Biomass: biogases

BIOGAS

Source

- Solid (wood, straw)
- Wet (waste, manure)
- Sugar/starch
- Oil crops

Process

- Combustion
- Gasification
- Pyrolysis
- Methanation
- Fermentation
- Extraction + esterification

Product

- Heat
- Woodgas
- Woodoil
- Biogas
- Bioethanol
- Biodiesel

Service

- Heat / CHP
- Electricity
- (Transport) Fuels
- Chemicals

Sources for biogas generation

=> essentially wet wastes, too inefficient too burn:

• organic industrial effluents	<5% organic dry matter
• sewage	5%
• farming residues	10%
• solid wastes (digesters, landfill)	>20%
– municipalities (≈20 m^3/yr.person)	MSW
– industry	ISW

– >100 m^3 biogas produced per tonne 'solid' waste (≈20% org. solids) (ca. 500 L biogas per kg organic dry matter)

When to *digest* waste?

Waste disposal scheme options, in particular for organics :

- incineration: for **solid** wastes
- composting: = aerobic; for farming (fertilising)
- **methanisation: = anaerobic digestion**
- landfill: as a lesser option, when none of the other options apply…; landfilling, however, is restricted in the case of organic wastes

=> most appropriate for **liquid** wastes with an organic fraction

EU ''waste-to-energy hierarchy''

Examples of waste-to-energy processes

Anaerobic digestion of organic waste where the digestate is recycled as a fertliser

Waste incineration and co-incineration operations with a high level of energy recovery
Reprocessing of waste into materials that are to be used as solid, liquid or gaseous fuels

Waste incineration and co-incineration operations with limited energy recovery
Utilisation of captured landfill gas

''The role of waste-to-energy in the circular economy'',
Brussels, 26.1.2017 COM(2017) 34 final

Anaerobic digestion - AD (1)

- =transformation of organic matter by microorganisms (bacteria) in absence of O_2
- internal reduction + oxidation breakdown of the biomass polymers (C-H-O) to the simplest building blocks :

  CH_4 (fully reduced) + CO_2 (fully oxidized) => biogas
- mature market technology
- drawback: lignine is nearly undigestable, cellulose is difficult to digest

  => AD is a slow process (10-20 days residence time), occurring at ≈35-55°C

Digestion process (2)

4 distinct steps in time; using 3 different bacterial groups

1. **Hydrolysis** (uses exo-enzymes)

   = the ***slowest*** of the 4 steps (rate-determining)

   breaks solid org. matter down to liquified monomeres & dimeres:

   cellulose → cellobiose + glucose

   starch → maltose + glucose

2. **Digestion**

   = formation of organic **acids**

   acetic / propionic / butyric acid (=C_2/C_3/C_4-OOH), lactic acid, ethanol, and little H_2 and CO_2

Digestion process (3)

3. '**Acidogenesis**'

   higher acids break down to CH_3COOH (**acetic acid**), H_2 and CO_2, approximatively as in the overall reaction:

   $C_6H_{12}O_6 + 2H_2O \rightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2$

4. '**Methanogenesis**':

   a. $2CH_3COOH \rightarrow 2\ \mathbf{CH_4} + 2\ CO_2$ (**70-80%** of CH_4 product)

   b. $CO_2 + 4\ H_2 \rightarrow \mathbf{CH_4} + 2\ H_2O$ (**20-30%** of CH_4 product)

   Reactions a & b take place upon different bacterial actions.

   These 2 parallel CH_4-synthesis reactions explain why biogas compositions typically are (60±5)% CH_4 and (40±5%) CO_2

Overall approximation: $C_6H_{12}O_6$ -> $3\ CH_4 + 3\ CO_2$

Anaerobic digestion - AD (4)

- The main objective for sewage and similar effluents (e.g. food industry) is waste **treatment**, i.e. **depollution** of liquid streams that are too heavily charged in organics, which cannot be discharged directly into the aquatic ecosystem; hence biogas is here mainly a **by-product** (energy recovered to power the ''depollution plant'')
- However, in the case of largely untapped farm waste (manure, crop residues) and MSW/ISW, biogas is not a by-product but an active **energy vector** (and especially for valorisation into electricity production, in gas **engines** or **fuel cells**)

Chemical formulae for biogas generation

'Buswell' formula:

$$C_a H_b O_c + \left[a - \tfrac{1}{4}b - \tfrac{1}{2}c\right] H_2O \rightarrow \left(\tfrac{1}{2}a + \tfrac{1}{8}b - \tfrac{1}{4}c\right) CH_4 + \left(\tfrac{1}{2}a - \tfrac{1}{8}b + \tfrac{1}{4}c\right) CO_2$$

e.g. for **manure**, approximated as $C_4H_8O_2$ (butyric acid):

$$C_4 H_8 O_2 + [4 - 2 - 1] H_2O \rightarrow \left(2 + 1 - \tfrac{1}{2}\right) CH_4 + \left(2 - 1 + \tfrac{1}{2}\right) CO_2 = \tfrac{5}{8} CH_4 + \tfrac{3}{8} CO_2$$

'Buswell-Boyle' (with N, S):

$$C_a H_b O_c N_d S_e + \frac{1}{4}\left[4a - b - 2c + 3d + 2e\right] H_2O$$
$$\rightarrow \frac{1}{8}(4a + b - 2c - 3d - 2e) CH_4$$
$$+ \frac{1}{8}(4a - b + 2c + 3d + 2e) CO_2$$
$$+ dNH_3 + eH_2S$$

Remark: CO_2, NH_3, H_2S dissolve better in H_2O than CH_4, hence the recovered gas is actually methane-enriched

Digestion is a batch process

- once a day, fresh organic substrate is filled in, and digested matter is removed from a batch reactor

- mean residence time (days):
  - saturation after 20 days

$$\theta = \frac{V_{reactor}\left[m^3\right]}{\dot{V}_{org}\left[m^3/d\right]}$$

- daily specific load (kg/m³.d)
  - M can designate fresh or dry organic matter

$$M_{day} = \dot{V}_{org} \cdot \frac{M}{V} = \frac{M}{\theta}$$

- biogas production can be expressed as:

$$m^3_{biogas}/m^3_{reactor}$$

$$m^3_{biogas}/kg_{org.matter}$$

Example:

Farm with 60 animals. Manure waste: 3 m^3/day. (≈3000 kg)

Organic dry matter = 50 kg/m^3 (=150 kg/day=5% organics)

Mean residence time θ = 20 days. Biogas production = 65 m^3/day. (≈433 L / kg d.m.)

- Reactor volume :

$$V_{reactor}\left[m^3\right] = \theta.\dot{V}_{org} = 20 * 3 = 60m^3$$

- Daily specific load:

$$M_{day} = \frac{M_{org}}{\theta} = \frac{50kg/m^3}{20days} = 2.5kg/m^3.day$$

- Specific biogas production:
  - per reactor volume:

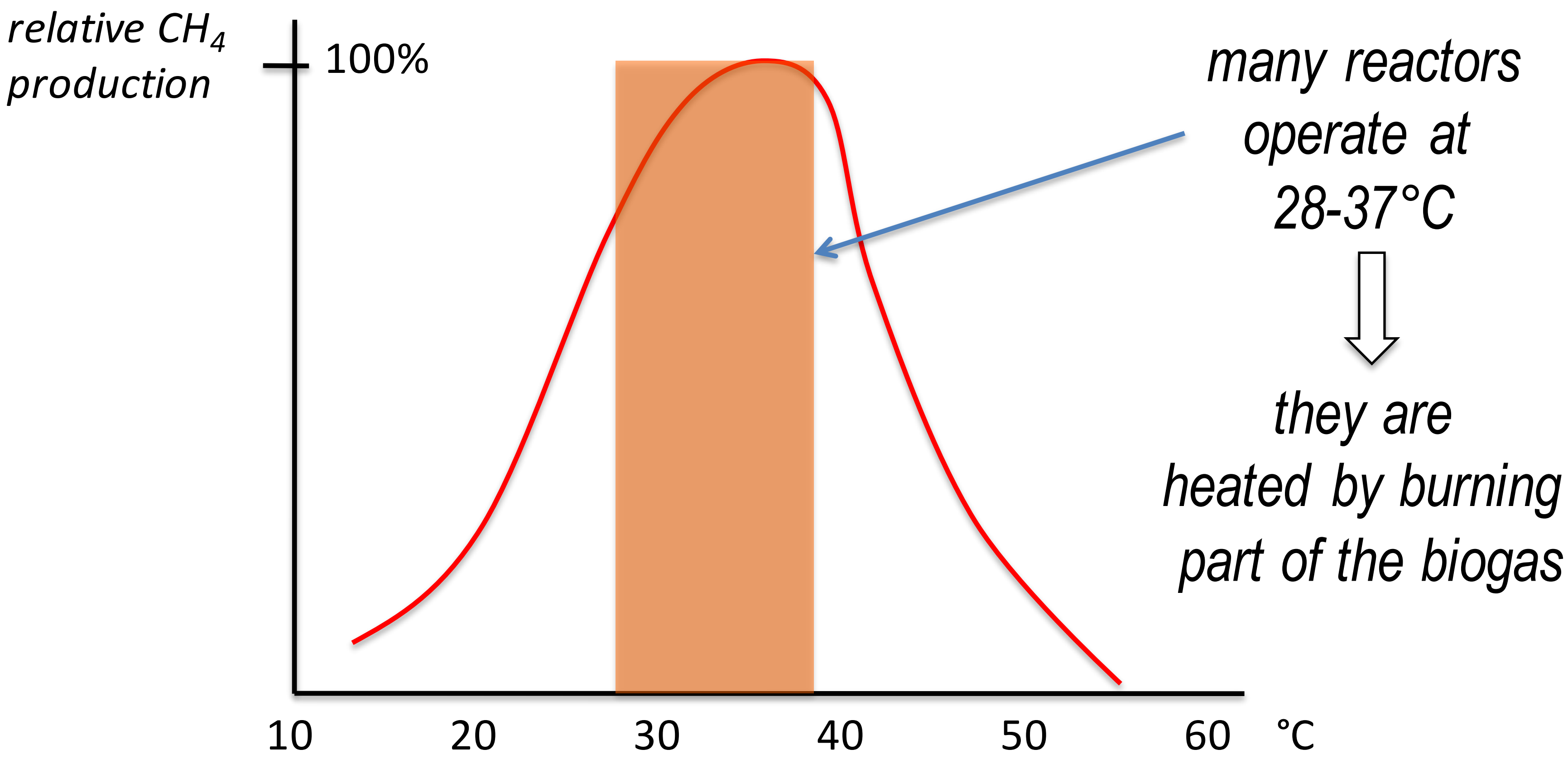
$$P = \frac{65m^3/d}{60m^3} = 1.08\frac{m^3/d}{m^3}$$

  - per organic matter:

$$P = \frac{65m^3/day}{M_{org}\left[\frac{kg}{m^3}\right].\frac{V_{reactor}\left[m^3\right]}{\theta\left[days\right]}} = \frac{65}{50.\frac{60}{20}} = 0.43\frac{m^3}{kg_{org.matter}}$$

Digestor reactor temperature

Enzyme	Optimal T range
'Psychrophilic'	20°C
'Mesophilic'	20-45°C
'Thermophilic'	>45°C



Experience values

- The determining factors in biogas production are:
  - **temperature**; part of the biogas is used to heat the reactor; the biogas production rate saturates at 40°C
  - **residence time** (days); saturates at 20 days
  - **organic** matter **charge** (usually 3-10%)

Production	Unit	Cows	Pigs
per animal and day	$m^3_{biogas} / head.day$	1.3 ± 0.3	1.5 ± 0.6
per mass	$m^3_{biogas} / kg_{org.matter}$	0.3 ± 0.05	0.5 ± 0.05

→1.5 m^3/day @ 20 MJ/m^3 = 30 MJ/day ≈ 8 kWh/day

= equivalent to 2 m^2 of thermal solar collectors

Any farm animal produces ca. 18-20 kg of manure per year per kg of its own body weight

Biogas vs. natural gas

Property	Unit	NG	BG (60% CH_4)
LHV	MJ / m^3	36	21.5
Density	kg/m^3	0.82	1.21
Ignition T	°C	620	700
Ignition speed in air	m/s	39	0.25
Air factor	-	9.5	5.7
Exhaust, max CO_2	Vol%	11.9	17.8
Exhaust, dew point	°C	59	60-160

Some characteristics of biogas production

- the digestate is a good quality **fertilizer** (2% nitrogen)
  - better than (air-)composted waste (<1% nitrogen)
- a significant part of the produced biogas is used for **heating of the digester** and the installation itself (farm,…)
- (cold) **desulfurisation** of the biogas is done with $FeCl_3$ solution (to precipitate FeS); sulfur is removed as it is poisonous (for the atmosphere but also in downstream CHP engines or fuel cells)

Biogas use and potential (EU)

	2007	gas engines	ultimate
Source	Use (PJ)	kW_e/site	Potential
Effluents	7	200 kW	140 PJ
Sewage	37	50-200	215
Manure	30	10-100	750
Solid agro	45		1370
MSW,ISW	15	0.1-1 MW	330
Landfill	120	1 MW	-
TOTAL	**254 PJ** (6 Mtoe)	*huge margin* →	**2805 PJ** (67 Mtoe)

⇩ 30% efficiency

20 TWh_{el} (0.6% of total)

⇩ =25% of NG import in EU

Biogas application examples (CH)

Source	Biogas m^3/day	% CH_4	% yr load	Installed power	Effi-ciency
Farm 37 cattle	70	57	60	**5 kW_{el}**	**18%**
Sewage 30'000 p.	1000	65	65	**130 kW_{el}**	**28%**
MSW 80'000 p.	1300	60	95	**90 kW_{el}**	**25%**

=> small power sites (gas engines); low (electrical) efficiency

Special case of landfill gas (LFG)

- (multi)MW_{el}-size sites (with gas engines, gas turbines)
- an important fraction of world biogas (20 Mtoe)
- 3 Mtoe in EU-27
- important anthropogenic GHG emitter! (as CH_4)
- often heavily contaminated (with F, Cl, NH_3, H_2S, Si,…)
- often of low calorific value (diluted with N_2/O_2)
  - engines stop running <45% CH_4
  - fuel-assisted flaring or venting !