

Heavy-Duty NOx Emissions Control: Reformer-Assisted vs. Plasma- Facilitated Lean NOx Catalysis

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Acknowledgements

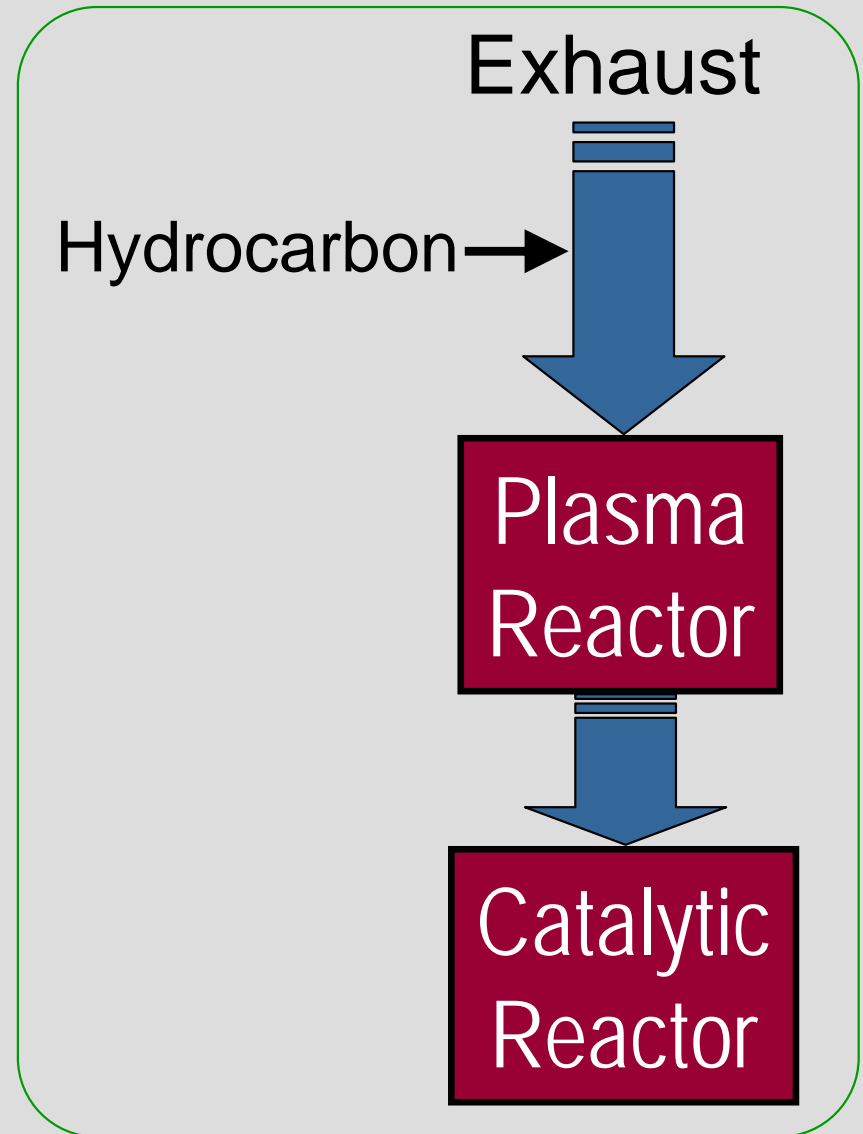
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- ▶ J. Hoard, C. Peden – LEP NTP CRADA
- ▶ G. Singh, K. Stork, DOE-OFCVT

Outline

- ▶ Background
 - Flowsheets
 - Motivation for examination reformers
 - Suitable reformation approaches
 - Current work
- ▶ Data on reformer-assisted lean NO_x catalysis
 - HC speciation using plasma reformer w/C₃H₆
 - Ag_xO/γ-Al₂O₃
 - Ba/zeolite-Y → Ag_xO/γ-Al₂O₃
- ▶ Comparison between PFC and RAC
- ▶ Summary and future plans

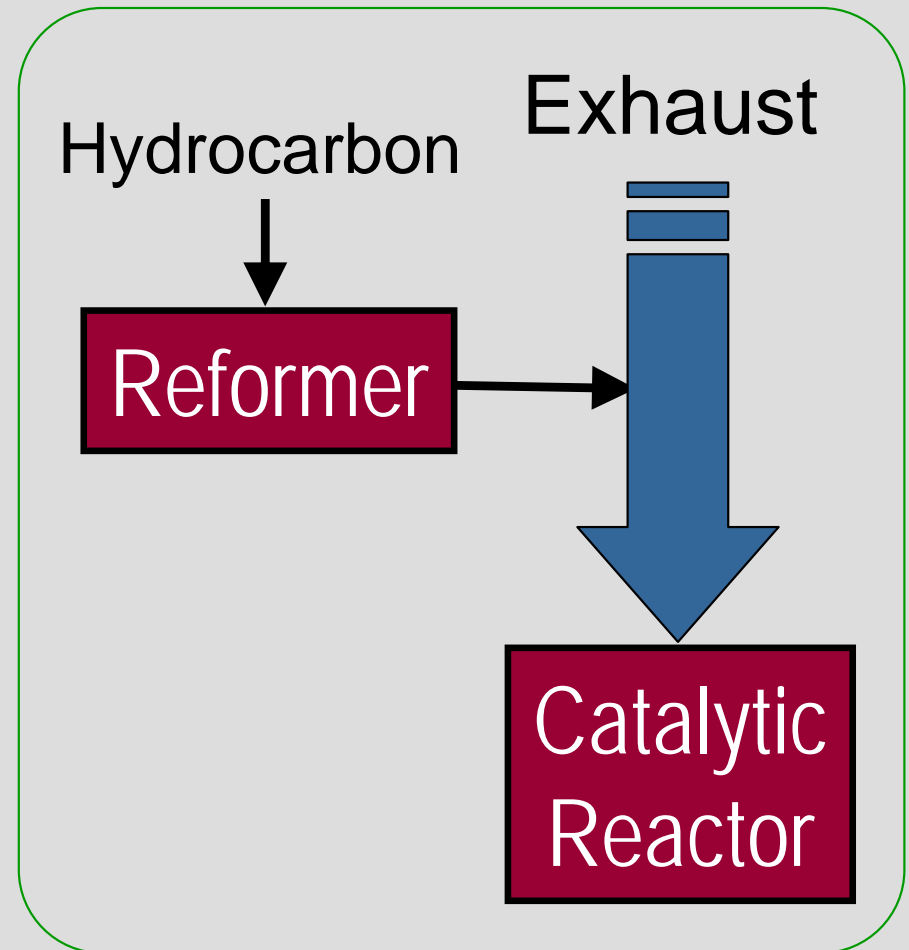
Plasma-Facilitated Lean NOx

- ▶ Step 1. Exhaust passed through NTP
 - Selective oxidation of NO to NO₂
 - Partial oxidation of hydrocarbon
- ▶ Step 2. NTP-treated exhaust passed over lean NOx catalyst
 - LD – zeolites; HD – alumina
 - NO & NO₂ reduced to N₂
 - Consumption of hydrocarbons



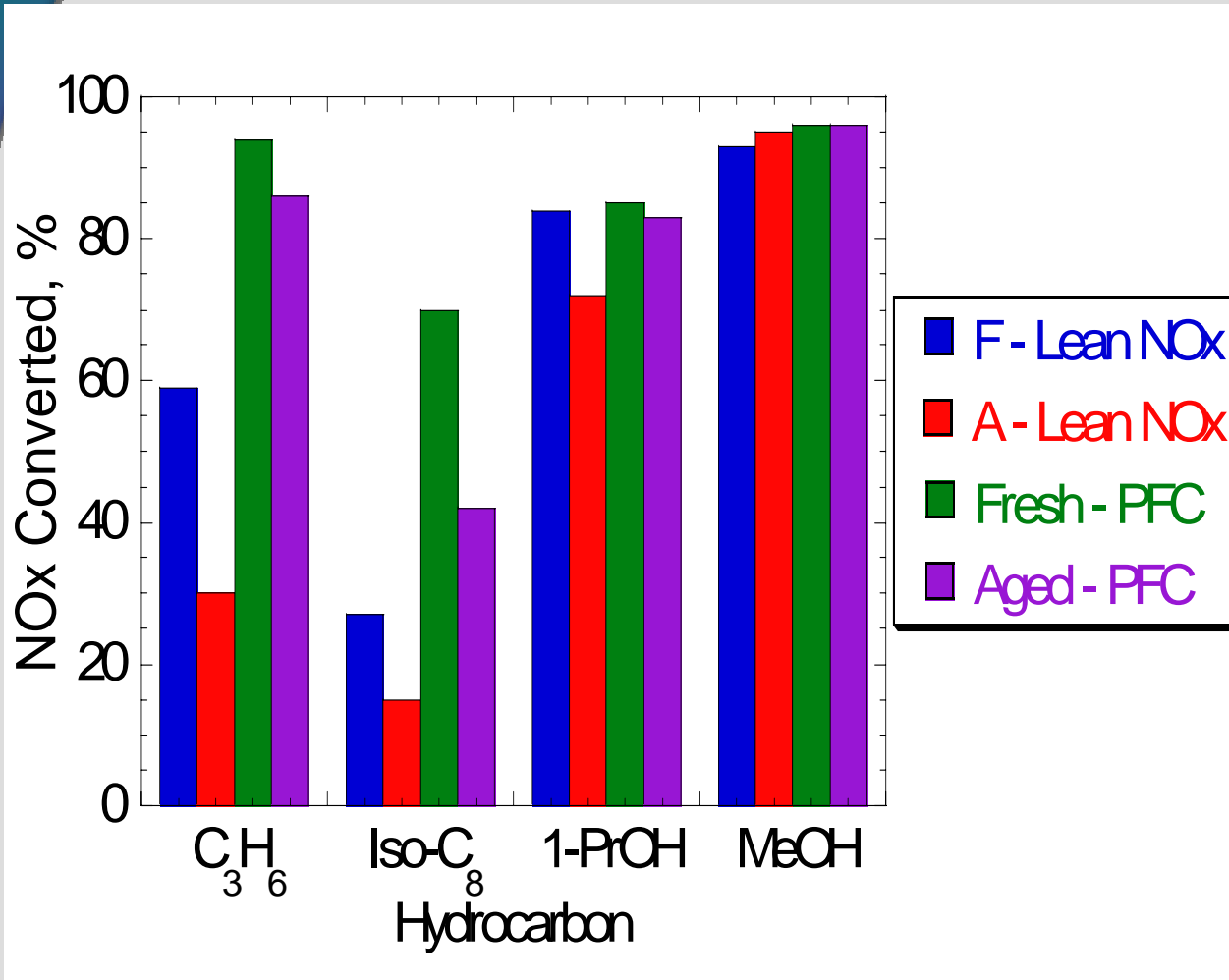
Reformer-Assisted Lean NOx

- ▶ Step 1. Hydrocarbon is treated in a side stream
 - Partial oxidation of hydrocarbon
- ▶ Step 2. Treated HC injected in to the exhaust prior to lean NOx catalyst
 - NO reduced to N₂
 - Consumption of hydrocarbons
 - Active catalyst should be similar to PFC



Motivation for RAC

350°C: $\text{In}_x\text{O}/\gamma\text{-Al}_2\text{O}_3$

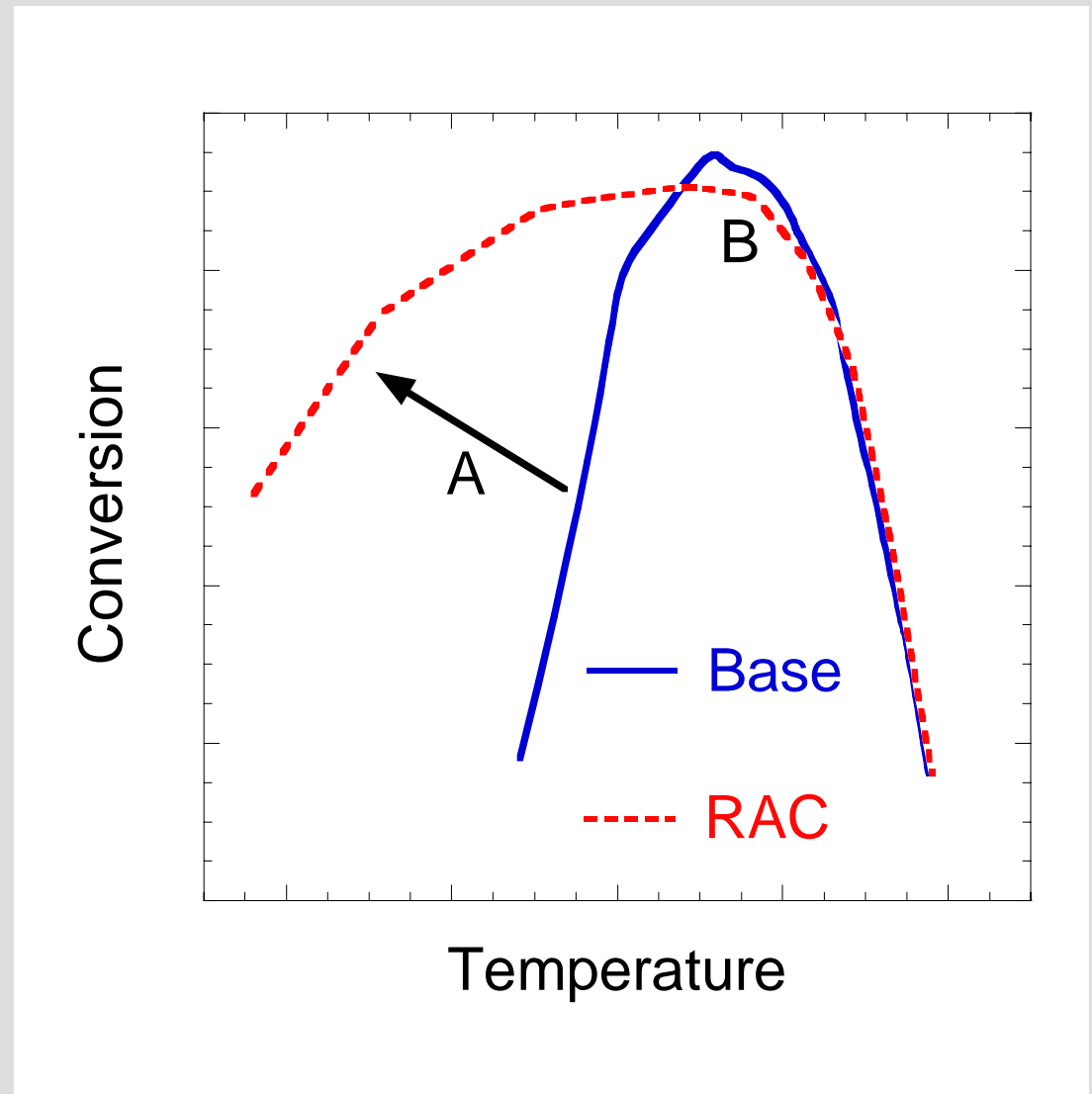


- ▶ Oxygenates result in higher activity on lean NOx catalysts
- ▶ Temperature range for high catalyst activity broadened
- ▶ Sulfur tolerance with oxygenates is better
- ▶ Potential to reduce energy cost (fuel penalty) and reduce the size of the system as a whole

Equal C_1 :NOx basis. Aging in 30 ppm SO_2 , 7% H_2O , 500 ppm NO, 7% O_2 for 250 Hrs.

What to Expect From RAC?

- ▶ A) Major benefit is broadening the active temperature window due to higher reactivity of oxygenates over catalyst at lower temperatures
- ▶ B) May be a slight loss in maximum level of reduction due to lower $C_1:NO_x$ over catalyst



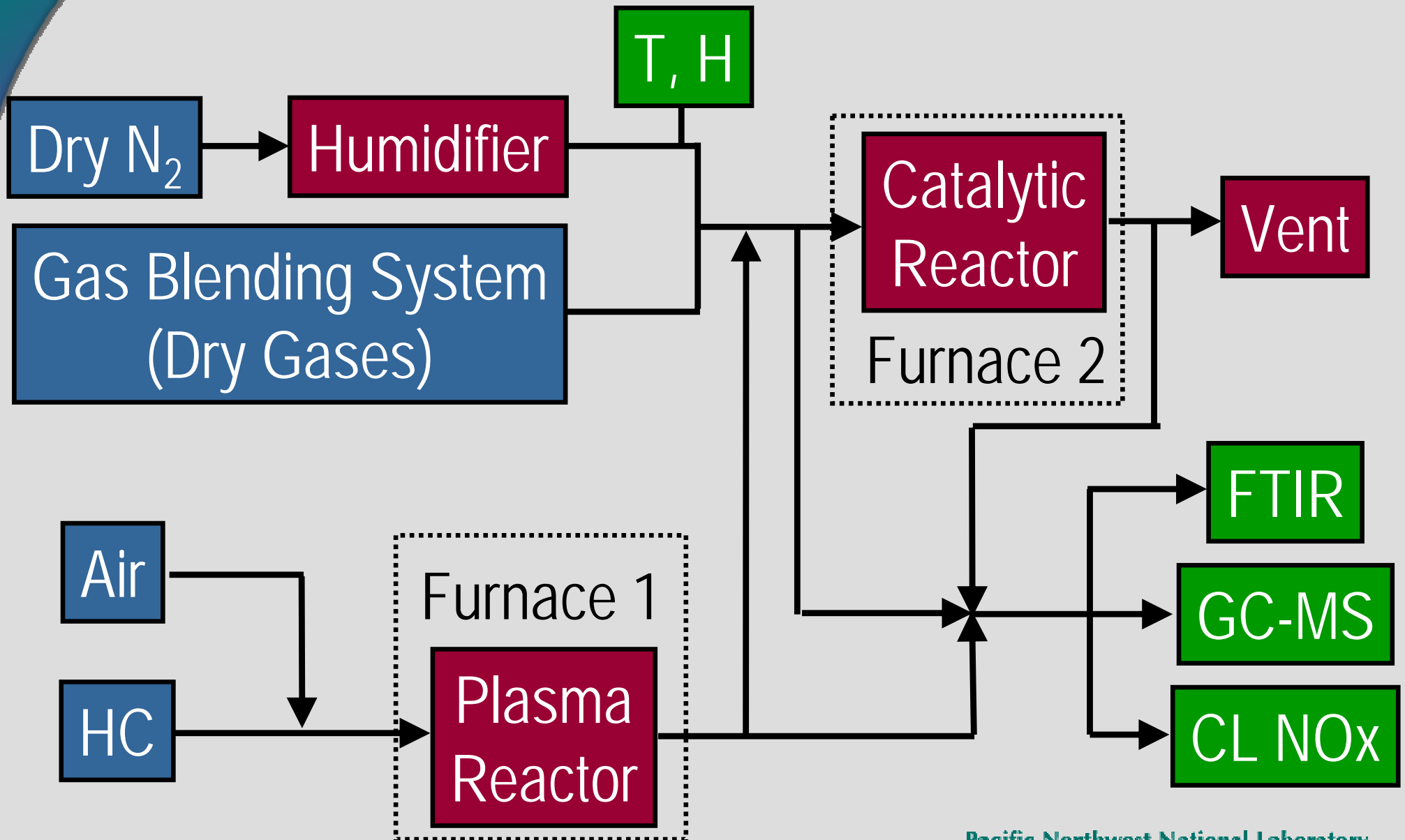
Reformer Options

- ▶ NTP alone
- ▶ NTP-catalyst combinations
- ▶ Thermal catalytic reformers
 - Partial oxidation of alkanes
 - Reform fuel to H_2/CO and use synthesis chemistry to obtain desired reducing agent

Ongoing Work of Interest

- ▶ First record: Engelhard USP #6176078
- ▶ PNNL-Caterpillar CRADA (Aardahl): Plasma-based oxygenate production
- ▶ GM (Schmieg): Thermal catalytic oxygenate production (LEP CRADA with PNNL)
- ▶ LANL (Borup) POx for olefin production from fuel
- ▶ Catalytica, NOxTech: Fuel reformers/converters for aftertreatment
- ▶ Potential sources of syngas
 - DOE-EERE Hydrogen Program: POx-LANL; Autothermal-ANL; SMR-PNNL
 - MIT (Bromberg): Plasmatrons
 - Seimens (Hammer), several others: Plasma SMR
 - Delphi (Fisher), Univ. Minn. (Schmidt): Millisecond POx

Bench Scale RAC System



Stream Compositions

▶ Catalytic Reactor

- Simulated exhaust composed of 2% water, 8% CO₂, 9% O₂, 500 ppm NO, and 300 ppm CO.
- Steady-state data taken: constant reactor temperature and reformer conditions for a given point.
- 3 grams of catalyst and 3 SLM flow.
 - Ag_xO/γ-alumina
 - Ba/zeolite Y → Ag_xO/γ-alumina

▶ Reformer

- Feed streams are house air and propene.
- Propene rate fed to the reformer maintains constant propene to NO_x ratio of 4 in the catalytic reactor. Values reported are feed ratios only, not actual HC:NO_x levels in the catalytic reactor.
- 1:1 to 15:1 C-to-O ratios examined
- Reformer held at 500°C and 6 kJ/L

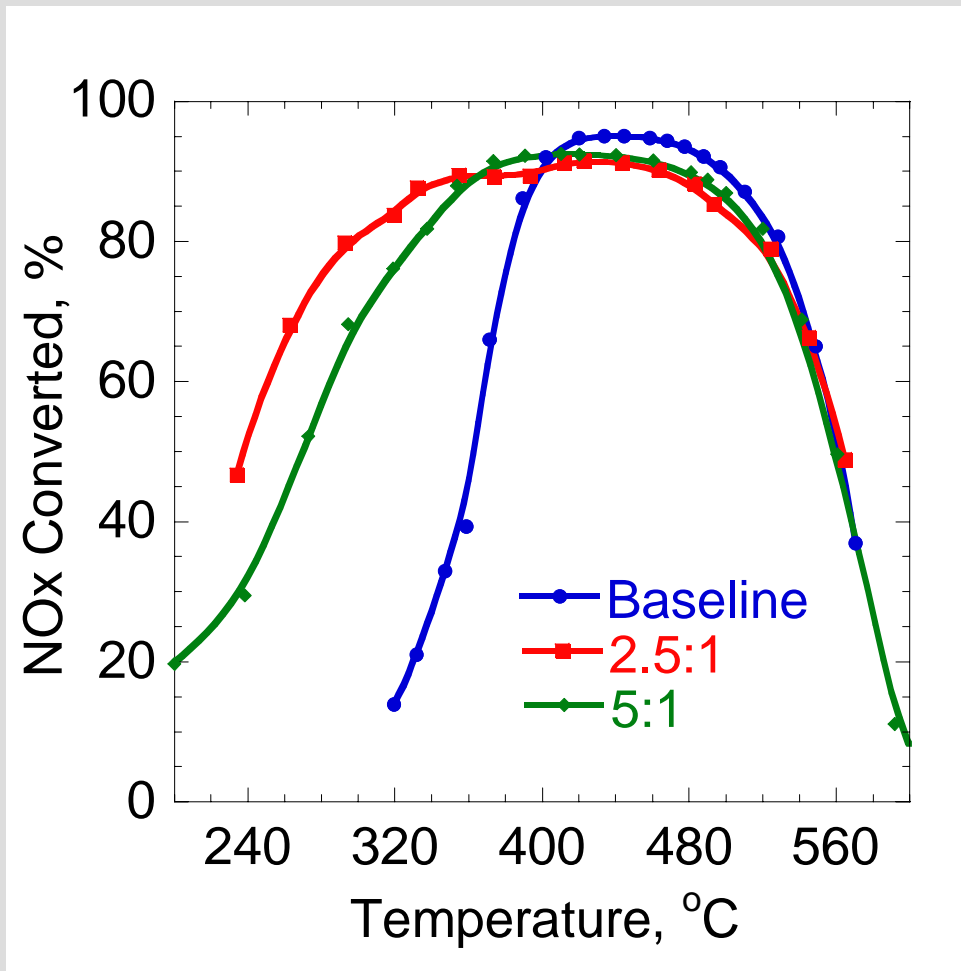
Reformer Chemistry for C₃H₆

- ▶ Higher energy density produces more oxygenates
- ▶ Observed compounds include acetaldehyde, propylene oxide, propanal, acetone, 2-propenal, 2-propanol, formaldehyde, methanol, ethanol, 1-propanol, 2-propen-1-ol, 1-hydroxy-2-propanone, carboxylic acids
- ▶ Higher power shifts alcohol production to somewhat higher C:O ratios
- ▶ Single pass propene conversion is less than 20% for conditions used.
- ▶ Limited CO₂ production at high C:O ratio. Selectivity deteriorates heavily below C:O = 2. Complete C balance still needed.

RAC Results: $\text{Ag}_x\text{O}/\gamma\text{-Al}_2\text{O}_3$

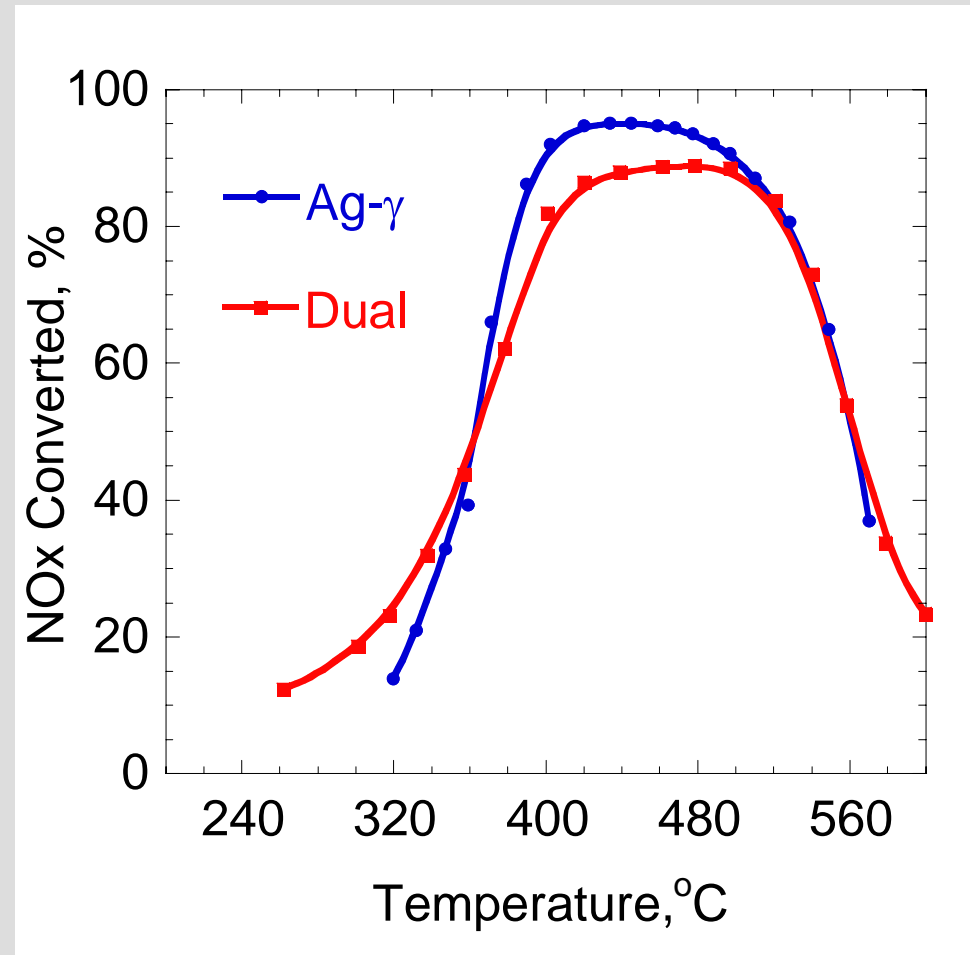
Reformer Operation: 500°C, 6 kJ/L

- ▶ Baseline is equivalent to lean NOx catalysis – no reformation
- ▶ As expected, temperature window broadened with slight loss in peak NOx reduction efficiency
- ▶ SV = 22000 1/hr



Lean NOx: Dual System vs Single Catalyst

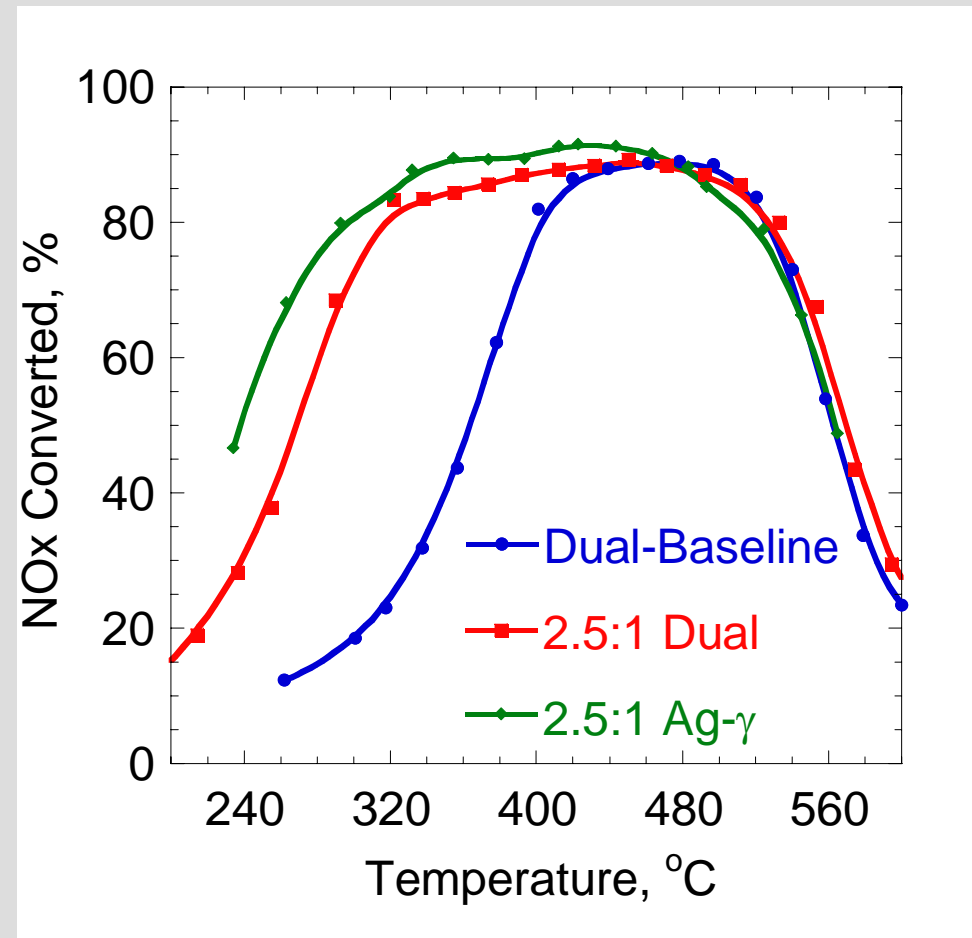
- ▶ $\text{Ag-}\gamma \equiv \text{Ag}_x\text{O}/\gamma\text{-Al}_2\text{O}_3$
- ▶ Dual catalyst represents Ba/zeolite Y followed by Ag- γ (SV = 28000 1/hr; SV=44000 based on Ag- γ alone)
- ▶ Total amount of catalyst by weight is the same for each case
- ▶ Drop in maximum efficiency due to SV effect. Ba/zeolite Y is not active with propene feed



RAC for Dual Catalyst System

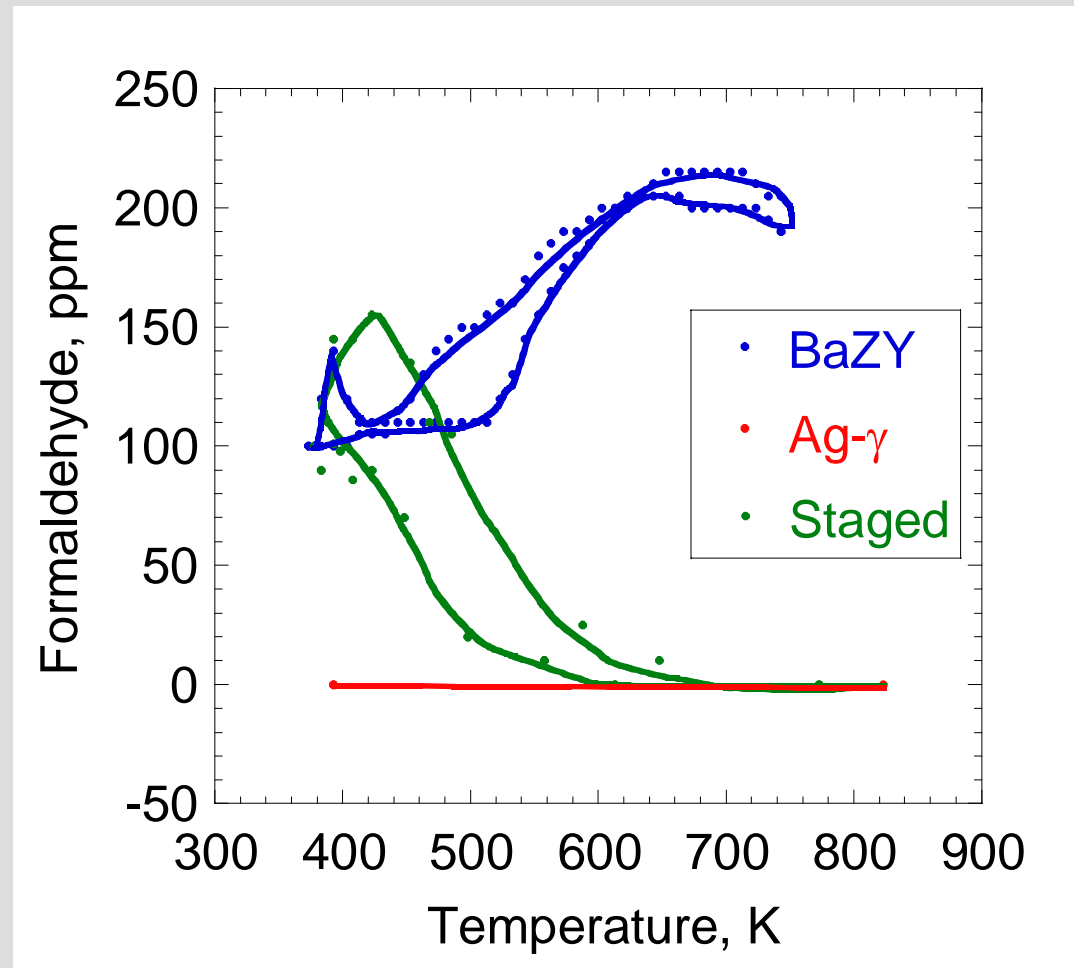
- ▶ Reformation shows improvement from lean NO_x baseline.
- ▶ Dual catalyst not better than Ag- γ alone.
- ▶ Likely that Ba/zeolite Y is not active with reformat as reducing agent.
- ▶ Drop in NO_x conversion in dual catalyst from Ag- γ due to SV effect.

Reformer Operation: 500°C, 6 kJ/L



Impact of Oxygenate Speciation

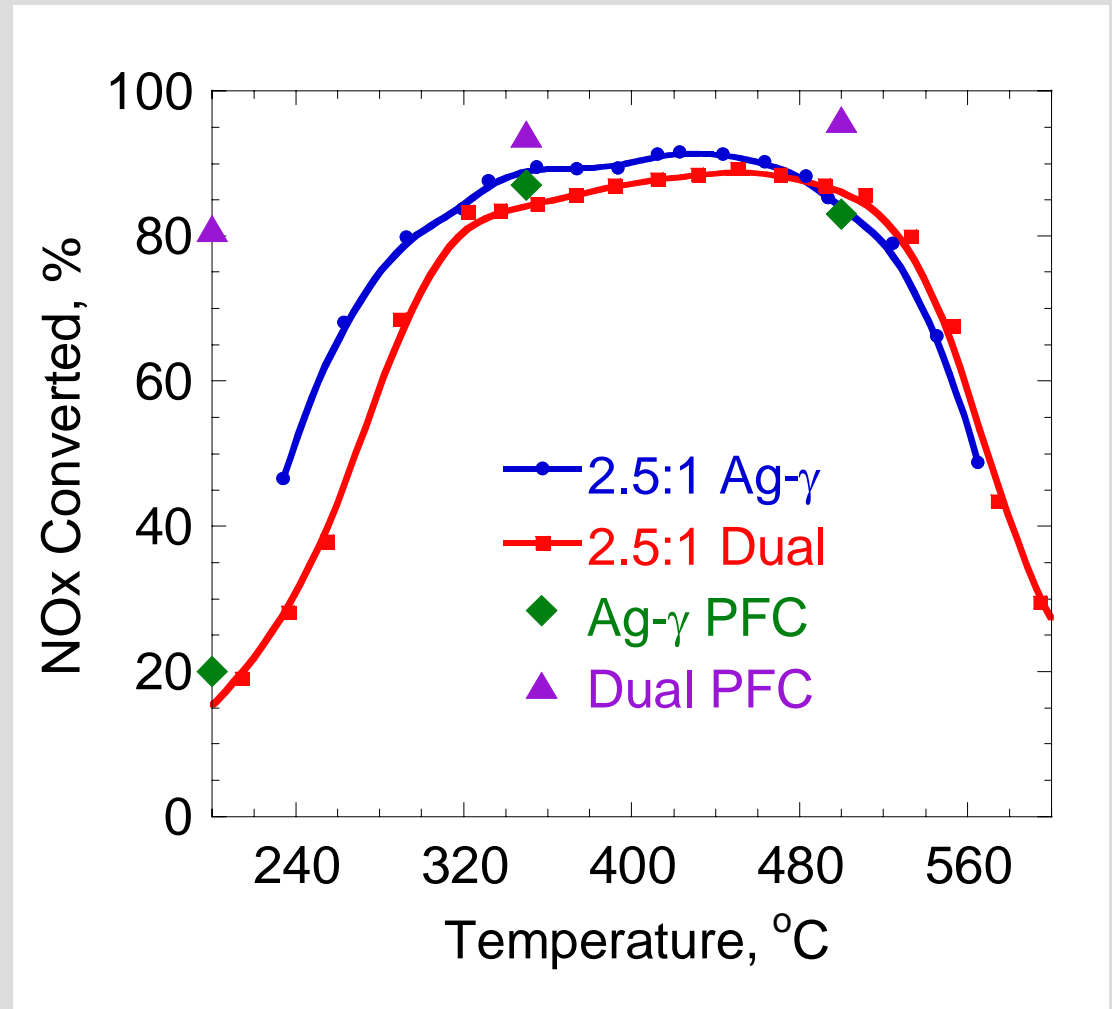
- ▶ RAC shows positive results for $\text{Ag}_x\text{O}/\gamma\text{-Al}_2\text{O}_3$, but not for the staged catalyst system with Ba/zeolite Y.
- ▶ **Hypothesis:** Oxygenates produced in the plasma can participate in the deNO_x chemistry over alumina, but not the zeolite.
- ▶ Observed before with formaldehyde.



Data taken by J. Hoard (Ford Research Labs)

Comparison: PFC vs RAC

- ▶ In the case of Ag- γ , RAC is equivalent to PFC (40 J/L).
- ▶ Still advantages for the dual catalyst system in using PFC.



Summary

- ▶ Reformer-assisted lean NO_x catalysis (RAC) is equivalent or better than plasma-facilitated catalysis (PFC) over Ag_xO/γ-Al₂O₃.
- ▶ The configuration of RAC used here (air:HC) was not successful in promoting NO_x reduction over Ba/zeolite Y. Other species in exhaust may be key to make ample amounts of acetaldehyde.

Outlook

- ▶ Currently looking at larger alkanes (dodecane and hexadecane) in the bench system
 - Fuel vaporizer required
 - Line heating an issue
 - Coking an issue?
- ▶ Catalytic NTP reforming could benefit
 - System is simple
 - Chemistry is not so simple
- ▶ Provided continued improvement examined, RAC will be examined at full scale during transient PFC testing at Caterpillar Tech. Center in Spring-Summer 2004.