Taking steps to reduce FCC NO\textsubscript{x} emissions
Taking steps to reduce FCC NO\textsubscript{X} emissions

Miray Genç, Aytaç Gül, Eda Bayraktar Dalgıcı, and Şeyma Avcılar, Tüpraş, along with Tom Ventham, Johnson Matthey
Temperatures in the fluid catalytic cracking (FCC) regenerator are insufficiently high to produce thermal NO\(_x\) from nitrogen in combustion air. However, in units with CO boilers that are typically found on partial burn FCC units (FCCUs), the introduction of direct firing will result in thermal nitrous oxides (NO\(_x\)) being produced downstream of the FCC regenerator. This is particularly true in cases where the CO boiler has not been fitted with low-NO\(_x\) burners.

Feed nitrogen that has been converted to coke in the reaction section can leave the process as NO\(_x\) in the flue gases when said coke is combusted in the regenerator. Approximately 40% of feed nitrogen will partition into coke. Nitrogen in coke will not automatically fully convert to NO\(_x\). Many different reaction paths exist. 75% of nitrogen in coke is converted to inert nitrogen (N\(_2\)), which leaves as a harmless inert. The remaining 25% will be converted to NO\(_x\) (NO, NO\(_2\), N\(_2\)O) or a reduced nitrogen species, such as hydrogen cyanide (HCN) or ammonia (NH\(_3\)). Reduced species will tend to form when available free oxygen is sparse; this is strongly the case in partial burn FCC regenerators and some full burn regenerators where radial mixing between spent catalyst and air is non-uniform. Reduced nitrogen species are readily converted to NO\(_x\) when they come into contact with oxygen, either in more oxygen-rich sections of the catalyst bed or vapour space, plenum, flue gas ducting or in the presence of excess air injected into the CO boiler.

Oxygen is a key factor in determining if nitrogen in coke forms N\(_2\) or NO\(_x\) in the FCC regenerator. A surfeit of oxygen will push the reaction further in the direction of NO\(_x\) rather than N\(_2\) in the oxygen rich environment of the downstream CO boiler. Similarly, a lack of oxygen will increase the formation of reduced nitrogen species, which terminates as NO\(_x\) rather than N\(_2\). The theoretical ‘sweet spot’ of oxygen would be the point between full burn and partial burn, i.e. close to zero excess O\(_2\) and ppm levels of CO in the flue gas. Although it is not a feasible regime to operate an FCC regenerator in a stable manner, combustor-type units and counter-current regenerators aim to be close to this sweet spot in key areas of the regenerator. Hence, these units tend to have lower levels of NO\(_x\) emissions from the outset. There may be separate drawbacks to this type of regenerator design in terms of other environmental emissions, but this discussion is not in the scope of this article.

In partial burn units, a higher CO/CO\(_2\) ratio implies more reductive atmosphere, which pushes nitrogen in coke through pathways leading to reduced N-species, such as HCN and NH\(_3\). These reduced species become fully oxidised to NO\(_x\) with surplus oxygen in the CO boiler.
Platinum (Pt) complexes that are present in CO promoters and antimony are strong catalysts in the generation of NOx from nitrogen in coke. Although it is plausible that the presence of CO can act to reduce NOx to N2 (2CO + 2NO → 2CO2 + N2), this may be very localised and heavily outweighed by the aforementioned significant generators of NOx.

CO promoters are used in FCCUs, more commonly in full burn than partial burn operations, to reduce afterburn. ‘Afterburn’ is defined as the positive temperature delta between the dilute phase of the regenerator and dense bed phase. This difference forms as a result of excess CO slipping from the dense bed, meeting an excess of O2 in the upper regenerator and fully oxidising through to CO2. The CO oxidation reaction is highly exothermic and the low density or heat capacity of the vapour space limits how much of this heat of combustion can be absorbed. Traditionally using platinum as the active material, CO promoters catalyse this final oxidation reaction within the dense bed, where the temperature is more effectively buffered by the surrounding catalyst.

CO promoters can be poisoned by lead and antimony. Lead (Pb) can irreversibly poison platinum CO promoters at a ratio of 100:1 Pb/Pt. Promotion activity may be reduced by 50% when using antimony. The amount of CO promoter required for a given operation to maintain effective afterburn control is conventionally termed ‘the level of promotion’. A fully-promoted system is when the amount of CO promoter in use results in 2 ppm of platinum present in the total circulating inventory at steady state. Units that find it challenging to maintain control of afterburn can increase this level. Other units may be able to achieve good control with less than 1 ppm of platinum.
Optimisation of the FCC

The push to minimise CO promoter use is prudent. Not only does it save on OPEX as precious metal containing additives are naturally expensive, but NO\textsubscript{x} emissions can be reduced significantly by limiting the amount of platinum or palladium added to the FCCU.

The first action to take is optimising the operation to minimise excess O\textsubscript{2} in full burn applications and reducing the CO percentage in partial burn applications. The next step for decreasing FCC NO\textsubscript{x} emissions is adding the CO promoter separately rather than pre-blending it with the catalyst. If the CO promoter is pre-blended with the catalyst, the control available to the operator to carefully optimise actual CO promoter requirement is made redundant. There is also concern if the CO promoter is truly ideally mixed with the catalyst and if the fresh catalyst addition system can add batches of catalyst in the accurate and semi-continuous way for the required application. With these factors acting against the pre-blended approach, progressive refiners often realise that separate addition with a reliable and accurate addition system is critical for reduced NO\textsubscript{x} emissions.

Refiners that pre-blend will find that CO promoter addition rate is set conservatively in an effort to overcome the issues during unstable operation. Moreover, transient high afterburn events can occur, particularly during a start-up, resulting in the need to inject additional promoter for a short period of time. If promoter is wholly pre-blended and there is no capability to add extra material, the pre-blend level may even be set for this worst-case/start-up operation, resulting in an over-addition of promoter in the vast majority of the operation.

Constantly changing the proportion of promoter included in the pre-blend catalyst is also unfeasible. Firstly, there is little way of checking the accuracy of this variable concentration due to the inability to accurately measure low levels of Pt. Also, the long-decay period of platinum in the catalysis of NO\textsubscript{x} and the short-decay period for CO promotion reactions means that targeting continuous optimal operation in a dynamic unit, such as the FCC, is almost impossible, especially when catalyst hopper turnover and delivery times extend the lead time that needs to be taken into account.
NO\textsubscript{x} reduction in full burn FCC

Following the optimisation of the FCC operation, the separation of CO promoter addition and the optimisation of promoter addition rate for stable afterburn control, the refiner may find that this improvement process has given an adequate reduction in NO\textsubscript{x} emissions to satisfy the environmental limits required. If this is not the case, the next step of switching to an effective non-platinum based CO promoter is typically sufficient to meet NO\textsubscript{x} reduction requirements for most European FCCUs – giving a reduction in NO\textsubscript{x} of up to 70%. In the unlikely event that further NO\textsubscript{x} reduction is required, specific NO\textsubscript{x} additives may also be used in certain FCCUs that show a sensitivity.
If the implementation of all the above steps does not give the required NO\textsubscript{x} reduction to achieve current or impending European regulations, it is likely that the design of the regenerator or mechanical failure in the regenerator is leading to elevated NO\textsubscript{x} emissions. In such a case, online improvements may not yield the reductions required and a radical redesign or maintenance shutdown will be necessary.

Alternatively, there are several end-of-pipe solutions that can be used in units with extreme NO\textsubscript{x} issues or partial burn units that are not able to take advantage of changes in CO promoter type (although partial burn units that use CO promoter can still benefit from switching to an effective non-platinum promoter). Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are among these technologies.

In SNCR, NH\textsubscript{3} or urea nozzles are installed in the convection section of CO boilers. These nozzles are used to atomise NH\textsubscript{3} at temperatures of 850 – 1030°C. NH\textsubscript{3} will react with NO\textsubscript{x} species through to N\textsubscript{2}. NH\textsubscript{4}HSO\textsubscript{4} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} salts can form as byproducts, causing plugging and corrosion downstream. NH\textsubscript{3} slip can reach as high as 20 ppm in the stack gas in an SNCR process, depending on the quality of NH\textsubscript{3}:NO ratio control in the reaction section.

In the SCR process, a V\textsubscript{2}O\textsubscript{5} or WO\textsubscript{3} based catalyst aids the formation of N\textsubscript{2} from NO\textsubscript{x}, using air and NH\textsubscript{3} as reactants. Optimum operational temperature is between 300 – 400°C and the catalyst life is typically between four to six years. The catalyst is mounted in a CO boiler or separate vessel. Salts can also cause plugging of the catalyst in this process.

NO\textsubscript{x} can be decreased by 40 – 75% by the SNCR process and 70 – 90% by the SCR process. In wet gas scrubbers, NO\textsubscript{x} is converted to N\textsubscript{2}O\textsubscript{5} and then to HNO\textsubscript{3} by ozone. Nitrogen leaves the process as NaNO\textsubscript{3} through reaction with NaOH. NO\textsubscript{x} removal is above 98% by WGS, but this is highly costly in terms of initial investment and operating cost. In addition, treatment of NaNO\textsubscript{3} and NaSO\textsubscript{4} enriched steams is typically required. Otherwise, crystallisation units are required to remove salts from the purge streams, resulting in further capital and operational costs.
Case study

Tüpras investigated NOX mitigation methods when challenged on this subject in 2011. The following section details the company’s experience when implementing its chosen technologies.

Tüpras Izmit Refinery has an FCCU that is designed for a feed rate of 1750 m³/d of HVGO/HCO/naphtha recycle. The unit is a UOP side-by-side configuration with a bubbling bed regenerator operating in full burn, a riser disengaging system with rough cut cyclones and feed injection at the bottom of the riser. The unit’s current operating capacity is 2250 m³/d.

The refinery began using Johnson Matthey’s non-platinum COP-NPTM CO promoter in April 2013, replacing a traditional platinum-based CO promoter that was pre-blended with the FCC fresh catalyst to a level of 2 ppm platinum. A later trial of the company’s NOXGETTERTM additive began in November 2013. An addition rate of 3 kg/d of COP-NP was required for this unit with 80 t of circulating catalyst inventory.

After the CO promoter switch, any platinum remaining in the inventory will continue to generate NOX long after the CO promotion capabilities have diminished. Therefore, Tüpras calculated a platinum decay profile based on a CSTR model (Figure 1). Based on this calculation, it takes more than 200 days to decrease platinum to a level below 1 ppm. There was a further interruption to the normal decay when catalyst pre-blended with platinum had to be loaded to the inventory in June 2013. This introduced a small deviation in inventory platinum concentration. However, towards the end of the period and by the start of the additive trial in November 2013, the platinum concentration had fallen to a low background level. The platinum decay profile approximates the turnover of the unit as a function of daily addition and withdrawal rates and the catalyst inventory of the system. Therefore, the fall in NOX at Tüpras Izmit Refinery followed the platinum decay curve after changing to non-platinum CO promoter (Figure 2).

Figure 1. Platinum decay during NOX reduction trials at Tüpras Izmit Refinery.

Figure 2. NOX emissions during reduction trials.

Figure 3. The relationship between NOX emissions at excess O₂ in the refinery’s FCCU.

Figure 4. NOX vs excess O₂, focusing on operation with COP-NP when platinum concentration has decayed to a low level.
While it is generally expected that NOx emissions will follow the platinum decay curve, moving from 2 ppm to 1 ppm platinum concentration is still a large amount of platinum present in the inventory. Moreover, despite being aged, it is still highly active in producing NOx. After the platinum-containing batch of catalyst had been consumed in June 2013, NOx began to decay with the platinum concentration. The platinum concentration also reduces below 1 ppm for a sustained period at this point (Figure 3).

At fixed excess O2, Johnson Matthey’s CO promoter was found to reduce NOx emissions by 32% in the latter part of the test when platinum in Ecatal has decayed to a lower level. However, it appeared that NOx emissions were continuing to decrease in line with further reductions in platinum concentration. Based on the final days of operation before the start of the next trial, NOx could be concluded to be 54% lower than the baseline. This is more in line with NOx reduction levels of ~60% that are expected when switching to an effective non-platinum CO promoter (Figure 4).

An important differentiator for Tüpras when exploring low-NOx CO promoters was the ability to maintain good afterburn control with a reduced amount of platinum or platinum alternative. Commercial data showed that COP-NP can provide effective afterburn control without the use of platinum. During the Izmit testing, no discernible difference in afterburn was observed when switching from platinum CO promoter to the replacement non-platinum CO promoter (Figures 5 and 6).

Figure 5. Cross-plot of afterburn vs excess O2.

Figure 6. Daily average afterburn in the base period using 2 ppm platinum-based CO promoter in fresh catalyst and Johnson Matthey non-platinum promoter.
To determine the potential for further reductions in NOX in the Izmit FCCU, a trial of separate NOX reduction additive was performed.

The trial strategy was to perform additions to attain 1% concentration in the FCC inventory and then towards 2%. Steady-state concentration was not achieved but over the course of this 25-day trial enough useful data was collected to analyse the additive effects (Figure 7).

Up to the start of the additive trial, further declines in the residual platinum concentration in the FCC inventory appeared to still dominate NOX generation. The additive proved to reduce a further 31% NOX emissions at constant Ecat platinum concentration (Figure 8).

The comparison at constant excess O2 is not as strongly correlated but still indicates significant NOX reduction with NOXGETTER, independent of the main driver of FCC NOX generation observed in full burn FCCUs (Figure 9).

Based on previous experience, it is not anticipated that feed nitrogen has a significant effect on FCC NOX generation. This is because the sensitivity of NOX emissions is primarily located in the regenerator in terms of the skew of reaction pathways to either N2 or NOX. Therefore, throughout the Tüpras Izmit NOX trials, no sensitivity with feed nitrogen was observed. Also, feed nitrogen was maintained in a similar range of 600 – 1200 ppm through the entirety of the base case and trial periods (Figure 10).

Figure 7. NOXGETTER addition protocol through the trial phase.

Figure 8. NOX vs Ecat platinum concentration through the additive trial.

Figure 9. NOX vs excess O2 during the additive trial.

Figure 10. NOX vs feed nitrogen during the NOX analysis period at the refinery.
Conclusion

Working alongside Johnson Matthey, Tüpras embarked on a comprehensive study of the possibilities for reducing NOx emissions from the İzmit FCCU. A NOx reduction of almost 75% was realised and a stepwise procedure was followed to achieve this reduction. A significant reduction in NOx was observed when switching to a separately added platinum-free CO promoter that is effective in afterburn control. This helped reduce NOx by almost 60%. A subsequent trial with an additive used reduced NOx to the point that the overall reduction was 74% on a constant excess O2 basis (Figure 11).

Feasibility studies of this kind can help companies approach current and future changes to environmental emission standards, following learning derived from the performance of short but rigorous plant trials.

Figure 11. NOx vs excess O2 over the whole NOx reduction period.
For further information on Johnson Matthey, please contact your local sales representative or visit our website. COP-NP and NOXGETTER are trademarks of the Johnson Matthey group of companies.

Billingham, UK
Tel: +44 (0) 1642 553601
Tel: + 1 732-223-4644
www.matthey.com