

"Nitrogen Chemistry and NO_x Control in a Fluid Catalytic Cracking Regenerator" was published in 1997 in *Industrial and Engineering Chemistry Research* and has been subsequently cited in more than 100 scientific papers. This fundamental work developed a complete nitrogen balance around the FCC and demonstrated that NO_x from the FCC regenerator is derived from feed nitrogen and not "thermal NO_x." This work was done in Grace's DCR™ Pilot Plant. The pilot plant scale allowed for studying process conditions not possible in a commercial unit, such as the elegant solution of using an oxygen/argon mix in the regenerator instead of air (oxygen/nitrogen) so the only nitrogen input to the FCC was feed nitrogen.

Today, refineries around the globe look to Grace to reduce NO_x and support environmental compliance, through both our operational insights and our products such as our DENOX® additive for standalone NO_x reduction.



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Nitrogen Chemistry and NO_x Control in a Fluid Catalytic Cracking Regenerator

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Emission of NO_x from the fluid catalytic cracking (FCC) regenerator is increasingly controlled by various state and local regulations. The FCC regenerator poses a very challenging environment for controlling NO_x. Other than NO, the high-temperature flue gas contains O_2, CO, CO_2, SO_2, SO_3, H_2O, and possibly other nitrogen or sulfur species. In this paper, we will first present a complete nitrogen balance around the fluid catalytic cracking unit by using a circulating pilot plant with continuous regeneration. We will also discuss the transformation of nitrogen species during the cracking and catalyst regeneration process, which has direct implications on the formation and reduction of NO_x in the regenerator. Pilot plant or commercial data on the effect of operating conditions, cracking feedstocks, and CO combustion promoter usage on NO_x emission will be discussed. With both thermodynamic analysis as well as experiments, we will show that the so-called "thermal NO_x" does not contribute to the FCC regenerator NO_x emission. On the basis of the understanding of the nitrogen chemistry we have obtained, we have successfully developed different catalytic NO_x control technologies for the FCC regenerator. Direct NO_x reduction additives and a new generation of CO combustion promoters which significantly reduced NO_x emissions will be discussed. Both laboratory and commercial trial data on some of the NO_x control additives as well as the mechanism for the NO_x control additives will also be presented. Finally, the future directions for NO_x control will be discussed.

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Emission of NO_x (i.e., NO, NO_2, and N_2O) from the fluid catalytic cracking regenerator is increasingly controlled by various state and local regulations. The FCC regenerator poses a very challenging environment for controlling NO_x. Other than NO, the high-temperature flue gas contains O_2, CO, CO_2, SO_2, SO_3, H_2O, and possibly other nitrogen oxygen species. Any NO_x control technology has to be designed in a way that it neither interferes with the catalytic cracking reaction in the riser nor substantially increases the emissions of other pollutants, e.g., CO or SO_2. NO_x levels in the FCC regenerator flue gas are typically in the range of 100-500 ppm. NO is the primary component of NO_x from the FCC regenerator. NO_2 is formed only after being released to the air, while N_2O exists typically at very low levels. The current paper will mostly focus on the emission and control of NO. In addition to the level of feed nitrogen, it is also known that operating conditions and hardware design of the regenerator can significantly affect NO_x emission. For example, higher excess oxygen in the flue gas is known to correlate with higher NO_x emission, which has led to the notion that NO_x is formed from the oxidation of molecular nitrogen from the air, or the so-called thermal NO_x. Until very recently, a few systematic studies existed on the formation and control of nitrogen oxide in the FCC regenerator. In the present paper, we will try to present and review what we learned about the NO_x chemistry through laboratory experiments on a pilot plant FCC unit and discuss the available approaches to control NO emission from FCC regenerators. The future directions of NO_x control in FCC will also be discussed.

Nitrogen Balance around FCC Unit

In order to understand the nitrogen chemistry in the regenerator, it is important to know where and how much of the feed nitrogen ends up in each of the FCC product streams. To answer these questions, we conducted nitrogen balance experiments in the Davison Circulating Riser (DCR), which is a pilot scale adiabatic circulating riser with continuous regeneration (Young, 1993; Zhao et al., 1996). Some of the preliminary nitrogen balance results have been presented in a previous paper (Peters et al., 1995). This unit processes about 1 kg of feed/h. All the operations are continuous, and the coked catalyst is continuously regenerated as in a commercial FCC unit. For the nitrogen balance experiments, two feedstocks with nitrogen contents of 0.12-0.32 wt% were processed in the unit. The feed properties are shown in Table 1. A commercial equilibrium catalyst was used for the experiments. The catalyst properties are shown in Table 2. All the product streams were collected for yield as well as nitrogen analyzes by gas chromatography and Leco analyzer. In order to exclude the nitrogen from air from our nitrogen experiments, we used a mixture of argon with 5% oxygen to regenerate the catalyst.

Description	Feed A F92-444	Feed B F93-247
API gravity @ 15°C	25.8	21.1
sulfur, wt%	0.3	0.77
total nitrogen, wt%	0.12	0.32
basic nitrogen, wt%	0.052	0.12
Conradson carbon, wt%	0.53	0.12
simulated distillation, vol %,°C		
10	298	288
50	421	403
90	530	495
K factor	11.78	11.39

Table 1. Feed Properties

Chemical Analysis (As Received)		
Al_2O_3	wt%	30.80
SiO_2	wt%	63.40
RE_2O_3	wt%	0.96
Na_2O	wt%	0.57
SO_4	wt%	0.35
Ni	wt%	0.166
V	wt%	0.119
Physical Properties (Thermal, 3 h/537°C)		
surface area	m^2/g	170
ZSA	m^2/g	139
MSA	m^2/g	31
peak height		
unit cell size	nm	2.427
ABD	g/cm^3	0.81

Table 2. Equilibrium Catalyst Properties

Figure 1 shows a schematic diagram of the nitrogen balance around the FCC pilot plant. Since the oxygen/ argon mixture was used for the regeneration, the only nitrogen input for the whole system was from the feed nitrogen. The nitrogen distributes among the liquid products (gasoline, light cycle oil, bottoms, and water condensed from stripping steam), vapor products from the top of the recovery column, and nitrogen containing species in the flue gas. If we assume the coke on the regenerated catalyst is negligible for a full combustion operation, the total nitrogen in the flue gas should equal to the nitrogen in the coked catalyst.

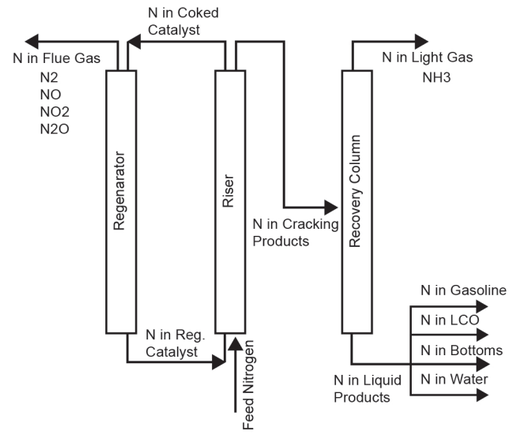

Figure 1. Nitrogen balance around Davison circulating riser.

Table 3 is the nitrogen balance from the DCR unit for both feeds. About half of the feed nitrogen appears in the liquid products. Most of the nitrogen in the liquid was concentrated in the heavy fractions. Figure 2 shows a distribution of the nitrogen in liquid products with five different feeds (including feed A and B). Since steam was used for product stripping as well as feed atomization, water was also recovered along with the liquid products. Titration of the water showed that about 5% of the feed nitrogen is converted into ammonium and recovered in the water.

Part of the ammonia appeared in the light gases. The ammonia in the light gases was measured by bubbling the gas product through a 0.1 N HCl water solution and titrating the amount of nitrogen in the liquid. The results of this procedure from an experiment in the DCR using Feed A at a 73% conversion level showed about 3% of the feed nitrogen appeared as ammonia in the light gases.

For the low-nitrogen feed A, only about 62 ppm of NO was detected in the flue gas, while the high-nitrogen feed B produced about 221 ppm of NO. In both cases, NO only accounted for less than 3% of the feed nitrogen. For both feeds, a significant amount of molecular nitrogen in the flue gas was measured by gas chromatography, which indicates the formation of molecular nitrogen coke in the regenerator. In the two balance experiments, 32 and 38 wt% of the feed nitrogen were recovered as molecular nitrogen. The total amounts of molecular nitrogen and NO in the flue gas are equivalent to about 61 and 145 ppm of nitrogen on the coked catalyst, or 1.4 and 2.6 wt% of the nitrogen in the coke.

		Feed A		Feed B	
	Unit	products, %	N/feed N, %	products, %	N/feed N, %
conversion	wt%	73.9		59.8	
C/O		8		7.7	
H2-C_4	wt%	18.1		13.2	
NH_3/water			3.0_a		3.0
liquid products	wt%	77.8	47.4	82.2	50.1
C_5 + gasoline	wt%	51.7		40.2	
LCO	wt%	15.5		22.6	
bottoms	wt%	10.6		19.4	
NH_3/water			5.0_a		5.0_a
coke	wt%	3.7		4.3	
total mass balance		99.6		99.7	
flue gas NO	ppm	62	2.6	211	2.7
flue gas N_2	ppm	450	38.0	1250	32.7
total N recovery			96.0		93.5

[a] Estimated from different experiments.

Table 3. Nitrogen Balance around a Riser Pilot Plant

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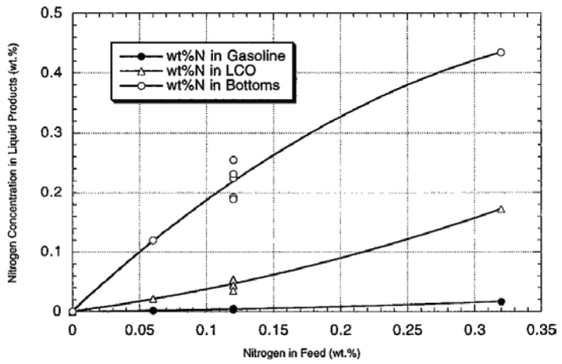

Figure 2. Nitrogen in FCC liquid products vs feed nitrogen.

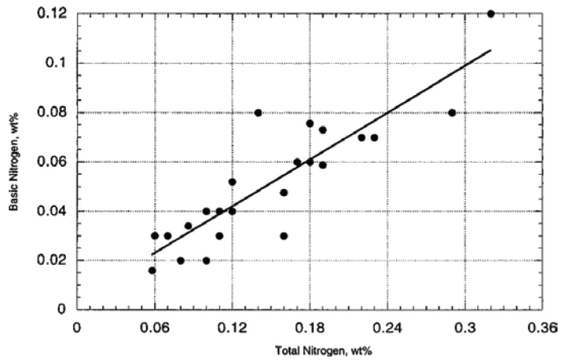

Figure 3. Basic vs total nitrogen in FCC feeds.

The results are in good agreement with direct measurement by a CNS analyzer shown in Figure 6 (done at Leco, St. Joseph, MI). It appears that 10%-15% of the nitrogen in the coke is converted to NO in the DCR regenerator at the conditions we are using. The rest is released as molecular nitrogen. In commercial FCC regenerators, the fraction of nitrogen released as NO varies from about 3% to 25%, depending on the regenerator design and operating conditions (Miller et al., 1996). The percentage of nitrogen converted to coke in the two cases are about 40.6% for feed A and 35.4% for feed B. The ratios are comparable to the percentage of basic nitrogen in total feed nitrogen: 43% for feed A and 37.5% for feed B.

It is worth noting that the balance of nitrogen in the FCCU is different from that of sulfur. Fifty to sixty percent of the sulfur in the feed appears in the liquid products, and most of the rest, 35% to 45%, appears as H_2S. Only 2%-5% appears in the coke, and nearly all of the sulfur in the coke is oxidized to sulfur oxides (Wormsbecher et al., 1993). The case of nitrogen is very different. About half of the feed nitrogen is present in the liquid products, less than 10% of nitrogen appears as ammonia, and the rest is present in the coke. Very little of the nitrogen in the coke is oxidized to NO. Most undergoes reduction to N_2 in the regenerator. It should be noted that although a smaller fraction of sulfur than nitrogen ends up in coke, the concentration of sulfur in coke is typically similar to that of nitrogen due to the high concentration of sulfur in the feed.

NO_x Chemistry

Nitrogen Compounds in Feeds

The nitrogen content in most FCC feeds is quite low, typically between 0.005 to about 0.5 wt%. Nitrogen is found at ppm levels in light and middle distillates, but increase significantly around 620 K (650°F). The nitrogen compounds are typically distinguished by their basicity. Much work has been reported to determine the basicity of each particular group of nitrogen compounds (Richter et al., 1952; McKay et al., 1975, 1976; Altgelt et al., 1994). According to their molecular structure, most of the nitrogen compounds fall into the following four groups with decreasing basicity: amines, pyridine derivatives, pyrrole derivatives, and amides. Typically, about one-third of the nitrogen is considered basic nitrogen according to titration analysis with perchloric acid (Figure 3). Most of the amine and pyridine types of nitrogen compounds are considered to be basic and are expected to be converted to coke. Literature also showed that these two types of nitrogen constitutes about one-third of the total nitrogen (Holmes, 1986). Most of the basic nitrogen is expected to be adsorbed on the acidic sites of the catalysts and be converted to coke during the cracking process, as we have shown in the nitrogen balance experiments. The percentage of nitrogen being converted to coke approximates the percentage of basic nitrogen in total nitrogen. Some of the nonbasic nitrogen may also contribute to coke. The fractions of nitrogen compounds left in the liquid products are expected to be the neutral or acidic types of nitrogen, e.g., pyrrole derivatives (Qian et al., 1995).

Nitrogen in Coke

Judging from the nature of the nitrogen compounds in the feed, a significant fraction of the nitrogen probably exists in aromatic rings. If one assumes the coke molecule contains about 15-20 aromatic rings, each molecule has to contain at least two nitrogen atoms at a nitrogen in a coke level of 5 wt% (Snape et al., 1995). One of the byproducts from the reaction between carbon and NO is C_2N_2. It has been speculated that the polymerization of C_2N_2 could in turn form a high melting point $(CN)_x$ polymer (Chu et al., 1993). Our own XPS characterization

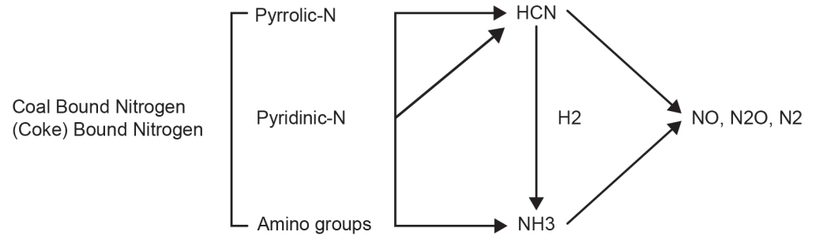

Figure 4. Schematic of the NO_x formation mechanisms (adapted from ref 16).

of the coke indicated the presence of two types of nitrogen structures in the coke. One is more strongly bonded to the catalyst surface than the other with a binding energy of 400.7 vs 398.4 eV (Qian et al., 1997).

Formation of NO_x

The exact chemistry on how the coke-bound nitrogen is being converted to NO_x/N_2 is not sufficiently understood. However, we can draw an analogy between the regeneration process (coke combustion) with fluidized bed coal combustion. There exists extensive literature on the nitrogen chemistry during coal combustion (Bassilakis et al., 1993; Wojtowicz et al., 1993). Systematic work was also reported for the formation of nitrogen compounds during the regeneration of spent hydroprocessing catalysts (Zeuthen et al., 1991; Furimsky et al., 1995, 1996). Figure 4 is a schematic showing of the transformation of coal-bound nitrogen during coal combustion (Wojtowicz et al., 1993).

Nitrogen in the coke has to go through some intermediates before being converted to NO or molecular nitrogen. For coal-bound nitrogen, HCN, and NH_3 are considered the intermediates for the formation of NO_x. Regeneration of spent hydroprocessing catalysts also follows the same mechanisms. It is expected that nitrogen in FCC coke would probably go through a similar route.

Regeneration of hydroprocessing catalysts indicated that the selectivity to $HCN/NH_3/N_2$ from fuel-bound nitrogen is strongly affected by the type of nitrogen in the coke, or originally in the feedstocks (Furimsky et al., 1995). Pyrrolic-N yields higher HCN than pyridinic nitrogen does. Model compounds studies for solid fuel combustion also showed that phenolic OH groups were found to increase the conversion of HCN to NH_3 (Hamalainen et al., 1994). Although there is very little evidence of amine groups in coal, the amine groups in FCC feed may be easily adsorbed on the catalyst and converted to coke. The nitrogen in amine groups are converted to ammonium intermediates before being further converted. Some of the amine groups may also be cracked and released as ammonia in the riser.

The subsequent destruction of HCN or NH_3 is more affected by the process or operating conditions. In a typical full combustion regenerator condition, most of the HCN and NH_3 should be oxidized to NO/N_2O as along as enough oxygen is available, especially with the presence of catalysts/metals. Part of the N_2O and NO can then go through reduction or decomposition to nitrogen. In the coal combustion process, there is evidence that N_2O is formed mainly from cyano species, whereas NH_3-based compounds tend to react toward NO. Laboratory experiments have shown (Tamhankar et al., 1996) than HCN is more readily oxidized than ammonia, through both are very reactive and are readily oxidized to N_2/NO_x. In partial combustion conditions, it is not difficult to imaging the presence of a significant amount of NH_3/HCN, which subsequently are converted to NO/N_2 in the downstream CO boiler. Thus, NO_x reduction in partial combustion requires different approaches from full combustion. The current paper will mostly deal with full combustion operations.

Reduction of NO_x

The nitrogen balance results described above show that nitrogen is produced in the regenerator during the burning of the nitrogen in the coke. This results suggests several possibilities. Nitrogen can be removed as either N_2 or as NO during initial combustion in the presence of coke. Another possibility is that the NO formed during combustion in the dense bed is further reduced to N_2 by reaction with either CO or carbon on an unregenerated catalyst.

Figure 5 demonstrates a laboratory simulated regeneration of a coked FCC catalyst by a temperature-programmed oxidation experiment. A coked catalyst is heated to 1010°F (550°C) in the presence of the oxygen/ helium mixture and held at that temperature for 20 min. At this point the temperature is again increased. During the initial heating most of the carbon is burned to CO_2, and very little NO is formed. During the second stage most of the NO is formed and relatively little CO_2. These results show that carbon and nitrogen are burned sequentially, first carbon and then nitrogen. It appears from these experiments that the oxidation of nitrogen to NO occurs

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at a higher temperature than the oxidation of carbon to CO_2 or to CO. These results would imply that as the amount of carbon on the regenerated catalyst decreases, the nitrogen content of the remaining coke increases. Direct measurements of nitrogen in coke have shown that this is the case (Figure 6). Nitrogen is removed last during regeneration in the DCR.

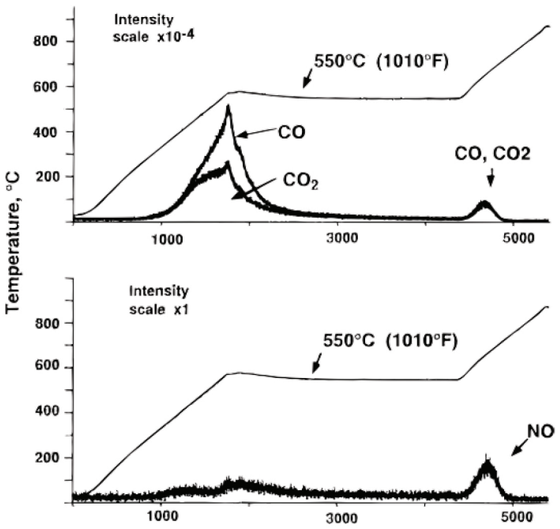

Figure 5. Regeneration of coked FCC catalyst (5 mol % oxygen in helium).

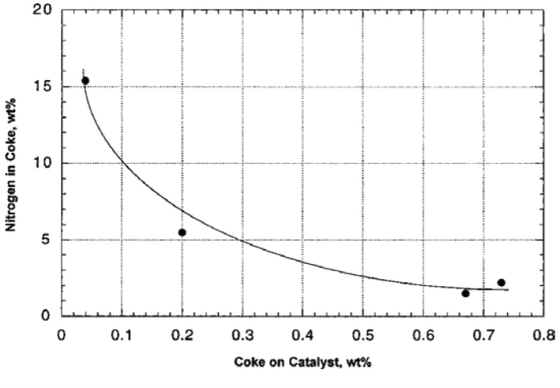

Figure 6. Nitrogen content in partially regenerated catalyst.

The reaction of NO with carbon has been reported previously as being as rapid or perhaps more rapid than the reaction of coke with oxygen (Chu et al., 1993). It is also well-known that NO can react with CO readily with the presence of various supported metal oxides or noble metals (Kobylinski et al., 1973, 1974). There is so far no conclusive evidence to differentiate the two mechanisms. The presence of carbon in the regenerator is always associated with the presence of CO. The fact that a CO combustion promoter substantially increases NO emission indicates that reduction of NO by CO is probably an important mechanism for NO conversion to N_2.

Another possible mechanism is the reaction of ammonia and NO_x competing with ammonia oxidation. As we have showed earlier, ammonia is a possible intermediate product of the NO_x formastion process and it is certainly present in the regenerator. Thus, it is conceivable that this reaction occurs. At the present, we do not have evidence to prove or disprove this mechanism. Further experimental work is necessary.

Thermal Oxidation of Nitrogen

It is often alluded that some of the NO_x emission is from thermal oxidation of nitrogen from the air (Mann, 1993; Tamhankar et al., 1996). Thermodynamic calculations show that the temperature needed for having an appreciable amount of NO_x is extremely high. The result of thermodynamic calculations for this process is shown in Figure 7. Even if this reaction goes completely to equilibrium, only less than 10 ppm of NO will be produced under typical regenerator conditions of 1% excess O_2 and temperatures between 730ºC (1340ºF) and 780ºC (1430ºF). Even at 1600ºF less than 30 ppm of NO is expected from this reaction. Since the concentration of NO in typical regenerators is considerably greater than the maximum equilibrium value of 30 ppm, the effect of this reaction, if it occurs, must be to convert NO back into molecular nitrogen. Consequently we feel that the oxidation of air makes no contribution to the observed NO_x in the FCCU flue gas.

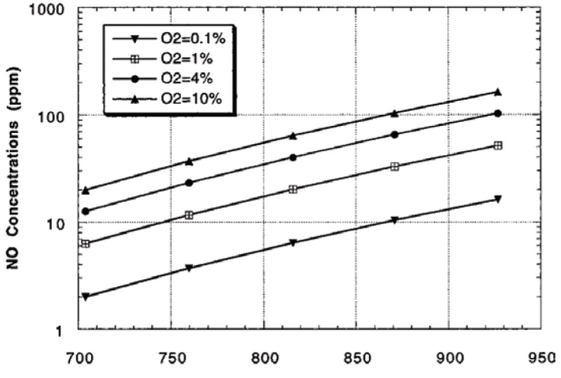

Figure 7. Equilibrium NO concentrations.

The fact that higher excess oxygen in flue gas correlated with higher NO is probably due to the decreasing CO concentrations with increasing excess oxygen, rather than the oxidation of molecular nitrogen to NO.

NO_x Emissions

From the analysis of nitrogen chemistry, we can expect the following conditions would create higher NO emissions from the FCC regenerator: high-nitrogen feed, excessive use of CO combustion promoter, and high excess oxygen.

A high-nitrogen feed produces more nitrogen-containing coke and thus emits more NO. Figure 8 shows the NO emission from a series of commercial units and the Davison circulating riser with feeds containing different levels of nitrogen. Although not all nitrogen in the feed contributes to NO emission in the same way, the general trend holds that a higher nitrogen feed typically produces more NO in the same unit.

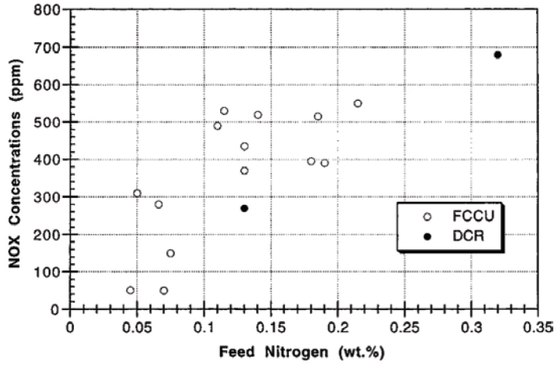

Figure 8. Correlation of NO emissions (promoted) with feed nitrogen. FCCU data from G. Bernstein, U.S. EPA Dockett no. A-79-09 (1982).

Compared with partial combustion, full combustion units would have less reducing agents (e.g., CO, coke, and NH_3) in the regenerator, thus allowing more NO to be released. Another related variable is the excess oxygen level in the regenerator. Higher excess oxygen favors the oxidation of CO, coke, and other reducing agents in the regenerator and increases the level of NO in the flue gas. A set of commercial data is shown in Figure 9 to illustrate the relationship. A similar relationship is also found in the laboratory DCR pilot plant. Contrary to some reports, the correlation between excess oxygen and NO_x emission is due to the change of reducing agents such as CO or NH_3, rather than the contribution of thermal NO_x.

Excessive use of a combustion promoter would deplete CO and other reductants in both the dense and the dilute phase in the

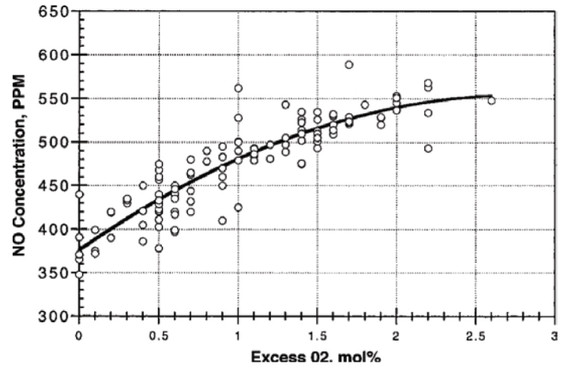

Figure 9. Excess oxygen vs NO_x emission in a commercial FCCU.

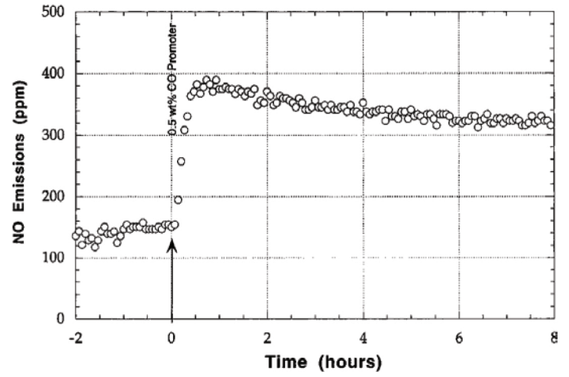

Figure 10. Effect of CO promoter on NO_x emission.

regenerator. As a result, more NO would be released. It is known from commercial observation as well as laboratory testing that a CO combustion promoter can significantly increase NO emission (Figure 10). There are speculations in the literature that a CO combustion promoter promotes the exothermic oxidation reaction so fast that is generates local hot spots. Part of the NO emission was attributed to the local high temperature. As shown in Figure 7, formation of any substantial amount of NO at thermodynamic equilibrium requires a temperature as high as 1700ºF. Also, the typical NO concentration is almost always higher than the equilibrium concentration; any occurrence of this reaction would actually reduce NO, rather than produce NO. We have also conducted an experiment in the Davison circulating riser with a feed containing no nitrogen. When a combustion promoter was added to the system, no increase of NO emission

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was observed as it did in the case of the nitrogen-containing feed. The results are shown in Figure 11.

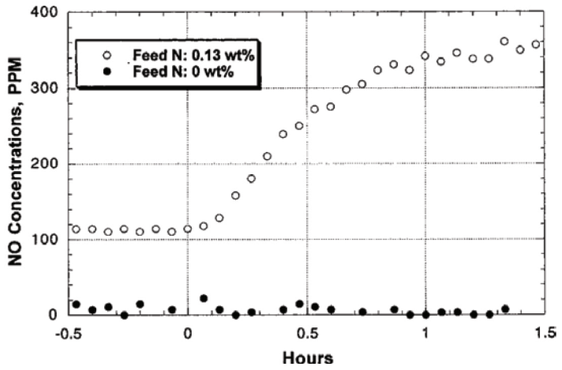

Figure 11. Effect of CO promoters on NO_x emission (EQ94-20, 0.5 wt% CP-5, 1% excess oxygen).

NO_x Control Technology

NO_x Control Additives

There are two schemes one can use to reduce NO emission: to control the formation of NO_x or to abate NO_x after its formation. Both can be accomplished by either catalytic or process approaches.

There have been numerous commercial products which claim to reduce NO_x emission when added to the FCC regenerators: commercial-based DESOX additives (Yoo et al., 1993; Cheng et al., 1997), perovskite-based NO_x additives (Dieckmann et al., 1994), and other metal oxide based additives (Chia, 1991). Reduction of NO to N_2 can also occur over a catalyst particle containing inorganic reduced components such as ceria (Figure 12). A ceria-containing material can be reduced in the riser by reacting with a hydrocarbon under cracking conditions and in the regenerator serves as a reducing agent to reduce NO to molecular nitrogen. All the additives require the presence of substantial amounts of reducing agents in the regenerator to maintain the redox process of cerium between Ce^{3+} and Ce^{4+}. Figure 13 illustrates the NO reduction activity of some ceria-based additives with the amount of coke combusted in the regenerator. Since high delta coke is also associated with higher CO in the regenerator, the correlation could well be due to higher CO, or both CO and coke, or even higher NH_3. The NO reduction activity is apparently enhanced by the presence of more reducing agents.

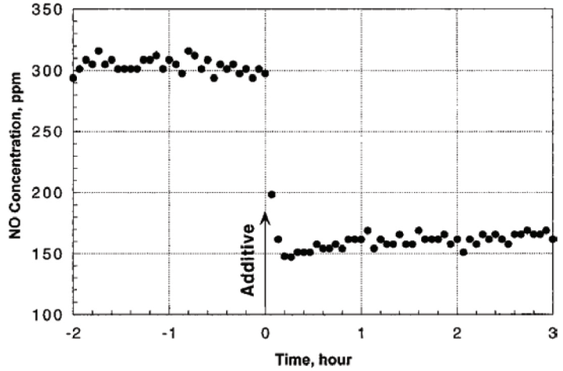

Figure 12. DCR testing of a ceria-based NO_x additive (0.5 wt% additive, 1% excess oxygen).

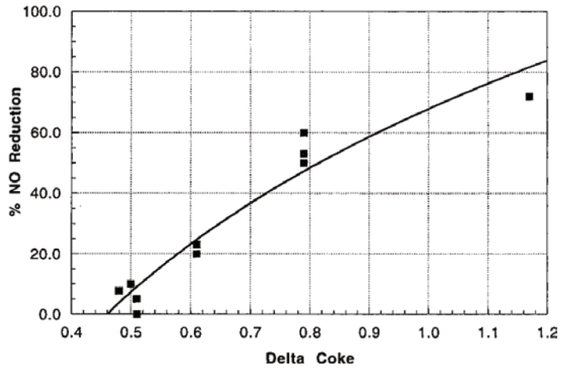

Figure 13. Effect of delta coke on the reduction of NO by Ce- based additives.

NO_x Control CO Combustion Promoter

The presence of reducing agents such as carbon monoxide can reduce NO_x emissions. Therefore, it is reasonable to expect an increase of NO emissions when CO is reduced or eliminated with the use of a combustion promoter. As we discussed earlier, the excessive use of a conventional CO combustion promoter substantially reduced the CO present in the dense phase as well as in the diluent phase of the regenerator.

A new generation of the combustion promoter has been developed at Grace Davison which selectively catalyzes the reaction between CO and NO while maintaining a good CO oxidation activity (Davey et al., 1996; Peters et al., 1996). The new generation combustion promoter does not increase NO_x emission

(Figure 14). In effect, it substantially reduces NO emissions, when compared with a conventional combustion promoter. The commercial application of the new combustion promoter has been reported elsewhere (Davey et al., 1996; Peters et al., 1996).

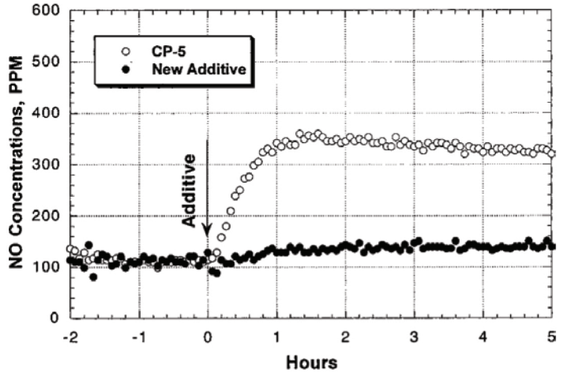

Figure 14. DCR testing of CO combustion promoters (gas oil feed, E-cat, 0.5 wt% additive, 1% excess oxygen).

Regenerator Design

NO_x reduction can be achieved by changes in the regenerator design. It has been reported that a countercurrent regenerator reduces NO_x emission due to the presence of a higher concentration of reducing agent at the top of the regenerator catalyst bed (Mann, 1993; Miller et al., 1996). Counter-current design allows a distribution of coked catalysts on the top of the regenerator catalyst bed surface. The chance of reduction of NO_x by CO or coke on catalyst is substantially improved. It is reported that the Kellog countercurrent design reduces the percentage of nitrogen in coke being released as NO_x to about 5% from 10%-20% in other regenerator designs (Miller et al., 1996). The UOP high-efficiency regenerator typically does not require the use of combustion promoters. Therefore, the NO_x emissions in general should be lower than those of the conventional regenerator design.

Partial Combustion

All of our discussion so far has focused on full combustion operation, i.e., regeneration with the presence of excess oxygen. For partial combustion, the presence of large amounts of carbon monoxide and coke on catalysts for partial combustion can substantially reduce the emission of NO. It is expected that most of NO is reduced to nitrogen. However, the absence of enough oxygen in the dense bed could also potentially affect the oxidation of the nitrogen-containing intermediates such as NH_3 and HCN. Instead of being released as NO, some of the nitrogen might be released as NH_3 or HCN. Thermo-dynamic equilibrium a concentration of ammonium of over 1% was reported from a simulation of a FCC regenerator at a low-temperature partial combustion operation (McArthur et al., 1981). In commercial FCC units, a CO boiler is often used with a partial combustion regeneration to facilitate the conversion of CO in the flue gas. In such cases, the nitrogen-containing intermediate species are converted to NO_x in the CO boiler, and the NO emission from the CO boiler rather than the regenerator becomes the main issue. NO_x control for such operations requires different strategies from those for full combustion operations. Since the combustion of nitrogen comes after the combustion of coke, partial combustion may also allow the accumulation of nitrogen on the regenerated catalysts and significantly affect the catalytic-cracking performance of the catalyst, especially for high-nitrogen feeds.

Oxygen enrichment is a technology where oxygen is introduced with the regeneration air to increase the flexibility of unit operation, especially for high coke making heavy resid processing units (Tamhankar et al., 1996). For partial combustion operation, oxygen enrichment can enhance the oxidation of reduced nitrogen species such as NH_3 and HCN. However, there will be a competing effect for full combustion. Oxygen enrichment enhances the oxidation of reduced-nitrogen species, but it could reduce the presence of CO and other reductants which contribute to the reduction of NO.

Future Horizons

With the increasing regulation of NO_x emissions, it is expected that refiners will demand more NO_x control technologies. From a process point of view, some of the new hardware design technologies will help the control of NO_x emissions. However, the majority of the refineries will have to rely on operation conditions optimization or catalytic approaches. Operation changes would include processing of low-nitrogen feeds through hydrotreating, partial combustion, and prudent use of combustion promoters. The catalyst approaches would include the use of combustion promoters which do not increase NO_x, or NO_x reduction additives.

Currently, there is still a lack of knowledge of the nitrogen chemistry on the formation or destruction of NO. A better understanding of the chemistry would no doubt help the development of new technology and more intelligent use of the available technologies. With the increasing numbers of units processing resid, units operating at partial combustion mode are expected to increase. The understanding of nitrogen chemistry in the partial combustion mode is essential. There lies another challenge for NO_x control due to its difference with SO_x control. SO_x control additives adsorb SO_3 after SO_2 oxidation in the regenerator. The sulfur is released in the riser where it is reduced to H_2S. In contrast, all the NO_x control technologies rely on the reduction of NO by the reducing agents

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available in the regenerators. Therefore, SO_x additives typically work better in a more oxidizing regenerator environment, while most of the NO_x additives work better in a more reducing regenerator environment. The simultaneous reduction of SO_x and NO_x would be a challenge for units which have both problems. It is expected many refineries will have both.

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Literature Cited

1. Altgelt, K. H.; Boduszynski, M. M.; *Composition and Analysis of Heavy Petroleum Fractions*; New York: Marcel Dekker, Inc., 1994.
2. Bassilakis, R.; Zhao, Y.; Soloman, P. R.; Serio, M. A. Sulfur and Nitrogen Evolution in the Argonne Coals: Experiments and Modeling. *Energy Fuels* **1993**, 7, 710-720.
3. Cheng, W.-C.; Kim, G.; Peters, A. W.; Zhao, X.; Rajagopalan, K.; Ziebarth, M.; Pereira, C. Environmental Fluid Catalytic Cracking Technology. *Catal. Rev.-Sci. Eng.* **1997**, accepted.
4. Chia, A. A. Reducing NOx Emissions with Zinc Catalyst. U.S.A. Patent 5,002,654, Mobil, 1991.
5. Chu, X.; Schmidt, L. D. Intrinsic Rates of NOx-Carbon Reactions. *Ind. Eng. Chem. Res.* **1993**, *32*, 1359-1366.
6. Davey, S. W.; Haley, J. T. *FCC Additive Technology Update*. Presented at the Oil & Gas Journal International Catalyst Conference & Exhibition, February 1-2, 1996, Houston, Texas, 1996.
7. Dieckmann, G. H.; Labrador, E. Q. Perovskite-Spinel FCC NOx Reduction Additive. U.S.A. Patent 5,364,517, Chevron, 1994.
8. Furimsky, E.; Nielsen, M.; Jurasek, P. Formation of Nitrogen Compounds from Nitrogen-Containing Rings during Oxidative Regeneration of Spent Hydroprocessing Catalysts. *Energy Fuels*, **1995**, 9, 439-447.
9. Furimsky, E.; Siukola, A.; Turenne, A. Effect of Temperature and O2 Concentration on N-Containing Emissions during Oxidative Regeneration of Hydroprocessing Catalysts. *Ind. Eng. Chem. Res.* **1996**, 35, 4406-4411.
10. Hamalainen, J. P.; Aho, M. J. Effect of fuel composition on the conversion of volatile solid fuel-N to N_2O and NO. *Fuel* **1994**, 74 (12), 1922-1924.
11. Holmes, S. A. Nitrogen Functional Groups in Utah Tar Sand Bitumen and Produced Oils. *AOSTRA J. Res.* **1986**, 2, 167- 175.
12. Kobylinski, T. P.; Taylor, B. W. The Catalytic Chemistry of Nitric Oxide. I. The Effect of Water on the Reduction of Nitric Oxide Over Supported Chromium and Iron Oxides. *J. Catal.*, **1973**, 31, 450-458.
13. Kobylinski, T. P.; Taylor, B. W. The Catalytic Chemistry of Nitric Oxide. II. Reduction of Nitric Oxide Over Noble Metal Catalysts *J. Catal.* **1974**, 33, 376-384.
14. Mann, R. Fluid Catalytic Cracking: Some Recent Developments in Catalyst Particle Design and Unit Hardware. *Catal. Today* **1993**, 18, 509-528.
15. McArthur, D. P.; Simpson, H. D.; Baron, K. Catalytic Control of FCC SOx Emission Looking Good. *Oil Gas J.* **1981**, 79 (2), 56- 59.
16. McKay, J. F.; Cogswell, T. E.; Weber, J. H.; Latham, D. R. Analysis of Acids in High-Boiling Petroleum Distillates. *Fuel* **1975**, 54, 50-61.
17. McKay, J. F.; Weber, J. H.; Latham, D. R. Characterization of Nitrogen Bases in High-Boiling Petroleum Distillates. *Anal. Chem.* **1976**, 48, 891-898.
18. Miller, R. B.; Johnson, T. E.; Santner, C. R.; Avidan, A. A.; Beech, J. H. *Comparison Between Single and Two-Stage FCC Regenerator*. Proceedings of the 1996 Annual NPRA Meeting, San Antonio, Texas, 1996.
19. Peters, A. W.; Weatherbee, G. D.; Zhao, X. Origin of NOx in the FCCU Regenerator. *Fuel Reformulation* **1995**, 5 (3), 45-50.
20. Peters, A. W.; Koranne, M.; Pereira, C.; Weatherbee, G. D.; Zhao, X.; Haley, J.; DAvey, S.; Lakhanpal, B. *Control and Origin of NOx in the FCCU Regenerator*. ACS Annual Meeting, Orlando, FL, 1996.
21. Qian, K.; Harding, R. H.; Zhao, X. *Impact of Conversion Level on Hydrocarbon Transformation in Fluid Catalytic Cracking Process Studies by Combined Chromatography and Mass Spectrometry*. Proceedings of the 43rd ASMS Conference on Mass Spectroscopy and Applied Topics, Atlanta, GA, 1995.
22. Qian, K.; Tomczaka, D.; Rakiewicza, E.; Harding, R.; Yaluris, G.; Cheng, W.-C.; Zhao, X.; Peters, A. W. A study of coke formation in fluid catalytic cracking process by combined catalytic techniques. *Energy Fuels* **1997**, 11 (3), 596-601.
23. Richter, F. P.; Caesar, P. D.; Miesel, S. L.; Offenhauer, R. D. Distribution of Nitrogen in Petroleum According to Basicity. *Ind. Eng. Chem.* **1952**, 44 (11), 2601-2605.
24. Snape, C. E.; McGhee, B. J.; Andresen, J. M.; Hughes, R.; Koon, C. L.; Hutchings, G. Characterization of Coke from FCC Refinery Catalysts by Quantitative Solid State 13C NMR. *Appl. Catal. A: General* **1995**, 129, 125-132.
25. Tamhankar, S.; Menon, R.; Chou, T.; Ramachandran, R.; Hull, R.; Watson, R. Enrichment Can Decrease NOx, SOx Formation. *Oil Gas J.* **1996**, 94, 60-68.
26. Wojtowicz, M. A.; Pels, J. R.; Moulijn, J. A.; Combustion of Coal as a Source of N_2O Emission. *Fuel Process. Technol.* **1993**, 34, 1-71.
27. Wormsbecher, R. F.; Weatherbee, G. D.; Kim, G.; Dougan, T. J.; *Emerging Technology for the Reduction of Sulfur in FCC Fuels*. Proceedings of the 1993 NPRA Annual Meeting, 1993.
28. Yoo, J. S.; Bhattacharyya, A. A.; Radlowski, C. A.; Karch, J. A. Mixed Spinels with Cerium-SOx Emission Control From Fluid Catalytic Cracking (FCC) Regenerator. In *New Frontiers in Catalysis*; Guczi, J., Ed.; Elsevier: Amsterdam, 1993; pp 1391- 1403.
29. Young, G. W. Realistic Assessment of FCC Catalyst Performance in the Laboratory. In *Fluid Catalytic Cracking: Science and Technology*. Magee, J. S., Mitchell, J. M. M. Eds.; Elsevier: Amsterdam, 1993; Vol. 76, pp 257-292.
30. Zeuthen, P.; Blom, P.; Massoth, F. E.; Characterization of Nitrogen on Aged Hydroprocessing Catalysts by Temperature-Programmed Oxidation. *Appl. Catal.* **1991**, 78, 265-276.
31. Zhao, X.; Weatherbee, G. D.; Rajagopalan, K. R. *Simulation of Commercial FCCU Operations by a Laboratory Circulation Riser Unit*. Proceedings of The Fifth World Congress of Chemical Engineering, San Diego, CA, 1996.

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