Fuel-Borne Reductants for NOx Aftertreatment: Preliminary EtOH SCR Study

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Caterpillar: Alexander Panov, Paul Park

Other contributors:

Williams-Pekin:	Fuel grade ethanol
GE Betz:	Blending agent, blend testing
Gromark:	Blended fuel
Illinois DOCCA:	Coordinated delivery

Sponsor: US DOE, OFCVT, Team Leader: Steve Goguen

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Background Leading to Current Effort

1. Previous work: E-diesel, urea SCR, adsorber catalysts.
2. HC SCR receiving less attention than other aftertreatment technologies.
3. ORNL formulated concepts for fuel-borne reductant systems. EtOH seen as a removable fuel-borne reductant for HC SCR
4. Caterpillar marketed an EtOH SCR system for stationary diesels. Co-operative effort developed between Caterpillar and ORNL

Comparison of Urea SCR to EtOH SCR

Urea SCR	EtOH SCR
Commercial technology for stationary engines	R&D, utility being explored
NOx Reduction > 90% achievable for 300-500°C	NOx Reduction ~ 80% thought to be possible for 400-500°C?
Uses ~ 1:1 NH_3/NOx mol ratio	Uses ≥ 3:1 C/NOx mole ratio
Aqueous solution injected into exhaust	Used undiluted, can be fuel-borne
32.5% urea freezes at 12°F	Freezing not an issue
Can produce/slip NH_3, N_2O, inert PM, reactive solids	Unwanted products/slip likely:, NH_3, N_2O, aldehydes, HC

Initial Project Objectives:

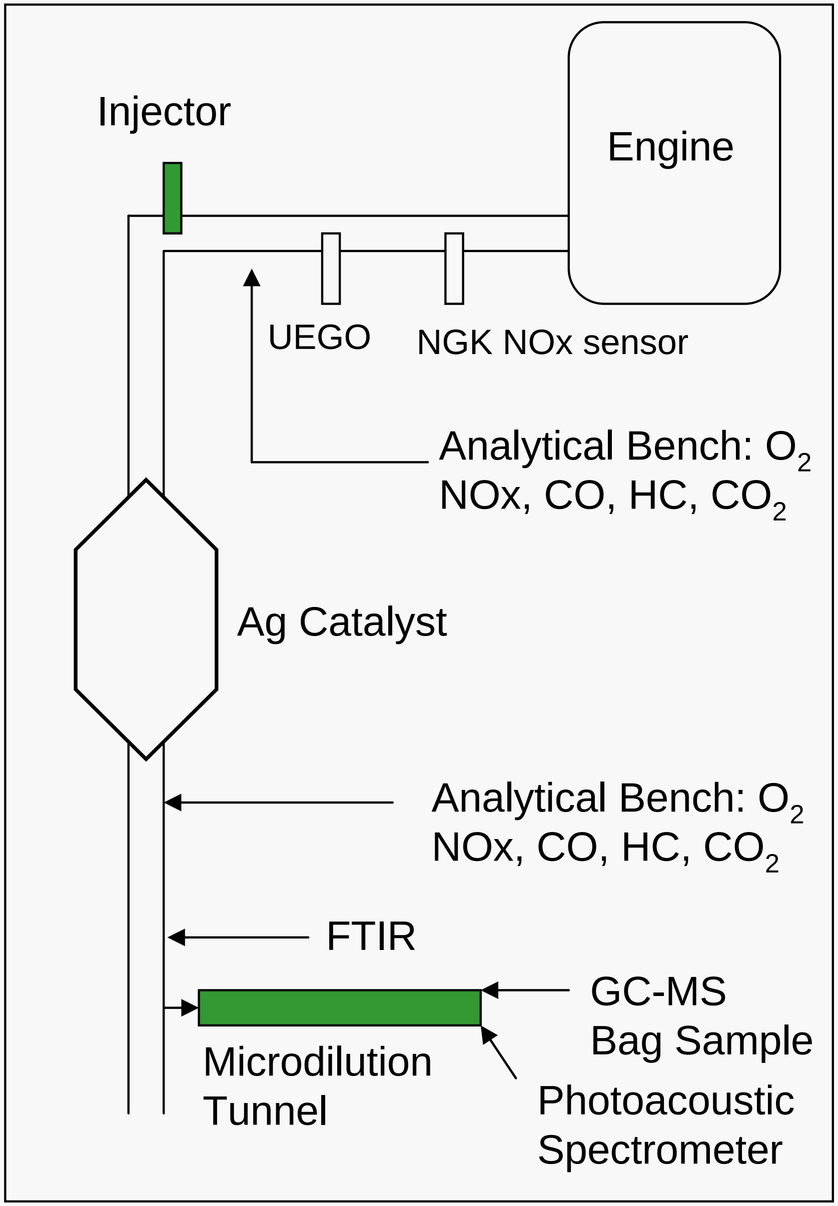
- Evaluate performance of EtOH reductant, Ag-Alumina SCR catalyst system on diesel exhaust. Look at unregulated emissions
- Demonstrate EtOH stripping from E-diesel & its usefulness for NOx reduction.
- Later: consider other fuel-borne reductants, catalysts

Ethanol Was Stripped From 15% E-Diesel

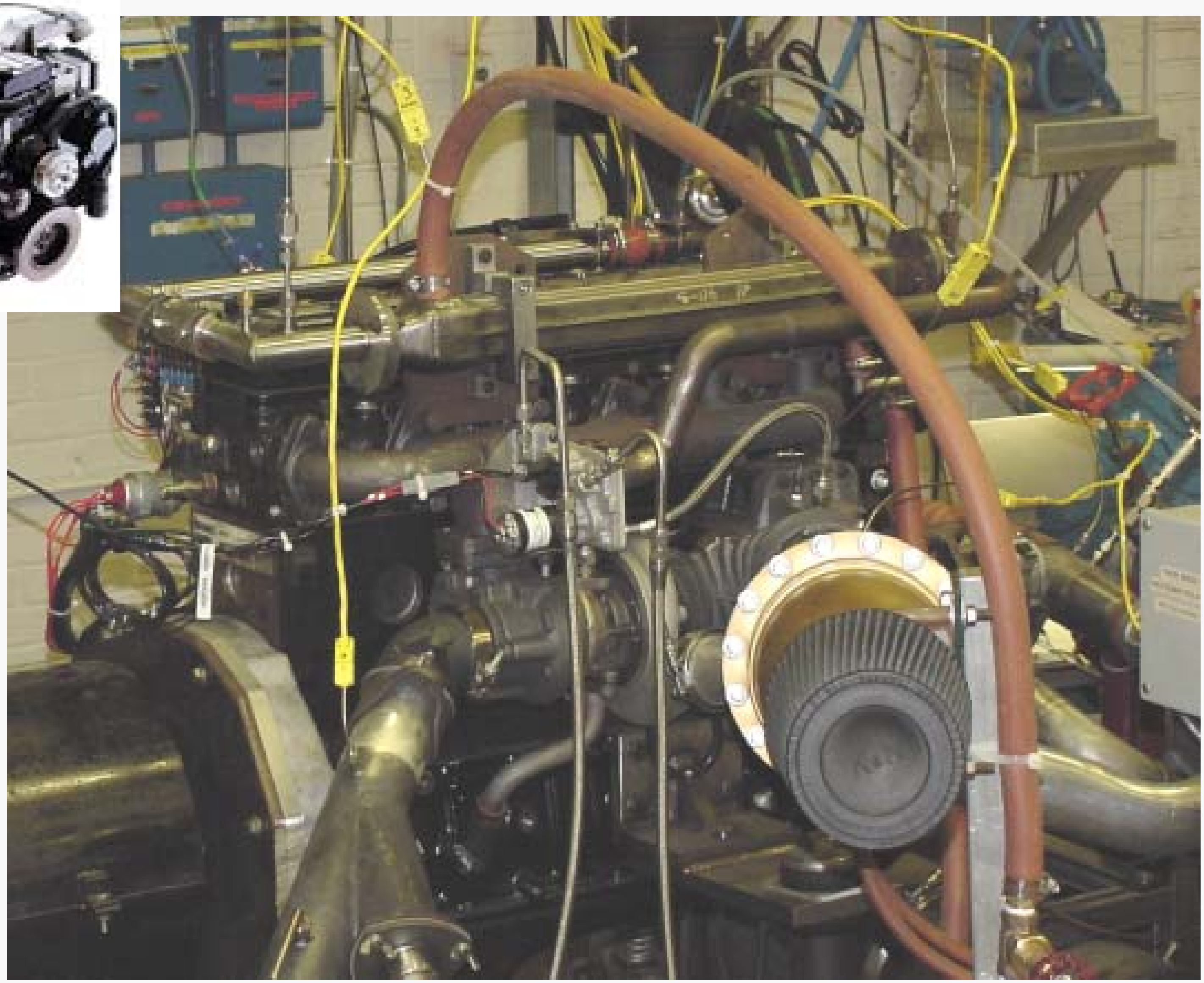
Using “mild distillation” nearly all EtOH was removed and then recovered

Experimental Configuration

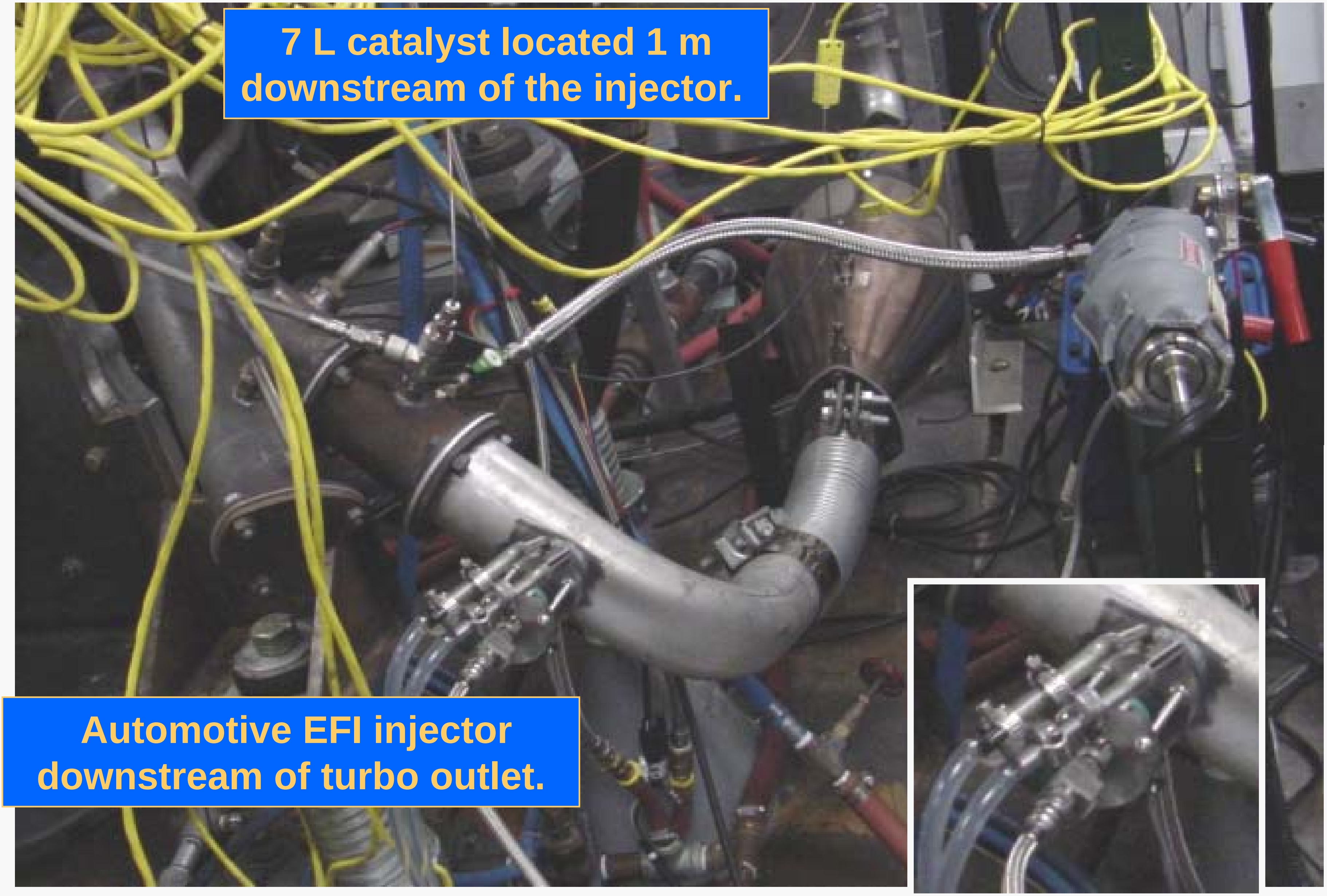
- Donated 1999 Cummins ISB, 5.9 L, With Cummins provided cooled EGR, upgraded fuel system, turbo., controls. Configured for “Near-2004” emissions.
- 285 hp DC motoring dynamometer
- Measured gases in exhaust via standard benches
- FTIR and GC-MS used to look for specific HCs, N_2O, NH_3, Acetaldehyde



Cummins 5.9 L Engine



Reductant Injector and Catalyst in the Exhaust
ORNL/NTRC Cell 3



SCR Performance Experimental Methodology

- **Shakedown, de-green** catalyst for ~10 hours at 400°C.

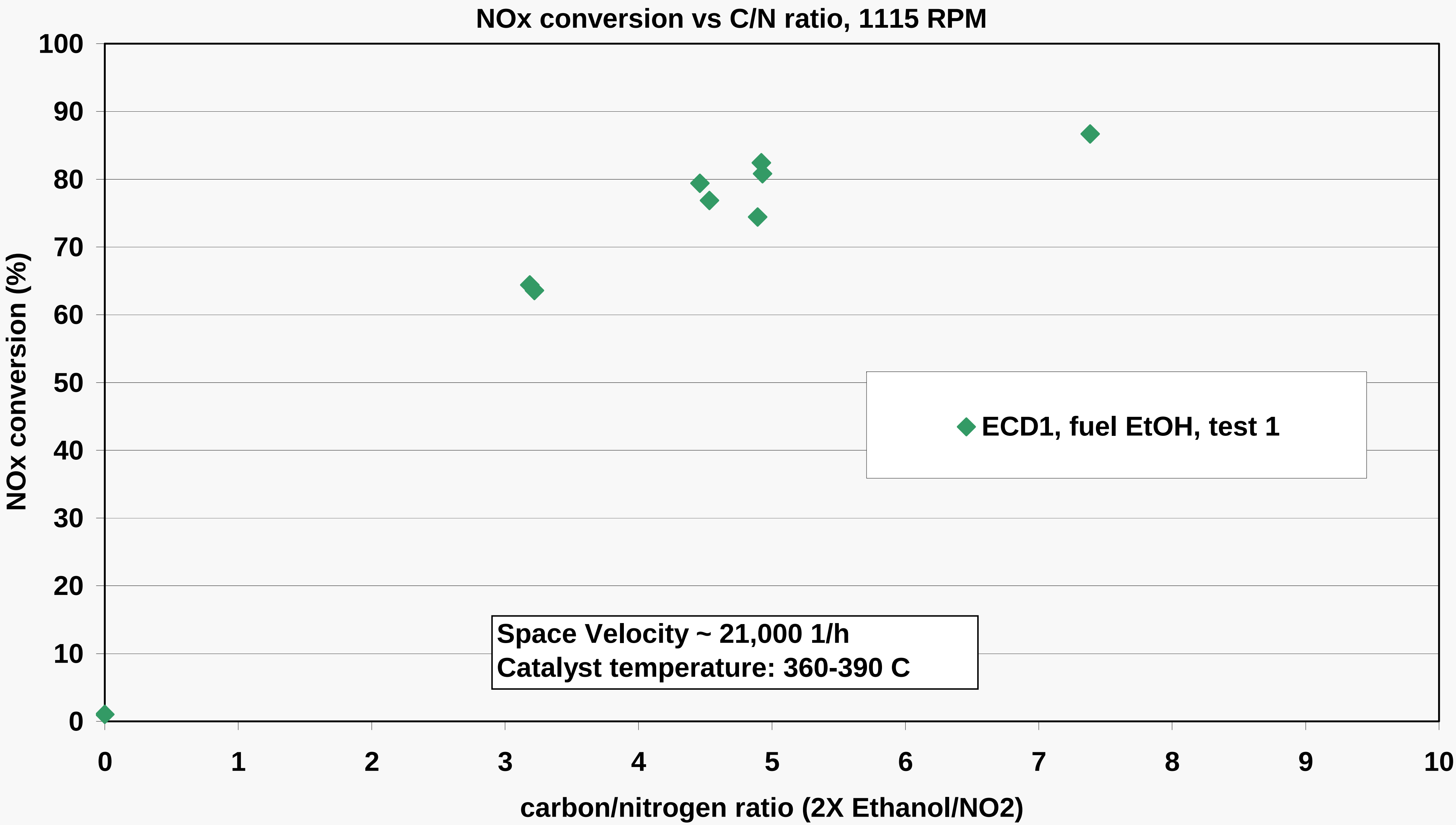
- **Performance Investigation at Two Engine Conditions / Space Velocities:** compared conversion at a low & high space velocity while maintaining similar catalyst temperature and NOx flux.

Test Setting	Speed RPM	Torque ft-lbs	SV 1/h	Cat T °C	NOx g/min
AVL8-M3	1115	230	21000	360-400	~1.5
~AVL8-M6	2225	180	57000	360-400	~2.1

Fuel-Reductant Combinations:

	Fuel	Reductant
1.	ECD-1	fuel-grade EtOH
2.	ECD-1	“stripped” fuel-grade EtOH
3.	E-diesel	“stripped” fuel-grade EtOH
4.	ECD-1	reagent grade EtOH

Excellent NOx Conversion Was Achieved at 21000/h, 360-400°C



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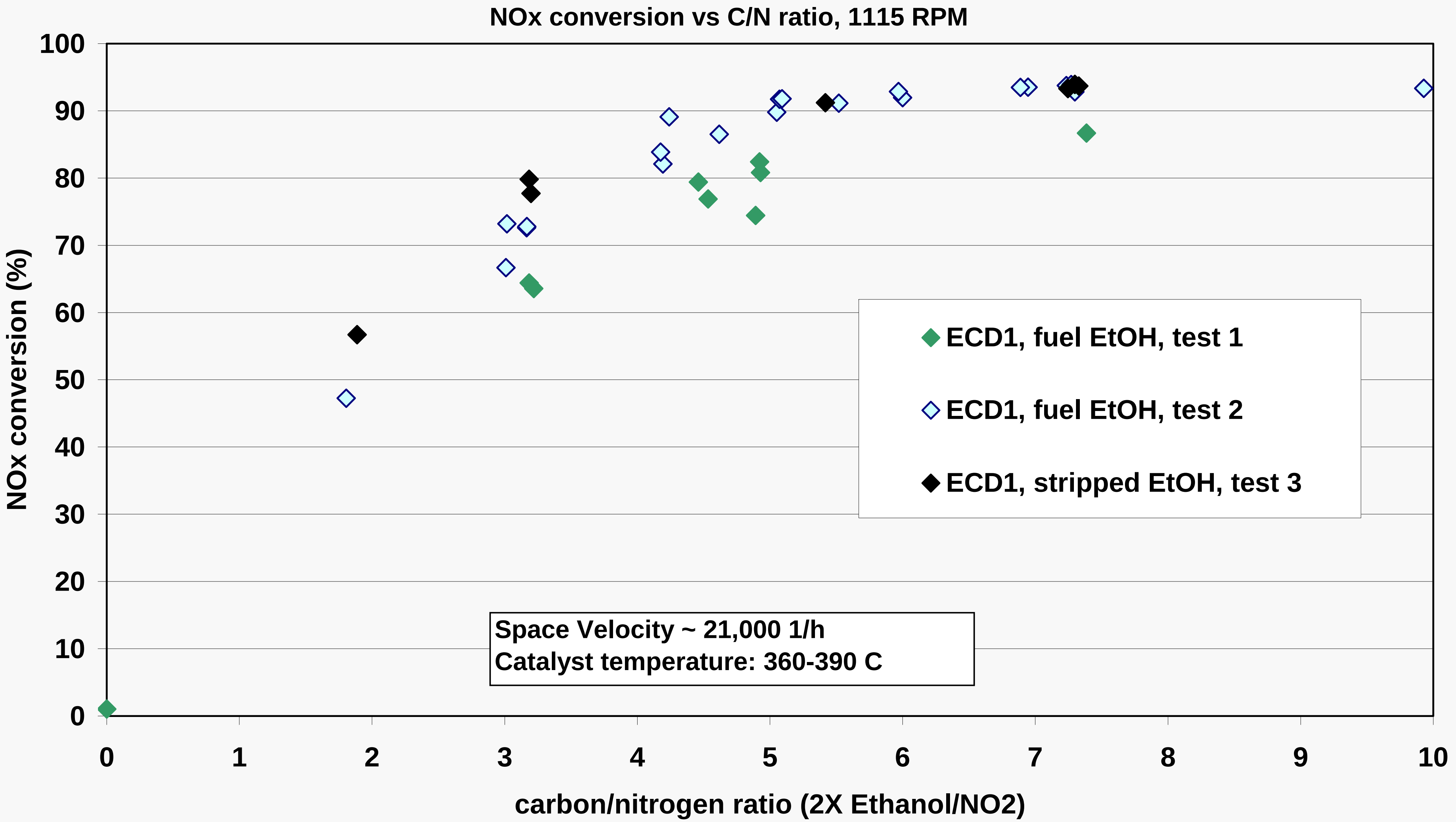
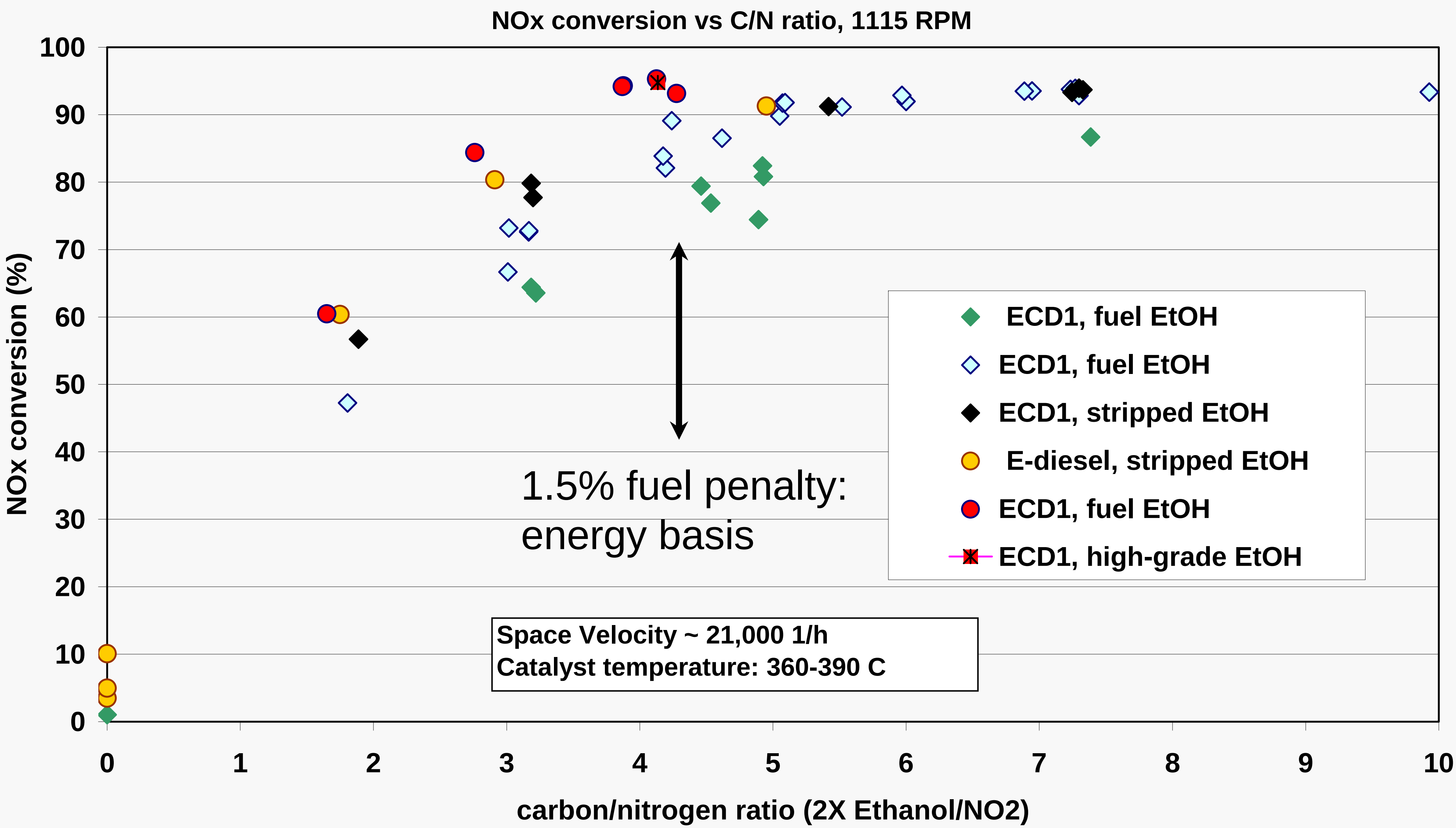
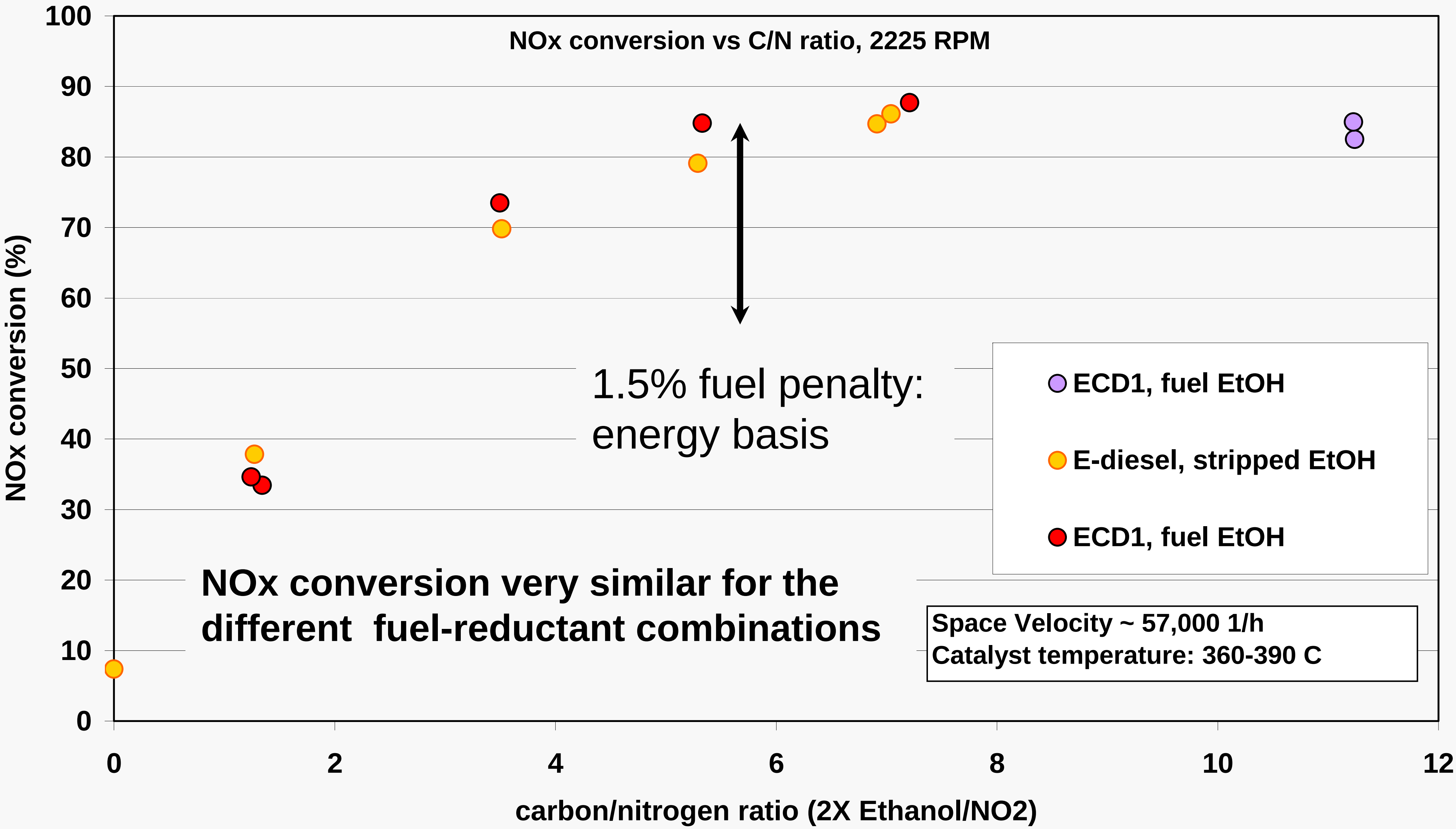


NOx Conversion Was Excellent at 21000/h and 360-400°C

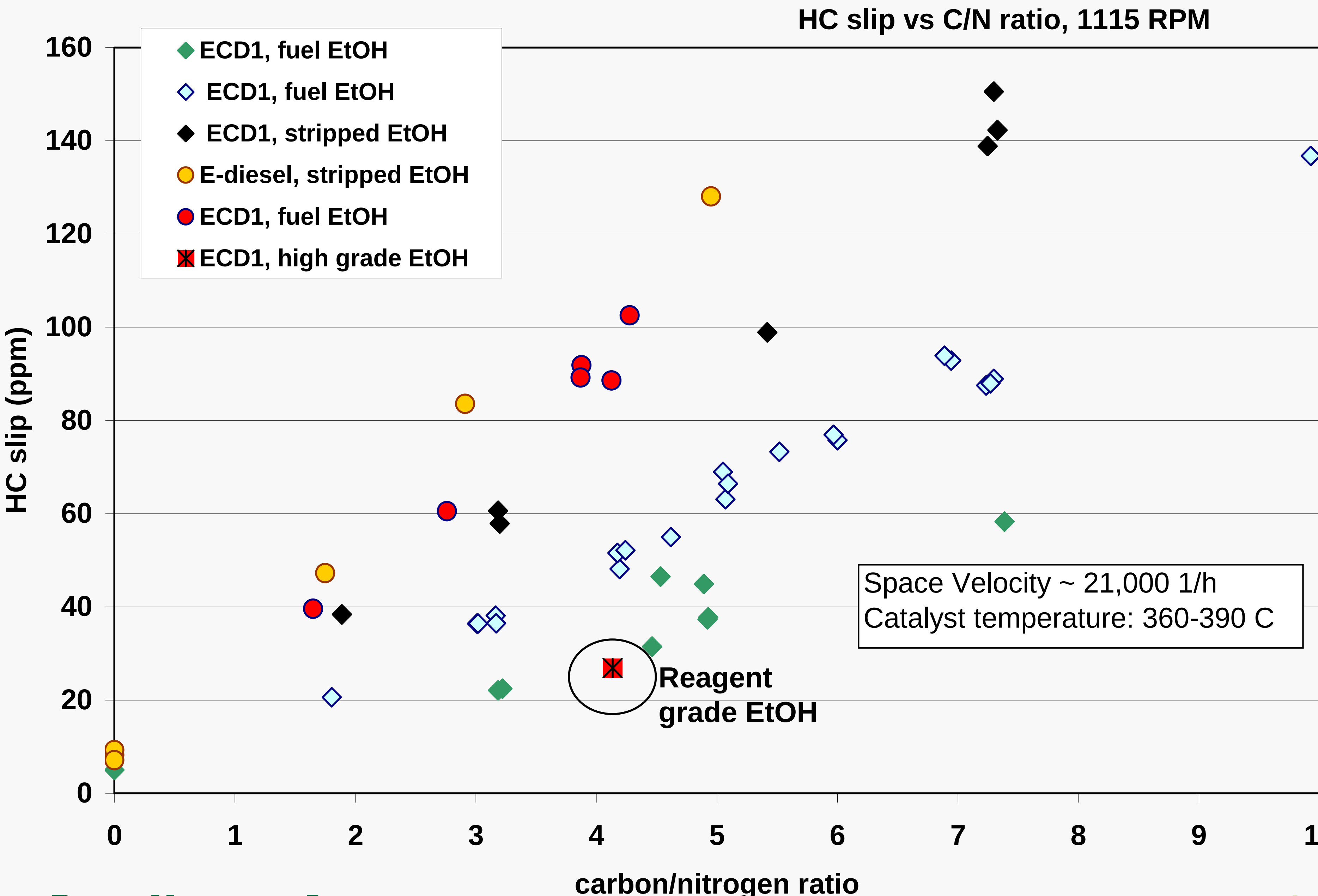
Selectivity appeared to improved as catalyst is exposed to more sulfur



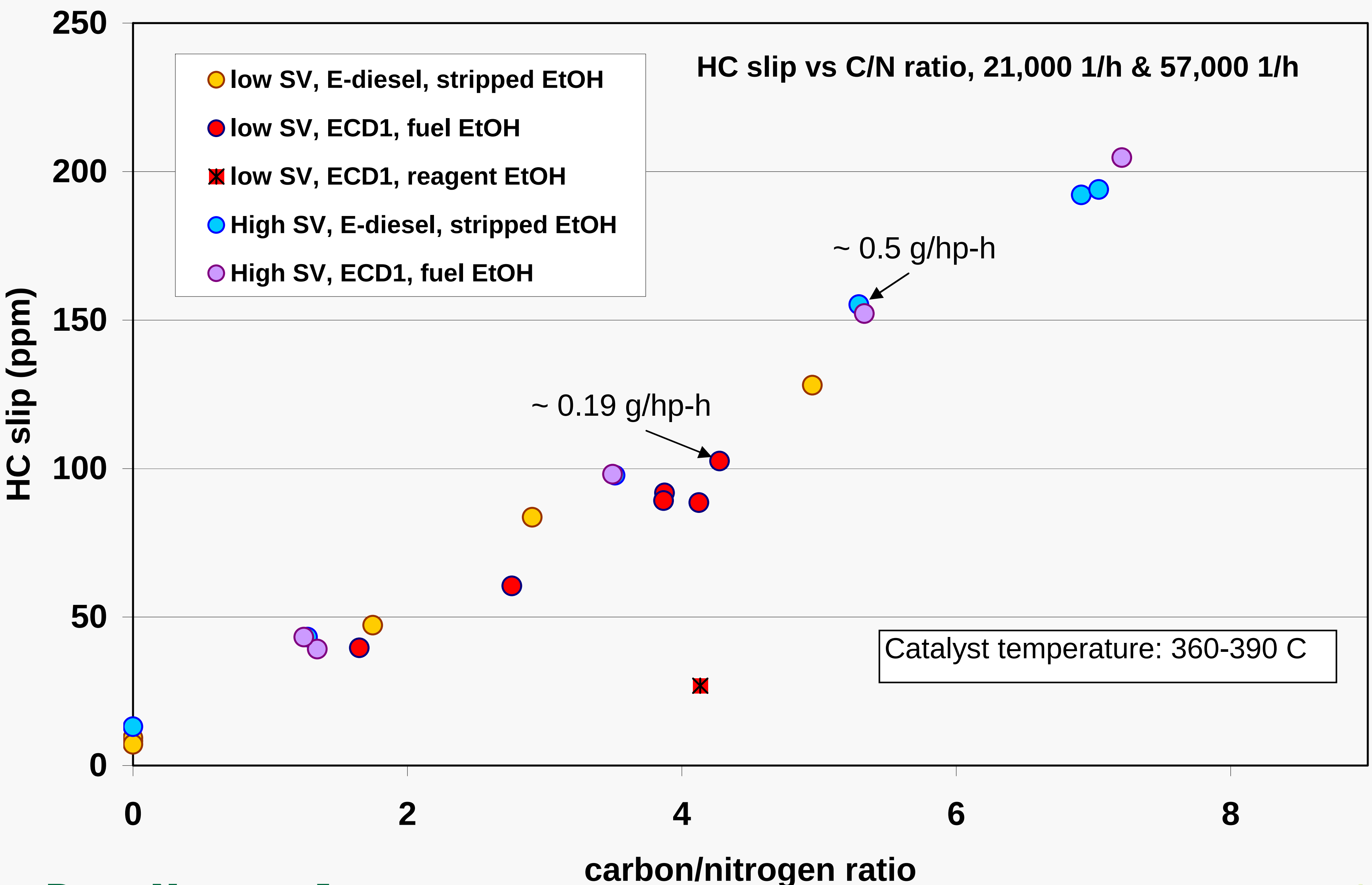
Good NOx Conversion Achieved at 57000/h and 360-400°C



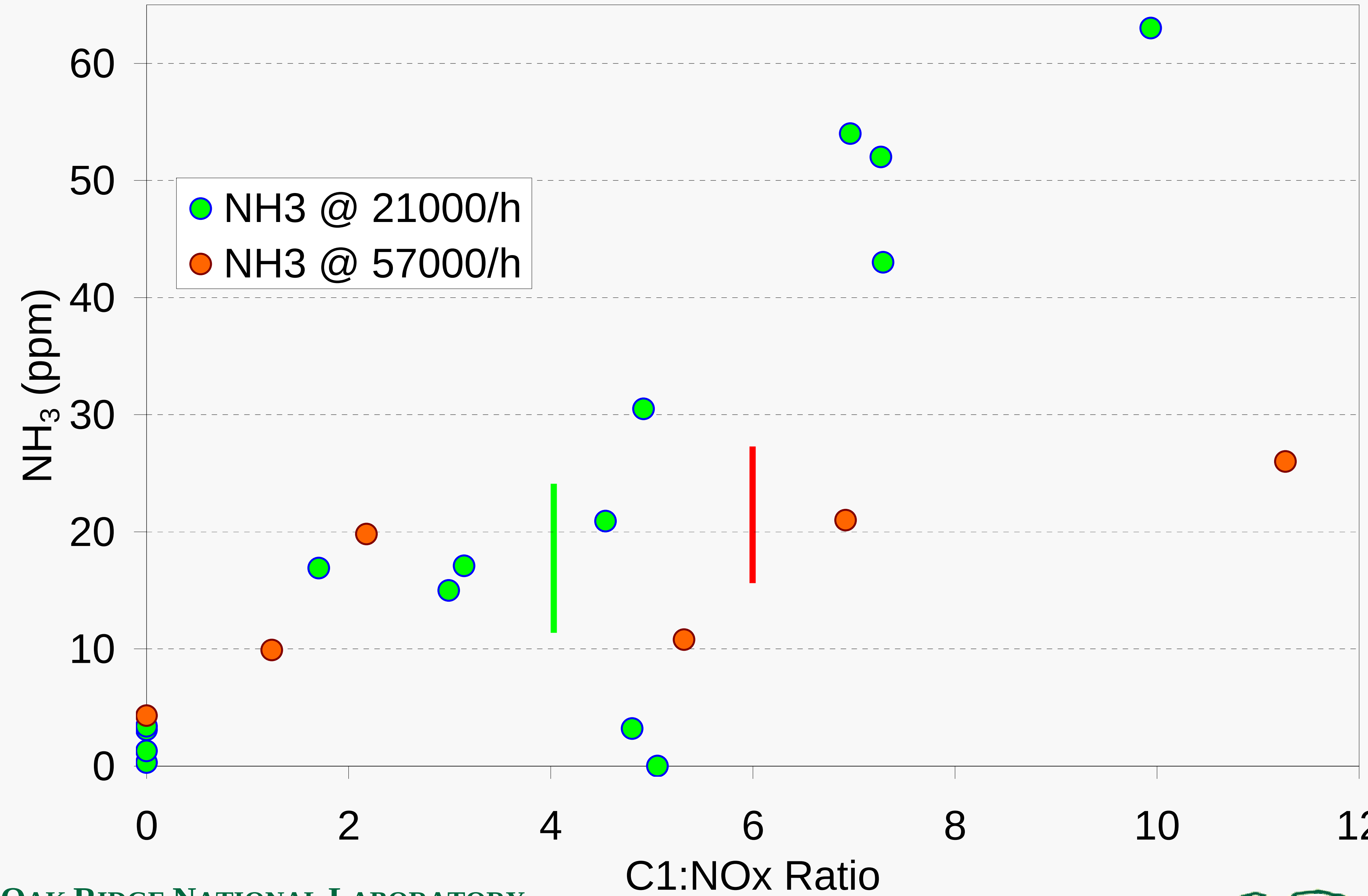
HC Slip Changed with Progression of Experiments



HC slip at high SV was about the same ppm level, mass flux is ~2.7 times greater

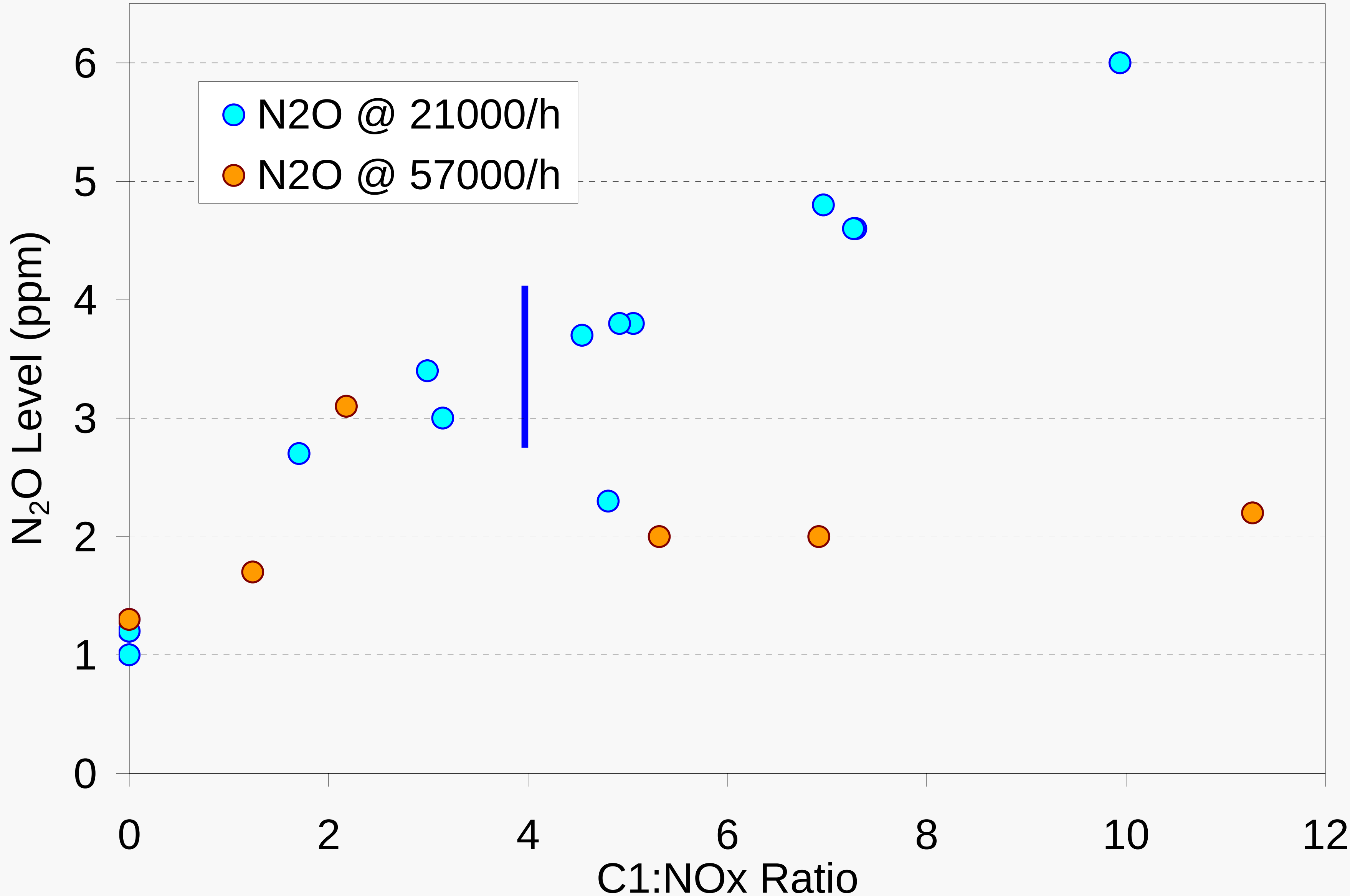


FTIR Results: Ammonia Emissions

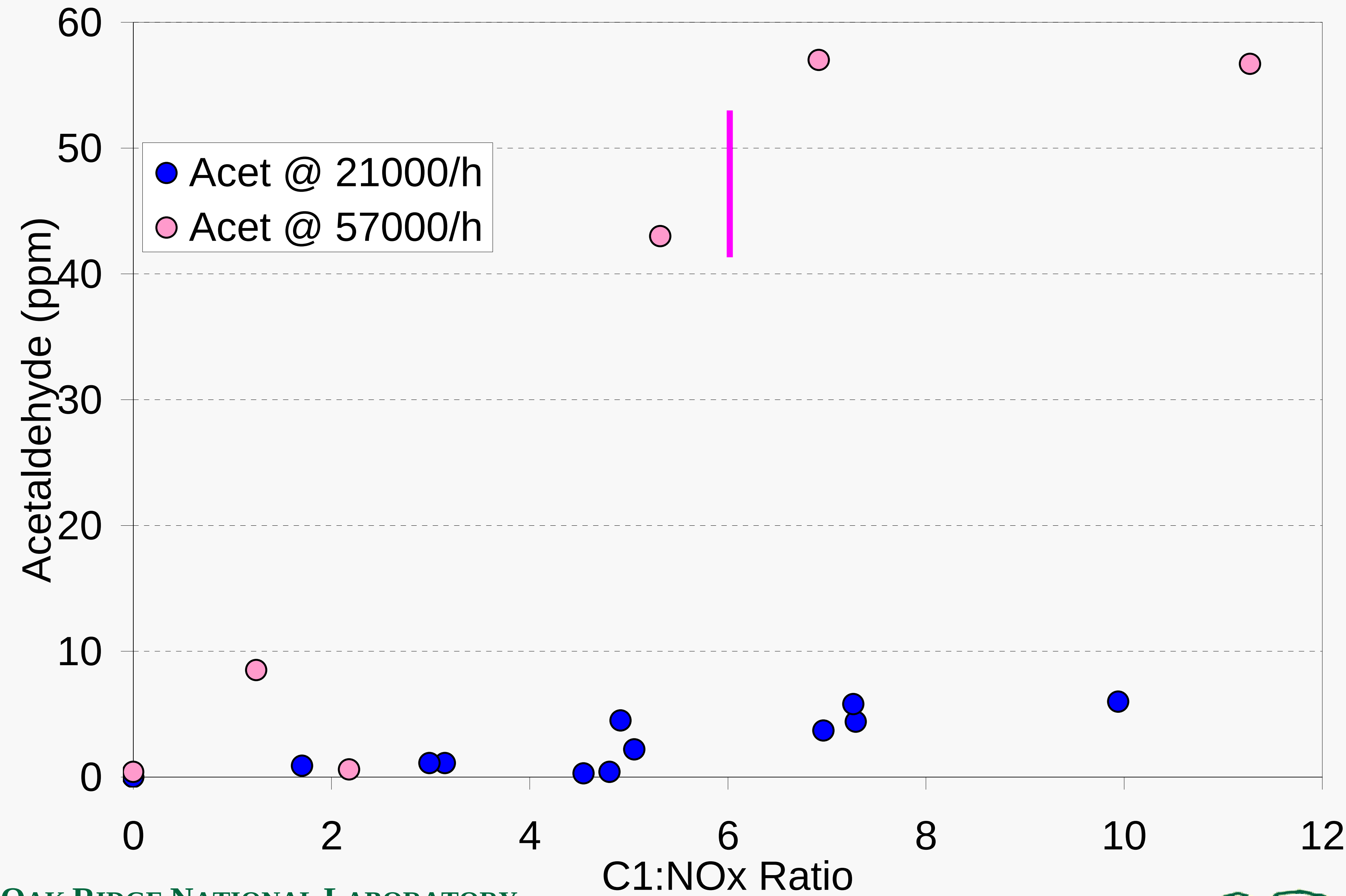


FTIR Results: N2O Emissions

In the past, some catalyst formed large amounts of N_2O

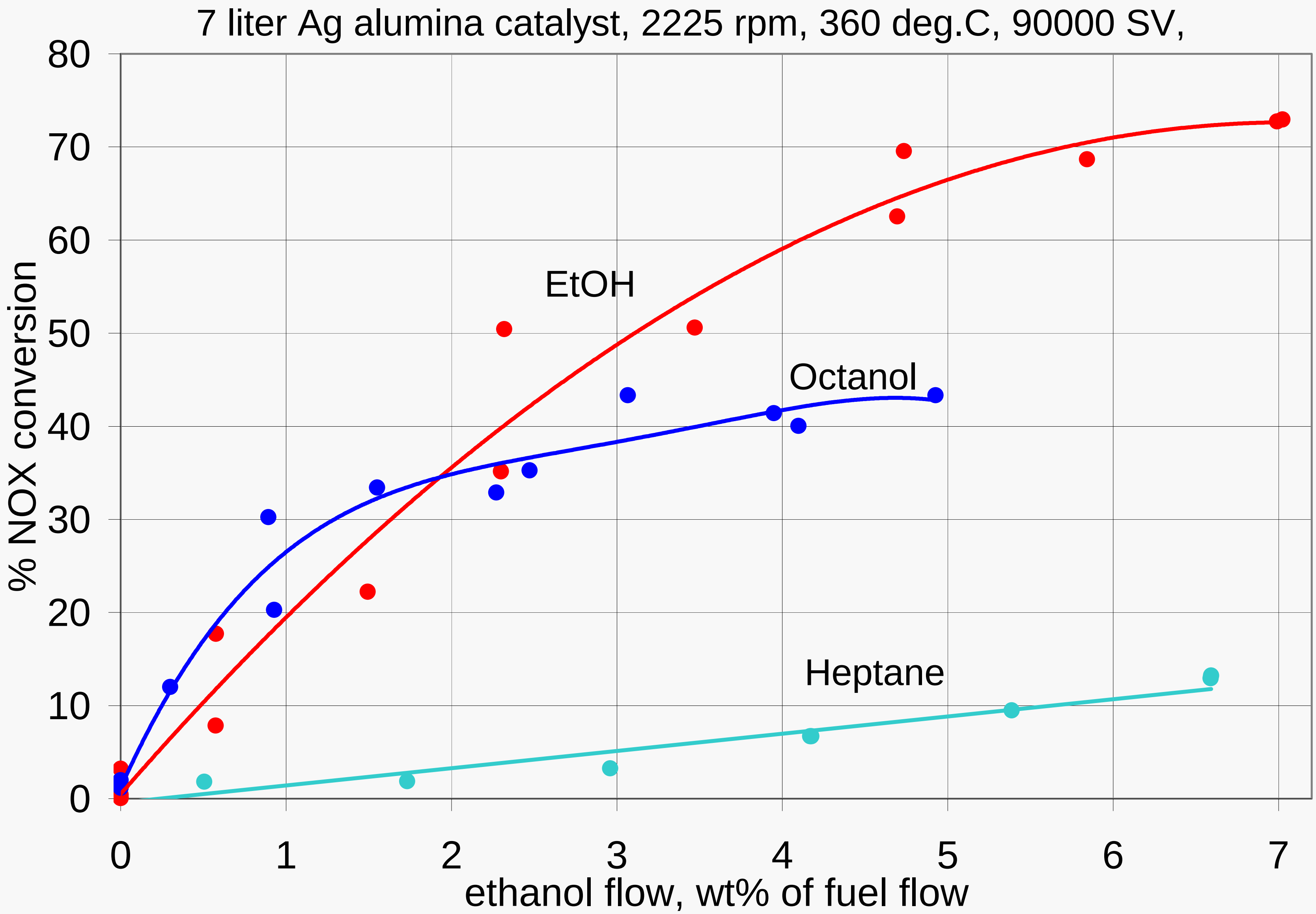


FTIR Results: NO_X, Versus Acetaldehyde Emissions



We Have Begun to Look at Other Fuel-borne Reductants

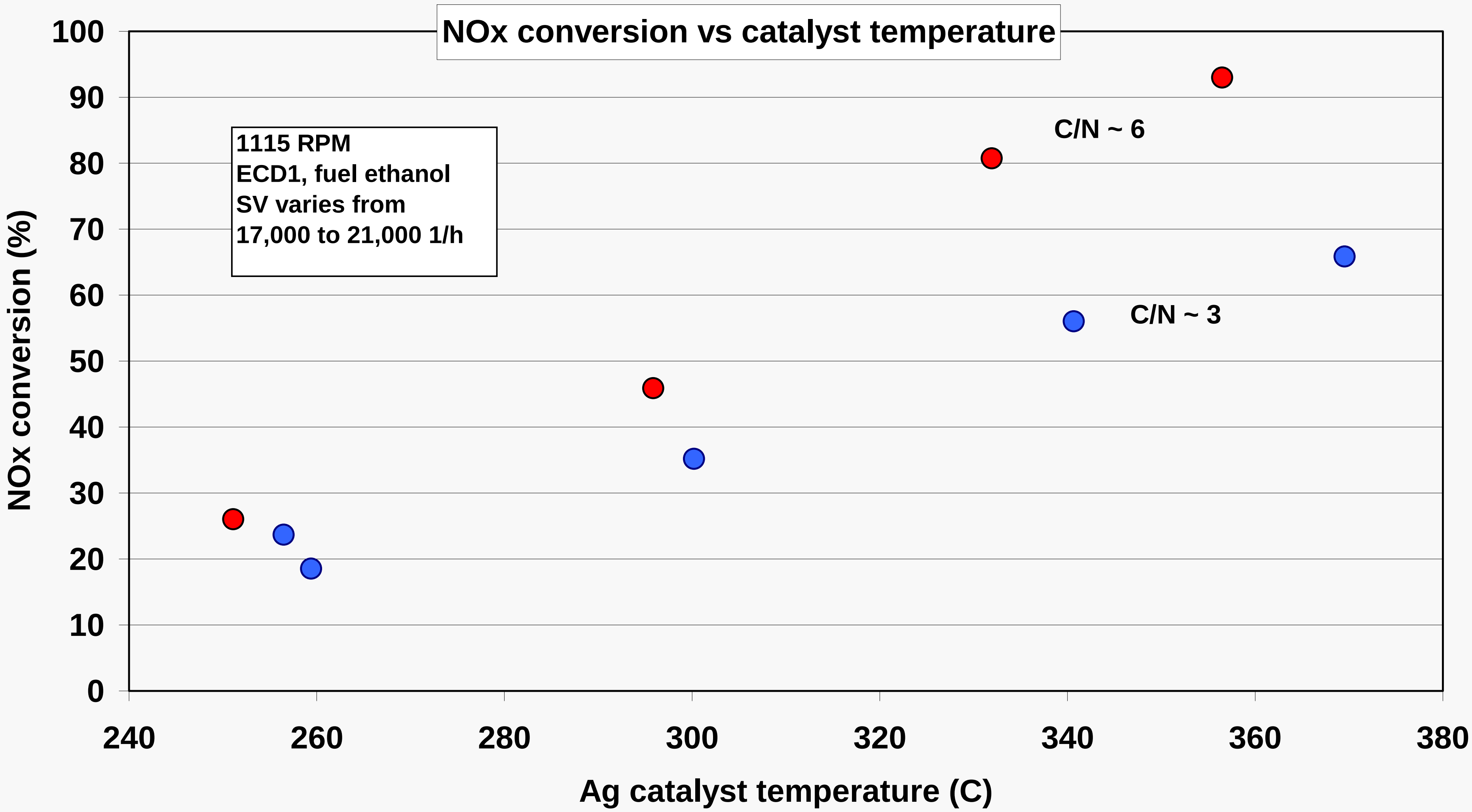
Note: much higher SV and NOx flux



Reductant stripping experiments

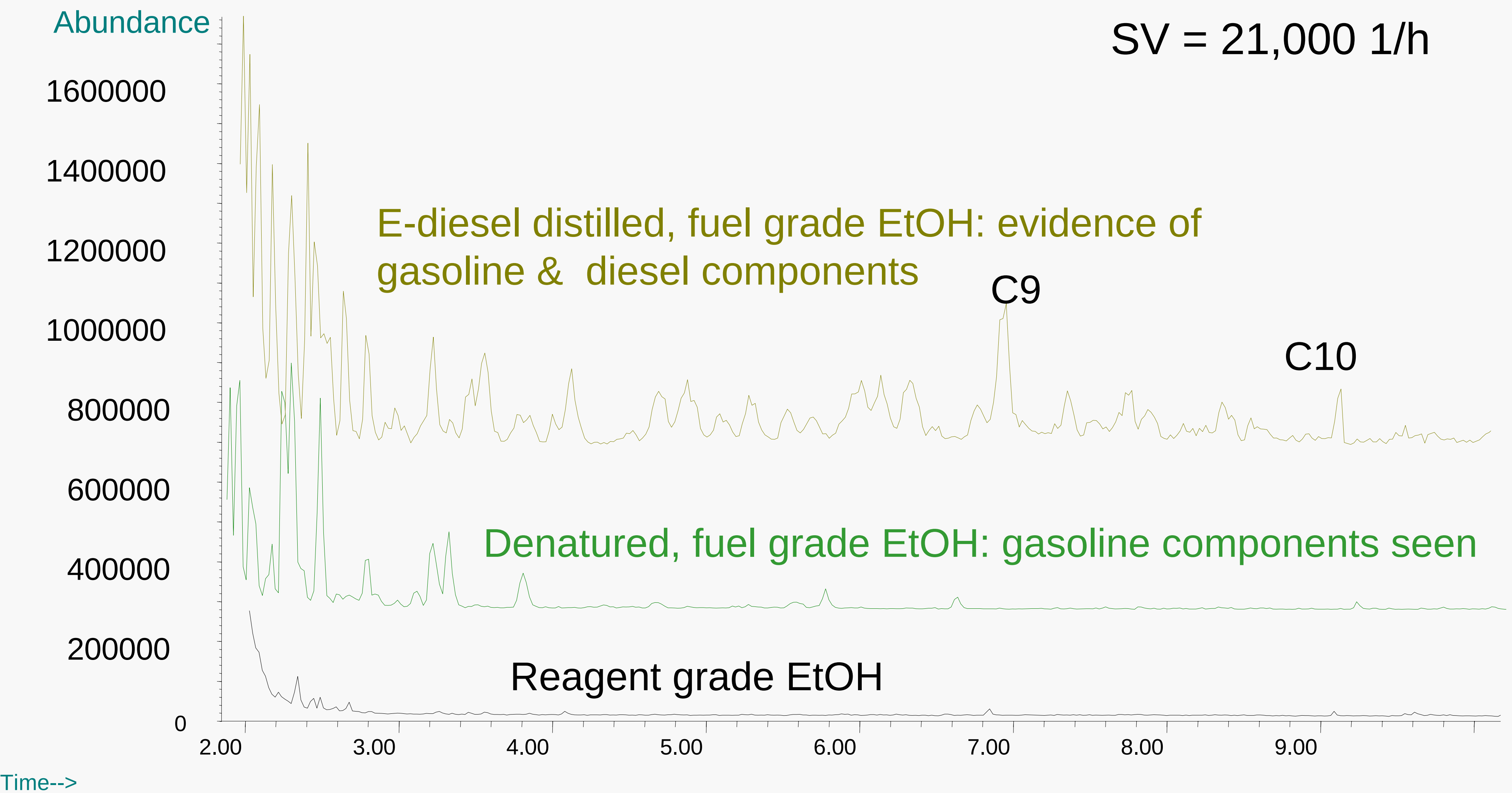
REDUCTANT	BOILING POINT, deg.C	% BLENDED IN ECD1 FUEL	% SEPARATED (rotovap, 100 CC, 10 minutes, 90 deg.C, 200 mm Hg vacuum)
ethanol	78	20	20
1-propanol	97	20	18
1-butanol	117	20	17.5
n-hexane	69	20	4.9
n-heptane	98	20	5
1-octanol	196	20	0

Low Temperature Effectiveness of Catalyst



Low Temperature Evaluation: For low SV, catalyst temperatures near 250°C, 300°C, 340°C and 370°C were examined at two C/N ratios

GC-MS Results Clearly Show Different Nature of Slip HC for The 3 EtOH “Grades”



Observations & Conclusions

- Ethanol SCR effectively reduced NOx emissions of diesel exhaust for catalyst temperatures between 360-400°C
  - moderate C1/NOx ratios
  - 90% for 21000/h and 80% for 57000/h
  - Some conversion observed at 250°C
- Saw catalyst performance improve with sulfur exposure
- Low levels of N_2O (< 6 ppm) were produced
- Ethanol was converted to acetaldehyde: slipped at 57000 1/h
- Ammonia was produced (high C/N, low SV), but may not be problematic
- Fuel-borne feasibility was demonstrated by stripping EtOH from E-diesel – use as reductant in the SCR system
- Technology may show promise - examining a broader set of parameters/conditions is warranted