Kick-Off Biomethane Regions May 24-27, 2011
Training Session – Train the Trainers, May 26

Biogas: Characteristics, Clean-up Technologies and Upgrading

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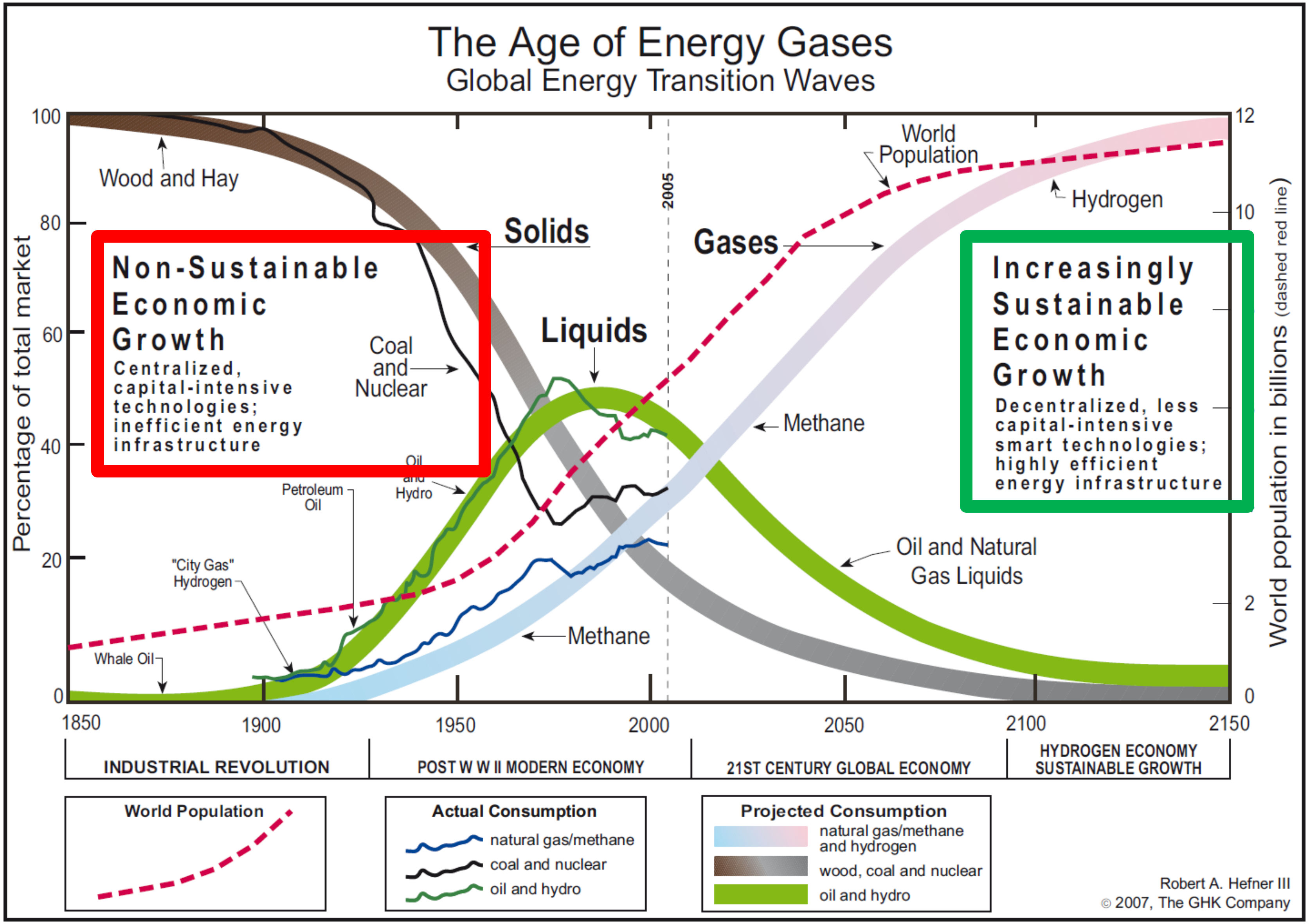
Agenda

- Characteristics of biogas
- Contaminations
- Characteristics of biomethane – regional differences
- Upgrading biogas
  - Preconditioning / pretreatment
  - Desulphurisation
  - Compression
  - Upgrading = CO2 + H2O separation
  - Final conditioning, offgas treatment
- Energy consumption and costs

What are the drivers ?



The Age of Energy Gases
Global Energy Transition Waves

Non-Sustainable Economic Growth
Centralized, capital-intensive technologies; inefficient energy infrastructure

Increasingly Sustainable Economic Growth
Decentralized, less capital-intensive smart technologies; highly efficient energy infrastructure

Robert A. Hefner III
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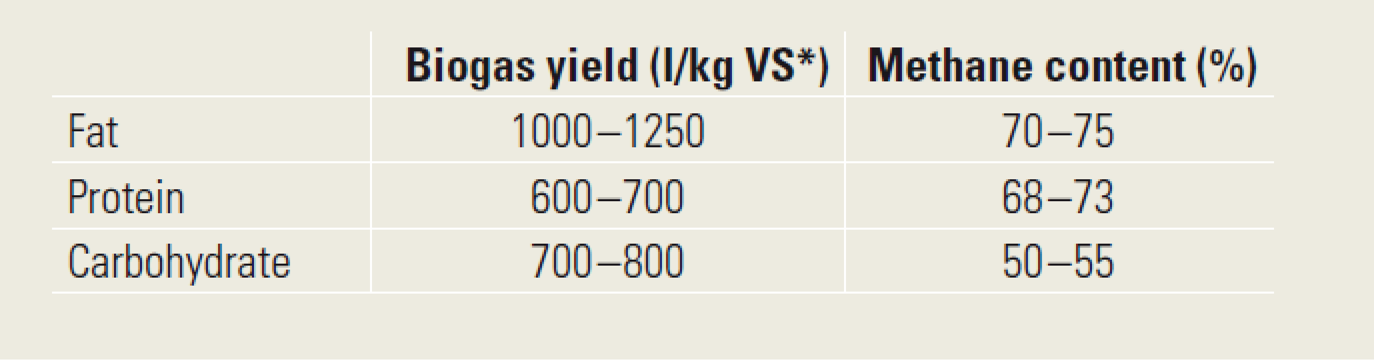
Biogas Composition and Natural Gas Standards



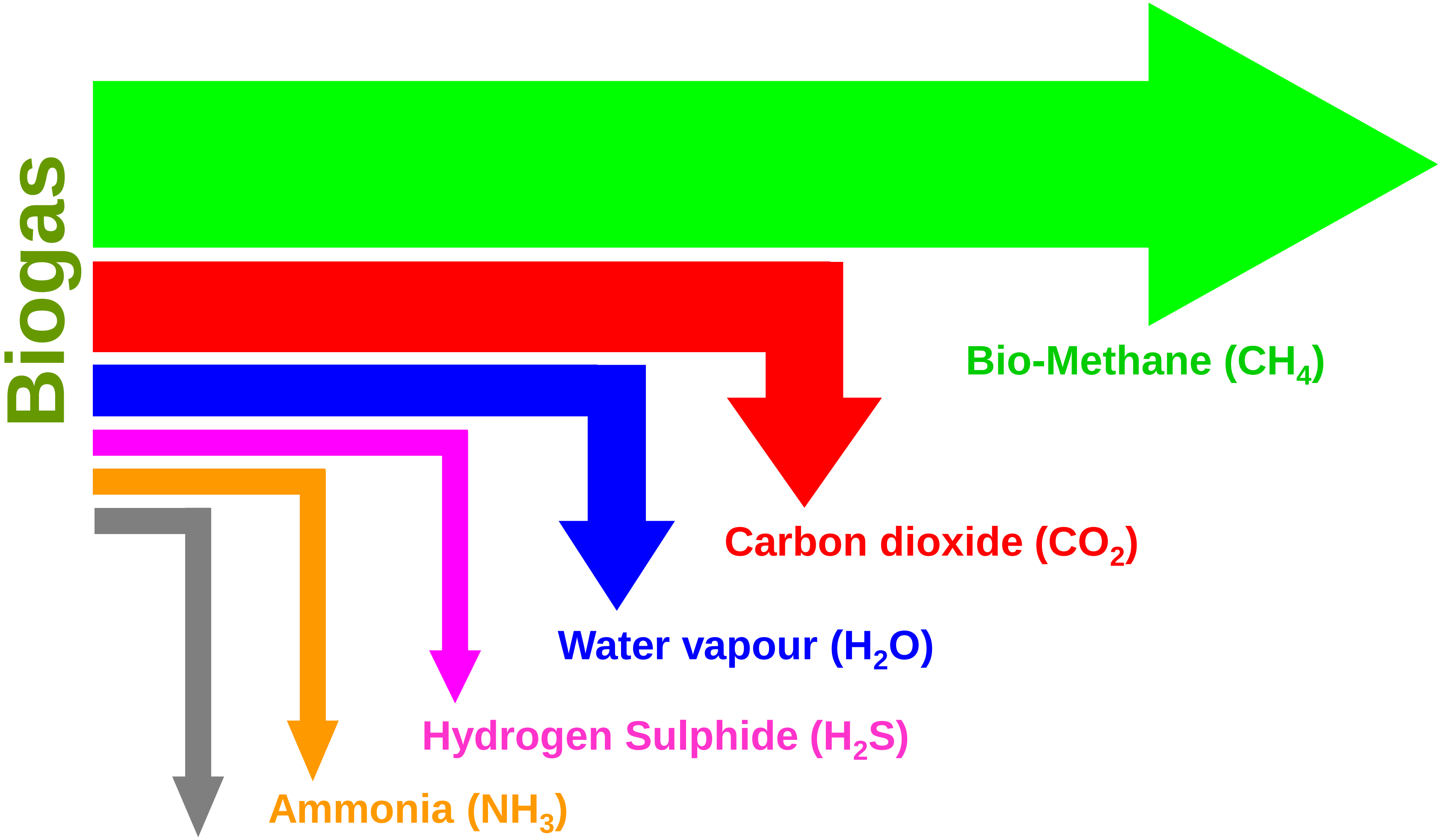
	Biogas yield (l/kg VS*)	Methane content (%)
Fat	1000–1250	70–75
Protein	600–700	68–73
Carbohydrate	700–800	50–55

*VS = Volatile Solids

[Wellinger et al., IEA Task37 (2009)]

Parameter	**Biogas**	**Specification according to ÖVGW G31**	**Unit**
methane	50 bis 70	-	[mole %]
carbon dioxide	25 bis 45	≤ 2,0	[mole %]
ammonia	up to 1.000	technically free	[mg/m_N^3]
hydrogen sulfide	up to 2.000	≤ 5	[mg/m_N^3]
oxygen	up to 2	≤ 0,5	[mole%]
nitrogen	up to 8	≤ 5	[mole %]
water vapour (dewpoint)	up to 37 @ 1 bar	≤ - 8 @ 40 bar	[°C]
upper heating value	6,7 - 8,4	10,7 - 12,8	kWh/m_N^3
Wobbe-Index	6,9 - 9,5	13,3 - 15,7	kWh/m_N^3

Biogas Upgrading – A Separation Problem



Biogas

Bio-Methane (CH_4)

Carbon dioxide (CO_2)

Water vapour (H_2O)

Hydrogen Sulphide (H_2S)

Ammonia (NH_3)

Other Contaminants (Particles, Droplets, Siloxanes, Hydrocarbons, Mercaptanes)

Trace components in raw biogas

- Raw biogas may contain following trace components :
  - longer alkanes, cycloalkanes and aromatic compounds
  - halogenated hydrocarbons
  - thiols and terpenes
  - volatile fatty acids and alcohols
  - siloxanes
  - particles
  - droplets (condensates, aerosols...)

- Possible adverse effects of trace components on compression, upgrading technology and gas grid of high importance
  - corrosion
  - performance decline
  - degradation of scrubbing solution, adsorption material or membranes

EU Legislative Basis for Biomethane Access to Gas Grids

- Directive 2003/55/EC of the European Parliament and of the Council of 26 June 2003 concerning common rules for the internal market in natural gas and repealing Directive 98/30/EC.

Preambel: Member States should ensure that, taking into account the necessary quality requirements, biogas and gas from biomass or other types of gas are granted nondiscriminatory access to the gas system, provided such access is permanently compatible with the relevant technical rules and safety standards. These rules and standards should ensure, that these gases can technically and safely be injected into, and transported through the natural gas system and should also address the chemical characteristics of these gases.

National Gas Quality Regulations

- Distribution of natural gas is governed mainly by national legislation concerning gas qualities.
- **H-gas** is distributed in most European countries whereas **L-gas** only is distributed in four countries (the Netherlands, France, Belgium and Germany).
- All nations with natural gas distribution systems have some kind of national regulations concerning gas composition.
- The key factor in these requirements is always the **Wobbe Index**. The WI- range and the sulphur content is always specified in all European regulations.

National Gas Quality Regulations II

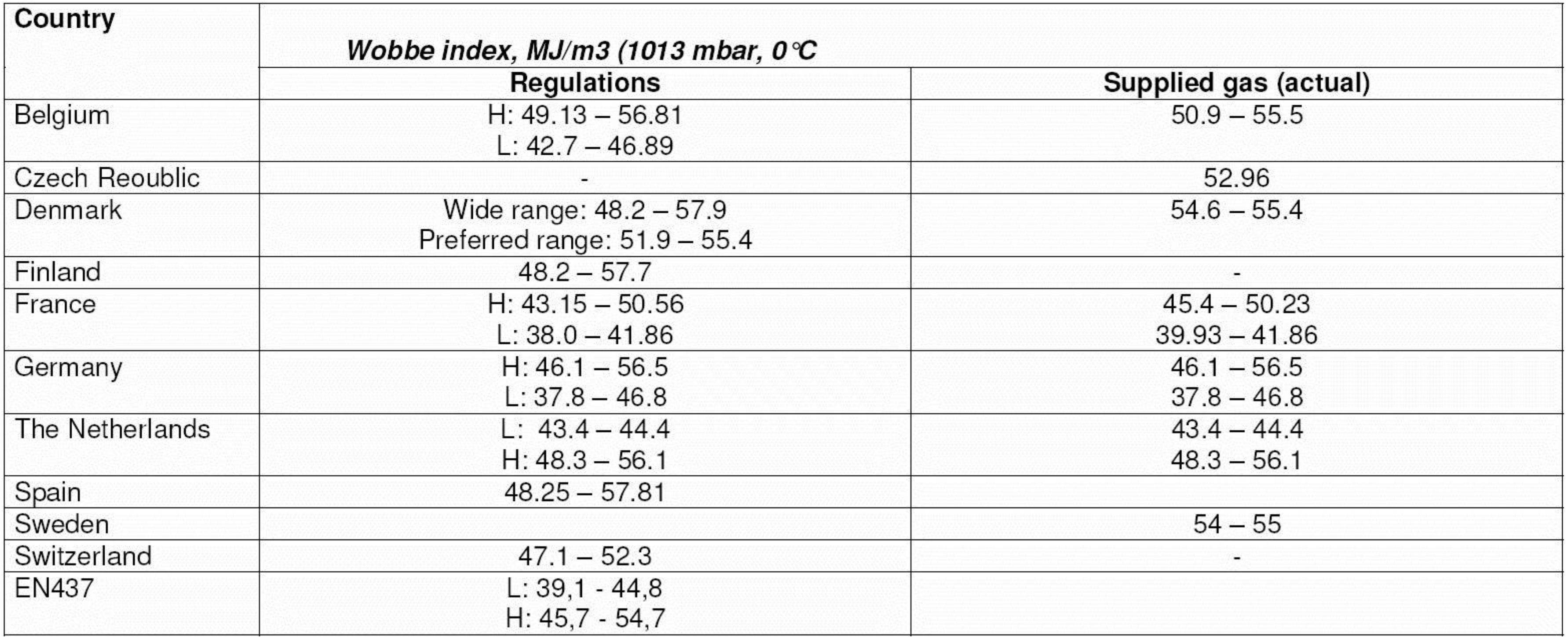
- Gas distributions grids in Europe are divided into two categories – L-gas grids and H-gas grids.
- The terms L and H refer to low and high Wobbe index according to the European standard EN437.
- L and H-gas are supplied to the customer in separate grids. The only present major source of L gas is in Holland but some minor sources also exist e.g. in the western part of Poland.
- In general, there is no direct legislation defining the quality of gas in the transmission lines in Europe.
- The gas composition is governed by national regulations, set by regulators in each individual country and **no common European standard** is available except the EN437.

Wobbe index ranges of natural gas in Europe

Wobbe Index definition: $W = H/(d)^{0,5}$

H…calorific value

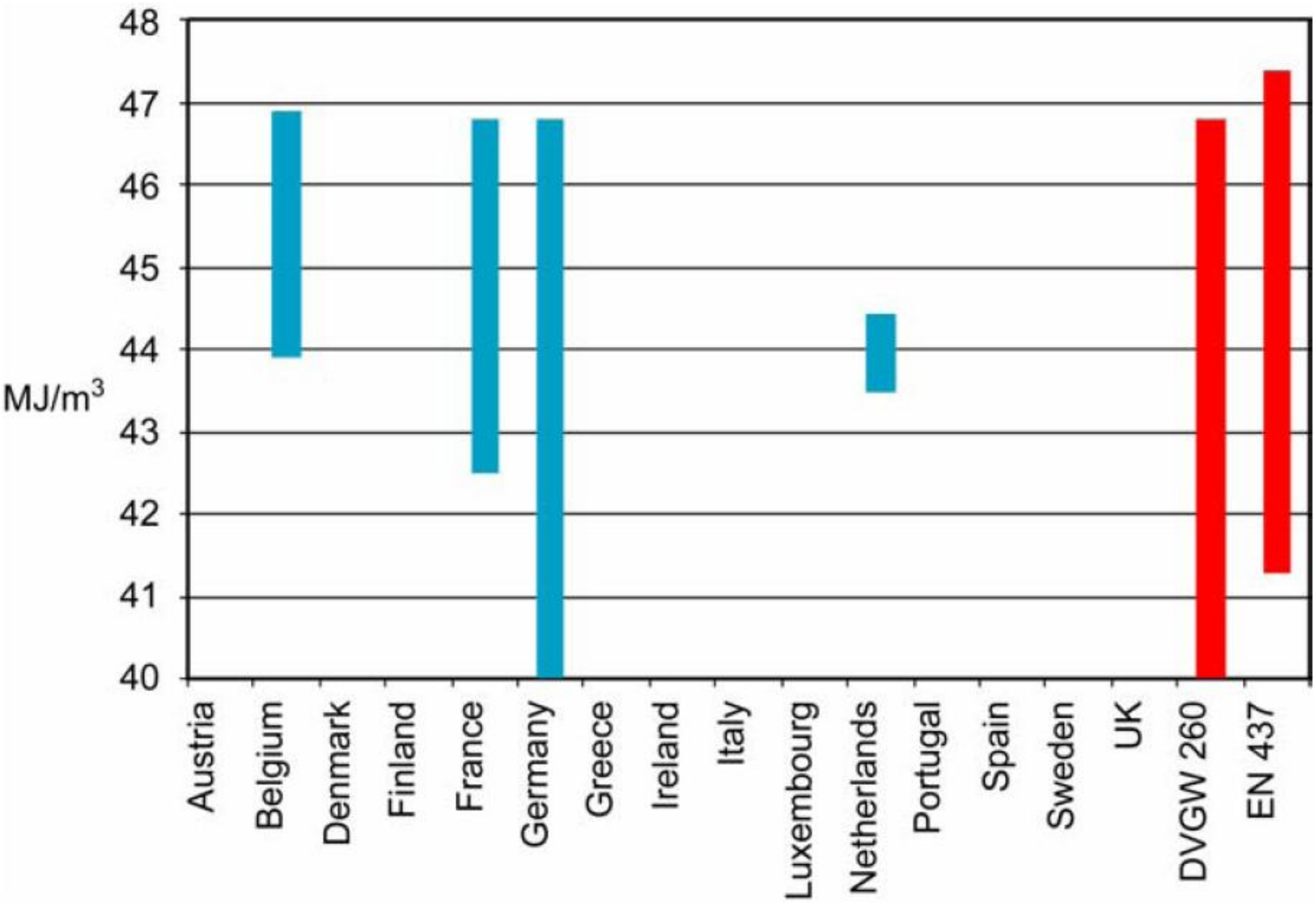
d…relative density of the gas



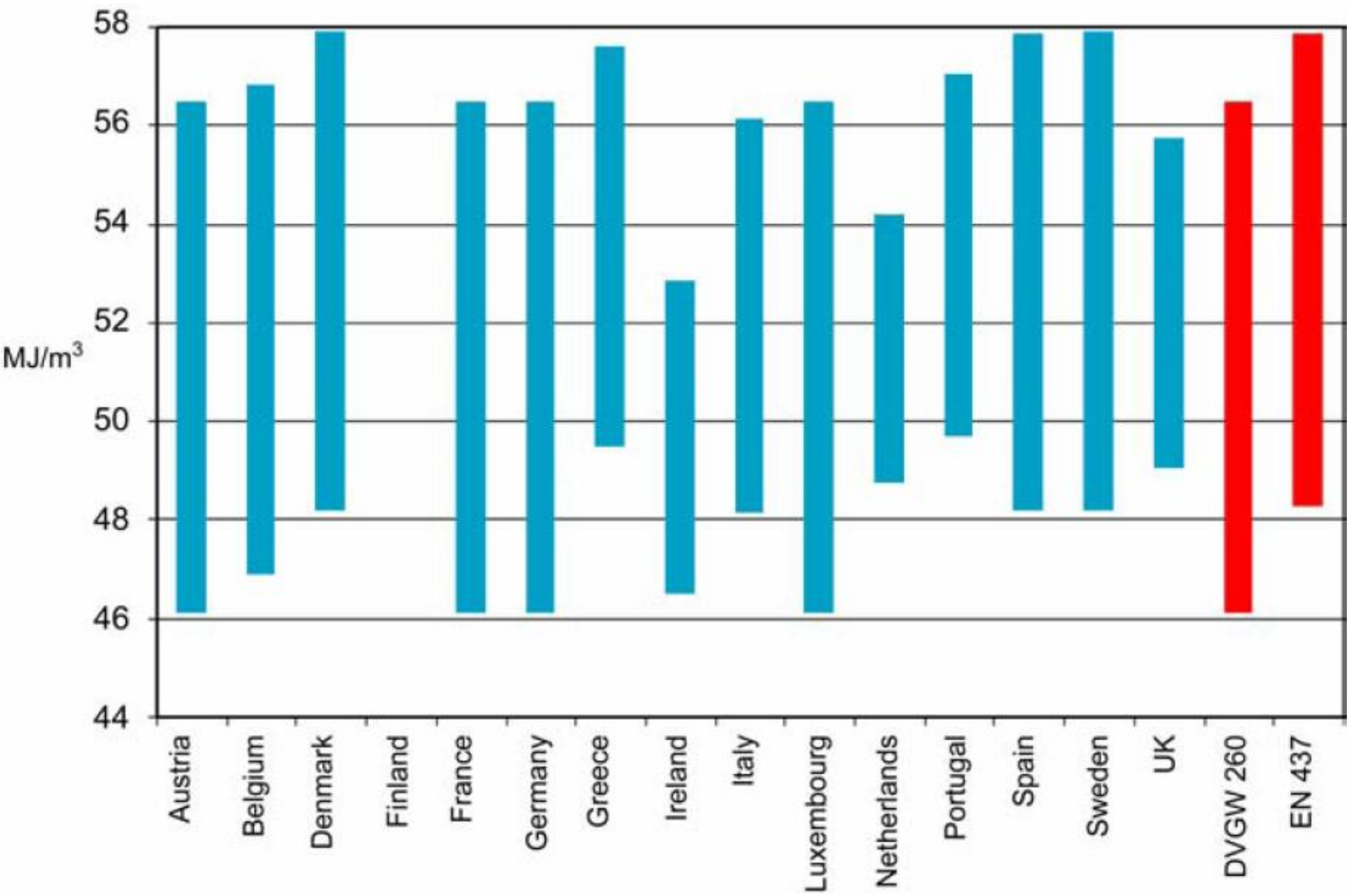
Country	*Wobbe index, MJ/m3 (1013 mbar, 0 °C*	
	Regulations	**Supplied gas (actual)**
Belgium	H: 49.13 – 56.81 L: 42.7 – 46.89	50.9 – 55.5
Czech Reoublic	-	52.96
Denmark	Wide range: 48.2 – 57.9 Preferred range: 51.9 – 55.4	54.6 – 55.4
Finland	48.2 – 57.7	-
France	H: 43.15 – 50.56 L: 38.0 – 41.86	45.4 – 50.23 39.93 – 41.86
Germany	H: 46.1 – 56.5 L: 37.8 – 46.8	46.1 – 56.5 37.8 – 46.8
The Netherlands	L: 43.4 – 44.4 H: 48.3 – 56.1	43.4 – 44.4 48.3 – 56.1
Spain	48.25 – 57.81	
Sweden		54 – 55
Switzerland	47.1 – 52.3	-
EN437	L: 39,1 - 44,8 H: 45,7 - 54,7	

- **IMPORTANT:** please check with your gas supplier / your authorities about the quality requirements (European Standard EN437 is a good start, however local regulations may vary!)

Permitted Wobbe Index, L Gas

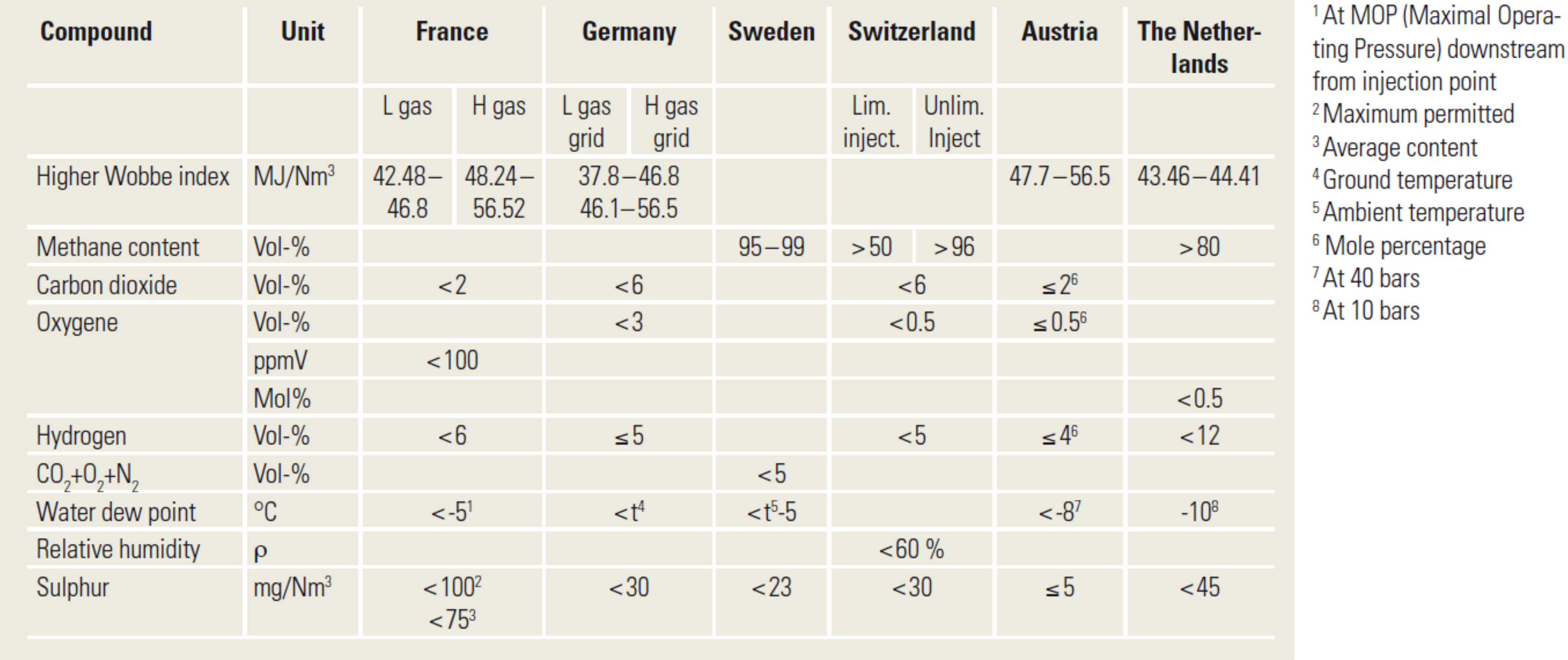


Permitted Wobbe Index, H Gas



Requirements for Grid Injection

- Selected standard requirements for grid injection or for utilization as vehicle fuel:



Compound	Unit	France		Germany		Sweden	Switzerland		Austria	The Netherlands
		L gas	H gas	L gas grid	H gas grid		Lim. inject.	Unlim. Inject		
Higher Wobbe index	MJ/Nm^3	42.48–46.8	48.24–56.52	37.8–46.8 46.1–56.5					47.7–56.5	43.46–44.41
Methane content	Vol-%					95–99	>50	>96		>80
Carbon dioxide	Vol-%	<2		<6			<6		≤2[6]	
Oxygene	Vol-%			<3			<0.5		≤0.5[6]	
	ppmV	<100								
	Mol%									<0.5
Hydrogen	Vol-%	<6		≤5			<5		≤4[6]	<12
CO_2+O_2+N_2	Vol-%					<5				
Water dew point	°C	<-5[1]		<t[4]		<t[5]-5			<-8[7]	-10[8]
Relative humidity	ρ						<60 %			
Sulphur	mg/Nm^3	<100[2] <75[3]		<30		<23	<30		≤5	<45

[1] At MOP (Maximal Operating Pressure) downstream from injection point
[2] Maximum permitted
[3] Average content
[4] Ground temperature
[5] Ambient temperature
[6] Mole percentage
[7] At 40 bars
[8] At 10 bars

[Wellinger et al., IEA Task37 (2009)]

- **Consequence:** again please check local requirements!

Recommendations – Raw Biogas Composition & Flow

- ✓ Ask for the raw biogas composition
- ✓ If the answer is not clear, be suspicious and measure yourself or consult a lab to run the analysis + ask for the feedstocks
- ✓ Remember: just to know the methane content is not enough!
- ✓ Ask for the biogas production capacity (volumetric flow rate) and its fluctuation

- ✓ The more you know, the better you go!

Biogas Upgrading Steps

1
- Preconditioning / pretreatment
- Removal of particles, droplets, siloxanes, other trace components

2
- Biogas desulphurisation

3
- Compression

4
- Biogas upgrading
- Separation of CO_2 and H_2O

5
- Final conditioning
- Dewpoint control, adjustment of heating value, offgas treatment

Preconditioning / Pretreatment

- ✓ **Particles, droplets:** use filter, demister
- ✓ **Siloxanes:** use carbon adsorption (water dewpoint control needed - place a chiller + reheater in front of the carbon adsorption tower)
- ✓ **Halogenated hydrocarbons, other hydrocarbons, fatty acids, terpenes:** use carbon adsorption (water dewpoint control needed - place a chiller + reheater in front of the carbon adsorption tower)

Desulphurisation – Removal of H_2S

- ✓ **Various technologies available:**
  - ✓ In-situ desulphurisation
  - ✓ Air injection
  - ✓ External biological desulphurisation
  - ✓ Chemical oxidation
  - ✓ Adsorptive removal (iron oxide, zinc oxide)
  - ✓ Catalytical oxidation and carbon adsorption (KI/I_2 – impregated carbon, needs stochiometric amount of oxygen)
  - ✓ Combined with upgrading: water/amine absorption
- ✓ Ask, if there is a desulphurisation currently used or implemented
- ✓ Check the H_2S concentration and feedstock related fluctuations

Compatible desulphurisation technologies

Compatible:

- External biological desulphurisation in combination with pure oxygen injection
- In-situ desulphurisation using iron salts
- **External chemical scrubber with oxidation using NaOH/H_2O_2, recommended for fluctuating H_2S concentrations in the biogas**
- Adsorptive desulphurisation technologies with low excess of O_2 (impregnated activated carbon adsorbents)

Not suitable / incompatible:

- Air injection
- External biological desulphurisation with air injection

1 2 3 4 5

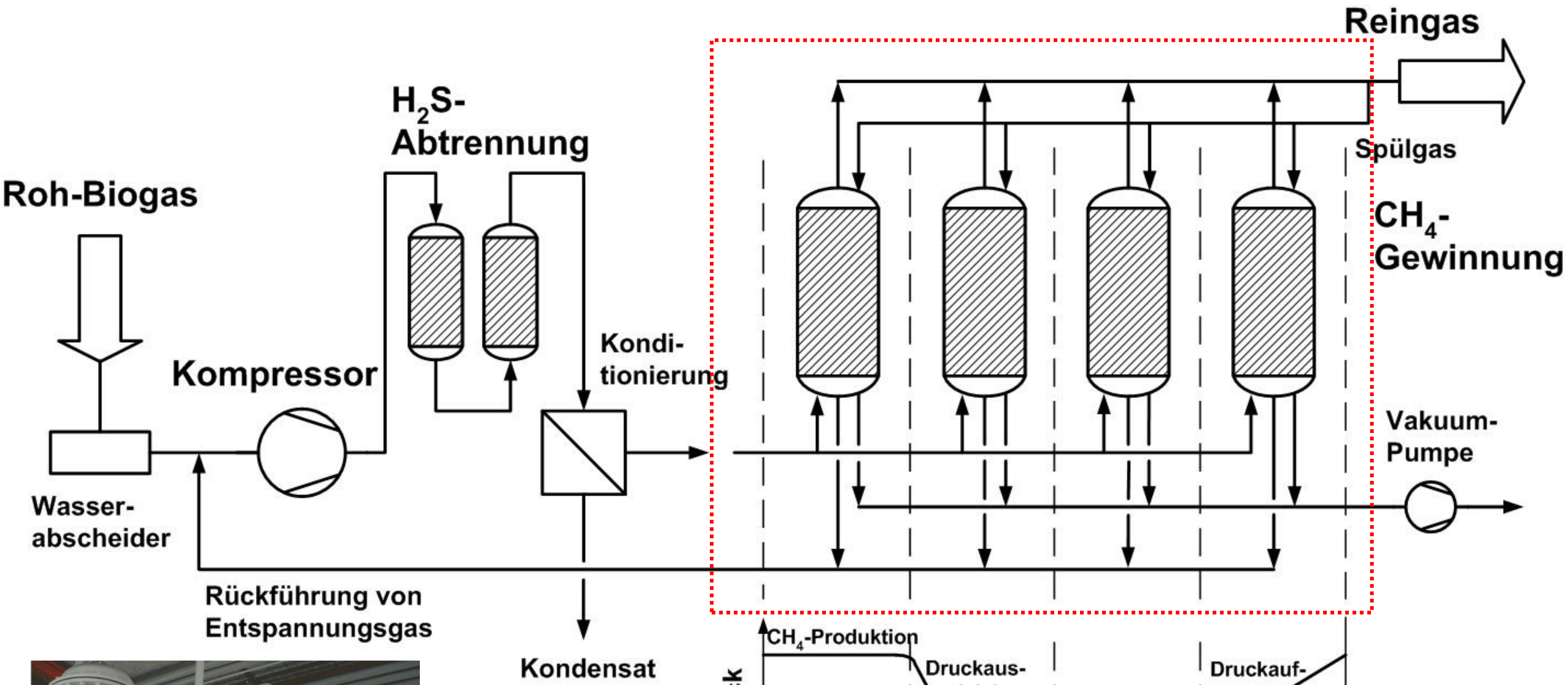
Compression

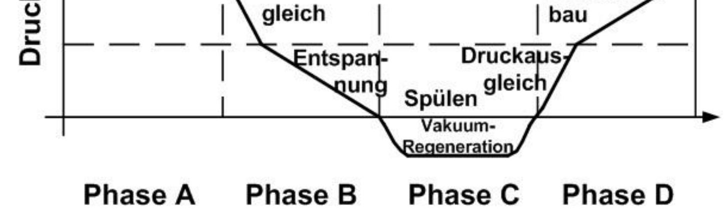
- **Various types of compressors available:**
  - Piston compressors
  - Screw compressors
  - Water ring pumps
  - Blowers
- Check range of load/capacity variation
- Check delivery pressure requirements
- Consider correct conversion volume flow to operating conditions (temperature, pressure), add recycle if needed
- Do not forget to account for water content / humidity
- Design for worst case and check turn-down ratio of compressor
- Check corrosion resistance, service intervals and lifetime
- Prefer oil-free systems (gear box lubrication only)
- Check cooling requirements – prefer water cooled systems

Biogas upgrading

- **Various technologies available**
  - Pressure swing adsorption
  - Water scrubbing
  - Selexol absorption
  - Amine absorption
  - Membrane separation
  - Cryo separation
  - Hybrid systems
- **Decide for suitable technology primarily NOT by investment costs – remember: cheap can be expensive!!**
- Select suitable technology according to:
  - upgrading capacity
  - turn-down ratio
  - shut-down / start-up performance and ease of operation
  - product quality needed
  - Chemicals and energy consumption

Pressure Swing Adsorption





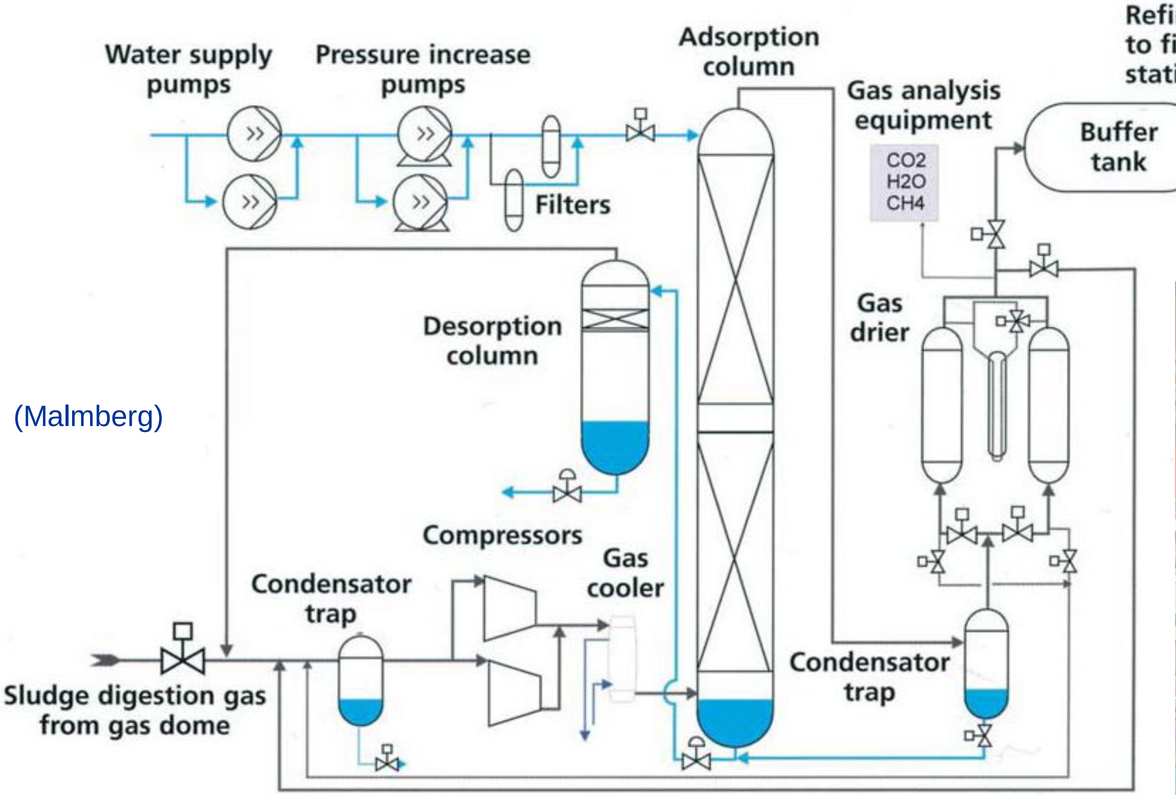
- Cyclic operation
- Many valves, precise timing needed

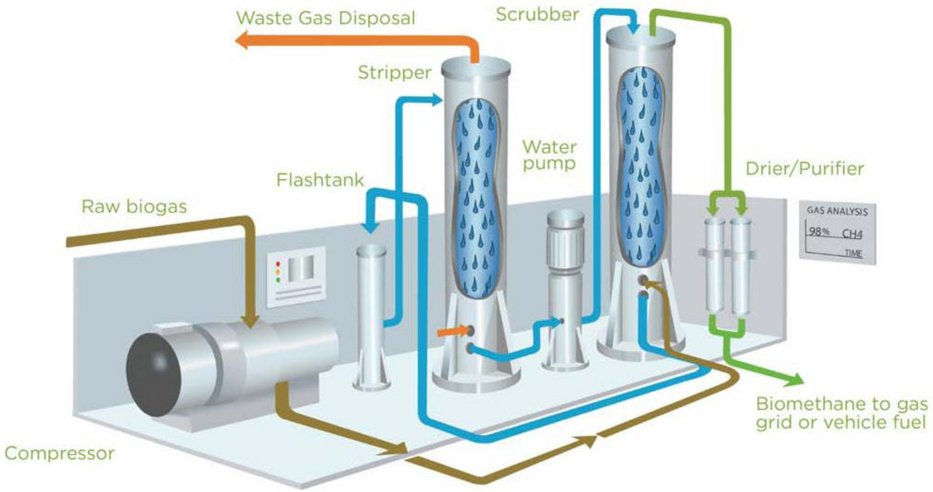
Project Pucking Pressure Swing Adsorption (PSA)

(Photos: M.Harasek)

Water Scrubbing / Absorption

(Malmberg)

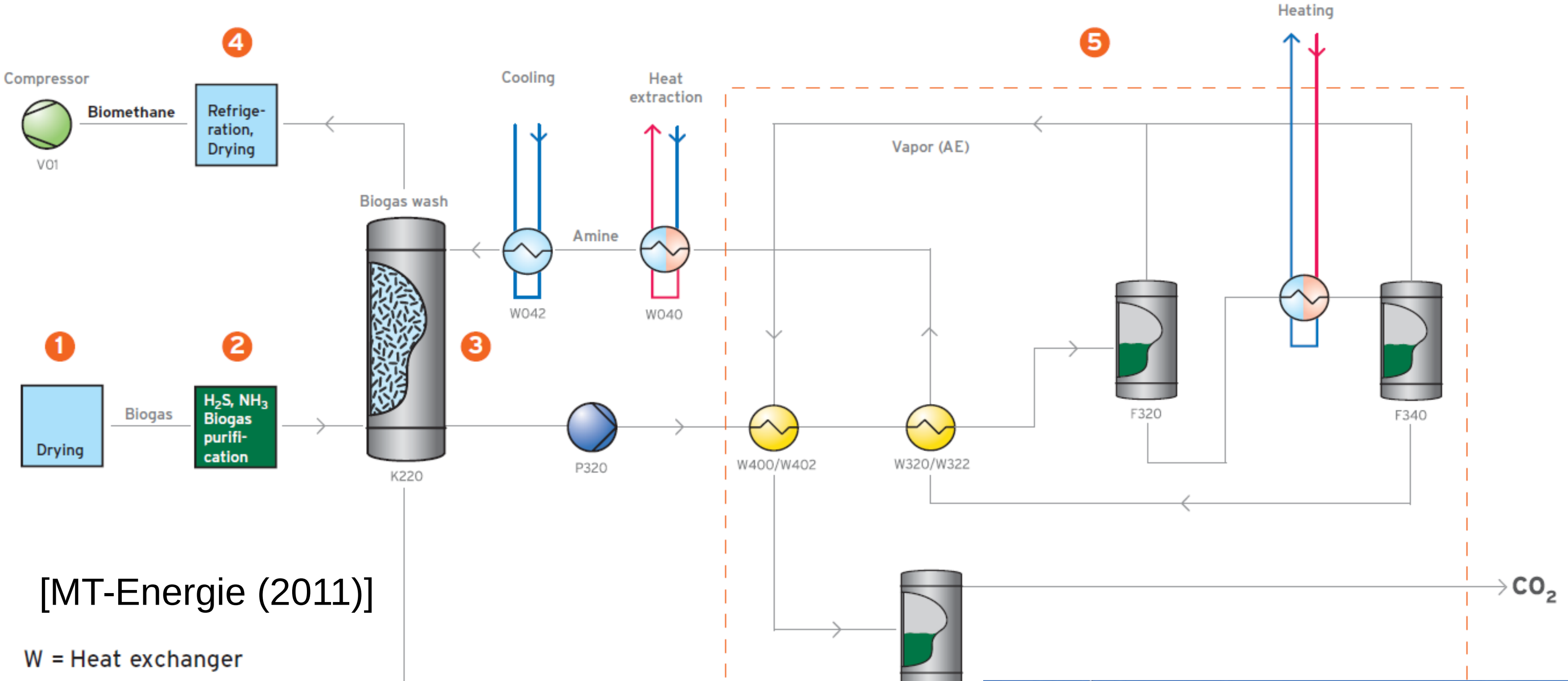




Large scale water scrubbing system

Malmberg 1250 m³/h water scrubbing system in Könnern (Germany)

Amine absorption



[MT-Energie (2011)]

W = Heat exchanger
P = Pump
F = Separator/reactor
K = Washing column

- Alkanol amines (MEA, DEA, MDEA) used for CO_2 absorption
- High desorption temperatures in recycle loops
- Low pressure operation possible

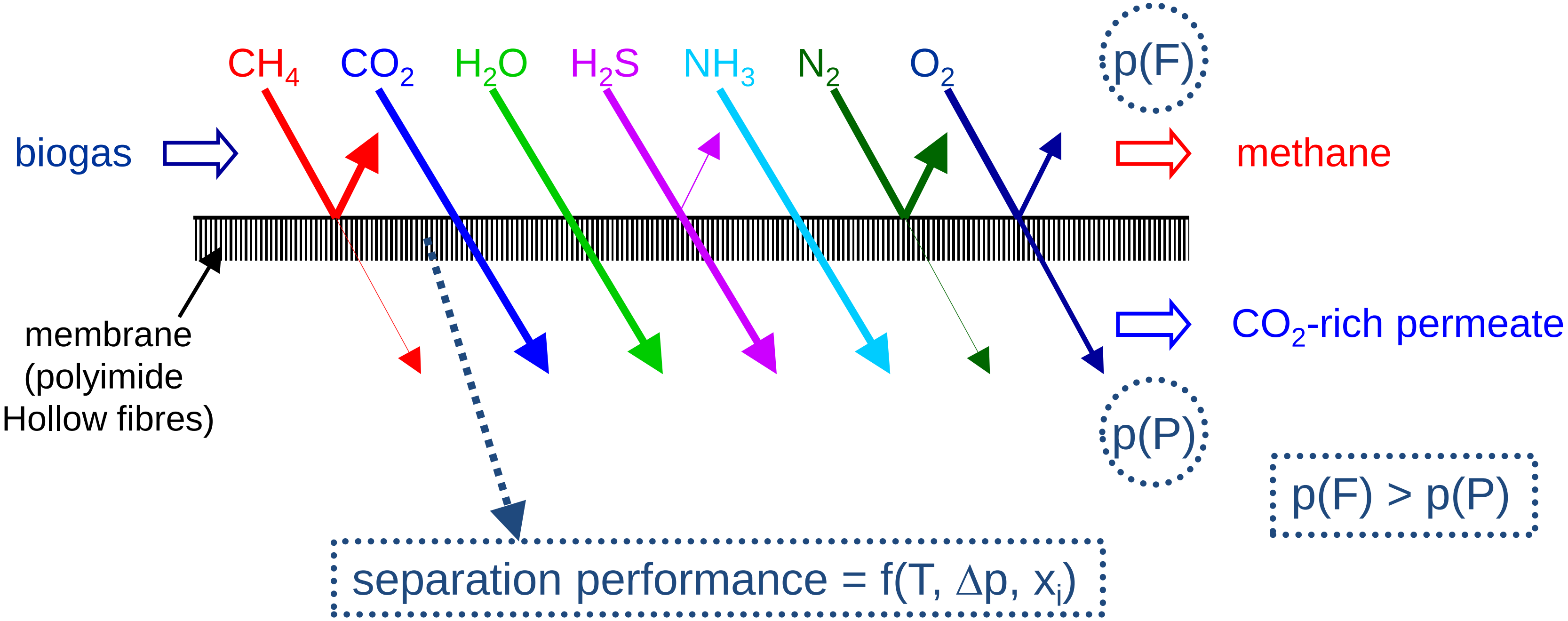
Amine Absorption / Biogas-upgrading in Leoben

- Project of Energie Steiermark Gas & Wärme
- Low pressure amine scrubbing system (delivery pressure 100 mbar)
- Full capacity of approx. 130 m³/h biomethane
- Start-up in 2009
- Temporary shut-down

[Machan (2009)]

Upgrading of biogas using gas permeation (GP)

- Separation principle: different permeabilities of methane and components to be separated.
- Important parameter: permeability ratio = selectivity.
- After compression biogas is fed to membrane modules.



CH_4 CO_2 H_2O H_2S NH_3 N_2 O_2

p(F)

biogas

methane

membrane (polyimide Hollow fibres)

CO_2-rich permeate

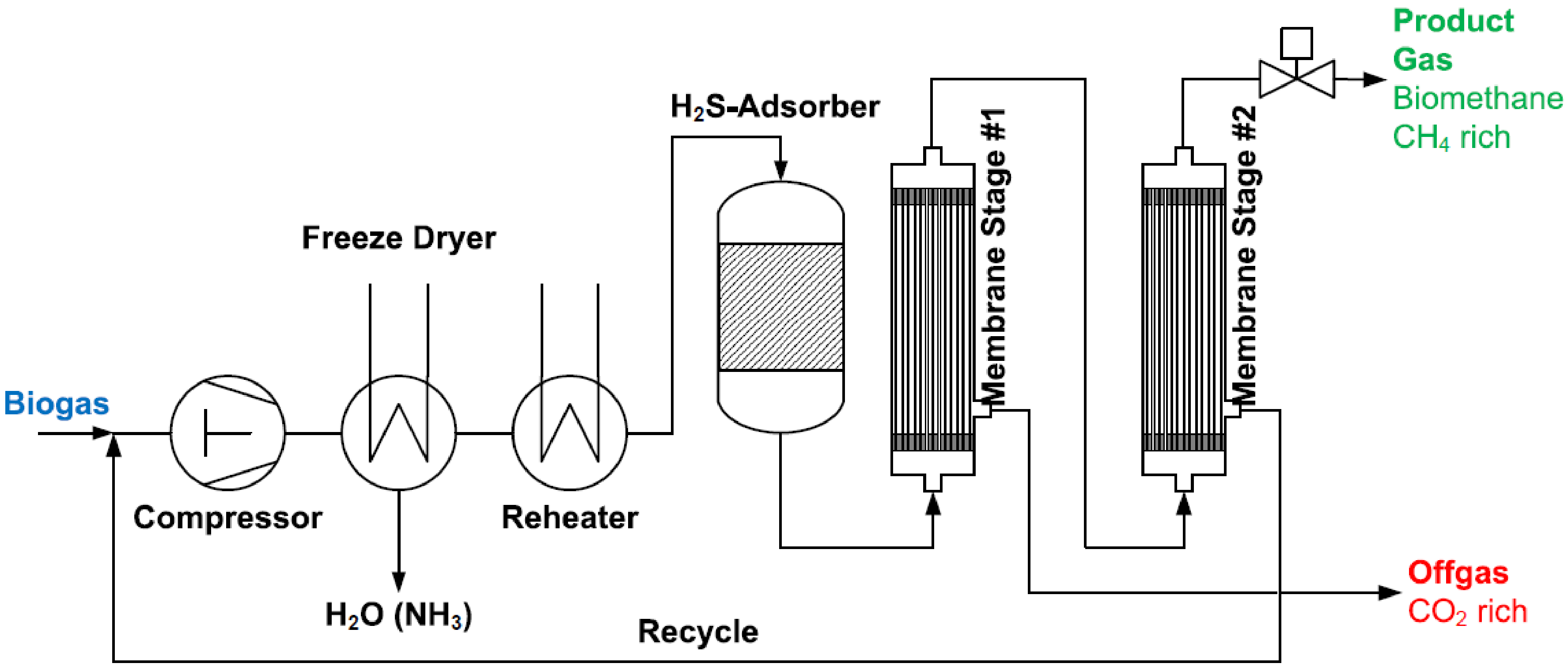
p(P)

p(F) > p(P)

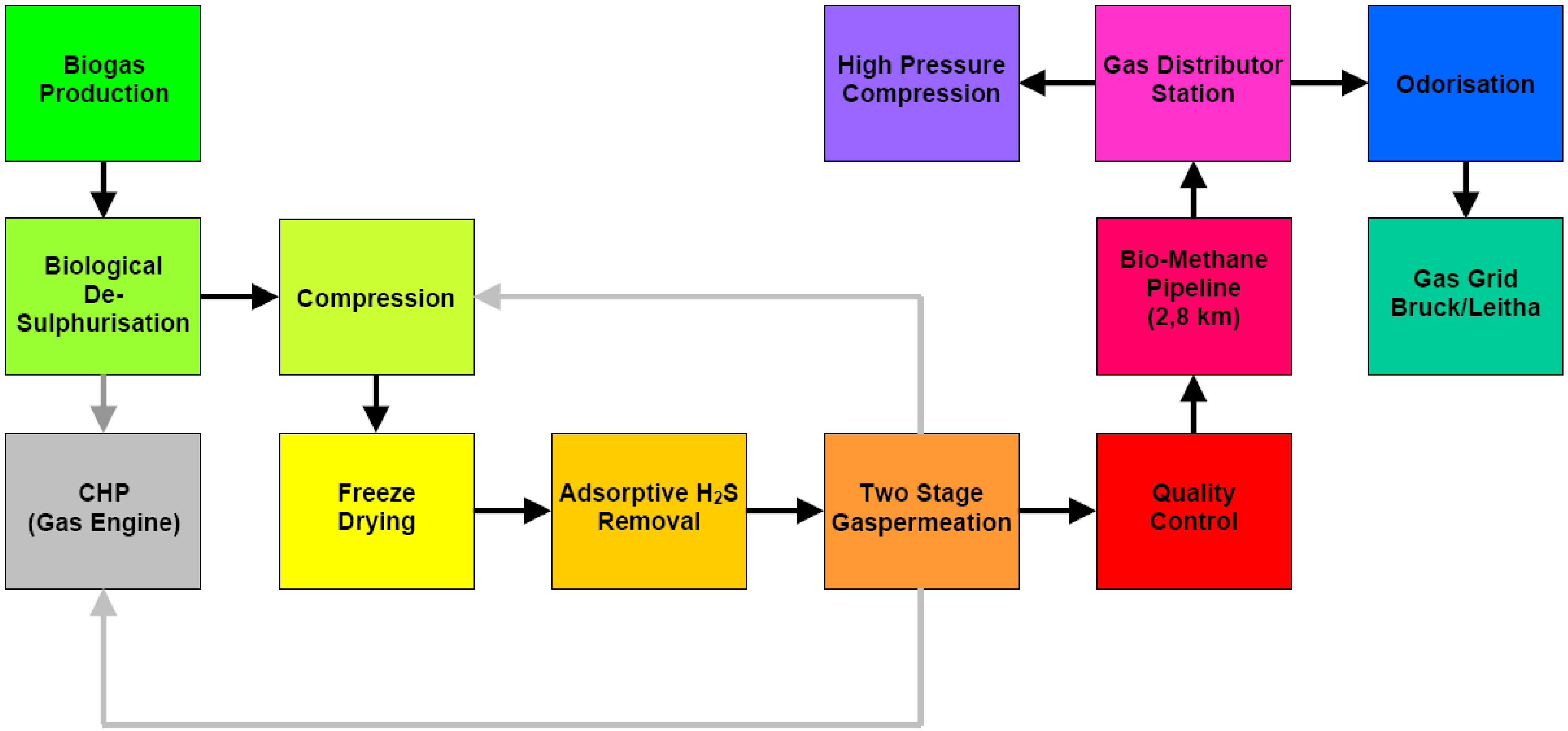
separation performance = f(T, Δp, x_i)

Process Scheme of a Two-stage Membrane System

- **Two-stage separation process** with recycle and a single compressor



Process Integration (Two-stage design)



- Biological desulphurisation prior to membrane treatment
- Permeate is recycled to CHP plant – „zero methane“ emission of upgrading system

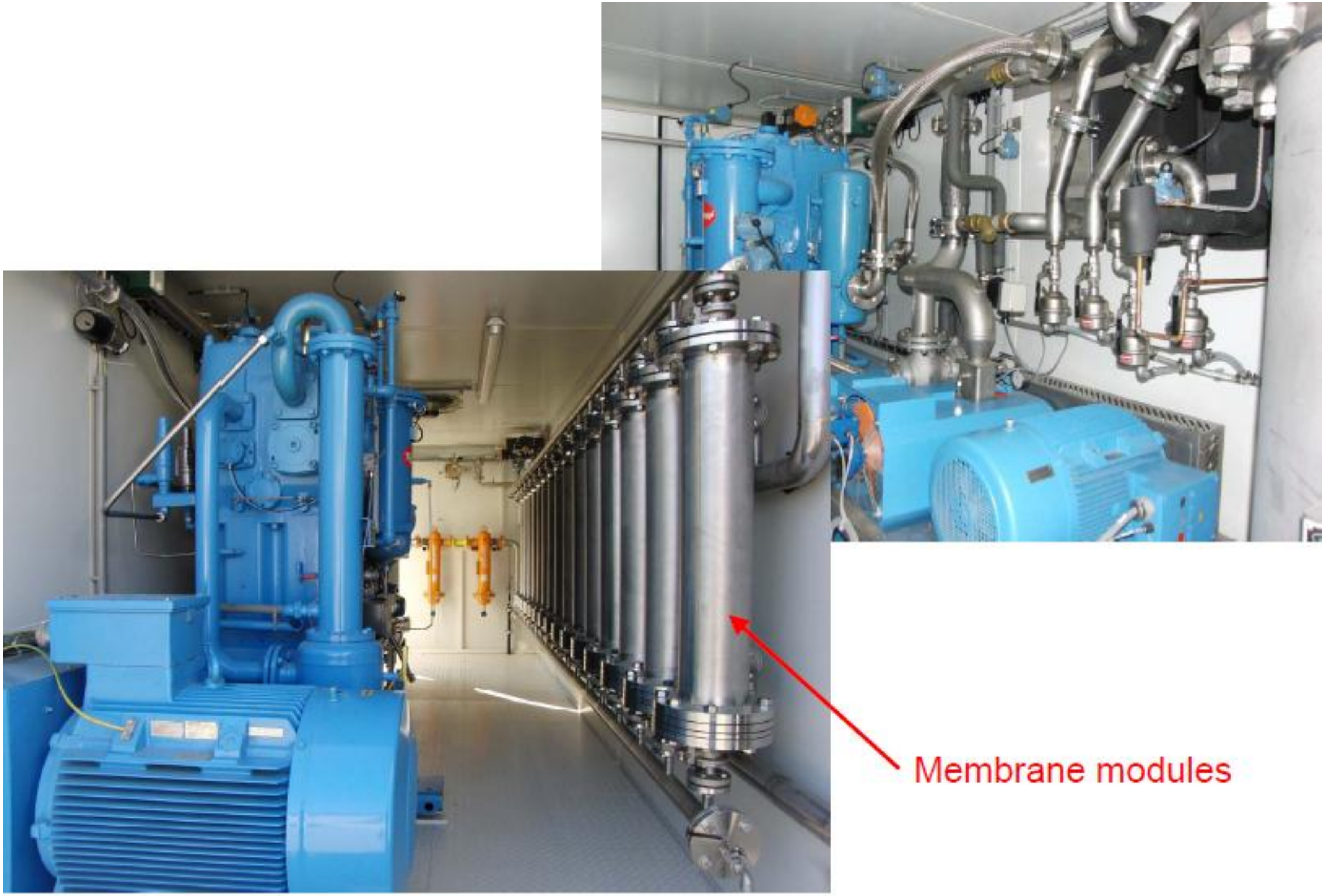
Upgrading plant in Bruck/Leitha

180 m³/h biogas / 100 m³(STP)/h biomethane @ 6 bar
Details: http://www.virtuellesbiogas.at

Membrane Biogas Upgrading Plant in Kisslegg (GE)

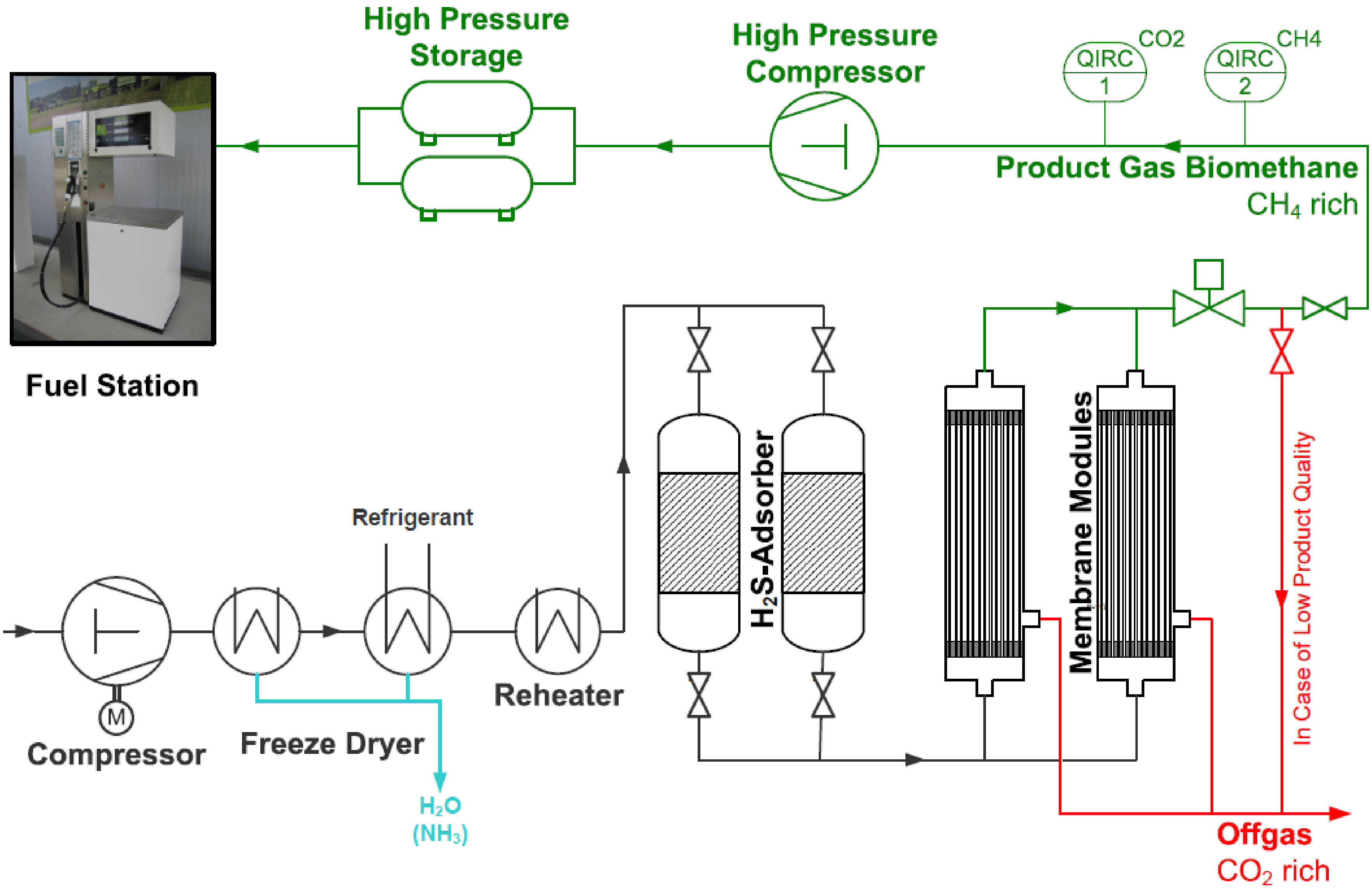
- Capacity 500 m³/h biogas, 300 m³/h biomethane, approx. 8 km pipeline for grid injection and high pressure compression to 60 bar

Membrane Biogas Upgrading Plant in Kisslegg (GE)



Membrane modules

Biomethane Fuel Station: Single Stage Upgrading

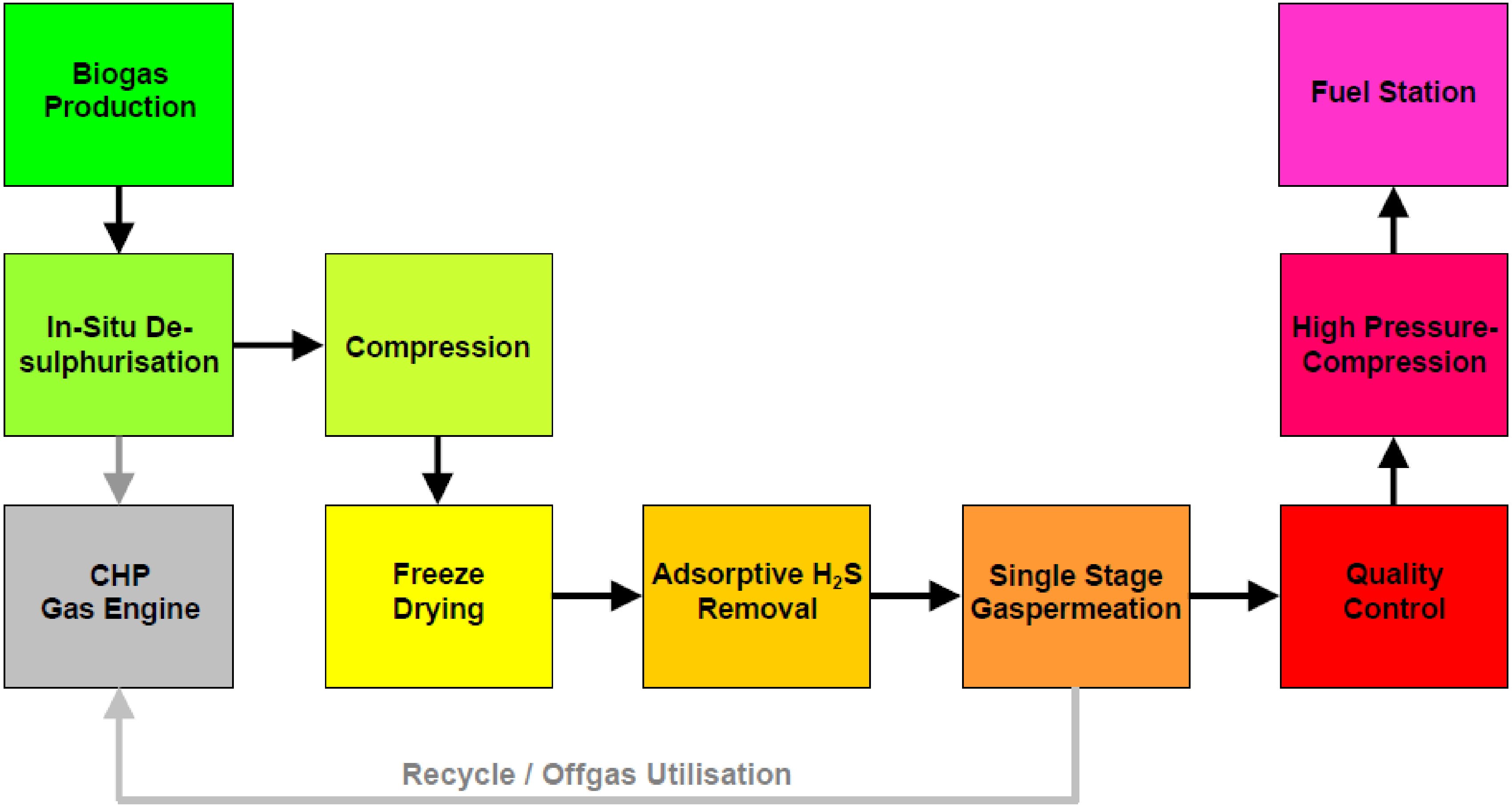


Biomethane Fuel Station using Membrane Technology

35 m^3/h biomethane

- Permeate recycle to CHP plant
- Further information:
  www.methapur.com, **bio.methan.at**
  Biomethane fuel station Margarethen/Moos

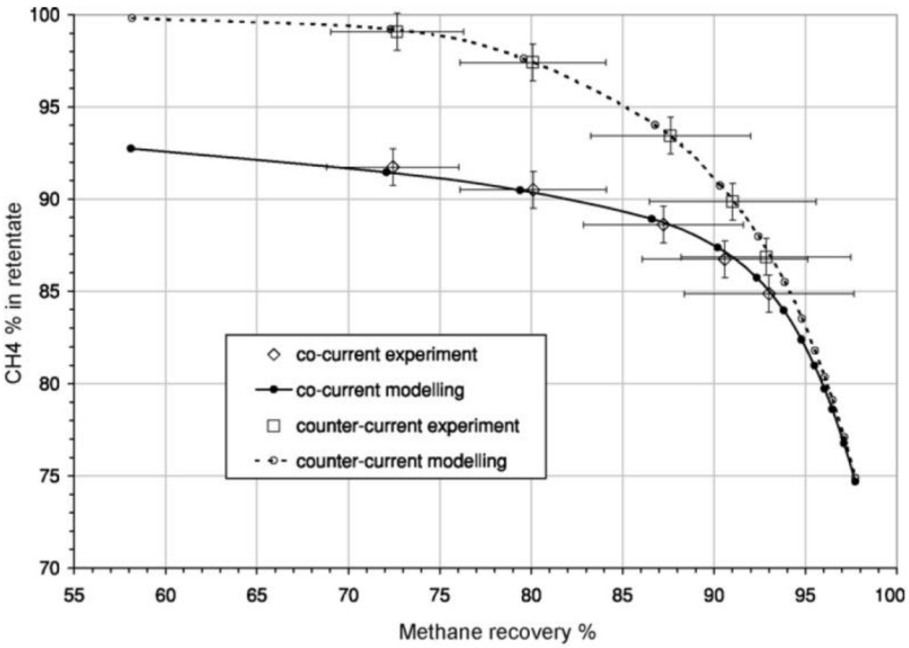
Process Integration (Margarethen am Moos)

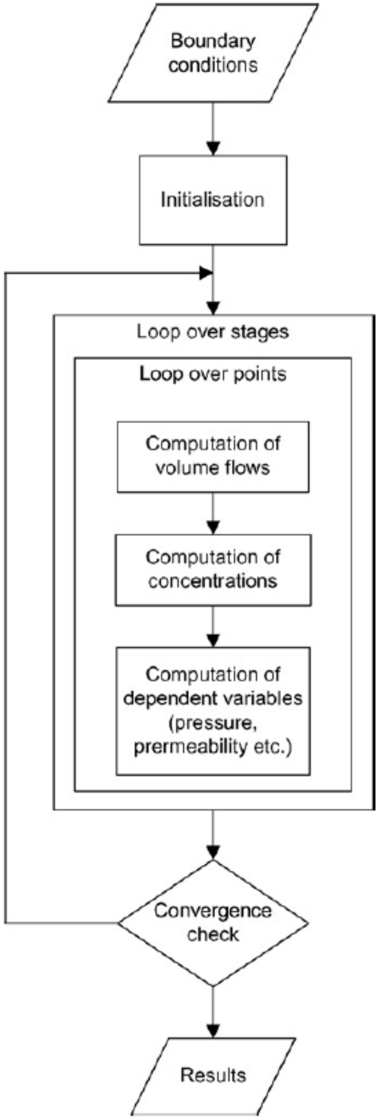


- In-situ desulphurisation (addition of iron salts into the fermentation broth to catch suphides)
- Permeate is recycled to CHP plant – „zero methane“ emission of upgrading system

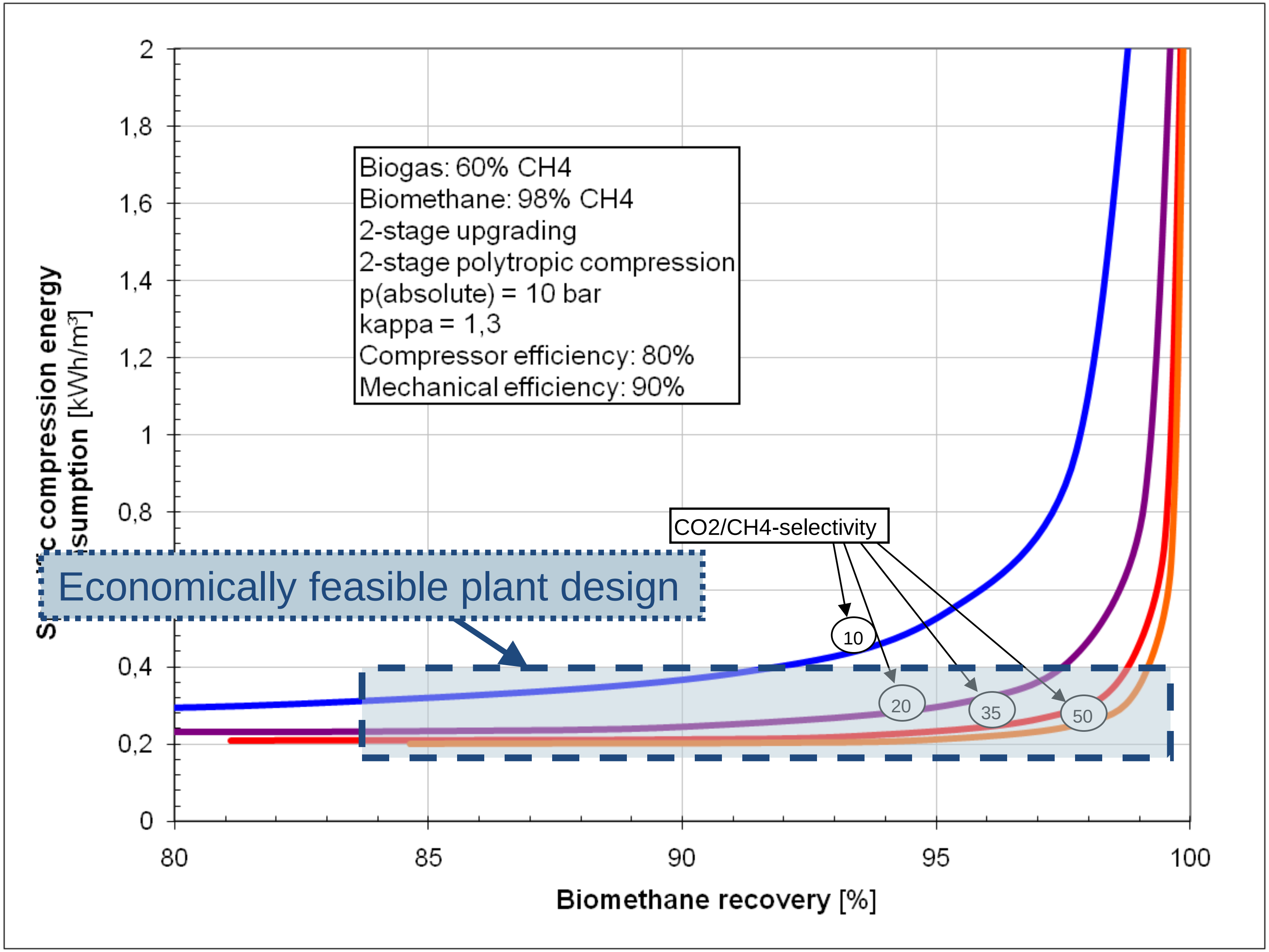
Process modelling of biogas upgrading

- Discrete solver for the modelling of multicomponent gas permeation systems
- Conservation equations in membrane permeation are discretised using finite difference method in one-dimension and solved using Gauß-Seidel approach (Makaruk & Harasek, J.Membrane Science 344 258-265)
- Modelling results were validated and provided good agreement with experimental results:

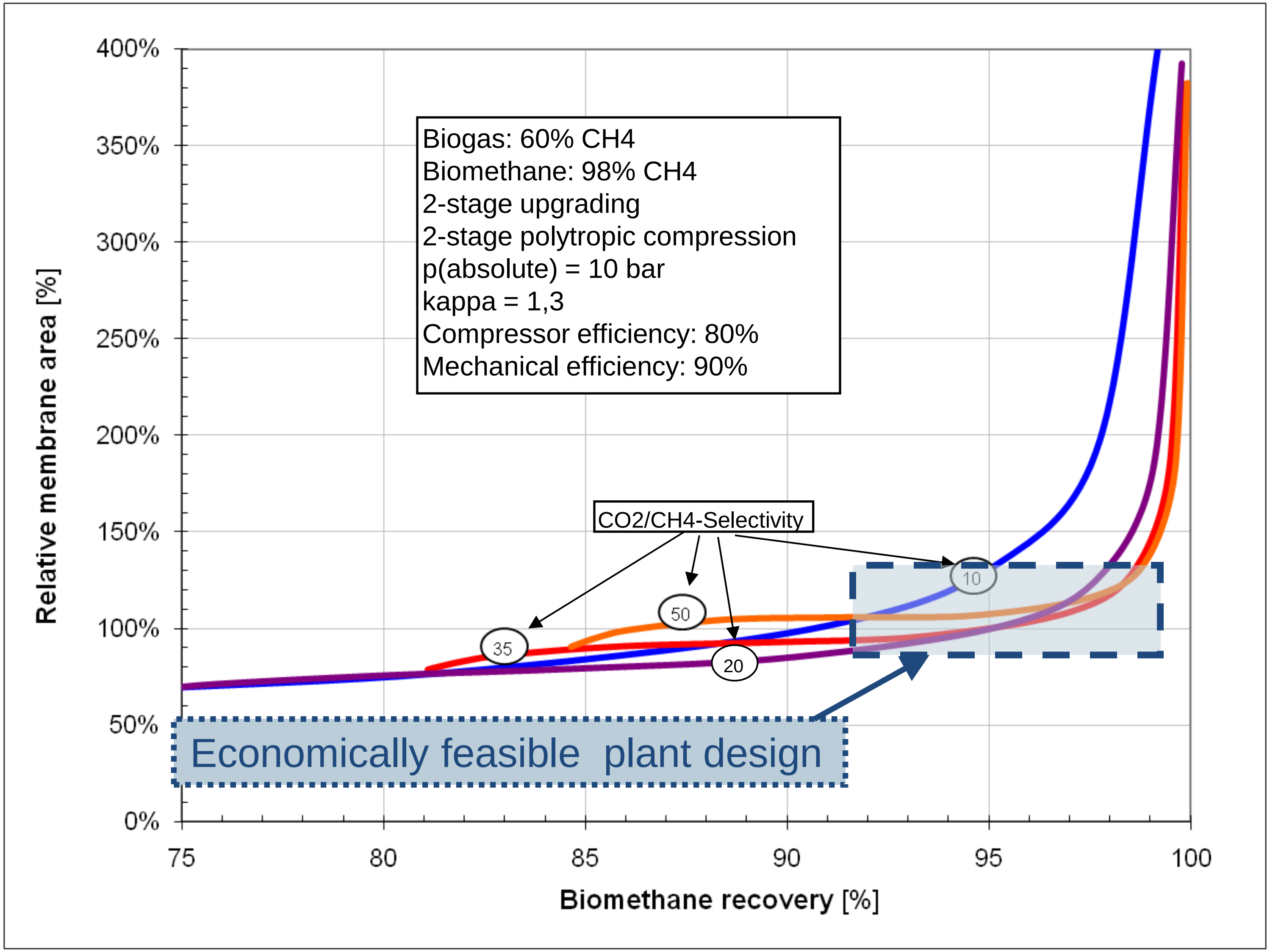




Compression Energy Consumption per m³ Product

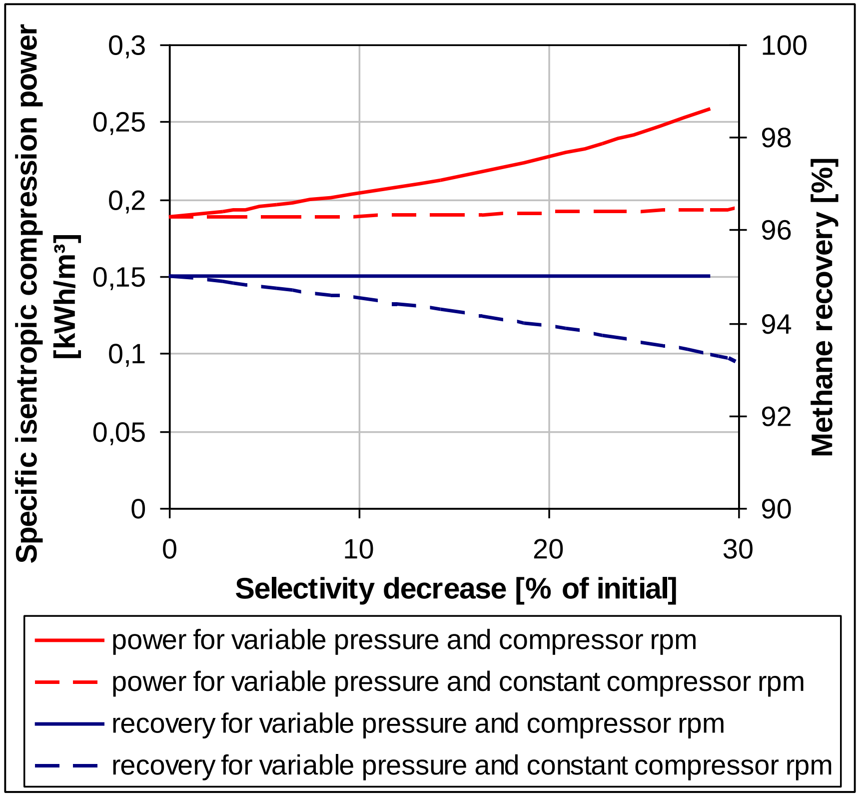


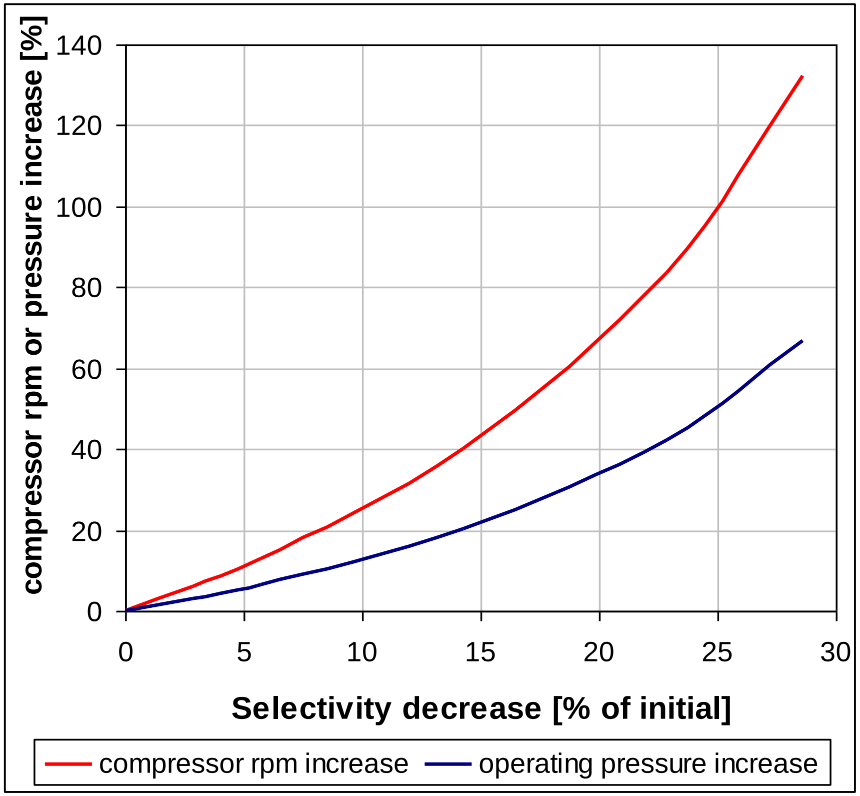
Membrane Area as Function of Recovery



Biogas: 60% CH4
Biomethane: 98% CH4
2-stage upgrading
2-stage polytropic compression
p(absolute) = 10 bar
kappa = 1,3
Compressor efficiency: 80%
Mechanical efficiency: 90%

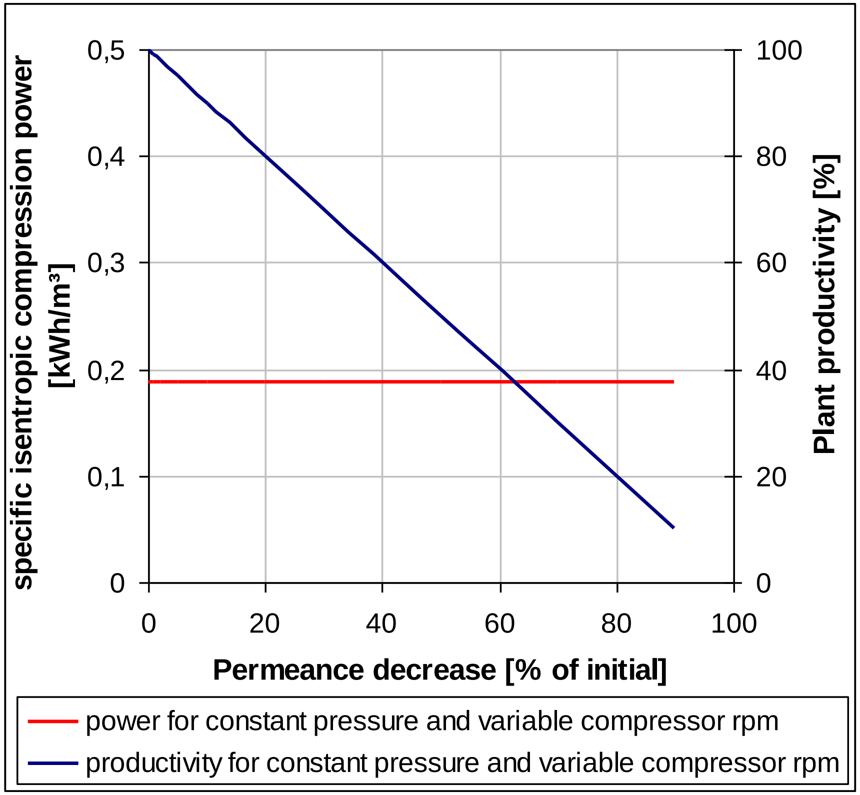
Simulation – Change of Membrane Selectivity

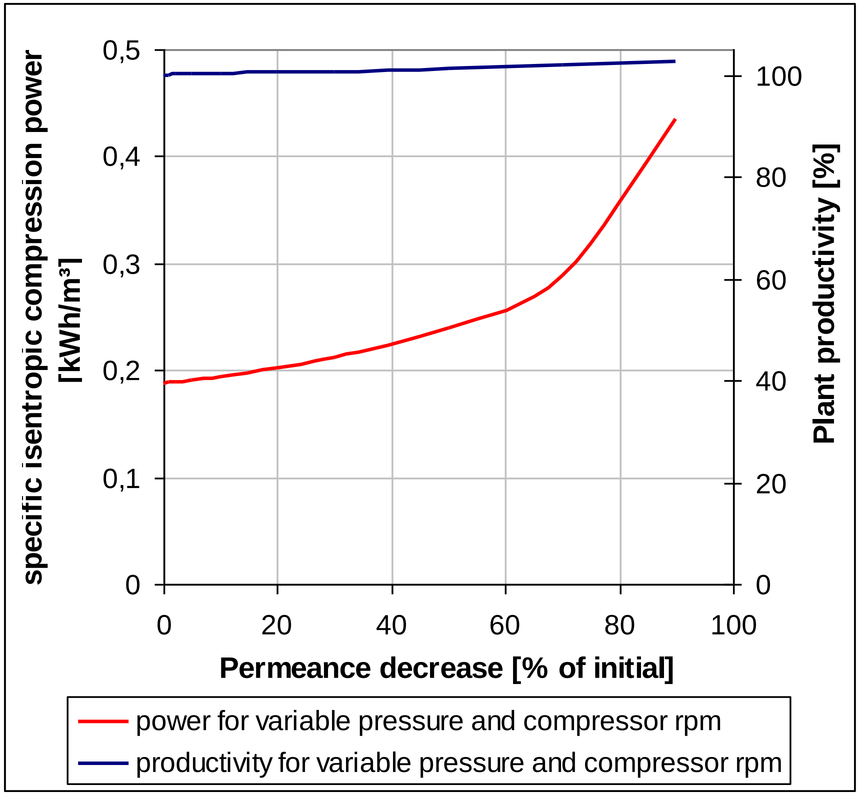




- Selectivity decline results in a reduction of methane recovery, the operating pressure must be adjusted to maintain the gas purity
- If methane content and methane recovery are to be invariable to the selectivity reduction, both pressure and compressor RPM need to be adjusted (higher specific energy consumption)

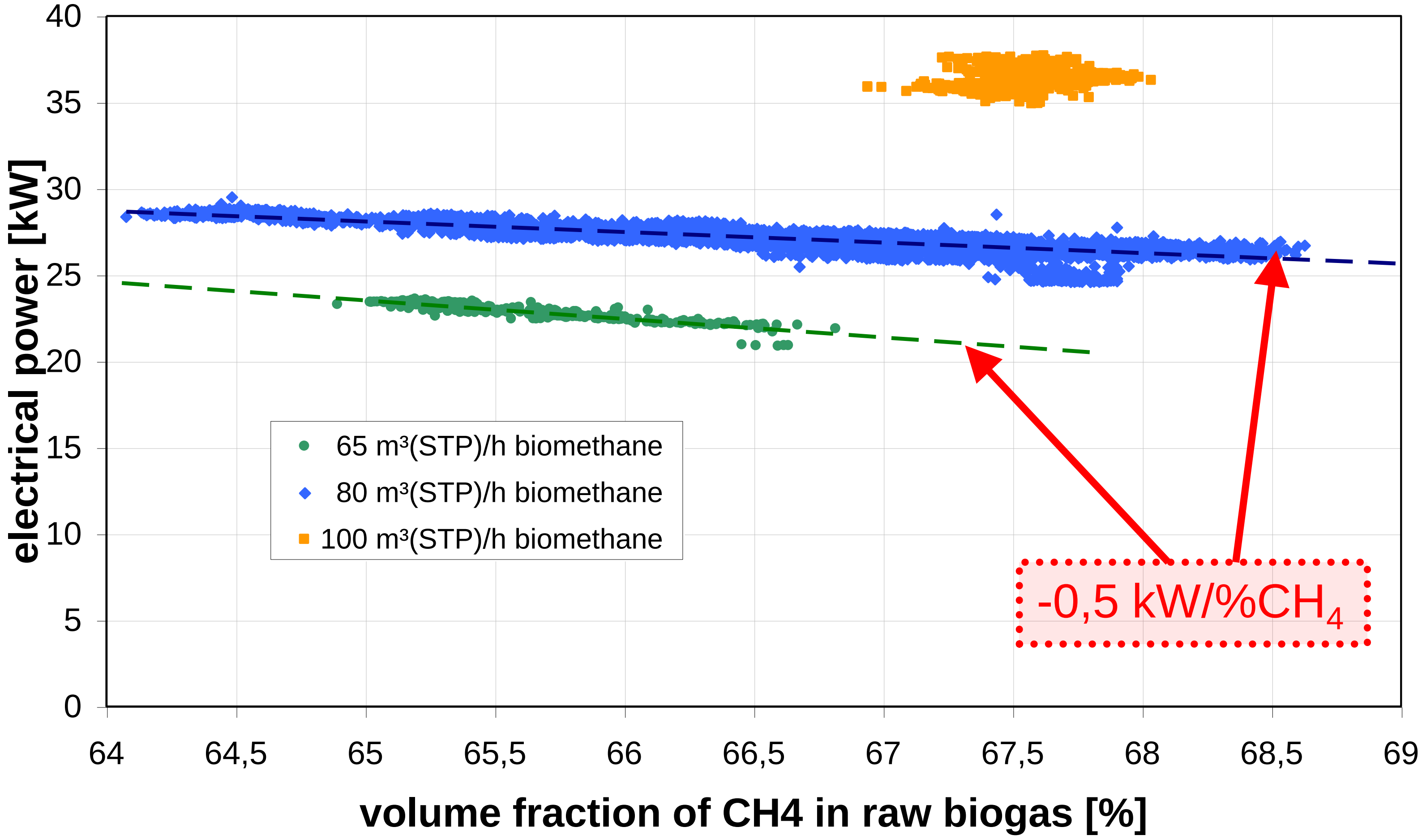
Simulation – Change of Membrane Performance





- Permeance decline leads to a decrease of plant productivity as the compressor volume flow has to be reduced to maintain the product gas methane content .
- If a constant productivity is to be maintained, the plant operating pressure needs to be increased while the compressor RPM may remain constant

Compressor Power Consumption (Bruck/Leitha)



Energy Consumption Analysis

- **Main energy consumer of upgrading is the raw biogas compressor.**
- Energy demand for constant product gas quality and quantity depends also on raw biogas methane content.
- **Effect of plant layout** (number of stages) on energy consumption:
  - **Two stage gas grid injection plant:** 0,378 kWh/m^{3}STP of product gas
  - **Single stage Bio-CNG-plant:** 0,280 kWh/m^{3}STP of product gas
- Related to the methane content of the produced biomethane gas stream:
  - **Two stage gas grid injection plant:** 3,2% (98,1vol% CH4)
  - **Single stage Bio-CNG-plant:** 2,8% (96,1vol% CH4)
- All values are valid for a product gas delivery pressure of max. 6 bar(g).

Offgas Treatment & Costs

- **Offgas treatment** depends on process integration:
  - Mixing with biogas and utilisation in CHP plants
  - Thermal oxidation (flameless oxidation systems or direct combustion of low-cal gas)
  - Catalytic oxidation
  - Further treatment using additional membrane separation stage
- **Membrane lifetime:**
  - In case of suitable biogas pre-treatment: > 2 years
- **Methane recovery:**
  - Process dependent, 92% to 98% - rest to offgas treatment
- **Specific costs of upgrading** (depends on plant capacity):
  - **Investment** (depreciation 10 years, 8%):
    0,05 – 0,08 €/m³ biomethane
  - **Operation** (> 8000 h/a):
    0,10 – 0,14 €/m³ biomethane

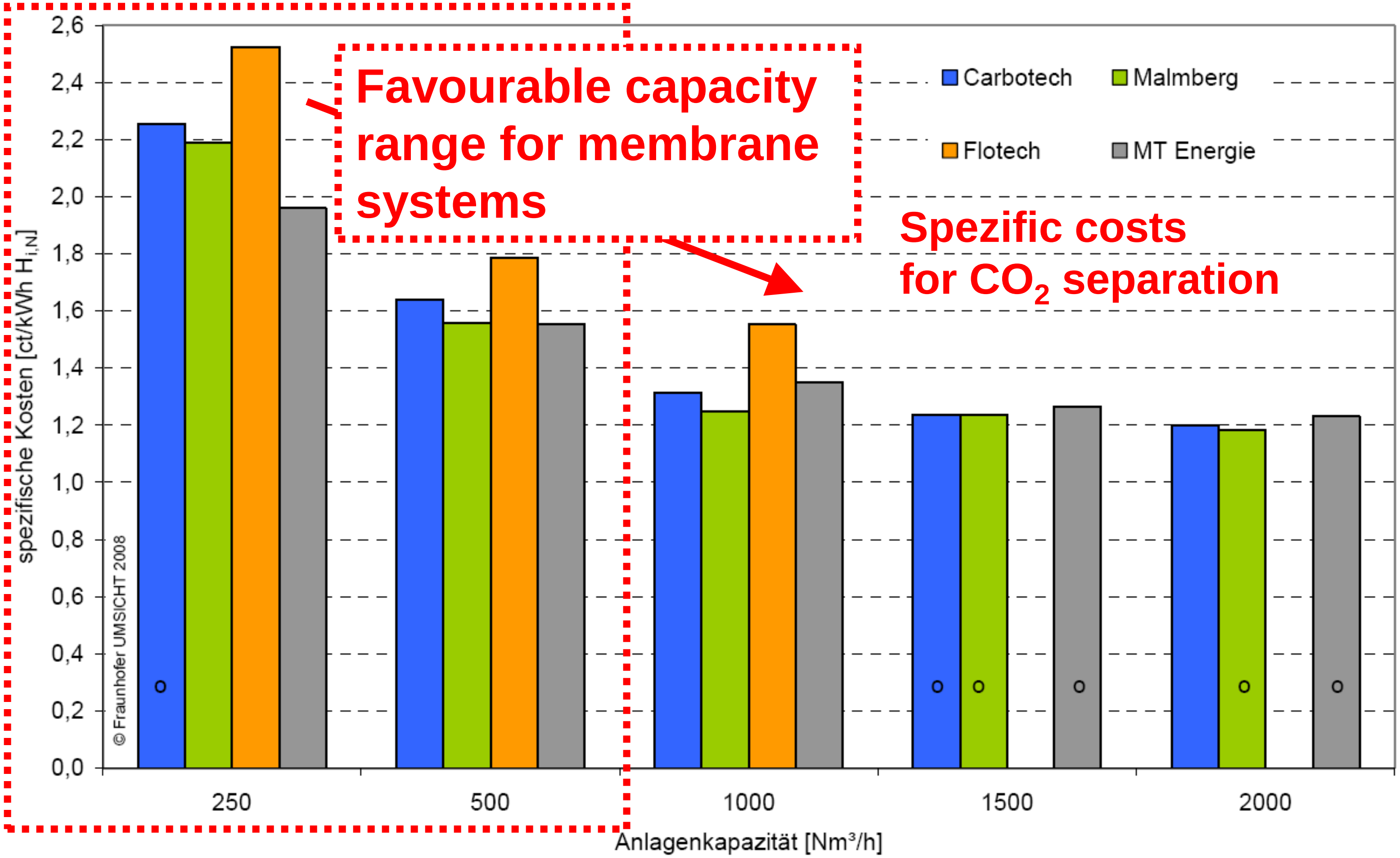
Final Conditioning / Offgas Treatment

- **Final conditioning needs depend on upgrading technology and requirements of gas grid or fuel use:**
  - All absorption based upgrading technologies (water scrubbing, selexol absorption, amine absorption) need gas drying by glycol scrubbing or molecular sieve adsorption
  - PSA may need mixing buffer tank to level out product concentration fluctuations
- Heating value correction: propane dosing to adjust heating value – consider need for gas quality and product gas flow measurement for dosing control
- Delivery pressure adjustment: pressure reduction or increase depends on feed-in conditions
- Odor dosing: e.g. THT (tetrahydrothiophene) or similar dosing equipment and control
- Gas quality measurement: local regulations and agreements may require continuous quality measurement (e.g. process gas chromatography – consider calibration needs!)

Gas quality Measurement / Offgas Treatment

Costs for CO_2 Separation

Calculations by Fraunhofer Institut UMSICHT (2008)

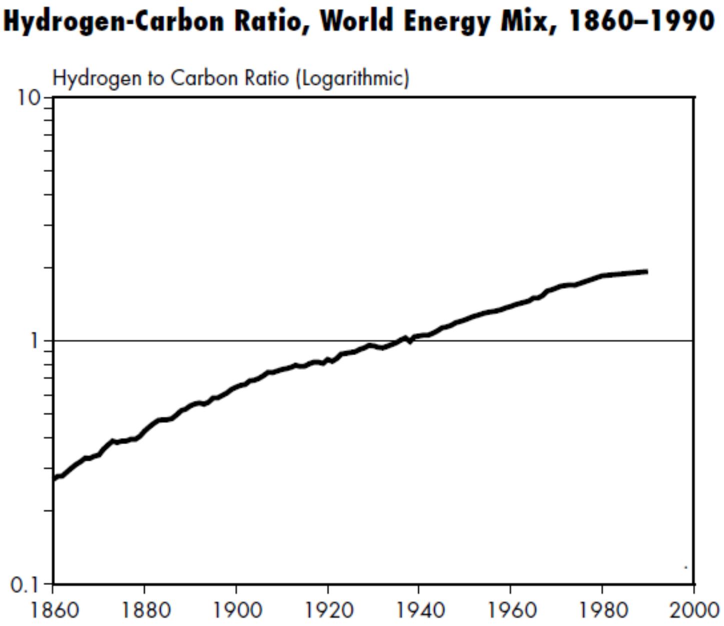


Favourable capacity range for membrane systems

Spezific costs for CO_2 separation

Lessons learned

- Various upgrading technologies available – choose according to your process needs!
- Define your upgrading tasks early & know your biogas composition early!
- Biogas upgrading is expensive and should therefore operate at design capacity for best economic results
- Fully automated systems available, but customised pretreatment design decides between success and failure!



Further informations – see our websites…

- Biogas upgrading: **www.virtuellesbiogas.at**
- CNG fuel station: **bio.methan.at**

Go biomethanic !