Question 15: What are your options for processing of disulfide oil from an extractive mercaptan removal unit? How will this oil affect a naphtha hydrotreater?

BURTON (Motiva Enterprises LLC)

Historically, disulfide oils would be blended back into the gasoline pool; but in the days of Tier 2 gasoline, this option is no longer available. The question of how to dispose of disulfide oils is one that comes up frequently within the company. Options that are often discussed are whether or not disulfide oils can be reprocessed in the cat cracker, the crude unit, or the coker. These operations have the potential for the disulfides to decompose back to the original mercaptan, setting up for a mercaptan/disulfide recycle loop. At the end of that day, the disulfides need to go to a hydrotreater and exit the refinery through the sulfur plant. Successful processing of disulfides at a hydrotreater requires sufficient protection to prevent caustic carryover from poisoning the hydrotreater catalyst, waterwash, sand filter, etc.

DUNHAM (UOP LLC, A Honeywell Company)

In the old days, we used to just draw the disulfide oil off and sell it to someone; but then they quit buying it. With the more efficient Merox™ units, in order to get down to lower levels, we now use a two-stage naphtha wash, and trace disulfide oil ends up in this hydrocarbon stream, which then can be sent to an FCC to destroy the mercaptan or thermal cracker. But I think the preferred method most people use is going to a naphtha hydrotreater where disulfide will be completely destroyed and converted to H_2S.

One concern about taking off this disulfide oil is that you want to make sure you get all of the proper equipment. That usually involves a sand filter, because cat crackers really do not appreciate you sending them a lot of sodium hydroxide.

DOMINIC VARRAVETO (Burns & McDonnell)

Does anyone consider putting the material to a Tier 3-type post-treater second stage and to what result? This would be in a two-stage Axens unit, for example, and putting that material into the second stage hydrotreater reactor.

BURTON (Motiva Enterprises LLC)

None of the sites are considering this option. Disulfide oils are going to naphtha hydrotreaters not associated with our Tier 2 or Tier 3 gasoline units.

KEADY (Technip USA)

This is not exactly a response to his question. But from my experience doing process design and overall refinery design, I know that this is a string that no one wants. If you have a mix of technologies and technology companies, you may have one group that produces this stream, but the other group does not want to receive the stream. So I would like to ask, as a design engineer, if, when you are doing your refinery work, you would figure out, before you come to us, who you are going to send this to [laughter], so we do not have to argue about it in the kickoff meeting and so we can avoid the situation of, "You have it." “No, you have it." That would be very helpful. So it would be great if you would please figure this out before you come to us. [Laughter]

MALCOLM SHARPE (Merichem Company)

I would just like to add that, in fact, many of our licensees do send this DSO (disulfided oil) purged stream to the hydrotreater feed tankage. As far as addressing the sodium concerns, you can install, as the panelist said, a sand filter at the outlet of the mercaptan extraction unit on a DSO-purge stream. However, your last and best line of defense is going to be sufficient residence time in your hydrotreater feed tank as that will allow any residual sodium to drop out.

RATHINA SABAPATHI [Kuwait National Petroleum Company (KNPC)]

We are looking for an alternate way to put it into the delayed coker or the naphtha hydrotreater stream. It was missed and not added as one of the feed streams during the design stage. Now neither licensor wants to process it in their licensed unit. What do you think is the best way to go about handling the delayed coker or the naphtha hydrotreater?

KEADY (Technip USA)

It depends on who has the technology for each one. It really comes down to who is willing to take the stream and use it. Who is saying, “Okay, send it here and make sure it does not have any sodium in it because this is what we want.”? I would say that would be where you have the least chance of poisoning your catalyst and contaminating your product. It is not an easy question.

DUNHAM (UOP LLC, A Honeywell Company)

So I think what Ginger is saying is that if you have UOP Merox™ unit and a UOP hydrotreater, then you send it to the coker. [Laughter]

KEADY (Technip USA)

You could not have said it better.

RATHINA SABAPATHI [Kuwait National Petroleum Company (KNPC)]

Without mentioning names, that is what I expected as the answer from you. Both the Merox™ and the NHT units are from UOP, so my question is directed toward Daryl of UOP.

DUNHAM (UOP LLC, A Honeywell Company)

Well, it will depend on your constraints in the refinery and whether you can effectively treat the disulfides in either one of these plants. If it is not going to cause you a problem in the naphtha hydrotreater, which is where most people send it, then I do not think it is going to be an issue because you are probably washing the Merox™ with naphtha anyway. So you can recover that naphtha if you send it through the hydrotreater. You will probably lose it if it goes to the coker where it will be downgraded.

ERIC LEETON (UOP LLC, A Honeywell Company)

One other consideration for sending it to the coker is if you have an HF alky unit and are running coker LPGs. In that case, you are sending sulfur to the coker where it will undergo change. So, you could get some sulfur – albeit lighter sulfur – into the HF alky that way. You would have to remove the sulfur from the coker product streams or consume the sulfur in the HF alky with the resultant acid losses, depending on how you processed those coker LPGs. So you have to look at the whole scenario.

WAYNE WOODARD (Valero Energy Corporation)

The issue with processing disulfide oil from a Mercaptan extraction process like Merox is that there is a small amount of caustic in the disulfide oil. If your naphtha hydrotreater is pressure drop-limited, then processing disulfide oil with trace amount of caustic will not shorten the NHT cycle length. If the NHT is catalyst activity-limited, then the caustic will deactivate some of the catalyst.

CHRIS STEVES (Norton Engineering)

There are a few options available for processing disulfide oil from an extractive mercaptan removal unit. The most common are to process the material in the riser of the FCC (usually by mixing with a slip stream of some other light oil) or to mix in with the feed to a hydrotreater (naphtha or distillate). When processing this material in the FCC or a hydrotreater, care must be taken to ensure that the stream is free of caustic in order to prevent sodium poisoning of the FCC catalyst or the hydrotreating catalyst.

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