JM

FCC NO_x reduction methods: Complying with regulations without capital investment

P. Hobbins - Placid Refining Co.
H. Blair, T. Hochheiser - Johnson Matthey

Reprinted from Hydrocarbon Processing January 2021

Johnson Matthey
Inspiring science, enhancing life

As fluid catalytic cracking (FCC) nitrogen oxides (NOx) emissions regulations become increasingly strict, refiners are driven to find the most economic compliance option. Multiple capital and non-capital project options are available to mitigate NOx emissions. Selective catalytic reduction, selective non-catalytic reduction, a proprietary NOx removal technology^a and regenerator hardware modifications are discussed in this article for capital project opportunities. A carbon monoxide (CO) promoter, optimization of oxygen (O_2) and CO, feed nitrogen reduction, flue gas ammonia injection and NOx additives are also covered for non-capital project options. These solutions are discussed, including their NOx reduction potential, and how they can be integrated into existing regenerator or flue gas systems.

The successful NOx reduction strategy at Placid Refining Co. is also described. This strategy includes the utilization of an additive for NOx reduction, combined with a non-platinum CO promoter. In addition, process variables are optimized to reliably control both NOx and CO emissions.

FCC NOx emissions regulations have been gradually tightening. In many countries, NOx emissions regulations have existed for decades, while others are just beginning to implement NOx limits. The range of NOx limits is substantial. For example, new FCC units (FCCUs) in India are limited to 260 parts per million (ppm), while many FCCUs in the U.S. have limits in the range of 25 ppm – 75 ppm. Based on proposed legislation, Southern California anticipates NOx regulations reaching as low as 2 ppm. A possibility exists for regulations on hydrogen time within the next several years.

With more stringent emissions limits, refiners must determine how to comply in the most efficient way possible. The following work examines several methods of NOx control that utilize both capital investment and non-capital strategies. FCC

NOx chemistry is also discussed, along with a case study from Placid Refining Co.'s refinery in Port Allen, Louisiana. NOx chemistry. In most FCCUs, 5 wt%–9 wt% of the feed is converted to coke. Coke comprises carbon, hydrogen and contaminants, including nitrogen. Typically, 40%–50% of trogen in coke reacts to form reduced nitrogen species [HCN and ammonia (NH_3)], some of which is oxidized to N_2 and NOx (FIG. 1). The amount of nitrogen that is converted to NOx is highly dependent on regenerator operation.

Many variables impact the formation of NOx in the regenerator. The type of feedstock will influence the amount of NOx formed. Processing heavier feeds (e.g., coker gasoil, residue or deasphalted oil) can increase regenerator NOx formation. Alternatively, hydrotreating FCCU feed reduces the amount of feed nitrogen, leading to lower NOx in the regenerator. Regenerator operating conditions impact NOx formation, as well. In full-burn regenerators, higher excess oxygen leads to increased NOx formation. Operators can minimize oxygen to minimize NOx formation; however, low amounts of O_2 will increase CO emissions. Therefore, a balance must be achieved.

In partial-burn regenerators, there are three contributors to CO boiler NOx emissions: NOx formed in the regenerator, NOx formed in the CO boiler from regenerator flue gases HCN and NH_3, and NOx formed in the CO boiler from air N_2. In the regenerator, HCN and NH_3 oxidize to form N_2 and NOx species, but this reaction is limited by oxygen availability. Consequently, reduced nitrogen species are present in the regenerator flue gas. In the CO boiler, these reduced nitrogen species are readily converted to NOx. The third source of NOx is from thermal oxidation of N_2 in the CO boiler burners. Thermal NOx can be minimized with lower flame temperatures and by optimizing air, fuel gas and flue gas mixing.

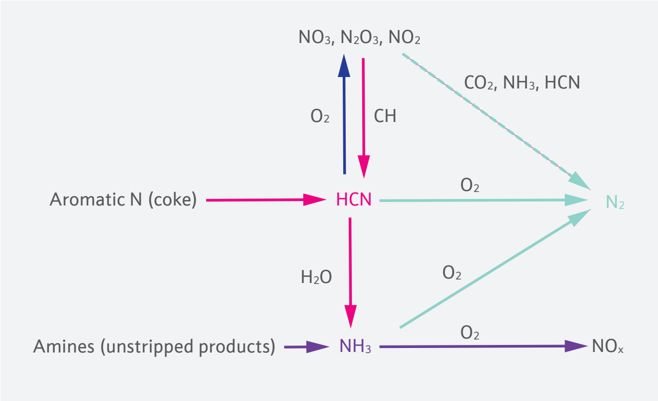

Figure 1: Regenerator nitrogen reaction pathways.

Regenerator design also has a major bearing on NOx formation. Well-mixed or counter-current regenerators help limit NOx formation due to consistent catalyst and air mixing. This avoids pockets with high or low oxygen content. Additional factors that impact NOx formation are the use of CO promoters and the use of antimony (Sb). Most U.S. refiners have switched from platinum-based promoters to palladium-based, but platinum is still widely used across the rest of the world.

Platinum catalyzes the formation of NOx and will continue to contribute to NOx while present in equilibrium catalysts (Ecat). Palladium promoters also generate NOx but to a lower extent than platinum. In addition, the NOx-generating half-life of palladium is lower than platinum.

Sb is often used for nickel (Ni) passivation, but this can also increase NOx.

NOx reduction options. Multiple strategies are available to decrease FCCU NOx emissions. These strategies can be divided into two main categories: capital investment projects and non-capital solutions. Most solutions involve some level of ongoing operating expense.

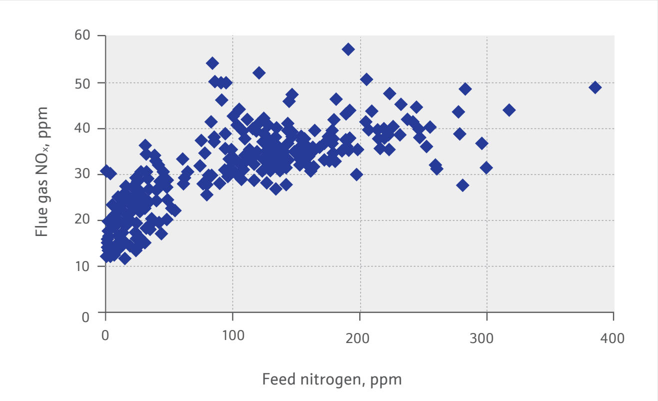

Figure 2: Impact of feed nitrogen on flue gas NOx.

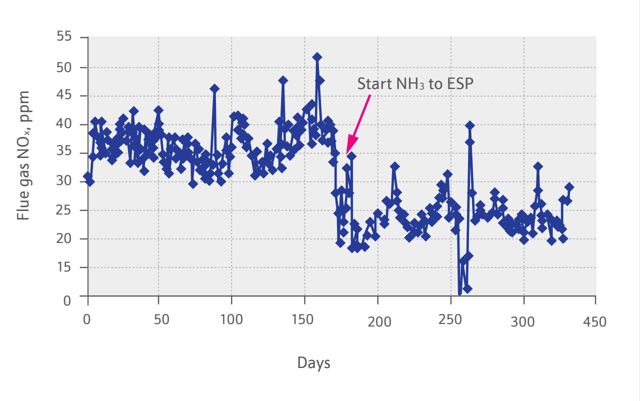

Figure 3: NOx reduction from ESP NH_3 injection.

Capital project options

The following are capital project options to reduce FCCU NOx emissions.

Regenerator hardware

Upgraded regenerator air grids, advanced spent catalyst distribution systems and well-mixed regenerator designs are becoming more common to reduce NOx emissions and optimize regenerator performance. The hardware improvements not only improve NOx control, but also provide other benefits, such as lower CO, lower afterburn and lower regenerated catalyst coke levels. Multiple licensors offer enhanced regenerator designs. These designs can be implemented either through revamps or through the installation of new regenerators. The various designs have different levels of achievable NOx reduction.

Selective catalytic reduction (SCR)

SCR is a process that involves the injection of NH_3 into the FCCU flue gas followed by reaction across a catalyst bed. The reaction occurs between 287°C–399°C (550°F–750°F) and produces N_2 and water vapor. The main reaction (1) as the majoirty of FCC NOx is NOx. The cost of the system is primarily driven by the SCR reactor, which must be incorporated in the flue gas system. In some FCCUs, feed-forward control is utilized. Flue gas NOx is measured upstream of the SCR unit and is used to control the NH_3 injection rate slightly above the molar equivalent ratio. Feedback control measures NOx downstream of the SCR and adjusts NH_3 injection accordingly. The process has operating costs for NH_3 and catalyst changeouts and can achieve up to 95% NOx reduction. The reduction chemistry is detailed below:

$$4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6\ H_2O \qquad (1)$$

$$2\ NO_2 + 4\ NH_3 + O_2 \longrightarrow 3\ N_2 + 6\ H_2O \qquad (2)$$

$$NO + NO_2 + 2\ NH_3 \longrightarrow 2\ N_2 + 3\ H_2O \qquad (3)$$

Selective non-catalytic reduction (SNCR).

SNCR is like SCR in that it uses NH_3 to react with NOx to form N_2 and water. The process is completed at a higher temperature than SCR, allowing it to be accomplished without a catalyst. The temperature must be maintained between 926°C–1,093°C (1,700°F– 2,000°F) for the reaction to take place; therefore, the SNCR system is incorporated with the CO boiler. Urea may be used instead of NH_3 due to the higher temperature of SNCR. The process includes an injection system with air, which is designed to produce effective mixing. Precautions include NH_3 slip at high injection and NOx breakthrough at low injection. SNCR can remove up to 50% NOx and is generally a lower capital investment than other NOx projects.

Proprietary NOx emissions reduction technology[a]

This proprietary process is a system that combines an ozone generator with a wet gas scrubber to remove NOx. The ozone generator converts supplied oxygen to ozone. The ozone selectively oxidizes insoluble NOx into soluble nitrogen species that can be removed in the wet gas scrubber. The process can remove up to 95% NOx , with low flue gas pressure drop. The associated operating costs include oxygen, power supply and caustic.

These four different capital project options"which can achieve different levels of NOx removal"have both benefits and precautions. The choice depends significantly on the existing flue gas system and how the different solutions could be integrated into the existing system. Non-capital investment options.

The following are noncapital investment project options to reduce FCCU NOx emissions:

CO promoter optimization.

All CO promoters contribute to NOx formation. To reduce NOx, the CO promoter addition rate should be minimized and, if feasible, stopped. If a CO promoter is required, utilizing a non-platinum rather than a CO promoter is a common first step to lower NOx. Non-platinum CO promoters typically utilize palladium to catalyze CO oxidation, although other metals can be used.

O_2/CO optimization.

The most prominent operating variable to control NOx is excess oxygen in a full-burn regenerator. Lower excess oxygen contributes to lower flue gas NOx. In partial-burn operations, NOx emissions are measured at the CO boiler outlet. Lower flue gas CO results in lower CO boiler NOx. NOx increases in deep partial burns because the amount of HCN and NH_3 in the regenerator flue gas increases. These reduced nitrogen species are converted to NOx in the CO boiler. Usually, the lowest NOx formation can be achieved when operating at the crossover point between full burn and partial burn.

Feed nitrogen reduction.

Minor changes in feed nitrogen do not typically have a noticeable impact on NOx formation. However, major changes in feed nitrogen have shown an impact on NOx. FIG. 2 is from an FCCU that was able to decrease its feed nitrogen by an order of magnitude by adjusting gasoil hydrotreater severity. This action allowed the operator to significantly reduce NOx formation. Another method that could significantly decrease feed nitrogen is by changing the feed source, such as removing residue or coker gasoil from the FCCU feed stream or changing the crude slate.

Flue gas NH_3 injection.

Some refiners have successfully reduced NOx through NH_3 injection into the flue gas system. This is done at a low temperature and without a NOx reduction catalyst system. The injection point is often upstream of the electrostatic precipitator (ESP), as NH_3 also improves ESP performance. FIG. 3 shows an FCCU that began injecting NH_3 upstream of the ESP and was able to achieve a 35% reduction in flue gas NOx emissions.

NOx reduction additive.

NOx reduction additives can be used to reduce both regenerator flue gas NOx and HCN. These additives are injected into the regenerator through an additive addition system. The additives are designed to catalyze the oxidation of HCN to N_2 (FIG. 4). The additives are used at 1 wt% – 2 wt% concentration in Ecat and can reduce NOx by up to 40%. Refiners can also use NOx reduction additives in combination with other technologies to optimize operating costs.

Case study from the Placid Refining Co. refinery. The Placid Refining Co. refinery was able to effectively manage its flue gas NOx emissions by using a strategic FCC additive regimen and process variable optimization. NOx emissions were first decreased by changing the combustion promoter from a platinum-based promoter to a palladium-based one. Emissions were further reduced with an NOx reduction additive specifically designed to catalyze the conversion of HCN and NH_3 to N_2.

Placid Refining operates a 25,000-bpd FCCU. The facility's crude slate is typically composed of Light Louisiana Sweet and Gulf Coast Sour crudes. The refinery's FCCU feed comprises 70%–80% gasoil and 20%–30% deasphalted oil. The feed basic nitrogen averages 440 ppm, with a typical API gravity of 20.9.

In 2010, Placid Refining began initial steps in overall NOx control by changing from a platinum-based CO promoter to a proprietary non-platinum promoterc. Removing the platinum promoter from the FCCU typically results in a 60%–70% reduction in NOx emissions.

In 2015, Placid Refining started analyzing the benefits of a capital project vs. a non-capital project solution to further reduce NOx emissions. This was in preparation for a new environmental regulation limiting NOx to a 45- pm rolling average limit. The proprietary non-platinum additive was trialed to determine if capital investment could be avoided.

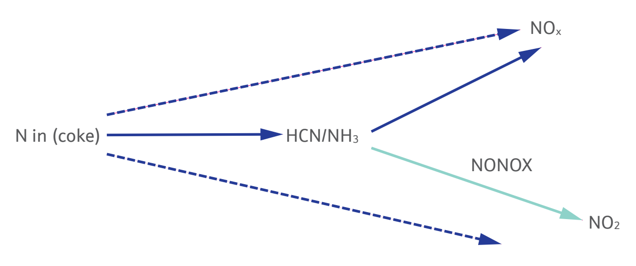

Figure 4: NOx reduction additive^b mechanism.

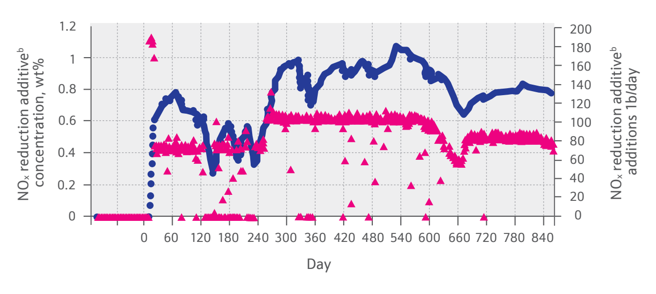

Figure 5: Proprietary non-platinum additive^c addition rate and concentration.

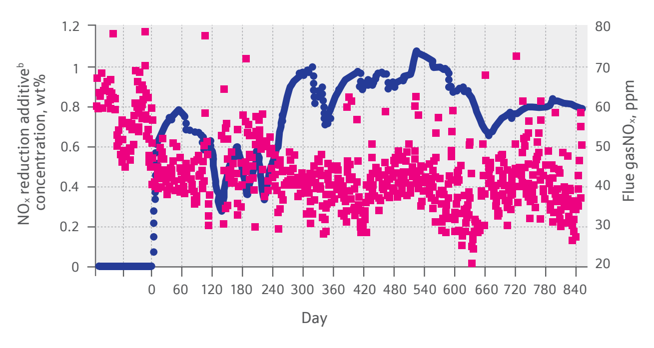

Figure 6: Proprietary NOx reduction additive^c reduced NOx emissions.

Placid Refining conducted a two-phase trial: 1 wt% concentration followed by 2 wt%. During each phase of the trial, noticeable reductions were observed in the level of NOx emissions. The trial was successful and proved that Placid Refining would be able to meet its emissions regulations without capital investment. The proprietary non-platinum additive was stopped after the trial and reintroduced once the NOx regulation went into effect. The following data is from when the proprietary NOx reduction additive was reintroduced to the FCCU.

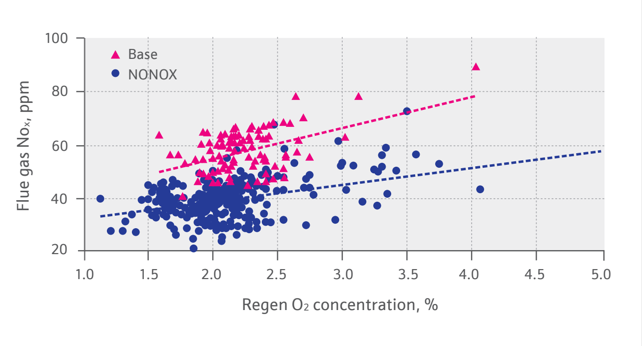

Figure 7: The proprietary NOx reduction additive reduced NOx emissions by 32%.

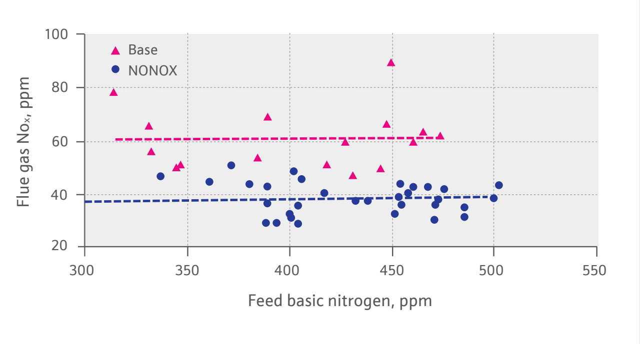

Figure 8: Feed nitrogen did not have an impact on NOx.

Placid Refining started with a 10-d baseload and has maintained an average of 0.8 wt% concentration since reintroduction. As the proprietary NOx reduction additive concentration increased, a reduction in NOx emissions was achieved (FIGS. 5 and 6).

Placid Refining optimizes process variables to ensure that the refinery is minimizing NOx while optimizing FCCU operation. Sb is used for Ni passivation, and Placid Refining closely monitor the Sb injection rate and Ecat Sb/Ni to ensure that the unit was not producing excess NOx . Steps have also been taken to minimize excess oxygen to a CO limit. A base period prior to the proprietary NOx reduction additive's use was compared against operation with the additive included. The proprietary NOx reduction additive use showed a clear reduction in NOx emissions at similar excess oxygen levels (FIG. 7). Placid Refining was able to achieve and maintain an NOx reduction of 32% relative to base emissions.

For additional insight, NOx emissions"as a function of feed nitrogen"were also analyzed. Placid Refining's feed nitrogen does not have an observable impact on NOx emissions. However, the reduction between the base data and the proprietary NOx reduction additive time period is transparent (FIG. 8).

Takeaway. Many different FCCU NOx reduction strategies can be employed to successfully meet emissions limits. The different strategies have varying levels of NOx reduction and can be integrated into different flue gas system designs. Some of the options require capital investment and affiliated operating expenses, while others can be successfully implemented without upfront investment.

Placid Refining was able to effectively use a NOx reduction additive to reduce FCCU NOx emissions by 32%. This enabled emissions limit compliance without having to invest in a sizeable project. The refiner continuously optimizes its regenerator excess oxygen level to operate in balance with CO limits. In addition, Sb is used to successfully passivate Ni without creating excess NOx.

Notes

a Linde's LoTOx process

b Johnson Matthey's NONOX additive

c Johnson Matthey's COP-NP non-platinum CO promoter

Patrick Hobbins

Patrick Hobbins is a Process Engineer for Placid Refining in Port Allen, Louisiana. He is responsible for technical support for the FCCU and alkylation unit, as well as gasoline blending. He has previously worked in all units of the refinery, including Crude/Vacuum, DHT, Reformer, CGHT, Treaters, SRUs and has provided engineering support for major revamps of the DHT and treater units. Mr. Hobbins earned a BS degree in chemical engineering from Louisiana State University and has 15 yr of experience in the refining and petrochemical industry.

Heather Blair

Heather Blair is an FCC Technical Engineer for Johnson Matthey. She is responsible for analysis, recommendations and customer interface in the FCC additives business. She started her career with HollyFrontier in Cheyenne, Wyoming, as a Product Blending Engineer. She held positions as a Process Engineer on the FCC and Alky, Crude Unit, Hydroprocessing Area and Process Safety. She has 10 yr of experience in the refining industry. Ms. Blair earned BS and MS degrees in chemical engineering from the University of Wyoming.

Todd Hochheiser

Todd Hochheiser is Manager of FCC Technical Service for Johnson Matthey. He is responsible for the engineering team that provides technical assistance on the use of additives and catalyst addition systems. Mr. Hochheiser earned his Bch degree in chemical engineering from the University of Delaware and an MBA from the University of California Irvine. Prior to joining Johnson Matthey, he held engineering, operations, and planning and economics positions with Valero Energy and ExxonMobil.

References

1. Sadeghbeigi, R. (2012). Fluid catalytic cracking handbook (3rd ed.) Waltham, MA: Elsevier Inc.
2. Jensen-Hom, H., Lindenhoff, P. (2010) Combating NOx from refinery sources using SCR, 2nd Annual World Refining Technology Summit and Exhibition, Abu Dhabi. Haldor Topsoe.
3. Kraus, K., Kwon, M. (2011) Controlling CO Boilers. Digital Refining article 1000742.
4. Hovey, K., Fisher, K. (2018) SOx and NOx emission abatement in the FCC. PTQ Q1 2018, Digital Refining Article 1001464.
5. Sorrels, J. (2019) Selective non-catalytic reduction. EPA Form 2220-1 (Rev 4-77).
6. Linde, LOTOX Leading the market for abatement efficiency, flexibility and cost competitiveness. Linde 2020. https://www.linde-gas.com/en/processes/emissions_solutions/lotox/index.html
7. Radcliffe, C. (2008) Reducing FCC Unit NOx emissions. Digital Refining article 1000303.
8. Ministry of Environment and Forests Notification (March 18, 2008) Part II, Section 3(i), New Delhi.
9. SCAQMD Proposed Rule 1109.1 NOx Working Group Meetings

Planting trees to catch carbon • Planting trees to catch carbon
XXXXXX
Printed on Carbon Captured paper

This document is printed on Essential silk paper, which contains material sourced from responsibly managed forests and is Elementary Chlorine Free (ECF). We are helping The Woodland Trust and The Woodland Carbon scheme, which aims to improve the landscape of Britain by planting more trees and protecting our national heritage of precious ancient woodland.

Designed and produced by www.houseoftype.co.uk

For further information on Johnson Matthey, please contact your local sales representative or visit our website. KATALCO is a trademark Johnson Matthey group of companies.

Billingham, UK
Tel +44 (0) 1642 553601
www.matthey.com

JM Johnson Matthey
Inspiring science, enhancing life