N_2O Abatement: Reaction Mechanisms and Methods for Improving Destruction Efficiency

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Outline: N$_2$O Kinetics

- Historical perspective
  - » NO$_x$ formation mechanisms
  - » Kinetic modeling of NO$_x$ formation
  - » Complex kinetics
  - » Available kinetic mechanism data bases

- Objectives of this work

- Kinetic modeling results
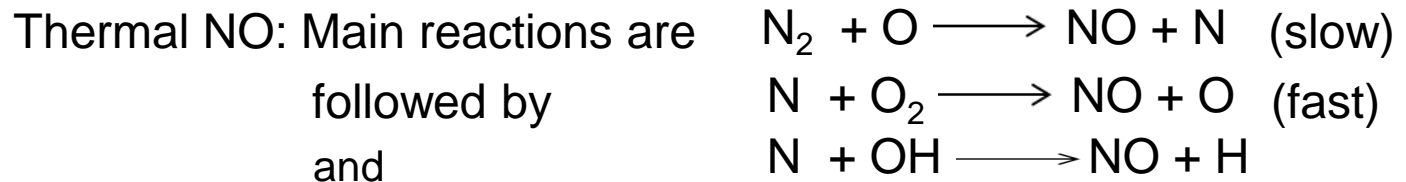
- Application example

- Future work

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History: NO$_x$ formation mechanisms -

- NO$_x$ (NO and NO$_2$) formation has been intensively studied since 1970.

- NO from combustion sources arises from two sources: fixation of atmospheric N$_2$ (**Thermal NO**), and oxidation of chemically bound nitrogen in the fuel (**Fuel NO**).

- Thermal NO formation – very sensitive to temperature. Formation is slow below 1800K. Sensitive to local air/fuel ratio (stoichiometric ratio, SR)

- Fuel NO (from, say NH$_3$ or HCN) – not so sensitive to temperature. Formation is rapid at moderate temperatures (<1800K). Sensitive to local SR.

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NOx formation (continued)

- Both Thermal NO_x and Fuel NO_x are formed by reactions involving free radicals (O, OH, H, CH, NH, N etc) formed at high temperatures during combustion of hydrocarbons. These are at levels above local equilibrium because of "chain branching" reactions.
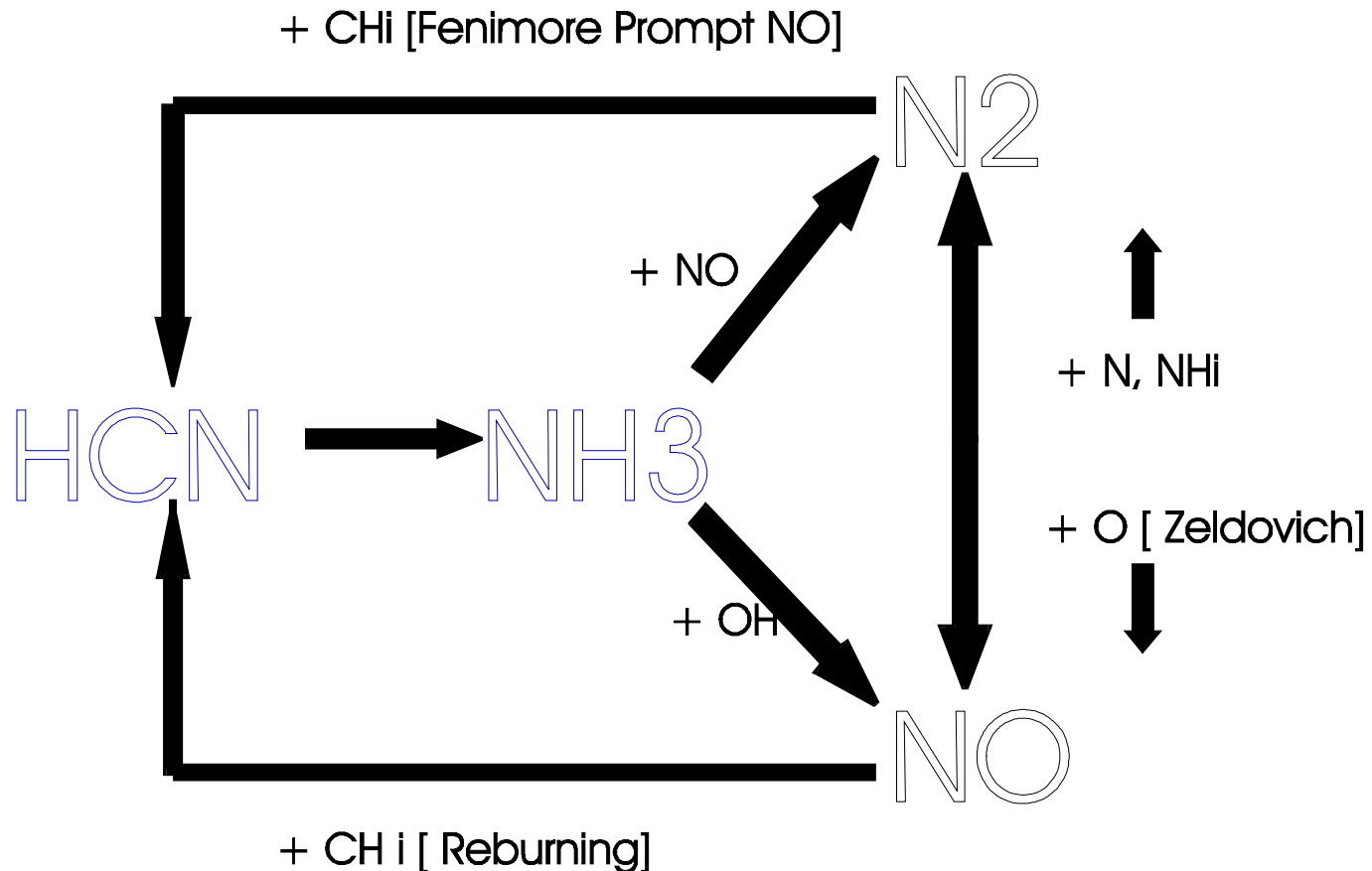
Thermal NO: Main reactions are $N_2 + O \longrightarrow NO + N$ (slow)

followed by $N + O_2 \longrightarrow NO + O$ (fast)

and $N + OH \longrightarrow NO + H$

Fuel NO : Main reactions involve oxidation of HCN, NH, etc to form *both* NO and N_2. NO is favored under local oxidizing conditions, N_2 under reducing conditions.

- More accurate detailed mechanisms include formation and destruction of N_2O.

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+ CHi [Fenimore Prompt NO]

N2

+ NO

+ N, NHi

HCN → NH3

+ O [Zeldovich]

+ OH

NO

+ CH i [Reburning]

How does N$_2$O fit into this?

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Question?

- Does N_2O behave like a Fuel Nitrogen compound leading to Fuel NO (weak temperature dependence)

or

- Does N_2O behave as part of the Thermal NO mechanism (i.e high temperature dependence)

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N_2O reactions embedded within overall NO_x formation mechanism (GRIMech3.0)

Reaction	A (cgs)	B (K)	E_A (cal/mol K)	Source
$N_2O + OH \leftrightarrow N_2 + HO_2$	0.200E+13	0.000	10000.000	JAM 9/87
$N_2O + O \leftrightarrow 2 NO$	0.100E+15	0.000	28200.000	PG
$N_2O + M \leftrightarrow N_2 + M + O$	6.900E+23	-2.500	64760.000	Bowman 1991
$N_2O + H \leftrightarrow N_2 + OH$	0.760E+14	0.000	15200.000	NH3 CST
$N_2O + O \leftrightarrow N_2 + O_2$	0.100E+15	0.000	28200.000	PG
$CN + N_2O \leftrightarrow NCO + NO$	0.100E+14	0.000	0.000	JAM
$NCO + NO \leftrightarrow N_2O + CO$	0.100E+14	0.000	-390.000	PEERY
$NH + NO \leftrightarrow N_2O + H$	1.400E+14	0.000	12700.000	Bowman 1991
$NNH + O \leftrightarrow N_2O + H$	0.100E+15	0.000	0.000	

All reactions are reversible.

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NO$_x$ prediction

- In order to predict trace species formation or destruction, one needs

   1. Simulation tools that allow easy handling (i.e input and integration) of many (100's) of "stiff" ODE's describing rates of formation and destruction of major and minor species

      These exist as available special purpose software packages, such as

      – e.g CHEMKIN, CANTERA, REKS

   2. Reaction rate coefficients (pre-exponential factors and activation energies etc) for the multiple (<1000) reactions that involve the major and minor species.

   3. Thermodynamic data for every species to be considered.

- Validated NOx formation kinetic mechanisms (including N2O as a minor species) are available:

   1. GRIMech3.0 Developed for trace species prediction from CH4 combustion by UCB for Gas Research Institute. Many validation studies for lean, rich, and reburning conditions. Contains N$_2$O kinetics embedded within.

   2. REI97 Developed by REI with emphasis on post flame selective non-catalytic destruction of NO in flue gases.

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Objectives of this work

- Completed work discussed here
  - » Phase I: Investigate key reaction mechanisms and parameters of N_2O destruction and NO_x formation.

- Future work
  - » Phase II: mechanism validation and parametric study to determine optimized reaction conditions to reduce NO_x formation
  - » Phase III: Extension of work to more complex reaction conditions and/or other species

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Summary- Phase 1

- Selected GRIMech 3.0 for the kinetic mechanism/thermodynamic data base to use in this project. Mechanism contains
    - » total of 53 species and 325 reaction steps overall
    - » 9 reaction steps for N_2O production/destruction
    - » 46 reaction steps for NO_x production/destruction
    - » N_2O can be converted to NO directly via three chemical pathways

- Performed chemical kinetics calculation to model the destruction of N_2O and corresponding formation of NO
    - » Findings from initial calculations indicate that NO_x production is increased by:
        - – Higher reaction temperatures
        - – Fuel lean reaction environments
        - – Premixing the N_2O and fuel in fuel lean conditions
    - » Results imply staged combustion (staged air injection) can reduce NOx

- To highlight the modeling capability, a chemical kinetic based model of a simplified practical system was performed using available tools and information

- With proper kinetics data, model can be extended to evaluate DRE of other species (i.e., Phase III)

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Kinetic modeling results
Focus on conversion of N_2O to NO

- Calculations were performed in a simple system consisting of an isothermal plug flow reactor (PFR)

- N_2O destruction and NO formation was calculated for the following conditions:
  - » 3 Temperatures
    - 1700K, 2000K, 2200K
  - » 2 Stoichiometries
    - Fuel rich (SR = 0.7)
    - Fuel lean (SR = 1.1)
  - » 2 N_2O Injection schemes
    - Premixed with fuel
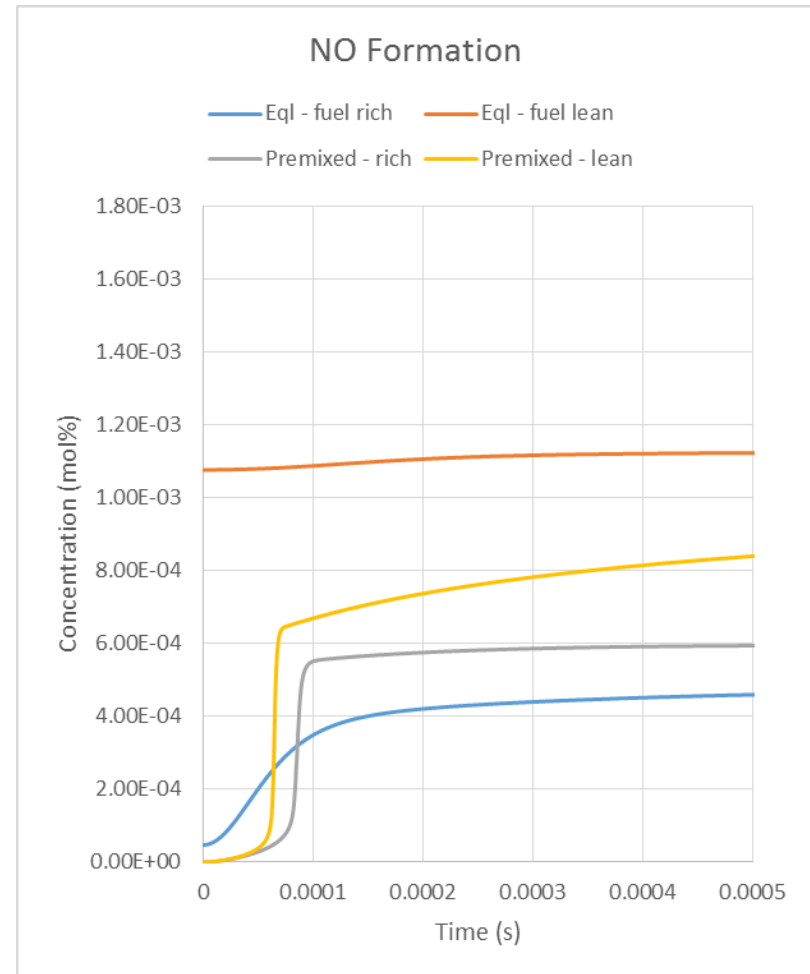   - Injected into flame

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Kinetic Calculations for N_2O to NO

- N_2O destruction was very rapid for all conditions
  - » Complete destruction on the order of a millisecond

N2O Destruction

Eql - fuel rich — Eql - fuel lean — Premixed - rich — Premixed - lean
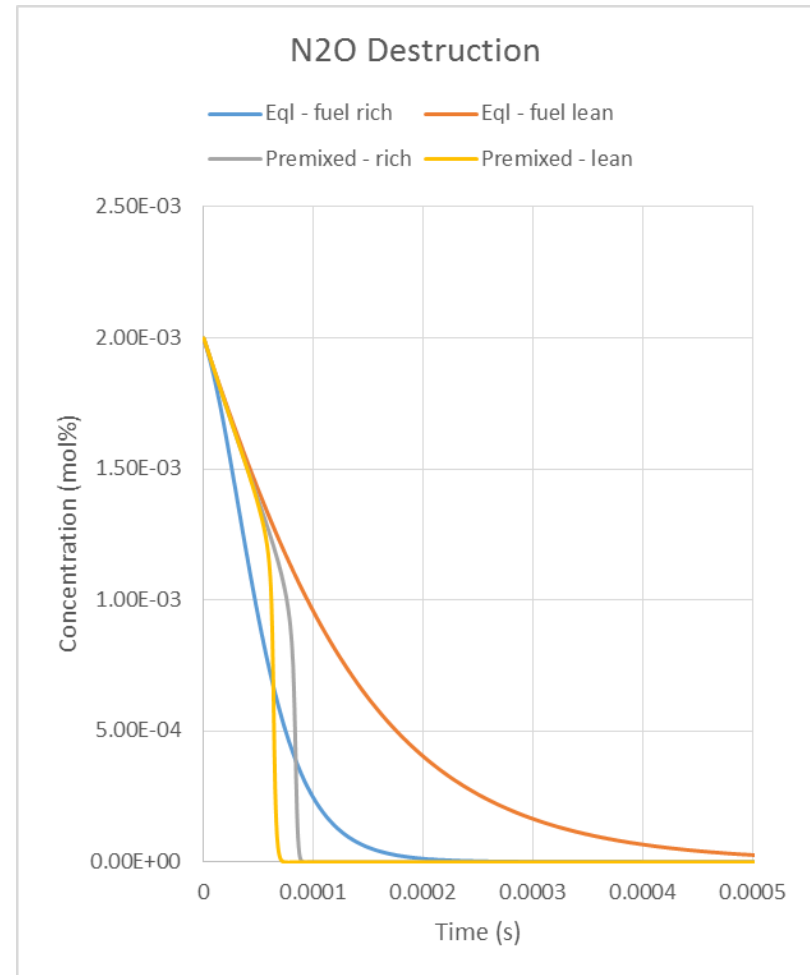
Kinetic Calculations for N₂O to NO – NOₓ Formation

- NOₓ formation results showed trends consistent with results found in the literature:

  » Fuel lean conditions → increased NOₓ production
  » Higher temperatures → increased NOₓ production
  » Premixing the N₂O and fuel → increased NOₓ production in fuel lean conditions

NO Formation

— Eql - fuel rich   — Eql - fuel lean
— Premixed - rich   — Premixed - lean

Y-axis: Concentration (mol%) — 0.00E+00, 2.00E-04, 4.00E-04, 6.00E-04, 8.00E-04, 1.00E-03, 1.20E-03, 1.40E-03, 1.60E-03, 1.80E-03

X-axis: Time (s) — 0, 0.0001, 0.0002, 0.0003, 0.0004, 0.0005

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N$_2$O Pathway Sensitivity Study – Individual Reactions

- 1 – $N_2O + OH \leftrightarrow N_2 + HO_2$

- 2 – $N_2O + O \leftrightarrow 2\ NO$

- 3 – $N_2O + M \Rightarrow N_2 + M + O$

- 4 – $N_2O + H \Rightarrow N_2 + OH$

- 5 – $N_2O + OH \leftrightarrow N_2 + HO_2$

- 6 – $CN + N_2O \leftrightarrow NCO + NO$

- 7 – $NCO + NO \leftrightarrow N_2O + CO$

- 8 – $NH + NO \Leftarrow N_2O + H$

- 9 – $NNH + O \leftrightarrow N_2O + H$

Reactions #3 and #4 appear to be suppressing NO production. Reaction #8 appears to be a very important pathway for NO production.
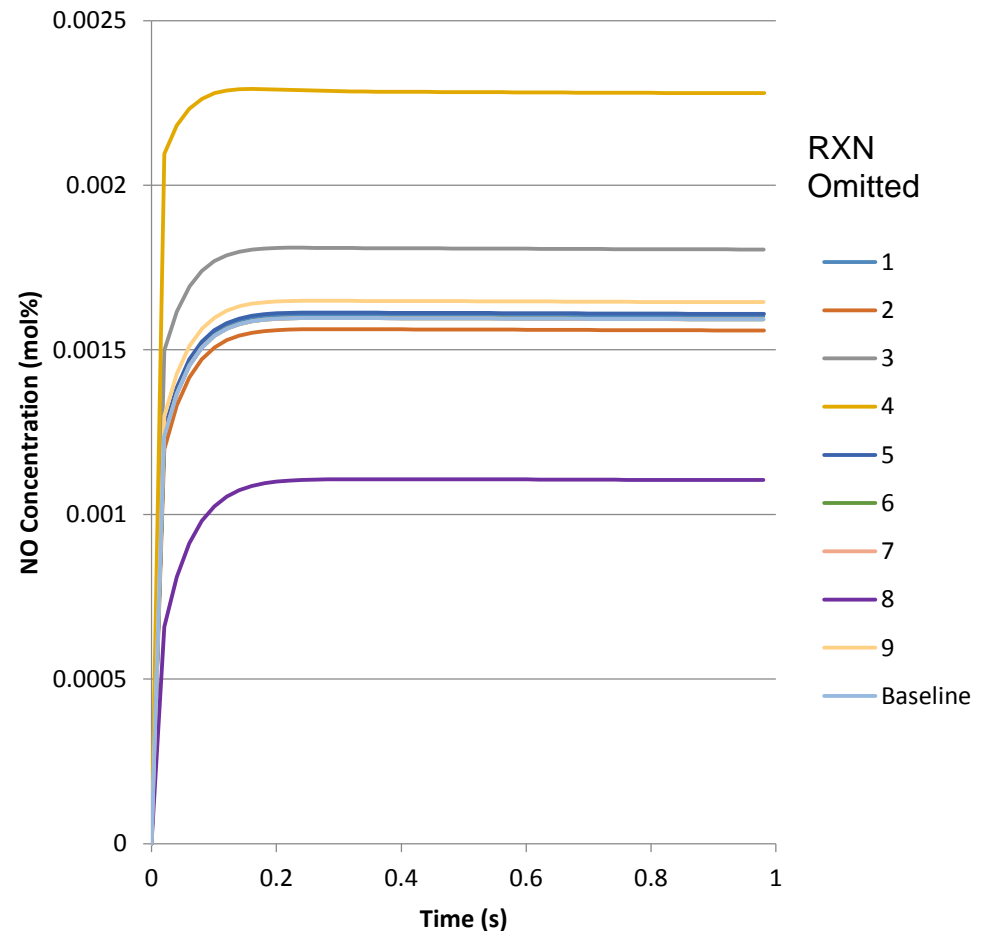
SR = 1.1   T = 2200K

To isolate NO formed from N_2O from that formed from N_2 in the air we explored N_2O Conversion in Argon/O_2 mixtures.

- Reactions were calculated for methane flame in lean O_2/Ar mixture
  - » N_2O only source of N, can determine amount of $N_2O \rightarrow$ NOx

- Results for fuel lean conditions showed that >80% of the N_2O reacted to become N_2, remainder became NO_x
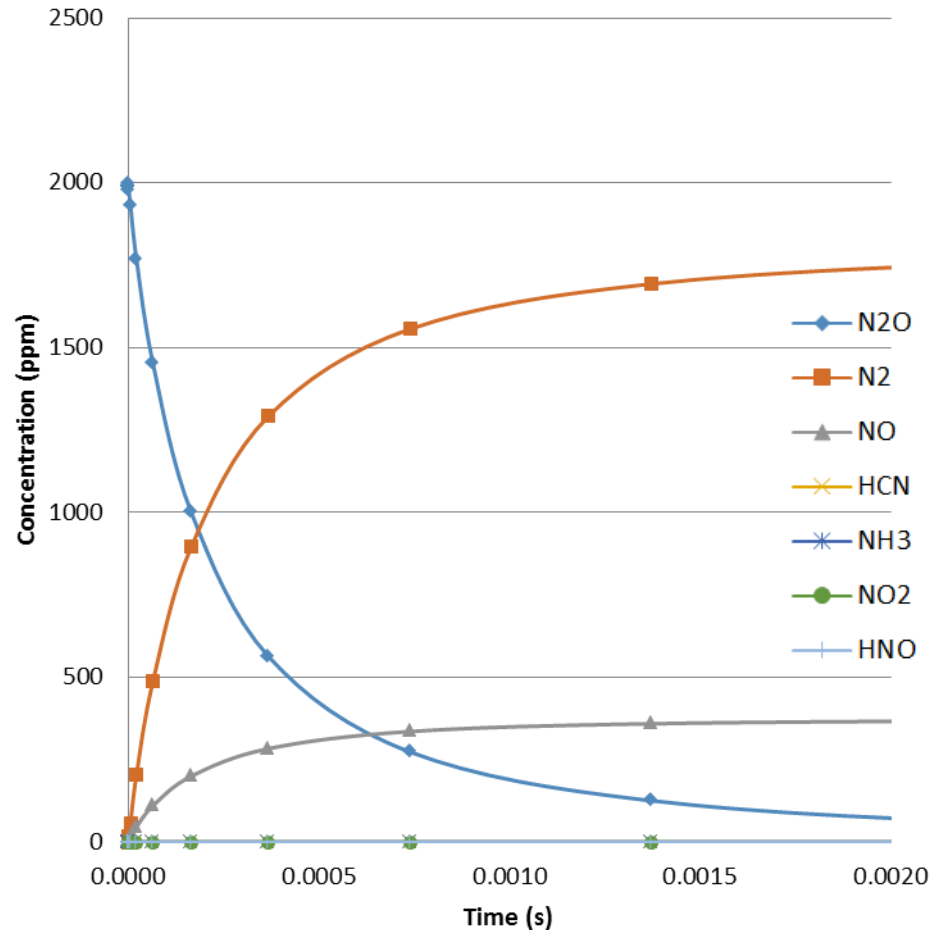
SR = 1.1, T = 1700K

N$_2$O Conversion Findings

- GRIMech 3.0 can be used to model the destruction of N$_2$O and the formation of NO$_x$

- Results follow trends identified in literature:
  - » NO$_x$ production is increased by:
    - Higher reaction temperatures
    - Fuel lean reaction environments
    - Premixing the N$_2$O with the fuel

- Majority of N$_2$O is converted to N$_2$
  - » N$_2$ production much higher for fuel rich conditions

- Possible methods of minimizing NO$_x$ production include temperature control, air staging, and injecting N$_2$O into the flame region (not premixed with fuel)

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We can explore how complex mixing can affect the kinetic results.
Specific example: application to Edwards Thermal Destruction Reactor

- The kinetic model can be applied to simulate possible complex thermal reactor conditions by coupling several simple reactors together.

- This model explored here was based on a specific thermal processing unit
  - » Temperatures and residence times based on information forwarded from Edwards

- The reactor was broken down into a series of smaller reaction zones
  - » Major mixing events were included as separate reaction zones
  - » Reactor was broken into several reaction zones to better approximate combustion products passing into the reactor

- Calculations were performed using Modlink, REI proprietary process flowsheet/kinetics software using GRIMech 3.0

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Process Model

PFR A – models the reactions during mixing of waste stream and O2 in the inlet tube

PFR B→D – represents the reactor, split into three zones to better represent NG and air products feeding in down the length of the reactor

PFR E – natural gas and air combustion reaction occurring in the ceramic annulus

Streams

1 – O_2 and waste (3.4% N_2O and CH_4) at SR = 0.7
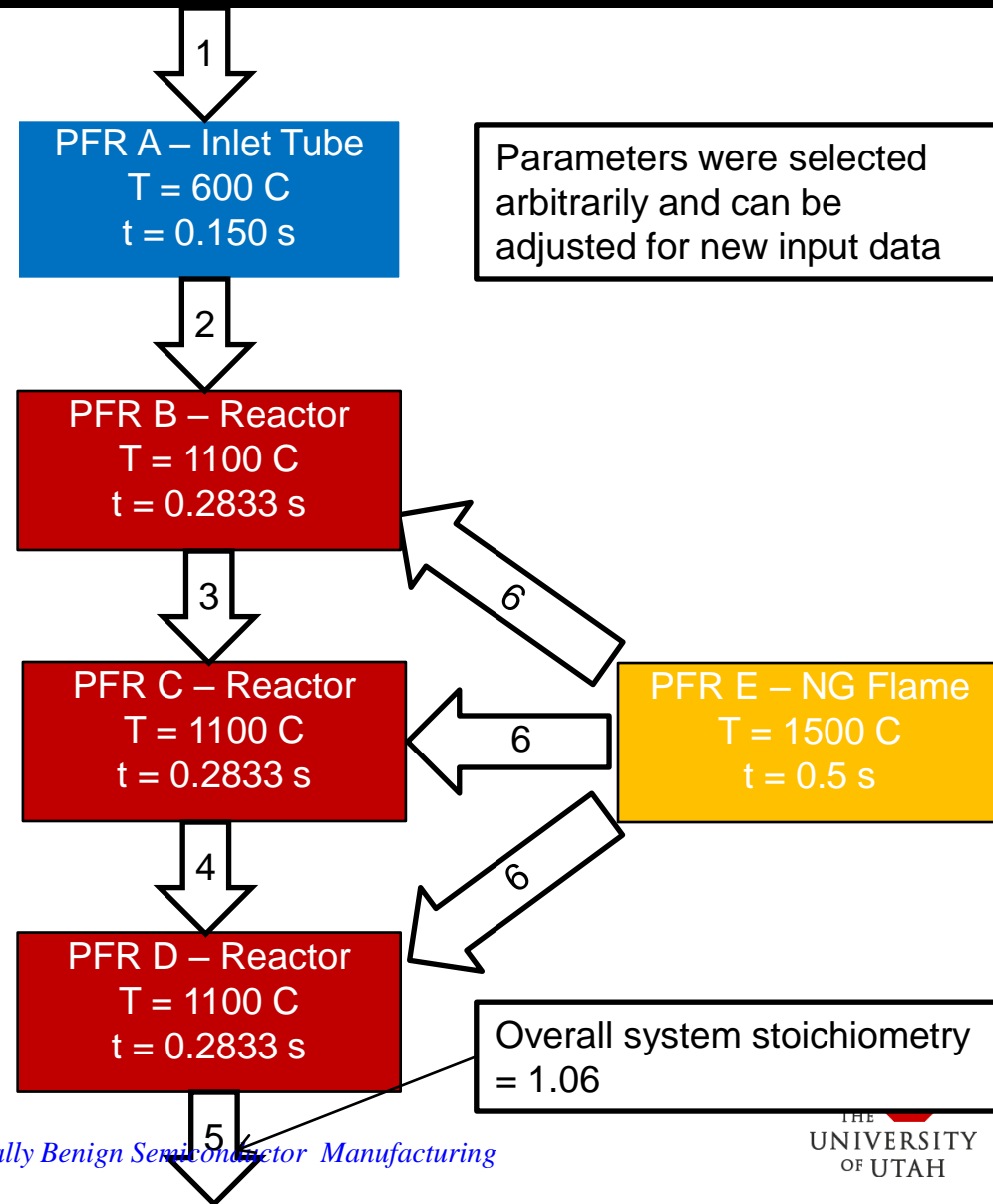
2 – O_2 and waste

3 → 5 - products of previous reactor

6 – products of NG and air combustion at SR = 1.1

Results (depend on input data)

NO at exit ~ 74ppm

N_2O at exit < 1ppm

1

PFR A – Inlet Tube
T = 600 C
t = 0.150 s

2

PFR B – Reactor
T = 1100 C
t = 0.2833 s

3

PFR C – Reactor
T = 1100 C
t = 0.2833 s

4

PFR D – Reactor
T = 1100 C
t = 0.2833 s

5

Parameters were selected arbitrarily and can be adjusted for new input data

6

6

6

PFR E – NG Flame
T = 1500 C
t = 0.5 s

Overall system stoichiometry = 1.06

Conclusions

- The UU/REI team has the capability and expertise to model the complex chemical kinetics involved in N_2O abatement reactors.

- Modeling has identified parameters that could potentially be exploited to reduce NO_x formation in the reactor
  - » Temperature control, air staging, waste stream injection scheme
  - » Other potential methods of NO_x control may become apparent with additional analysis.

- With proper kinetics and thermodynamics data, the model can be extended to other pollutant species involving Cl, F, Si, or PFC's.
  - » Appreciable information on H-C/CL and H-C/Br mechanisms is available. Theoretical techniques will be necessary to extrapolate to F reactions.

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Future work

- Task 1. Mechanism validation.
    - » Conduct an in-depth literature survey to identify available data sets on N2O destruction in simple flames. Purpose is to validate kinetic mechanisms without complicated mixing effects. Review paper by Kramlich and Linak (1996)
    - » comprises a good starting point.
    - » If such data do not exist, suggest appropriate validation experiments to be conducted by interested research organizations in the Sematech Team.

- Task 2: Configuration optimization for N_2O destruction and NO minimization.
    - » Explore effects of
        - – Peak temperature
        - – Temperature quench rate
        - – Stoichiometry
        - – Input N_2O level
        - – Staged combustion configurations
    - » Determine optimum combination of variables to allow destruction of NO with minimal NO formation.

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Future work (continued)

- Task 3: Explore effects of fluorine compounds in the fuel on N_2O destruction and NO formation.
    - » Use *simplified mechanisms* that focus on interactions between F, HF, F_2 and the free radicals O, OH, and H that are known to have a first order influence on NO formation.
    - » Rates for reactions involving Fluorine will be gleaned from the literature, or estimated using crude correlations (as opposed to *ab-initio* quantum mechanical calculations)
    - » Objective shall be to determine whether F chemistry is likely to have a first order adverse effect on N_2O/NO chemistry, and whether more sophisticated modeling is likely to be needed.

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