
Question 11: What operating variables lead to increases in organic fluorides in LPG product streams in a hydrofluoric (HF) acid alkylation unit? What operating variables lead to increases in organic sulfates in sulfuric acid alkylation units and where do these compounds concentrate?

DUNHAM (UOP LLC, A Honeywell Company)

The HF alkylation reaction is a two-step process. The first step of the reaction goes rather quickly, and anything that slows a reaction down will allow a stable organic fluoride to form. So the factors that increase organic fluoride formation are temperature at I/O ratio and usually acid strength.

So, temperature is an important factor. If the reactors run below 80°F, we see much higher organic fluoride formation because the reaction slows down. So, the organic fluorides are mostly made in the reactor. The predominant organic fluoride is propyl fluoride, which generally will boil in the isobutane range. So, we will see a lot of that circulating in the recycled isobutane.

If you have high isobutane content at your normal butane product, your organic fluorides will generally be higher as a result. The organic fluoride that goes out with the propane is generally ethyl fluoride. So, if you get ethylene in your feed, it almost completely goes to ethyl fluoride; so, you want to keep ethylene out of your feed. That, of course, goes back to the cat cracker operation. So, it is the cat, guys. Keep that out of the feed.

Once it is made, some of the units have provisions for chemical deformation. Some of the reactors have contacting trays or long resinous time where the reaction can reverse, and you will recover the HF. There are external recontactors that Phillips had designed and put on some units. There is thermal deformation if you have a unit with fire reboiler on your fractionator. The high temperatures in the reboiler circuit will call some of that organic fluoride to break back down.

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2015