Question 9: Is there a limit on the amount of time acid can remain stagnant in the reaction section of the alkylation unit? What adverse effects may occur if this limit is exceeded? What issues could arise on a restart from a stagnant-acid condition?

FRY (Delek Refining Ltd)

We have found that if we can bring the unit down in a controlled fashion – specifically, if we can clean up the acid by circulating isobutane for a few hours and clear the acid of any reactants, then we can let it sit there for 24 to 36 hours, maybe even 48 hours, without any kind of issue. However, if the unit came down because of something unexpected (e.g., a power outage), you will not have an opportunity to circulate isobutane, nor will you be able to bring the unit back up within 12 to 24 hours. At that point, you might need to consider dumping the acid because it could form polymers and acid-soluble oils. If you go for an extended period of time, even beyond that, then the acid might even set up and you will not be able to flow anything. So the practice we use is that if the shutdown is controlled, then you will have a 36 to 48 hours. If it was not controlled, then get ready to dump the acid after 24 hours.

DUNHAM (UOP LLC, A Honeywell Company)

Fortunately, AGIP (Azienda Generale Italiana Petroli/General Italian Oil Company) is a little more stable. And if you are not bringing in olefin feed, there is usually no problem with letting the reactor just sit. The HF alkylation reaction takes places very quickly. HF mixes readily with hydrocarbons, and it separates readily from the hydrocarbon. So, unless you are going to be down more than about four weeks, it is okay to just let the reactor sit. If you are going to be down for an extended period of time, we recommend that you dump the acid, just from the safety standpoint, to get it out of the reactor loop where there are a lot more connections that can leak. Get it into a storage drum where you can isolate it from the process.

There are some reactions that can take place. The polymer that is in the acid can get a little heavier. There are other problems that may happen if you have leakage into the unit. So what we recommend on startup of the unit is that if the acid and hydrocarbon are still on the settler, you must get isobutane recycle established to ensure good acid circulation. Then, check the acid strength to make sure you have acid within your target strength. If you do not do this, there is a chance that when you bring in the olefin feed too quickly, the unit could run away.

BURTON (Motiva Enterprises LLC)

For sulfuric acid plants, our recommendation is very similar to what Emerson said. For a controlled

shutdown, the reactors are flushed with isobutane to consume reactive components contained in the acid. The reactor will then store isobutane-full of the acid transferred to and stored in the settler. If the reaction section will be back up in, say, less than a week, then we will not dump the acid. If the down time is anticipated to be any longer, then we recommend removing the acid from the reactor system.

RANDY PETERSON (DuPont Clean Technologies)

This is a frequently asked question from those refiners who have STRATCO® sulfuric acid alkylation units. During a typical FCC three- to four-week turnaround, many refiners choose to minimize work within the alkylation unit by performing any reaction zone maintenance either before or after the FCC shutdown period. If the entire alkylation unit reaction zone or just a portion of it will not be entered during the shutdown, we typically recommend NOT neutralizing that equipment and leaving the acid in-situ.

However, we DO recommend pushing the acid from the Contactor™ reactors up to the acid settlers and stopping all feeds as they could potentially contain wet hydrocarbon. Hydrocarbon can be left in the reaction zone as well, as long as the relief system is functional. During this period, the reaction zone should not be entirely liquid full in order to leave room for thermal expansion.

The neutralization of carbon steel removes the protective layer of iron sulfate which will form again after exposure to acid. Avoiding unnecessary neutralization avoids this metal loss. Leaving acid in the reaction zone saves labor hours (shutdown and startup), as well as the cost of the acid.

Once the acid is within the acid settler(s), it will slowly degrade and can form acid sludge over time. The major concern is that this sludge can clog small bore piping and fittings and foul the vessel internals. The decomposition reaction rate increases with temperature, so a refiner in a cool climate can safely store acid longer than in a warm climate. We have not heard of problems occurring when refiners have stored intermediate-strength acid (92%+) in their acid settlers for three to four weeks.

$H_2SO_4 + CH_x \; ? \; H_2O + SO_2 + CH_{x-2}$

If the duration of storage is expected to be significantly longer than three to four weeks, then we recommend draining the reaction zone of all acid and neutralizing it.

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