Question 40: Are there instances where mercaptan treatment of refinery gasoline or naphtha streams is necessary? What are the applicable treatment methods?

Praveen Gunaseelan (Vantage Point Consulting)

As mercaptans are sulfur-bearing compounds, they are one among numerous target species for sulfur removal from naphtha or gasoline streams to meet reactor feed or finished product sulfur specifications. Streams that need to be aggressively treated to low sulfur levels, such as naphtha feed to catalytic reformers, or ultra-low-sulfur gasoline product or blend stock, often require hydrotreating, which targets removal of a broad array of contaminants, including mercaptans.

However, there are a number of instances that warrant targeted removal of mercaptans species from refinery naphtha and gasoline streams (generally achieved through mercaptans extraction or sweetening). Some examples are provided below.

For light gasolines with a high proportion of mercaptans sulfur, selective extraction of mercaptans may be a competitive alternative to hydrotreating. For example, light straight run naphtha or FCC light naphtha with a high proportion of mercaptans sulfur may require only caustic extraction to be rendered acceptable as gasoline blendstock. In the case of FCC light naphtha, caustic treating for mercaptans can help avoid octane loss from olefin saturation during hydrotreating.

Light (C1-C6) mercaptans have an objectionable odor and corrosion potential and are prone to accumulate in refinery naphtha and lighter streams. In instances where naphtha is segregated, such as for use as a feedstock for downstream processing, there may be a need to reduce light mercaptans content to render the material transportable, regardless of the total sulfur content. In such instances, caustic sweetening of the naphtha may be appropriate, where the light mercaptans are oxidized to odorless disulfides.

Besides meeting sulfur specifications, gasoline streams may require meeting a mercaptans specification, such as a negative Doctor test. If the mercaptans specification is difficult to achieve through hydrotreating (for instance, due to recombinant mercaptans), mercaptans sweetening of the stream may be required.

Selective hydrotreating of FCC gasoline can result in the formation of recombinant heavy mercaptans due to the reaction of olefinic species with H_2S. Depending on the sulfur level, these mercaptans may either have to be extracted (to meet the minimum sulfur specification) or sweetened to disulfide to render the gasoline acceptable as blendstock. Proprietary reagents are typically required in such instances.

For tank inventories or cargoes of gasoline or naphtha that are off-spec due to high mercaptans levels, mercaptans scavengers are typically used to treat the material to specification in a batch/semi-batch setting. Continuous treatment of liquid streams for scavengers is not typically performed because it is uneconomical compared to dedicated treatment processes.

Michael Windham (UOP)

Gasoline and naphtha streams if routed to gasoline pool should meet the following specs: Total S, mercaptan sulfur, Doctor test, CuStrip and Silver strip corrosion. If total sulfur is not required, Minalk Merox can be used to meet all of these specs. However, if total sulfur reduction is required, an extraction Merox should be used.

Of course, mild hydrotreating can also be used if reduction of sulfur is a must. However, for increased flexibility of the hydrotreating severity, a Minalk should be installed on its product.

Brad Palmer (ConocoPhillips)

Besides the obvious need to meet gasoline sulfur specifications, mercaptans tend to be malodorous and some tend to promote fuel instability by acting to aid initiation of gum formation by peroxidation. To deal with these situations, refiners can employ either mercaptan removal using strong caustic (extraction) or mercaptan oxidation that converts mercaptans in-situ to disulfides (sweetening).

Extraction is viable for the lowest molecular weight mercaptans. As the hydrocarbon chain containing the mercaptan group grows, the less water soluble the mercaptan becomes. Extraction efficiency drops off rapidly after ethyl mercaptan. Only lighter gasoline fractions will contain mainly methyl and ethyl mercaptans, (light cat or coker naphtha, C5-C7 paraffins). Heavier gasoline fractions will contain not only heavier mercaptans, but also other sulfur compounds that will neither be subject to caustic extraction nor sweetening.

Extraction can be done on a "once-through" or regenerative basis. Since extraction is equilibrium limited, once-through treating can become costly as only a small portion of the caustic value can be consumed before a significant breakthrough to the finished product occurs. Regenerative extraction processes such as UOP's Merox™ and Merichem's Thiolex™ allow the lightly loaded caustic to be reused. Distillation regeneration as well as oxidation regeneration is available, with oxidation being the most widely employed. However, distillation regeneration is not likely to be used in gasoline extraction as the extraction of heavier mercaptans will be limited by the residual methyl mercaptan content of the lean caustic from the regeneration.

Oxidative regeneration is accomplished using air and cobalt based oxidation catalyst to convert dissolved sodium mercaptide salts from the extraction into disulfide oils. The disulfide oils are nearly insoluble in the caustic and can be gravity separated from the regenerated caustic stream. Merox™ and Thiolex™ use variations of the contact, oxidation, and disulfide separation stages to accomplish extraction. Both technologies employ naphtha wash of the regenerated caustic to re-absorb trace disulfide oil that may be entrained in the lean caustic from the disulfide separation stage to prevent "re-entry" sulfur.

Sweetening is not an option for low sulfur gasolines as the mercaptan to disulfide conversion is done in-situ, that is, the sulfur content of the gasoline does not change. Sweetening can be used after extraction to aid in product stability and odor control.

Malcolm Sharpe (Merichem Company)

In the low-sulfur (< 10 wppm total S) gasoline world, there are potentially three (3) applications where wet treating can be utilized to remove mercaptans from FCC gasoline. Two of these solutions require that a FCC gasoline splitter be installed and the third removes mercaptans from selectively hydrotreated FCC gasoline.

In the case of splitter-derived FCC gasoline, the mercaptans can either, one, be extracted from the light FCC gasoline fraction using caustic-based FIBER FILM® technology (THIOLEXTM/REGEN®) or, two, be sweetened using caustic/catalyst/air-based FIBER FILM® technology (MERICATTM II) ahead of the gasoline splitter to convert the mercaptans contained in the light gasoline fraction into the heavier disulfide oil (DSO) molecule. This DSO leaves with the heavy FCC gasoline destined for the hydrotreater. The suitability of these applications is refinery-specific and is especially dependent on the light FCC gasoline cut-point and gasoline pool blending tolerances with respect to sulfur. The mercaptan extraction method (THIOLEXTM/REGEN®) can also be used to treat light straight-run naphtha subject to the same refinery-specific operating criteria.

Third, in some cases refiners may encounter recombinant mercaptan sulfur in selectively hydrotreated FCC gasoline. The presence of high levels of hydrogen sulfide and olefins at the outlet conditions of the selective reactor can lead to the formation of heavy molecular weight recombinant mercaptan compounds. Rather than increasing hydrotreater severity, at the expense of octane loss and hydrogen consumption, to battle this increase in product sulfur, it can be optimized using EXOMERTM technology which is designed to extract the recombinant mercaptans as they form. In this way operating expense and octane reduction are minimized while reaching target gasoline sulfur specifications.

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