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SENEFFE, BELGIUM

Introduction to biogas purification

Julien Estager, Benoît Kartheuser, 1st April 2025

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Certech – Centre de ressources technologiques en Chimie

R&D partner and supplier of analytical and technological services for companies involved in activities related to chemicals, life science & plastics

Flanders (2023)

€ 53,8 billions turnover

66.184 direct jobs

31% of Flanders exports

€ 2,9 billions in R&D

Source : essenscia

Wallonia (2023)

€ 12,4 billions turnover

24% of industrial employment

30.365 direct jobs

68.000 indirect jobs

€ 3,4 billions in R&D

Hauts-de-France (2021)

29.000 direct jobs

500 different companies (95% SMEs)

3rd region in France in term of employees

Grand Est (2021)

15.894 employés,

370 different companies

Source : France Chimie

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ENVIRONMENT

Air quality
Health & safety
Energy
Circular Economy

MATERIALS

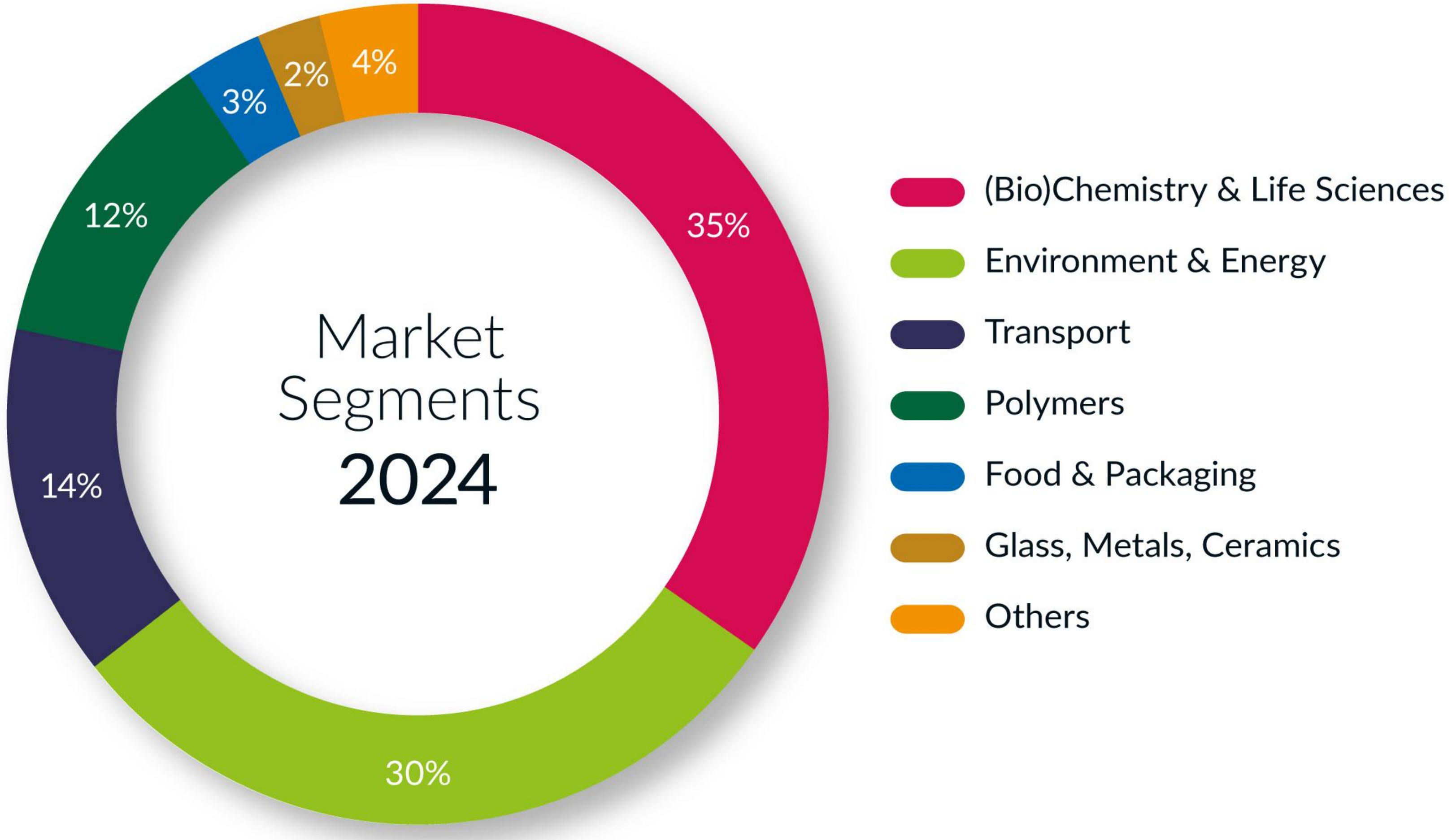
(Bio-based) polymers & composites
Emissions and odours from materials
Lightweight materials
Mechanical Recycling

CHEMISTRY & INDUSTRIAL PROCESSES

Micro / Meso fluidic technologies
Catalysis and synthesis
Chemical Recycling

ANALYTICAL & TECHNOLOGICAL SERVICES

Extended characterization platform / reverse engineering
Pilot equipment
Products and processes improvement



750 industrial contracts in 2024

34 employees

1780 industrials partners since 2000

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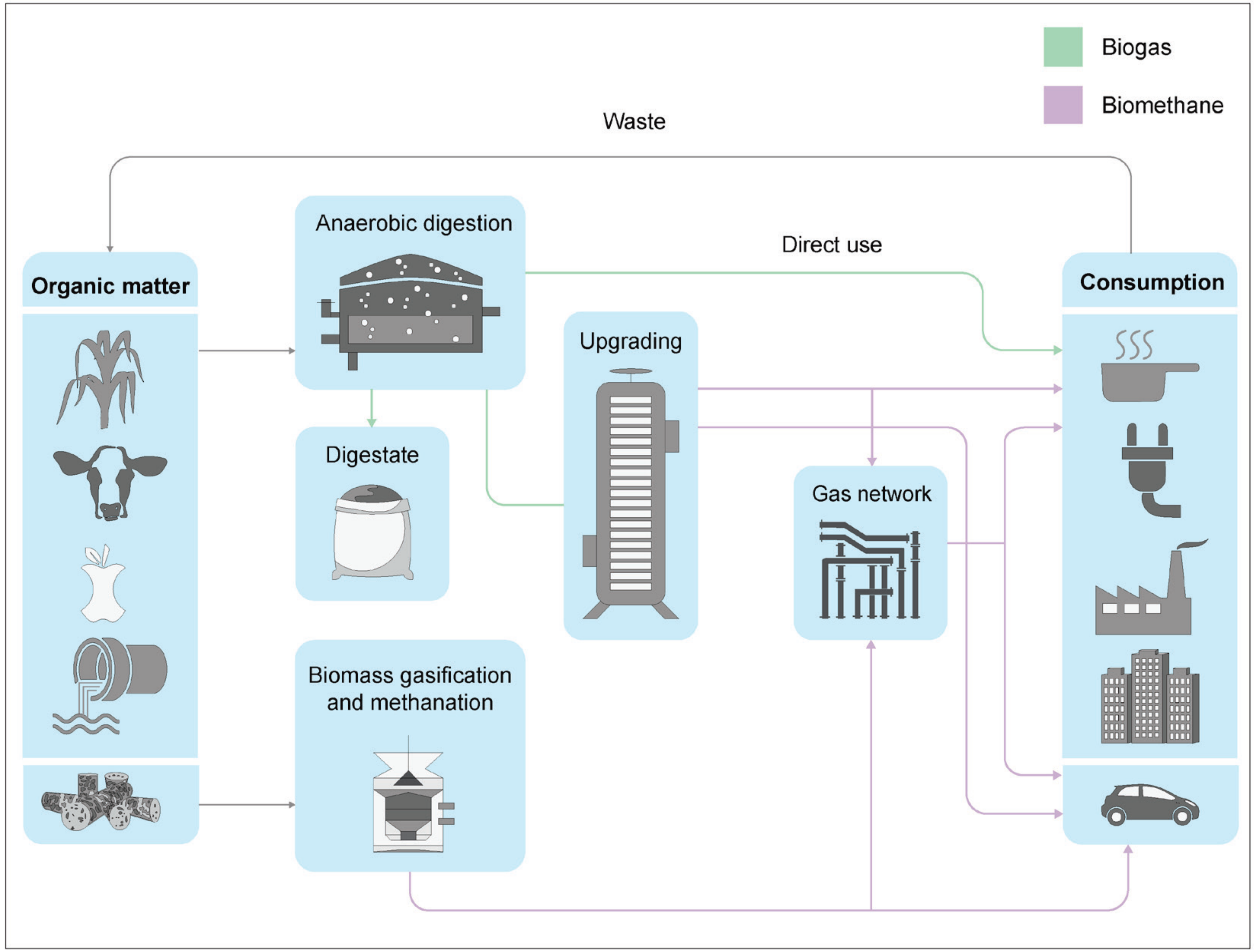
So, what is biogas ?

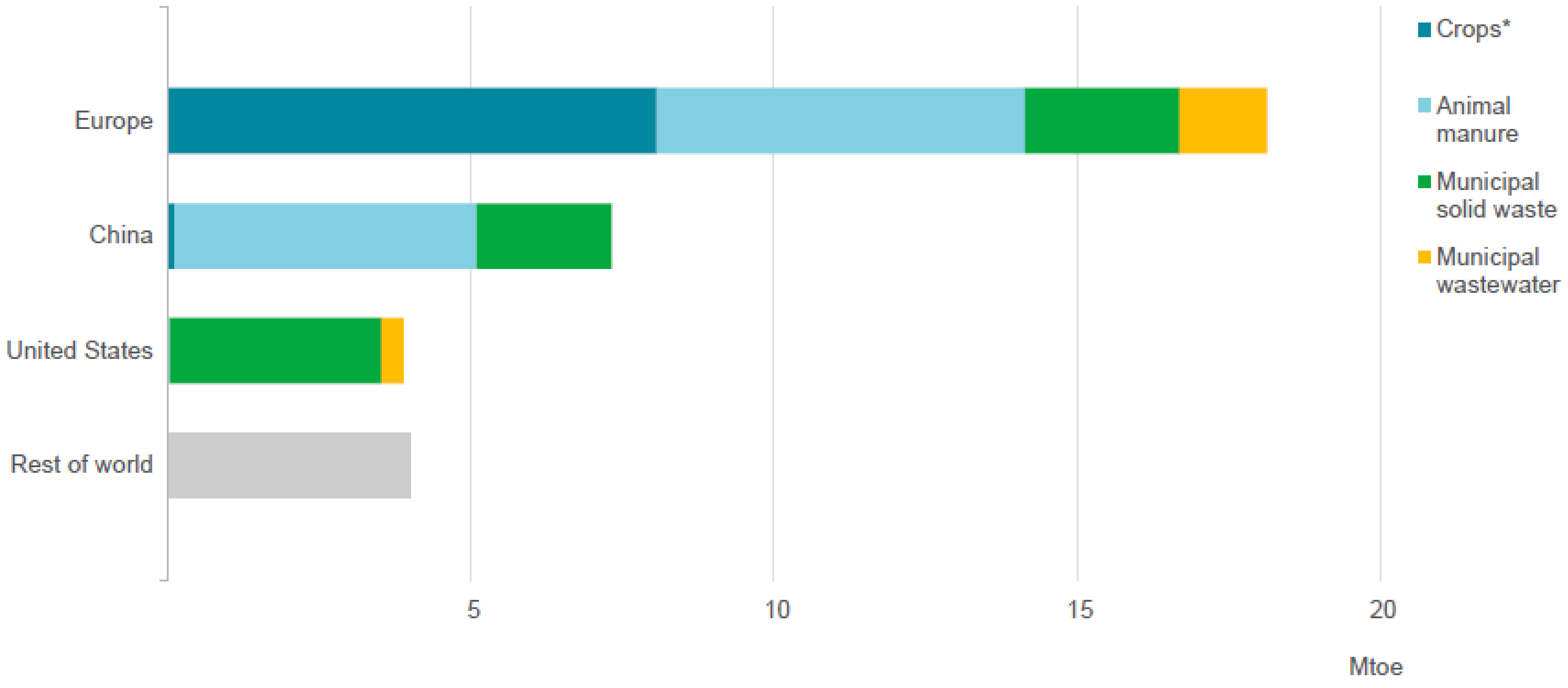
According to Wikipedia : A gaseous energy source produced from raw materials such as agricultural waste, manure, municipal waste, plant material, green waste, wastewater, and food waste. Biogas is produced by anaerobic digestion with anaerobic organisms or methanogens inside an anaerobic digester or bioreactor.

According to the European Environment Agency : A gas, rich in methane, which is produced by the fermentation of animal dung, human sewage or crop residues in an air-tight container. Biogas fuels do not usually cause any pollution to the atmosphere, and because they come from renewable resources they have great potential for future use.

https://www.eea.europa.eu/help/glossary/eea-glossary/biogas

Where does it come from ?





About feedstock :

Crops – Residues from wheat, maize, rice, sugar beet, sugar cane, soybean, oilseeds, do not compete with food

Animal manure – Cattle, pigs, poultry, sheep

Organic waste – Food, leaves, paper, cardboard, wood

Waste water – semi-solid organic material from treatment plants

Outlook for biogas and biomethane – prospect for organic growth, IEA

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How is biogas obtained – in one slide ?

Forth steps process, close to our own digestion actually

Hydrolyse long molecules into short ones using so called aquatic bacteria

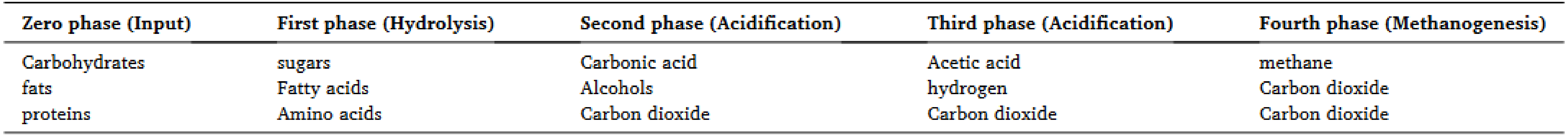
Breakdown of these molecules into so called volatile acids

Third phase consist in converting those into molecules suitable for methanogenesis

Methanogenic bacteria convert molecules in methane and CO_2

Final products : biogas, liquid/solid phase (digestate, used as soil amendment, contains notably minerals – N, K, P, Ca,… – and nutriments (Zn, Cu, Fe,…)

https://www.lalibre.be/network/entreprises/2024/03/01/le-hainaut-a-la-chance-davoir-du-biogaz-DTZPCUDHD5GQ5A463CXVN22OQ4/



Zero phase (Input)	First phase (Hydrolysis)	Second phase (Acidification)	Third phase (Acidification)	Fourth phase (Methanogenesis)
Carbohydrates	sugars	Carbonic acid	Acetic acid	methane
fats	Fatty acids	Alcohols	hydrogen	Carbon dioxide
proteins	Amino acids	Carbon dioxide	Carbon dioxide	Carbon dioxide

Jameel *et al.*, *Results in Chem.*, **2024**, *7*, 101549

Not what we will discuss today – still a very interesting topic:

Taken into account in the OBIWAN project

Please refer to Prof. André Pauss' Team from UTC Compiègne on that matter

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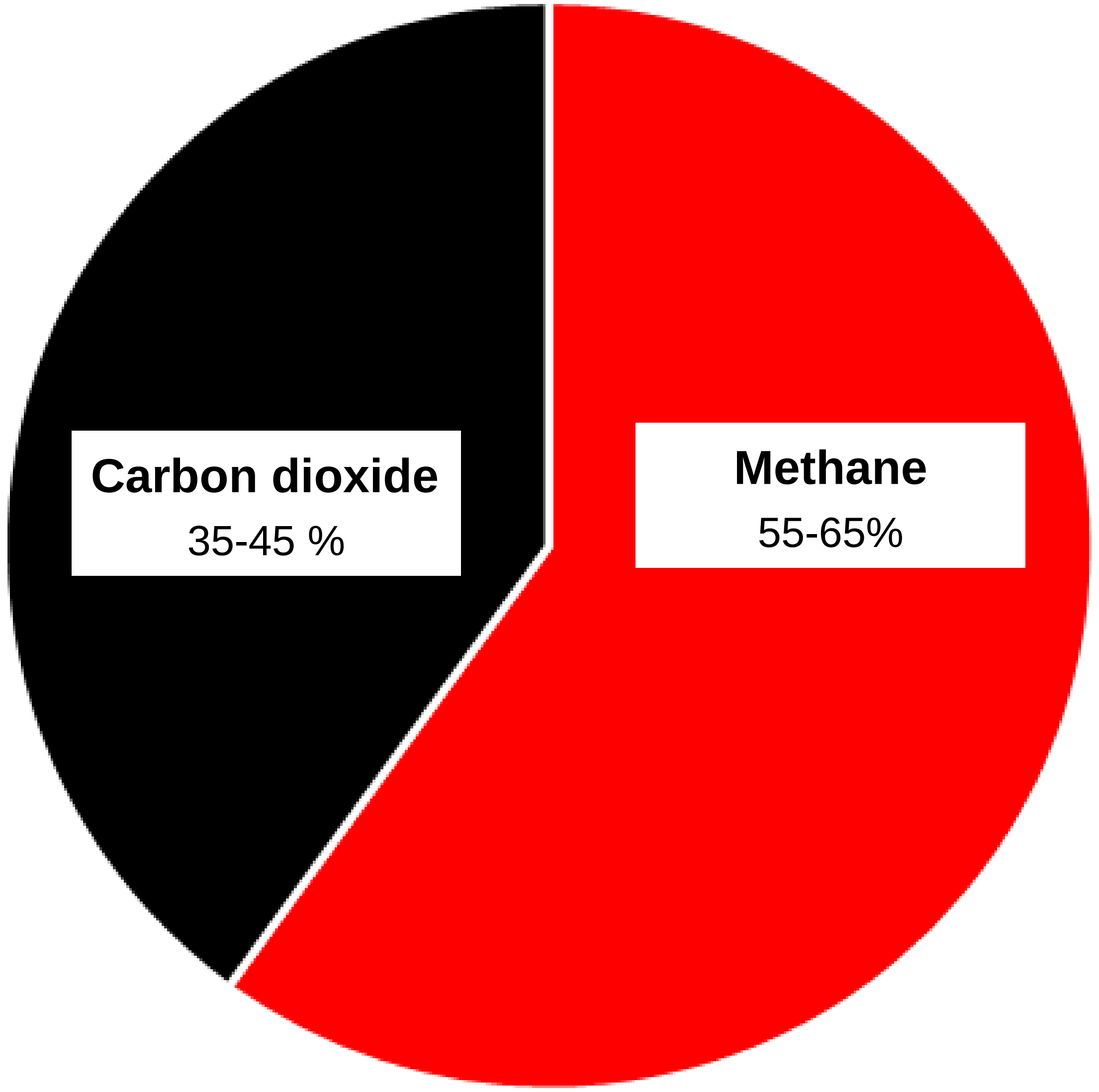
What is its general composition – CO_2 and methane

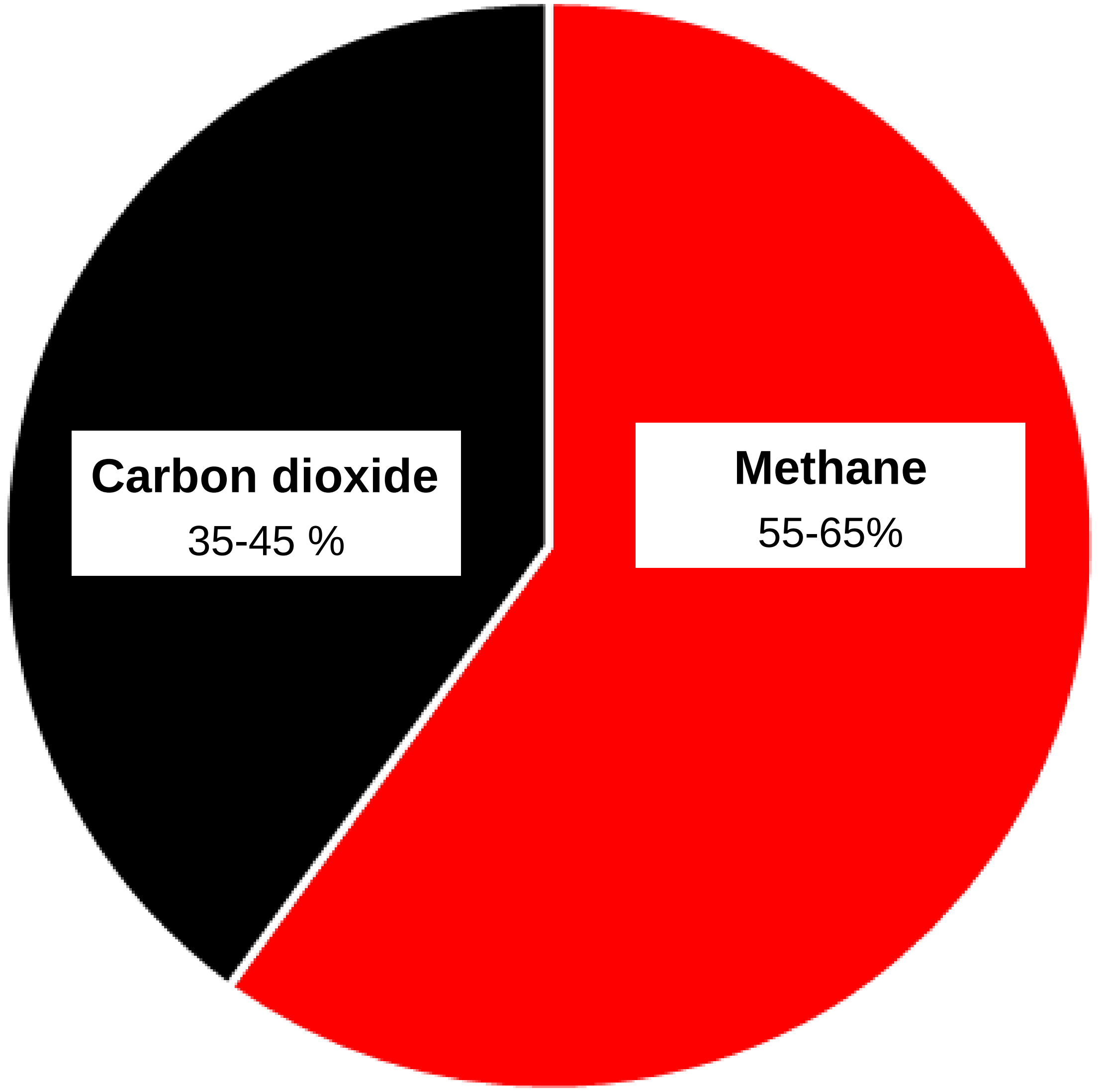


Spoiler alert : note that this pie-graph is inaccurate and will be updated in a few slides

Methane – often wrongfully referred to as “Natural Gas”

Used as fuel, for heater, heat our stove or water, heat turbine, steam boiler, …
Heat value of **55MJ/kg and 39,8MJ/m^3** vs. 142MJ/kg and 12,7MJ/m^3 for H_2, making it a very valuable source of energy [www.engineeringtoolbox.com]
Methane is responsible of one third of the global warning today and is warming potential is **80 times greater than CO_2** according to UN [UN environment programme]

What is its general composition – CO_2 and methane



Carbon dioxide – the usual suspect of GHW effect

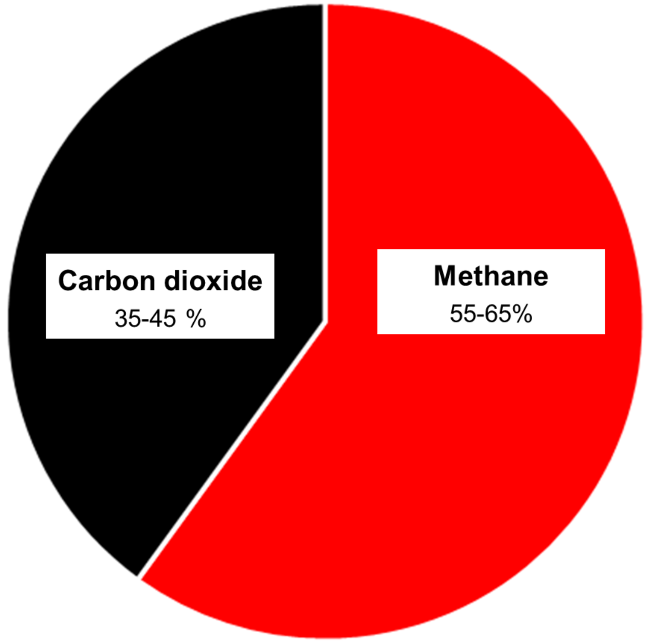
Extremely stable gas, often generated by oxidative combustion of carbon-based materials
Heat value of **0MJ/kg**, you just cannot burn it as it is fully oxidised
CO_2 is a well-known contributor to greenhouse effect and most process should consider should consider its capture either for storage (CCS) or for its valorisation (CCUS)

Conversion of CO_2 is a very hot topic these days :

Taken into account in the OBIWAN project

For instance refer to Prof. Andreï Khodakov to come

What is its general composition – CO_2 and methane



Based on these previous information :

Methane is a very efficient fuel, CO_2 is not at all, so mixtures are intermediates
Methane has a lower heat value of 50MJ/m³, $\text{biogas}_{75\%CH4}$ 28MJ/m³ and $\text{biogas}_{45\%CH4}$ generates 16MJ/m³ [https://knowledge4policy.ec.europa.eu/glossary-item/biogas_en]
Therefore, both biogas and its upgraded version can be used as fuels

Some interesting data [International Energy Agency]:

Biotmethane is today about 0,1% of natural gas demand, meaning 3,5Mtoe (million of ton oil equivalent)
Ratio of upgraded biogas is highly region dependant (35% S.Am., 15% N.Am., 10% Europe, 2% Asia)
It is however crucial for non energy valorisation (and legislation may change as well…)

Upgrade of CO_2 is an important stage of biogas valorisation:

Taken into account in the OBIWAN project and CO_2/CH_4 separation will be the subject of one specific presentation by Certech

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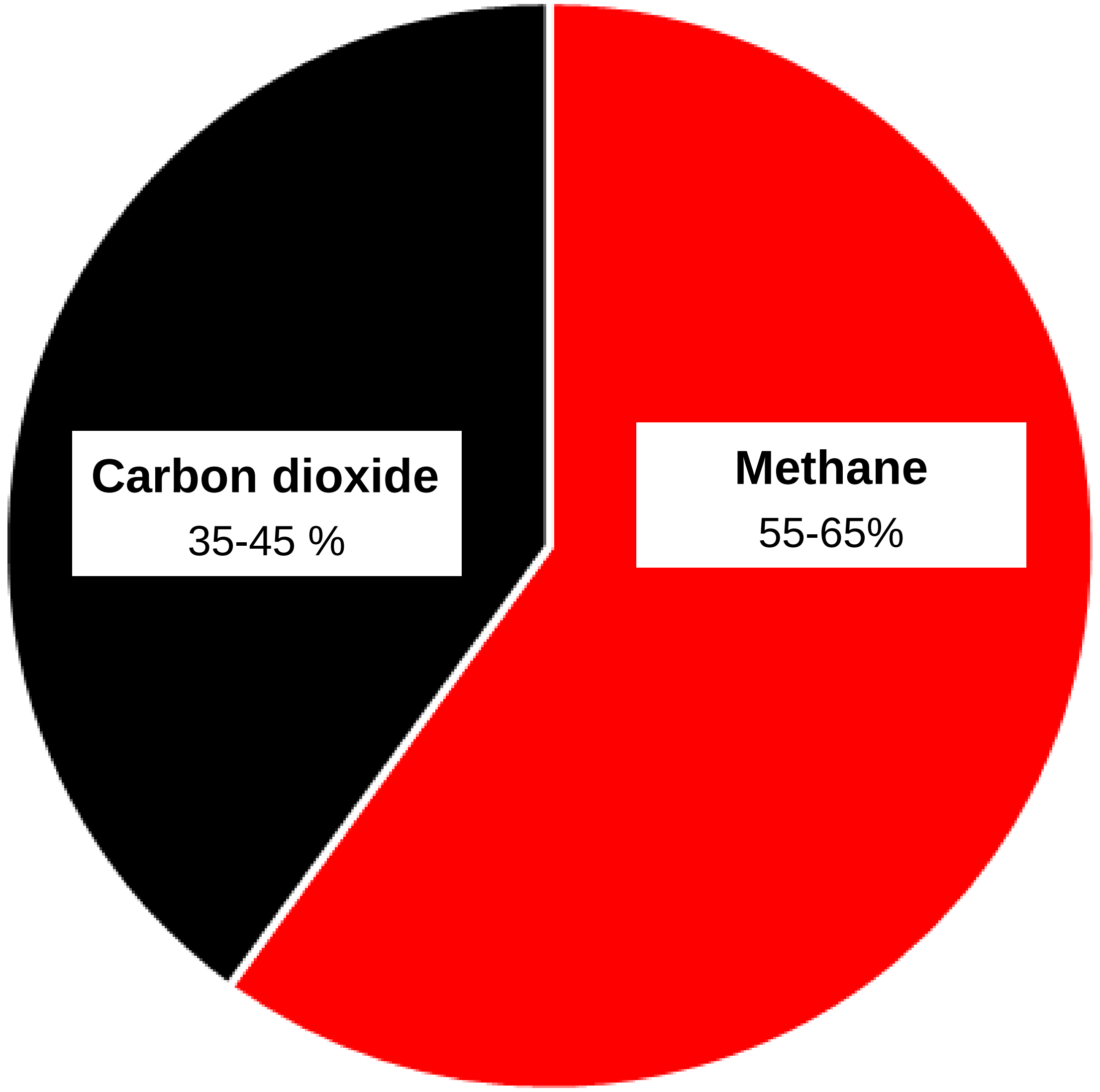
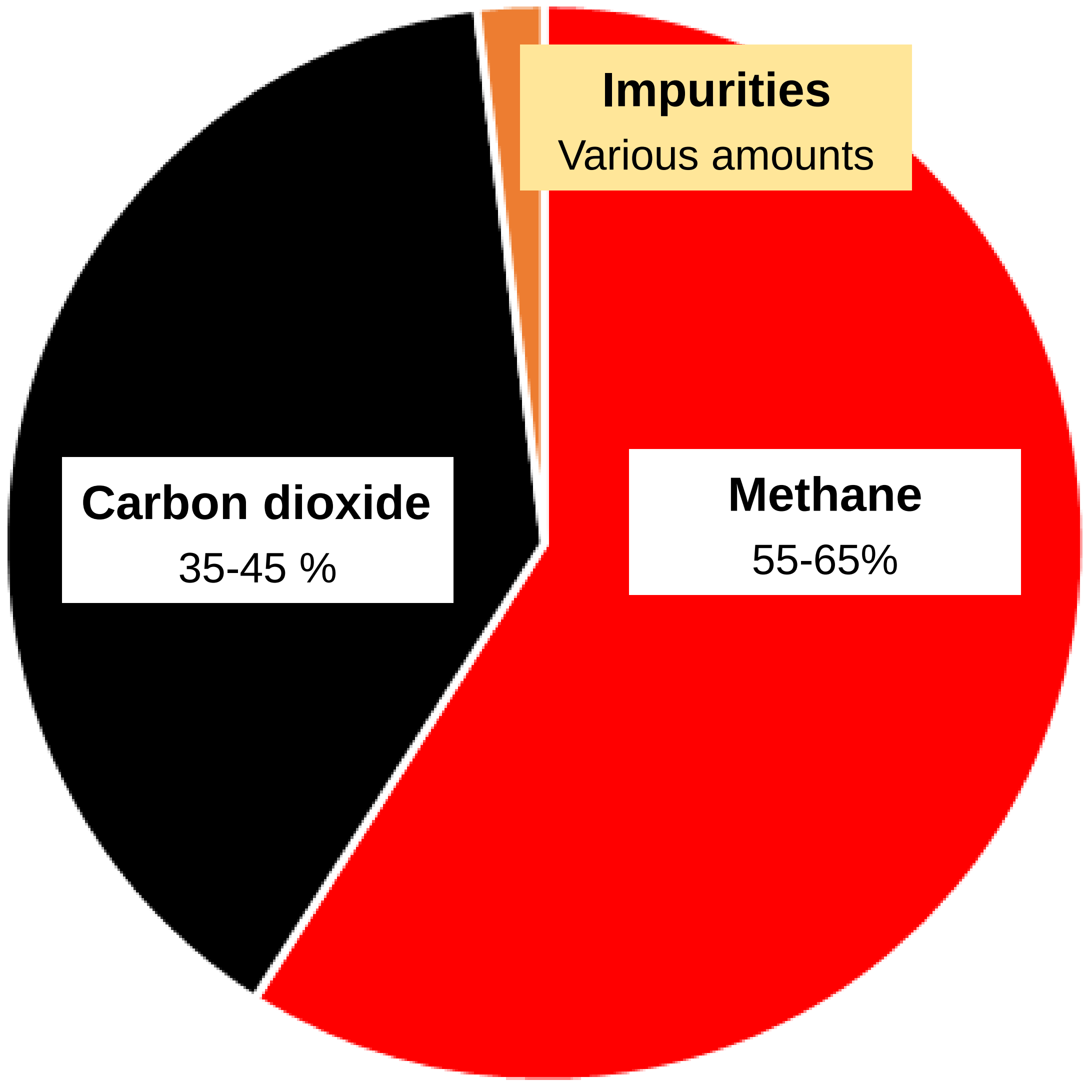
What is its real composition – the truth revealed

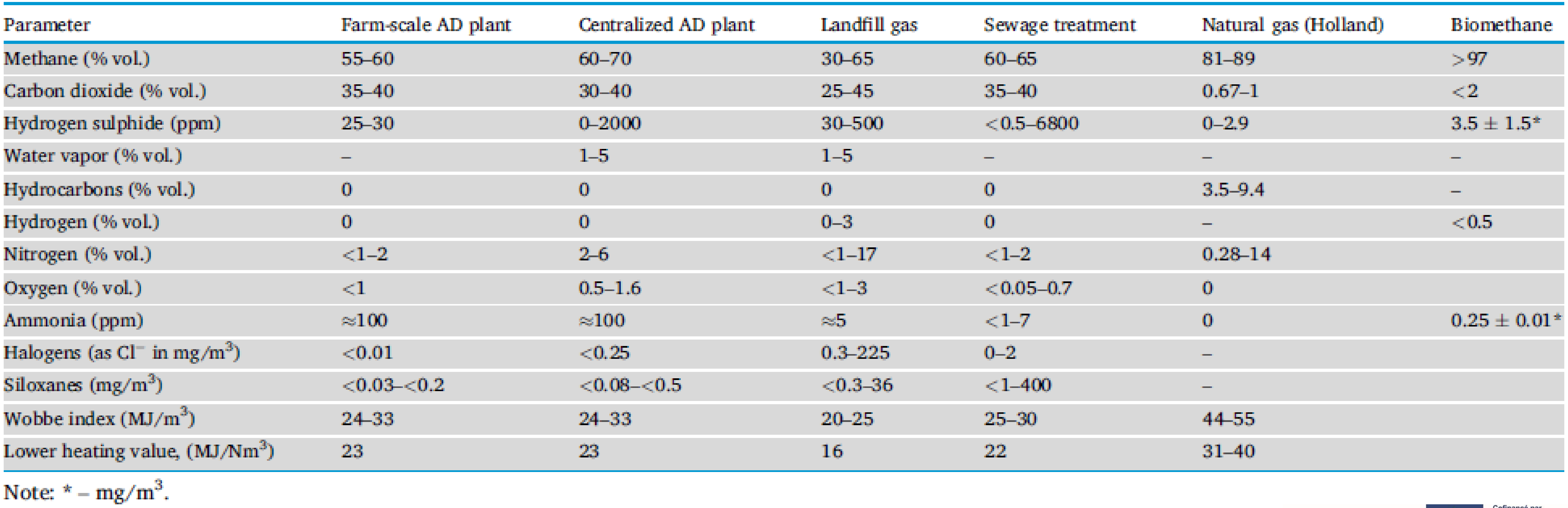




Impurities are also present in the biogas and is in some cases highly problematic (and that’s the object of this presentation)

What are the impurities present in biogas ?

The nature and the amount of the impurities highly depends on the process used for the biogas production



Parameter	Farm-scale AD plant	Centralized AD plant	Landfill gas	Sewage treatment	Natural gas (Holland)	Biomethane
Methane (% vol.)	55–60	60–70	30–65	60–65	81–89	>97
Carbon dioxide (% vol.)	35–40	30–40	25–45	35–40	0.67–1	<2
Hydrogen sulphide (ppm)	25–30	0–2000	30–500	<0.5–6800	0–2.9	3.5 ± 1.5*
Water vapor (% vol.)	–	1–5	1–5	–	–	–
Hydrocarbons (% vol.)	0	0	0	0	3.5–9.4	–
Hydrogen (% vol.)	0	0	0–3	0	–	<0.5
Nitrogen (% vol.)	<1–2	2–6	<1–17	<1–2	0.28–14	
Oxygen (% vol.)	<1	0.5–1.6	<1–3	<0.05–0.7	0	
Ammonia (ppm)	≈100	≈100	≈5	<1–7	0	0.25 ± 0.01*
Halogens (as Cl^- in 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	

Note: * – mg/m^3.

Reproduced from A.A. Werkneh, *Heliyon*, **2022**, *8*, e10929

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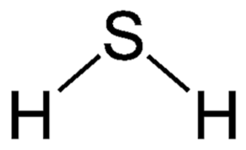
Such impurities can be highly problematic

Hydrogen sulfide –



- Highly odorous chemical (rotten egg) even at low concentration (0,0008-0,2 mg/m³)
- Toxic by inhalation (from headache at 0,008 ppm to neurological effect as low as 20 ppm in air), labelled as fatal by inhalation (nerve poison)
- Hazardous for environment, with for instance acid rains, corrosive for pipelines
- Generate process problem including corrosion or poisoning of eventual catalysts as well as killing some adsorption processes

World Health organisation, Government of Western Australia dpt of Health

MSDS from Airgas, an Air Liquide Company

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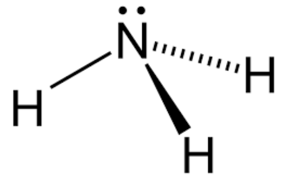
Such impurities can be highly problematic

Ammonia –



- Bad smell (urine, detection limit 5-53 ppm), harmful to health
- Kills anaerobic bacteria so not good if present during the digestion process
- Convert into NOx during combustion (generating smog, acid rains, harmful to health,…)
- Generate process problem including corrosion when presence of water (less than H_2S)

National institutes of health,

MSDS from Airgas, an Air Liquide Company

Such impurities can be also problematic

Water –

- Wet gas is not nice to burn and water accumulates in pipelines…
- Water generates corrosion with NH_3 and acid rains with H_2S, potential freezing,…

Nitrogen –

- Decrease the quality of the biogas during combustion, toxic to anaerobic bacteria

Siloxanes –

- Damages the equipment by forming SiO_2 and quartz during combustion, abrasion,…

Particles –

- Can plug the equipment as well as the adsorbing systems

VOCs –

- Can be toxic, can affect elastomers or plastics, can form soot during combustion, safety for end-user…

Atelge *at al.*, *Sustainability*, **2021**, *13*, 11515

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Purification of biogas – H_2S

As mentioned, hydrogen sulfide is an highly problematic compound, and generally no more than 10 ppm for kitchen stove or 50-500 ppm for combustion engines Jbiogas upgrading, Evaluation of méthodes for H_2S removal, Danish Technological Institute, 20014

Most popular methods of purification consist in chemical and physical capture of the sulfur compound

- Adsorption methods
- Absorption methods (sometimes referred to as scrubbing)
- Membrane separation
- Precipitation

Purification of biogas – H_2S – adsorption

Generalities about adsorption

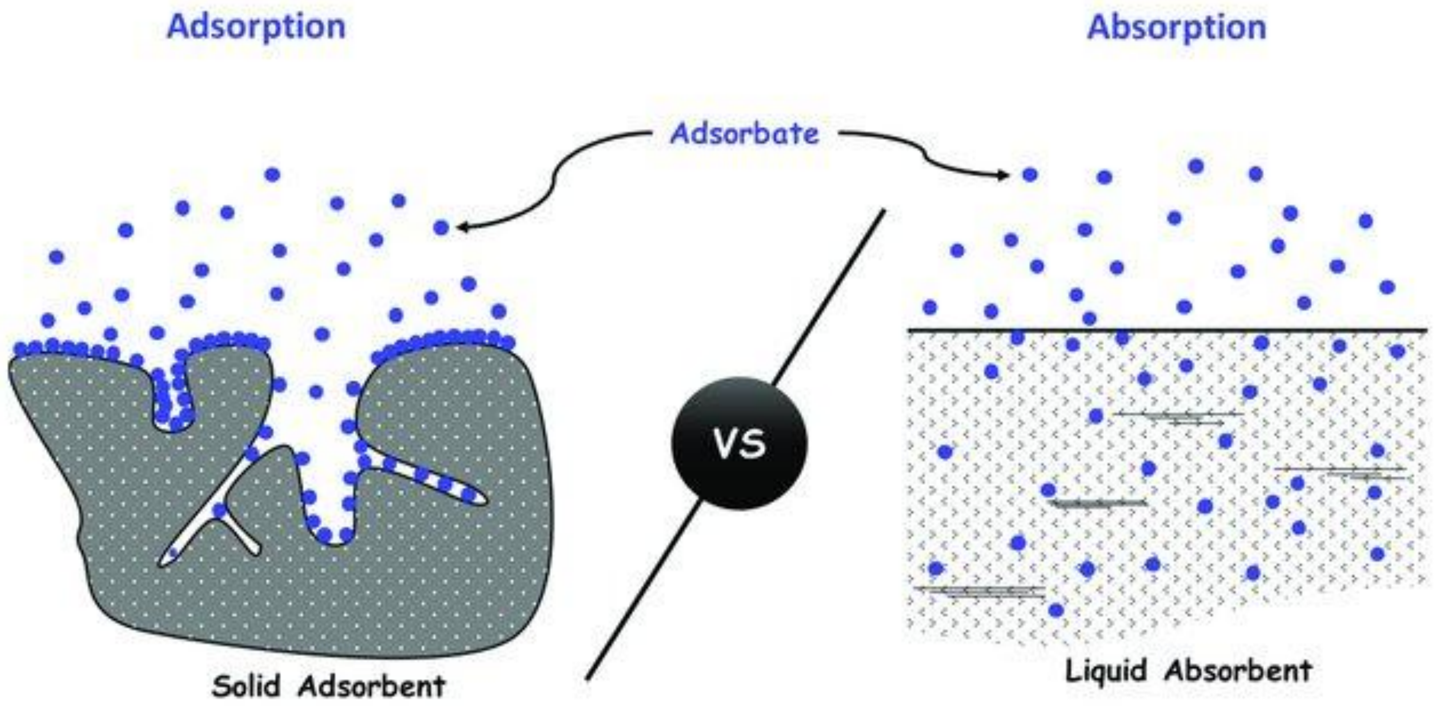
A**d**sorption consist in trapping a compound **on the surface** of a specific solid in opposition to a**b**sportion where the product diffuse in the bulk of the material

Key point of an adsorbant

Good specific surface and porosity

Well-known for biogas purification

Can imply physical effect (formation of weak physical interaction VdW, ionic,…) and/or chemical effect (creation of chemical bounds)



Zbair *et al.*, *Energies*, **2021**, *14*(11), 3105

Purification of biogas – H_2S – adsorption

Generalities about adsorption of H_2S for biogas

Adsorption systems are generally suitable for flow rates 10-10,000 m³/h with a pollutant concentration around 0,1-8 g/m³ Biotechnologiy for odor and air pollution, Eds. Z. Shareefseen, A. Singh, Springer-Verlaag Berling Heidelber 2005

Historically used on facilities capturing less than 200 kg/S per day

As the pollutant is blocked on the surface and in the pore of the materials, a saturation limit exist and reactivation procedure must be implemented

Traditional adsorbents for H_2S include impregnated activated charcoal and iron-oxide or hydroxide

Purification of biogas – H_2S – adsorption with AC

- H_2S can be trapped by physical adsorption
- H_2S can better trapped when the Activated Charcoal is impregnated
- Impregnated by species that partially oxidise H_2S in the presence of air (20-30% moisture and oxygen)

$$2\ H_2S + O_2 \rightarrow \tfrac{1}{4}\ S_8 + 2\ H_2O$$

- Species to be impregnated include KI, NaOH, KOH, Na_2CO_3, $KMnO_4$,…
- Update to 120/140 kgH_2S/m^3 vs. 10-20 kgH_2S/m^3 if virgin carbon but recycling

https://norit.com/applications/biogas-rng/hydrogen-sulfide-removal2005

Purification of biogas – H_2S – adsorption with Fe (III)

- H_2S be converted in iron sulfide, a solid specie thus removed from the gas phase

  $Fe_2O_3 + 3\ H_2S \rightarrow Fe_2S_3 + 3\ H_2O$ (from Iron (III) oxide to Iron (III) sulfide)

  $2\ Fe(OH)_3 + 3\ H_2S \rightarrow Fe_2S_3 + 6\ H_2O$ (from Iron (III) hydroxide)

- Reaction are endothermic, performed around 25-50°C for residence 1-15 min
- Performed with $[H_2S]$ up to 100ppm with reduction rate up to 99%, water can generate sticking of the material via condensation, decreasing efficiency
- Material is regenerated by an highly exothermic process, generating S(0)

  $2\ Fe_2S_3 + 3\ O_2 \rightarrow 2\ Fe_2O_3 + 6\ S$

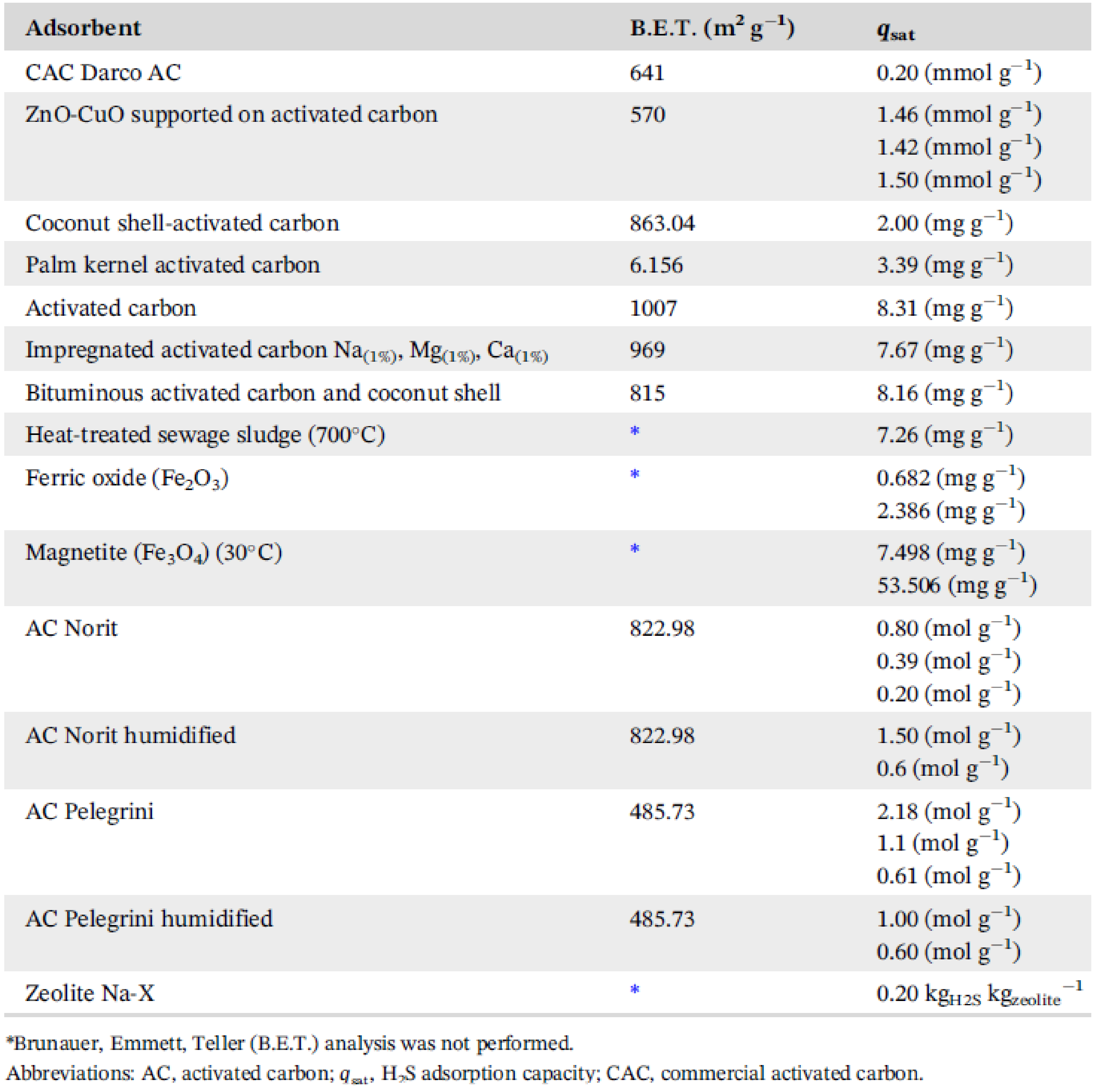
Biogas Fundamentals, process and Operation, Eds. M. Tabatabeai, H. Ghanavati, Springer, Cham, Switzerland

Limited regeneration because surface will be covered by sulfur

Specific Iron oxide are commercially available using different optimisation (Sulfatreat, Soxia, Sulfa-Bind,…)

Purification of biogas – H_2S – study of some materials

Measurement of H_2S adsorption capacity of some classical materials

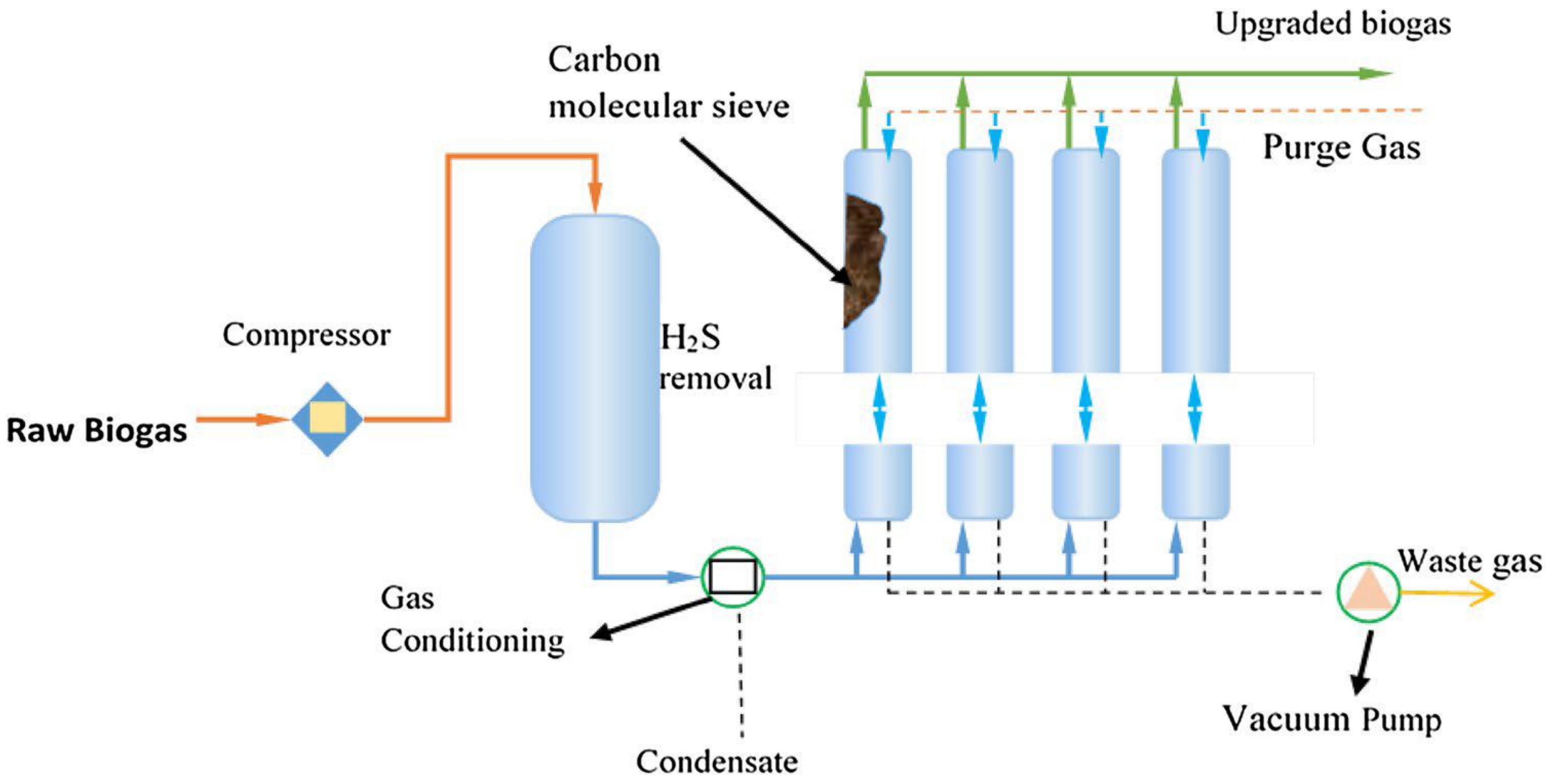


Adsorbent	B.E.T. ($m^2\ g^{-1}$)	q_{sat}
CAC Darco AC	641	0.20 ($mmol\ g^{-1}$)
ZnO-CuO supported on activated carbon	570	1.46 ($mmol\ g^{-1}$) 1.42 ($mmol\ g^{-1}$) 1.50 ($mmol\ g^{-1}$)
Coconut shell-activated carbon	863.04	2.00 ($mg\ g^{-1}$)
Palm kernel activated carbon	6.156	3.39 ($mg\ g^{-1}$)
Activated carbon	1007	8.31 ($mg\ g^{-1}$)
Impregnated activated carbon $Na_{(1\%)}$, $Mg_{(1\%)}$, $Ca_{(1\%)}$	969	7.67 ($mg\ g^{-1}$)
Bituminous activated carbon and coconut shell	815	8.16 ($mg\ g^{-1}$)
Heat-treated sewage sludge (700°C)	*	7.26 ($mg\ g^{-1}$)
Ferric oxide (Fe_2O_3)	*	0.682 ($mg\ g^{-1}$) 2.386 ($mg\ g^{-1}$)
Magnetite (Fe_3O_4) (30°C)	*	7.498 ($mg\ g^{-1}$) 53.506 ($mg\ g^{-1}$)
AC Norit	822.98	0.80 ($mol\ g^{-1}$) 0.39 ($mol\ g^{-1}$) 0.20 ($mol\ g^{-1}$)
AC Norit humidified	822.98	1.50 ($mol\ g^{-1}$) 0.6 ($mol\ g^{-1}$)
AC Pelegrini	485.73	2.18 ($mol\ g^{-1}$) 1.1 ($mol\ g^{-1}$) 0.61 ($mol\ g^{-1}$)
AC Pelegrini humidified	485.73	1.00 ($mol\ g^{-1}$) 0.60 ($mol\ g^{-1}$)
Zeolite Na-X	*	0.20 $kg_{H2S}\ kg_{zeolite}^{-1}$

*Brunauer, Emmett, Teller (B.E.T.) analysis was not performed.

Abbreviations: AC, activated carbon; q_{sat}, H_2S adsorption capacity; CAC, commercial activated carbon.

Oliveira *et al.*, *Canadian J. Chem. Eng.*, **2023**, *101*, 2361-2390



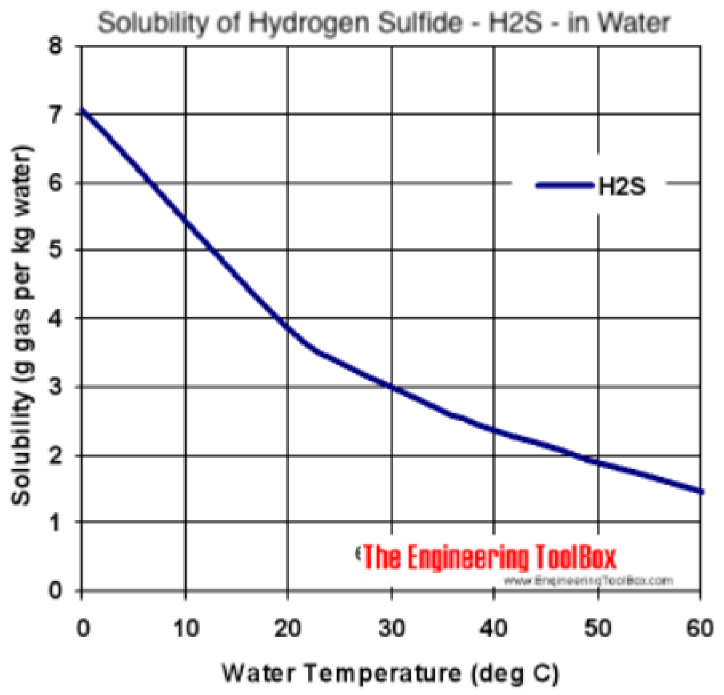
Regeneration by steam injection in general

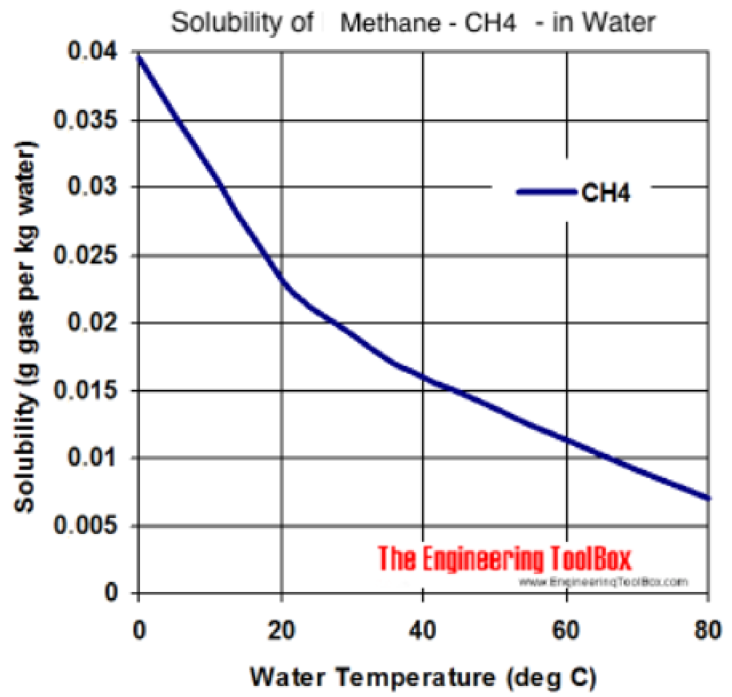
Replacement of adsorbent if it is fully coated by sulphur for instance

Water and dust to be removed prior to adsorption

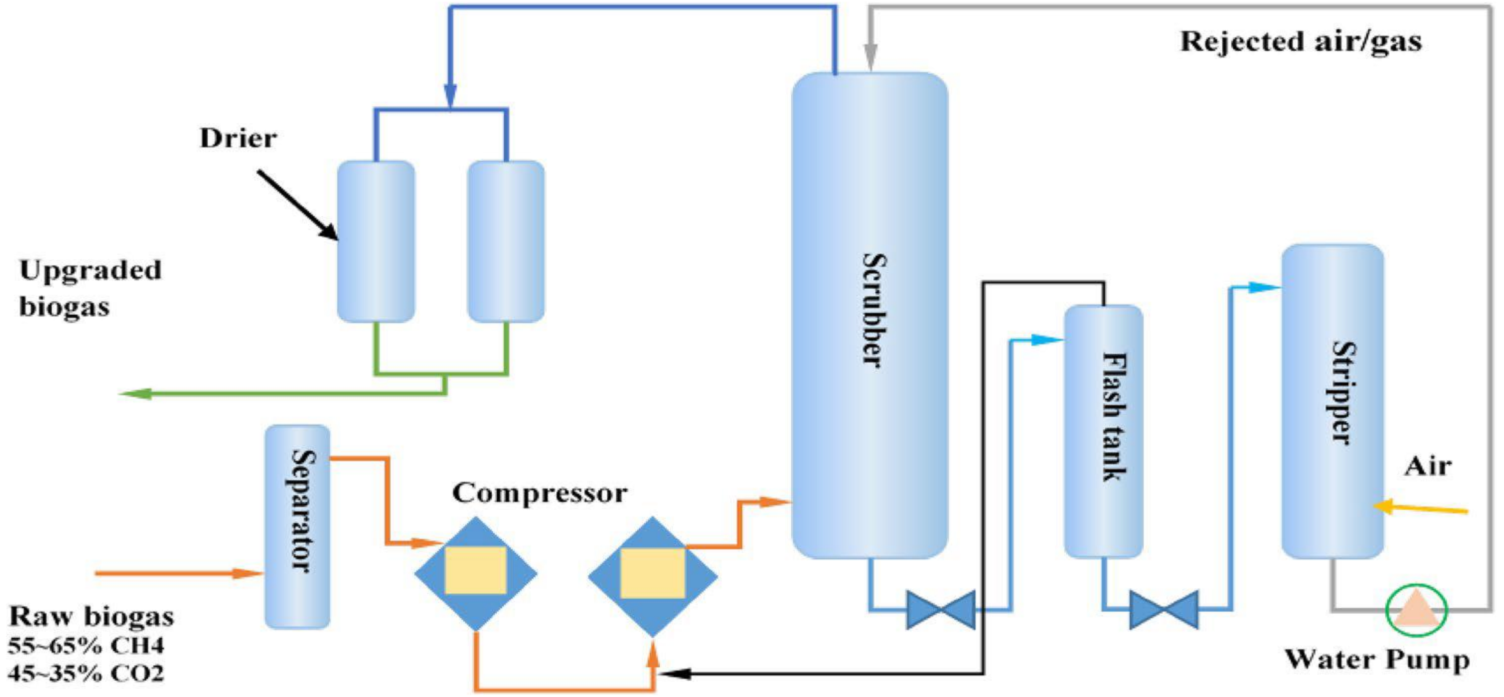
Purification of biogas – H_2S – use of scrubbers - water

- H_2S can be removed using a liquid phase, called scrubber
- Water can be used to “wash” the gas, removing impurities such as H_2S or CO_2
- Hydrogen sulfide is 80 times more soluble than methane in water





https://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html



Awe *et al.*, *Waste Biomass Val.*, **2017**, *8*(2), 267

- Concept is generally to use high pressure processes to concentrate H_2S
- Process can be regenerative or not, but not regenerative need high volume of water (150l/Nm³), 10 times less if regenerated

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Jbiogas upgrading, Evaluation of méthodes for H_2S removal, Danish Technological Institute, 2014

Purification of biogas – H_2S – use of scrubbers - chemicals

- Other scrubbers can be used by means of either physical or chemical capture

1°) Organic solvents with high affinity to H_2S can be used for physical capture, including ethylene glycols, propylene carbonate,… the most common one being used for Selexol^{TM} processes (polyglycol dimethyl ethers) owned by UOP

2°) Catalytic solutions can be used for chemical stripping for instance using redox reaction with Iron (III) with chelatant such as EDTA for instance

$$H_2S + 2\,[Fe^{3+}] \rightarrow S + 2\,[Fe^{2+}] + 2\,H^+$$

The chelatant prevent the precipitation of iron sulfide so Fe^{2+} can the be reoxidised using air stripping

$$2\,[Fe^{2+}] + 2\,H^+ \rightarrow 2\,[Fe^{3+}] + H_2O$$

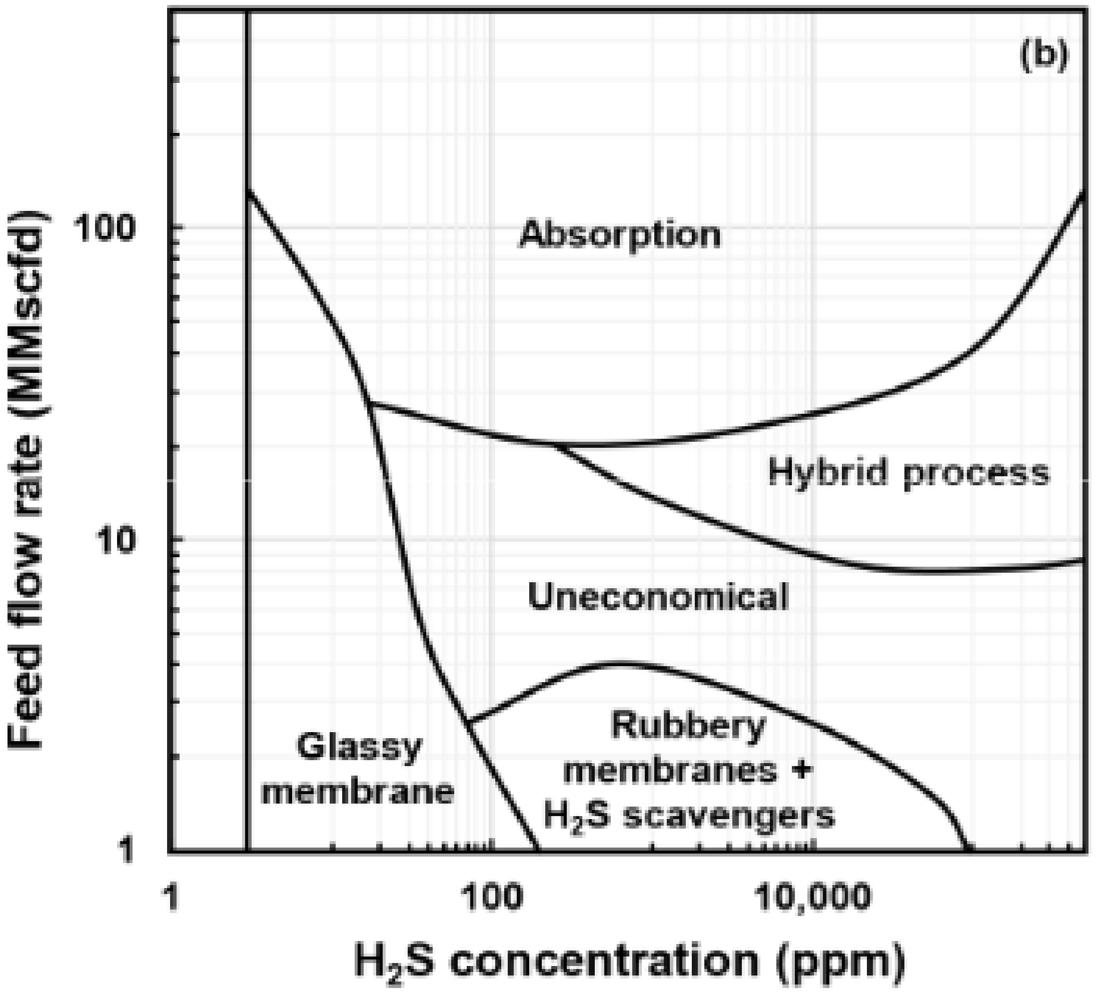
Issues with potential clogging or foaming but commercial systems are available

Biogas upgrading, Evaluation of méthodes for H_2S removal, Danish Technological Institute, 2014

Purification of biogas – H_2S – membrane separation

Membranes can be used to separate H_2S from CH_4

- Various effect can occur including solution-diffusion and size exclusion effect (later not very good for CH_4/H_2S)
- Selectivity is key to prevent CH_4 loss (and thus cost)
- Specific problem like H_2S induced plasticization or aging can occur



Polymer	H_2S/CH_4 Selectivity	CO_2/CH_4 Selectivity	Strategies for Improving Sour Gas Performance
CA	20–25	15–20	Limited scope for improvement. Best suited to sweet natural gases.
Polyimide	20–25	~30	Crosslinking to improve resistance to H_2S plasticization.
Microporous polymers	>50	~10	Incorporation of functional groups to improve CO_2 and H_2S solubility. Limited scope for improving CO_2/CH_4 selectivity.
PEO	>50	~10	Crosslinking, sub-ambient operation may improve CO_2/CH_4 selectivity.

Rao *et al.*, *Energies*, **2023**, *16*, 5713

Purification of biogas – H_2S – precipitation

- It is possible to decrease the amount of H_2S in the gas by trapping it directly during the fermentation by :

1°) Adding Fe(II)Cl_2 (liq.) or, less employed Fe(III)$(OH)_3$, Fe(II)$(OH)_2$ or Fe(III)Cl_3

- Fe(II)+ + $S^{2-} \rightarrow FeS$
- $2\,Fe(OH)_3 + H_2S \rightarrow 2\,Fe(OH)_2 + S + H_2O$ then $Fe(OH)_2 + H_2S \rightarrow FeS + 2\,H_2O$
- $2\,FeCl_3 + 3\,H_2S \rightarrow 2\,FeS\,(sol) + S\,(sol) + 6\,HCl$

Considered as partial removal (max 100ppm at the end)

2°) Bacteria (such as Thiobacilius) can be use to perform oxidation of H_2S into S(0) or sulphate. Nutriments will be performed by the digestate and O_2 will be obtained by adding air to the mixture

Jbiogas upgrading, Evaluation of méthodes for H_2S removal, Danish Technological Institute, 2014

Purification of biogas – H_2S – summary

Method	Advantages	Drawbacks
AC (impregnated KI)	High efficiency, high purification rate Compact and high loading capacity Low operating temperature	High CAPEX and OPEX H_2O and O_2 block the sites Regeneration 450°C / possible residues
Iron(II) oxide/hydroxide	High removal efficiency Low CAPEX, compact Handle 0,3/500 kg/d of H_2S	High OPEX, sensitive to water Release dust, exothermic regeneration Reduce activity per cycle, reagent disposal
Water adsorption	Cheap if water available Remove also CO_2	Not regenerative so water treatment High pressure/low temperature
Membrane	High removal capacity, can also remove CO_2	Expensive OPEX and maintenance Hignly complex solution
Iron Chlorides in digester	Cheap investment, low energy and heat, cheap operation cost (0,024€/m³), remove H_2S prior to other operations, form S(0)	Low efficiency, expensive materials (Fe), changes the pH condition of the digestion, correct dosing is difficult and process generaly requires specialised supervision

Awe *et al.*, *Waste anf Biomass Valor.*, **2017**, *8*(2), 267

Purification of biogas - water

Water can be added during the purification process, for example often saturated after desulfurisation (5%$_{w/w}$ at 35°C) and should be addressed

Ryckebosch *et al.*, *Biomass and Bioenergy*, **2011**, *35*(5), 1633-1645

- Water can be also removed by absorption (glycols, $CaCl_2$ sol.,…) or use of dessicants (silica gel, molecular sieves, …) with same issues as previously. Note that some adsorbent like AC can multitask. Solvents like glycols can be used as well. Two column systems are the common way to go.
- Water can be used by cooling the gas to condensate it using air/water-cooled heat exchangers, chillers,…) and/or by pressurisation/expansion which is effective but can be costly

Purification of biogas – O_2, N_2

- Despite loose regulation, the minimum CH_4 regulation implies a strict control of this pollutant
- Low acceptable O_2 level in biomethane (generally <0,5%) implies the control of air intrusion during the digestion
- Expensive end-of-pipe removal generally involving PSA (AC or molecular sieves) or membrane system

Purification of biogas – ammonia

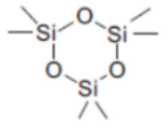
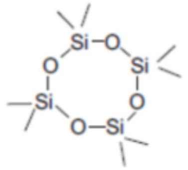
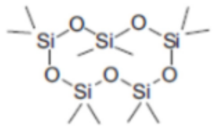
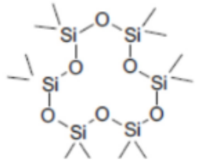
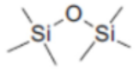
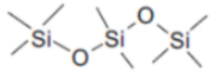
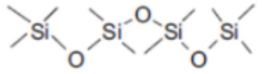
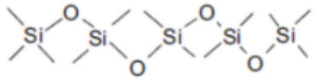
If needed, strategies for the removal of ammonia are often implemented during the fermentation process as it can inhibit anaerobic bacterias and is formed by degradation of proteins (so not end-of-line)

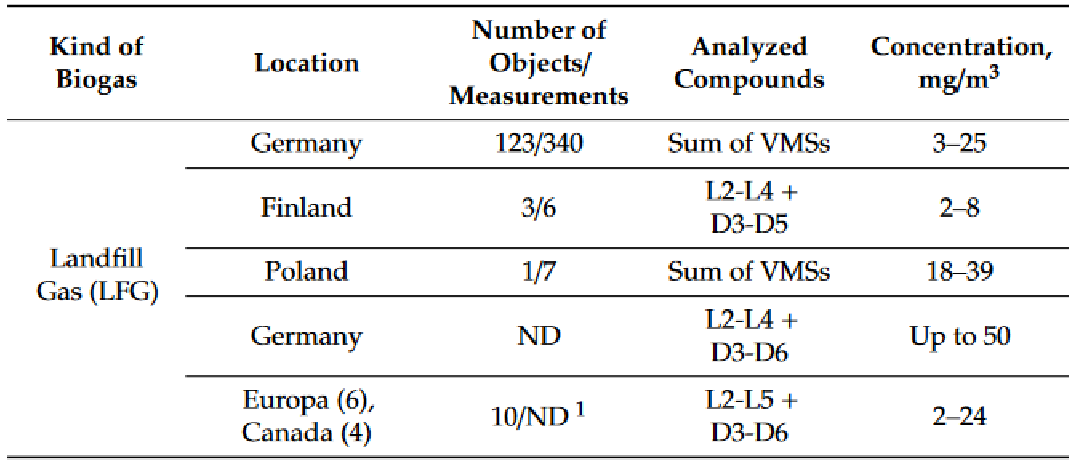
Traditional methods include :

- Bioaugmentation – add of bacteria to hinder the formation of the pollutant
- Reactive adsorption of supports that are impregnated with acid *via* formation of ammonium
- During digestion, it ammonia can be removed by continuous stripping of the biogas

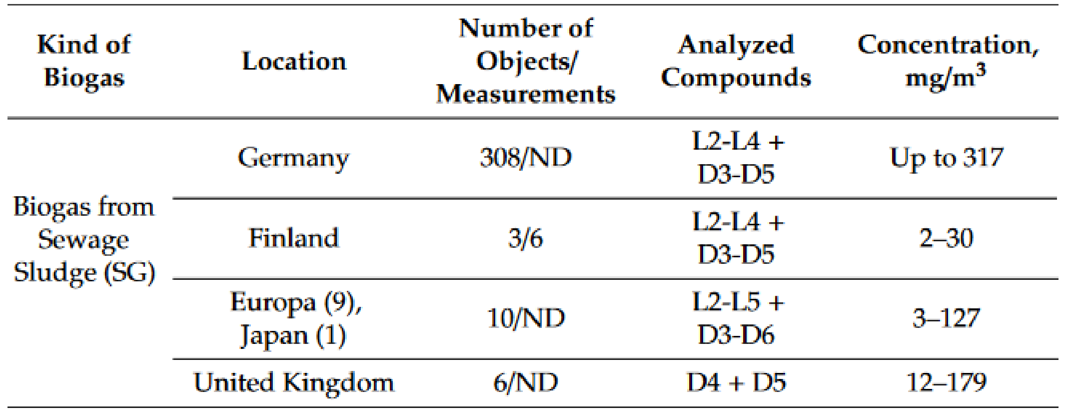
Purification of biogas – Siloxane

Siloxanes are chemicals that contains Si-O-Si functions with general formula R_2SiO and is word derivative from **sil**icium, **ox**ygen and alk**anes**. Some can be volatiles.

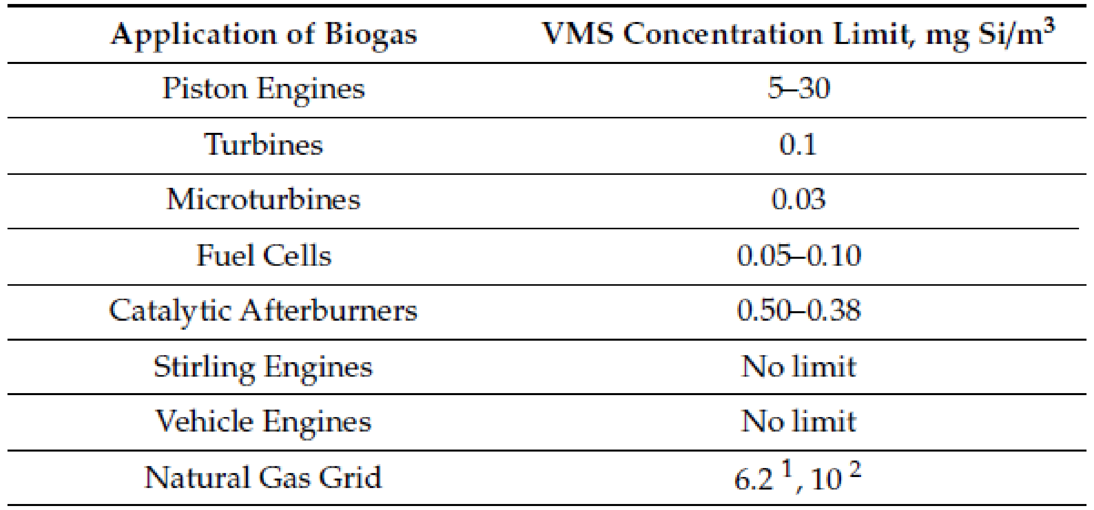
Chemical Name	Abbreviations	CAS	Chemical Formula	Structural Pattern
Hexamethylcyclotrisiloxane	D3 (HMCTS)	541-05-9	Si_3-O_3-$(CH_3)_6$	
Octamethylcyclotetrasiloxane	D4 (OMCTS)	556-67-2	Si_4-O_4-$(CH_3)_8$	
Decamethylcyclopentasiloxane	D5	541-02-6	Si_5-O_5-$(CH_3)_{10}$	
Dodecamethylcyclohexasiloxane	D6	540-97-6	Si_6-O_6-$(CH_3)_{12}$	
Hexamethyldisiloxane	L2 (HMDS)	107-46-0	Si_2-O-$(CH_3)_6$	
Octamethyltrisiloxane	L3 (MDM)	107-51-7	Si_3-O_2-$(CH_3)_8$	
Decamethyltetrasiloxane	L4 (MD_2M)	141-62-8	Si_4-O_3-$(CH_3)_{10}$	
Dodecamethylpentasiloxane	L5 (MD_3M)	141-63-9	Si_5-O_4-$(CH_3)_{12}$	



Kind of Biogas	Location	Number of Objects/ Measurements	Analyzed Compounds	Concentration, mg/m^3
Landfill Gas (LFG)	Germany	123/340	Sum of VMSs	3–25
	Finland	3/6	L2-L4 + D3-D5	2–8
	Poland	1/7	Sum of VMSs	18–39
	Germany	ND	L2-L4 + D3-D6	Up to 50
	Europa (6), Canada (4)	10/ND [1]	L2-L5 + D3-D6	2–24



Kind of Biogas	Location	Number of Objects/ Measurements	Analyzed Compounds	Concentration, mg/m^3
Biogas from Sewage Sludge (SG)	Germany	308/ND	L2-L4 + D3-D5	Up to 317
	Finland	3/6	L2-L4 + D3-D5	2–30
	Europa (9), Japan (1)	10/ND	L2-L5 + D3-D6	3–127
	United Kingdom	6/ND	D4 + D5	12–179



Application of Biogas	VMS Concentration Limit, mg Si/m^3
Piston Engines	5–30
Turbines	0.1
Microturbines	0.03
Fuel Cells	0.05–0.10
Catalytic Afterburners	0.50–0.38
Stirling Engines	No limit
Vehicle Engines	No limit
Natural Gas Grid	6.2 [1], 10 [2]

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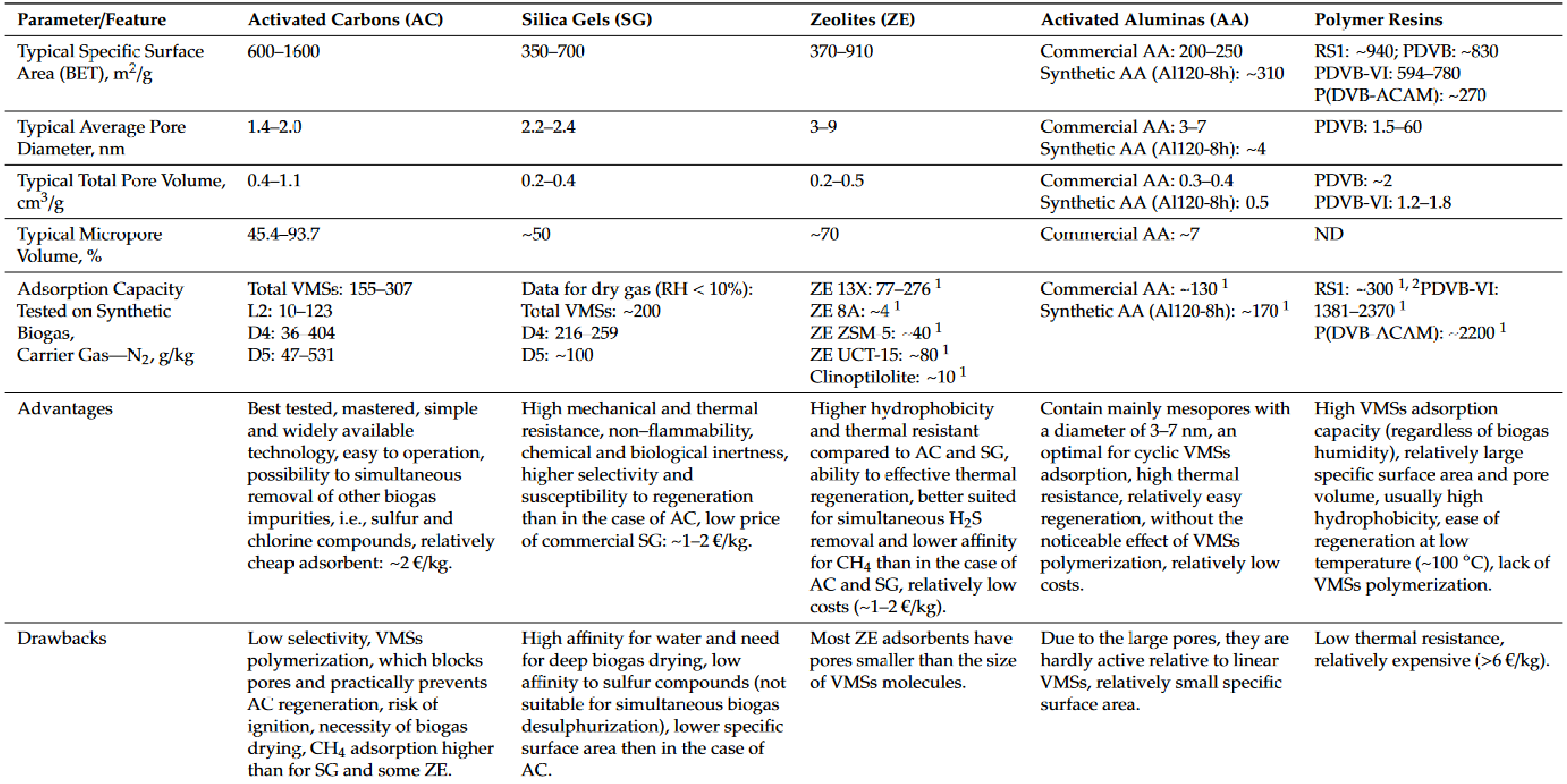
K. Gaj, *Energies*, **2020**, *13*, 2605

Purification of biogas – Siloxane

Many chemical adsorbents can be used for siloxane trapping, with pros and cons



Parameter/Feature	Activated Carbons (AC)	Silica Gels (SG)	Zeolites (ZE)	Activated Aluminas (AA)	Polymer Resins
Typical Specific Surface Area (BET), m^2/g	600–1600	350–700	370–910	Commercial AA: 200–250 Synthetic AA (Al120-8h): ~310	RS1: ~940; PDVB: ~830 PDVB-VI: 594–780 P(DVB-ACAM): ~270
Typical Average Pore Diameter, nm	1.4–2.0	2.2–2.4	3–9	Commercial AA: 3–7 Synthetic AA (Al120-8h): ~4	PDVB: 1.5–60
Typical Total Pore Volume, cm^3/g	0.4–1.1	0.2–0.4	0.2–0.5	Commercial AA: 0.3–0.4 Synthetic AA (Al120-8h): 0.5	PDVB: ~2 PDVB-VI: 1.2–1.8
Typical Micropore Volume, %	45.4–93.7	~50	~70	Commercial AA: ~7	ND
Adsorption Capacity Tested on Synthetic Biogas, Carrier Gas—N_2, g/kg	Total VMSs: 155–307 L2: 10–123 D4: 36–404 D5: 47–531	Data for dry gas (RH < 10%): Total VMSs: ~200 D4: 216–259 D5: ~100	ZE 13X: 77–276 [1] ZE 8A: ~4 [1] ZE ZSM-5: ~40 [1] ZE UCT-15: ~80 [1] Clinoptilolite: ~10 [1]	Commercial AA: ~130 [1] Synthetic AA (Al120-8h): ~170 [1]	RS1: ~300 [1, 2]PDVB-VI: 1381–2370 [1] P(DVB-ACAM): ~2200 [1]
Advantages	Best tested, mastered, simple and widely available technology, easy to operation, possibility to simultaneous removal of other biogas impurities, i.e., sulfur and chlorine compounds, relatively cheap adsorbent: ~2 €/kg.	High mechanical and thermal resistance, non–flammability, chemical and biological inertness, higher selectivity and susceptibility to regeneration than in the case of AC, low price of commercial SG: ~1–2 €/kg.	Higher hydrophobicity and thermal resistant compared to AC and SG, ability to effective thermal regeneration, better suited for simultaneous H_2S removal and lower affinity for CH_4 than in the case of AC and SG, relatively low costs (~1–2 €/kg).	Contain mainly mesopores with a diameter of 3–7 nm, an optimal for cyclic VMSs adsorption, high thermal resistance, relatively easy regeneration, without the noticeable effect of VMSs polymerization, relatively low costs.	High VMSs adsorption capacity (regardless of biogas humidity), relatively large specific surface area and pore volume, usually high hydrophobicity, ease of regeneration at low temperature (~100 °C), lack of VMSs polymerization.
Drawbacks	Low selectivity, VMSs polymerization, which blocks pores and practically prevents AC regeneration, risk of ignition, necessity of biogas drying, CH_4 adsorption higher than for SG and some ZE.	High affinity for water and need for deep biogas drying, low affinity to sulfur compounds (not suitable for simultaneous biogas desulphurization), lower specific surface area then in the case of AC.	Most ZE adsorbents have pores smaller than the size of VMSs molecules.	Due to the large pores, they are hardly active relative to linear VMSs, relatively small specific surface area.	Low thermal resistance, relatively expensive (>6 €/kg).

K. Gaj, *Energies*, **2020**, *13*, 2605

Purification of biogas – Siloxane

- Different chemical adsorbents can be used for siloxane trapping, with pros and cons, including methanol or Selexol (dimethyl ethers of PEGs) for instance.

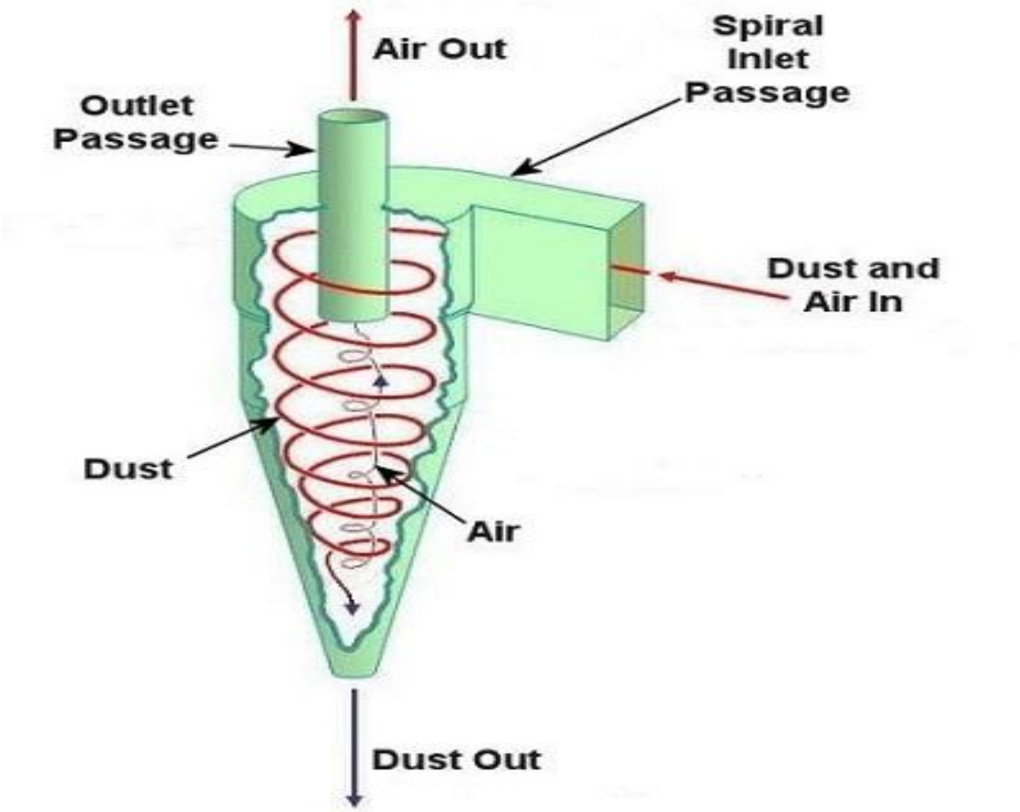
Efficiency is high, operating cost as well (energy for regeneration, cooling and compression,…) and can raise HSE issues (toxicity, flammability)

- Refrigeration and condensation processes are also used full scale thanks to their simplicity, usefulness for also drying the gas as well as not needing solvent (no reagent cost, no product to be disposed). However, they are quite energy intensive and therefore costly

G. Soreanu *et al.*, *Canadian Biosys. Eng.*, **2011**, *53*, 8.1

Purification of biogas – particles

Cyclone filters

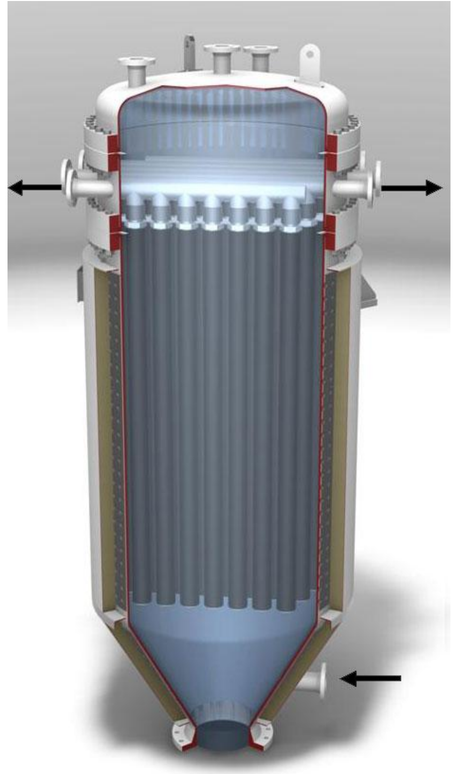


source: engineeringexpert.net

Pocket filters

source: Fleco Filtration Co.

Metallic candle



source: Steri technologies.

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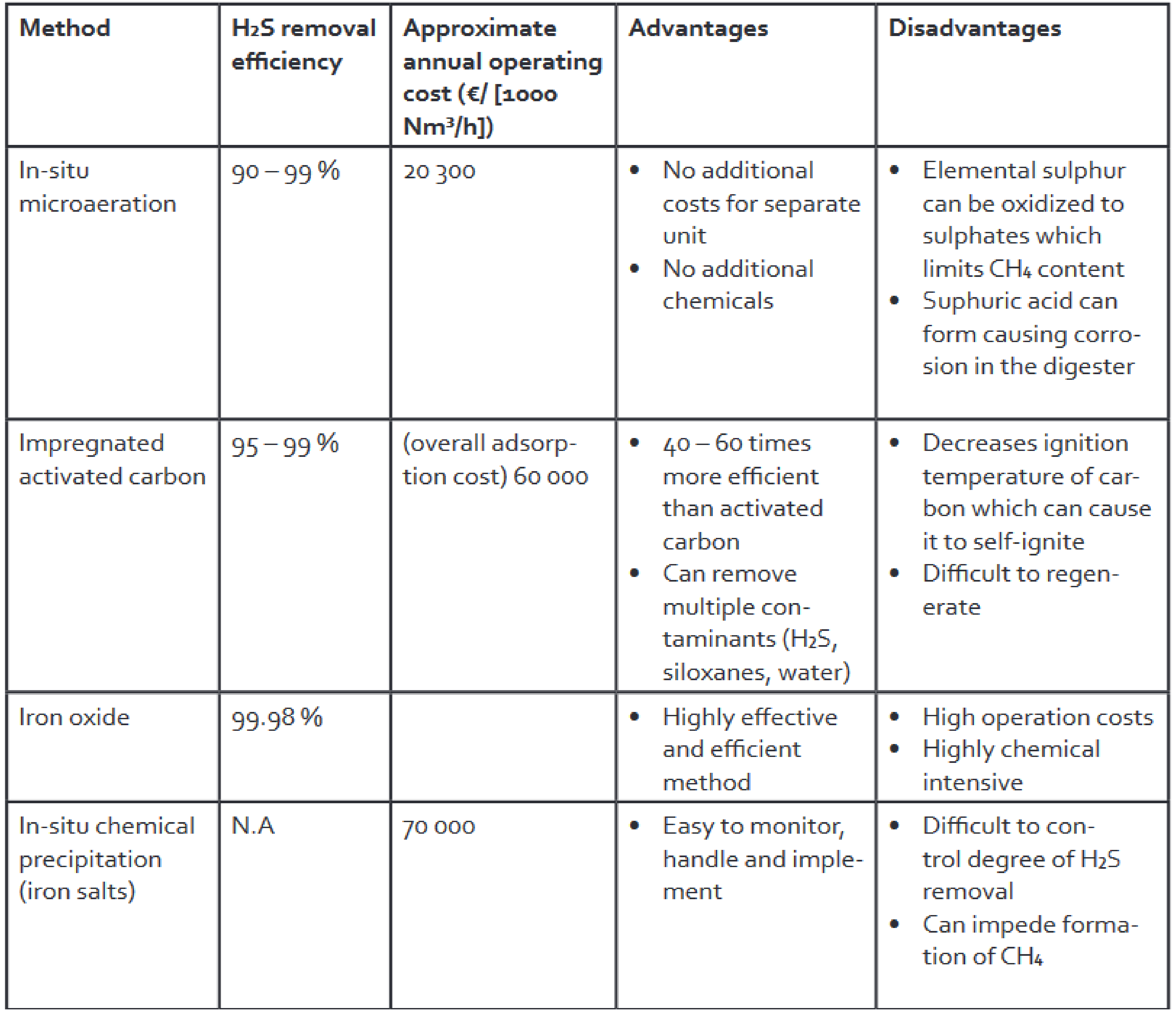
Purification of biogas – conclusion – One word on rentability



Method	H_2S removal efficiency	Approximate annual operating cost (€/ [1000 Nm^3/h])	Advantages	Disadvantages
In-situ microaeration	90 – 99 %	20 300	• No additional costs for separate unit • No additional chemicals	• Elemental sulphur can be oxidized to sulphates which limits CH_4 content • Suphuric acid can form causing corrosion in the digester
Impregnated activated carbon	95 – 99 %	(overall adsorption cost) 60 000	• 40 – 60 times more efficient than activated carbon • Can remove multiple contaminants (H_2S, siloxanes, water)	• Decreases ignition temperature of carbon which can cause it to self-ignite • Difficult to regenerate
Iron oxide	99.98 %		• Highly effective and efficient method	• High operation costs • Highly chemical intensive
In-situ chemical precipitation (iron salts)	N.A	70 000	• Easy to monitor, handle and implement	• Difficult to control degree of H_2S removal • Can impede formation of CH_4

Each purification step or system comes with a cost in both OPEX and CAPEX

Target your purification strategy based on :

- The nature of your biogas
- Your target based on the application you want (as well as local legislation)
- OPEX, CAPEX, maintenance cost as well as throughput targets

Biogas Drying and purification methods, Mwacharo *et al.*, Centria University of Applied Science, 2020

Notion of gas upgrading – in one slide as a teaser

Once purified, biogas can be burnt directly (if regulation is reached) or upgraded

Upgrade of biogas = increase of CH_4 content → removal of CO_2

Biogas is then mentioned as “biomethane” (vs. natural gas for the fossil one)

Additionally, some application implies the use of only (bio)methane (or only CO_2) and therefore efficient upgrade are required

Techniques for methane/CO_2 separation will be for another lecture but valorisation of such product – here carbon dioxide – will be discussed later on by Prof. Khodakov from CNRS

Acknowledgements

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