

Using CHEMKIN to Study Heterogeneous/Homogeneous Combustion Systems



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Outline

■ Heterogeneous/Homogeneous Reactions



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- Wall Effects of Laminar and Steady H₂ and CH₄ in a Shear Layer Flow
- Reduction of Fuel-NO_x in a Hybrid Combustor with Low Heating Value Fuel
- J. Andrae, PhD Thesis, KTH, Stockholm, 2002

Outline

■ Heterogeneous Reactions

- Development of H₂/O₂ Oxidation Mechanism on Pd at High Temperatures and Low Pressures (1300 K, 13 Pa, 100 SCCM)
- Ignition of Simulated Gasified Biomass on Platinum in a High-pressure System (p=0.5-1.6 MPa)
- Global Kinetic Model for Catalytic Combustion of CH₄/Air Mixtures over Alumina-supported Palladium Catalysts



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Heterogeneous/Homogeneous Reactions



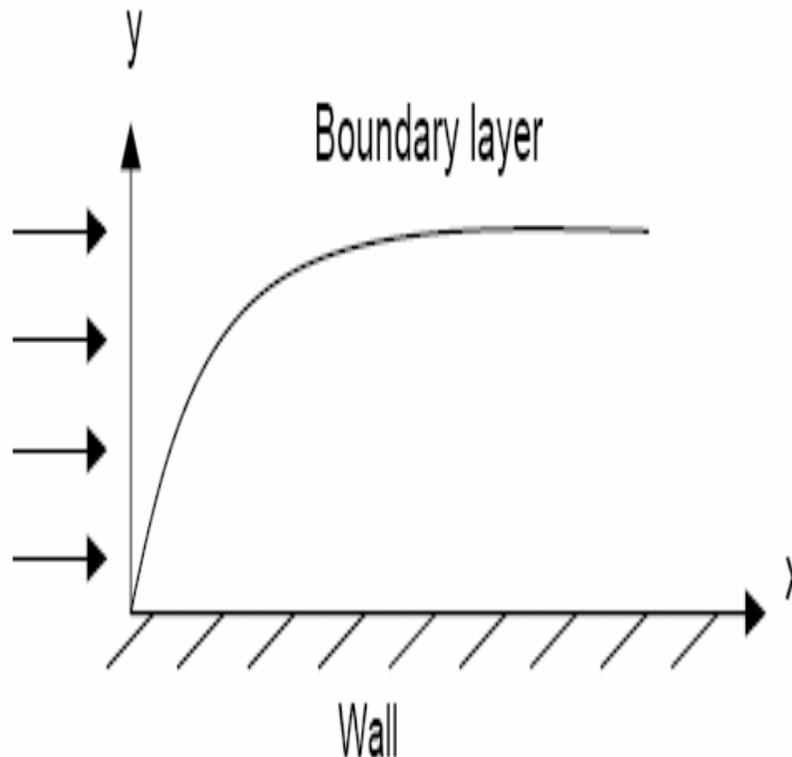
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- Wall Effects of Laminar and Steady H₂ and CH₄ Flames in a Shear Layer Flow
- Reduction of Fuel-NO_x in a Hybrid Combustor with Low Heating Value Fuel

Wall Effects of Laminar and Steady H₂ and CH₄ Flames in a Shear Layer Flow



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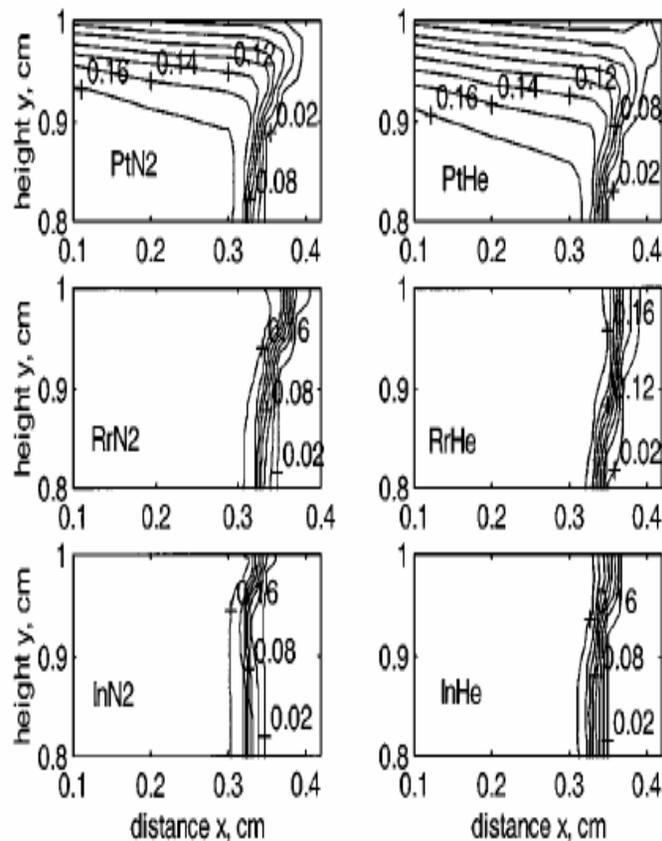
- CRESLAF code (Chemkin Release 3.x).
- Effect of surface chemistry investigated by changing wall boundary conditions.
- Effect of mass transfer investigated by changing carrier gas from N₂ to Helium.

Contours of Near-wall Fuel Concentration for Different Wall Boundary Conditions, $\phi = 0.5$



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Andrae and
Björnbom,
AIChE J. 46, 2000.



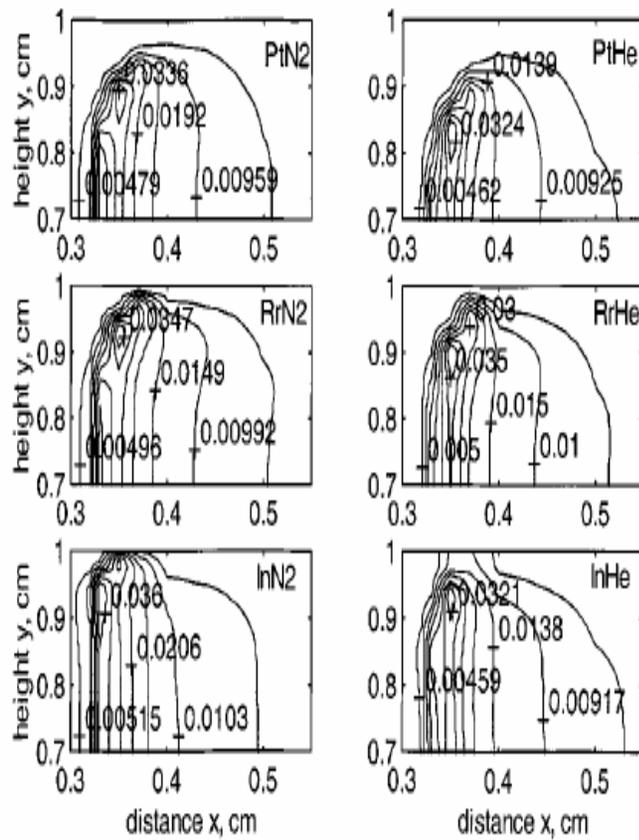
- H_2 in Air
- $T_o = 975 \text{ K}$
 $T_{\text{wall}} = 600 \text{ K}$ (constant)
 $p = 1 \text{ atm}$
 $u_o = 900 \text{ cm/s}$
- Slower overall combustion rate for Platinum wall sustaining catalytic combustion.

Contours of Near-wall H Atom Concentration for Different Wall Boundary Conditions, $\phi = 0.5$



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Andrae and Björnbom, *AIChE J.* 46, 2000.



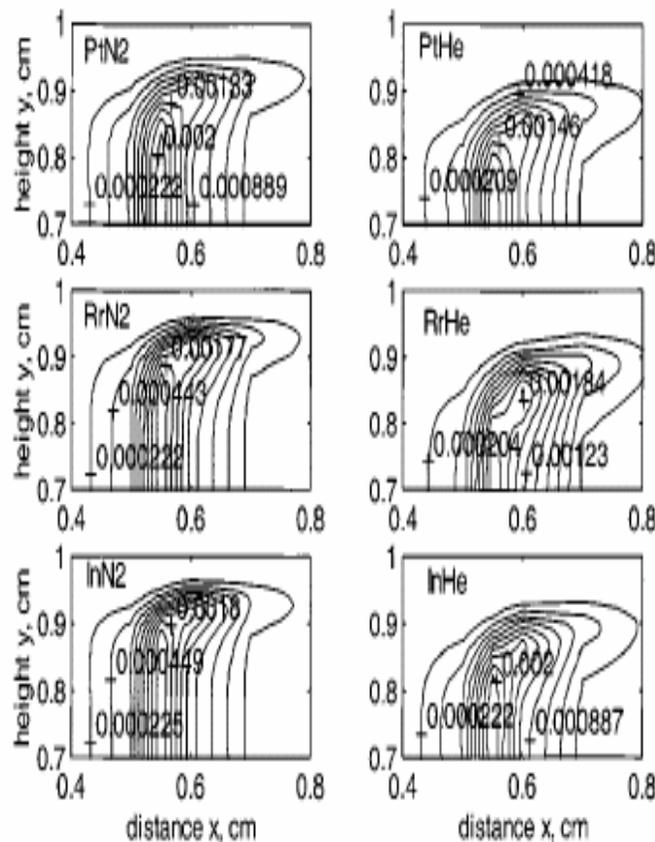
- $\phi = 0.5$, $T_o = 975$ K
 $T_{\text{wall}} = 600$ K (constant),
 $p = 1$ atm, $u_o = 900$ cm/s
- H atoms depleted near wall for Platinum wall sustaining catalytic combustion.
- Analysis show that catalytically formed H_2O slows down oxidation in boundary layer in reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ (Catalytic Flame Quenching)

Contours of Near-wall H Atom Concentration for Different Wall Boundary Conditions, $\phi = 0.1$



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Andrae and
Björnbom,
AIChE J. 46, 2000.

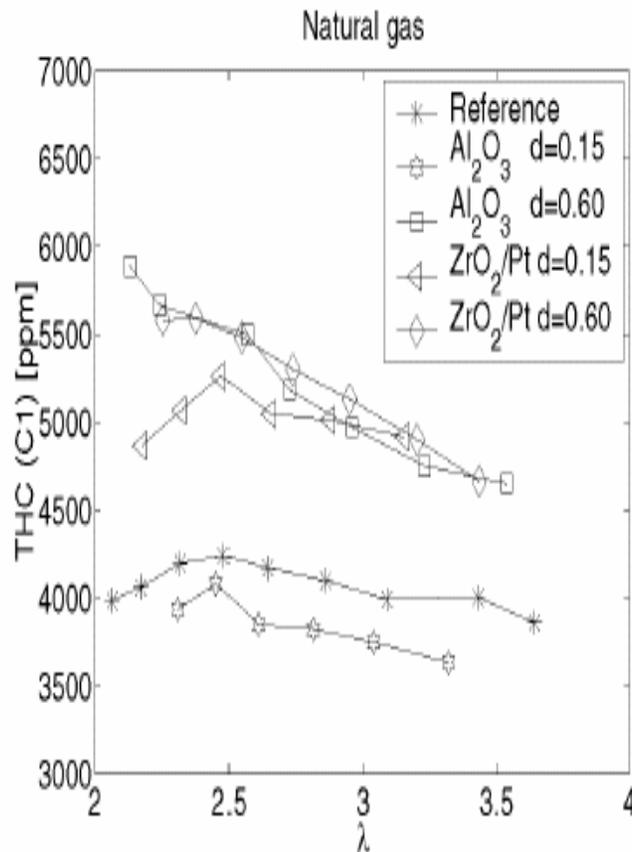


- $\phi = 0.1$, $T_o = 975$ K
 $T_{\text{wall}} = 600$ K (constant)
 $p = 1$ atm, $u_o = 900$ cm/s
- $\phi = 0.1$: Difference between boundary conditions small
- $\phi = 0.1$: Thermal and velocity boundary layer thicker than at $\phi = 0.5$
- $\phi = 0.1$: Heat and momentum transfer more important for wall effects

Catalytic Coatings on Cylinder Head and Valve Gave Increased UHC's Emissions From Natural Gas Fuelled HCCI Engine



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Ref: A. Hultqvist, M. Christensen, B. Johansson, SAE Paper 2000-01-1833

Heterogeneous/Homogeneous Reactions



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- Steady H_2 and CH_4 flames studied for different wall boundary conditions including catalytic walls
- Reduction of Fuel- NO_x in a Hybrid Combustor with Low Heating Value Fuel

LHV Fuel in form of Synthetic Gasified Biomass

Carbon dioxide neutral fuel but contains compounds (e.g. NH_3) which gives extensive formation of fuel- NO_x

Fuel	Molfr.	LHV (kJ/mol)
	-	
CH_4	0.05	802
CO	0.15	283
H_2	0.10	242
N_2	Balance	
NH_3	0.001	
H_2O	0.11	
CO_2	0.14	
LHV (kJ/mol)		107
LHV (MJ/kg)		4.1



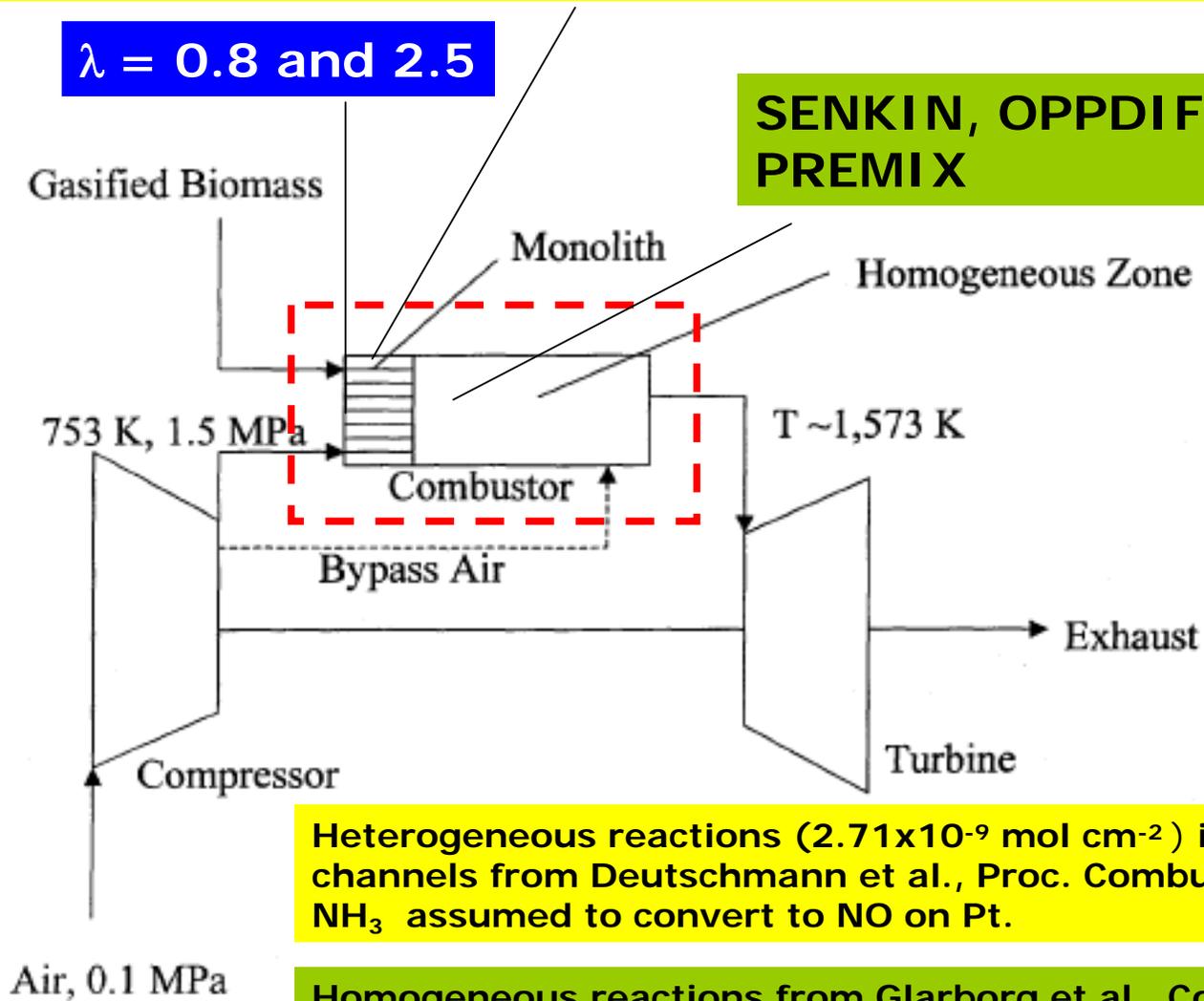
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Monolith consists of active (Pt) and passive channels

Individual channel modelled with CRESLAF (CHEMKIN, Release 3.6)

$\lambda = 0.8$ and 2.5

SENKIN, OPPDIF,
PREMIX



Heterogeneous reactions (2.71×10^{-9} mol cm^{-2}) in active channels from Deutschmann et al., Proc. Combust. Inst. 1996, NH_3 assumed to convert to NO on Pt.

Homogeneous reactions from Glarborg et al., Combust. Flame 1998 (460 reactions, 66 species)



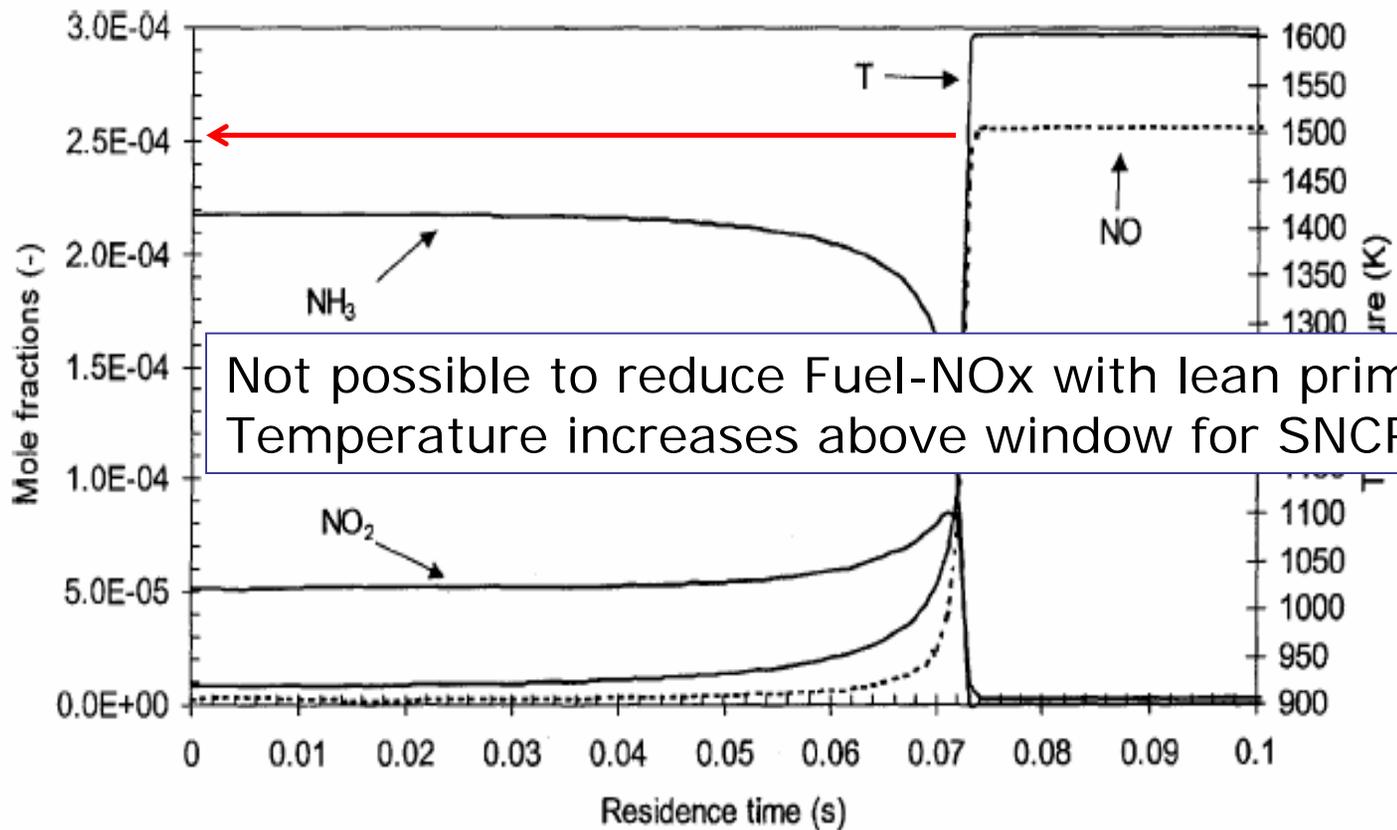
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Andrae et al.
AIChE J. 49, 2003.

NH₃ consumption and NO formation in homogeneous zone: $\lambda_{\text{primary}} = 2.5$ Ratio Active/Passive Channels = 0.2



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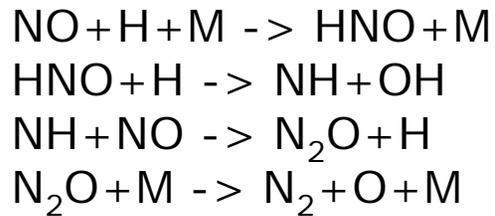


Andrae et al.
AIChE J. 49, 2003.

NO and N₂ evolution in homogeneous zone: $\lambda_{\text{primary}} = 0.8$

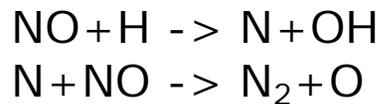
Ratio Active/Passive Channels = 0.17

Channel II:

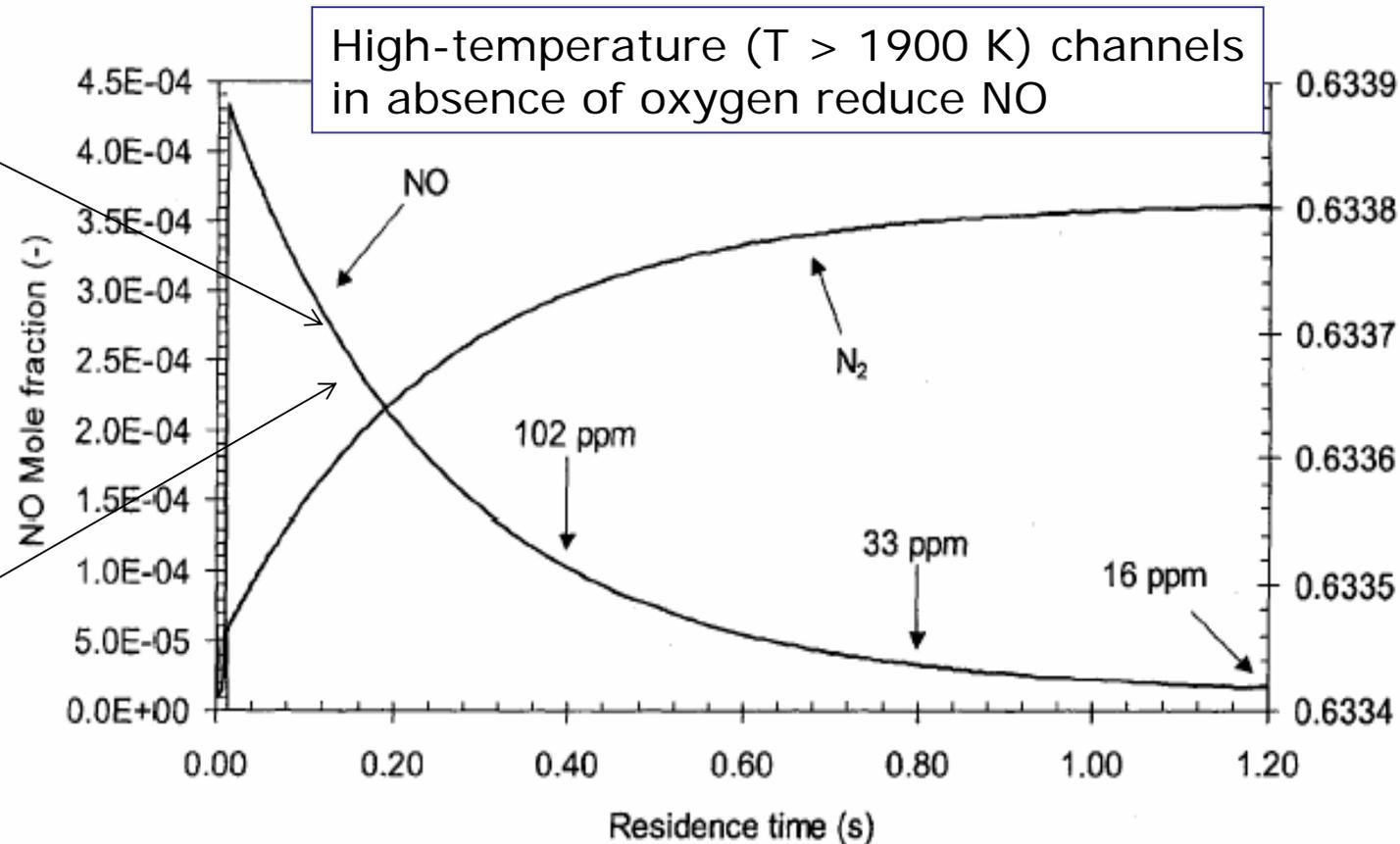


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Channel I:



Andrae et al.
AIChE J. 49, 2003.



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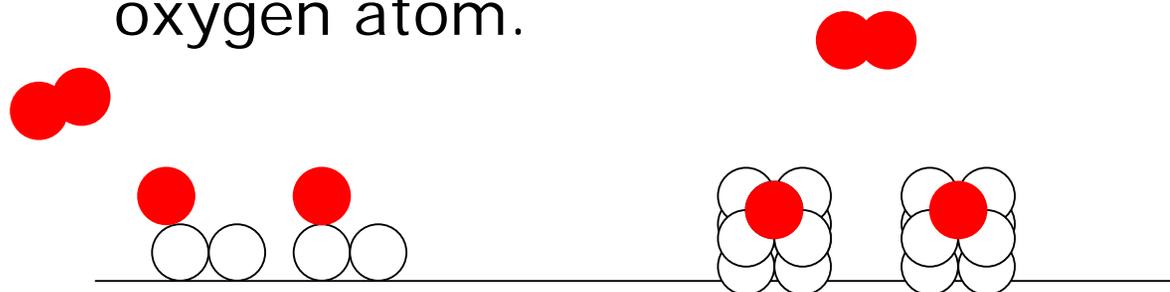
- Development of H₂/O₂ Oxidation Mechanism on Pd at High Temperatures and Low Pressures (1300 K, 13 Pa, 100 SCCM)
- Ignition of Simulated Gasified Biomass on Pt in a High-pressure System (p=5-16 bar)
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Limited understanding of the palladium catalyst at high temperatures and moderate pressures.

- Saturation coverage for O atoms on single crystals has been determined to be 0.25 for Pd(1 1 1) and Pd(1 0 0), which indicates that essentially four surface atoms are required for each adsorbed oxygen atom.



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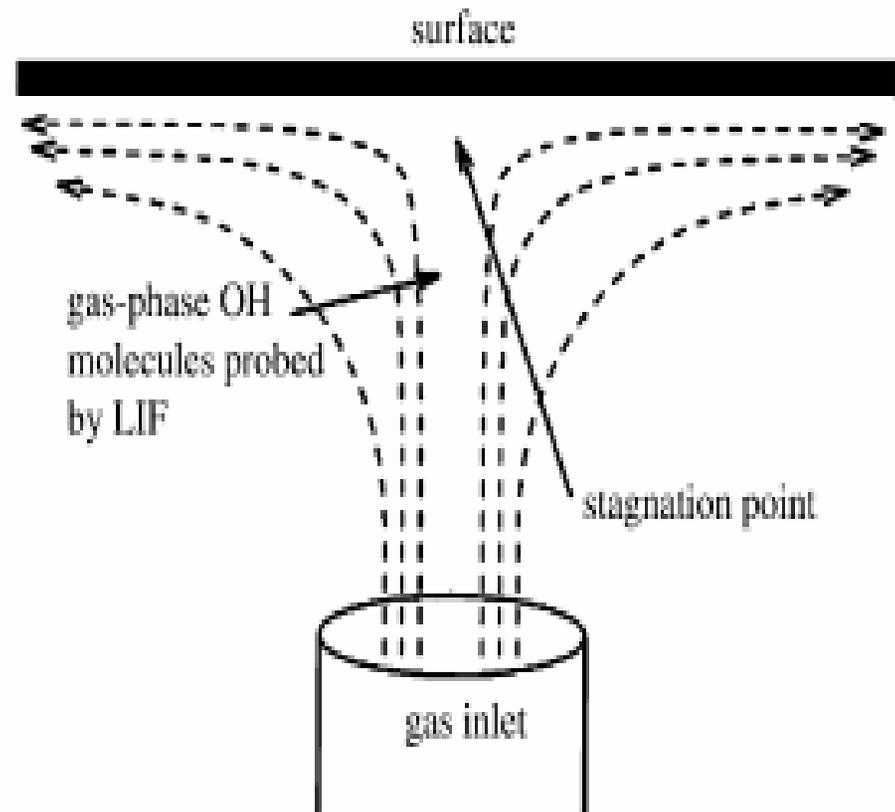


Experiments and Modelling



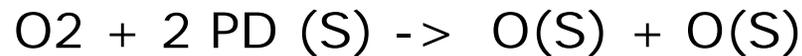
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- Yield of OH measured with LIF
- Water formation measured with microcalorimetry
- SPIN application (CHEMKIN Release 3.7) in order to model a stagnation point flow and compare with experiments



Model Formulation

- Previous model, max. O coverage 100%



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- New model, max. O coverage 25%

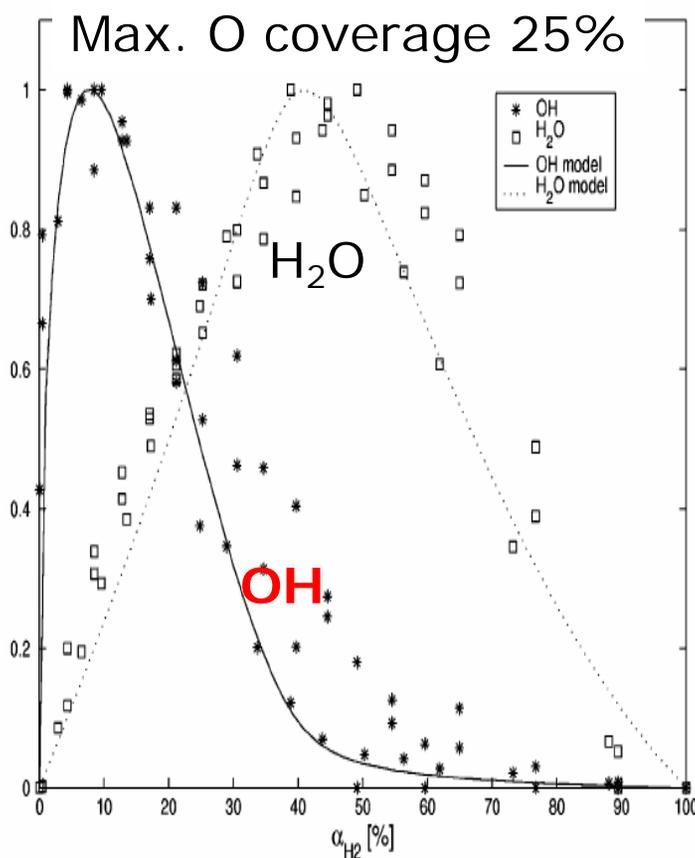


The OH desorption intensity and water production against α_{H_2} for palladium at a pressure of 13 Pa and a flow of 100 SCCM (Lines – model predictions)

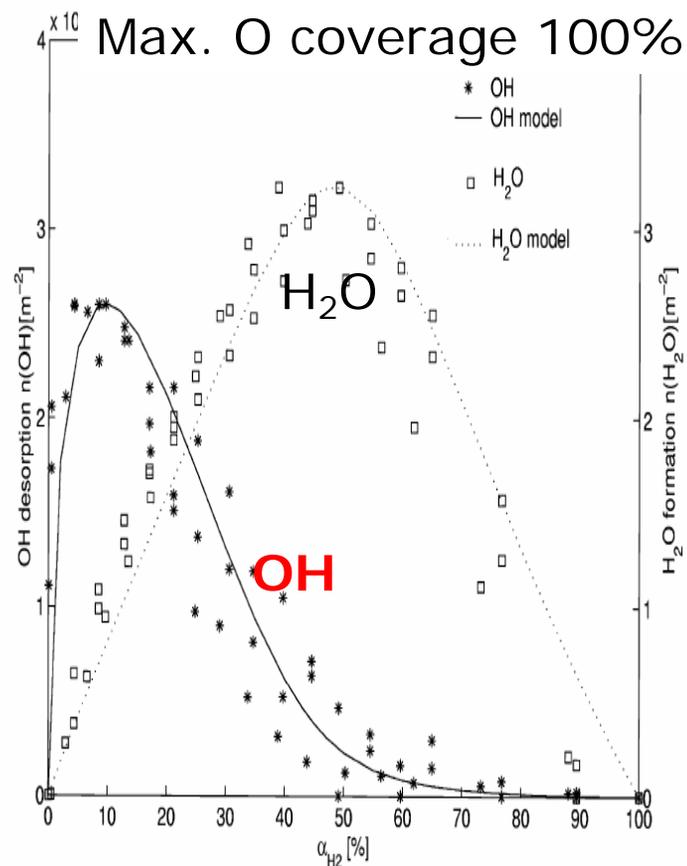


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$$\alpha_{H_2} = \frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$



Andrae et al.
Surf. Sci. 563, 2004



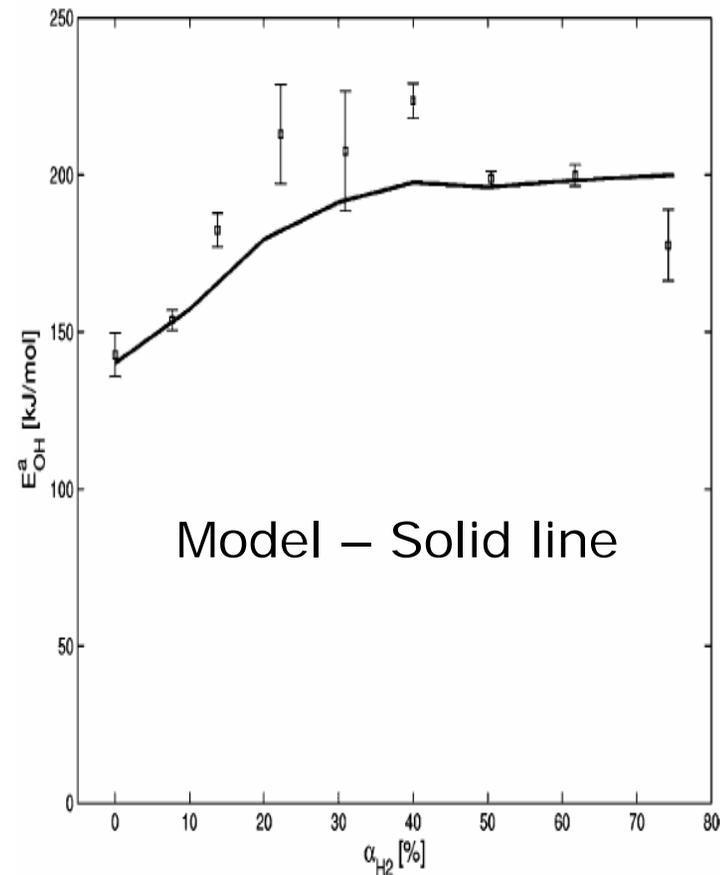
Johansson et al.
Surf. Sci. 529, 2003

New model also developed against apparent desorption energy of OH vs α_{H_2} at inlet with good result



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- The apparent desorption energy was measured with LIF as a function of α_{H_2} .
- The apparent desorption energy was for each α_{H_2} calculated from a traditional Arrhenius plot.
- Apparent desorption energy was calculated with CHEMKIN using the desorbed flux of OH predicted from the model.



Heterogeneous Reactions



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Purpose



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- Investigate the effect of pressure in catalytic ignition of synthetic gasified biomass in a hybrid combustor (partially coated monolith)
- Validate a detailed surface kinetic model* for oxidation of Methane, Carbon Monoxide and Hydrogen on Platinum

*Mhadeshwar et al., Proc. Combust. Inst. 29, 2002

Fuel

Composition of gasified biomass fuel (mole fractions)

	Fuel	LHV (kJ/mol)
CO	0.332	283
H ₂	0.240	242
CH ₄	0.106	802
CO ₂	0.322	–
LHV (kJ/mol)	237	–
LHV (MJ/kg)	9.24	–



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CHEMKIN Release 4.0 used to set up calculations for an individual channel in partially coated (Pt) monolith

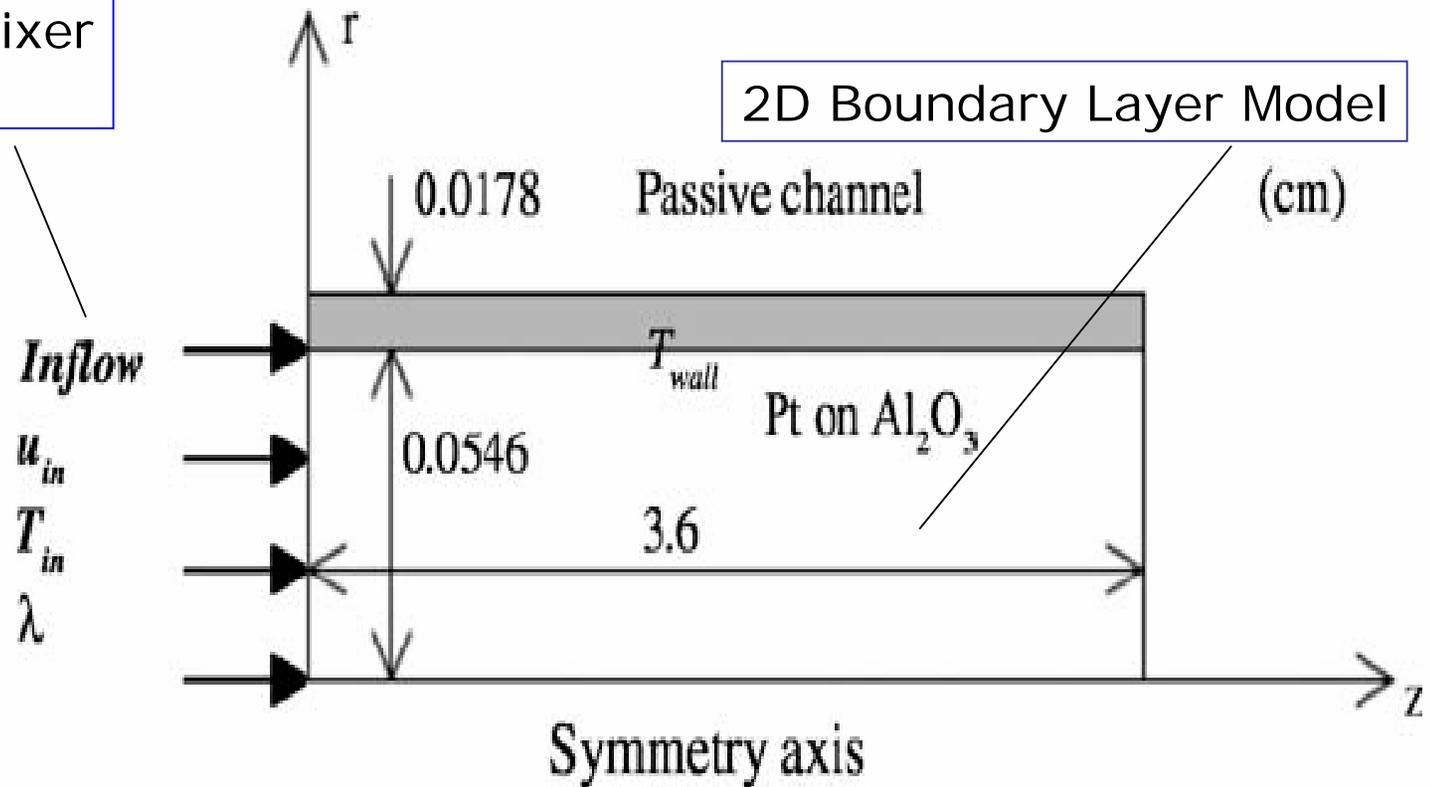


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Gas Mixer Model

$\lambda = 4-6$
 $u_{in} \sim 550 \text{ cm/s}$
 $P = 5-16 \text{ bar}$
 $T_{in} = 218-257 \text{ }^\circ\text{C}$
 $Re_d = 820-2360$

2D Boundary Layer Model



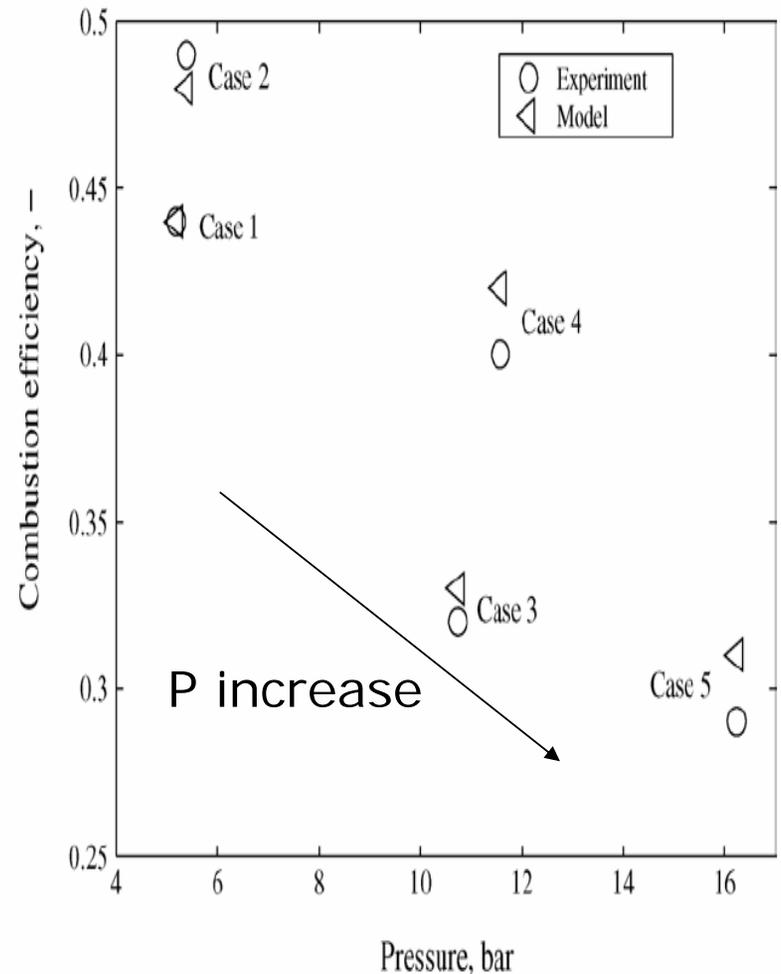
Effect of pressure for constant residence time



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- 2D boundary layer model coupled to the multi-step surface mechanism could predict with good accuracy that the combustion efficiency decreased with increasing pressure.
- The surface kinetic model could also predict the negative pressure dependence for the availability of free surface sites, $PT(S)$

Andrae et al.
Appl. Cat. A 293, 2005



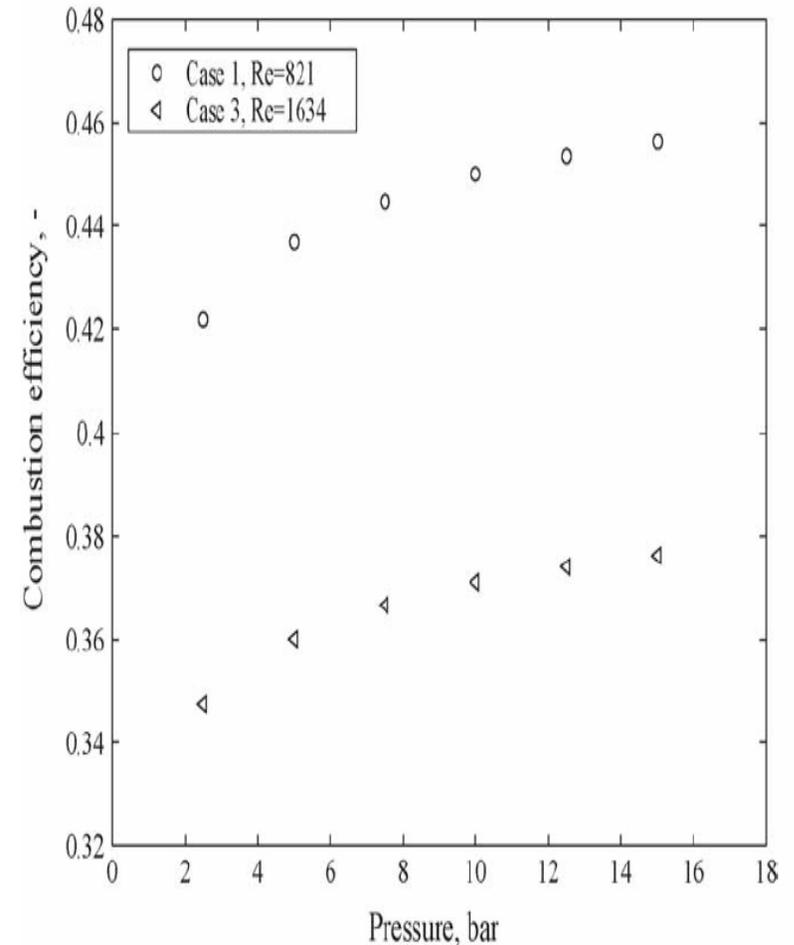
Effect of pressure for constant mass flow

- The combustion efficiency increase with pressure, the increment more significant up to around 10 bar
- Increased residence times at higher pressures compensates for the decreasing diffusion velocities (increasing mass transfer limitations).



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Andrae et al.
Appl. Cat. A 293, 2005



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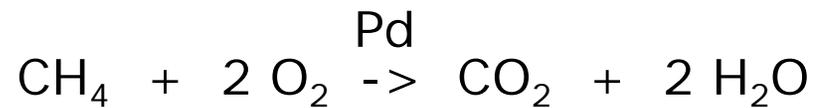
A Global Kinetic Model for Catalytic Combustion of CH₄/Air Mixtures over Alumina-supported Palladium Catalysts



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- CHEMKIN Release 4.0 was used to develop a global kinetic model with methane/air mixtures for $T_{in} = 300-475^{\circ}\text{C}$.
- After validation with lab-scale kinetic data, the model is compared to results obtained for conditions relevant to gas turbine combustion (i.e high pressures and flow rates).

Proposed Global Model



$$-r_{\text{CH}_4} = k [\text{CH}_4]^\alpha [\text{O}_2]^\beta \text{ mol}/(\text{cm}^2 \cdot \text{s}) \quad \text{Rate law}$$



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$$k = A T^n e^{(-E_a/RT)} \quad \text{Rate constant}$$

$$\alpha = 0.9 \quad (\text{e.g. Ribeiro et al. 1994, Aryafar and Zaera 1997, van Giezen et al. 1999})$$

$$\beta = 0.0 \quad (\text{e.g. Ribeiro et al. 1994, Aryafar and Zaera 1997, van Giezen et al. 1999})$$

$$E_a = 92 \text{ kJ/mol} \quad (\text{Baldwin and Burch 1990})$$

$$A = 2.64 \text{E} + 08 \quad \text{mol}^{(0.1)} \cdot \text{cm}^{(0.7)} / \text{s}$$

$$n = -1.0$$

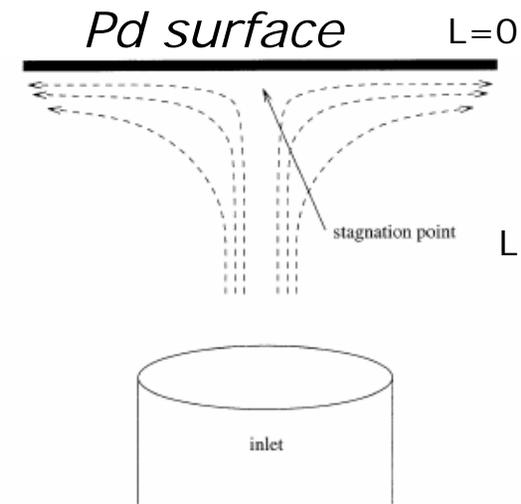
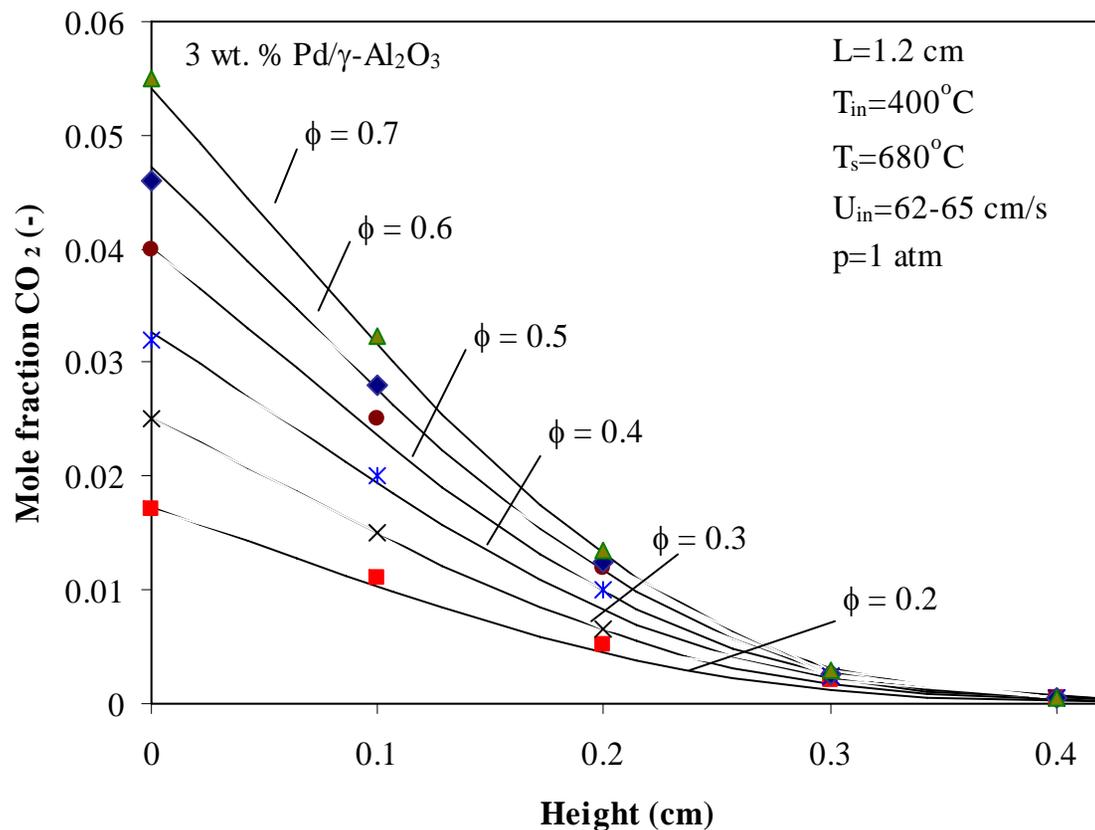
$$300 < T_{\text{in}} < 475 \text{ }^\circ\text{C}$$

Andrae,
EUROPACAT VII
2005

Global Model Validation - Stagnation Point Flow (1 atm)



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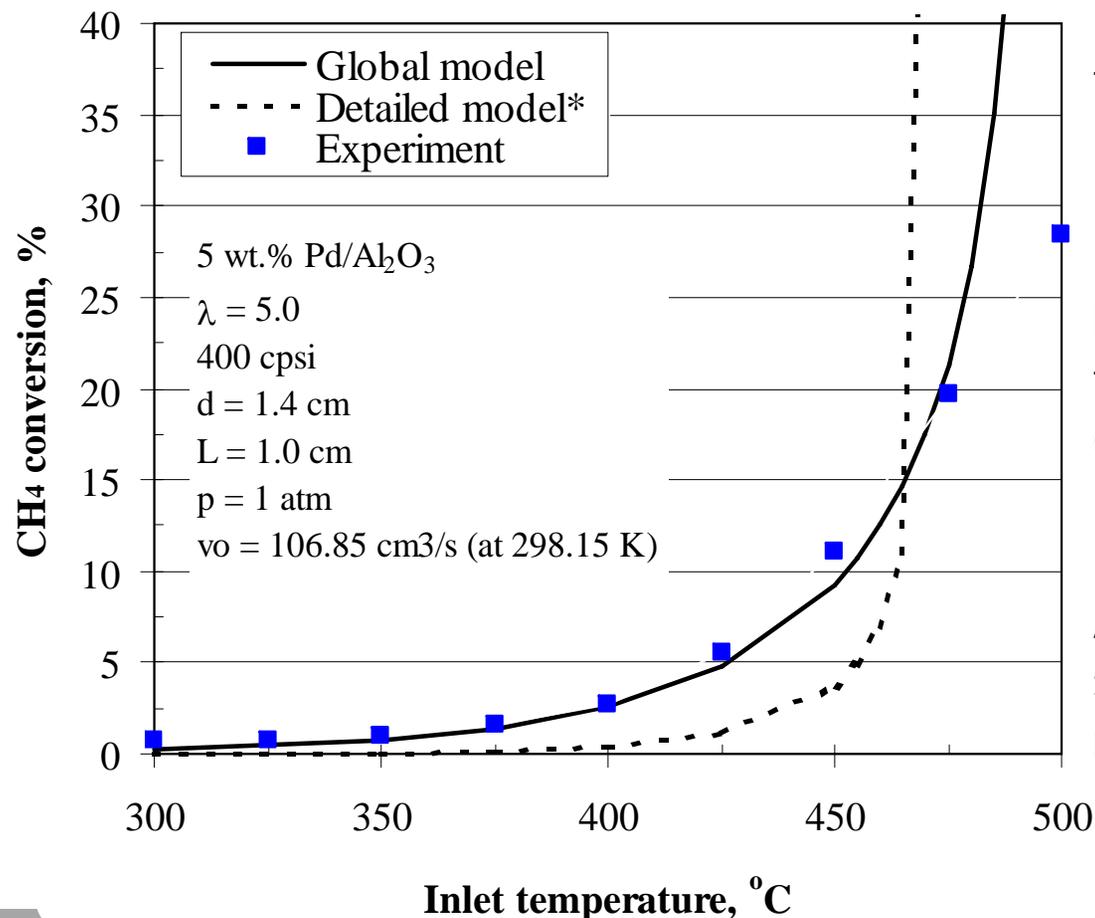
Andrae,
 EUROPACAT VII
 2005

Lines = Model prediction, Symbols = Experiment Sidwell et al, Appl. Cat A 2003.

Global Model Validation – Lab Scale Tubular Reactor (1 atm)



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2D Boundary layer
fluid mechanics model
is used.

Not possible to use
Monolith Model (Plug
flow) provided in
CHEMKIN 4.0

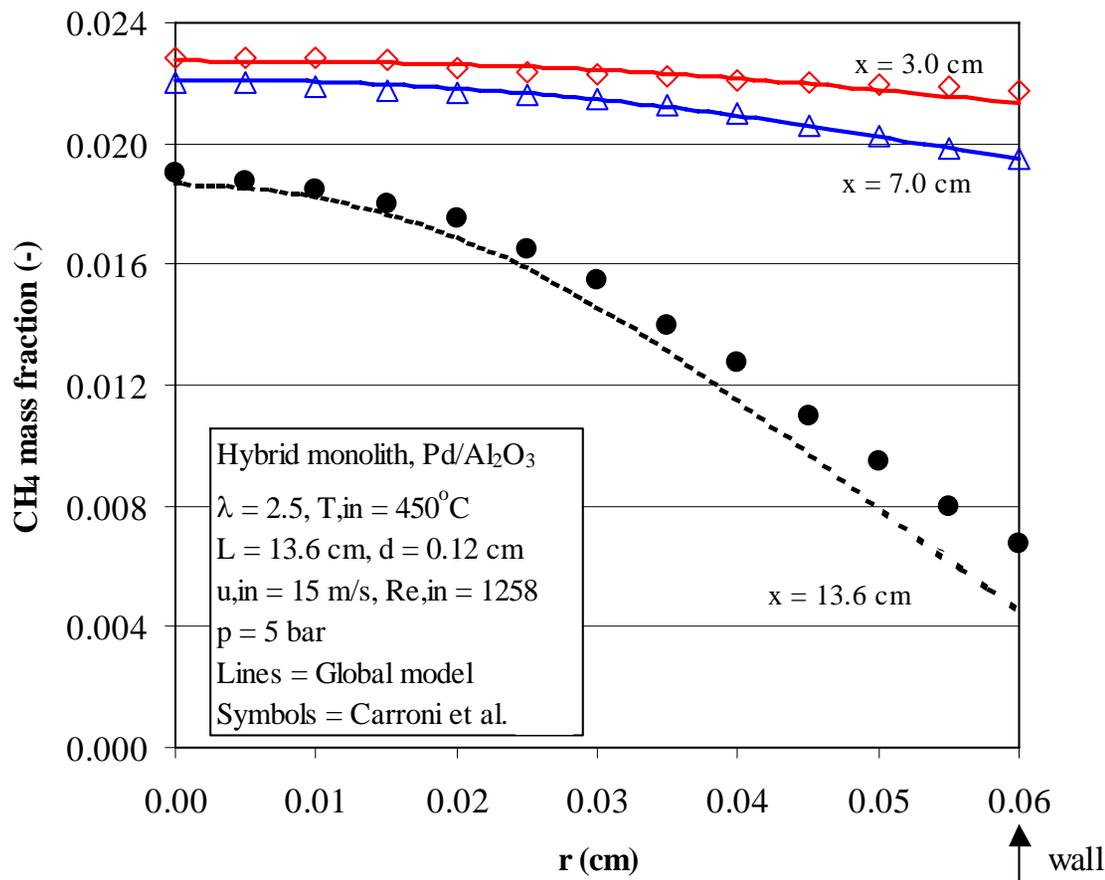
*Zhu and Jackson,
ASME 2001-GT-0520,
site density $1.30E-09$
mol/cm².

Andrae,
EUROPACAT VII
2005

Model-model Comparison at Elevated Pressures: $p=5$ bar, $Re_d=1258$



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Radial profiles of computed methane mass fractions for three stream-wise distances.

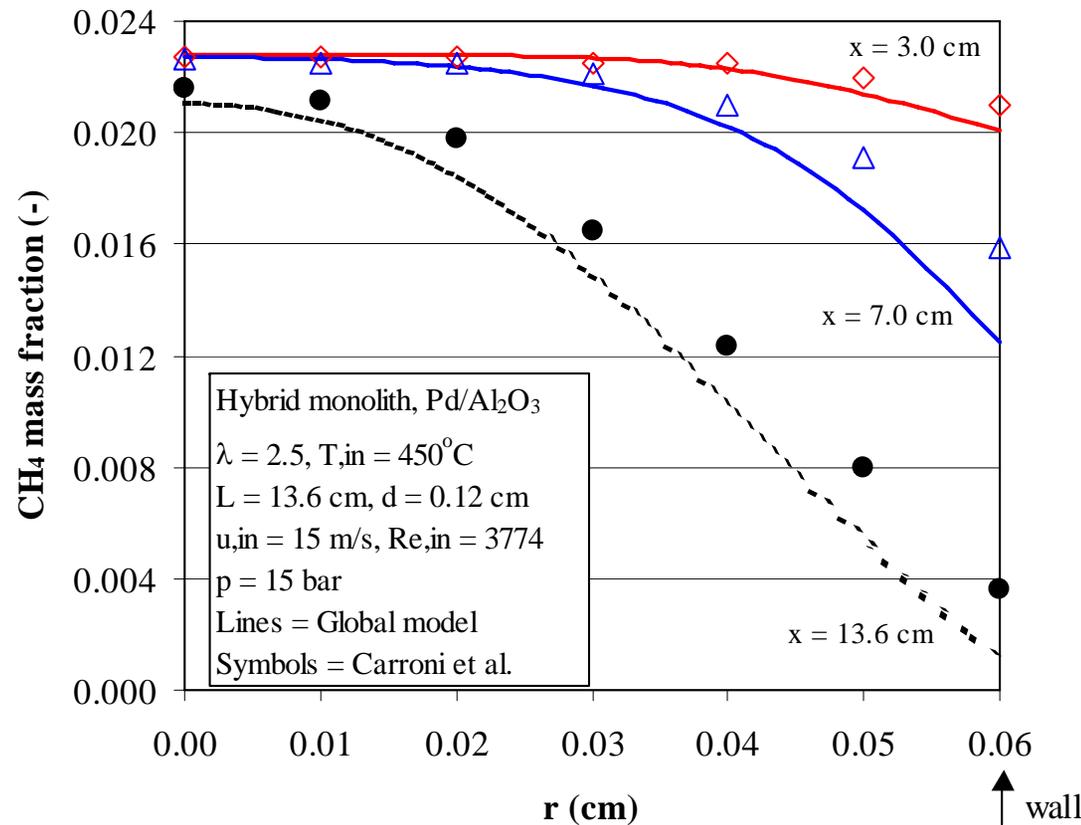
2D Boundary layer fluid mechanics model is used (lines).

Carroni et al. Cat. Tod. 83, 2003 (symbols) make use of an elliptic fluid mechanics model.

Model-model Comparison at Elevated Pressures: $p=15$ bar, $Re_d=3774$



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Radial profiles of computed methane mass fractions for three stream-wise distances.

2D Boundary layer fluid mechanics model is used (lines).

Carroni et al. Cat. Tod. 83, 2003 (symbols) make use of an elliptic fluid mechanics model.

Conclusions

- CHEMKIN is a valuable simulation/modelling tool for investigating complex systems involving heterogeneous and homogeneous reactions such as catalytic combustion
- CHEMKIN has been improved significantly in the latest releases, helping researchers improve their performance, e.g.
 - Reactor networks and mixing models
 - Extended options for formulating gas- and surface chemistry



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