Chemical kinetics

Procida June 2015

Module 4

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Module 4

- Challenges in combustion chemistry (PG)
- Future modeling possibilities in OpenSMOKE (AC)
- Task 3: Flame inhibitors
  - Introduction (AC)
  - Solving using OpenSMOKE++ (AC, PG)

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

Challenges in fuel oxidation chemistry

- Extend fuel range to large hydrocarbons and oxygenated hydrocarbons (”practical fuels”)
- Secure the modeling foundation: H_2 and small hydrocarbons
- Extend range of characterization to high pressure

Current challenges in combustion chemistry

- Extend fuel range to large hydrocarbons and oxygenated hydrocarbons (”practical fuels”)
- Secure the modeling foundation: H_2 and small hydrocarbons
- Extend range of characterization to high pressure

High-pressure flow reactor

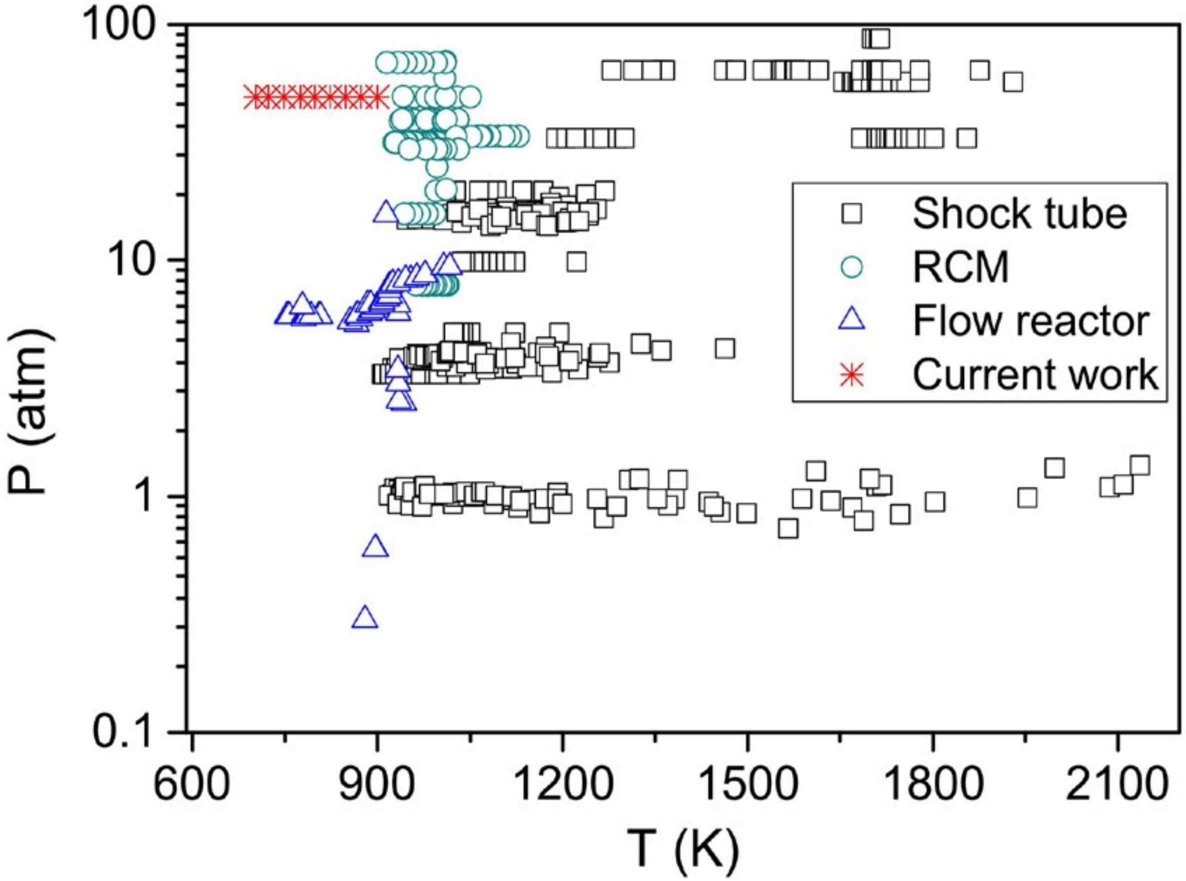
- Temperature: $<925\,K$
- Pressure: 10–100 bar
- Flow: 1–5 NL/min
- Reaction zone: $\sim$50 cm
- Residence time: 2–60 s

- Quartz reactor to minimize surface reactions
- Measurable species: H_2, O_2, N_2, CO, CO_2, most hydrocarbons/oxygenates, SO_2, H_2S, NO_x, CH_3NO_2

High-pressure chemistry program: Background

- Generally few data available for hydrocarbon oxidation at high pressure
  - Shock tubes and rapid compression engines (mostly > 1000 K and < 50 bar)
  - Flow reactors and jet-stirred reactors (mostly < 15 bar)
  - Laminar premixed flames (diagnostic limitations at high pressure)
  - Super-critical oxidation reactors
- High pressure, medium temperature chemistry important for
  - Gas-to-liquid processes
  - Ignition in engines
  - Extension of the boundaries of kinetic model development and validation

High-pressure H_2 ignition and oxidation



Hashemi et al. (2014)

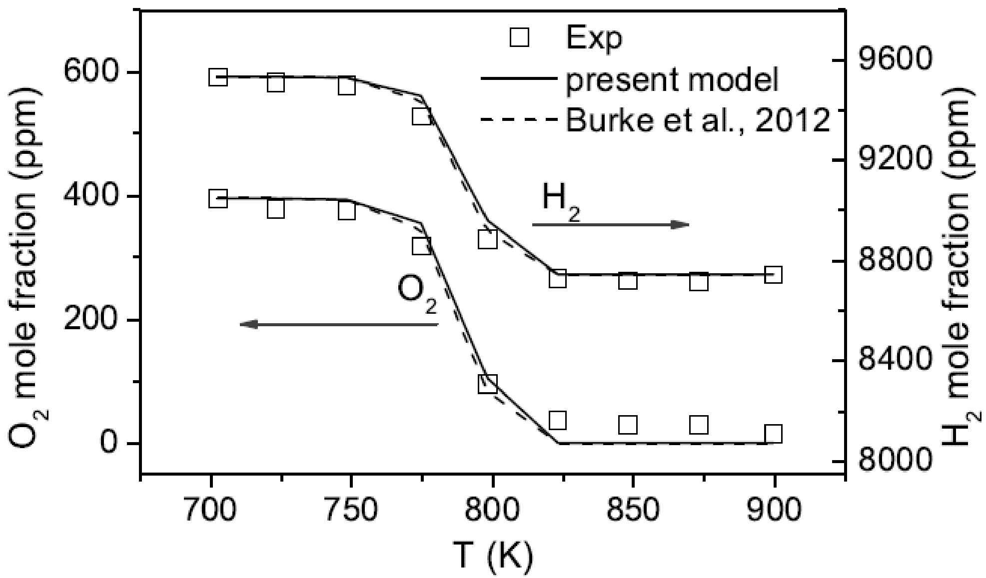
Objectives of high-pressure program

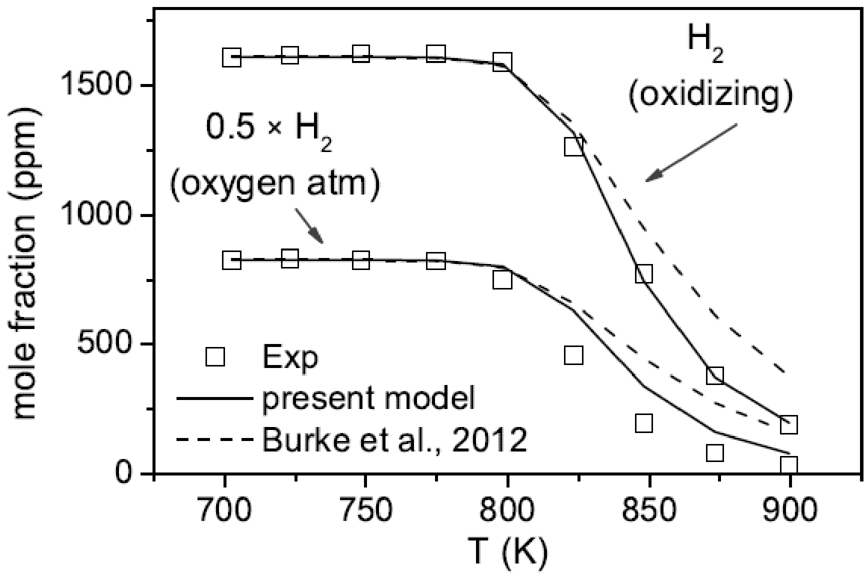
- Characterize experimentally high-pressure oxidation at 600-925 K, varying the following parameters
  - Fuels
    - H_2
    - CH_4, C_2H_6, CH_4/C_2H_6 blends, C_2H_4, C_2H_2
    - CH_3OH, C_2H_5OH, DME
    - Diesel surrogates
  - Pressure (20-100 bar)
  - Temperature (600-925 K)
  - Stoichiometry ($0.2 < \lambda < 20$)
  - Presence / absence of NO_x
- Analyze results in terms of a detailed reaction mechanism

H_2 oxidation at 50 bar

Rich (φ=12)

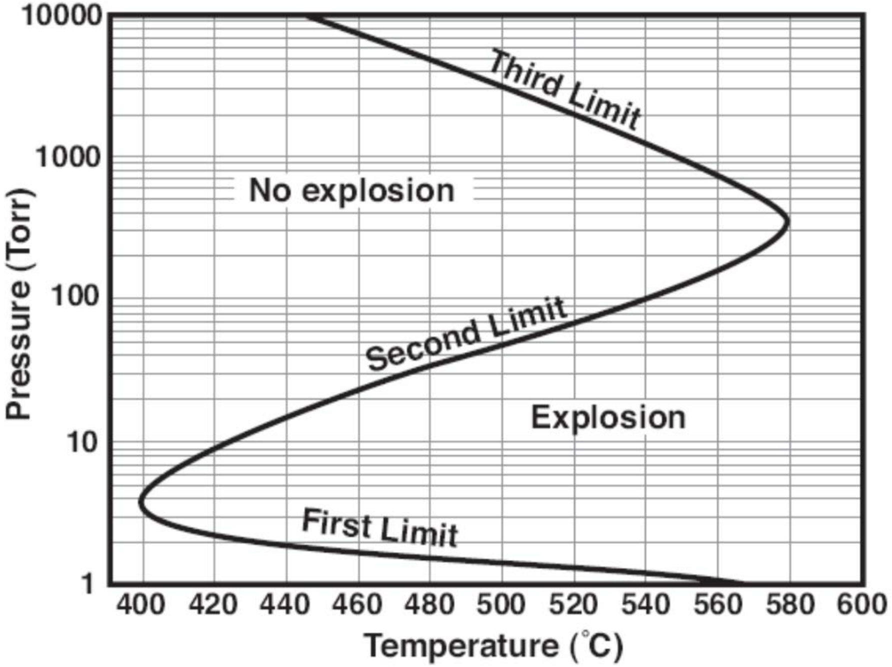
Lean (φ=0.05 / 0.0009)





Hashemi et al. (2014)

Third explosion limit for H_2



Chain-branching:

$H_2 + HO_2 \rightarrow H_2O_2 + H$

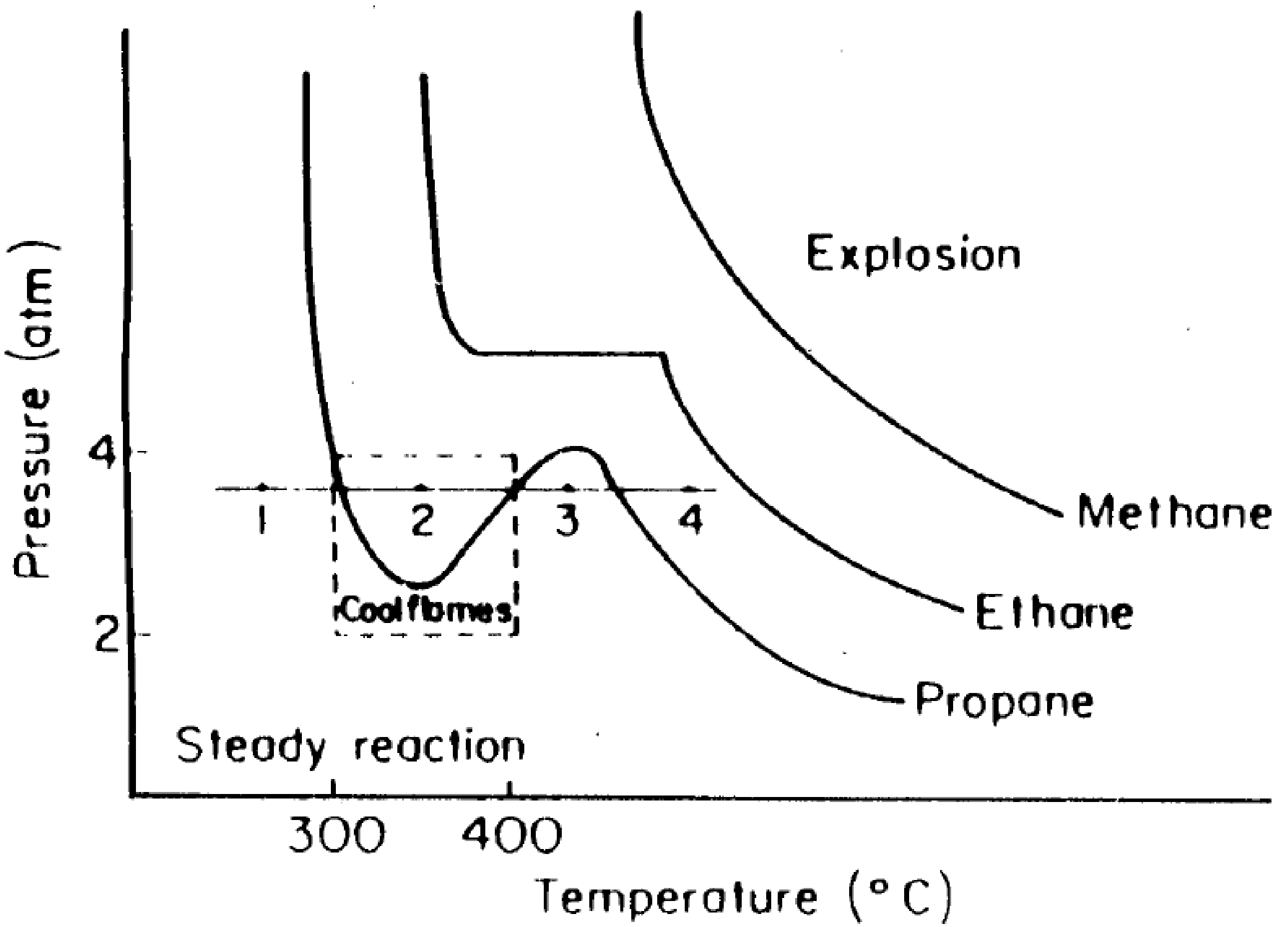
$H_2O_2\ (+M) \rightarrow OH + OH(+M)$

Termination:

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 + OH \rightarrow H_2O + O_2$

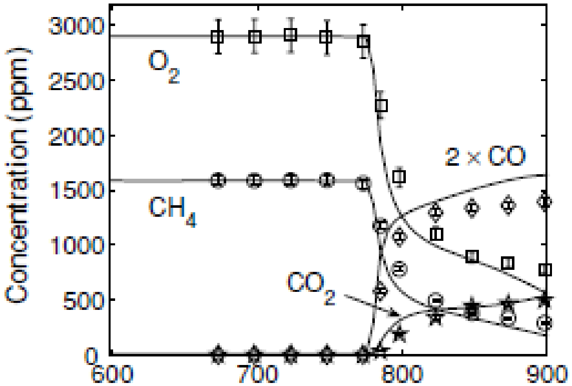
Explosion limits



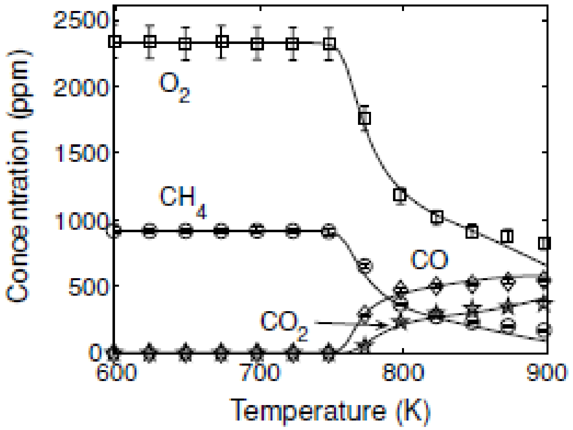
Effect of high pressure on fuel oxidation

- The $H+O_2+M = HO_2+M$ reaction is promoted compared to $H+O_2 = O+OH$
- Rate constants for pressure-dependent reactions approach high-pressure limit
- Addition reactions may become more important
    - Addition of OH to fuel molecule
    - Addition of HO_2 to fuel molecule
    - Addition of O_2 to fuel-derived radicals

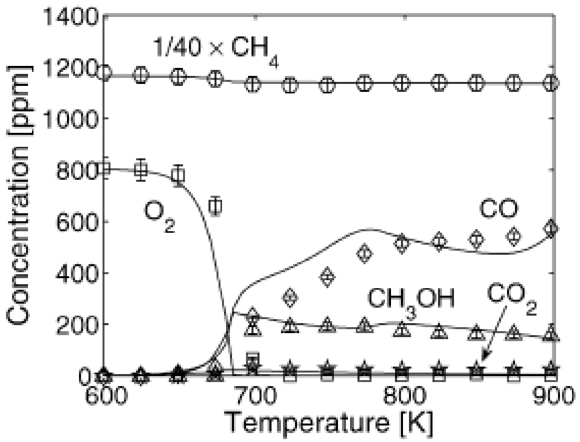
High-pressure oxidation of CH_4 (100 atm)

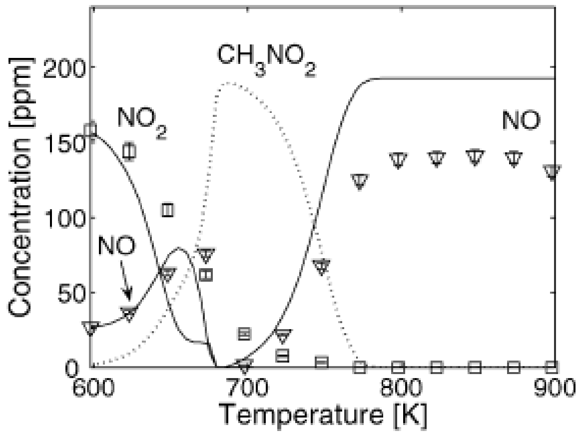


CH_4



CH_4/C_2H_6

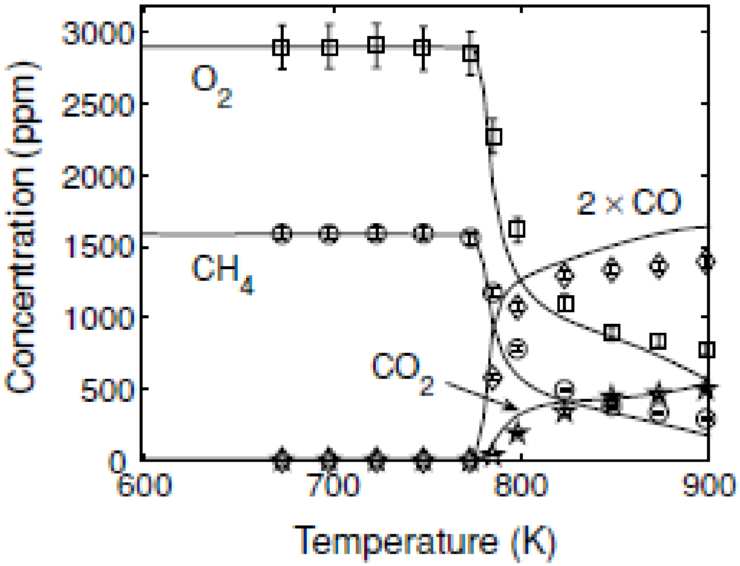


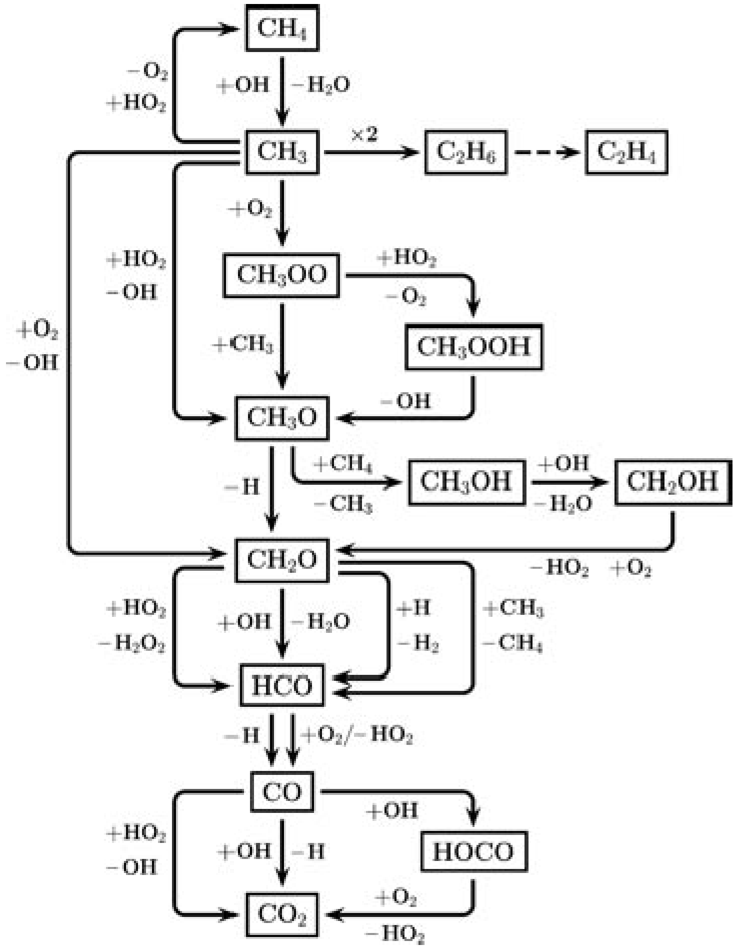


CH_4/NO_x

Rasmussen et al., 2008

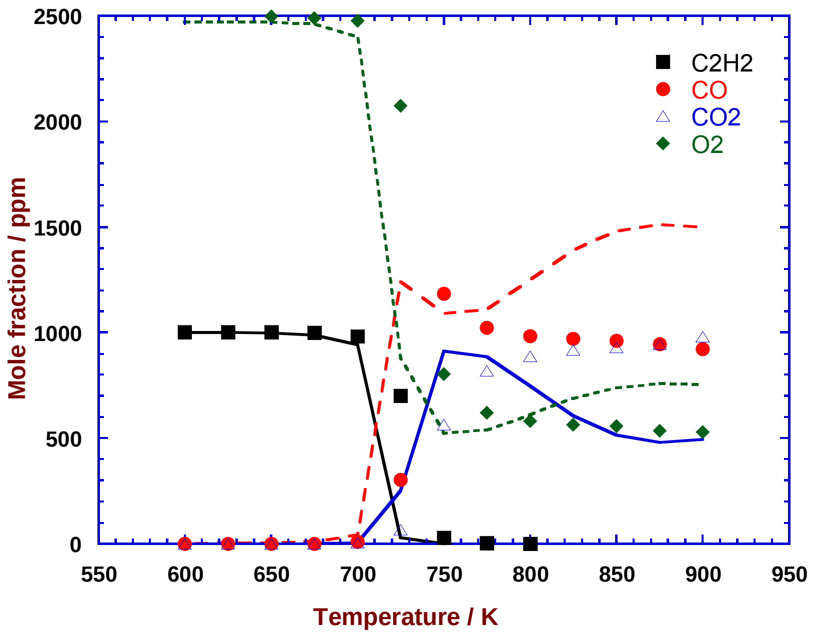
Reaction pathways for CH_4 at high pressure





Rasmussen et al. (2008)

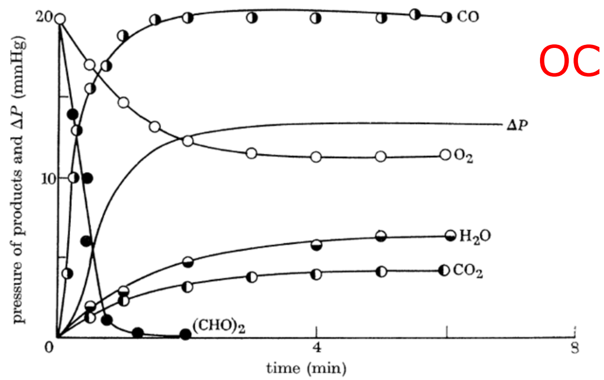
High-pressure oxidation of C_2H_2
- and related chemistry



C_2H_2

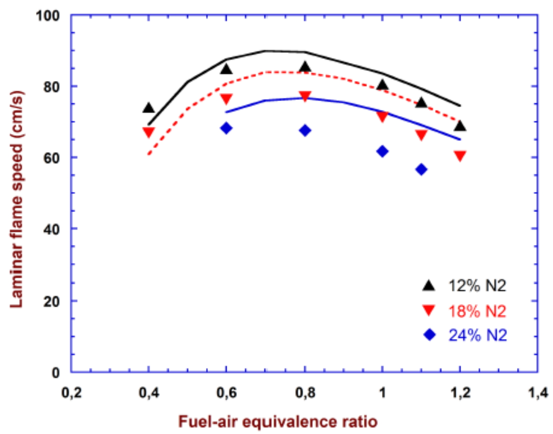
Flow reactor (60 atm)
Gimenez et al. (unpublished)

$$C_2H_2 \xrightarrow{+OH} C_2H_2OH \xrightarrow{+O_2} \begin{array}{l} OCHCHO + OH \\ HOCHO + HCO \end{array}$$



OCHCHO

Oxidation in static reactor (603 K)
Hay and Norrish (1965)

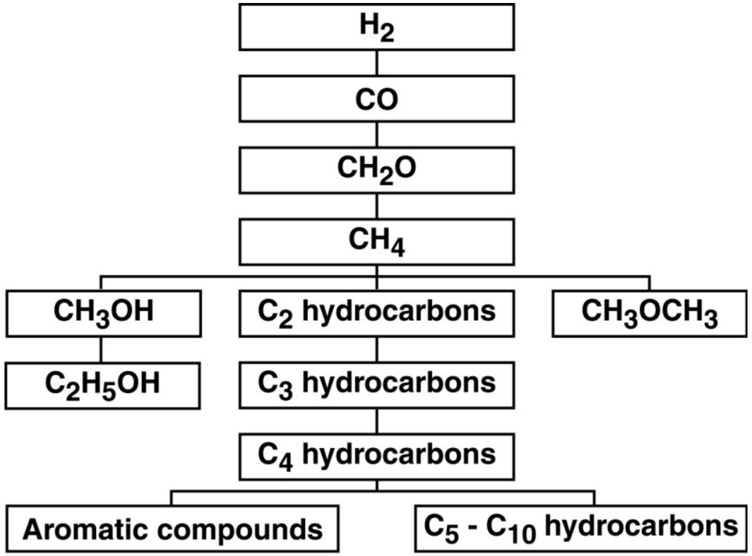


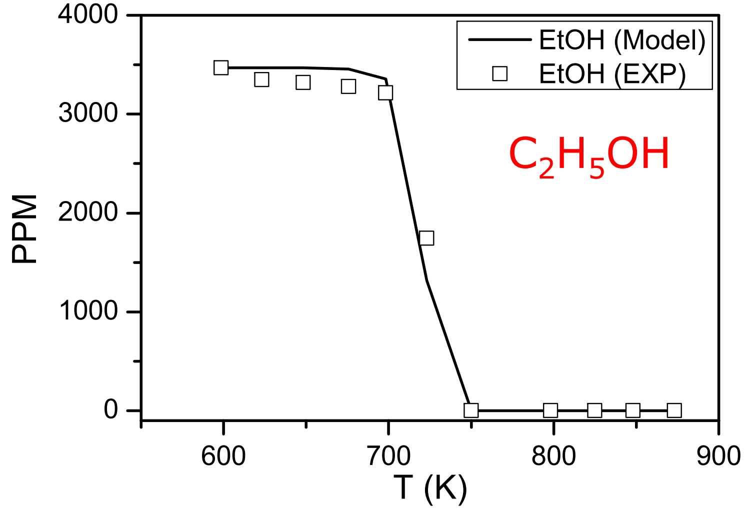
HOCHO

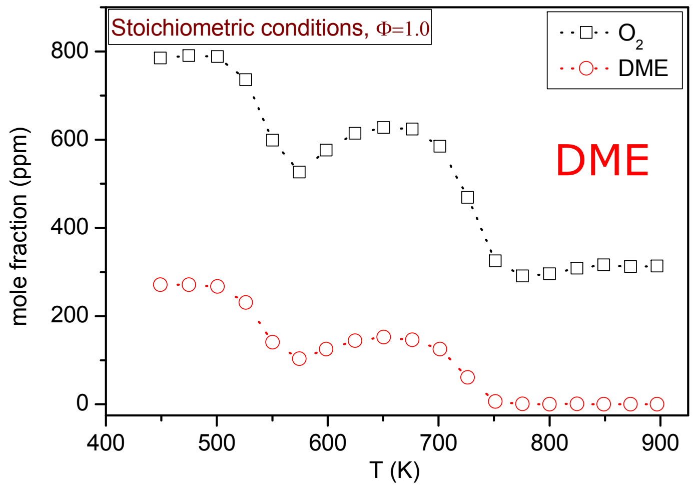
Laminar flame speed (433 K)
De Wilde and van Tiggelen (1968)
Marshall and Glarborg (2014)

Hydrocarbon oxidation – high pressure

High pressure, medium temperature chemistry:
- Ignition in engines
- Gas-to-liquid processes
- Extension of the boundaries of kinetic model development and validation



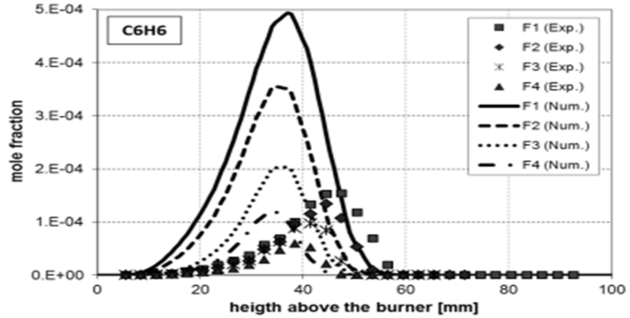




Flow reactor, 50 bar (Hashemi et al., 2013)

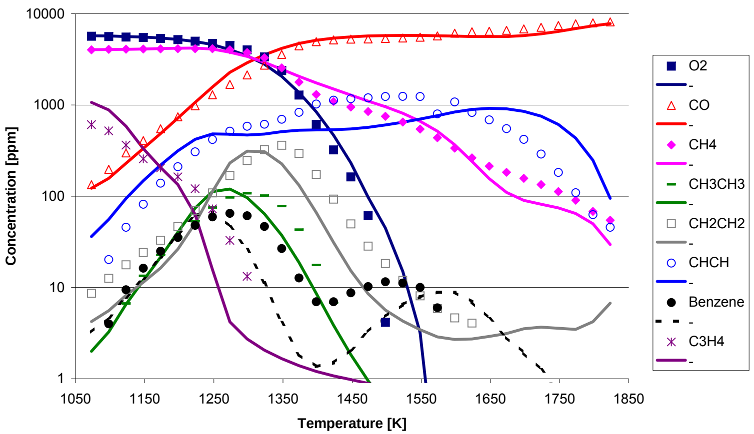
Formation of PAH and soot

CH$_4$/air co-flow flame



Couci et al. (2012)

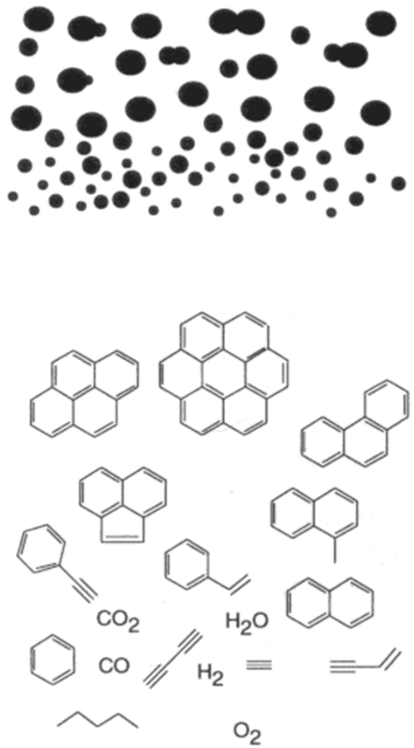
CH$_4$/C$_3$H$_4$ oxidation in flow reactor



Rasmussen et al. (2004)

Combine flow reactor and advanced diagnostics:

- Increase temperature in steps
- Step through fuel → C$_6$H$_6$ → PAH → soot



Nitrogen chemistry

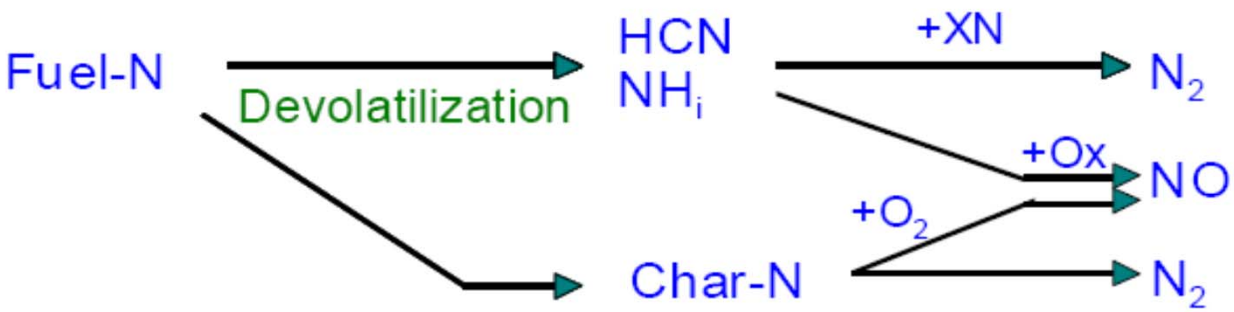
- Emissions of nitrogen oxides have been a concern since the 1970’s
- Extensive R&D has lead to efficient measures
- New challenges
  - Regulations increasingly stringent
  - New fuels and fuel mixtures
    - Natural gas (Thermal NO, prompt NO)
    - Biomass (Fuel-NO, mostly from amines)
  - Low-NO_x burners and Selective Catalytic Reduction of NO (SCR) not applicable for range of fuels and technologies

Formation mechanisms for NO

Fixation of atmospheric N_2

$$O + N_2 \rightarrow NO + N \qquad (>1800\ K)$$
$$CH + N_2 \rightarrow HCN + N$$
$$O + N_2 + M \rightarrow N_2O + M \qquad (\text{High pressure})$$

Conversion of fuel nitrogen

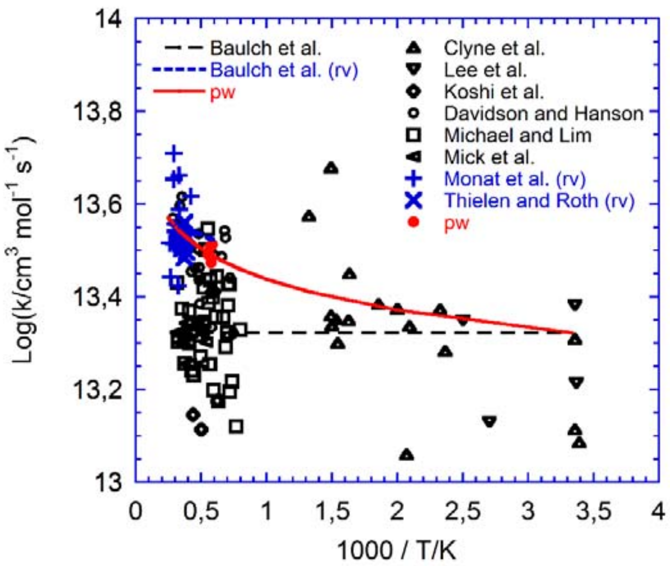


Thermal NO formation

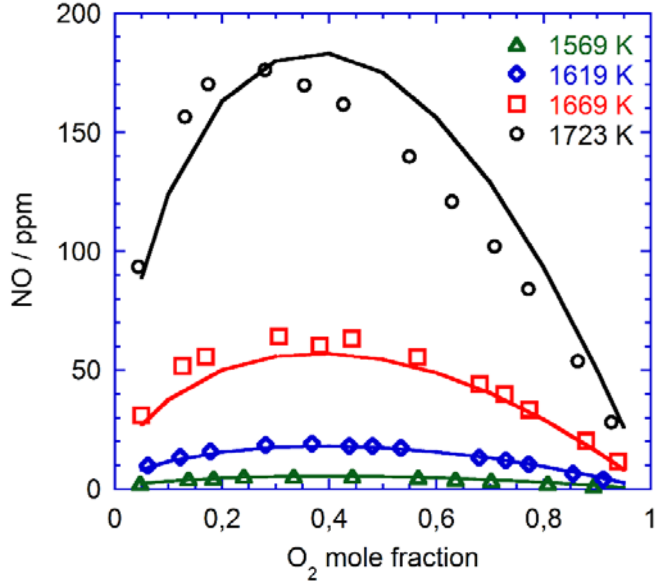
- Mechanism well known
- $O+N_2$ = N+NO rate limiting
- The rate constant accurate only within a factor of two
- Present work:
    - N_2/O_2 in a flow reactor
    - Compare model with literature data

Abian et al. (2014)

N+NO → N_2+O



Flow reactor results

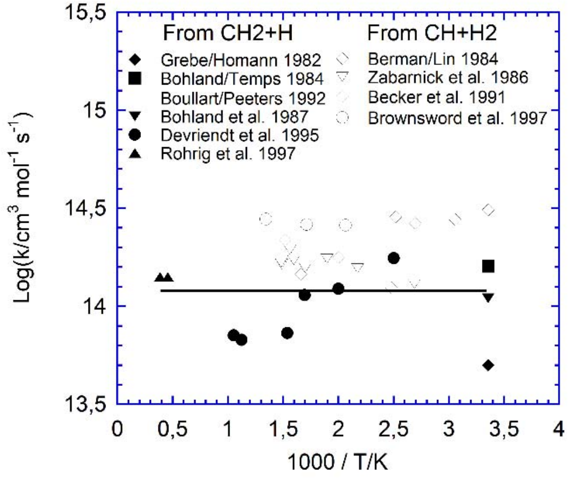


Prompt NO formation

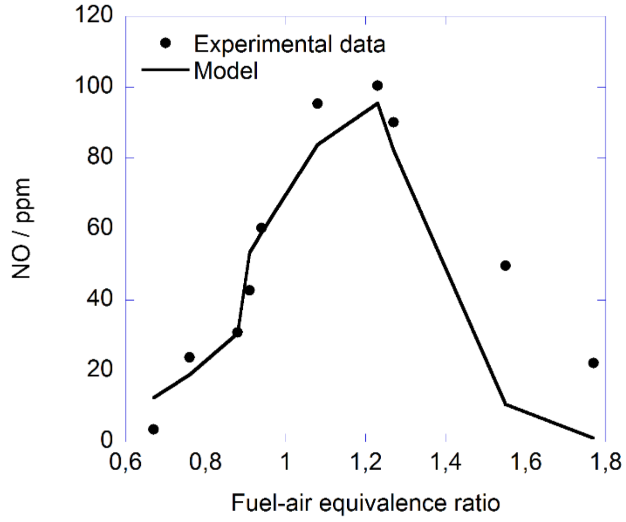
- Mechanism:
  - $CH+N_2$ = NCN+H
  - $NCN+O_x \rightarrow NO, N_2$
- Uncertainties:
  - Heat of formation of NCN
  - NCN+H rate constant
  - Formation and destruction of CH_i radicals
- Present work:
  - High level theory
    - $\Delta H_{f,298}$(NCN)
    - NCN+H, CH_2+O_2, $CH+H_2O$
  - Compare model with literature data

Klippenstein et al. (2014)

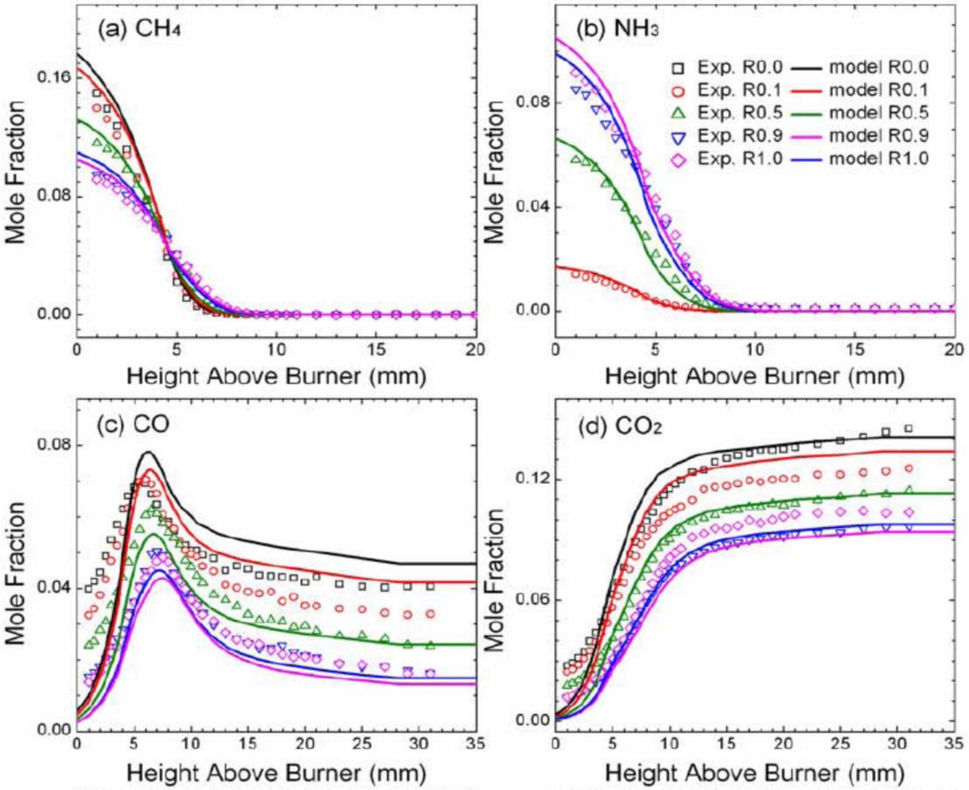
$CH_2+H \rightarrow CH+H_2$



Jet-stirred reactor results (CH_4/air; Bartok et al., 1972)



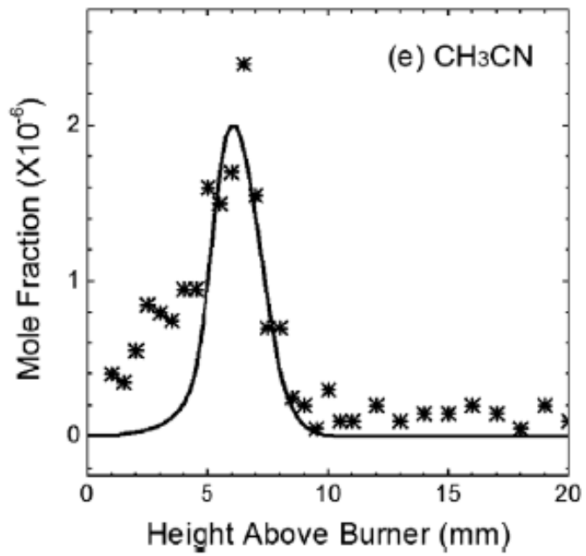
Homogeneous fuel nitrogen chemistry



$CH_4/O_2/Ar$ flames doped with NH_3

Tian et al. (2009)

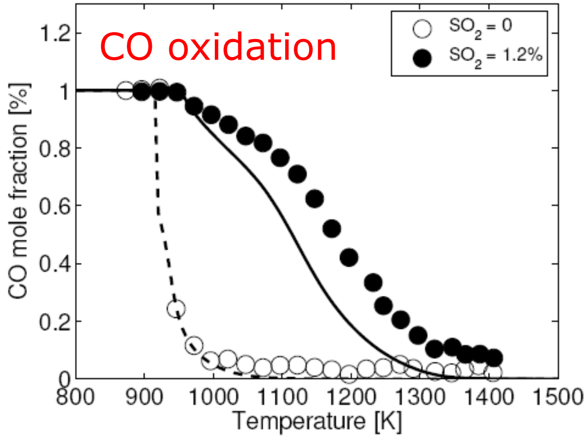
- Expand species range
    - fuels
    - diagnostics



Sulfur chemistry

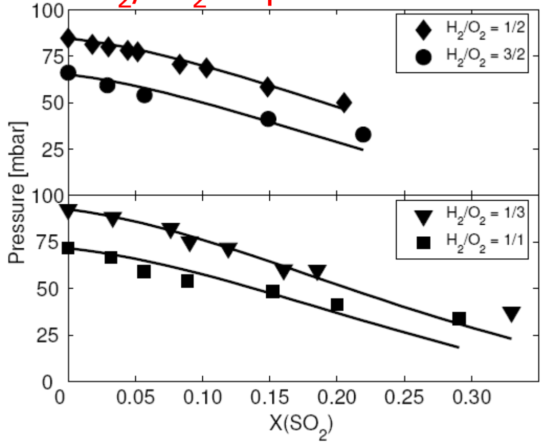
- Gas-phase sulfur chemistry is important in a variety of industrial processes
- Homogeneous oxidation of SO_2 to SO_3, as well as the interaction with the O/H radical pool, is fairly well understood
- Challenges:
  - The chemistry of reduced sulfur species like H_2S, COS, and CS_2 is not understood in detail
  - The interaction of sulfur species with alkali and halogen species is under investigation
  - The interaction of sulfur with hydrocarbons is a mystery

Influence of SO_2 on the radical pool



Flow reactor data: Dagaut et al., 2004

H2/ O_2 explosion limits



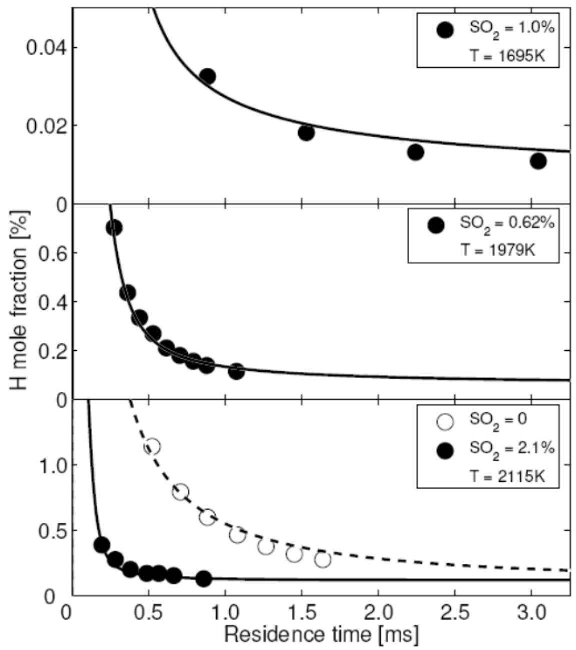
Batch reactor data (784 K):
Webster and Walsh, 1965

Inhibition mechanism:

$H+SO_2(+M) \rightarrow HOSO(+M)$

$HOSO+H \rightarrow SO+H_2O$

$SO+OH \rightarrow SO_2+H$



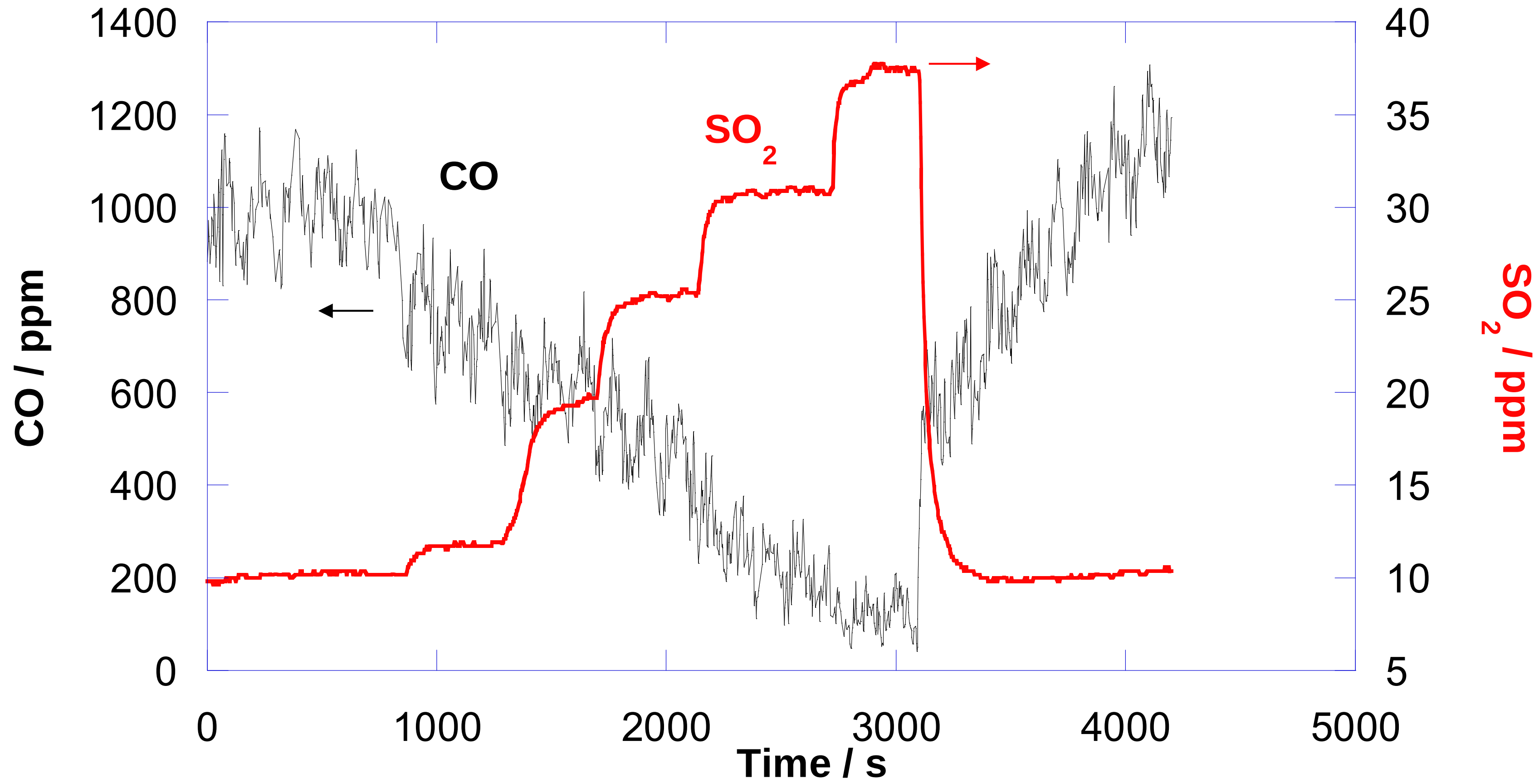
Post-flame [H] decay

Laminar premixed flames
Kallend, 1972

Rasmussen et al., 2007

Sensitization by SO_2

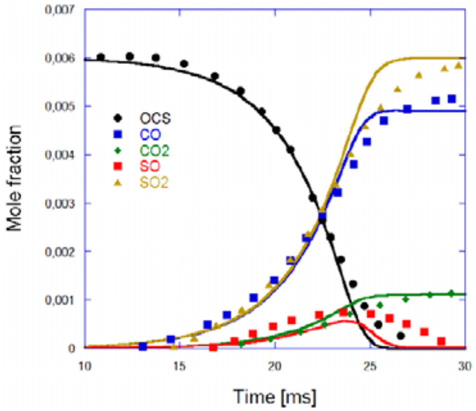
Swirl-stabilized natural gas flame (35 kW, $\Phi \sim 1.0$)

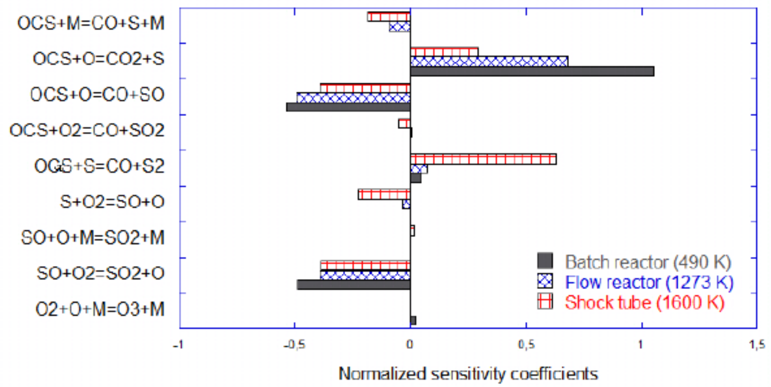


Andersen, 2006

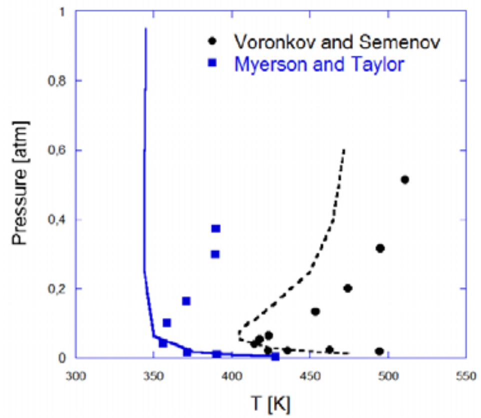
Oxidation chemistry of reduced sulphur species

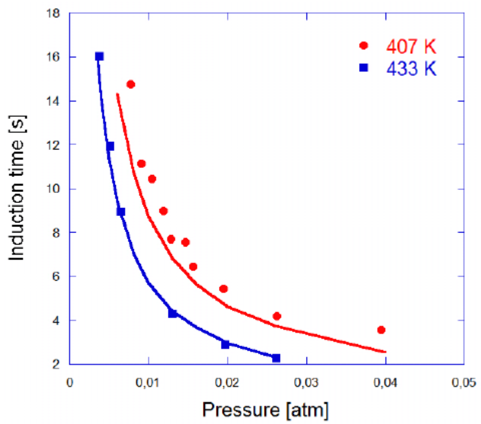
Data: Homann et al., 1969





OCS oxidation at 1273 K; sensitivity coefficients (Glarborg and Marshall, 2013)





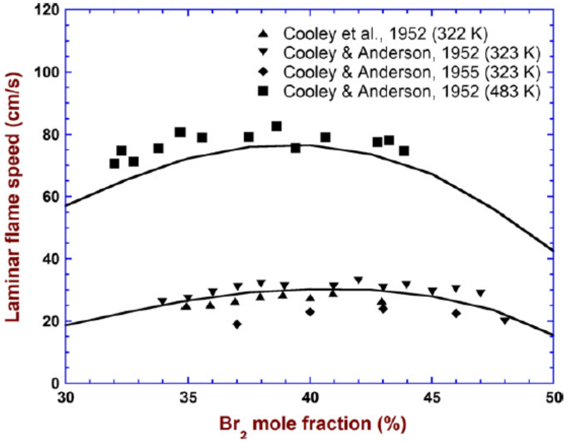
CS_2 explosion limits and ignition delay (Glarborg, Marshall, Troe, et al., 2013)

Halogen chemistry

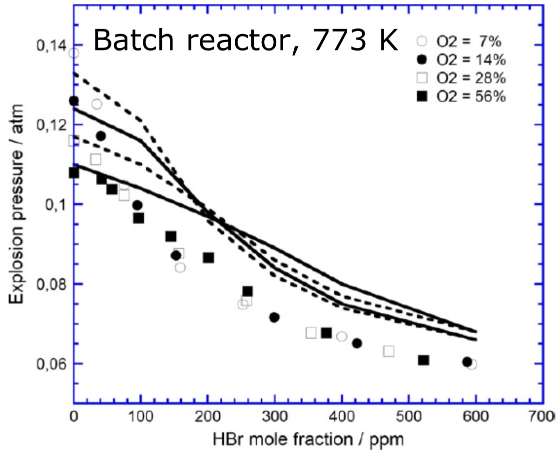
- Gas-phase halogen chemistry is important in a variety of industrial processes
- Brominated hydrocarbons used as flame retardants and (still) important in incineration
- Most solid fuels contain considerable amounts of chlorine
  - Deposition and corrosion
  - Pollutant formation (HCl, dioxin, aerosols)
  - Chlorinated species other than HCl may represent a challenge in gasification gas clean-up
- Detailed models for high-temperature halogen chemistry are available, but only with limited predictive capabilities

Recent work in halogen chemistry: bromine

H_2/Br_2 flame speeds

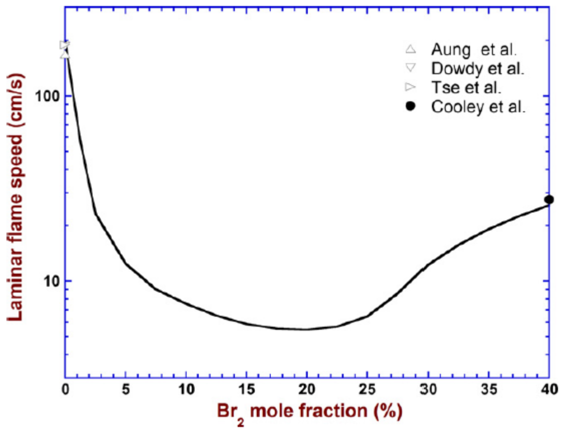


$H_2/O_2/HBr$ explosion limits



Data:
Clarke et al., 1970

H_2/air/Br_2 flame speeds

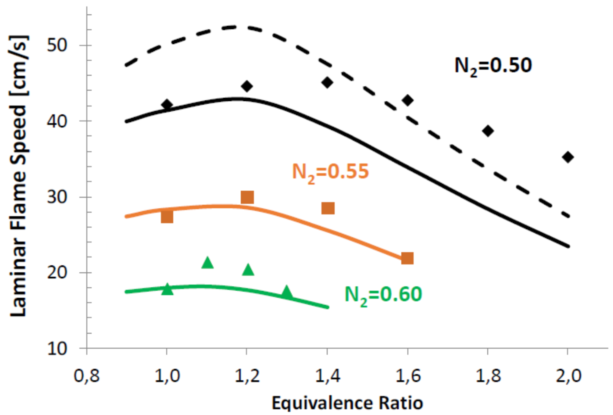


Dixon-Lewis et al., 2012
(Sugden Prize 2013)

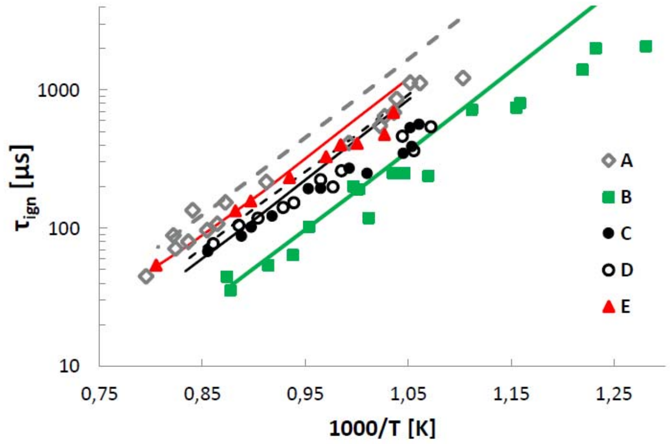
Collaboration:
Leeds University (GB)
University of North Texas (US)
Argonne National Laboratory (US)
Technion (Israel)
DLR (Germany)
Politecnico di Milano (Italy)

Recent work in halogen chemistry: chlorine

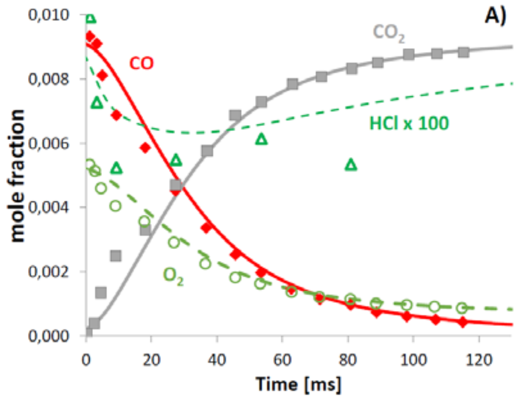
H_2/Cl_2 flame speeds
Data: Leylegian et al., 2005



H_2/Cl_2 ignition delay times
Lifshitz and Schechner, 1975



Oxidation of $CO/HCl/H_2O/O_2/N_2$ in a flow reactor
Data:Roesler et al., 1992



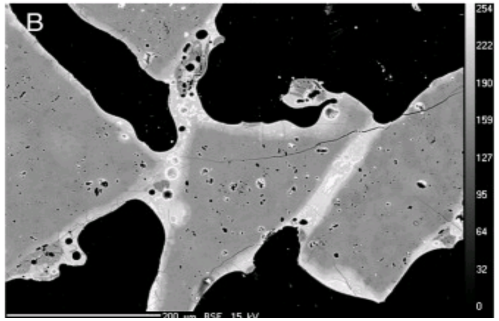
Pelucchi et al., 2015

Alkali chemistry:
KCl related issues in biomass combustion

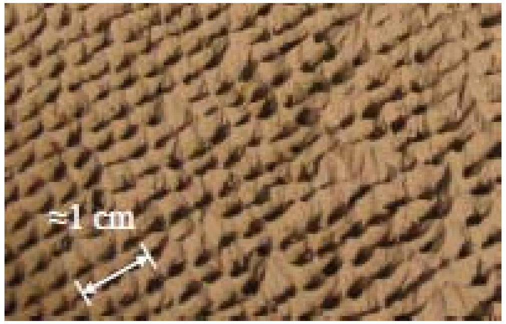
Ash deposition

Corrosion

KCl



Bed agglomeration



SCR deactivation

Gas-phase K/S/Cl transformations

Proposed KCl sulfation mechanism:

$SO_2 + ½O_2 \rightarrow SO_3$ (global, rate limiting)

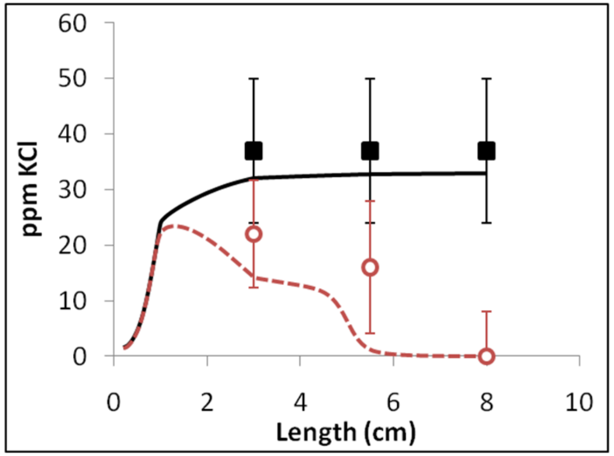
$KCl + SO_3\ (+M) \rightarrow KSO_3Cl\ (+M)$ (fast)

$KSO_3Cl + H_2O \rightarrow KHSO_4 + HCl$ (fast)

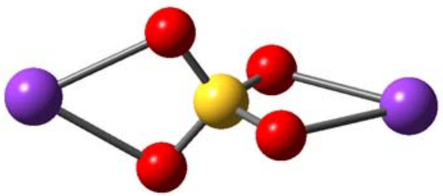
$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$ (fast)

$2KCl + SO_2 + ½O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$ (net)

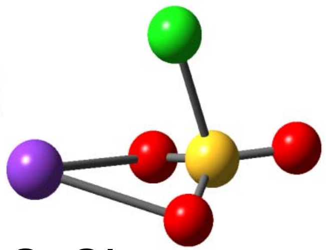
Post-flame sulphation of KCl



Li et al. (2012)

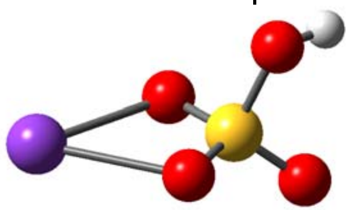


K_2SO_4



KSO_3Cl

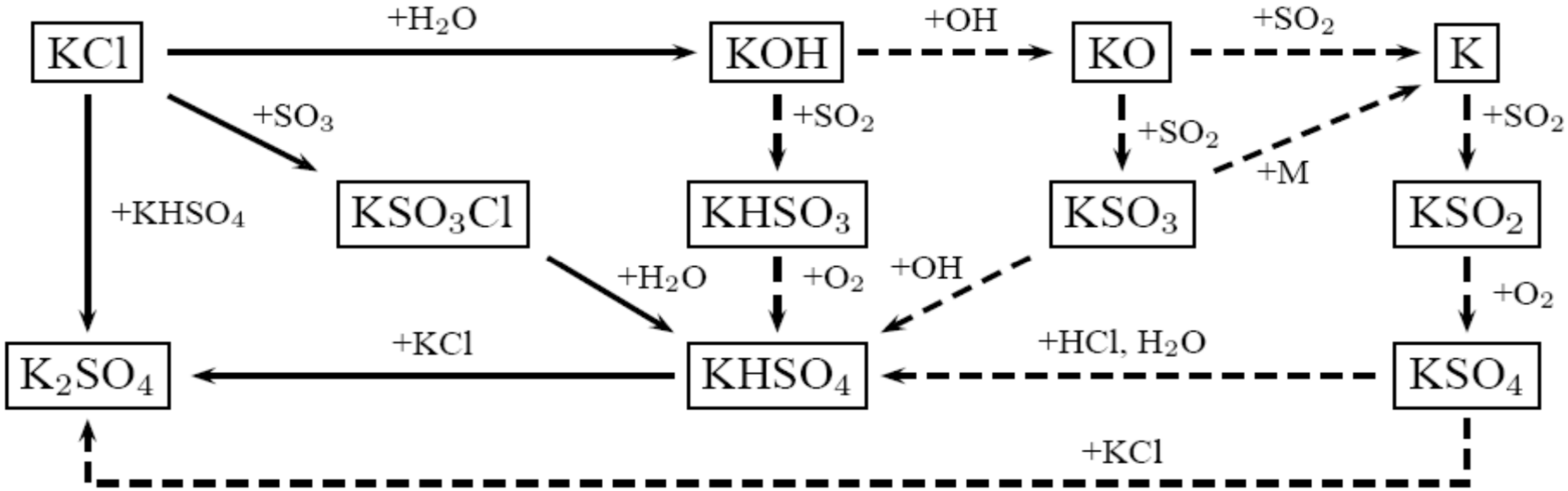
$KHSO_4$

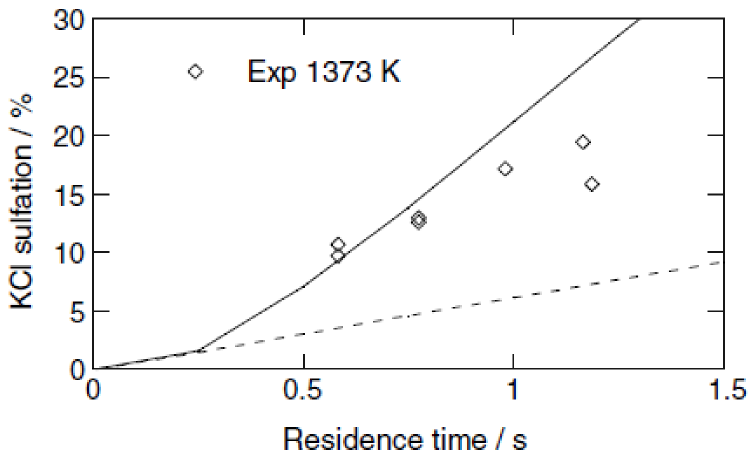


Glarborg and Marshall (2005)

- No experimental data for key intermediates
- Mechanism only a hypothesis

A mechanism for sulfation of KCl





Sulphation of KCl

Entrained flow reactor
Data: Iisa et al., 1999

Hindiyarti et al., 2008

Homogeneous KCl sulfation

Gas-phase mechanism:

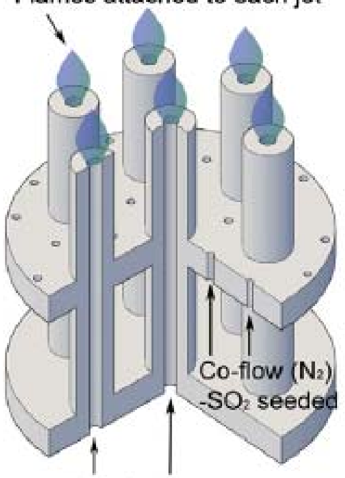
$SO_2 + O_x \rightarrow SO_3$

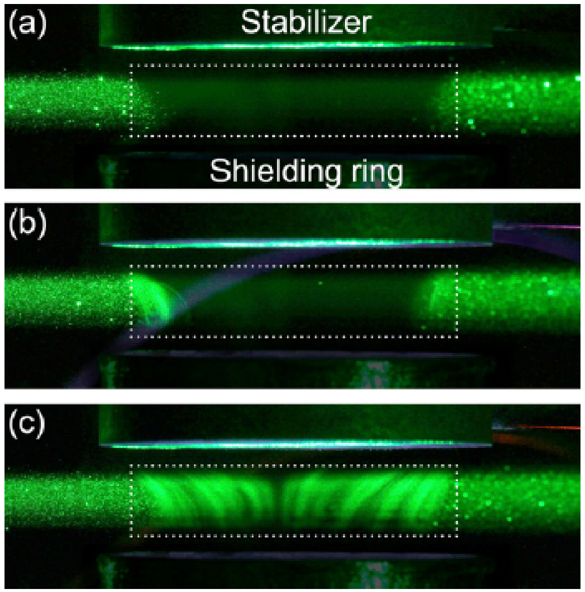
$KCl + SO_3\ (+M) \rightarrow KSO_3Cl\ (+M)$

$KSO_3Cl + H_2O \rightarrow KHSO_4 + HCl$

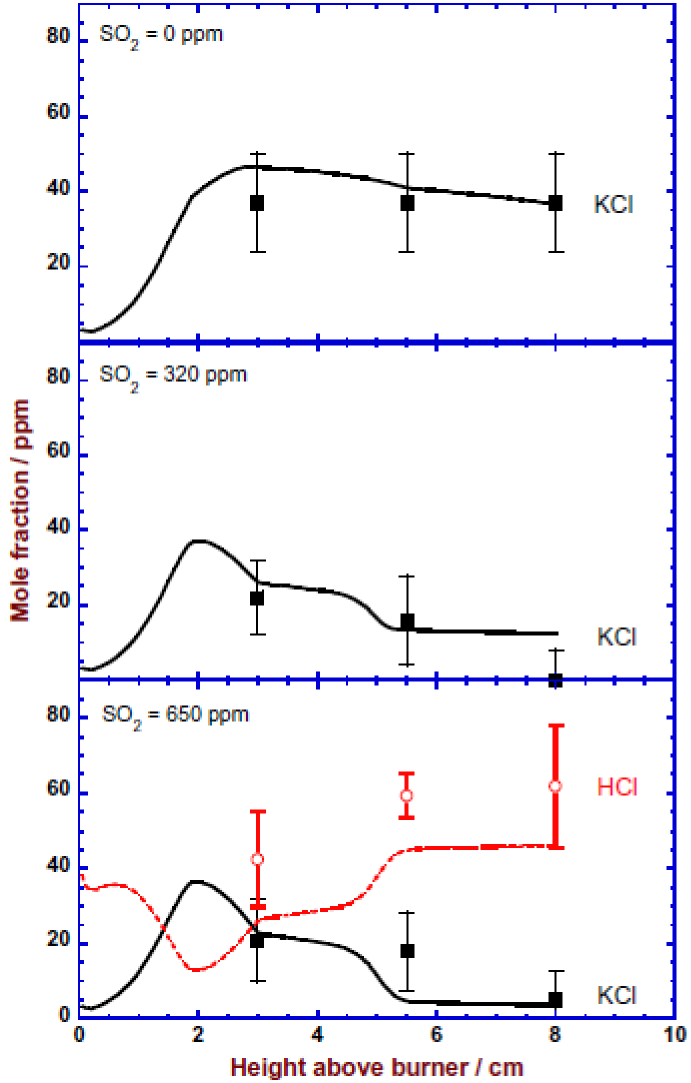
$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$

$K_2SO_4 \rightarrow$ aerosol



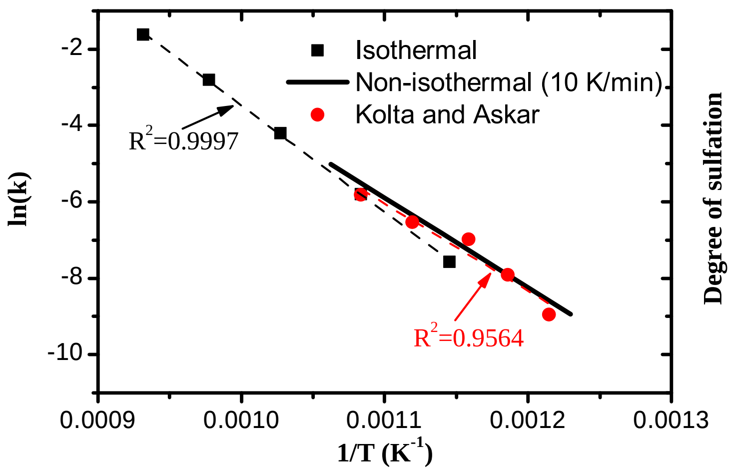


Post-flame sulphation of KCl

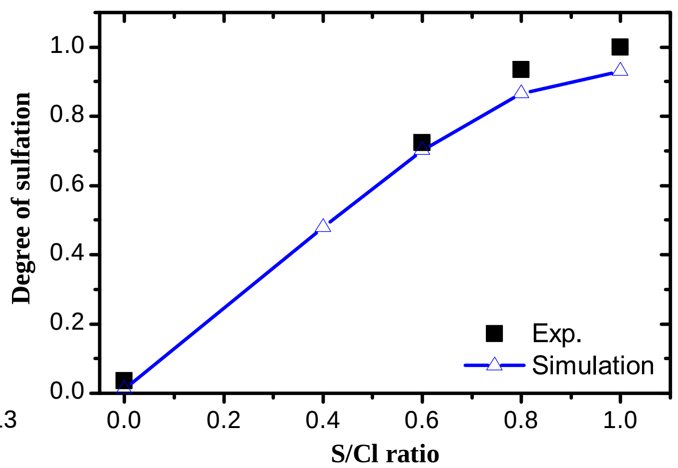


Li et al. (2012)

Sulphate additives for KCl control

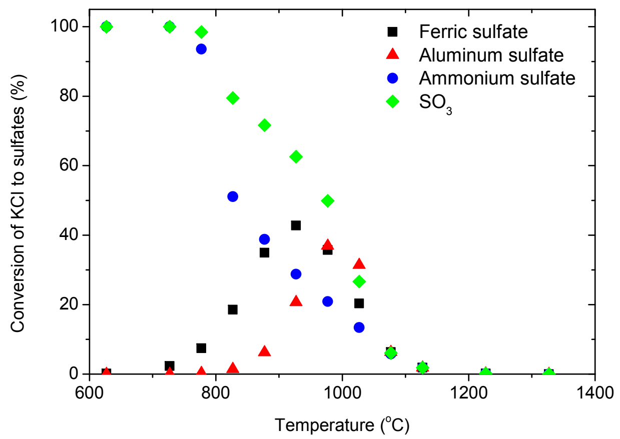


Ferric sulphate decomposition (TGA)



Ferric sulphate addition for KCl control
(VTT pilot-scale reactor)

Wu et al.
(2013a)



Additive temperature windows
Wu et al. (2013b)

Collaboration:
VTT (Finland)

Some concluding remarks

- Novel challenges in thermal fuel conversion
  - Production of bio-fuels (pyrolysis, gasification)
  - Use and kinetics of bio-derived fuels
  - Combustion of alternative fuels
- And an old challenge, still not resolved
  - Prediction of PAH and soot formation and destruction
- Measures:
  - Combine advanced diagnostics with new experimental settings
  - Refine and extend modelling tools
- Bridging fundamental research and application is required to meet the challenges