FCC Regenerator Off Gas:
Cost Effective Emissions Control

Chris Leger, David Lenhert, and John Scalise, all with Praxair, Inc.*

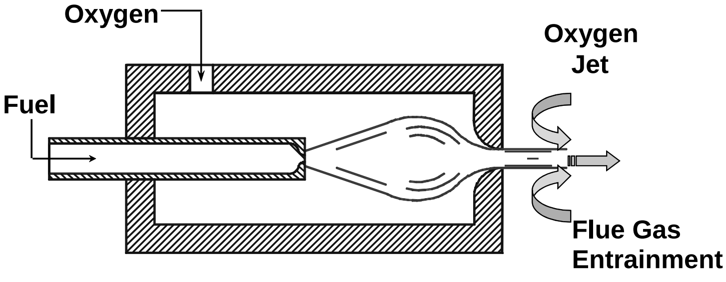
**Presenter Contact Information:*

Chris Leger
Refining Business Development Manager
Praxair, Inc.
1585 Sawdust Road
Spring, TX 77380 USA

Phone: 1-800-772-9247
Email: Chris_Leger@Praxair.com

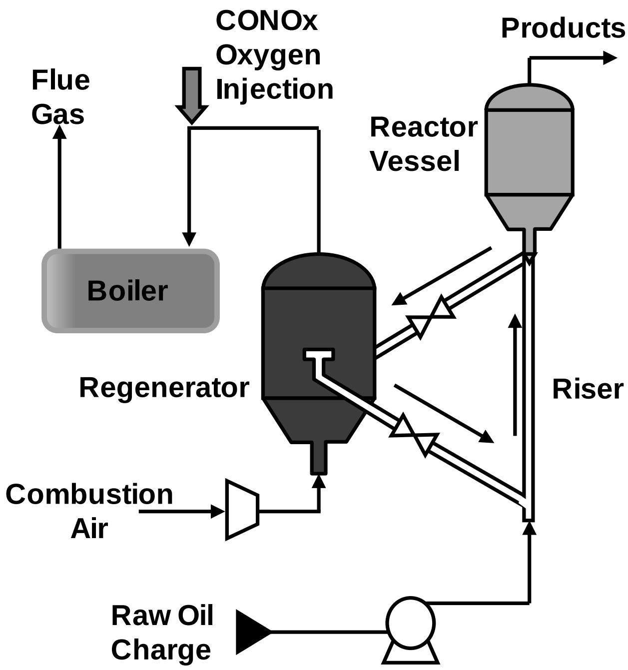
I. Introduction

FCC regenerator flue gas is one of the larger CO and NOx emission sources in the refinery and will continue to be regulated heavily in attempts to minimize the refinery's environmental impact. Praxair's CONOx technology[1] is a flexible, low capital cost technology that significantly reduces both CO and NOx emissions and energy usage in CO boilers. Due to the low capital cost of implementing this technology, it can be used in conjunction with other emissions control devices to achieve an even larger reduction in emissions. This technology also may enable more profitable operation through increased feed rate, improved yield, or reduced fuel consumption.



Praxair's CONOx technology is based on a specialized lance[2], which injects heated oxygen into the flue gas duct between the regenerator and the CO boiler or heat recovery boiler. The key to the technology is a high velocity jet of heated oxygen that rapidly mixes with process gases. The lance also creates high concentrations of free radicals, enabling rapid reactions at lower bulk temperatures. Due to the extraordinary jet mixing characteristics and the free radicals achieved, the CONOx technology is significantly more effective at initiating low temperature reactions than a standard oxygen jet.

For full burn regenerators, the CONOx technology enables operators to minimize NOx emissions by operating the regenerator at very low excess oxygen levels (e.g., < 1% excess O_2), causing CO levels to rise. Any CO slip in the flue gas duct is effectively oxidized at temperatures less than 760^oC, which is usually manageable within existing flue gas ductwork without modification. These temperatures are not high enough to create thermal NOx, so no additional NOx is created. Thus, stack emission requirements for both NOx and CO are met.



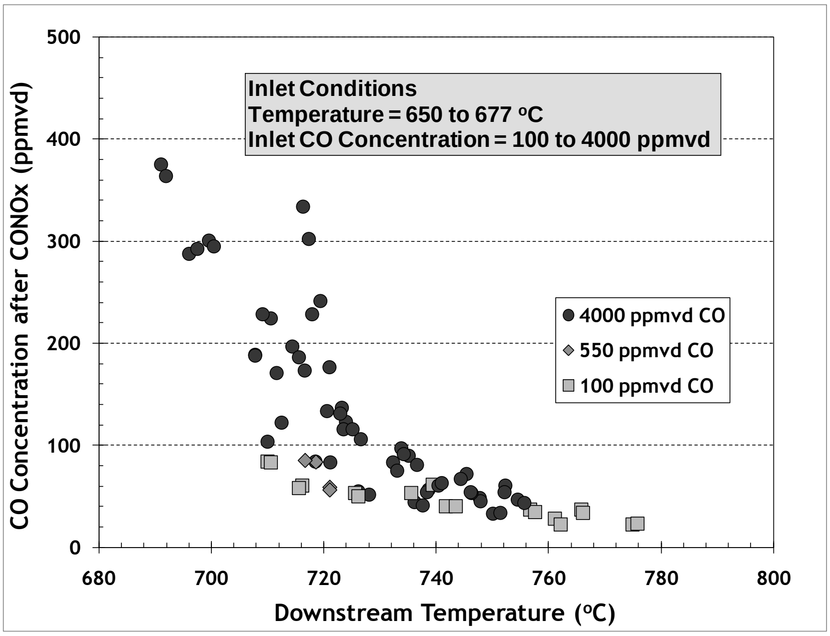
In partial burn regenerators, the lance is operated such that the flue gas remains deficient in oxygen after all oxygen from the lance is consumed, resulting in significant reductions in NOx precursors, namely NH_3 and HCN. By reducing the availability of NOx precursors in the duct prior to conversion to NOx in the CO boiler, stack NOx can be reduced considerably. Consequently, Praxair's CONOx technology can be used to debottleneck operations due to CO boiler or NOx limits, thus enabling a wider regenerator operating window while still achieving low NOx emissions.

The actual amount of NOx reduction in full and partial burn units will vary depending on feed, catalyst properties, regenerator design, CO boiler, and other constraints on the units. However, NOx reductions of up to 60% can be achieved in both full burn and partial burn regenerators. This paper reviews several case studies where Praxair's CONOx technology can be used to reduce FCC stack emissions while improving productivity and in one case reducing total fuel consumption.

II. Full Burn Operation

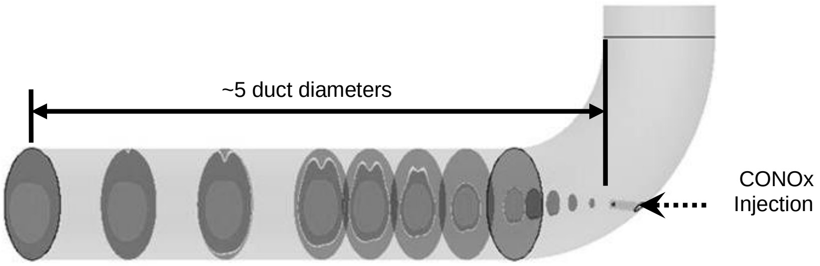
In full burn units Praxair's CONOx technology destroys CO in the regenerator flue gas without increasing NOx. This unique ability allows the regenerator to be operated with less excess oxygen resulting in significantly less NOx being produced.

To characterize the performance under full burn conditions, a test program was developed and completed at Praxair's Technology Center in a pilot-scale test furnace. The pilot furnace allowed precise control of the temperature and composition of the flue gas. The test program investigated the effects of flue gas temperature, composition, and lance operating conditions on CO and NOx emissions. The figure below shows representative samples of the experimental results for CO concentration after Praxair's CONOx technology for several inlet conditions against the resulting flue gas temperatures. Inlet CO concentrations had little impact on the resulting downstream CO concentration, provided sufficient oxidant was injected to fully mix with the flue gases. Downstream bulk temperature was the dominant variable controlling outlet CO concentrations, and for final flue gas temperatures of 732^{o}C or higher, CO levels of less than 100 part per million by volume dry basis (ppmvd) were achieved. This superior CO oxidation performance is due to the excellent mixing capability of the lance as well as the high reactivity of the heated oxygen jet. Corresponding NOx measurements showed no generation of NOx during the CO oxidation tests.



III. Case Study 1: Full Burn Operation

Both CO and NOx annual emission limits were limiting one refiner. In this case, the CO levels required to meet the annual emissions limit was easily achieved using CONOx technology as long as adequate mixing was achieved. The ability of the lance to achieve mixing within five duct diameters was critical to meeting the required emissions. Praxair used CFD modeling to determine the best location for installing the lance, as shown below. The CFD predictions of the lance in the 1.5m diameter flue gas line show that within five duct diameters, all of the flue gas has mixed sufficiently with the reactive oxygen jet to destroy the CO.

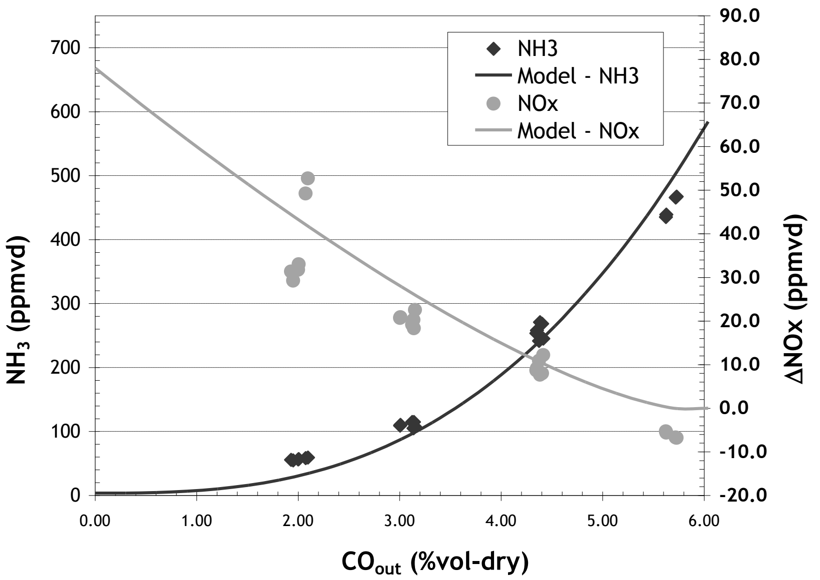


The refinery evaluated the regenerator NOx response to excess oxygen by reducing excess oxygen and allowing CO to increase. They determined that their NOx goals could be achieved by operating at reduced excess oxygen while maintaining full charge rates. CO levels leaving the regenerator would increase, but the CONOx technology would oxidize CO to acceptable levels. Since refinery economics did not always dictate operating the FCC at full rate, the low installed cost and ability to only operate the lance as desired made Praxair's CONOx technology a great fit for this situation.

IV. Partial Burn Operation

As noted previously, the flue gas from a partial burn FCC regenerator usually contains little or no NOx. A majority of the NOx is formed downstream in the CO boiler or incinerator when the NOx precursors (NH_3 and HCN) in the regenerator flue gas are combusted. Praxair's CONOx technology initiates destruction of these precursors with little or no generation of NOx. Using this technology can typically reduce the NOx leaving the CO boiler between 30% and 60%. To characterize the performance of the lance under partial burn conditions, a test program was conducted in the same pilot scale test furnace used for the full burn tests. The test program investigated the effects of flue gas temperature, composition, and lance operating conditions on CO, NOx, and NH_3 concentrations under conditions representative of partial burn operation.

The graph below demonstrates the capability of the CONOx technology to destroy NOx precursors with little or no NOx increase. The graph shows a representative sample of the experimental measurements for NH_3 and NOx at inlet concentrations of 6.0% CO and 580ppm NH_3. The lines in the graph represent the predictions of a proprietary engineering model. NH_3 concentration decays quite rapidly as oxygen flow through the lance is increased (equivalent to decreasing % CO_{out} or moving to the left on the graph). Most of the NH_3 can be destroyed with only a modest amount being converted to NOx. In fact, NH_3 was destroyed preferentially to CO for a given oxygen flow from the lance. Furthermore, these experiments illustrate an important feature observed with the CONOx technology: there is no NOx generated and perhaps some NOx reduction when only a small percentage of the CO is destroyed with the lance. Adding more oxygen to drive more destruction of NH_3 causes the NOx to trend upward. Thus, minimum stack NOx is a balance between NOx formed by the lance and the NOx formed by the remaining precursors converted to NOx in the CO boiler. A refiner can also leverage the ability of Praxair's CONOx technology to destroy the NOx precursors to go deeper into partial burn while maintaining or improving NOx performance.

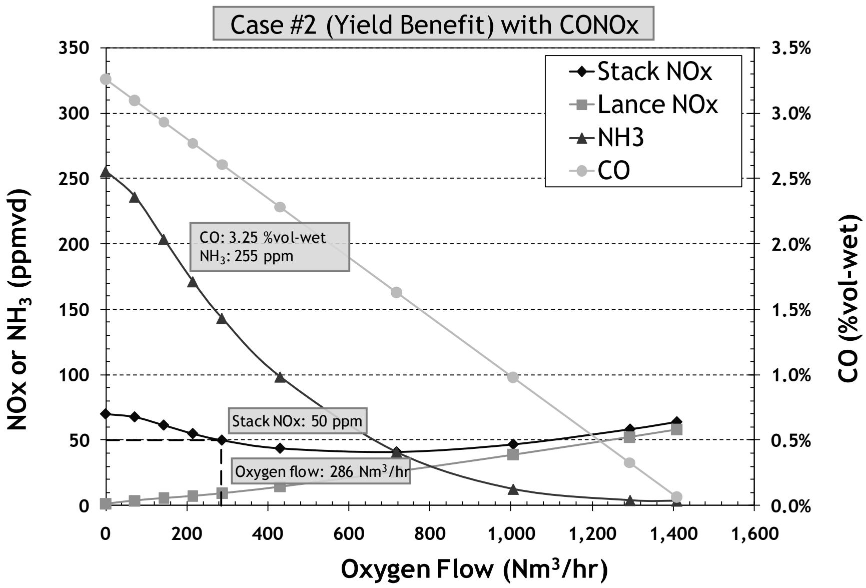


As show above, an engineering model has been developed based on regressions over a wide range of initial conditions investigated in the pilot scale facility. This model can be used to predict CONOx performance in partial burn flue gas. The model calculates CONOx NH_3 destruction and conversion to NOx as a function of initial concentrations and CO residual values. The engineering model then uses these intermediate concentrations and additional assumptions about CO boiler performance to predict stack NOx. The model allows the quick evaluation of CONOx technology for a specific refiner's operating conditions to predict emissions performance and energy benefits, as will be shown in the following cases.

V. Case Study 2: Partial burn operation – Yield Benefit

A refiner was struggling to control NOx from the regenerator and was taking a significant conversion penalty to keep NOx emissions below permitted limits. In this case, an increase in flue gas CO of 0.75% would increase the yield of motor fuel products by about 0.5%. The yield improvement is based on operating at a higher catalyst to oil ratio at constant reactor temperature, allowed by the lower regenerator temperature. However, the higher CO levels also bring higher levels of NOx precursors and ultimately higher stack NOx emissions. Applying Praxair's CONOx technology would allow them to go deeper into partial burn to achieve the yield benefit without exceeding their NOx limits.

The study showed that the refiner could leverage the technology's ability to destroy the NOx precursors to maintain their current NOx performance (50ppmvd) when operating deeper in partial burn at 3.25 %vol-wet CO, up from the current level of 2.5%. The graph below shows the engineering model predictions. At zero oxygen flow, stack NOx emissions are attributable solely to the CO boiler combusting NOx precursors, and the duct temperature is 724^{o}C. As oxygen flow increases, stack NOx drops as NH_3 is initially destroyed, and for low oxygen flows, performance is limited by incomplete mixing. As oxygen flow is increased still further, mixing becomes complete and a minimum stack NOx level below 40 ppmvd is achieved. However, this level of reduction is not necessary to meet the permit level



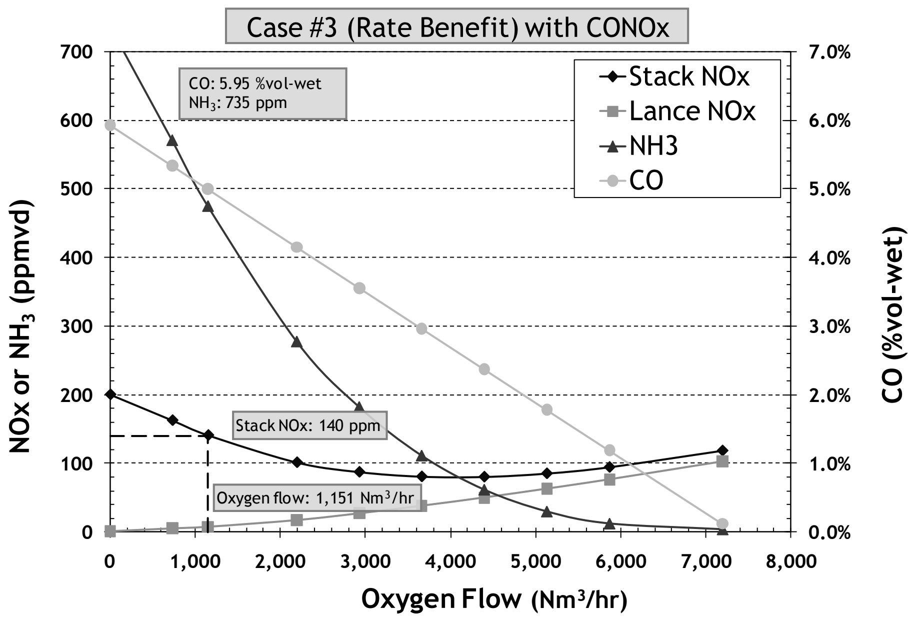
of 50 ppmvd, and the temperature rise is excessive. Operating at 286 Nm^3/hr of oxygen results in approximately 50 ppmvd stack NOx and flue duct temperatures around 776^oC while minimizing oxygen cost. Lower NOx levels could be achieved at higher oxygen flow rates, but some accommodations would have to be made for the higher duct temperatures. This illustrates another key advantage of the CONOx technology; the lance can be tuned very rapidly to deliver the exact amount of NOx reduction needed at that time. A small increase in oxygen flow could mitigate a spike in stack NOx emissions, or alternately the oxygen could be decreased (minimizing OPEX) if stack emissions are lower than permit levels.

Case Study 2 Process Data		***Base Case***	***Case 2 with CONOx***	***Difference***	***€/day***
FCCU Rate (bbl/day @ €5.36/bbl)		18,900	18,900	-	-
FCCU Yield Improvement (%)		-	0.5%	0.5%	€2,500
Regenerator CO Concentration (%vol-wet)		2.50	3.25	0.75	-
Regenerator Exhaust Temperature (°C)		729	724	(5)	-
Oxygen Flow	**(Nm^3/hr)**	-	286.7	286.7	(€776)
	(t/day @ €79/t)	-	9.82	9.82	
Fuel Flow	**(Nm^3/hr)**	-	17.9	17.9	(€46)
	(MJ/hr @ €0.003/MJ)	-	631.7	631.7	
COB Inlet CO Concentration (%vol-wet)		2.50	2.60	0.10	-
COB Inlet Temperature (°C)		729	776	47	-
COB Fuel Gas Flow	**(Nm^3/hr)**	1,548.2	1,339.6	(208.6)	€390
	(MJ/hr @ €0.003/MJ)	39,631.4	34,291.3	(5,340.1)	
COB Steam Rate (t/hr @ 1.1 x Fuel Cost)		43.99	43.99	-	-
Total Stack Flow (Nm^3/hr)		110,452	105,726	(4,726)	-
				Net	€2,068
				Simple Payback	0.95 years

The refinery determined that the yield benefit covered the required capital payback and operating expense associated with the installation of Praxair's CONOx technology. This was mostly the result of the low installed cost for the system. In addition, implementing flue gas duct modifications to accommodate a larger temperature rise would allow for further stack NOx reductions to meet future emission limits.

VI. Case Study 3: Partial burn operation – Rate Benefit

A refiner was struggling to control NOx from the regenerator and was taking a significant rate penalty to keep NOx emissions below permitted limits. When applied, the CONOx technology would allow them to increase rate and maintain current NOx levels (140 ppmvd) by destroying the NOx precursors while operating deeper in partial burn at the increased rate. The graph below shows the predictions of the engineering model for the higher rate case. At zero oxygen flow, stack NOx emissions are attributable solely to the CO boiler combusting NOx precursors and would be above permit limits. As oxygen flow increases, a minimum stack NOx level of 70 ppmvd is achieved. However, this level of reduction is not necessary to meet the permit level of 140ppmvd, and the temperature rise is excessive. To minimize oxygen usage and thus operating cost, an oxygen flow rate of approximately 1,151 Nm^3/hr would be preferred, giving approximately 140 ppmvd stack NOx and flue duct temperatures around 791°C.

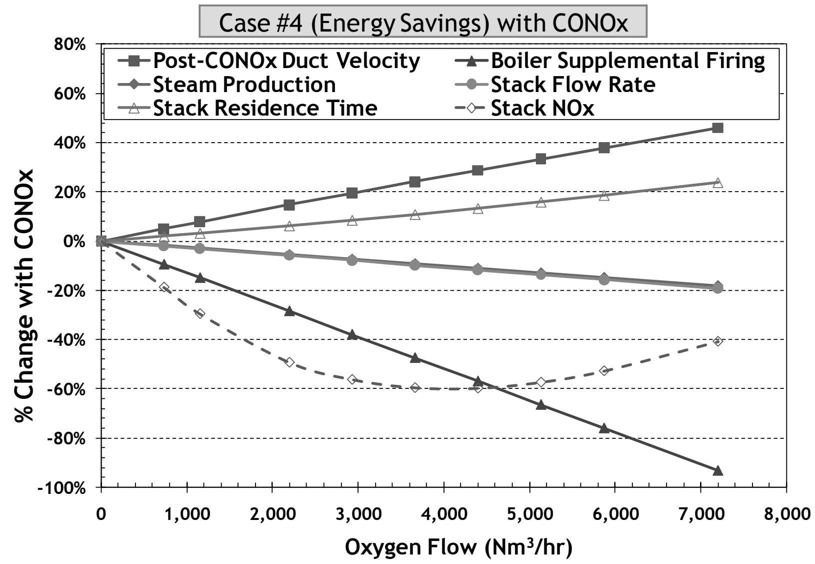


The refinery determined that the rate benefit could easily cover the required capital payback and operating expense associated with the installation of the lance. This was mostly the result of the low installed cost for the system. With some flue gas piping modifications to accommodate a higher temperature, the outlet NOx could be lowered further by leveraging the capabilities of the CONOx technology.

Case Study 3 Process Data	*Reduced Rate*	*Full Rate with CONOx*	*Difference*	*€/day*
FCCU Rate (bbl/day @ €5.36/bbl)	55,000	57,000	2,000	€10,720
FCCU Yield Improvement (%)	-	-	-	-
Regenerator CO Concentration (%vol-wet)	4.25	5.95	1.70	-
Regenerator Exhaust Temperature (°C)	724	715	(9)	-
Oxygen Flow **(Nm^3/hr)**	-	1,151.0	1,151.0	(€3,115)
Oxygen Flow **(t/day @ €79/t)**	-	39.43	39.43	
Fuel Flow **(Nm^3/hr)**	-	71.9	71.9	(€330)
Fuel Flow **(MJ/hr @ €0.0054/MJ)**	-	2,536.4	2,536.4	
COB Inlet CO Concentration (%vol-wet)	4.25	5.00	0.75	-
COB Inlet Temperature (°C)	724	791	67	-
COB Fuel Gas Flow **(Nm^3/hr)**	3,882.7	3,882.7	0.00	€0
COB Fuel Gas Flow **(MJ/hr @ €0.0054/MJ)**	161,156.9	161,156.9	0.00	
COB Steam Rate (t/hr @ 1.1 x Fuel Cost)	150.68	167.88	17.20	€5,721
Total Stack Flow (Nm^3/hr)	297,583	303,574	5,991	-
			Net	€12,996
			Simple Payback	0.15 years

VII. Case Study 4: Partial burn operation – Energy Savings

A refiner wanted to reduce CO boiler operating costs. Since Praxair's CONOx technology reacts oxygen with CO in the flue gas line, there will be a drop in CO and a rise in flue gas temperature going to the CO boiler. This allows a reduction in CO boiler supplemental fuel firing and steam make. When CO boiler steam production can be reduced (steam long) or moved to a more efficient boiler, the use of CONOx technology can reduce fuel costs. In the figure below, burner fuel gas and combustion air have been adjusted to maintain constant excess oxygen and firebox temperature in the CO boiler to maintain stack CO performance. The total flue gas from the CO boiler (shown in the figure as Stack Flow Rate) is reduced as combustion air is replaced by oxygen from the lance. Lower combustion air significantly reduces boiler supplemental firing, as less fuel gas and corresponding air are needed to maintain firebox temperatures. This increases flue gas residence time, which improves operation of downstream pollution control equipment. Although supplemental firing could be eliminated in this case, steam production would only decrease by 19%.



The CO boiler fuel savings covers the capital payback and operating expense associated with Praxair's CONOx technology. As a side benefit, stack NOx is reduced by 30% or more. The low capital cost and ability to tune operation according to economic needs make this technology well suited for cost conscious times.

Case Study 4 Process Data		***Base Case***	***Case 4 with CONOx***	***Difference***	***€/day***
FCCU Rate (bbl/day @ €5.36/bbl)		57,000	57,000	-	-
FCCU Yield Improvement (%)		-	-	-	-
Regenerator CO Concentration (%vol-wet)		5.95	5.95	-	-
Regenerator Exhaust Temperature (ºC)		715	715	-	-
Oxygen Flow	**(Nm³/hr)** **(t/day @ €79/t)**	- -	1,151.0 39.43	1,151.0 39.43	(€3,115)
Fuel Flow	**(Nm³/hr)** **(MJ/hr @ €0.0105/MJ)**	- -	71.9 2,536.4	71.9 2,536.4	(€639)
COB Inlet CO Concentration (%vol-wet)		5.90	5.00	(0.90)	-
COB Inlet Temperature (ºC)		724	791	67	-
COB Fuel Gas Flow	**(Nm³/hr)** **(MJ/hr @ €0.0105/MJ)**	2,754.1 114,331.3	2,343.3 97,262.7	(410.8) (17,068.6)	€4,299
COB Steam Rate (t/hr @ 0.0 x Fuel Cost)		150.68	146.32	(4.36)	€0.00
Total Stack Flow (Nm³/hr)		293,329	284,321	(9,008)	-
				Net	€491
				Simple Payback	4.0 years

Summary

Praxair has developed a unique technology, which injects heated oxygen into the FCC regenerator flue gas duct between the regenerator and CO boiler or heat recovery unit. In partial burn units, CONOx technology destroys NOx precursors, such as ammonia and hydrogen cyanide, before they can be converted to NOx in the CO boiler. This technology also converts a portion of the CO to CO_2, thus reducing the air and fuel requirements in the CO boiler. In full burn units, CONOx technology enables operators to minimize NOx emissions when operating the regenerator at very low excess oxygen levels. Any CO slip from the regenerator would then be converted to CO_2 by the oxygen lance. In either case, the CONOx technology helps refiners meet both NOx and CO stack emission requirements. In four case studies, the CONOx technology is shown to provide NOx emission reduction while achieving other operational benefits for net economic gains.

Major points about Praxair's CONOx technology are:

- Provides additional flexibility for FCCs to meet CO and NOx emission limits as conditions or requirements change.
- Achieves up to 60% reductions in stack NOx for both full and partial burn units.
- Is a relatively low capital cost technology.
- Can be used in combination with other control technologies to achieve more cost effective NOx control.
- Effectively increases regenerator and CO boiler capacity due to the operating flexibility provided by CONOx technology.

VIII. References

[1] Reduction of CO and NOx in Regenerator Flue Gas, US Patent No. 7,470,412.

[2] Thermal Nozzle Combustion Method, US Patent No. 5,266,024; EU Patent No. EP0590572.