents formation of the zwitterion, AmH^+COS^-, and Reaction (7) describes its deprotonation reaction. Any base, B, present in solution deprotonates the zwitterion, but the amine must be primary or secondary for Reaction (6) to take place. These reactions are responsible for quite significant COS removal by such amines, but do not occur with tertiary amines. Reaction (4) is known to be equilibrium limited. The rate of reverse reaction is observed to be *extremely slow* for Reaction (5), implying that for *any* amine, COS will completely hydrolyse to CO_2 and H_2S only in the fullness of time. However, for a primary or secondary amine, Reaction (7) occurs irreversibly at a much faster rate than Reaction (5). To the extent that H_2S removal does not seriously deplete the free amine concentration in the solvent, this renders COS relatively inert from the inhibiting effect of dissolved H_2S. Thus, in a column, COS reacts at a roughly constant rate across all the trays because neither DEA nor COS concentrations change greatly from tray to tray.

Figure 8 shows that MDEA, being tertiary, does little towards COS removal whereas the other amines are either primary or secondary (including piperazine). MDEA alone removes only 0.4% of the COS in this example, whilst the other amines removed between 24% (MDEA + piperazine) and 72% (MMEA). Caustic though removes 99.6% of the COS. These amines are effective for COS even in the presence of significant H_2S because their reaction with COS is irreversible and H_2S cannot reverse it.

Effect of Solvent Flow Rate

The effect of solvent flow rate on removal of H_2S, COS, and mercaptans under base case conditions is shown in Figure 9. Considering H_2S, if the solvent rate is too low the treater will be rich-end pinched and performance becomes capacity limited. If it's very high, performance becomes lean-end pinched.

The removal of COS is driven to a certain extent by the behavior of H_2S. If H_2S is rich-end pinched most of the amine has already been consumed by the time the amine solvent has progressed towards the center of the column so alkalinity has depreciated considerably and there is insufficient alkalinity to catalyze thiocarbamate decomposition. COS removal is limited by the equilibrium of Reaction (6) instead of being driven forward by the decomposition Reaction (7).

Mercaptans remain stubbornly in the LPG phase because, as alluded above, even quite small concentrations of H_2S negatively affect the equilibrium of the mercaptan protonation reaction by acidifying the solvent, thereby preventing mercaptan protonation.

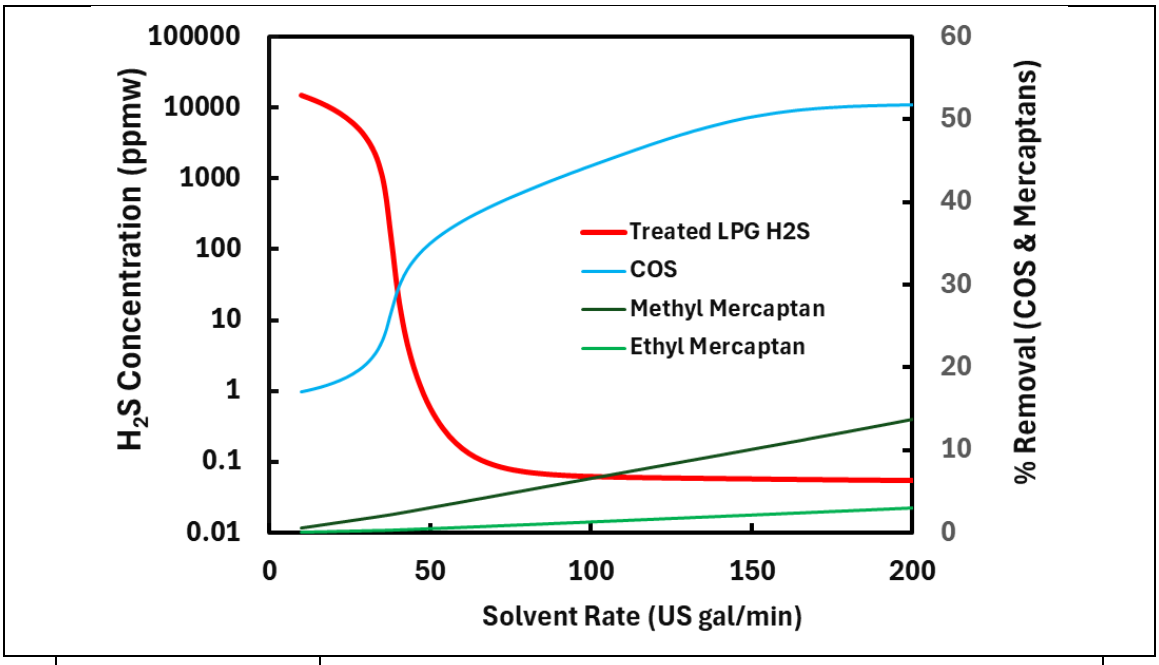

Figure 9	Effect of Solvent Rate on Removal of Sulfur Compounds

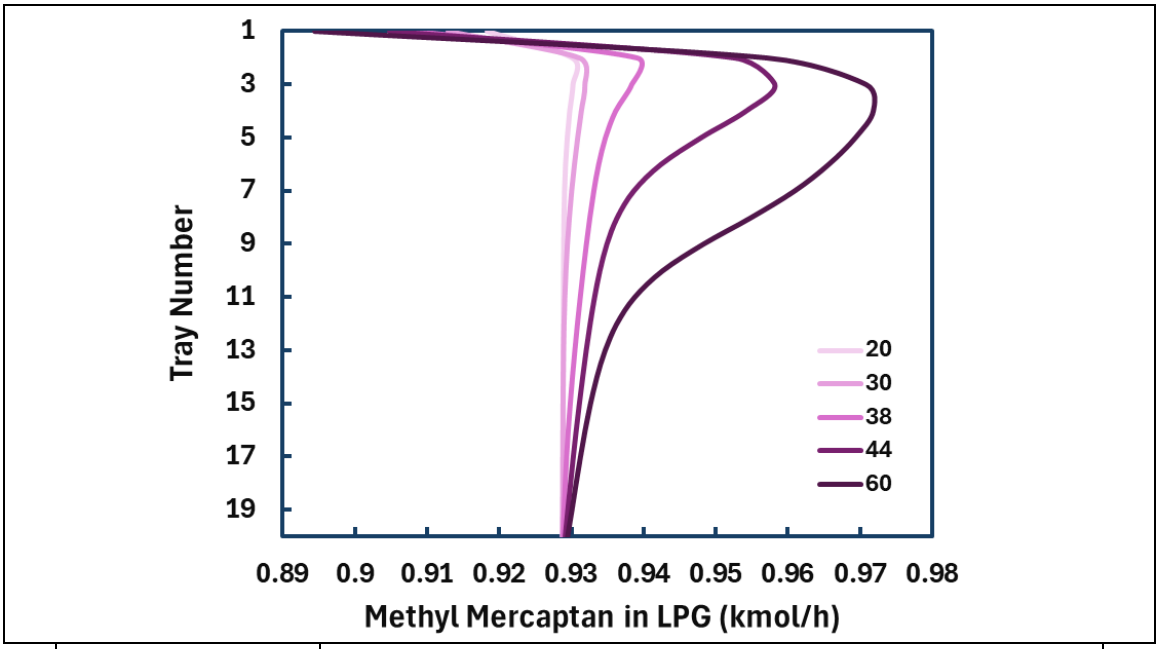

Figure 10	Effect of Solvent Rate on Size and Position of the C_1SH Bubble in the Treater

Figure 10 shows the C_1SH up-flow rate in the raffinate as a function of tray number from the top of the treater. Although not large, the bubble is nonetheless obvious — the flow rate of methyl mercaptan entering the tower with the LPG is 0.929 kmol/h and it remains

well above that value until the very uppermost tray. Increasing the solvent flow from 20 to 60 USgpm only reduces the flowrate of remaining C_1SH from 0.919 to 0.894 kmol/h, probably not measurable in a commercial treater. One must conclude that the battle to remove mercaptans from liquid streams containing much more than a trace of H_2S are almost always likely to be lost.

Effect of Solvent Strength

This topic can be adequately addressed by limiting our attention to DEA. Figure 11 shows how treating responds to changing solvent flowrate in the operating region where the tower goes from rich-end pinched through inadequate solvent flow to the region where there is neither a rich-end nor a lean-end pinch condition. Once 80–90 USgpm solvent rate is reached, the treater's H2S removal performance is no longer limited by solvent rate, and it becomes lean-end pinched. However, COS continues to be extracted because there is an increasing unreacted DEA level which catalyzes thiocarbamate decomposition and continues gradually to drive the irreversible reaction with COS forward.

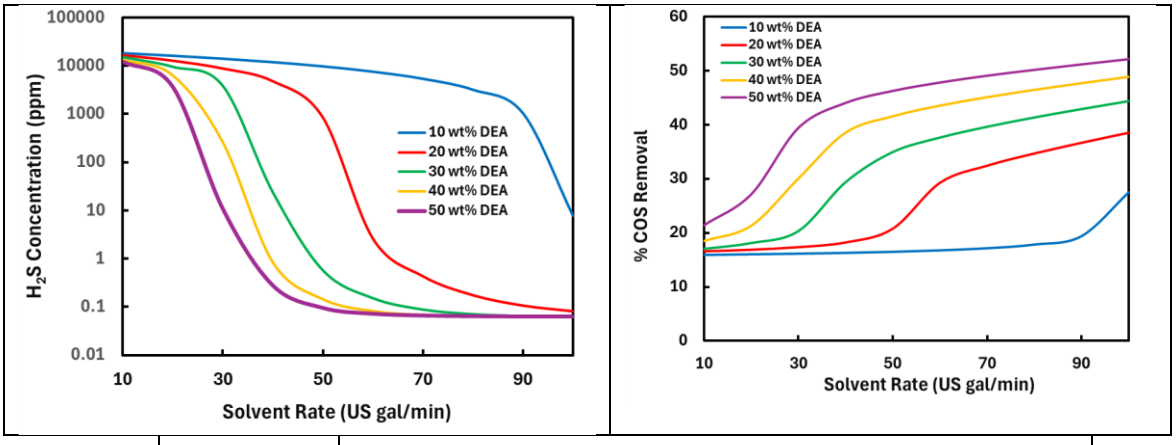

Figure 11	**Effect of DEA Strength on Residual H_2S (left) in the Treated Raffinate, and %COS Removal (right)**

Tray Characteristics

The main physical characteristics of the treater pertain to circumstances for raffinate flow as represented by sieve hole diameter, percentage of the tray area consisting of perforations (% hole area), and tray spacing. Tray spacing is an easy to discuss parameter. If tray spacing doubles or triples, the volume of biphase between each pair of trays also doubles or triples, and with 20 trays the entire volume of the tower and the interfacial area for mass transfer does so also. Figure 12 shows the same simulated behavior, albeit not quite linear.

In addition, Figure 12 also shows how COS removal responds to *sieve hole diameter* and tray *%open area*. The fractional area of the tray consisting of perforations does not have a pronounced effect; however, the size of the sieve holes does. Large holes, of course, mean

larger diameter drops but fewer of them. Overall, the interfacial area is reduced when the drops are large, reducing extraction rates.

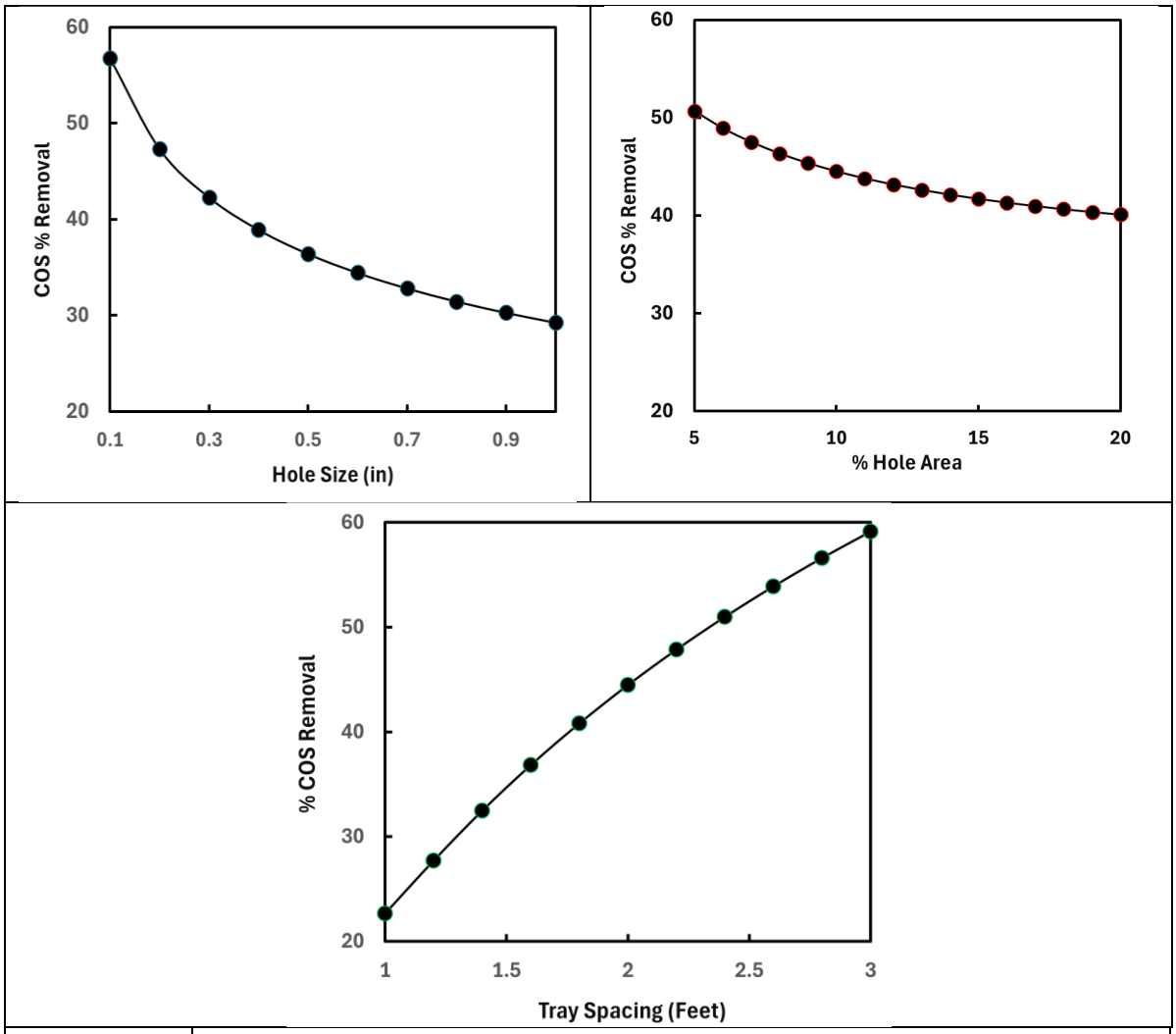

Figure 12	**Effect of Sieve Hole Diameter (left) and the Tray %Open Area (right) and Tray Spacing (bottom) on COS Removal**

In terms of fundamentals, interfacial area and Sauter Mean Diameter of the drops are interesting parameters. For all other variables and parameters such as hole size and open area fixed, Figure 13 shows how changing just the LPG feed rate to the treater affects these characteristics. Low LPG flowrate means slow flow through the sieve holes which produces larger drops with reduced frequency. The net result is low interfacial area. Hole velocity is limited if for no other reasons than higher pressure drops across the trays and the turbulence generated by high jetting velocity. Interestingly, the drop diameter is not a strong function of the LPG flowrate through holes of fixed specific diameter. In our experience, literature correlations when applied in the present context invariably result in drop diameters in the 5-8 mm range. This suggests that larger drops in LPG-amine systems

are hydraulically unstable; they will break into smaller drops (and very small drops will coalesce into larger ones).

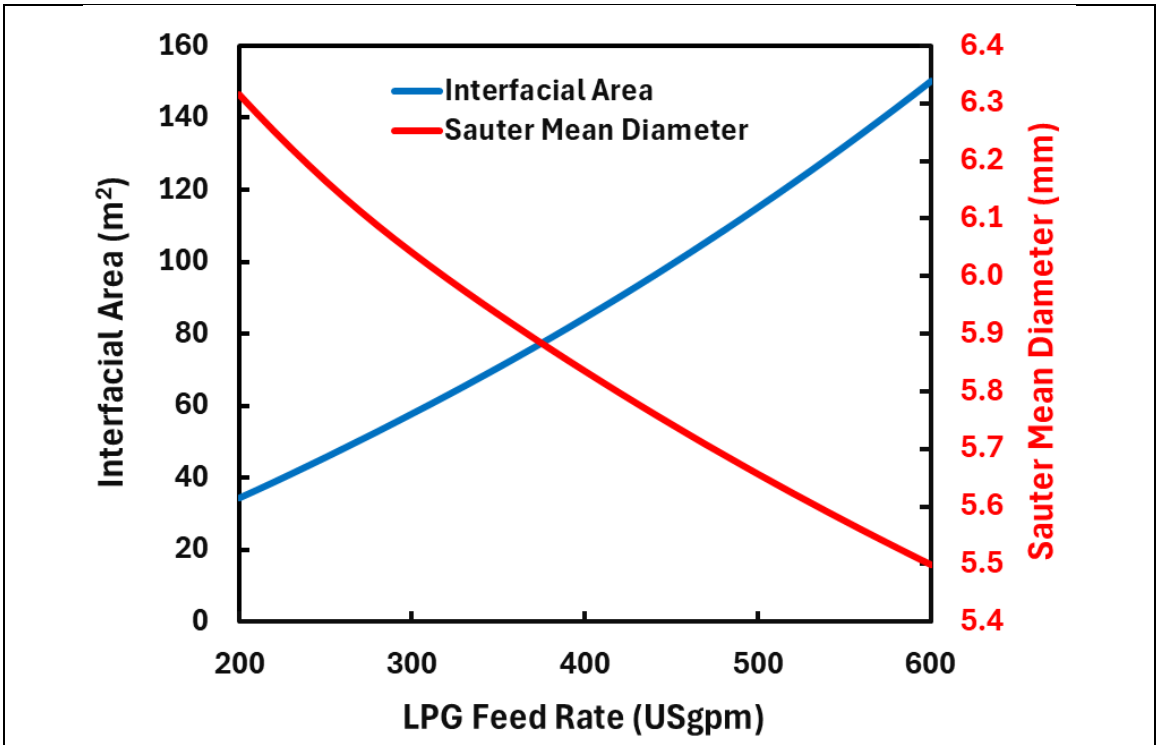

Figure 13	Effect of LPG Flowrate on Sauter Mean Drop Diameter and per Tray Interfacial Area

Packing

The remaining question concerns random and structured packing and the effect of packing size, type, and material on COS removal from LPG in a packed treater. Figure 14 summarizes the results of a parametric study to compare ½–3-inch Raschig Rings, both metal and ceramic (both materials see frequent use commercially), with structured packing of equivalent specific (dry) surface area.

The variation between commercial packings of the same nominal size but different material is largely the result of the same nominal sizes in different materials and packing types having different specific areas. Ceramic packings tend to have smaller specific area than their nominally-sized brethren in metal random and structured packings—this might lead to larger drops. However, ceramic packings have thicker walls, hence smaller void fraction (0.70–0.77 vs. 0.92–0.95 for metal rings and 0.70–0.85 for structured packing). This will result in higher flow velocities of LPG though the ceramic packed bed, thus smaller drops. When the geometric and material factors are all considered, there seems to be little to choose between packing type and material as long as the packing is nominally 2-inch size or larger. There is also only a minor advantage to using packings 1-inch size or smaller, but with the potential disadvantage of plugging. Of course, there may be other reasons for

choosing a smaller packing. For example, large packings are likely to be more prone to maldistribution, one of the banes of using packed beds in multi-phase systems.

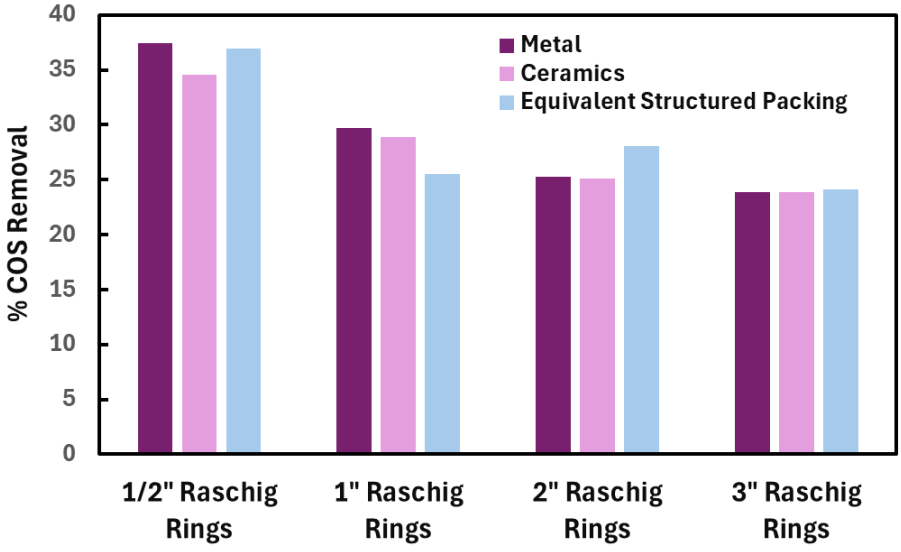

Figure 14	Effect of LPG Flowrate on Sauter Mean Drop Diameter and per Tray Interfacial Area

Summary

This work presents a new mass-transfer rate-based model for predicting the performance of LPG treaters. The model incorporates rigorous electrolyte thermodynamics, reaction kinetics, diffusional mass transfer, droplet behavior, and detailed internal geometry for trays and packing. The model has been validated against a set of 15 commercial operating plant data.

The parametric study that was conducted using this model reveals how solvent type, strength, flow and tray/packing characteristics influence the treating performance. H_2S removal is largely solvent independent due to its instantaneous reactivity. Any resistance to mass transfer is dominated by the hydrocarbon phase. Mercaptans removal is poor with amines in the presence of H_2S. COS removal is strongly influenced by the reactivity of the solvent. Although, caustic is shown to be effective in removal of both mercaptans, and COS. Tray properties have noticeable effect on mass transfer through its small but non-negligible effect on droplet diameter and the interfacial area. Packing selection is shown to have negligible effect on mass transfer characteristics as long as adequately large interfacial area and void fraction is guaranteed.

Historically, engineers have relied on ideal-stage methods combined with rough efficiency assumptions and HETP estimates, approaches that are often highly unreliable due to the complex hydrodynamics, transport, and reactive chemistry in real treaters. With the introduction of this model, for the first time, engineers can analyze and predict the performance of trayed and packed treaters in acid-gas liquid-hydrocarbon service with the

same reliability that rate-based simulation of gas treatment using amines has provided for the past 30 years. We are currently adding other types of contacting devices and non-stationary internals to those already available and are addressing other applications of liquid extraction, including aromatics removal from pyrolysis gasoline fractions in refineries, and aromatics removal from lube oils.

Rate-based simulation of liquid-liquid systems is truly revolutionary and opens the door to reliable, predictive simulation of a whole new world of unit operations that until now has had to rely on antiquated rules of thumb, gross approximations, and hope.

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