Question 76 The regeneration of feed dryers/sulfur guard beds on butane isomerization units generates a butane slop stream. Will processing this butane slop stream in an HF or sulfuric acid alkylation unit cause any problems? If so, what else may be done with this slop stream?

QUINTANA (Valero Energy Corporation)
The spent Isom regenerant will contain butanes that are attractive to recover. They can come from generally any of three sources: either the treated normal butane feed downstream of the on-stream dryer, the fractionated isobutene from the Deisobutanizer fractionator overhead, or the isomerate product is used as the regenerant source. The spent regenerant also contains all of the sulfur and oxygenate impurities that were previously accumulated on the sieve; and after the spent regenerant coalescer, it will also be saturated with water. We should also keep in mind that these impurities will generally co-boil with the normal butanes since that's how they got to the Isom feed dryer to begin with. This should be kept in mind when determining disposition of the spent regenerant. Furthermore, while the impurity concentrations vary during the regeneration, you will generally hit a peak during hottest part of the regeneration as well. That high level can possibly overload some of the downstream systems that the regenerant is directed to.
The spent regenerant may be attractive to recover as alkylation unit feed, especially where it has significant amounts of isobutene. Clearly, if you're using the Isom feed (with low amounts of isobutene) as your regenerant, then it's just going to take up hydraulic space in the alky unit, and another alternative may be preferred.
The feed dryers at the alky unit won't remove much of these impurities other than moisture with three primary consequences. You'll get consumption of acid from sulfur and oxygenate reactions, but they won't be completely converted. Then, these acid consumption byproducts will increase the load on the acid regenerator while the unconverted impurities that remain will end up back in the fractionated normal butane cut that goes to the Isom unit feed. As a result of that, the recycled impurities from the spent regenerant will add on to the level that is in the fresh C4 feed. As the level builds, it will wind up in the feed to the Isom dryers and potentially overload it, leading to breakthrough between regenerations, and possibly deactivate Isom catalyst.

The windup effect is illustrated in this figure where the dotted line represents the recycle of the spent regenerant to the alky feed. Each time a regeneration is under way, the impurity level in the alky unit will likely increase, which will increase that load on the alky regenerator and produce more ASO. And as Allen indicated back in Question 72, oxygenates in an HF unit are particularly a problem as they will make lighter ASO compounds. We've seen as much as a 100°F drop in the ASO IBP from oxygenates in alky unit feeds. In order to get rid of those byproducts in the acid regenerator, you have to drop your regenerator cut-point, which will substantially increase the physical acid losses that go out with the spent regenerant.
Since the conversion of the impurities to ASO compounds is not complete, those residual impurities in an alky unit will wind up, again, in the Isom feed and load up the dryers, and the cycle is repeated. The tolerance of a given unit to that wind-up really depends on the amount of available dryer capacity. But if

you have a unit that has increased throughput over the years and you have less time between regenerations, you may not have enough drier capacity between regenerations to tolerate that wind-up. And additionally, depending on how much sulfur you have in the refinery, clearly that will have an impact on how much load there is on those dryers as well.

So the most effective alternative is to break the wind-up loop and not have a recycle that's going to contribute to that increased concentration and basically send the spent regenerant to where it can be more completely converted. What we found to be most effective is to send it to a hydrotreating unit, typically the naphtha unit, and there the impurities will be completely converted; subsequently, the treated butanes can combine with other refinery butanes and be sent back to the Isom feed. In this way, you don't have the accumulation effect described earlier.

Gasoline ProcessesGasoline Processes•Tolerance to sulfur wind-up varies with the amount of slack drier capacity, amount of sulfur in the refineryIsom Regenerant DispositionAlky UnitDIBIsomDriersIsomUnitAlkylateSpent IsomRegenerantC4 FeedASOiC4 RecyclenC4

Other alternatives can include fueling spent regenerant although that depends on the refinery fuel balance and may present an economic downgrade of butane. It may also affect stack emissions because of the sulfur compounds in that regenerant. Alternately, you could recycle it further upstream to the butane sweetening unit; but again, you're not going to get as completed conversion as in the hydrotreating unit itself.

We have seen some units, in my previous days at UOP overseas, that were equipped with a large spent regenerant drum that was large enough to contain all of the spent regenerants from the full regeneration. That way, variability of the contaminant concentration could be limited and it could be sent ratably to the downstream destination.

METKA (Sunoco, Inc.)

We operate a Butamer within our HF alky complex. Originally, normal butane was used as the dryer guard bed regenerant, and we routed the spent stream to gasoline blending. Over the years, we had no reported issues resulting from this operation. Approximately three years ago, we performed a study to evaluate using stabilizers bottoms from the Butamer as the regenerant stream and then subsequently reprocessing it in the alky.

The stabilizer bottoms is a dry stream and its relatively high isobutane content results in less alkylation unit impact than would be expected with a normal butane stream. As part of the study, the cycle up of contaminants that Javier discussed was reviewed and its potential impact on the unit was determined to be manageable. We made the piping modifications to route the stabilizer bottoms to the guard beds and to also allow the spent stream to be rerouted back to the HF alky where it is treated and then dried with the BB feed. We've had no adverse effects to date with this operation.

Tags

Alkylation

Sulphuric Alkylation

Year

2008

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