
Question 9: What are the latest strategies for feed dispersion and mixing in HF and sulfuric acid alkylation? How does mixing affect alkylate endpoint? Does better mixing allow for operations at reduced I/O ratios via increased olefin charge rate or operating against isobutane constraints?

BULLEN (UOP LLC, A Honeywell Company)

I am going to address the HF units again. For the first question, it is more of an issue of, "If it ain't broke," we are not going to fix it. The types of mixers are simple in the HF unit. An orifice-type mixer is used for mixing the olefin and the isobutane recycle, and then a spray nozzle is used to mix the isobutane in the olefin into the acid. What we have experienced is it does not matter whether or not a fancy nozzle or a simple nozzle is used. As long as the pressure drop across the mixer with the acid is 10 pounds or more, you will get good mixing. There has not really been an incentive to improve that design.

As to the endpoint, if you get poor mixing, you certainly will create more ASO (acid-soluble oils) and your octane will drop. We have not actually seen the endpoint change, but we suggest that it will happen if you get the ASO really high. However, you will get more organic fluorides if you have poor mixing; so that is another problem that might happen.

We do not think changing the mixing nozzle will allow you to lower the I/O ratio. However, we have different reactor designs that allow you to lower the overall ratio. The names of those are the Phillips Split Olefin Feed Technology (SOFT) and the UOP Split Feed Series Recycle (SPFS) Technology.

MELDRUM (Phillips 66)

As Patrick mentioned, the desired alkylation reaction environment is well-mixed hydrocarbons: the olefins with the isorecycle that are then well-dispersed into the acid catalyst. This is achieved with good acid circulation and feed mixed into the acid. Poor mixing has been attributed to some high alkylate endpoints. However, mixing performance is hard to quantify, so defining a correlation between mixing and endpoint is difficult.

Sulfuric acid alkylation uses the feed distribution and significant impeller mixing in the reaction zone. The feed distributor pressure drop, mixer motor ramps, and mix zone DP (differential pressure) for a STRATCO-type unit should all be part of routine unit monitoring. At turnarounds, all the work scope should include inspecting and renewing or replacement of any the mixing components.

For the HF alkylation process, mixing is achieved through the feed nozzles. The solubility of the hydrocarbon in HF acid is greater than that of the hydrocarbon and sulfuric acid, so impeller mixing is

not used in the HF technology. Routine unit monitoring should include the feed zone pressure drop. The same comment for the sulfuric units. All of the turnaround work scopes on HF units should include inspecting and then renewing or replacement of the feed system components as necessary. I do not know of any experience where additional mixing has been used to offset lower I/O (isobutane/olefin) ratios.

ADRIÁN GUZMÁN (YPF Tecnología S.A.)

In one of our refineries in Argentina, we have an HF alkylation unit in which we are experiencing deposit formation and plugging of the spray nozzles. The analysis indicates that the deposits are mainly organic and inorganic fluorides. Can you comment on this?

The second part of my question is about the design of the spray nozzles. According to your experience, does it have an impact on the tendency to form deposits?

DARYL DUNHAM (UOP LLC, A Honeywell Company)

We are familiar with your problem, but we rarely see it. When we talk about mixing in a riser reactor with a Phillips design, we evaluate droplet size and residence time. One issue we often review is how to mix the isobutane recycle with the olefin feed ahead of the spray nozzles, because there is often enough acid in the isobutane recycle that could start the alkylation reaction before getting to the spray nozzles. So, we always emphasize that this mixing should take place as close to the riser as possible to minimize that mixing time, which may be what is producing your organic fluorides and possibly some polymer that could contribute to the mixing or to the fouling of the spray nozzles.

Now in the older designs, we used to put in fewer spray nozzles with larger orifices. With some of the newer designs, we found that their smaller nozzles produce smaller droplets; so, we tend to go with more spray nozzles but smaller. In your case, we may want to look at modifying the number of your spray nozzles and going with fewer nozzles of larger diameter while staying within the differential pressure range we need. The number analysis really depends on the flow rate. So, looking at the number of nozzles and the pressure drop for each one will dictate how they are sized.

PATRICK BULLEN (UOP LLC, A Honeywell Company)

The mixing device designs in the HF alkylation Process have not changed significantly for many years. A simple orifice type in-line mixer is typically used for blending the olefin feed into the isobutane recycle, and spray nozzles are used to mix the isobutane and olefin into the acid. For the spray nozzles, UOP's experience is that the pressure drop across the nozzle appears to be more important than the specific spray design of the nozzles. In Heritage-UOP design HF alkylation Process units: There is some evidence that plain round drilled holes provide approximately the same performance as the special spray nozzles, as long as the pressure drop across the plain drilled holes is above about 10 psi (pounds per

square inch).

Experience shows that poor mixing can cause lower alkylate octane and higher acid-soluble oil (ASO) yield. UOP has not seen data that proves that poor mixing causes higher alkylate endpoint; but if the ASO yield goes up, it is possible that the alkylate endpoint could go up at the same time (although the two are not necessarily tied to one another). UOP has feedback from one refiner who saw an increase in organic fluorides in the product stream that was caused by poor mixing.

A change in the type of mixing nozzles would not allow for operation at lower I/O ratios. However, there are reactor section designs that allow mixing the olefin and isobutane at different points in the reactor section, and this can allow operation at a lower overall I/O ratio or at a higher total olefin feed rate for a given isobutane recycle rate. Two such designs are the Heritage-Phillips Split Olefin Feed Technology (SOFT) and the Heritage-UOP Split Feed Series Recycle (SFSR) technology.

CRAIG MELDRUM (Phillips 66)

The desired alkylation reaction environment is mixed hydrocarbons (olefins and isobutane) that are well dispersed into the acid catalyst (acid continuous phase). This is achieved with good acid circulation and feed mixing into the acid. Poor mixing is attributed to high alkylate endpoint; however, mixing performance is hard to quantify, so defining a correlation of mixing with endpoint is difficult.

- Sulfuric acid alkylation uses feed distribution and significant mixing in the reaction zone. The feed distributor DP, mixer motor amps, and mix zone DP should be part of the unit monitoring. It is recommended that inspection and renewing or replacing the mixing components be included in each turnaround work scope.
- HF acid alkylation mixing is achieved through the feed nozzles. The solubility of hydrocarbon in HF acid is greater than in sulfuric acid, so impeller mixing is not used. The feed nozzle DP should be part of the HF alkylation unit monitoring, and feed nozzle inspection and renewal or replacement should be part of each turnaround work scope.

I do not know of any experience where additional mixing has been used to offset low I/O ratios.

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