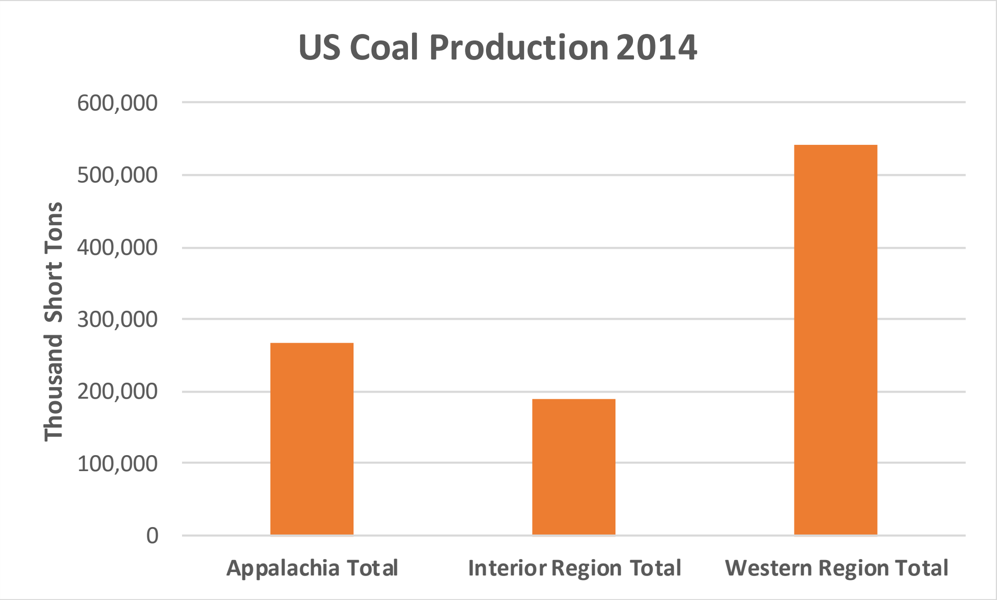
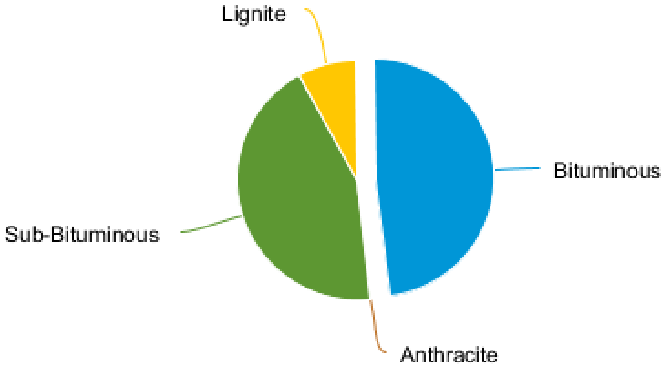
US Coal Production



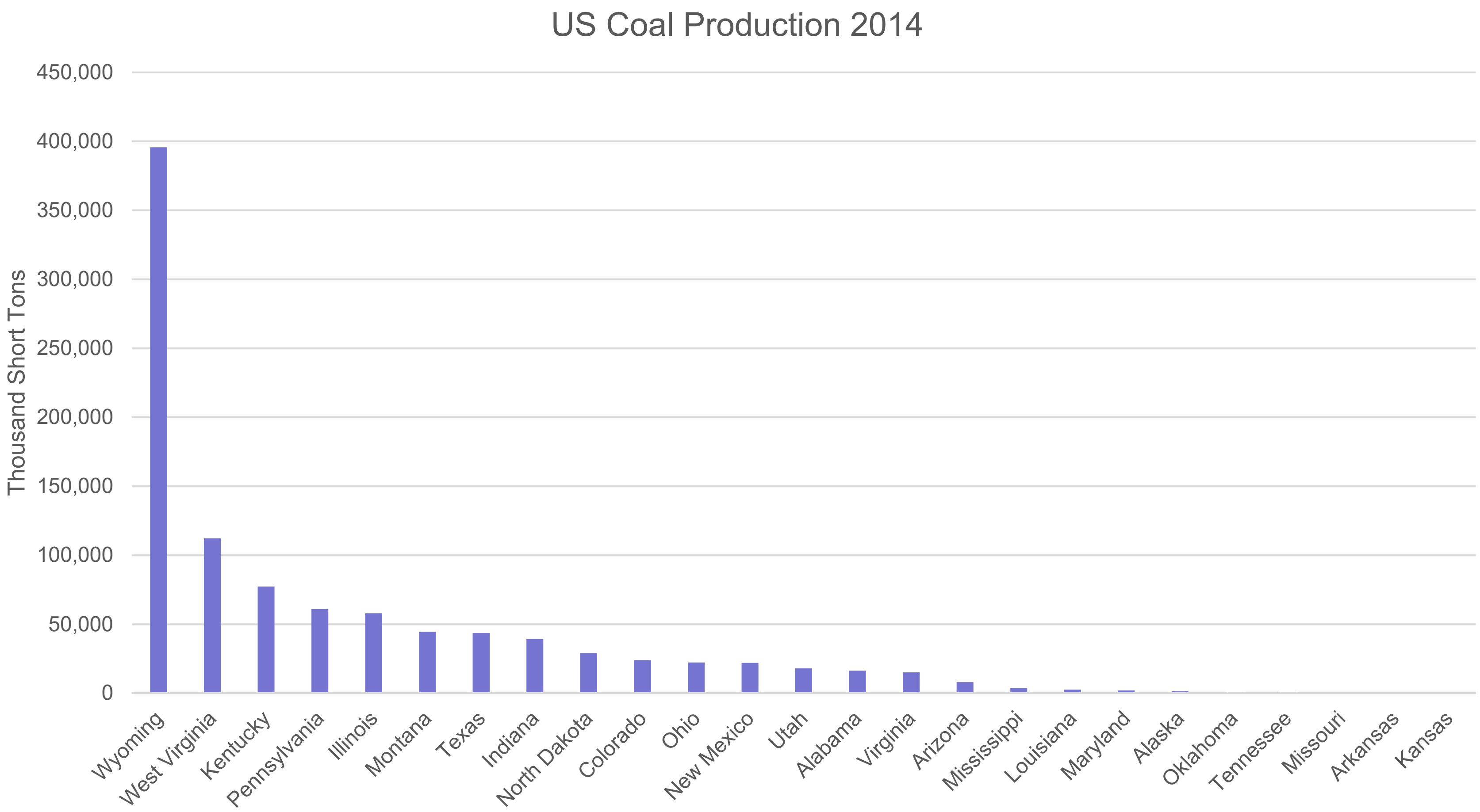
U.S. coal production by rank, 2014

total: 1,000,049 thousand short tons

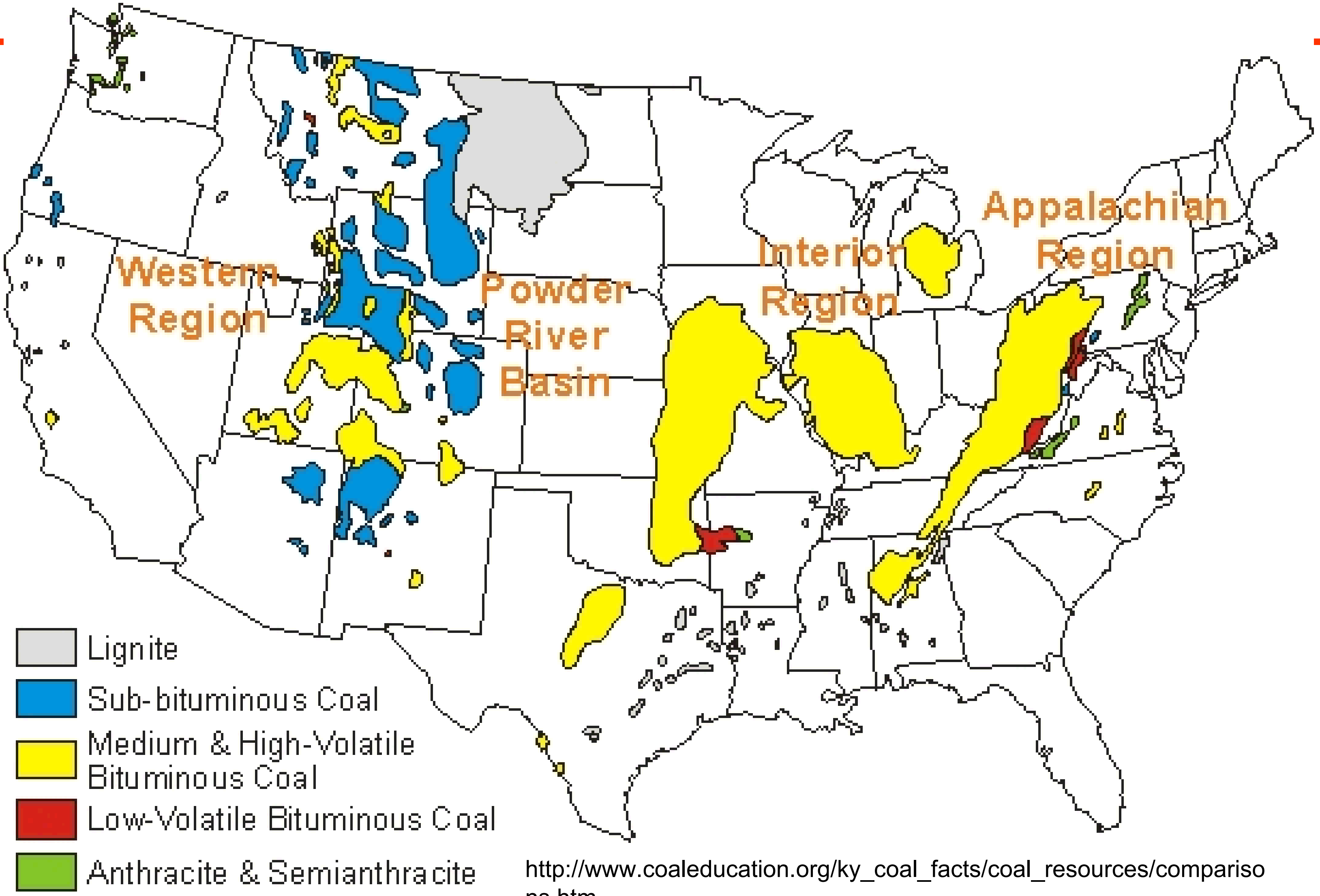


eia Source: Annual Coal Report Table 6.

US Coal Production



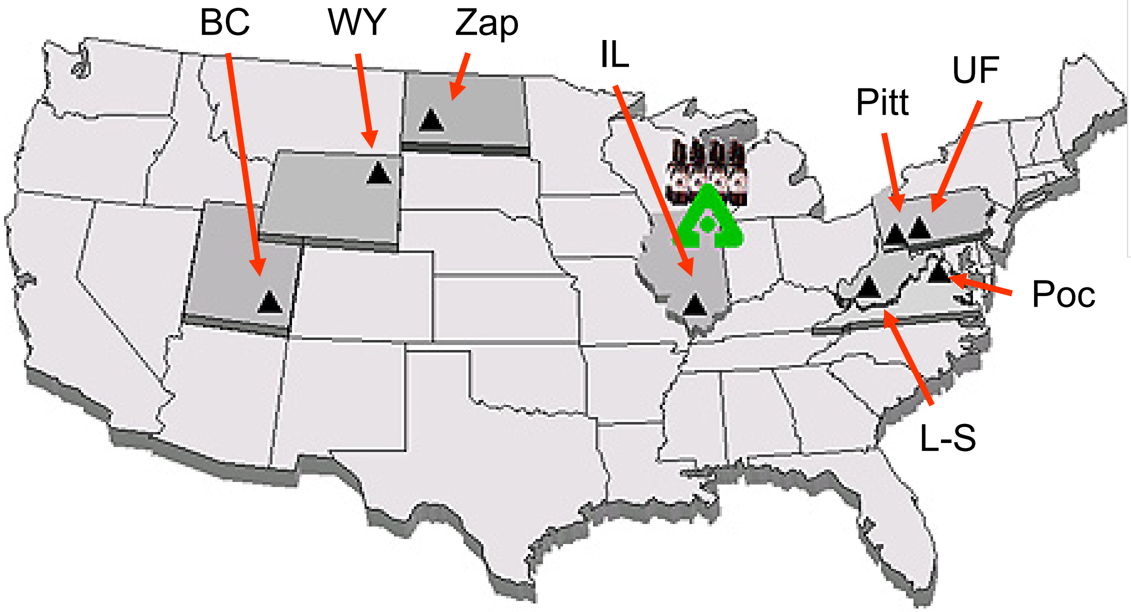
U.S. Coal Fields

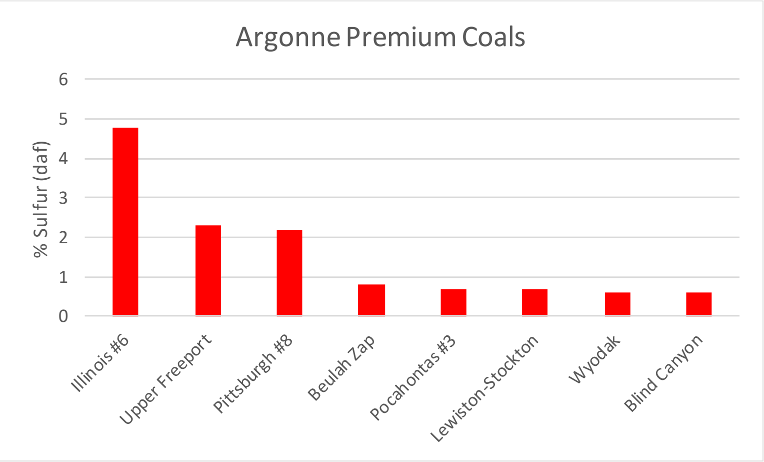


http://www.coaleducation.org/ky_coal_facts/coal_resources/comparisons.htm

Source: Developed from the U.S. Geological Survey

Sulfur





Rank	Rank	% S (daf)
Illinois #6	hvc bit	4.8
Upper Freeport	mv bit	2.3
Pittsburgh #8	hva bit	2.2
Beulah Zap	lignite	0.8
Pocahontas #3	lv bit	0.7
Lewiston-Stockton	hva bit	0.7
Wyodak	subbit	0.6
Blind Canyon	hvb bit	0.6

Price of Coal

Average price of coal delivered to end-use sector, 2008-14

Source: Annual Coal Report Table 34.

Class 14

NO_x from Coal

Outline

- NO_x environmental effects
- General forms of NO_x
- Forms of Nitrogen in Coal
- Nitrogen Release Mechanisms
- NO_x Control Strategies

NO_x Environmental Effects

1. Describe the environmental problems associated with emission of the following chemicals (at both ground level and in the upper atmosphere):
    - NO
    - NO_2
    - NH_3
    - HCN
    - N_2O

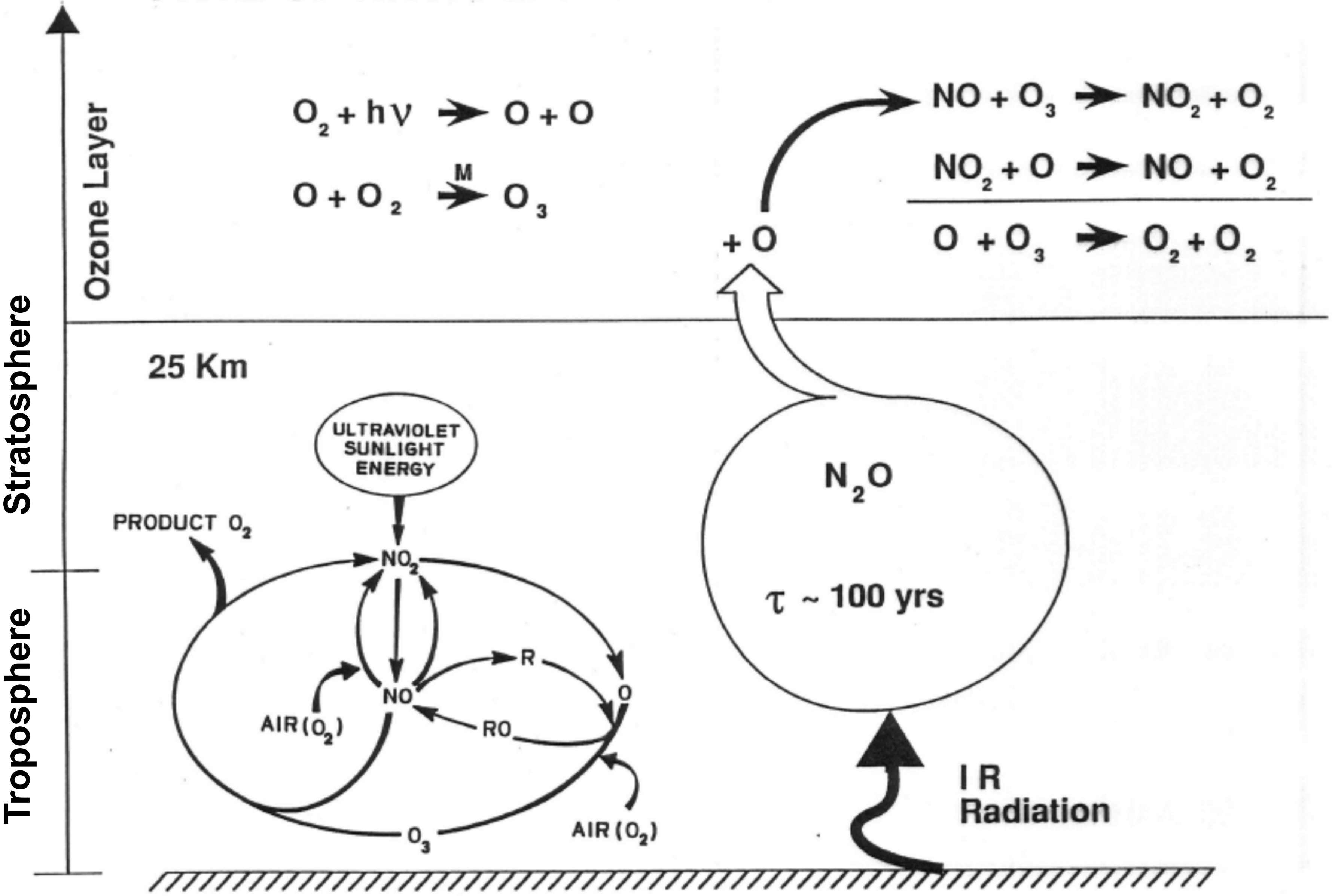
Nitrogen Pollution from Combustion

What is NOx?	**Names?**	**Why is this a problem?**
NO	nitric oxide	Forms NO_2 and nitrates that turn into PM10
NO_2 (reddish brown gas)	nitrogen dioxide	a. Helps form smog (ozone) b. Toxic (respiratory hazard) above 5 ppm c. Forms nitrates that turn into PM10
N_2O (laughing gas)	dinitrogen oxide (nitrous oxide)	Depletes ozone in upper atmosphere

Other species often considered are:

HCN	Hydrogen Cyanide	Extremely toxic (poisonous gas used to execute people)
NH_3	Ammonia	Respiratory hazard

FATE OF NITROGEN OXIDES IN THE ATMOSPHERE



$O_2 + h\nu \rightarrow O + O$

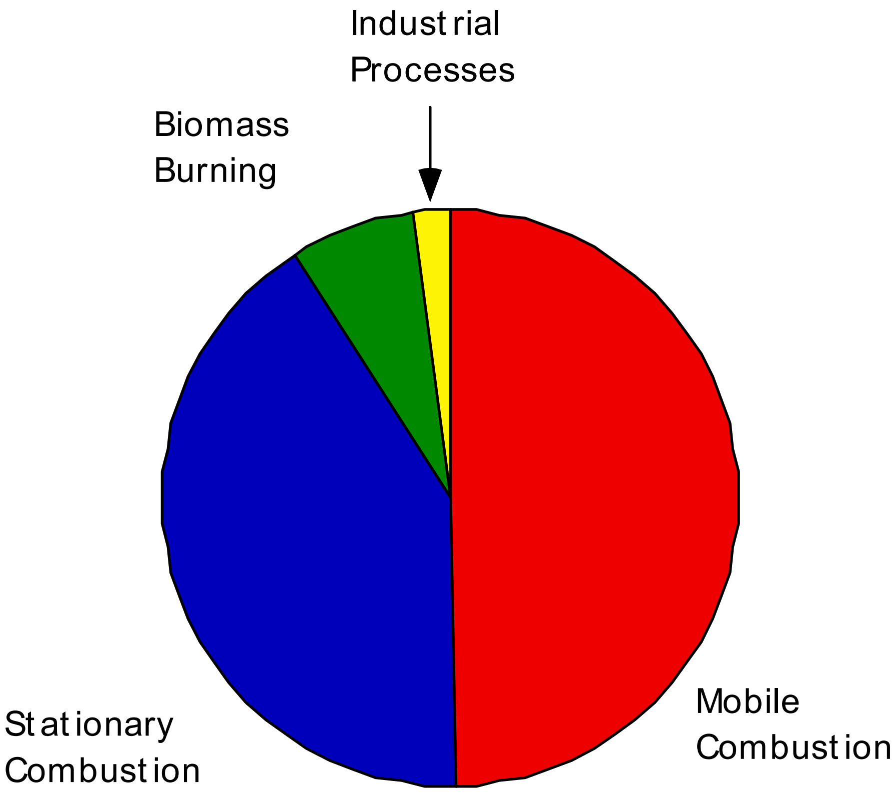
$O + O_2 \xrightarrow{M} O_3$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

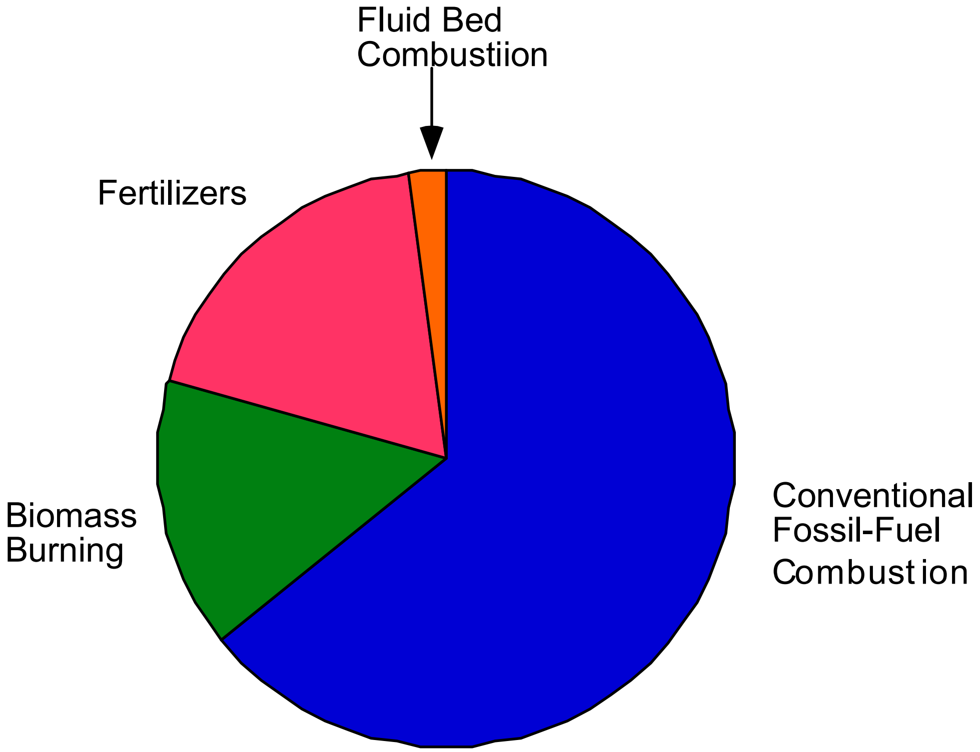
$O + O_3 \rightarrow O_2 + O_2$

Sources of Man-Made Nitrogen Oxide Emissions



$NO_x = NO + NO_2$

Total: 1.5 x 10^{10} kg N / yr



N_2O

Total: 0.1 x 10^{10} kg N / yr

2. General Forms of NO_x

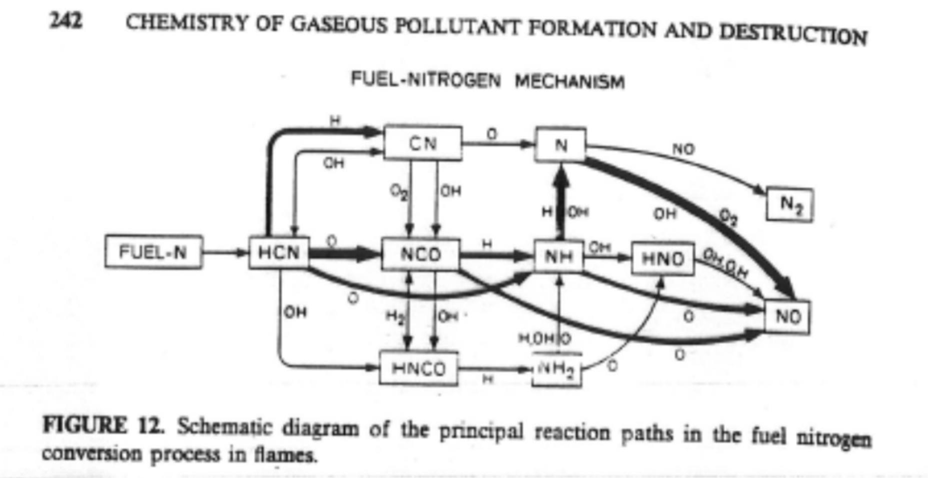


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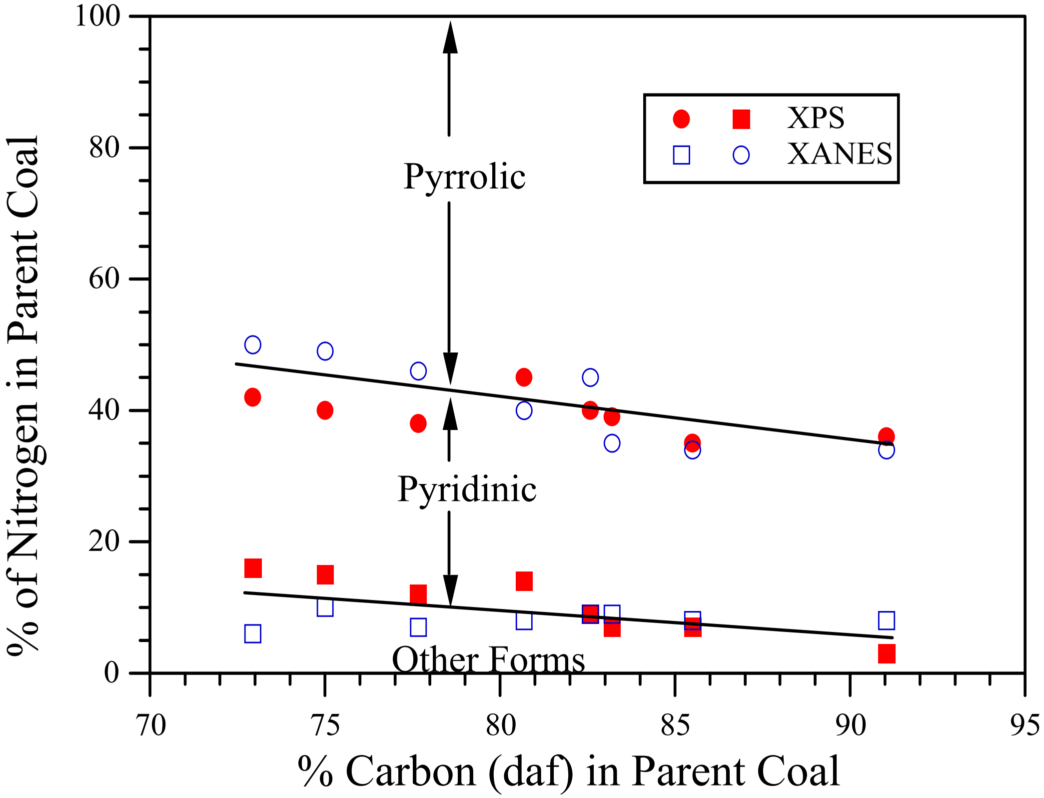
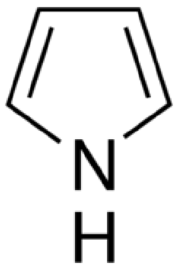
FIGURE 12. Schematic diagram of the principal reaction paths in the fuel nitrogen conversion process in flames.

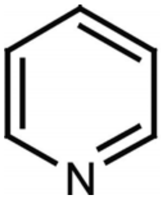
- Thermal NO_x
  - $N_2 + O_2 \rightarrow 2NO$
  - N_2 and O_2 only, no other major species
  - Dominant source of NO_x in gaseous hydrocarbon combustion (CH_4, etc.)
- Fuel NO_x
  - Nitrogen in fuel → → NO, NO_2, and N_2O
  - Example: pyridine combustion $C_6H_5N \rightarrow NO_x$
  - Dominant source of NO_x in coal combustion
- Prompt NO_x
  - CH or $CH_2 + N_2 \rightarrow HCN \rightarrow NO$, etc.
  - Hard to quantify because radical concentrations are hard to measure
  - Not usually a dominant source of NO_x in combustion

Forms of Nitrogen in Parent Coal





pyrrole



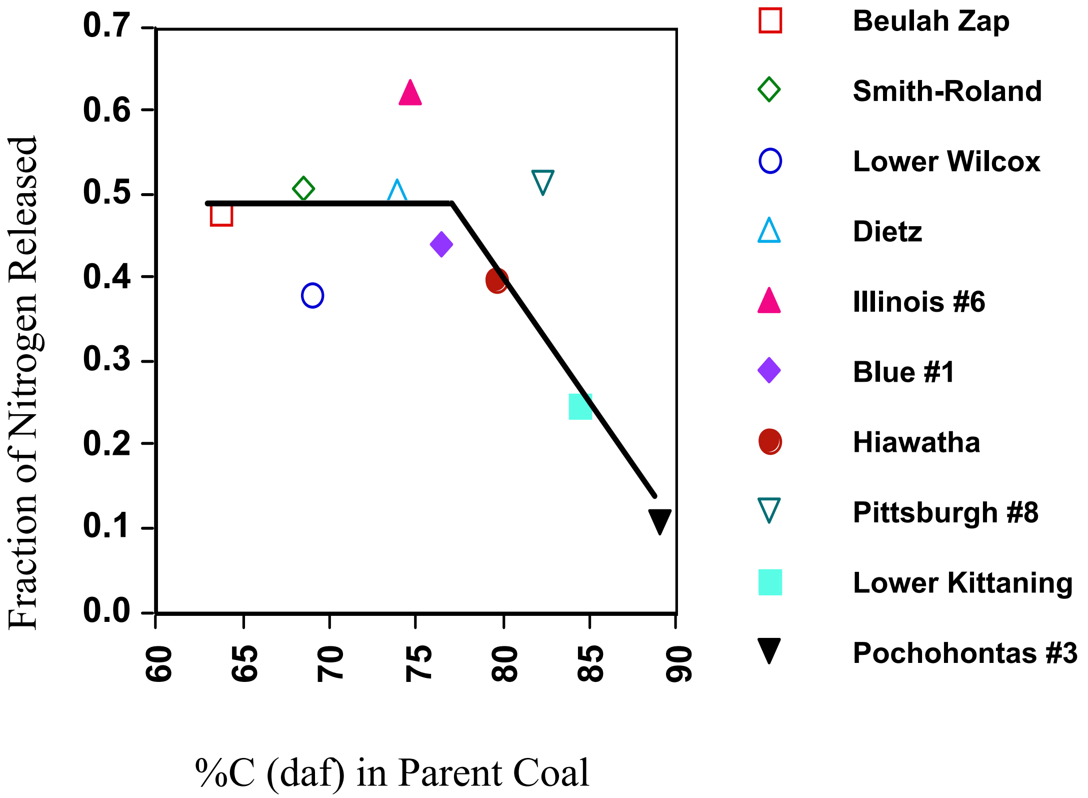
pyridine

Argonne Premium Coals, XPS data from Kelemen et al. (1993), XANES data from Mitra-Kirtley et al. (1993)

N Release Mechanisms

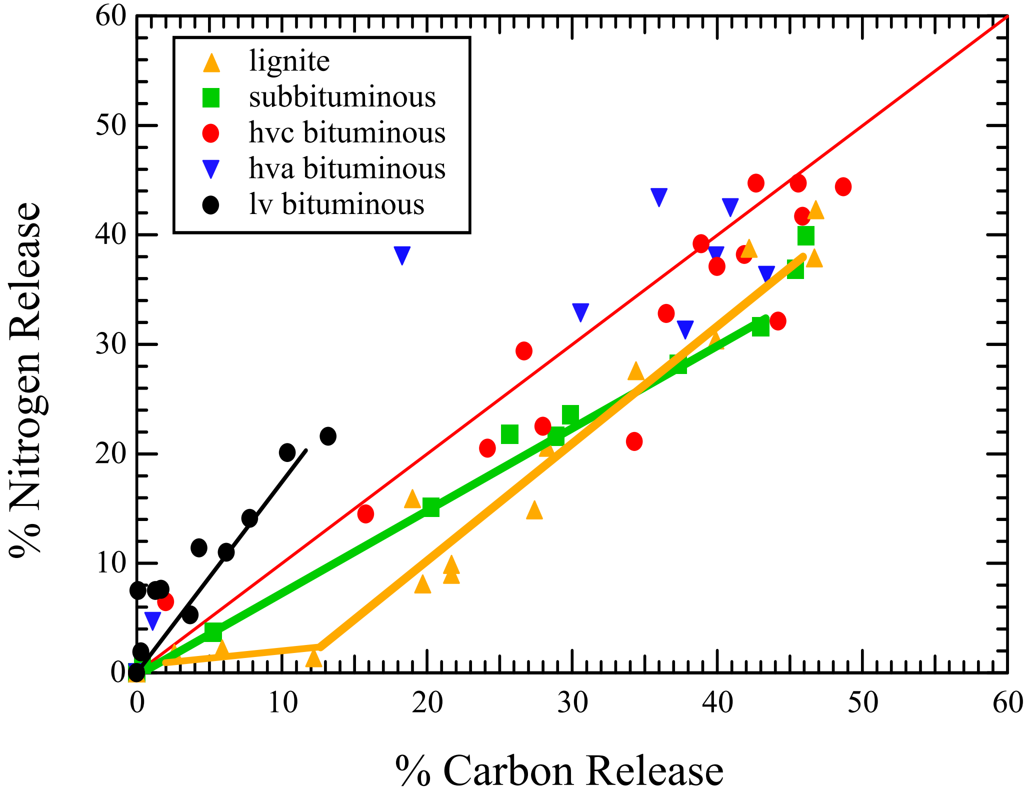
3a. Pyrolysis

Nitrogen Release vs. Coal Rank



DOE/PETC coals pyrolyzed in 6-mole-% O_2 in flat flame methane burner, residence time of 47 ms, 5×10^4 K/s (Mitchell, et al., Sandia, 1992)

Rate of Release of Nitrogen During Devolatilization



Entrained flow devolatlization of DOE/PETC coals, 10^4 K/s to 1250 K, Fletcher and Hardesty, Sandia (1992)

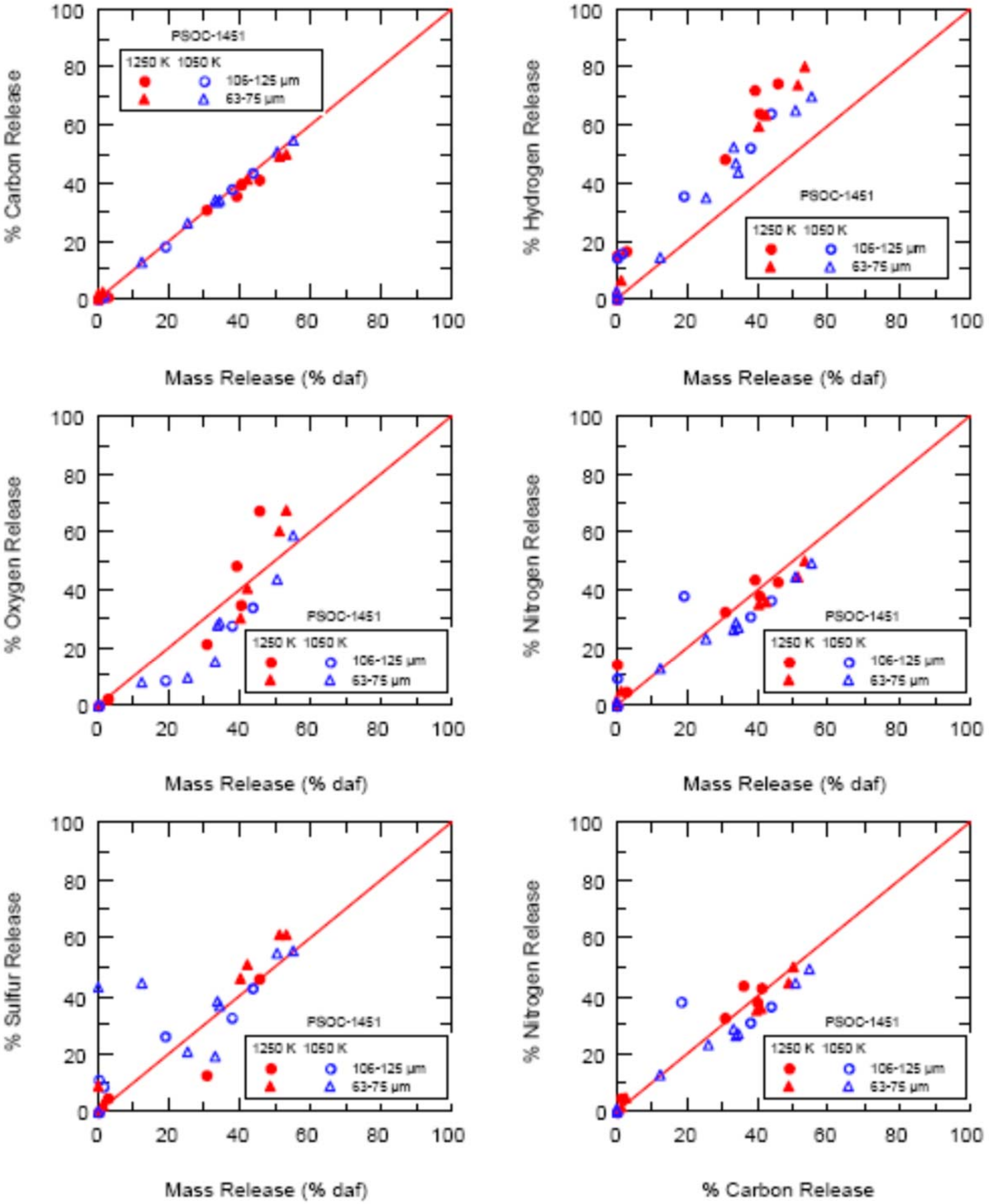


Figure 5.34 Elemental mass release rates for PSOC-1451D Pittsburgh #8 hva bituminous coal particles (106-125 and 63-75 µm) during devolatilization in 100% N_2 in the CDL.

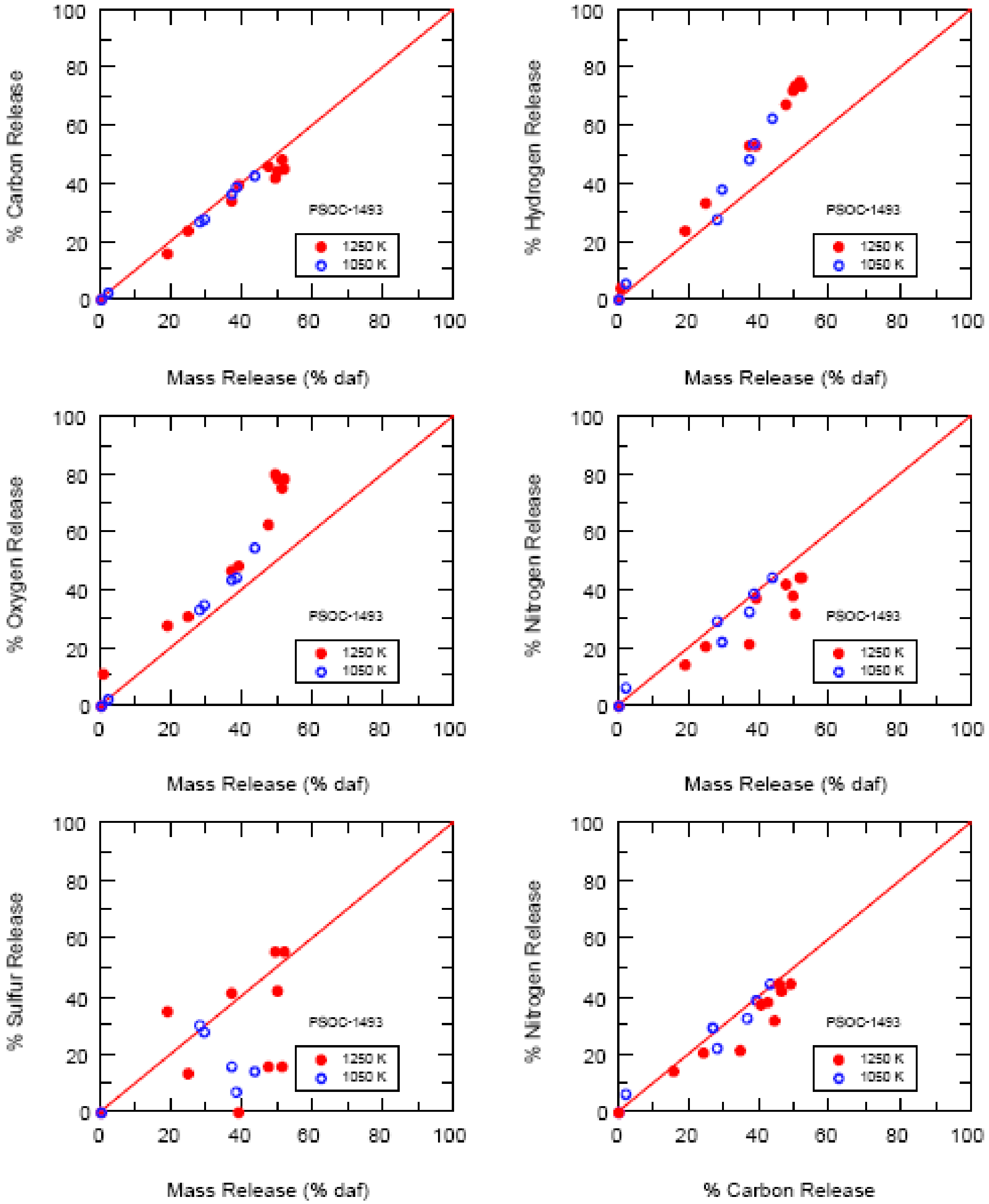


Figure 5.35 Elemental mass release rates for PSOC-1493D Illinois #6 hvb bituminous coal particles (106-125 μm) during devolatilization in 100% N_2 in the CDL.

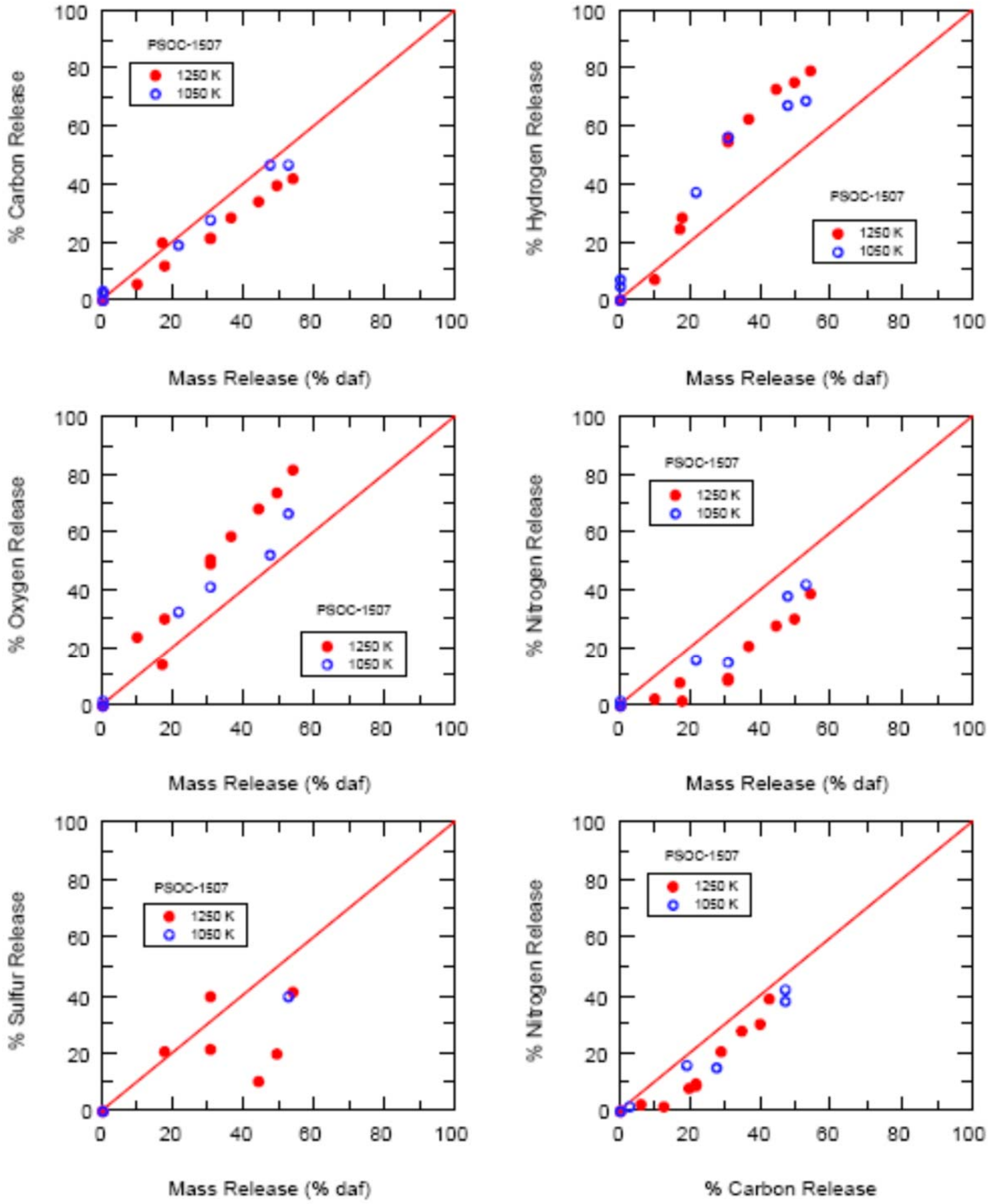


Figure 5.36 Elemental mass release rates for PSOC-1507D North Dakota Beulah Zap lignite particles (75-106 μm) during devolatilization in 100% N_2 in the CDL.

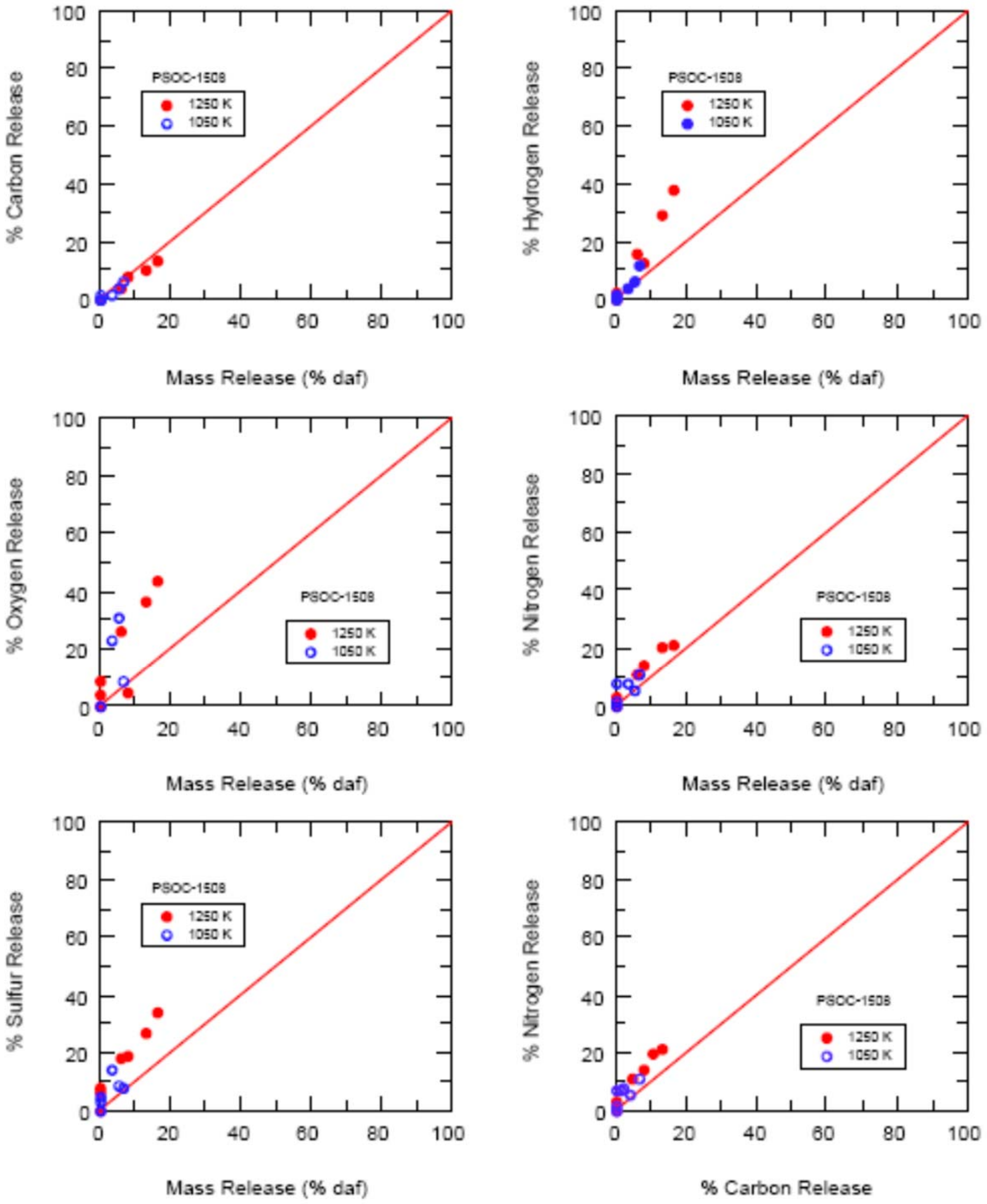
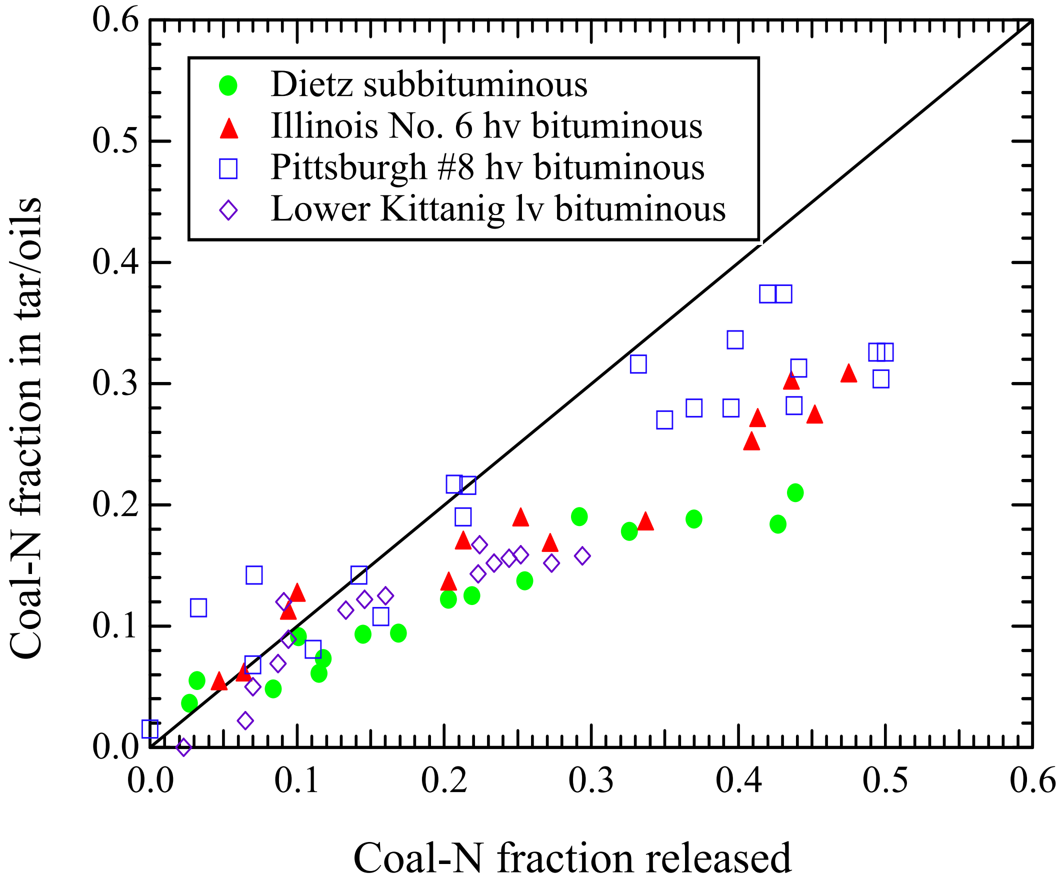


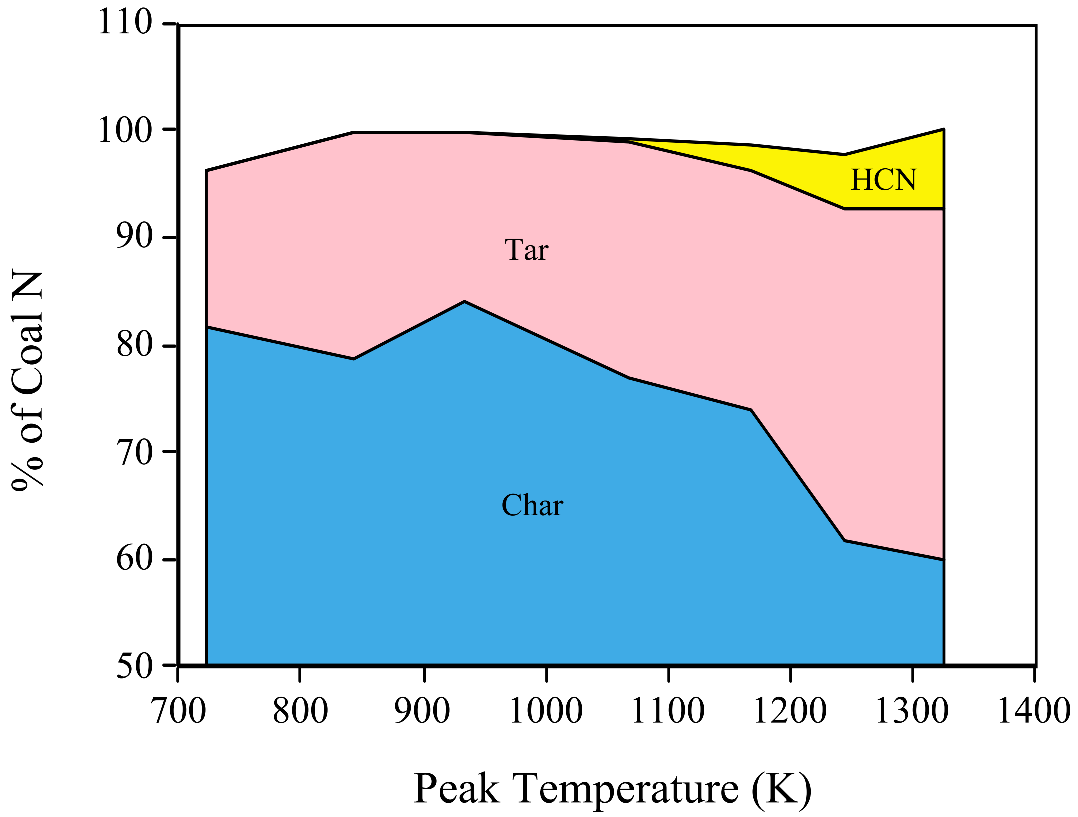
Figure 5.37 Elemental mass release rates for PSOC-1508D West Virginia Pocahontas #3 lv bituminous coal particles (106-125 μm) during devolatilization in 100% N_2 in the CDL.

Tar Does Not Contain All Pyrolyzed Nitrogen, Especially for Low Rank Coals



Pulverized coal particles in a radiant drop tube reactor (Chen, Stanford University, 1991)

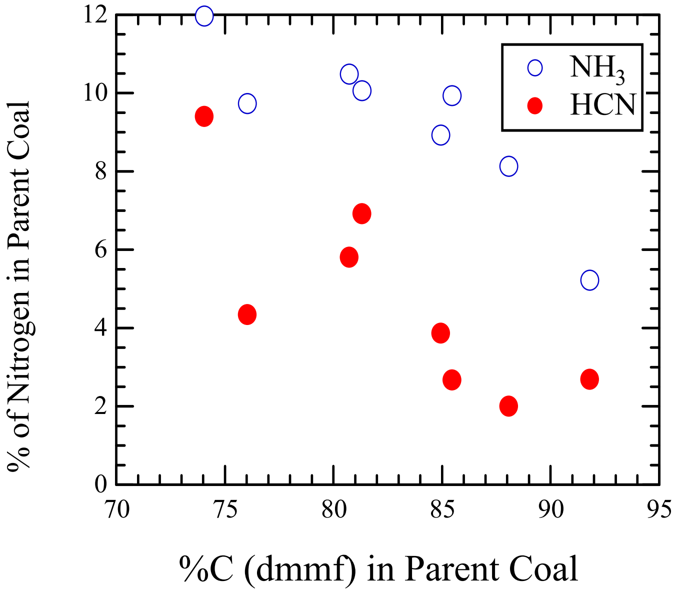
HCN Is Evolved Late in the Devolatilization Process

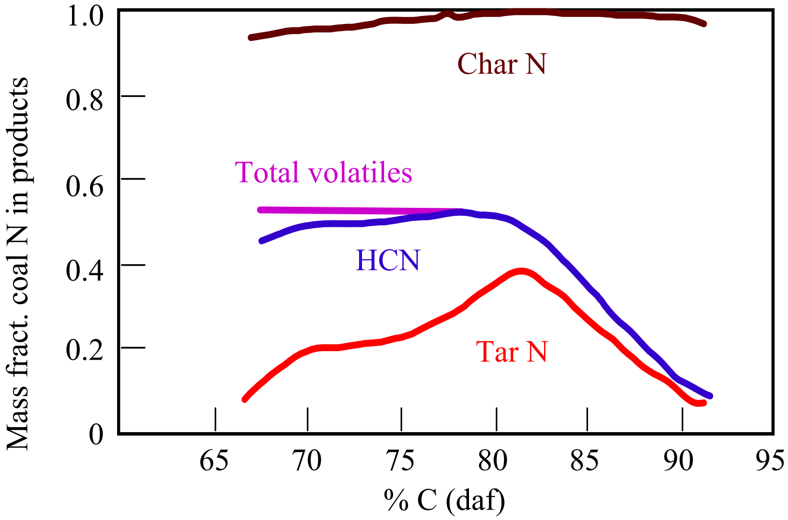


No NH_3 detected!

Pittsburgh No. 8 hv bituminous coal in radiant drop tube furnace, 20-30 μm
(Freihaut et al., Comb. Sci. Tech., 1993)

NH_3 Production Seems To Be A Function of Heating Rate and Char Contact Time



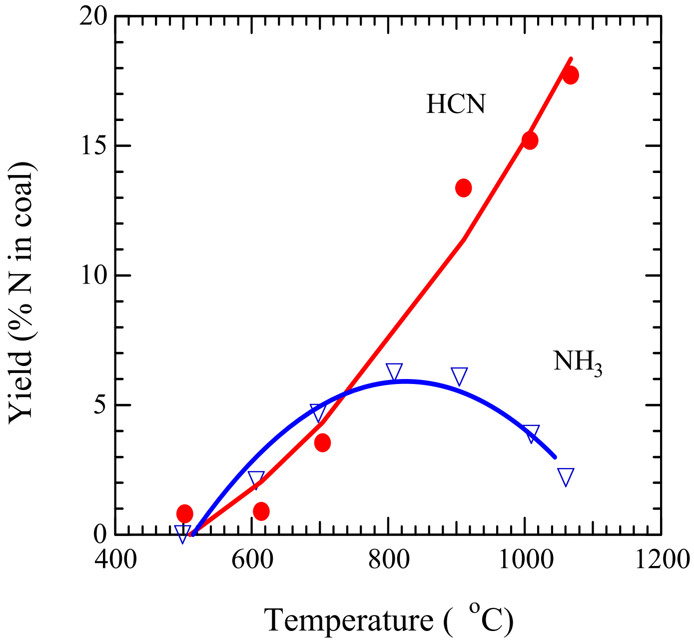


No NH_3 observed!

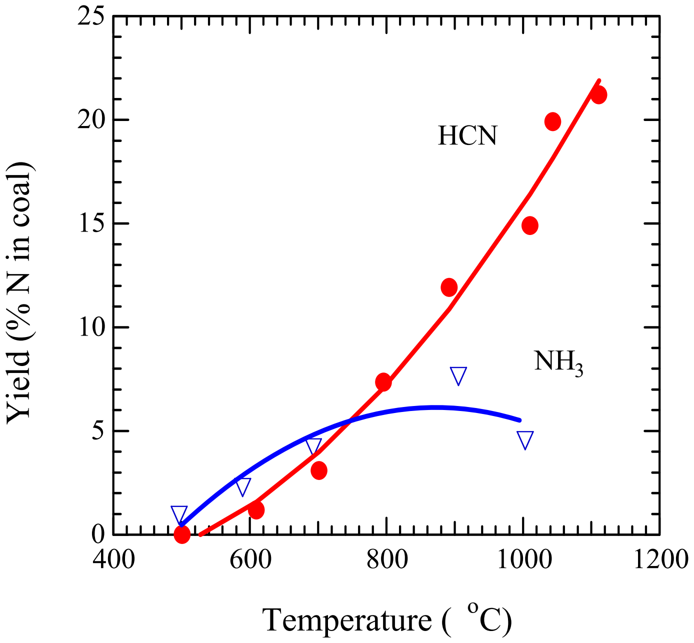
TGA yields of N gas species, 0.5 K/s to 900 °C (Bassilakis, et al., E&F, 1993). No NH_3 seen in EFR experiments (10^4 K/s).

Heated grid data, 500 K/s to 1273 K, 4 s hold time in vacuum (Freihaut, et al., UTRC, 1989)

NH_3 Is Also Seen in Fluidized Bed Pyrolysis Experiments



Yallourn (low rank coal)

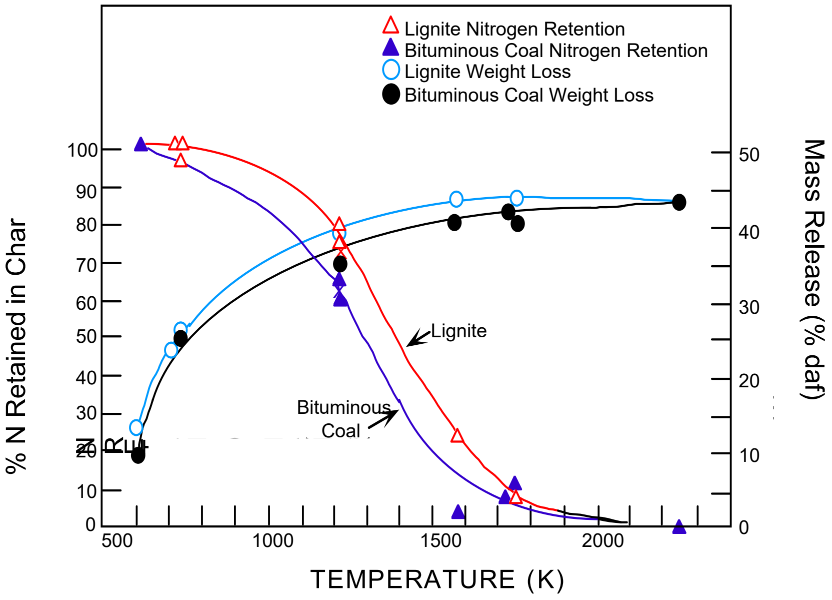


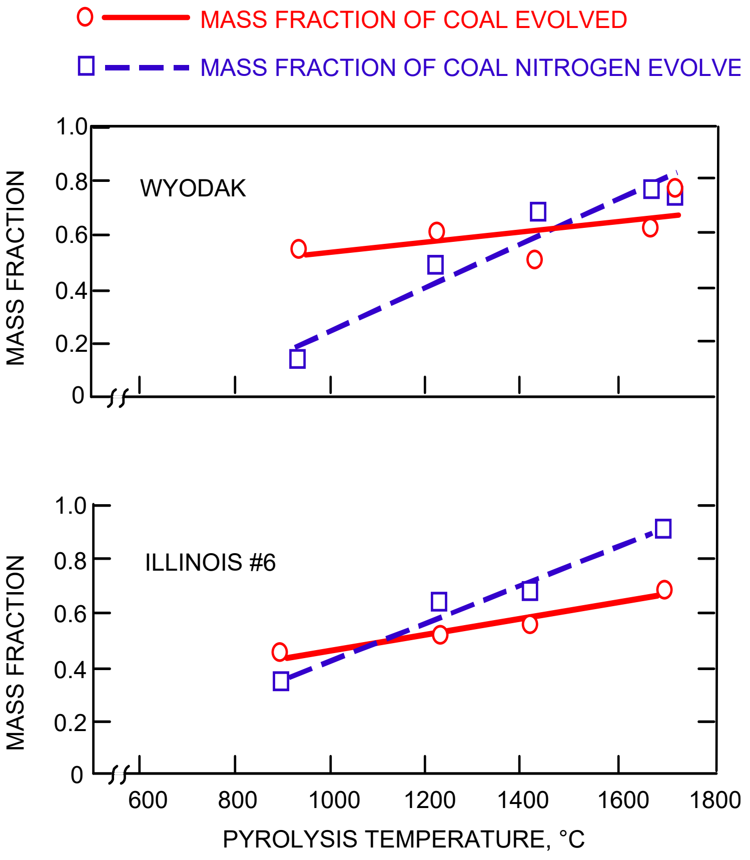
Blair Athol (bituminous coal)

Initial heating rate of 10^4 K/s, residence times of 0.3 to 0.5 s (Nelson, et al., 24th Symp., 1992)

Nitrogen Release Increases with Increasing Temperature

(In contrast to total volatiles yields)



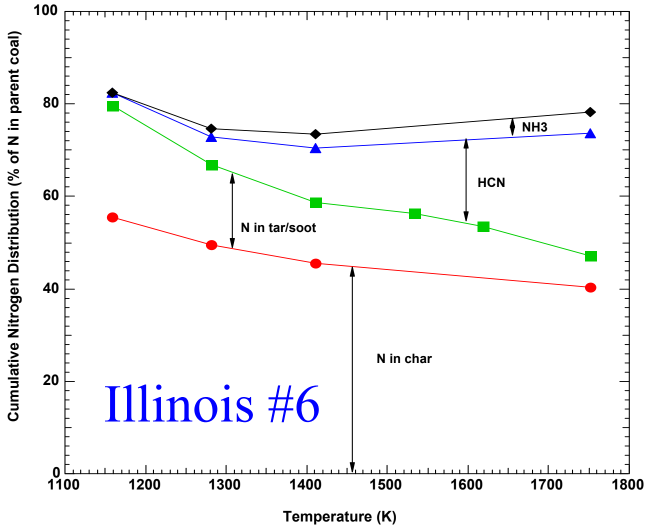


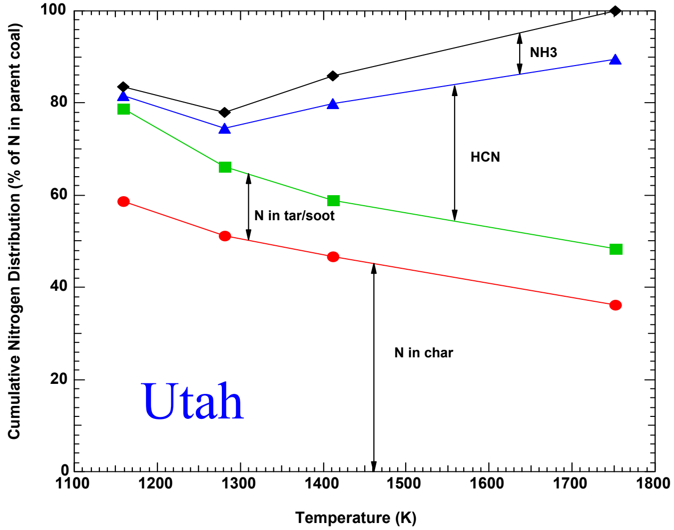
Crucible data from Pohl and Sarofim, 16th Symp. (1976)

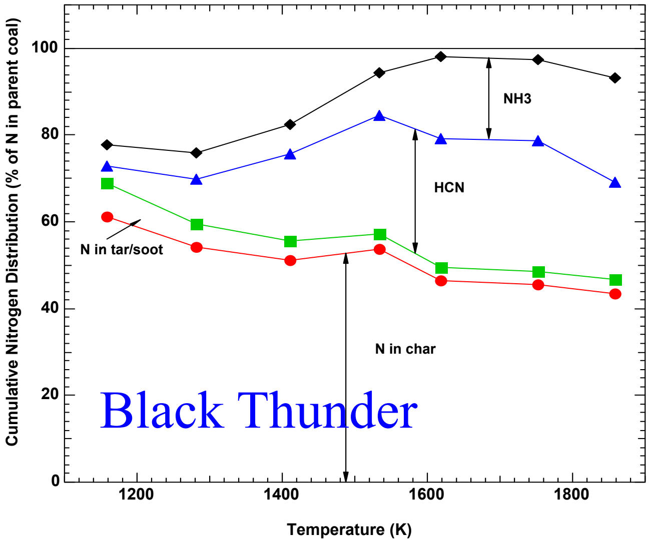
Heated graphite ribbon data from Blair, et al., 16th Symp. (1976)

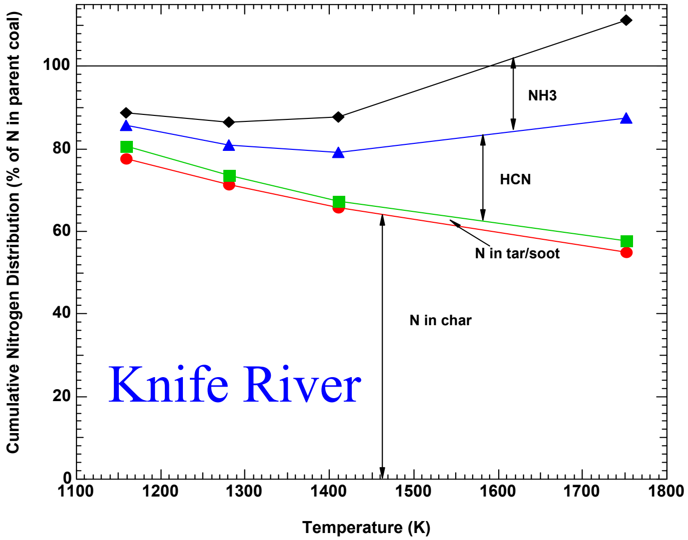
N distribution

(from Zhang, 2001, FFB data)

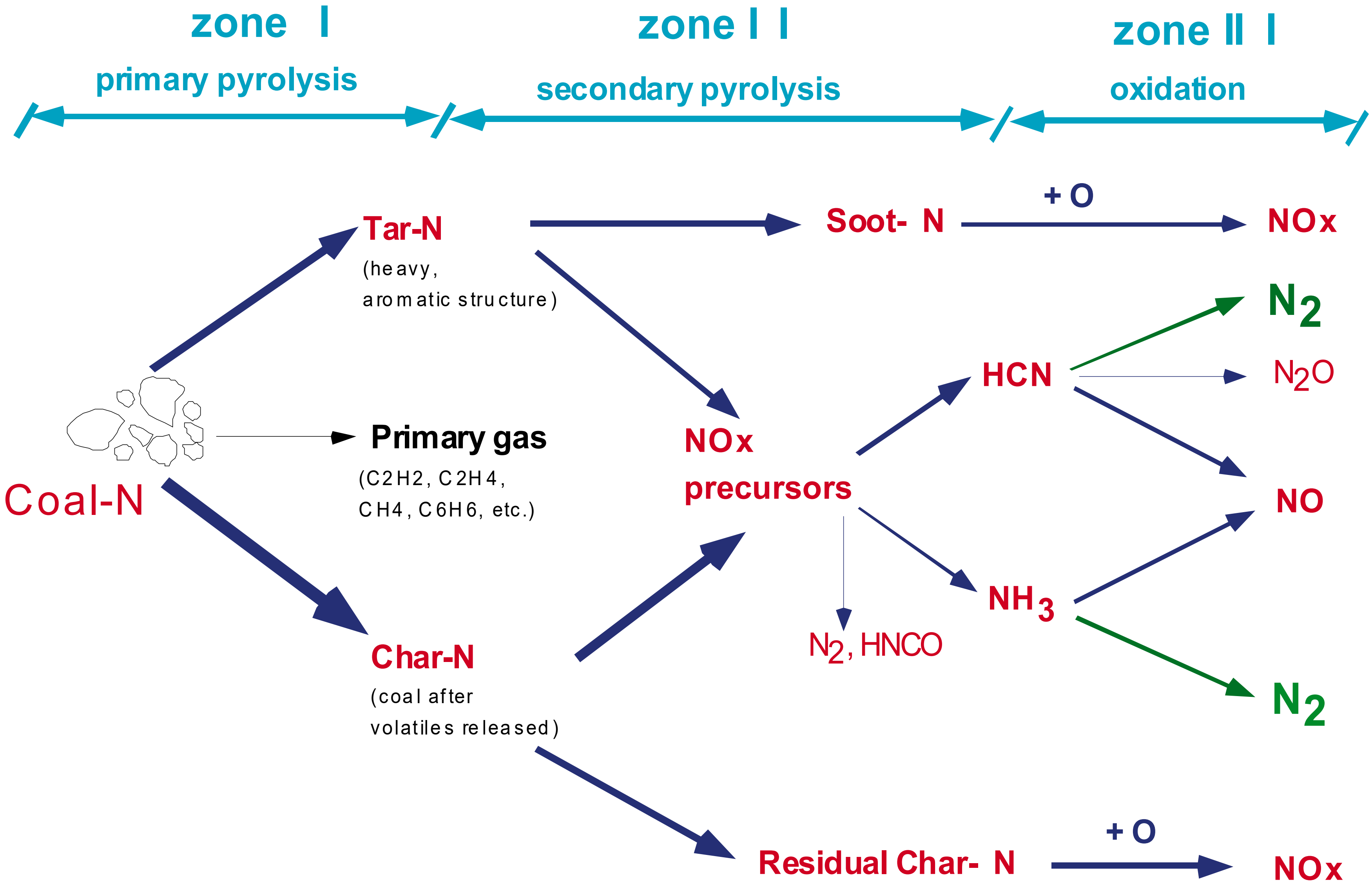








N transformations during Coal Combustion



zone I

primary pyrolysis

zone II

secondary pyrolysis

zone III

oxidation

Coal-N

Tar-N

(heavy, aromatic structure)

Primary gas

(C2H2, C2H4, CH4, C6H6, etc.)

Char-N

(coal after volatiles released)

Soot- N

+ O

NOx

NOx precursors

N_2, HNCO

HCN

$\mathbf{NH_3}$

$\mathbf{N_2}$

N_2O

NO

$\mathbf{N_2}$

Residual Char- N

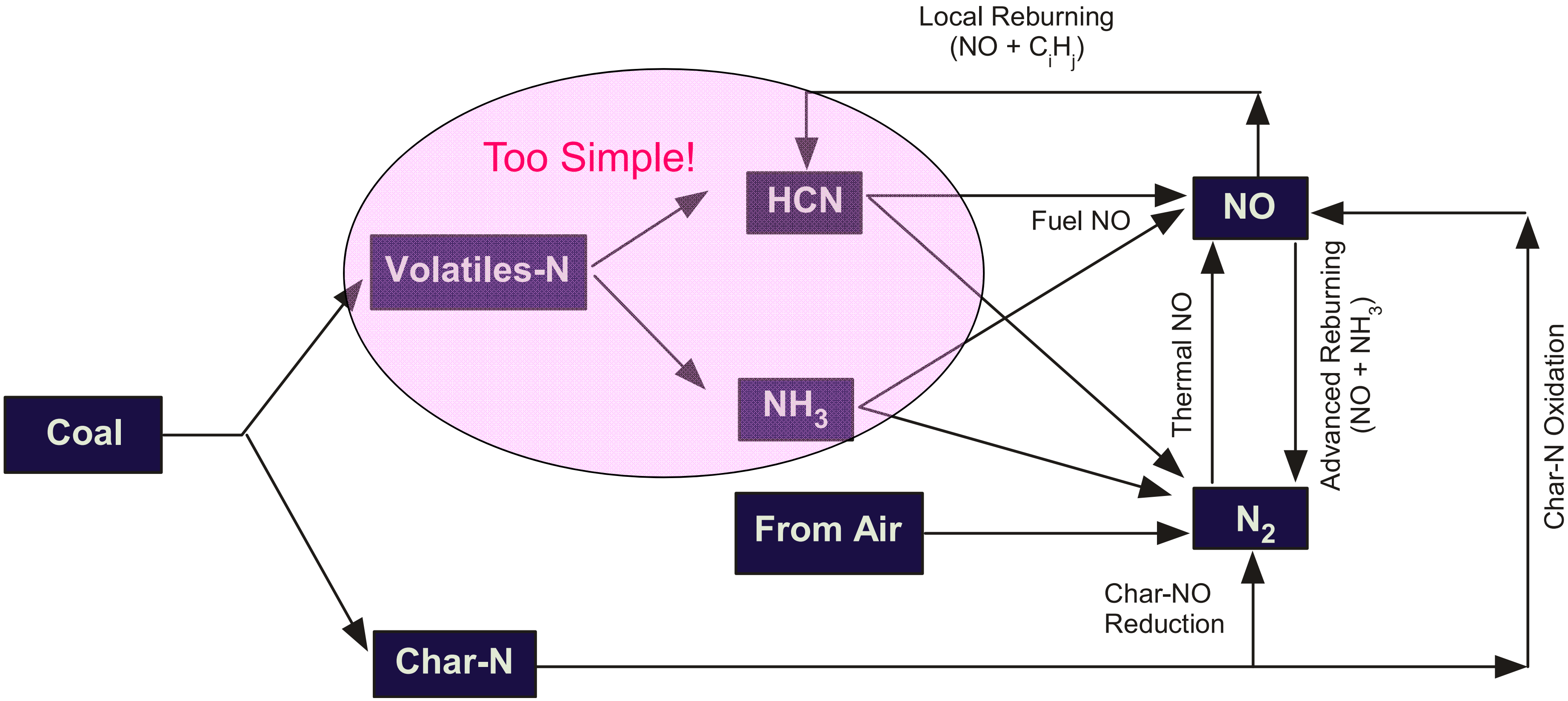
+ O

NOx

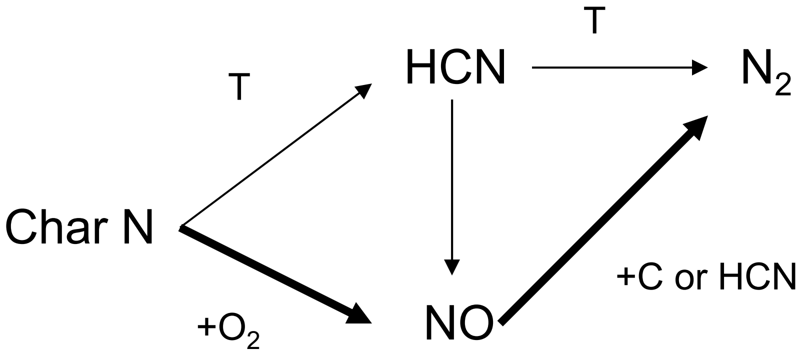
Summary of Primary Devolatilization of Nitrogen

- N exists as pyrrolic and pyridinic structures in coals
  - No ammonia or nitrate groups!
- N release ↑ as T ↑
  - Total volatiles yield reaches asymptote
- In rapid heating entrained flow, N release is proportional to carbon release (not mass release)
- Primary HCN release occurs late in the devolatilization process
- Little primary NH_3 release seen in entrained flow
- Little correlation between form of N in coal (pyrrolic vs. pyridinic) and N pyrolysis products

NO_x Pathways in Coal Combustion



3b. Char NO



- Result:
  - Often only 10-20% of char N → NO
- Control
  - Overfire air
  - Char NO not affected by low-NO_x burners
- Bottom line:
  - More N in volatiles means NO_x control through low-NO_x burners and air staging

4a. NO_x Control Strategies

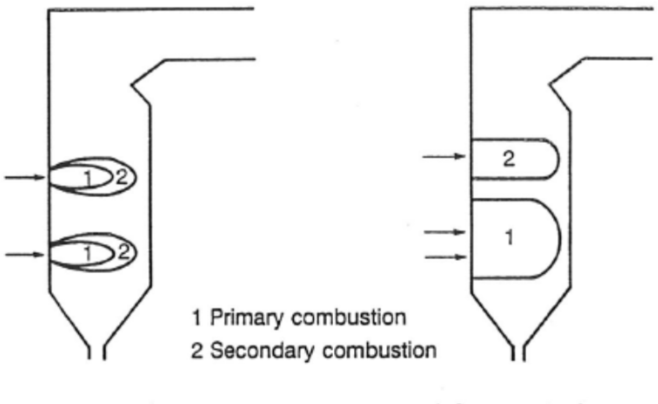
Combustion Modifications

TABLE 6.6

Achievable emissions reduction for selected stationary combustion NO_x control technologies

Abatement Technology	Percentage NO_x Reduction Possible			Advantages[116]	Disadvantages[116]
	Coal[114]	Nat. Gas [116]	Resid. Oil[116]		
Low excess air	0-15%	0-15%	0-20%	No significant capital cost, increased boiler efficiency	Oxygen trim system requires maintenance
Flue gas recirculation	0-5%	10-30%	5-20%	Retrofits are usually possible, can easily be combined with other technologies, very effective in reducing thermal NO	Requires high-temperature duct work and fans, higher capital cost than staged air or staged fuel to achieve equal or greater emissions reductions
Air staging	10-50% 30% typical	30-40%	30-40%	Low to moderate operating costs, can be adapted to existing boilers by taking selected burners out of service	May not be applicable to package boilers, access for secondary air ports may not be available
Fuel staging or low NO_x burners	30-75% 50 % typical	30-40%	30-40%	Low capital costs, retrofits normally possible, low operating and maintenance costs	Some increase in static pressure, may require package boilers to operate at a lower rate
Low NO_x burners and air staging and/or fuel staging	25-80% 70% typical	-	-	Highest reduction efficiency without resort to flue-gas treatment technologies, retrofit of existing combustors normally possible	May require boiler to be taken off line for an extended period during retrofit, may require package boilers to operate at reduced rates

Staging



a burner staging

b furnace staging

Figure 3 **Air staging in the burner and the furnace**

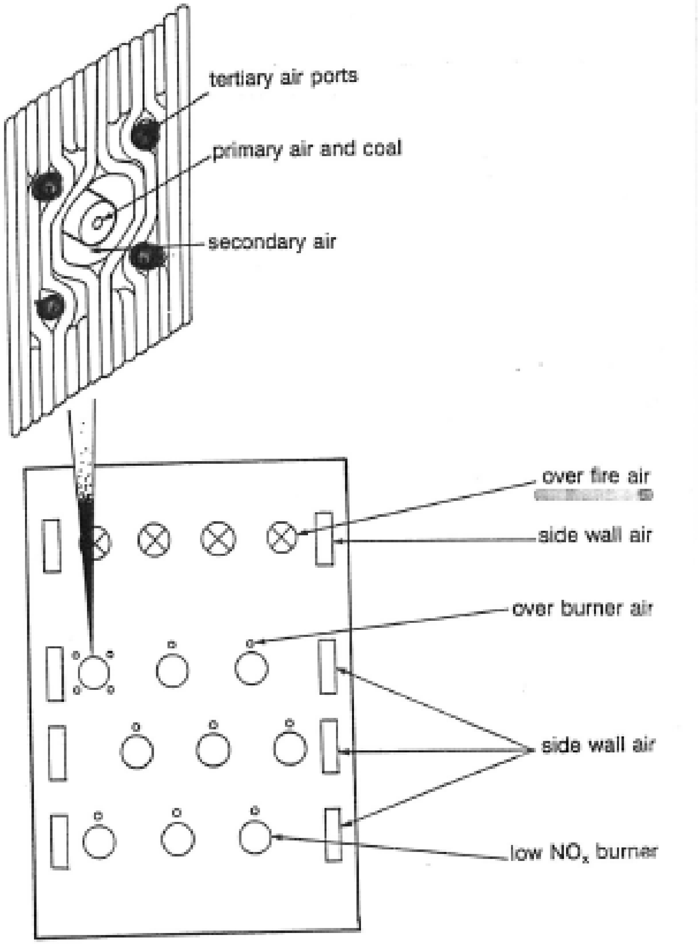
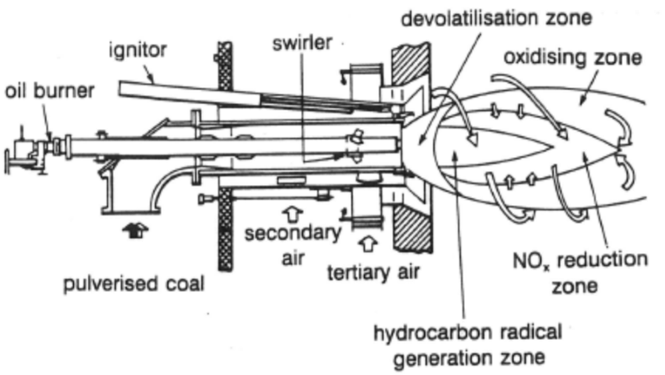
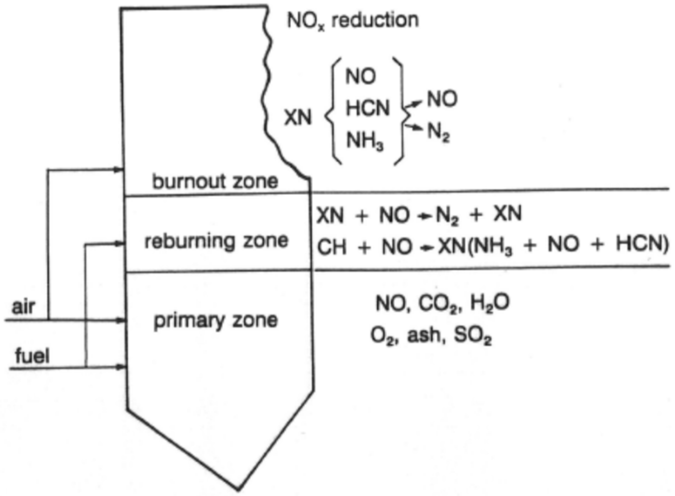


Figure 4 **Example of different locations of staged air on a furnace wall and in a burner (wall-fired boiler**

Low NO$_x$ Burner, Reburning

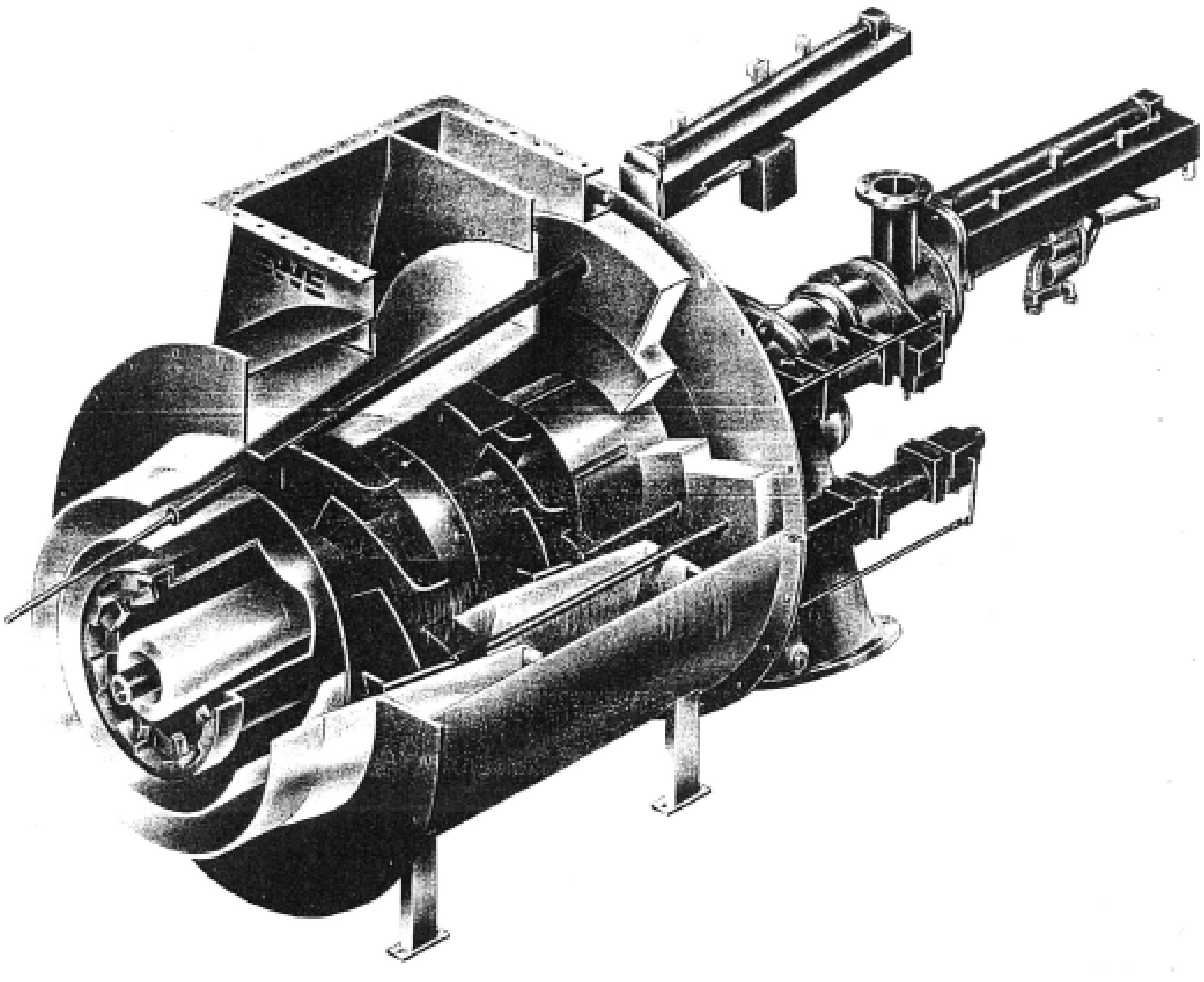


Example of an advanced low NO$_x$ burner
(LaRue and others, 1987)



Principle of fuel staging (reburning) in a furnace (McCarthy and others, 1987)

BWE Type 4AF Attached Flame Low-NOx Burners



Foster Wheeler

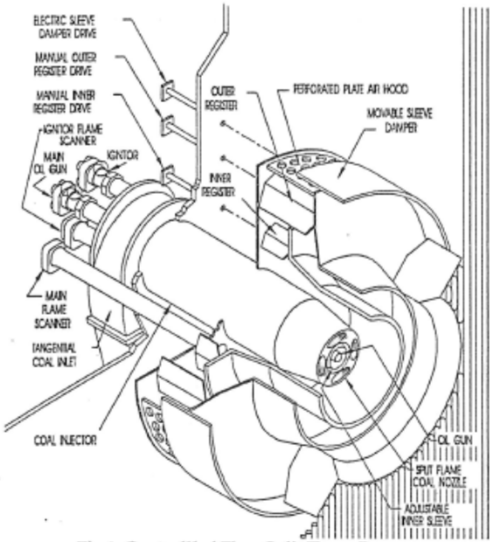


Fig 1. Controllled Flow Split Flame Burner

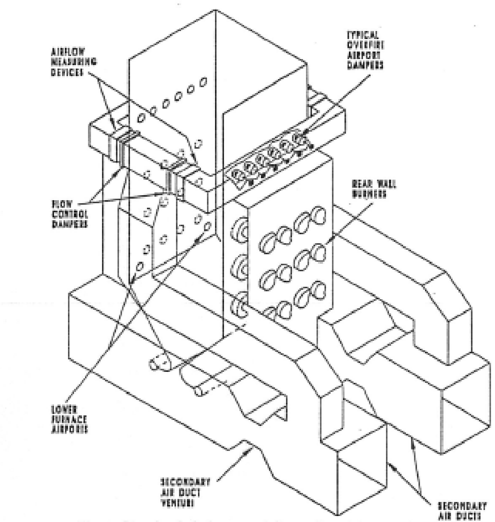
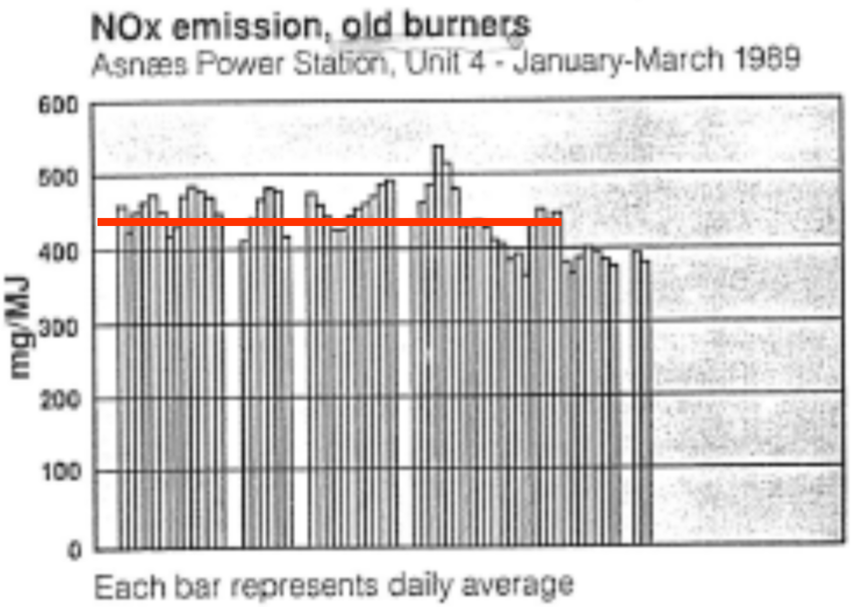


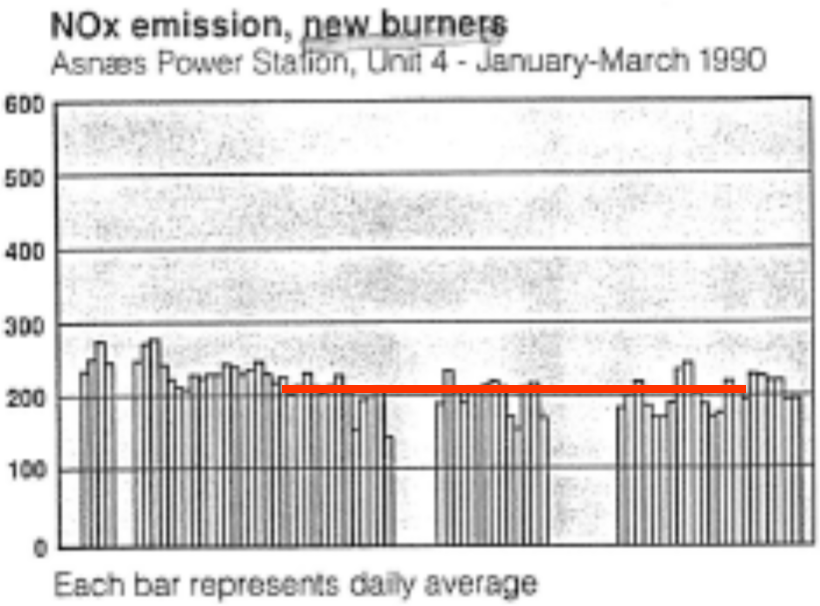
Fig 2. Typical Advanced Overfire Airport System



NOx emission, old burners

Asnæs Power Station, Unit 4 - January-March 1989

Each bar represents daily average



NOx emission, new burners

Asnæs Power Station, Unit 4 - January-March 1990

Each bar represents daily average

Reduction from ~440 mg/MJ to ~200 mg/MJ

4b. NO_x Control Strategies

Post-Combustion Control

Post-Combustion NO_x Abatement

$$4\ NO + 4\ NH_3 \rightarrow 4\ N_2 + 6\ H_2O$$

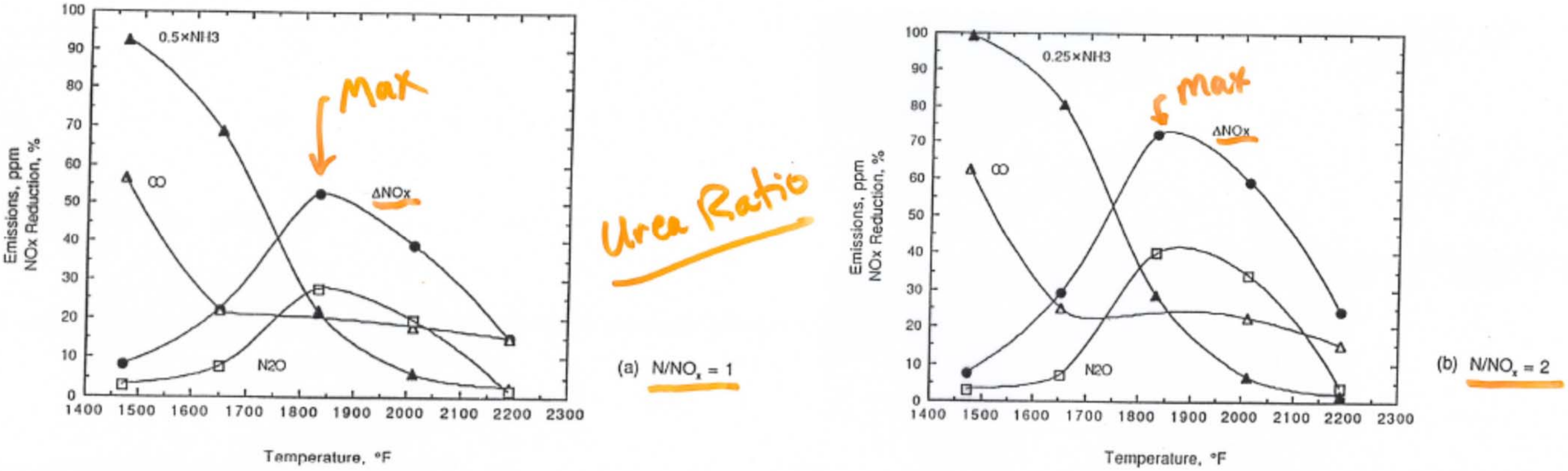
Selective Noncatalytic Reduction (SNCR)

- NH_3 or urea injected (900 to 1100°C)
- Up to 80% NO_x reduction
- Moderate capital cost
- NH_3 slip
- Good mixing required
- Careful control for varying loads

Selective Reduction (SCR)

- Mix combustion gases with reducing agent over catalyst
- Up to 90% NO_x reduction
- High capital cost
- NH_3 slip
- Problems with catalyst deactivation and disposal

Urea Addition



(a) $N/NO_x = 1$

Urea Ratio

(b) $N/NO_x = 2$

Figure 3. NO_x Reduction and Byproduct Emissions with Urea Injection (Initial NO_x = 250 ppm)

Selective Non-Catalytic Reduction (SNCR)

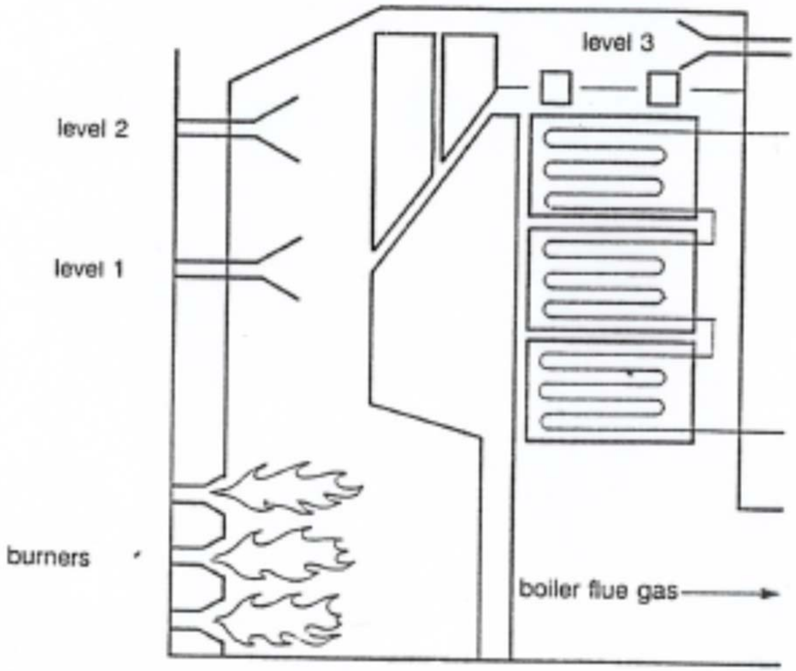
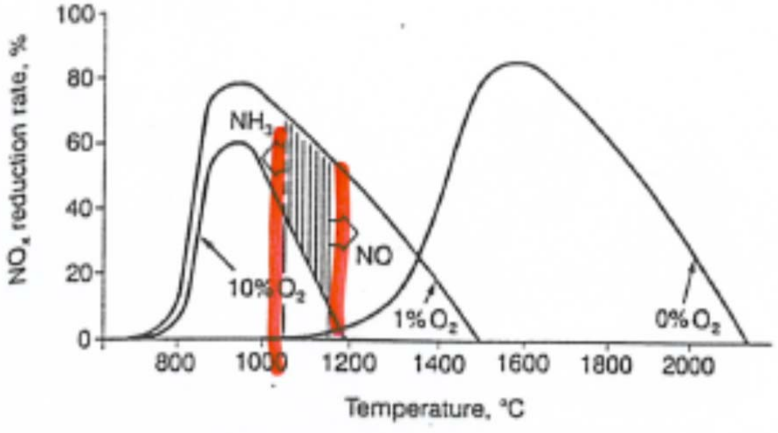


Figure 30 Injection at multiple levels for SNCR (Epperly and others, 1988)

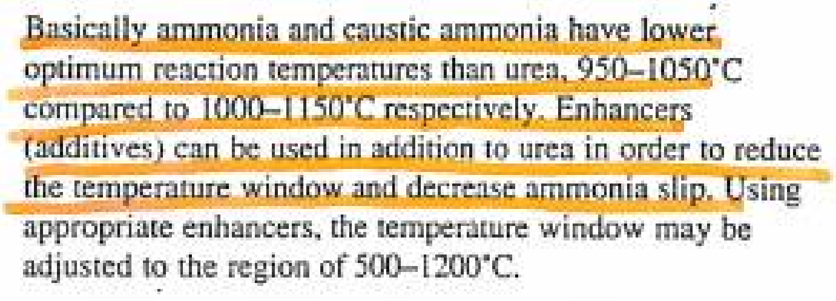
- Temperature window
  - 900-1100°C
- Common chemicals
  - Ammonia (NH_3)
  - Urea ($CO(NH_2)_2$)
- Must follow local temperature as load changes
- Problems
  - Ammonia slip
  - Ammonium bisulphate (clogging in air preheater)

SNCR



NO concentration = 100 ppm
NH$_3$ concentration = 100 ppm

Figure 31 Temperature window for SNCR NO$_x$ reduction rate as a function of temperature and O$_2$ concentration (Gebel and others, 1989)



Basically ammonia and caustic ammonia have lower optimum reaction temperatures than urea, 950–1050°C compared to 1000–1150°C respectively. Enhancers (additives) can be used in addition to urea in order to reduce the temperature window and decrease ammonia slip. Using appropriate enhancers, the temperature window may be adjusted to the region of 500–1200°C.

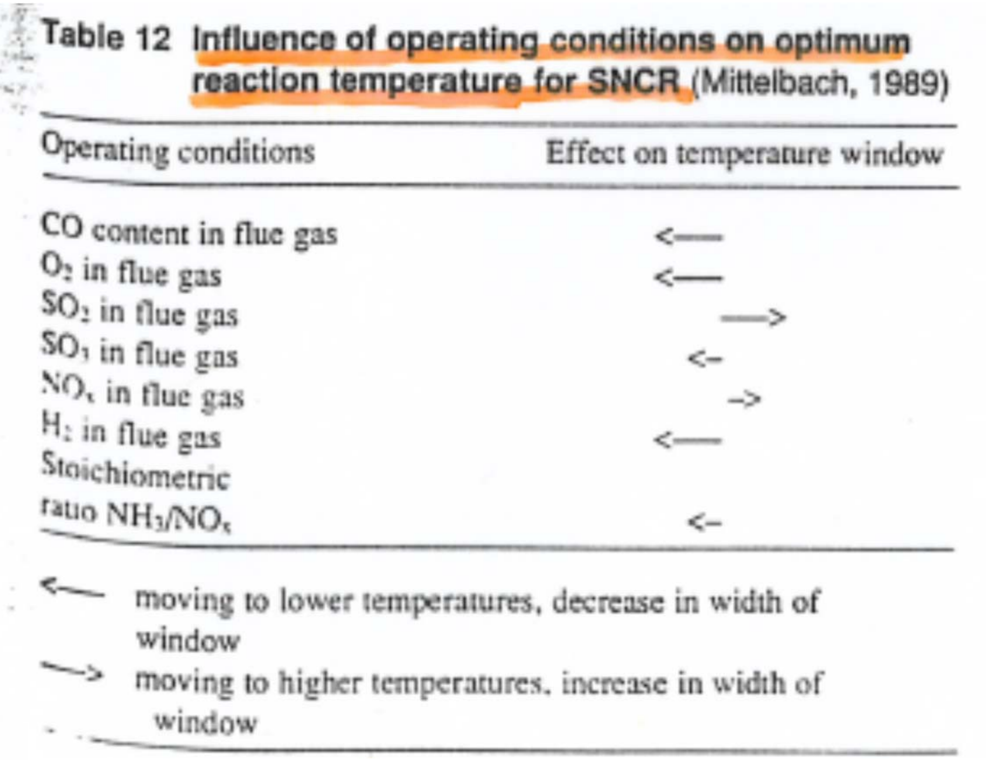
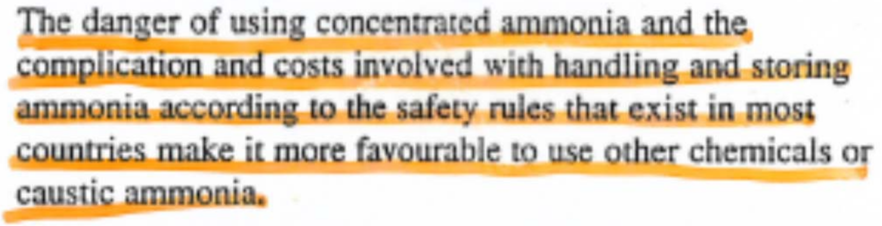


Table 12 Influence of operating conditions on optimum reaction temperature for SNCR (Mittelbach, 1989)

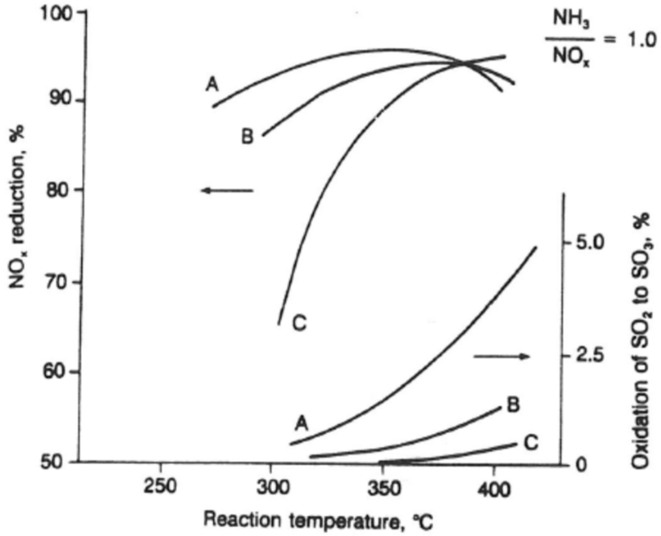
Operating conditions	Effect on temperature window
CO content in flue gas	<——
O$_2$ in flue gas	<——
SO$_2$ in flue gas	——>
SO$_3$ in flue gas	<–
NO$_x$ in flue gas	–>
H$_2$ in flue gas	<——
Stoichiometric ratio NH$_3$/NO$_x$	<–

<—— moving to lower temperatures, decrease in width of window
——> moving to higher temperatures, increase in width of window



The danger of using concentrated ammonia and the complication and costs involved with handling and storing ammonia according to the safety rules that exist in most countries make it more favourable to use other chemicals or caustic ammonia.

Selective Catalytic Reduction (SCR)



Type	Activity	Field of application	Type of fuel at high dust
A	high	clean gas	gas
B	average	clean gas	oil
C	low	raw gas	coal

NO_x reduction and oxidation of sulphur dioxide as a function of reaction temperature for different types of catalysts (Hüls, 1986)

- Reducing agents
  - Typically NH_3
  - Hydrocarbons
- Typical catalysts
  - V_2O_5/TiO_2
  - Metal-exchanged zeolites

SCR

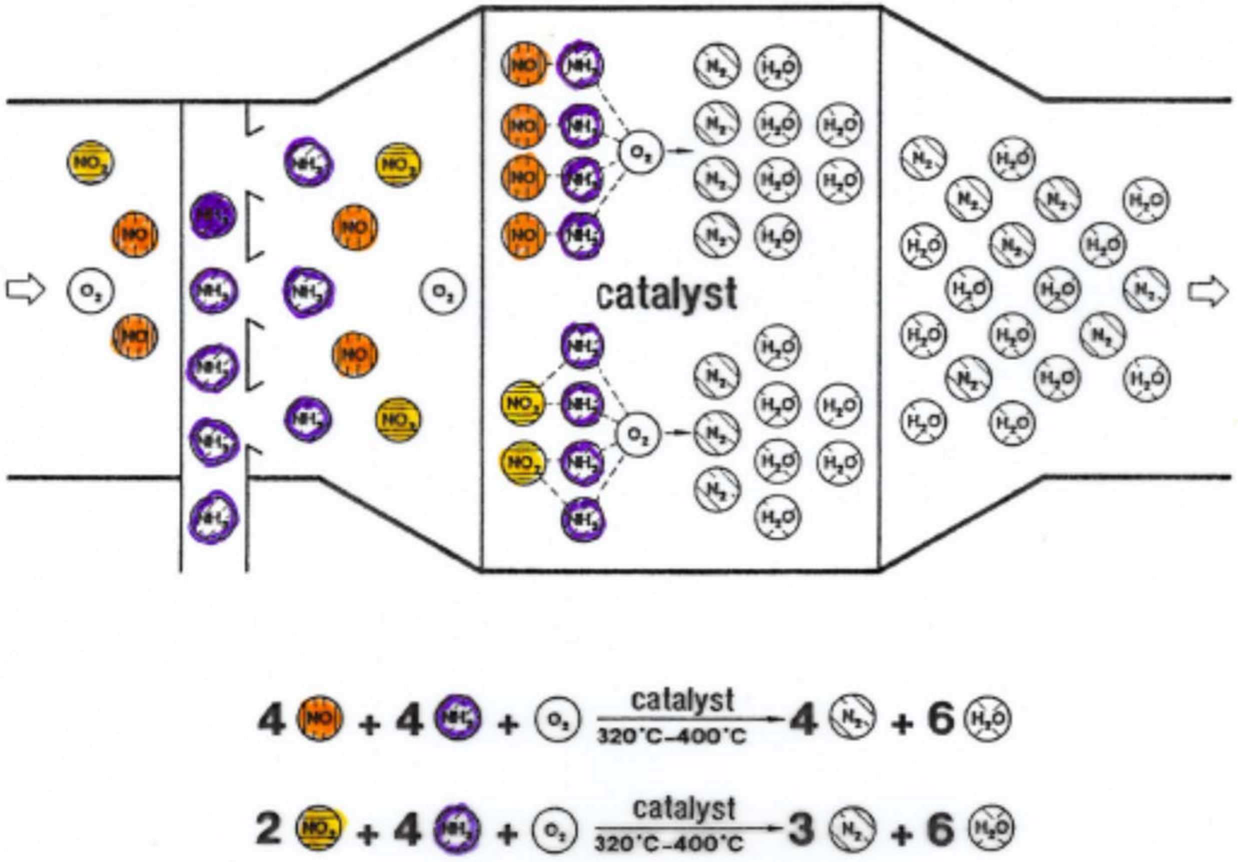


Figure 3. Principals of the SCR-Process

SCR

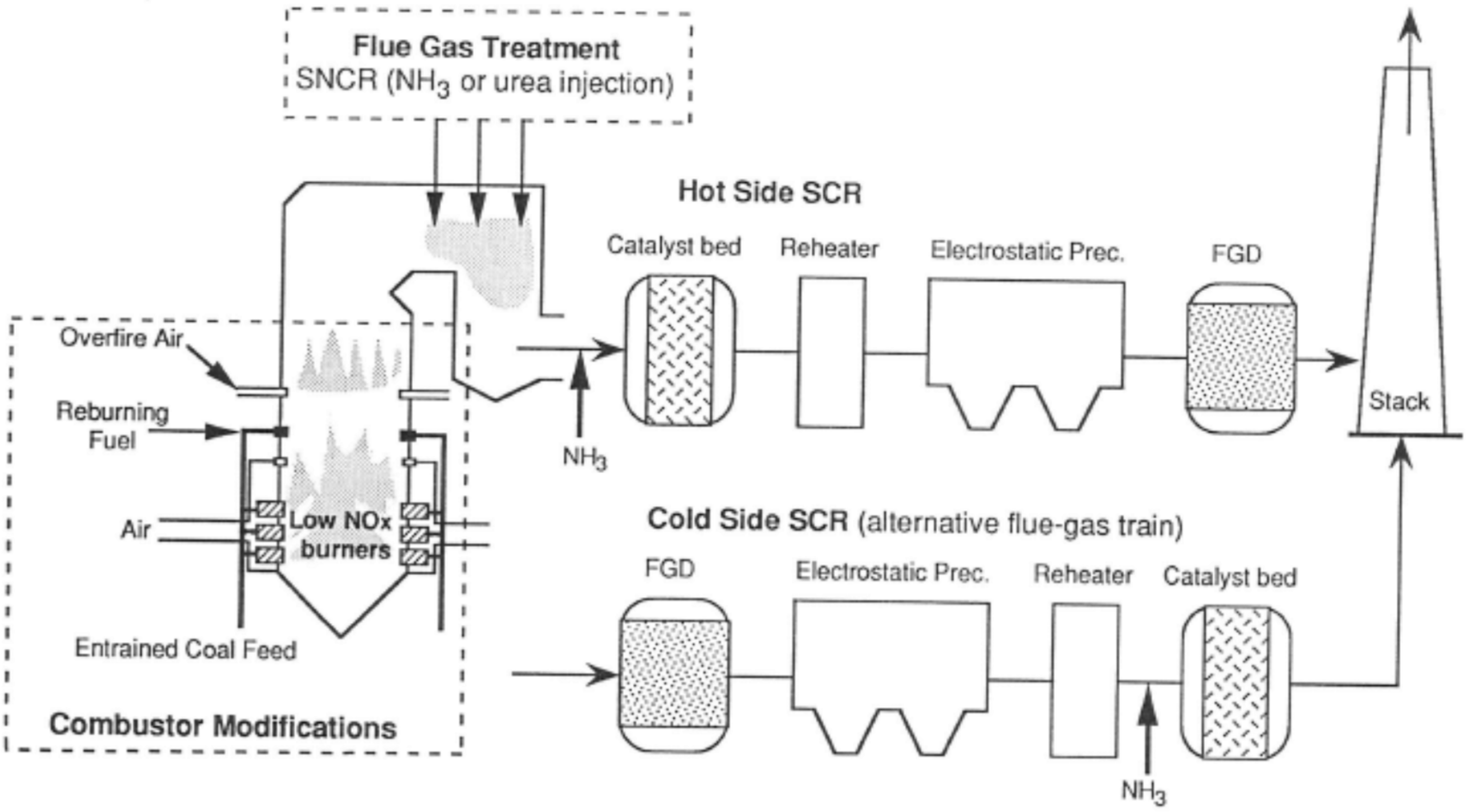
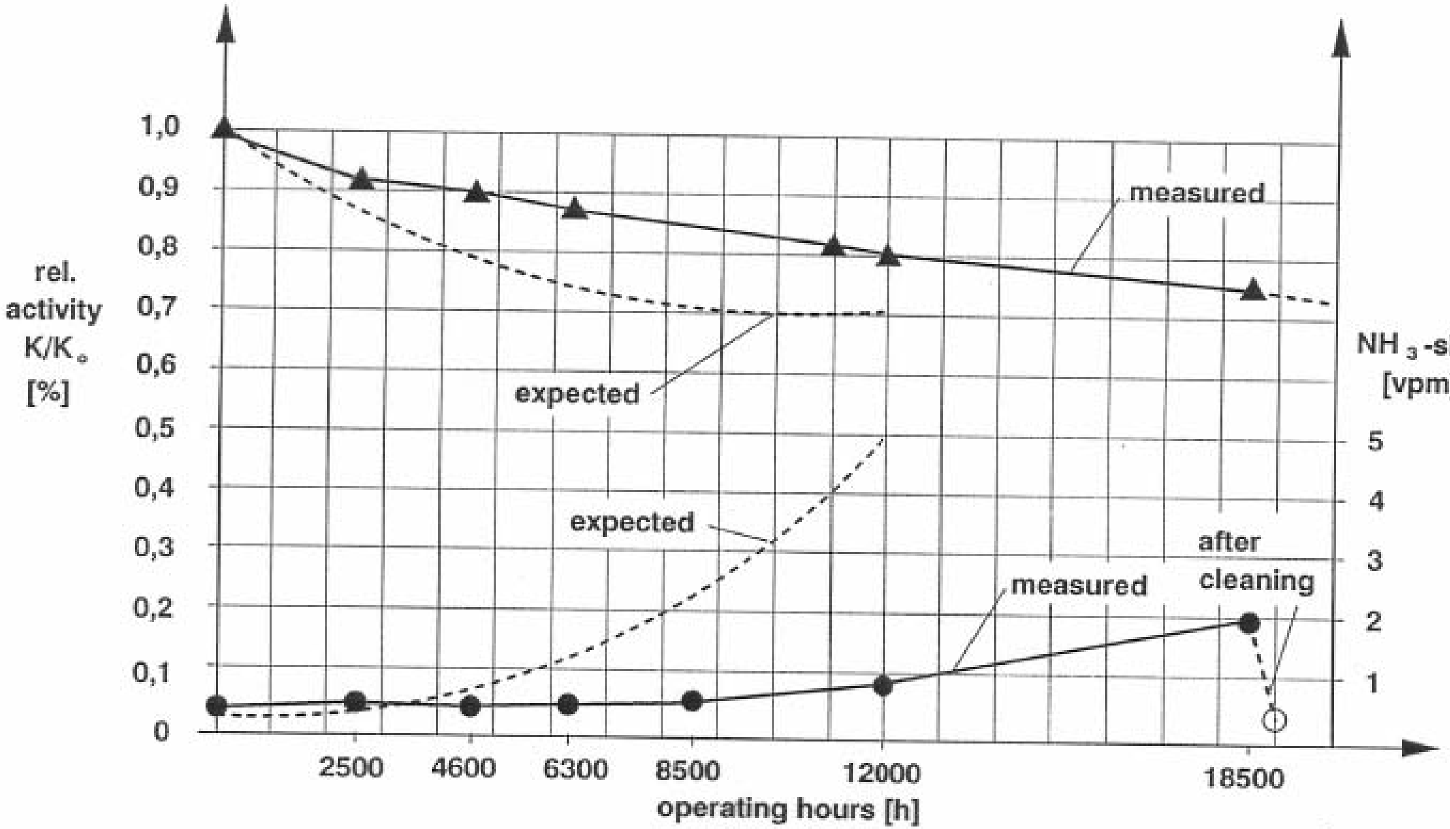


Fig. 6.14 Schematic drawing of NO_x abatement control technologies and their point of application. SNCR = Selective Non-Catalytic Reduction; SCR = Selective Catalytic Reduction; FGD = Flue Gas Desulfurization.

Catalyst Life



500 days

771 days

Figure 5. Heilbronn power station unit 7; DENOX-plant. Loss of activity and ammonia slip

$SO_xNO_xRO_xBO_x$

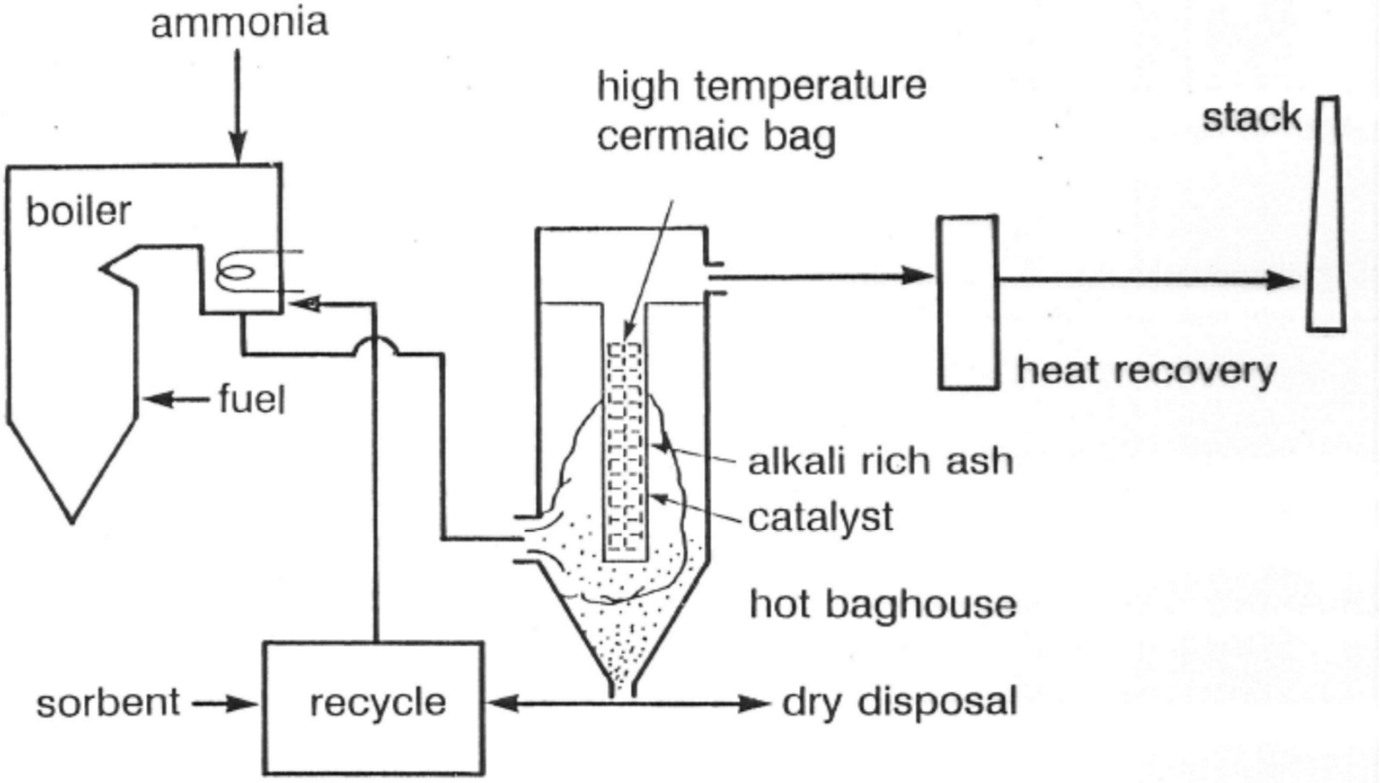


Figure 34 **$SO_xNO_xRO_xBO_x$ hot bag filter process for combined SO_2, NO_x and particulate removal** (Kitto, 1989)

NO$_x$ Reduction Comparison

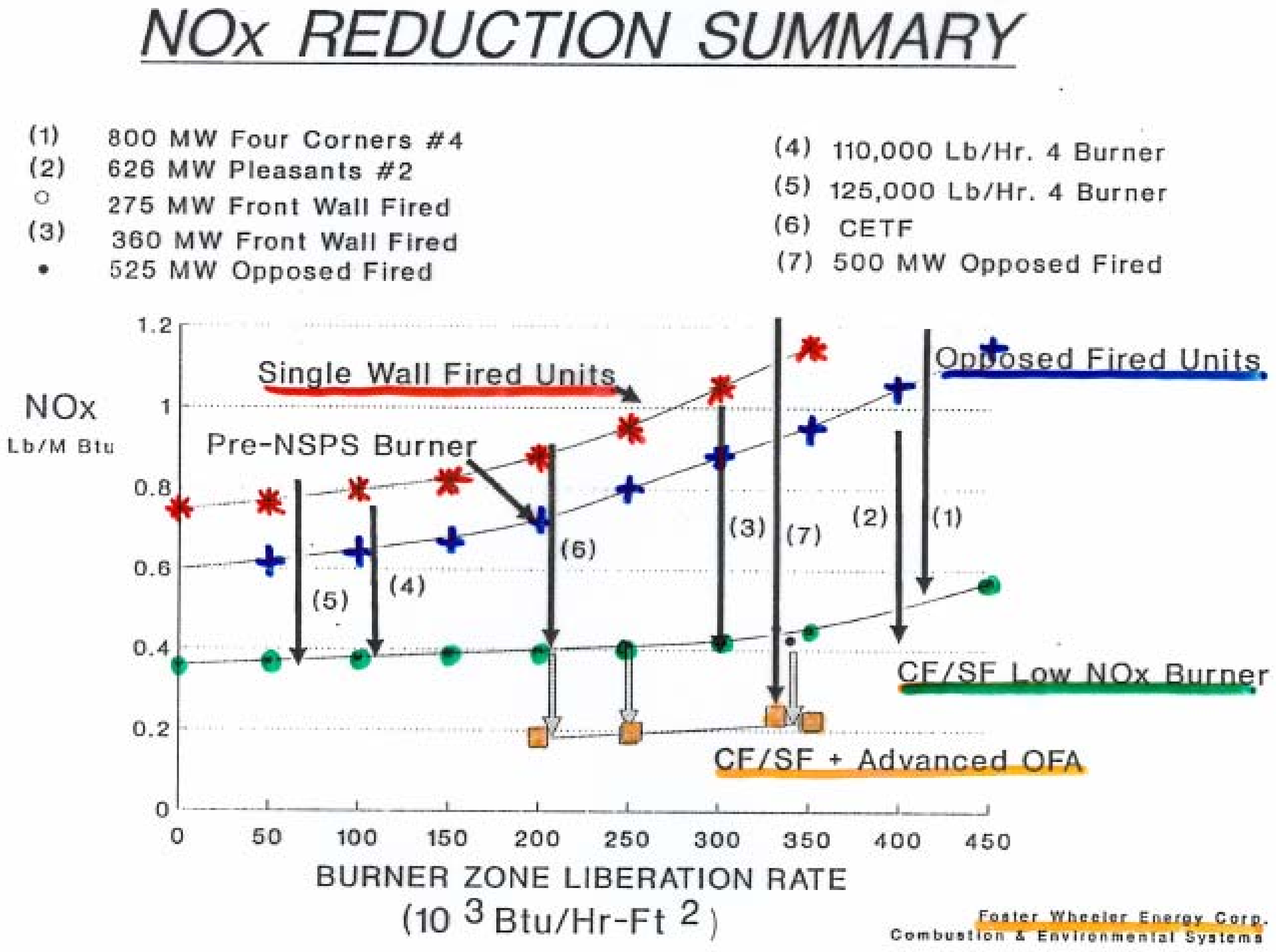


Figure 3

5. Cost Comparison

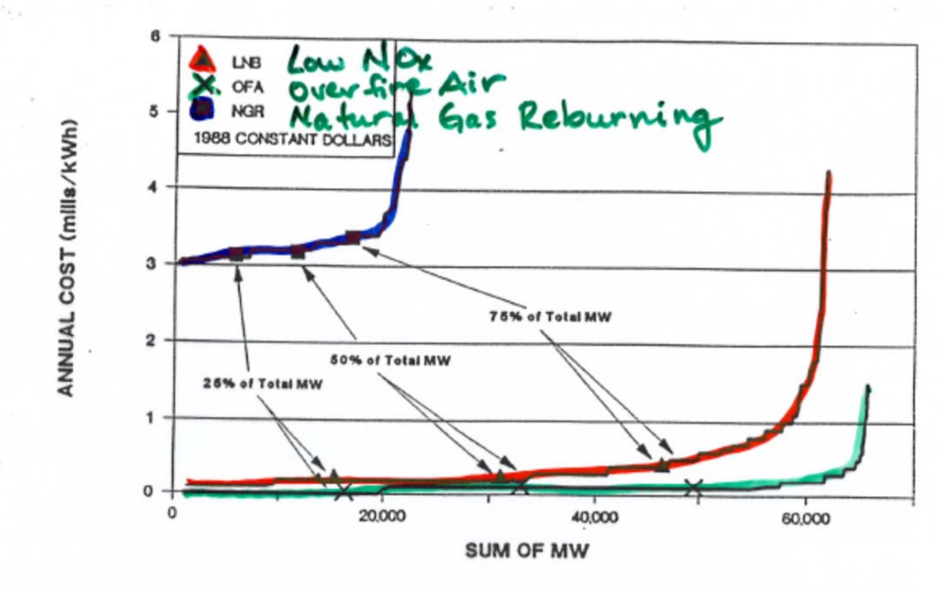


FIGURE 4. SUMMARY OF ANNUAL COST RESULTS FOR LOW NOx COMBUSTION

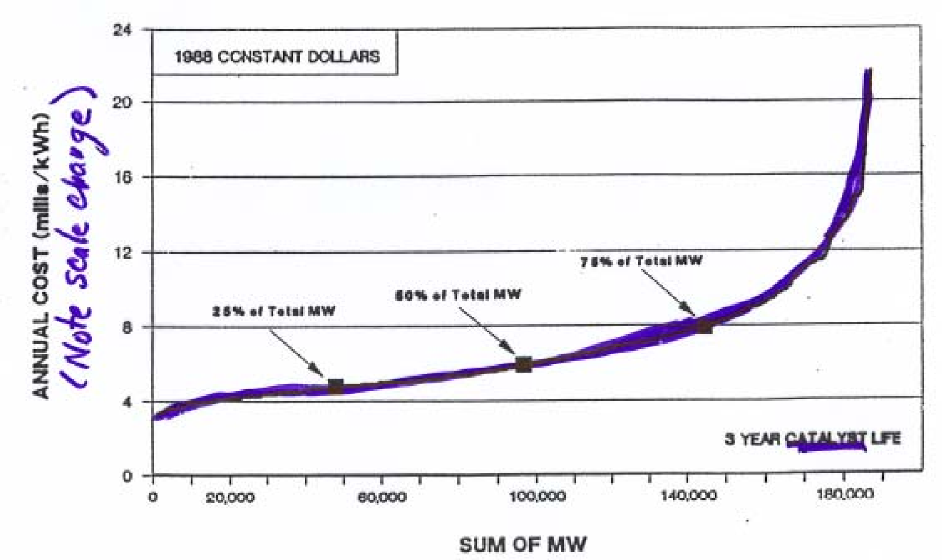


FIGURE 5. SUMMARY OF ANNUAL COST RESULTS FOR SELECTIVE CATALYTIC REDUCTION.

(from Radian corp.)

Review

- Why NO_x is bad
- Categories of NO_x formation
  - Thermal
  - Fuel
  - Prompt
- Forms of N in coal
- N release mechanisms
  - Pyrolysis
  - Char oxidation
- NO_x reduction strategies
  - Overfire air
  - Low NO_x burners
    - Wall-fired units
    - Tangential-fired units
  - Reburning
  - SNCR
    - Ammonia
    - Urea
    - Others
  - SCR
    - Hot side
    - Cold side