Plasma-Enhanced SCR of NOx in Simulated Heavy-Duty Exhaust: Sulfur, Hydrocarbon, and Temperature Effects

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Outline

Background Information

High-Temperature Plasma System

Results from Catalyst Testing
- Temperature Effects
- Efficiencies
- Hydrocarbon Quantity and Form
- Sulfur Effects

Future Plans

Plasma Catalysis Program (3/99 Start)

Challenges

Stability, Durability, and Activity over a Broad Temperature Range
- -Focus on Higher End of Temperature Range
- -Numerous other Programs Examining the Low End

Large Exhaust Flow and Low HC Concentration

Technical Approach

Design a High-Temperature Plasma Reactor
Develop Novel High-Temperature Catalysts
- PNNL – Synthesis, Characterization, Plasma Testing
- Caterpillar – Synthesis, Characterization, Engine Testing

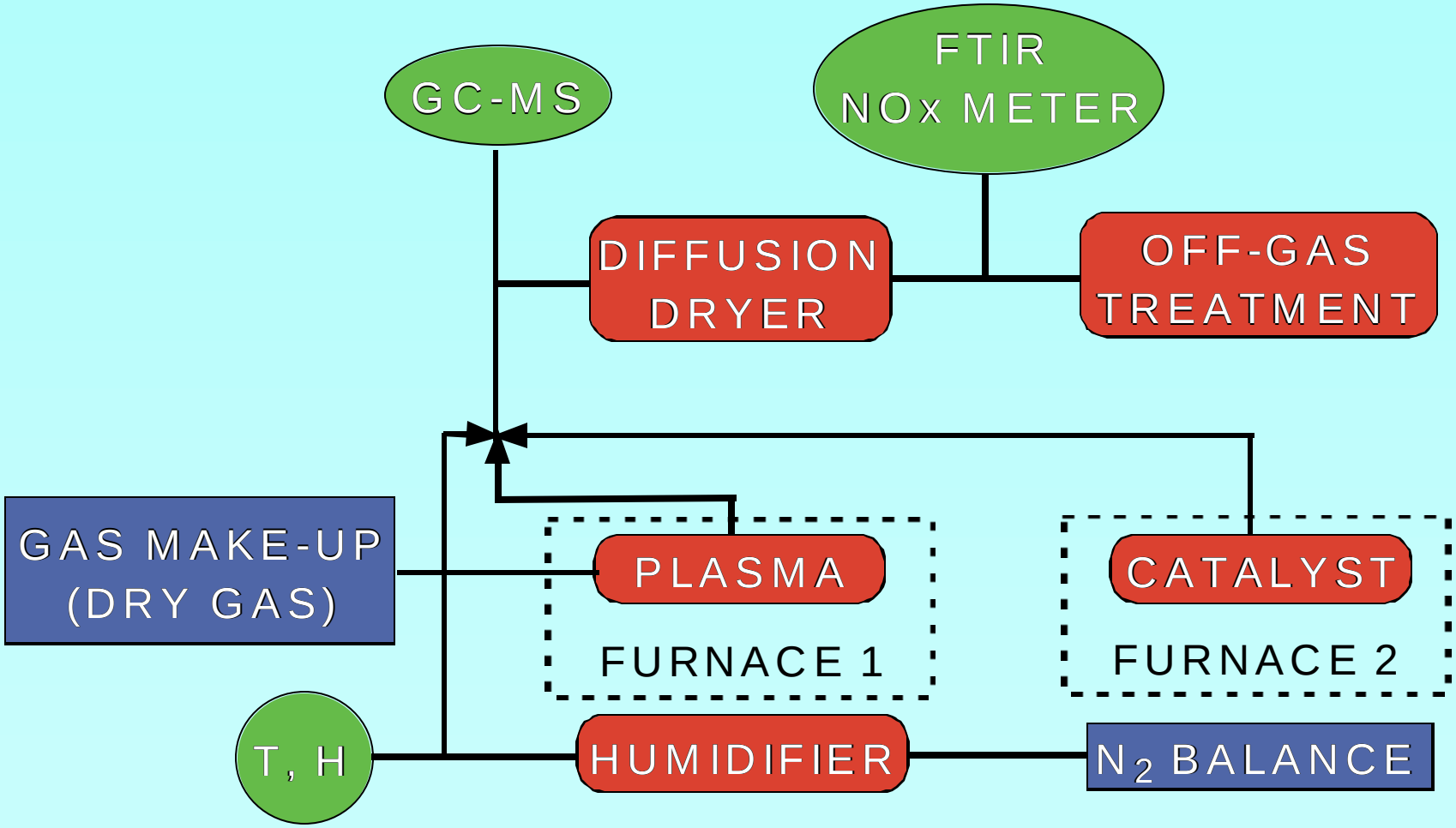
Develop Mechanistic Understanding
- Reactant Variation (NOx, SO_2, HC, H_2O)
- Catalyst Surface Analysis Pre- and Post-Mortem

Plasma Chemistry

Ideal Reaction:	$NO + N\bullet \rightarrow N_2 + O\bullet$
Reactions that Dominate:	$NO + O\bullet \rightarrow NO_2$ $NO_2 + O\bullet \rightarrow NO + O_2$ $NO_2 + \bullet OH \rightarrow HNO_3$
HC Is an O• and •OH Getter:	$C_3H_6 + O\bullet \rightarrow \bullet C_2H_5 + HCO\bullet$ $C_3H_6 + O\bullet \rightarrow \bullet CH_2CO + \bullet CH_3 + H\bullet$ $C_3H_6 + \bullet OH \rightarrow C_3H_5 + H_2O$ $C_3H_6 + \bullet OH \rightarrow C_3H_6OH$
Oxidation Products Form $HO_2\bullet$:	$CH_3O\bullet + O_2 \rightarrow CH_2O + HO_2\bullet$ $HCO\bullet + O_2 \rightarrow CO + HO_2\bullet$ $H\bullet + O_2 \rightarrow HO_2\bullet$
$HO_2\bullet$ Reacts Quickly w/NO:	$NO + HO_2\bullet \rightarrow NO_2 + OH\bullet$

Penetrante *et al.* (SAE SP-1395)

Process Flow Sheet



Gas Composition and Test Conditions

Make-Up

NO	500 ppm
SO_2	0/20 ppm
O_2	9%
CO	300 ppm
C_3H_6	500–2000 ppm
CO_2	8%
H_2O	1.5%
N2	balance

Catalyst: 1 gram

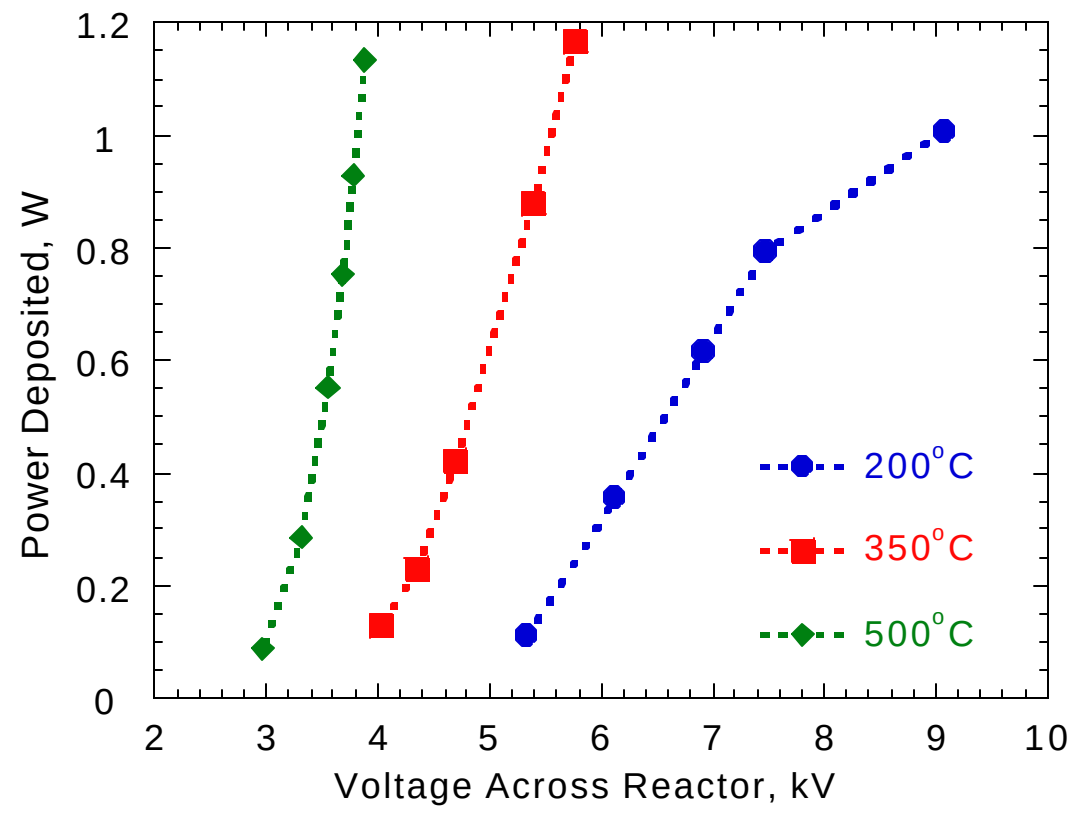
Bulk Sp. Grav.: 0.25–0.40

Flowrate: 1 SLM

Space Velocity:
15,000–25,000 1/hr

Power Deposition vs. Temperature

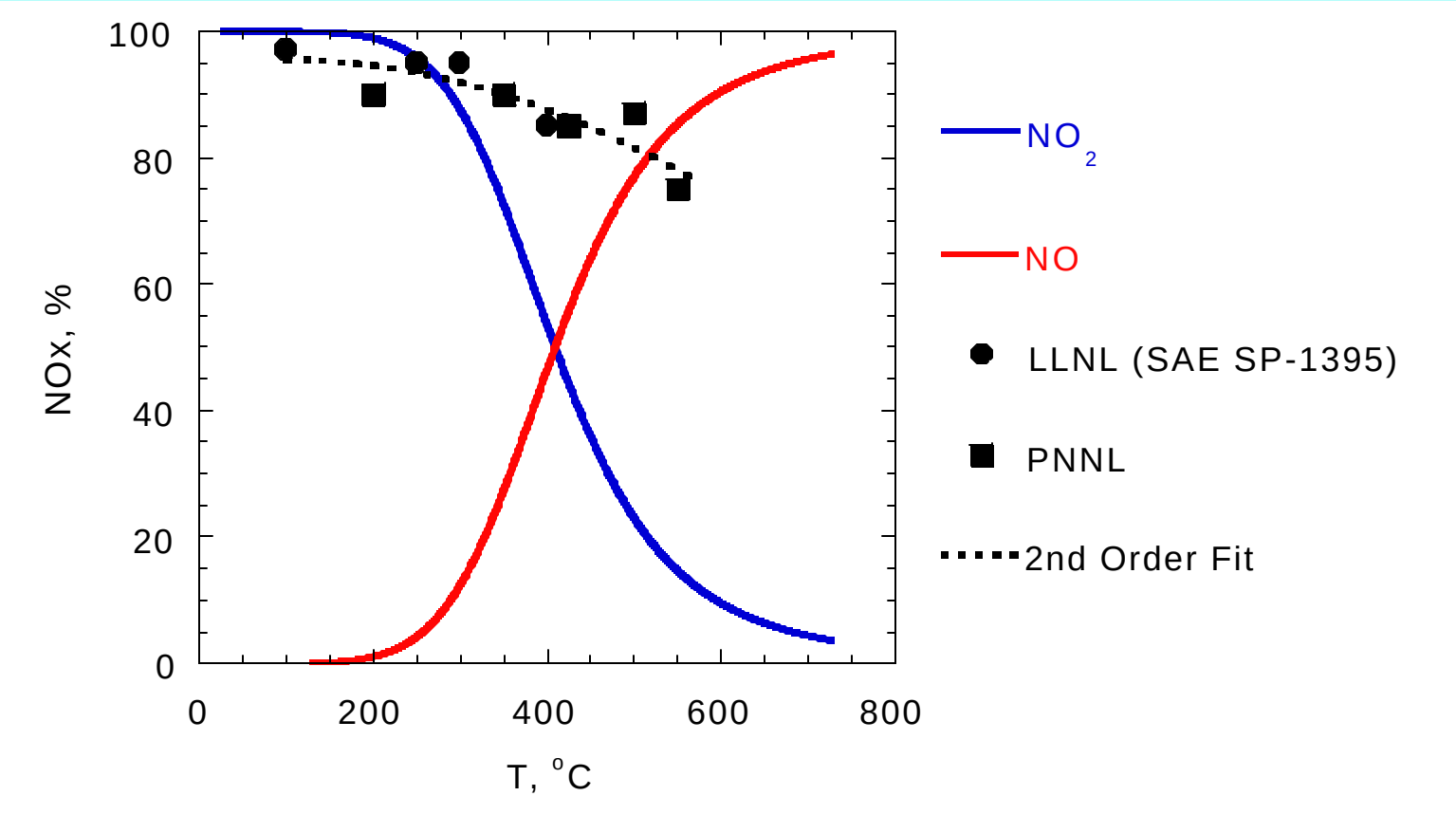
1 SLM on small-scale reactor



- Packed-bed and single-barrier reactors failed
- High-temperature stability gained by using dual-dielectric barrier system
- Power vs. voltage better as T↑ because electron mean free path increases.

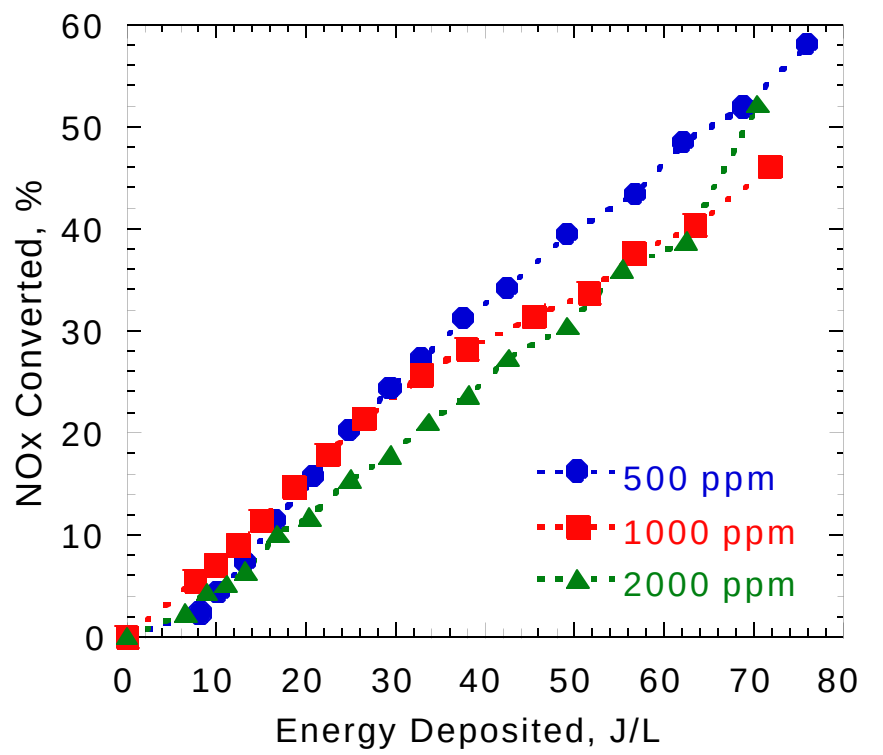
Thermodynamics Effects on NO ® NO_2

$$NO + \frac{1}{2} O_2 \rightarrow NO_2$$

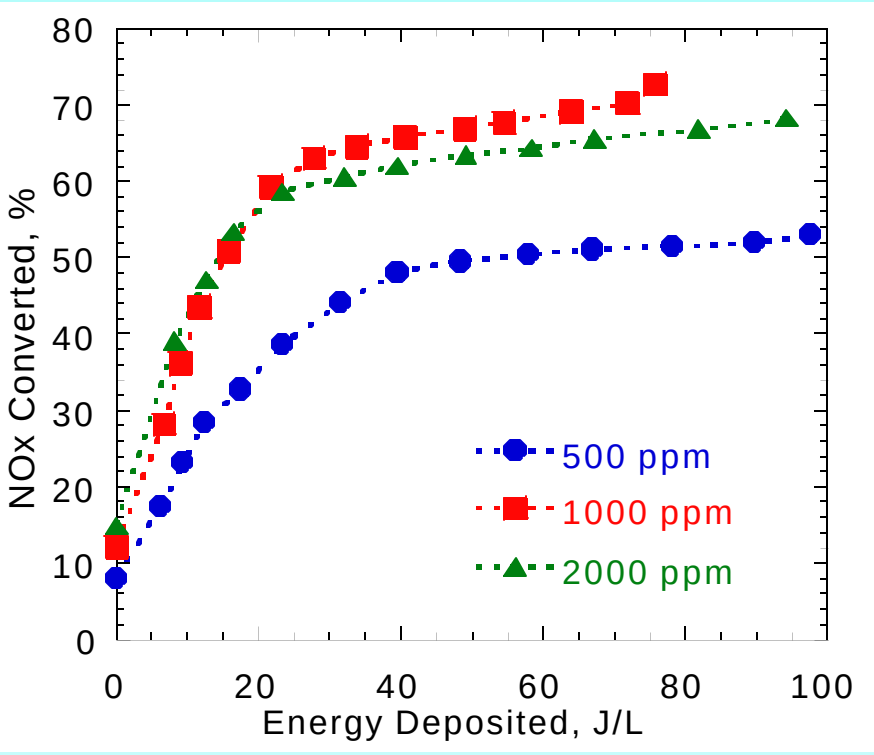


HC Level Study (PF#1)

200°C

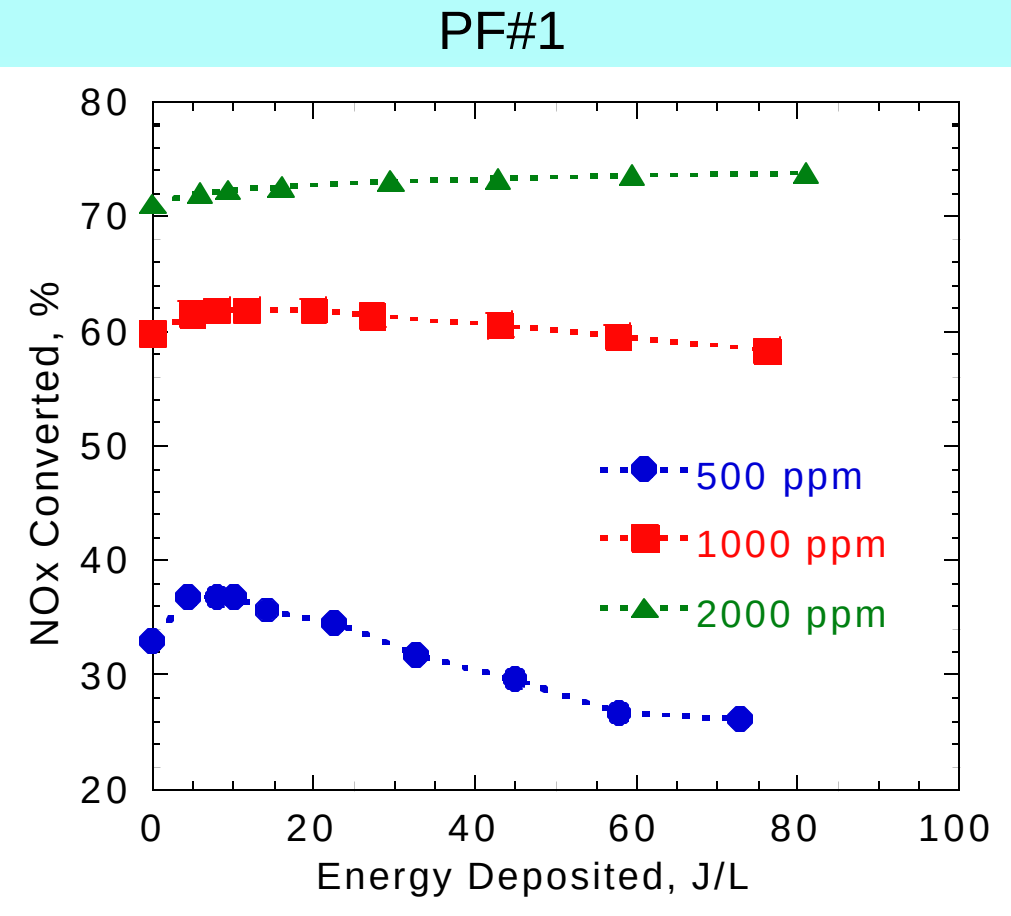


350°C



No SO_2 used in this study.

HC Level Study–500°C



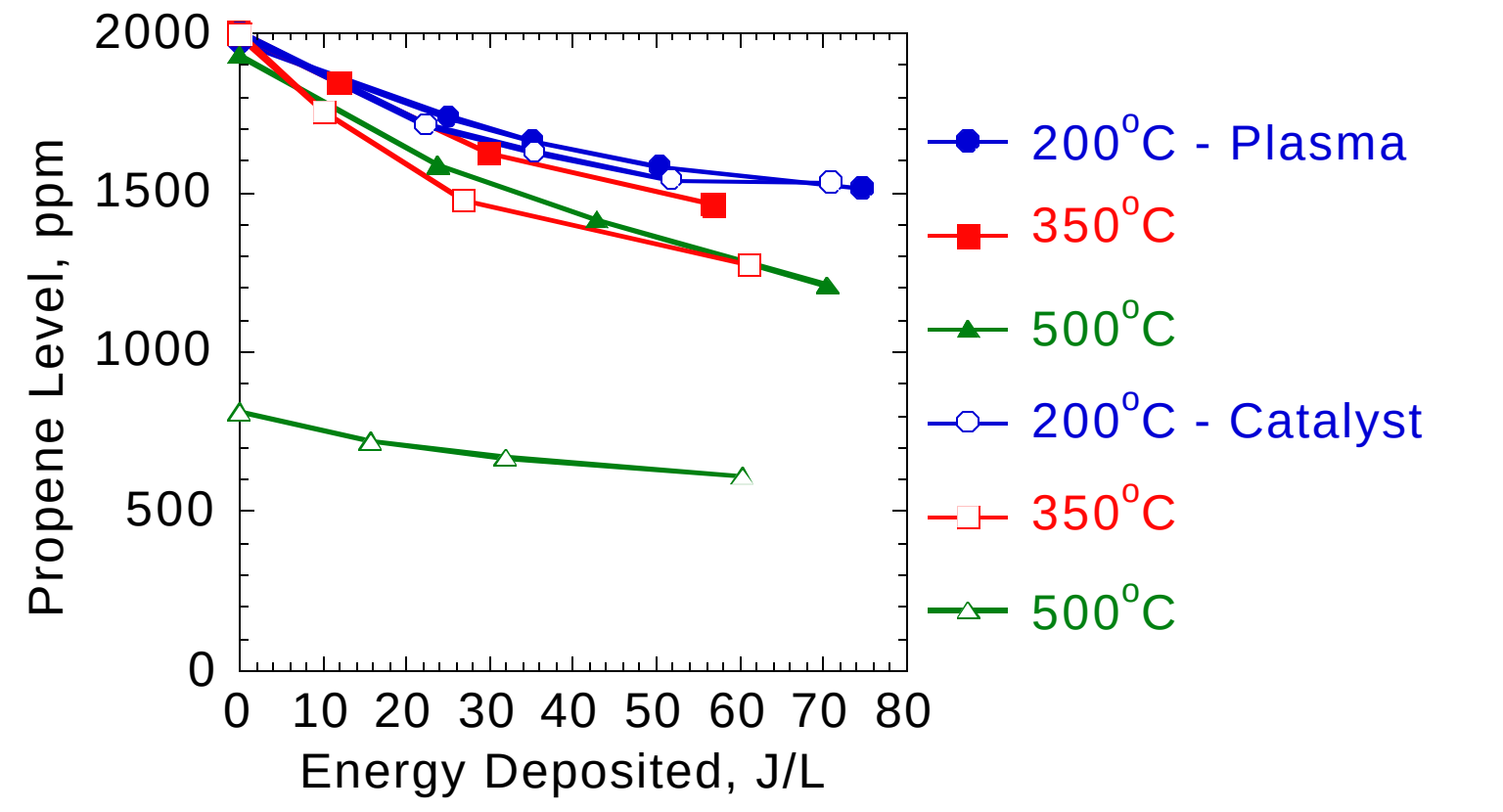
As temperature increases, optimal C_1:NOx ratio also increases

200°C: 3:1 sufficient

350°C: 6:1

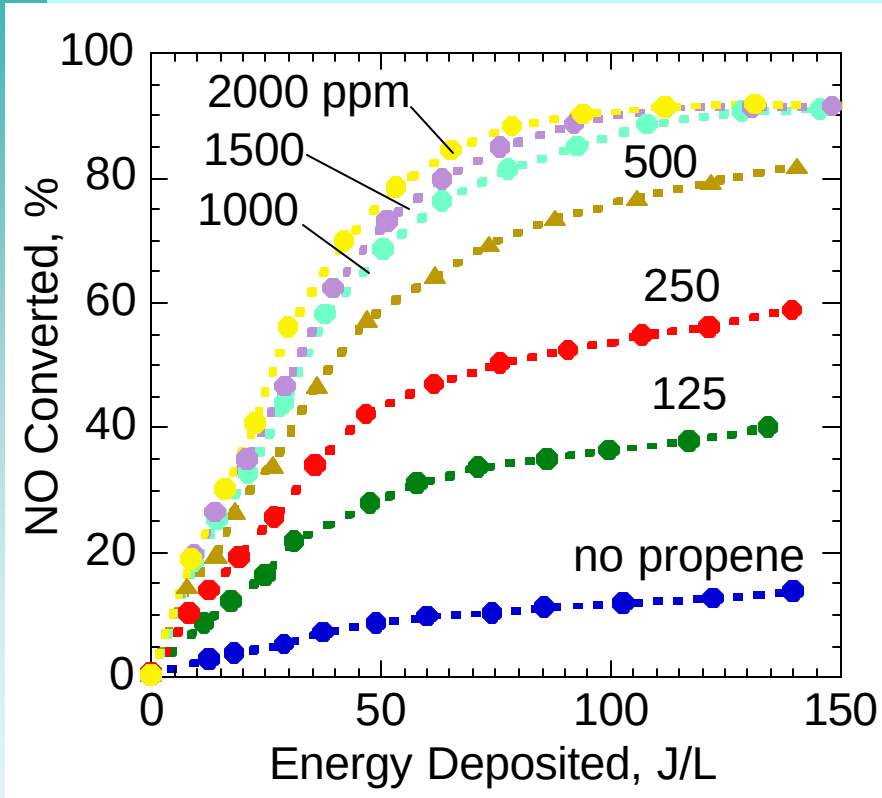
500°C: 12:1 (greater?)

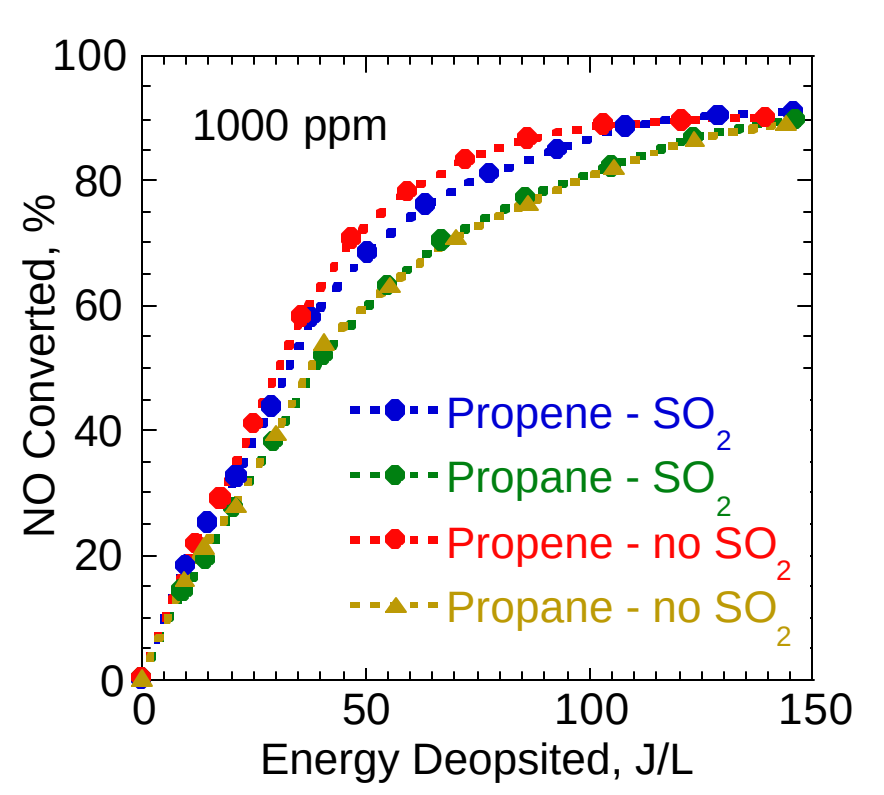
HC Consumption vs. Temperature



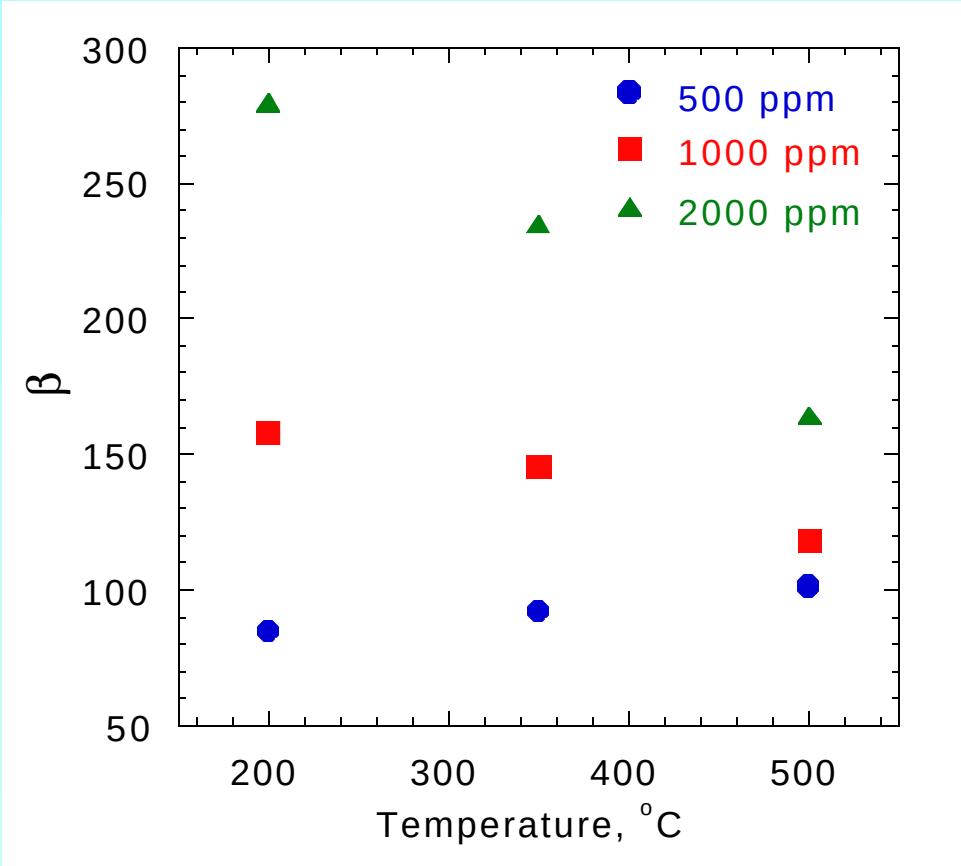
NO to NO_2 (Plasma)

350°C





Energetics of Propene Oxidation

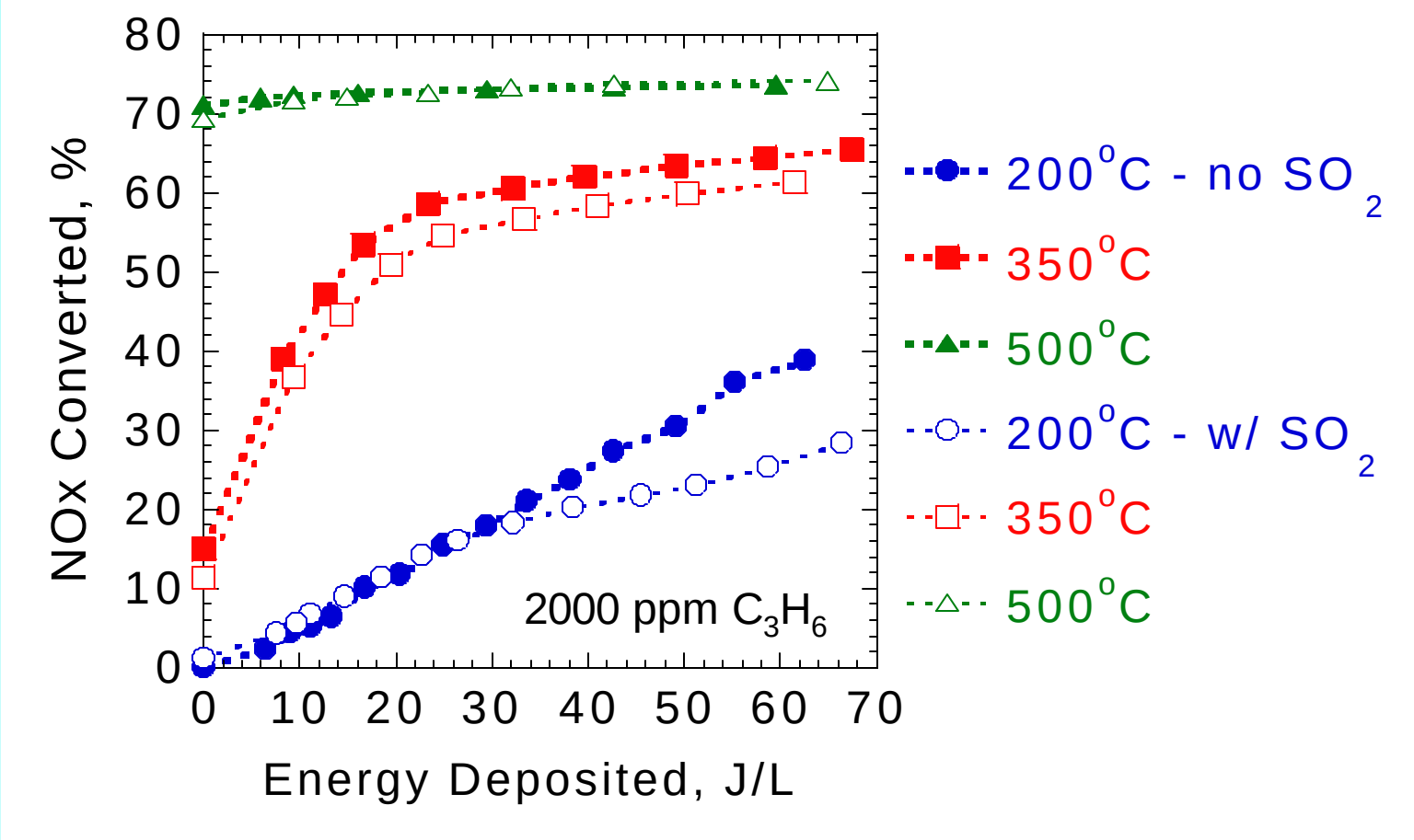


$$C = C_i \exp\left(-\frac{E}{\beta}\right)$$

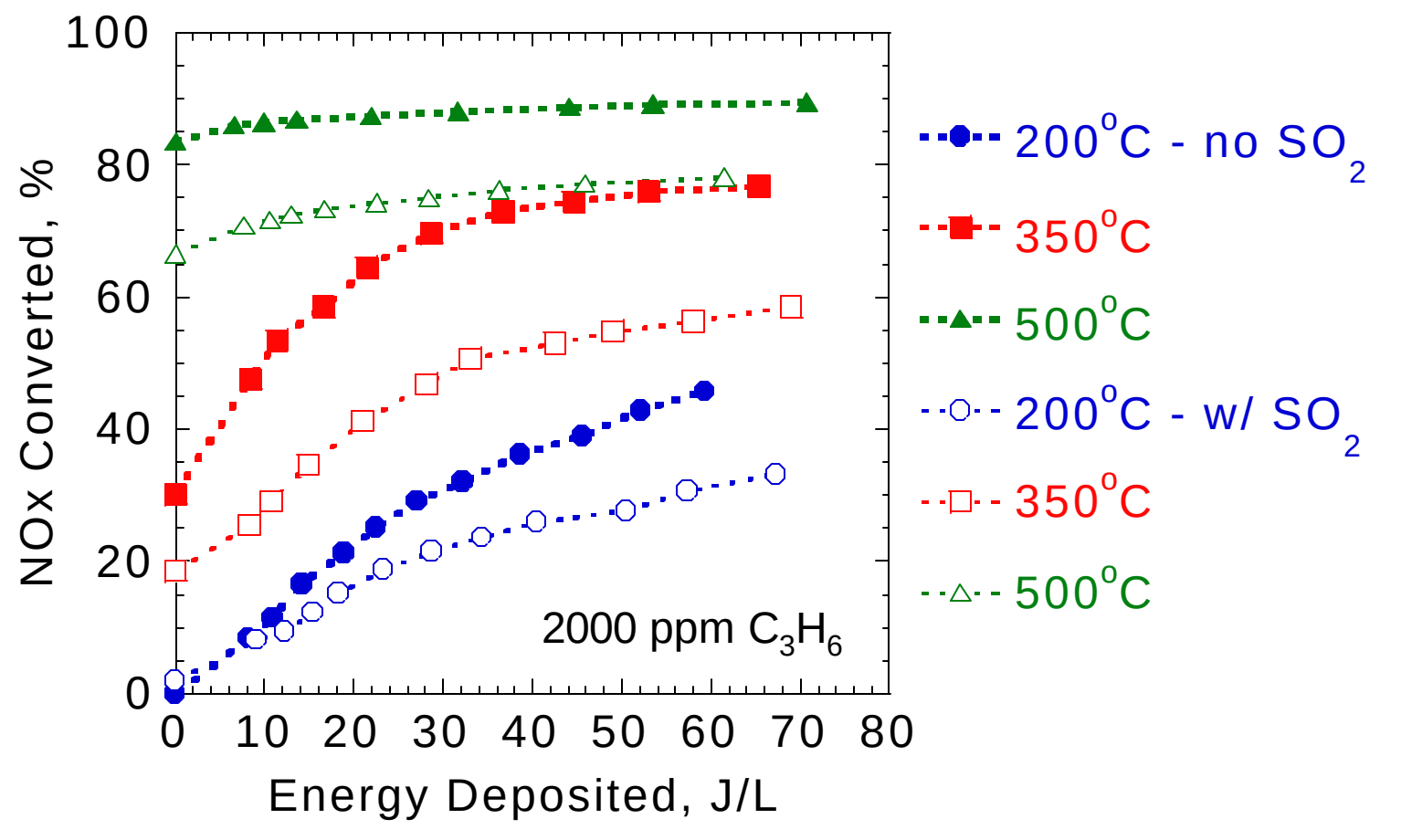
As HC level increases:

- More difficult to oxidize same fraction of HC at a given temperature (higher β).
- Enhanced oxidation due to increased temperature is more significant.

Sulfur Tolerance of PF#1

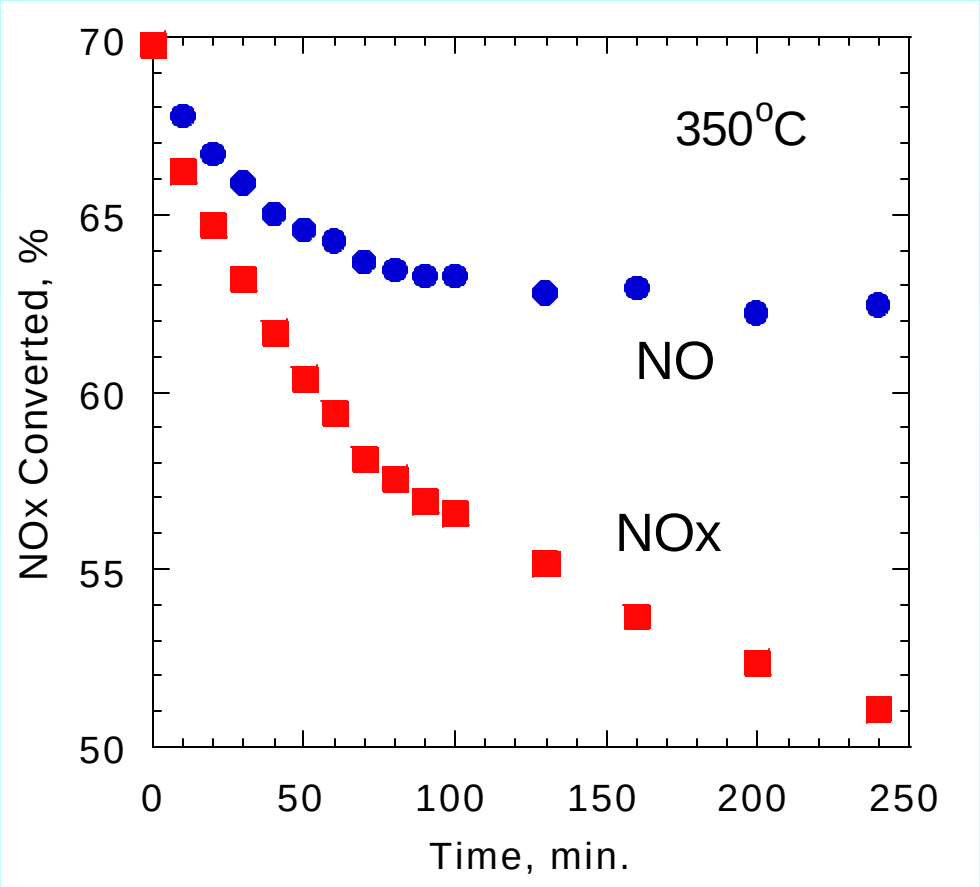


Sulfur Tolerance of PF#2



Transient Response to SO_2

PF#2



20 ppm SO_2 added at t = 0

Energy deposition held at 61 J/L

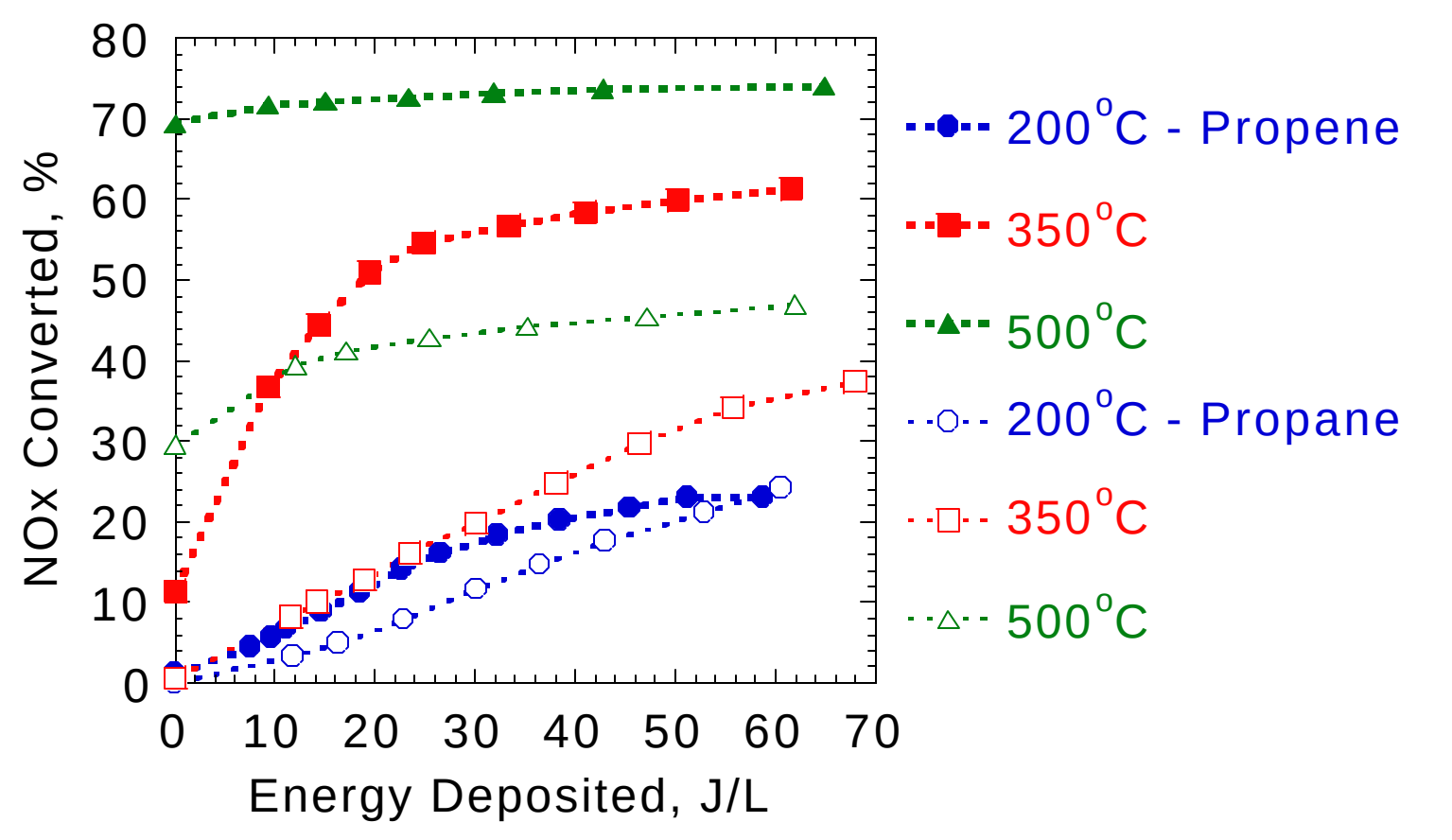
Poisoning takes place over 4-6 hours at 2000 ppm HC.

Poisoning is irreversible.

Loss in efficiency shows up as NO and NO_2.

Saturated vs. Unsaturated HC

PF#1–2000 ppm HC



Conclusions

1. High-temperature plasma is possible and reliable.

2. Optimum HC level changes with temperature due to changes in NO conversion, HC oxidation, and catalyst activity. May be beneficial to inject post-plasma. Optimal HC levels are too high.

3. Sulfur poisoning is a problem for certain catalysts. Other formulations show relatively minor degradation in activity. More aging and long-term studies needed.