Hvordan foredle biogass og redde verden i samme slengen

(English: How to purify biogas and save the world!)

Presenter: Fred Martin Kaaby, MSc. Organic Chemistry

Target audience: Technicians, CEOs, decision makers, engineers

Todays agenda

IFE

Institute For Energy Technology's vision: Internationally leading research institute

Turnover:
1
BNOK

Annual publications:
120

1948: IFA
1980: IFE

Employees:
300

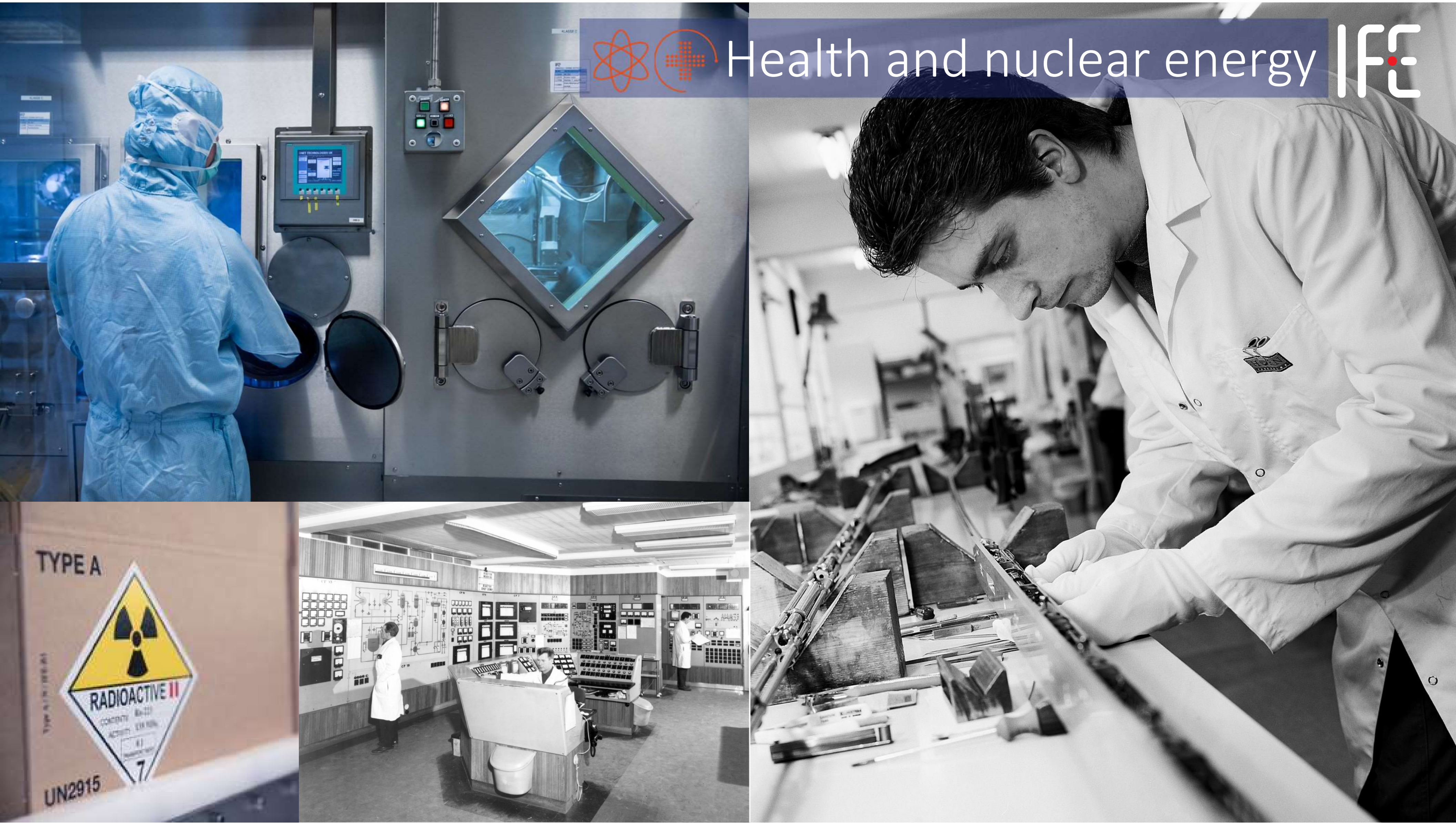
Nationalities: 32
Researchers: 218
PhDs: 105

14.000
Annual visitors

Advanced laboratories:
24

Centres for renewable energy:
2

International projects:
>30%


Health and nuclear energy
IFE
TYPE A
RADIOACTIVE II
7
UN2915

Renewables and environment

Reservoir Technology Department

- Finding smart solutions for a better future

Greener and more efficient exploration and production of methane (hydrocarbons)

Becoming carbon neutral by embracing the energy transition and CO_2 storage.

Protect the environment by monitoring pollution and fluid flow in landfills.

Photo by Neta Wechsler

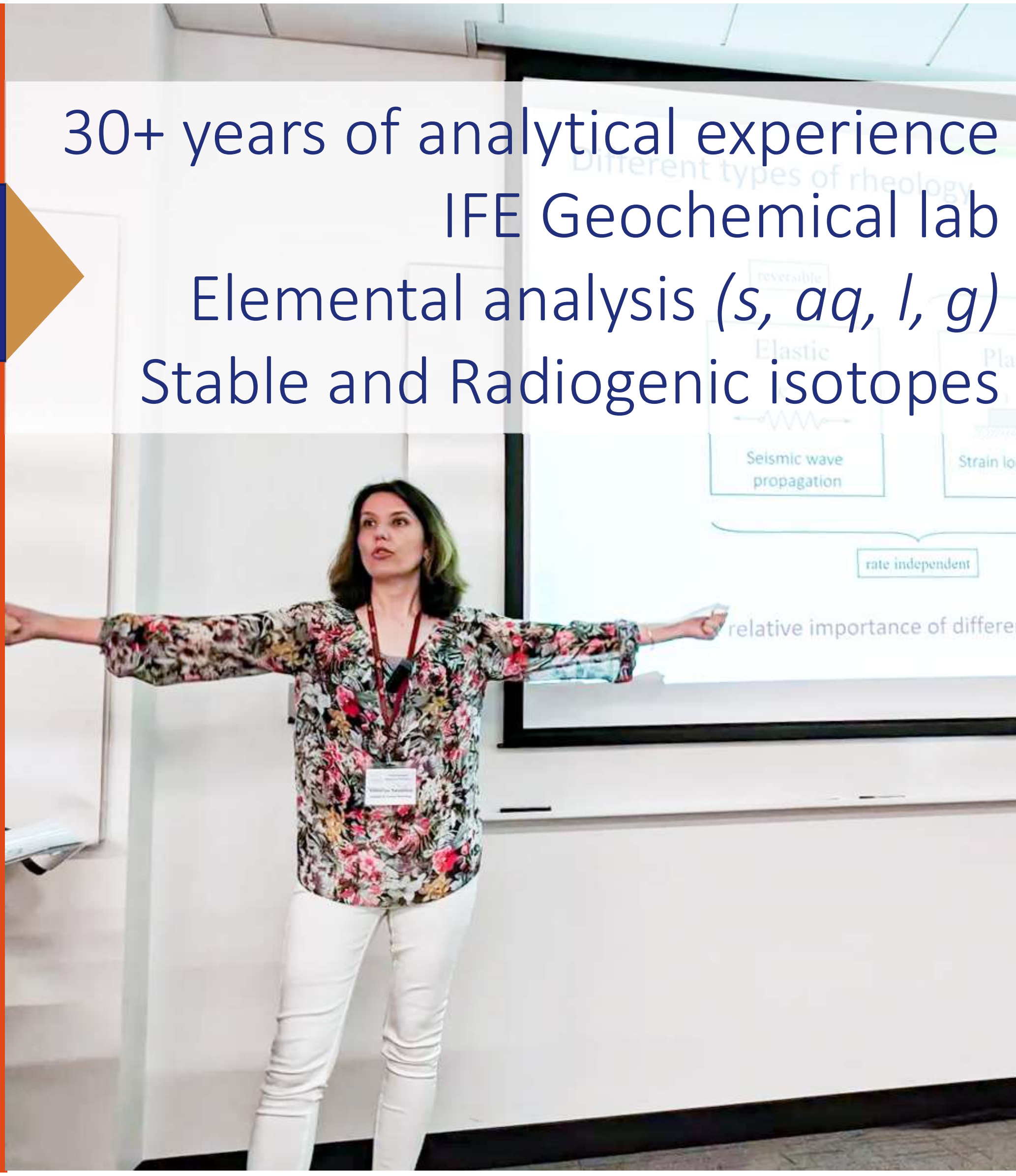
IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring



30+ years of analytical experience

IFE Geochemical lab

Elemental analysis *(s, aq, l, g)*

Stable and Radiogenic isotopes

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Verify sensor calibration

Range, precision and accuracy

No interferences

All gaseous species

Easy to sample and send

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Verify purification/filtration

Know your contaminants

Essential for Risk Evaluation

Part of preventive maintenance

Requirement from CHP* suppliers

*Combined heat and power usually with Combined-cycle Gas Turbin

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Thrustworthy monitoring

Sampling is AΩ for quality!

Support/Analytical expertise

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

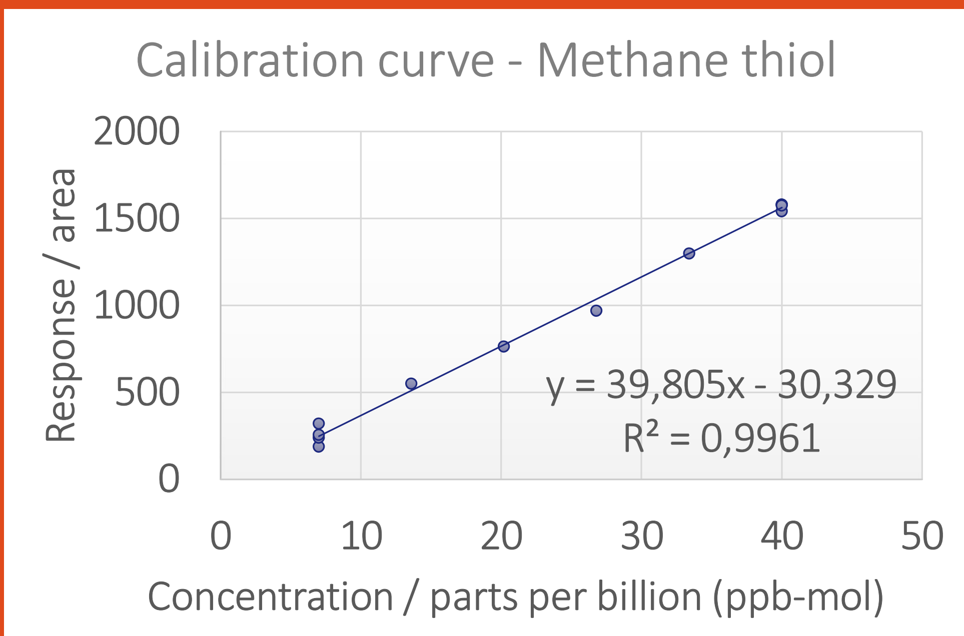
Stability control of process

Certification

Tracing leachate and pollutants

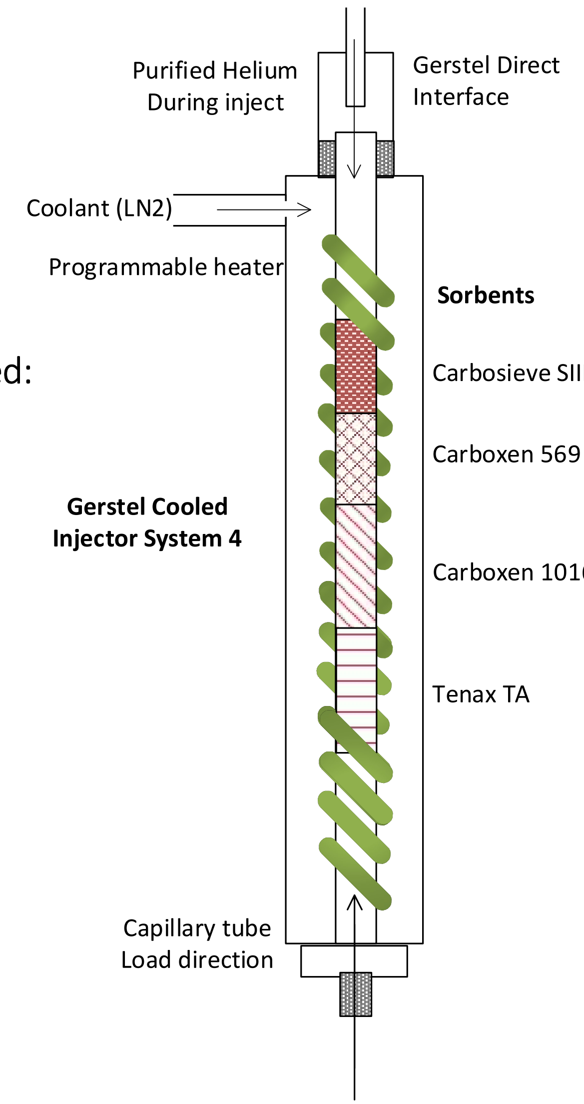
METROLOGY for HYDROGEN VEHICLES

Quantification of hydrogen gas impurities according to EN17124



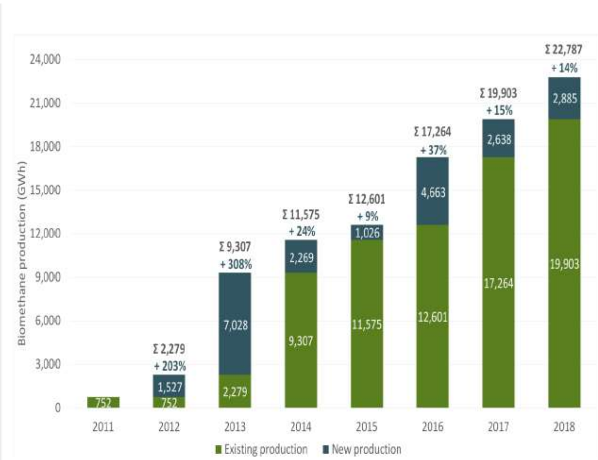
Impurities measured:

H_2S
CS_2
COS
MeSH
Methanol
Ethanol
Acetone
nC2-nC6
Ethylene
Propylene
Cl_2



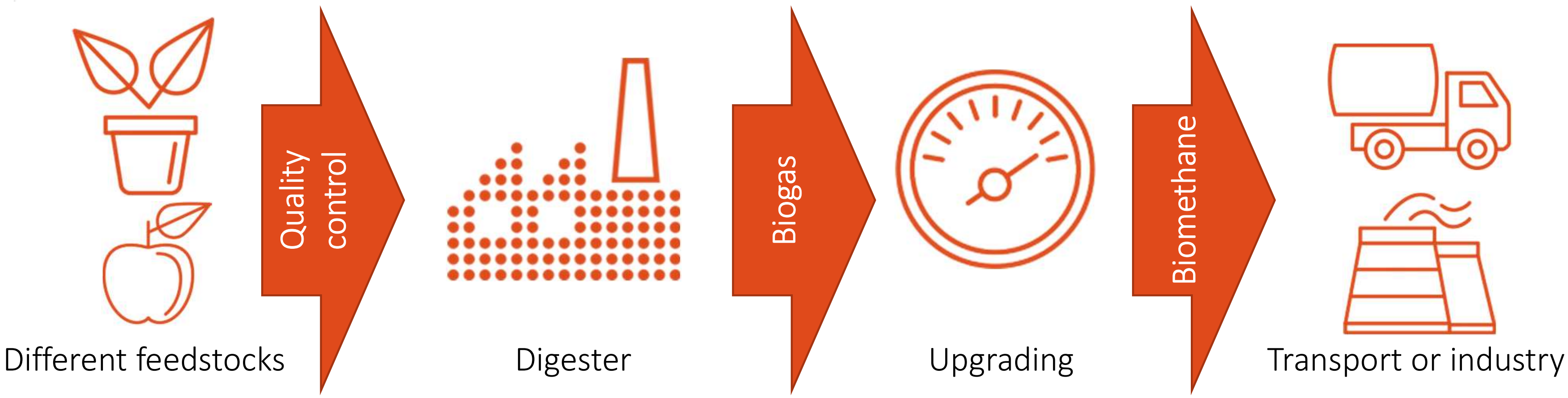
Agenda

Biogas is climate neutral



EBA European Biogas Association

Biogas potential in Europe: 1170 TWh (2050)



Hydrogen from biomethane?

Steam-methane reforming reaction

$CH_4 + H_2O \rightarrow CO + 3H_2$

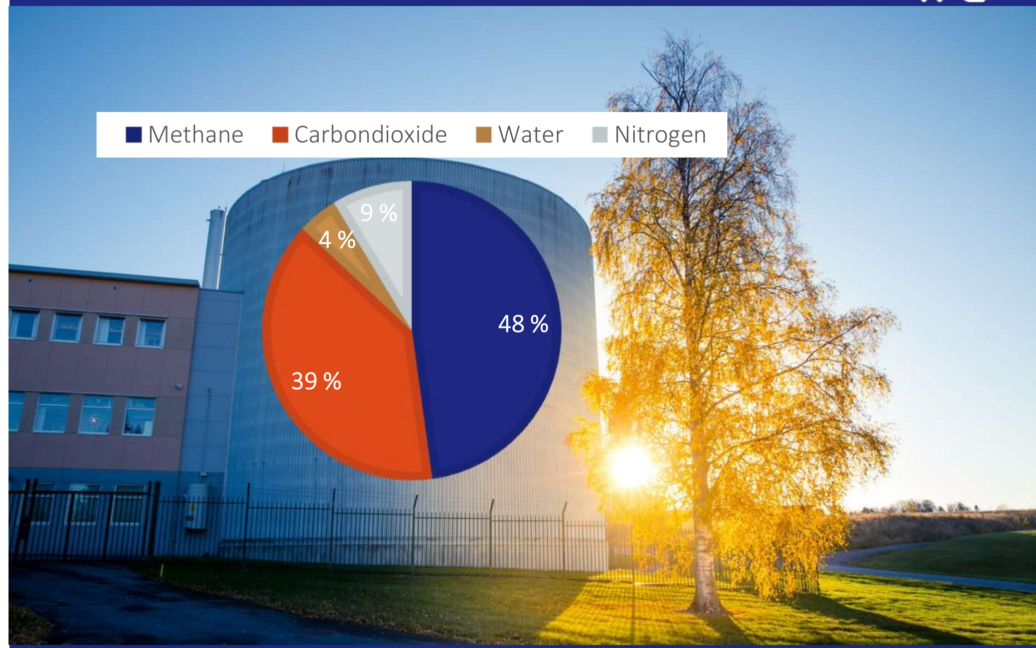
Water-gas shift reaction

$CO + H_2O \rightarrow CO_2 + H_2$

Agenda

Biogas (biowaste) content

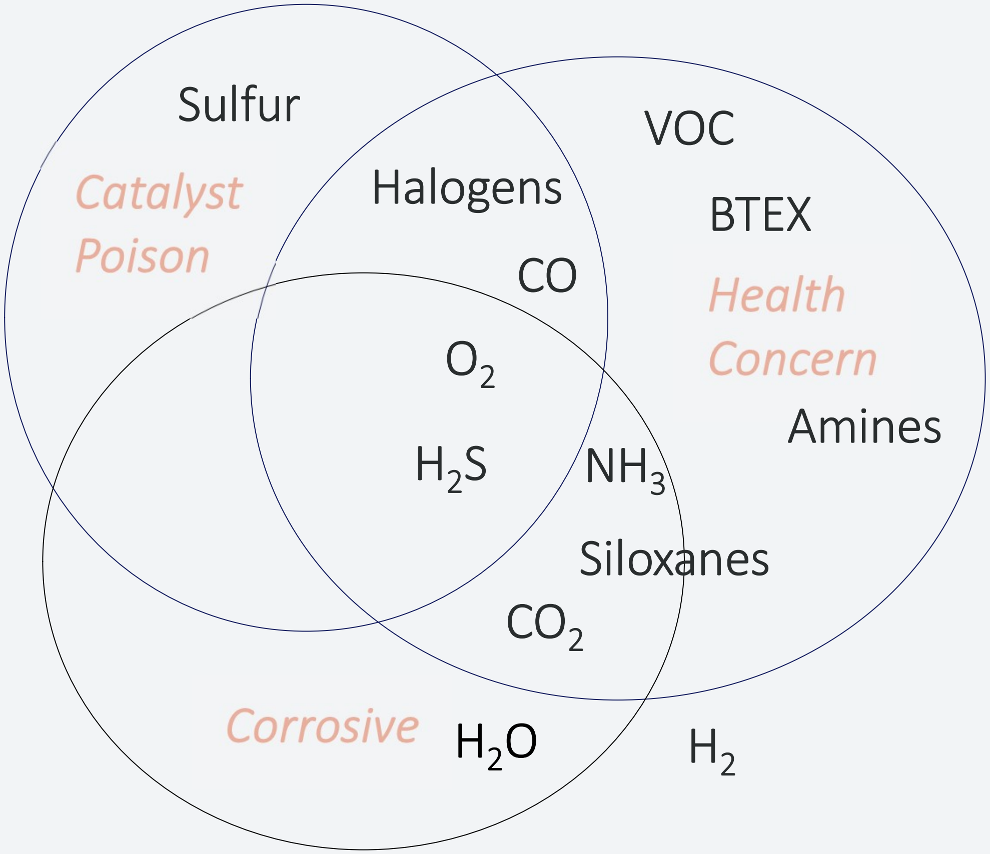
Methane (CH_4)	55–70%
Carbon dioxide (CO_2)	30–45%
Nitrogen (N_2)	< 15%
Oxygen (O_2)	< 3%
Water (H_2O)	< 5%
Hydrogen sulfide (H_2S)	< 1%
Ammonia (NH_3)	< 0.1%
Siloxanes	< 0.1%
Terpenes	< 0.1%



Volatile organic compounds (VOC)
All organic compounds with high vapor pressure and low water solubility.

Biogas impurities and risks

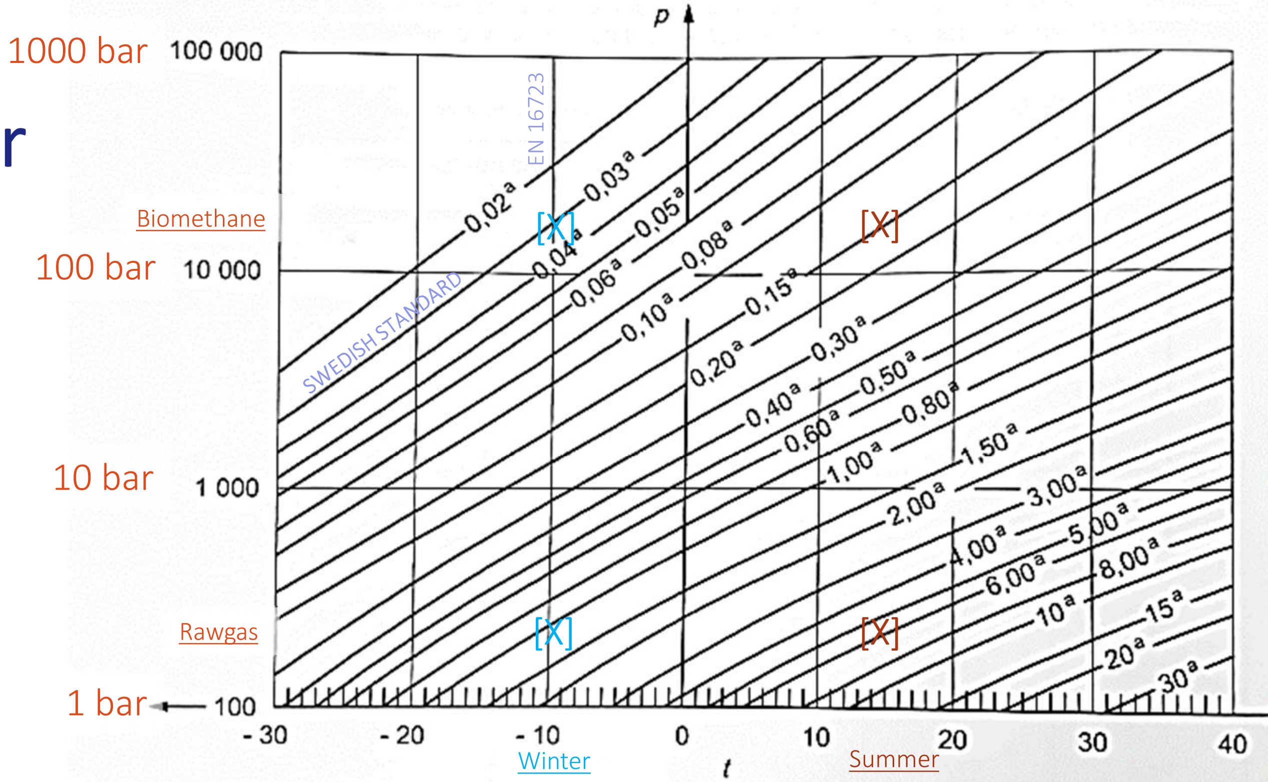
Methane is flammable!



How to handle water

The art of manipulation of P and T

Water saturation limits – dew point (g/m³)

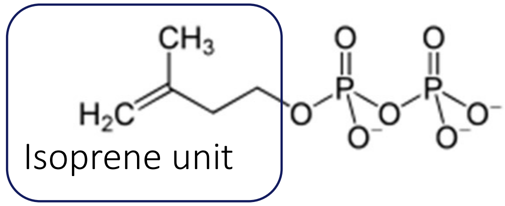


Key

t temperature, °C

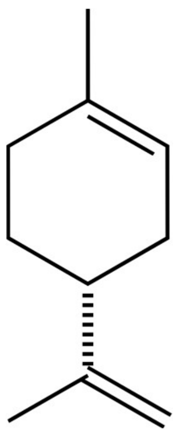
p absolute pressure, kPa

a Water content of natural gases in g/m³ (0 °C, 101,325 kPa, dry)

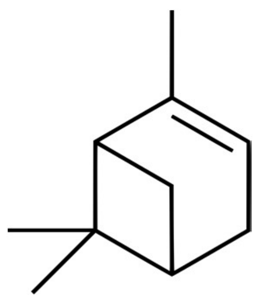


Terpenes and terpenoids

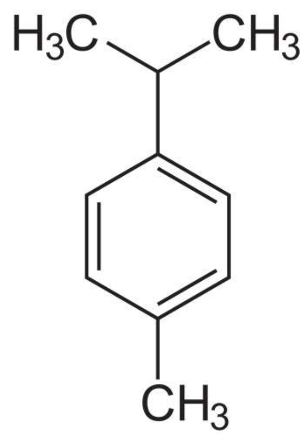
Built by nature from isoprene units.



Limonene gives lemon its smell

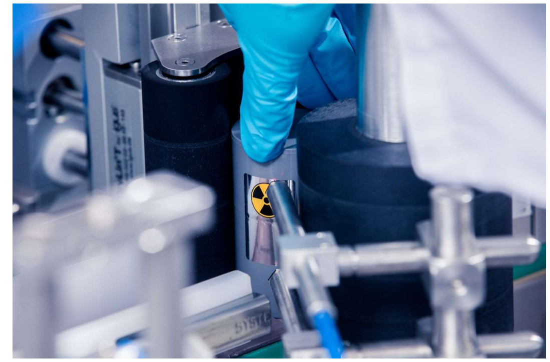


Pinene is main constituent in terpentine

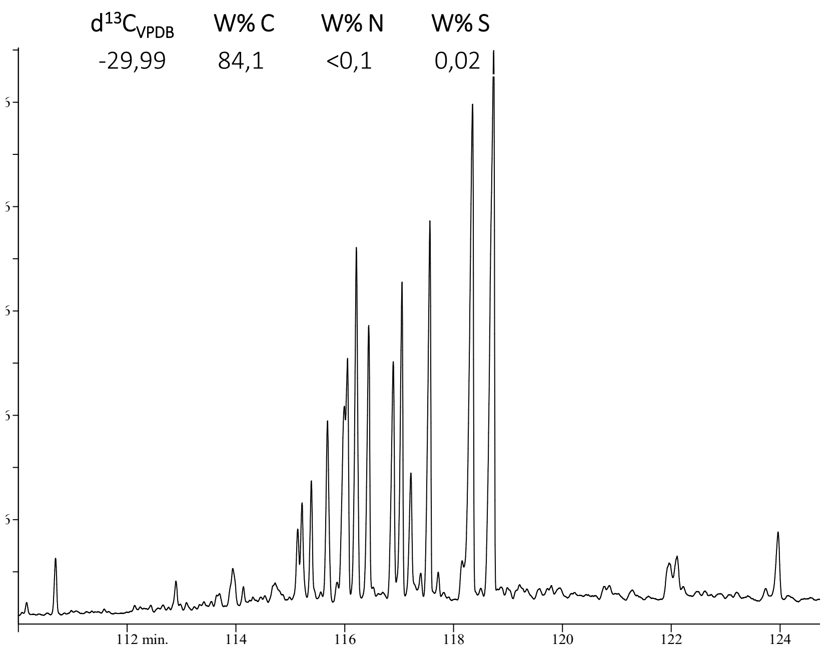


Cymene is a naturally occurring aromatic organic compound

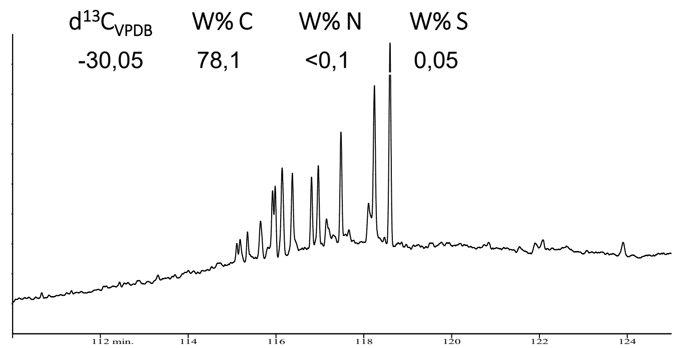
Please verify the compatability of your raw biogas with rubbers and seals

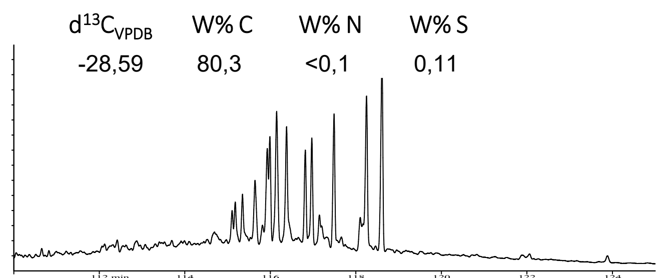


The challenge with compressor oil



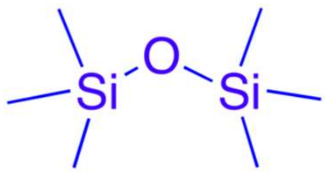
Compressor oil (Mobile rarus SHC 1015) from ***biomethane plant***





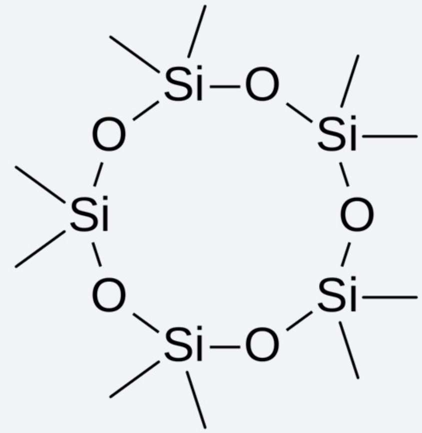
Oil filter and gas supply line on ***biomethane truck***

Siloxanes



Dimethyl siloxane

Combustion of siloxanes creates silicon dioxide (glas).



D5 – Decamethylcyclopentasiloxane
- Is listed in The Candidate List of Substances of Very High Concern (SVHC).

ICP-MS analysis of scales on underside of exhaust vent and injection vent from A damaged motor inside a ***biomethane truck***

Agenda

Biomethane for Automotive fuel (EN 16723-2)

Total silicon (siloxanes) [b]	< 0.5 mg/m^3
Hydrogen	< 2 %
Hydrocarbons (including terpenes)	< -2 °C dew point
Oxygen	< 1 %
Total sulfur	< 5 mg/m^3
Methane	> 65 % (High grade 80)
Compressor oil	de deminis[a]
Dust	de deminis[a]
Amines (including NH_3)	< 10 mg/m^3
Water	< -10 °C dew point

a) de deminis - Does not render the fuel unacceptable for use in end user applications
b) Some gas turbines manufacturers have set < 0.1 mg/m^3 limits.

The biomethane monitoring caveat:

«Of all the requirements, only methane, CO2, hydrogen sulfide, oxygen is monitored real-time.»

Hydrogen specification for PEM fuel cells (EN 17124:2018)

Nitrogen	< 300	µmol/mol
Methane	< 100	
Water	< 5	
Oxygen	< 5	
Carbon dioxide	< 2	
Total hydrocarbons (except CH4)	< 2	
Carbon monoxide	< 0.2	
Formic acid	< 0.2	
Ammonia	< 0.1	
Halogenated compounds*	< 0.05	
Formaldehyde	< 0.2	
Total CO, formic acid, formaldehyde	< 0.2	
Total sulphur compounds	< 0.004	
Particulate	< 1 mg/kg	

IFE

Hydrogen production from biomethane?

Purification is even more essential!

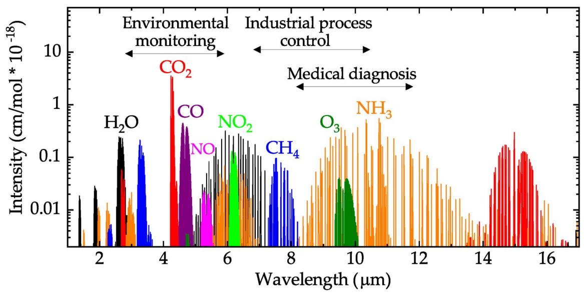
Biomethane gas quality standards

	Natural gas network	Automotive fuel	Swedish standard	Suggested test methods
	EN 16723-1	EN 16723-2	SS 15 54 38:1999	
Total silicon (siloxanes) [c]	< 0.3 (pure) - 1 (diluted) mg/m³	< 0.5 mg/m³		EN 16017-1
Hydrogen		< 2 %		ISO 6974, 6975
Hydrocarbons		< -2 °C dew point		ISO 23874, 11150, 12148, 6974
Oxygen		< 1 %	< 1 %	ISO 6974, 6975
Total sulfur	< 20 mg/m³	< 5 mg/m³	< 23 mg/m³	ISO 6326, 19739
Methane		> 65 % (High grade 80)	97 % ± 2	EN 16726
Compressor oil	de deminis[a]	de deminis[a]		ISO 8573-2
Dust	de deminis[a]	de deminis[a]		ISO 8573-4
Amines	< 10 mg/m³	< 10 mg/m³	< 20 mg/m³	VDI 2467 Blatt2: 1991-08
Water		< -10 °C dew point	< 32 mg/m³	ISO 10101, 6327, 11541
Chlorinated compounds	de deminis[a]			ISO 6142-1, HCl: EN 1911
Fluorinated compounds	de deminis[a]			NF X43-304, ISO 15713
Carbon monoxide	< 0.1 %			ISO 6974
Ammonia	< 10 mg/m³		< 20 mg/m³	NEN 2826, VDI 3496 Blatt 1:1982-04, NF X43-303
Wobbe index			43,9 - 47,3 MJ/m³	ISO 6976, 6974
Carbon dioxide + Nitrogen			< 3-4 %	ISO 6974
Motoroktantall (MON) [b]			> 130	ISO 15403

Sampling according to ISO 10715, 16726

a) de deminis - Does not render the fuel unacceptable for use in end user applications
b) MON = 137,78*metan+181,233*CO2+26,994*N2
c) Some gas turbines manufacturers have set < 0.1 mg/m³ limits.

Agenda



Nondispersive infrared spectra of common gases

Common online sensors and their limitations

Wikimedia Commons@Daniel Popa and Florin Udrea

Oxygen

Mostly electrochemical, finite lifespan (2-3 years).

Calibration check:
3 months.

Hydrogen sulfide

Mostly electrochemical, finite lifespan (1-2 years). Cross-sensitive to hydrogen.

Calibration check:
3 months. Requires personell handling of toxic gas. Gas mixtures have limited «shelf-time».

Carbondioxide/Methane

Nondispersive infrared sensors are bulky and expensive, but robust!

Calibration check:
6 months

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Verify sensor calibration

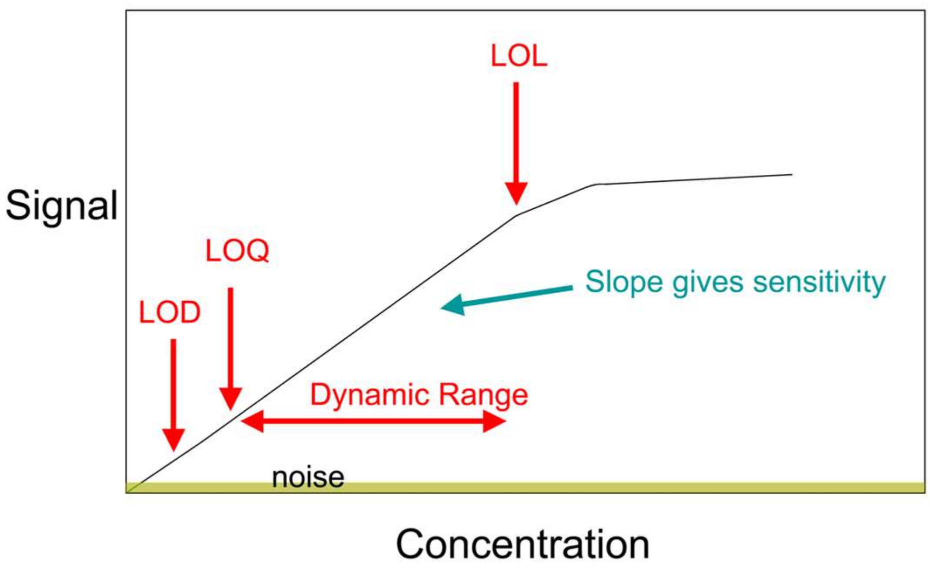
Range, precision and accuracy

No interferences

All gaseous species

Easy to sample and send

Frequent calibration is key for accuracy in online monitoring



Five habits for a good calibration of sensors

1. Learn the basics on handling pressurised gas before continuing.
2. Always include background (zero) points
3. Minimum two calibration points excluding background.
4. Calibrate with certified standards within expected «shelf-time».
5. Purge thoroughly the gas to wash out background air and saturate lines.

Agenda

Periodic measurements

Twice/year and after feedstock/process changes according to EN16723

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Verify purification/filtration
Know your contaminants
Essential for Risk Evaluation
Part of preventive maintenance
Requirement from CHP* suppliers

*Combined heat and power usually with Combined-cycle Gas Turbin

IFE Biogas analysis service

Gas composition analysis

Periodic measurements

Training

Stable Isotope Monitoring

Stability control of process

Certification

Tracing leachate and pollutants

Five good habits on sampling gas with bags

1. Make sure you are using the correct type of gas bag for the purpose of the sampling
2. Remember even empty gas bags contains air.
3. Never reuse a gas bag.
4. Always use soft-tubing which are inert to your gas.
5. Purge well and thoroughly all lines before sampling.

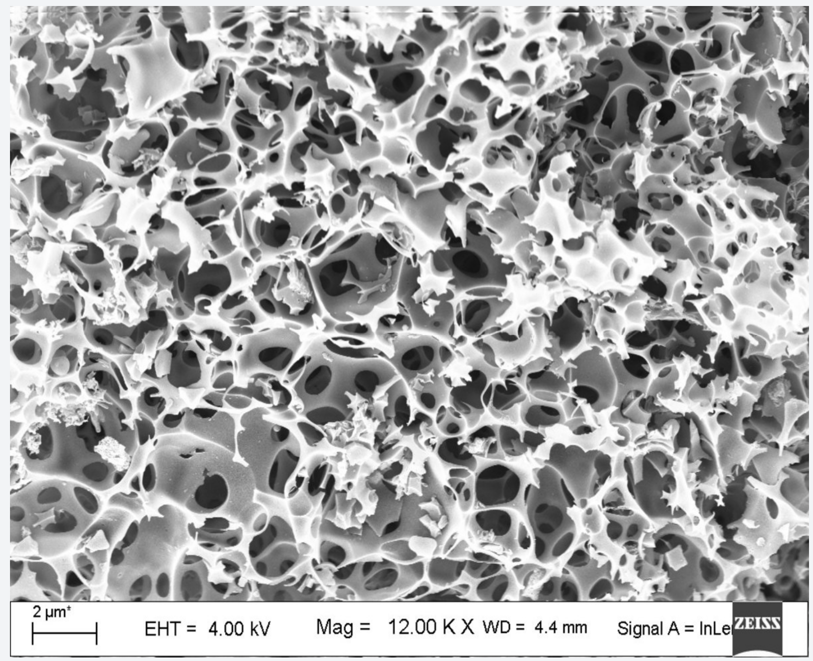
Five good habits on sampling gas with TD-tubes

1. Always sample in the middle of the flow! VOC's creeps on the tubing walls.
2. Start sampling on a «training tube» to assert flow readings.
3. Split the flow, don't restrict it, to get a accurate sample within the limits of your tube.
4. Inertness of tubing and equipment is very important in VOC-analysis.
5. Sample several tubes with different sampling-times. Example: <15s, 30s, 1', 2'> at 80-100 mL/min

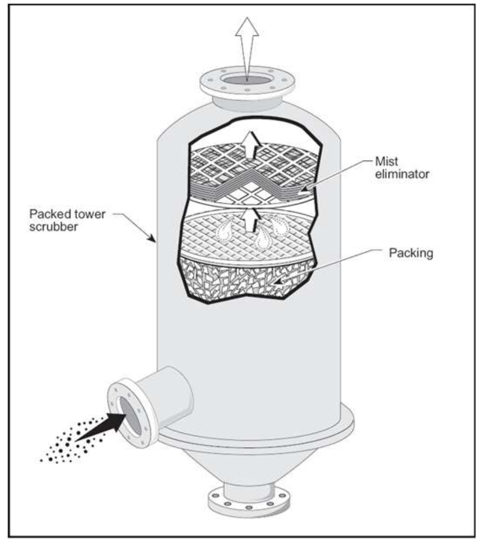
Agenda

Biogas upgrading

Absorbents, adsorbents / chemisorption vs physisorption

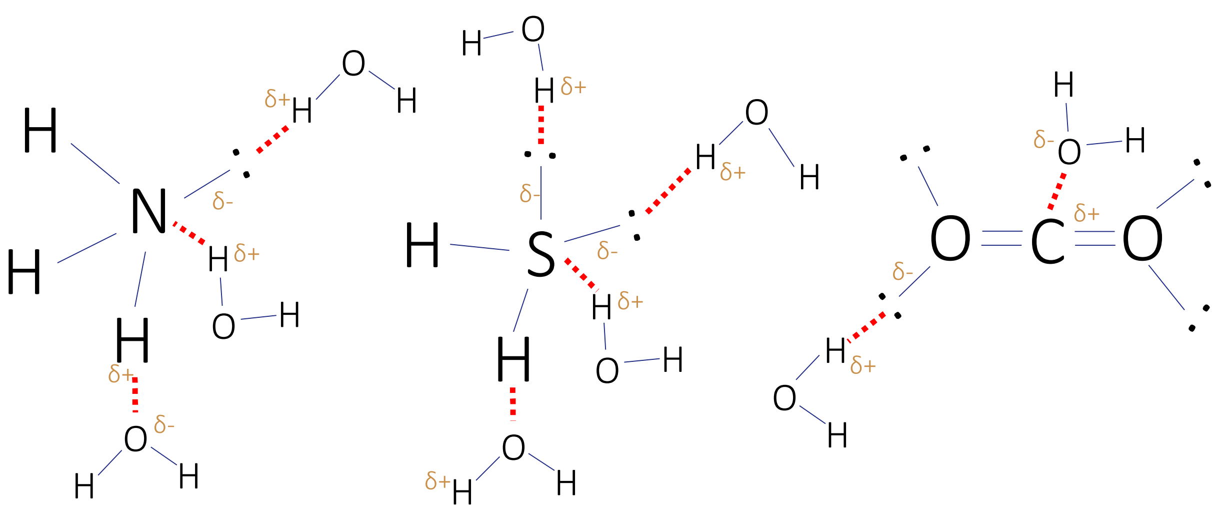


$$2\ H_2S\ (g) + 3\ O_2\ (g) \rightarrow 2\ SO_2\ (g) + 2\ H_2O\ (l)$$



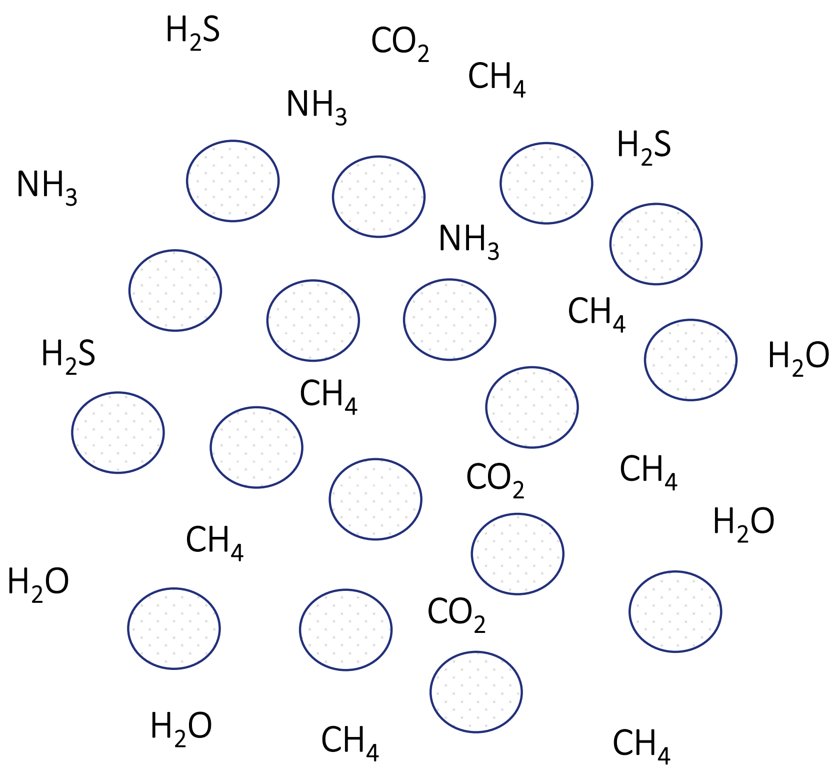
Scrub the gas!

Use the power of hydrogen-bonds



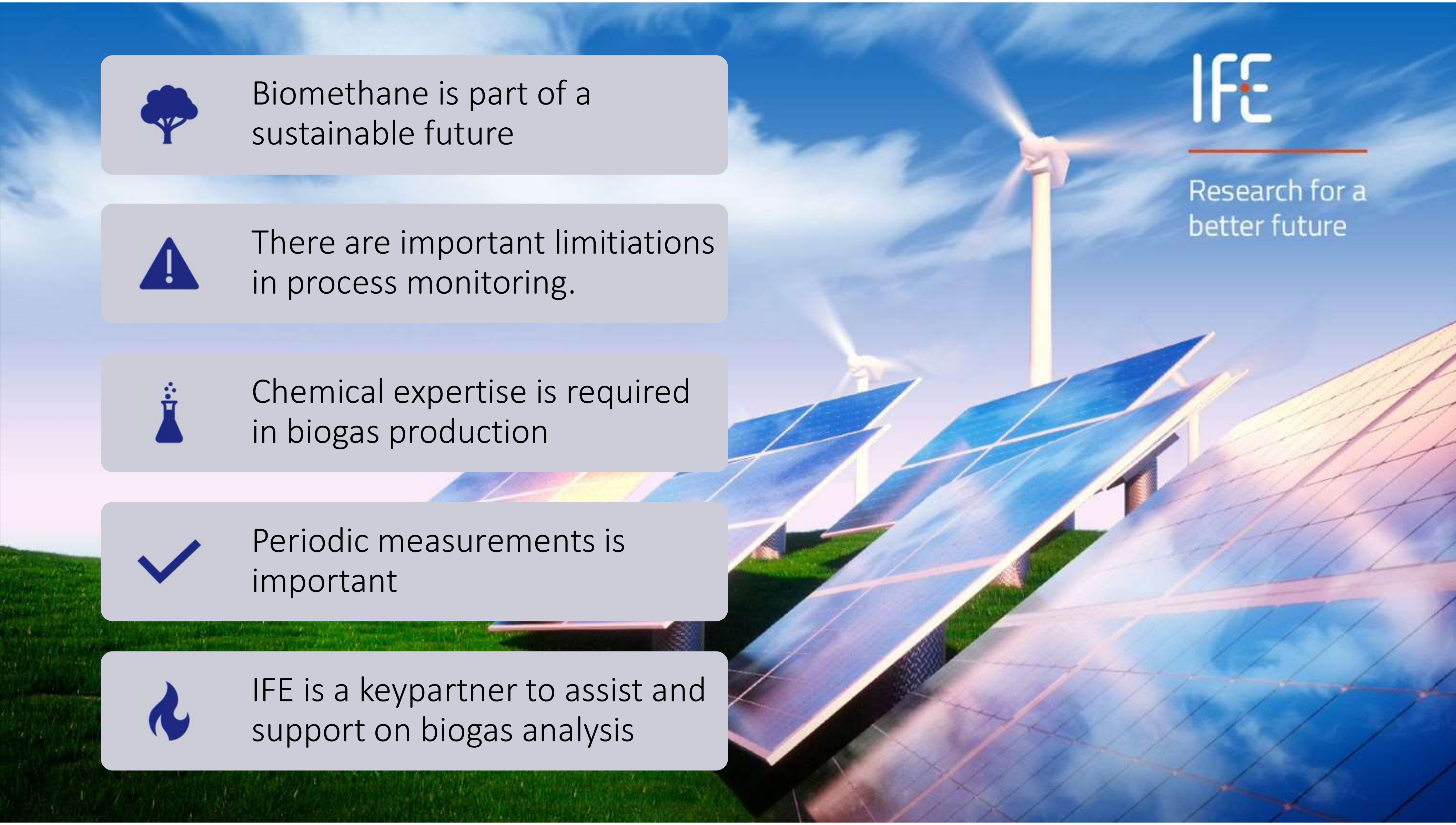
Pressure swing adsorption

Pressure manipulation increases adsorption.



There are many other upgrading technologies not mentioned here. Example: Membrane-technology have come a long way.

Agenda


Biomethane is part of a sustainable future
There are important limitiations in process monitoring.
Chemical expertise is required in biogas production
Periodic measurements is important
IFE is a keypartner to assist and support on biogas analysis
IFE
Research for a better future

Thank you for your attention!

Fred Martin Kaaby
Process engineer, Msc. Organic Chemistry

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