Question 95: What NOx reduction additives have been successfully used to rapidly decrease NOx during operational excursions or hardware failure? What alternatives to additives and hardware exist for NOx reduction? Is there a synergy for combining NOx reduction control methods that may reduce operating or project costs?

Ray Fletcher (Intercat)

Intercat has developed a line of highly successful NOx abatement additive for use in the FCC unit. These additives tend to be most effective when added on a steady state basis. These include a platinum free combustion promoter and an additive designed to reduce NOx emissions for those refineries not using platinum promoters. The NOx reducing additive is typically added at 2-3 wt% and requires base loading. Both additives will provide benefit to the refiner needing to reduce NOx emissions.

The two most common causes for NOx step changes include maldistribution within the regenerator generally caused by mechanical damage to an air grid or spent catalyst distributor and a large increase in excess oxygen. Several techniques exist for identification of maldistribution within the regenerator. The simplest technique includes plotting SOx emissions versus delta cyclone set outlet temperatures (i.e., cyclone set #1 minus cyclone set #2, etc.). Side-by-side analysis of the NOx versus delta temperature plots will indicate whether there has been a step change in temperature profile indicating maldistribution. A second technique is to use a Reaction Mix Sampling device with a portable gas analyzer. This technique involves identifying fittings that can be accessed on the regenerator, inserting the probe into the regenerator, and measuring oxygen, CO, and CO_2 levels. A third method is to use multivariable linear regression to identify independent variables impacting not emissions. One refinery observed an increase in particular emissions and maldistribution when increasing their supplemental air blower rate by 20%. A second refiner observed a substantial increase in maldistribution when increasing the rate of one of three air blowers.

An additional solution to step change increases in NOx emissions is to analyze the FCC feed slate. Multivariable linear regression is often required for refineries charging multiple feeds to the refinery. Identification to a specific feedstock may lead to a rapid solution to NOx emissions.

Refiners faced with a step change increase in NOx emissions should

1) reduce flue gas excess oxygen to the lowest stable level possible,

2) avoid adding platinum-based combustion promoters,

3) for those units which are over promoted inserter adding antimony as a way to deactivate the platinum currently in the circulating inventory,

4) determine the root cause for maldistribution, and where possible, make operating adjustments to

minimize this maldistribution and

5) identify any feedstocks contribute to NOx emissions.

Finally, Intercat is developing catalytic technology for post-regenerator removal of NOx emissions with highly promising results observed to date. Unfortunately, it is premature to describe this technology until additional commercial trials have been completed.

Matthew Meyers (Western Refining)

The most effective alternative other than additives and hardware is a systematic approach to stabilize the regenerator burn. Once this is accomplished, excess oxygen can be controlled to limit NOx formation. Stabilizing the regenerator burn can be complicated and involves a number of steps:

•Determine the precise regenerator level maximum (before catalyst is dropped) and minimum (the level at which the catalyst drop is stopped). The addition of a dense bed density transmitter can be useful in this regard. The spent catalyst should be entering at least 1-2 ft above the dense bed at all times.

•Spent catalyst stripper operation can be tested by changing steam rates. A single coked nozzle on a steam distributor can allow entrained hydrocarbon into the regenerator causing severe temperature maldistribution.

•A pressure survey can help find additional opportunities such as the air grid, standpipe fluidization problems, nozzle plugging or partial stripper blockage.

•Conduct multivariable linear regression to determine other opportunities. This technique has been used with success.

•The use of non-platinum combustion promoter is a very effective means of stabilizing and minimizing afterburn.

Once the regenerator burn is stable, a DMC model can be developed with an excess O_2 control variable, assuming the O_2 analyzer is well maintained. The controller should manipulate the main air blower (enriched O_2 if applicable) to minimize excess O_2 but not allow the excess O_2 to drop below the operator minimum set point. Regenerator velocity can become a limit as feed rate or coke burn is maximized but can be mitigated somewhat with the use of non-platinum CO promoter. In the case of enriched O_2, DMC may preferentially increase enriched O_2 versus air to limit the high velocity. By controlling excess O_2 between 0.7% and 1.1% excess O_2, the NOx should drop substantially.

Eric Griesinger (Grace Davison Refining Technologies)

NOx reduction additives generally fall under two categories: standalone NOx reduction additives, and low NOx combustion promoters.

Standalone NOx reduction additives are catalytic based NOx control technologies that provide NOx reduction, without providing combustion promotional activity. Generally, this NOx control technology has provided slow response to mitigating elevated NOx concentrations. Grace Davison has developed a catalytic NOx reduction additive, GDNOX™ 1, which shows prospect of providing a quicker ability to curb NOx emissions. Additionally, GDNOX™ 1 has not been vulnerable to material surcharges. GDNOX™ 1 applications should be reviewed local Grace Davison sales and technical service representative for additional insight specific to the application.

Current generation of low NOx combustion promoters are typically formulated with a noble metal other than platinum. Historically, the use of platinum has been demonstrated to exhibit a correlation with elevated, and prolonged, NOx concentrations in regenerator flue stack gases. Applications of Grace Davison's current generation low NOx combustion promoter, CP® P, when dosed in higher-than-normal rates, whether intentionally to correct other FCCU conditions or unintentionally, has shown a shortened duration of elevated NOx emissions is likely. This observation of shortened NOx emission excursion interval can provide refiner's benefit when striving to satisfy rolling day average, or other time-based NOx emission limit constraints.

Operational variables that often have an effect on NOx emission have been found to include excess O2, regenerator hydrodynamics, platinum formulated combustion promoter, antimony-based nickel passivators, and feed nitrogen. Generally, a decrease in excess O2 will directionally lead to lower NOx emissions. While regenerator hydrodynamics are complex, a change in dense bed level, and/or temperatures, may provide conditions favorable to reduced NOx emissions. Use of platinum formulated combustion promoters and/or antimony has also been widely observed to correlate with increased NOx emissions. Oddly enough, while feed nitrogen has been found to be the contributing source to NOx emissions, typically these other variables have a stronger influence over the actual NOx emissions.

Tags

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