The role of advanced diagnostics in combustion chemistry research

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Introduction: The problem

- Clean combustion: high efficiency, low emissions
- Alternative transportation fuels: new chemistry
- Novel combustion regimes: influences of p, T, phi, mixture

Needed: Systematic knowledge on combustion chemistry

Probing flame chemistry: Wanted

- In situ information on unknown species mix: identification.
- Large dynamic range of mole fractions, labile species.
- Quantitative set of concentration-reaction time profiles.

**Example:** butane combustion, ~ 40 species.

Laser spectroscopy: Raman, LIF, CRDS, IR absorption, etc.
Quantitative, non-intrusive, small molecules: e.g. CH, C₂
Not suitable for complete flame analysis

Small species and chemical mechanisms

- One species **cannot** validate mechanisms.
- Small species are at **end** of reaction chain.

Probing flame chemistry: mass spectrometry

- Molecular-beam mass spectrometry (MBMS):
  - Complete species set (!?); structure-sensitive, isomers
  - Quantitative – but: fragmentation, overlaps, sampling, …. 
Species- and structure-selective analysis

- Tunable VUV single-photon PI-MBMS:
- Distinction of intermediates in C/H, C/H/O, and C/H/O/N systems
- Mass & photoionization efficiency (PIE) spectra as discriminators

C.A. Taatjes et al, PCCP 10, 2008, 1
B. Yang et al, Combust Flame 148, 2007, 198
A. Lucassen et al, PROCI 34, 2012
Combining high mass + energy resolution

- Fuel complexity: hydrocarbons → oxygenates → fuel-N.
- More elements need better mass separation: → EI-MBMS.
- Fuel structure and intermediate mix need isomer separation: → PI-MBMS.
- Example: morpholine flame.

A. Lucassen et al, PROCI 32, 2009, 1269
Combining EI-MBMS+PI-MBMS+LIF+CRDS

- MBMS results for HCN, NH$_3$, NO, HNCO, CH$_3$, ...
- LIF temperature measurement
- CRDS results for NH$_2$, CN, CH, OH, ...

P. Nau et al, Exp Fluids 32, 2009,1269
**Experiment vs. model: (un)disturbed T profile**

- **T profile** for optical or MBMS sampling must be considered in comparison with models – no shifts!
- **Example:** butanol flames.


M. Sarathy et al, Combust Flame 159, 2012, 2028
New combustion details: study of isomeric fuels

- Quantitative but *relative* species measurement is more forgiving.
- Chemical trends are more obvious.
- Model can probe mechanistic differences.
- **Example:** ethanol and DME addition to propene.

A. Frassoldati et al, Combust Flame 158, 2011, 1264
Fuel-N conversion: biomass components

- **Isomeric** fuel decomposition pathways different.
- Ethylamine breakdown suggests early NH$_3$ formation.
- Substantial HCN mole fractions expected for both fuels.
- **Example**: ethylamine and dimethylamine combustion.

A. Lucassen et al, Combust Flame 159, 2012, 2254
Ethylamine vs. dimethylamine combustion

- \( \text{NH}_3 \) mole fractions much higher for EA.
- Model under-predicts \( \text{NH}_3 \) in both flame sets.
- High HCN mole fractions of up to 12%.
- Model under-predicts HCN.

A. Lucassen et al, Combust Flame 159, 2012, 2254
Sampling from highly-diluted, preheated, partially-premixed DME flame at 1 bar with $T = 1400$ K.

Partially-premixing species profiles are position-dependent.

K. Zhang et al, PROCI 34, 2012
Low-temperature combustion chemistry

- Highly diluted preheated DME combustion.
- Three stoichiometries: 0.85, 1.0, and 1.2.
  *Intermediate-T* behavior; e.g. CH$_3$ vs. CH$_2$O.

K. Zhang et al, PROCI 34, 2012
Low-temperature combustion chemistry

- Highly diluted DME oxidation in flow reactor.
- Three stoichiometries: 0.8, 1.0, and 1.2.
  *Expected* low-T behavior.
- Compare with model/to EtOH: →WIP!

F. Herrmann et al, PROCI 34, 2012

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1st International Workshop on Flame Chemistry, Warsaw, Poland, July 28-29, 2012
DME oxidation in low-T flow reactor.

High mass resolution: fuel DME (46.042) and formic acid (46.010) at $T_h = 583$ K are separated.

Methyl formate is detected.

More species, VUV-PI-MBMS: →WIP!

F. Herrmann et al, PROCI 34, 2012

1E07 Mon, W5P072 Fri
EI-MBMS and GC from the same volume

- In-situ isomer separation + EI-MBMS
- Example: butene flames, C$_5$H$_8$ m/z 68
Butene combustion as C4 chemistry subset

- Different fuel breakdown schemes for the 3 butene isomers.
- **C3 route** is of high importance for all butenes, almost exclusive for i-butene.
- Additional **C4 route** exists for the 2 linear butenes.

M. Schenk et al, Combust Flame 2012, submitted
Highly complex chemistry: Biomass pyrolysis

- Tunable VUV PI-MBMS for analysis of pyrolysis profiles (T, time) of second-generation biofuels.
- Fast-growing poplar wood as potential corn replacement; carbon conversion to biofuels.

J. Weng et al, PROCI 34, 2012
Poplar pyrolysis set-up

- Qstar triple quadrupole TOF-MS with mass range 30-20000 Da, **resolution 10000**.
- Reactor is heated to specific temperature, then sample inside the quartz pole is pushed into the furnace.
- Pyrolysis products pass through a repeller plate into the photoionization region, photoions are analyzed by the QTOF mass spectrometer.

J. Weng et al, PROCI 34, 2012
Major products from poplar pyrolysis

C$_2$H$_4$O$_2$ (86) / 2,3-Butanedione
C$_6$H$_5$O (94) H Phenol
C$_6$H$_9$O$_2$ (102) H Valeric acid / o-Cresol
C$_7$H$_8$O$_2$ (108) H Dihydroxybenzenes 4-Hydroxy-5,6-dihydro-2H-pyran-2-one
C$_8$H$_6$O$_3$ (114) / 2-Methoxyphenol

C$_6$H$_5$O$_3$ (126) / 5-Hydroxymethyl-furfural
C$_6$H$_8$O$_2$ (136) H 2-Hydroxy-5-methylbenzaldehyde
C$_6$H$_9$O$_2$ (138) G 4-Methylguaiacol
C$_8$H$_8$O$_2$ (150) G 4-Vinylguaiacol
C$_8$H$_6$O$_3$ (152) G Vanillin
C$_8$H$_8$O$_2$ (152) G 4-Ethylguaiacol
C$_8$H$_6$O$_3$ (154) S 2,6-Dimethoxyphenol

C$_6$H$_8$O$_2$ (162) / Levoglucosan
C$_{10}$H$_{12}$O$_2$ (164) G Eugenol
C$_{10}$H$_{12}$O$_2$ (164) G Isoeugenol
C$_{10}$H$_{10}$O$_3$ (166) G Apocynin
C$_{10}$H$_{10}$O$_3$ (168) S 4-Methyl-2,6-dimethoxyphenol
C$_{10}$H$_{12}$O$_3$ (178) G Coniferyl aldehyde
C$_{10}$H$_{12}$O$_3$ (180) S Vinlylsyringol

C$_{10}$H$_{12}$O$_3$ (182) G Coniferyl alcohol
C$_{9}$H$_{10}$O$_4$ (182) S Syringaldehyde
C$_{11}$H$_{14}$O$_3$ (194) S 4-Propenylsyringol
C$_{11}$H$_{12}$O$_3$ (196) S 1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone
C$_{11}$H$_{12}$O$_4$ (208) S Sinapyl alcohol
C$_{11}$H$_{14}$O$_3$ (210) S Sinapyl alcohol
Time-resolved pyrolysis profiles

Time: 115 s

Time: 90 s

Time: 60 s

Time: 90 s

(a) total ion current

(b) m/z 114 hemicellulose

(c) m/z 180 lignin

(d) m/z 124 lignin

(e) m/z 138 lignin

(f) m/z 110 lignin

500 ºC
10.5 eV

J. Weng et al, PROCI 34, 2012
MBMS in non-premixed flames

- \( \text{C}_2\text{H}_2 \) flame at 30 Torr
- Mole fractions vs. fuel outlet
- Agreement with model by Jim Miller

S.A. Skeen et al, PROCI 34, 2012
MBMS in non-premixed flames

- Radicals can be detected.
- Profiles appear shifted vs. model.

S.A. Skeen et al., PROCI 34, 2012
Flame-sampling aerosol mass spectrometry
Flame-sampling aerosol mass spectrometry

- Gas phase species and **50-100 nm particles** are sampled from 700 Torr counterflow flame with quartz microprobe.

- Particles are focused with aero-dynamic lens onto heated copper plate and flash-vaporized.

- Molecular constituents are VUV-photoionized and detected by TOF mass spectrometry.
Particle chemical composition: surprises

- Mass spectra map chemical composition of the particles vs. distance from the fuel outlet; PIE spectra permit identification.
- Example m/z=116, normally only identified as indene, but PIE curve shows also *phenyl-substituted allene and propynes*. 
Soot formation beyond benzene

- Many species beyond benzene to ~1000 Da.
- Mass spectra peak at around 202 Da, i.e. pyrene.
- Detailed analysis in progress.
Perspectives: Future trends and needs?

- **New combustion chemistry**: more elements, higher mass range, structure-selective quantitative analysis.
- **New measurement domains**: larger p and T range, pyrolysis vs. highly-diluted oxidative systems, particles, aerosols, homogeneous vs. heterogeneous combustion chemistry.
- **Time-resolved** analysis.
- **Support by theory**: ionization energies, structures, simulation of spectra, kinetics, thermochemistry.
- **Combination of methods**: optical&MS techniques, in situ GC-MBMS, IR-absorption, MS-MS, PEPICO, ….
- **Caveat**: Let‘s get sampling problem solved!
THANK YOU

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