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: $C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2$

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:

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

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

$$C_4H_8O_2 + \left[4 - 2 - 1\right]H_2O \rightarrow \left(2 + 1 - \tfrac{1}{2}\right)CH_4 + \left(2 - 1 + \tfrac{1}{2}\right)CO_2 = \tfrac{5}{8}CH_4 + \tfrac{3}{8}CO_2$$

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

$$C_aH_bO_cN_dS_e + \frac{1}{4}\left[4a - b - 2c + 3d + 2e\right]H_2O$$

$$\rightarrow \frac{1}{8}\left(4a + b - 2c - 3d - 2e\right)CH_4$$

$$+ \frac{1}{8}\left(4a - b + 2c + 3d + 2e\right)CO_2$$

$$+ dNH_3 + eH_2S$$

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 <u>batch</u> 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/m[3].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)

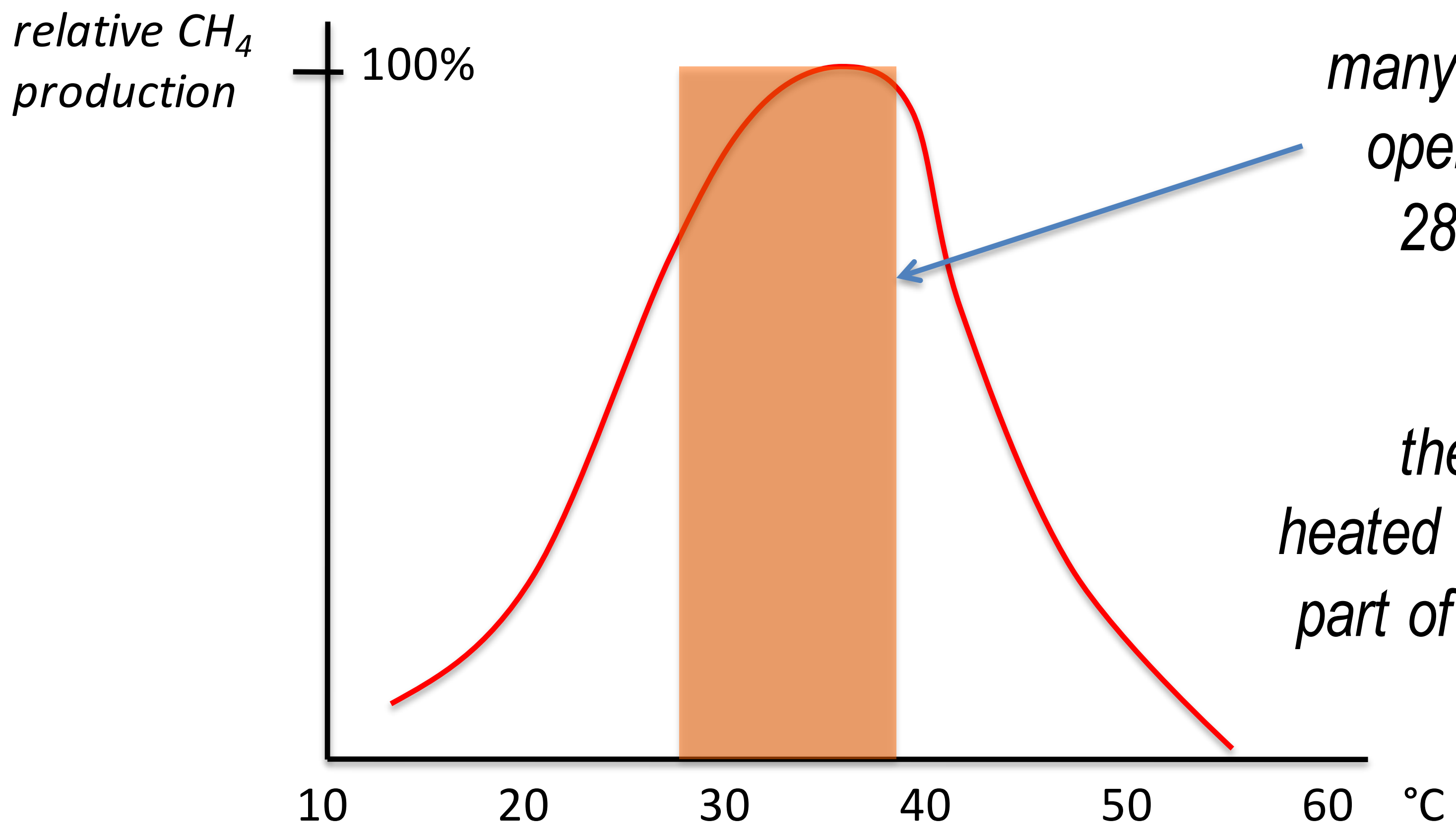
Organic dry matter = 50 kg/m^3 (=150 kg/day=5% organics)

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

- Reactor volume : $$V_{reactor}\left[m^3\right] = \theta.\dot{V}_{org} = 20 * 3 = 60 m^3$$
- Daily specific load: $$M_{day} = \frac{M_{org}}{\theta} = \frac{50 kg/m^3}{20 days} = 2.5 kg/m^3.day$$
- Specific biogas production:
  - per reactor volume: $$P = \frac{65 m^3/d}{60 m^3} = 1.08 \frac{m^3/d}{m^3}$$
  - per organic matter: $$P = \frac{65 m^3/day}{M_{org}\left[\frac{kg}{m^3}\right] . V_{reactor}\left[m^3\right] / \theta\left[days\right]} = \frac{65}{50.\frac{60}{20}} = 0.43 \frac{m^3}{kg_{org.matter}}$$

Digestor reactor temperature

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



many reactors operate at 28-37°C

⇩

they are heated by burning part of the biogas

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 $\pm$ 0.3	1.5 $\pm$ 0.6
per mass	$m^3_{biogas} / kg_{org.matter}$	0.3 $\pm$ 0.05	0.5 $\pm$ 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 !