Ag-Al_2O_3 Catalyst HC-SCR; Performance with Light Alcohols and Other Reductants

Oak Ridge National Laboratory: John Thomas, Sam Lewis, Bruce Bunting
John Storey, Mike Kass, Ron Graves,

Caterpillar: Paul Park

Sponsor: US DOE, OFCVT

Fuels Technologies Team Leader: Steve Goguen

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Motivation for HC-SCR, Ag-Al_2O_3 Effort

1. Major attraction is potential for a simple system using a fuel-borne reductant.
2. HC-SCR - generally considered less attractive than LNTs & urea SCR due to modest NOx reduction (20-50%)
3. A notable exception is the Ag-Al_2O_3 catalyst.

"Despite the large body of data for SCR-HC catalysts, very few formulations possess adequate NOx conversion levels … Alumina supported silver catalysts hold promise".

CRC project No. AVFL-7, June 2002

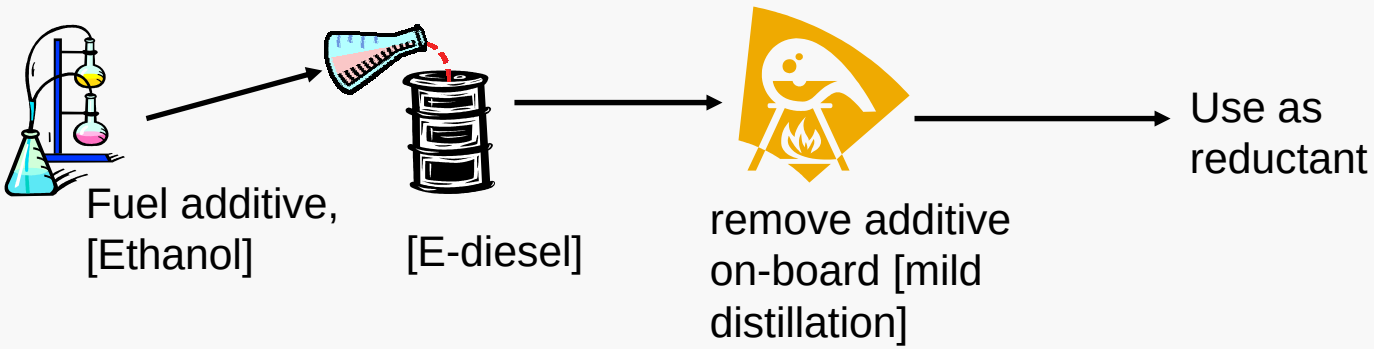
4. Previous work gave good results using ethanol

Earlier $Ag\text{-}Al_2O_3$ SCR Effort (9th DEER)

- Co-operation between Caterpillar & ORNL (2002).

  Caterpillar provided $Ag\text{-}Al_2O_3$ catalysts & expertise.
- Demonstrated 80-90% NOx reduction using ethanol on a 5.9 L engine with a 7 liter catalyst for 350-400 ˚C diesel exhaust. Measured regulated & unregulated emissions.
- Demonstrated feasibility of ethanol being fuel-borne reductant using E-diesel (ethanol-diesel) .

  Fuel-borne reductant – fuel additive that is removed and used as a reductant:



Current Effort

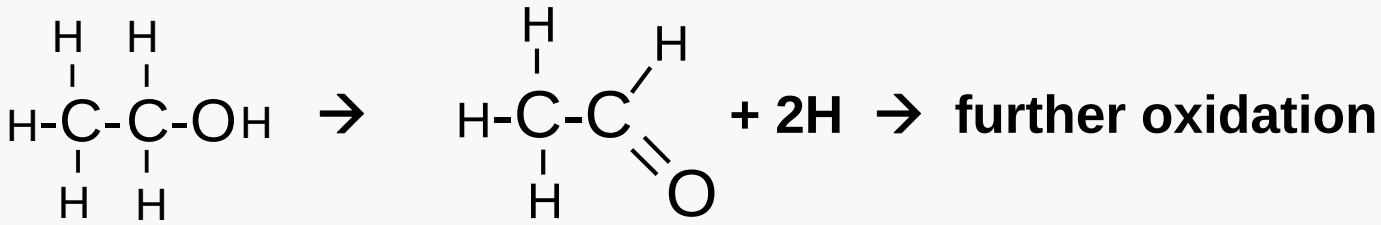
Goals:

1) Find new, effective reductants for the Ag catalyst – particularly if they can be fuel-borne.

2) Gain understanding of reductant – catalyst mechanisms, role of chemical functional group & other properties

What Makes a Good Reductant?

- **Ethanol → acetaldehyde; 1-propanol → propionaldehyde**



- **Aldehydes appear to be good reductants - further oxidation drives the NOx reduction**
- **What properties make ethanol a good reductant?**
  - **reactive,**
  - **very polar,**
  - **highly water soluble, can compete for surface sites**
  - **volatile, may have good surface mobility (diffusion)**

- **Miscible with diesel fuel – can be removed for use as reductant**

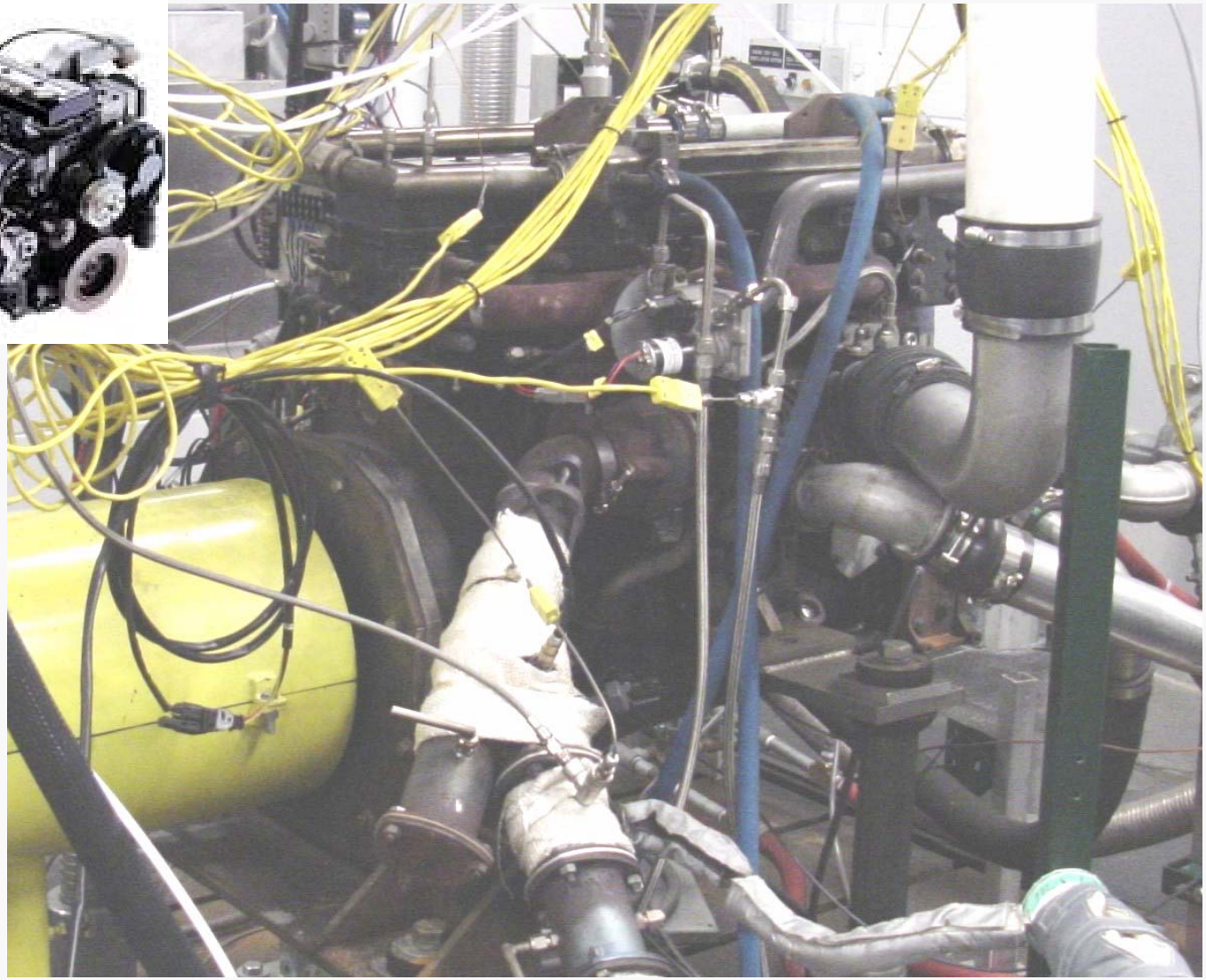
Experimental Matrix Design

- Engine set points

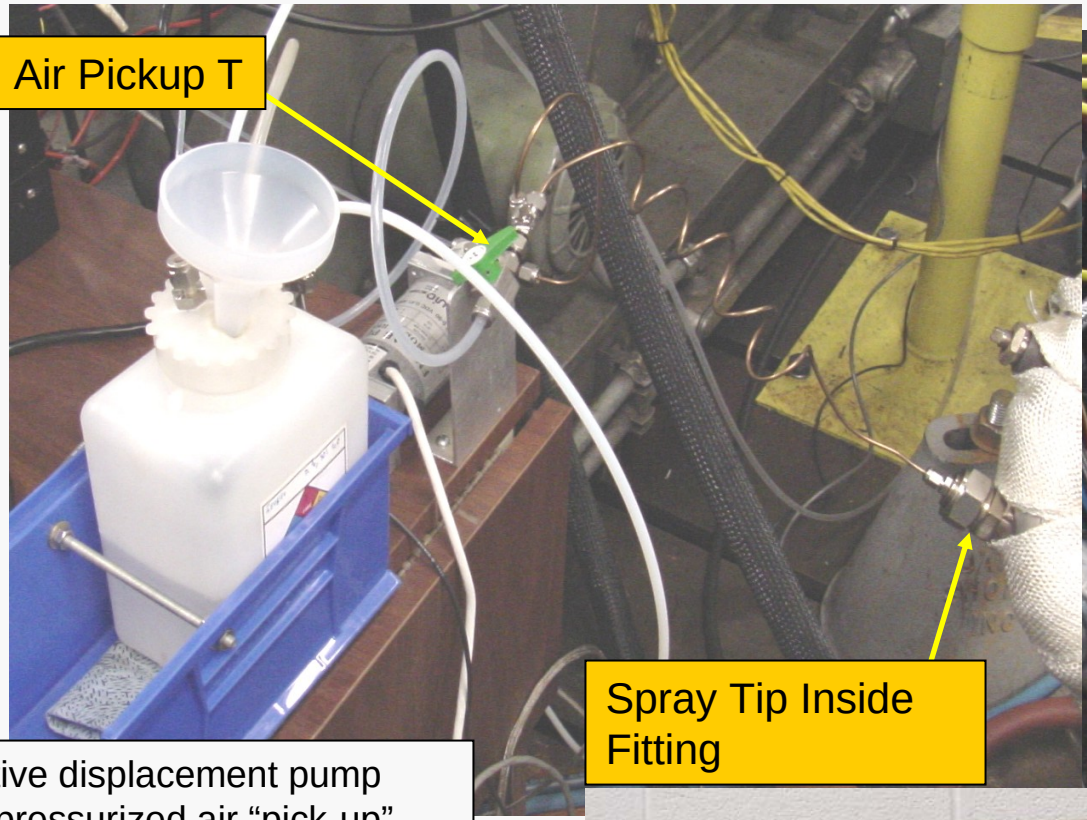
Test Condi-tion	SV (1/h)	Catalyst inlet Temperature (°C)	O_2 conc. (%)	CO_2 conc. (%)	H_2O conc. (%)
1	50K	260	13.2	4.8	6.5
2	50K	295	12.3	5.4	7.1
3	50K	335	10.6	6.5	8.2
4	50K	390	8.5	7.8	9.6
5	50K	465	5.5	9.8	11.9
6	100K	380	10.5	6.5	8.2

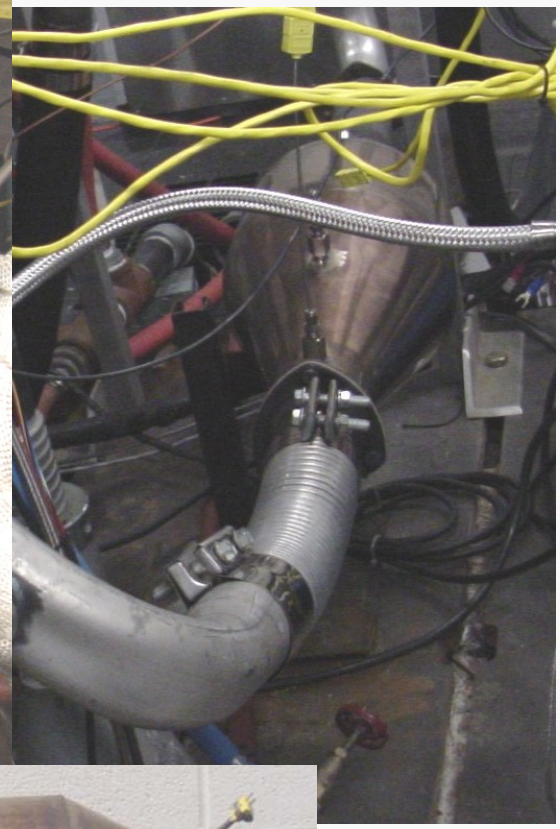
- Cummins 5.9 L engine with controlled EGR – controlled NOx to 200-240 ppm
- Reductant injection range: C/N from 0 to 10 +
- Reductants: various alcohols, diols, ketone, acetate, non-oxygenated hydrocarbons

Cummins 5.9 L Engine: ORNL, NTRC cell 3



Air-assisted atomization injection was used. Reductant dispersion was verified.

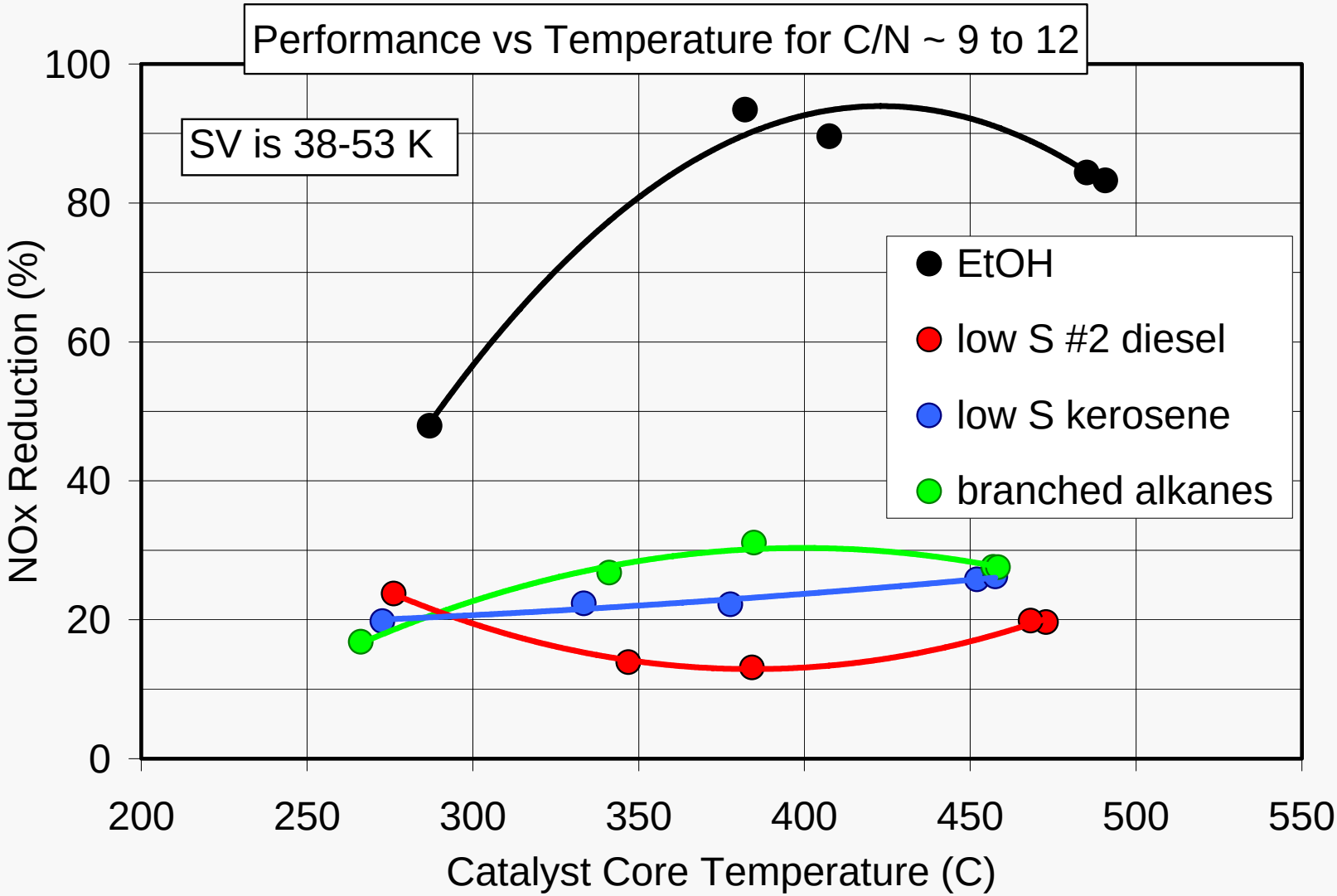




Positive displacement pump with pressurized air “pick-up” and spray tip

Caterpillar silver catalyst

Earlier tests: fuel hydrocarbons are poor reductants. n-heptane tests also gave poor results (not shown)

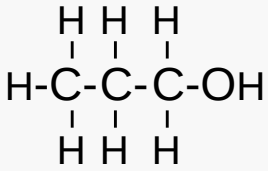


Eleven alcohols tested as reductants

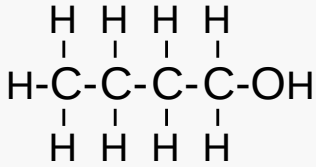
Primary alcohols:

Ethanol

1-propanol



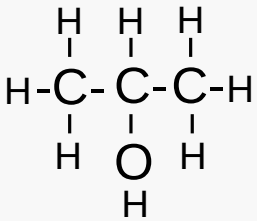
1-butanol



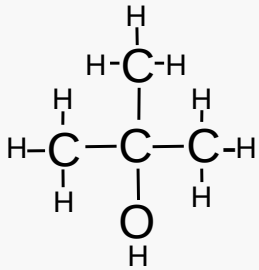
1-hexanol $C_6H_{14}O$

1-octanol $C_8H_{18}O$

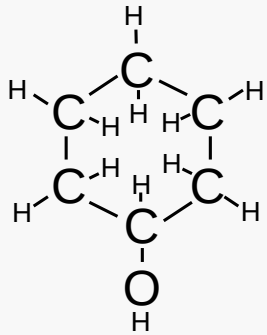
2-propanol



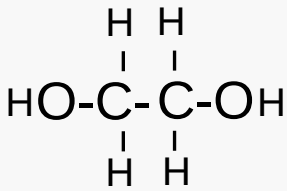
tert-butanol



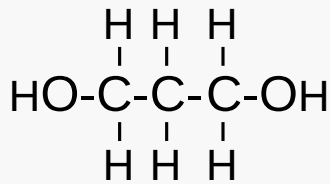
cyclohexanol



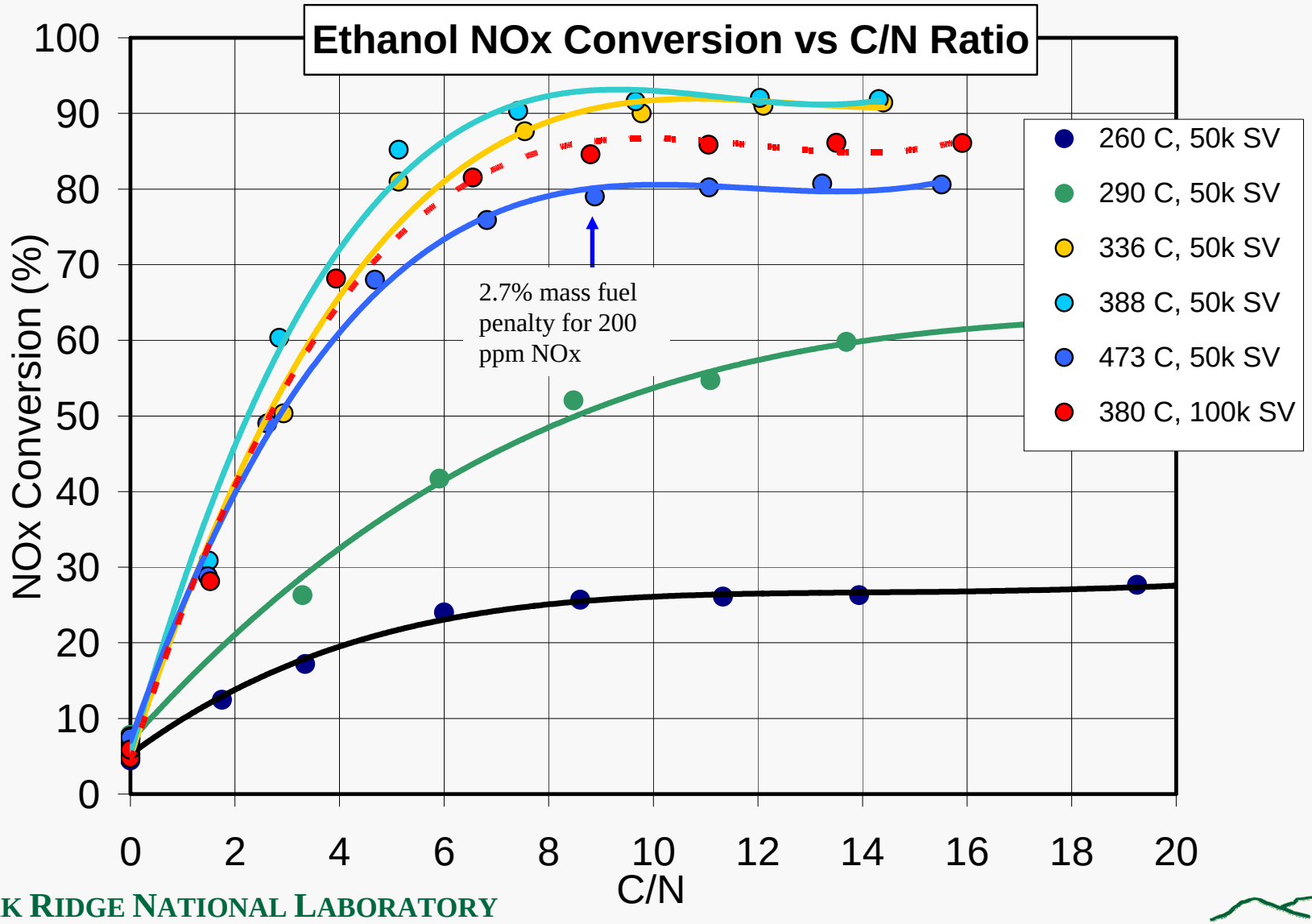
ethylene glycol C_2H_6O



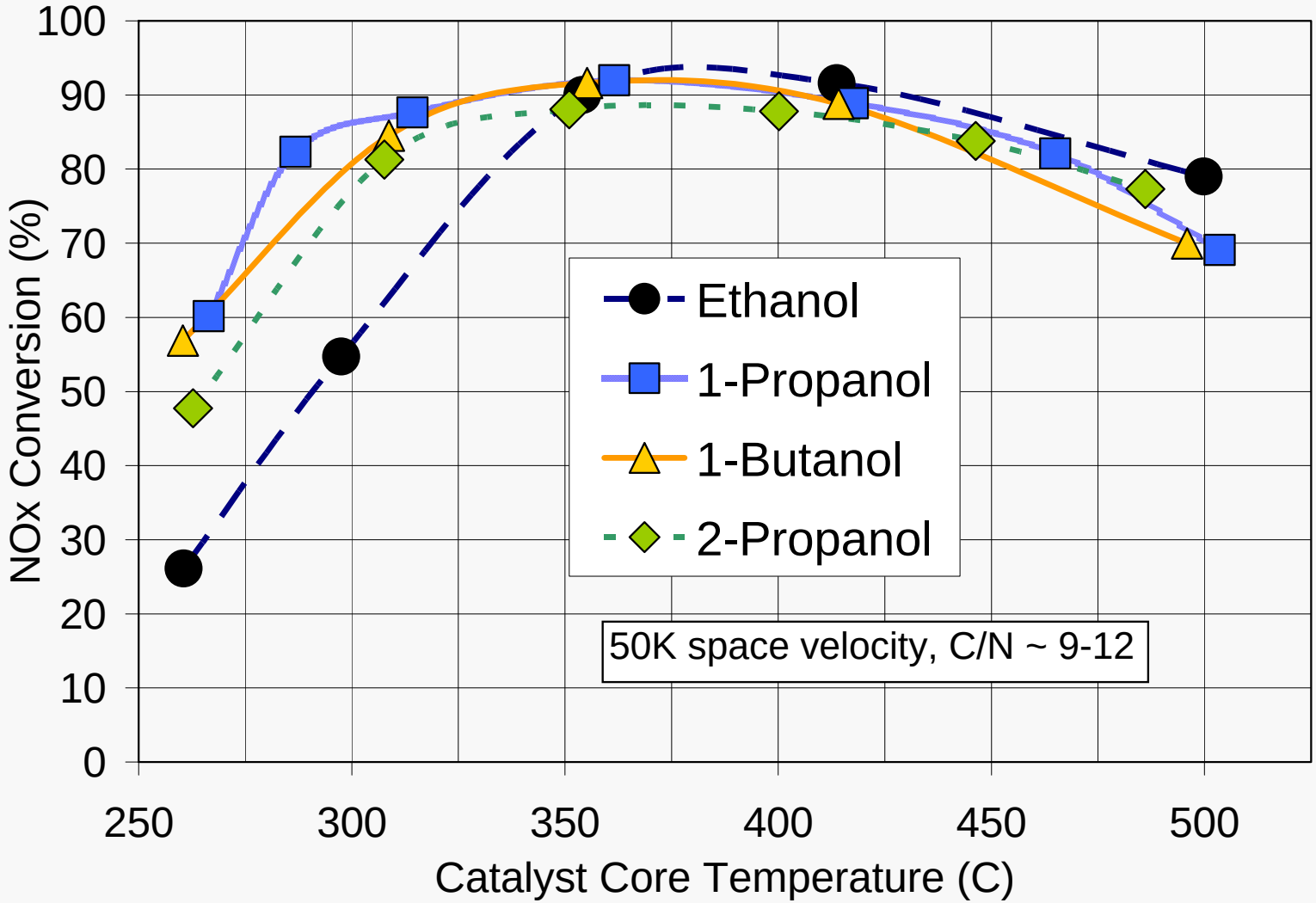
1,3-propanediol $C_3H_8O_2$



Ethanol Data Set: > 90% conversion is possible

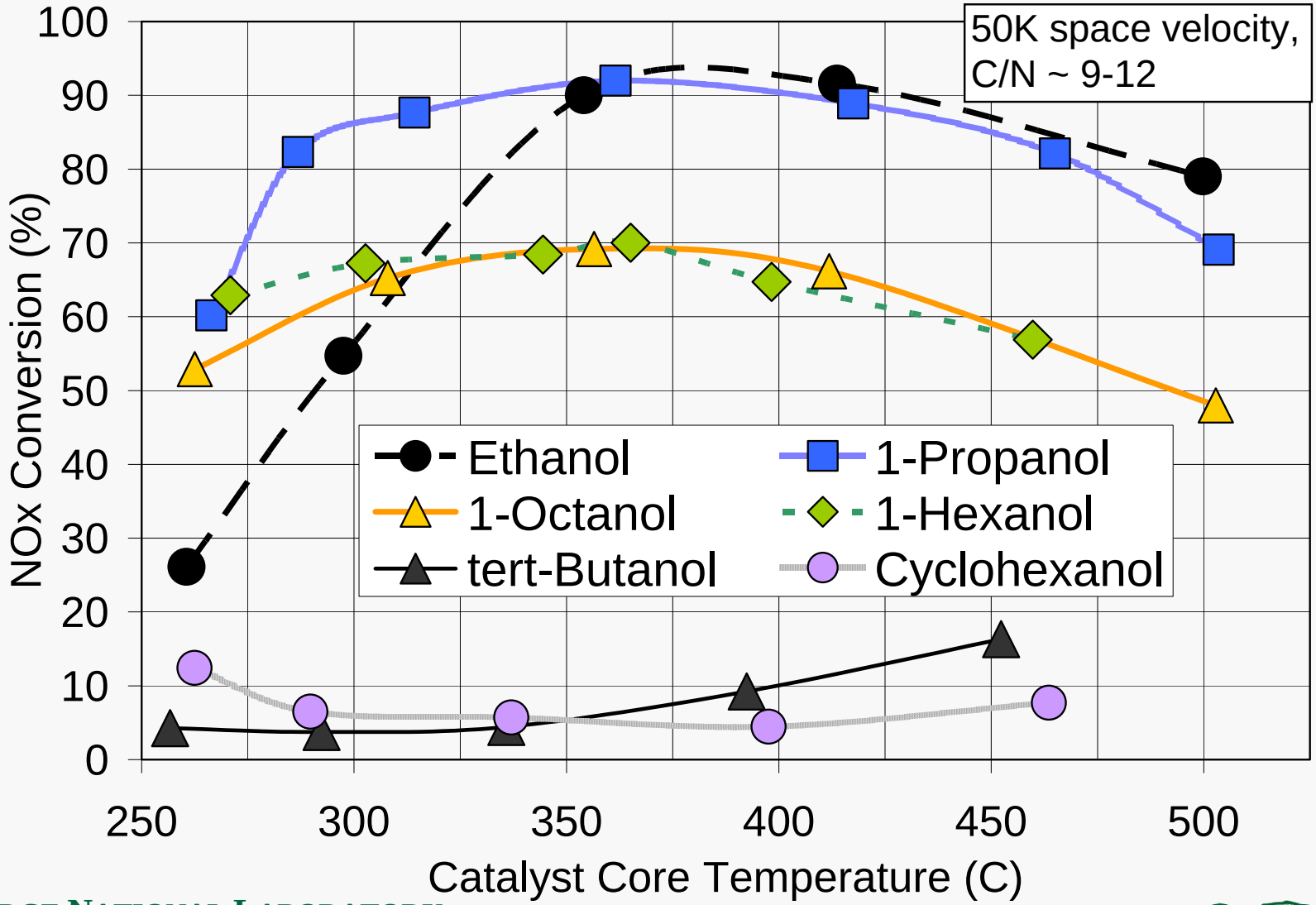


1-propanol, 2-propanol, butanol extend good performance to lower temperatures vs. ethanol

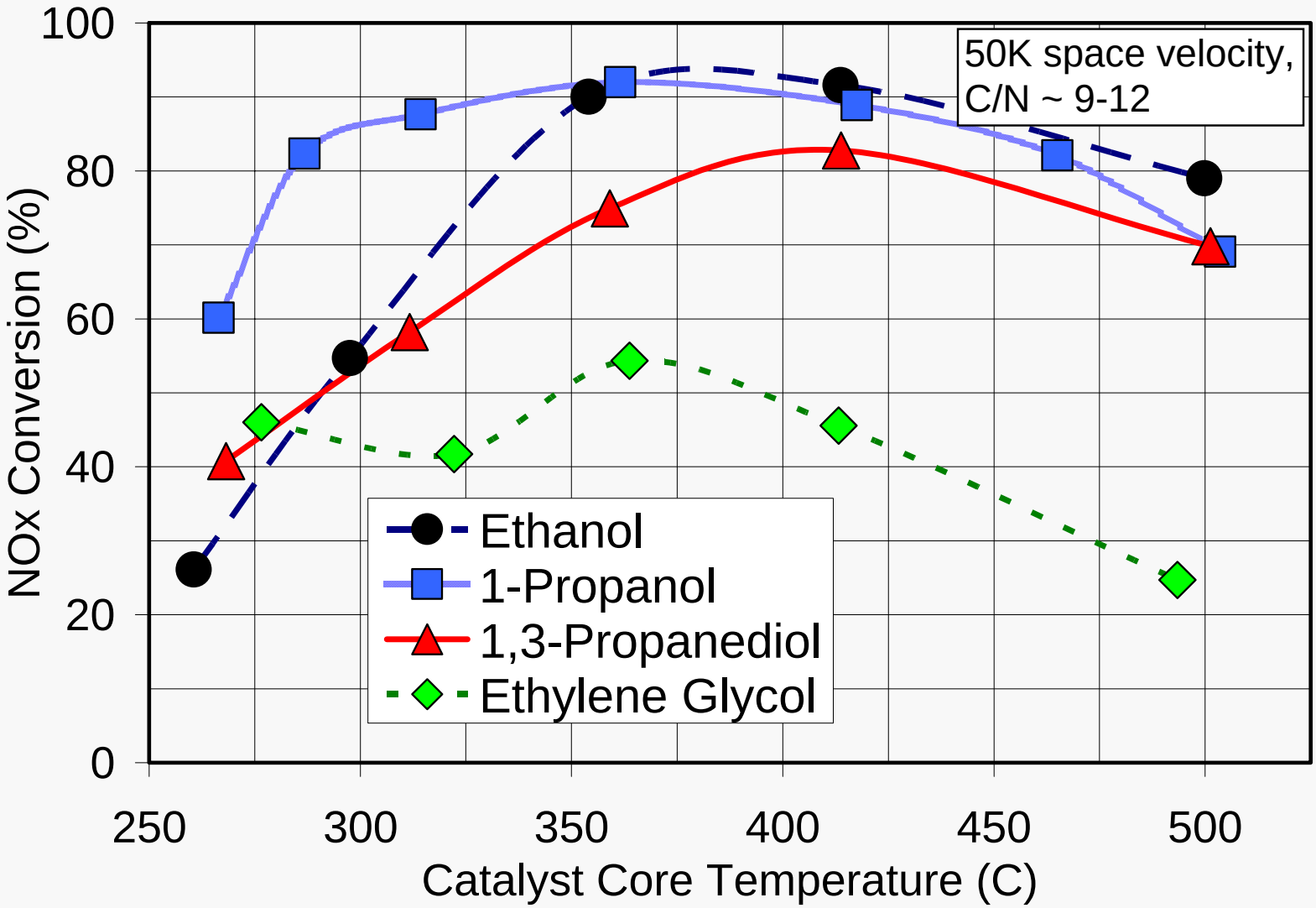


Hexanol, octanol, don't perform like ethanol & 1-propanol.

t-butanol, cyclohexanol do not act as reductants

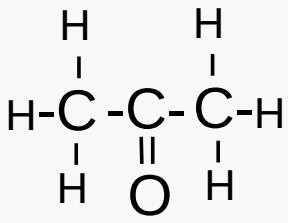


Diols did not perform as well as light 1-alcohols, except at ~ 260 °C point

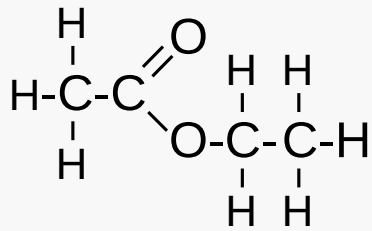


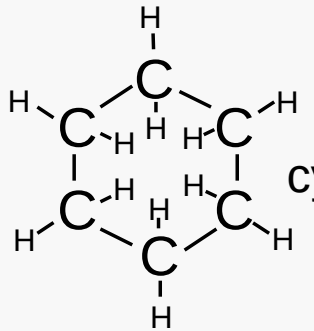
Other reductants tested: acetone, ethyl acetate, cyclohexane

acetone C_3H_6O



ethyl acetate $C_4H_8O_2$



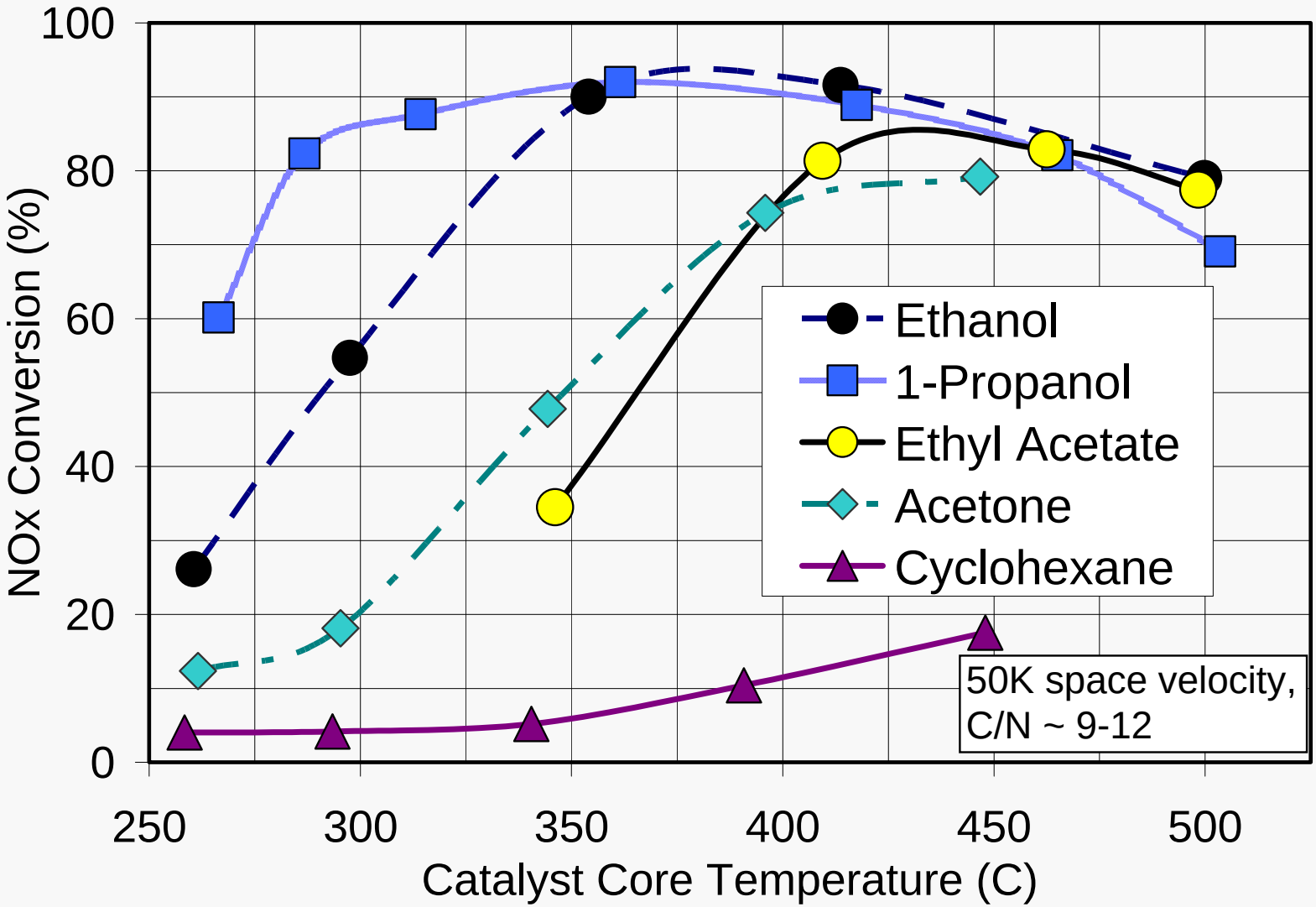


cyclohexane C_6H_{12}

cyclic HCs are common in oil-sand derived fuel

Acetone, ethyl acetate are inactive at low temperatures.

Cyclohexane does not perform as a reductant



Results Summary

Reductant	Performance	Explanation, notes
ethanol, 1-propanol 1-butanol, 2-propanol	55-90 % reduction, best reductants. Propanol, butanol better than ethanol at low temps.	polar, reactive, highly water soluble, mobile. Found new reductants
1,3-propandiol	40-80% reduction, reasonable at low T	non-polar, reactive, water soluble
1-hexanol, 1-octanol	40-60% reduction, reasonable at low T temp.	less polar, less mobile, may carbonize at some conditions
ethylene glycol	some reduction at low T, otherwise poor	water soluble, non-polar, may oxidize readily
ethyl acetate, acetone	good performance at ~ 400 C +	molecule stable at lower T range

Results summary

Reductant	Performance	Explanation, notes
tert-butanol cyclohexanol	very unreactive	very stable molecule?
cyclohexane, n-heptane, #2 diesel, kerosene, iso-paraffins	unreactive to very unreactive	non-polar, non-oxygenated

Goals: 1) find new reductants & 2) understand more about what makes this system work well

- 1-propanol & 1-butanol have been successfully blended with diesel fuel (ECD-1) and recovered by mild distillation.
- Good reductant: small molecule, polar, very water soluble, reactive, mobile

Thank you for this opportunity

- **Questions?**