



The CONTACTOR™

Published Monthly by Optimized Gas Treating, Inc.
Volume 16, Issue 5, May, 2022

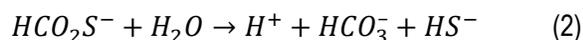
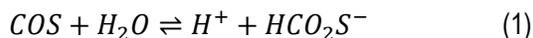
COS Removal: Finally, Accurate Simulation

Natural gas, refinery gas and hydrocarbon liquid streams such as propane (LPG) need to be cleaned of CO₂, H₂S and other sulphides such as COS and mercaptans. Failure to adequately do so will cause LPG, for example, to fail a copper-strip test. Even LPG that passes the copper strip test will fail later if there is much residual COS because of the gradual conversion of COS to CO₂ and H₂S.

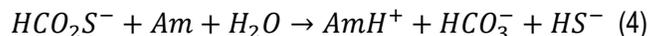
Amines have excellent H₂S removal characteristics but they're notoriously poor solvents for other trace sulphur species that are less-acidic such as COS and mercaptans. Heretofore, no simulator has been able to model COS and mercaptans removal adequately. For mercaptans the basic problem appears to be insufficient, inaccurate phase equilibrium data. For COS, one of the main issues has been the fact that the simulators have ignored the reactive nature of COS in aqueous amine solutions, by the over-simplification of a purely physical dissolved solute. Thus, the capacity of the solvent is wrongly assessed, and its absorption rate is wrongly computed because the calculations fail to account for absorption rate enhancement of COS through the chemical reactions of COS with solvent species.

Reactions

The reaction mechanisms and kinetics for COS in amines are well established in the literature (Vaidya and Kenig[†]). COS reacts in aqueous solutions by the following reactions to form thiocarbonate which further hydrolyses to bicarbonate and bisulfide:



The combined form of these two reactions along with other speciation reactions of CO₂ and H₂S is equivalent to the overall hydrolysis of COS to CO₂ and H₂S. Reactions (1) and (2) are very slow unless there is a base in the solution to catalyse the reactions. In the presence of amines, it's postulated that COS reacts by a base-catalysed mechanism as given below:



In addition to these reactions, COS forms thiocarbamate with primary and secondary amines via a zwitterion mechanism:



Equation (5) represents the zwitterion mechanism and Equation (6) describes its deprotonation reaction. Any base, B, present in solution deprotonates the zwitterion.

Reaction (3) is known to be equilibrium limited. The rate of reverse reaction is observed to be practically zero for reaction (4) thus indicating that COS will completely hydrolyse to CO₂ and H₂S in the fullness of time.

Thiocarbamate formation is significantly limited by the deprotonation step (6). In fact, for several amines, the COS absorption rate is almost completely determined by the rate of deprotonation. This is unlike CO₂ where the zwitterion deprotonation rate has much less influence on the overall conversion. As a result of these factors, it's reported that the COS-amine reaction rate is roughly two orders of magnitude slower than CO₂. Nevertheless, COS reaction rates are significant enough for a substantial fraction of the COS in a typical feed gas to be removed by primary and secondary amines. Such is not the case for mercaptans, however, because they are very weak acids and are easily displaced by co-absorbed CO₂ and H₂S.

Recently, OGT developed a model for COS absorption by treating it as a rigorous mass transfer rate-controlled component and implemented it along with its reaction kinetics into OGT|ProTreat®. The results of the model were validated against a range of proprietary field-performance data for various amine systems. The model allows *accurate* simulation of COS removal in amine absorbers for the first time ever. What follows is a case study showing the importance of a mass transfer rate-based model for COS removal and comparing the performance of DEA against MDEA in a simple absorber.

[†] P. D. Vaidya & E. Y. Kenig, *Kinetics of carbonyl sulfide reaction with alkanolamines: a review*, Chem. Eng. J., 148, 207–211 (2009).

Case Study

Figure 1 shows the simulation of two simple absorbers, one using a 3M solution of DEA and other using MDEA at the same molar strength and circulation rate. In both cases, the feed gas is 5 mol% CO₂ and 2 mol% H₂S; 500 ppmv of COS was assigned to the inlet gas. Callouts attached to the gas streams show the gas analyses.

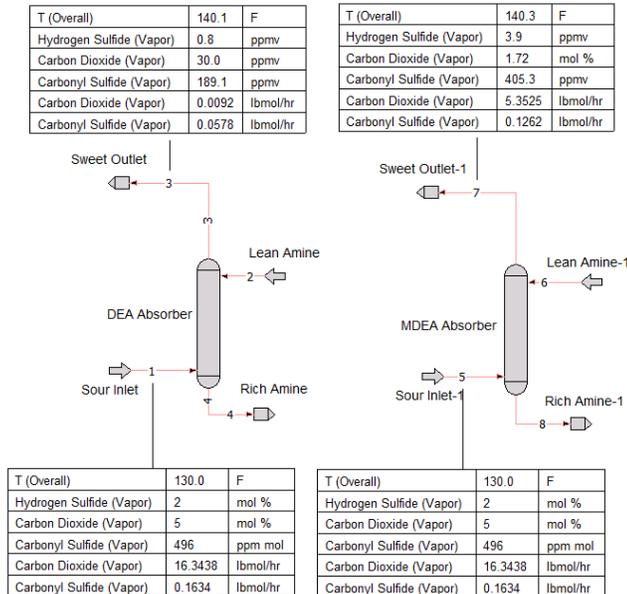


Figure 1 Absorber Models

For MDEA and DEA respectively, the CO₂ removal efficiency is about 67% and 99% compared with 23% and 65% for COS. As expected, amines don't remove COS as effectively as CO₂, although a significant amount of pick-up is seen. In addition, DEA, a secondary amine, reacts much faster with COS by forming thiocarbamate via the zwitterion mechanism. This leads to almost three times greater efficiency than MDEA which, as a tertiary amine, can't form thiocarbamate.

Table 1 compares ProTreat's predictions using our new model for COS absorption ("Kinetic" in table) with what has been the only type of simulation commercially available until now ("Legacy" in table). The Legacy and Kinetic Models

Table 1 Comparison between Legacy and Kinetic Models*

Model	DEA			MDEA		
	CO ₂	H ₂ S	COS	CO ₂	H ₂ S	COS
Legacy (Equilibrium)	30	0.8	523†	1.7‡	3.9	508†
Kinetic (Reaction Rate)	30	0.8	189	1.7‡	3.9	405

* Treated Gas Concentrations in ppmv ‡ Concentration in mole %
 † Removal of CO₂ and H₂S concentrates COS above its 500 ppmv inlet value

give identical predictions of CO₂ and H₂S removal as one might expect. However, the Legacy Model predicts 2% of the COS is removed by DEA and 3.3% by MDEA; whereas, the Kinetic Model predicts removal of 65% and 23% by DEA and MDEA, respectively. Users of Legacy simulators have complained for years that predicted COS removal has been far removed from observations. That deviancy has now been rectified — ProTreat's Kinetic Model predictions conform well.

Figures 2 and 3 show how the Kinetic Model predicts that CO₂ and COS approach final outlet values in the DEA absorber. The gentler decrease in COS partial pressure reflects the much slower reaction kinetics of COS. In DEA, CO₂ falls rapidly from 5 mol% to a few ppmv; whereas, the same 20 trays only take COS from 500 ppmv to 189 ppmv. But relative to MDEA, both CO₂ and COS decrease rapidly simply because DEA reacts with both. MDEA does not.

In a typical amine absorber, COS is severely mass transfer rate limited. This is supported by the present cases where the COS equilibrium partial pressures are almost coincident with the y-axis. The driving force is high but the absorption rate is slow. COS can't be properly simulated using only its physical (Henry's Law) solubility. COS reacts with primary and secondary amines at rates that enhance its absorption and therefore affect the ability of any absorber to remove it from the inlet gas. For accuracy, it's imperative that the latest Version (7.0) of only OGT|ProTreat's rigorous mass transfer rate-based simulator is used to simulate COS removal in gas treating.

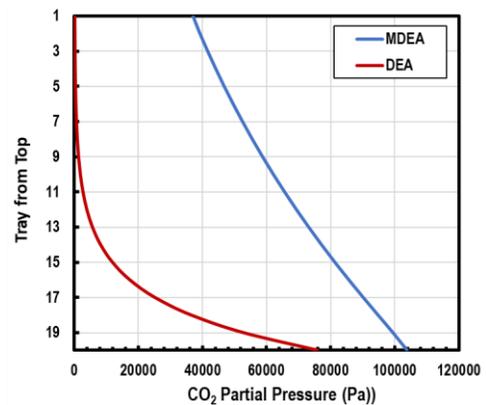


Figure 2 CO₂ Partial Pressure Profiles

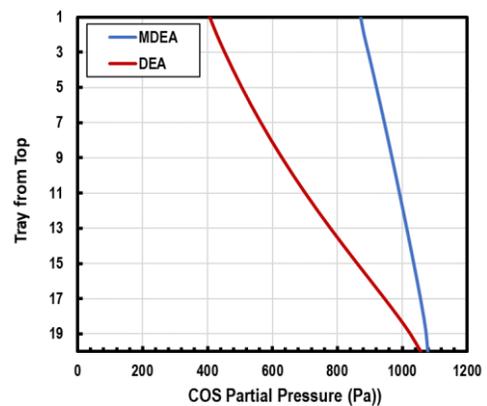


Figure 3 COS Partial Pressure Profiles

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.

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