Chemical kinetics
Procida June 2015

Module 3

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

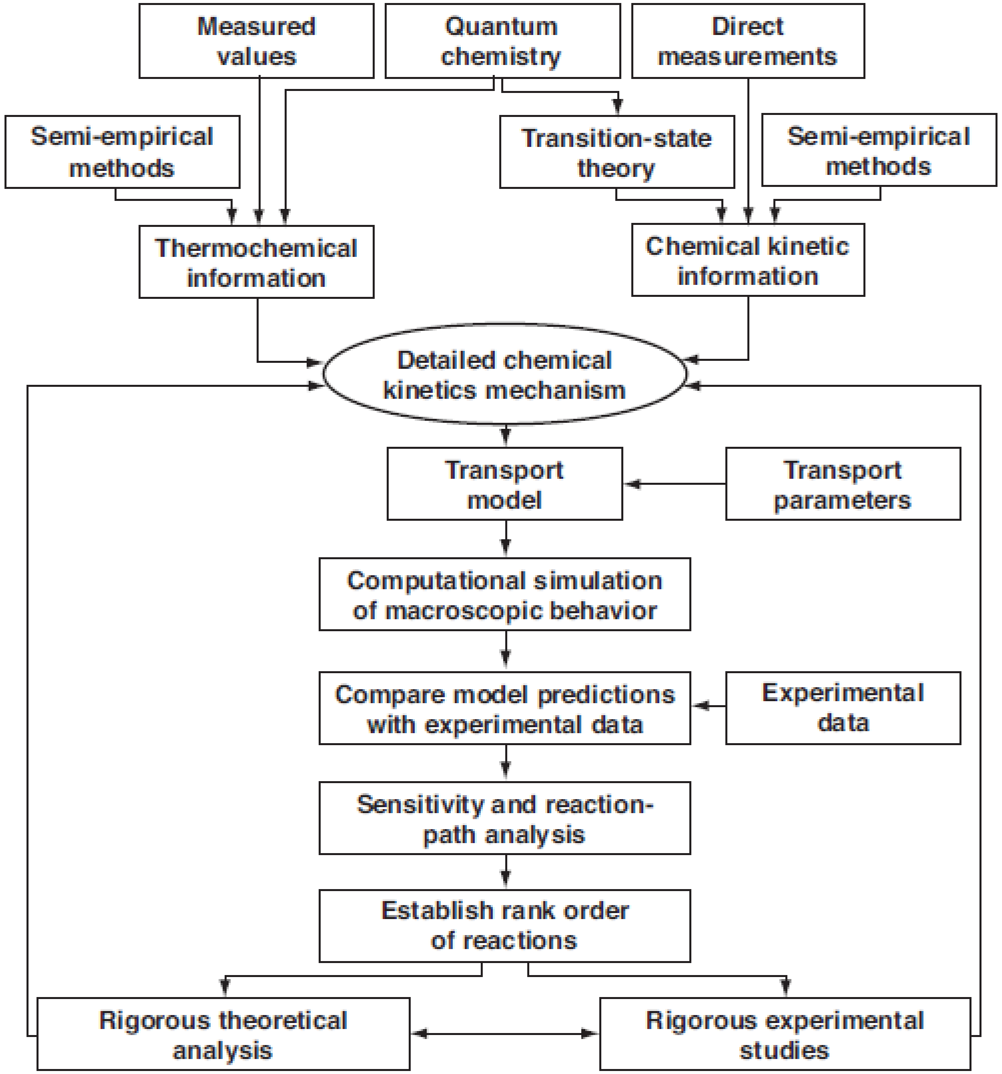
Module 3

- Developing detailed chemical kinetic models (PG)
  - Approach
  - Experimental validation
  - Analysis tools
- Task 2: Engine exhaust oxidation of unburned hydrocarbons
  - Introduction (AC)
  - Solving using OpenSMOKE++ (AC, PG)

Developing a detailed chemical kinetic model

- Compile the best available species and reaction specific data
  - Experiment
  - Theory
  - Analogy / empirical
- Compare modeling predictions with the best available non-reaction-specific experimental data
  - Ignition delays, flame speeds, explosion limits
  - Detailed characterization data (species concentrations, etc.)
- Refine
  - Microscopic accuracy (fundamental model)
  - Macroscopic accuracy (engineering model)

Development of chemical kinetic model



Kinetic experiments

- Microscopic

  Characterization of elementary reaction

  – Determine rate coefficients

  – Identify products

- Macroscopic

  Characterization of process

  – Identify mechanism

  – Validate model

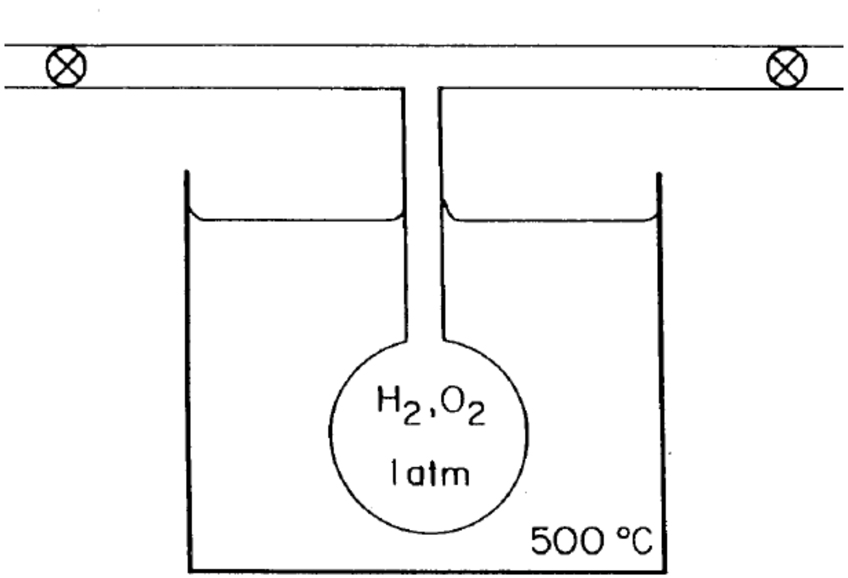
Macroscopic experimental techniques

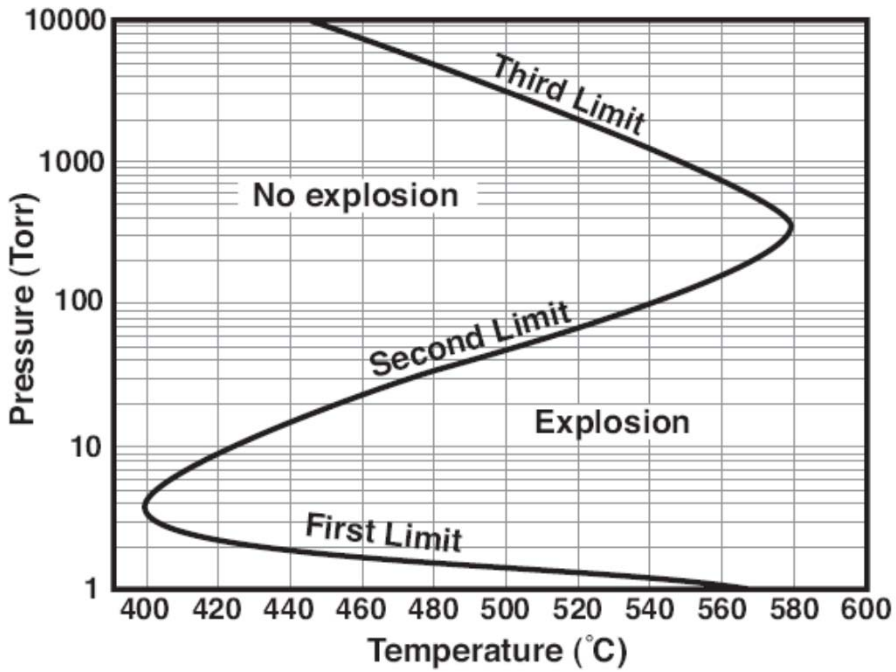
- Batch reactor
  - Low to medium temperature, low to medium pressure
- Flow reactor
  - Low to high temperature, low to high pressure
- Jet-stirred reactor
  - Medium to high temperature, medium pressure
- Shock tube
  - Medium to high temperature, medium to high pressure
- Rapid Compression Machine (RCM)
  - Medium temperature, medium to high pressure
- Laminar, premixed flames
  - Medium to high temperature, low to medium pressure

Experimental techniques for model validation

	Pressure	Temperature	Dilution	Stoichiometry limits	Transport effects
Static/batch reactor	atm.	< 1000 K	yes	none	no
Stirred reactor	atm. - high	800 - 1400 K	yes / no	no (ext. heat) Flammability limits	no
Plug-flow reactor	atm. - high	800 - 1400 K	yes	none	no
Shock tube	atm. - high	> 1300 K	yes	none	no
Flames	atm. - low	800 - 2500 K	no	Flammability limits	yes

Batch reactor

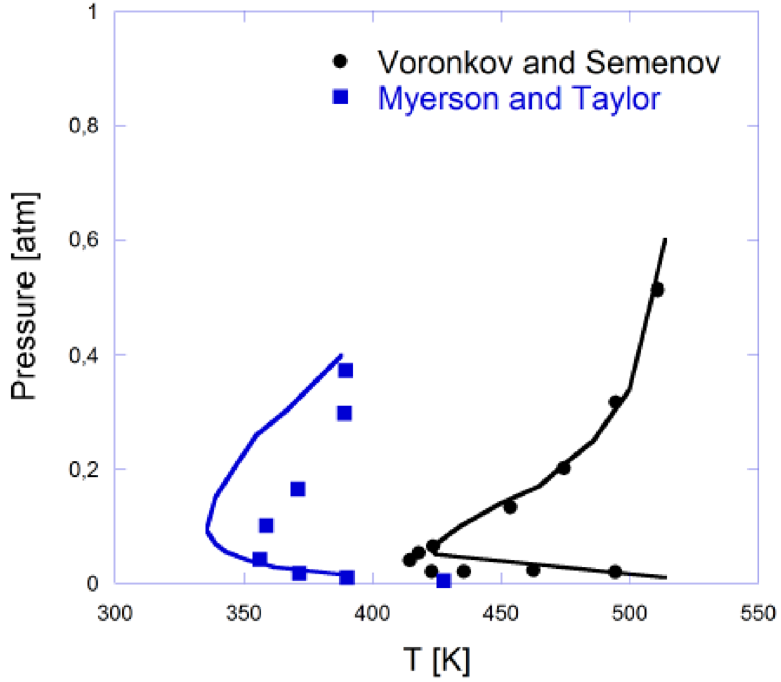




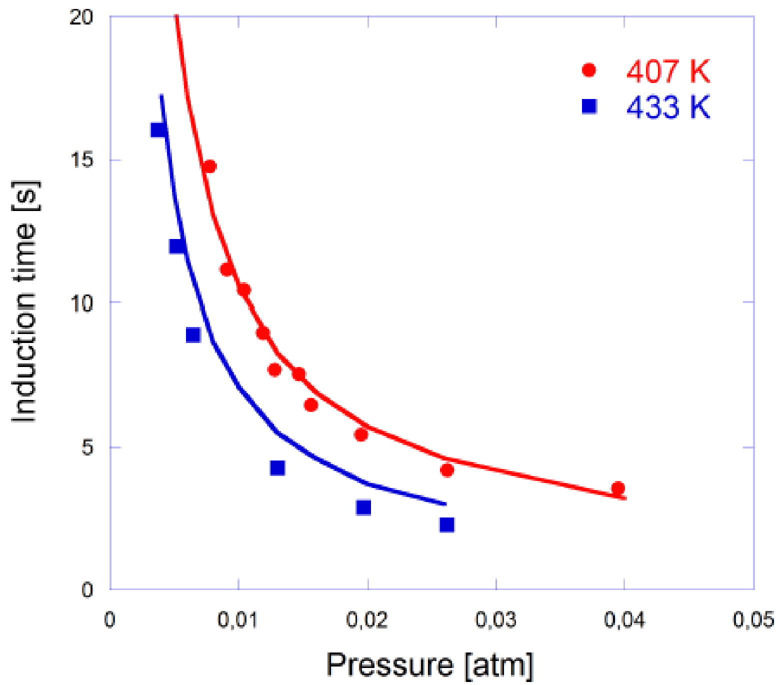
H_2/O_2 explosion limits
Data: Lewis and von Elbe (1987);
Figure: Kee et al. (2003)

Batch reactor
- CS_2 ignition

Explosion limits

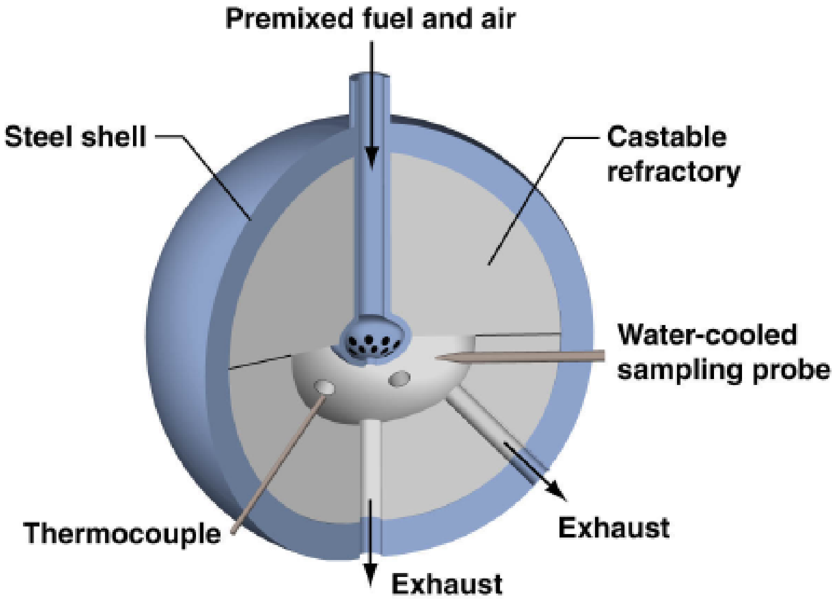


Ignition delay

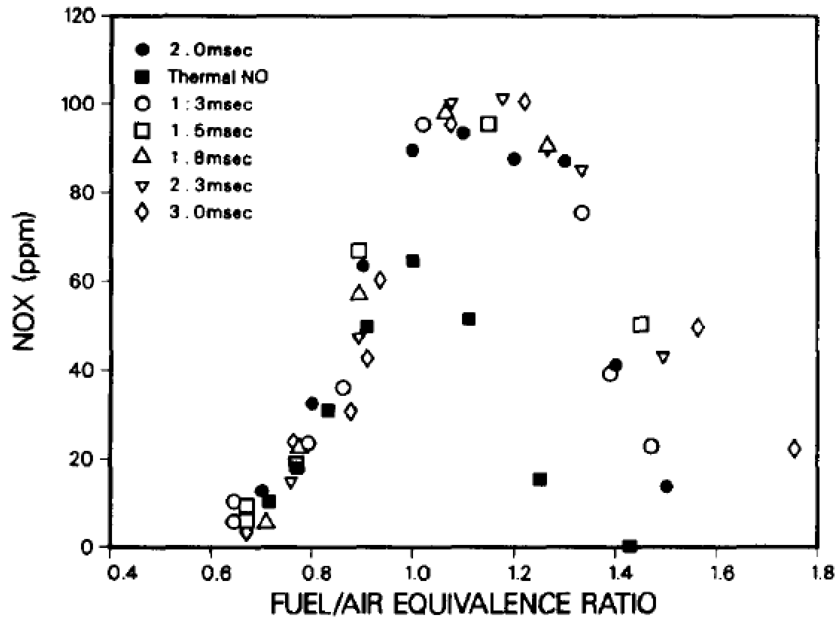


Glarborg et al. (2014)

Jet-stirred reactor

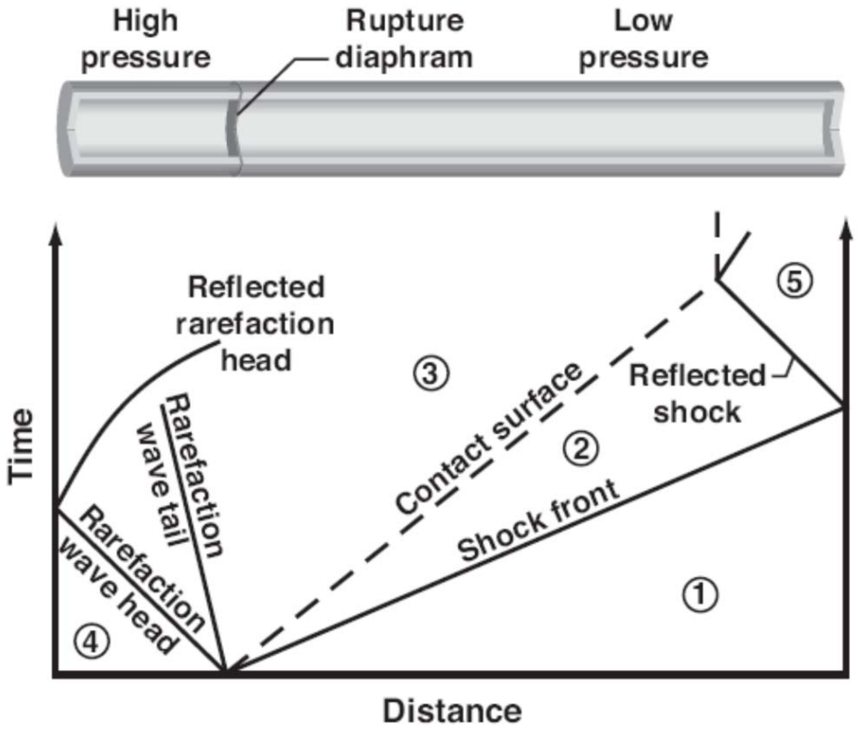


CH_4 oxidation (1600-2000 K)
Experimental data: Bartok et al. (1972)

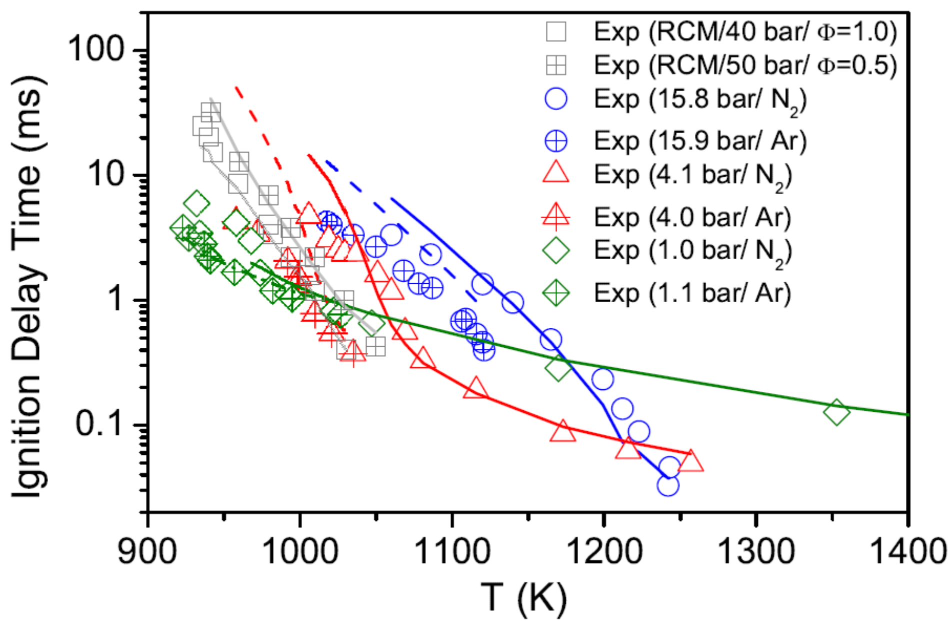


Glarborg et al. (1986)

Shock tube



Ignition delay for H_2



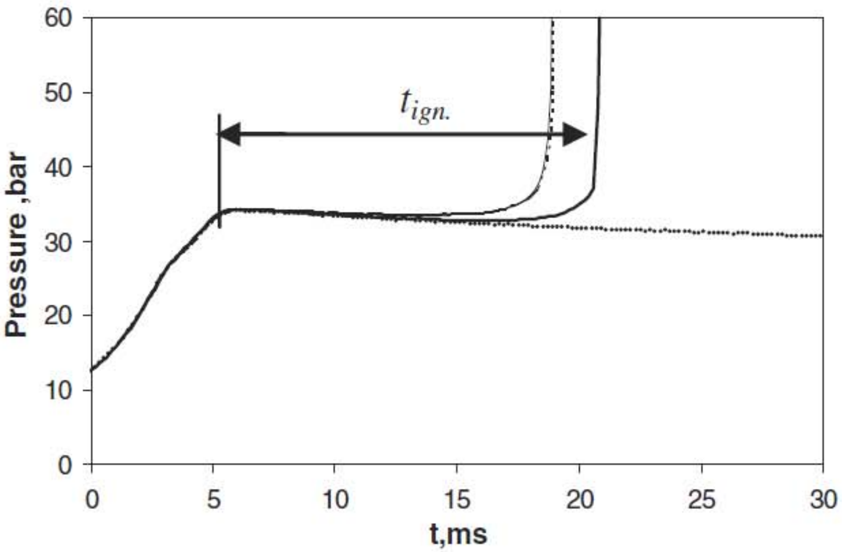
Hashemi et al. (2014)

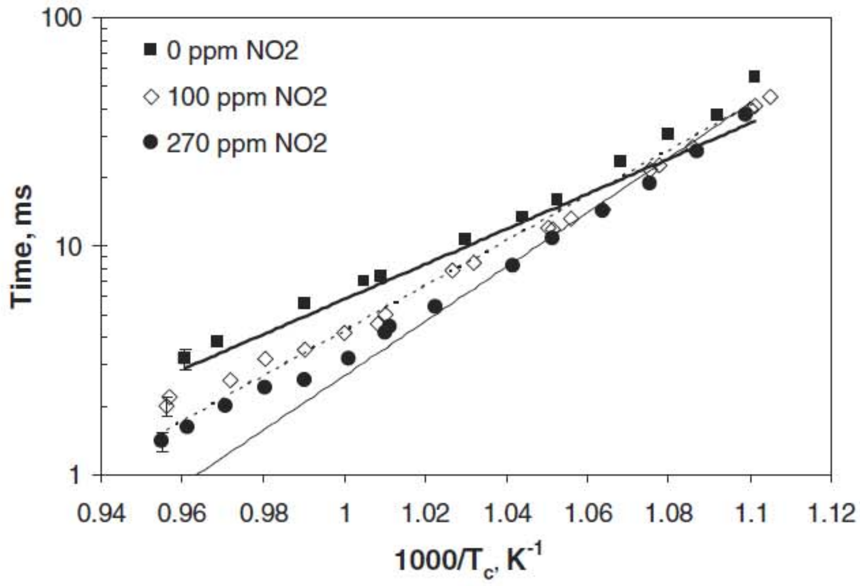
Rapid Compression Machine

Henry Curran

Rapid Compression Machine

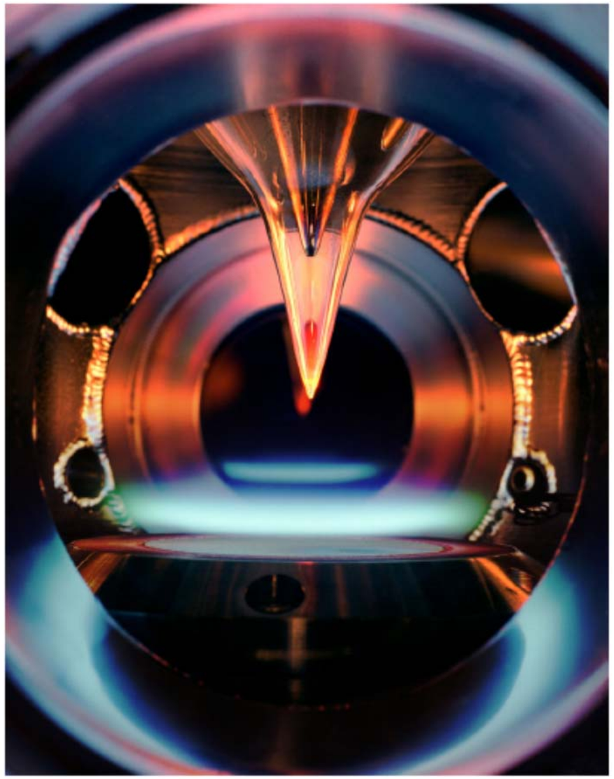
Ignition delay for CH_4

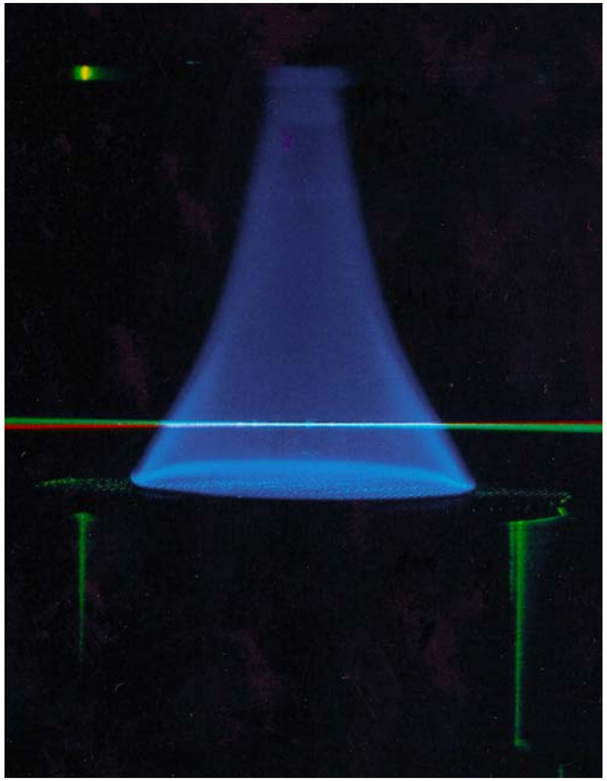




Gersen et al. (2011)

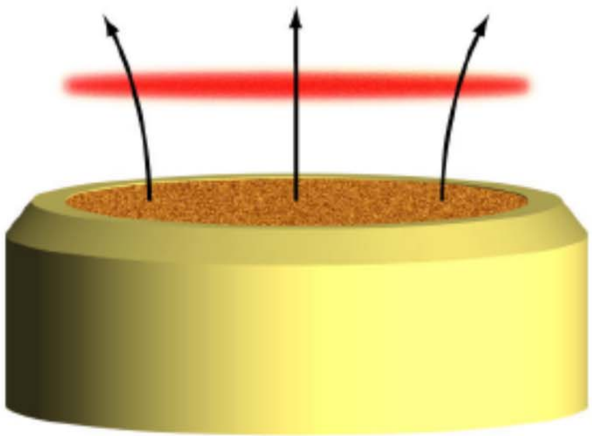
Low-pressure premixed flames

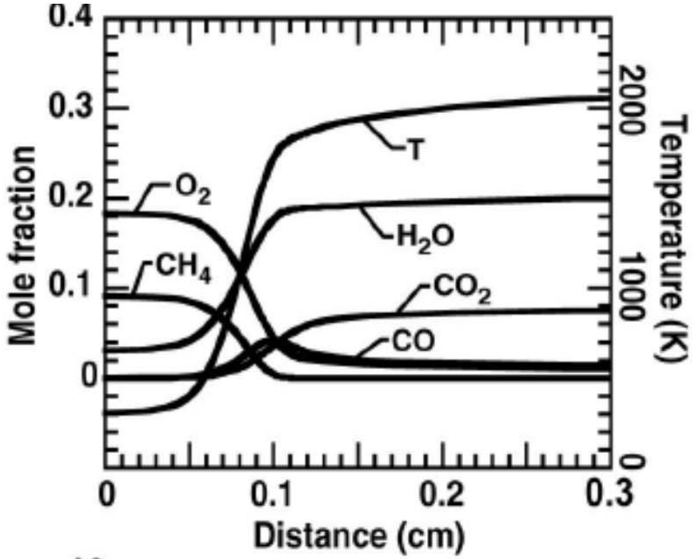


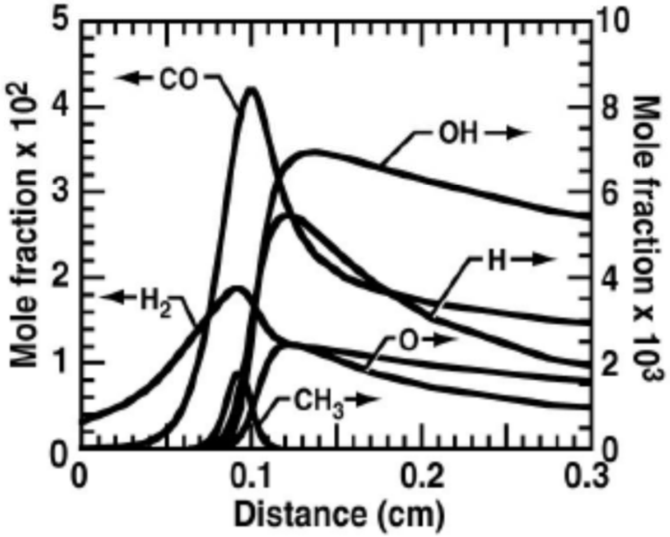


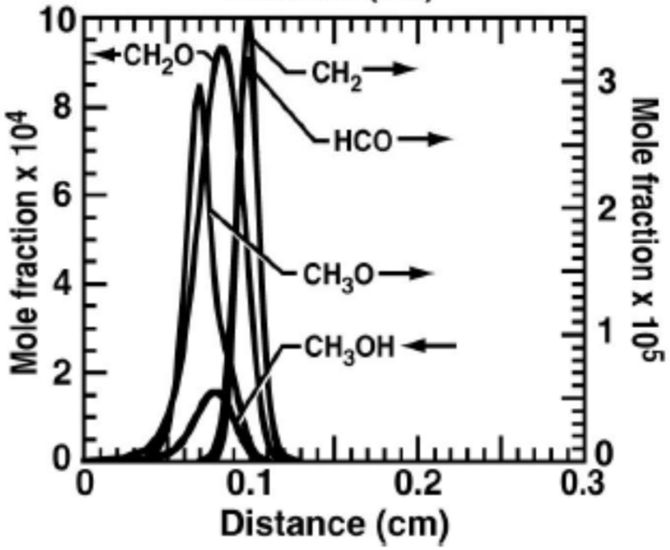
Photos: Sandia National Laboratories

Premixed flame

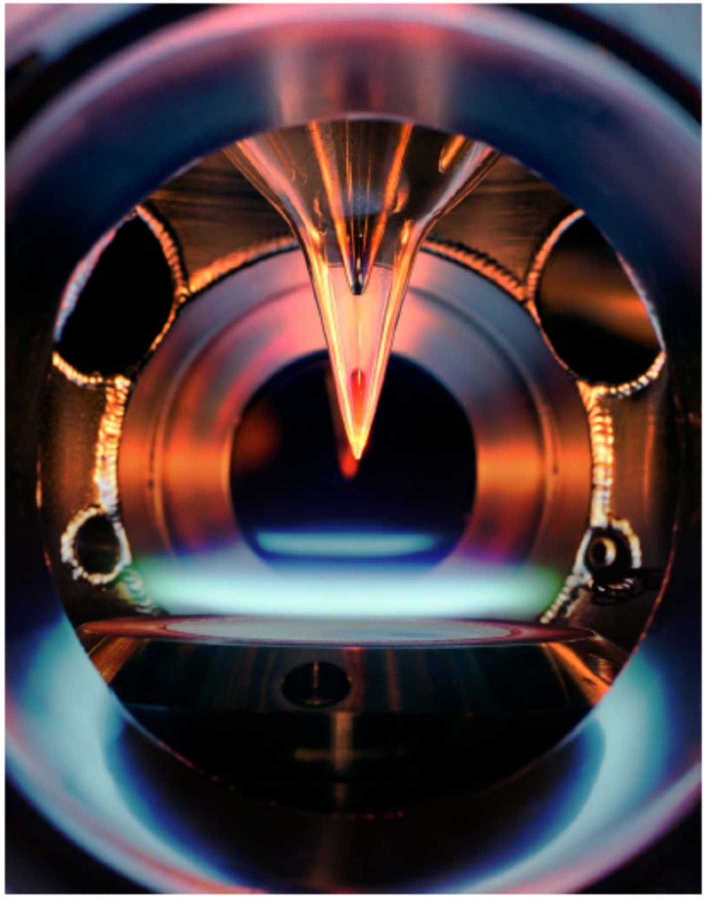




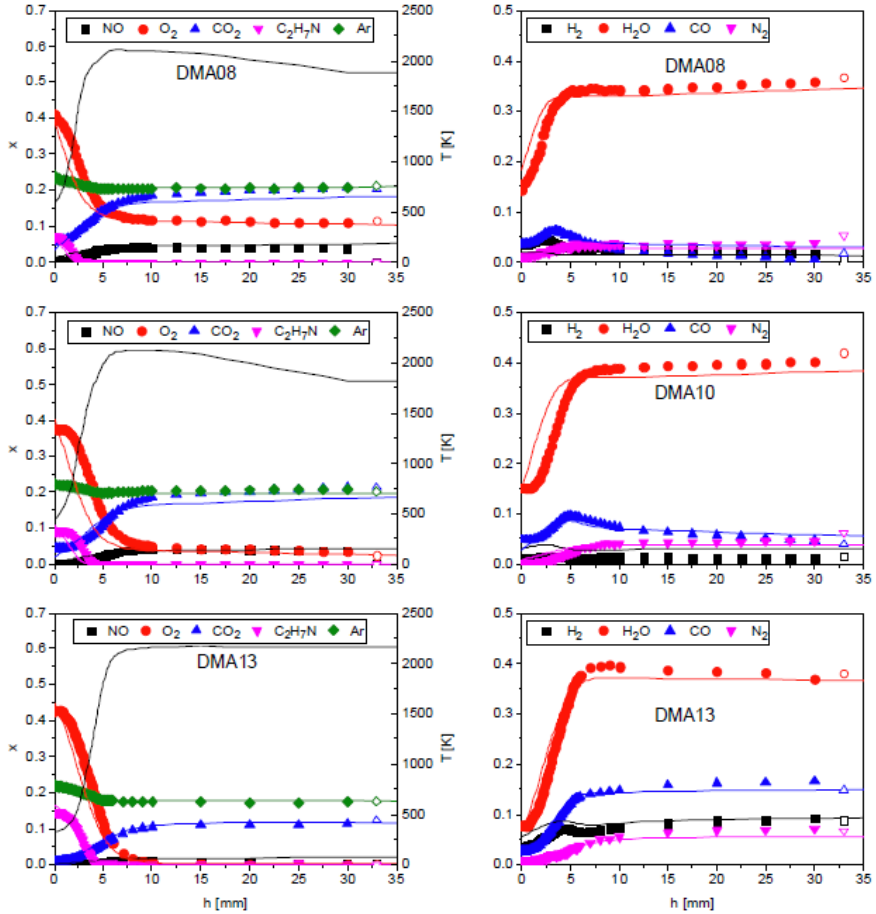




Low-pressure, premixed flame



C_2-amine oxidation

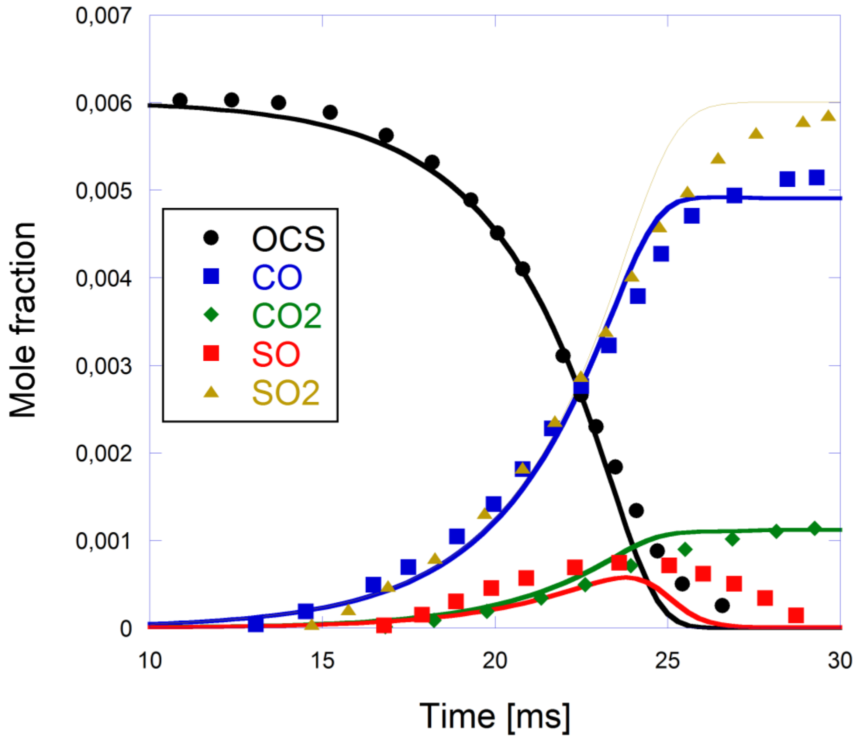


Lucassen et al. (2012)

Flow reactor

OCS oxidation
1200 K, 0.056 atm

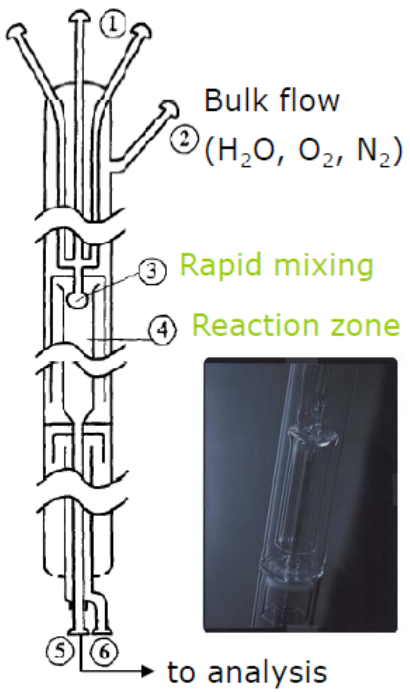
Experimental data:
  Homann et al. (1969)
Modeling:
  Glarborg and Marshall (2013)



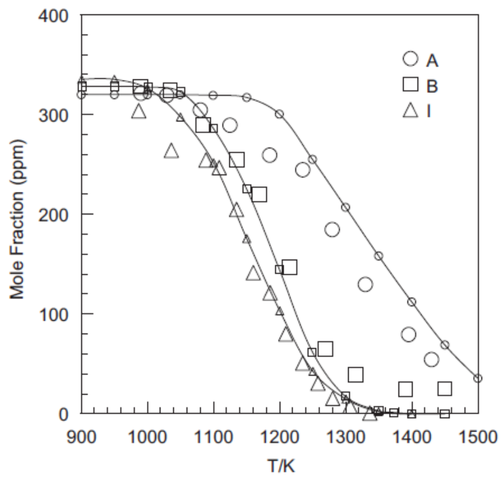
Flow reactors for high-temperature or high-pressure chemistry

Injector flows
(HCN, N_2)

1 atm, 600-1300 K

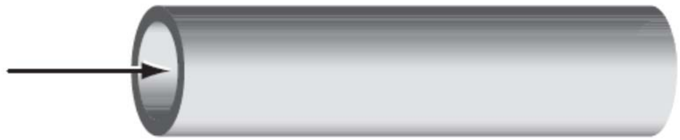


HCN, 1 atm

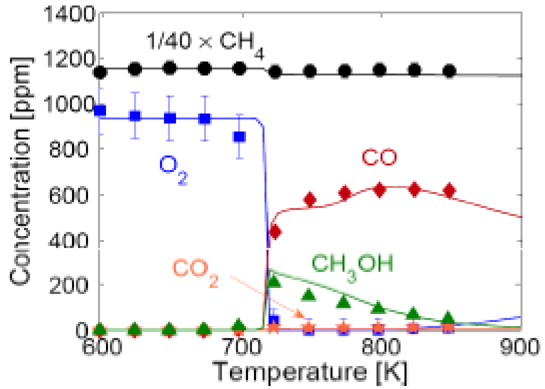


Dagaut et al., 2008

1 atm, 600-1850 K
20-100 atm, 600-925 K

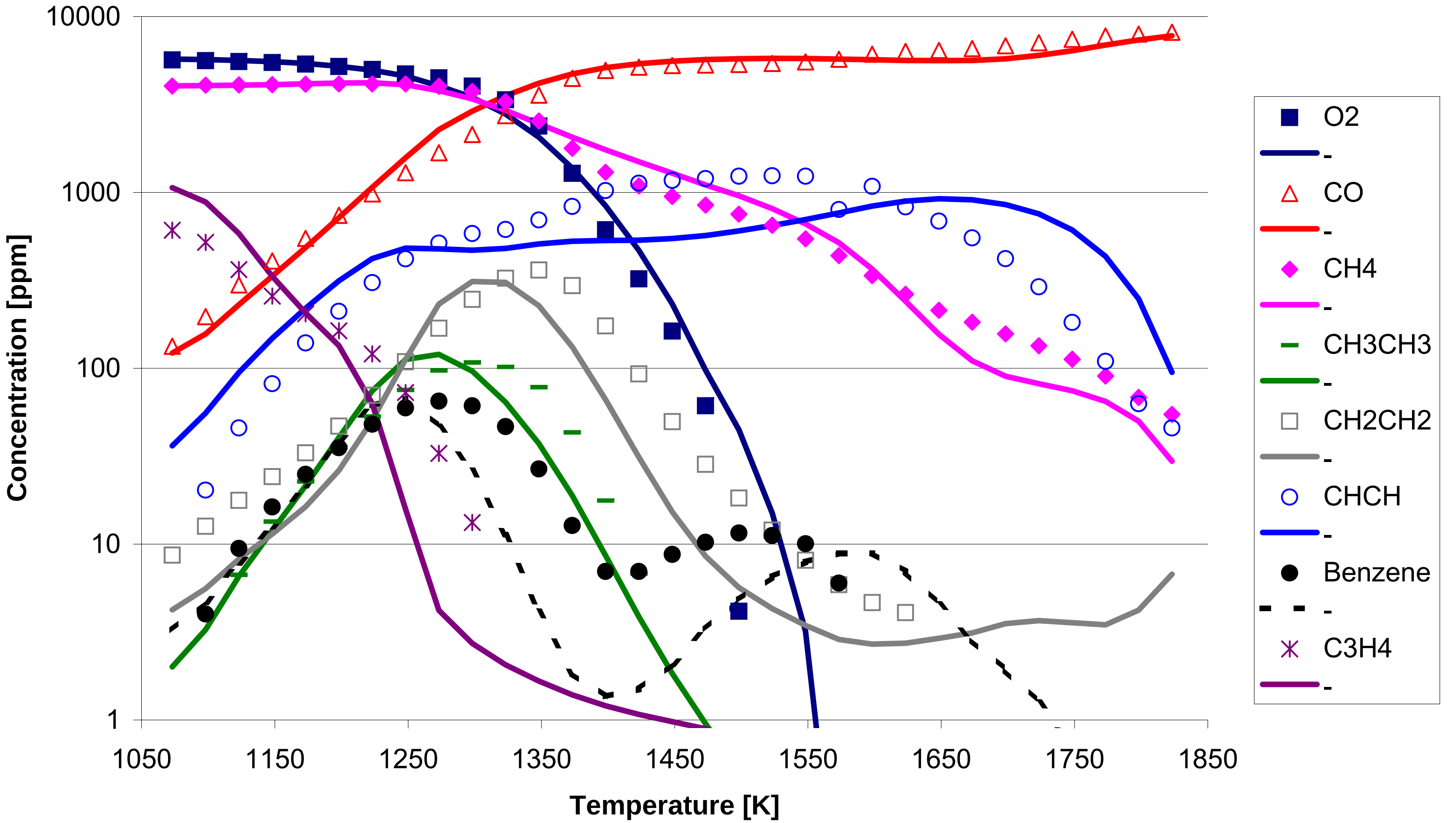


CH_4, 100 atm



Rasmussen et al., 2008

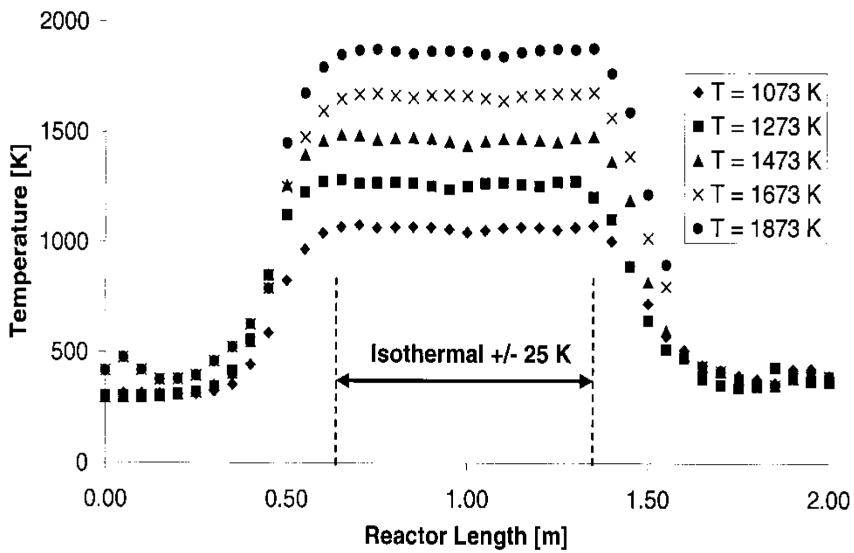
Flow reactor: Oxidation of CH_4 / C_3H_4 mixture



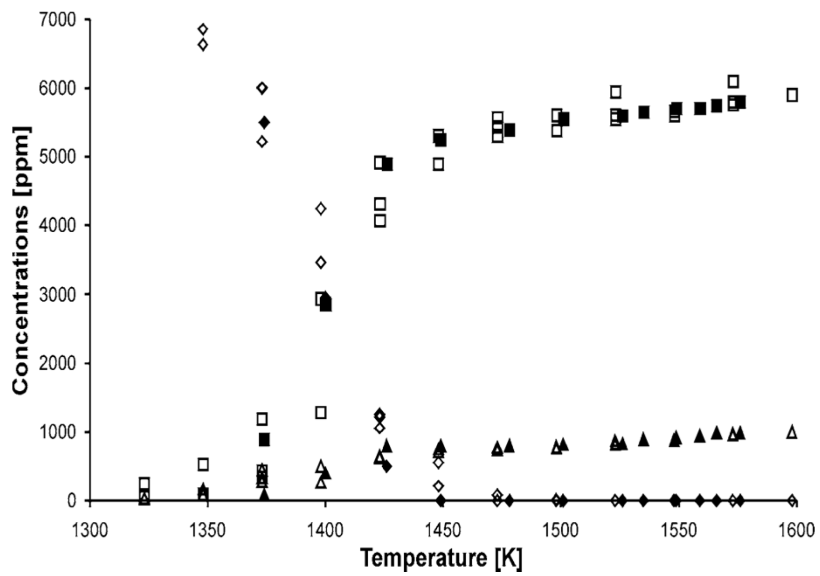
Skjøth-Rasmussen et al. (2002)

Flow reactor issues

Temperature



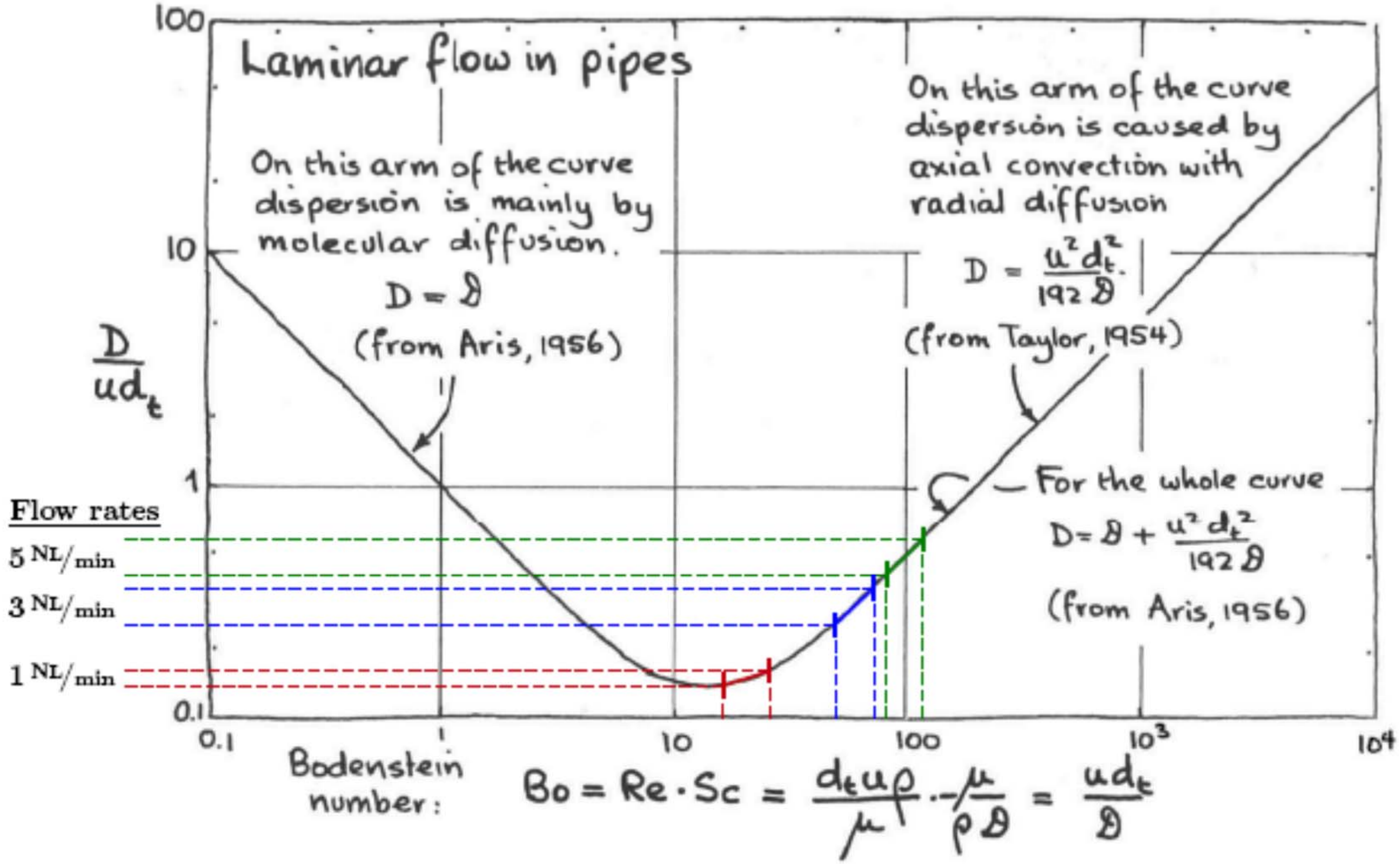
Surface reactions



CH_4 oxidation: 1.0% CH_4, 0.75% O_2; N_2
Quartz reactor (closed symbols)
Alumina reactor (open symbols)

Skjøth-Rasmussen et al. (2004)

The plug-flow approximation: Axial dispersion in the laminar flow regime



Levenspiel: The Chemical Reactor Omnibook

Macroscopic experimental techniques - concerns

- Batch reactor
  - Surface reactions, conditioning, temperature
- Flow reactor
  - Surface reactions, conditioning, temperature
- Jet-stirred reactor
  - Mixing, probe system
- Shock tube
  - Temperature and pressure
- Rapid Compression Machine (RCM)
  - Temperature and pressure
- Laminar, premixed flames
  - Interaction with burner surface, stabilization, probe effects

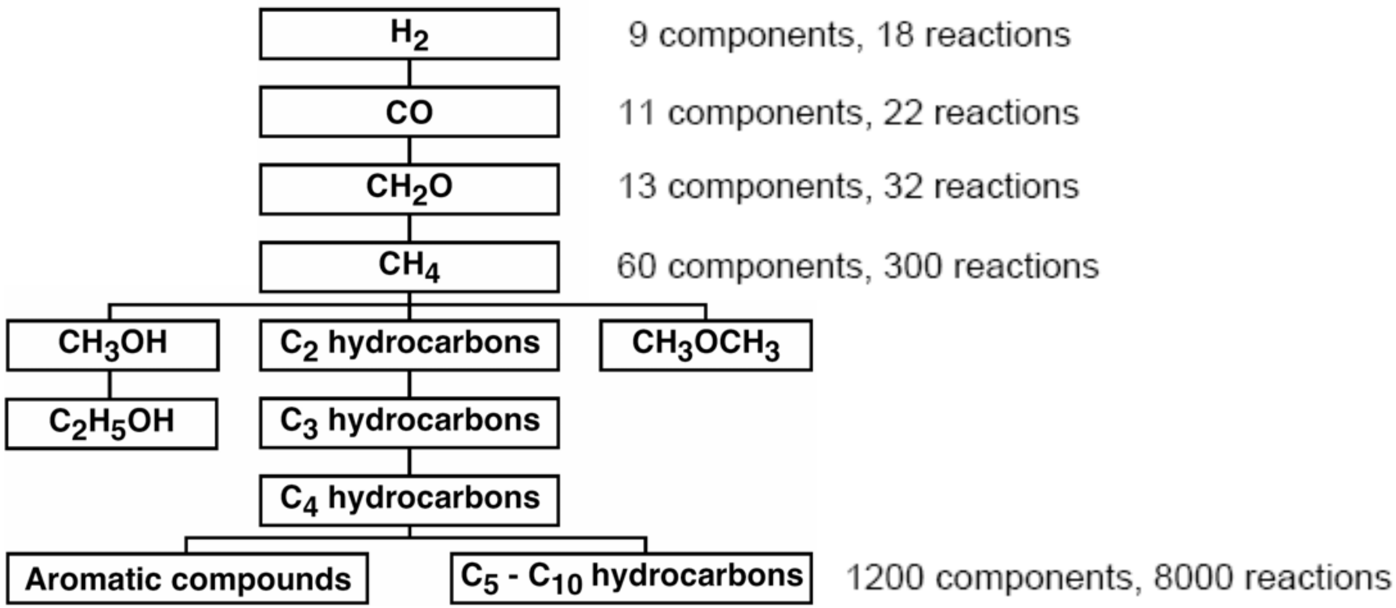
Development of reaction mechanism

	Known territory	Unknown territory
Small mechanism	H_2 oxidation	CH_4+H_2S oxidation
Large mechanism	Heptane oxidation	Biofuel(s) oxidation

Small mechanism: manageable in hand

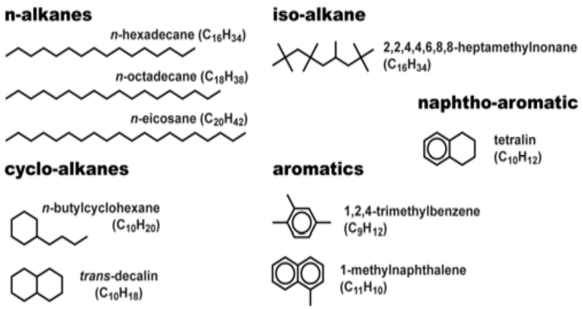
Known territory: detailed mechanisms available
with some predictive reliability

Hierarchichal structure of combustion chemistry

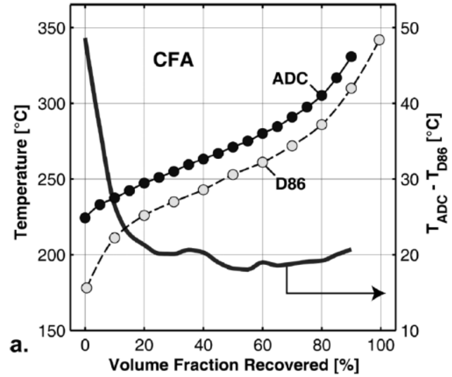


Why are (some) mechanisms so large?

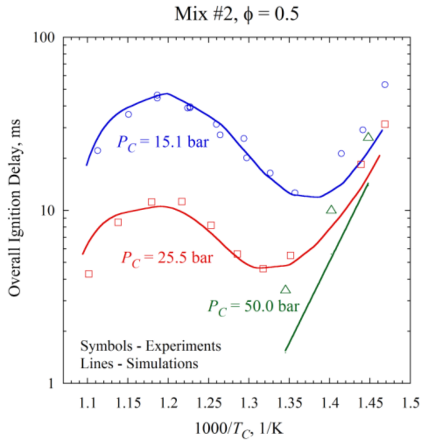
Need to predict complex behavior in "real" fuels



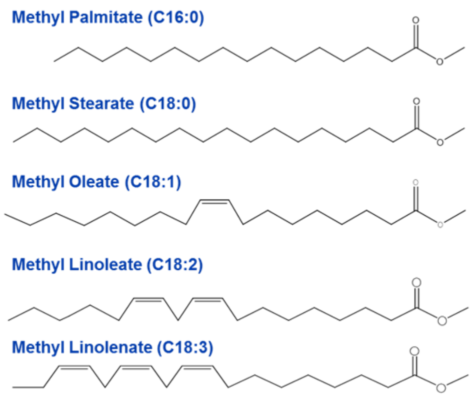
Many fuel components



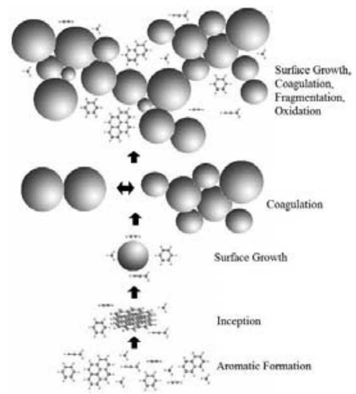
Fuel vaporization



Low temperature chemistry



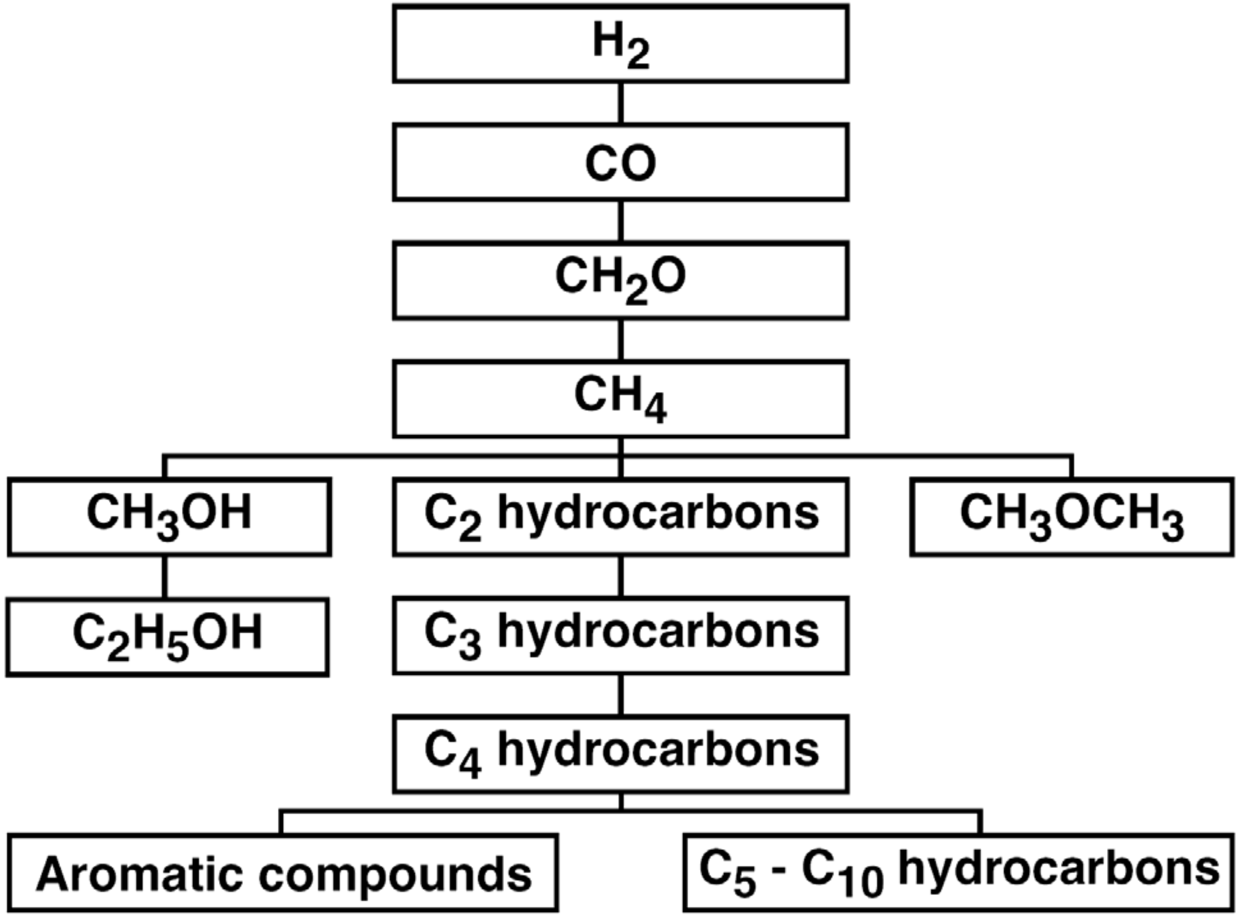
New fuel components



Soot

Slide courtesy of William Pitz, Henry Curran

Hierarchichal structure of combustion chemistry

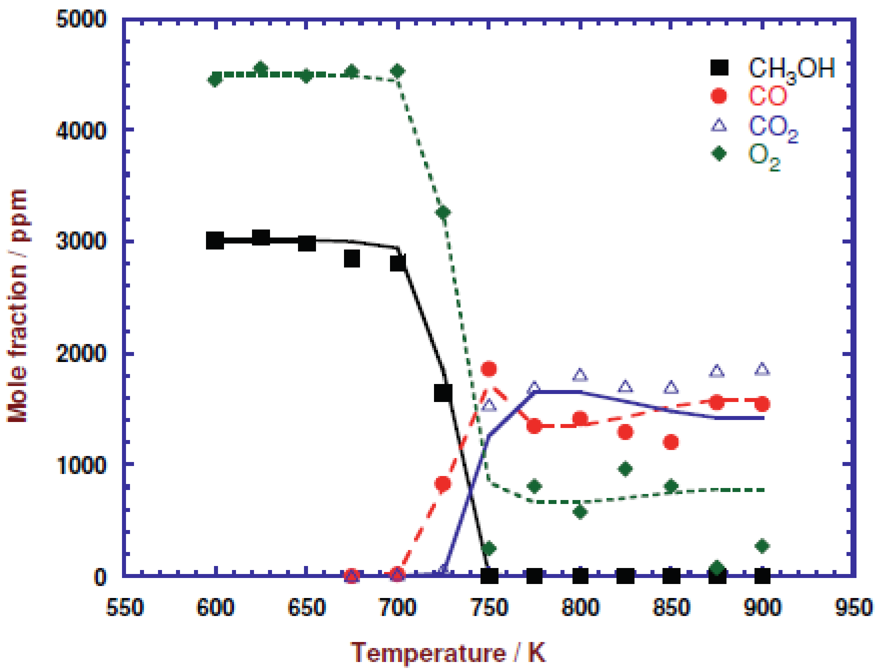


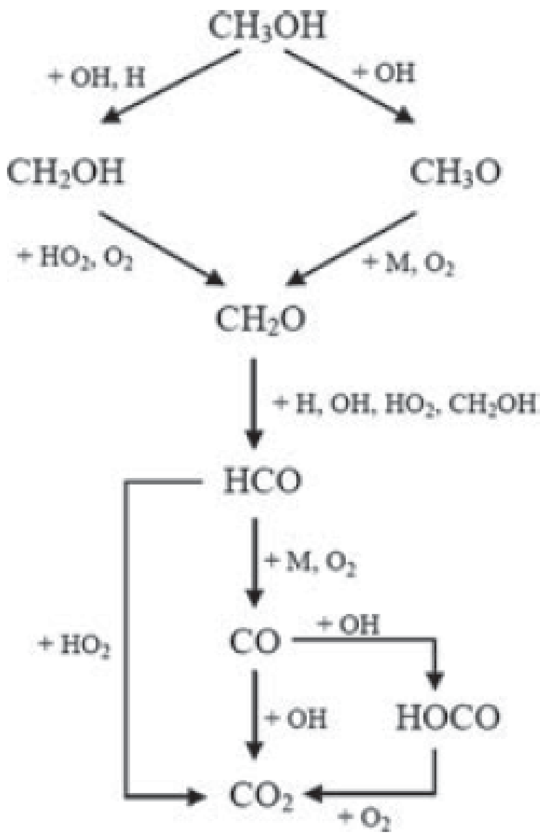
Analysis tools for mechanism development

- Sensitivity analysis
- Rate-of-production analysis

High-pressure oxidation of CH_3OH

Stoichiometric, 100 bar





Aranda et al. (2013)

Sensitivity analysis

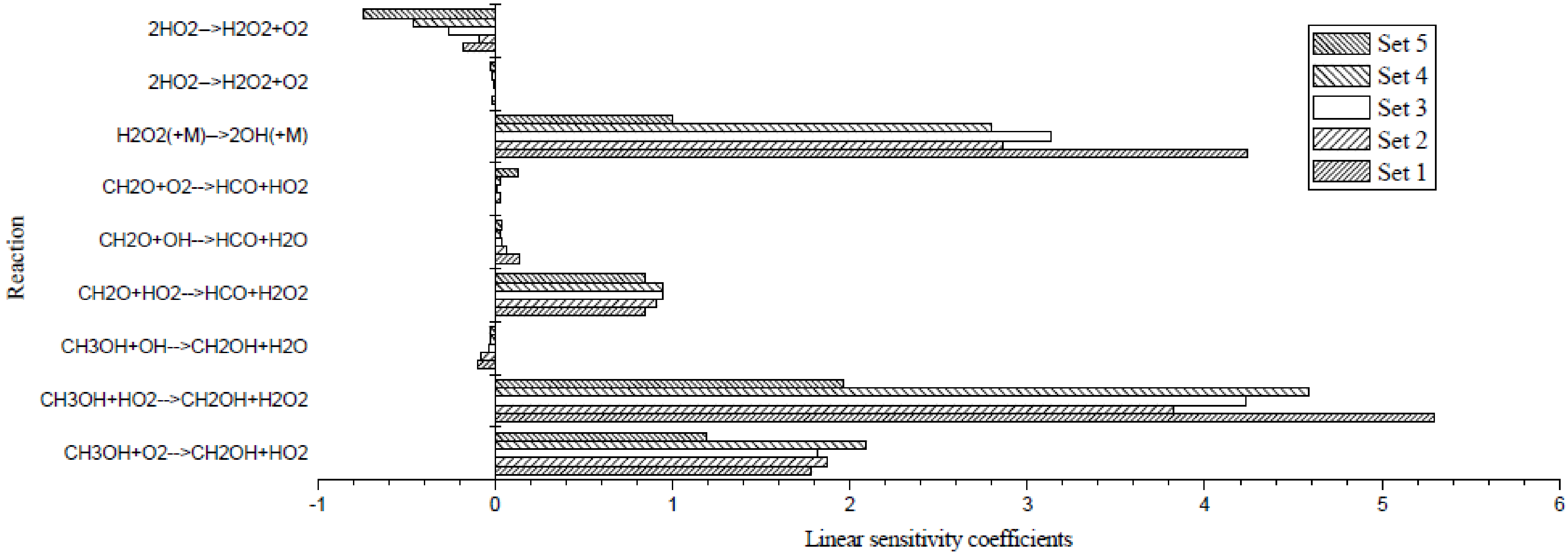
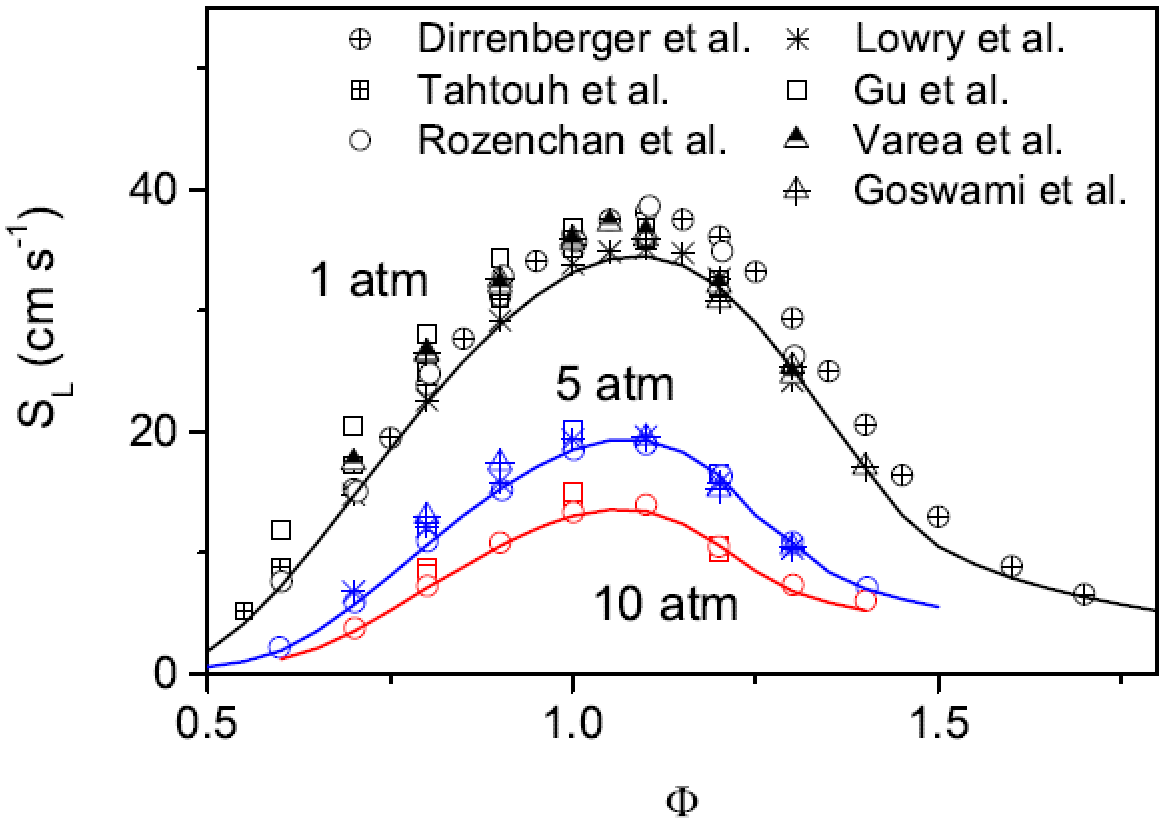
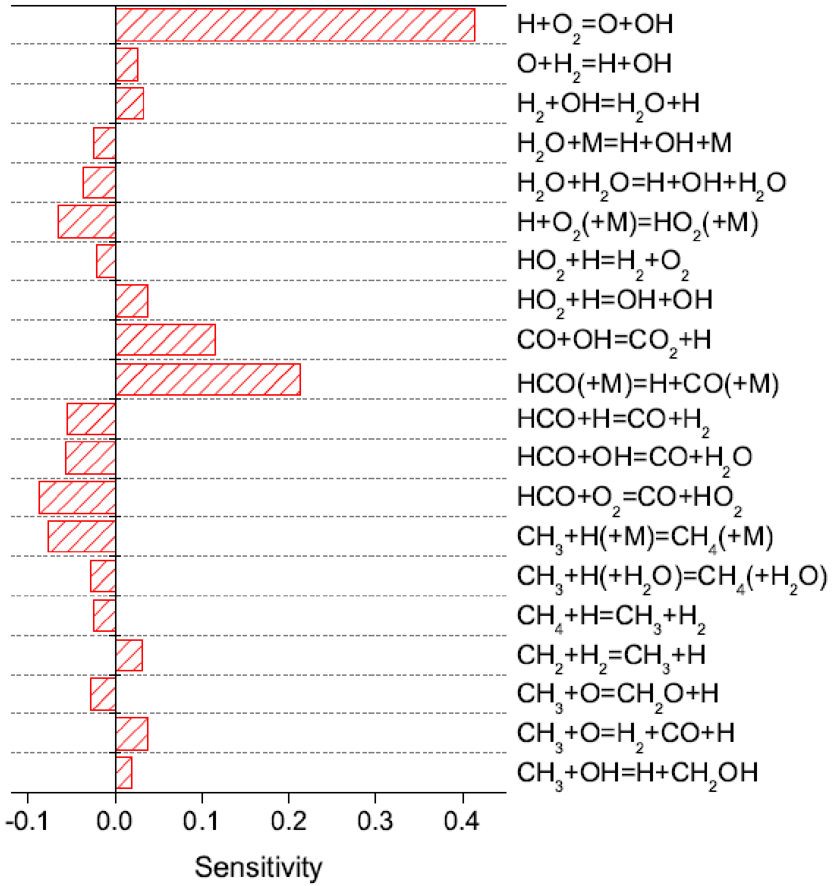


Figure 4: Linear sensitivity coefficients for CO for sets 1-5 given as $(A_i/Y_j)\cdot(\delta Y_j/\delta A_i)$.

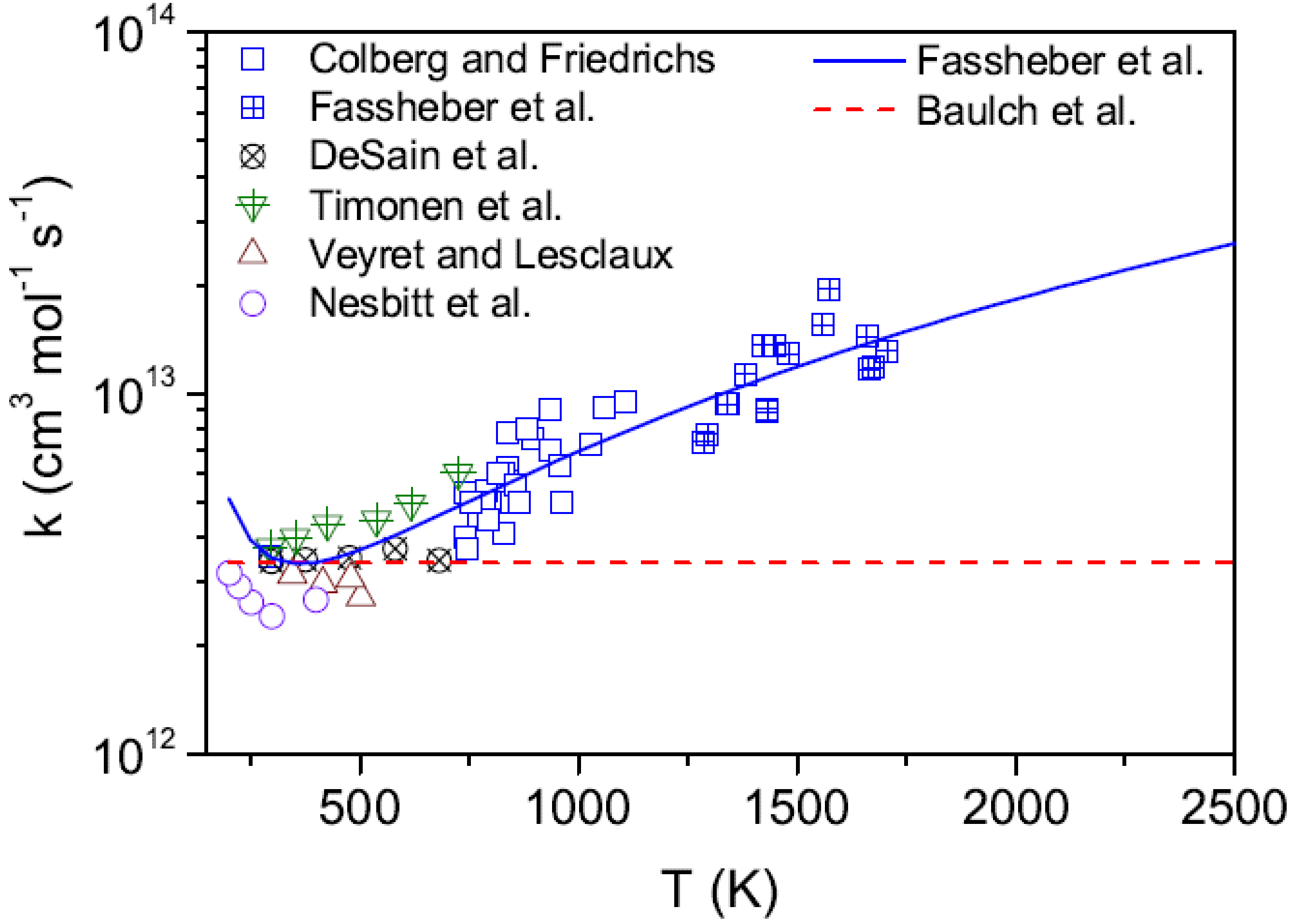
Laminar flame speed for CH_4



CH_4 flame speed – sensitivity analysis

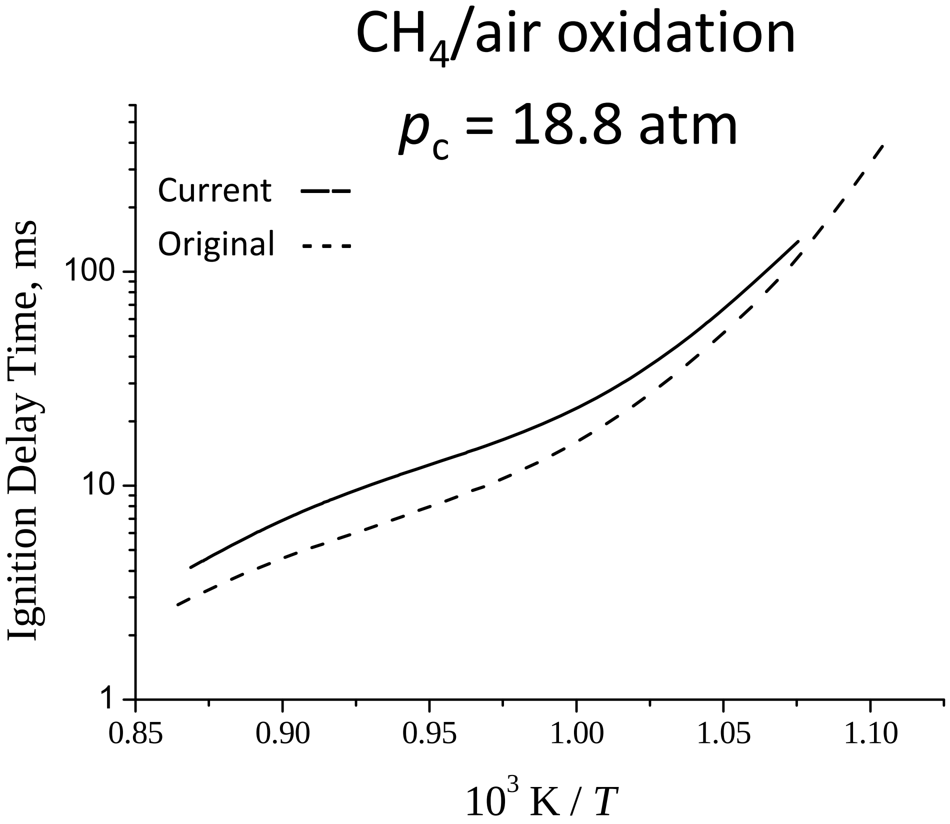


Rate constant for $HCO+O_2$



Effect of thermochemistry

- $\dot{C}H_3 + O_2 \rightleftharpoons CH_3\dot{O}_2$
- $CH_3\dot{O}_2 + \dot{C}H_3 = CH_3\dot{O} + CH_3\dot{O}$



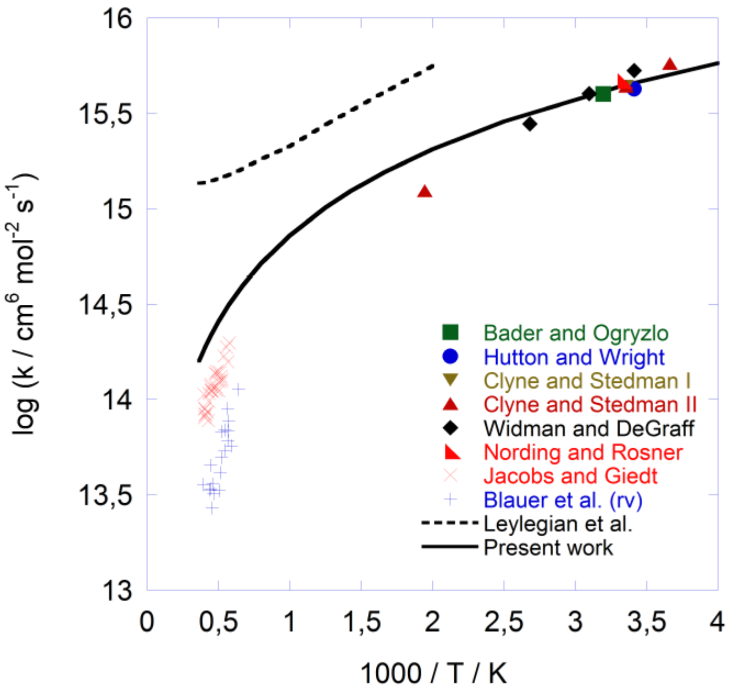
Slide courtesy of Henry Curran

Developing a detailed chemical kinetic model

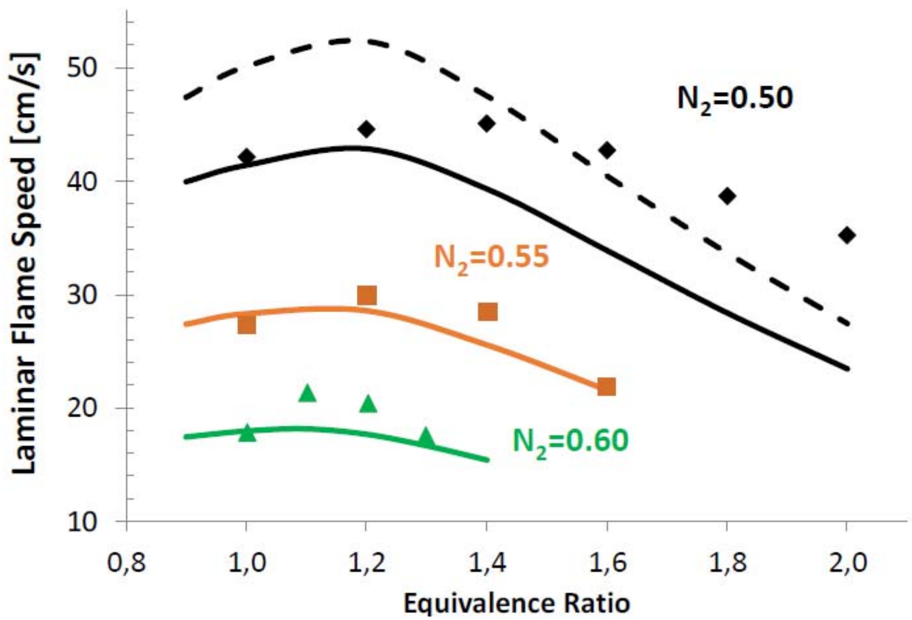
- Compile the best available species and reaction specific data
  - Experiment
  - Theory
  - Analogy / empirical
- Compare modeling predictions with the best available non-reaction-specific experimental data
  - Ignition delays, flame speeds, explosion limits
  - Detailed characterization data (species concentrations, etc.)
- Refine
  - Microscopic accuracy (fundamental model)
  - Macroscopic accuracy (engineering model)

Modeling approaches

Microscopic accuracy



Macroscopic accuracy



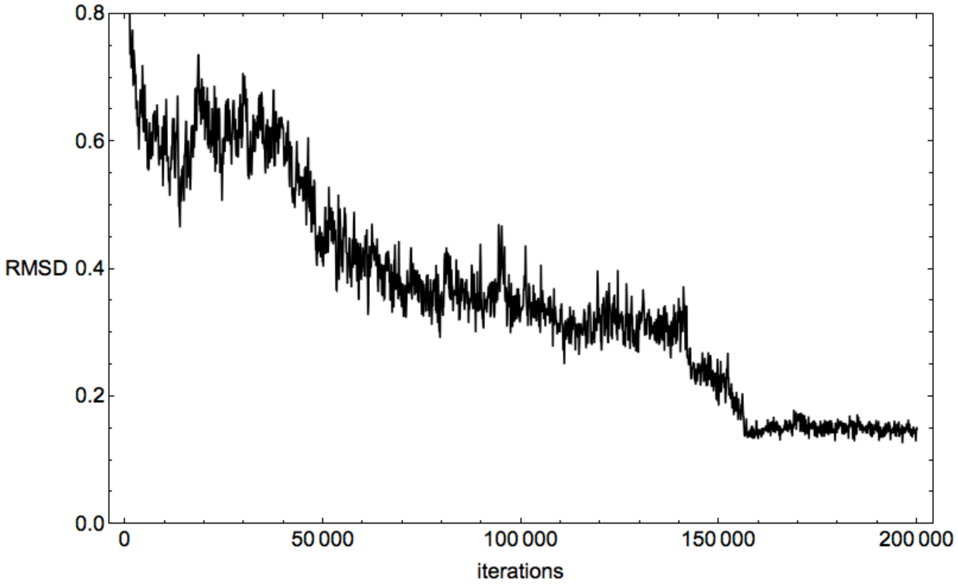
Engineering (optimized) models

Do not make changes

- Thermo
- Rate constants

- Often impressive predictive capabilities
- Tend to disguise scientific issues

Fundamental (non-optimized) models



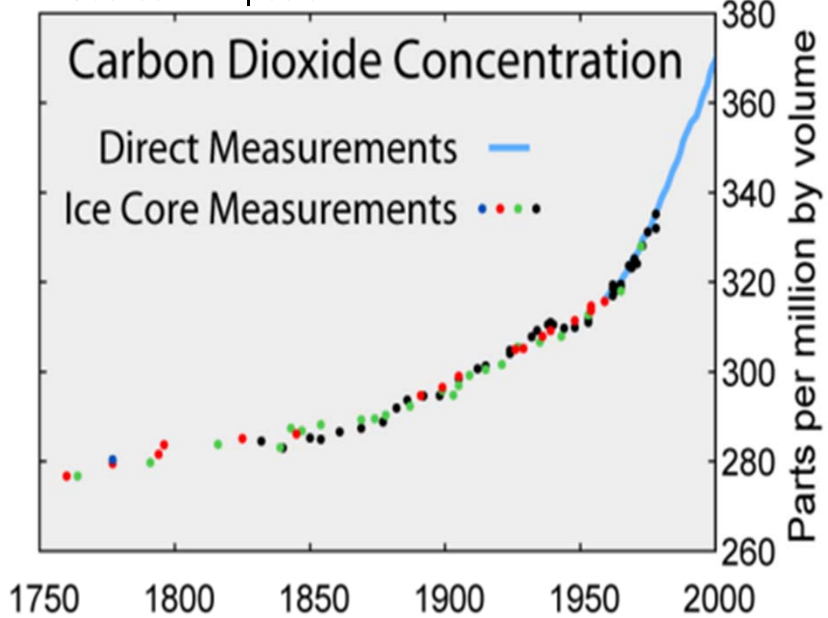
- Scientifically sound
- Represent the present understanding of the chemistry
- Often lower accuracy compared to engineering models (within optimized regime)

Research issues

- Control pollutant formation
  - Unburned hydrocarbons
  - PAH
  - Soot
  - Nitrogen oxides
- Abate global warming
  - Use of biomass and bio-derived fuels
    - Formation of liquid bio-derived fuels
    - Kinetics of bio-derived fuels
    - Use of alcohols such as ethanol in Diesel engines
    - Chemistry of KCl
  - Oxy-fuel combustion
  - Formation and oxidation of soot

The largest challenge: the climate issue

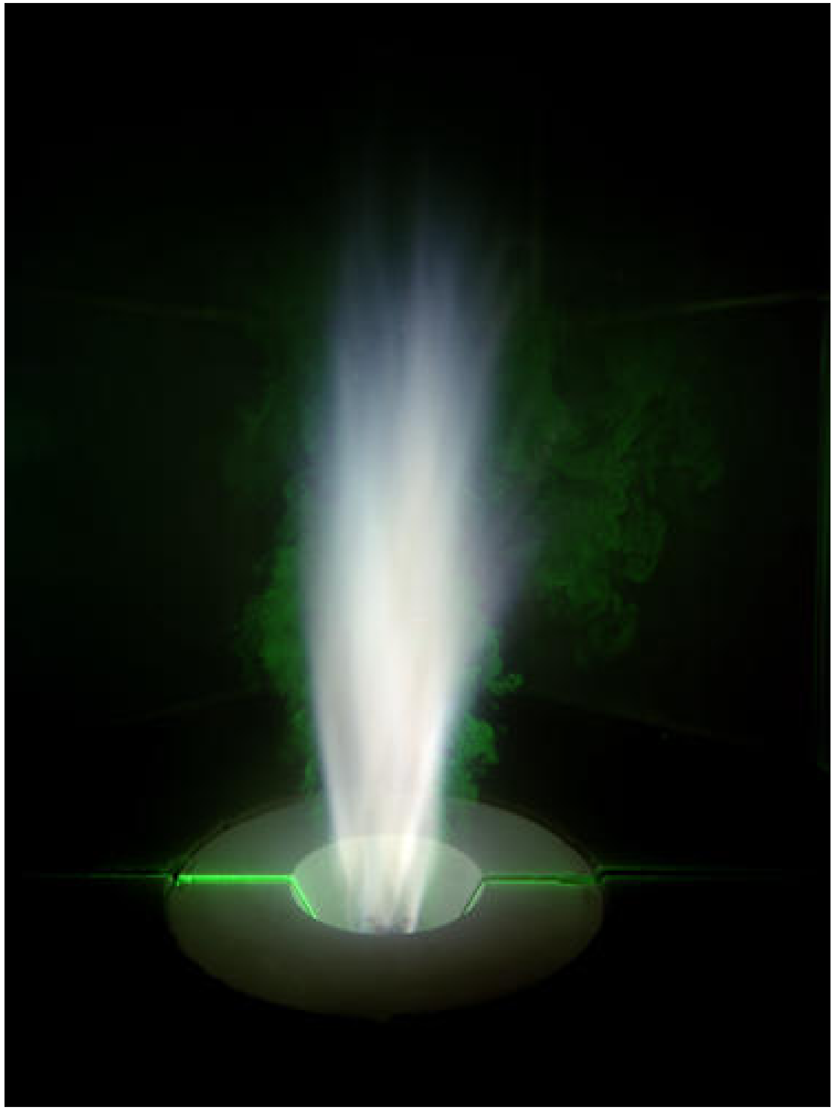
Source: Wikipedia



- A dramatic reduction of the CO_2 emission is required, according to UN recommendations
- The power industry, as a major contributor, is dedicated to this challenge

Clean thermal energy: Combustion of hydrogen

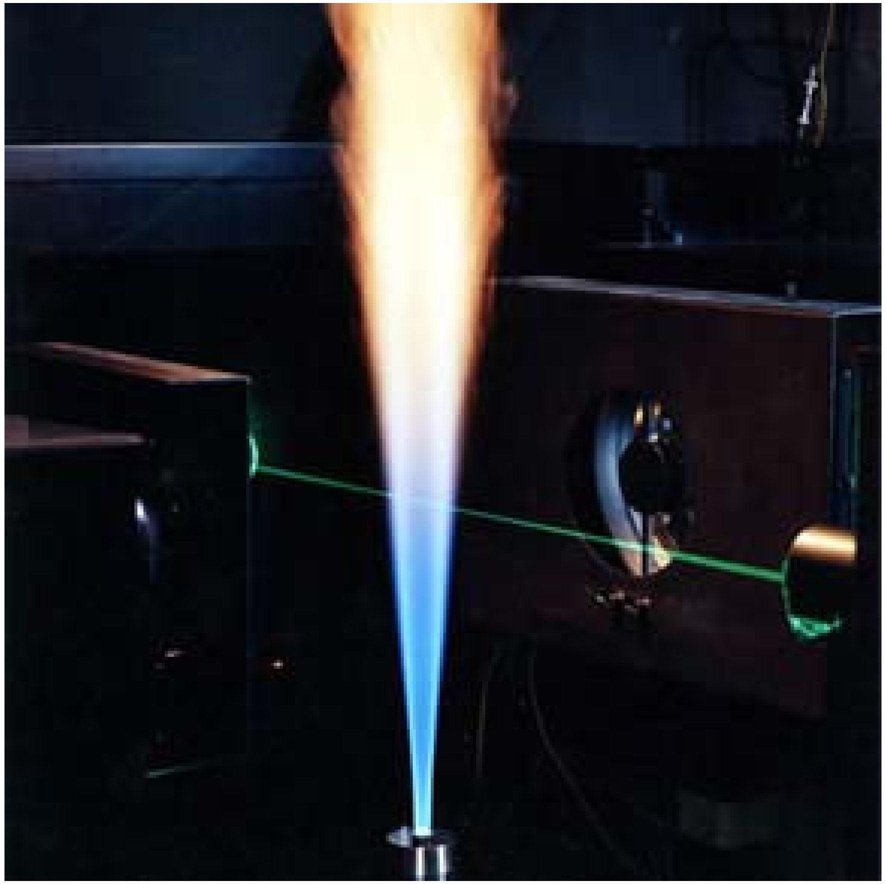
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$



The cleanest fossil fuel: natural gas

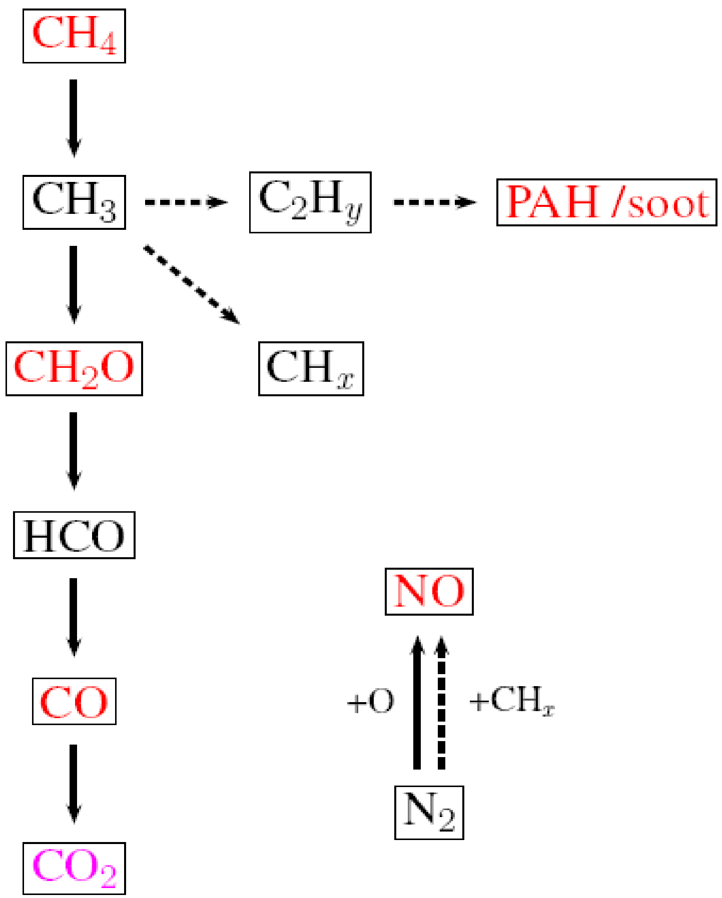
Natural gas is an easy fuel

Yilmaz et al., 2009



Source: Sandia National Laboratories

Pollutant formation
- gaseous fuels



Fuel-lean Fuel-rich

Emission control:

Combustion modification

Flue gas cleaning

Change of fuel

Increase efficiency

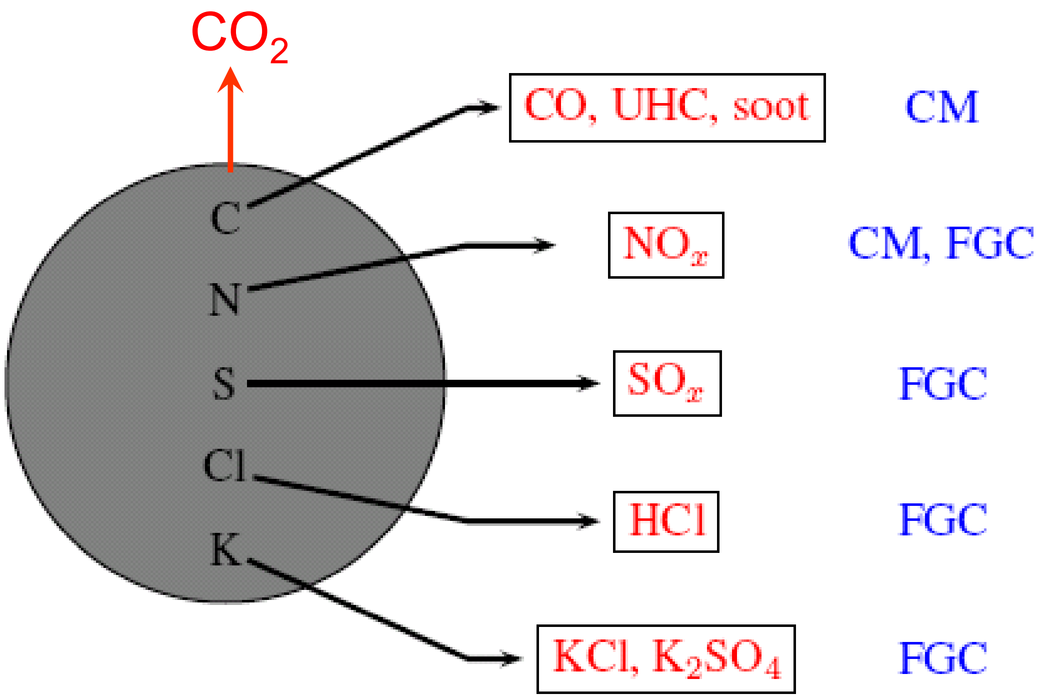
Solid fuels

Solid fuels are challenging:

handling, combustion, emissions, residual products

For coal: also CO_2

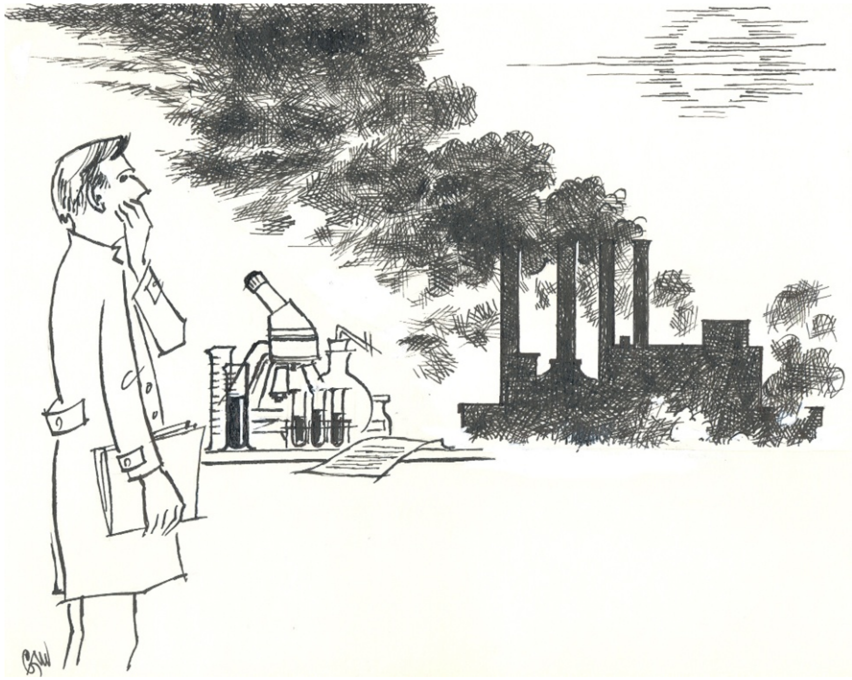
Pollutant formation – solid fuels



CM: Combustion modification

FGC: Flue gas cleaning

Sustainable Thermal Processes - Challenges



- Thermal processes remain important:
  - Heat and power production
  - Transport
  - Industrial processes
- Challenges:
  - Pollutant formation
  - Greenhouse gases
    - Efficiency
    - Fuel switching
    - New thermal processes