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Optimising FCC economics against changing market dynamics

CO promoters are a frequently overlooked parameter for better control of afterburning, as demonstrated in a case study amidst a changing platinum group metals marketplace

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Co promoters are used in the majority of fluid catalytic cracking (FCC) operations. They are generally used in low quantities and, as a result, are often overlooked as an important point for optimisation. CO promoter optimisation and an understanding of coke burning fundamentals, afterburning, and methods for its control can lead to significant cost savings. Better control of afterburning helps limit downtime and allows for higher feed rates or the processing of more challenging feeds.

In addition to elaboration on the development of the new **COP-NP™ HD** promoter, the fundamentals of coke combustion, afterburn, CO promoter usage, and optimisation will be discussed, including a case study demonstrating the successful use of **COP-NP HD** in a commercial application. Reviewing the current status of the platinum group metals marketplace and drivers for innovation are also forthcoming.

FCC regenerator and heat balance

The FCC regenerator restores catalyst activity by removing coke from spent catalyst. This coke combustion provides the main source of heat necessary to drive the FCC process. Additional heat is also supplied from fresh and recycle feed preheat, steam, compression of air at the main air blower, and other minor sources. The total heat from these sources, especially coke combustion, provides the heat necessary for the FCC operation and keeps the system in energy balance (energy in equals energy out).

The FCC requires energy for the following: to vaporise feed and recycles and raise their temperature to the reactor temperature; to supply the energy for the endothermic cracking reaction (heat required to break the bonds); to heat steam to process temperatures in the riser, stripper, and standpipes; to heat the air from the blower discharge to the flue gas temperature; and to account for heat losses (such as catalyst cooler) in the system.

Coke combustion in regenerator and heat generation

Carbon and hydrogen in coke are combusted in the FCC regenerator by reaction with oxygen to form carbon dioxide, carbon monoxide, water, and heat:

$$\text{Coke} + O_2 \longrightarrow CO_2 + CO + H_2O + \text{Heat}$$

Coke combustion also yields SOx and NOx since portions of feed nitrogen and sulphur also convert to coke which is also exothermic, but the heat produced is small and usually not included in heat balance calculations.

$$\text{S in Coke} + O_2 \longrightarrow SO_2 + SO_3 + COS + H_2S + \text{Heat}$$

$$\text{N in Coke} + O_2 \longrightarrow N_2 + NOx + HCN + \text{Heat}$$

Coke combustion is kinetically limited; increasing the rate of coke combustion helps limit afterburn by keeping this reaction in the dense bed where there is more catalyst available to absorb the heat produced. Higher excess oxygen increases oxygen partial pressure, which in turn increases the coke burning rate. Higher regenerator pressure also increases oxygen partial pressure and reduces the superficial velocity, thereby increasing residence time. Higher regenerator dense bed temperature increases the rate of coke combustion, and the even distribution of catalyst and air improves coke combustion.

Incomplete combustion in the regenerator dense phase can result in CO and O_2 breaking through to the dilute phase. Combustion of CO in the dilute phase is called afterburning.

Dealing with different types of afterburn

When CO is combusted to CO_2 in the dilute phase above the regenerator dense bed, it causes a large temperature rise because there is insufficient catalyst to absorb the heat released. In order to minimise afterburn in full burn units, CO is minimised leaving the dense bed, and in partial burn units O_2 is minimised leaving the dense bed.

In many cases, afterburn can be controlled or minimised using a CO promoter or methods that increase the rate of coke combustion outlined previously. It is much easier to control afterburn that is uniform across the regenerator, as indicated by consistent dilute phase and cyclone temperatures.

Afterburn caused by poor catalyst and/or air distribution is more difficult to manage. Usually, this type of afterburning results from damage to the regenerator internals, such as the air grid or catalyst distributor. It can also occur due to maldistribution resulting from poor regenerator operation or design that does not allow for good catalyst and air mixing throughout the bed.

To mitigate this type of afterburn, air distribution to the individual grids or rings can be adjusted or lift air relative to the main air blower, and regenerator bed levels can be optimised. CO promoter can be added and will be effective if there is enough CO and O_2 present. However, sometimes the only method of resolution for this type of afterburn is a shutdown with modification to the air grid or catalyst distribution.
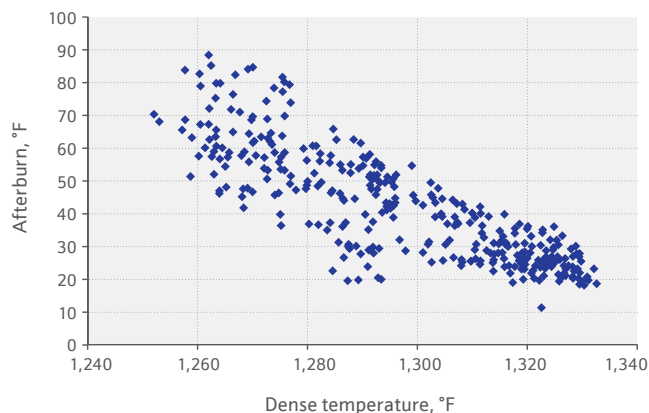
Figure 1. Afterburn vs dense bed temperature

Importance and mitigation of afterburning

Afterburning has two major consequences in the FCC. First, the dilute phase temperature limits the feed rate and flexibility to run opportunity feeds. Second is potential serious damage to cyclones and flue gas systems from operating at excessively high temperatures, which can lead to premature shutdowns and costly repairs.

Higher dense bed temperature increases the rate of combustion of CO to CO_2, thereby avoiding CO breakthrough to the dilute phase. Figure 1 shows a common example of afterburn decreasing with increasing dense bed temperature.

Regenerator bed level can have a major impact on CO breakthrough and afterburn. Higher bed levels often help minimise CO breakthrough because of increased residence time. Understanding how different regenerator levels impact CO, NOx, and O_2 can help refiners define their optimum operating window. It is also important to observe CO, NOx, and O_2 when undertaking catalyst withdrawals. If CO or afterburn are increasing significantly at lower bed levels or during catalyst withdrawals, it is generally advised to operate at a higher bed level and decrease time intervals between withdrawals. Higher bed levels can also cause increases in catalyst carryover, especially if transport disengaging height (TDH), where the catalyst concentration in the flue gas stays constant, is not maintained.[1]

Other afterburn indicators can be observed in the regenerator by looking at dense, dilute, and cyclone temperatures. Typically, these temperatures should trend with one another. Dense phase temperatures increase together, dilute phase temperatures increase together and so on, and the delta between temperatures in similar axial locations should trend together. If one or more of

the temperature indicators (TIs) start to divert, this can be a sign of uneven distribution or damage. Regenerated e-cat should be uniform in colour; if there are very dark-coloured particles mixed with very white particles (salt and pepper), this is an indicator of uneven distribution that can lead to afterburn and CO breakthrough.

Combustion promoters to mitigate afterburn

Use of CO promoters is the most common and effective way to mitigate afterburn. Combustion promoters help increase the rate of reaction of CO to CO_2 through the following equation:

$$CO + \tfrac{1}{2}O_2 \quad \longrightarrow \quad CO_2$$

CO promoters, present in the dense phase, help move this reaction into the dense phase. A good guideline is to start by adding 1 to 2 ppm platinum or platinum equivalent based on total catalyst replacement (for example, a CO promoter containing 500 ppm used at a rate of 2 lb per 1000 lb total additions results in 1 ppm Pt at steady state). However, actual CO promoter requirements can vary significantly based on regenerator conditions, changes in feed, and contaminant metals. CO promoter can be added via a small shot pot loader, an additive loader (preferred), or pre-blended with the catalyst. Ideally, spreading the addition of the promoter throughout the day as opposed to a small amount when afterburn begins to increase is much more effective. This allows the regenerator temperature and promotion level to be more constant and creates an environment for consistent CO promotion.

Platinum was originally chosen as an oxidation catalyst because it was the only metal that could be used in low enough concentrations to catalyse CO oxidation without catalysing undesirable de-hydrogenation reactions (other metals yielded higher amounts of hydrogen and methane). However, platinum also promotes nitrogen oxide (NOx) formation in the flue gas from nitrogen in coke. Platinum-based promoters can increase NOx emissions by up to four to five times base emissions.

NOx emissions are harmful to human health and the environment. They cause harmful effects on the human respiratory system. Besides, NO_2 reacts with water to produce nitric acid and contributes to acid rain. NOx is also considered a greenhouse gas. Nitrous oxide has about 300 times the warming power of carbon dioxide and stays in the atmosphere for more than 100 years.[2] For these reasons, NOx emissions regulations are becoming more stringent.
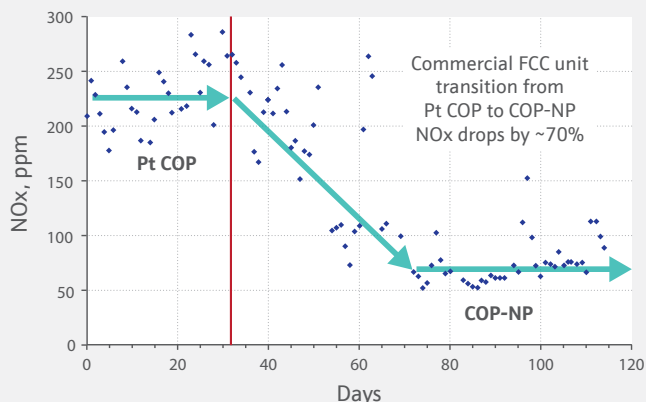
Figure 2. Reduction of NOx emissions by 70% at an FCC unit switching from a platinum-based to a non-platinum based promoter

Figure 3. Platinum and palladium price evolution over the last six years, $/TOz[4]

In geographical areas with fewer restrictions on NOx emissions, platinum-based promoters are still widely used due to their affordability and high performance. For geographical areas where NOx emissions are strongly regulated, palladium-based promoters are often used in place of platinum. Switching from a platinum-based promoter to a non-platinum-based (palladium) promoter usually leads to a reduction of NOx emissions by 60 to 70%, as shown in Figure 2.

In recent years, many refiners using palladium-based promoters have started to switch back to platinum-based promoters due to increased palladium costs. These refiners either have some room in their NOx emissions limits or a post-treater for NOx, such as SCR (selective catalytic reduction), SNCR (selective non-catalytic reduction), or LoTOx (low-temperature oxidation for NOx control). For refiners that have these options available, understanding the cost difference between platinum and non-platinum promoters weighted against post-treater costs such as catalyst, electricity, and ammonia can provide an opportunity for cost savings.

Cost of platinum vs non-platinum promoters

Due to their high content in platinum-group metals (PGM), combustion promoters bear the brunt of PGM price fluctuations, which are mainly influenced by changes in supply and demand.

As far as platinum is concerned, about one-third is used in autocatalyst (mainly for light and heavy-duty diesel vehicles), about 30% in industrial segments (petrochemicals, petroleum refining, glass industries), 25% in jewellery, and the rest in investment.[3] During the Covid crisis, autocatalyst demand plunged by 22%, with steep falls in European diesel car production. Meanwhile,
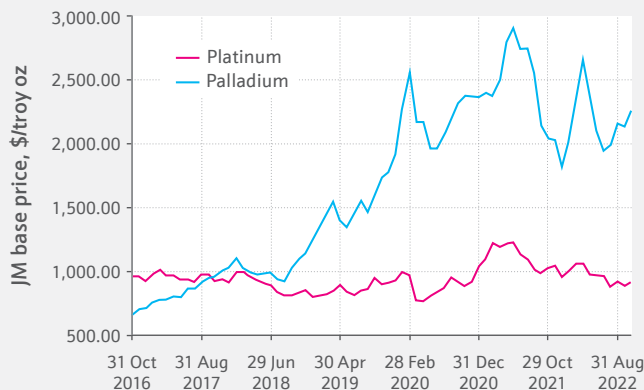
supply also contracted by 20% due to processing outages and pandemic-related disruption in South Africa. As overall changes in supply and demand were nearly identical, the platinum market continued to be in moderate deficit, as it was pre-pandemic. The platinum market moved into surplus in 2021 as supplies recovered and investment purchasing collapsed. Consequently, platinum prices have been decreasing.

Regarding palladium, the vast majority is used in autocatalysts (85%) and about 15% in industrial applications (chemical, dental, and electronic industries).[3] During the Covid crisis, the plunge in vehicle output was partly offset by higher palladium loadings on gasoline vehicles, and therefore led to a less drastic decrease in demand in auto- catalyst (about -12% vs pre-pandemic).

Meanwhile, supply was severely hit by mine closures and processing outages. Consequently, the palladium market remained in significant deficit, driving the price above $2,000/TOz from early 2020. Availability of palladium improved progressively as South African supplies recovered from processing outages. However, palladium prices remain high and volatile, recently reflecting the exposure to Russian supply.

Palladium prices increased steadily over the last five years or so, whereas platinum prices remained relatively stable at around $1,000/Oz (see Figure 3). Palladium is now at a premium of ~125% vs platinum. This overall change in palladium vs platinum has driven Johnson Matthey to complete extensive research on a lower palladium content CO promoter with optimised metal dispersion over the additive.

CO promoter additive with high metal dispersion – laboratory-scale study

Johnson Matthey has leveraged knowledge gained from the hydrogen, renewables, and autocatalyst industries to optimise the metal support interaction and disperse palladium more efficiently, hence enhancing CO promotion efficiency on the palladium-based promoter.

A uniform metal distribution across the CO promoter particle allows optimal distance between the active metal clusters, which in turn reduces their rate of sintering. Sintering is the agglomeration of metal particles under operating conditions that leads to permanent loss of CO promotion activity (deactivation). Modifying the support to provide a strong metal-support interaction further reduces the rate of agglomeration by inhibiting migration of the active metal clusters.

Figure 4 exhibits electron probe micro-analyser (EPMA) cross-sectional images showing the enhanced dispersion in the modified support. Strong metal-support interaction ensures the metal is anchored as firmly as possible, lowering the rate of sintering.
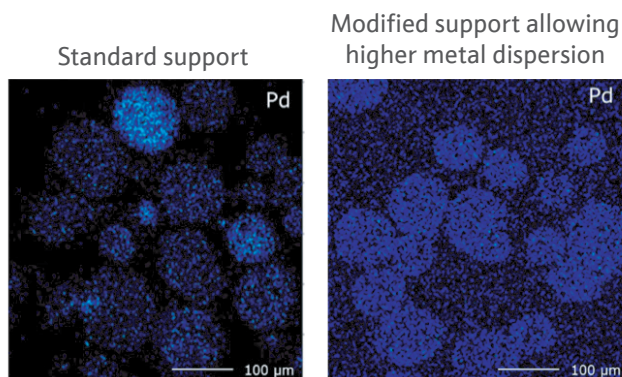
In addition to reducing sintering, optimised metal distribution throughout the mesoporous support particles further increases active sites available to anchor CO and O_2 required to carry out the CO oxidation reaction.

Metal dispersion level and CO reduction efficiency were measured for three CO promoters with the same active metal loading and various dispersion levels, both fresh and steam deactivated (788°C/95%H_2O/20h) (see Figure 5).

The additive with the highest metal dispersion exhibits the highest CO reduction efficiency, for both fresh and steam deactivated versions.

Metal dispersion in general has an inverse correlation with metal loading. Hence, it is critical to optimise the metal loading to identify the 'sweet spot' where the highest activity level is obtained.

Steamed CO promoter additives with various metal loadings were assessed for metal dispersion and CO reduction efficiency (see Figure 6). The less metal content in the CO promoter additive, the higher dispersion was observed, leading to a volcano shape of activity vs metal loading.

Based on these findings, we developed a new CO promoter additive with greatly improved CO reduction efficiency. The new additive has been successfully used in multiple refineries.

CO promoter additive with high metal dispersion – refinery case study

Following successful testing at laboratory scale, the performance of the new CO promoter additive, **COP-NP HD**, was compared with our best-selling CO promoter **COP-NP** at a North American refinery. The purpose of the trial was to match performance to **COP-NP** at a reduced metals cost. This FCC unit operates in full burn and has had a long history of successful use of non-platinum promoter.

Standard support | Modified support allowing higher metal dispersion

Figure 4. 1 EPMA elemental mapping assessing palladium dispersion on standard vs modified support
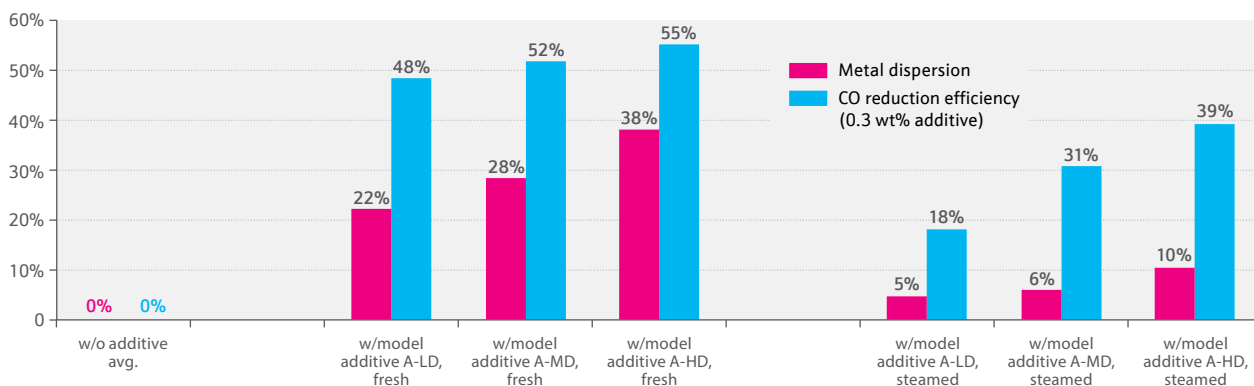

Figure 5. Metal dispersion and relative CO reduction efficiency during temperature programmed oxidation (TPO) of spent catalysts with CO promoter additives at the same metal loading. LD = low dispersion, MD = medium dispersion, HD = high dispersion
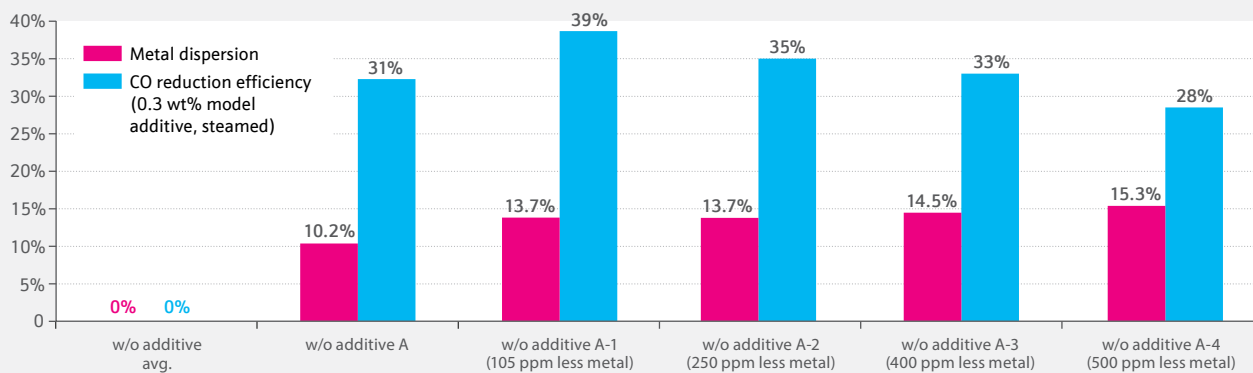
Figure 6. Metal dispersion and relative CO reduction efficiency during TPO of spent catalysts of CO additives with different metal loadings
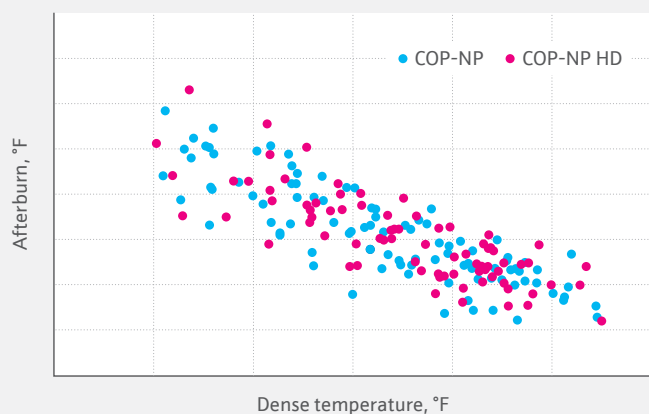
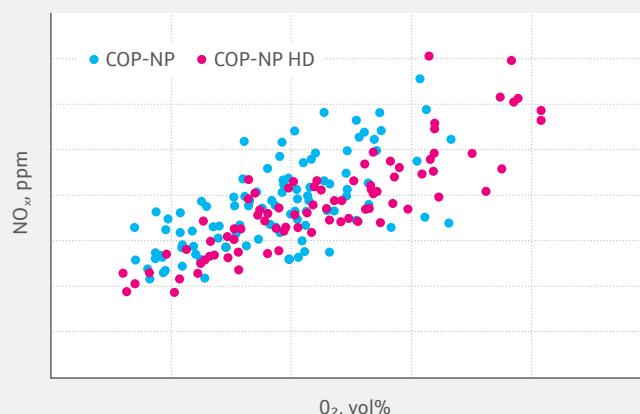

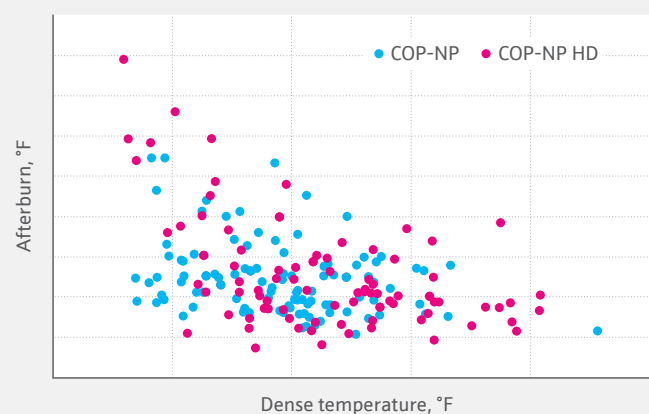Figure 7. Afterburn vs dense bed temperature

Figure 9. NOx vs excess O_2

Figure 8. CO and afterburn vs excess O_2

Results from this trial showed equivalent afterburn and CO control using the highly dispersed non-platinum promoter with no change in NOx emissions. Performance between the two promoters was compared at similar dense bed temperatures (see Figure 7) and excess O_2 (see Figure 8).

Both CO and afterburn are a function of dense bed temperature, as discussed previously in this article. Higher dense bed temperatures lead to reduced afterburn, as seen in Figure 7. Both **COP-NP** and **COP-NP HD** follow very similar trends at this refinery. CO and afterburn are also dependent on excess O_2. At this refinery, excess O_2 has an impact on CO emissions, and both **COP-NP** and **COP-NP HD** showed similar performance (see Figure 8). Excess O_2 can impact afterburn as well but had minimal effect at this refinery. Both additives performed similarly.

The last important variable in the study is NOx. Excess O_2 has a major impact on NOx; however, both additives showed similar NOx performance at varying ranges of excess O_2 (see Figure 9).

The addition rate difference between the two additives was equal within error. Hence, the new CO promoter with lower palladium content, **COP-NP HD**, showed equivalent performance to **COP-NP**. **COP-NP HD** opens opportunities for significant metal cost savings to refiners. Similar results have been obtained at multiple North American refineries where **COP-NP HD** has been used.

Conclusions

Afterburning in the FCC regenerator is a key constraint in many FCC operations. Controlling afterburning is very important but often under-emphasised to help maximise FCC profitability and reliability.

COP-NP HD, with improved metals dispersion and metal-support interaction, is an attractive choice of combustion promoter that allows metal cost savings while maintaining the low NOx benefit of **COP-NP.**

Understanding coke fundamentals, regenerator operation, and changes that impact CO and afterburn combined with the overall economic picture of changing metals prices and the costs affiliated with post-treaters provides major opportunities for FCC operation optimisation. The ability to understand and optimise leads to reduced downtime and the ability to process more opportunity feeds and operate at higher unit feed rates.

References

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4 Johnson Matthey, PGM Management, 2022, https://matthey.com/ products-and-markets/pgms-and-circularity/pgm-management (accessed Nov 2022).

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