



Afterburn relief

How to prevent FCC afterburn in the downstream industry

Afterburn Relief

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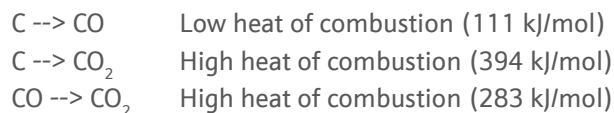
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Heartburn can ruin someone's day if it is not controlled or prevented. For a fluid catalytic cracking (FCC) engineer or operator, 'afterburn' can also ruin a day if it is not controlled or prevented. Afterburning is any increase in the flue gas temperature that may occur in the dilute phase, cyclones, or flue gas where there is less catalyst present to absorb the heat of combustion. It can lead to regenerator inefficiency, high cyclone temperatures, lower than optimum riser temperatures (if circulation limited) and carbon monoxide (CO) emission excursions. CO promoting additives are used to control afterburning and minimise CO emissions. Both platinum and non-platinum based CO promoters can achieve afterburn and CO emissions control. However, platinum based promoters generally increase NO_x emissions substantially, while non-platinum based promoters are normally used to minimise NO_x emissions.

The basic function of the FCC regenerator is to remove the carbon, in the form of coke, from the circulating catalyst to restore the equilibrium catalyst activity for cracking in the riser. Carbon combustion can be considered to take place in two steps in the FCC regenerator.



The first reaction step burns the carbon on the coked catalyst to CO with a low heat of reaction. The second reaction oxidises the CO to carbon dioxide (CO₂) with a much higher heat of reaction. The second reaction needs to take place in the dense bed of the regenerator where the catalyst can utilise its higher specific heat capacity vs the gas phase to absorb the heat of combustion, which is transferred to the riser to heat and vaporise the feed and help drive the endothermic catalytic cracking reactions. In most full burn units, some of the carbon is not fully oxidised to CO₂ in the dense phase because of slip, imperfect mixing, or simply because the residence time in the regenerator bed is insufficient to complete this reaction. The dense bed coke burning capacity can become limited due to insufficient oxygen (air blower

capacity), poor air distribution, high feed carbon content, low catalyst levels in the regenerator or higher than normal feed rates. If all the CO is not burnt to CO₂ in the dense bed, the remaining CO will continue to burn in the dilute phase where there is insufficient catalyst present to absorb the heat of CO oxidation, thus resulting in a high temperature rise of the flue gas that is referred to as 'afterburning'.



Regenerator afterburning

The increase in flue gas temperature as a result of afterburning may limit overall unit throughput or feedstock flexibility. High levels of afterburning may also result in serious damage to internals, leading to premature shutdown and costly repairs. Typically, there are two types of afterburn observed: kinetic limited and distribution induced. Kinetic limited afterburning occurs due to insufficient regenerator bed residence time for complete combustion. Distribution induced afterburning is caused by poor air and/or catalyst distribution, and is frequently caused by inherent design features and/or air grid mechanical failures.

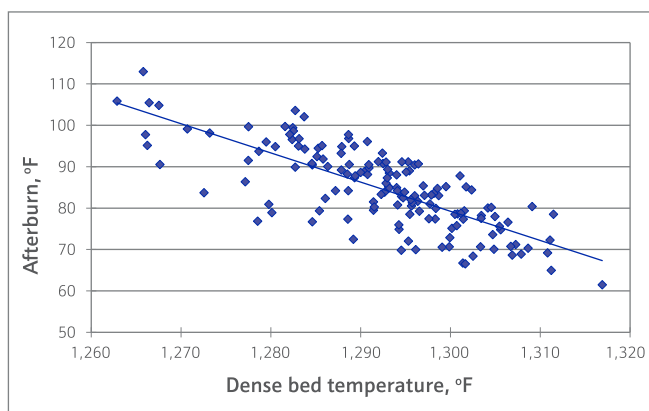


Figure 1. Afterburn vs regenerator dense bed temperature

Kinetic limited afterburning

Kinetic limited afterburning is characterised by well dispersed afterburning across regenerator cross section, high superficial velocities, low bed levels and low bed temperatures. The typical solution is to raise the bed level, increase bed temperatures and add CO promoter. Kinetically limited units generally respond well to CO promoter (Figure 1).

Distribution induced afterburning

Distribution induced afterburning is characterised by localised afterburning, which is induced by poor air and/or catalyst distribution, resulting in the mixing of CO and O₂ rich zones above the dense bed. This type of afterburning does not respond as well to CO promoter. If possible, the hotspot temperature should be monitored as promoter concentration increases. The hotspot temperature will decrease until the excess O₂ is fully consumed in the affected region. Continuing to increase promoter additions after the temperature drop has ceased has little or no effect on the regionalised afterburning. A normally well functioning unit, which begins to have increased afterburn along with a change in losses or equilibrium of power spectral density (PSD) indicates air grid damage (Figure 2).

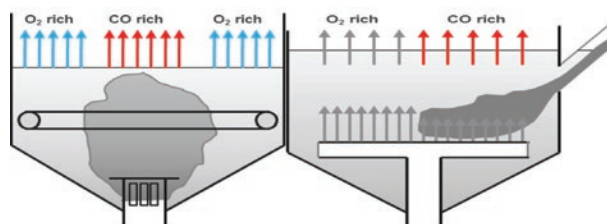


Figure 2. FCC Air distributors¹

CO promoters

There are two basic types of CO promoters that improve the kinetics (speed) of the oxidation of CO to CO₂ in the regenerator: platinum and non-platinum promoters. Platinum based promoters can improve the kinetics (speed up the reaction of CO to CO₂) but have a high propensity to catalyse the production of NO_x from feed nitrogen that ends up in the coke.

Non-platinum based promoters incorporate a proprietary mixture of metals that also improve the kinetics of CO to CO₂, while producing significantly less NO_x than platinum containing additives.



CO promoter NO_x response

Commercial data shows the decrease in NO_x emissions with the shift from platinum based CO promoters to non-platinum CO promoters such as Johnson Matthey's **COP-NP**[™] that contains no platinum (Figure 3)

NO_x emissions are directly related to the equilibrium catalyst COP platinum content (Figure 4). **COP-NP** controls the regenerator afterburn, allowing lower addition rates (Figure 5).

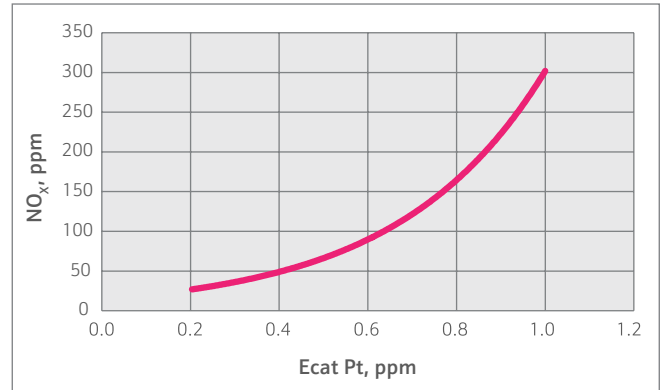


Figure 4. NO_x ppm vs Ecat Pt ppm

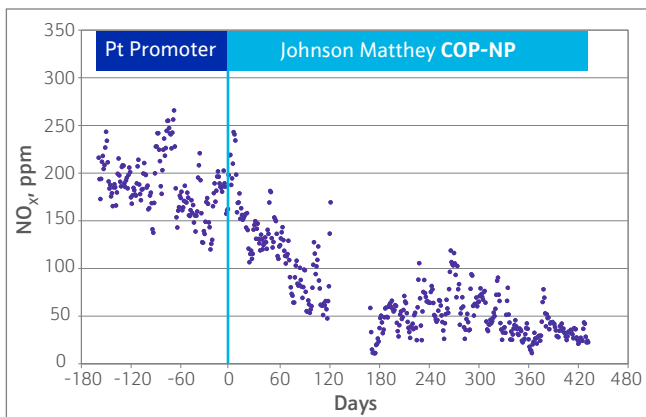


Figure 3. NO_x emissions (ppm vs days)

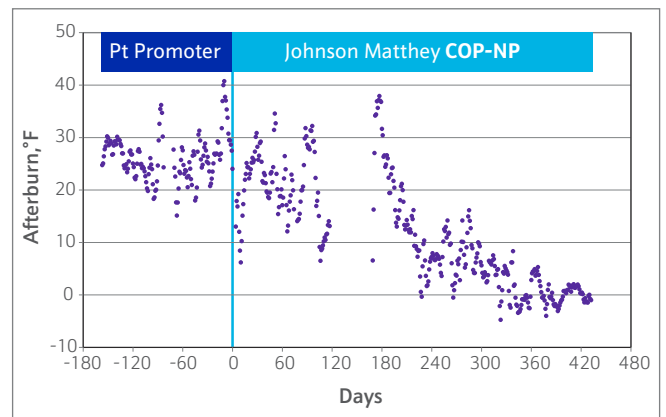


Figure 5. Afterburn vs days

Back-to-back commercial data

A major western European refinery performed a set of three back-to-back trials on the FCC unit to find the optimum low NO_x CO promoter for operations. In this case, NO_x emissions are a concern because the refiner elected to use antimony to passivate the negative effects of nickel coming in with the feed. Use of antimony, which is common with residue FCC units and FCC units that suffer from wet gas compressor or delta coke constraints, has been observed to significantly increase NO_x in many cases. The NO_x producing effect of antimony can be magnified, for example, in a unit that has mitigated other sources of NO_x, such as removing platinum based CO promoter, minimising maldistribution of spent catalyst and air, and reducing excess oxygen to the lowest level for stable operation. There are also cases where the regenerator design greatly impacts the sensitivity of NO_x to antimony use, e.g. combustor-style regenerators generally produce low baseline levels of NO_x, hence these types of unit can be susceptible to relatively large NO_x increases when introducing a NO_x catalysing material such as antimony.

In the case of this European refiner, historical attempts to introduce antimony had resulted in a 300% increase in NO_x. In another case, a small amount of foreign antimony entered the FCC unit and increased NO_x by 130%. If the refiner performing this back-to-back test was to be permitted to add antimony to its FCC operation continuously, then its baseline NO_x would have to be brought down sufficiently to allow the increased NO_x (expected when introducing antimony) to be accommodated without exceeding maximum NO_x emissions limits.

Three low NO_x CO promoters were tested in a commercial FCC unit in sequence (Table 1).

	Average NO _x (ppm)	Average additions (lb/d)
Additive X	48	95
Additive P	43	75
JM COP-NP	40	59

Table 1. Johnson Matthey's COP-NP effectively controls NO_x

NO_x control

NO_x reduction was improved by 17% when using **COP-NP**, compared to the base case. The observed NO_x emissions were also more stable for this promoter, at 15 – 17% lower than the base case (Figure 6).

CO promoter addition rates

Each promoter was placed at a consecutively lower average daily addition rate. Since all low NO_x CO promoters can catalyse the formation of NO_x, lower observed NO_x emissions can be derived from requiring to add less CO promoter. This is only achievable if the CO promoter that is being used is more effective for afterburn and CO control. The required **COP-NP** average daily addition for effective afterburn control was 37% lower than the base case (Figure 7).

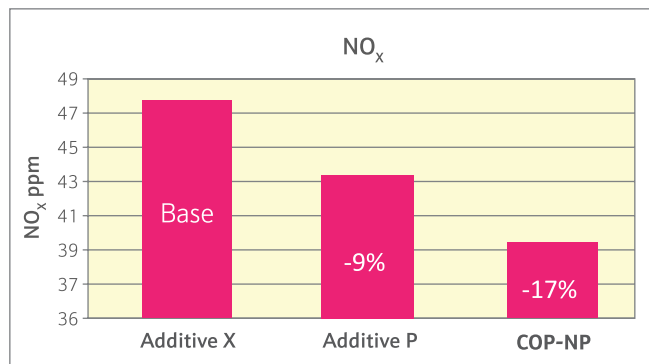


Figure 6. NO_x ppm decrease

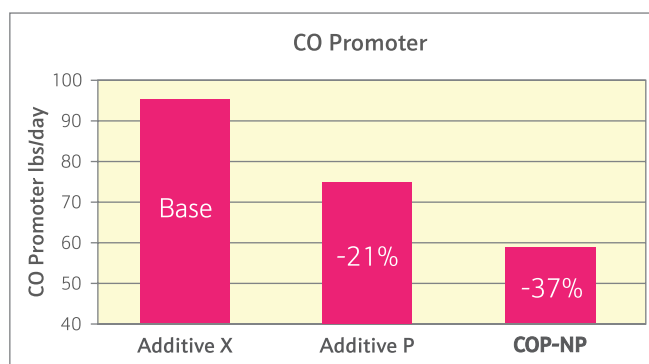


Figure 7. CO promoter decrease

NO_x and promoter addition rates

The company's promoter provides low NO_x emissions with a tight distribution. This can be of critical importance as the repeatability of response can be equally or even more important to refiners to ensure confidence that emissions limits will not be exceeded when the operation is otherwise stable.

Part of the reason for the disturbed and inconsistent response in the first low NO_x CO promoter trial may be due to the CO promoter being added as a pre-blend in the fresh catalyst. This approach gives many disadvantages as blending additional additive components can be non-ideal, meaning variable amounts of CO promoter are unintentionally entering the process, resulting in a fluctuating response.

In addition, CO promoter is not a concentration based additive as it is highly effective at reducing afterburning when initially added, and its use should be minimised to avoid excessive NO_x. CO promoter daily addition rates are typically fixed at the minimum addition level to control normal levels of afterburning, while supplementary manual additions are made or the addition rate is adjusted if afterburning changes are observed. By blending in a

fixed concentration with the fresh catalyst, the ability to optimise afterburning at minimum NO_x is lost. For example, additional amounts of CO promoter are added to the unit when increasing the fresh catalyst addition rate. This additional promoter is usually unnecessary and unadvised (due to increased NO_x and costs). In addition, pre-blended CO promoter is typically blended at an elevated level for the worst case scenario or for periods of low fresh catalyst addition, in the cases where no supplementary addition is possible. This means normal CO promoter addition is excessive, only giving negative connotations.

To achieve tight control of FCC NO_x emissions, it is vital that a high quality low NO_x or non-platinum CO promoter is added separately through a reliable and accurate addition device. A second low NO_x promoter trialled was added separately through a non-Johnson Matthey addition system. And the final trial with **COP-NP** used the company's **INTERCAT**[™] additive addition system. In the back-to-back trials, **COP-NP** was effective at much lower addition rates (Figures 8 and 9).

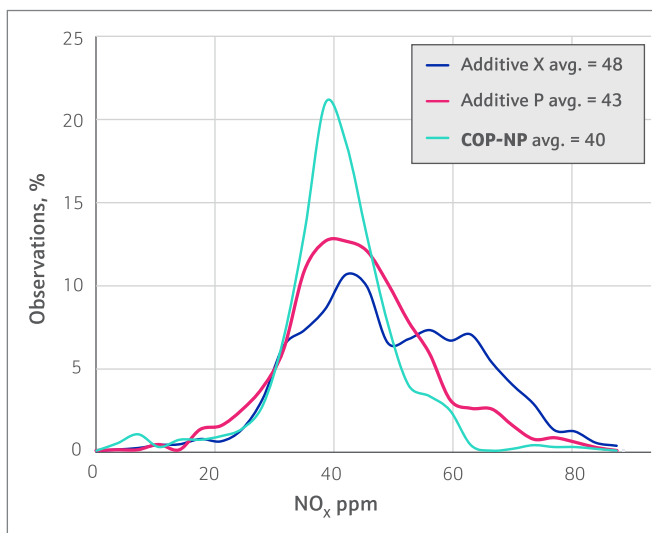


Figure 8. NO_x ppm histogram

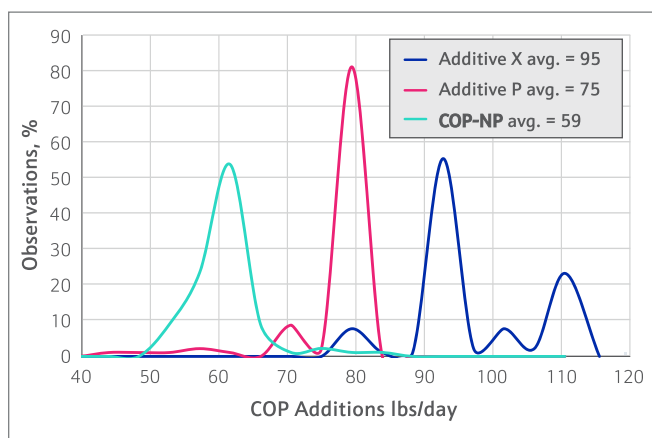


Figure 9. CO promoter usage histogram

Conclusion

Afterburn can be a big problem just like heartburn if it is not controlled or prevented. FCC afterburn results when the coke on a catalyst is not burned completely to CO₂ in the regenerator dense bed. The remaining CO will continue to oxidise in the dilute phase and upper portions of the regenerator. The high heat of combustion for CO to CO₂ and the low catalyst density can result in higher than desired temperatures, which can cause serious damage to internals that leads to premature shutdown and costly repairs. Kinetic limited afterburning is due to insufficient reaction volume in the dense phase and can be effectively controlled with CO promoter additives. Distribution induced afterburning is characterised by localised afterburning, which is induced by poor air and/or catalyst distribution and may, or may not, be effectively controlled with platinum or non-platinum based CO promoter additives. Platinum based CO promoters can increase NO_x formed from combustion of nitrogen in coke. Avoiding platinum by using a non-platinum promoter allows for more effective afterburning control where there is a need to minimise the production of NO_x in the regenerator.

References

1. WILSON, J. W., 'FCC Regenerator Afterburn Causes and Cures', Wilson P.E., Barns and Click, Inc., AFPM Annual Meeting 2003, AM-03-44.

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