Lecture 15 - NO_x - Chp 5, 15.

3 NO_x Mechanisms

1. Thermal NO_x: Zeldovich
2. Prompt NO_x: Fenimore — Includes Fuel NO_x.
3. N_2O - intermediate

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1. High T: wide range of ϕ (slow)
2. Fast, Rich
3. Lean, Low - T.

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1. Zeldovich:

$$O + N_2 = NO + N$$
$$N + O_2 = NO + O$$
$$N + OH = NO + H$$

- 3 Rxns
- NO product — To recall.
- $N_2 + O$, $O_2 + N$, $N + OH$

- Rate Dep on fuel chemistry through O_2, N_2 O, OH, N

But combust is way faster than NO_x

[See PPT slide] $O(20\ ms)$ vs $O(0.2\ ms)$

→ 100 x.

- → Decouple the chemistry. Assume eq O, N etc.

NO has a small impact on (O), (N_2) < 5%

- Neglect Rev. Rxns → $\frac{d(NO)}{dt} = 2k\,(O)_{eq}(N_2)_{eq}$.

Good up to ~75 ms (see HW 5)

- In Flame zones → not equilibrium

higher [O] than equilibrium. ✱ Superequilibrium O → higher Rates.

- Thermal NO_x > 1800 K !

- See HW5

(2) Prompt NO_x

- Flame Zone
- Combustion chemistry
- Fast

* $CH + N_2 = HCN + N$ * Primary, Rate limiting

$C + N_2 = CN + N$

- Then HCN $\xrightarrow[\text{steps}]{}$ NO

$\phi > 1.2$, $\phi < 1.2$.

- Can be complex.

- Fuel NO_x : $N \rightarrow HCN \xrightarrow[\text{prompt}]{} NO$

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(1) Note $(NO/NO_2)_{eq} \approx 6000$ (Thats equib!)
Not actual output.

Modlink → about same spread!

2226 K → NO_2 Destroyed.

* At lower T NO_2 formed

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(3) N_2O Not Discussed

NO_x emission & Control.

- In many ways Pollutant emissions Drive our study of Combustion and our Design of equipment.
- NO_x is one of the king Pollutants.
- Premixed / Nonpremixed Categories
  - Chemistry is The Same, but get Different properties Due to mixing & Composition variations.

- Contributions – Table 15.2
  - Pressure: Low → Prompt
  - ϕ rich
  - ϕ lean.

See PPT

NO_x Control

(1) – Combustion Controls
(2) – Post Combustion Controls.

(1) mainly for Thermal NO_x

- Figures : NO_x vs ϕ — Control = Time, Temp, O_2
  NO_x vs T

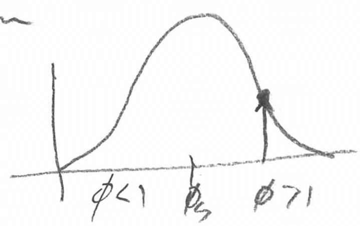
  - NO_x peaks lean $\phi = 0.85$ = 0.9
    = peak [O]
  - NO_x Takes off for T > 1800 : high E_{act}.
  - NO_x is "slow" as we've seen.

  * Control by (1) reducing Temperatures
  (2) Changing ϕ
  (3) Going fast.

- See PPT NO_x vs ϕ

(Q) If we want To run slightly lean : say $\phi = 0.9$ overall, but minimize NO_x. How Can we use The above properties to ~~Do~~ Do This? →

- Staged Combustion: rich → lean
  - Burn partially rich
  - Then : quickly mix in more air
  - Then burn out lean.



- Others :

See PPT Fig 15.13.

  - Staging
  - Reduce T
  - remove NO from Fuel
  - Remove NO from Products.

Staging

- Over-fire air
- Low NO_x burners — See PPT — 10-40% reduction
- Biased firing
- Reburn (up to 60%)

Temperature

- water injection
- FGR

} 50-85%

SNCR

- inject ammonia, urea, cyanuric acid to "reduce" NO_x
- ~ 1250 K

SCR

- $NO \xrightarrow{NH_3} N_2$ 480-780 K
- expensive
- High reduction

Use a combo. of methods.

Examples - See PPT

Limits on NO_x

- See Table 15.6 ~ 15-40 ppm
- Equilibrium values ~ 3000 PPM
- Uncontrolled NO_x → Table 15.5

Fuel NO_x - Coal : 20-40% of Fuel N → NO_x = ~$\frac{1}{2}$ total NO_x

- Combustion control → Thermal NO_x
- Rest via Post-combustion

Chemical Engineering 633

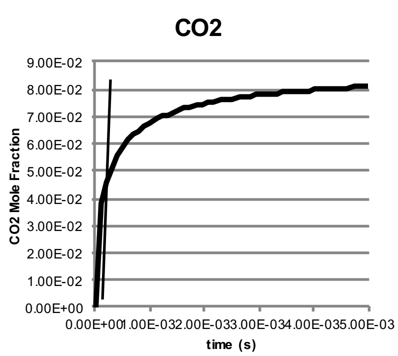
Combustion Processes

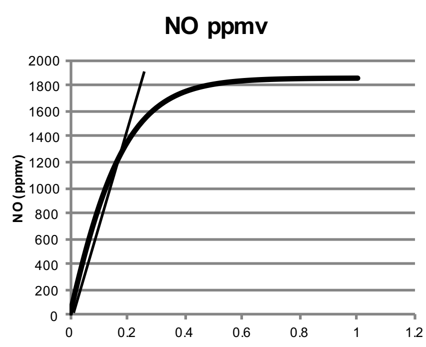
NO_x

1

Timescales

2





CH4 + air at constant 2226 K

NO formation at 2226 K with CH4+air equilibrium products)

Fenimore/Promt NO

3

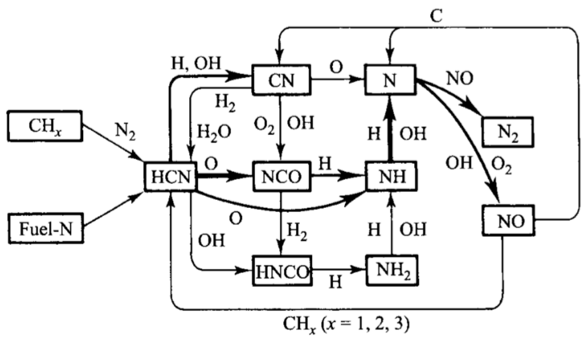


Figure 5.6 Production of NO associated with the Fenimore prompt mechanism.
SOURCE: Reprinted from Ref. [25] by permission of The Combustion Institute.

NO Contributions

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Flame	Φ	P(atm)	Total NO_x (ppm)	Fraction of Total NO Formation: Equilibrium Thermal	Superequilibrium	$HC–N_2$	N_2O
Premixed, laminar, CH_4–air [22]	1	0.1	9 @ 5 ms	0.04	0.22	0.73	0.01
	1	1.0	111	0.50	0.35	0.10	0.05
	1	10.0	315	0.54	0.15	0.21	0.10
Premixed, laminar, CH_4–air [23]	1.05	1	29 @ 5 mm	0.53	0.30	0.17	—
	1.16	1	20	0.30	0.20	0.50	—
	1.27	1	20	0.05	0.05	0.90	—
	1.32	1	23	0.02	0.03	0.95	—
Well-stirred reactor, CH_4–air [23, 24]	0.7	1	12 @ 3 ms	≈0	0.65	0.05	0.30
	0.8	1	20	—	0.85	0.10	0.05
	1.0	1	70	—	0.30	0.70	—
	1.2	1	110	—	0.10	0.90	—
	1.4	1	55	—	—	1.00	—

Lean Premixed

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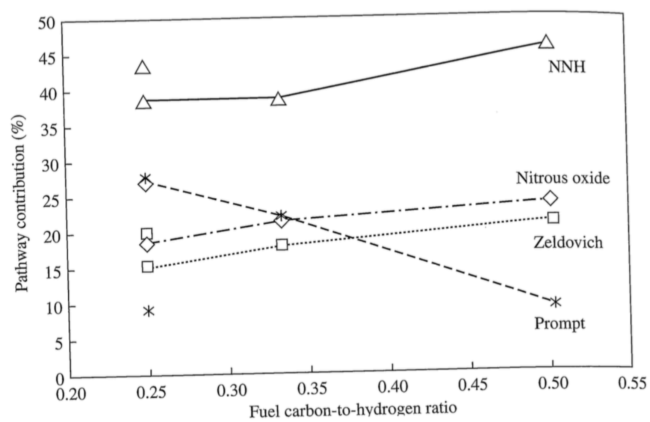

Figure 15.2 The results from the modeling study of Rutar *et al.* [36] show the contributions of various NO-formation pathways to the total NO formed for lean premixed combustion for Φ = 0.61, 1 atm, and 1790 K. A sequence of perfectly stirred reactors was modeled to simulate the experiments used for comparison.

Lean Premixed

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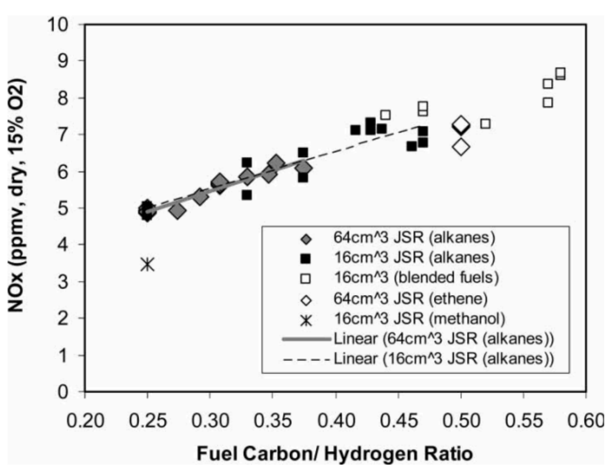
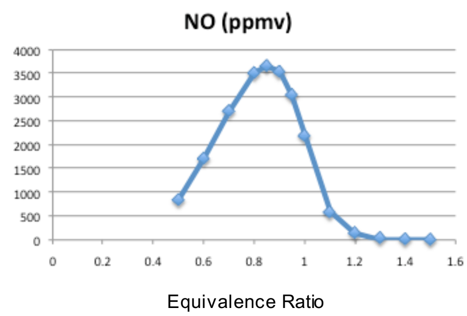
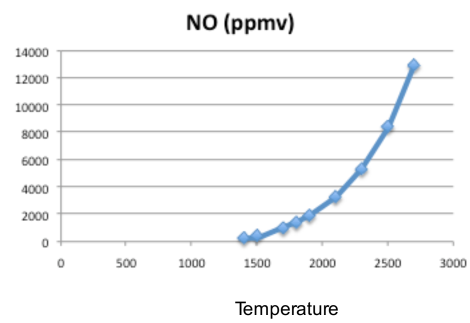


Equilibrium NOx (methane)





NOx Levels

Process	Range, ppm at 3% O_2
High-temperature direct	
High preheat	500–2,000
Low preheat	200–800
High-temperature indirect	200–600
Low temperature	30–100
Boilers	25–100

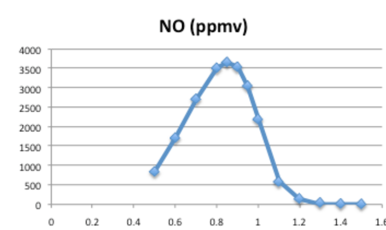


Table 15.6 The NO_x emission regulations for industrial sources (California SCAQMD) [70]

Process	Limit	Rule No.
Gas-fired industrial boilers	30 ppm (3% O_2)	1146, 1146.1
Refining heaters	0.03 lb/MMBtu	1109
Glass-melting furnaces	4 lb/ton of glass	1117
Gas turbines (no SCR)	12 ppm (15% O_2)	1134
Gas turbines (SCR)	9 ppm (15% O_2)	1134
Others	Best available current technology	

- Limits ~ 12-30 ppm
- Equilibrium ~ 3000 ppm
- (Raw Emm. ~ 25-2000 ppm)

NOx Control Strategies

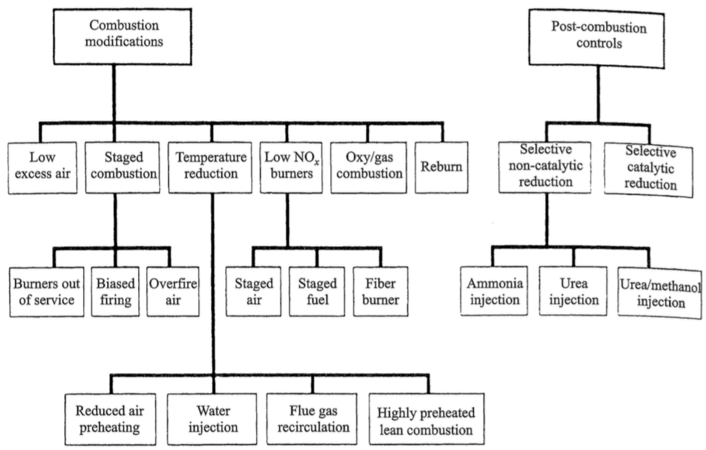


Figure 15.13 The NO_x control technologies for gas–fired industrial combustion equipment.
SOURCE: Adapted from Ref. [71] with permission of the Gas Research Institute.

Low-Nox Burner