IEA Bioenergy

Workshop Report

IEA Bioenergy: Task 33: 08 2019

Gas cleaning, experiences, new developments, analytics and diagnostics

KIT Campus North, June 6th 2019

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Edited by: Berend Vreugdenhil, Jitka Hrbek

INTRODUCTION

Gasification is a technology widely applied for the production of heat and power. Two trends can be observed, the first that the feedstock base is broadening to more difficult feedstocks and the second that the end use of the gas is also requiring more advanced gas cleaning techniques. These developments can only be made possible with advanced analytics and diagnostics. This workshop is organized to bring together the various companies and research organisation active in the field of gas cleaning and gas analysis.

SPEAKERS

HANS LEIBOLD – KIT
BEREND VREUGDENHIL – ECN.TNO
TIM BENSTEAD – Rath Filtration
SERGE BIOLLAZ – Paul Scherrer Institut
YORG NEUBAUER – TU Berlin
ALEXANDER FATEEV – DTU
MAX SCHMID – Uni Stuttgart
EFTHYMIOS KANTARELIS - KTH
PATRICK NAU – DLR
FLORIAN SCHMIDT – UMEA University

GOAL

The goal of the workshop is to share new knowledge and ideas about improvements for gas cleaning. The organising committee suggest reading the thorough report on gas analysis guidelines from IEA Bioenergy Task 33 when joining the workshop

http://task33.ieabioenergy.com/content/Task%2033%20Projects

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Introduction

Gasification is generally acknowledged as one of the technologies which could enable the large-scale production of biofuels and chemicals from biomass and waste. One of the main technical challenges associated to the deployment of biomass gasification as a commercial technology is the cleaning and upgrading of the product gas. The contaminants in the product gas from biomass/waste gasification include dust, tars, alkali metals, BTX, sulphur-, nitrogen- and chlorine compounds, heavy metals and further undesirable components.

Thus, proper measurement of the components and contaminants of the product gas is essential for the monitoring of gasification-based plants (efficiency, product quality, by-products), as well as for the design of the downstream gas cleaning train (for example, scrubbers, sorbents, etc.).

In practice, a trade-off between reliability, accuracy and cost has to be reached when selecting the analysis technique for a specific application. The deployment and implementation of inexpensive yet accurate gas analysis techniques to monitor the fate of gas contaminants might play an important role in the commercialization of biomass and waste gasification processes.

The workshop "Gas cleaning, experiences, new developments, analytics and diagnostics", which was organized by IEA Bioenergy Task 33 and hosted by KIT (Germany), offered an overview on actual developments in product gas cleaning and analytics. The highlights of the presentations are summarized in the following chapter. Presentations details can found on the Task 33 website:

http://www.ieatask33.org/content/home/minutes_and_presentations/2019_June_WS/

Hot gas cleaning – Experience and improvements at the bioliq pilot plant

H. Leibold, KIT

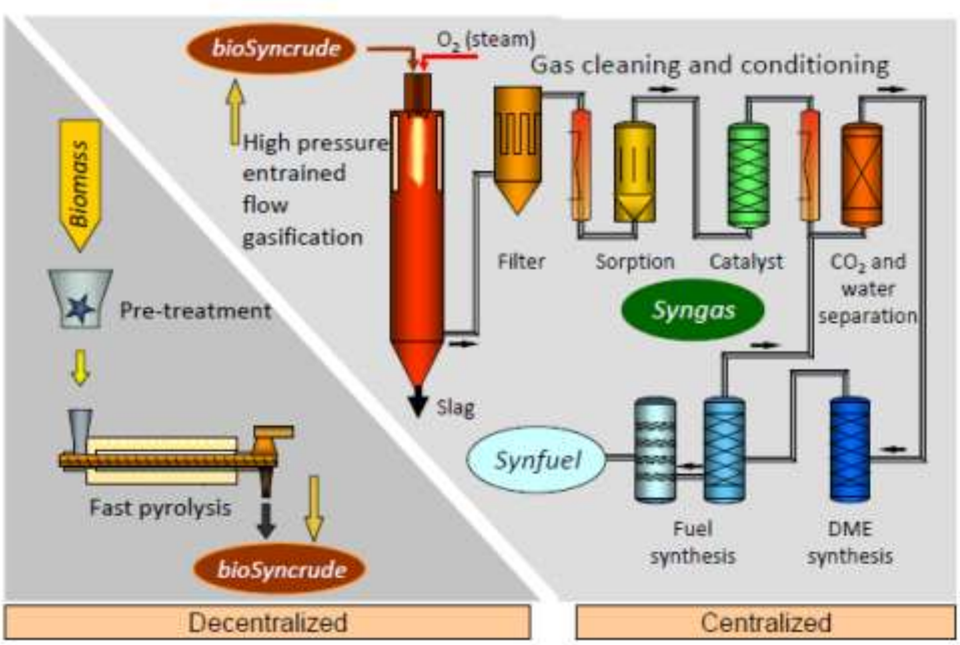


Figure 1: The bioliq process

The bioliq process is a combination of decentralized and centralized concepts. The biomass is pretreated using fast pyrolysis in decentralized units, produced bioSyncrude is then transported to a centralized entrained flow gasification unit. Here the synfuel from syngas is produced. The details concerning gas cleaning can be seen in the following figure.

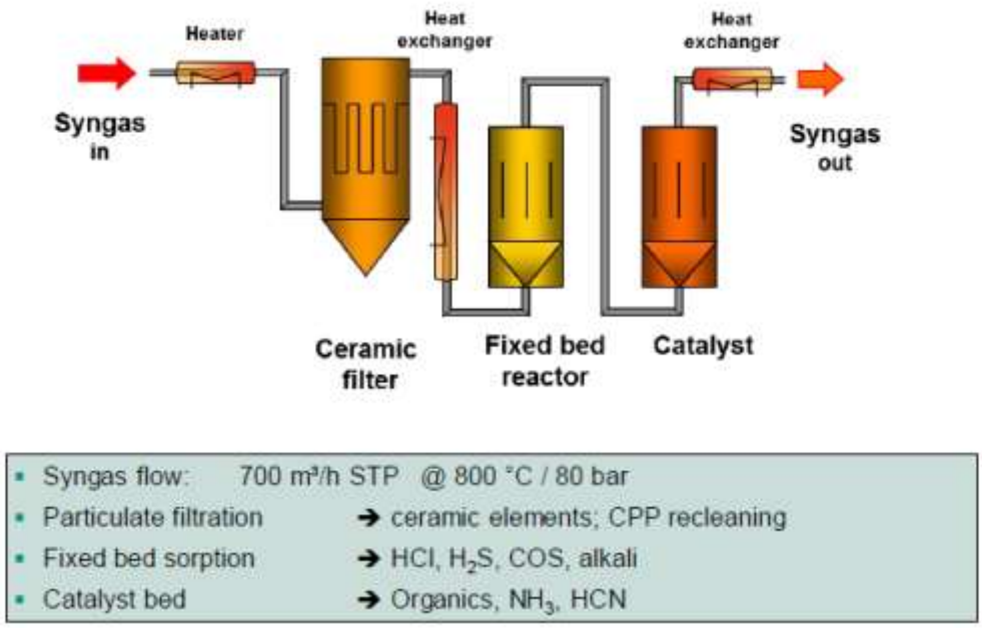


Figure 2: Dry HTHP cleaning bioliq

The sticky and reacting particles are filtrated using ceramic filter, the trace contaminants such as HCl, H_2S, COS, alkali species are removed by dry fixed bed sorption and finally, by catalytic decomposition

NH_3, HCN and trace organics are removed. Integrated syngas treatment enables scalability and long-term performance, for details see the following figure.

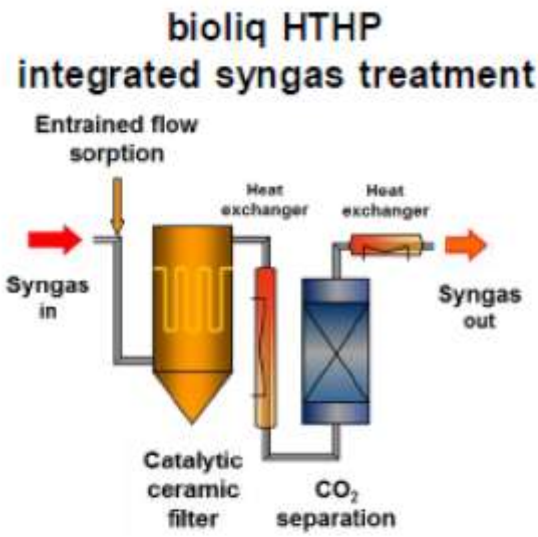


Figure 3: bioliq HTHP integrated syngas treatment

Entrained flow sorption process is characterized by the following points:

- Enables continuous sorption process for trace contaminants
- Adapts to variable contaminants` concentrations
- Utilizes pulverized sorbents to enhance sorption process
- Sorption properties instead of thermo-mechanical properties
- Excludes channelling and bypassing
- Utilizes liquid sorbents dispersions
- Enables further process integration

CALIDA (combined HT filtration and entrained flow sorption facility)

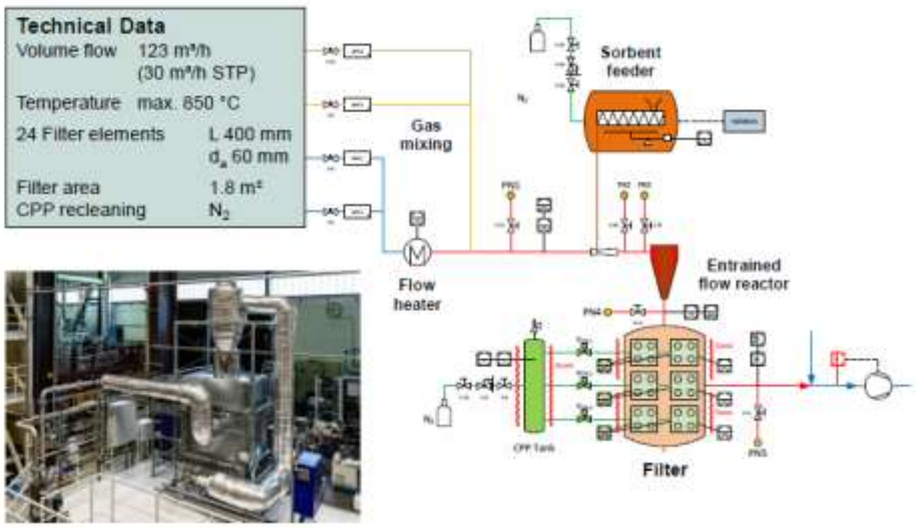


Figure 4: CALIDA

Summary and outlook:

- The bioliq dry HTHP syngas cleaning process chain provides a solution for the most relevant trace contaminants.
- The conversion of N-species in a catalytic step is still to be done
- Development of an entrained flow sorption process for trace contaminants.

- Basic investigations on sorption kinetics of the most critical H_2S on mineral Na and Ca sorbents reveal a strong influence of temperature.
- Na based sorbents show the fastest H_2S sorption kinetic.
- Detailed investigation on the sorption process during entrained flow sorption.
- The PDU CALIDA will provide design parameter for the bioliq process.
- Investigations on CuO based sorbents for HT polishing filters are ongoing.
- Catalytic impregnation of ceramic fiber filters are under development.

MILENA gasification as a platform towards heat and power and sustainable fuels and chemicals

B. Vreugdenhil, ECN part of TNO

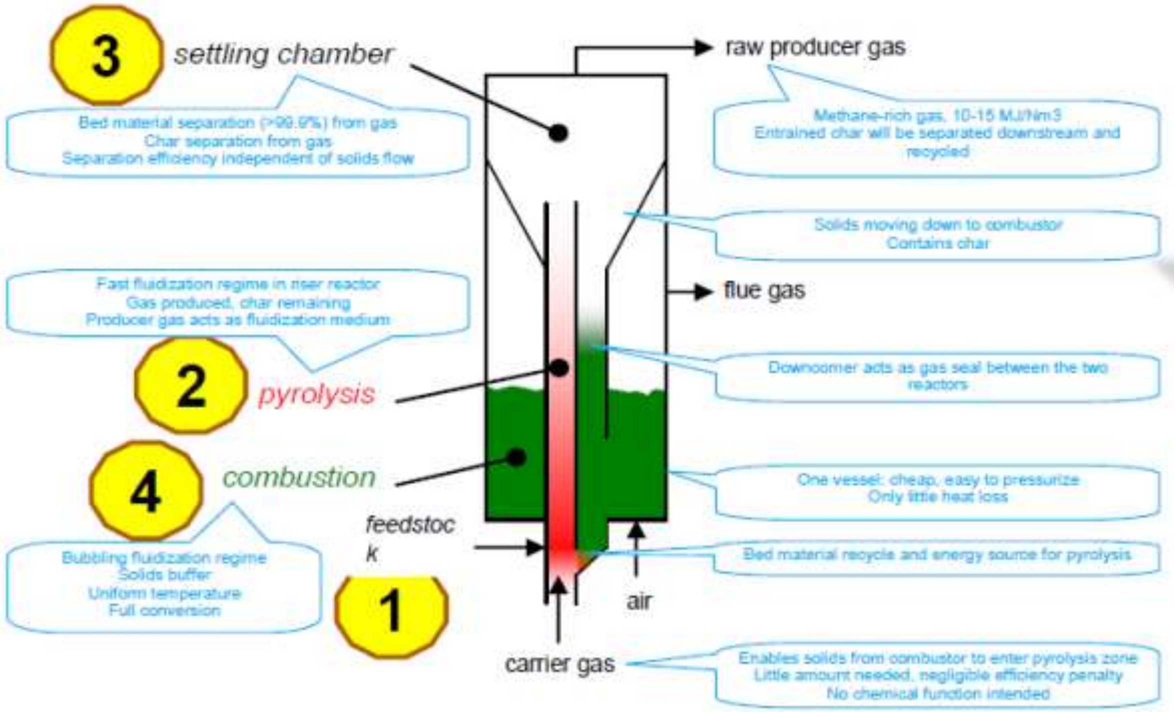


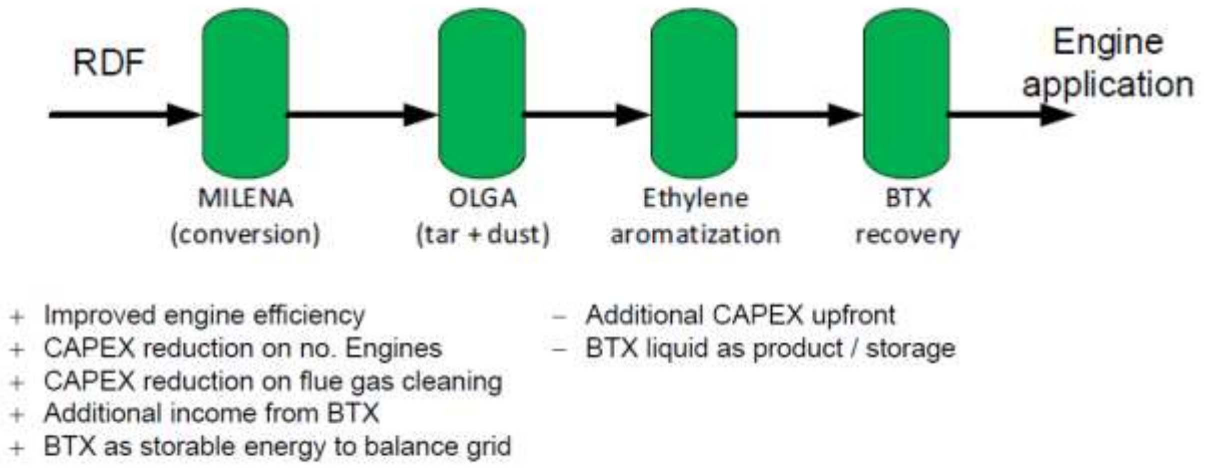
Figure 5: MILENA technology

The MILENA gasification process and OLGA tar removal is commercial available technology for Green Gas production and for Waste to Energy applications. Synova is currently building a facility in Thailand to produce heat and power (6MWth to 1,5 MWel.)

Figure 6: Synova facility in Thailand

Berend explained that the future for waste to energy lies in co-producing chemicals with heat/power. A scheme showing a possible future lay-out is give below.

Future for waste-to-enery:



ECN.TNO is investing also in new infrastructure to perform state of the art R&D on biofuel production in combination with gasificaiton. The following figure depicts the new infra.

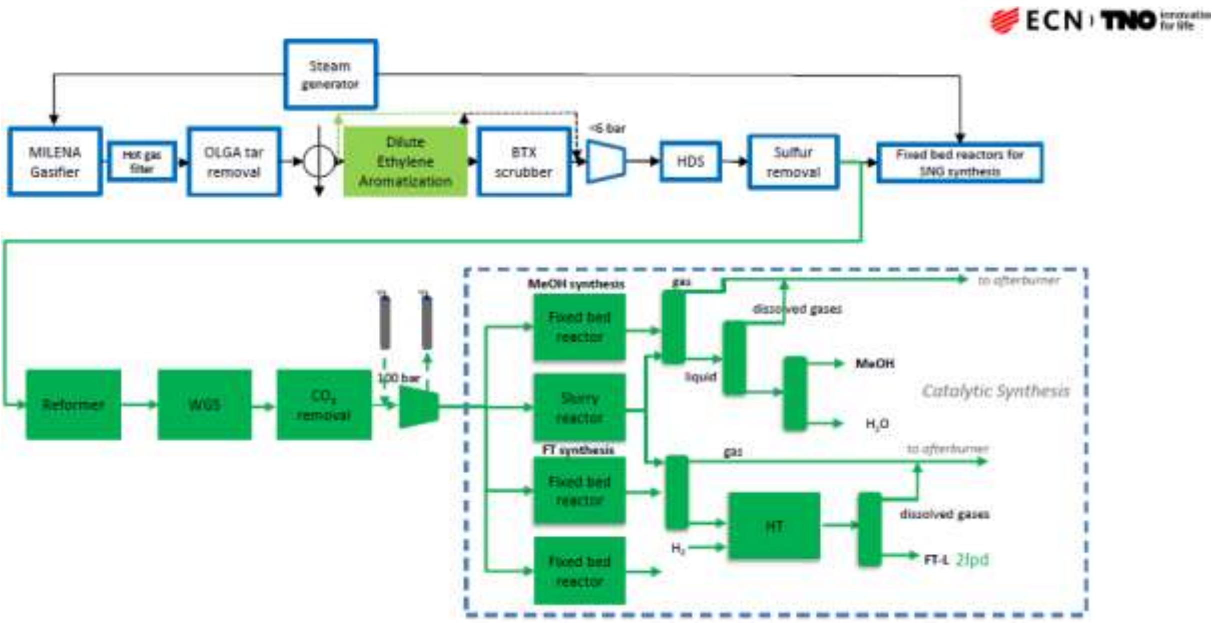


Figure 7: Biofuels laboratory at ECN.TNO

Latest developments in ceramic filter-based hot gas filtration

T. Benstead, RATH

What is fine particulate and how can be controlled:

- Combustion particles, organic compounds, metals etc. < 2,5µm
- Dry electrostatic precipitation, which is a non-barrier filter process in which fine dust particles are removed from the contaminated gas stream. The positively-charged (ionised) particles flow over negatively charged collector plates to which they are attracted
- The baghouse filter system is a barrier filter process in which fine dust particles are removed from the contaminated gas flow. Filtration occurs when the raw gas is passed through the wall of a long, cylindrical bag filter made of woven or felt material
- The fine particulate trapped on the outer surface of the fabric filter is then removed via a shaking, sonic horn or "reverse jet-pulsed air" process

What is hot gas filtration and how does it work:

- Hot Gas Filtration (HGF) is generally taken to refer to the use of a barrier filtration technique to control process or exhaust emissions in the temperature range 250-1000°C
- Developed in the 1980s, rigid, low density ceramic filter (CF) element technology - typically in candle form - is particularly suited to HGF applications
- High temperature wool (HTIW) is a mineral-based material comprising a collection of synthetically produced fibres of various lengths and diameters
- Temperature-resistant VFP are playing an increasingly important role in thermal insulation thanks to their variety of shapes and outstanding properties
- The moldings are made from high-quality mineral, alkaline or polycrystalline wool with a high aluminium oxide content
- VFP made from high purity PCW (i.e. with an aluminium oxide content > 72% are not classified according to "EU-REACH") and offer very high corrosion and temperature resistance

Ceramic filter elements – surface filtration

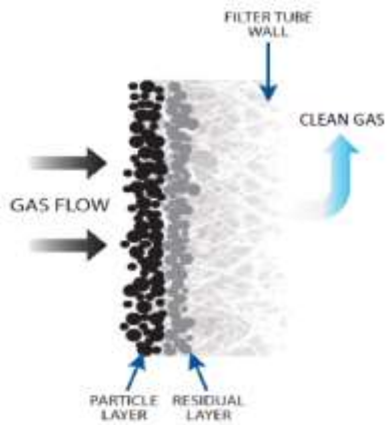


Figure 8: Ceramic filter elements

- High efficiency dedusting (HEPA*-rated)
- Filtration efficiency further enhanced via residual „primary" dust layer (>99,99%)
- Negligible penetration of dust into the filter body
- Primary dust layer provides greater resistance to blockage, masking and poisoning and hence to an overall improvement in filter performance and durability
- Rigid, low density ceramic filter elements are not subject to expansion or bending
- Dedusting via "reverse jet-pulsed air" system
- Suitable for operation with variable dust loads

What is catalytic hot gas filtration:

- Hot gas filtration is generally taken to refer to the use of a barrier filtration technique to control process or exhaust emissions in the temperature range 250-1000°C

- Catalytic HGF takes this concept one step further with the addition of an SCR-Catalyst-coating to the filter fibres. This enables "multi-pollutant control" of the particulate, acid gases1 (SO_2, HCL, HF) and oxides of nitrogen2 (NOx)
- SCR Technology is limited to a max. inlet temperature of 420°C
- It is similar to the technology in use on today's "Euro 6" Diesels cars which employ similar "DeDust & DeNOx" techniques…. albeit with some subtle differences!

Table 1: Industrial applications of hot gas filtration

Industry		Sector / Branch	Potential Pollutants	Demand
	Glass Manufacturing	Container Glass, Flat Glass, Tableware Glass, Special Glass, etc.	Dust, acid gases, NOx / NH_3, CO, heavy metals	2017+
	Cement & Lime Manufacturing	Main Furnace, Clinker Cooler, Alkali-Bypass, „xmercury"	Dust, acid gases, NOx / NH_3, dioxins / furans, CO, Hg, heavy metals	2018+
	Chemical & Petrochemical Industry	Catalysts, Pigments, usw.	Dust, acid gases, NOx / NH_3, dioxins / furans, CO, VOC, Hg, heavy metals	2019+
	Metal Processing Industries	Iron & Steel, Non-Ferrous	Dust, acid gases, NOx / NH_3, CO, VOC, heavy metals	2020+
	Biomass & Waste Incineration	Also Gasification, Recycling, Remediation	Dust, acid gases, NOx / NH_3, CO, dioxins / furans, Hg, heavy metals	2021+
	Energie / Power Generation	Power Plants, Stationary / Marine Engines, Gas Turbines, usw.	Dust, acid gases, NOx / NH_3, CO, VOC	2022+

Gas analysis working group (GAW): Status and perspective

Y. Neubauer, TCKON, S. Biollaz, PSI

Motivation:

- Exchange and sharing information and experiences on recent methodologies in gas sampling and gas analysis for bioenergy processes (gasification, biogas, combustion, pyrolysis, ...)

The way we work together:

- Website, Wikis, Online Polls and Virtual Task Boards (VTB) to provide information on current status of analytical technologies in the fields of interest
- Workshops and Webinars on all issues regarding gas sampling and analysis, as well as on general issues which are relevant for GAW (ELN, HAZOP, …)
- Working together in joint measurement campaigns to gain and deepen specific knowledge and intensify direct personal exchange (host site).

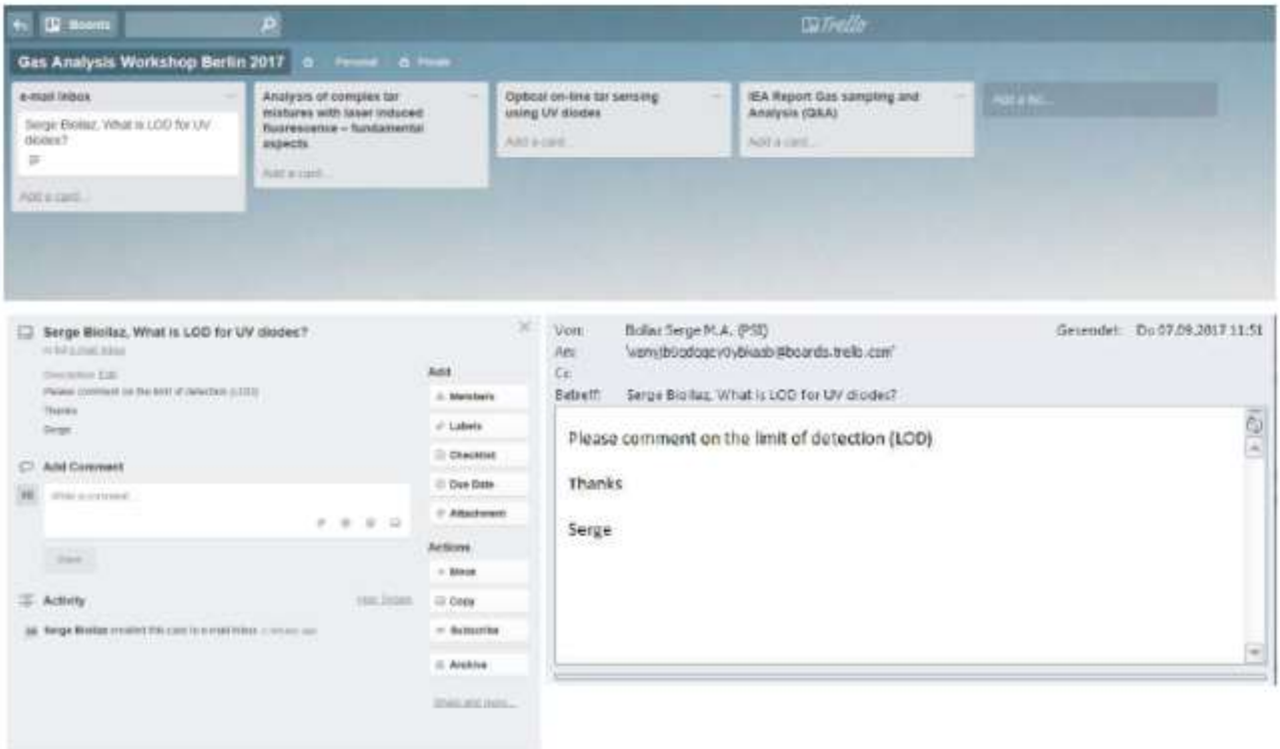


Figure 9: Trello as a platform for feedback & questions

Continous on-line tar monitoring and tar analysis with UV-fluorescence

Y. Neubauer, TCKON

Scientists wants	**Industry needs**
Fast and detailed results	A reliable, robust, easy to operate and to maintain measurement or monitoring instrument.
Preferred inline measurements revealing reactor insights on time	A 'translation' of the physical tar species properties and amounts into a useful value, characterizing the current status of the respective plant section.
Continuous monitoring	A device that can be taken care of by a technician - rather than a scientist !
Validated, spatial resolved data for modelling and simulation	A tool that handles tar loaded gas which stays longer in operation than the monitored part of the plant itself! Such a device needs to be applicable in the industrial environment (temperature, vibrations, dust, ex proof zones). To assure a long operating and life time, the direct contact of the measuring unit with the tar species especially in 'raw' gases needs to be avoided.

Optical techniques such as UV-fluorescence spectroscopy offer a number of benefits for this purpose

Principal setups for fundamental examinations can be seen in the following figure. As can be seen, the methodology is suitable for liquid and gas phases.

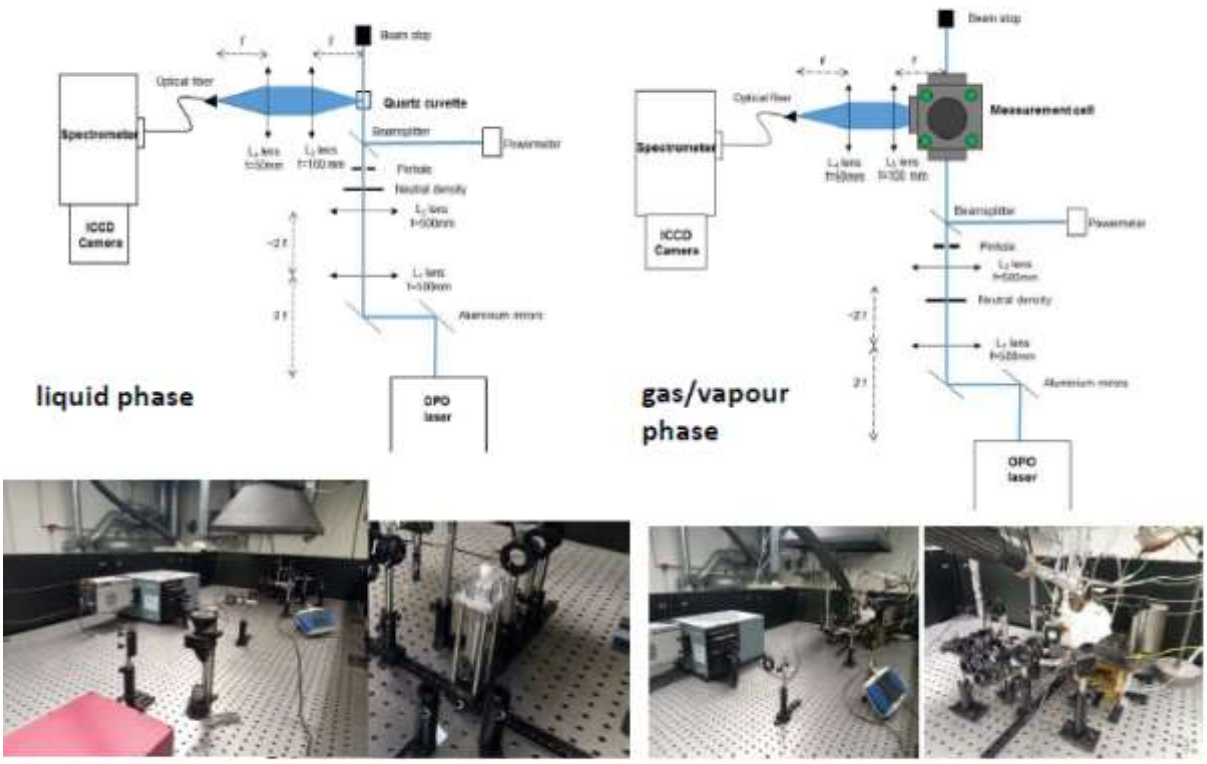


Figure 10: Principal setups for fundamental examinations

Industrial application for tar monitoring using UV-fluorescence – advantages:

- Robust and reliable
- As much and as long as possible unmanned operation
- Little maintenance requirements by technicians, not analytic experts
- Less expensive and with robust components
- Eliminating further influencing factors

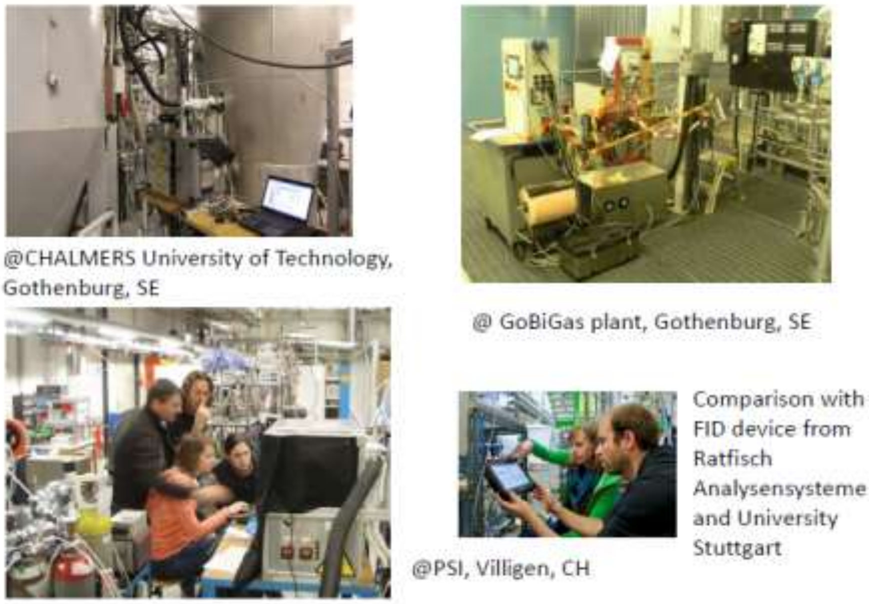


Figure 11: Field deployable set-ups

On line UV/IR measurements of tars and other gas compounds

A. Fateev, DTU

Choice of spectral range depends on different factors:

IR (MIR: 600-8000cm-1):

- Classic tool for H_2O, CO_2 and H_xC_y+
- Databases available (HITRAN, PNNL)
- in situ or on-line measurements

UV (200nm<l):

- superb sensitivity for (complex) organics
- (very) strong light absorption
- in situ or on-line measurements

Special for gasification: no O_2

- possibility to go further down (120nm<l): far-UV
- superb sensitivity for major/minor gas components
- compact system
- in situ or on-line measurements

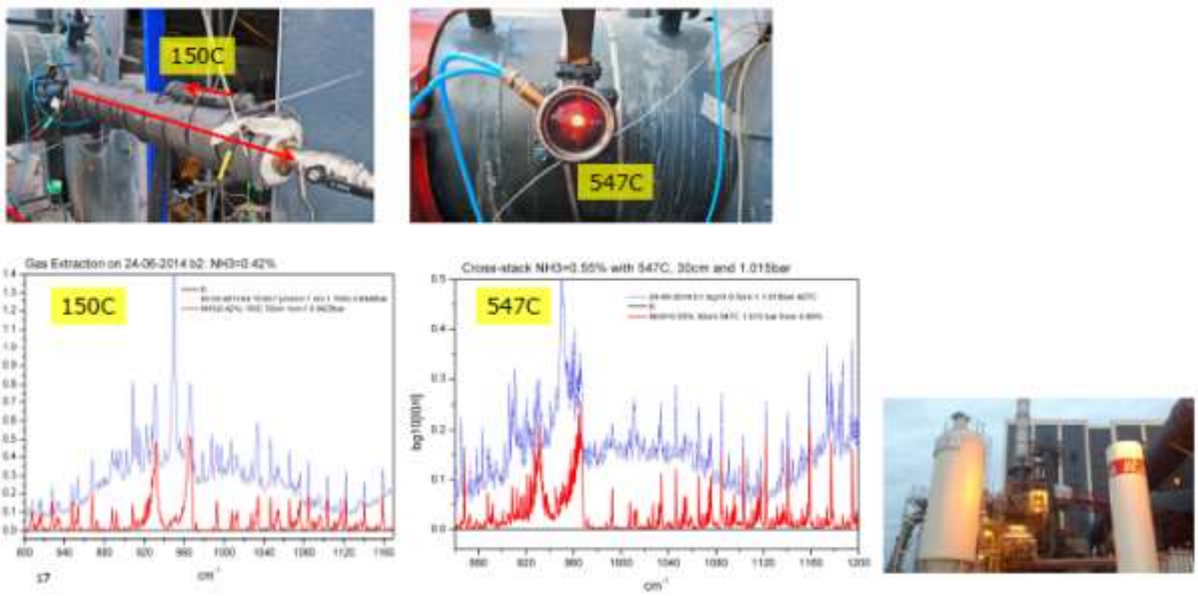


Figure 12: Field measurements at 6 MW demo plant

As an example, the details from field measurements can be seen in the figure above.

Data of the measurements:

- Straw gasification
- Gas feed into burner
- Target: NH_3, HCN, NO and H_2O
- NH_3 extraction: ca. 24% less than in situ
- NH_3 trapping by condensing acids/tars

Another example which was presented were the field measurements at Viking gasification unit. The details can be seen below.

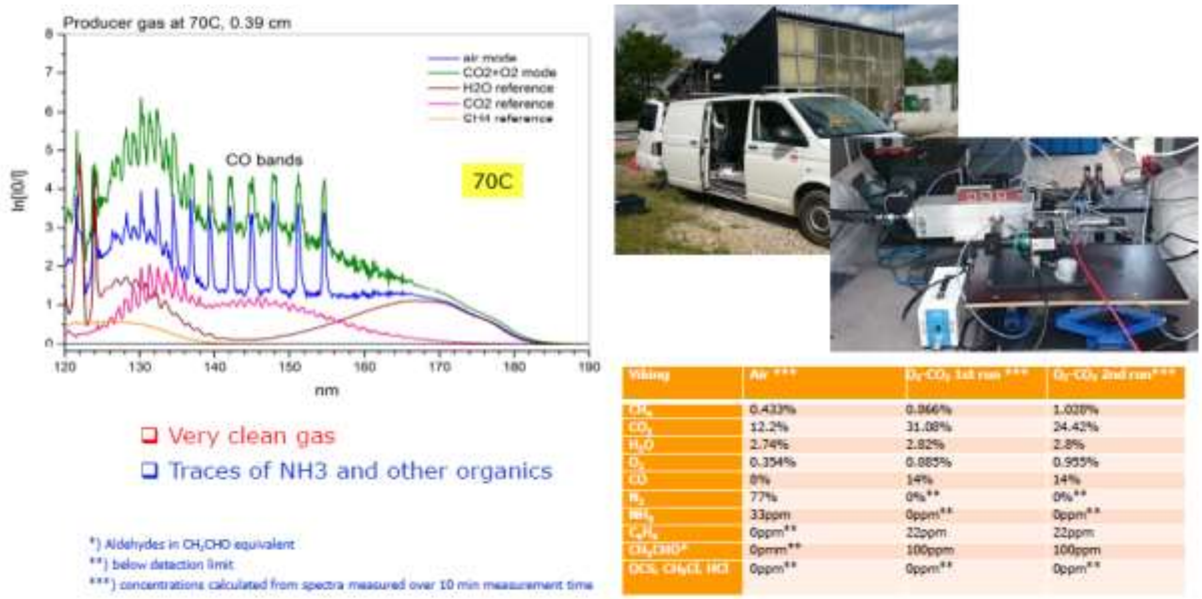


Figure 13: Field measurements at Viking gasification unit

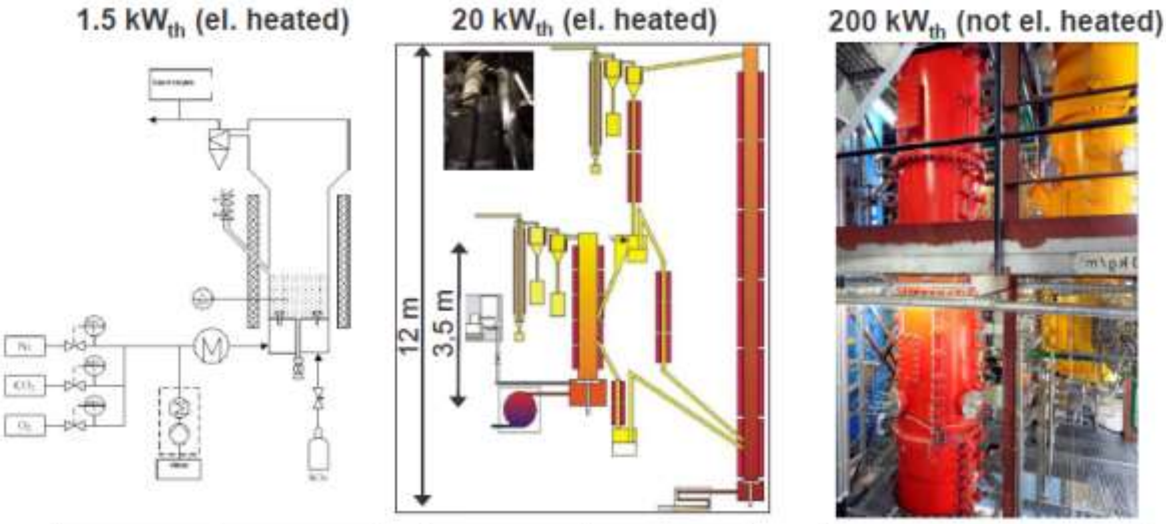
Conclusions:

- Broad-band absorption spectroscopy is a powerful and robust tool for tar and major/minor gas components in situ and on line measurements and process monitoring: buy all for 1 price concept
- T-dependent cross section databases can be generated on request (support instrument/sensor development
- Successful demonstration of in situ/on line approaches in measurements in various environments (low/high temperature gasification and combustion)
- Far-UV (160nm<) can be used for tar/BTX in situ measurements (absolute or relative) by simple weighting of the 195-230 nm and 170-200 nm areas under an absorption spectrum
- Ability unexpansive far UV small spectrometers opens possibility for a new in situ tar/BTX sensor development when a complex tar/BTX sampling can be avoided.

Tar and sulphur measurements and monitoring for biogenic residue gasification

M. Schmid, G. Schefknecht, University of Stuttgart

Fluidized bed research and pilot facilities at the Institute were presented.



Height	0.65 m
Fuel rate	Up to 1 kg/h
Fluidization	BFB

Height	3,5-12 m
Fuel rate	1-5 kg/h
Fluidization	BFB/CFB

Height	6-10 m
Fuel rate	20-50 kg/h
Fluidization	BFB/CFB

University of Stuttgart - Institute of Combustion and Power Plant Technology - M.Sc. Max Schmid

Figure 14: Research facilities at Institute of Combustion and Power Plant Technology

Tar measurement
The tars are measured using FID online Total Tar Analyzer TTA300, which is comparative with "Tar protocol" and it is a suitable device for raw gas monitoring.

Sulphur measurement
H_2S and COS are measured via micro-GS

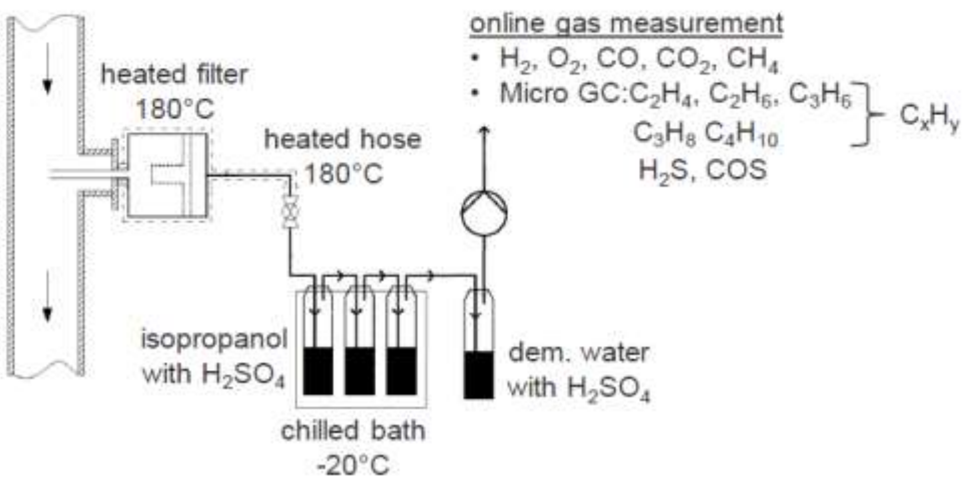


Figure 15: Measurement set up

- gas washing with isopropanol and water necessary to protect online gas analysers
- sour washing liquid enablesH2S and COS to pass the gas washing bottles
- H2S and COS can be measured down to~5 ppm

Tar protocol – wet chemical sampling

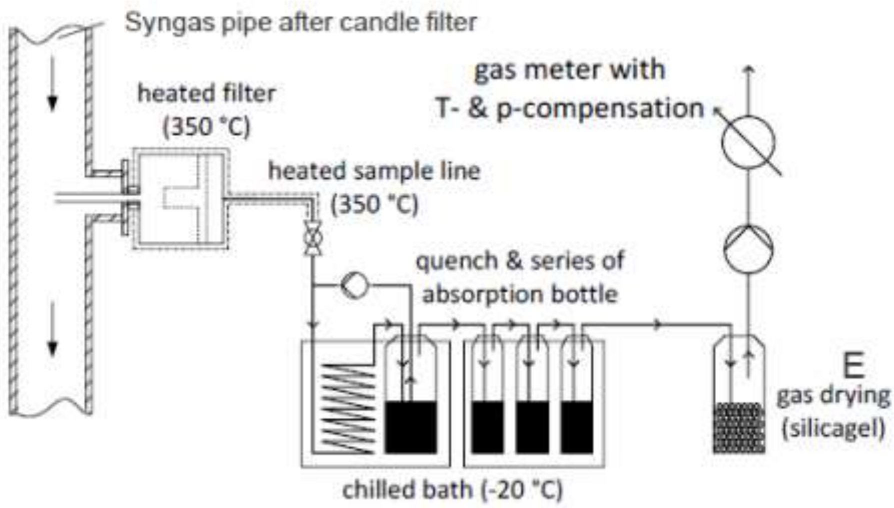


Figure 16: Wet chemical sampling measurement setup

Absorption liquid: Isopropanol

Liquid is sampled and analysed

- gravimetrically at IFK
- GC-FID at FAU
- GC-FID and GC-SCD at PSI
- additional N and S-containing tars for residue gasification

Summary:

- TTA 300 has good comparability to tar protocol and is an available device for raw gas monitoring
- H_2S and COS measurement with micro-GC is reliable for raw gas in residue gasification
- liquid sampling / tar protocol is still needed to characterize tars
    - for residue gasification additional GC detectable tar species need to be considered
    - solid formation needs to be considered for gravimetric analysis
    - endeavour to reduce liquid sampling effort by PSI’s automatic liquid quench system
- new online GC planned at IFK

Effect of gas phase K and H2S on catalytic tar reforming using commercial Ni catalysts downstream a biomass gasifier

E. Kantarelis, KTH – Chemical Engineering Department

- Reproducible dosing of gas-phase K and elimination of transient effects catalyst sintering and sulphur passivation allow for investigation of K/S effects using real gasification gas
- Contradictory literature results of gas phase K effects on methane and tar reforming activity
- K uptakes of <100 μg/m2 catalyst under reforming conditions
- As θK increase on the catalyst the θS on Ni sites decreases improving conversion (Plausible K-induced Ni-S bond weakening)
- Suppport-sorbed K has some effect on conversion of bigger tar molecules and almost no effect on CH_4
- Tailoring K and H_2S concentrations in the gas allows for virtually carbon-free operation

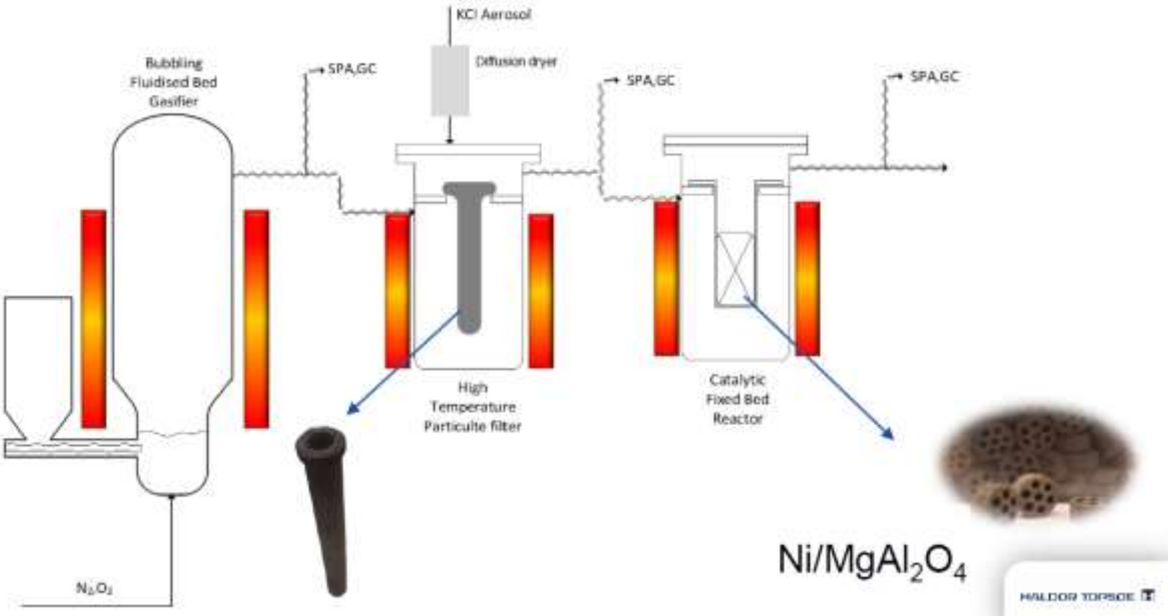


Figure 17: Experimental set up for tar reforming research

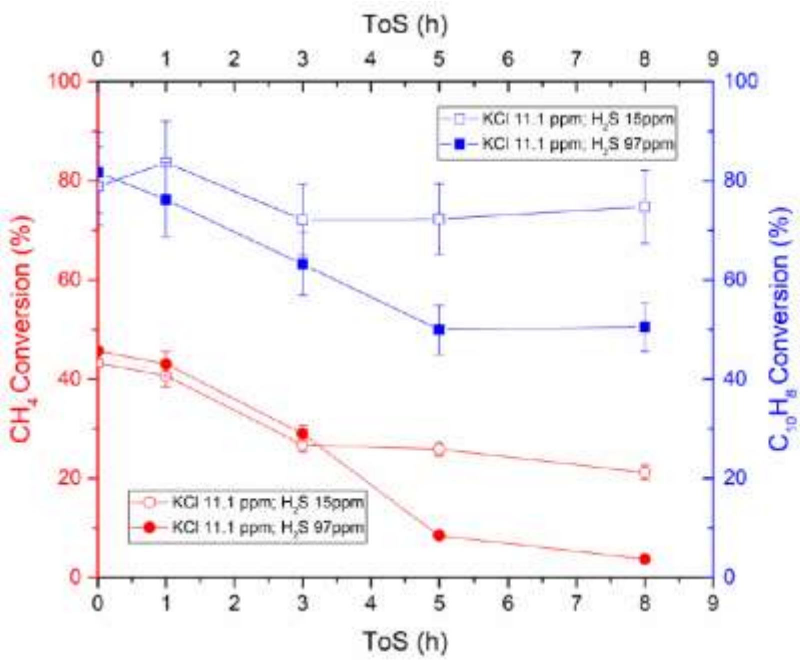


Figure 18: Results- 850°C Reduced Ni-catalyst

Gradual sulphur coverage affects the rate limiting step of conversion of different molecules.

Tunable diode laser absorption spectroscopy (TDLAS) for gas analysis in gasifiers

P. Nau, German Aerospace Center (DLR)

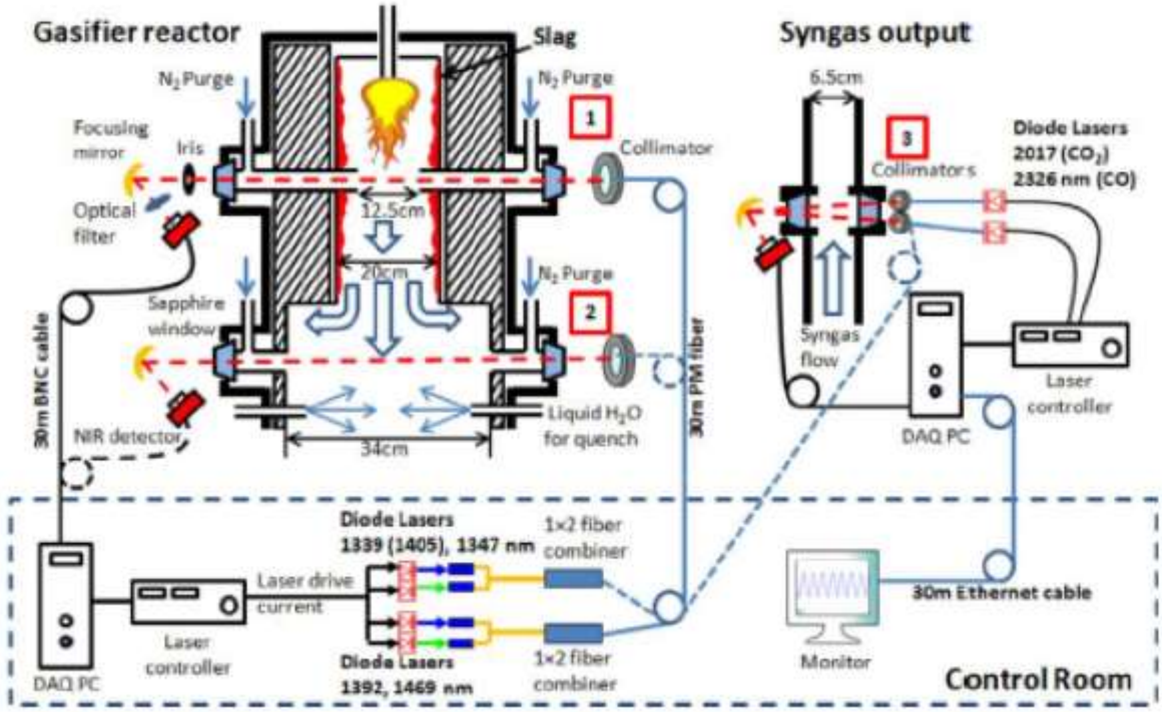


Figure 19: Optical access of measuring device

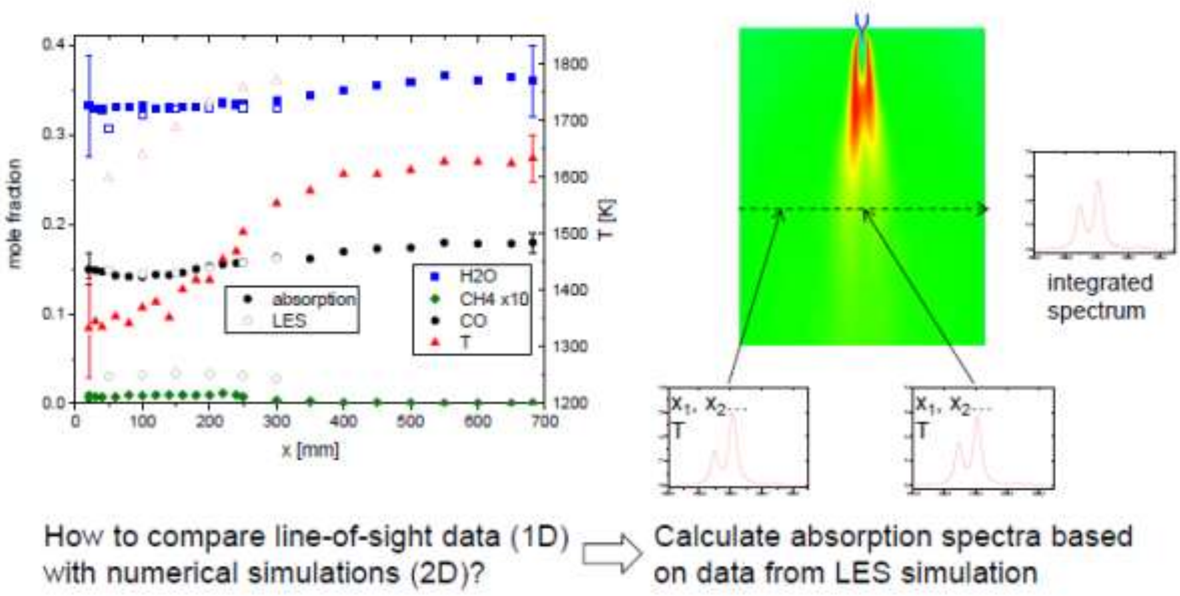


Figure 20: Comparison with numerical simulation

Laser absorption enables temperature and species mole fraction measurements

•Direct absorption: straightforward and calibration free
•WMS: higher sensitivity but more complicated data evaluation
•Careful line selection necessary
•Robust optical fibre setup
•Application at high pressure limited by pressure broadening of absorption lines and scanning range of diode laser

TDLAS-based in situ measurements of potassium in entrained flow gasifiers

F. Schmidt, Umea University

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

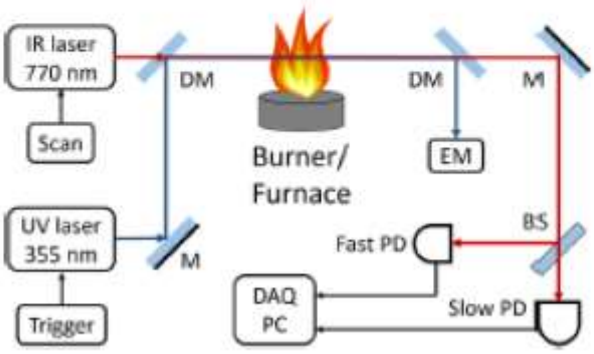


Figure 21: KOH detection – photofragmentation

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

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.

TDLAS is well-suited for real-time in situ measurements of process parameters in the reactor zone (small- and large-scale) and 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.

Summary

Some developments in gasification and gas cleaning were presented. These developments all show improvements in cost reduction, scale enlargement and or application potential. From these technologies it became clear that also measuring gas phase components is necessary in order to operate a technology to its fullest potential.

From the remaining presentations we learned that there are a lot of different techniques available, which are also constantly improved. The challenge is all of this lies in what is practical from an industrial perspective versus what are the specific components needed to be analysed. These two views are not aligned as became clear from York Neubauer's perspective.

A structurized approach in dealing with gas analysis is something that the R&D and industrial community could benefit from. Serge Biollaz's presentation showed how this can be realized and how he is already doing this together with other researchers. Also the combined report made by IEA Bioenergy Task 33 on gas analysis (as referred to on the first page) is a good example on how much knowledge is readily available within this (and broader) community.