Question 85: Olefins that are formed in the catalytic reforming process must be removed or converted when the reformate is processed in an aromatics extraction unit. Historically, what unit operations have been used to remove/convert the olefins in the reformate? Are there any good alternatives to clay treating? How do the alternatives compare to clay treating with respect to capital cost, maintenance, operating cost, environmental impact, and effectiveness of olefin removal?

QUINTANA (Valero Energy Corporation)

The olefin content of the reformate is determined by thermodynamics at the last reforming reactor. With higher severity, whether it's from a leaner feed, lower pressure, lower hydrogen-to-hydrocarbon ratio or higher octane, you will produce higher olefin content in the reformate. Those olefins are going to be distributed more towards the lighter end; that is, the C6 fraction has higher olefins than the C7 fraction, which is higher than the C8 fraction, and so on. While the olefins can be managed in the extraction unit, the octane economics generally are going to dictate reforming severity. Olefins that result are incidental to that the reforming economics. The olefin management strategy that you pursue really depends on the type of extraction unit you have. This question wasn't very clear as to specifically what type of extraction unit it is, whether it's a solvent extraction unit or an adsorptive extraction unit for paraxylene production that might be of concern.

The solvent extraction units don't typically require feed treating except in the case of raw pyrolysis gasoline from a steam cracker, but typically that hydrotreating is done within the boundary of the steam cracker itself. In the extraction unit, we can optimize unit operations to limit the build-up of olefins in the internal recycle loop, and you end up rejecting in excess of 99% of the olefins in the feed to the raffinate stream without any additional treating.

Managing that potential olefin buildup, though, in the internal recycle stream becomes an important part of the operating strategy because if it builds up excessively, it can create some equipment constraints and it can cause you to back out throughput. There are various optimization techniques available to maintain on-spec performance with feed olefin levels at the extraction unit in excess of 3%. That can occur if you're taking a fairly light benzene fraction as the extractor feed. If you have a wider range BTX fraction, then you will have a lower olefin content and it's generally easier to manage.

The residual olefins in the extract stream are typically fairly dilute. You measure the Bromine Index, which is typically in the range of 50 to 100, which translates to a concentration of about 250 wt ppm to 500 wt ppm. And at those concentrations, clay treating is an effective solution with demonstrated clay lives often in excess of a year without affecting benzene purity. In those situations, you can use fairly high activity clays. Clay treating is going to work by alkylating the olefins with an aromatic molecule and you'll leave a heavy byproduct that will be removed by fractionation.

The figure in the slide shows an illustration of the potential location of clay treating systems and contrasts the solvent extraction system versus an absorptive extraction unit. If you split the reformate between the extraction unit feed overhead and heavy reformate production, the heavy reformate will either be sent to blending or to a xylene column to produce isomer grade mix xylenes or to feed an adsorptive extraction unit. If you're going to upgrade the heavy reformate in this fashion, then generally you need to clay treat it to remove olefins that would foul the adsorbent and result in diminished capacity. If you're producing mixed xylenes by fractionation that are going to be sold, then you still have to clay treat. Some people have tried clay treating on the xylene product, but then you end up with the clay treating byproduct as a heavy tail in those xylenes.

The heavy reformate treater is a much more severe treating application than the extract treater behind the solvent extraction unit. The olefins at that point are at about 10 to 15 times higher than in the extract application because the extraction unit has managed to reject most olefins to the raffinate stream.

Because of the severity of the treating, you will have some competing side reactions, such as transalkylation, that can actually lead to tangible xylene losses where you'll start making some benzene, some toluene, and then some heavier aromatics through the transalkylation reaction. You'll also have more of the heavy foulants that occur from these reactions. That higher severity has often resulted in clay lives as short as four to eight weeks, which can become a bit of a maintenance headache. We should note that you do have to do that clay treating ahead of the xylene column to remove the heavy byproduct by fractionation to protect the absorbent system if you have the adsorbent extraction unit in the facility. A complicating factor is that to make the xylenes by fractionation only is going to require higher reformer severity, so generally those systems tend to have a much higher olefin content as a result of the higher reformer severity.

We do understand that there are alternatives to clay treating in the form of more selective and stable alkylation catalysts and selective saturation catalysts that have recently been commercialized, but we understand that there's limited commercial experience on those so far. I would suggest that you discuss that with the various technology licensers directly for what their experience has been on that.

GRUBB (Chevron USA, Inc.)
In the Pascagoula refinery, we have experience with a benzene unit and a xylene unit; not your typically BTX process, but we do have experience with each one individually. On the benzene unit, we have a selective hydrogenation reactor for removing the diolefins in front of the extractive distillation unit. The olefins are allowed to just go through and they end up out with the raffinate, so we have a SHU there. But on the xylene unit, we have a clay treater. We clay treat a C8+ stream and it does give us, I guess you might want to say, fits. We experience short activity and high differential pressures at times on these. So we set out to see if we could solve this by using another technology. So we looked at a SHU there, but it was too expensive; it was a little bit unproven. We would have had to pipe in hydrogen, and we would have also had to add some vessels to separate the vapor and liquid afterwards, so it became too expensive.

We settled with more of a predictive tool. We look at the output of the reformers and predict how much olefins will be coming out. We look at how they're operating and then decide, a month down the road, what it's going to look like. Based on that, we're able to predict when our clay treaters are going to die sooner. We also went down the route of trying to arrange where we could do a quicker turnaround on the clay treaters, either have a load of clay onsite or have one at a manufacturing plant ready to be shipped with a couple of days notice. Using those tools, we're satisfied with how we're handling our clay treaters now.

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