
Question 10: Where is carbonyl sulfide found in alkylation units? What effects can it have on the unit, and what are the prevalent management strategies?

FRY (Delek Refining Ltd)

Again, I am focusing mostly on sulfuric acid units because that is where I have experience. Carbonyl sulfide (COS) is a noncombustible gas that will follow propane and propylene. So, if you are running all of your FCC olefins, then you will get it into the reactor and into the refrigeration section. If you are using a C3/C4 splitter on the front end, then it will go out with your propylene product overhead of the splitter. It can cause issues in both locations. We have had experience with COS hydrolyzing to form H₂S and failing copper strip corrosion tests on the propylene product stream.

The other location where you can have issues – one where we do not have much experience, but I understand others do – is when COS gets in the refrigeration section. It can hydrolyze with any water, form H₂S, and cause copper strip corrosion failure in your propane stream. One way to deal with this issue is to use solid KOH (potassium hydroxide). At our facility in Tyler, we have never had issues with our propane because we do have KOH beds. So, if any COS does slip in with the feed, it is neutralized there and does not cause any issues. Having the proper feed treaters – say, using a DEA (diethanolamine) amine – to treat your feed will also help.

I also understand that there are a number of facilities which have had success using alumina or mol sieve. The objective with those methods is to hydrolyze the H₂S at that location and then neutralize it with an absorbent before it goes into your feed. If you use an amine process to treat your alky feed, then consider using DEA DGA (diglycolamine?). MEA (monoethanolamine) will react and form a non-regenerable urea. You can try using MEA as an additive in other applications, but certainly not in your amine unit. MDEA (methyl diethanolamine) is not effective in removing COS.

KEADY (Technip USA)

Emerson did a great job and basically covered everything. I have a lot of experience removing COS because many of our high propylene FCC units to produce polymer grade propylene. We designed contaminant removable beds. The sequence of the beds is very important. You need to work with your design engineers to get the sequence of the beds correct. In many of our units, we use Selexsorb™ COS to ensure the quality of propylene. And you are right: It does follow propane and propylene.

DUNHAM (UOP LLC, A Honeywell Company)

In an HF alky unit, the carbonyl sulfide is one of the few sulfur compounds that can get all the way

through the reactor unreacted. When it goes out with the propane stream, it will hydrolyze in the alumina treater because it is running 400°F, there is water and a catalyst present, and it will form H₂S there. The H₂S will be captured in the downstream, solid bed KOH treater, because that is where the water will dissolve the KOH, and then that will absorb the H₂S. There is a safety concern here that when you drain that brine of KOH in water, it contains H₂S. Most people do not understand that H₂S can be present in an HF alky unit. When that gets into the sewer, if it gets neutralized anywhere or goes into an acidic situation, the H₂S will sprang. So, this has proven to be a safety concern in HF alky units. We have had refiners whose H₂S detectors have gone off while they were draining this brine off the KOH treater.

ADRIAN SKIPPER (Phillips 66)

How do you limit the amount that gets into the unit? Is there anything you can do back at the catalytic cracker to decrease/stip the carbonyl sulfide?

FRY (Delek Refining Ltd)

When we were having issues with copper strip corrosion of our propylene, we tried changing caustic more frequently at our treaters and adding MEA into the makeup caustic. Neither approach had a long-lasting impact. However, we did observe that lowering the FCC riser temperature seemed to coincide with when we stopped failing copper strip corrosion.

ERIC LEETON (UOP LLC, A Honeywell Company)

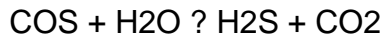
You mentioned the causes of CO obviously with the FCC. Much of the COS formation is driven by reactor severity. If you look at the reaction for the formation of COS, it is not fully understood; however, most parties assume that it is formed from the CO and H₂S that is entrained with the catalyst. So anything you do to increase catalyst circulation – raising reactor temperature or potentially changing catalyst formulation – can re-entrain more CO or H₂S. There are some other theories about what causes the formation in the FCC; but again, a lot of it is severity driven. Some of the different feedstocks we are running seem to contribute more to COS formation. So typically, the harder you push the catalyst with higher severity, the more COS you will make. If you want to make a lighter yield – i.e., you are pushing the unit towards your lighter products, then you can expect to push the unit towards the lighter sulfur species. These changes will shift from mercaptan formation to the formation of H₂S and, therefore, COS in the reactor as well.

SHANE PRESLEY (DuPont Clean Technologies)

Carbonyl sulfide (COS) enters the alkylation unit in the olefin feed from the FCC unit. We have received feedback from numerous customers that COS is found in sulfuric acid alkylation units in the propane

purge or propane product stream. To our knowledge, a material balance has not been performed to determine if all of the COS freely passes through the reaction section or if a portion of it stays with the sulfuric acid.

In many cases, customers have reported that carbonyl sulfide was originally discovered because of a failed copper strip corrosion test on the propane product. While the COS itself was not to blame for the failed test, it is believed that a hydrolysis reaction, which is catalyzed by molecular sieve in the dryers, produced H₂S. The reaction is shown below:



Regarding treatment steps, it is well understood that caustic systems do not adequately remove COS. Amine systems, on the other hand, are known to remove COS. Another option is to promote the hydrolysis reaction using molecular sieve dryers to produce H₂S and then treat the H₂S.

GINGER KEADY (Technip)

Carbonyl sulfide (COS) is produced during the cracking reaction and is not easily removed by solvents. COS has the tendency to hydrolyze, forming corrosive H₂S and CO₂. COS follows the propylene/propane and propylene.

The sequence of contaminant removal is important: H₂O, CO₂, and H₂S. The structure of the adsorbent must be carefully determined, depending on contaminants.

Selexsorb COS is a smooth, spherical adsorbent with a demonstrated ability to remove COS, CO₂, H₂S, and CS₂ from hydrocarbon streams (regenerable). It is typically considered part of the Performance Protection & Enhancement Program for any refinery or petrochemical catalyst that is sensitive to sulfur compounds.

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