UNIVERSIDADE FEDERAL DE LAVRAS

EPFL

BIOMASS CONVERSION COURSE

Doctoral School
EPFL

Biomethanation

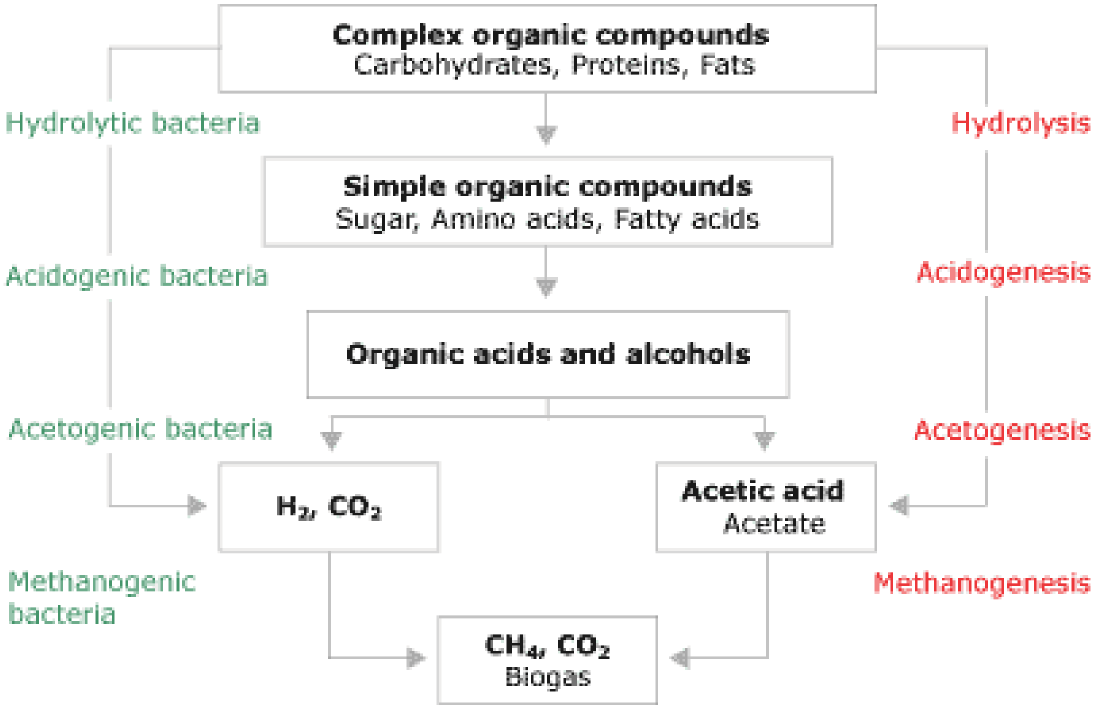
Anaerobic digestion

- Series of processes where microorganisms break down biodegradable materials usually in the absence of oxygen.

- Four phases of biomass conversion to biogas

1. Hydrolysis
2. Acidification
3. Acetogenesis
4. Methanogenesis

Anaerobic digestion



Source: http://www.schaumann-bioenergy.com

Hydrolysis: carbon hydrates -> simple sugars
proteins -> amino acids
fats -> fatty acids
Acidogenesis: organic acids and low alcohols are produced.
Acetogenesis: acetic acid, CO2 and H2 are formed
Methanogenesis: CH4 is formed .

Anaerobic digestion

- Methane formation - **pH** 6.5 - 8.5 (optimum **7.0 - 8.0**).

- pH increases by ammonia accumulation during degradation of proteins.
- pH decreases by the accumulation of VFA.

- Acetic acid is usually present in higher concentration
- Propionic and butyric acids are more inhibitory effective to methanogens

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Anaerobic digestion

- Undissolved compounds like cellulose, proteins or fats are cracked slowly into monomers - **several days**
- Hydrolysis of soluble carbohydrates - **few hours**.
- Process must be well **adapted to the substrate** properties and the speed of step of the conversion.

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Biogas

- Quality and quantity of biogas is varying due to the mixture of the used substratum.
- 2/3 of methane (CH_4)
- 1/3 of carbon dioxide (CO_2).

Traces of: VFA, alcohols

compound	**concentration**
Methane (CH_4)	50-75 Vol.-%
Carbon dioxide (CO_2)	25-45 Vol.-%
Water (H_2O)	2-7 Vol.-% (20-40°C)
Hydrosulfide (H_2S)	20-20000 ppm
Nitrogen (N_2)	< 2 Vol.-%
Oxygen (O_2)	< 2 Vol.-%
Hydrogen (H_2)	< 1 Vol.-%

Biogas

- Basic Reaction

$$C_cH_hO_oN_nS_s + y\,H_2O \rightarrow x\,CH_4 + n\,NH_3 + s\,H_2S + (c-x)CO_2$$

$$x = 1/8\cdot(4c + h - 20 - 3n - 2s)$$

$$y = 1/4\cdot(4c - h - 20 + 3n + 3s)$$

Carbohydrates:	$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$
Fats:	$C_{12}H_{24}O_6 + 3H_2O \rightarrow 4.5CO_2 + 7.5CH_4$
Proteins:	$C_{13}H_{25}O_7N_3S + 6H_2O \rightarrow 6.5CO_2 + 6.5CH_4 + 3NH_3 + H_2S$

$$CH_4 : CO_2 = 71\% : 29\%$$

Control Parameters

- **CHEMICAL OXYGEN DEMAND (COD) :**

Amount of oxygen, which is used for oxidation of the complete organic matter in a fluid medium.

- **DRY MATTER**

Mineral and organic compounds left after complete dewatering

- **ORGANIC DRY MATTER:**

Energetically useable part of substances used in biogas plants

Temperature

Temperature changes or fluctuations affect the biogas production negatively

The digestion process takes place at different conditions

- mesophilic (35–42 °C): tolerate +/- 3ºC temperature variation.
- thermophilic (45–60 °C): higher productivity, problem with ammonia inhibition and temperature variation.

Temperature

Mesophilic process: about 37°C.

Heating system (inlet 80°C, outlet 55°C).

Network of pipes inside the digester walls or on the inner wall surface.

Heat supply

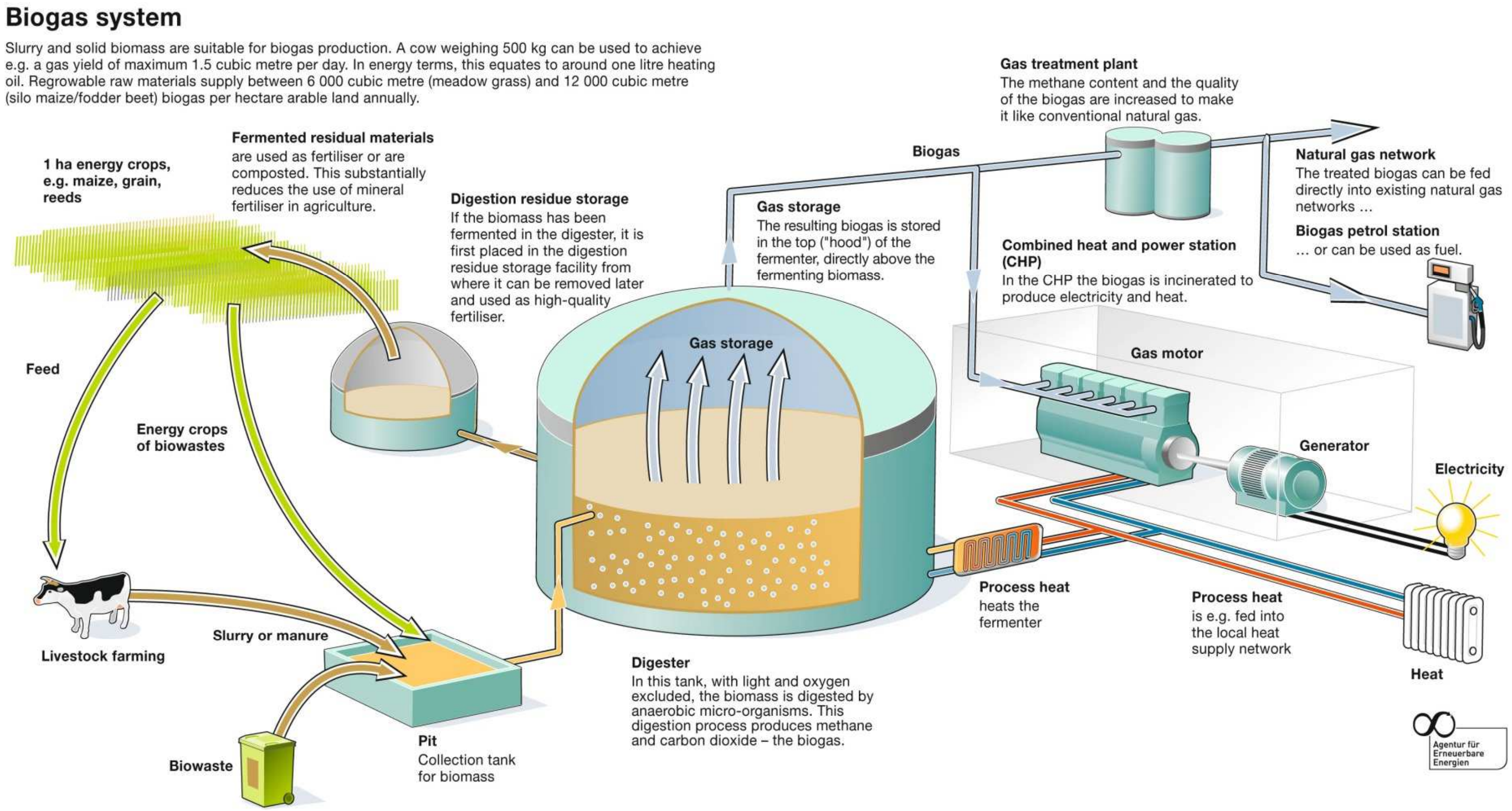
- Boilers fuelled by biogas, natural gas

or their mixture

- Cogeneration with biogas engines

Source: http://zorg-biogas.com

Biogas plant



Nutrients

- Macronutrients are carbon, nitrogen, phosphorus and sulfur (C:N:P:S=600:15:5:1 is sufficient).

- Micro-nutrients like iron, nickel, cobalt, selenium, molybdenum, and tungsten are important for the growth rate of microorganisms

➢ Nickel is required by methanogenic bacteria.

Feedstock

- Carbohydrates, proteins, fats, cellulose, hemicelluloses are main components of biomass for biogas production.

- Only strong lignified organic substances, e.g., wood, are not suitable due to the slowly anaerobic decomposition.

Feedstock

- Fats provide the highest biogas yield, but require a long retention time.
- Carbohydrates and proteins show much faster conversion rates but lower gas yields.

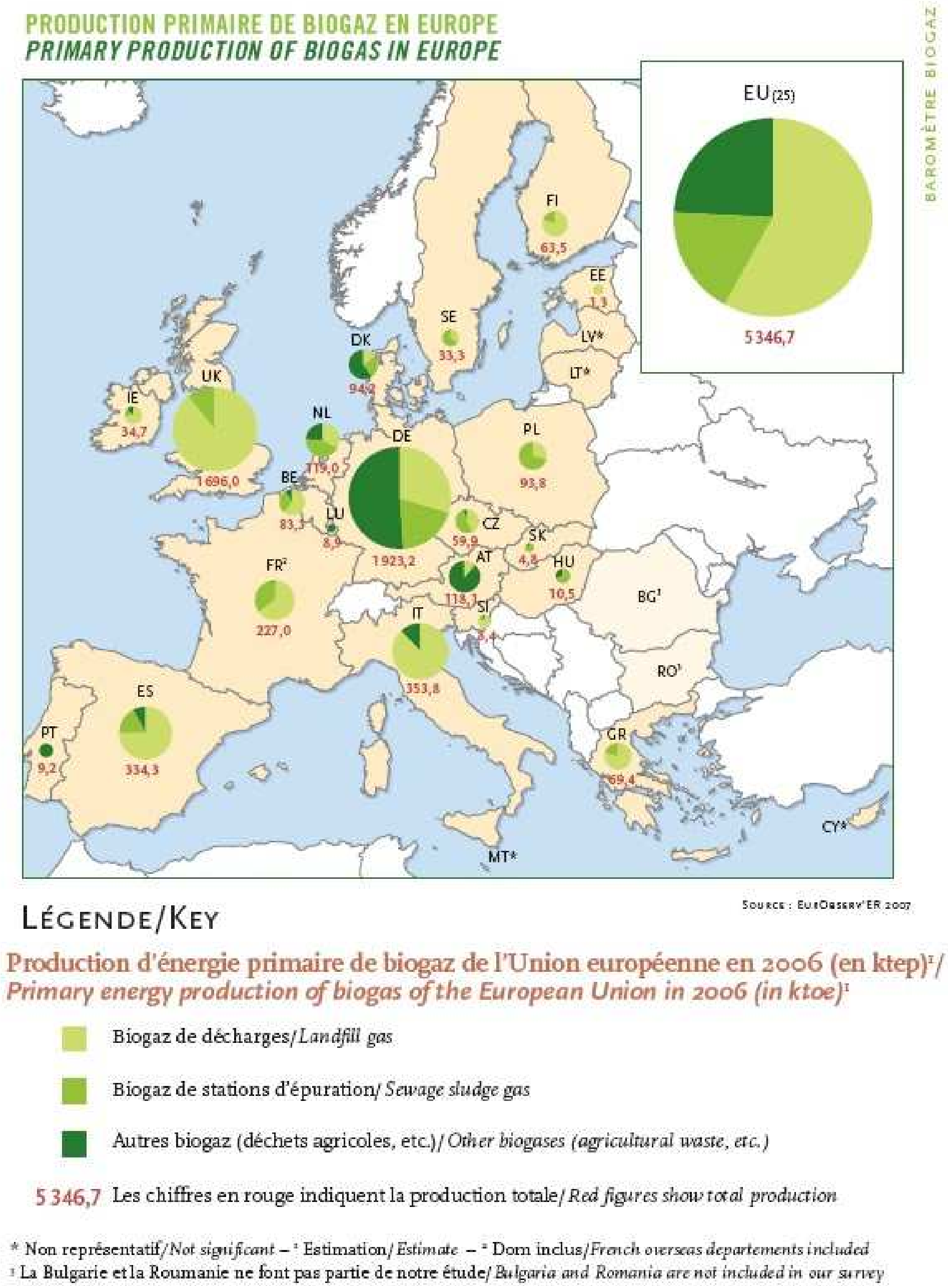
Table 1 Maximal gas yields and theoretical methane contents (Baserga U 1998)

Substrate	Biogas (Nm^3/t TS)	CH_4 (%)	CO_2 (%)
Carbohydrates[a]	790–800	50	50
Raw protein	700	70–71	29–30
Raw fat	1,200–1,250	67–68	32–33
Lignin	0	0	0

[a] Only polymers from hexoses, not inulins and single hexoses

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Biogas Production in Europe



Biogas potential

Crop	Crop yield (t FM/ha)	Biogas yield (Nm^3/(t VS))	Methane content (%)
Sugar beet	40–70	730–770	53
Fodder beet	80–120	750–800	53
Maize	40–60	560–650	52
Corn cob mix	10–15	660–680	53
Wheat	30–50	650–700	54
Triticale	28–33	590–620	54
Sorghum	40–80	520–580	55
Grass	22–31	530–600	54
Red clover	17–25	530 -620	56
Sunflower	31–42	420–540	55
Wheat grain	6–10	700–750	53
Rye grain	4–7	560–780	53

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Process techology

Pretreatment -> increase of the degradation rate

- Mechanical
- Thermal
- Chemical
- Enzymatic

• Process is faster with smaller particle size (does not necessarily increase the methane yield).

Process techology

- **Wet digestion** – total solids below 10%

Application of completely stirred tank digesters (Batch and continuous)

- Energy crops -> input must be mixed with liquid manure or recycled process water in order to achieve pumpable slurries.

90% of modern biogas plants in Germany

stirring must be implemented, using mechanical, hydraulic, or pneumatic mixing

Source: http://www.entec-biogas.com/en/services/technology-system-cstr.php

Process techology

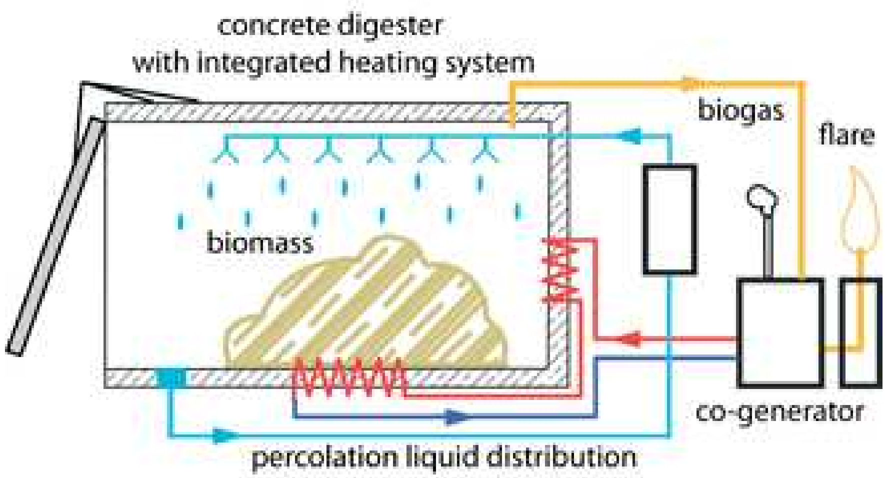
- **Dry digestion** – total solids 15% - 50%.
- Only batch operated processes are applied.

Advantage: Pumping and stirring units are not needed

- Simpler and robust to

that of wet fermentation

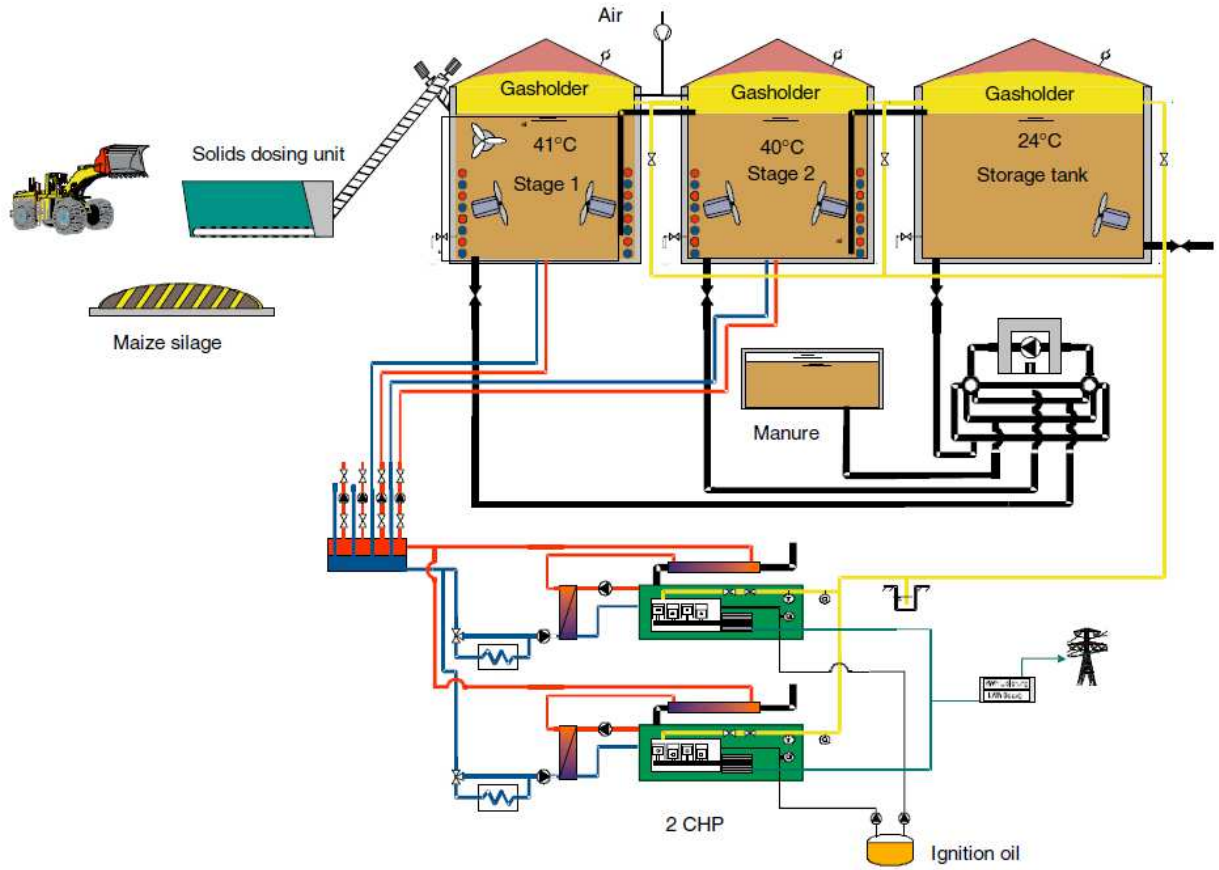
plants.



Source: http://zorg-biogas.com

Energy crops digestion: two-stage

1) high-loaded main fermenter for hydrolysis phase
2) low-loaded secondary fermenter in series which treats the digestate from the first stage.



Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Energy crops digestion: two-stage

- **Higher gas yields**
- Reduced residual methane potential of the digestate
- pH range for hydrolysis (5.5–6.5) and methanation (6.8–7.2)

Drawback:

Difficult control of the operation

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Equipment

reactor

Mixers

heater

Solid-liquid Separator

Gas Holder

Source: http://zorg-biogas.com

Desulphurization

- Biogas must be desulphurizated and dried before utilization to **prevent damage** of the gas utilization units.
- Co-fermentation of manure with energy crops or harvesting residues - H2S between 100 and 3,000 ppm.
- CHPs need levels of H2S below 250 ppm.

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Desulphurization

Biological desulphurization (inside the reactor):

- Oxidation of H_2S by injection of a small amount of air (2–5%) into the raw biogas.

- The air can be injected directly in the headspace of the digester, and the reaction occurs on the floating layer, on reactor wall, and on other surfaces in the gas room.

- *Sulfobacter oxydans* bacteria can convert H_2S into elementary sulfur and sulfurous acid.

- *S. oxydans* does not have to be added, because it is present inside the digester.

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Desulphurization

Biological desulfurization (outside the reactor)

- installations filled with plastic support materials on which the microorganisms can grow

a) Raw biogas and air are injected in the bottom of the column

b) Aqueous solution of nutrients are injected in the top in order to wash out acidic products and to supply nutrients to the microorganisms.

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Desulphurization

Desulfurization chemical process

- Done by adding a commercial ferrous solution to the digester
- Ferrous compounds bind sulphur in an insoluble compound in the liquid phase, preventing the production of gaseous hydrogen sulphide
- Expensive method

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Biogas Utilization

- IC Engines (gas or dual fuel) - electric efficiencies of up to 43% can be achieved.
- Microturbines - electric efficiency (25–31%) - availability of the exhaust heat
- Fuel cells - higher electric efficiency but need an efficient gas cleaning

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860

Biogas Upgrade – grid quality

- Upgraded gas must have a methane content of more than 95%.

- Methods of removing carbon dioxide from biogas:

- water scrubbing or scrubbing with organic solvents like polyethylene glycol
- pressure swing adsorption using activated carbon or molecular sieves
- chemical washing by alkanol amines like monoethanolamine or dimethylethanolamine
- membranes
- cryogenic separation at low temperature

Source: Peter Weiland. Appl Microbiol Biotechnol (2010) 85:849–860