
Question 81: How do CO (carbon monoxide) and NOx (nitrogen oxide) emissions change when you operate at low regenerator temperatures? What can be done to mitigate any increases?

BULL (Valero Energy Corporation)

I will initially address this question from a CO standpoint and then discuss the NOx. CO emissions typically increase if the regenerator falls below a certain temperature threshold. That temperature threshold will vary based on your regenerator configuration and definitely on the type of air distribution. In general, well-mixed regenerators with longer residence times can be run at significantly lower temperatures before CO emissions increase, compared to a poorly mixed regenerator with lower residence time.

Mitigation of CO Emissions at Low Regen Temps

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- Add non-Pt CO promoter to limit NO_x
- Modify your operation to increase your delta coke
 - Catalyst or Operational Change
- Increase pressure in the Regenerator
- Modify the Regenerator to increase mixing

In the absence of a CO combustion promoter, large variations in the CO₂ (carbon dioxide)-to-CO ratios are observed. At the catalyst surface, it is believed that that CO₂-to-CO ratio is an intrinsic function of the temperature at the burning site. However, the CO exiting the burning site may be further oxidized to CO₂ at a rate dependent on the temperature, amount of CO and O₂, water partial pressure, and active metals on the catalyst.

To mitigate CO emissions at low regenerator temperature, we add a non-platinum CO promoter to limit the NO_x. Other solutions include increasing 1) your delta coke, 2) the pressure in the regenerator, or 3) the mixing by modifying the regenerator. The amount of NO_x emitted from the regenerator is highly dependent upon several variables such as operation regenerator style, excess O₂, promoter concentration co-distribution, feed nitrogen, and dense bed temperatures. So, there are many variables that determine the overall NO_x equation. NO_x formation chemistry inside the regenerator is difficult to pin down. Studies have shown that about half of the feed nitrogen becomes coke on the catalyst, but only a small portion of that actually becomes NO_x. It is also believed that NO_x emissions are limited by the reaction of CO plus NO (nitric oxide) to form N₂ (nitrogen gas) and CO₂. Thus, when you have platinum CO promoters added to the unit, CO is converted to CO₂ so quickly that there is less CO available for that reaction to occur.

We do have an experience of the regenerator being in true countercurrent flow. With platinum promoter in the unit, it is able to run NO_x levels that are very low; but, I will say that is a rarity. In our system, if there is normally a platinum promoter, then you will see elevated NO_x levels. In partial-burn operation, there is always CO available to react with the NO_x; so emissions are lower. Good coke and air distribution is important to ensure that the concentration of CO, O₂, and NO_x are evenly distributed throughout the regenerator. The results have been better and more efficient control of the burn zone so that oxygen is used more efficiently and the regenerator can be operated at lower levels of excess oxygen to completely burn the coke to CO₂. Generally, you do not need to use platinum promoter. Finally, uniform residence time distribution minimizes the duration that spent catalyst remains the regenerator.

Importance of Good Mixing and Burn Control in the Regen

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- Oxygen is used more efficiently, requiring lower levels of O_2 to completely burn the coke to CO_2 while minimizing the CO emissions
- Generally no Platinum combustion promoter is needed (at design rates) to accelerate the burn to completion
- The uniform residence time distribution permits the time spent in the Regenerator to be minimized

Due to the interaction between CO, NO_x, and the FCC regenerator, I recommend that you actually conduct testing to determine the tipping point where you start going up in CO emissions because there are benefits from lowering the oxygen at that time. Running O₂ in excess slightly above that tipping point provides a good NO_x baseline of your minimum level on the unit. If that level is still too high, then you have other options which include LoTO_x[™], WGS+[™], CONO_x[™], and SCR (selective catalytic reduction). We have all of these applications across our system. We have very little experience with NO_x reduction additives.

GIM (Technip Stone & Webster)

The low regen temperature used to be beneficial. However, with the advent of tight oil and light feed stock, actually too much of a good thing is now bad. So let us first consider what causes some of these low regen temperature phenomena.

The first cause is a result of better feed stock qualities, such as lower Conradson carbon, lower nitrogen, and metals. Second, lower operating severities, such as lower reactor outlet temperature and lower catalyst activity, will reduce regenerator temperatures. The third cause is catalyst regeneration, including full- versus partial-burn, CO promoters (platinum-based or non-platinum-based), and supplemental oxygen that has been turned off.

Jeff described many of these aspects, but I thought it would be worthwhile to summarize all of the factors into three main categories. One is, obviously, the combustion kinetics. Second is the hardware of the actual generator design; and third, to a certain aspect, are the feed contaminants such as feed nitrogen. In terms of combustion kinetics, a lot of these items have been discussed multiple times in past panels, so I will just go over the basics and summarize them. The lower regenerator temperature increases the CO but decreases the NO_x or NO₂; the promoter lowers the CO. But in terms of the distinction between a platinum and non-platinum base, the promoters can be either increased NO₂ or NO₂ neutral. The higher O₂ concentration lowers the CO and increases the NO_x. Again, these are some of the factors that you can use to counteract the formation of CO and NO₂.

CO & NO_x at Low Regenerator Temperature

		CO	NO _x
Combustion kinetics	Regenerator Temperature	Lower temperature increases CO	Lower temperature decreases NO _x
	CO promoter	Promoter (platinum or non-platinum) lowers CO	Pt-based promoter increases NO _x . Non Pt-based promoter are neutral to NO _x formation
	Excess O ₂	Higher O ₂ level lowers CO	Higher O ₂ level increases NO _x
	Torch Oil	Usage of torch oil lowers CO	Usage of torch oil increases NO _x
Hardware	Regenerator Air distribution		Partial burn reduces NO _x Poor distribution increases NO _x
	Catalyst distribution		Poor distribution increases NO _x
	Nitrogen		A small percentage of feed nitrogen forms NO _x . Small correlation between feed nitrogen and NO _x .

BART de GRAAF (Johnson Matthey INTERCAT, Inc.)

All of the speakers mentioned that the low temperature does affect the CO oxidation and the formation of NO_x. The nitrogen kinetics in the regenerator are not affected by the lower temperature. Nitrogen in coke can be converted into nitrogen in NO_x, hydrocyanide, and ammonia. As was suggested, non-platinum combustion promoter can be used to steer the oxidation reactions from HCN and NH₃ towards N₂ instead of NO_x. Partial-burn operation is one example where you can see that the CO concentration does affect high NO_x. But at the same time, in a partial-burn operation, after the CO boiler, you frequently see a higher NO_x level than you would have in a full-burn operation because of the high temperature oxidation in CO boiler.

KEN BRUNO (Albemarle Corporation)

I want to point out that Albemarle has a detailed answer in the Answer Book. But in summary, Albemarle's non-platinum promoter, ElimiNO_x[™], provides high CO promotion, excellent afterburn, and minimal impact on NO_x emissions.

ROBERT "BOB" LUDOLPH [Shell Global Solutions (US) Inc.]

If you are an oxygen enrichment operator or considering oxygen enrichment, this is your opportunity to raise your bed temperature at the same coke burning rate and shift the CO and NO_x distribution within the bed. In turn, the control of NO_x and CO emissions could improve.

MICHAEL WARDINSKY (Phillips 66)

We have done a lot of modeling around NO_x and CO emissions for additive use. We have seen NO_x emissions decrease with higher regen temperatures in almost all of the modeling cases. From our experience, we also know that the non-platinum promoters can increase NO_x emission, although not as severely as a platinum-based promoter. We have moved partial-burn units from deep partial-burn to full-burn and observed the NO_x emissions decrease substantially. I think it was from the gentleman from INTERCAT who mentioned that in partial-burn, you are releasing ammonia and HCN (hydrogen cyanide) off the regenerator in greater quantities than during full-burn operations. However, these reduced nitrogen species are combusted across the CO boiler to NO_x, so your partial-burn units always appear to emit higher NO_x emissions than operating in full-burn, even after accounting for thermal NO_x generated in the CO boiler.

JEFFREY BULL (Valero Energy Corporation)

CO emissions will increase if the regenerator falls below a certain temperature threshold. That temperature threshold varies based on the regenerator configuration and the type of air distribution. In general, well mixed regenerators with longer residence times can be run at significantly lower temperatures before CO emissions increase compared to a poorly mixed regenerator with lower residence times. In the absence of a CO combustor promoter, large variations in CO₂/CO ratios are observed. At the catalyst surface, it is believed that the ratio of CO₂/CO is an intrinsic function of the temperature at the burning site ("Arthur's ratio"). However, the CO exiting the burning site may be further oxidized to CO₂ at a rate dependent on temperature; CO, O₂, and H₂O partial pressures; active metals on the catalyst; carbon/oxygen distributions within the fluidized bed; and even the catalyst presence.

To mitigate CO emissions at low regenerator temperatures you can:

- Add non-Pt (platinum) CO promoter to limit NO_x,
- Modify your operation to increase your delta coke (catalyst or operational changes),
- Increase pressure in the regenerator, and/or
- Modify the regenerator to increase mixing.

The amount of NO_x emitted from the regenerator is highly dependent upon several variables such as mode of operation, regenerator style, excess O₂, promoter concentration, coke distribution, feed N₂, and dense bed temperature. Studies have shown that about half of the feed N₂ goes to coke on catalyst, but only a small portion of the N₂ in coke goes to NO_x. It is believed that the NO_x emission is limited by the reaction of CO + NO to form N₂ and CO₂. Thus, when Pt CO promoter is added to a unit, CO is converted to CO₂ so quickly that there is less CO available to react with the NO_x; so NO_x emissions increase. We do have experience with a regenerator that is in true countercurrent flow, and the operator is able to run at low NO_x levels with platinum promoter in the unit. In a partial-burn operation, there is always CO available to react with the NO_x formed; so, emissions are lower. Good coke and air distribution are important so that concentrations of CO, O₂, and NO_x are evenly distributed throughout the regenerator.

The results of the better, more efficient control of the burn zone in a regenerator are that:

- Oxygen is used more efficiently so that lower levels of excess oxygen are required to completely burn the coke to CO₂ while minimizing CO emissions.
- Generally, no Pt combustion promoter is needed (at design rates) to accelerate the burn to completion.
- The uniform residence time distribution permits the time spent in the regenerator to be minimized.

Due to the interaction between CO and NO_x in an FCC regenerator, testing should be conducted for your individual regenerator to determine the "tipping point" where a reduction in excess O₂ causes CO emissions to increase dramatically. Running at an excess O₂ slightly higher than the "tipping point" provides a baseline NO_x that you can expect for your unit. If this level is too high, then you will either need to modify your regenerator for better mixing or use an alternate method of NO_x reduction like

LoTOx™, WGS+™, CONOx™, or an SCR. We have four LoTOx™ applications, one WGS+, one CONOx™, and one SCR in our system. In some cases, a catalyst additive can reduce NOx, but we have limited experience with this application.

STEVE GIM (Technip Stone & Webster)

Why lower regenerator temperatures? Let us first examine some of the factors leading to lower regenerator temperatures: first, better feedstock qualities (such as lower Conradson carbon), lower nitrogen, and metals. Second, lower operating severities, such as lower reactor outlet temperature and lower catalyst activity, will lower regenerator temperatures. Third, catalyst regeneration, including full versus partial-burn, CO promoters (platinum-based or non-platinum-based), and supplemental oxygen turned off are additional options.

Factors Directly Affecting CO and NOx: Many of these directly affect the formation of both CO and NOx in the regenerator. Some of these factors influence the formation of these two species in opposite direction. I have summarized these factors into three categories and their directional changes of the CO and NOx. Many of these items are obvious and have been extensively discussed in the past panels, but I thought it would be a good summary.

		CO	NO _x
Combustion Kinetics	Regenerator Temperature	Lower temperature increases CO.	Lower temperature decreases NO _x .
	CO Promoter	Promoter (platinum or non-platinum) lowers CO.	Pt-based promoter increases NO _x . Non-Pt-based promoters are neutral to NO _x formation.
	Excess O ₂ level	Higher O ₂ level lowers CO.	Higher O ₂ level increases NO _x .
	Torch Oil	Usage of torch oils lower CO.	Usage of torch oil increases NO _x .
Hardware	Regenerator Design		Partial-burn reduces NO _x .
	Air Distribution		Poor distribution increases NO _x .
	Catalyst Distribution		Poor distribution increases NO _x .
Feedstock Contaminants	Nitrogen		A small percentage of feed nitrogen forms NO _x . Small correlation between feed nitrogen and NO _x .

Interactions Between CO and NOx: Reductant-like CO converts NOx to elemental nitrogen in the presence of O2. Lower regenerator temperature can be the direct result of higher CO to CO2 ratio in partial-burn units, which in turn will lower the NOx.

CHRIS STEVES (Norton Engineering)

The impact of low regenerator temperature on CO and NOx emissions can be very unit-specific, depending especially on regenerator design and the distribution of air and coke in the regenerator. In full-burn units, operation at low regenerator temperature will generally result in higher CO emissions and lower NOx emissions. The use of CO promoter can help in reducing CO formation, but use of platinum-based promoters is well documented as increasing NOx emissions. Non-Pt-based promoters are widely used today to allow for control of CO (and afterburning associated with CO) while limiting NOx emissions.

RYAN NICKELL (Albemarle Corporation)

Though not directly stated, this question is most applicable to FCC units concerned with after-burn. Lowering the regenerator temperature can indeed lead to an increase in CO and NO to N2 and CO2. A platinum-based combustion promoter can be used to reduce CO emissions with excellent success. However, NO will increase as intermediates, such as HCN and NH3 (ammonia), are also oxidized by platinum. As a result, many refiners prefer a non-Pt-based promoter such as Albemarle's ElimiNOx™. This additive provides high CO promotion activity but acts less on the aforementioned intermediates containing nitrogen. ElimiNOx™ provides excellent after-burn control and minimal impact on NOx emissions.

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