Migrating CHEMKIN Applications to the MATLAB/SIMULINK Environment for Simulating NO_x Conversion in a TWCC

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Outline

- Brief review of CHEMKIN and CHEMKIN applications
- Migrating to MATLAB/SIMULINK
- Model Problem chosen from literature
- SIMULINK demonstration
- Conclude

Brief Review Of CHEMKIN

- **A collection of subroutines designed to facilitate the solution of problems involving chemically reacting flow systems**
  - **Developed by Sandia National Laboratories**
  - **General-purpose, problem-independent algorithms to manage computation and provide information**

    Species (composition, concentration, charge, site occupancy, etc.)

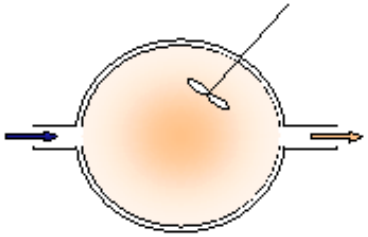
    Reactions (kinetic parameters, stoichiometric coefficients, etc.)

    Chemical production rates, thermodynamic properties, other utilities
  - **Gas-phase reaction mechanisms (CHEMKIN)**
  - **Surface reaction mechanisms (SURFACE CHEMKIN)**

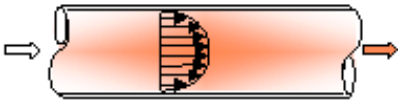
- **Includes a suite of application 0-, 1-, and 2-D applications codes**

- **Currently distributed commercially by** RD REACTION DESIGN

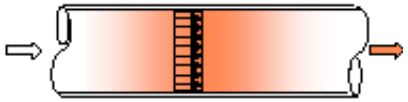
Application Codes Included In The RD Distribution



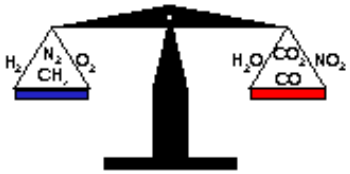
Stirred Tank



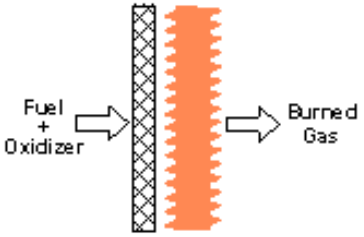
Boundary-Layer



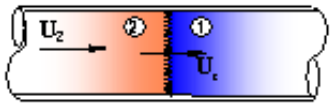
Plug Flow



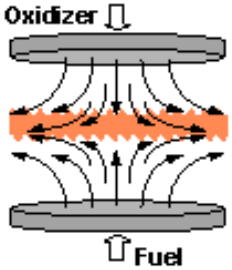
Equilibrium



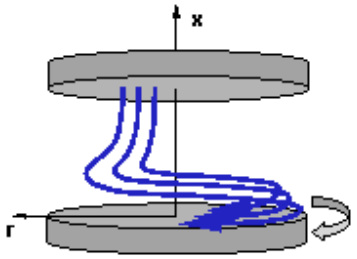
Premixed Flame



Shock Tube



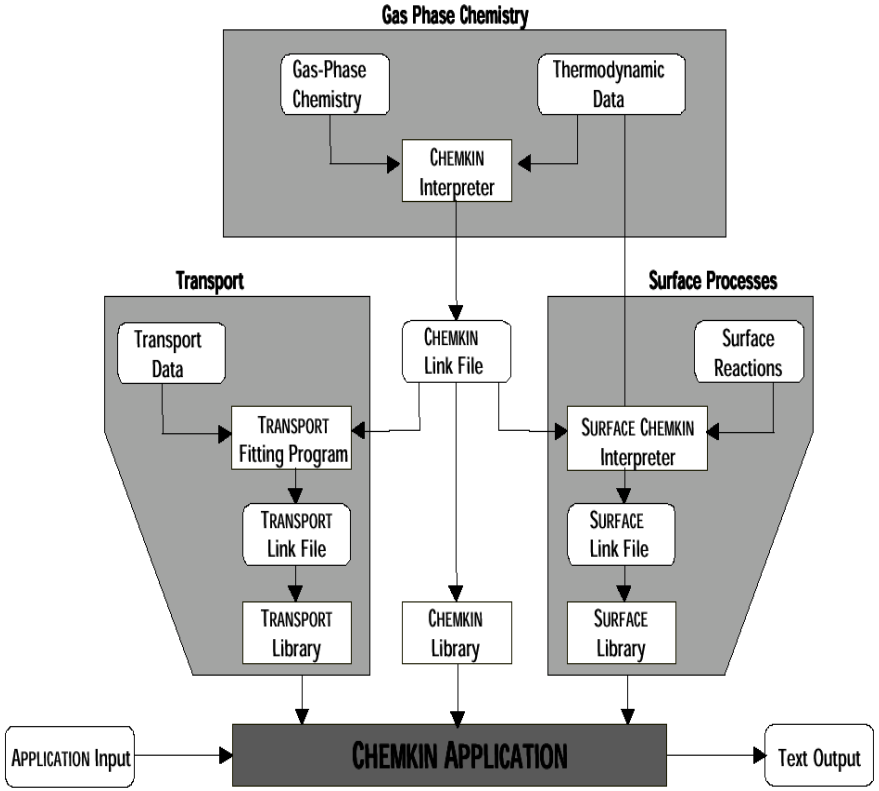
Opposed Diffusion



Rotating Disk

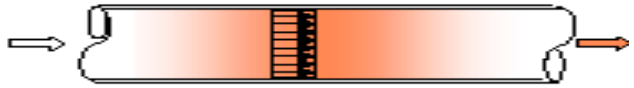
Program Structure

- Gas-phase chemistry, surface chemistry, and transport libraries compiled with application code
- Input files specify gas, surface, and transport processes
  - Databases and reaction mechanisms
  - Interpreters generate linking files that communicate with application code
- Subroutine calls to CHEMKIN libraries simplify program structure



Plug Flow Model Of TWCC

Number of square cells	62,000	m^{-2}
Reactor length	0.09	m
Length/diameter ratio	1	—
Wall thickness	180	µm
Washcoat thickness	39	µm
Converter void fraction	0.69	—
Space velocity	14	s^{-1}
Nusselt number	2.98	—
Sherwood number	2.98	—
Catalytic surface area	1.4×10^4	$m^2_{\text{Noble Metal}}\, m^{-3}_{\text{reactor}}$
Total surface sites concentration	2.7×10^{-5}	$\text{mol}\, m^{-2}_{\text{Noble Metal}}$

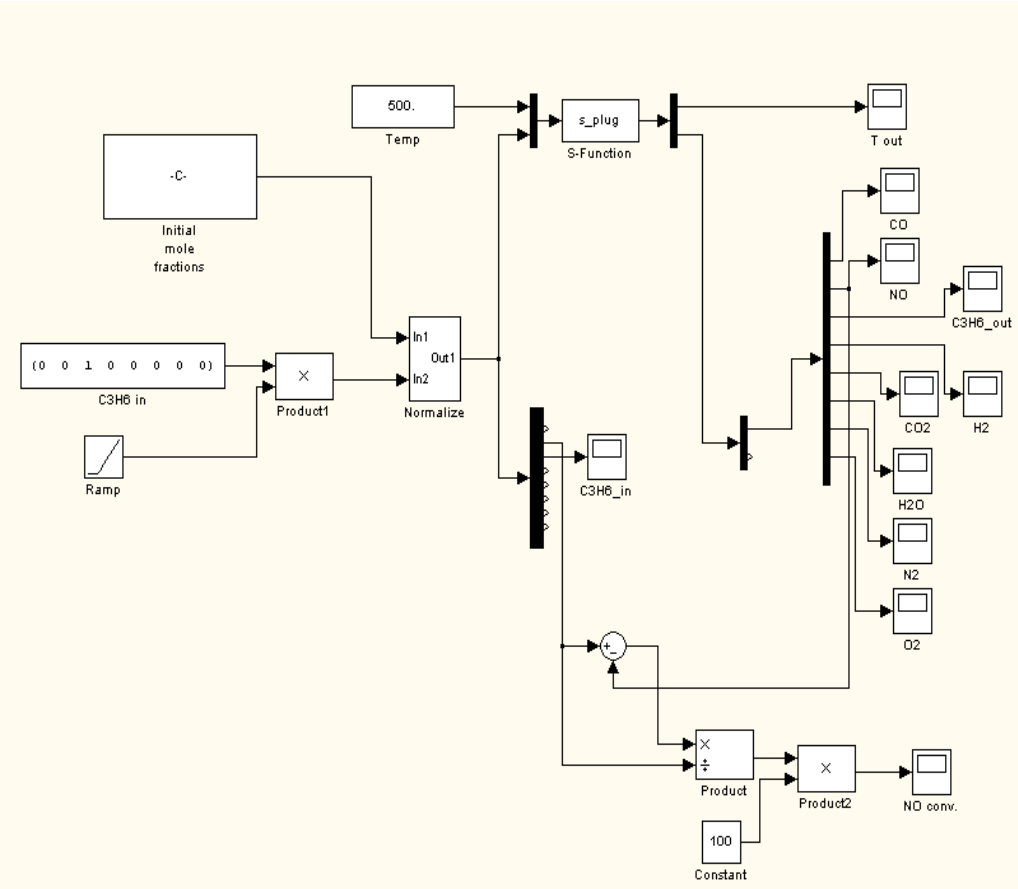


Inlet Gas	%Vol.
CO	1.40
O_2	1.69
NO	0.11
C_3H_6	---
H_2	0.47
H_2O	10.00
CO_2	14.00
N_2	72.27

- **Non-dispersive, one-dimensional, reacting flow in conduit of arbitrary geometry**
  - **Differential/algebraic equations solved implicitly using DASSL**
  - **Optional external energy transfer using overall heat transfer coefficient**
- **Example problem taken from J.H.B.J. Hoebink et al., Chemical Engineering Sciences, 55 (2000) pg 1573-1581**

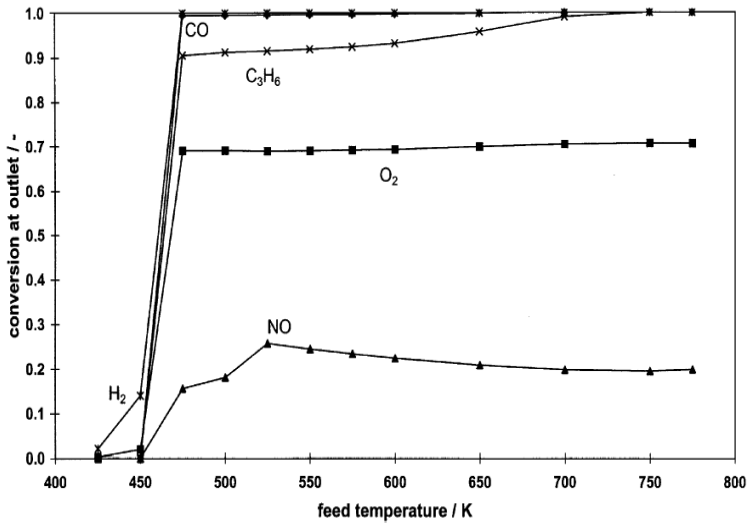
SIMULINK Model

- Routine gradually increases C_3H_6 concentration
  - NO_x conversion
  - O_2 conversion
  - Exit temperature
- CHEMKIN PLUG interfaced through s-function
  - Brute force
  - Limited flexibility
- More elegant approaches possible
  - Use SIMULINK solvers
  - Recast CHEMKIN routines as SIMULINK library modules



Model Chemistry From Hoebink et al.

- **Mechanism and rate parameters taken from various literature sources**
  - **Combination of elementary and global reactions**
- **Predict light-off behavior in laboratory systems**



$$\mathrm{CO} + * \overset{k_{a,\mathrm{CO}}}{\underset{k_{d,\mathrm{CO}}}{\rightleftharpoons}} \mathrm{CO}*$$

$$\mathrm{O_2} + 2* \overset{k_{a,\mathrm{O2}}}{\underset{k_{d,\mathrm{O2}}}{\rightleftharpoons}} 2\mathrm{O}*$$

$$\mathrm{NO} + * \overset{k_{a,\mathrm{CO}}}{\underset{k_{d,\mathrm{CO}}}{\rightleftharpoons}} \mathrm{NO}*$$

$$\mathrm{C_3H_6} + 3* \overset{k_{a,\mathrm{C_3H_6}}}{\underset{k_{d,\mathrm{C_3H_6}}}{\rightleftharpoons}} \mathrm{C_3H_6}***$$

$$\mathrm{H_2} + 2* \overset{k_{a,\mathrm{H_2}}}{\underset{k_{d,\mathrm{H2}}}{\rightleftharpoons}} 2\mathrm{H}*$$

$$\mathrm{NO}* + * \xrightarrow{k_{\mathrm{dias}}} \mathrm{N}* + \mathrm{O}*$$

$$\mathrm{CO}* + \mathrm{O}* \xrightarrow{k_{\mathrm{CO_2}}} \mathrm{CO_2} + 2*$$

$$\mathrm{NO}* + \mathrm{N}* \xrightarrow{k_{\mathrm{N2,1}}} \mathrm{N_2} + \mathrm{O}* + *$$

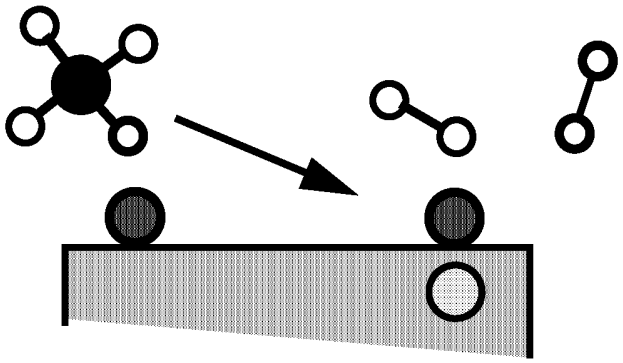
$$2\mathrm{N}* \xrightarrow{k_{\mathrm{N2,1}}} \mathrm{N_2} + 2*$$

$$\mathrm{C_3H_6}*** + 6\mathrm{O}* \xrightarrow{k_{\mathrm{H20,1}}} 3\mathrm{CO}* + 3\mathrm{H_2O} + 6*$$

$$2\mathrm{H}* + \mathrm{O}* \xrightarrow{k_{\mathrm{H20,2}}} \mathrm{H_2O} + 3*$$

Simple Conversion Of Model Chemistry To CHEMKIN Format

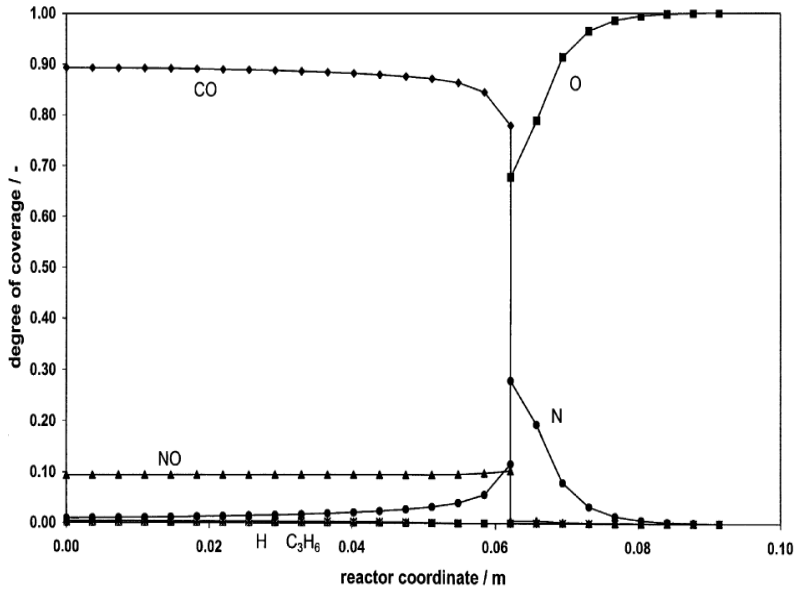
- **Symbolic representation of elements, species, and reactions (alphanumeric characters)**
- **No surface thermochemistry required**
  - **Forward and reverse rates specified**
- **Pre-exponential factors converted to (cm^2 mol^{-1} s^{-1}) using site density**

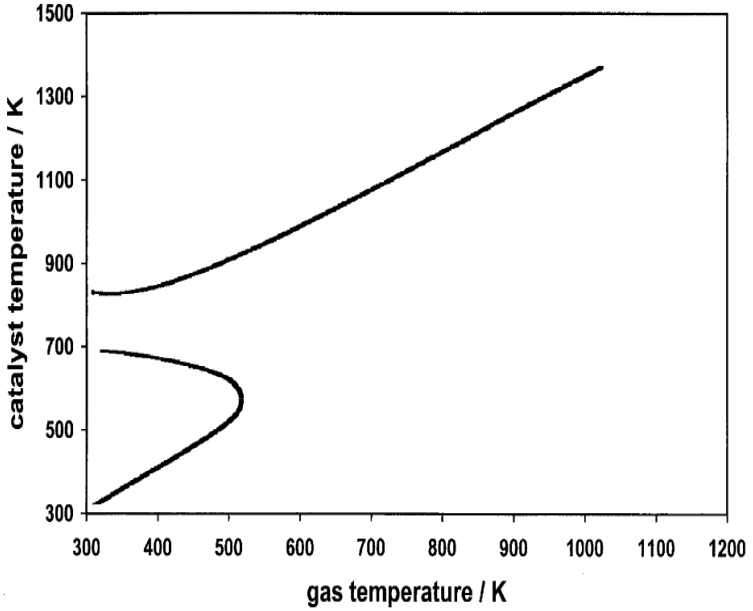


```
SURFACE REACTIONS CONSIDERED                          A        b        E

 1. CO+PT(s)=>CO(s)                                5.00E-01    0.0        0.0
    Forward order PT(s)    1.000E+00
    Coefficients are sticking parameters...
 2. CO(s)=>CO+PT(s)                                1.60E+14    0.0      112.0
 3. O2+2PT(s)=>O(s)+O(s)                           1.00E-02    0.0        0.0
    Forward order PT(s)    1.000E+00
    Coefficients are sticking parameters...
 4. O(s)+O(s)=>O2+2PT(s)                           1.85E+21    0.0      217.5
 5. NO+PT(s)=>NO(s)                                5.00E-01    0.0        0.0
    Forward order PT(s)    1.000E+00
    Coefficients are sticking parameters...
 6. NO(s)=>NO+PT(s)                                5.00E+13    0.0      108.7
 7. C3H6+3PT(s)=>C3H6(3s)                          3.50E-01    0.0        0.0
    Forward order PT(s)    1.000E+00
    Coefficients are sticking parameters...
 8. C3H6(3s)=>C3H6+3PT(s)                          1.00E+13    0.0       57.3
 9. H2+2PT(s)=>H(s)+H(s)                           4.60E-02    0.0        0.0
    Forward order PT(s)    1.000E+00
    Coefficients are sticking parameters...
10. H(s)+H(s)=>H2+2PT(s)                           3.70E+21    0.0       67.4
11. NO(s)+PT(s)=>N(s)+O(s)                         1.11E+19    0.0       79.4
12. CO(s)+O(s)=>CO2+2PT(s)                         3.70E+20    0.0       60.0
13. NO(s)+N(s)=>N2+O(s)+PT(s)                      7.41E+17    0.0       87.8
14. N(s)+N(s)=>N2+2PT(s)                           1.11E+19    0.0      120.0
15. C3H6(3s)+6O(s)=>3CO(s)+3H2O+6PT(s)             2.22E+22    0.0       62.7
    Forward order C3H6(3s)    1.000E+00
    Forward order O(s)    1.000E+00
16. 2H(s)+O(s)=>H2O+3PT(s)                         3.70E+21    0.0       17.4
    Forward order H(s)    1.000E+00
    Forward order O(s)    1.000E+00
```


Stiff System Of Differential Equations / Multiple Steady States



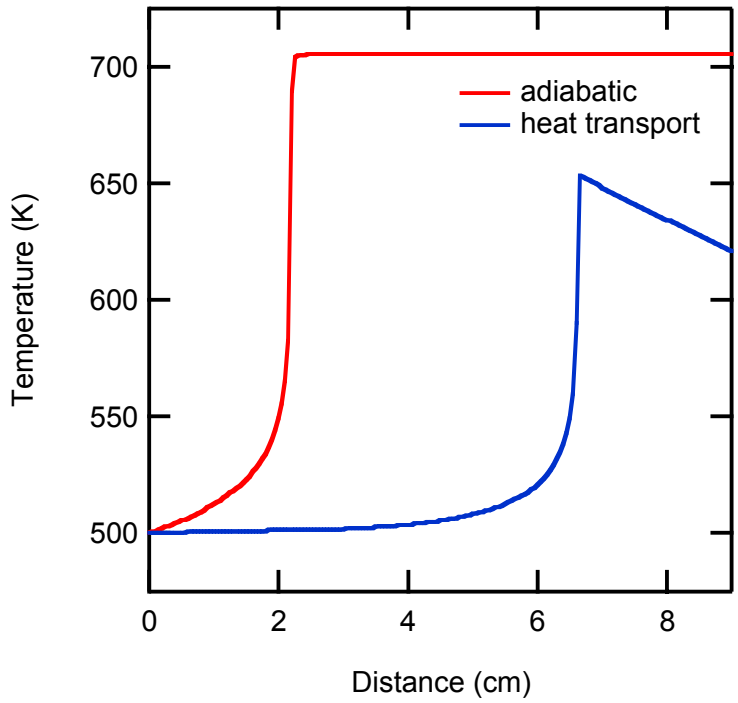


- **Solutions from Hoebink et al.**
  - **Abrupt light-off behavior, fast reactions, large heat release, multiple solutions**
- **Hoebink et al. had to stabilize their numerical integrator to solve problem**
  - **Analytical Jacobian, artificial washcoat temperature, continuation methods**

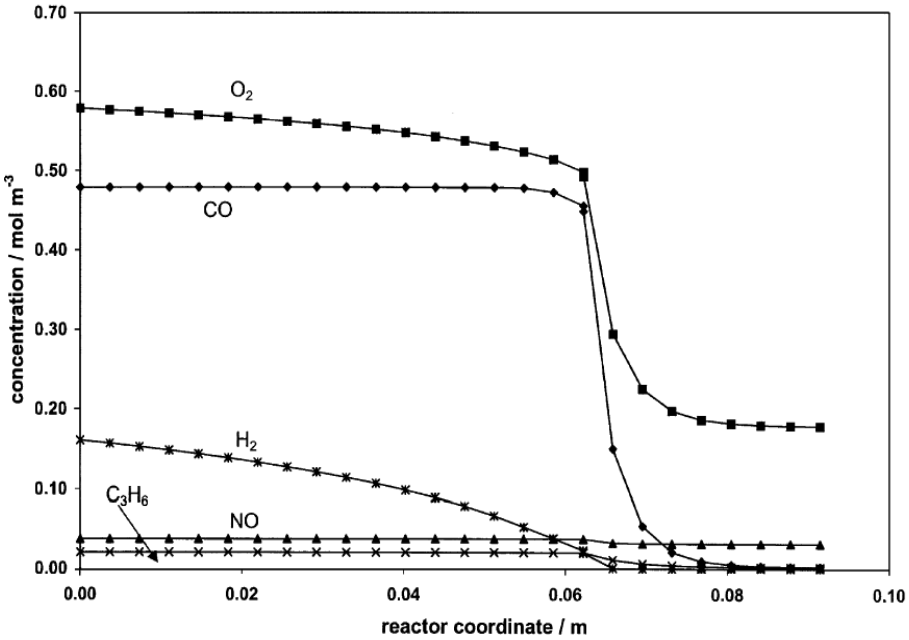
CHEMKIN / PLUG Solution

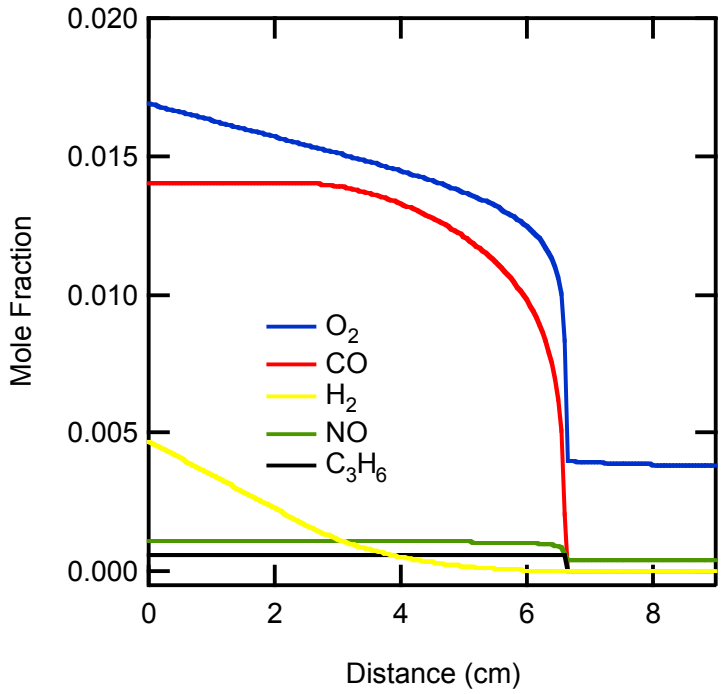
- **DASSL able to grind through light-off condition**
  - **No need to invoke methods used by Hoebink et al.**
- **Solution very sensitive to external heat transfer**
  - **Position of light-off tuned by heat transfer coefficient**

Inlet Gas	%Vol.
CO	1.40
O_2	1.69
NO	0.11
C_3H_6	0.06
H_2	0.47
H_2O	10.00
CO_2	14.00
N_2	72.27



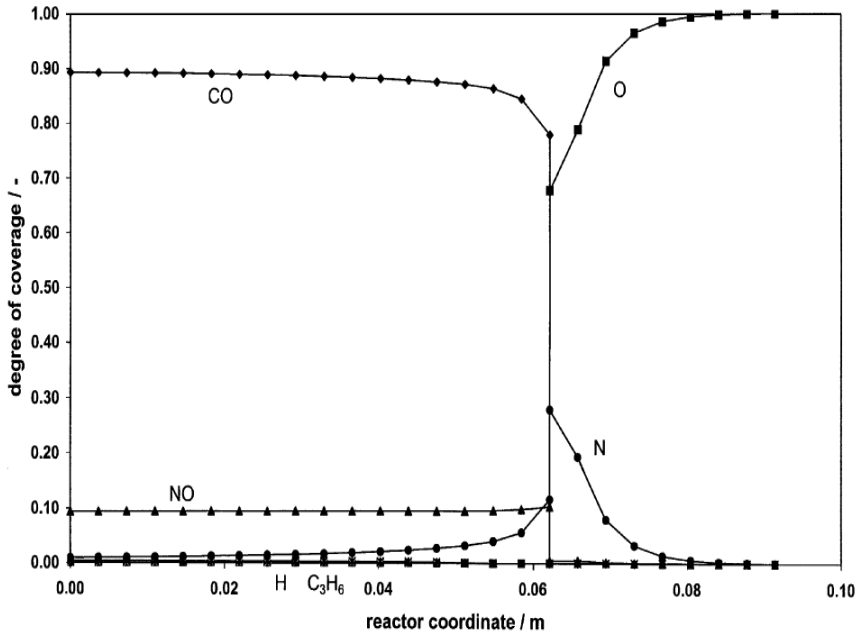
Compare PLUG Solution With Model Problem

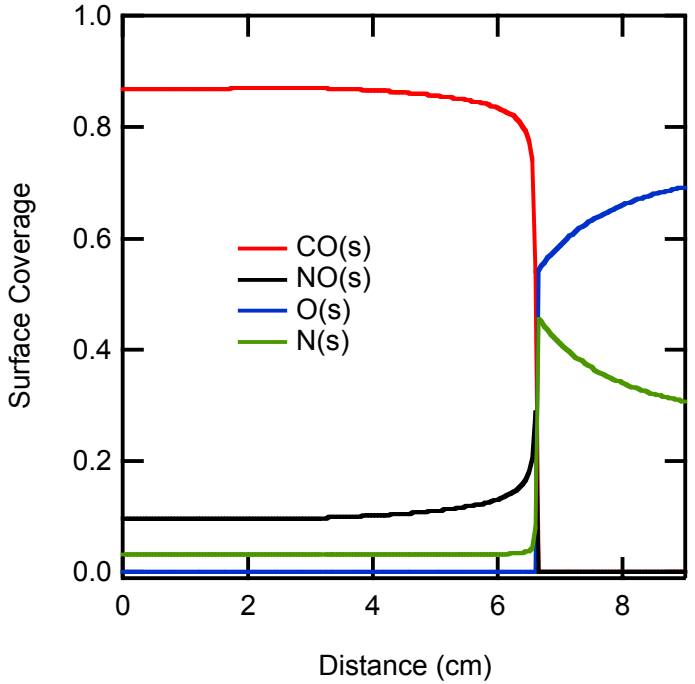




- **Species mole fractions subtlety different**
  - **Solution methods vary**
  - **Heat transfer term in energy balance not identical**

Compare PLUG Solution With Model Problem





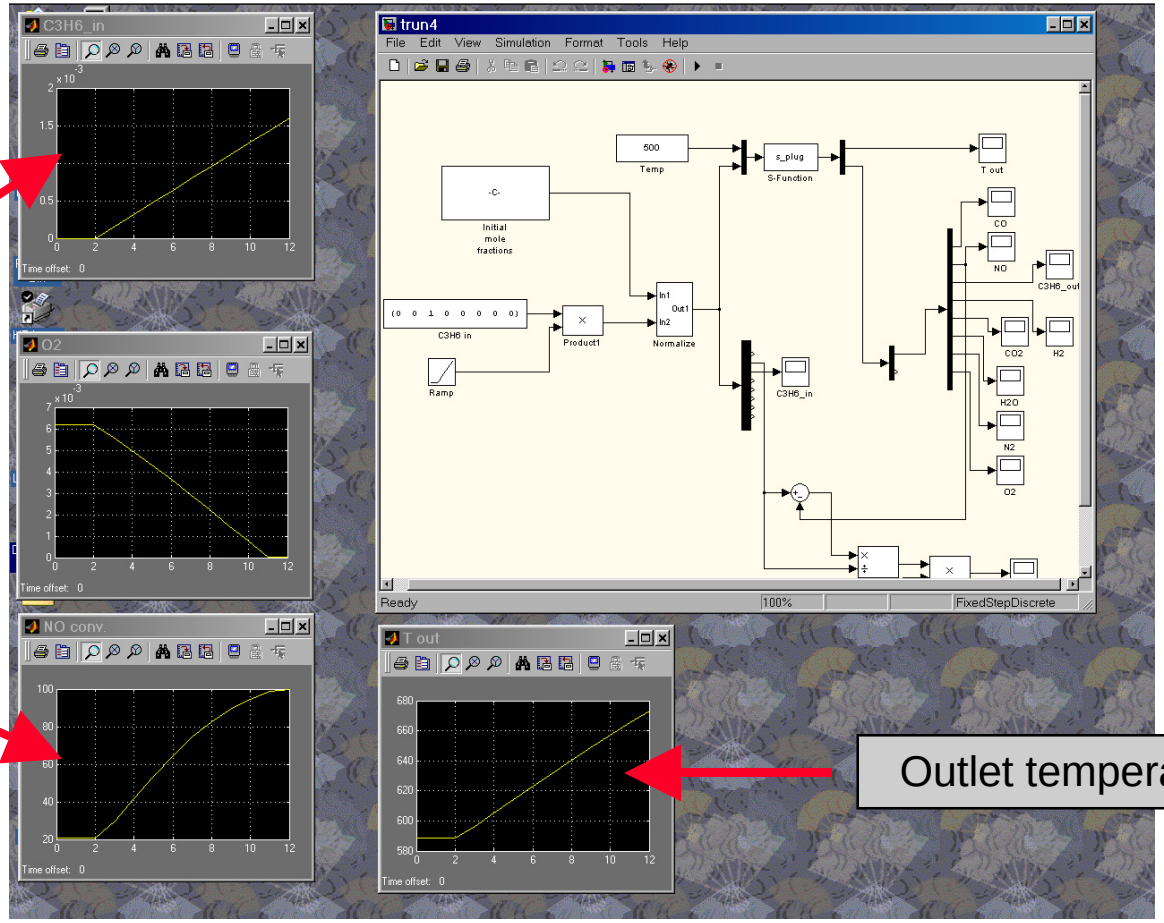
- **Abrupt change in surface coverage indicates light-off position**
  - **Create difficulty for numerical integrator**
- **Final temperature predicted by PLUG lower than model problem**
  - **Affects steady-state O(s) and N(s) coverage after light-off**

MATLAB/SIMULINK

DEMONSTRATION

Sandia National Laboratories
Combustion Research Facility

MATLAB/SIMULINK Output From Laptop Computer



C_3H_6 inlet

NO conversion

Outlet temperature

- **Total simulation time for 12 PLUG calculations less than 1 minute**
  - **Affect of a gradual ramp in the C_3H_6 inlet concentration at 500 K**

Development Of Simulation Tools

- **More efficient integrators for solving stiff problems**
  - **DASSL works in some cases, but still has trouble**
- **General, problem independent platforms**
  - **Handling kinetic and thermochemical information (CHEMKIN)**
  - **Standardize reactor models (include realistic treatment of transport)**
- **Advanced applications possible under CHEMKIN/SIMULINK environment**