Question 4: The economic benefit for propylene and amylene alkylation is improving. What considerations do you use in the feed pretreatment and alkylation unit operations before increasing these feeds?

CHRIS STEVES (Norton Engineering)

Increased processing of propylene and amylene feedstocks in alkylation (alky) units does bring challenges, but most will depend on the configuration of the existing unit and whether any of these feedstocks have been processed before.

Modification of a butylene-only alkylation unit to handle larger volumes of propylene may involve significant capital modifications to add or expand the capacity of C3 handling equipment. Examples include the depropanizer, C3 defluorinations (in HFalky units), and refrigeration equipment (for sulfuric acid alky units). With sulfuric acid alky plants, consideration will also be required for treating the reactor hydrocarbon stream before fractionation. Caustic treating systems may require the caustic circulation rate to increase by as much as twice the butylene-only rate to treat and remove esters from the reactor effluent of a propylene alky unit. In addition, the temperature required to break down these esters in the caustic treater will need to increase, potentially as much as 40°F above current operating temperatures, due to the higher stability of esters in the reactor effluent of a propylene alky unit.

In sulfuric acid alkylation units, separate reactors for propylene-rich and butylene-rich streams can help in managing acid consumption, as the different feedstocks respond differently with regard to acid consumption at different acid strengths and operating temperatures. A strategy of processing a propylene-rich stream in the high strength reactor and the butylene-rich stream in the low acid strength contactor can help to minimize overall unit acid consumption.

In addition to alkylation unit modifications for propylene alkylation, the alky feed treating will need to be reviewed to ensure that the sulfur is adequately handled and that C2is properly stripped from the alky feed stream. For addition of propylene feed, removal of H2S (hydrogen sulfide) with amine and/or expansion of the caustic pre-wash equipment should be considered so as to not negatively impact the operation of the mercaptan removal system with the production of non-regenerable sodium sulfide.

Addition of amylene to alky feed may also typically require modifications to the alky unit equipment. The extent of the modifications will depend on the desired level of amylene. Some considerations include the following:

In sulfuric acid alkylation units, amylene alkylation can be safely practiced at lower acid strengths than with propylene or butylene alkylation. With a separate reactor for amylene processing, the overall acid consumption on the unit can be minimized by allowing the final spending strength to fall lower than what would be practiced with butylene alkylation.

In sulfuric acid units, amylene alkylation is more sensitive to temperature than butylene alkylation; but with limited propane in a separate amylene reactor, the desired lower temperature may be difficult to

achieve. Modifications to the refrigeration system may be required to optimize the individual reactor sections with regard to operating temperature.

In both sulfuric acid and HF alkylation, introduction of amylene feeds will increase production of isopentane through hydrogen transfer reactions (although at higher rates in HF alkylation). Removal of isopentane from alkylate may require fractionation changes in the alky unit. The isopentane production can be minimized through recycling of isopentane from the fractionation section back into the reaction zone, but this process would require additional fractionation equipment.

Amylene alkylation will also require a review of the alky feed treating system. Introduction of heavier feedstocks to the mercaptan treating section may impact the overall sulfur of the alky feed (which will then impact acid consumption), as the heavier mercaptans are more difficult to extract. Introduction of heavier feedstocks to the alky feed can also bring undesirable species into the alky feed, such as cyclopentane and diolefins which consume acid at a significant rate. While cyclopentane can usually be excluded from the alky feed via upstream fractionation, treatment of diolefins may require separate reaction systems to remove them from alky unit feed.

KURT DETRICK (Honeywell UOP)

The issues in an HFAlkylation unit are different for propylene and amylenes.

<u>For Propylene:</u>

The types of contaminants and the concentrations of those contaminants that must be removed in the feed pretreatment section is not much different from butylene. The one difference is that there can be some ethane and ethylene that comes in with the propylene feed. Ethane tends to act as a Non condensable and requires venting from the depolarizer overhead system, which will cause increased acid losses. Ethylene does not react with iC4 in the HF alky unit but tends to make ethyl fluoride, which will cause higher organic fluoride content in the untreated propane and resulting in higher alumina consumption in the propane defluorinations.

The operational issues with propylene are primarily increased consumption of isobutane and propane rejection. The increased isobutane consumption is due to the fact that about 20% of the propylene will undergo a hydrogen transfer reaction where one molecule of propylene will react with two molecules of isobutane to produce one molecule of propane and one molecule of isooctane (C8 alkylate). This reaction actually helps improve the alkylate octane, but it causes a somewhat higher consumption of isobutane than might otherwise be expected.

The propane rejection issue is often the controlling factor in how much propylene feed can be handled in each particular unit. There is a limit to how much propane the fractionation and stripping columns can handle, and that limit is dependent on the specific unit design. One problem that can occur as the amount of propane coming though the unit increases is that the concentration of propane in the main fractionator or isostripper overhead vapor increases, causing a decrease in the condensation temperature, and this temperature reduction can “pinch out” the overhead condenser, thus limiting the available cooling duty of this exchanger.

For Amylenes:

The types of contaminants present in the amylenes are a little different from the propylene and butylene feed. Also, the concentration of contaminants such as sulfur and diolefins is higher. These changes can require adjustment of the operation–or even the design –of the feed pretreatment units. For example, the heavier mercaptans that co-boil with amylenes have a lower solubility in caustic, and they tend to be present in higher concentrations; therefore, a higher caustic circulation rate may be required for the mercaptan extraction unit in the feed pretreatment section.

Amylenes can also undergo a hydrogen transfer reaction in which one molecule of amylene will react with two molecules of isobutane to produce one molecule of isopentane and one molecule of isooctane (C8 alkylate). As with the propylene hydrogen transfer reaction, the amylene hydrogen transfer reaction actually helps improve the alkylate octane; however, it causes a somewhat higher consumption of isobutane. The amount of amylene that undergoes this hydrogen transfer reaction depends on several factors and can be anywhere between 30% and 60%.

The isopentane that results from feeding amylenes (both in the amylene feed itself and that which is produced by the hydrogen transfer reaction) can cause the alkylate to have a somewhat higher Reid Vapor Pressure (RVP). It may be necessary to draw some of the isopentane out with the n-butane product if a relatively low RVP alkylate product is desired.

For Both Propylene and Amylenes:

The octane number –both RON and MON (motor octane number)–of the C7 and C9 alkylate that is produced is about 5 to 10 numbers lower than the RON and MON of C8 alkylate. So, higher concentrations of propylene or amylene in the feed will decrease the alkylate octane if all other variables are held constant. Of course, if the addition of propylene or amylene to the feed results in more total olefin in the feed to the unit, the isobutane-to-olefin ratio may decrease, which will cause lower alkylate octane and higher ASO production.

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