Question 41: What is your best method for detecting nitrogen levels in reformer feeds? How effective is naphtha hydrotreating in reducing nitrogen levels?

Praveen Gunaseelan (Vantage Point Consulting)

Nitrogen in naphtha feedstock can be detected using analyzers based on pyro chemiluminescence or electrochemical measurement. Pyro chemiluminescence-based analyzers appear to be more prevalent in the industry and can detect nitrogen levels over a wide range (from ppb levels to several hundred ppm) in a matter of minutes. ASTM D4629 is a standard test method for trace nitrogen detection in liquids based on pyro chemiluminescence.

As refiners increasingly process heavy crudes using cokers, the nitrogen content in naphtha feed to reformers will tend to increase. While conventional naphtha hydrotreaters can theoretically be operated at higher severity to increase nitrogen removal, there are practical limits on such operation due to potential undesirable outcomes, such as higher sulfur levels in the reformer feed due to recombination. Accordingly, preventing high nitrogen levels in reformer feeds may require specialized approaches such as using high-activity denitrification catalyst in a reactor section or a separate reactor. In extreme cases where nitrogen content is excessive and cannot be adequately removed, it may be required to limit the volume of coker naphtha processed in the reformer.

Ujjal Roy (Indian Oil Corporation)

In our refineries, ASTM D4629 is being mostly used for nitrogen detection. This method can detect 0.3 to 100 ppmw of total nitrogen with good reproducibility. Also, in some units, we are using licensors' recommended test methods using their recommended apparatus for testing basic nitrogen.

Some naphtha hydrotreaters, having cracked material in feedstock, are designed to produce < 0.5 ppm nitrogen for feeding to reformers. Higher nitrogen level cannot be tolerated to avoid catalyst deactivation and downstream equipment fouling. These units are operated at about 50 kg/cm2 pressure using Ni-Mo catalyst. We are effectively able to control nitrogen within 0.5 ppmw in reformer feed.

Brad Palmer (ConocoPhillips)

The state-of-the-art in total nitrogen detection for naphtha and distillate streams is oxidative combustion with chemiluminescence detection. The standard test method for this technique is ASTM D4629-10. Direct injection of the sample into a vertically oriented combustion furnace will provide the best sensitivity. The reported quantitation limit for this technique is 300ppb.

Naphtha hydrotreaters are very effective at removing nitrogen IF:

1. Loaded with NiMo catalyst,

2. Catalyst replaced before denitrification reactions have stopped due to Si poisoning,

3. A proper water wash system is employed for salt removal upstream of the stripper,

4. Robust NH3 removal occurs in a reboiled stripper,

5. Nitrogen analyses on feed and product is done frequently with a low detection level

Erik Myers (Valero)

In general, Reforming units prefer low levels of nitrogen in the feed. The problem with nitrogen in the reforming feed is the deposition of salt in the cold sections of the reforming unit. Typical locations for salt deposit are cold areas of the recycle gas circuit and the top of the stabilizer system. Most naphtha hydrotreaters operate in a 300 to 700 psig range of design pressures. This means that sulfur removal is essentially 100% while nitrogen removal from the feed is seldom greater than 80%. Therefore, there is always nitrogen in the feed to the Reforming unit. Since the Reforming unit has abundant chloride present the rate of salt deposits is entirely dependent on nitrogen slip through the NHT unit.

At 0.5 ppm nitrogen in the feed each 10 mbpd will produce almost a ton per year of ammonium chloride. The ratio of chloride to nitrogen is 2.5 lbs of chloride to 1 lb. of nitrogen.

One best practice that Valero implements is to water wash the reformer recycle compressor when the unit is down to remove the salts that form during normal operation. This prevents imbalance from the sloughing off of salts that may take place during thermal cycles of the unit.

Soni O. Oyekan, PhD (Marathon Petroleum Company)

According to an analytical chemist, nitrogen determination in naphtha can be conducted via the use of an analytical procedure that incorporates an Antek Model 9000. The equipment is interfaced with an auto sampler and computer system containing an Antek 393 software. Nitrogen concentrations as low as 0.1 wppm and as high as hundreds wppm can be measured. Samples containing high nitrogen are diluted with isooctane before nitrogen determinations are made. Samples of isooctane blanks are also used as reference for zero nitrogen.

For the second part of the question, a key requirement is that the refiner has a good analytical procedure for determining nitrogen in hydrotreated naphtha and the response to the first part of this question addressed that challenge. Having established a reliable database and current hydrotreated product sulfur, nitrogen and other data, it is then possible to determine the effectiveness of a naphtha hydrotreater for nitrogen removal or reduction.

It is known that while 99.9 % hydrodesulfurization of organosulfur compounds can be achieved in naphtha hydrotreaters, hydrodenitrogenation (HDN) of organo nitrogen compounds is limited to the range of 75 % to 90 % conversion to ammonia. Therefore, the residual concentration of nitrogen compounds in hydrotreated naphtha is relatable to feed nitrogen and other factors.

The effectiveness of naphtha hydrotreating (NHT) for reducing nitrogen is highly dependent on the type of catalyst used, hydrodenitrogenation (HDN) activity of the catalyst, process conditions, concentration of metal contaminants in the feed, composition of the naphtha mix and the percentage of cracked naphtha in the naphtha mix and especially the percentage of coker naphtha in the NHT feed mix. Achievable HDN is also dependent on the degree of upgrading of naphtha from unconventional oils in the feed mix to the NHT. In addition, naphtha processing schemes are also important for the effective removal of nitrogen for straight run naphtha and especially for naphtha mixes containing other contaminants such as metals, olefins and dioolefins.

For modest concentrations of nitrogen of <2 wppm in the feed to the NHT and negligible concentrations of metal contaminants such as arsenic and silicon, the processing of the naphtha leads to hydrotreated naphtha with nitrogen in the range of 0.1 wppm to 0.5 wppm. For NHT naphtha feed containing high percentages of cracked naphtha (such as coker naphtha) and high concentrations of contaminants such as olefins, diolefins, arsenic and silicon, HDN could be limited if the concentration of organo nitrogen compounds are higher than 2 wppm with respect to meeting target nitrogen in the hydrotreated naphtha for the refiner.

The following factors are relevant for effective reduction of nitrogen in hydrotreated naphtha

1. Catalyst

For optimizing HDN, NiMo catalysts are usually preferred relative to CoMo catalysts Single reactors, moderate pressures, high quality treat gas and rates, reactor temperatures in the range of 500 to 615 F are used and the high temperature is usually limited by mercaptan reversion reactions. As the organo nitrogen compounds increase as well as other contaminants such arsenic and silicon, stacked catalysts are used in reactors to incorporate demetalization catalysts or metals scavengers to manage metal contaminants that can negatively impact HDN relative to HDS. In order to optimize organo nitrogen reductions, refiners should work closely with technology providers who offer a variety of catalysts and adsorbents for enhancing the effectiveness of the naphtha hydrotreating process for HDS and HDN.

2. Naphtha Processing Schemes

As the concentrations of nitrogen and other contaminants increase in mix naphtha feeds, refiners processing schemes include medium and high pressure stacked reactors, and multi stages of reactors (two and three reactors) to manage unsaturated compounds and metal contaminants in order to enhance HDN of the naphtha. Several catalysts are then used for effective reduction of organo nitrogen and other contaminants metals, sulfur, olefins and diolefins. As indicated, your technology provider companies will be pleased to support your efforts and plans.

3. NHT Stripper

As part of the reference database, the NHT stripper operations should be checked and determined to be operating as designed. Upsets in the NHT Stripper would also falsely suggest ineffective naphtha hydrotreating and high nitrogen (NH3) in the hydrotreated naphtha and in those cases high sulfur (H2S) and possibly water would also be carried into the catalytic reformer.

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