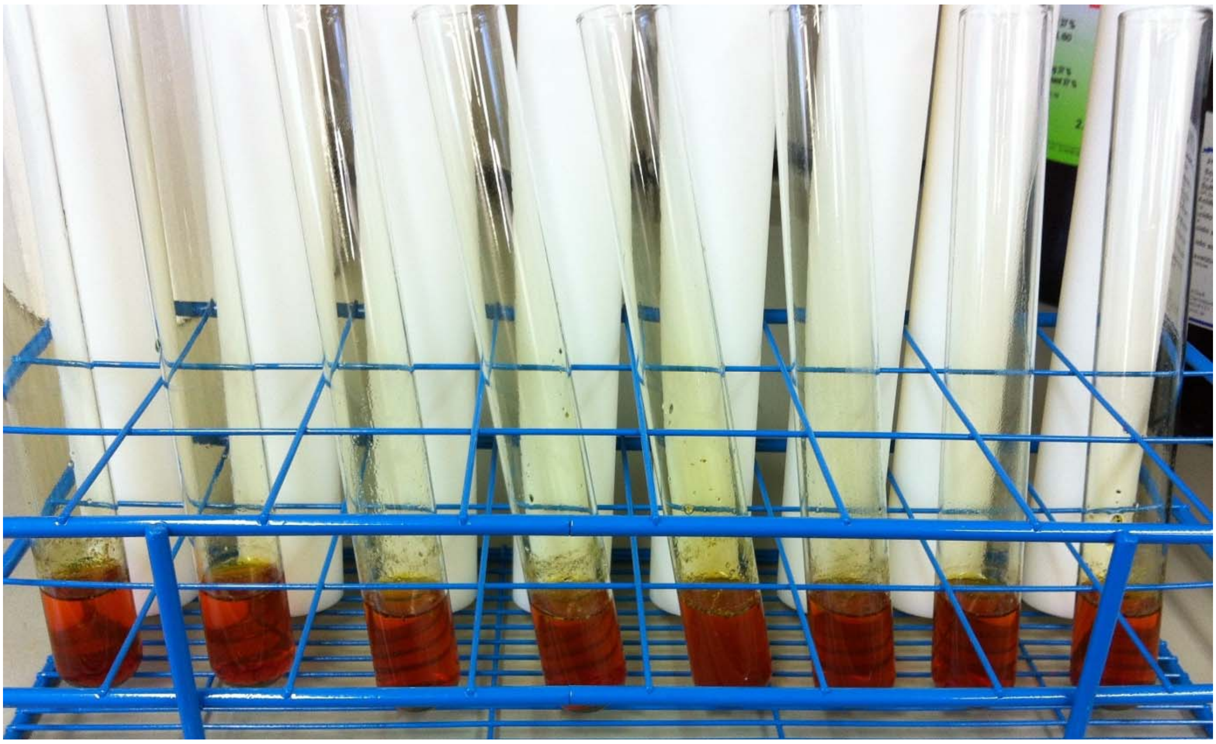

IEA Bioenergy, Task 33 –Gasification of Biomass and Waste

Workshop

Gas sampling, measurement and analysis (GSMA) in thermal gasification processes

26. October 2016, Lucerne, Switzerland

Summary by Dr. Jitka Hrbek, Vienna University of Technology

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Introduction

Technologies like the gasification of biomass for power generation or as a basis for further products from synthesis gas have strict quality requirements.

Trace components like H_2S, NH_3, HCN, dust or organic components like tar are responsible for corrosion, deposits, catalyst impairment and cause increased emissions. To prevent components, assemblies and processes from damages the gas quality at typical plant conditions have to be measured. There are many different principles to determinate the concentration of different pollutants.

Workshop "Gas sampling, Measurement and Analysis (GSMA) in Thermal Gasification Processes" was divided into three sessions:

- General overview for Energy Gas Applications
- Gas sampling, Measurement and Analysis Science
- Gas Sampling, Measurement and Analysis on Pilot, Demonstration and early Commercial Plants

Gas sampling, measurement and analysis (GSMA) in thermal gasification processes

workshop presentations

Session I: General overview for Energy Gas Applications

Overview energy gas specifications

Oliver Stankiewitz, Nordur Power Grid Association

Starting point is the overall purpose of product specifications is to provide a true & fair presentation of its 'Inner Quality'. The 'Insetting' of technical aspects and sustainable benefits along the whole value chain is the key driver for a premium energy gas product and should be reflected by its specifications as a true & fair presentation.

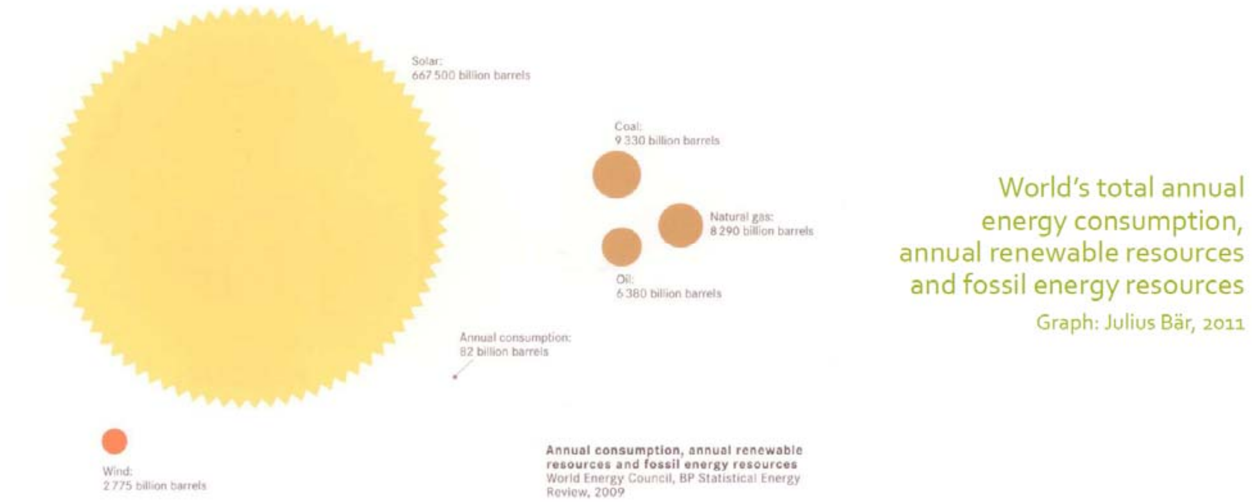


Figure 1: Renewable energy and security of supply

In contrast to other global challenges like biodiversity, water, soil, etc. energy itself is available in general.

To ensure a secure, reliable and sustainable energy supply we have to consider:

- Strategy: On what kind of resources do we have to focus?

- Technology: What are the best available technologies to harvest?

- Partnership: Who are the most reliable partners at the long-run?

The Global Grid (ETHZ 2013)

• Smoothing out supply and demand

• Minimizing power reserves

• Reducing the storage problem

• Lower volatility of electricity price

• Enhancing power system security

• Additional benefits ('Green Economy')

There is a fundamental need for international cooperation to reduce fossil fuel consumption and to phase-out nuclear power.

Swiss Gas Market

• In 2014, the total primary energy supply (TPES) in Switzerland was 26,7 million tons of oil equivalent (Mtoe), reflecting an increase of 0.5% per year over the last decade

• Fossil fuels account for 52% (13,9 Mtoe) of TPES. Switzerland has a significant share of oil in TPES at 40%, but low shares of natural gas (12%) and coal (< 1%). Nuclear also makes a large contribution to the energy mix with 25%. Renewable energy sources account for 23% (6,2 Mtoe), mainly hydro (12%) and biofuels/waste (9%). Other RES, such as solar and wind, have much smaller shares

• Most of the growth in energy supply is from increases in natural gas, biomass and waste, and geothermal (heat pumps). The country's self-sufficiency, as the share of domestic energy production in TPES, is around 48%

In 2014 the total final energy consumption was 825'770 TJ. The residential sector is the largest consumer, accounting for 31% (6.5 Mtoe). Transport consumed 29%, industry 21% and the commercial sector 19%. Natural gas and renewable energy have increased their share in residential energy consumption. Oil accounts for 95% of transport energy, electricity 4.5%, natural gas 0.3% and biofuels 0.1%.

Switzerland has around 85 gas utilities, most of them are local monopolies owned by the Cantons and Municipalities. They are also often involved in other activities, such as supplying electricity, heat or water. In 2014, the 9 biggest utilities, owned by the largest cities, sold half of the gas, whereas the 42 smallest utilities accounted for only 10% of total sales.

Facts and Figures related to the Swiss Gas Sector (2014)	
Number of municipalities in Switzerland	2'324
Number of gas supplied municipalities	961
Population in gas supplied municipalities	6'150'000
Number of residential buildings	1'696'000
Number of gas heaters in residential buildings	270'000
Gas consumption of residential buildings (in TWh)	11,8
Number of gas fueling stations	135
Number of biogas plants (feeding into gas network)	23
Biogas fed into gas network (in GWh)	213
Length of Swiss gas network (in km)	19'500
Value of gas infrastructure (in CHF)	13-20 Bn
Investments of the gas sector (in CHF)	323 Mn
Gas consumption (in TWh)	30
Swiss share of EU total consumption	0,7%

Table 1: Swiss Gas Sector - facts and figures

Vertical integration in gas transmission and distribution is strong. For the gas procurement, the local monopolies have set up 4 regional companies:

• Gasverbund Mittelland AG

• Erdgas Ostschweiz AG

• Gaznat SA

• Erdgas Zentralschweiz AG

Each regional company operates its own HP-grid and procures most of the gas through Swissgas AG, the gas industry's vehicle for imports. The regional companies also have direct import contracts with foreign suppliers.

Conclusions and next steps:

• Think globally – a basic need of our time

• Demonstrate your co-benefits

• Do the externalization of the internal benefits

• Generate an added value to bridge the gap

• Let's bring sustainable projects as a real asset to

the ground

Just add hydrogen – Making the most out of a limited source

Ilkka Hannula, VTT

The presentation especially motivated by arguments like:

- ”Electric vehicles will do the job”
- ”Decarbonisation of fuel important, but only after electricity and heat”
- ”Sustainable biomass is a scarce resource and therefore cannot do the job”

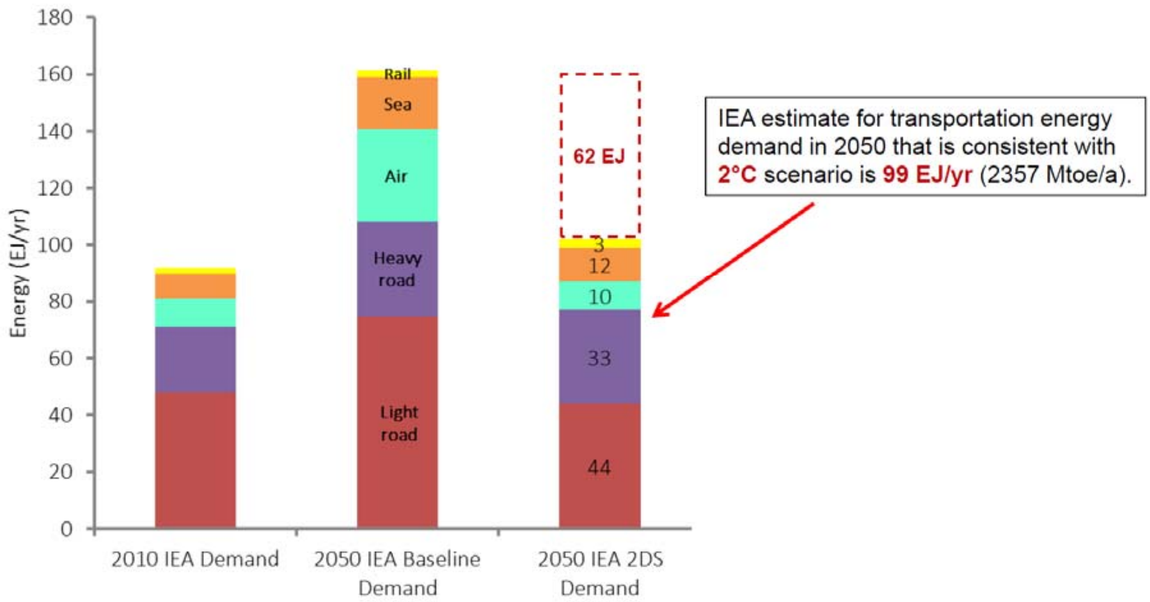


Figure 2: Global transportation energy demand in 2050

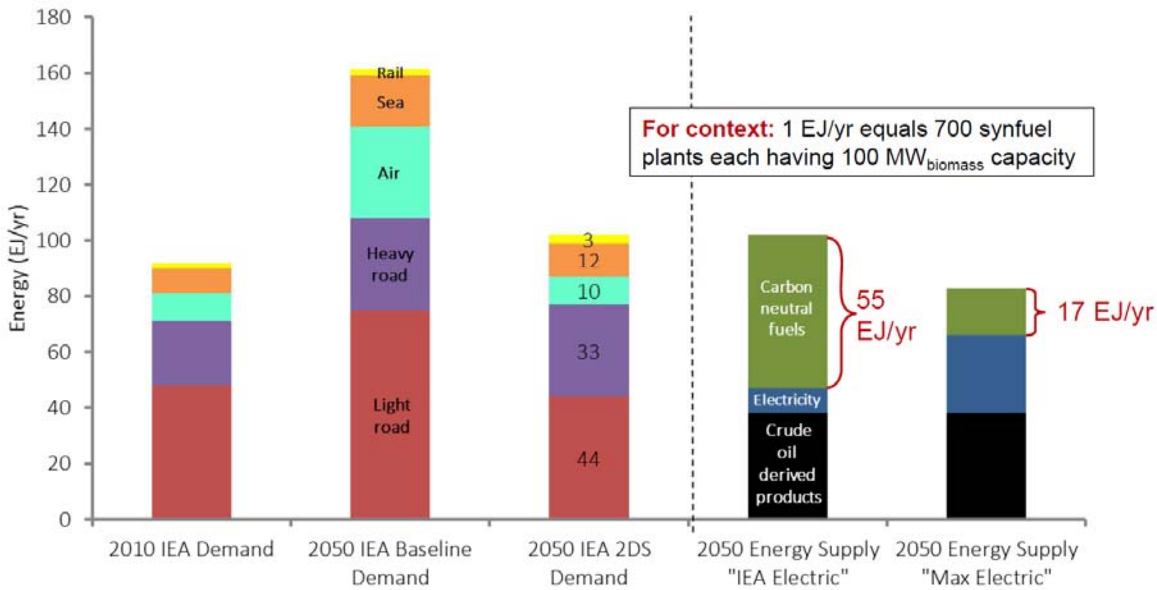


Figure 3: Global transportation energy thought experiment (adapted from GEA, 2012)

What is the supply potential of sustainable biomass?

From AR5 (IPCC, 2014):

"…This assessment agrees on a technical bioenergy potential of around 100 EJ (medium evidence, high agreement), and possibly 300 EJ and higher (limited evidence, low agreement) …"

From IEA (2011):

"…with a sound policy framework in place, it should be possible to provide … 145 EJ of total biomass for biofuels, heat and electricity from residues and wastes, along with sustainably grown energy crops."

- 80 EJ of biomass assumed for generating heat and power
- 65 EJ of biomass assumed available for biofuel feedstock

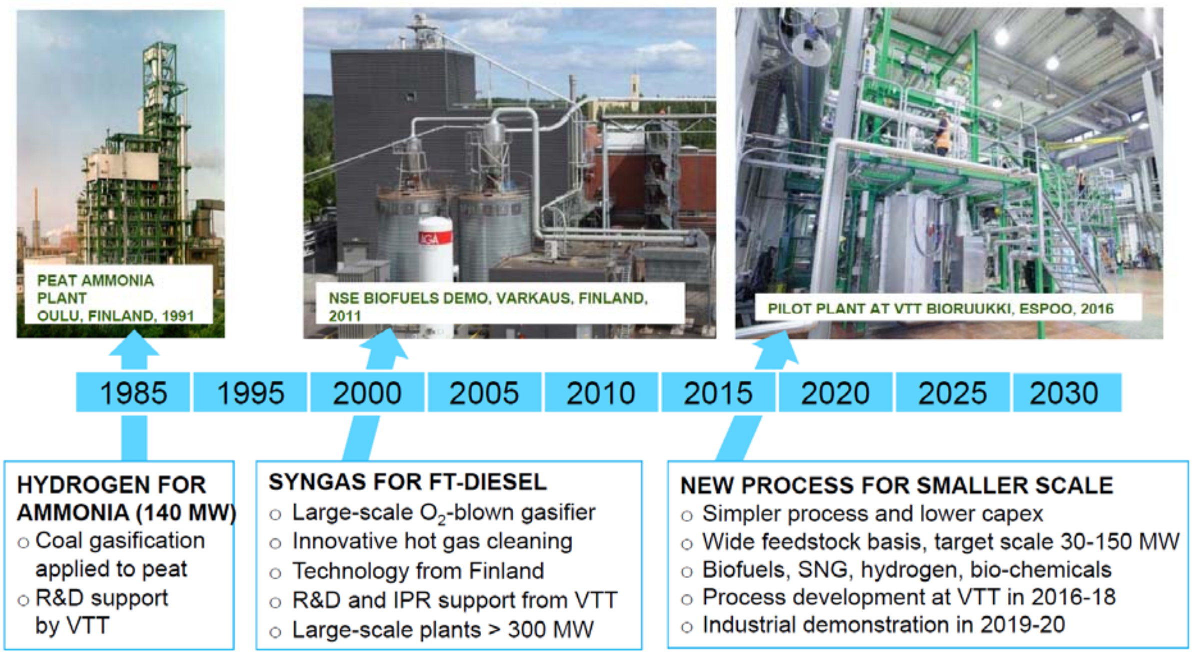


Figure 4: Biomass gasification for advanced biofuels in Finland

Biomass can be converted to synfuels with an efficiency in the range of 50 – 60 % (LHV), depending on the process configuration and end-product. If by-product heat from the process is also utilized, additional 20 – 30 %-point improvement can be attained, leading to ~ 80 % overall efficiency.

Despite the high energy efficiency, more than half of feedstock carbon is rejected from the process, as there is not enough hydrogen to convert it into fuels. The traditional conversion route is therefore hydrogen constrained.

By adding hydrogen from external source (enhancement), the surplus carbon could be hydrogenated to fuel as well. But the surplus carbon is in the form of CO2 instead of CO!

Implications:

- Only methane and methanol have reaction routes via CO2

- MoreH2 is required to produce one mole of fuel from CO2 than from CO

- CO2 has higher activation energy than CO

- Byproduct water from CO2 hydrogenation inhibits methanol catalysts

Despite challenges related to CO2 hydrogenation, the potential increase in fuel output is significant. The process is not sensitive to the source of hydrogen, but production from water via electrolysis using low-carbon electricity is considered in this presentation.

SUMMARY

When the maximally enhanced by an external H2 source, following increases in fuel output can be observed:

- 2.2-fold (methane) or 1.9-fold (gasoline) for steam gasification;
- 3.1-fold (methane) or 2.6-fold (gasoline) for oxygen gasification.

Overall carbon conversions for enhanced configurations:

- 67.0% (methane) and 58.4% (gasoline) for steam gasification;
- 98.0% (methane) and 79.4% (gasoline) for oxygen gasification.

Econ. feasible over base case when low-GHG H2 cost lower than

- 2.2 €/kg (methane) and 2.7 €/kg (gasoline) for steam gasification;
- 2.4 €/kg (methane) and 2.8 €/kg (gasoline) for oxygen gasification.

Gasification and combustion, comparison of the potential

Thomas Nussbaumer, Verenum, Task 32

Energy wood in Switzerland and trends and potentials were presented.

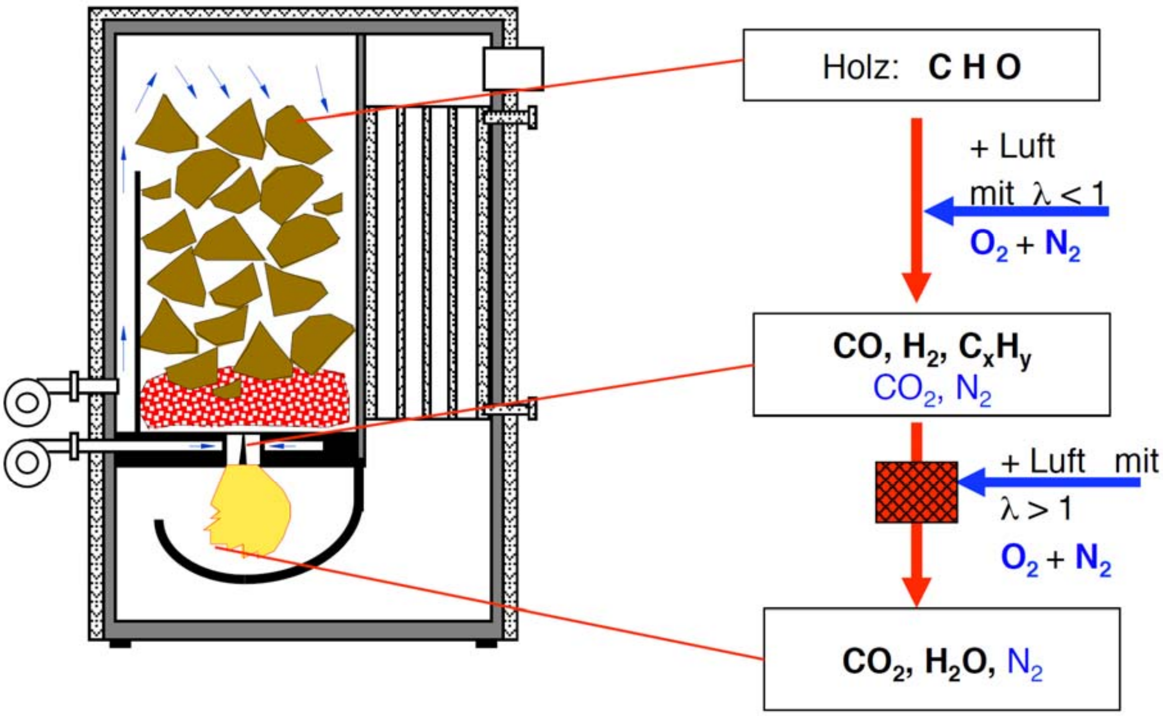


Figure 5: Two stage combustion (gasification?) in boilers

Nowadays automatic biomass plants e.g. for district heating are well established.

Current project to improve load range and reduce fuel NOx

- Multi-sector grate and flue gas recirculation
- Fuel bed model presented

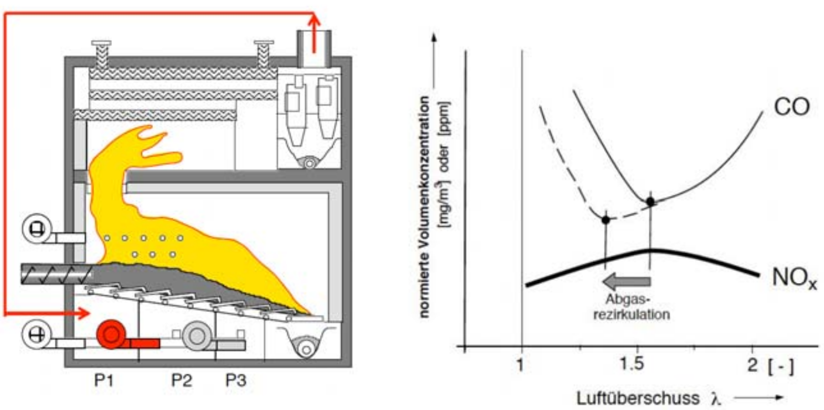


Figure 6: Multi-sector grate and flue gas recirculation

Conclusions

Biomass combustion is established

– for heat at reasonable cost but with PM and NOX

– for CHP with low electrical efficiency and at high cost

Biomass gasification exhibits a potential

– for heat with faster operation and low PM and NOX

– for CHP with higher electrical efficiency and at lower cost

Gasification exhibits a gap between the claim and the reality

– Advantages (PM, NOX, el. efficiency) have been demonstrated

– Costs and complexity are claimed to be low (TRUE or FALSE ?)

– Reliability is claimed to be high (TRUE or FALSE ?)

Session II: Gas Sampling, Measurement and Analysis Science

Gas Analysis Working Group (GAW) – Status and perspectives

York Neubauer, TU Berlin

Conclusions from the 1st workshop on "tar measurement" in 2010 were:

- Different interpretations of the 'standard' tar protocol
- No overview about the status of other known concepts for measuring
- Would be nice to have an international workshop

After workshop in Berlin in 2011 came the idea "**to setup an international working group to optimize the basis of knowledge about sampling, analysis and evaluation of impurities in product gases from thermochemical gasification, pyrolysis gases and conditioned synthesis gases**"

Motivation for the Gas Analysis Working Group (GAW):

- Workshops and internet based Webinars on all issues regarding gas analysis and more generally analytical tasks in gas producing processes
- Exchange of information on recent methodologies in product gas sampling and analysis
- Sharing knowledge and experiences
- Working together to learn, improve and to gain and deepen personal contacts (host site)
- Provide information on current status of analytical technologies in this field via Website and Wikis.

Advantages:

- Interaction via internet makes collaborative working in virtual teams possible!
- Find other groups with very similar interests
- Try to understand the common motivation
- Perform round robin tests with real teams: Example PSI November 2013

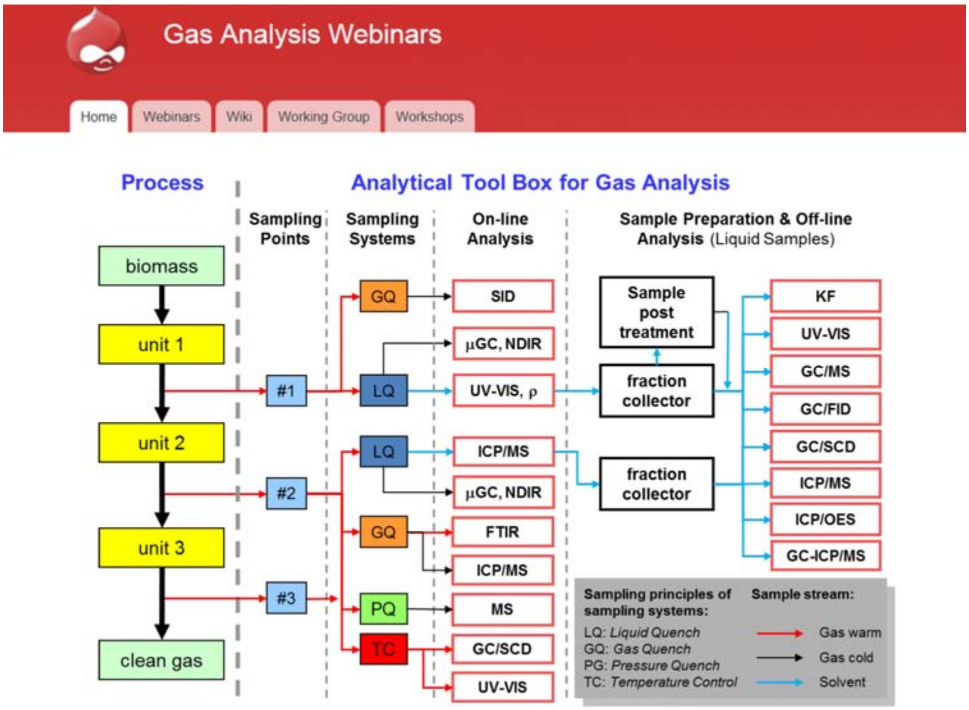


Figure 7: Gas Analysis Webinars

Measurement and characterization of tars using the SPA method

Kevin Whitty, University of Utah

Biomass gasification tars

- Production of condensable polyaromatic “tars” is inherent in most biomass gasification processes
- Tars foul and can plug equipment downstream of the gasifier
- Challenging to remove from syngas
- Reduce energy efficiency of gasification process
- Reports of as much as 10% of biomass carbon ending up in the form of tars

Tar analysis – common steps

1. Sampling of the tar: Generally collected from a side stream, including more or less complicated sampling equipment to attain a representative sample.

2. Storage of sample: Only valid for offline methods.

3. Pre-preparation/conditioning of the sample:

- Offline methods: The collected tars are extracted to or dissolved in an appropriate solvent for further chemical analysis.
- Online measurements: Conditioning such as drying of gas removal of particulates etc. may be required depending on the analytical technique.

4. Analysis of sample: Chemical analysis of pre-prepared/conditioned tar sample. Most common analytical techniques are based on gas chromatography (GC) or high pressure liquid chromatography (HPLC).

“Conventional” Tar Analysis	**Solid Phase Absorption (SPA) for Analysis of Biomass Gasification Char**
- Tar protocol developed over several projects supported by IEA Bioenergy Task 33, US DOE and European Commission 1998-2005 • Significant contributions by ECN, VTT, KTH, DTI, BTG, NREL - Adopted as CEN standard for tar sampling - Procedure • Draw specific volume of process gas through filter then series of cold impingers to collect tar • Evaporate solvent to measure gravimetric (total) tars • Analyze tars by GC-MS to evaluate composition - Quantitative, but very laborious	- SPA sampling and analysis method was developed by KTH in the 1990’s - SPA used for measurement of the concentration(mass) of individual light aromatic hydrocarbons and phenols - The SPA-method is restricted to GC-available (GA) compounds only - These compounds are, however, significant process markers that provide good measures of reactor performance and gas quality - At 900°C the GA-compounds roughly correspond to the total tar amount

Table 2: Conventional tar analysis vs. SPA method

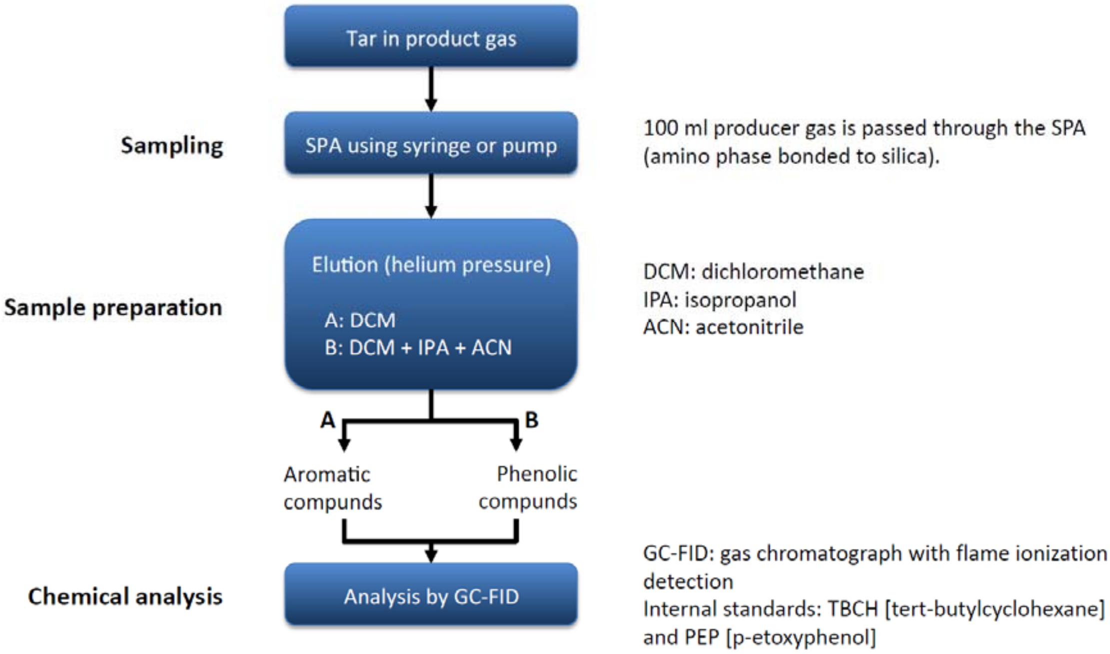


Figure 8: Solid phase absorption (SPA) analysis

Challenges of SPA Method

- Inleakage of air, especially for sub-atmospheric pressure systems
- Using temperature high enough to avoid tar condensation yet low enough not to melt septum
- Plugging of needle by septum material
- Condensation of tars in needle of syringe
- Undesirable heating of SPE column during sampling due to temperature, steam condensation
- Possible conversion of tars by upstream filter material or filter cake
- Breakthrough of light tars (BTX)
- Desorption of light components from SPE cartridge during storage
- Efficient elution of aromatic and phenolic compounds
- Inability to measure heaviest tars
- Consistency of procedures for sampling and analysis

Conclusions

- Dealing with tars a significant challenge for biomass gasification systems
- Simple, low-cost, yet robust means of measuring and characterizing tars is desirable
- Impinger-based method of standard tar protocol is relatively robust but time consuming and laborious
- SPA method much simpler and equally as good for many situations, but does have drawbacks
- Variants of SPA method allow for more complete quantification or analysis of other components
- Continued development of SPA procedure will improve robustness and utility of the method

Synergies in gas sampling research bioenergy Task 32 and Task 33

Thomas Nussbaumer, Verenum

Targets

1. increase efficiency for biomass heat and power

2. increase fuel flexibility

3. reduce the impact on ambient air by:

- Particulate Matter PM10 caused

- by primary PM: primary organic aerosol (POA), BC, fly ash

- NMVOC as precursors for secondary organic aerosol (SOA)

- NOX

Gas sampling and analysis in fuel bed ('pyrolysis gas') and flue gas (presented by S. Roth)

Parameter	Pyrolysis Gas		Flue Gas	
	Measurement	Modeling	Measurement	Modeling
T	Type K 0..1200°C	+	Type K 0..1200°C	+
O_2	Paramag. 0..25 %	+	Paramag. 0..25 %	+
H_2	TCP 0..25 %	+	-	+
CO_2	NDIR 0..25 %	+	-	+
CO	NDIR 0..30 %	+	NDIR 0..2500 ppm NDIR 0..5 %	+
CH_4	NDIR 0..5 %	+	(VOC – NMVOC)	+
VOC	FID 0..10 %	-	FID 0..10 %	-
NMVOC	(VOC – CH_4)	"Tar" = C_6H_6	FID 0..10 %	"Tar" = C_6H_6
H_2O	Cap. 0..50 %	+	-	+
NH_3	-	+	-	+
HCN	-	+	-	+
NO	-	+	NDIR 0..2500 ppm	+
PM mass	-	-	Filter Sampling	-
PM number/size	-	-	SMPS 20..700 nm OAS 0.3..20 µm	-

Table 3: Gas sampling and analysis at Hochschule Luzern

Further steps
1. On-line detection of gas species (CO, H2, CH4, H2O, VOC)
from gasification section in a boiler is established
2. Data can be used for model validation
3. Compared to the measurements, the model predicts the wood gas flows out
of the bed sharper. Explanations:
– In the 1D-FBM only an upright velocity component out of the bed is

simulated, while mixing along the bed is neglected.
– Currently, the fuel particles are assumed as thermally thin, which is not accurate for practical fuel particles (e.g. > 10 mm)

Synergies to Gasification
1. Comparison of model approaches and data for validation
2. Exchange of experience on sampling:
– avoid clogging
– increase positioning and accuracy
3. Interest on additional species:
– "tar": indicators, other species than "NMVOC" ?
– N-species for NOX formation: NO, HCN, NH3, ..

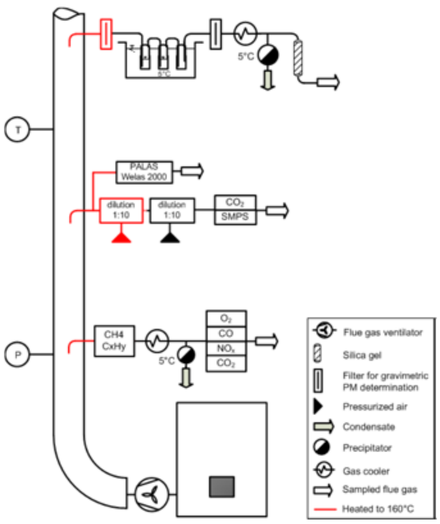


Figure 9: Experimental setup for flue gas sampling

Session III: Gas Sampling, Measurement and Analyses on Pilot, Demonstration and early Commercial Plants

Gas sampling, measurement and analysis on the bioliq - EFG

Mark Eberhard, KIT

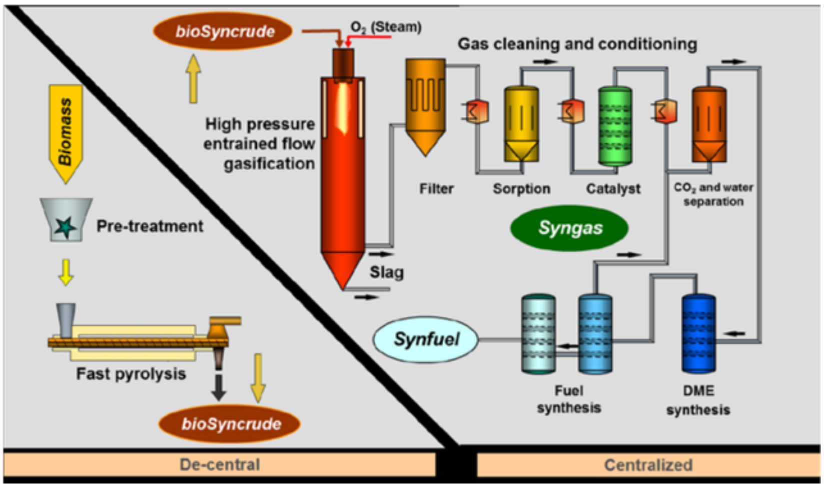


Figure 10: The Bioliq® BtL Process

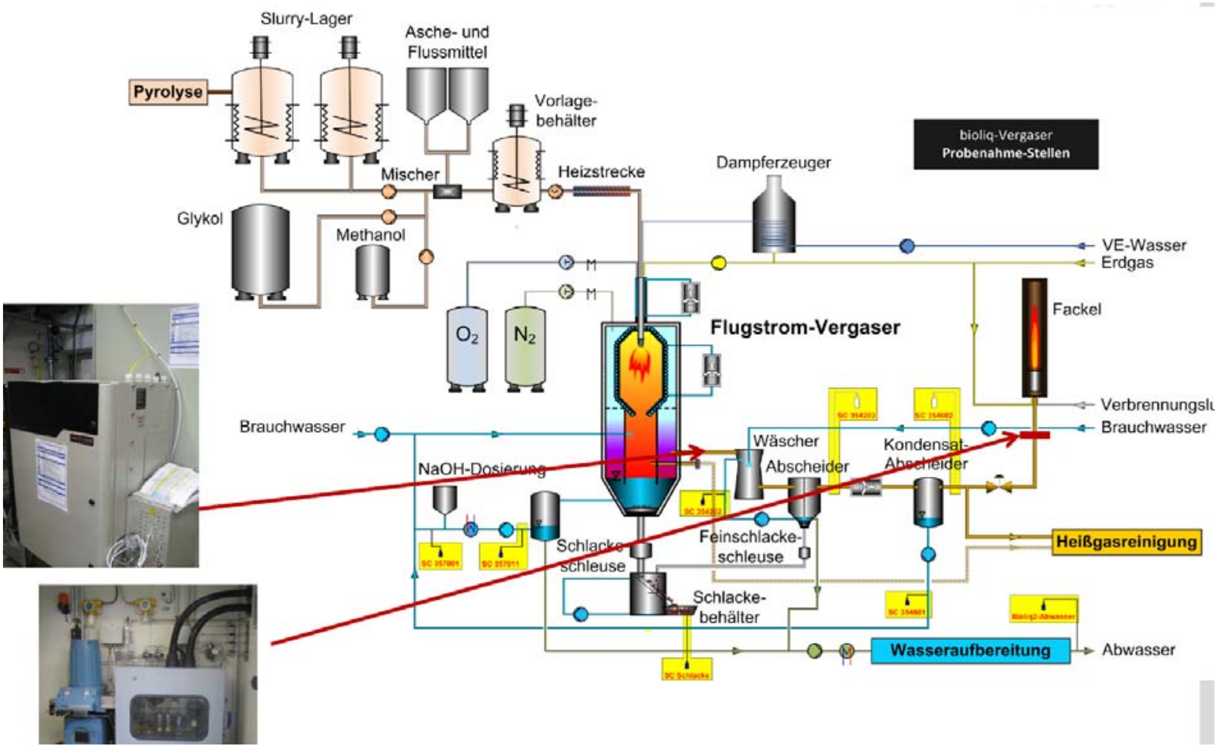
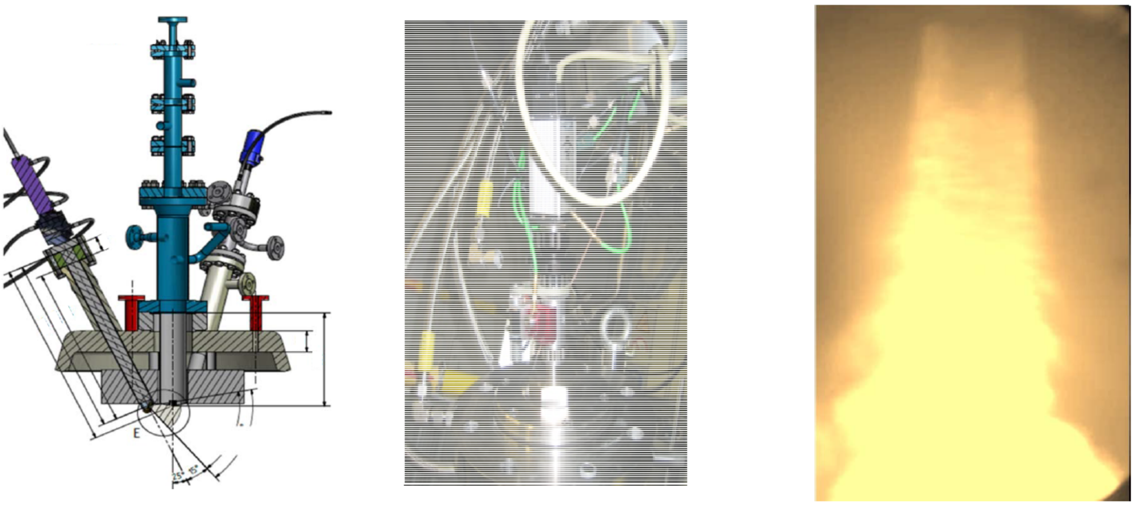


Figure 11: Points for sampling

Development of diagnostic methods for gasifiers

- Emission spectroscopy
  - Broad range of stable and meta stable combustion products and elements detectable.
- Laser induced incandescence (LII)
  - Measurement of soot volume fraction and particle size
- Laser induced breakdown spectroscopy (LIBS)
  - Measurement of the elemental composition in the gas phase.
- Absorption spectroscopy
  - Measurement of species concentration (e.g. H_2O, CO, CO_2 CH_4, NO, NO_2, HCN, O_2, HCl, NH_3)

Bioliq – High pressure optical borescope



gasifier flame at 40 bar

Figure 12: Camera based systems for analysis of atomization

Gas Sampling, Measurement and Analyses at Güssing - DFB Biomass gasification

Reinhard Rauch, Vienna University of Technology, bioenergy 2020+

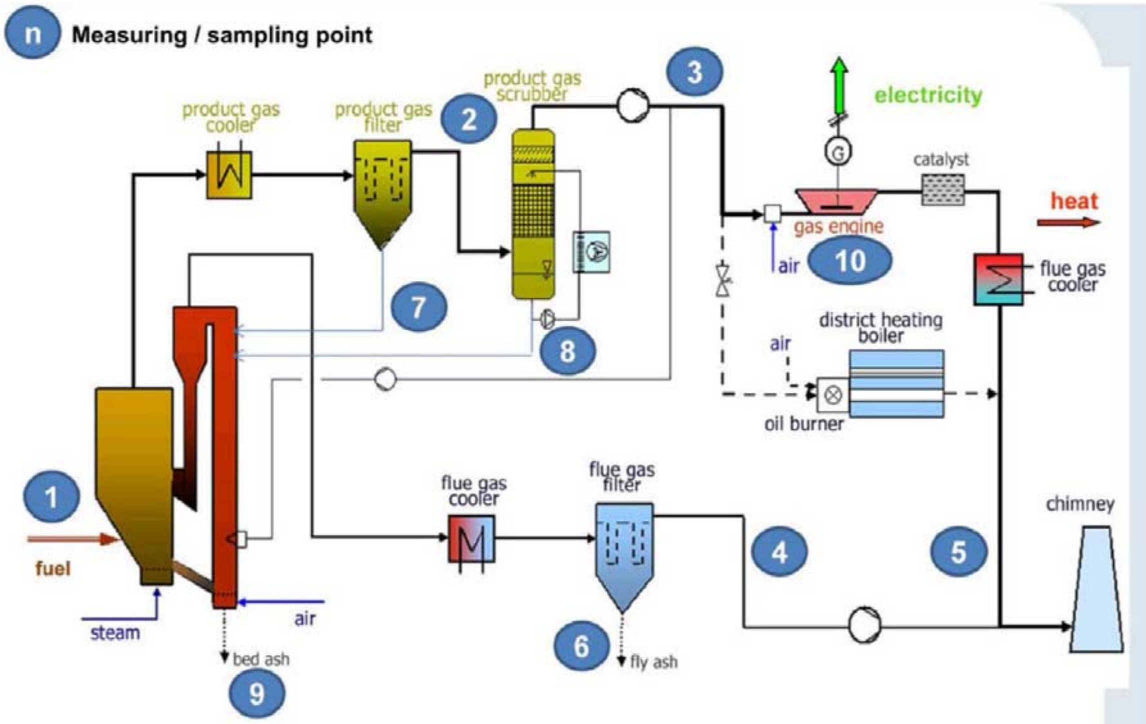


Figure 13 : Gasification plant in Güssing – sampling points

CHP standard operation

- Fast results are necessary, so only online systems are used
- For normal operation only gas components are analysed (CO, CO2, O2), here typical online analysers are used (infrared, paramagnetic)
- Main difficulty is to clean the gas and to bring it into the analyser with good availability
- Analysis of the engine oil is also quite important as it shows the quality of the gas treatment

Analysis for commissioning/optimisation of the process

- All permanent gases in the producer gas (by GC)
- Flue gas in combustor and gas engine (CO, NOx, SOx, PAH, …)
- Tar and particles in gas phase (gravimetric and GC-MS), here TU Vienna uses the standard method, only a different solvent (toluene) is used
- Hydrocarbons / tar content in solvents (e.g. tar content in RME)
- Bed material and ashes (activation of the bed material)

Analytics

• Sulphur
– In the gas phase by GC-SCD,
– sampling is done by Tedlar bags

• Chlorine, Ammonia, HCN
– Sampling in liquids (e.g. H2SO4),
– analysis by IC

• BTX, Naphthalene
– Sampling by Tedlar bags or online
– Analyzed by GC

• Metals, Carbonyls
– Done by external organizations

Conclusiones

• Analytics for standard CHP are established and work well
• They are only too expansive and/or too much maintenance is necessary
• Species analyzed for synthesis gas are different than CHP (focus more on inorganic)
• Analytics for synthesis applications are more difficult, as the range from **ppm** is changed to **ppb**
• In addition to the analytics long term tests in pilot scale are really necessary, because you do not know, if you miss one catalyst poison

GSMA at the CHP-Plant Stans

Bernhard Boecker-Riese, BR-Engineering

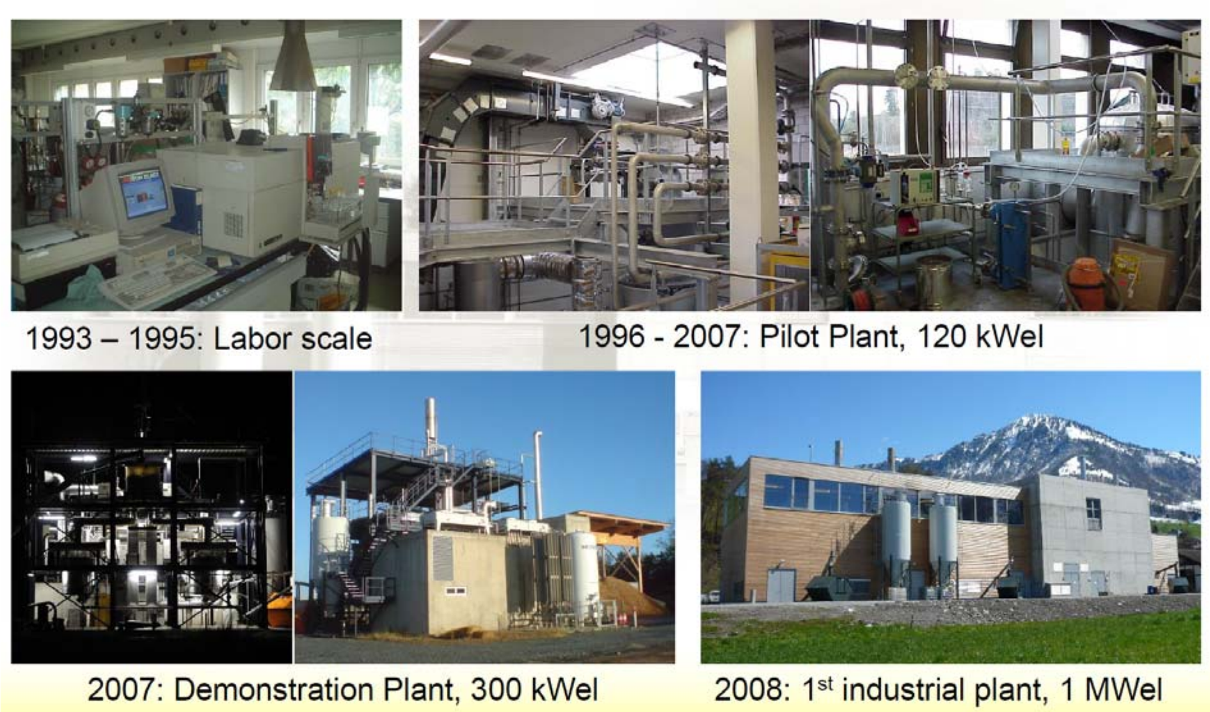


Figure 14: Development of the plant in Stans

SIRION: modular arrangement - benefits

- Up to 8 reactors in one block
  - Max. 1,4 MWel/ block
- Redundant gas production
  - By using several reactors in one block the gas production has an extremely high availability
  - if one reactor is offline, the others keep working
    - ✓ No shutdown of the whole plant, only a reduction of the power output
    - ✓ Maintenance can be done in the regular shift without any work peak
- One service reactor in addition
  - Full gas production even during the annual reactor revision

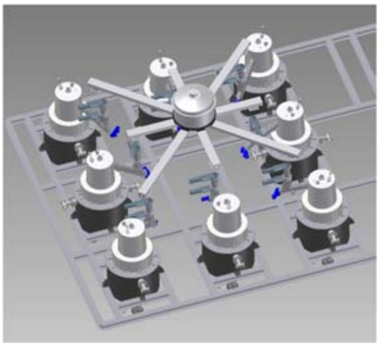


Figure 15: Sirion modular arrangement

Gas composition measurement

-Measurement principle NDIR / UV
-Gas has to be free of particles and condensate
-Daily maintenance
-Heated extraction unit seems to work better than heated extraction pipe
-Back pressure regulation for constant gas flow

Oxygen content measurement

-Measurement principles
-Paramagnetic (PO2)
-Electrochemical (EO2)
-Gas has to be free of particles and condensate
-Daily/weekly maintenance

CO detection

-Reactors and gas cleaning system are working under negative pressure
No toxic gas can leak from the system, only air can break in
Entrapped air is immediately detected by an redundant 02monitoring system
LEL at 4%, shutdown at 2% O2
No ATEX-equipment necessary

-Only the CHP room contains pressured gas pipes
Secured by CO monitoring and automatic ventilation systems

-Additional operator protection by portable CO monitor

Laws and proof of legal emissions from biomass conversion installations

Christioph Baltzer, BECO (Dep. Environment Bern)

BECO is responsible for the execution of the Federal Act on the Protection of the Environment (EPA), especially for the Ordinance on air Pollution Control (OPAC) in the Canton Bern.

What they do:

- call up . . .
- measure . . .
- evaluate measurement reports of . . .
- carry out negotiations on deadlines for retrofitting . . .
- issue the necessary limitations until the retrofit of . . .
- . . many kinds of stationary installations, such as:

Measurement of a Wood Gasifier

- Limit values of stationary internal combustion engines (OPAC, appendix 2, number 81) which uses biogas from aggriculture
- dust (solids) 10 mg/m³ (before 01.01.2016: 50 mg/m³)
- nitrogen oxides (NOX) 250 mg/m³ (before 01.01.2016: 400 mg/m³)
- carbon monoxide (CO) 650 mg/m³ (before 01.01.2016: 650 mg/m³)

Is IGCC a viable option for biomass?

Jürgen Karg, Siemens AG Power and Gas Division, Germany

IGCC = Integrated Gasification Combined Cycle

Data regarding Primary feedstock for gasification, numbers of gasifiers by primary feedstock, gasification capacity by application, cumulative worldwide gasification capacity and growth (total for all applications), as well as cumulative global IGCC net power capacity and yearly capacity additions were presented.

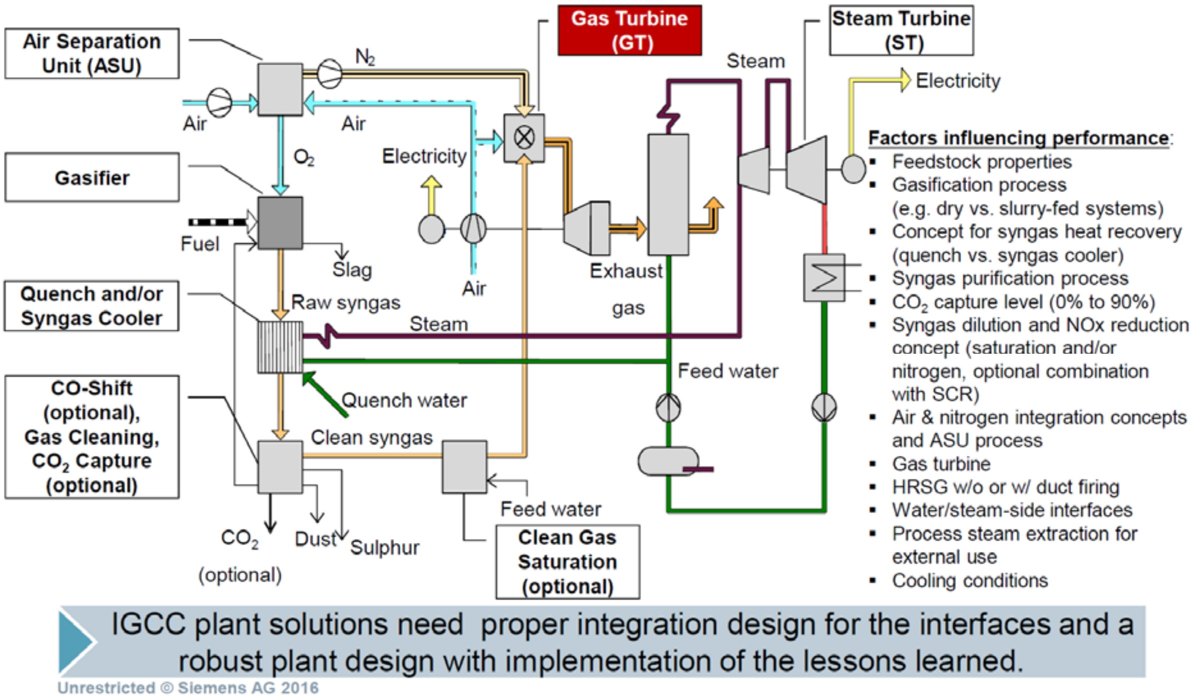


Figure 16: IGCC in principle

General considerations for application of syngas as gas turbine fuel:

• The fuel has to meet the typical gas turbine fuel purity requirements

• Due to the hydrogen content in the fuel, syngas has to be combusted in diffusion-type burners

• Depending on the syngas composition, dilution with nitrogen and/or steam may be required for reactivity and/or NOx emission control

• In case of low LHV and/or low fuel reactivity, natural gas may need to be added

• In any case a project/fuel-specific evaluation is needed from combustion point of view

• Especially the lower LHV design limits have to be checked in conjunction with fuel composition and reactivity, respectively

Gas turbine fuel purity requirements:

- Contaminants for which limit values in low ppm range are defined:
  Na, K, V, Pb, Ca, dust, H_2S, total S

- Contaminants for which limit values in ppb range are defined:
  Fe, Ni and related carbonyls ($Ni(CO)_4$, $Fe(CO)_5$)

Fuel purity requirements are defined for standard fuels with high LHV. Limit values have to be corrected for syngas applications with LHV ratio.

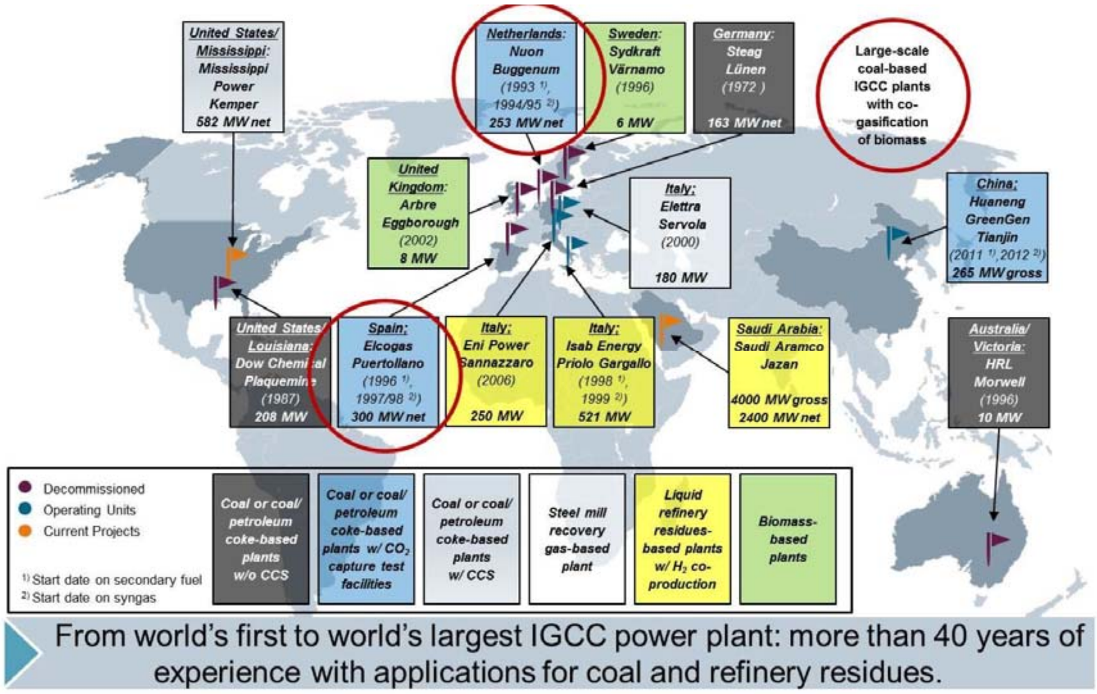


Figure 17: Global syngas/IGCC projects incorporating Siemens GT or CCPP technologies

Conclusions and outlook

• In general, IGCC power plants are still a niche application for gasification and in the power industry

• Coal-based IGCC still has significant development potential

• …but needs incentives in competition with SPP for power only applications

• …and is more attractive in combination with co-production of higher value products

• Refinery residues-based IGCC plants are commercially applied on (very) large scale

• …typically co-produce hydrogen and process steam for refinery supply

• …future application depending on refinery capacity additions and/or upgrades

• Biomass-based IGCC so far with very limited experience in small-scale units

• …co-gasification of biomass in large coal-based plants may be more attractive

• …co-firing of syngas in boilers or use of syngas in gas engines expected to be commercially more viable for small-scale gasification plants

• …higher value (chemical) products may be more attractive than power

Summary

The workshop offered a very good overview and important information on Gas sampling, measurement and analysis in thermal gasification processes; an attendance of the workshop has shown that this topic is very present and need to be discussed also in the future.

All the presentations can be found at the Task 33 website. (task33.ieabioenergy.com)