Improved Catalysis for Fuel Cells, Fuel Reformation and Efficient Hydrogen Production. Task 4: Detailed Modeling of Methanol and Ethanol Catalytic Reaction

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Start Date = 9/30/04
Planned Completion =3/30/06

Research Goals and Objectives

- Develop codes for fully resolved 2-D gas-phase and surface kinetic models using Cantera and Matlab
- Implement methanol and ethanol steam reforming kinetics over copper based catalysts in these codes
- Comparison with experiments (Experiments run by David Hahn)
- Modify the kinetic models for more accurate predictions
- Extend work to similar problems, including catalytic combustion

Relevance to Current State-of-the-Art

- Very few models exist for the study of multi-dimensional reacting flows with both surface and gas phase reactions
- Application of computational methodology is not limited to reforming, but can also be applied to such important topics as catalytic combustion

Relevance to NASA

•Extension of this work into areas like catalytic combustion of hydrogen is important for the development of low NOx/low CO2 gas turbines

Budget, Schedule and Deliverables

Budget: $42,162 allocated/$63,514 requested

Original Schedule and Deliverables

- 1st Quarter: n/a
- 2nd Quarter: First cut at methanol kinetic mechanism.
- 3rd Quarter: Improved methanol mechanism and first cut at ethanol mechanism.
- 4th Quarter: Mechanistic model for ethanol oxidation as a function of model catalyst properties, kinetic model for ethanol oxidation under flow conditions.

Modified to refocus on catalytic combustion as NASA interest in reforming has waned. First three Quarters deliverables completed, except for extentionb to ethanol. Refocused on palladium model development as there is more interest in that area.

Anticipated Technology End Use

- Hydrogen production and development of new catalysts for hydrogen production
- Analysis of hydrogen production systems that use catalysts
- Eventual application in the analysis of catalytic combustion systems for power generation, especially for low NOx/low CO2 systems

Accomplishments and Results

- Wrote code for the analysis of reacting boundary layers using Cantera and Matlab
- Tested code with computations of hydrogen/air combustion on a platinum based catalyst using the Deutchmann model
- Partially completed development of a Cantera/Matlab code for the analysis of reacting inlet problems
- Implemented a **modified** Peppley model for reaction of methanol and water over a copper based catalyst and made initial comparisons with the experiments of Hahn for boundary layer flow
  - Original Peppley code was not suitable for detailed kinetic studies due to the deletion of important reaction pathways by removing **CH_2O** from the mechanism
  - H2 yield predictions are too low
  - Rapid change in rate of growth in hydrogen yield in the first centimeter

Accomplishments and Results - continued

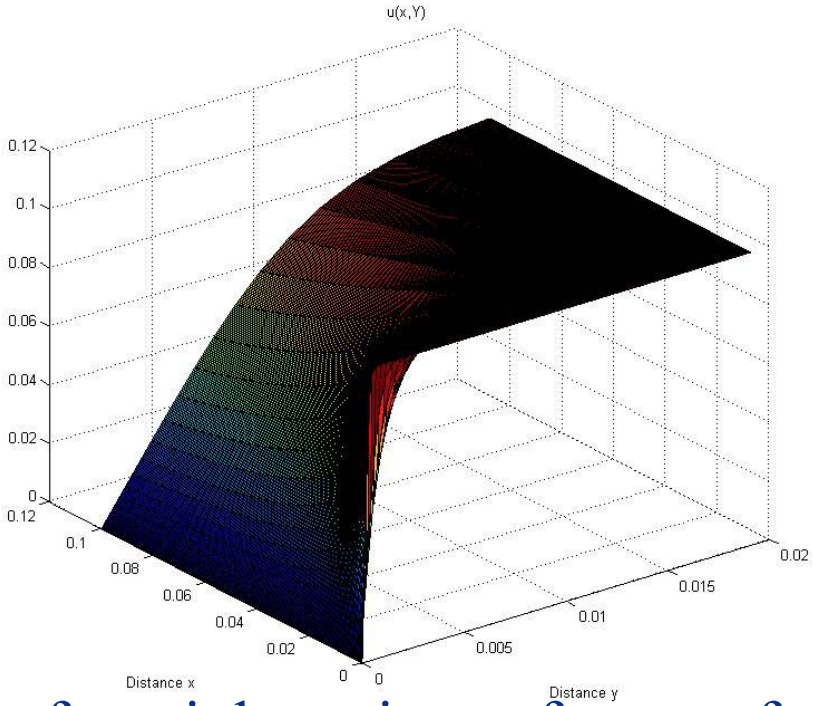
CH_2O Problem Resolution

CH_2O quickly reaches quasi-steady-state.

One can either put it in quasi-steady-state **OR** model its destruction with a rapid reaction. We chose the later, but with the difficulty that it adds additional stiffness to the computational problem.

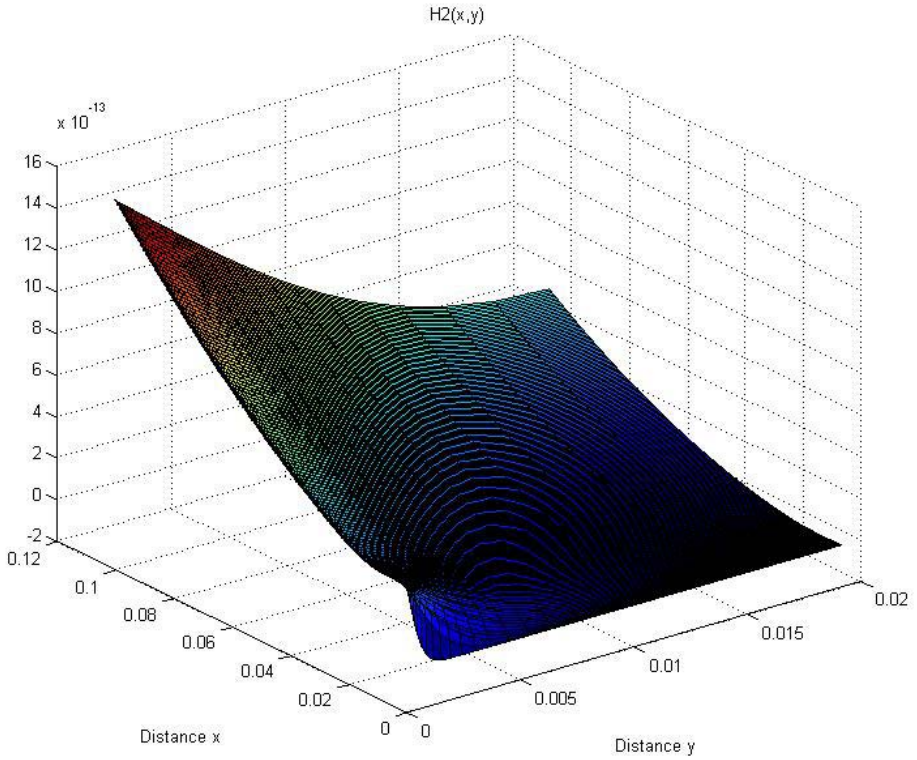
Accomplishments and Results - continued

Axial velocity field for the developing, reacting boundary layer



u in m/s – x in cm from inlet, y in cm from surface – stoichiometric methanol/water, u_{inlet} = 0.1 m/s, T_{inlet} = 500 K, P = 1 atm example

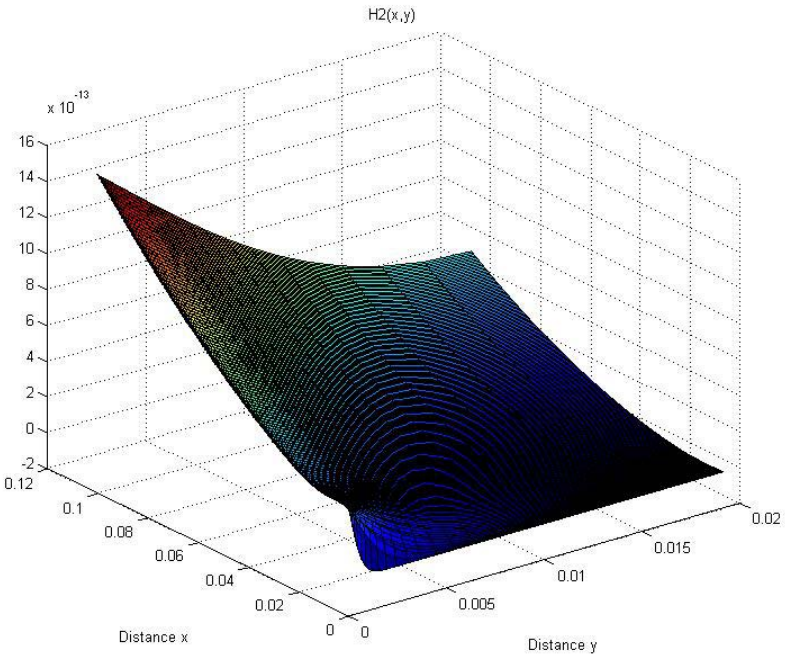
Accomplishments and Results - continued

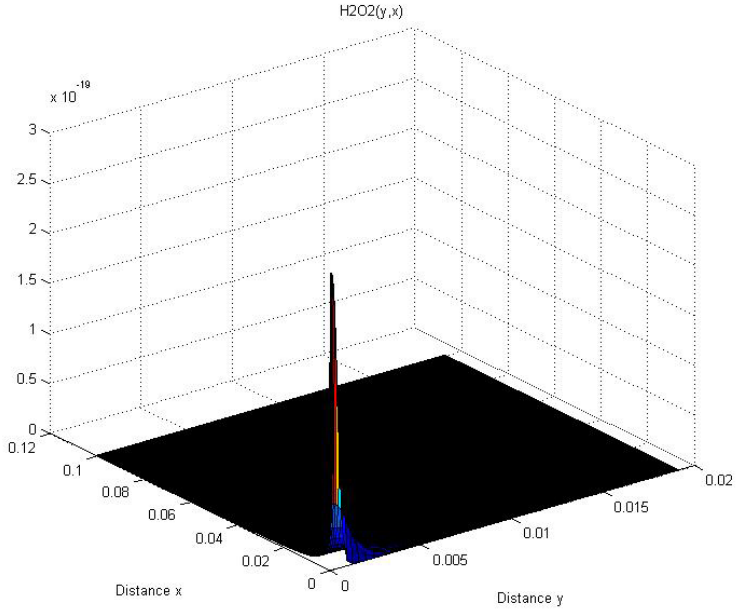


Predicted mass fraction of H2 example– x in cm from inlet, y in cm from surface – stoichiometric, Vinlet = 0.1 m/s, Tinlet = 500 K, P = 1 atm

Accomplishments and Results - continued

- Change in growth rate of H2 in the first centimeter is explained.





REASON: A low temperature chain branching with hydrogen peroxide intermediate is active in the gas phase initially. The surface adsorbs H radicals and terminates the chain branching mechanism

Accomplishments and Results - continued

- Change in growth rate of H2 in the first centimeter is explained - continued.

This detail found near the inlet could not be detected by using a 1-D analysis

Accomplishments and Results - continued

Proposed H2/O2 surface mechanism on a palladium catalyst

Hydrogen/Oxygen Only:

OH(S) + OH(S) <=> H2O + PD(S) + O(S)

O2 + 2 PD(S) => 2 O(S)

2 O(S) => O2 + 2 PD(S)

CO + PD(S) => CO(S)

H2 + 2 PD(S) => 2 H(S)

H2 + O(S) + PD(S) => OH(S) + H(S)

2 H(S) => H2 + 2 PD(S)

H(S) + O(S) <=> OH(S) + PD(S)

Accomplishments and Results - continued

Proposed additional surface mechanism on a palladium catalyst for methane/carbon monoxide chemistry

CH4 + O(S) + PD(S) => CH3(S) + OH(S)
CH3(S) + O(S) => CH2(S)s + OH(S)
CH2(S)s + O(S) => CH(S) + OH(S)
CH(S) + O(S) => C(S) + OH(S)
C(S) + O(S) => CO(S) + PD(S)
CO(S) + O(S) => CO2(S) + PD(S)
CO(S) => CO + PD(S)
CO2(S) => CO2 + PD(S)

Future Plans

- Complete modifications to Peppley model to improve agreement with experiments of Hahn and write paper
- Complete development of gas phase/surface reaction model for inlet flows and write paper
- Continue new work in the development of kinetic models for the catalytic combustion of hydrogen on palladium based catalysts – extend work to C1 chemistry for catalytic combustion of methane and syngas
- Implement the palladium based kinetic models and analyze multidimensional problems
- Continue collaborations started with this project