VALORGAS

Lecture 15: Biogas upgrading

RE1 Biogas Technology for sustainable Second Generation Biofuel Production

Prasad Kaparaju

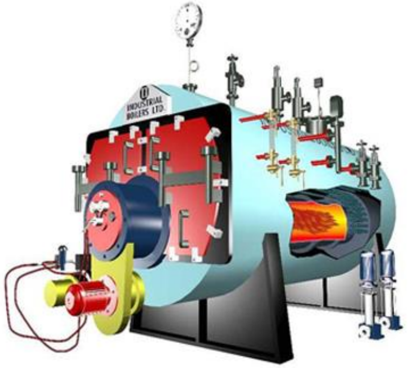
SEVENTH FRAMEWORK PROGRAMME

Content

- Biogas utilization
- Biogas composition
- Biogas upgrading technologies

BIOGAS UTILIZATION

- Traditional
  - Cooking, Lighting
- Commercial
  - Heat and steam
  - Electricity and/or heat (cogeneration in CHP)
  - Vehicle fuel
  - Fuel cells
  - Injection to natural gas grid



Why to clean and upgrade biogas?

- Meet the requirement of gas applications
  - Removing trace compounds prevent mechanical wear & corrosion
- Improve the calorific value
  - High methane content means high energy value fuel
- Standardization of the gas
  - Uniform gas/fuel quality for grid injection
  - National standards for upgraded biogas fuel
  - Standards by vehicle manufactures
- Reduce harmful effects on environment
  - Trace compounds removal
- Biogas upgrading take 3-6% of biogas energy & costs € 10/GJ

Definition

- Biogas cleaning:
  - Removal of water, H_2S and other undesired trace contaminants from the biogas like dust, Halogenated compounds, siloxanes, ammonia, etc.
- Biogas upgrading:
  - Removal of CO_2 to achieve gas quality for injection in gas grid or vehicle fuel use
- Biomethane:
  - Upgraded biogas used for grid injection or vehicle fuel

Biogas sources

- Biogas is produced through biodegradation of various organic materials (sugars, proteins and fats) under anaerobic conditions
- There are different sources of biogas - feedstock/AD system

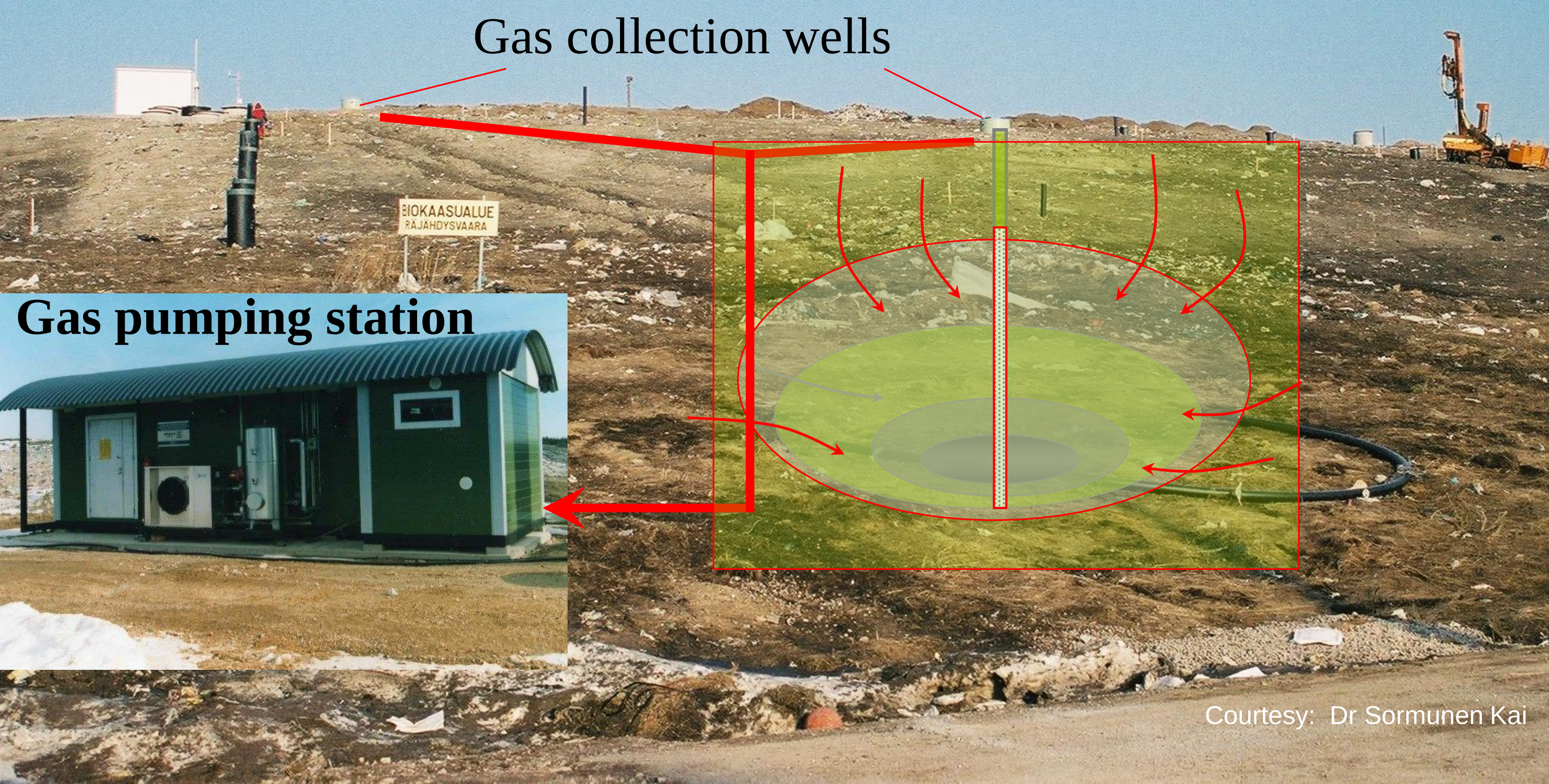
Feedstock	AD system	Produced gas
Sewage sludge	Wastewater treatment plant	Sewage gas
Agricultural wastes, manures, energy crops, crop residues etc.	Farm-scale biogas plants	Biogas
Co-digestion of industrial wastes with manures	Centralized-biogas plants	Biogas
Municipal waste	Landfills	Landfill gas

Biogas composition

Parameter	Farm-scale AD-plant	Centralised AD-plant	Landfill	Sewage Treatment plant	Natural gas (Holland)
CH_4 (vol-%)	55-60	60-70	30-65	60-65	81-89
Other hydro carbons (vol-%)	0	0	0	0	3.5-9.4
H_2 (vol-%)	0	0	0-3	0	-
CO_2 (vol-%)	35-40	30-40	25-45	35-40	0.67-1
N_2 (vol-%)	<1-2	2-6	<1-17	<1-2	0.28-14
O_2 (vol-%)	<1	0.5-1.6	<1-3	<0.05-0.7	0
H_2S (ppm)	25-30	0-2000	30-500	<0.5-6800	0-2.9
NH_3 (ppm)	≈100	≈100	≈5	<1-7	0
Halogenated compounds (as Cl^-, mg/m^3)	<0.01	<0.25	0.3-225	0-2	-
Siloxanes (mg/m^3)	<0.03-<0.2	<0.08-<0.5	<0.3-36	<1-400	-
Wobbe index (MJ/m^3)	24 – 33	24 – 33	20 - 25	25 - 30	44-55
Lower heating value (MJ/Nm^3)	23	23	16	22	31-40

The composition of biogas depends on several variables such as the type of waste or the treatment process used to digest it.

Biogas collection from landfills

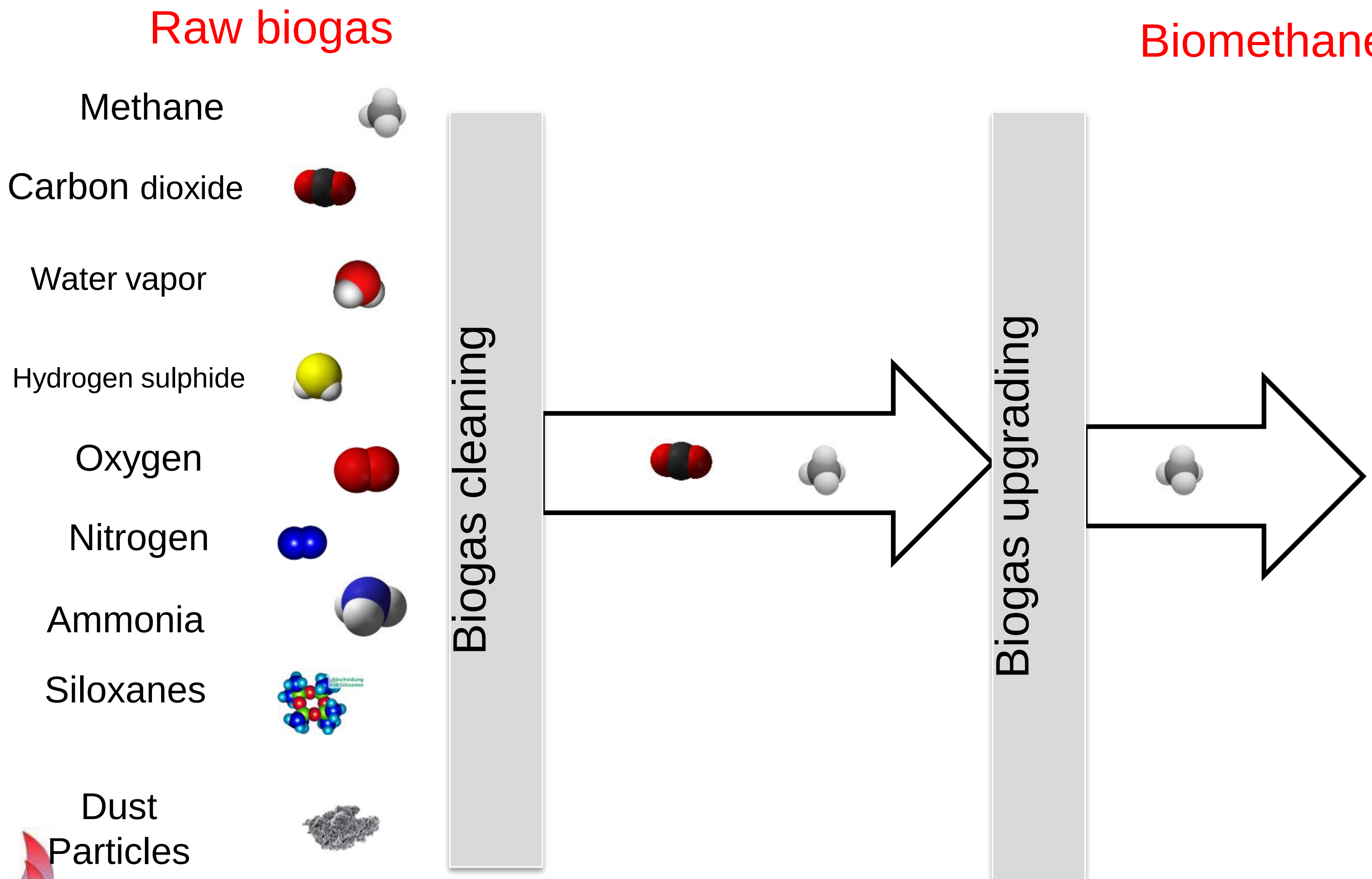


Biogas treatment requirements

Application	H_2S	CO_2	H_2O	Siloxane
Cooking	Yes	No	No	No
Gas heater (boiler)	< 1000 ppm	No	No	No
Stationary gas engine (CHP)	< 500 ppm	No	No condensation	Yes
Vehicle fuel	Yes	Recommended	Yes	Yes
Natural gas grid injection	Yes	Yes	Yes	Yes
Hot fuel cells	Yes	No	No condensation	Yes
High pressure compression	Yes	Recommended	Yes	No

Removal of water, H_2S and other possible contaminants required for all commonly used gas applications

Concept for biogas upgrading



Biogas cleaning

- Dust and particles
- **Water**
- **Sulphur compounds**
- Halogenated compounds
- Ammonia
- Oxygen and nitrogen
- **Siloxanes**

Water

- Condensate in the gas line
- Contributes to corrosion
- Lowers the efficiency of purification techniques
  - active carbon adsorption
  - silica gel treatment
- Problem in cryogenic treatment due to ice formation

Technique	Media	Principle
Cooling (approx. 2–5 °C)		Water condensation. The gas is chilled below water dew point
Adsorption	Silica gel Active carbon Molecule sieve	The water binds to the solid adsorbent (the dew point of –20 °C is reached). Reversible process
Absorption	Glycol, Tri-ethylene-glycol or hygroscopic salts	The water is absorbed into a tri-ethylene-glycol solution

Water removal

- Adsorption
  - Water vapour is adsorbed and reversely bounded on the surface of adsorbents like molecular sieves, silica gel or activated carbon
  - Adsorption and regeneration mode (desorbed)
  - Regeneration of adsorbent
    - Heating to 200°C
    - At atmp pressure – using air or vacuum pump
    - At high pressure – using minor amount of dried, depressurised gas

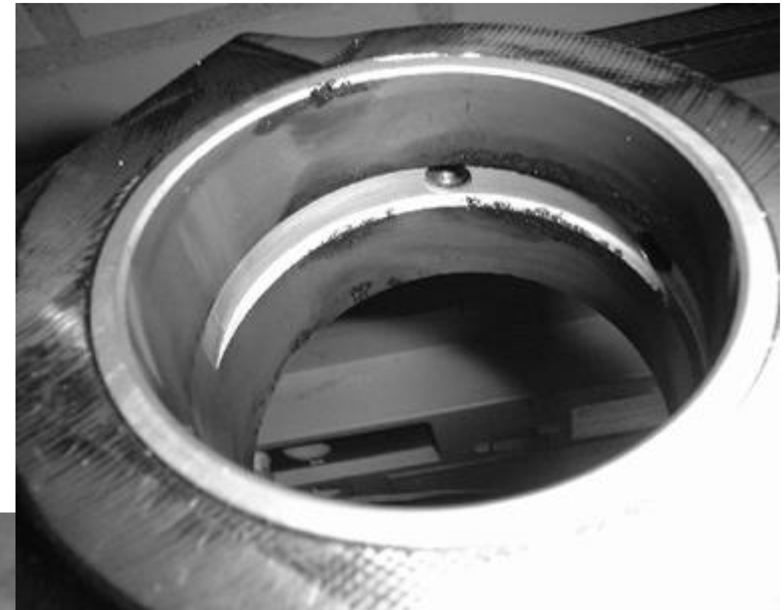
Sulphur compounds

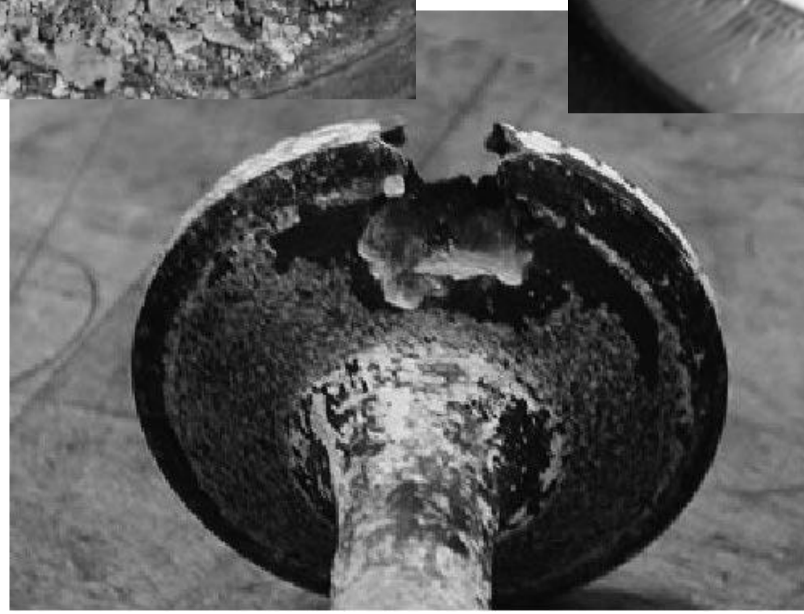
- Sulphides, disulphides & thiols
- Raw biogas contain H_2S 1000 -5000 ppm
- On combustion, SO2 and SO3 are produced which reacts with water to form H_2SO_4
  - Causes severe corrosion of compressors, gas storage tanks and engines
- H_2S limits for CHP is of 250 ppm

$$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$$

$$2\ S + 2\ H_2O + 3\ O_2 \rightarrow 2\ H_2SO4$$

Sulphur deposits in gas engine





(Source: Duller 2005)

Damage caused by H_2S

Source: Applied Filter Technology

Removal of Sulphur

Technique	Principle
Oxygen/air dosing	Biological oxidation Microbes oxidize sulphur into elemental sulphur, sulphate and sulphite
Chemical flocculation	Flocculation by ferrous chloride, iron salts or with lime
Adsorption	Activated Carbon
Chemical Adsorption	Sulphur reacts with KI, Fe(OH)3, (marsh ore or limonite), ferrous oxide or with ZnO
Catalytic scrubber	Chelate solution

Air/oxygen dosing

$2H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$ (*Thiobacillus spp.*)

Iron sponge (hydrated ferric oxide)

$Fe2O3 \cdot H2O + 3H2S \rightarrow Fe2S3 + 4H2O$

Ferric Chloride Injection

$3H2S + 2FeCl3 \rightarrow S + 2FeS + 6HCl$

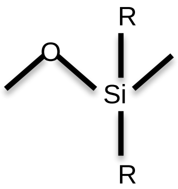
Biological oxidation

- Removal efficiency is high (80-99%)
  - Conc. can reach down to 20-100 ppm

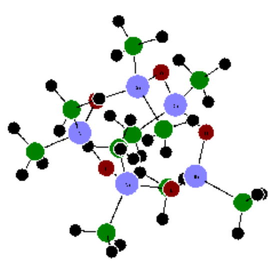
$$H_2S + ½ O_2 = H_2O + S°$$

Biofilters

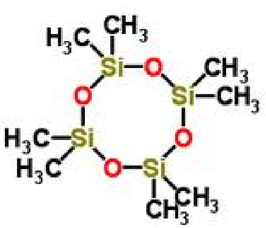
Siloxanes



- Volatile silicones compounds bonded by organic radicals
- R – Si – O – Si – R
- Common in landfill and sewage gas only (D4 and D5)
- Absent in natural gas or biogas from agricultural biogas plants.
- Main source is consumer products
- Oxidised to SiO_2 during combustion
- Deposits on valves, cylinder walls and liners → cause extensive damage by erosion or blockage

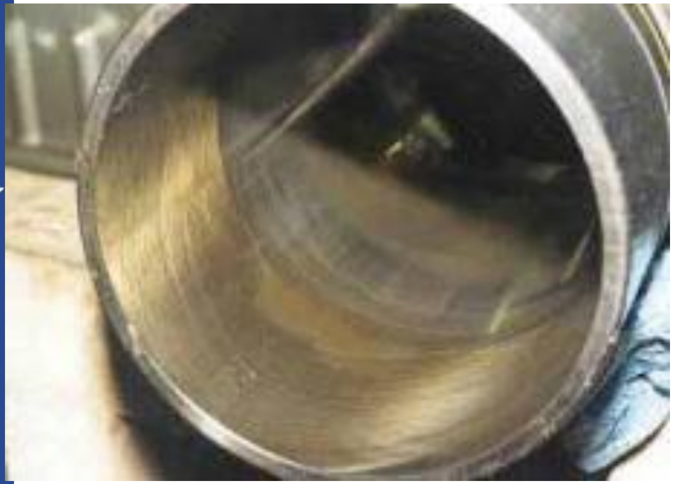


Decamethylcyclopentasiloxane (D5)

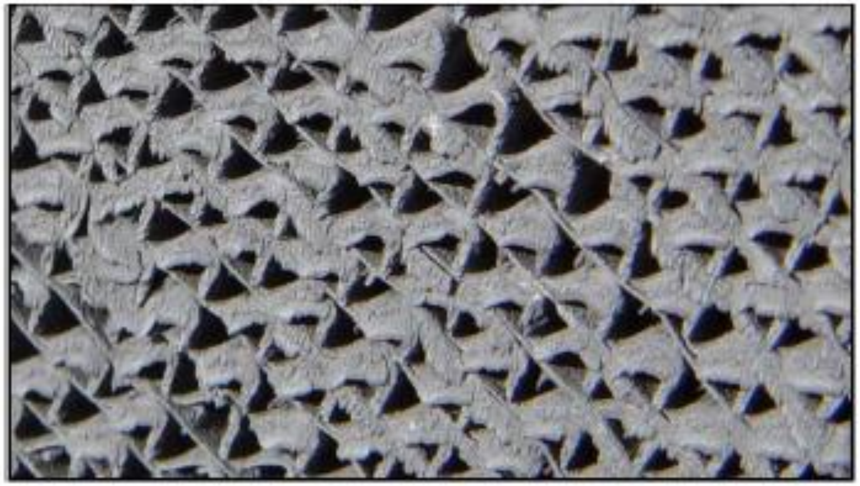


Octamethylcyclotetrasiloxane (D4)

Siloxane and silicate depositions

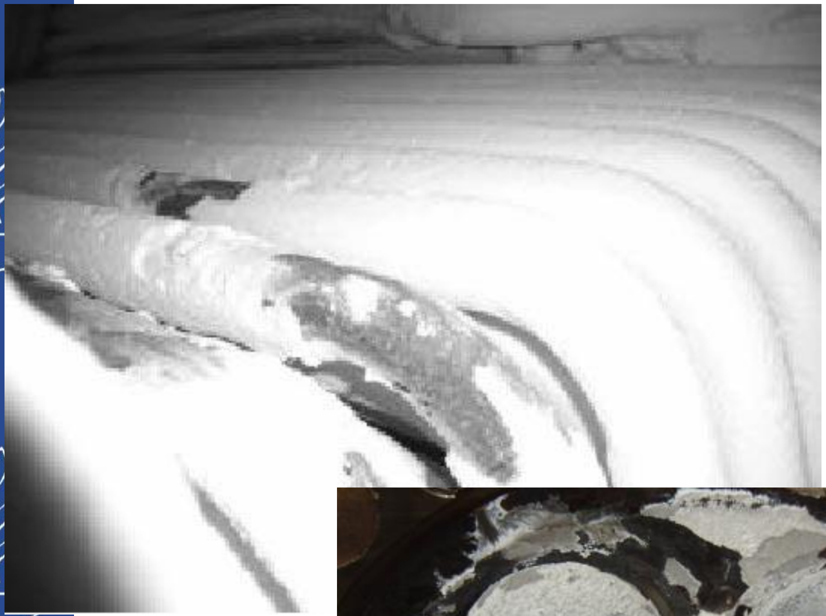


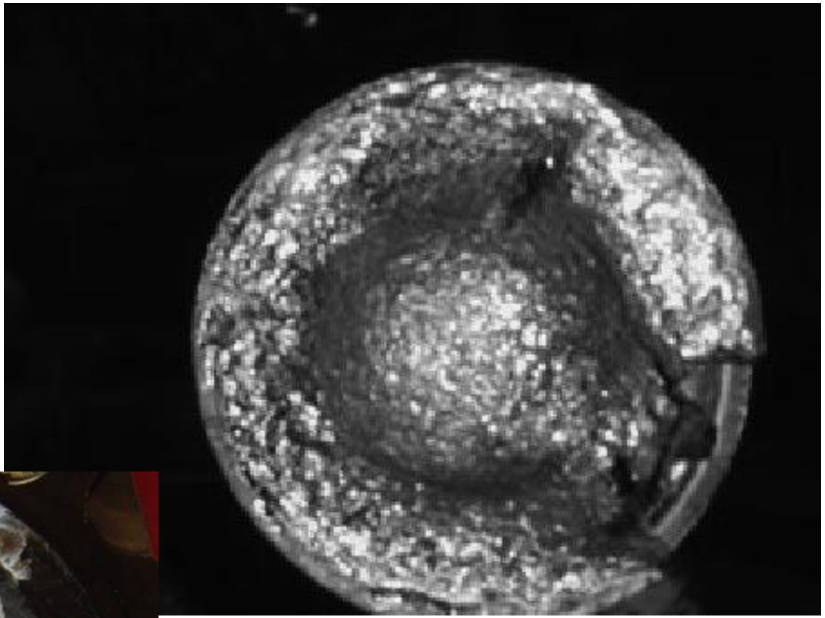
Gold-coloured siloxane layer on the inner surfaces of a cylinder Source: Environmental Agency (2002)



Silicate layers on a catalytic after-burner Source: Pierce (2005)

SiO_2 depositions on boiler tubes and damage to an engine piston



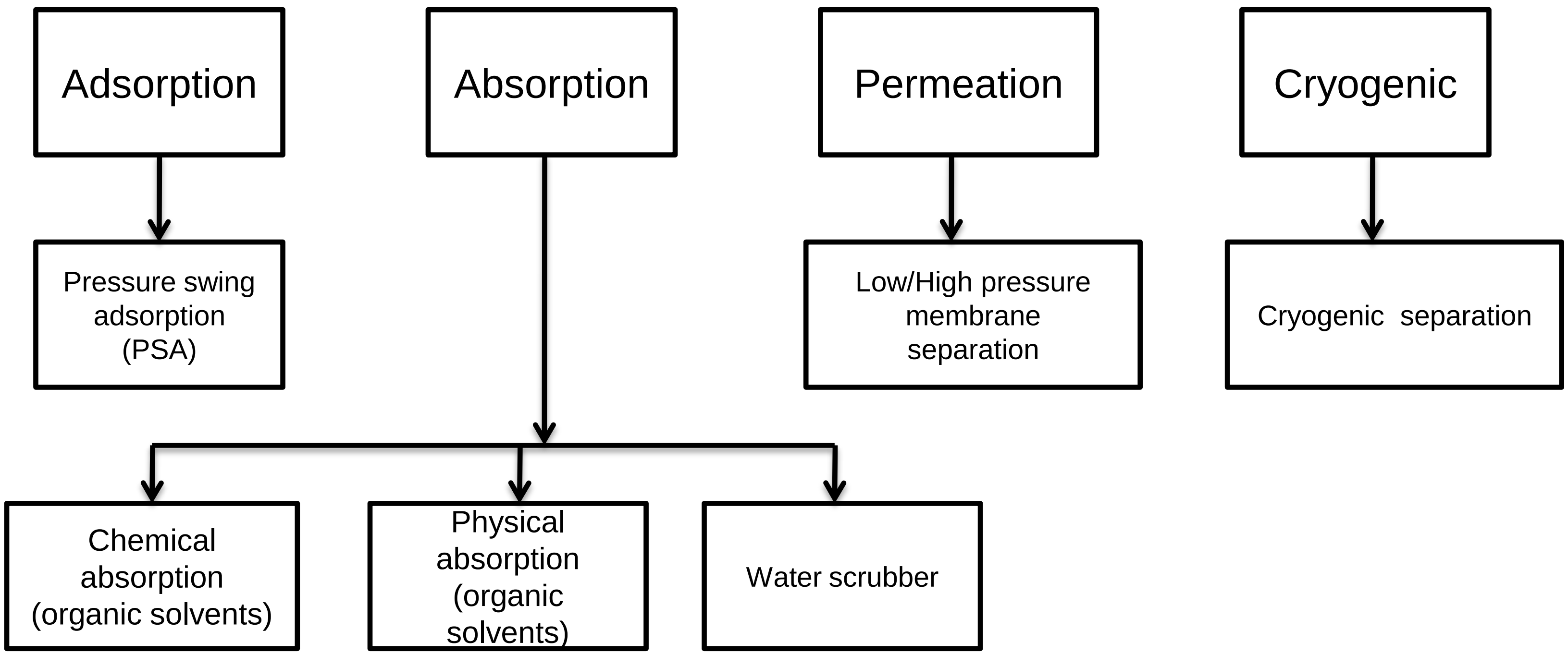


Source: Applied Filter Technology

SILOXANE REMOVAL

- Adsorption with activated carbon
  - Regeneration of activated carbon is not possible
  - Biogas has to be heated before the treatment to prevent water saturation of activated carbon
  - At 24 bars and 4.4 °C – 10 to 15 g siloxanes/kg activated carbon
- Adsorption with silica gel or activated aluminium
- Absorption in a liquid medium (organic solvents)
  - Counter flow columns with or without regeneration of the scrubbing liquid
- Cooling (-23 °C)
  - Most of the silicon components are removed at low temp.

Overview biogas upgrading technologies (for CO_2 - removal)

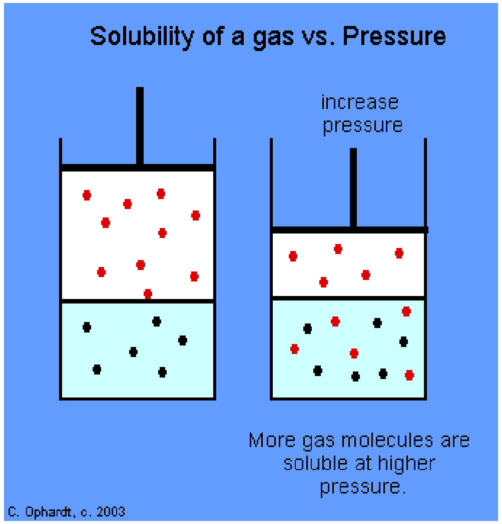


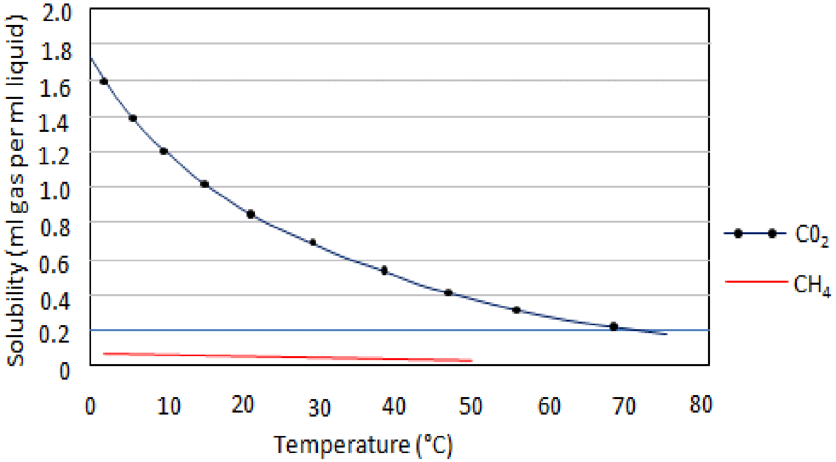
1. Absorption

- Principle: Pollutants from gas stream are dissolved into a solvent liquid stream by mass transfer
  - a. Physical absorption: Pollutant from the gas stream is physically absorbed in a non-reactive solvent fluid
  - b. Chemical absorption: Pollutant from the gas stream reacts chemically with the component of liquid solvent
- Absorption process is also called ”washing” or ”scrubbing” process as soluble gas components are ”washed out ” by the absorption liquid

a. Physical absorption

- CO_2 is removed based on the difference in solubilities of the gaseous components of biogas in an absorption liquid.
- Solubility of CO_2 is 55 times higher than CH_4
- $H_2S >> CO_2 > CH_4$
- Solubility increases with increase in pressure and decrease in temperature





Solubility of CO_2 and CH_4 at 1 atmosphere (101.325 kPa) and temperature

Solubility of CO_2 in water

- The solubility of CO_2 in water decreases with increase in temp and increases with increase in pressure

	Temp (°C)			
Pressure (bar)	0	10	20	30
1	0.4	0.25	0.15	0.10
20	3.15	2.15	1.30	0.90
50	7.70	6.95	6.0	4.80

1. Water scrubbing

- Most common biogas upgrading technology
- Principle: CO_2 & H_2S are more soluble in water than CH_4
- Other trace compounds viz., NH_3, SO_2, halogenated compounds etc can also be removed.
- Water scrubbing
  - with regeneration of wash water
  - Without regeneration of wash water (single pass)

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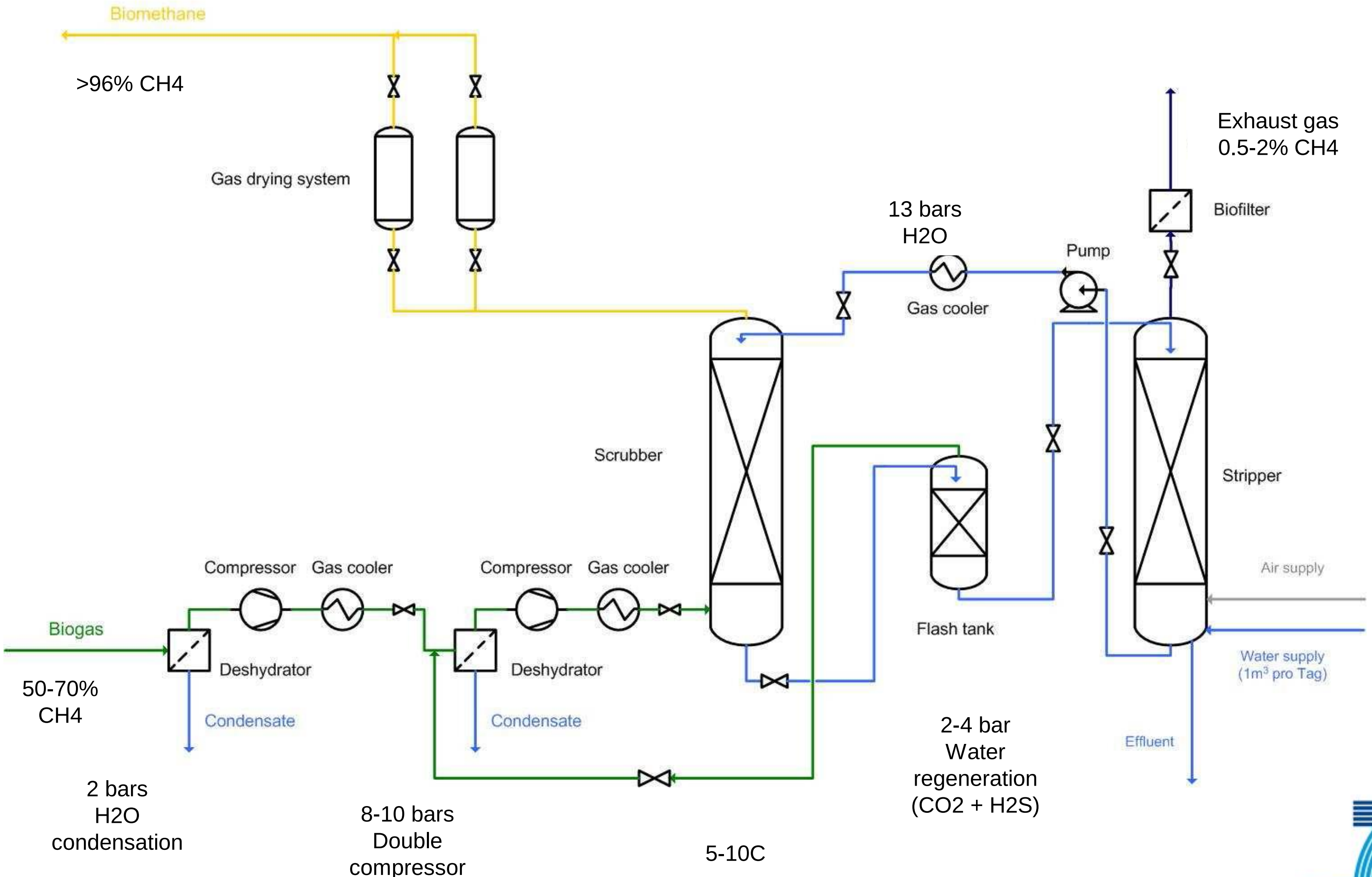
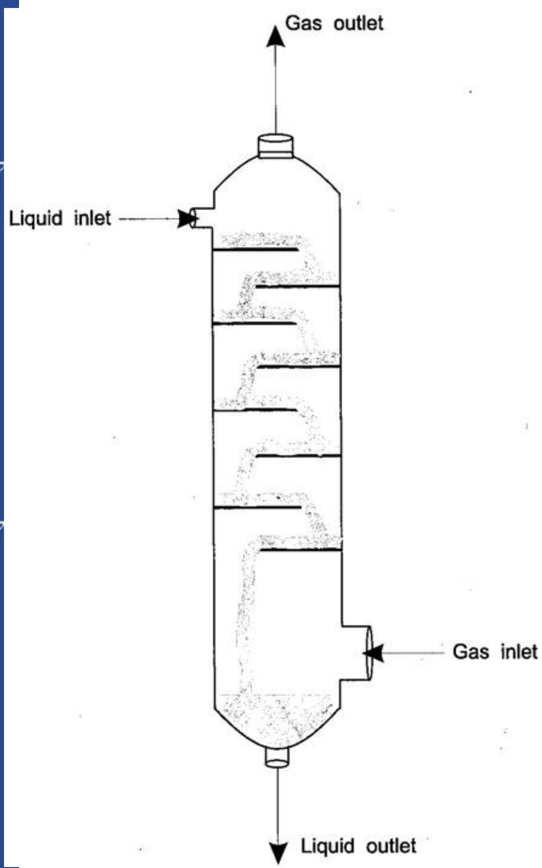
1. Water scrubbing technology (regeneration of wash water)

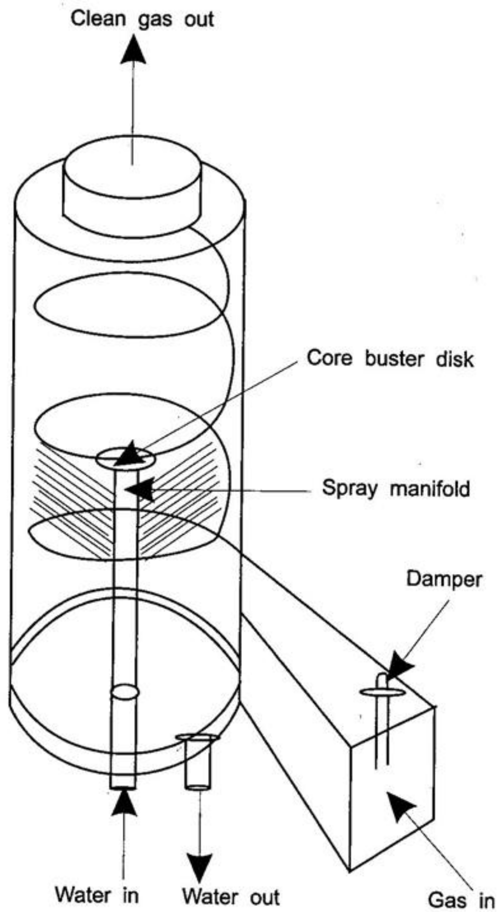


(Courtesy: ISET, 2008)

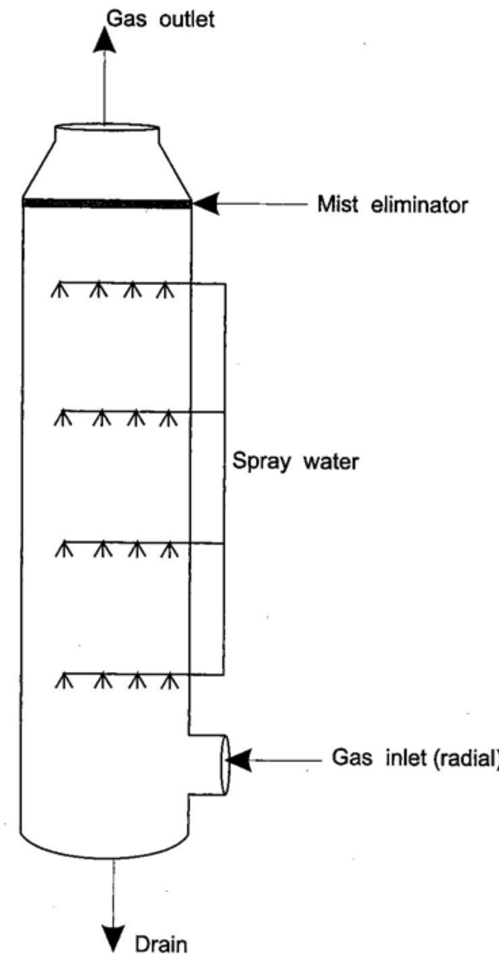
Different absorption designs



Counter-current



Co-current flow

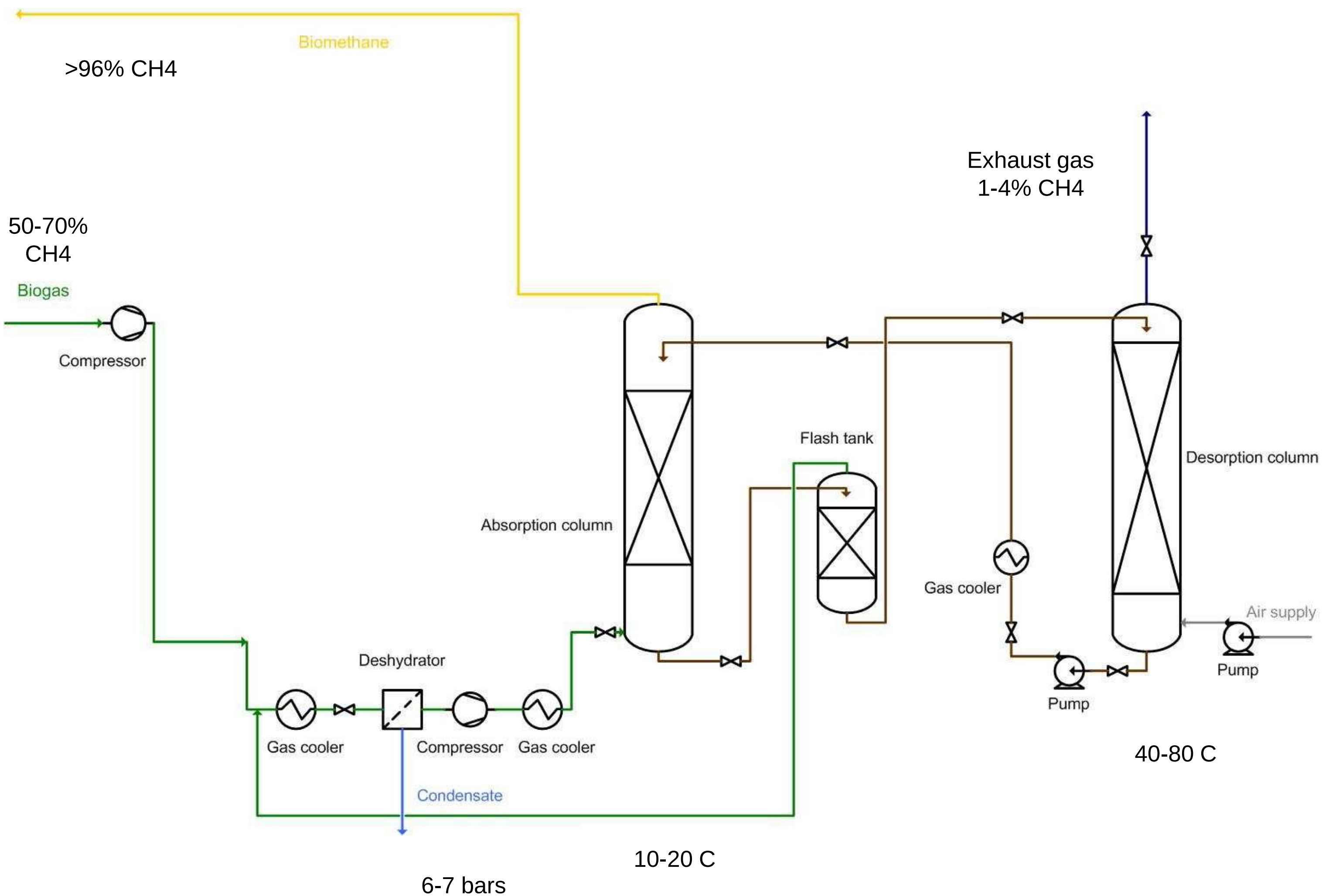


Tower

Other absorption liquids

- **Polyethylene glycol (PEG)**
- Upgrading principle is similar to water scrubbing process with regeneration of the wash water
- Main difference is that CO_2 and H_2S are more soluble in PEG than in water
  - Lower solvent demand
  - Reduced pumping (circulation of PEG)
- Water and hydrocarbons are also absorbed in PEG
  - Biomethane is low water content and does not need drying
- Selexol™ is trade name for dimethylester of PEG
- H_2S removal beforehand is recommended
- 93-98% CH4 in product gas

Physical absorption using organic solvent



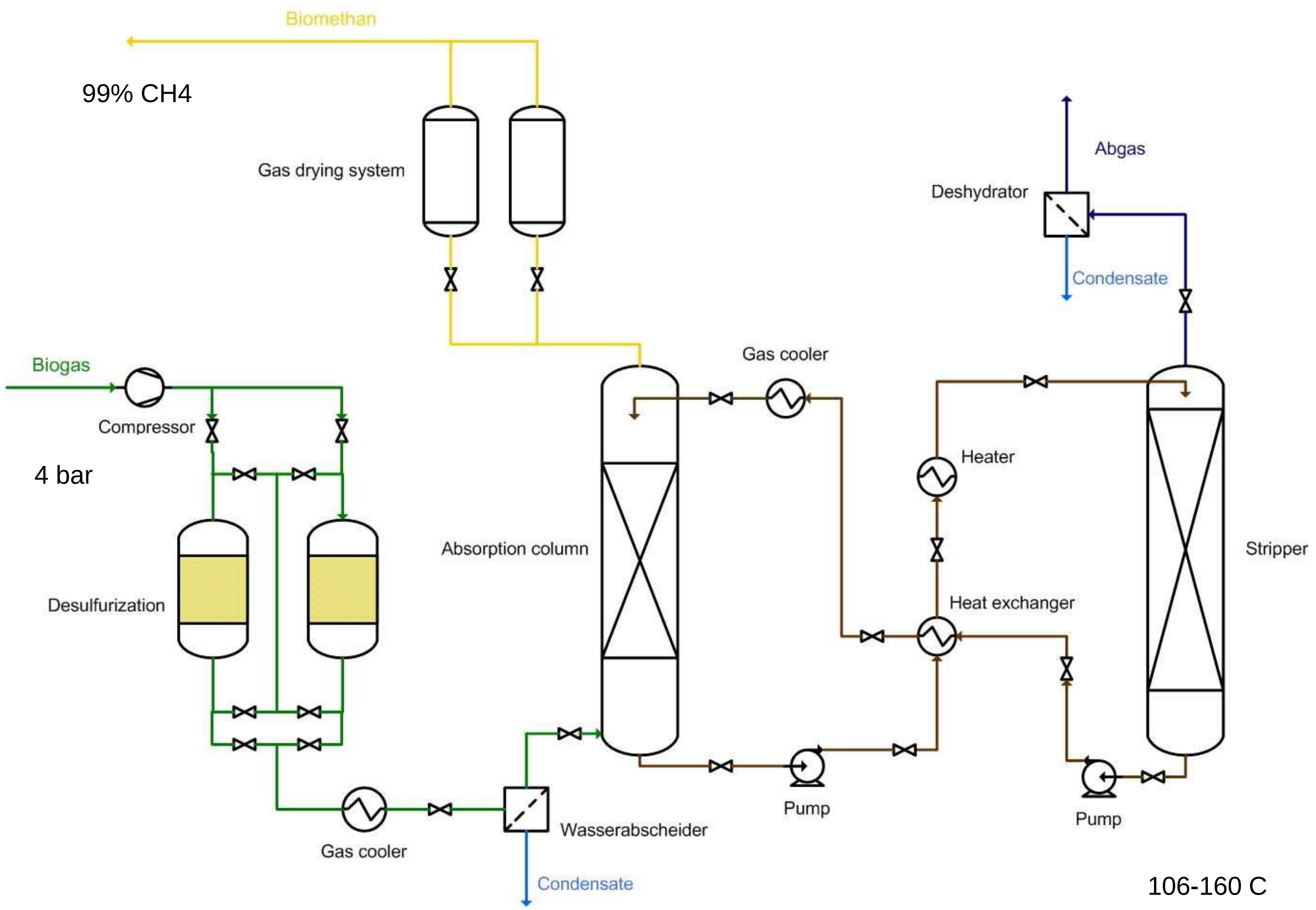
(Courtesy: ISET, 2008)

b. Chemical absorption

- Chemicals:
  - Alkanol amines : mono ethanol amine (MEA) or di-methyl ethanol amine (DMEA)
  - Potassium carbonate solutions
- Gas components do not simply dissolve in the solvent but react chemically
- CO2, H2S absorbed (H2S removal is required)
- N2 cannot be absorbed
- Highly selective reaction between amine & CO_2
- More CO_2 per unit volume is absorbed than WS system
  - smaller volumes and plant sizes
- Operated at very low partial pressure
- Chemical is regenerated by heat and/or vacuum

Chemical scrubbing

- CO_2 absorption using aqueous amino acid salt solutions:



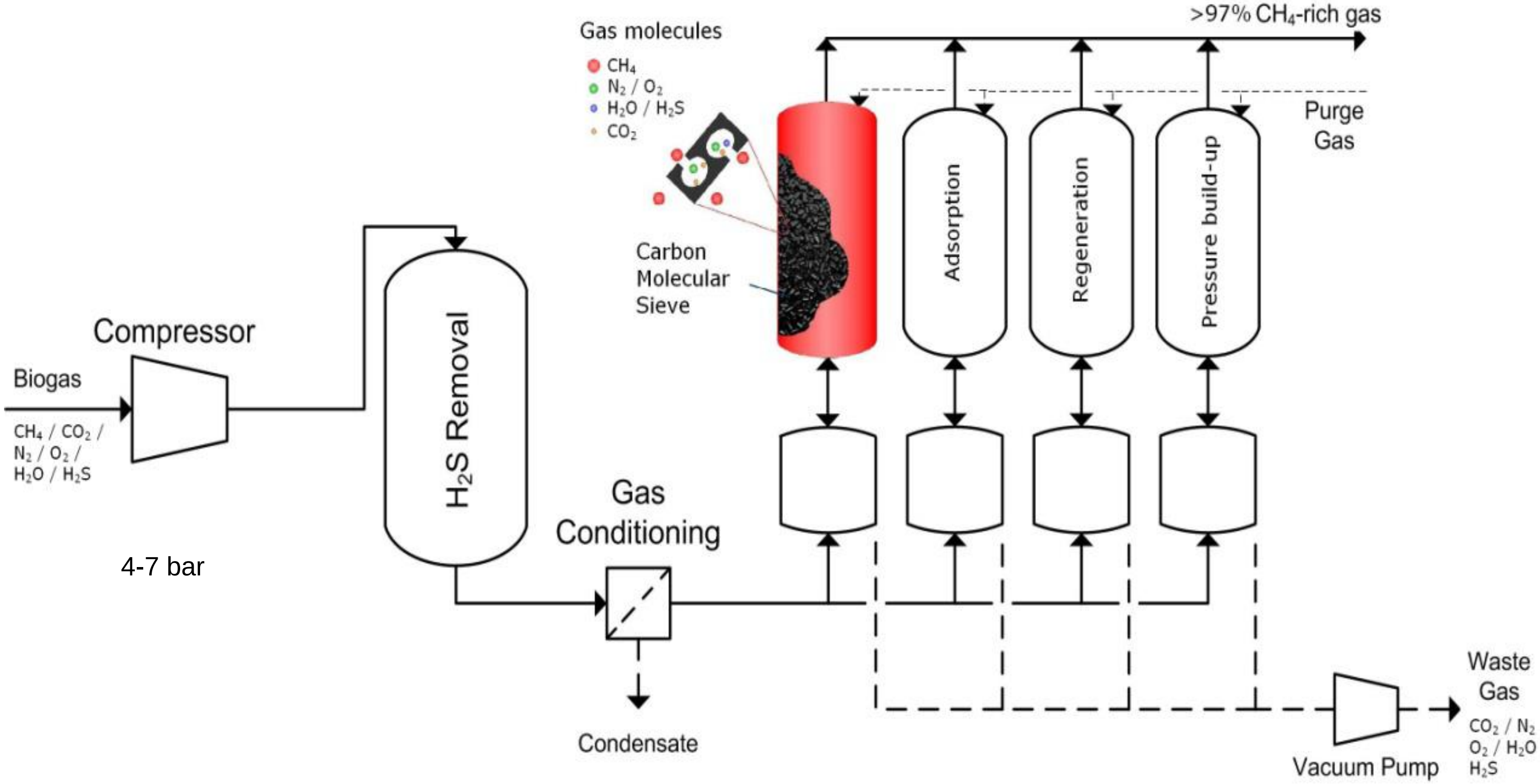
1 bar

(Courtesy: ISET, 2008)

Adsorption

- **Pressure swing adsorption (PSA)**
- Ability of various adsorbent materials to selectively retain one or more components of a gas mixture under varying pressure
- CH_4 (3.8 Å)/CO_2 (3.4 Å) separated by an adsorbent with a pore size of 3.7 Å.
- H2S, NH3 and H2O can also be separated
- Most commonn adsorption materials:
  - Activated carbon, zeolites and molecular sieves
- Two cycles
  - Upgrading at high pressure (7-10 bars)
  - Desorption at low pressure (2-4 bars)
- Adsorbent is regenerated by decreasing pressure or increasing temperature (desorption)

Pressure-swing adsorption



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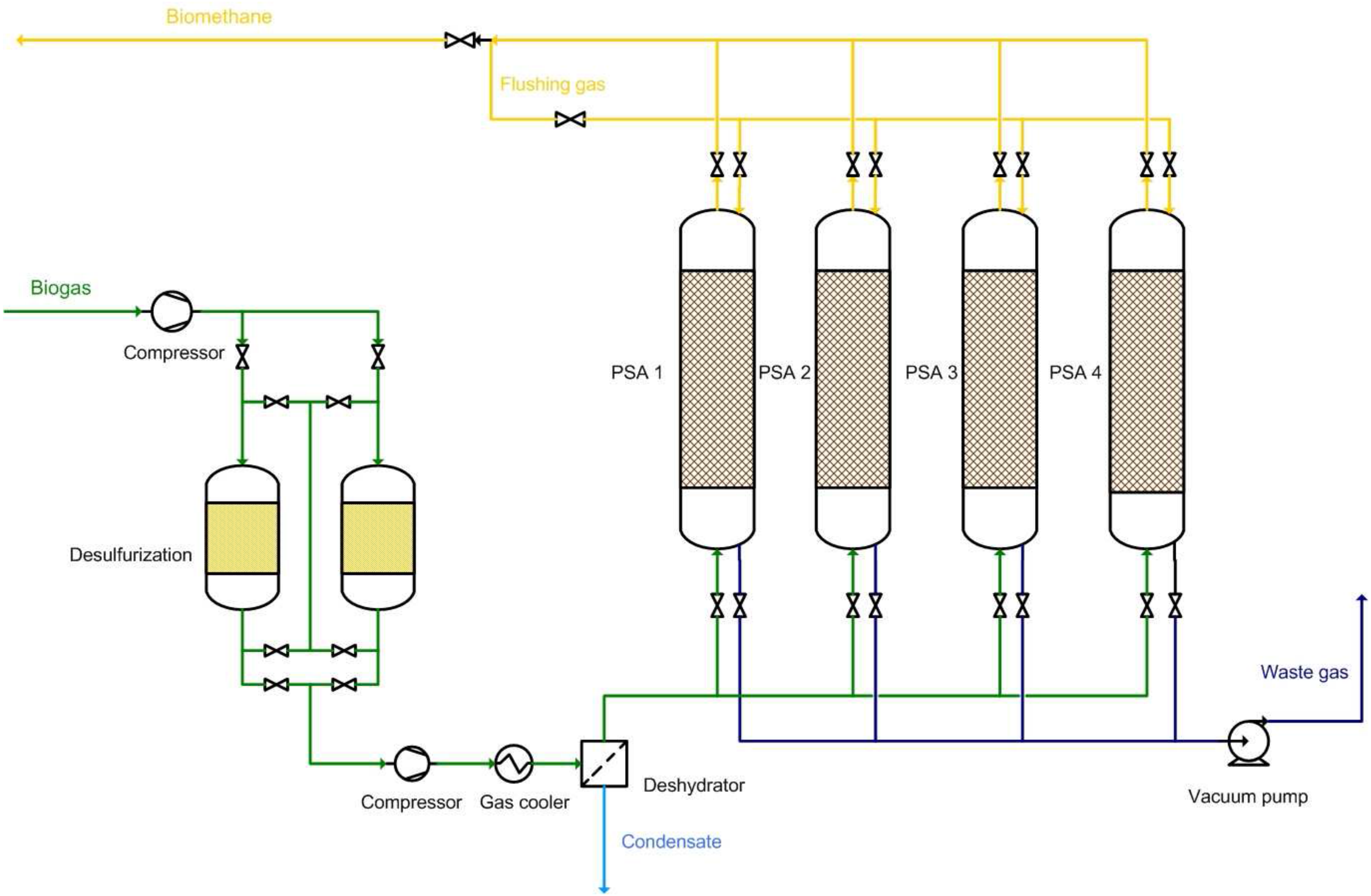
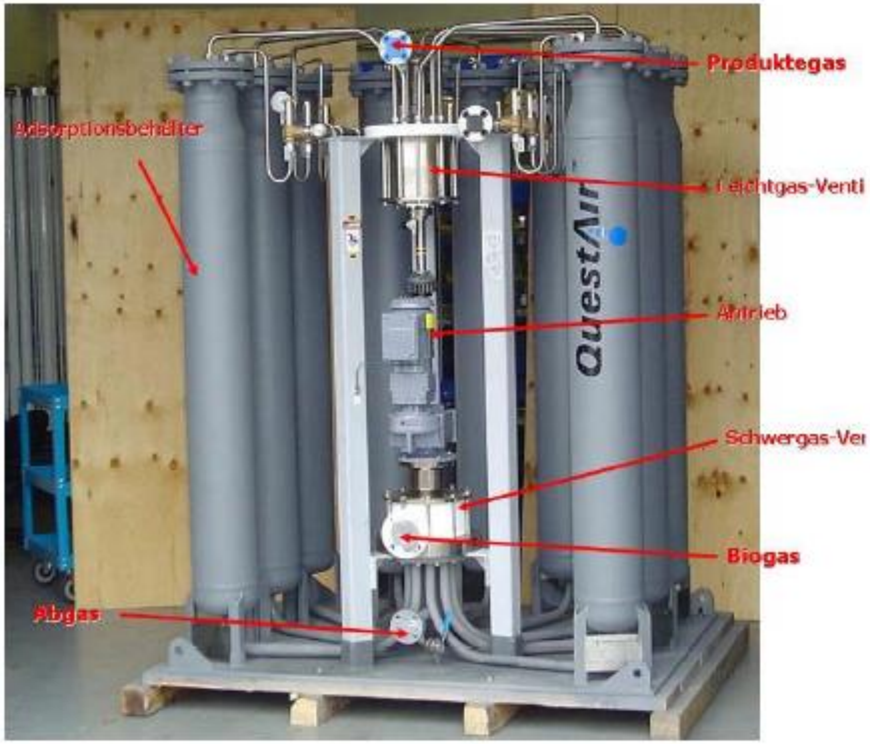


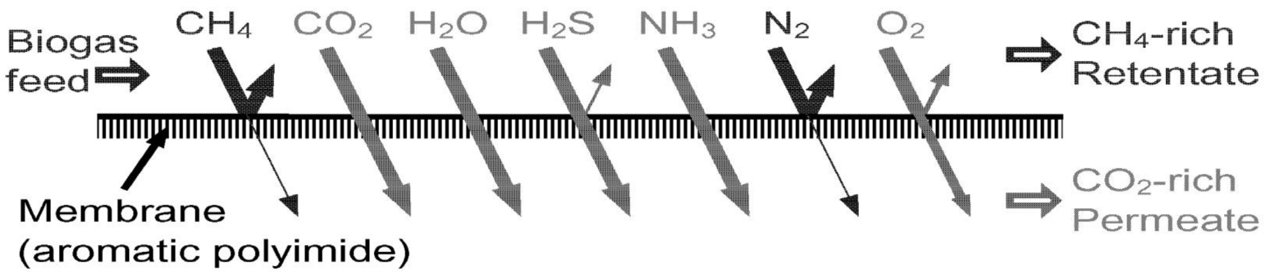
(Courtesy: ISET, 2008)

PSA with activated carbon



Membrane technology

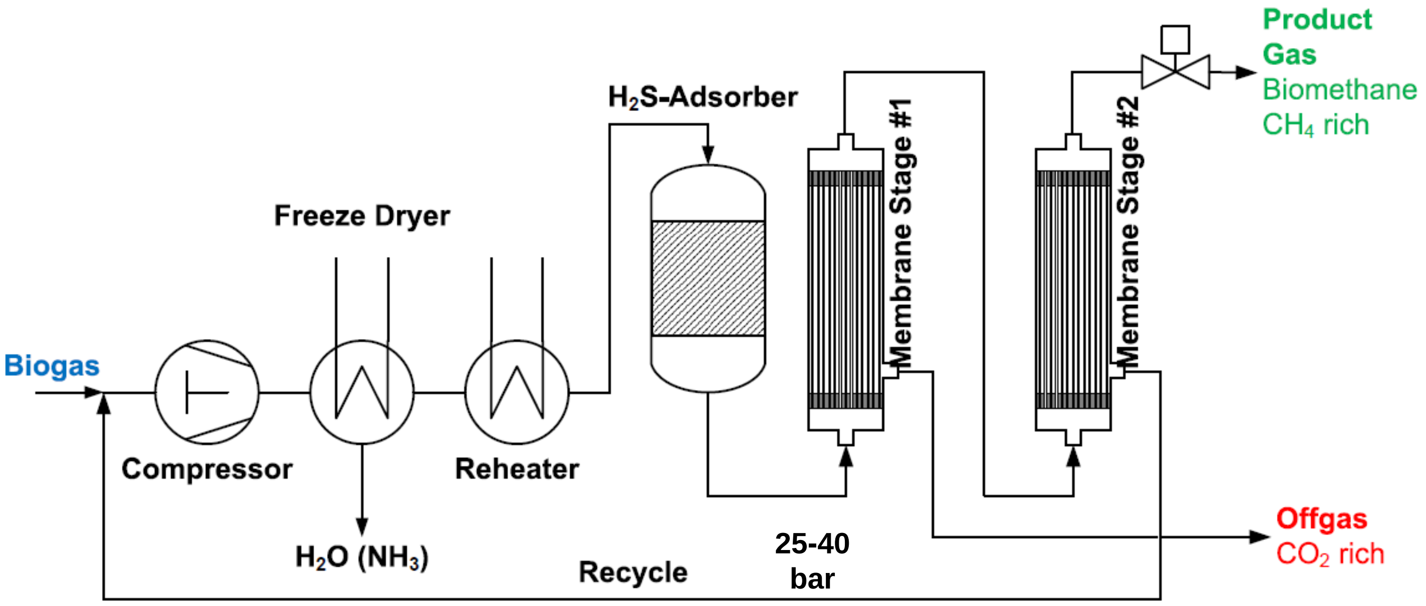
- Different molecules in a gas mixture have different permeation rate through a given permeable membranes
- Important parameter: permeability ratio = selectivity
- Permeation rate is dependent on the gas ability to dissolve in and diffuse through the membrane
- Driving force for the flux of each component is the difference in partial pressure over the membrane
- For good separation – high permeability between the components



Membrane technology

- Membranes
  - Usually constructed as hallow fibre modules for large surface area
  - Several modules are used for specific gas separation
  - Polymers used as solid membranes
  - Acetate-cellulose membrane: Permeability of H_2S is 60 times and CO_2 is 20 times than CH_4
- Membrane separation
  - High pressure (25-40 bars)
  - Low pressure (9 bars)

Two-stage membrane system



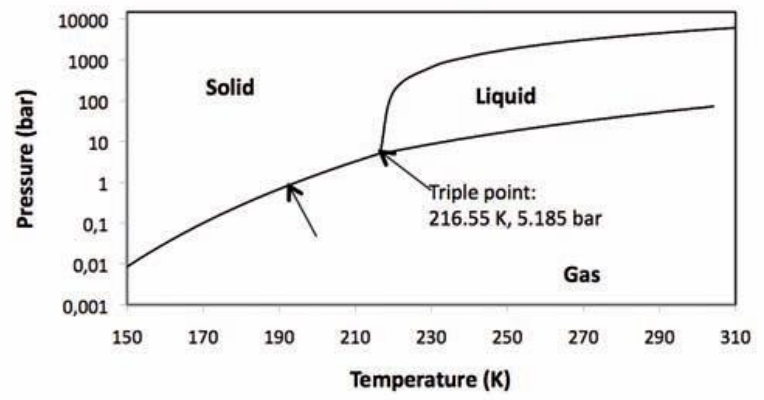
Courtesy: Biogas Upgrading Plant in Bruck/Leitha (Austria)

Membrane technology

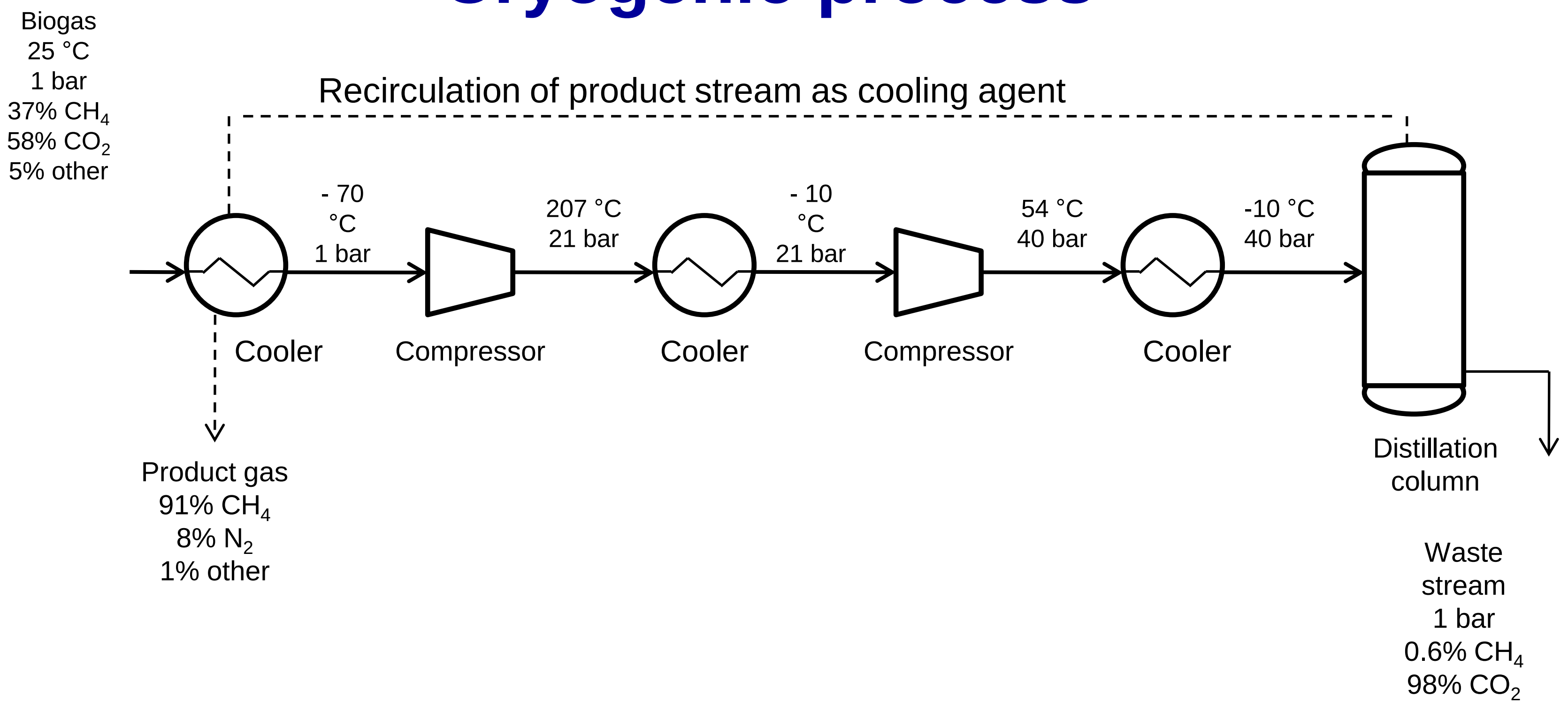
Courtesy: Biogas Upgrading Plant in Bruck/Leitha (Austria)

Cryogenic separation

- Each contaminant have different boiling points and thus liquefies at a different temperature-pressure domain
  - CO_2 -78 °C and CH_4 -160 °C
- The raw biogas is cooled down to the temperatures where the CO_2 in the gas condenses or sublimates (194.5 K) and can be separated as a liquid or a solid fraction



Cryogenic process



- Raw gas is compressed in multi stage with intercooling using chillers and heat exchangers
- CH_4 accumulates in the gas phase
- CO_2 is further processed for enrichment

Off-gas CH_4 treatment

- Off-gas seldom contains high concentrations to maintain a flame without adding natural gas or biogas
- Methane loses should be kept as low as possible
  - Loss of energy
  - GHG emissions
- CH_4 can be present
  - In the off-gas leaving a PSA-column
  - In air from a water scrubber with water circulation
  - In water in a water scrubber with water recirculation
- **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

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Comparison of biogas upgrading technologies

	Water scrubbing	Chemical (amine) scrubbing	PSA	Membrane	Cryogenic
Working pressure (bars)	7 - 10	Atmp	4 – 7	8 - 10	25- 40
Maximum achievable yield (%)	94	90	91	98	98
Maximum achievable purity (%)	98	98	98	89.5	91
CH_4-losses	<2	<0.1	<2	–	<2-10
Produced gas dryer required	Yes -	Yes -	No +	No +	No +
H_2S pre treatment required	No +	Yes -	Yes -	Yes -	Yes -
Waste gas treatment required	No +	Yes -	No +	No +	Yes -
Technical availability per year (%)	96	91	94	98	98
Energy requirement (kWh/m^3 of upgraded biogas)	0.43	0.646	0.335	0.769	–
Investment cost (€/yr)	265,000	353,000[a] -869,000[d]	680,000	233,000[a] -749,000[b]	908,500
Maintenance cost (€/yr)	110,000	134,000[a] -179,500[b]	187,250	81,750[a]-126,000[b]	397,500
Cost price per Nm^3 biogas upgraded (euros)	0.13	0.17[a] -0.28[b]	0.25	0.12[a]-0.22[b]	0.44
References	32	9	33	4	1

Source: de Hullu et al. 2008; Berndt, 2006; Beil, 2009; Patterson et al., 2009

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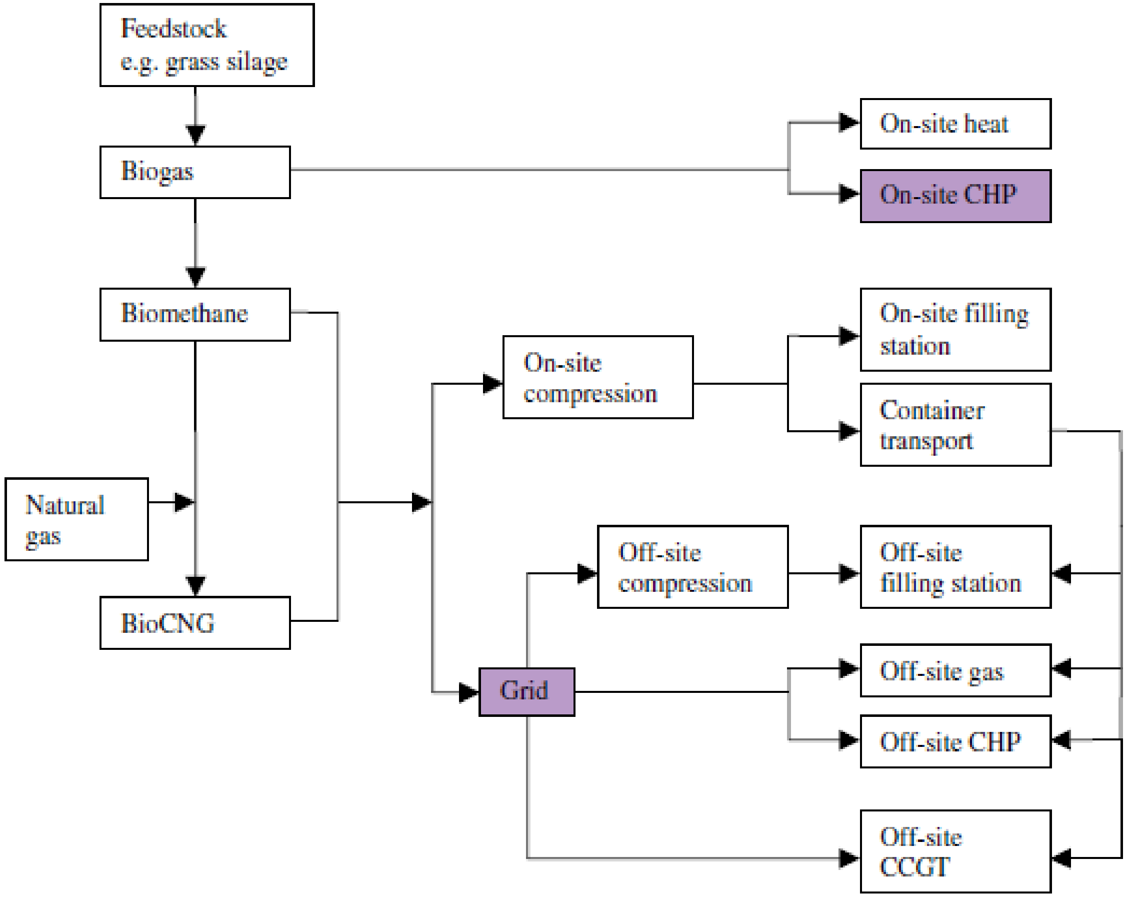
Uses of biomethane



Biogas as vehicle fuel

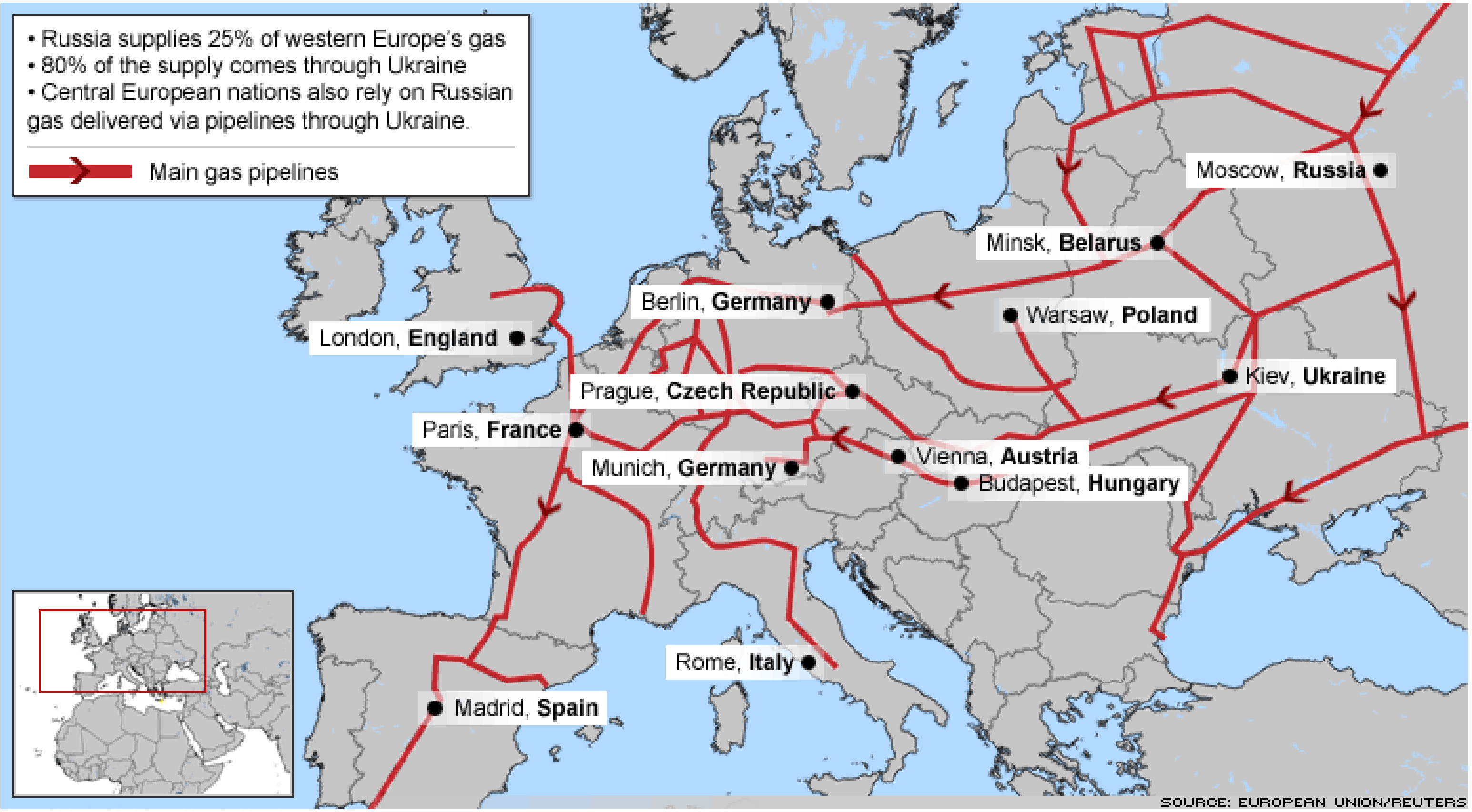
- Biomethane can be used in vehicles operated with natural gas without any engine modification.
- Bifuel vehicles use gas and gasoline
  - Range with gas 200-400 km
- Dual fuel vehicles use methane and diesel
- Biomethane is compressed to 200 bars for on-site storage or transport by road.
- It is also distributed through natural gas grid or separate on-site fuelling stations

Biogas as vehicle fuel

Biogas injection to natural gas grid

- Biogas can be distributed via natural gas grid
- Biogas plants usually locates in rural areas → grid connects the production site with more densely populated areas
  - New customers
  - Improves the local security of supply
- Some countries have standards for gas injection to grid
  - Methane, carbon dioxide, sulphur compounds, moisture, Wobbe index, siloxanes…
  - Low- and High value gas
- In most cases biogas needs to be upgraded before gas grid injection
  - Wobbe index

EU natural gas grid



Biomethane standards for grid injection or vehicle fuel use

Compound	France[1]		Germany[2]		Sweden[3]	Switzerland[4]		Austria[5]	Holland[6]
	L gas	H gas	L gas	H gas		Limited injection	Unlimited injection		
Lower Wobbe Index (MJ/Nm^3)					43.9-47.3				
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
CH_4 (vol-%)					97	>50	>96		>80
CO_2 (vol-%)	<2		<6			<6		<2[6]	
O_2 (vol-%)	<0.01		<3		<1	<0.5		<0.5[6]	
H_2 (vol-%)	<6		<5			<5		<4[6]	<12
$CO_2+O_2+N_2$ (vol-%)					<5				
Water dew point (°C)	<-5 (at MOP downstream from injection point		<t[4]		<t[4]-5			<-8[7]	-10[8]
Relative humidity (%)			0.55-0.75			<60%			
Total S (mg/Nm^3)	<100 (instant content) <75 (Annual average)		<30		<23	<30		<5	<45
MON (Motor octane number)					>130				
NH_3 (mg/Nm^3)					<20				
H_2S (mg/Nm^3)						<30			

[1]National guidance no. 2004-555 (2004) and technical specifications (2006); [2]Standards DVGW G260 and G262; [3]Standard SS155468; [4]Directive SSIGE G13; [5]Directive OVGW G31 and G33; [6]Proposition for Dutch gas suppliers

Adapted after IEA Bioenergy, (2009).

Upgrading Technology	Advantages	Disadvantages
Chemical absorption	1. Almost complete H_2S removal 2. Cost effective on larger scale 3. Good energy efficiency & operating costs	1. Safety – solvent is dangerous to handle 2. Risk of pollution by chemical contamination 3. Uneconomic capital and energy costs for gas streams with high CO2 loadings (>20%) 4. Does not remove inerts (e.g. O2 and N2) 5.Only removal of one component in column 6. Expensive catalyst
High pressure water scrubbing	1. Removal gases and particulate matter 2. High purity, good yield 3. No special chemicals or equipment required 4. Neutralization of corrosive gases 5. Excellent safety; proven performance 6. Reliable, simple and easy to maintain 7. Low capital and operating cost 8. Siloxanes effectively removed	1.Limitation of H_2S absorption due to changing pH 2.H_2S damages equipment 3.Requires a lot of water, even with the regeneration process 4. Practical capacity limit ≈ 2200 Nm3/h per unit 5. Does not remove inerts (e.g. O2 and N2)
Pressure swing adsorption	1. More than 97% CH4 enrichment 2. Low power demand 3. Low level of emissions 4. Adsorption of N_2 and O_2 5. Can remove some inert gases, but sometimes requires an additional process module 6. Cost effective on small scale	1. Media becomes poisoned and needs replacement 2. Process difficult to control – problems maintaining high CH4 recovery 3. Upstream H_2S removal required step needed
Membrane process	1. Simple & compact plant 2. Low capital cost 3. Low maintenance 4. Low energy requirements 5. Easy process	1. Relatively low CH_4 yield (92% max.) 2. H2S removal step needed 3. Membranes can be expensive 4. High energy consumption 5. Membranes foul and require replacement 6. Does not remove inerts (e.g. O2 and N2)
Cryogenic separation	1.Can produce large quantities with high purity 2. Can produce LNG 3. Cost effective on very large scale 4. Easy scaling up 5. No chemicals used in the process	1. Complex plant, high capital and operating costs 2. Operational problems due to solid CO2 formation on heat exchangers. 3. Very low temperatures and high pressures create potentially hazardous plants 4. A lot of equipment is required

Source: de Hullu et al. 2008; Berndt, 2006; Beil, 2009; Patterson et al., 2009

Definition

- Wobbe index (WI): Actual heating value of natural gas arriving, from the gas line, at the orifice where a burner is located.

$$\frac{calorific\ value\ (MJ/\ m^3)}{\sqrt{relative\ density}}$$

- Relative density: The ratio of the density of gas to air at STP

- Higher heating value (HHV): Energy released when one normal cubic meter (Nm^3) of biogas is combusted and the water vapour formed in the combustion is condensed.
- Lower heating value (LHV): Energy formed when the water vapour is still not condensed.
- Examples : biogas (60 % CH4): 21.5 MJ/Nm^3 & pure CH4: 35.8 MJ/Nm^3.

Biogas upgrading technologies

- Separation of CH_4 and CO_2 of the pre-cleaned biogas in order to obtain the calorific value, Wobbe index and relative density required for the final use
- If gas is injected to gas grid – gas is compressed and dried to condensation point of the ground temperature at the actual pressure
- If gas is injected into a low pressure pipe of the natural gas grid – small amounts of sulphurous compounds (mercaptans & tetrahydrotiophen) are added (odourization)