Part 1: Biomethane production: Microbiology of Biomethane production

Md. Maksudur Rahman Khan

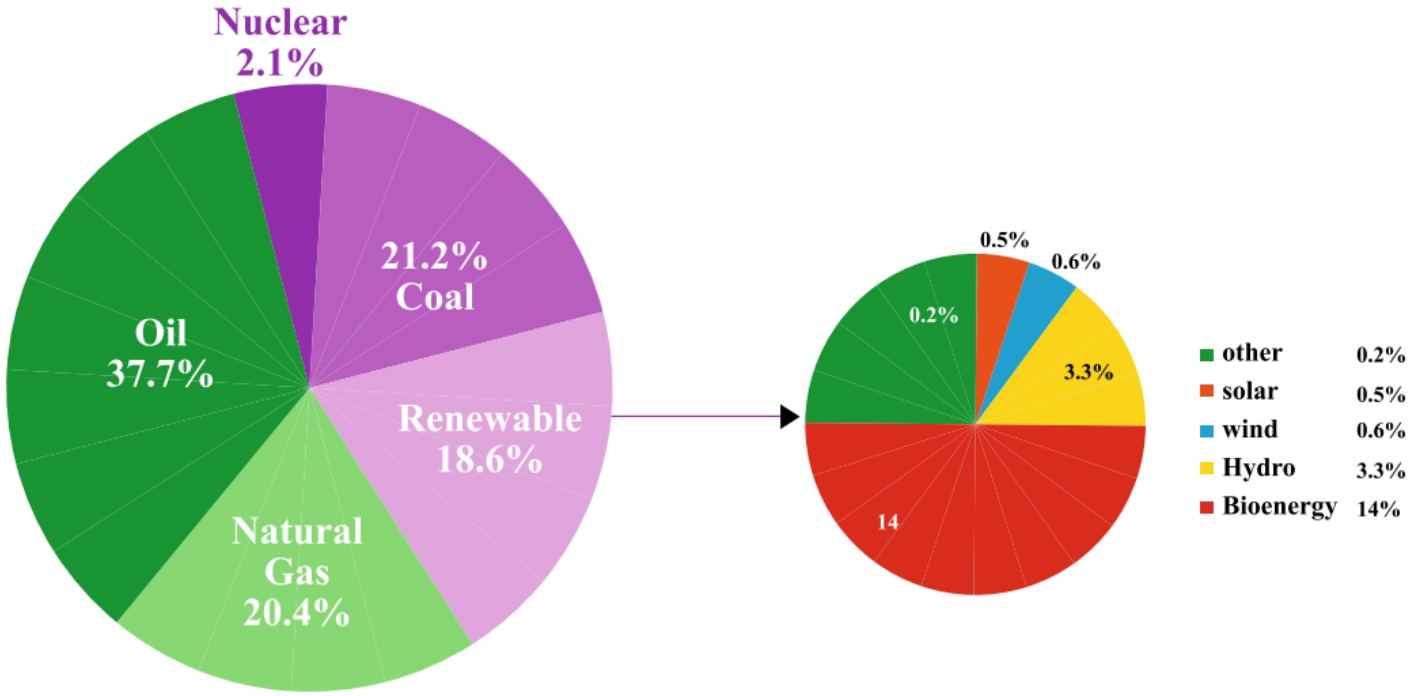
Professor, Department of Chemical Engineering

Universiti Malaysia Pahang

Biomethane Background

- Biogas was used for heating bath water in Assyria during the l0th century BC and in Persia during the 16th century
- In 1630, Jan Baptist van Helmont discovered that organic material in decomposition produced flammable gases
- In 1776, Alessandro Volta discovered methane by collecting gas emerging from Lake Maggiore in Italy
- The concept of anaerobic digestion (AD) was introduced around 1870 with the development of the septic tank system by Jean-Louis Mouras

Gross global energy consumption by fuel in 2014



Source: Sirichai K., Pruk A., James M., Green Energy and Technology, Springer Nature Singapore Pte Ltd. 2020

Biogas and Biomethane - definition

- Biogas is a mixture of methane, CO2 and small quantities of other gases produced by anaerobic digestion of organic matter in an oxygen-free environment.
- Biomethane (also known as “renewable natural gas”) is a near-pure source of methane produced either by “upgrading” biogas (a process that removes any CO2 and other contaminants present in the biogas) or through the gasification of solid biomass followed by methanation:
- Upgrading biogas: Conventionally, biogas upgradation (BU) is performed by physico-chemical (absorption, adsorption, membrane seperation, and cryogenic) and biological (in situ and ex situ) processes which are site/case specific
- Thermal gasification of solid biomass followed by methanation: Woody biomass is first broken down at high temperature (between 700-800°C) and high pressure in a low-oxygen environment. Under these conditions, the biomass is converted into a mixture of gases, mainly carbon monoxide, hydrogen and methane (sometimes collectively called syngas). To produce a pure stream of biomethane, this syngas is cleaned to remove any acidic and corrosive components. The methanation process then uses a catalyst to promote a reaction between the hydrogen and carbon monoxide or CO2 to produce methane. Any remaining CO2 or water is removed at the end of this process.

Advantages of Biomethane

- It is a renewable energy source.
- When burned, it emits less pollution compared with diesel or gasoline. The emissions from these fuels are compared in Table 1.5.
- Biomethane can be produced from locally made biogas.
- Byproducts from the production of biogas can be used or sold as natural fertilizer.
- Organic waste from farms is sometimes disposed of in natural waterways causing pollution to marine life. Processing this waste into biomethane reduces this aquatic pollution.
- An increased share of biomethane from within a country's own borders makes a nation's natural gas supply more reliable.
- Biomethane is economically attractive, in terms of reducing the costs of importing fuel and increasing local employment in the production chain.
- Rural areas especially profit from biomethane production because a considerable part of the revenue along the value chain is generated there.

Biogas to Biomethane

Biogas

Biogas is is mainly methane (50-80%) with other impurities suchas CO2, H2s, N2, O2 etc. It is produced from organic matter via anaerobic digestion.

Table 1.1 General composition of biogas

Biogas composition	Concentration levels
Methane (CH_4)	50–80% by Vol.
Carbon dioxide (CO_2)	20–50% by Vol.
Ammonia (NH_3)	0–300 ppm
Hydrogen sulfide (H_2S)	50–5000 ppm
Nitrogen (N_2)	1–4% by Vol.
Oxygen (O_2)	<1% by Vol.
Moisture (H_2O)	Saturated 2–5% by mass

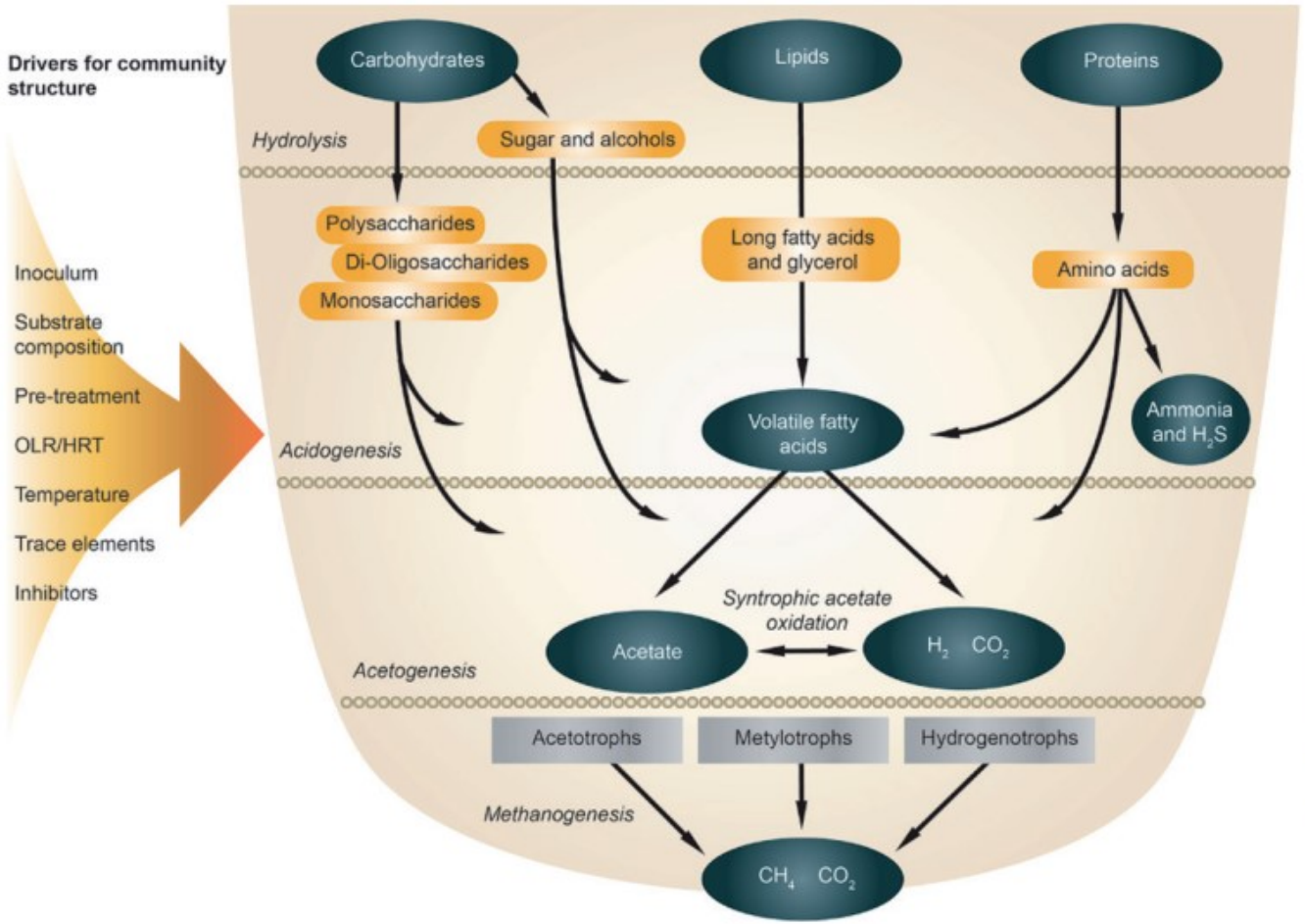
Biomethane

Biomethane is a gas that results from a process that improves the quality of biogas by reducing its levels of carbon dioxide, hydrogen sulfide, moisture, and other gases. Biogas upgraded to biomethane has a higher percentage of pure methane.

Components	SAE J1616 (1994)	CARB (1992)	NZS 5442 (1999)	CPUC Rule 30 (2002)
CH_4	–	88% (at least)	–	–
C_2H_6	–	6% (max)	–	–
C_3+	–	3% (max)	–	–
C_4+	–	–	–	–
C_6+	–	0.2% (max)	–	–
N_2	–	–	–	–
CO_2	3% (max)	0.1% (max)	–	3% (max)
Inert gas ($CO_2 + N_2 + O_2$)	–	1.5–4.5%	–	4% (max)
Sulfur	8–30 ppm	16 ppm (max)	50 mg/m^3	0.75 g/100scf (max)
Methane number	–	–	–	–
Heating value	–	–	–	36.1–42.8 MJ/m^3 (max)
Specific gravity			0.8 (max)	
Wobbe index	48.5–52.9	–	46–52	±10%

Note All percentages expressed as a mole. Except as otherwise shown

BIOGAS PRODUCTION BY ANAEROBIC DIGESTION



The microbial aspect of biomethane production involves 4 major steps if light, sulfate, and nitrate are limiting:

- ❑ HYDROLYSIS
- ❑ ACIDOGENESIS
- ❑ ACETOGENESIS
- ❑ METHANOGENESIS

1. Hydrolysis: Degradation of complex high-molecular-weight organic macromolecules into low-molecular-weight monomers.
2. Acidogenesis: Conversion of soluble monomers to various metabolic products.
3. Acetogenesis: Conversion of products from acidogenesis to acetic acid and hydrogen.
4. Methanogenesis: Methane production.

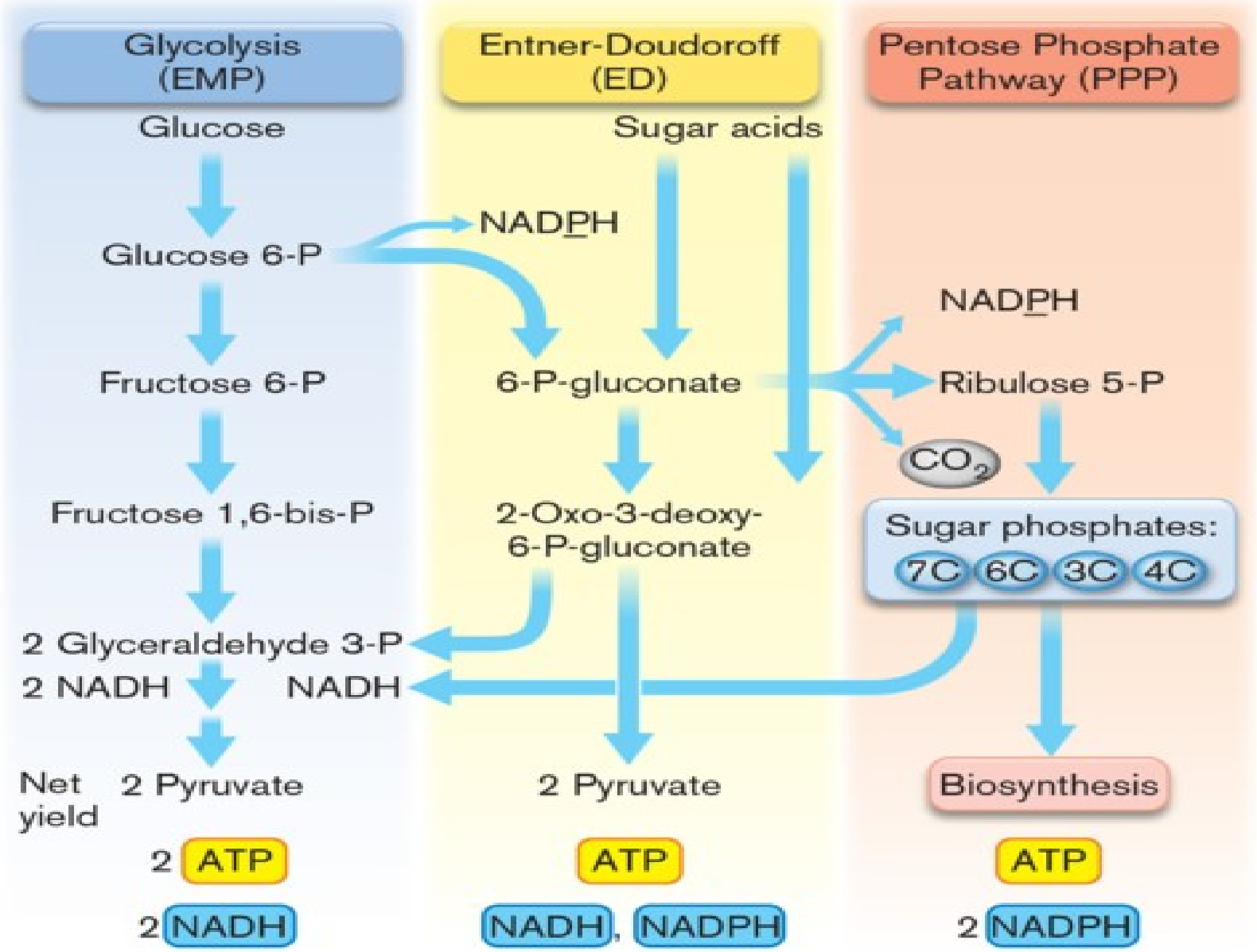
Anaerobic degradation of carbohydrates, lipids, and proteins and the phyla commonly reported to be involved in the different steps. Biogas digester parameters identified as main drivers for community structure is depicted.
The figure is adapted from Kougias et al. [Kougias PG, Angelidaki I. Biogas and its opportunities—A review. Frontiers of Environmental Science &Engineering. 2018;12:14. DOI: 10.1007/s11783-018-1037-8]

HYDROLYSIS

- The hydrolization of complex polymers to monomers is known as hydrolysis
- The organic molecules are converted to simple sugars, amino acids and fatty acids
- The process is carried out by hydrolytic microorganisms
- Facilitated by extracellular organism

HYDROLYSIS

- The process of hydrolysis is dependent on the polymeric compound to be decomposed.
- Harder or intricate lignocellulosic structures lead to low rates
- The microbes (Eg. Bacillus, Cellulomonas etc) involved in lignocellulose degradation use extracellular enzymes or cell-anchored enzyme systems such as cellulosomes
- Pathways involved in hydrolysis –
  - The Embden–Meyerhof–Parnas (EMP) pathway
  - The Enter–Doudoroff (ED) pathway

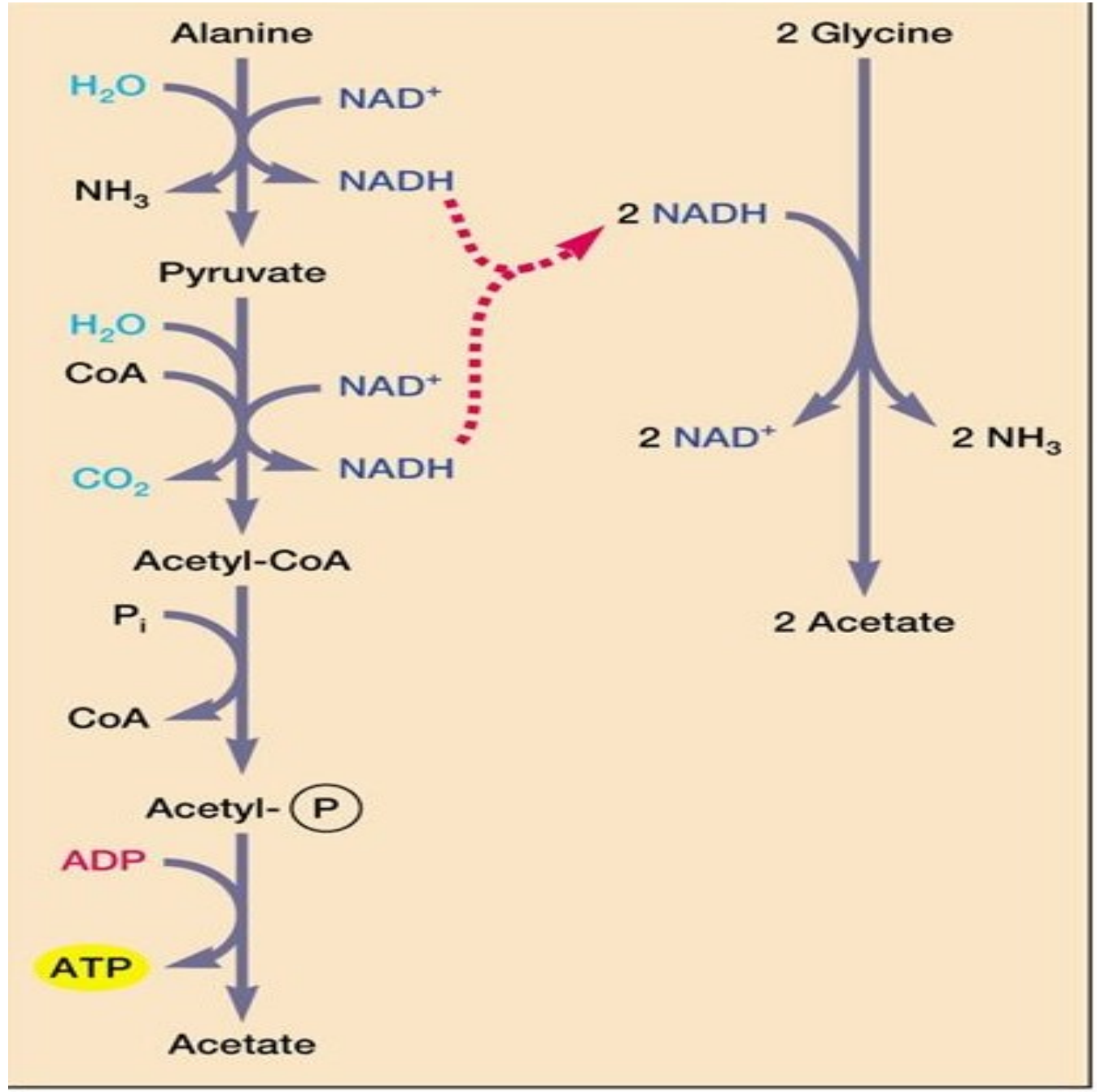

Glycolysis (EMP)
Entner-Doudoroff (ED)
Pentose Phosphate Pathway (PPP)
Glucose
Sugar acids
NADPH
Glucose 6-P
NADPH
Fructose 6-P
6-P-gluconate
Ribulose 5-P
CO2
Fructose 1,6-bis-P
2-Oxo-3-deoxy-6-P-gluconate
Sugar phosphates:
7C 6C 3C 4C
2 Glyceraldehyde 3-P
2 NADH
NADH
Net yield
2 Pyruvate
2 Pyruvate
Biosynthesis
2 ATP
ATP
ATP
2 NADH
NADH, NADPH
2 NADPH

ACIDOGENESIS

- The remnants after hydrolysis are further broken down by acidogenic bacteria (Eg. Propionibacterium, Butyrivibrio, Acetivibrio)
- Trace amounts are consumed by fermentative bacteria
- This steps produces various components which include
    - Hydrogen
    - Carbon dioxide
    - Hydrogen suphide
    - Fatty acids
    - Carbonic acids
    - Alcohols

ACIDOGENESIS

- Sugar oxidation leads to pyruvate as an intermediate, resulting in pyruvate being used as an internal electron acceptor for re-oxidation of NADH leading to C2–C6 products
- Pathways used-
  - Stickland reaction
    - Coupled oxidation/reduction processes destroy pairs of amino acids. One amino acid functions as an electron donor, while the other functions as an electron acceptor. The electron donor amino acid is oxidised to an unstable carboxylic acid with fewer carbon atoms than the initial amino acid.
  - Uncoupled oxidation and release of electrons as hydrogen is an alternate mechanism.


Alanine
H_2O
NH_3
NAD^+
NADH
Pyruvate
H_2O
CoA
CO_2
NAD^+
NADH
Acetyl-CoA
P_i
CoA
Acetyl- P
ADP
ATP
Acetate
2 Glycine
2 NADH
2 NAD^+
2 NH_3
2 Acetate

ACETOGENESIS

- The digestion to acetic acid, carbohydrate and hydrogen by the presence of acetogenic bacteria (eg. Eubacterium limosum) using the products of acidogenesis is known as acetogenesis
- Metabolizes intermediates - propionate
- Types of acetogens
    - Obligate hydrogen producing acetogens – OHPA
    - Homoacetogens – less dominant

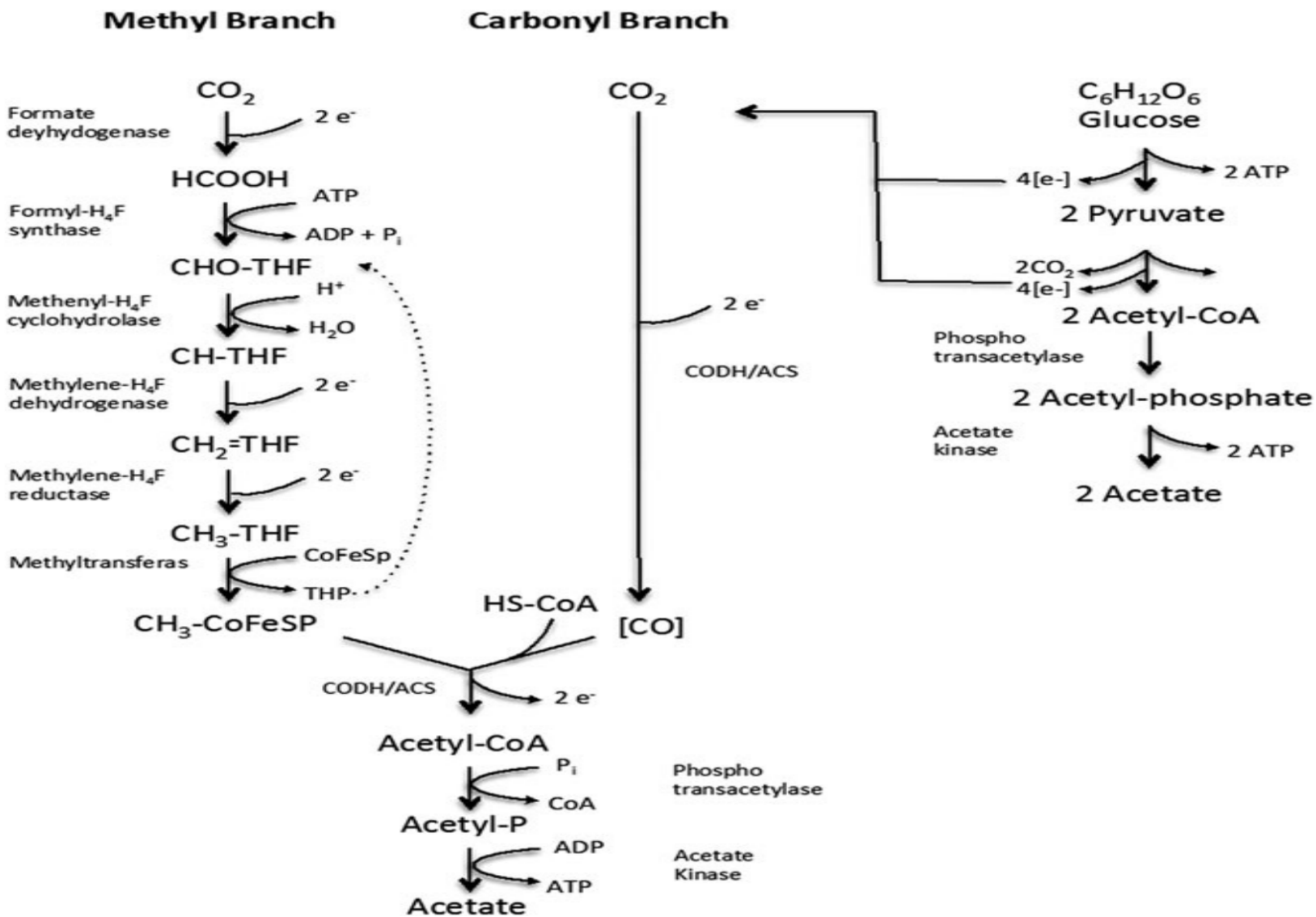
ACETOGENESIS

Acetogenesis is distinguished by the conversion of carbon dioxide (CO_2) to the acetyl moiety of acetyl-coenzyme A (CoA) via the Wood–Ljungdahl (W–L) pathway, by a phylogenetically distinct microbial group (acetogens).

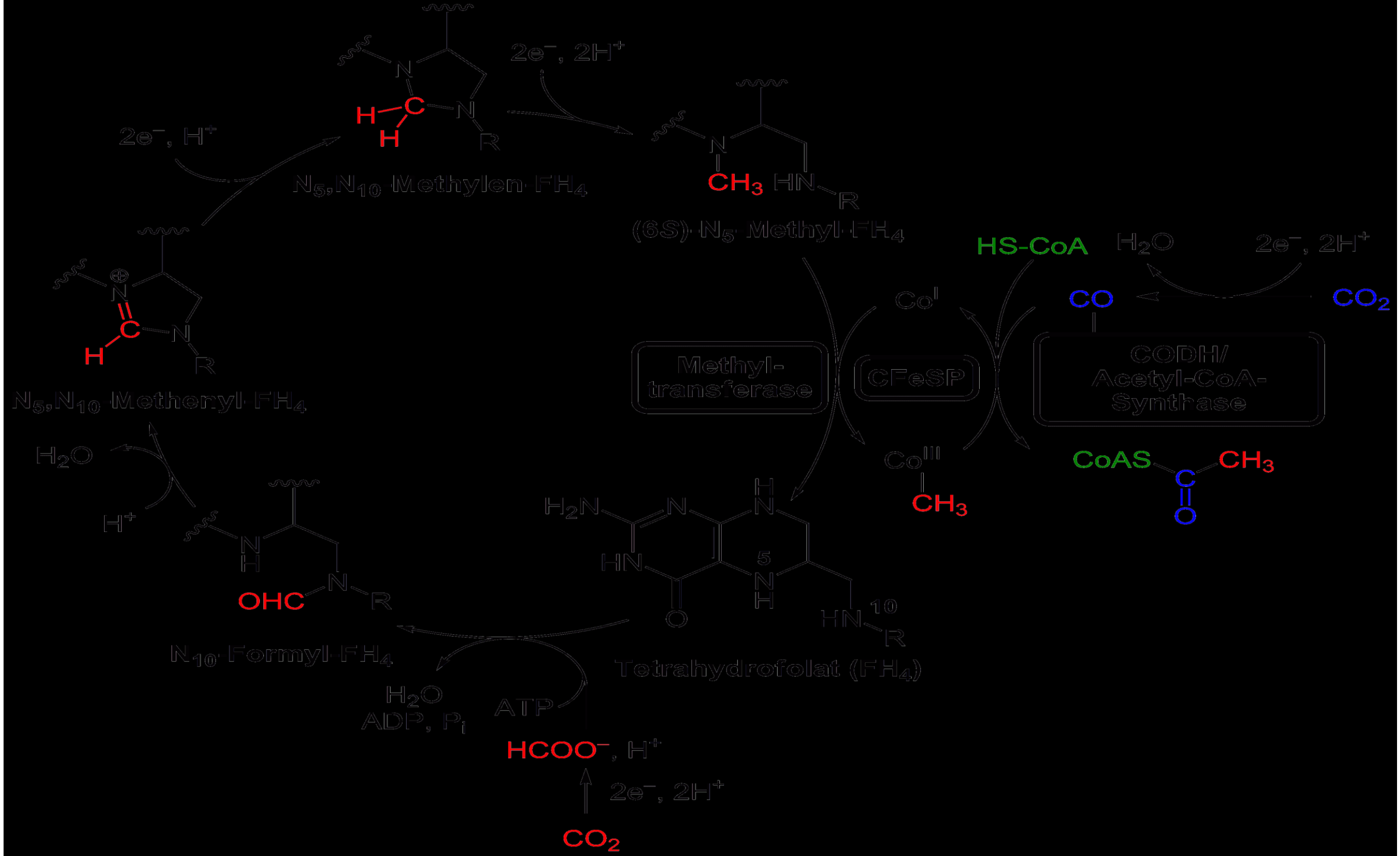
The W–L pathway has two functions:

It accepts electrons and conserves energy, and it also serves as a carbon assimilation pathway. Sugars are metabolised to pyruvate via the EMP (Embden Meyerhof Parnas) and pentose phosphate pathways in heterotrophic growth circumstances. Carbon dioxide, electrons, and exogenous CO_2 are shuttled into the W–L route from the decarboxylation of pyruvate by a pyruvate ferredoxin oxidoreductase.

Acetogenesis (Wood–Ljungdahl pathway)



Source: Anna Schruner 2016


2e⁻, 2H⁺
2e⁻, H⁺
N5,N10 Methylen FH4
(6S) N5 Methyl FH4
N5,N10 Metheryl FH4
HS-CoA
H2O
2e⁻, 2H⁺
CO
CO2
Co I
Methyl-transferase
CFeSP
CODH/ Acetyl-CoA-Synthase
Co III
CH3
CoAS
CH3
H2O
H+
OHC
N10 Formyl FH4
Tetrahydrofolat (FH4)
H2O
ADP, Pi
ATP
HCOO⁻, H⁺
2e⁻, 2H⁺
CO2

- The final stage wherein the intermediate products are converted to methane, water and carbon dioxide.
- The biogas finally produced contain the above mentioned components
- The process is carried out by methanogenic bacteria
- Eg. Archaebacteria

METHANOGENSIS

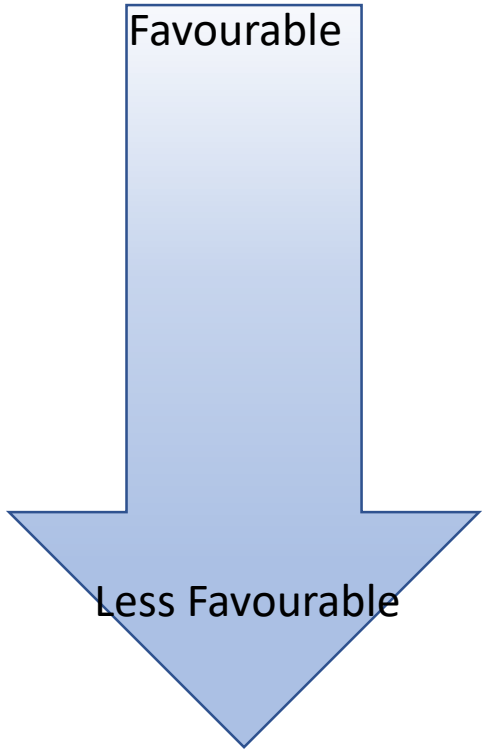
- Methanogens are strict anaerobes which share a complex biochemistry for methane synthesis as part of their energy metabolism
- Methanogens are categorized depending on the substrate and pathway they use: hydrogenotrophs and methylotrophs.
- The hydrogenotrophs get their energy from formate or hydrogen and CO2 is converted to methane. Certain alcohols can also be used as an electron donor by some methanogens in this group.
- Methylotrophs utilizes hydrogen and CO2, acetate, CO, methyl compounds, such as methanol, methyl amines. Here the methyl group is reduced to methane: the substrate reaches the process as methyl-S-CoM in methanogenesis via methanol, methylamines, and other sources. Hydrogen or methyl disproportionation, such as oxidation of another methyl-S-CoM to carbon dioxide, provide electrons for the reduction of methyl-S-CoM to methane.

DIVERSITY OF METHANOGENS: Key Microorganisms of the Methane Fermentation Process

- 61 species (including 5 synonymous) of hydrogenotrophs oxidize H2 and reduce CO2 to form methane and formatotrophs oxidize formate to form methane
- Twenty species (including one synonymous) of methylotrophs use methyl compounds as methanol, methylamines, or dimethylsulfide and of which 13 species are obligate methylotrophs
- Nine species (including 1 synonymous) of aceticlastic (or acetotrophic) methanogens utilize acetate to produce methane,

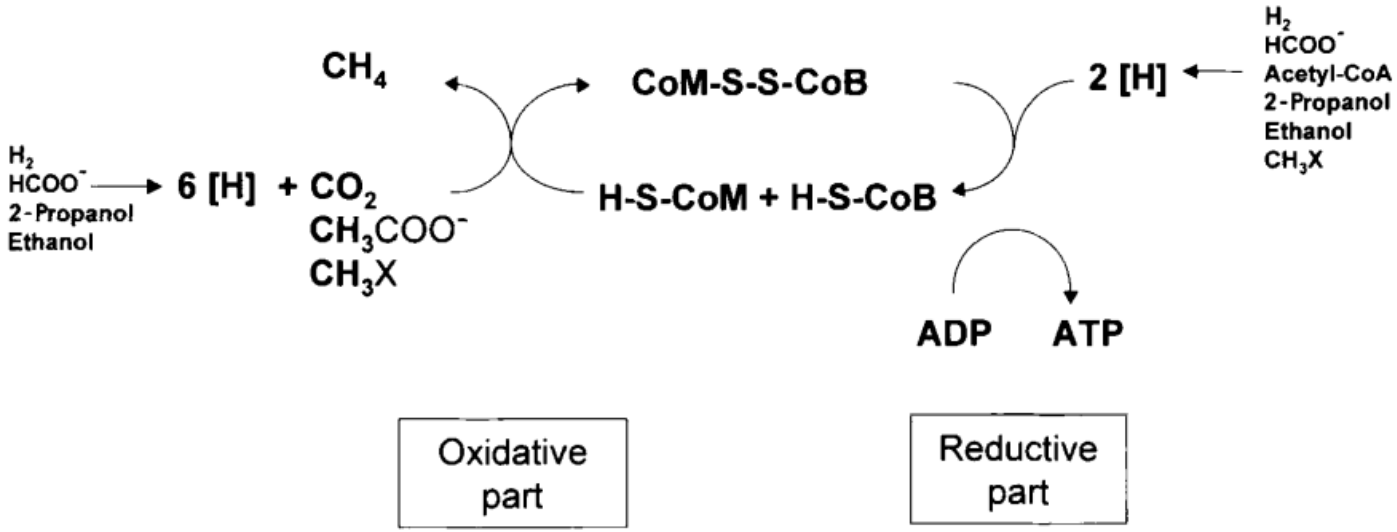
REACTION AND STANDARD CHANGES IN FREE ENERGIES FOR METHANOGENESIS

Reaction	$\Delta G^{\circ\prime}$ (KJ/mol CH_4)
$4\ H_2+CO_2 \rightarrow CH_4+2H_2O$	−135.6
$4\ Formate \rightarrow CH_4+3CO_2+2H_2O$	−130.1
$2\ Ethanol+CO_2 \rightarrow CH_4+2\ Acetate$	−116.3
$Methanol+H_2 \rightarrow CH_4+H_2O$	−112.5
$4\ Methanol \rightarrow 3CH_4+CO_2+2H_2O$	−104.9
$4\ Methylamine+2H_2O \rightarrow 3CH_4+CO_2+4NH_4^+$	−75.0
$4\ Trimethylamine+6H_2O \rightarrow 9CH_4+3CO_2+4NH_4^+$	−74.3
$2\ Dimethylsulfide+2H_2O \rightarrow 3CH_4+CO_2+H_2S$	−73.8
$2\ Dimethylamine+2H_2O \rightarrow 3CH_4+CO_2+2NH_4^+$	−73.2
$4\ 2\text{-}Propanol+CO_2 \rightarrow CH_4+4\ Acetone+2H_2O$	−36.5
$Acetate \rightarrow CH_4+CO_2$	−31.0



Energy metabolism of methanoarchaea

The energy metabolism of methanogens can be viewed to consist of two parts: an oxidative part in which coenzyme M (H-S-CoM, 2-thioethanesulfonate) and coenzyme B (H-S-COB, 7 thioheptanoylthreonine-phosphate) are oxidized to the heterodisulphide CoM-S-S-COB; and a reductive part in which the heterodisulphide of coenzyme M and coenzyme B is re-reduced.



Energy metabolism of methanogenic archaea. In the oxidative part, coenzyme M (H-S-CoM) and coenzyme B (H-S-COB) are oxidized to the heterodisulphide CoM-S-S-COB by CO,, acetate or reduced C, compounds (CH,-X) such as methanol, methylthiols and methylamines, which in turn are reduced to CH,; in the reductive part, the heterodisulphide is reduced to coenzyme M and coenzyme B, the electron transport from the electron donors being coupled with phosphorylation.

$$CH_3\text{-S-CoM} + \text{H-S-CoB} \rightarrow CH_4 + \text{CoM-S-S-CoB} \qquad \Delta G^{0\prime} = -45\ \text{kJ mol}^{-1}$$

Why H_2S is present in Biogas?

The biogas produced in industrial biogas digesters mainly consists of methane and carbon dioxide, but also small amounts of other gases such as hydrogen sulphide (H_2S).

- H_2S has corrosive properties causing damage on equipment
- H_2S may also cause inhibition to the microbial community by direct toxic effects or by precipitation of trace metals needed for enzymatic activity

The production of sulphides is influenced by different factors:
(i) The amount of sulphur-containing amino acids in the incoming material
(ii) The level of sulphate in the incoming material
(iii) The presence of SRB in inoculum

- In the presence of sulphate in a biogas process, SRB and methanogens compete for the same substrate, i.e. acetate and hydrogen/carbon dioxide.
- SRB typically win this competition owing to several interacting factors:

(i) anaerobic respiration with sulphate as the final electron acceptor yields more energy for growth compared with carbon dioxide;

(ii) SRB possess higher affinity for both hydrogen and acetate, enabling them to consume substrates below levels possible for use by methanogens;

(iii) SRB generally have a higher specific growth rate than methanogens.

- Many different groups of bacteria within the anaerobic digester compete for the same substrate and electron acceptor.
- Methane is produced by methane-forming bacteria and a variety of acids and alcohols are produced by sulfate reducing bacteria.
- Hydrogen is used with sulfate (SO_4^{2-}) by sulfate-reducing bacteria and hydrogen sulfide (H_2S) is produced

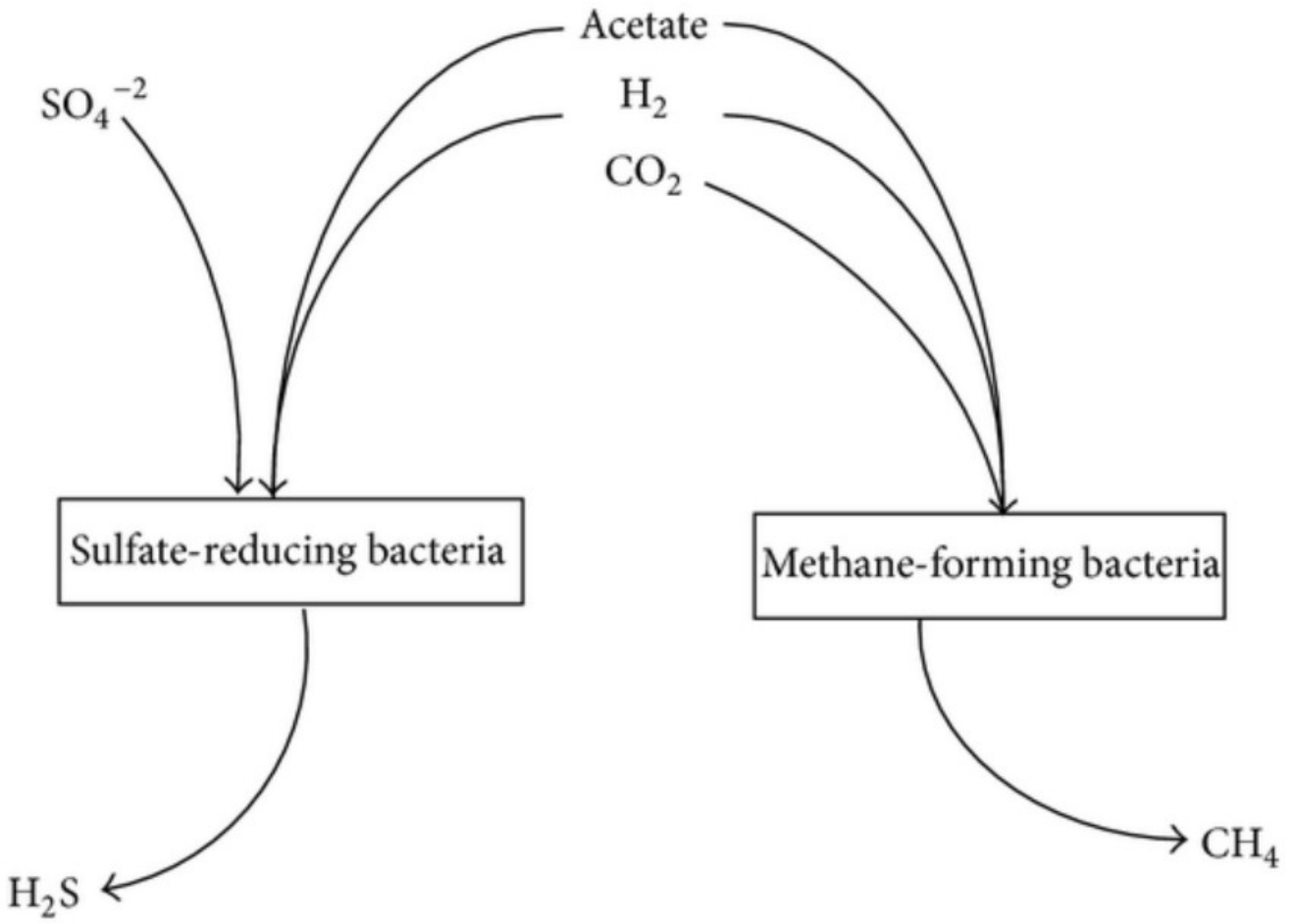


Table: Acetogenic and methanogenic reactions, and sulfate-reducing reactions involved in the degradation of organic matter in methanogenic bioreactors, and sulfate-reducing bioreactors, respectively.

- Propionate-degrading bacteria: Syntrophobacter sp. (Syntrophobacter wolinii, Syntrophobacter pfennigii and Syntrophobacter fumaroxidans
- Butyrate-degrading bacteria: Syntrophomonas and Syntrophospora
- Syntrophobacter species appear to be sulfate reducers
- Syntrophobacter sp. degrades propionate via the so-called methylmalonyl-CoA pathway

	$\Delta G^{o\prime}$ [kJ/reaction]
Acetogenic reactions	
$Propionate^- + 3\ H_2O \rightarrow Acetate^- + HCO_3^- + H^+ + 3\ H_2$	+76.1
$Butyrate^- + 2\ H_2O \rightarrow 2\ Acetate^- + H^+ + 2\ H_2$	+48.3
$2\ Propionate^- \rightarrow Acetate^- + butyrate^-$	0
Methanogenic reactions	
$4\ H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\ H_2O$	−135.6
$Acetate^- + H_2O \rightarrow CH_4 + HCO_3^-$	−31.0
Sulfate-reducing reactions	
$4\ H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\ H_2O$	−151.9
$Acetate^- + SO_4^{2-} \rightarrow 2\ HCO_3^- + HS^-$	−47.6
$Propionate^- + \frac{3}{4}\ SO_4^{2-} \rightarrow Acetate^- + HCO_3^- + \frac{3}{4}\ HS^- + \frac{1}{4}\ H^+$	−37.7
$Butyrate^- + \frac{1}{2}\ SO_4^{2-} \rightarrow 2\ Acetate^- + \frac{1}{2}\ HS^- + \frac{1}{2}\ H^+$	−27.8
Homoacetogenic reactions	
$4\ H_2 + 2\ HCO_3^- + H^+ \rightarrow Acetate^- + 4\ H_2O$	−104.6

Competition of sulfate reducers with methanogens and acetogens

- Direct competition between methanogens and sulfate reducers will occur for hydrogen and acetate.
- Compared with methanogens, SRB are much more versatile than methanogens.
- Compounds like propionate and butyrate, which require syntrophic consortia in methanogenic environments, are degraded directly by single species of SRB in environments where sufficient sulfate is present

How to suppress SRB?

- The abundance of SRB was only marginally influenced by the choice of the incoming material and process parameters.
- Two parameters have a significant effect on SRB abundance:

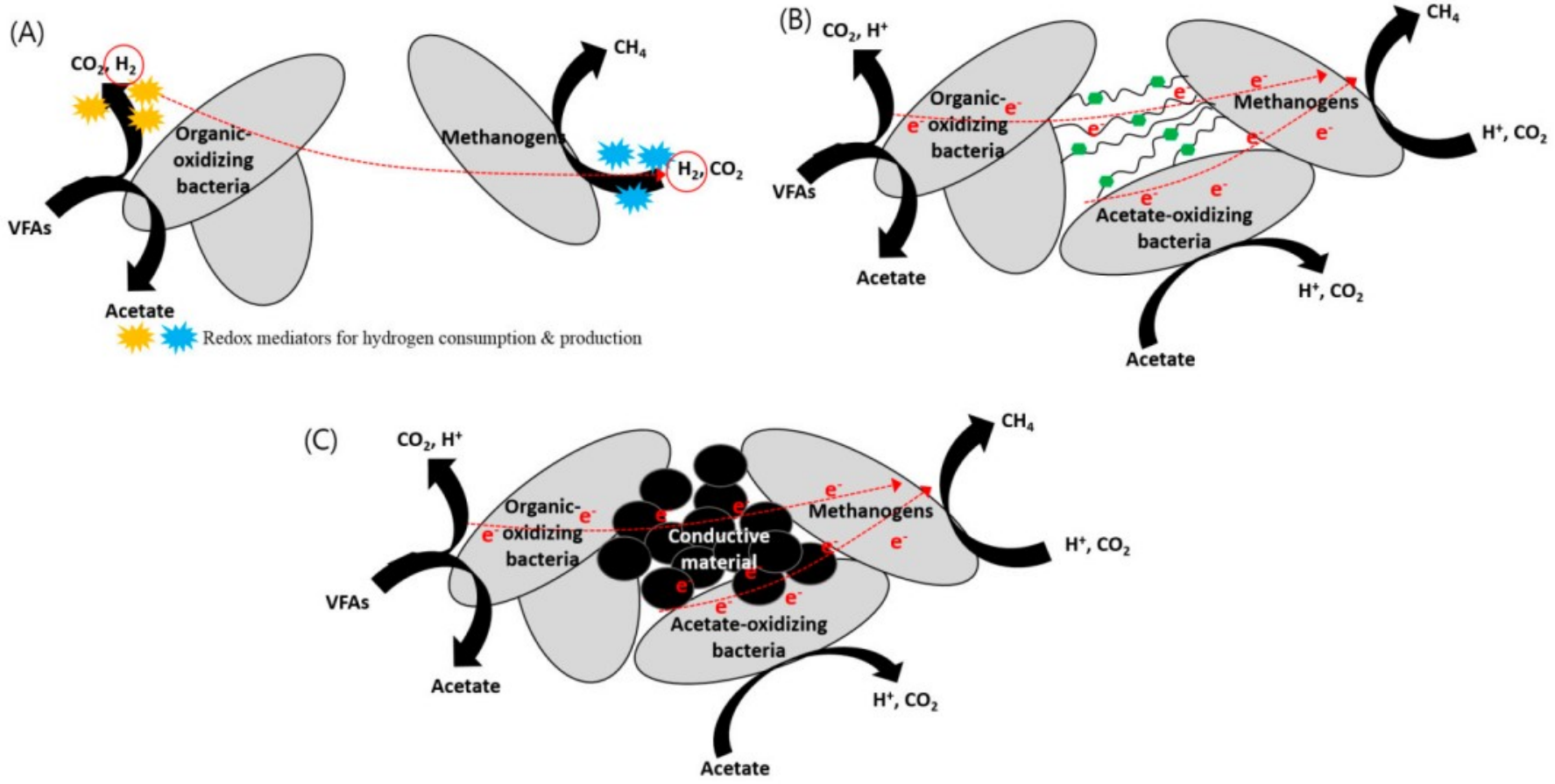
(i) High levels of nitrogen (Ammonia) result in lower levels of SRB. high ammonia concentrations have been shown to select for methane production by syntrophic acetate oxidation instead of acetoclastic methanogenesis (Caution: very high concentrations of free ammoniacal nitrogen can be a major cause of operational failure)

(ii) Addition of excess sulphate results in increased growth of SRB (selection of substrates with lower sulphur content)

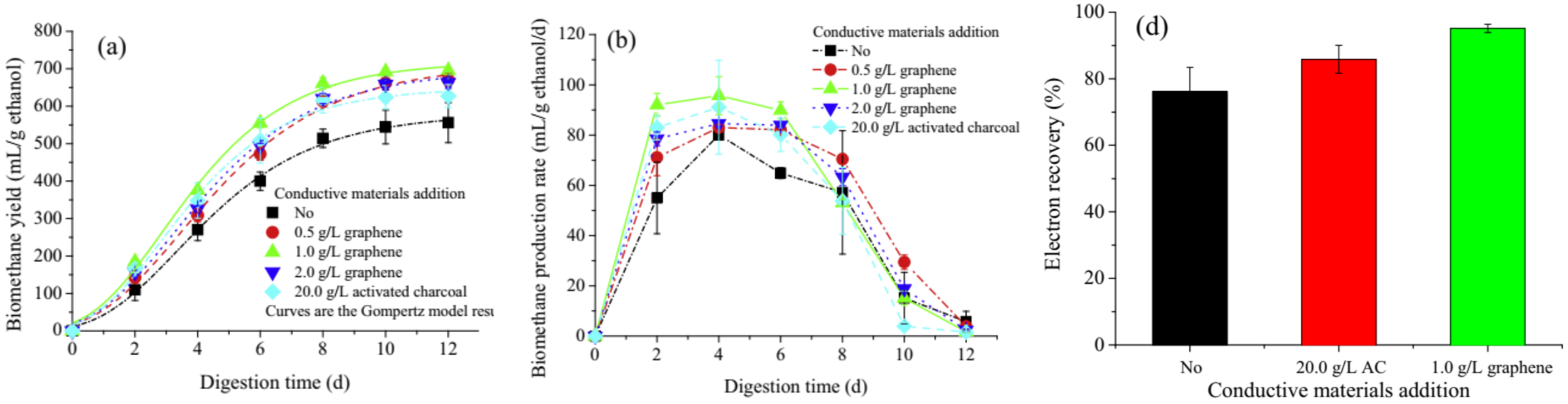
How to improve methanogenesis?

- **Stable and fast interspecies electron transfer (IET)** between volatile fatty acid-oxidizing bacteria and hydrogenotrophic methanogens is crucial for efficient methanogenesis. *(In this syntrophic interaction, electrons are exchanged via redox mediators such as hydrogen and formate.)*
- Microorganisms undergoing DIET form interspecies electrical connections via membrane-associated cytochromes and conductive pili; thus, redox mediators are not required for electron exchange. This indicates that DIET is more thermodynamically favorable than indirect IET.
- Conductive materials (e.g., iron oxides, activated carbon, biochar, and carbon fibers) can mediate direct electrical connections for DIET.

Mechanisms of (A) indirect interspecies electron transfer (IIET) via hydrogen, (B) biological direct interspecies electron transfer (DIET), and (C) conductive material-mediated DIET



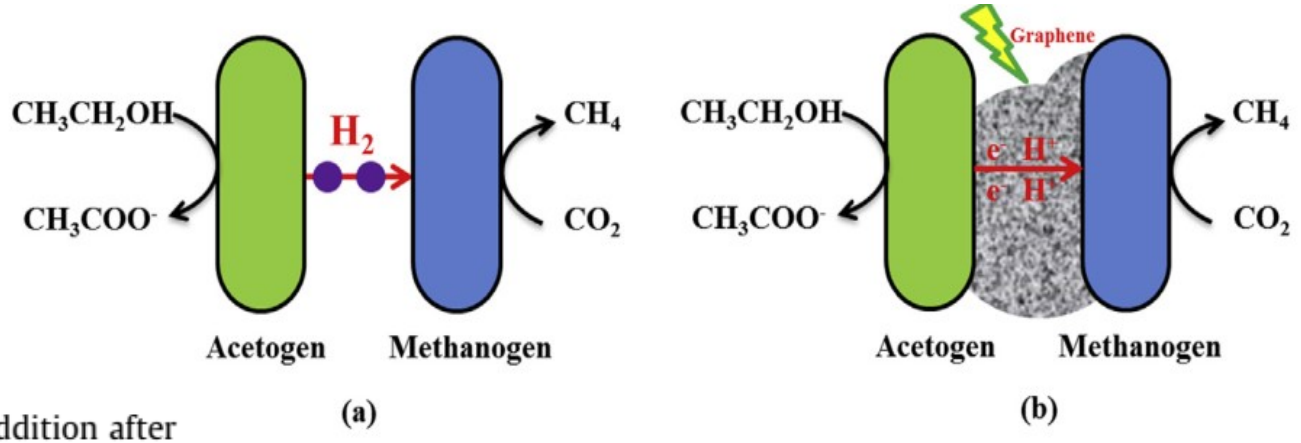
Source: Gahyun Baek and Jaai Kim and Jinsu Kim and Changsoo Lee , Role and Potential of Direct Interspecies Electron Transfer in Anaerobic Digestion,Energies,2018, 11, p.107



Effects of graphene and activated charcoal on biomethane yield and production rate from ethanol: (a) biomethane yield, (b) biomethane production rate (d) overall electron recovery

Source: R. Lin et al. / Bioresource Technology 239 (2017) 345–352

Figure: Mechanisms for extracellular cell-to-cell electron transfer in anaerobic digestion: (a) mediated interspecies electron transfer, (b) direct interspecies electron transfer via graphene



Bacterial community structures at genus level with/without graphene addition after anaerobic digestion of ethanol. Genera with less than 1% abundances were classified into others.

Genera	Relative abundance in different anaerobic digestates (%)		
	Inoculum	Digestate without graphene	Digestate with 1.0 g/L graphene
Geobacter	0.29	8.43	9.94
Pseudomonas	0.43	1.91	6.85
Levilinea	7.64	11.59	6.2
Clostridium	10.09	8.57	5.15
Thermovirga	3.34	2.71	2.98
Victivallis	0.38	2.89	2.73
Aminobacterium	3.98	2.14	2.24
Longilinea	0.85	2.71	2.22
Desulfovibrio	0.05	2.27	1.96
Synergistes	3.09	1.97	1.72
Smithella	2.86	2.03	1.45
Syntrophomonas	1.4	2.13	1.27
Meniscus	1.86	1.69	1.24
Bellilinea	1.27	1.54	0.9
Others	42.92	34.04	39.39
unclassified	19.55	13.38	13.76

Archaeal community structures at genus level with/without graphene addition after anaerobic digestion of ethanol. Genera with less than 1% abundances were classified into others.

Genera	Relative abundance in different anaerobic digestates (%)		
	Inoculum	Digestate without graphene	Digestate with 1.0 g/L graphene
Methanosaeta	86.08	50.14	39.75
Methanobacterium	2.68	24.02	34.87
Methanolinea	6.44	20.19	9.84
Methanospirillum	1.14	2.15	7.76
Unclassified	2.27	2.07	4.66
Others	1.39	1.43	3.12

Source: R. Lin et al. / Bioresource Technology 239 (2017) 345–352

Part 2:
Biomass Sources for Biomethane Generation

Strengths, weaknesses, opportunities, and threats analysis of

Strengths	Weaknesses
• Biomethane is a flexible and mature energy carrier giving it versatile and immediate application • Use of existing gas grid infrastructure enables cheap, large-scale, and long-term energy storage • Use of existing biogas infrastructure • Valorization of waste CO_2 streams • Valorize renewable power outside of the electricity sector, which only covers a minor part of the total energy demand • Reduced dependency of biomass for production of renewable carbon-based fuel	• Low H_2 solubility entails high energy demand (gas–liquid mixing) and/or demand for construction of additional reactor volume (*ex situ* step) • Additional investment cost compared to direct usage of electricity or H_2 as an energy carrier • Inevitable energy loss compared to direct usage of H_2 gas as an energy carrier • Requires continued implementation of renewable power production based on wind and sun
Opportunities	**Threats**
• Binding and more ambitious targets for renewable transport fuels • Use of biomethane as a building block for production of base chemicals through intermediates such as synthetic gas • Breakthrough in electrolysis investment costs • Increasing taxes on CO_2 emission • Continued implementation of renewable power production based on wind and sun	• Continued low fossil natural gas prices or decreased value of green gas certificates • No significant breakthrough in gas–liquid mass transfer technologies • Lack of political awareness and un-adapted legislation • Continued high electricity prices caused by transmission and system operation levies • Development of competing power-to-X technologies

Source: Agneessens, 2018)

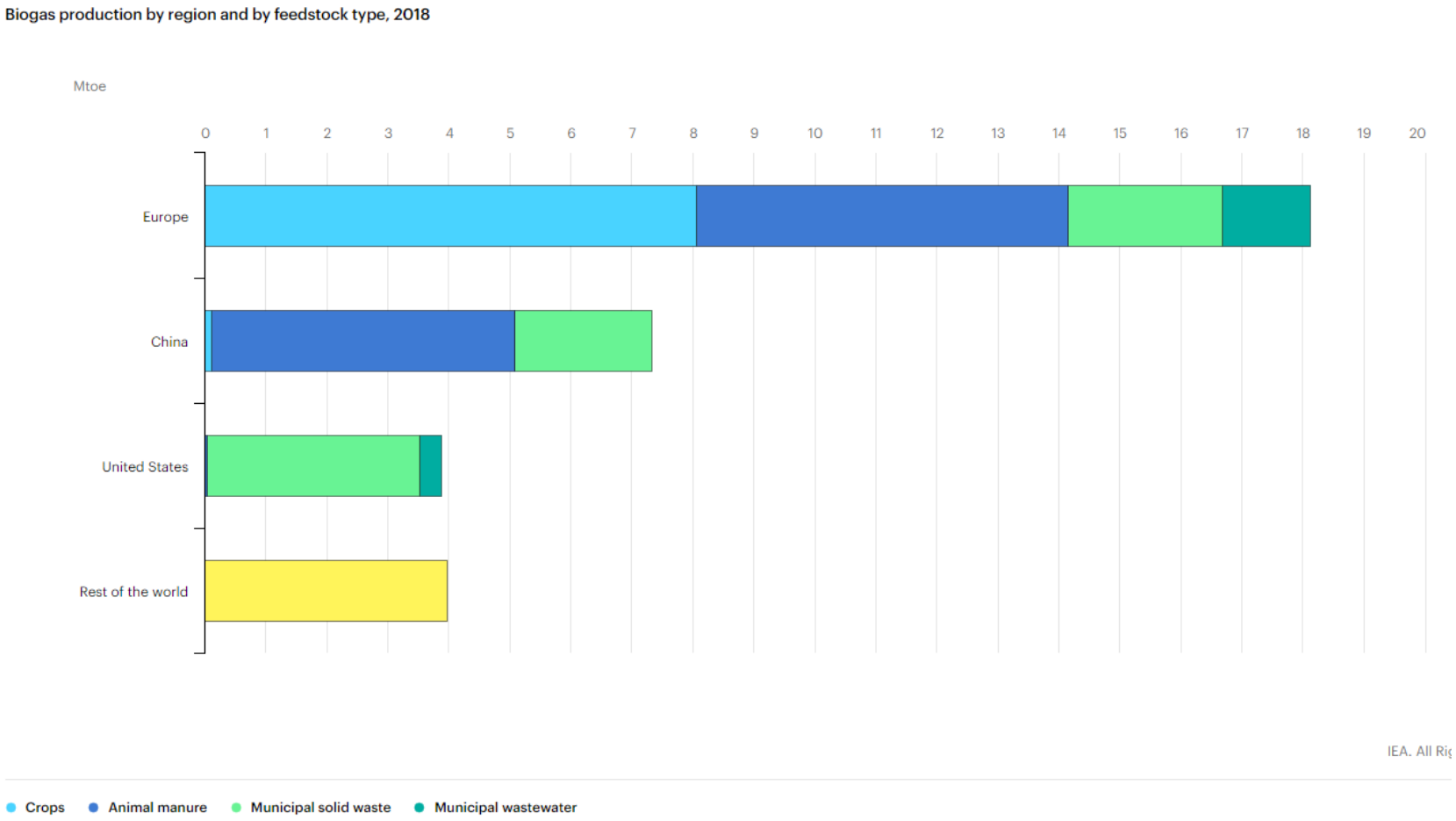
Raw materials for Biogas

- Biomass is the general term used to describe all biologically produced matter and therefore includes all kinds of materials and substances derived from living organisms.
- Biomass originating from forestry and agriculture
- Biomass originating from industrial and municipal residues and wastes
- Industrial and domestic wastewater

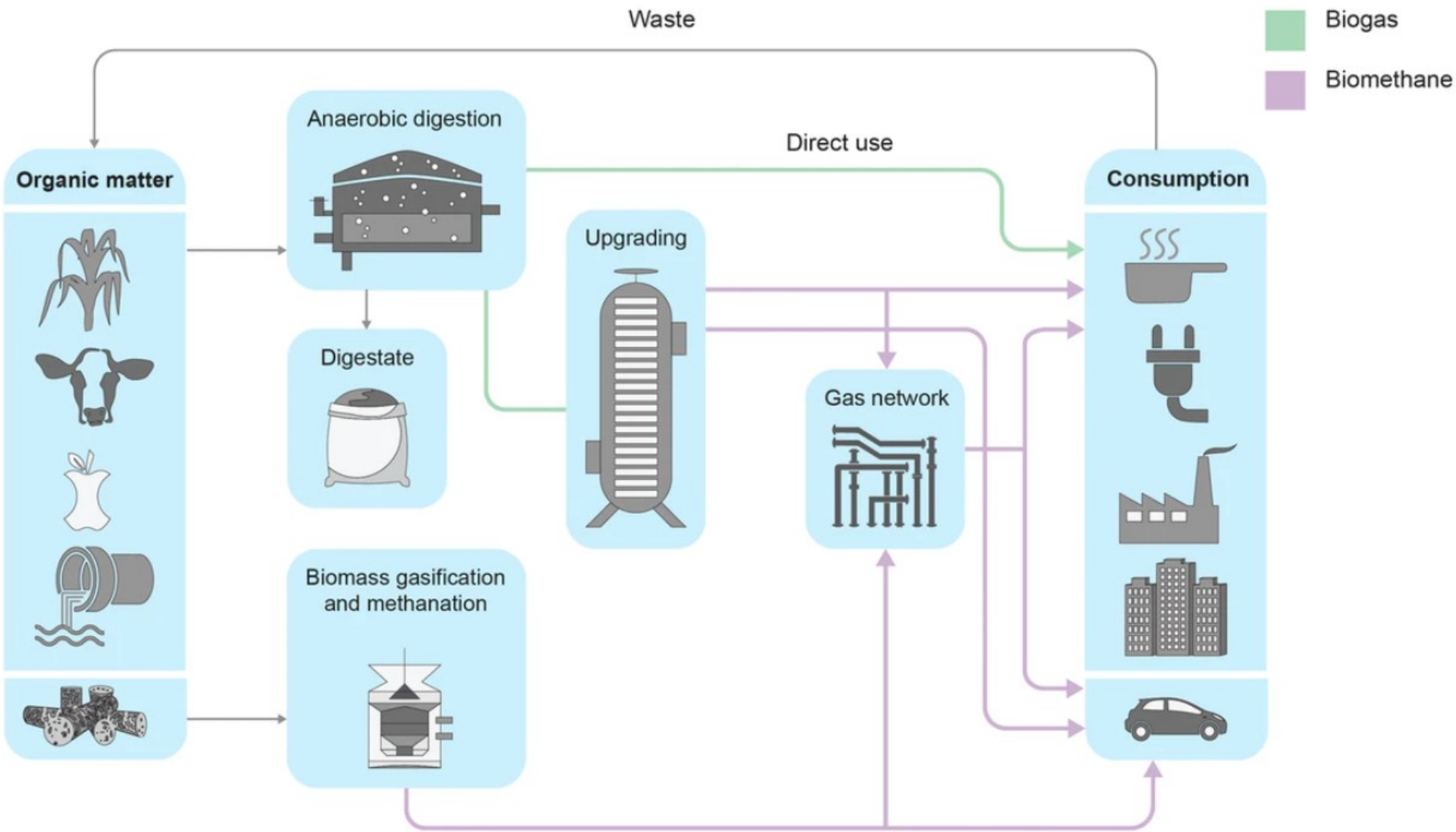
Feedstock for Biogas/Biomethane

- Crop residues
- Energy crops
- Animal manure
- Organic fraction of MSW
- Wastewater sludge
- Lignocellulosic Biomass/Woody Biomass/Forest residues

Biogas Feedstock



Source: https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth/an-introduction-to-biogas-and-biomethane



Source: https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth/an-introduction-to-biogas-and-biomethane

Biofuel classification based on feedstock

- **First-generation biofuels:** Produced from edible plants.
- **Second-generation biofuels**: Produced from agricultural waste and non-edible plants.
- **Third-generation biofuels**: Produced from algal biomass.

Different feedstock for the production of first-generation biogas and its performance

- The studies presented in this table were conducted under mesophilic conditions at temperature rang ing 30–38 °C, at a interval of pH between 7 and 8 with hydraulic residence time (HRT) of 30–60 days

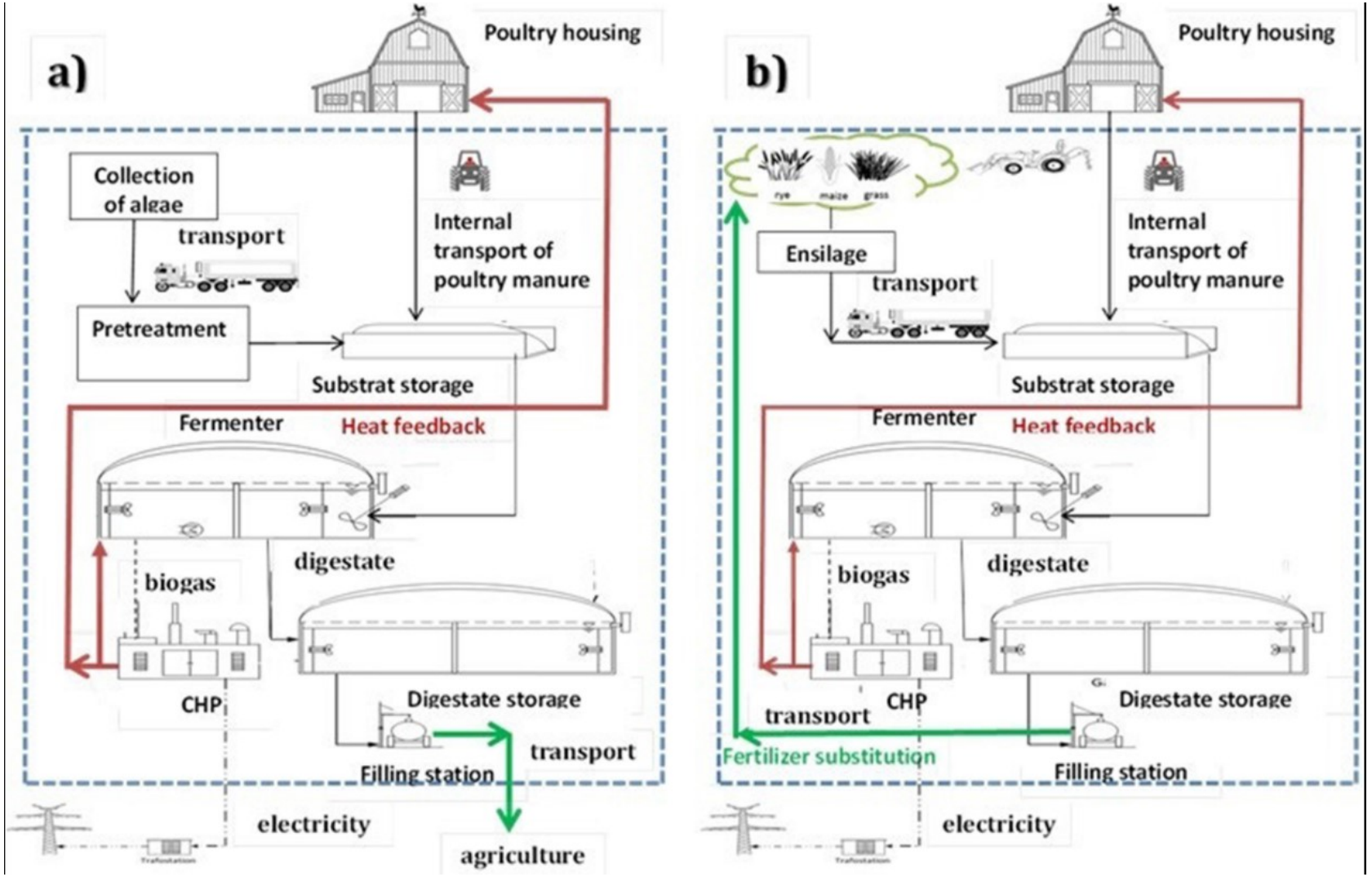
Biomass	Inoculum	Operation conditions	Type of reactor	Pretreatment	Methane yield	Methane yield[a], $m^3\ ha^{-1}\ year^{-1}$	Crop yield t DS $ha^{-1}\ year^{-1}$	References
Maize and amaranth	Mixture of microorganisms	37.5 °C	Batch assays (100 mL syringes)	Ensiling techniques	349.5 mL $CH_4\ g^{-1}$ ODM	–	–	Haag et al. (2015)
[redacted]								Pakarinen et al. (2011)
Maize silage	Methanogenic	37 °C, pH 7.2, 21 days	Batch (1 L)	Microbial consortium with high cellulolytic activity	393.3 mL g^{-1}	3933–8652	10–22[b,c]	Poszytek et al. (2016)
Zea mays (maize)	Anaerobic sludge	39 °C, HRT = 60 days	Continuously stirred tank reactors (CSTRs)	Ensiling	330.0 mL $CH_4\ g^{-1}$ VS	2970–6536	10–22[b,c]	Klimiuk et al. (2010)
Sorghum	Digestates	35 °C, 30 days	Batch (2 L Glass vessel)	Silage	341.0–378.0 mL g^{-1} ODM	6479.0–7182	19[c]	Herrmann et al. (2011)
Barley	Inoculum from anaerobic reactor	37 °C	Batch	Milled	314.8 mL g^{-1} VS	1416	5[d]	Himanshu et al. (2017)
Sugar beet	Digestate	35 °C, pH 8.1, 30 days	Batch (2 L)	Silage	350.4–399.4 mL g^{-1} ODM	4905–5591	14[e]	Herrmann et al. (2016)
Sunflowers	Digestate	35 °C, pH 8.1, 30 days	Batch (2 L)	Silage	210–286.1 mL g^{-1} ODM	2100–3147	10–11[d,e]	Herrmann et al. (2016)
Winter wheat	Digestate	35 °C, pH 8.1, 30 days	Batch (2 L)	Silage	269.2–327.6 mL g^{-1} ODM	1346–3277	5–10[d,e]	Herrmann et al. (2016)

Table: Different feedstock for the production of second generation of biogas

Biomass	Inoculum	Operation conditions	Type of reactor	Pretreatment	Methane yield	Methane yield[a], $m^3\ ha^{-1}\ year^{-1}$	Crop yield *t* DS $ha^{-1}\ year^{-1}$	References
Rice straw	Anaerobic sludge	35 °C at 100 rpm	Batch flasks	Citric acid to (100–140 °C)	322.1 mL biogas g^{-1} rice straw	128.8–966.3	0.4–3[b]	Amnuaycheewa et al. (2016)
Rice straw	Sludge from manure compost (seed)	55 °C, pH 6.8	Semi-batch bioreactor of 250 mL containing carbon fiber textile	Premilled nanofiltration	260 mLCH_4 g^{-1} VS	104–780	0.4–3[b]	Sasaki et al. (2016)
Corn stover	Mixture from biogas plant	37.5 °C, 49 days	Batch fermenters	Steam explosion (160 °C for 2 min)	585 mL g^{-1} VS	783.9	1.34[c]	Lizasoain et al. (2017)
Grass silage	Manure and crops	55 °C, 63 days		Anaerobic inocula	405 mLCH_4 g^{-1} VS	4374	12[d]	Voelklein et al. (2016)
Agave tequilana bagasse	Anaerobic granular sludge	35 °C pH 7, 4 g COD L^{-1} day and HRT 4–5 days and 30 g VSS L^{-1}	UASB	Acid or enzymatic hydrolysis	240 mL CH_4 g^{-1} COD			Arreola-Vargas et al. (2016)
Wheat straw Sugarcane bagasse	Sludge wastewater	35.1 °C, pH 6.5–7.0 30 days	Batch (2 L)	Thermal Acid Alkaline (30%) Alkaline-peroxide	200–240 mL CH_4 g^{-1} VS	612–2304	3.4–9.6[e]	Bolado-Rodríguez et al. (2016)
Sunflower stalks	Granular sludge	35 °C, pH 7	Batch anaerobic flasks	Acid and thermal (170 °C)	302 mLCH_4 g^{-1} VS			Monlau et al. (2013a)
Miscanthus sacchariflorus	Anaerobic sludge	39 °C, HRT = 60 days	Continuously stirred tank reactors (CSTRs)	Ensilage	190 mLCH_4 g^{-1} VS	2223–5700	13–30[f]	Klimiuk et al. (2010)

Table: Different feedstock for the production of Third generation of biogas

Biomass	Inoculum	Operation conditions	Type of reactor	CH_4 conversion efficiency (%)	Yield	Methane yield[a], m^3 ha^{-1} $year^{-1}$	Crop yield *t* DS ha $year^{-1}$	References
Ipomoea aquatica and *Eichhornia crassipes*	Cow dung slurry	Agitation manual twice daily, 25.5–35.5 °C, 119 days	Batch assays working volume of 15 dm^3	–	290 mL biogas kg^{-1} VS $days^{-1}$	–	–	Adanikin et al. (2017)
Typha latifolia	Anaerobic sludge	37 °C, 60 days	Batch assays	–	151 mL CH_4 g^{-1} VS	2147	15.8[b]	Nkemka et al. (2015)
Eichhornia crassipes	Sludge of wastewater	38 °C, pH 7–8	Pilot scale, batch	–	140 mL CH_4 g^{-1} VS	7560–12,600	60–100[c]	O'Sullivan et al. (2010)
Eichhornia crassipes	Sludge	35 °C	Batch	–	170 mL CH_4 g^{-1} VS	9180–15,300	60–100[c]	Gao et al. (2013)
Cabomba	Sludge of wastewater	38 °C, pH 7–8	Pilot scale, batch	–	109 mL CH_4 g^{-1} VS	–	–	O'Sullivan et al. (2010)
Elodea nuttallii	Anaerobic sludge	37 °C and 100 rpm, 14 days	Batch assays	61.4	299 mL CH_4 g^{-1} TS	–	–	Koyama et al. (2014)
Egeria densa	Anaerobic sludge	37 °C and 100 rpm, 14 days	Batch assays	60.6	234 mL CH_4 g^{-1} TS	7020	30[d]	Koyama et al. (2014)
Potamogeton malaianu	Anaerobic sludge	37 °C and 100 rpm, 14 days	Batch assays	72.2	156 mL CH_4 g^{-1} TS	528.8–1332.4	3.39–8.54[e]	Koyama et al. (2014)
Duckweed (aquatic plant):cattle dung in a 1:1 ratio	Cattle dung	38 °C, pH 7.2, 55 days	Batch	–	580 mL $days^{-1}$	–	–	Yadav et al. (2017)
Egeria densa	Anaerobic sludge	35 °C, 300 rpm, HRT = 45 days	Semi-continuous reactor	–	231 mL CH_4 g^{-1} VS	6930	30[d]	Kobayashi et al. (2015)
Potamogeton maackianus	Anaerobic sludge	–	Semi-continuous operation	53.6	255.9 mL CH_4 g^{-1} VS	857.5–2185	3.39–8.54[e]	Koyama et al. (2017b)

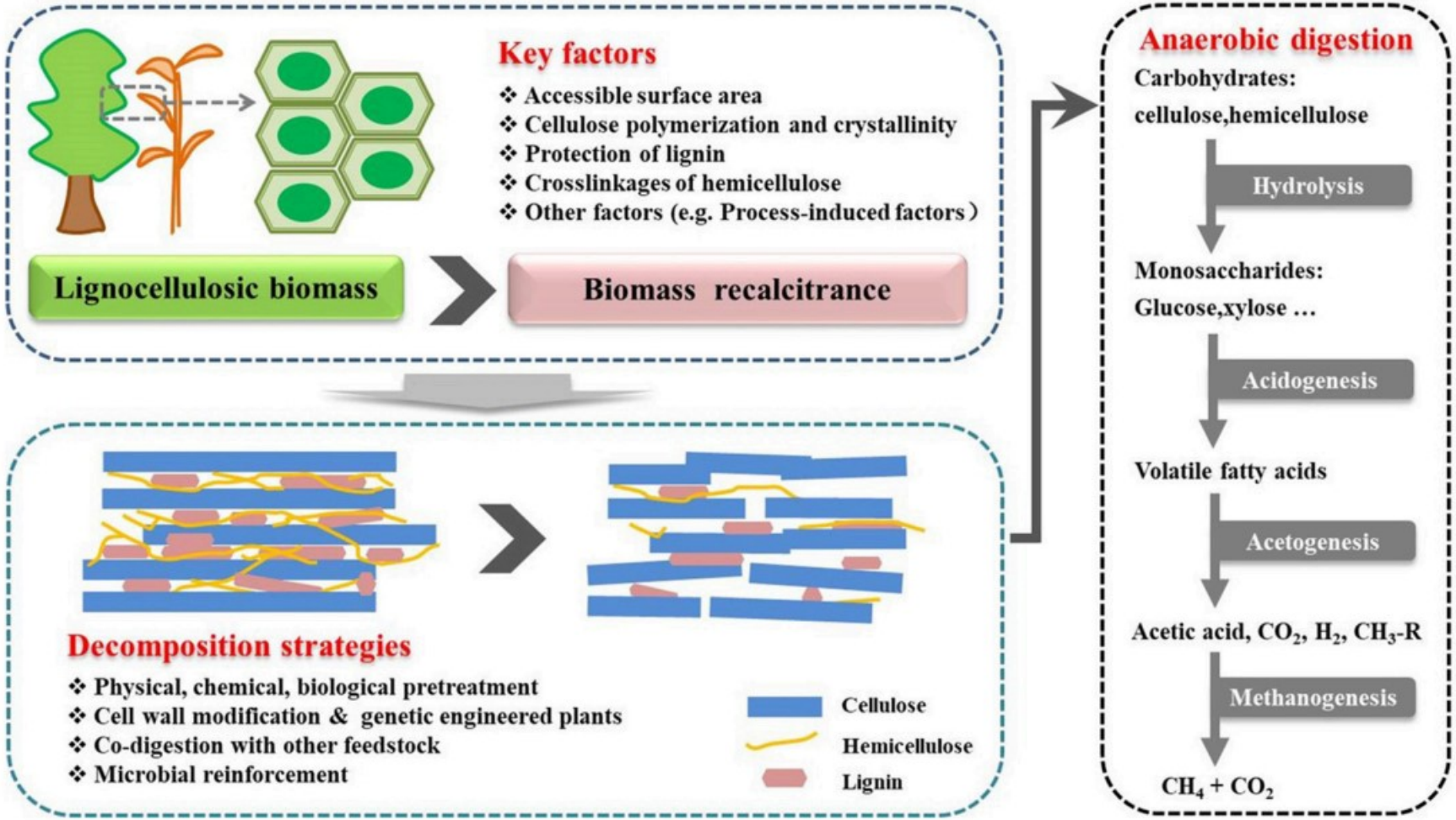


Findings: marine macroalgae: mixture of brown (20%) and red algae (80%) as feedstock in an industrial scale biogas plant. This plant operates with the co-digestion of maize (27%), grass (54%), rye (8%) and chicken manure (11) and produces 500 kWh energy.

Impact of the codigestion of algae with chicken manure on the emission reductions: 52%, 83%, 41% and 8% lower global warming, acidification, eutrophication and land transformation potentials, respectively per 1 MJ of energy generation, moreover, 84% and 6% lower acidification and land transformation potentials per kg of feedstock.

Figure: Energy production from the co-digestion of chicken manure with a) Macroalgae and b) Energy crops.

Source: Funda CansuErtem, Peter Neubauer, Stefan Junne, Environmental life cycle assessment of biogas production from marine macroalgal feedstock for the substitution of energy crops, Journal of Cleaner Production 2017, 144, pp. 977-985



Biomethane production is a naturally occurring biological process, which can be divided into four stages. Recalcitrance of lignocellulose restricts the hydrolysis during the first stage. **Pretreatment is necessary step for biomethane production.**

The positive effects of pretreatment strategies can help to facilitate the hydrolysis of lignocellulosic in the first stage

Figure: Process stages of the conversion of lignocellulosic biomass to biomethane.

Source: Biomethane Production From Lignocellulose: Biomass Recalcitrance and Its Impacts on Anaerobic Digestion, Front. Bioeng. Biotechnol., 08 August 2019 | https://doi.org/10.3389/fbioe.2019.00191

Lignocellulosic biomass recalcitrance

Biomass	Cellulose	Hemicellulose	Lignin
Sunflower stalk	31.0	15.6	29.2
Barley straw	34.3	23.0	13.3
Wheat straw	35.0	22.3	15.6
Miscanthus	38.2	24.3	25.1
Rice straw	38.6	19.7	13.6
Pine	43.3	21.5	28.3
Polar	44.5	22.5	19.5
Corn straw	45.4	22.7	10.8
Spruce	45.5	22.9	27.9
Eucalyptus	54.1	18.4	21.5

Factors	Relative effects
Epidermal protection	The epidermal tissue of the plant body, particularly the bark, cuticle and epicuticular waxes
Cellulose characteristic	High degree of CrI and DP of cellulose, challenges for enzymes acting on insoluble substrate
Chemical compositions	Heterogeneity and complexity of constituents, degree of lignification, and complexity of chemical cross-linkages
Cell wall physical structure	Arrangement and density of the vascular bundles; the relative amount of sclerenchymatous tissue
Process-induced causes	Inhibitors are generated during conversion processes (e.g., cellulose realignment)

Source: Biomethane Production From Lignocellulose: Biomass Recalcitrance and Its Impacts on Anaerobic Digestion, Front. Bioeng. Biotechnol., 08 August 2019 | https://doi.org/10.3389/fbioe.2019.00191

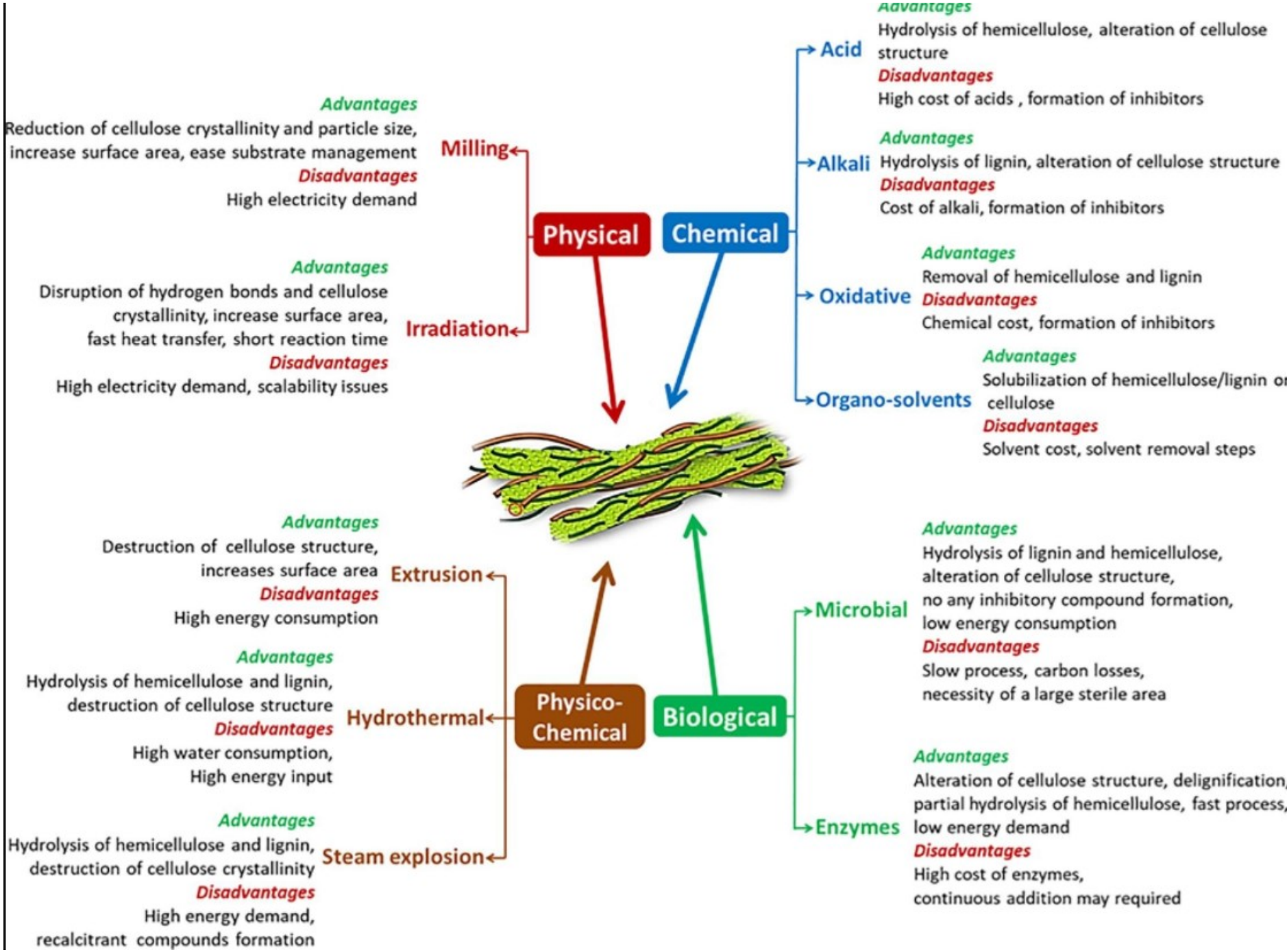
Cellulose

- Cellulose forms the core portion of lignocellulose, which is bounded by a hemicellulose matrix and an outer lignin layer
- Cellulose is the major constituent in biomass and forms liner homopolymer chains of 100 to 140,000 units. Each unit is made up of a glucose disaccharide (cellobiose), which are linked by a β-1,4-glycosidic bond
- Even though cellulose is hydrophilic, but its large size makes it less soluble in water.
- Cellulose crystallinity plays noticeable role in affecting initial hydrolysis of cellulose. The yield of monosaccharides decreased with the increased crystallinity of the substrate, indicating that amorphous domains are hydrolyzed first before the hydrolysis of crystalline parts.

Hemicellulose And Lignin

- Hemicellulose is a heteropolysaccharide with a degree of polymerization of between 200 and 700 and is composed of different combinations of monomers, such as pentoses, hexoses, and sugar acids with xylan as the major structural unit
- Hemicellulose is non-covalently attached to cellulose fibres and acts as a matrix material in lignocellulosic biomass. The amorphous structure and lower degree of polymerization of hemicellulose causes it to be more susceptible to physical, chemical, and biological degradation than cellulose
- Lignin is a heteropolymer consisting of monomeric units of coniferyl, sinapyl, and coumaryl alcohols
- The AD process can digest both cellulose and hemicellulose portion of lignocellulosic substrate, whereas lignin remains undigested.
- Lignosulfonate is commercially used as a plasticizer in the cement industry, a binder in animal feed and as a substrate for the production of a flavoring agent, vanillin

Pre-treatment methods

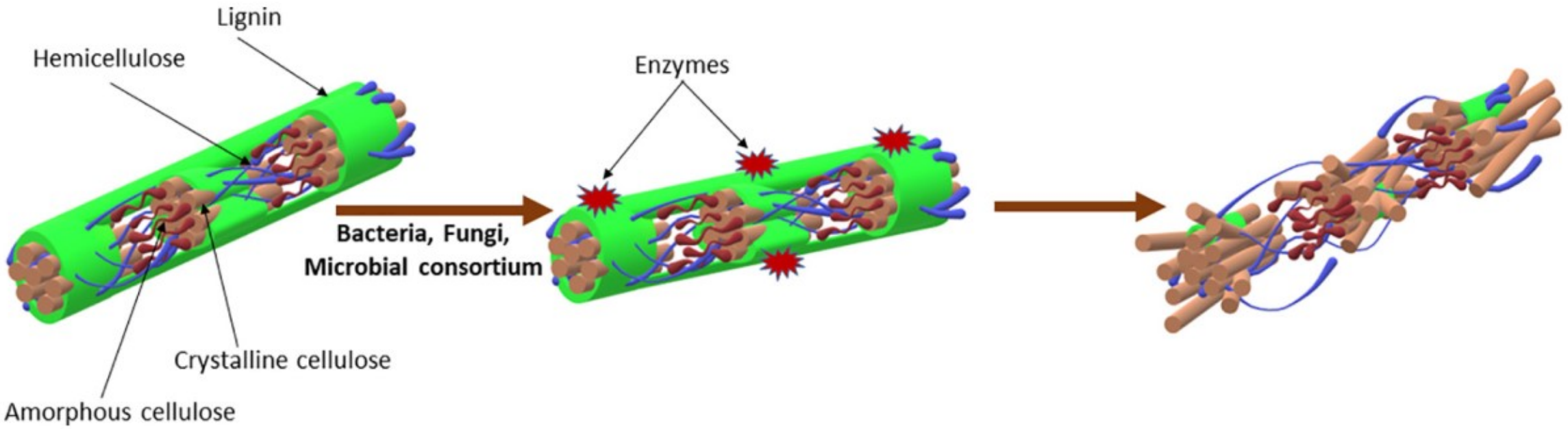


Biological Pretreatment: more compatible with AD

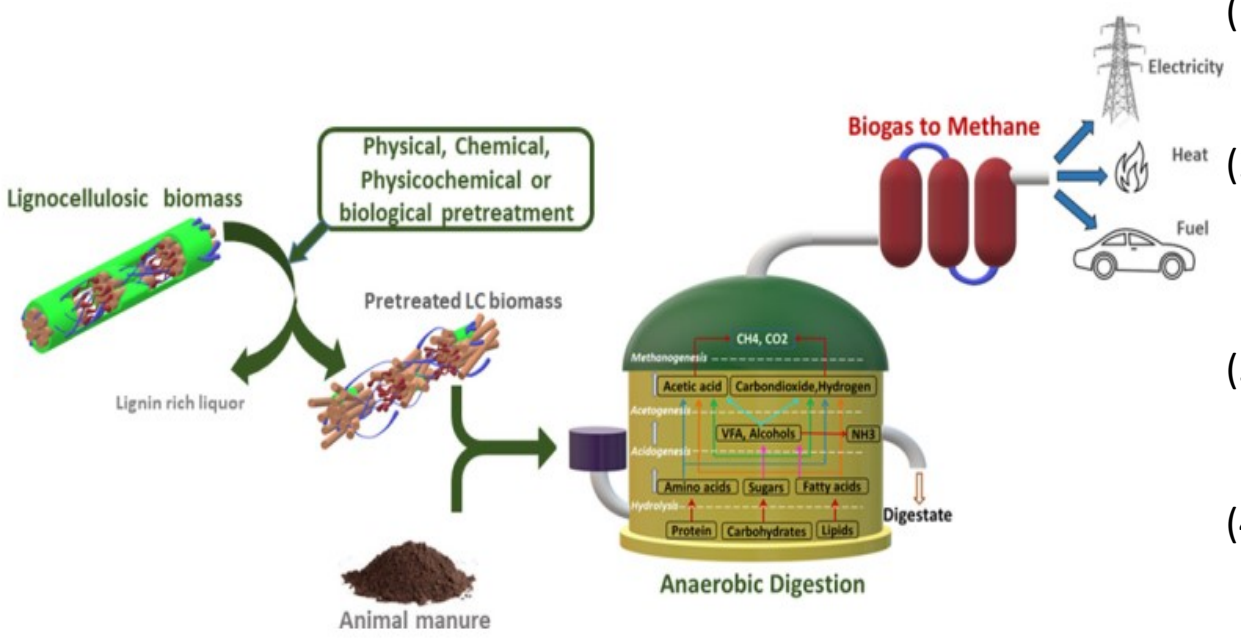
Different biological pretreatment methods for enhanced biogas production.

Pretreatment methods	Microorganism used for pretreatment	Biomass	AD conditions	Effect on methane or biogas production
Fungal pretreatment	*Polyporusbrumalis*	Wheat straw	Batch, 36 °C, 57 days	52% higher methane yield
	Trametes versicolor	Corn silage	Semi-continuous, 37 °C, 21 days	Methane generation rate 0.236 m^3 CH4 $kgVS^{-1}$ (Control 0.167 m^3 CH4 $kgVS^{-1}$)
	Pleurotus eryngii	Corn stover	Batch, Mesophilic, 40 days	19% higher biogas production
	Flammulina velutipes	*Agropyrone longatum*	Batch, 37 °C, 24 days	120% higher biogas production
	Pleurotus ostreatus	Rice straw	Batch (SS), 37 °C, 45 days	120% higher methane yield
	Trichoderma reesei	Rice straw	Batch (SS), 37 °C, 45 days	78.3% higher methane yield
	Ceriporiopsis subvermispora	Albizia chips	Batch (SS), 37 °C, 58 days	3.7-fold higher methane yield
	Ceriporiopsis subvermispora	Yard trimmings	Batch (SS),37 °C, 45 days	106% higher methane yield
Bacterial pretreatment	*Bacillus* sp.	Rice straw	Batch (SS), 37 °C, 50 days	76% higher biogas production
	Bacillus subtilis	Corn straw	Batch (SS), 37 °C, 50 days	17.35% higher methane yield
	Citrobacter werkmanii VKVVG4	Water hyacinth	Batch (SS), Mesophilic, 80 days	3.07 times higher biogas production
Microbial consortium pretreatment	Microbial consortium TC-5	Wheat straw	Batch, 45 °C, 35 days	36.6% higher methane yield
	Microbial consortium	Saw dust	Batch, Mesophilic, 28 days	25.6% higher biogas production
	Rumen fluid	Rice straw	Batch, 35 °C, 30 days	82.6% higher methane yield
	Microbial consortium	Wheat straw	Batch, 37 °C, 20 days	80.34% higher methane yield
Enzyme pretreatment	Cellulase	Corn stover	Batch, 37 °C, 18 days	36.9% higher biogas production
	Endoglucanase + Xylanase + Pectinase	Spent hops	Semi-batch, 37 °C	13% higher biogas production
	Cellulase + Cellobiase	Switch grass	Batch, 50 °C, 30 days	Methane yield 274.28 mL g^{-1} (VS), (Control 197.39 mL g^{-1} (VS))
	Endoglucanase + Xylanase + Pectinase	Sugar beet pulp silage	Batch, 37 °C, 30 days	27.9% higher biogas production
	Endoglucanase + Exoglucanase + Xylanase	Sorghum forage	Batch, 35 °C, 30 days	15% higher methane yield
	Laccase	Corn stover	Batch, 37 °C, 30 days	25% higher methane yield
	Mn Peroxidase + Versetile Peroxidase	Corn stover	Batch, 37 °C, 30 days	17% higher methane yield

Biological Pretreatment



Biomethane from Lignocellulosic biomass: Challenges and ways forward



(1) correlation between biomass degradability and its structural and compositional properties on the relative contributions of each feature to lignocellulose resistance to biodegradation;

(2) Adaption of anaerobic bacteria to lignocellulosic feedstocks following different pretreatment methods and the effect of different pretreatment methods on the microbial population inside the raw biomass and subsequent AD processes;

(3) Effects of ethanol fermentation inhibitors (i.e. furfural, HMF, and phenolic compounds) and chemical residues of chemical pretreatment processes on the AD process;

(4) Combination of AD with biofuel processes (bioethanol, biohydrogen, or biobutanol) to increase the energy efficiency of the biorefinery process, e.g. the byproducts of bioethanol and biohydrogen production can produce biogas via AD

(5) Development of new and low cost pretreatment methods that are suitable for AD processes. Most current AD studies focus on the evaluation of various kinds of pretreatment methods developed for cellulosic ethanol processes.

Part 3:
Biomethane Production Systems

Biogas production

- AD can be divided into wet anaerobic digestion (WAD) and dry anaerobic digestion (DAD) depending on the total solid (TS) content of biomass feedstock:
- WAD handles biomass with TS < 15% and consume around 1m3 fresh water per ton of organic biomass digestion (Submerged AD)
- DAD treats high solid content biomasses (with TS > 20%)

Factors affecting biogas production

- Hydrolysis - a key rate-limiting factor during AD
- pH: A near neutral pH (6.87.4) is considered as the ideal pH for the enrichment, growth, and relative abundance of methanogenic microbial community towards increasing the CH4 production
- C/N ratio: Lower C/N ratios decrease nitrogen inhibition, which is toxic to methanogens and leads to reduced utilization of carbon sources. A higher nitrogen content causes toxic effects, while lower quantities of nitrogen cause nutrient limitation. The C/N ratio range of 20:1 to 35:1 is considered optimum, and the ratio of 25:1 is considered ideal for the AD process.
- Hydraulic retention time: Maximum CH4 production and its upgradation essentially occur at
- optimized HRTs. The optimized HRT mainly depends on the type of biocatalyst (mixed or pure culture) and the OLR.

Comparison: WAD vs DAD

Parameters	Wet Anaerobic Digestion (WAD)	Dry Anaerobic Digestion (DAD)
Total Solids (TS) content	<15%	>20%
External water use	1 m^3/ton of biomass	10 times lower than WAD
Abrasion of digester	Frequent clogging and abrasion from digestate (sand, dirt, and grit etc.) result operational difficulties	Very little to lower possibility of clogging and abrasion
Loss of volatile solids (VS)	Higher loss during biomass pretreatment	No loss
Organic loading rate (OLR) (kg VS/m^3/d)	2–5	5–12
Maximum biogas yield (m^3CH_4/kg VS)	0.417	0.622

	(WASSA[a] process)	(DRANCO[a] process)
Volume of digester	Larger volume required	Smaller volume required
Phases involved	At least two phases	Single phase
Dispersion of inhibitors	More dispersion due to homogeneous mixing	Less dispersion because of no mixing
Digestate dewatering	Extensive dewatering required	Not required
Wastewater and compost	More wastewater and less compost formed from digestate	Less to no wastewater and more compost formed as by product
Digestate characteristics	Less stable with high VS	More stable than WAD

[a]Commercial AD process

Main Challenges in DAD

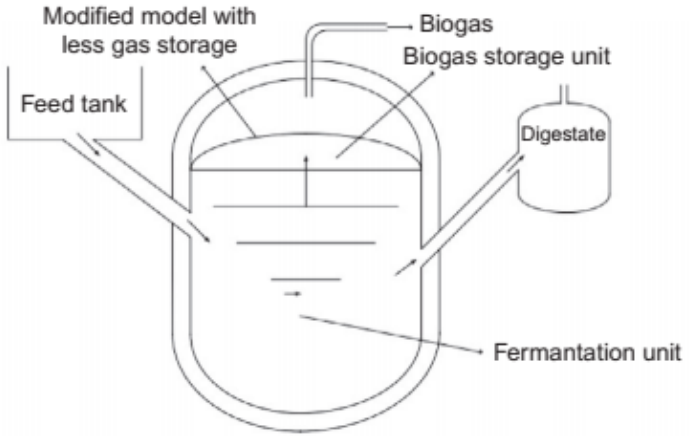
Advantages of DAD over the WAD

- TS content can be 20 - 40% compared to maximum 20% for LAF
- Smaller reactor volume
- Lower energy requirements for heating
- Minimal material handling
- Lower total parasitic energy loss
- Tolerant process for wide range of contaminants (plastics, paper, glass)
- Digestate can be used as fertilizer
- Less maintenance required
- Less complex process compared to LAF process

Challenges

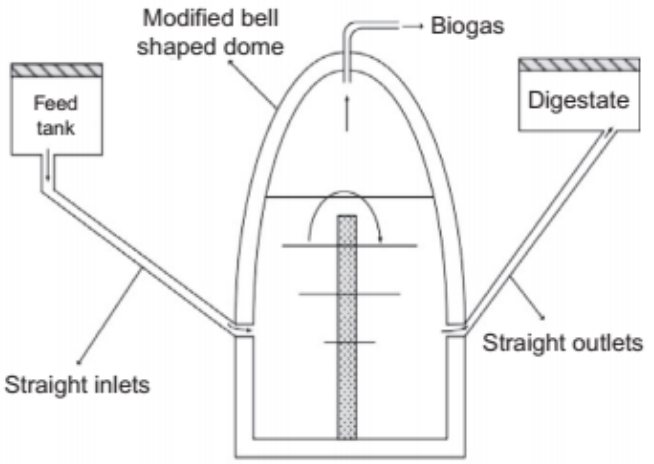
- Long retention time,
- Poor startup performance
- incomplete mixing
- Accumulation of volatile fatty acids (VFAs)

Different types of household digesters



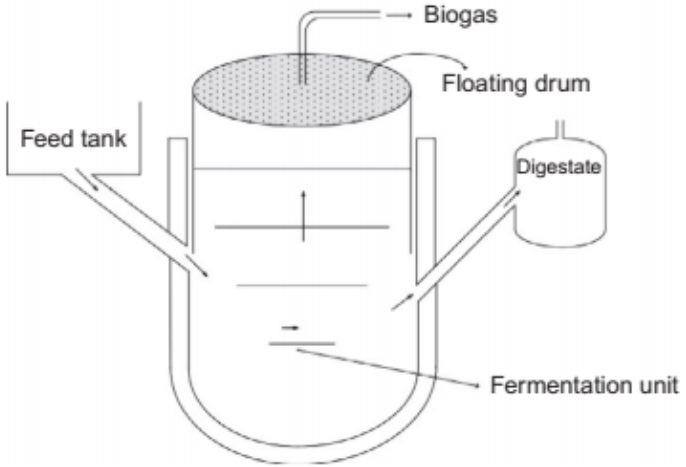
Fixed dome digester (1)

(a)



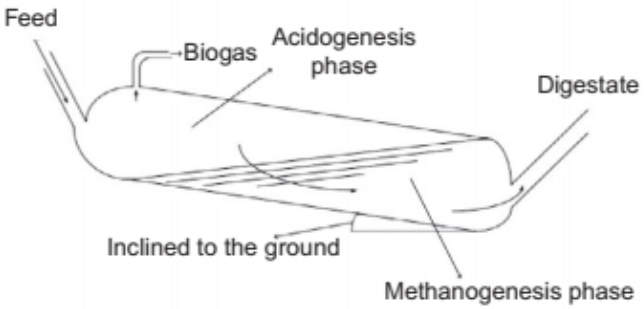
Fixed dome digester (2)

(b)



Floating drum digester

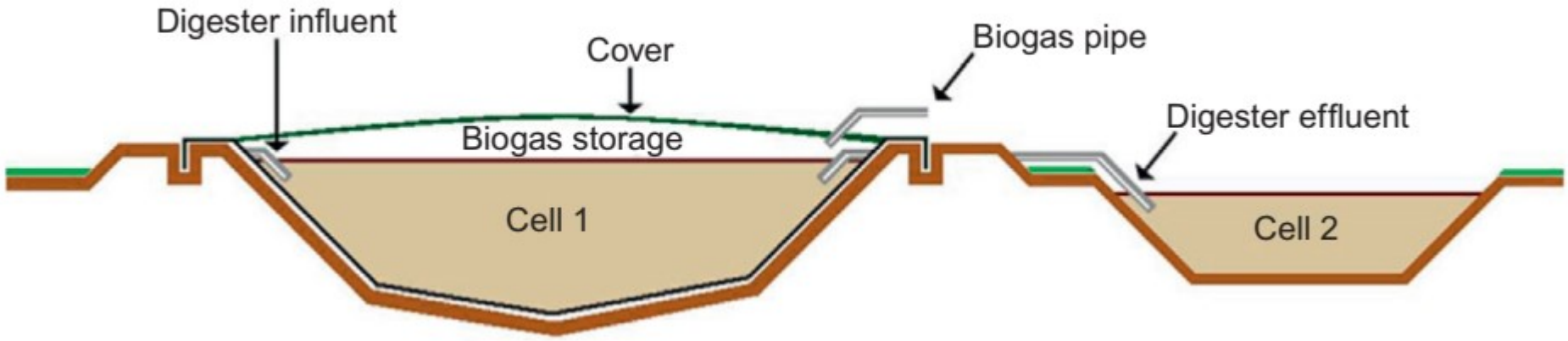
(c)



Plug flow digester

(d)

Fixed dome system: Covered anaerobic lagoon



ENHANCED BIOREACTORS FOR LARGE-SCALE APPLICATIONS

- Enhanced bioreactors for large-scale applications benefit from optimization in energy, mass, momentum transfer, and reaction process
- Computational modeling, like computational fluid dynamics (CFD) modeling, is widely used to simulate the energy, mass transfer, and configuration in biogas reactors in order to designor improve biogas production.

ENERGY TRANSFER

- Gas production, VFA, OLR (organic loading rate), and stability of the thermophilic two-step reactor was superior to that of the reactors under mesophilic conditions (source: 25 ch 3)
- It was observed that the methane content of the produced biogas would increase up to 99.3% in a 7 m3 household digester with heat insulation by increasing the temperature 7.5C and changing the substrate from crop residues to cattle dung (Source: 26).
- The significance of heat transfer in the anaerobic digestion process by modeling a plug-flow digester combined with solar energy operated on a monthly basis temperature condition was validated (Fig a). A positive net energy flux was always found in this digester model, revealing that solar energy was able to keep the digester working without extra energy input. However, the total methane production changed remarkably with temperature conditions (Figure b).

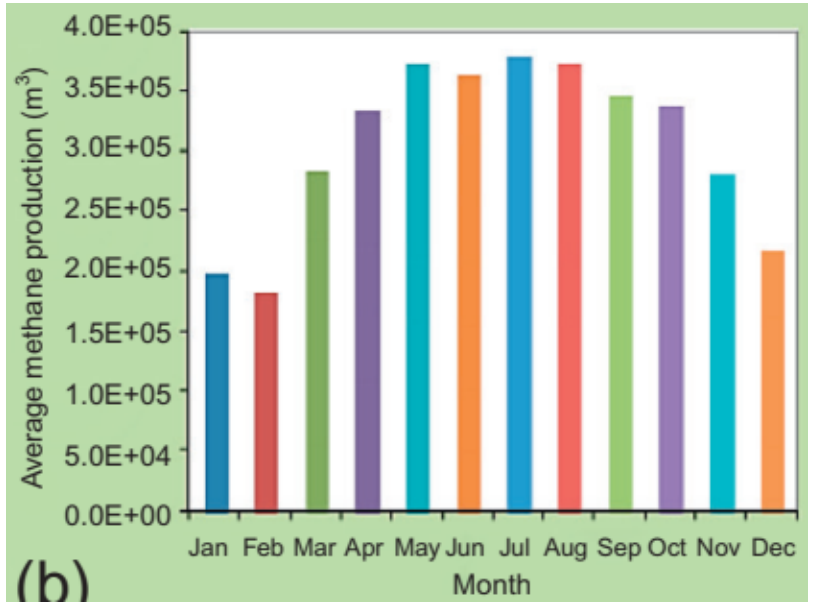
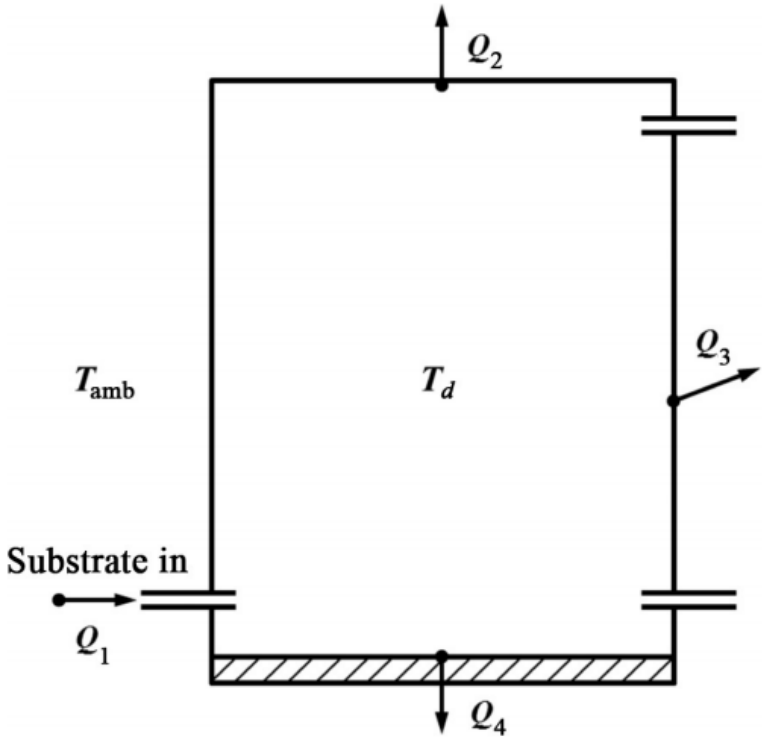


Figure (a) Plot of velocity vectors when operated in January; (b) Predictions of monthly methane production in 12 months of the plug-flow digester.

Heat loss due to mass flow



The heat loss due to heating up input feedstock (Q1)

$$Q_1 = C_p m\left(T_{\text{dig}} - T_\infty\right)$$

Heat loss through the digesters Cover (Q2)

$$Q_2 = \frac{T_{\text{dig}} - T_\infty}{\frac{1}{h_{c1}} + \sum R_{\text{cover}} + \frac{1}{h_{c2}}} A_{\text{cover}}$$

Heat loss through the digesters Wall (Q3)

$$Q_3 = q_{\text{walls}} A_{\text{walls}}$$

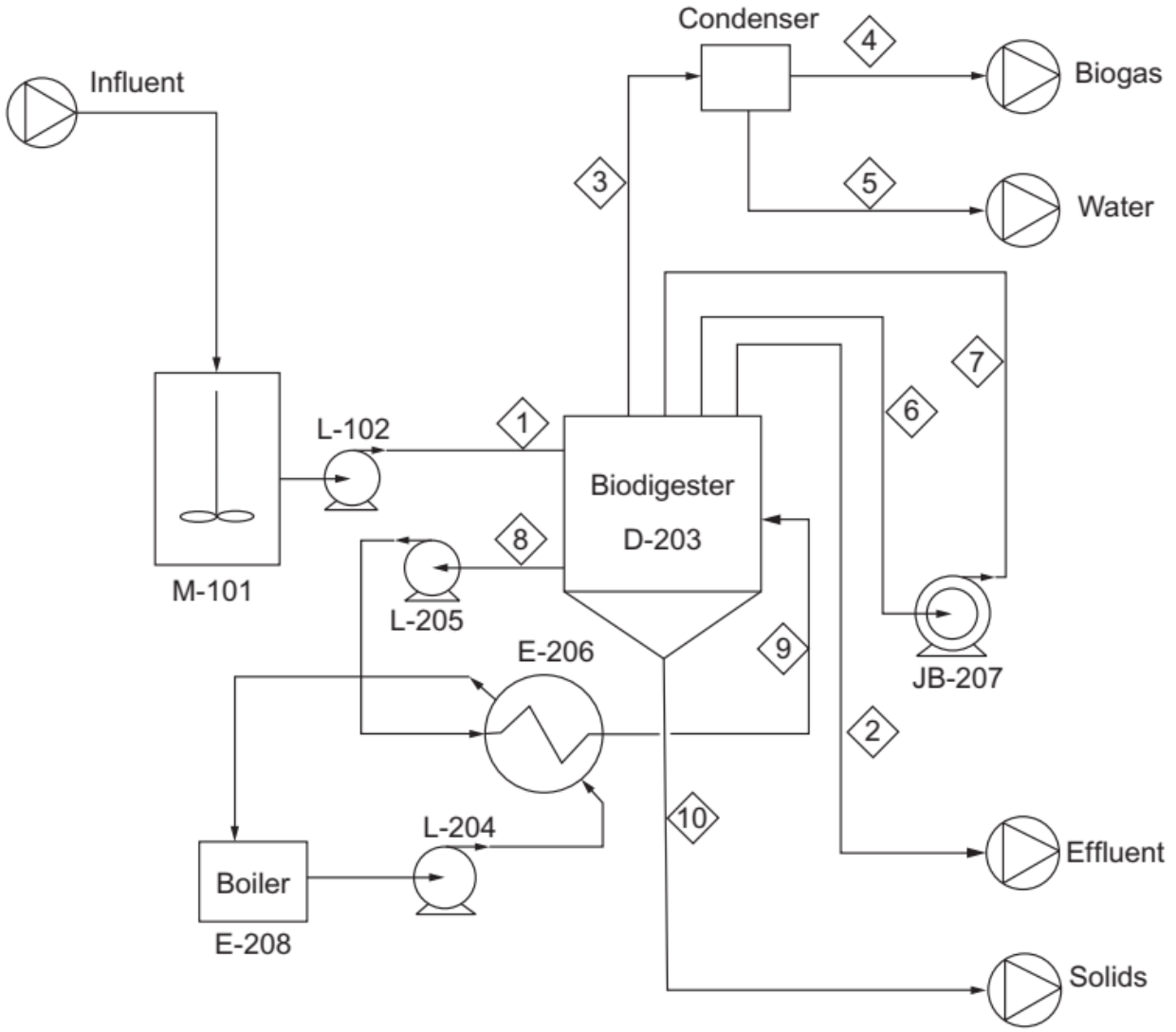
$$= \frac{(T_{\text{walls}} - T_\infty)}{\sum R_{\text{walls}} + \frac{1}{h_{c2}}} A_{\text{walls}}$$

Heat loss through the digesters Floor (Q4)

$$Q_4 = q_{\text{floor}} A_{\text{floor}}$$

$$= \frac{(T_{\text{floor}} - T_{\text{soil}})}{\sum R_{\text{floor}}} A_{\text{floor}}$$

Process diagram of a thermophilic anaerobic pilot plant



Heat transfer Enhancement

There are various ways to improve the heat transfer of heat exchangers used in an outside heating loop of a biogas reactor:

- increasing the heat transfer area, mentioned in the former sector of inside heating, by adding fins to the tube surface;
- changing tube materials to those with higher heat conductivity coefficient;
- increasing the convective heat transfer coefficient on both sides via facilities such as baffles in the shell side.

Waste heat recovery

Why?

- In the energy consumption of a biogas system, more than 80% or sometimes 90% of energy is used for heating substrate, indicating that recovering waste heat from the substrate is an important way to reduce the total energy consumption.

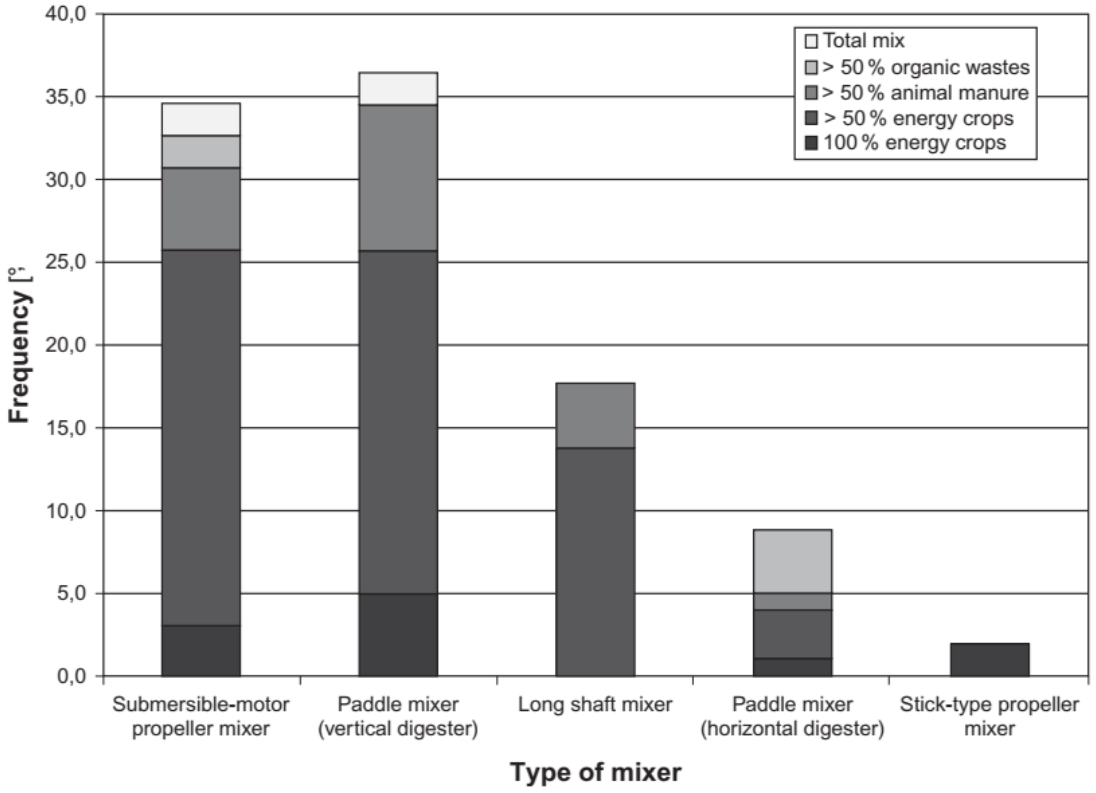
How?

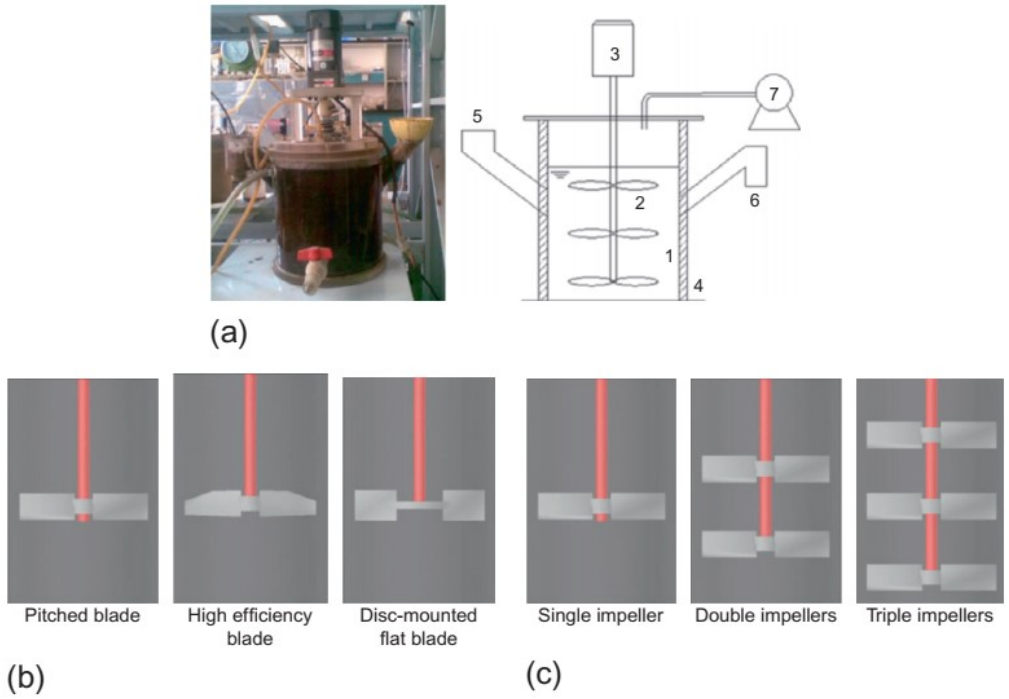
- In the CHP unit, 55% of the biogas energy is converted to heat, and waste heat can be recycled from a series of three heat exchangers.
- The heating water from the standard CHP unit is released at 90C and returned at 70C after heating the sludge and digesters.
- The heat can be used to preheat the therphilic anaerobic sludge.

STIRRING AND MIXING IN BIOGAS REACTORS

- Mixing improves the contact between substrate and bacterial consortium, which is essential to increases the biogas production.
- Mixing can eliminate concentration and temperature gradients in the anaerobic digestion.
- The homogenization of nutrients within the entire volume of the digester and avoiding the accumulation of VFA’s and pH inhibitions.
- Mixing also aids in particle size reduction as digestion progresses and in removal of gas from the mixture
- The mixing influences biogas production depending on the type of reactor, the type of agitator used, and the substrate.
- Excessive mixing may reduce the biogas production. Continuous mixing was found inhibitory at higher loading rates.

Mechanical stirring





(a) Diagram of the anaerobic digester (1, digestion tank; 2, blade; 3, motor, 4, jacket for water bath; 5, inlet; 6, outlet; 7, gas flow meter); (b) Types of stirring impellers for anaerobic digestion; (c) Number ofimpellers

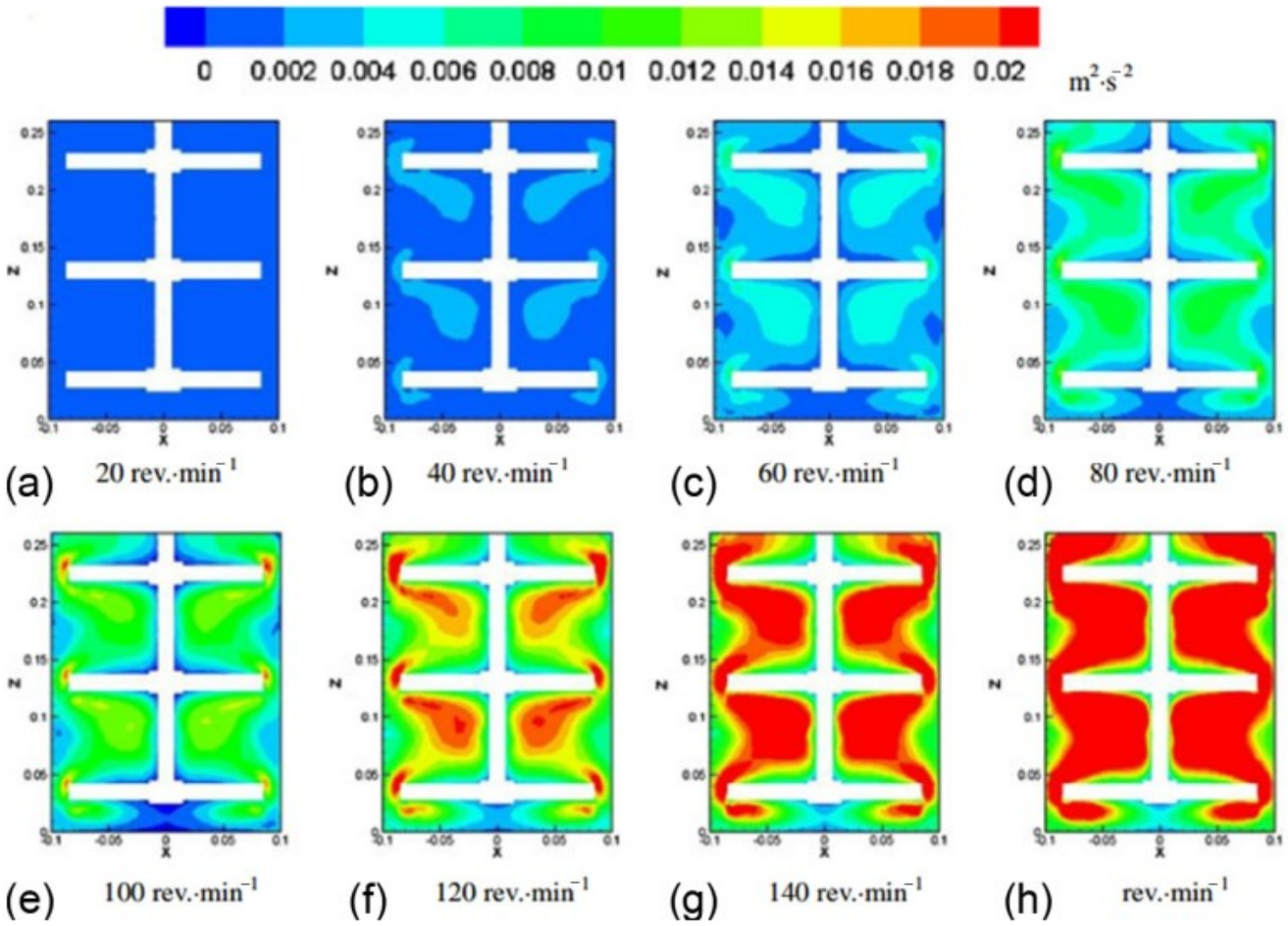
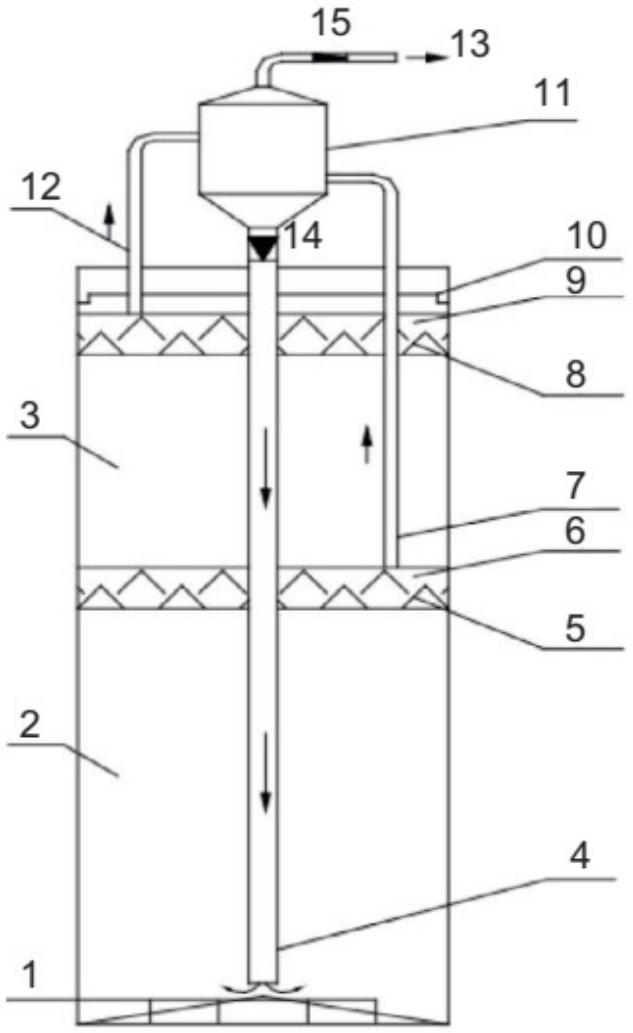


Figure: Volume fraction of the solid phase at different stirring rate.

- Not all parts of a digester need to be mixed equally, and continuous shear force brought by excess stirring negatively impacts the microbial consortiums, with unmixed strata at the base of the digester demonstrating methane producing activity 1.5 times of that in mixed zones
- The mixing intensity decreases with an increase in TS.

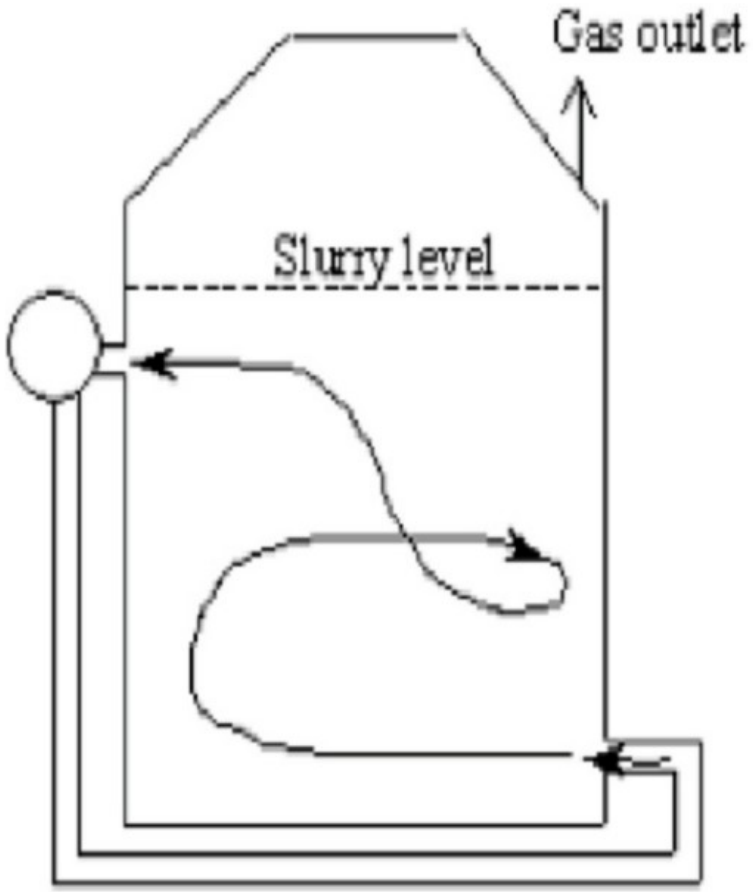
Hydromechanical mixing: Air lifting

- Airlifting biogas reactors use the rising tendency of produced biogas bubbles as the power source to agitate and further reduce the cost of mixing.



(1) the influent distributor, (2) the first reaction chamber, (3) the second reaction chamber, (4) the returned mixture pipe, (5) the first tri-phase separator, (6) the first reaction biogas chamber, (7) the first reaction biogas lift pipe, (8) the second tri-phase separator, (9) the second reaction biogas chamber, (10) the effluent zone, (11) the segregated bag, (12) the second reaction biogas lift pipe, (13) the effluent biogas pipe, (14) the flow meter of the returned mixture pipe, and (15) the biogas flow meter of the effluent biogas pipe

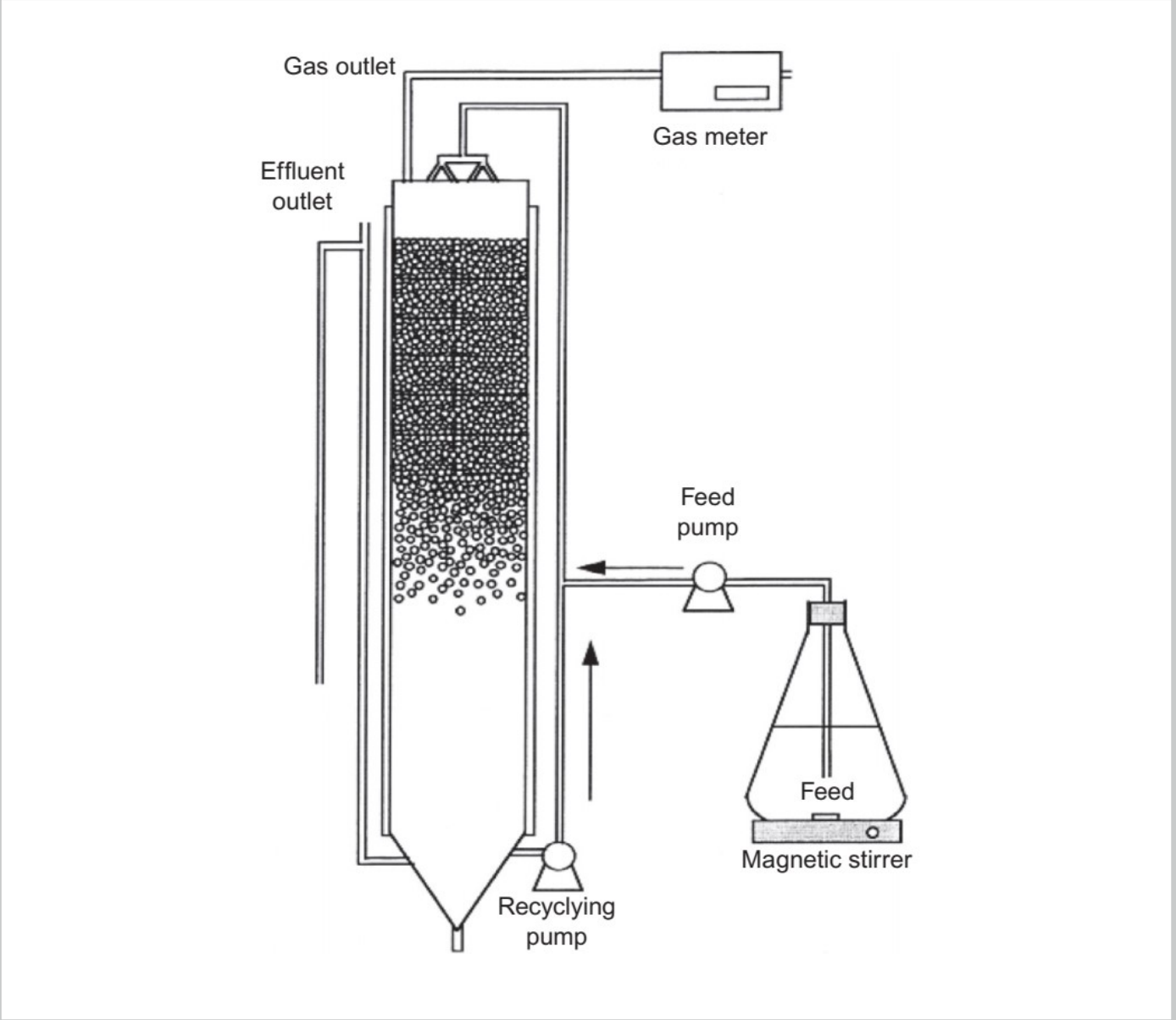
Hydraulic mixing via slurry recirculation



- Hydraulic mixing accomplishes stirring and mixing via the slurry-recirculation by pumping it out and back to the digester
- Compared to the artificial agitation in the whole digester, slurry-recirculation is more cost efficient.

Fluidized bed

- Fluidized bed biogas reactors combine immobilization and hydraulic mixing to achieve a high reactor biomass hold-up and a long mean cell residence time
- The density of carrier or supported materials needs to be smaller than the substrate to maintain floating.
- In order to realize excellent supports for cell immobilization, high porosity and surface area are also needed



Research Progress on Immobilization

- Considering the low growth rate of methanogenic bacteria, a very long residence time is necessary in most anaerobic digesters to guarantee high biomass concentrations
- via immobilization to support materials such as polymers it can be easier for methanogenic bacteria to adjust to unstable environments such as feeding, which can raise the treat rate and prevent the loss of bacteria with feeding and ejection.

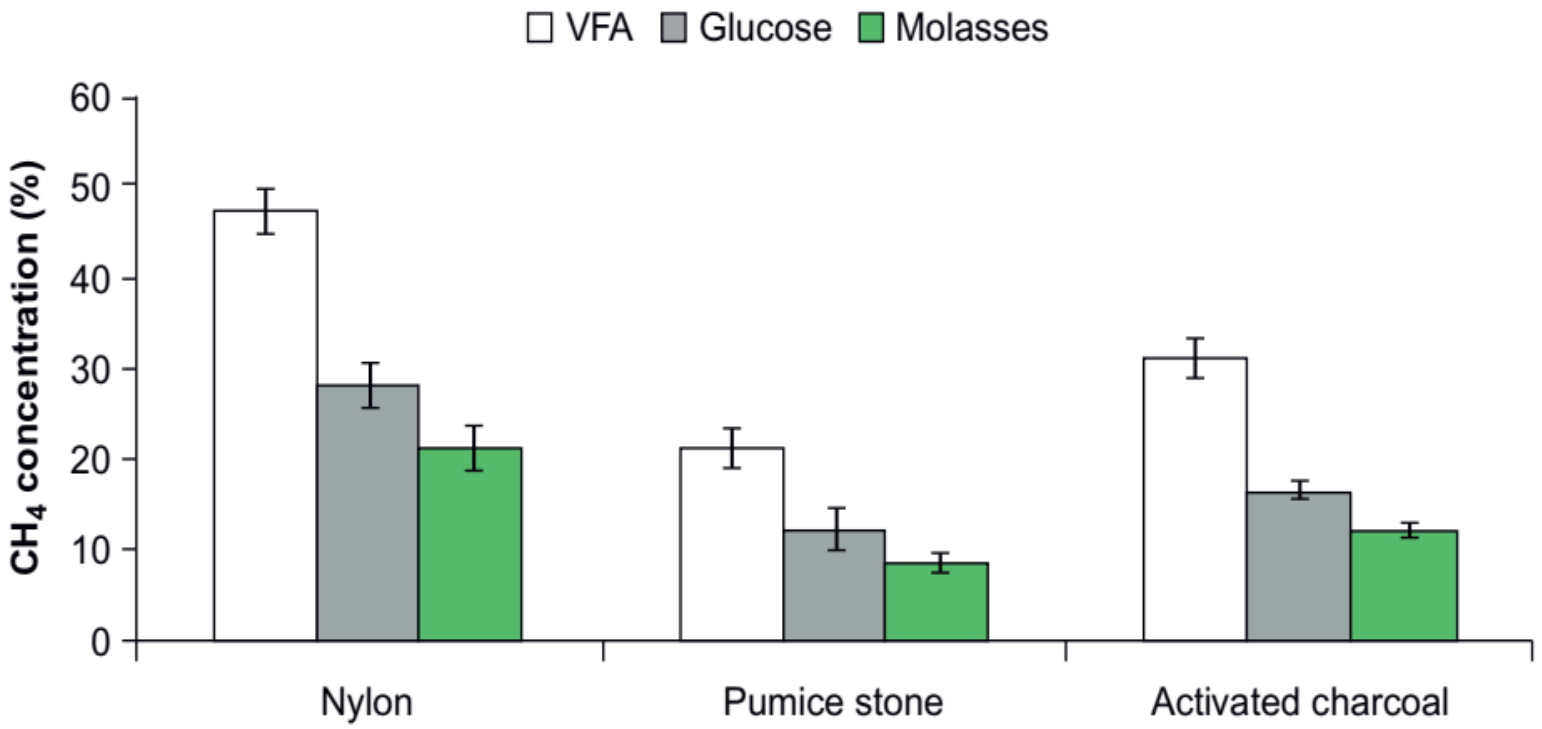
Operating Parameters of Steady-state Methanogenic Processes at various Organic Loading Rate a (immobilized methanogenic bacteria to a co-polymer of acrylonitrile (90%) and acrylamide (10%) to treat vinasse wastewater)

Retention Time (d)	**10**	**5**	**3**
OLR(kg COD m^{-3} d^{-1})[b]	2.04	4.1	6.8
COD_i[c] (kg m^{-3})	20.4	20.4	20.4
COD_r[d] (kg m^{-3})	18.8	16.7	15.9
R^M (m^3 CH_4 m^{-3} d^{-1})[e]	0.62	1.07	1.78
Y^M (m^3 CH_4 kg^{-1} COD_r)[f]	0.32	0.33	0.33

[a]The values given in the table are average of at least three times repeated experiments.
[b]OLR = Organic loading rate, kg COD m^{-3} reactor day^{-1}.
[c]COD_i = COD, influent.
[d]COD_r = COD, removal.
[e]R^M = Methane production rate, m^3 CH_4 m^{-3} reactor day^{-1}.
[f]Y^M = Methane production yield, m^3 CH_4 kg^{-1} COD.

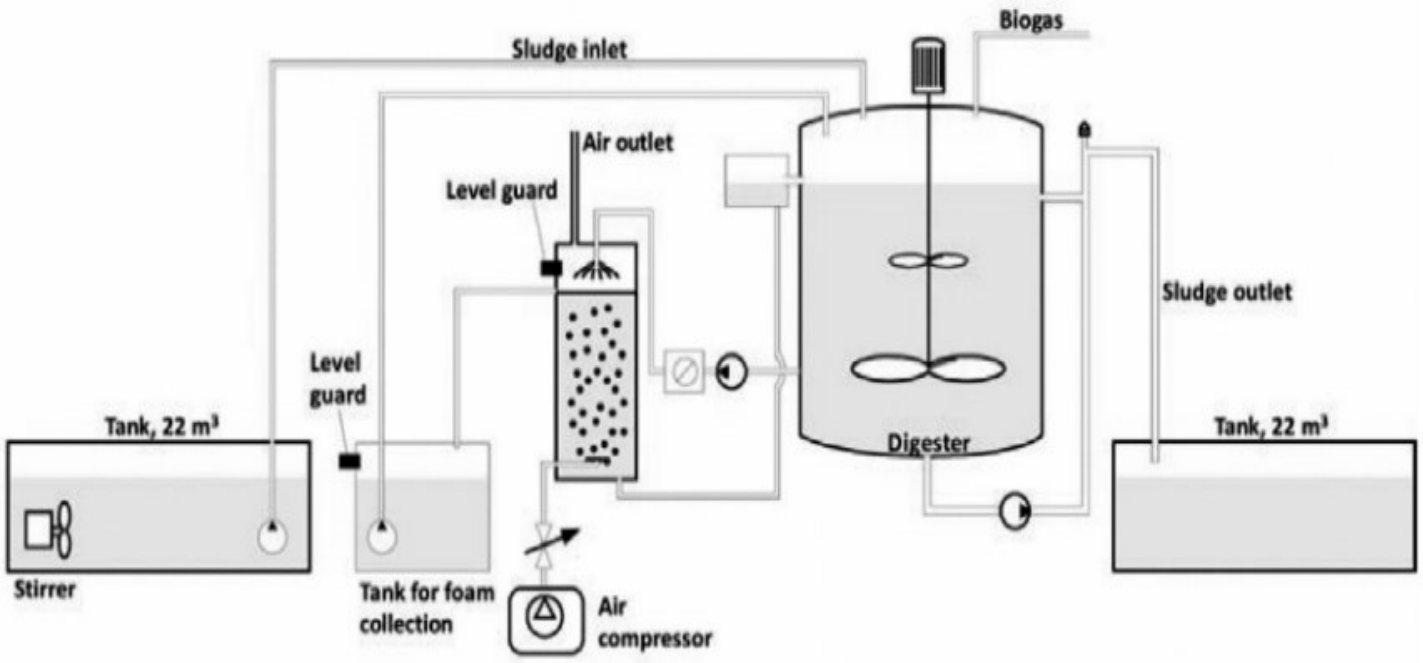
Lalov IG, Krysteva MA, Phelouzat JL. Improvement of biogas production from vinasse via covalently immobilized methanogens. Bioresour Technol 2001;79(1):83–5.

Effect of support on methane production



Methane production obtained from the bio-film grown on different support materials in batch reactors maintained with different substrates at 37 °C.

IN-SITU METHANE ENRICHMENT



Schematic view of an in-situ methane enrichment research plant

- For those small- or medium-scaled plants with relative low biogas production, a cost-efficient biogas upgrading technology is necessary. In-situ methane enrichment combines biogas production and upgrading processes by pumping sludge rich in soluble CO_2 to the desorption column to accomplish CO_2 separation and then back to digester.
- Unlike other upgrading technologies, the in-situ methane enrichment process, which separates CO_2 and CH_4 in the sludge, could decrease the methane loss down to <2% and increase the methane content to >95%.

Biogas Upgradation (BU)

Electrochemically induced biogas upgradation

- BU depends on the syntrophic interactions between fermentative and methanogenic microorganisms to increase electron transfer via mediated/direct interspecies electron transfer (MIET/DIET) to increase the H2 utilization and other electron carriers and redox intermediates towards enhanced CH4 production.
- Microbial interactions for increased electrogenic activity could be triggered for increased performance during AD, with the polarized potential developed due to electrode placement or by the external supplementation of potential towards higher CH4 production, described as electromethanogenesis (EM). Electrode placement or applied potential to a microenvironment influences on increasing the reaction/electron transfer rates with respect to conventional fermentations towards increasing the CH4 content in total biogas.
- The EM strategy in the presence of electrodes or applied potential helps in efficiently neutralizing/reducing the overpotentials and electrochemical losses to overcome the limitations of BU.
- EM in synergy with microbeelectrode interactions and the specific microenvironment helps in regulating metabolite biosynthesis for CH4 production and could be considered as an essential unit operation in the waste biorefinery.

Chemical absorption—amine absorption/stripping technology for BU

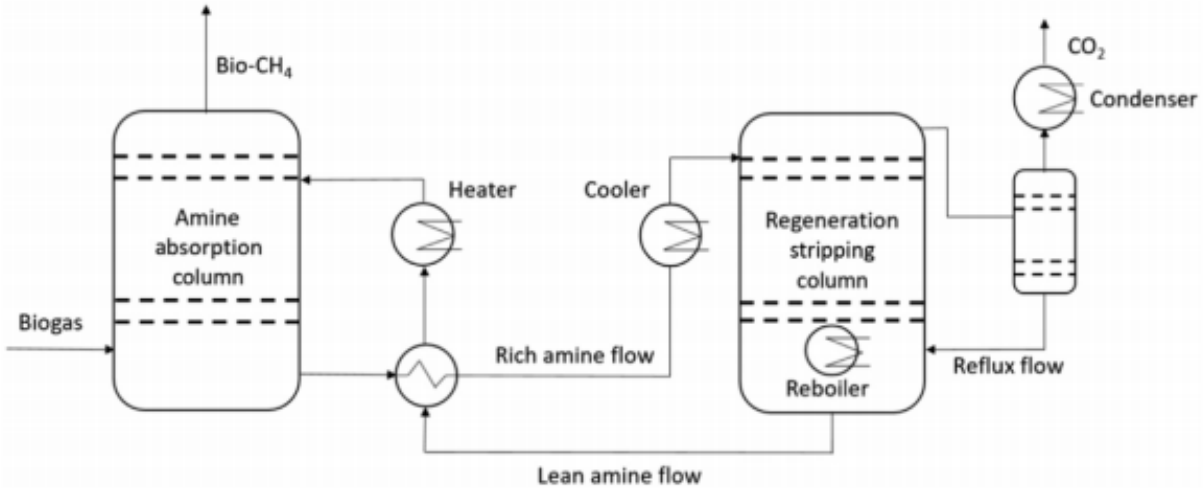


Figure: Simplified process flow diagram of an amine scrubber

Advantages	Disadvantages
High efficiency (> 99% CH_4) Cheap operation Regenerative More CO_2 dissolved per unit of volume (compared to water) Very low CH_4 losses (<0.1%)	Expensive investment Heat required for regeneration Corrosion Decomposition and poisoning of the amines by O_2 or other chemicals Precipitation of salts Foaming possible

$$2RR'NH + CO_2 \leftrightharpoons R'NH^+COO^- + RR'NH_2^+$$

$$RR' + NCOO^- + H_2O \leftrightharpoons RR'NH + HCO_3^-$$

$$CO_2 + H_2O + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^-$$

Amines: methyl diethanolamine (MDEA), diethanolamine (DEA), and monoethanolamine MEA

Amine absorption: R&D direction

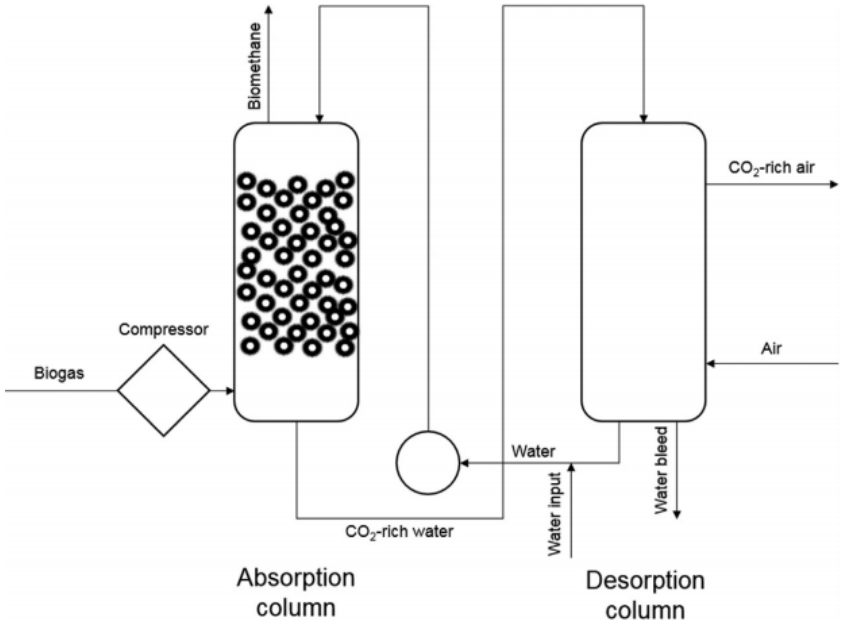
- Development of novel efficient absorbent: amino acid solutions (AASs) demonstrates higher $S_{CO2/CH4}$.
- Development of Amine-functionalized solid sorbents
- Process optimization: Regeneration of absorbents; energy and cost minimization

Water scrubbing for BU

- In water scrubbing, CO2 molecules are sorbed by means of weak molecular forces into the liquid matrix, and it is usually performed at low temperatures and high pressure to further increase CO2 solubility.
- Absorption of CO2 can be significantly improved by using an alkaline solution instead of water. Difficulty of regenerating the alkaline solution is the main issue.
- Absorption in K2CO3 solutions

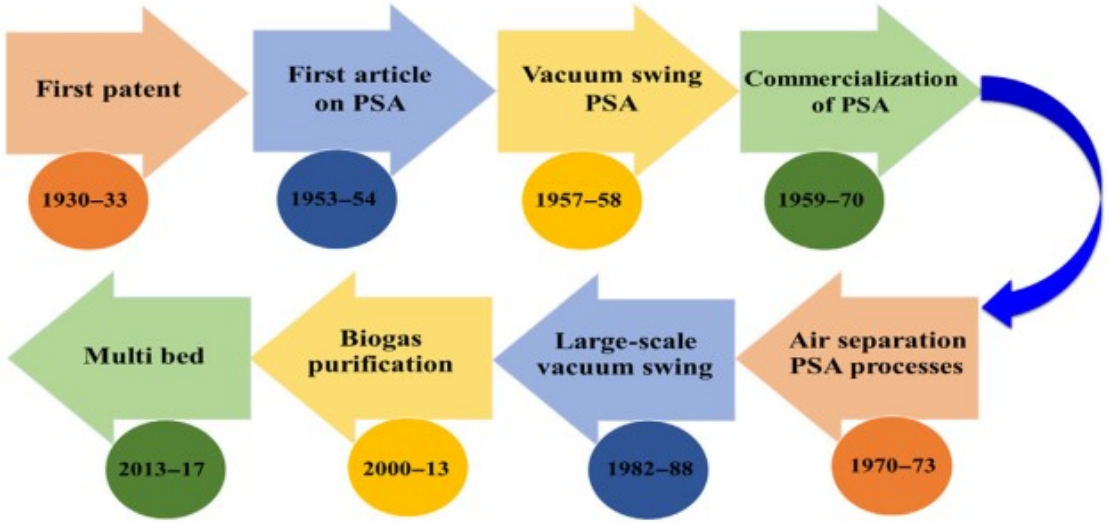
Table: Henry's constant

Species name	H^{cp} at 298.15 K (mol/m^{-3} Pa^{-1})
CO_2	3.4×10^{-2}
CH_4	1.4×10^{-5}
H_2S	1.0×10^{-3}



BU: pressure swing adsorption (PSA)

- CO2 is adsorbed onto a porous solid surface such as activated carbon and then desorbed by changes in pressure.



Temperature swing adsorption:

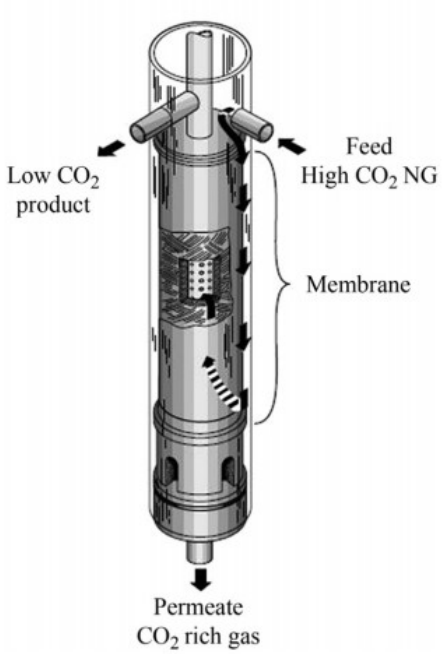
- Adsorption: At low temperature;
- Desorption: By heating the bed to remove impurities;
- Cooling: To return to the adsorption step.

Electric swing adsorption (ESA):

- feeding
- Electrification (raising the temperature of the bed using a direct Joule effect low-voltage current)
- cooling for biogas upgradation

Membrane-based technology for methane separation from biogas

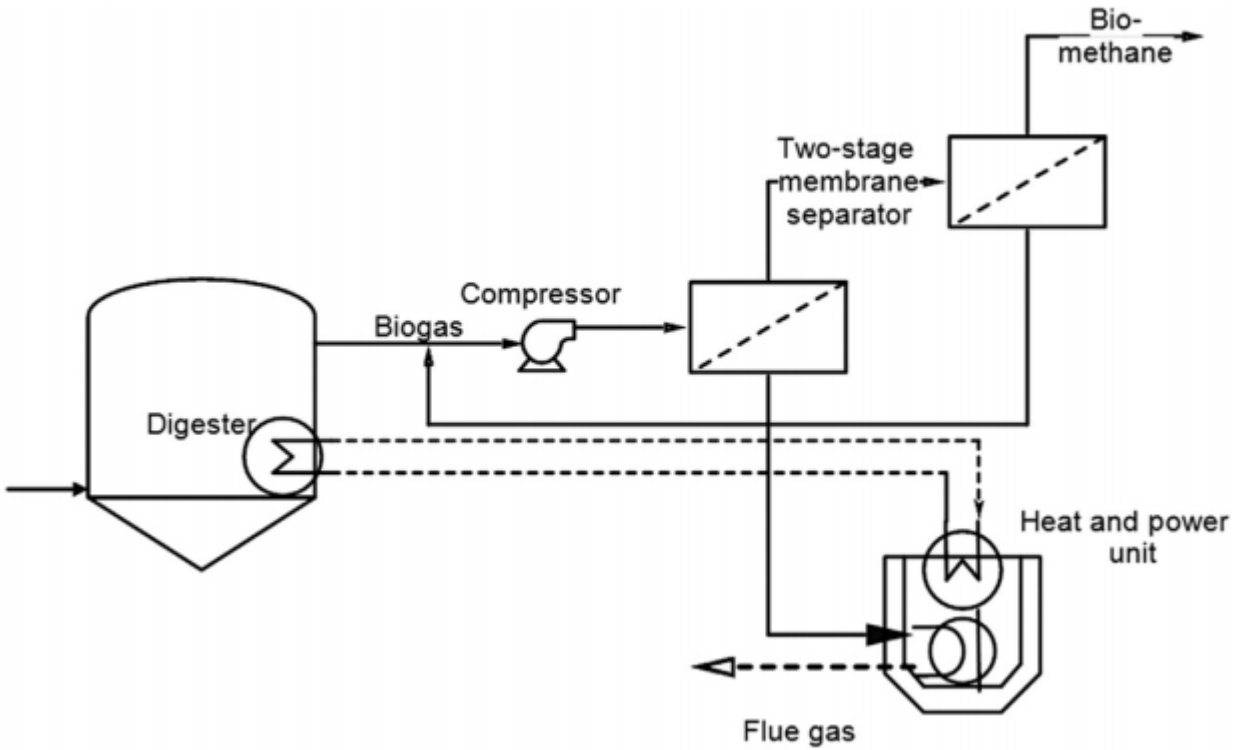
- Practically all materials used for fabrication of membranes for CO2 removal are polymer-based, for example, CA, PIs, polyamides, PS, polycarbonates, and polyetherimide.
- Most commercial membranes are made as asymmetric membranes consisting of a thick porous layer or support, on the top of which a thin membrane layer is placed. This layer governs the separation and is also referred to as the selective layer or skin layer.



Common polymer membrane materials and their gas transport properties for the CO2/CH4 binary gas mixture.

Polymer	P (CO_2) Barrer	α (CO_2/CH_4)
Cellulose acetate (CA)	8.9	20–25
Polyimide (PI)	65–110	25–15
	25–368	13.1–34.5
Polyamide (PA)	—	12.8–14.4
Polysulfone (PSf)	5.6	22.4
Polycarbonate (PC)	6.8	19
Polyetherimide (PEI)	1.25	17.5

Membrane-based technology for methane separation from biogas



Recently a two-stage biogas upgrading process using dense hollow-fiber membranes made of polyester carbonate. The breakthrough of this study was the use of membrane modules resistant to the presence of water and H2S. Due to this implementation, the pretreatment for desulfurization and drying could be avoided, and the upgrading was achieved as a single-step method. Lower energy consumption combined with high CO2/CH4 selectivity resulted in 96% vol/vol CH4 purity and reduced capital expenditures when compared to other methods.

Future Trends

- In-situ BU (in-situ methanation of CO2): Biological approach combined with electrochemical/Photocatalytic/photoelectrocatalytic approach
- Development of efficient membrane modules for CO2 separation and its further utilization to offset CO2 emission.
- Reactor development for versatile feed: energy optimization
- Process parameter optimization