Question 33: How do refiners avoid De-isobutanizer (DIB) column/reboiler fouling in sulfuric acid alkylation? What process conditions on the column do you use to detect this fouling? What process modifications do you take to minimize the impact of this fouling?

Randy Peterson (STRATCO)

Fouling in the DIB column is almost always caused by salt deposits. These salts are typically sodium sulfate and sodium sulfite but can also contain calcium or magnesium if the effluent treating water is not demineralized. If these water-soluble salts are present in the DIB feed, the water will evaporate once inside the column leaving the solids behind. The salt deposits are typically found on or near the feed tray.

The long-term solution is to make changes to the effluent treating system. The quickest operational change is to increase the water makeup rate to the system to dilute the aqueous salt concentration. Monitor conductivity in the water effluent and maintain a level less than 5000 ?mhos/cm (microSiemens/cm) to minimize salt carryover.

Properly designed and functioning water wash static mixers are very important to wash any salts out of the tower feed. A retrofit of coalescing media should be considered in all effluent treating vessels to minimize carryover of the salt-containing aqueous phase. If the unit does not have a water wash downstream of an alkaline water wash, a water wash coalescer with static mixer should be considered.

Improving the water quality with softer water can also help. However, it is important to note that some refiners have experienced foaming problems in their water washes when using water that is too soft. Mixing a little hard water with the demineralized (soft) water typically solves the problem (40-50 ppm total hardness in the makeup water is a good target).

A quick fix to improve DIB operations while running is to perform an online water wash. Although this carries some risks, several refiners have successfully restored column operations. The typical method is to add water to the column feed. In doing so, the salts fouling the feed tray are made soluble. The salts are then carried away from the feed tray and redeposited on nearby trays as the water evaporates. This is not a permanent solution as the salts typically remain in the column until washed properly off-line. It is best to add the water as close to the tower feed nozzle as possible to avoid stagnant pools of water in the feed line which can lead to corrosion in low points.

Reboiler Fouling

Reboiler fouling is almost always caused by ineffective effluent treating. If the reaction intermediate esters (typically propyl or butyl sulfates) are not decomposed within the treating system, they enter the DIB and travel down the tower. When they reach the hot reboiler, they thermally decompose releasing SO2 while the organic component fouls the reboiler tube bundle. An indication that this is happening is low pH and high iron in the DIB overhead accumulator water draw. The evolved SO2 and water forms corrosive sulfurous acid. A good target pH is 6.5 – 7.5 with less than 10 ppm iron.

To avoid reboiler fouling, an increase in the temperature of the effluent treating water wash temperatures (>120 F) may help break the esters down. Typically, new static mixers, designed specifically for immiscible fluids, are required.

Some refiners report success with online water washing of the reboiler. Either water is directly added to the reboiler hydrocarbon inlet or enough water is added to the feed so that water goes down the column to the reboiler. In many cases, the boiling water breaks up the foulant and sends it downstream. If not severely fouled, the reboiler performance is restored. Care should be taken with the resulting wash water as it will have low pH (1-2) and will contain solids. In severe cases, the tube bundle requires pulling and hydroblasting to mechanically remove the foulant.

John Clower (Chevron)

DIB fouling typically starts in the alkylation unit reaction section. As reaction conditions deteriorate with increased feed rates (higher contactor temperatures, lower I:O, higher OSV) the amount of side reactions increase.

One critical side reactant with respect to DIB fouling is neutral esters. Neutral ester removal occurs at the alkaline water wash upstream of the DIB.

Increased rates through the alkaline water wash can result in declining separation of the hydrocarbon and aqueous phases, and underperformance of the heat input in the treatment section – the outlet of the alkaline water wash must be maintained above 120 °F to decompose the neutral esters, as high as 150°F If feeding large amounts of C3 olefins. Left unchecked, these esters will decompose and foul either trays in the DIB or its reboiler.

To avoid DIB fouling where heat input is the limitation, the installation of a trim heater is appropriate. If the outlet temperature is above 120 °F and fouling still exists, a second treatment step can be added as a water coalescer downstream of the alkaline water wash. The coalescer uses fresh water to polish any dissolved solids carried from the alkaline water wash.

The column dP above the feed tray is the most immediate way to detect column fouling. This can identify fouling 6 months before column performance is negatively affected. Overall column dP may not indicate fouling with the upper trays become more loaded, and the lower trays become less loaded as salts plate out on the feed tray.

Increasing column pressure can prolong run length once fouling is detected at the expense of iC4 recovery from the DIB.

Mark Meterna (Sulzer Chemtech USA)

Distillation is essential to the alkylation unit, where efficiently working trays produce a high purity isobutane recycle stream to the reactors with minimum energy consumption. Trace sulphuric acid and acidic by-products from the alkylation reaction may cause corrosion of distillation internals and damage the capability of trays and heat exchangers.

It is easy to detect corrosion and fouling of the distillation internals and to prevent further corrosion by understanding the mechanism by which it occurs. Corrosion of these internals can be further minimized by effectively operating and monitoring the treating section directly before the distillation columns. The refiner should monitor Deisobutanizer reboiler duty, Deisobutanizer overhead accumulator water pH, and separation efficiency (overlap in product distillation). Trends in any of these items may indicate that adjustments are required to the operation of the treating section. The presence of iron in the overhead accumulator water is another indication that metal losses are occurring upstream as a result of corrosion.

The net effluent stream from the reactor section contains corrosive components such as trace free sulfuric acid, alkyl sulfates and di-alkyl sulfates. These alkyl sulfates, or esters, are reaction intermediates produced during the alkylation reaction and if not treated in the treating section will foul and corrode process equipment and distillation internals.

If the trace acid and esters are left untreated before entering the deisobutanizer, they not only cause corrosion, but the alkyl sulphates will produce solid, tar-like material in the bottom of the column and on the reboiler due to the high temperature. During the formation of the tars, SO2 is released and travels up the column to collect in the overhead system. In contact with water in the overhead, SO2 causes corrosion of the overhead system equipment and piping and also of the rectifying section distillation trays. This reduces the fractionation between isobutane and n-butane resulting in poor purity of the isobutane recycle stream to the reactors.

Another form of corrosion in the Deisobutanizer is caused by water carryover if the treating section is finished with a water treating or caustic vessel. If water or caustic is carried into the column, the feed tray can be fouled with salts which will deposit when the water evaporates.

Though there are various treating section configuration and designs, the main principles hold true for all; efficiently mix the treating agent with the net effluent to maximize the contact between the two fluids, and effectively settle the two fluids before the next process step. The net effluent stream from the reactor section contains corrosive components such as trace free sulphuric acid and reaction intermediates (esters, or alkyl sulphates and di-alkyl sulphates). With well-mixed effluent and treating fluid, the trace acid and esters can be neutralized and removed from the hydrocarbon stream. Both mixing and separation can be improved with static mixers such as Sulzer SMV static mixers which develop the optimal droplet size to improve the contact between the two fluids, while minimizing small droplets and creating the chance of an emulsion to form. An emulsion of the hydrocarbon stream and the treating fluid can be challenging to separate. Separator internals, such as Sulzer Mellaplate, can also be installed in the separator vessel to improve separation between the two fluids. Increased separation capability and efficiency reduce the risk of water or caustic carryover to the deisobutanizer and minimize the chance of corrosion and fouling. Sulzer VG AF™ Trays can also be used in the deisobutanizer to reduce the impact of fouling and accumulation on trays. Sulzer VG AF™ Trays are designed with large, fixed valves that allow vapor to still pass through the trays. They are also designed with push valve technology, which reduce accumulation on the tray deck in stagnant regions and use high performance downcomers to help reduce accumulation. Tailored design features make VG AF™ Trays less sensitive to plugging and increase the run time of fouling applications while delivering high capacity and efficiency.

Procedures for online water washes can be developed to wash away the fouling material on the lower trays as well as the tar on the reboiler but monitoring the unit and minimizing the water carryover from the treating section will help reduce the need for column water washes. Monitoring the amount of water in the overhead accumulator, and the pH and iron content of the water are good indicators of how the treating section is performing and will help reduce the amount of corrosion to the distillation equipment.

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