TDLAS-BASED IN SITU MEASUREMENTS OF POTASSIUM IN ENTRAINED FLOW GASIFIERS

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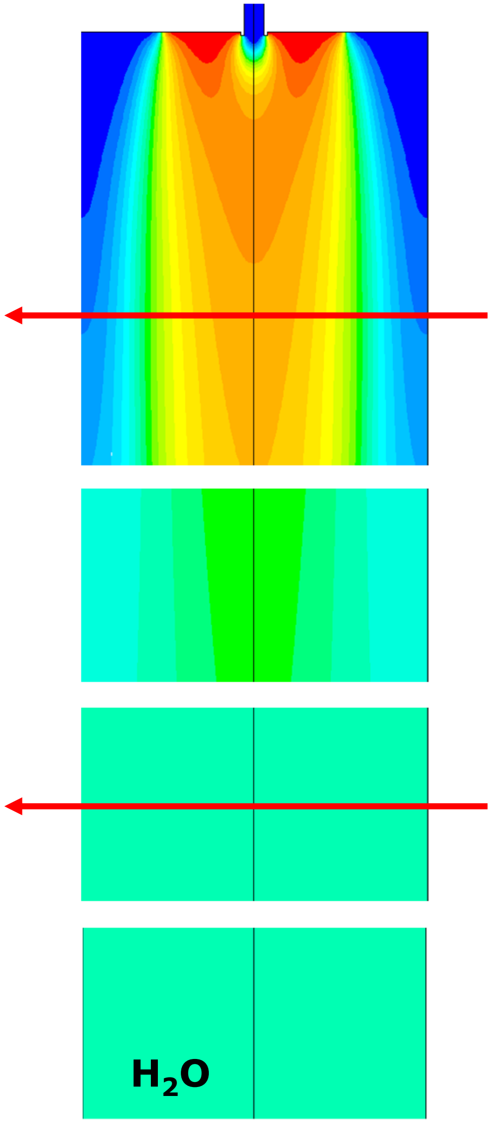
MOTIVATION



Main technical issues

- ➢ Fuel-flexibility
- ➢ Process efficiency
- ➢ Ash-related operational problems and emissions
- ➢ Resource recovery

Development of laser-based diagnostics

- Allow in situ, real-time measurements in reactor core
- Gain increased understanding about biomass conversion in combustion and gasification
- Complement established offline and extractive methods
- Model verification
- Identification of key-parameters for online process monitoring and control

➢ Application in fundamental laboratory studies

➢ Application in larger (pilot-) scale gasifiers

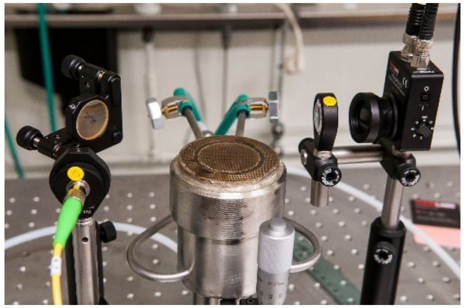
Groups Involved - SFC

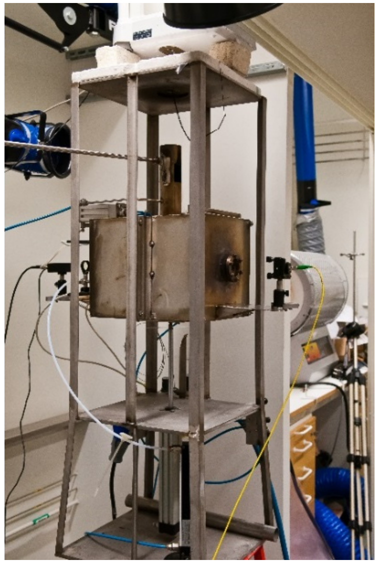
- **Combustion Physics, Lund University** (Prof. Per-Erik Bengtsson)
  - Soot volume fractions, soot formation, tars, PAHs, ash particles
  - Elastic light scattering (ELS), Laser-induced incandescence (LII), Laser-induced fluorescence (LIF), Chemiluminescence

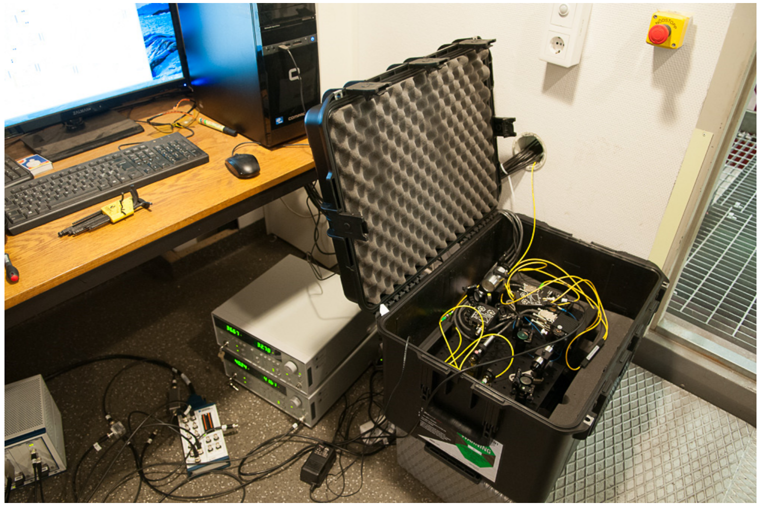
- **RISE Energy Technology Center Piteå** (Dr. Alexey Sepman)
  - Major species (CO, CO_2, H_2O), temperature, soot, fuel feeding
  - Tunable diode laser absorption spectroscopy (TDLAS), Laser extinction, pyrometry, camera-based sensors

- **TEC-Lab, Umeå University** (Dr. Florian Schmidt)
  - Temperature, H_2O, atomic potassium K(g), KOH, soot
  - Tunable diode laser absorption spectroscopy (TDLAS), Photofragmentation spectroscopy

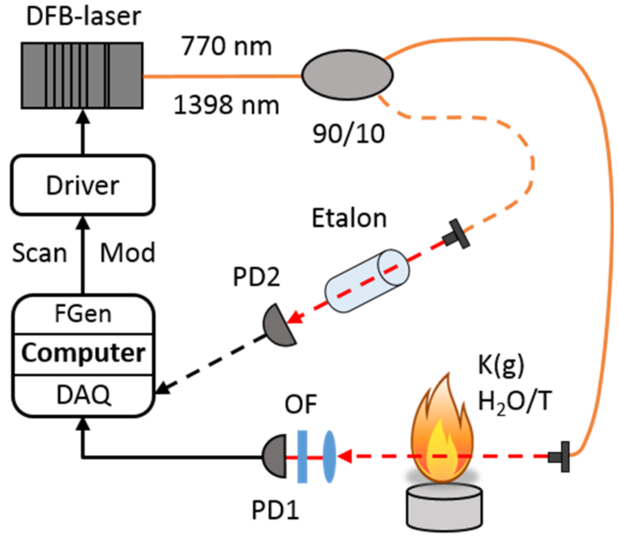
Facilities

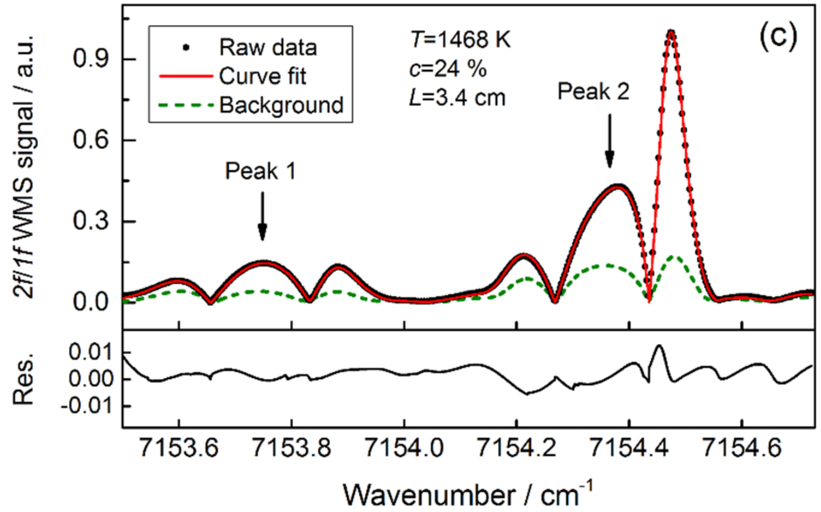






TDLAS Sensor – H_2O, T, K(g), Soot



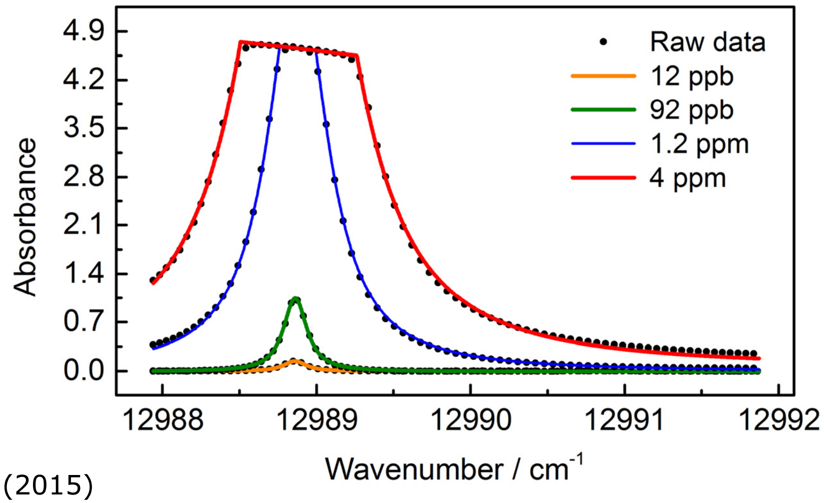


Calibration-free WMS at 1398 nm for H_2O and Temp

- Linear T dependence: 1200-1800 K
- Density-weighted path-averaged temperature

Direct TDLAS at 769.9 nm for atomic potassium, K(g)

- Optically thick conditions
- Dynamic range: 40 pptv·cm to 40 ppmv·cm



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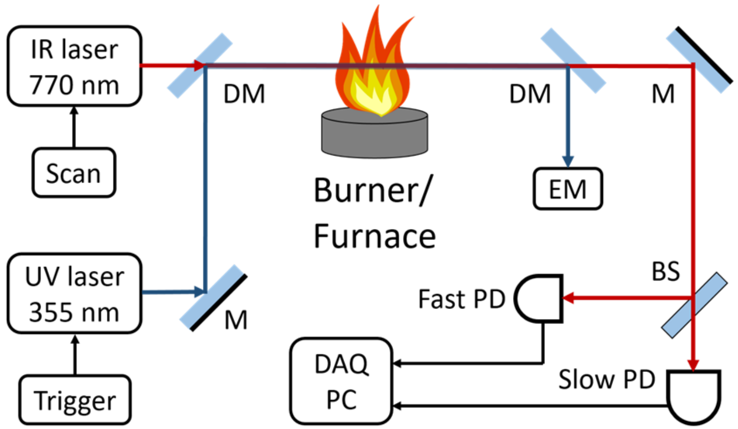
Z. Qu, E. Steinvall, R. Ghorbani, F. M. Schmidt, *Anal. Chem.* **88**, 3754−3760 (2016)

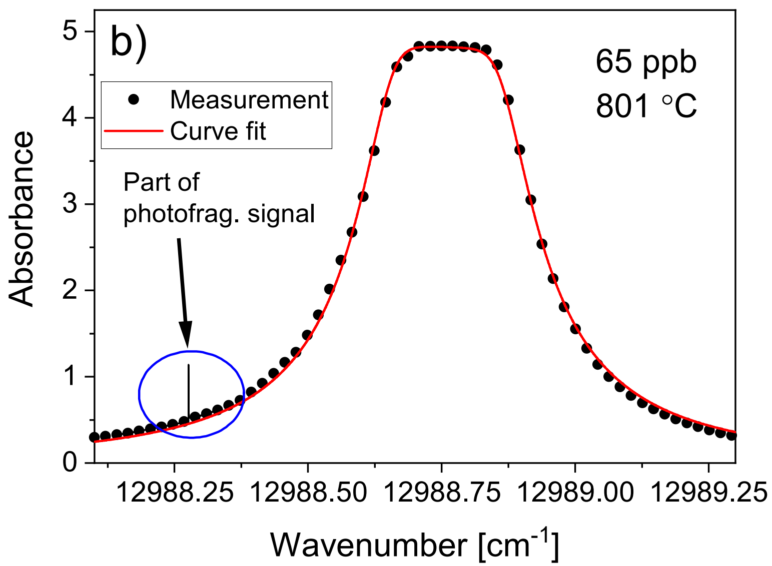
A. Sepman, Y. Öhgren, Z. Qu, H. Wiinikka, F. M. Schmidt, *Proc. Combust. Inst.* **36**, 4541-4548 (2017)

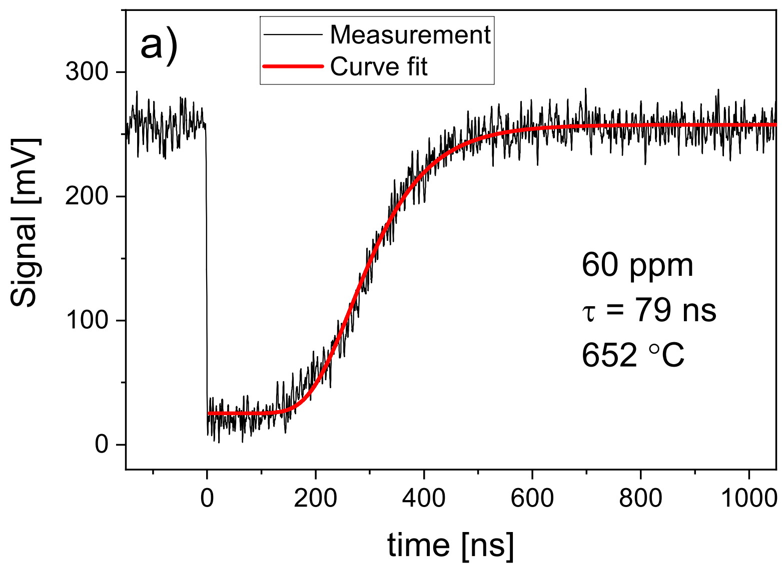
KOH Detection - Photofragmentation

Photofragmentation spectroscopy

- UV laser pulse fragments KOH – detect increase in K(g)
- Combine with TDLAS of K(g)
- Simultaneous detection of K(g), KOH and KCl in wide dynamic range







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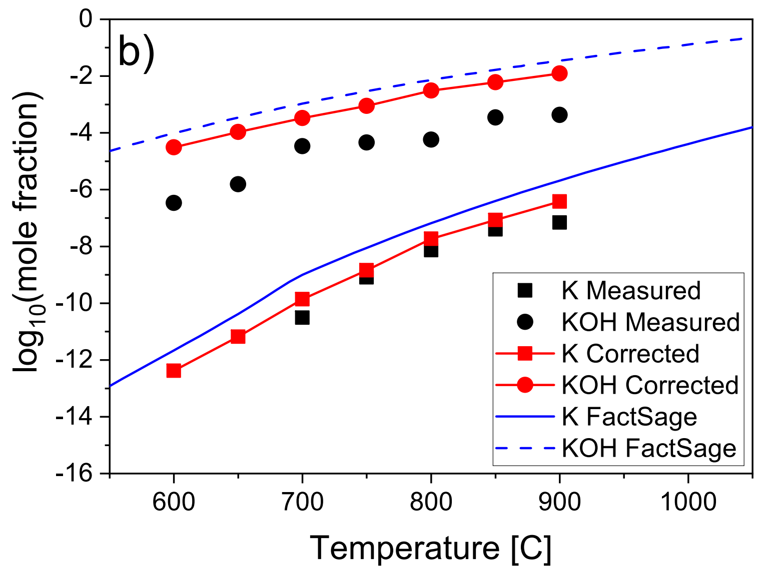
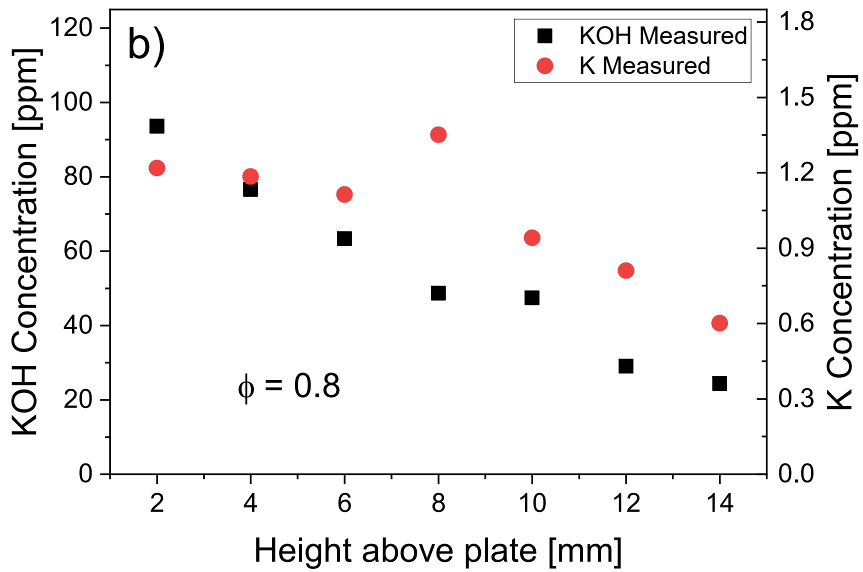
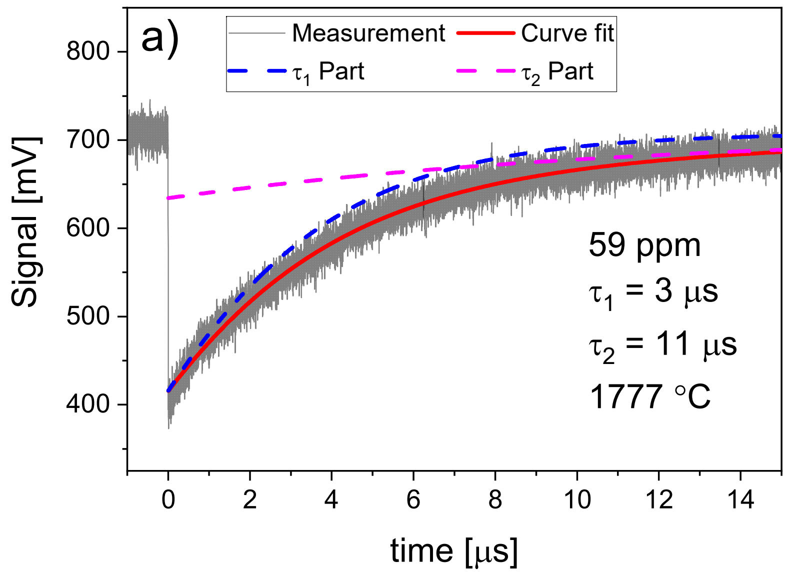
KOH, K(g) Setup Validation

- Tube furnace: Saturated vapour pressure of KOH(g) and K(g)
- 600-900 °C



- Methane/air flat flame: KOH evaporates from platinum plate, 1300-1600 °C.





Why Potassium?

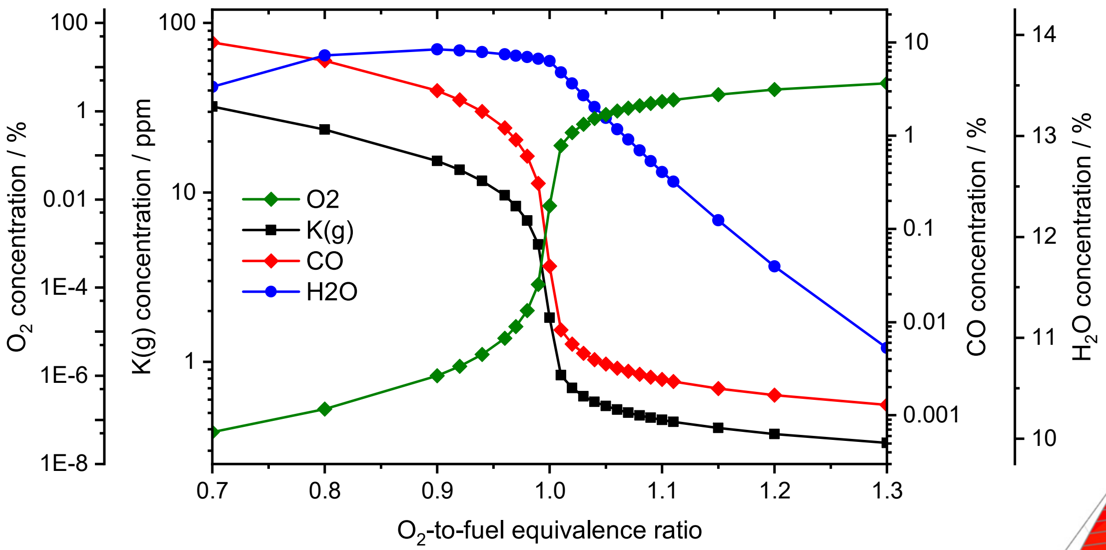
- One of the most abundant inorganic compound in biomass
- Released to gas phase - reactive species K, KOH and KCl.
- Concentrations dependent on e.g. fuel composition, equivalence ratio and temperature
- Participates in ash-forming reactions and influences extent of operational problems and emissions.
- Fly ash, slagging, corrosion, agglomeration, pre-coursers for soot and particle formation
- Catalytic effect?

- Detailed fundamental investigations of K species
- Process Monitoring of K, KOH KCl

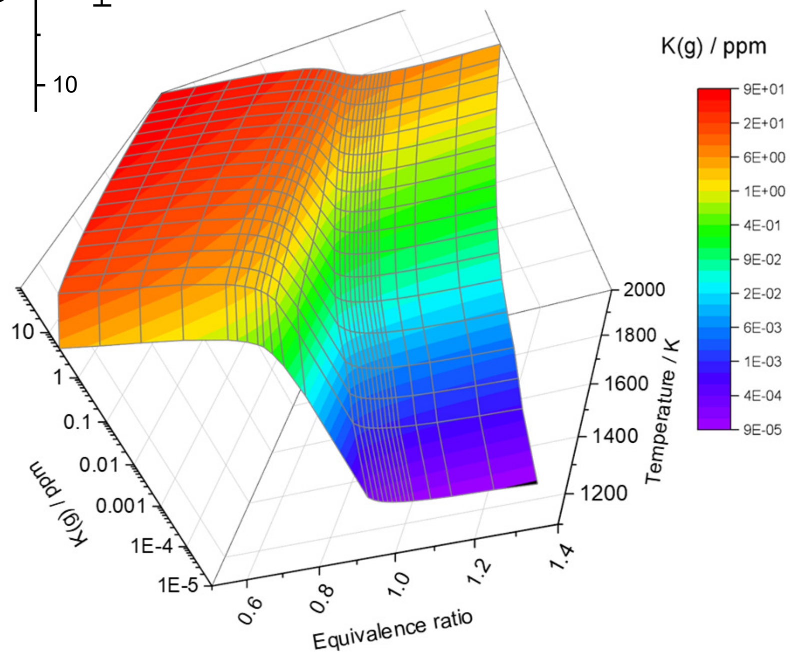
- Intermediate species K(g) interesting (as we will see) and relatively simple to measure.

K(g) vs. Lambda – Equilibrium Calc.

Thermodynamic equilibrium calculations
as a function of equivalence ratio and temperature.



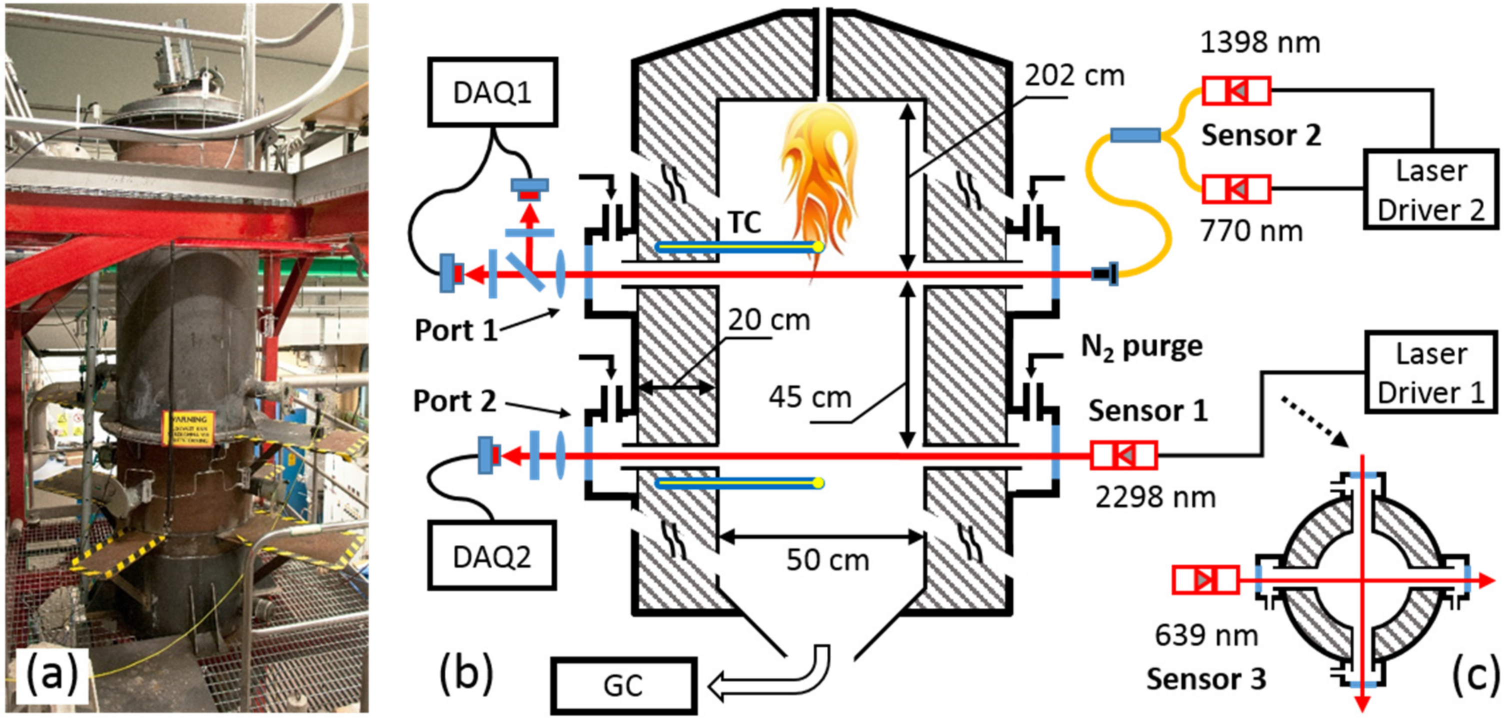
- Temperature dependence of S-shaped K(g) curve
- Difference combustion-gasification decreases with increasing temperature



- S-shaped curve for K(g) similar to CO.
- K(g) and CO high in gasification, low in combustion (orders of magnitude).
- Opposite behaviour for O_2.
- Small changes for H_2O.

PILOT-SCALE ENTRAINED-FLOW REACTOR

Entrained-flow gasifier - VAFF, RISE ETC Piteå, Sweden

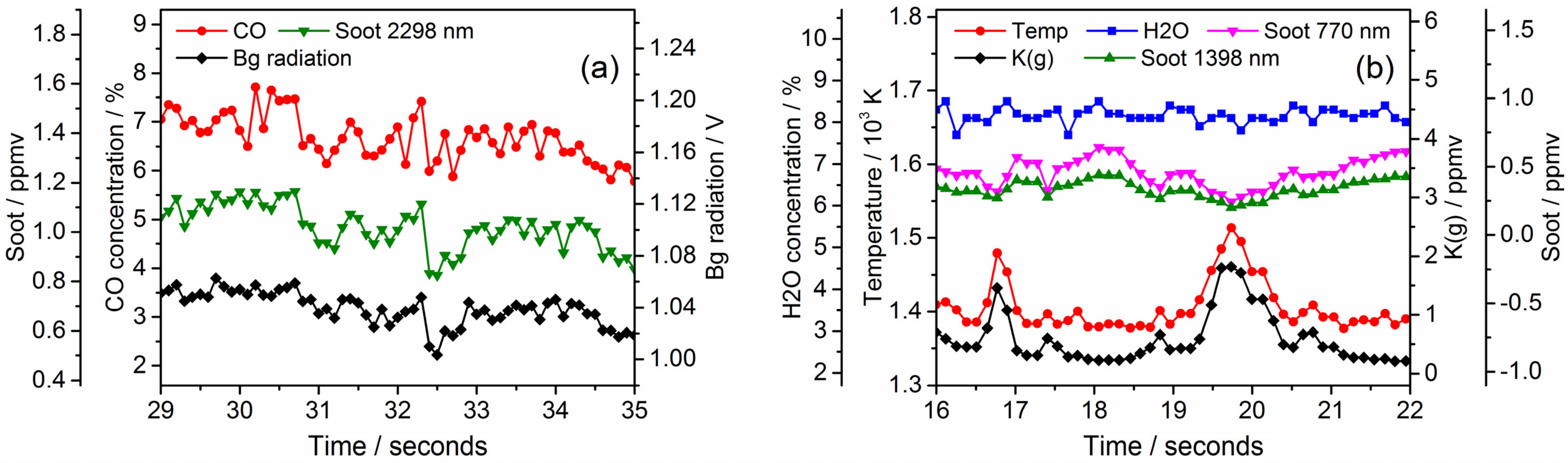


- Length: 4 m
- Operated at 0.1 MW_{th}

A. Sepman, Y. Öhgren, Z. Qu, H. Wiinikka, F. M. Schmidt, *Proc. Combust. Inst.* **36**, 4541-4548 (2017)

Z. Qu, P. Holmgren, N. Skoglund, D. R. Wagner, M. Broström, F. M. Schmidt, *Combust. Flame* (accepted, 2017)

VAFF - Real-Time Performance



- Clear correlation between CO, soot and background radiation
- Soot closely related to carbon species
- Background radiation partly from soot emission

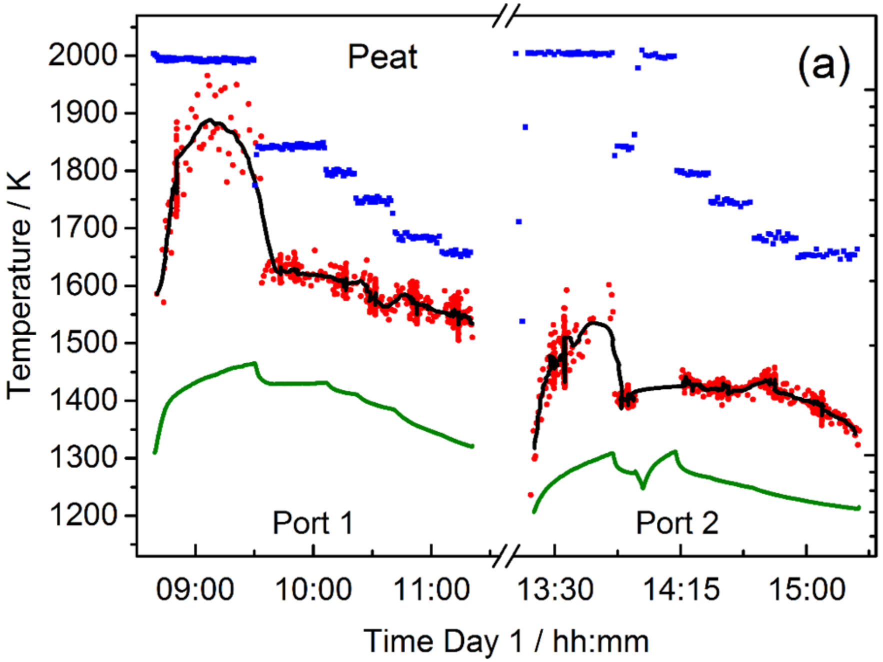
- Positive correlation between *T* and K(g) due to chemistry
- Negative correlation of *T*, K(g) with soot
- No correlation with H_2O

➢ Short-term (and long-term) variations could be related to fluctuations in the fuel feeding, e.g. changes in local equivalence ratio.

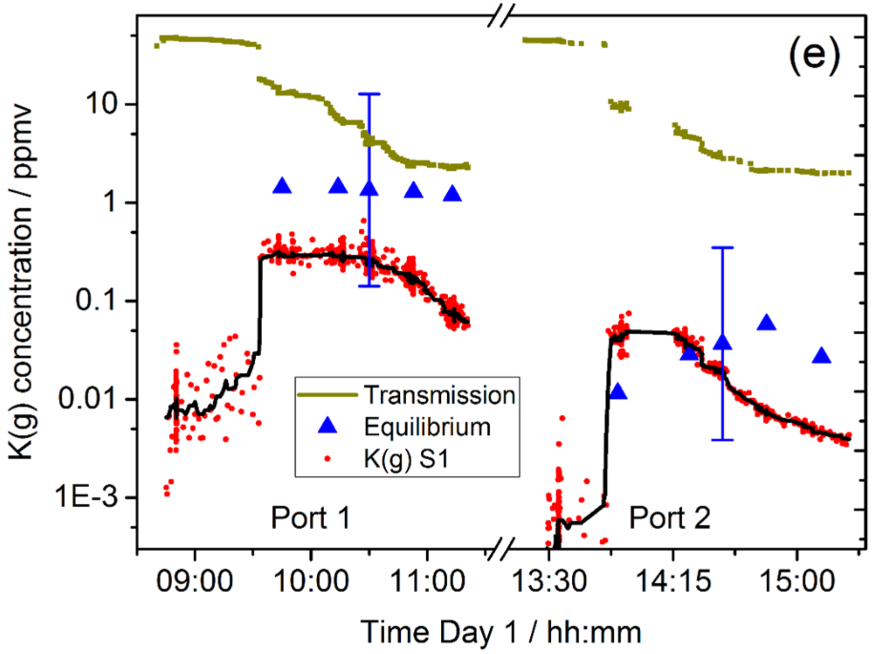
A. Sepman, Y. Öhgren, Z. Qu, H. Wiinikka, F. M. Schmidt, *Proc. Combust. Inst.* **36**, 4541-4548 (2017)

VAFF Reactor Core

Gas temperature



Atomic potassium



- Uncorrected thermocouple measurements (gasifier center) underestimate the actual gas temperature by 100-200 K in gasification.
- Chemical reactions involving K(g) are very fast and depend on fuel compositions. Equilibrium is reached (only) at the end of conversion.

A. Sepman, Y. Öhgren, Z. Qu, H. Wiinikka, F. M. Schmidt, *Proc. Combust. Inst.* **36**, 4541-4548 (2017)

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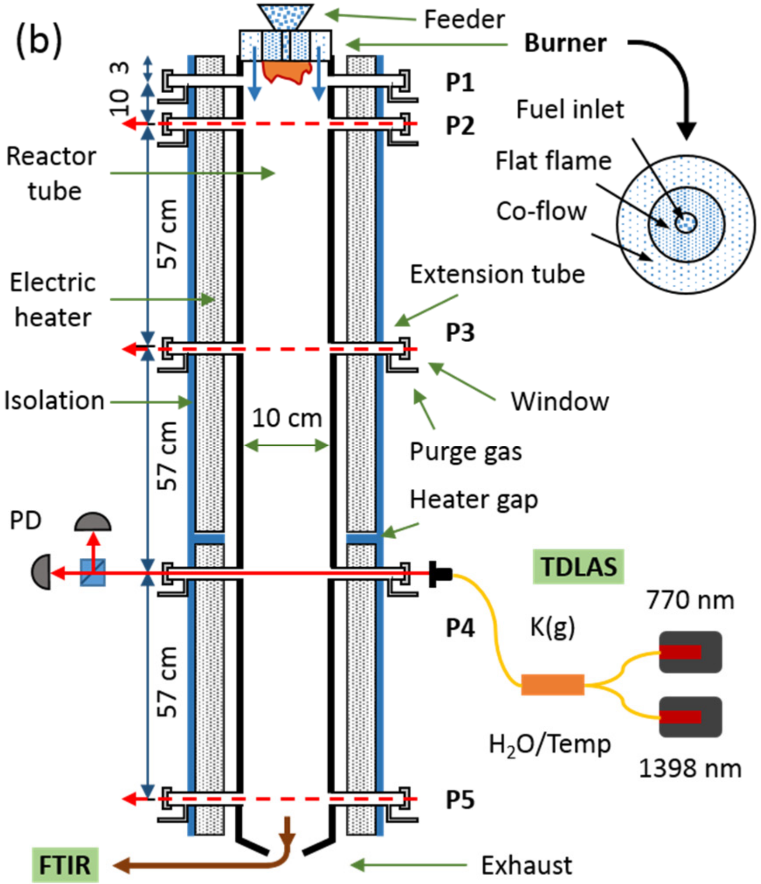
ENTRAINED-FLOW DROPTUBE REACTOR

Atmospheric laminar lab-scale EFR at Umeå University

- Length: 2 m
- Optical ports: 5
- Electrical heaters
- Propane/air flat flame burner
- Powder-fed
- PIV
- Laminar gas flow
- Low particle Stokes number

➢ Global thermodynamic equilibrium



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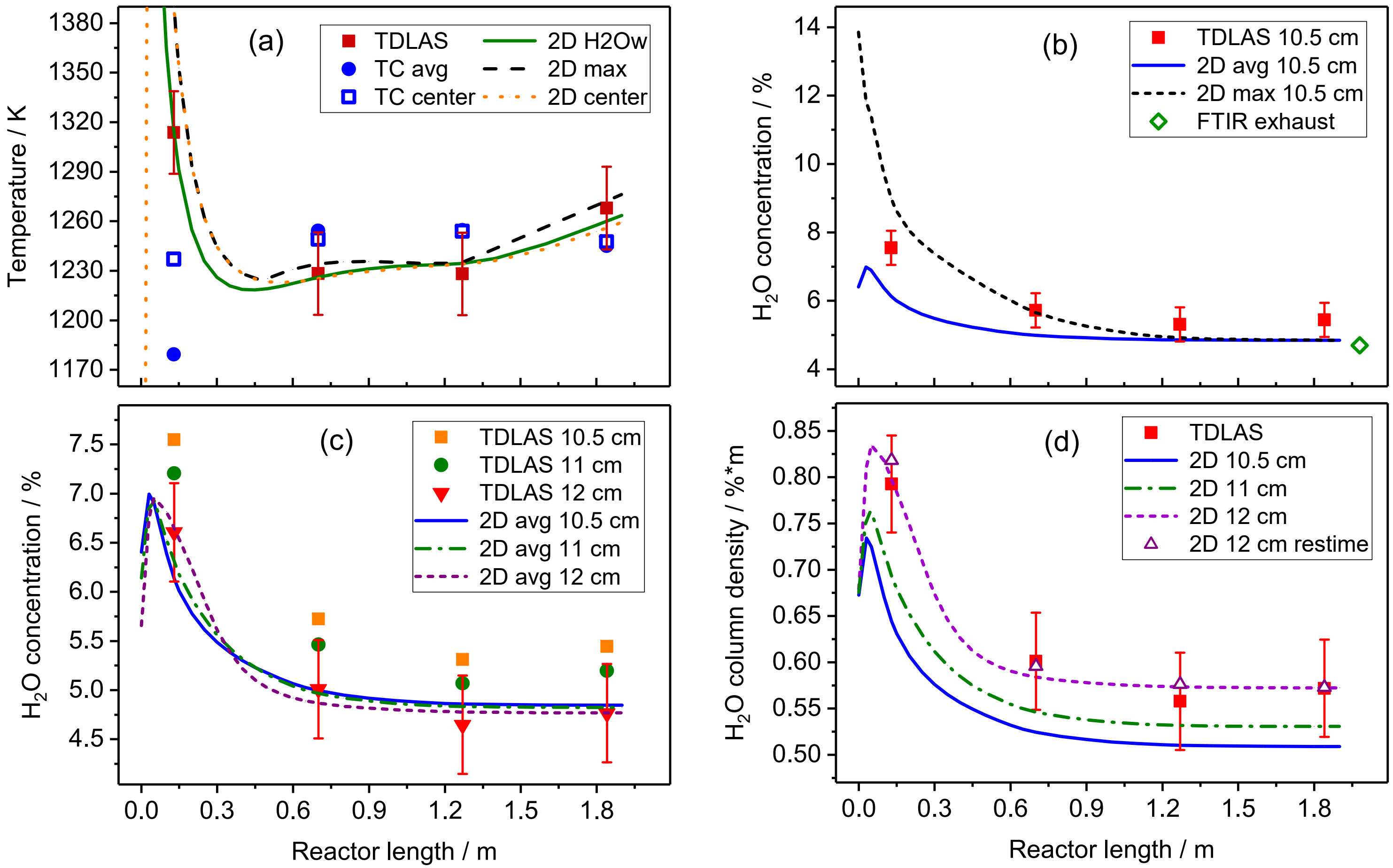
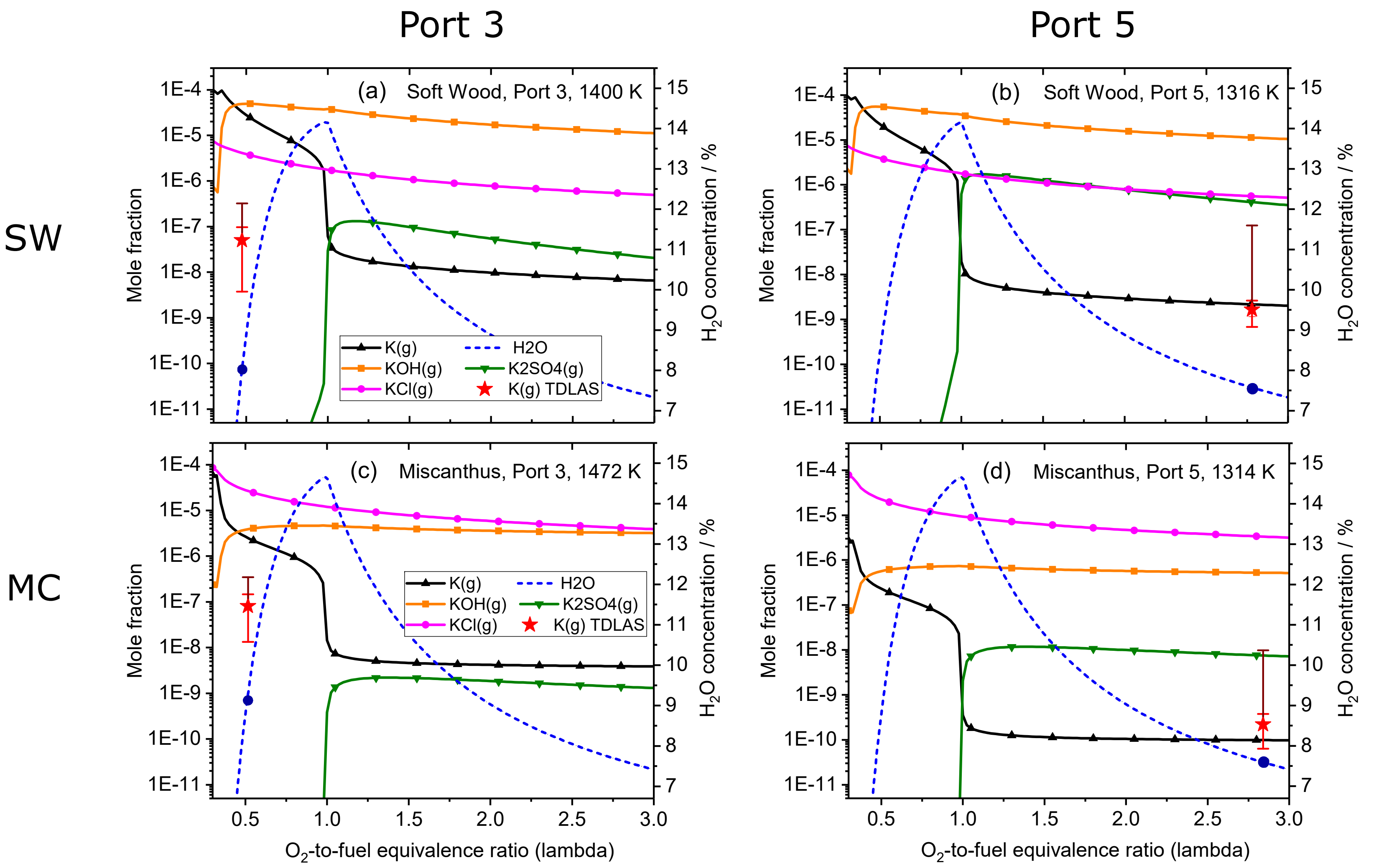
TDLAS vs. CFD – Propane Flame

Temperature, H_2O concentration and H_2O column density



- Temperature: CFD, thermocouple and TDLAS agree well at Ports 3-5.
- H_2O: CFD and TDLAS agree well. Small discrepancy suggest a slight path length increase.

Biomass Conversion vs. Equilibrium

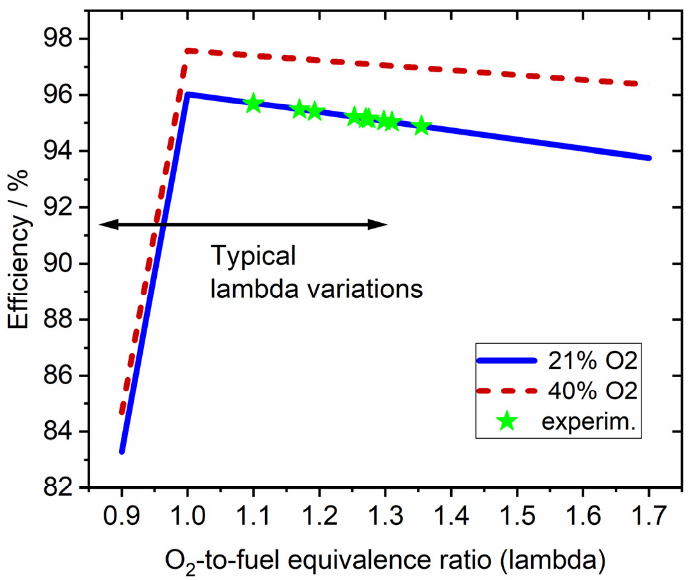


- Primary K(g) ash transformation reaction have already taken place at Port 3.
- K(g) ash transformation reactions at or close-to equilibrium at Port 5 for both fuels.

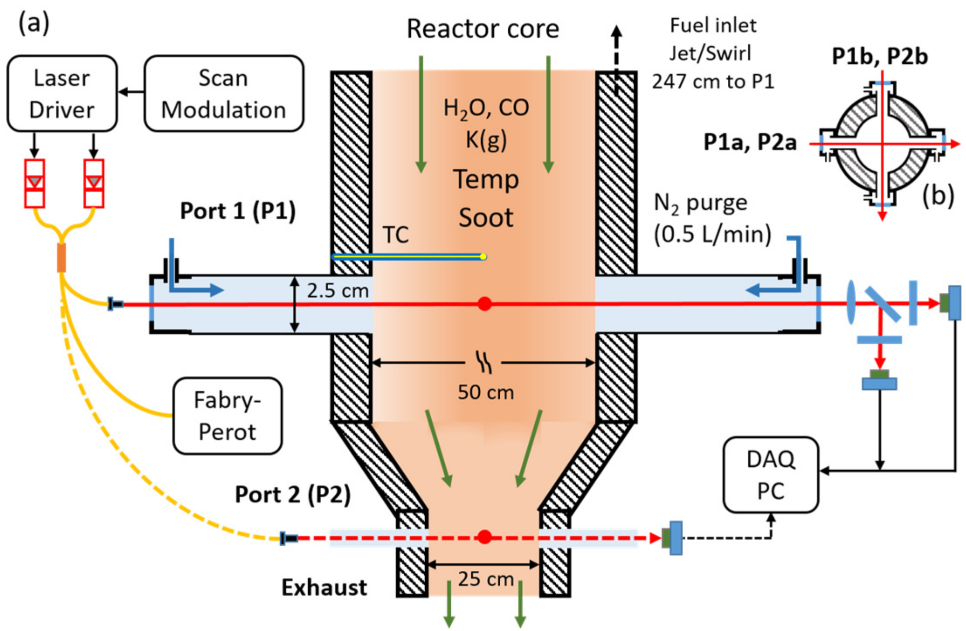
VAFF 2 – Close to Stoichiometry

In situ measurements close to stoichiometry
– local lambda fluctuations

- K(g), soot, CO, H_2O and temperature
- 2 burners (jet and swirl)
- 3 oxygen enrichment levels (21%, 30%, 40%)
- 2 ports (reactor core and exhaust)



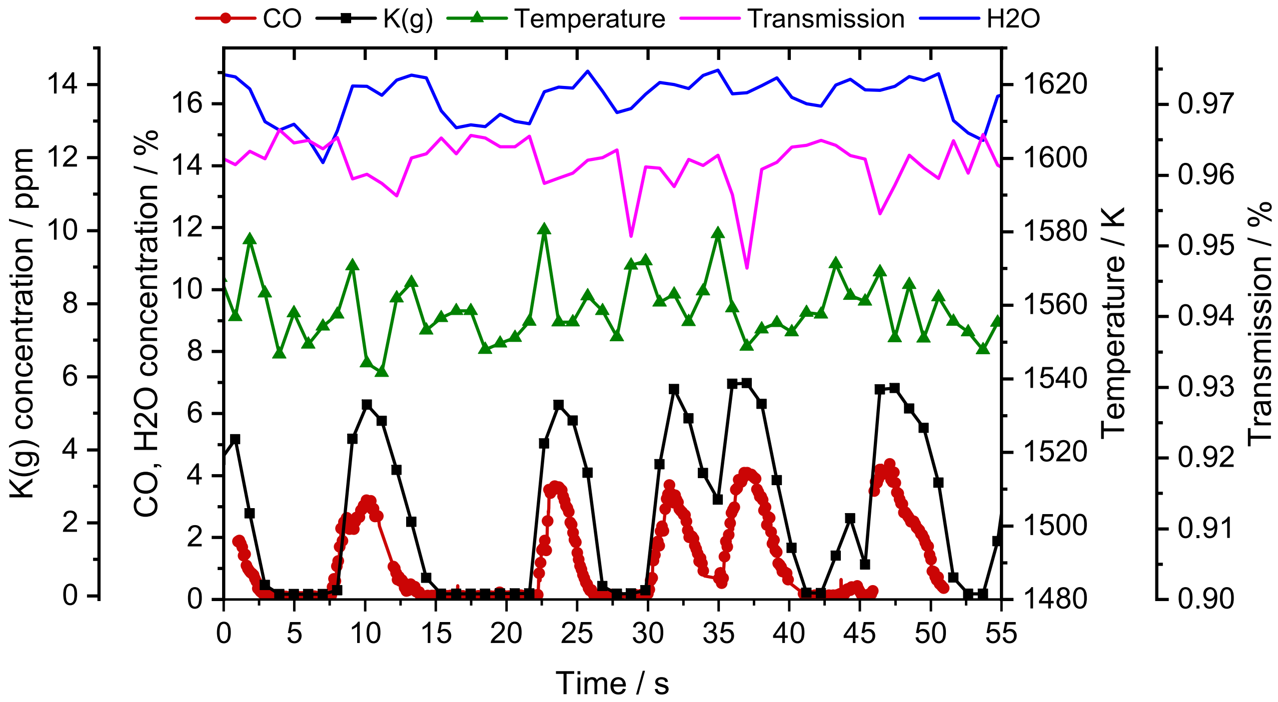
Theoretical process efficiency



Entrained-flow reactor at ETC (VAFF)

VAFF 2 - Real-time Detection

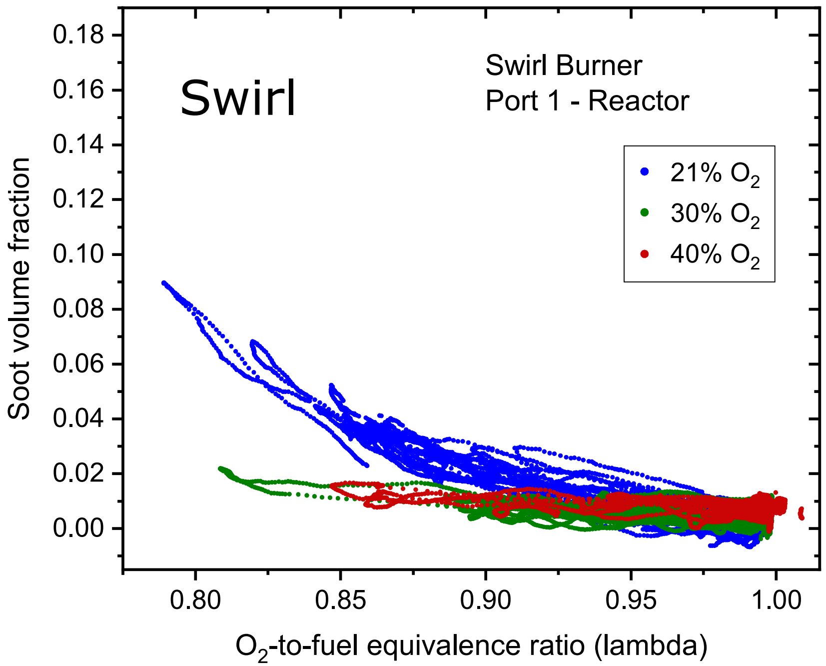
Simultaneous measurement of K(g), CO, H2O, temperature and transmission/soot.

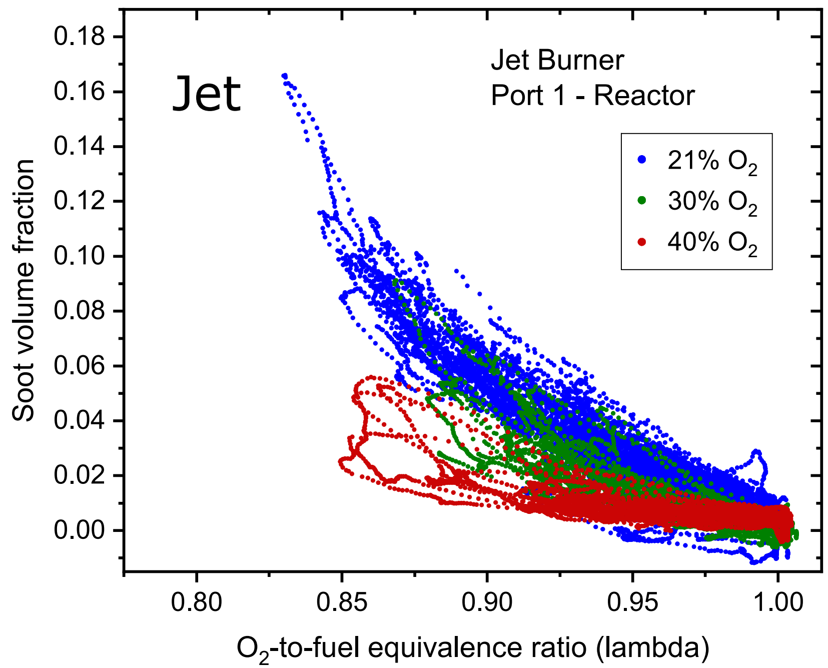


- Correlation between K(g), CO and soot.
- Correlation with gas temperature and H_2O not obvious.
- Low CO concentrations not detectable, but low K(g) accurate.

VAFF 2 - Soot vs. Lambda

Soot volume fraction as a function of equivalence ratio for 3 O_2 levels. Local lambda from CO compared to TEC.

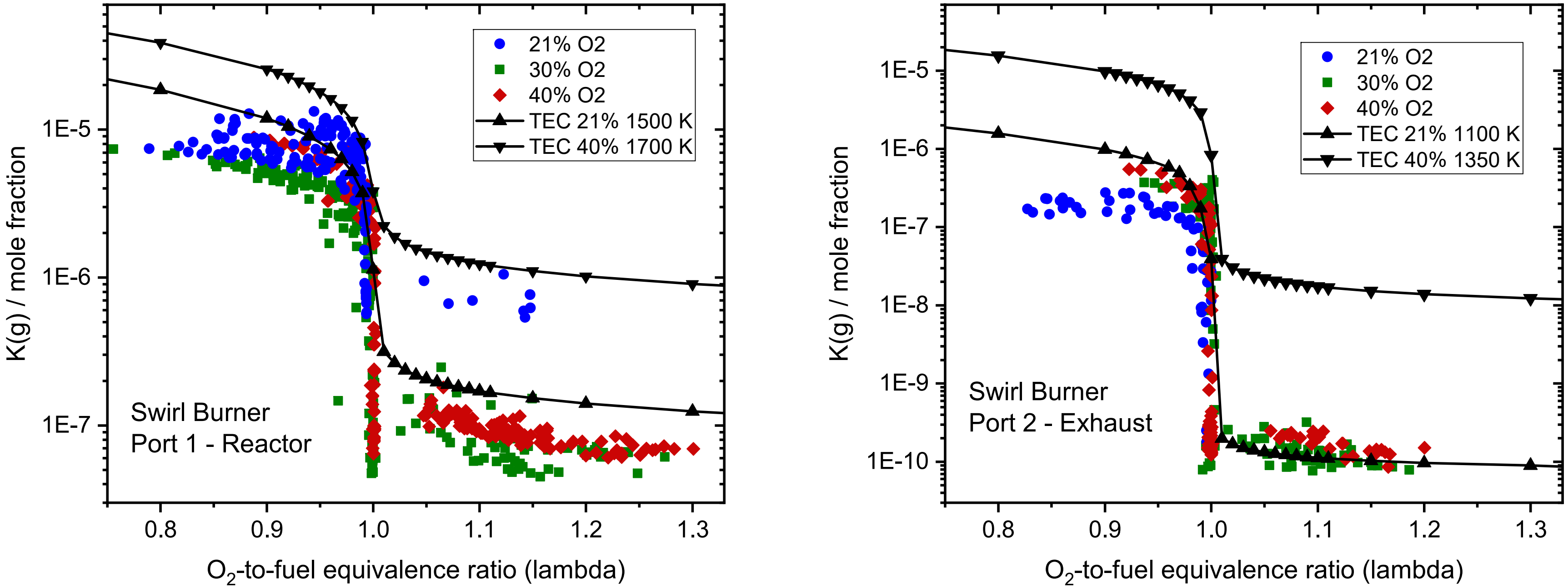




- Local lambda varies in a wide range.
- Less soot for swirl burner
- Soot decreases for increasing O_2 enrichment.

VAFF 2 - K(g) vs. Lambda

K(g) as a function of equivalence ratio for 3 O_2 levels.
Local lambda from CO and H_2O compared to TEC



- K(g) S-shape observable, discrimination combustion-gasification, lambda sensor, feedback control to keep lambda =1.
- K(g) below equilibrium at Port 2.
- K(g) at equilibrium at exhaust (both swirl and jet, any O_2).

Laboratory Burner Studies

KOH converted in premixed methane/air flat flame

- Characterized by TDLAS
- Homogeneous horizontal temperature and concentration profiles

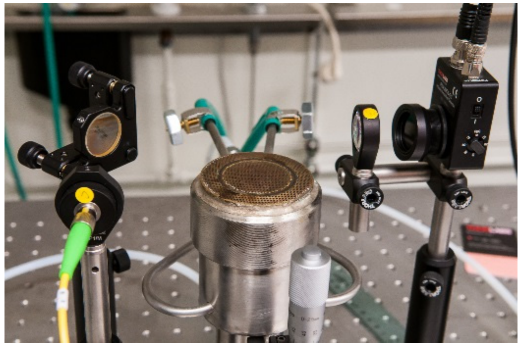
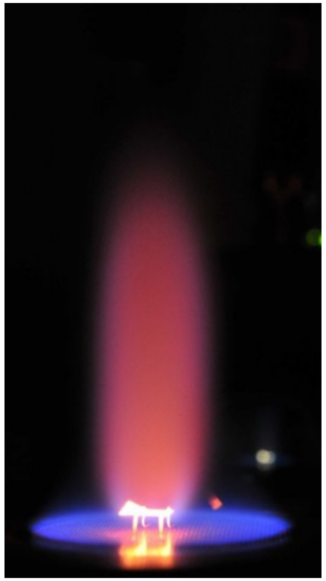


Photo KOH/K plume

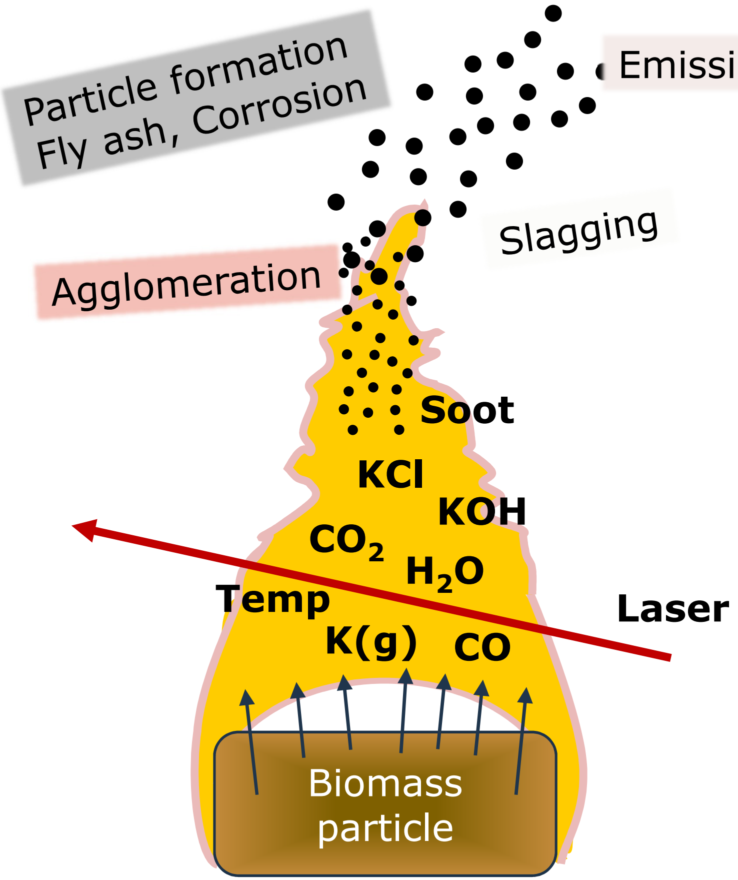


Simulated KOH(g)

Simulated K(g)

- K(g) and KOH as a function of residence time and equivalence ratio
- Simultaneously measure temperature, H_2O, CO and CO_2.
- Compare with 2D reaction kinetics simulations including potassium.

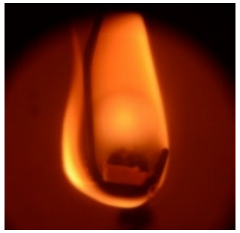
Single-Particle Studies

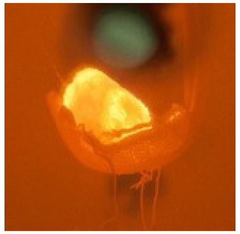


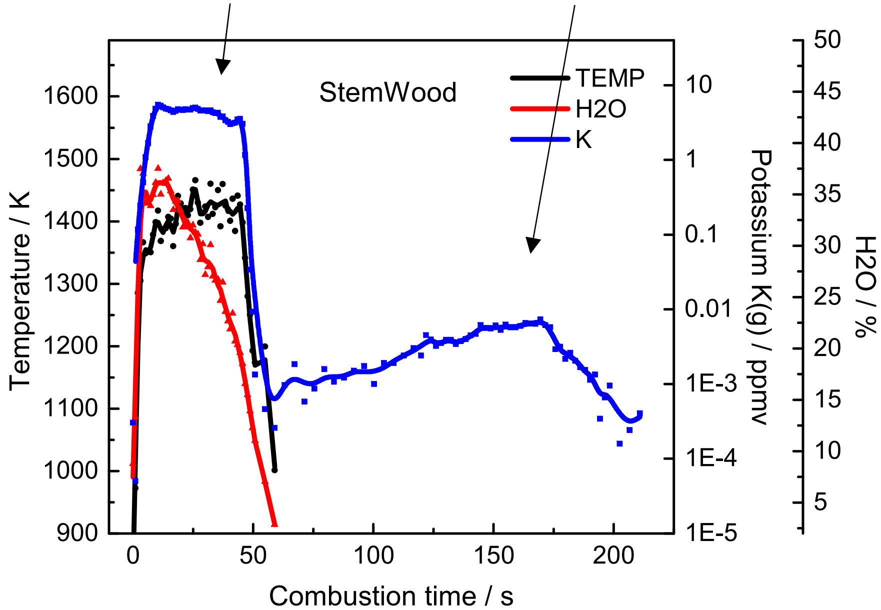
Compare to biomass particle model

Single-particle conversion

Devolatilization Char conversion







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Z. Qu, E. Steinvall, R. Ghorbani, F. M. Schmidt, *Anal. Chem.* **88**, 3754–3760 (2016)

CONCLUSIONS AND OUTLOOK

- TDLAS is well-suited for real-time in situ measurements of process parameters in the reactor zone (small- and large-scale).
- TDLAS can give real-time info on local equivalence ratio; and evaluate performance differences (burner, oxygen-enrichment).
- Experimental verification: Significant K(g) concentrations (on the order of KOH, KCl) under fuel-rich conditions
- Experimental verification: K(g) agrees with equilibrium calculations at end of conversion, and of K(g) behaviour around stoichiometry.
- Evidence that the ash-forming elements, not the K content in the fuel, determine the observed K(g) concentrations.
- Inorganic ash-transformation reactions seem to approach equilibrium fast.
- K(g) could be used a lambda sensor.

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SFC

BIO4ENERGY

Swedish Energy Agency

VETENSKAPSRÅDET
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