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Dark fermentative hydrogen production
–
potentials and opportunities

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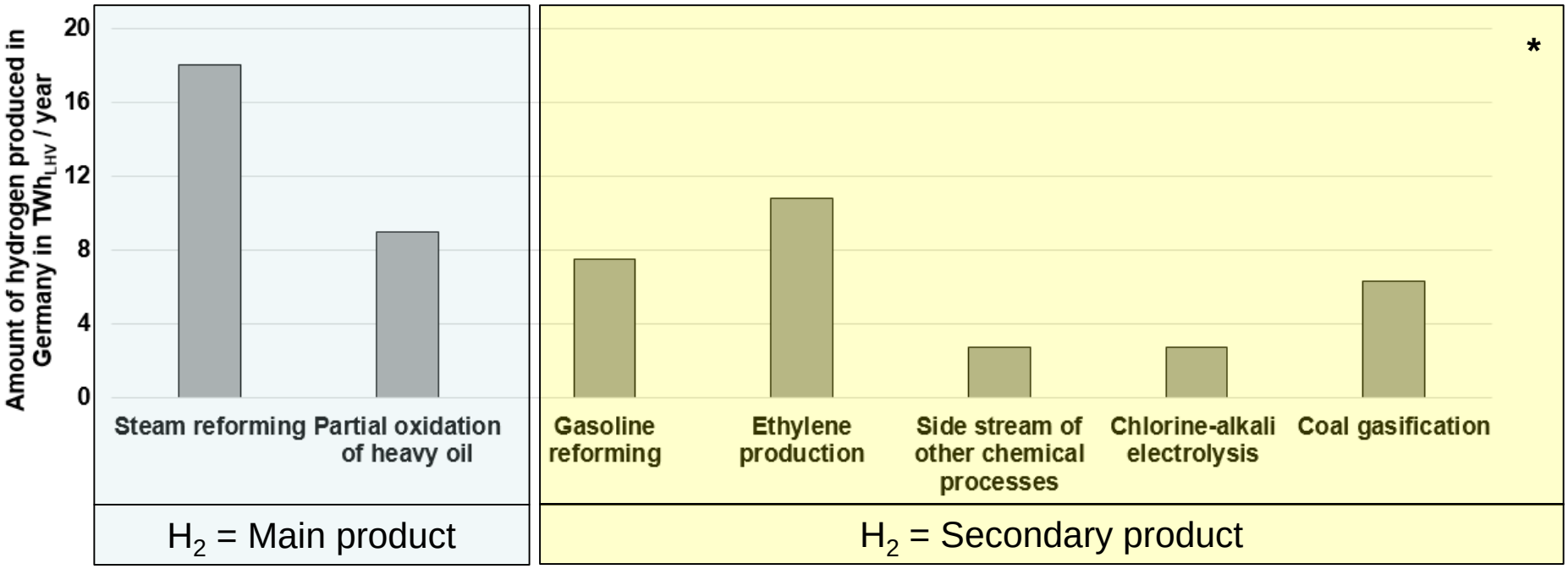
Agenda

- Hydrogen – Status quo
- Options to produce climate neutral hydrogen
- Hydrogen production from biomass
- Concept of dark fermentation
- Embedding dark fermentation into the biorefinery sector
- Conclusion

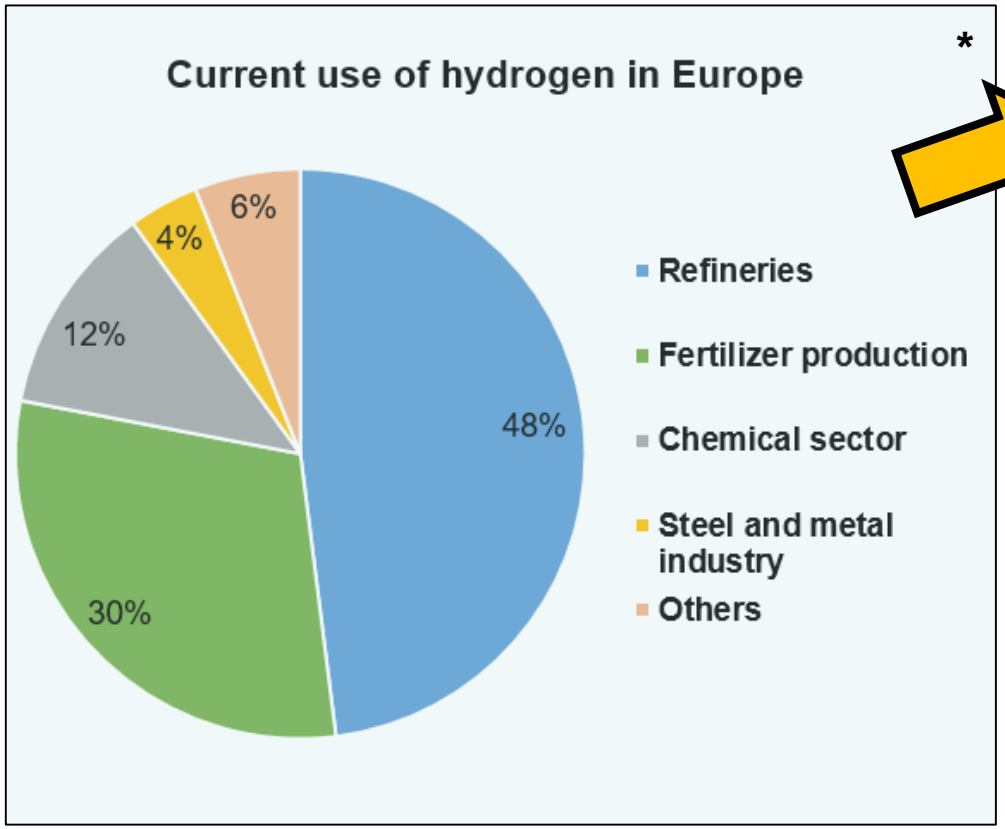
Hydrogen – Status quo



- So far, the majority of the hydrogen produced is a by-product of other processes.
- Most of the hydrogen produced to date comes from fossil sources and is accordingly accompanied by the release of climate-impacting emissions.

* Kreidlmeyer et al. (2020), Kosten und Transformationspfade für strombasierte Energieträger

Hydrogen – Status quo



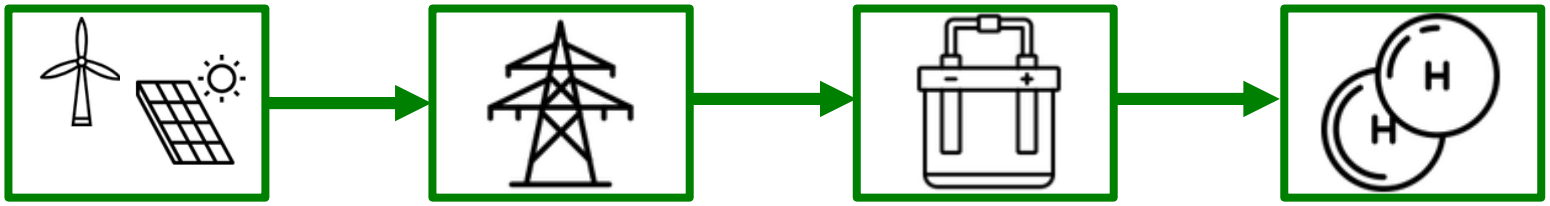
Strategic future markets (according to the national hydrogen strategy 2020)

- Industry
- Mobility
- Heat

- It is assumed that the demand of hydrogen will increase sharply in the next years.
- This is only compatible with climate protection targets if hydrogen production will be fossil-free.

* Kreidlmeyer et al. (2020), Kosten und Transformationspfade für strombasierte Energieträger

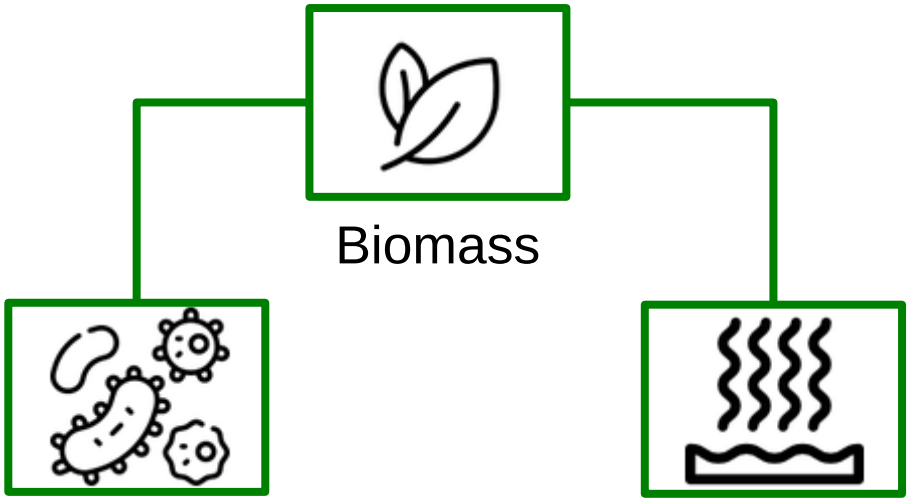
Green hydrogen



Renewable energy → Electricity → Electrolysis → Green hydrogen

- The production pathway shown is not the only way to produce hydrogen from renewable sources.
- Since renewable electricity is limited and hydrogen production based on electrolysis faces numerous challenges, the hydrogen production from biomass could play a supporting role.

Hydrogen production from biomass



Main product

- Bio-photolysis → H_2, O_2
- Dark fermentation → H_2, Acids
- Photo fermentation → H_2, CO_2
- Pyrolysis → CH_4, CO
- Gasification → CH_4, CO

Feedstocks for reforming

Types of biomass

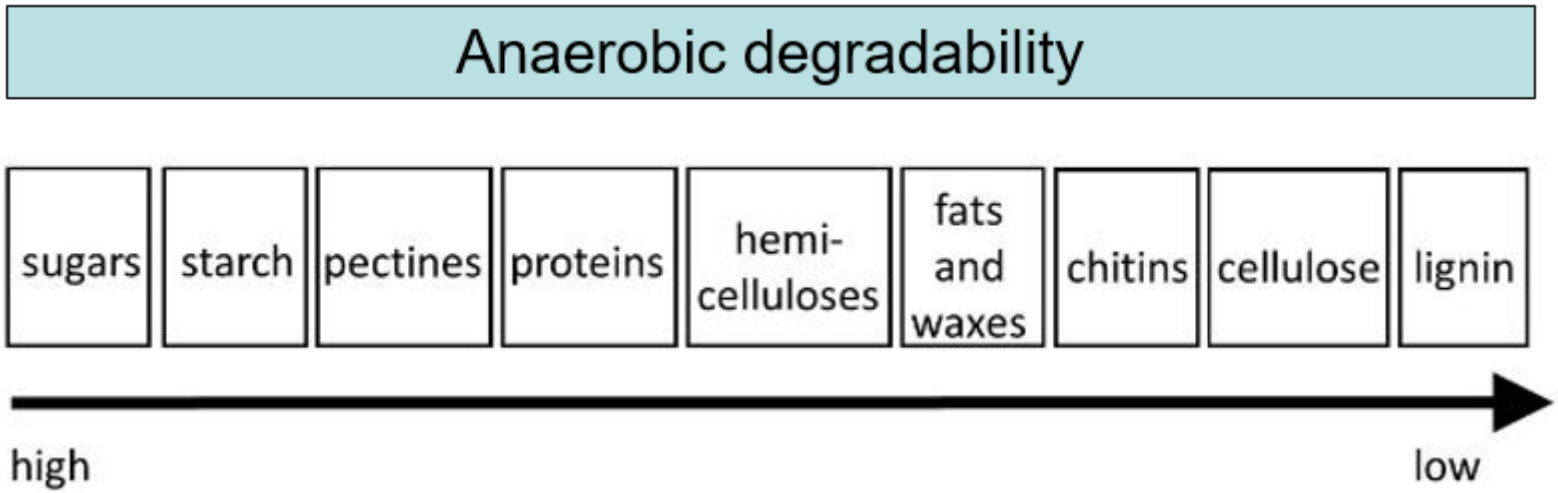
Definition of the term „biomass“

All substances of organic origin (i.e. carbonaceous matter)

- the phyto and zoomass (plants and animal) living in nature
- the resulting residues (e.g. animal excrements)
- dead (but not yet fossil) phyto and zoomass (e.g. straw)
- in a broader sense, all substances that are produced by a technical transformation and / or material use (e.g. organic household waste)

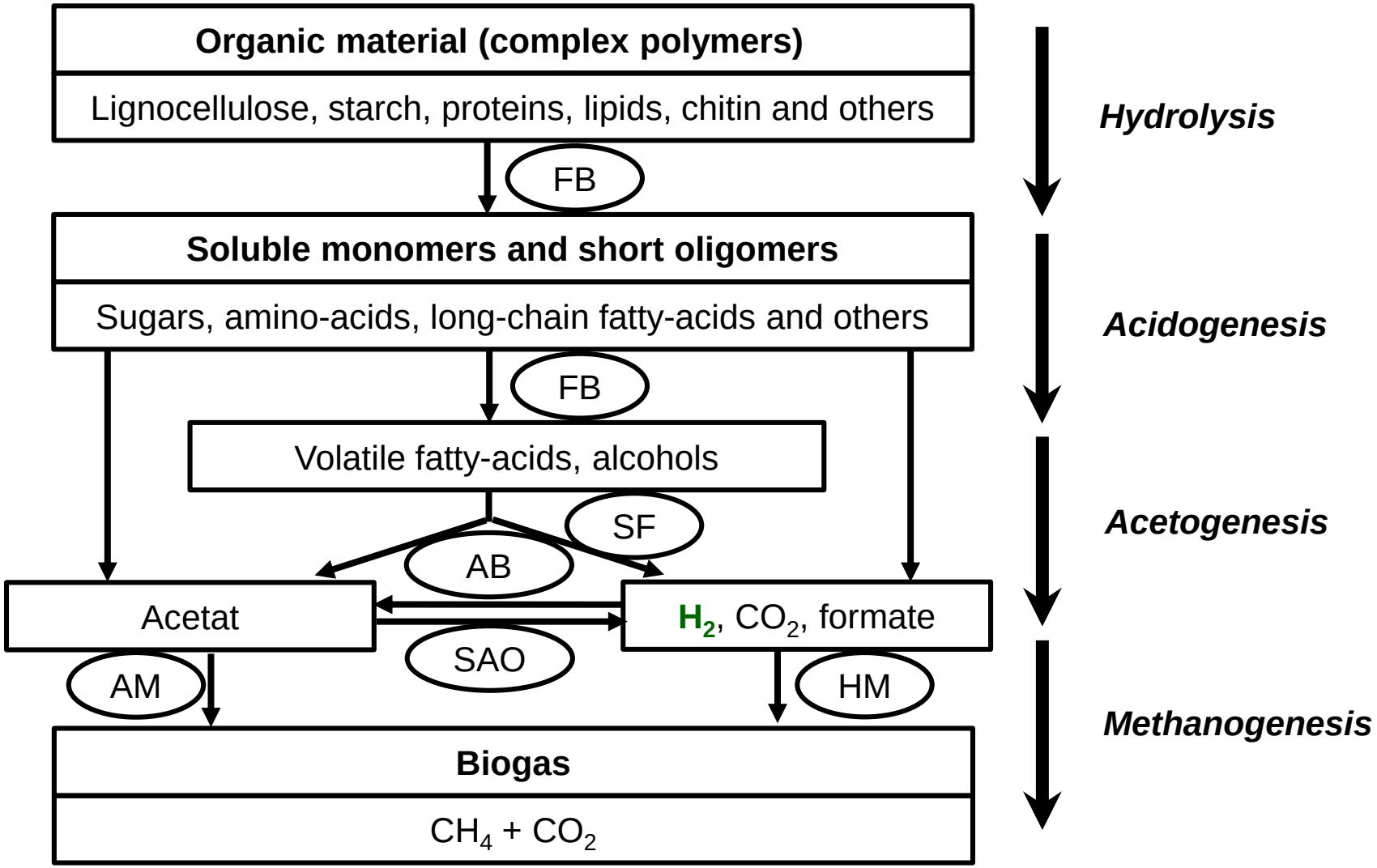



Biomass components and their degradability



- Not all types of biomass are suitable as substrates for dark fermentation (e.g. lignin cannot be degraded anaerobically).
- The content of organic substance should be appropriate for the selected fermentation process and its technical properties.
- The conditions occurring in the process are also largely due to the chosen substrate.

Connection between anaerobic digestion and dark fermentation

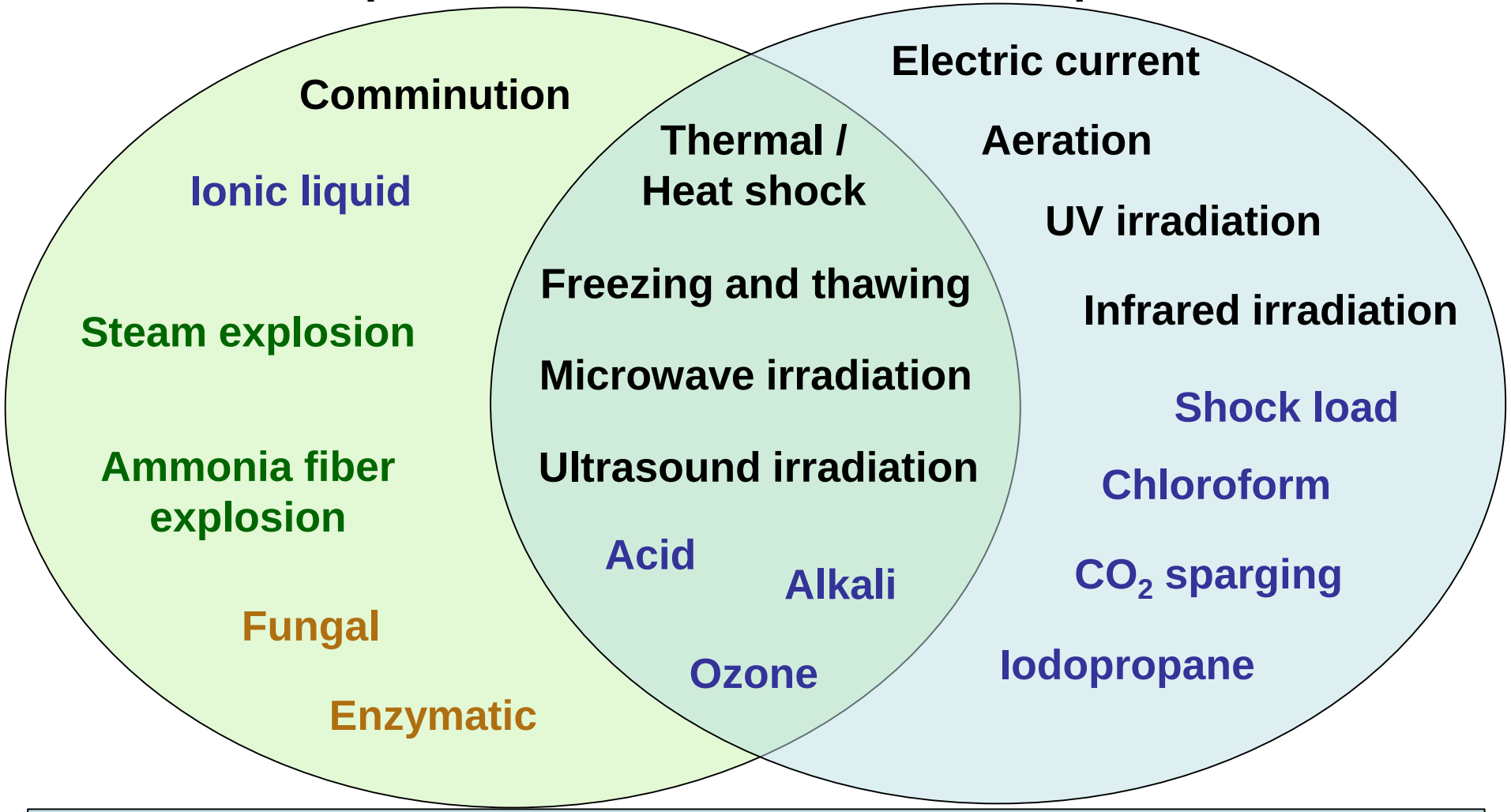


FB = fermentative bacteria; SF = secondary fermentative bacteria; AB = acetogenic bacteria; SAO = syntrophic acetate oxidizers; AM = acetoclastic methanogens; HM = hydrogenotrophic methanogens

Selection of microorganism cultures

	Pure cultures (e. g. *Clostridium sp.*)	Mixed cultures (e. g. anaerobic sludge)
Pros	• Easy detection of metabolic shifts due to the low diversity of microbial biomass • Relatively high H_2 yields	• Relatively simple in terms of process control and operation • Applicable to a large number of different substrates • No need for sterile conditions
Cons	• Not always feasible due to indigenous bacteria on the substrates • Reduced hydrolytic degradation of substrates	• Presence of H_2 consuming microorganisms (e. g. methanogenic archaea) • **Need for inoculum pre-treatment**

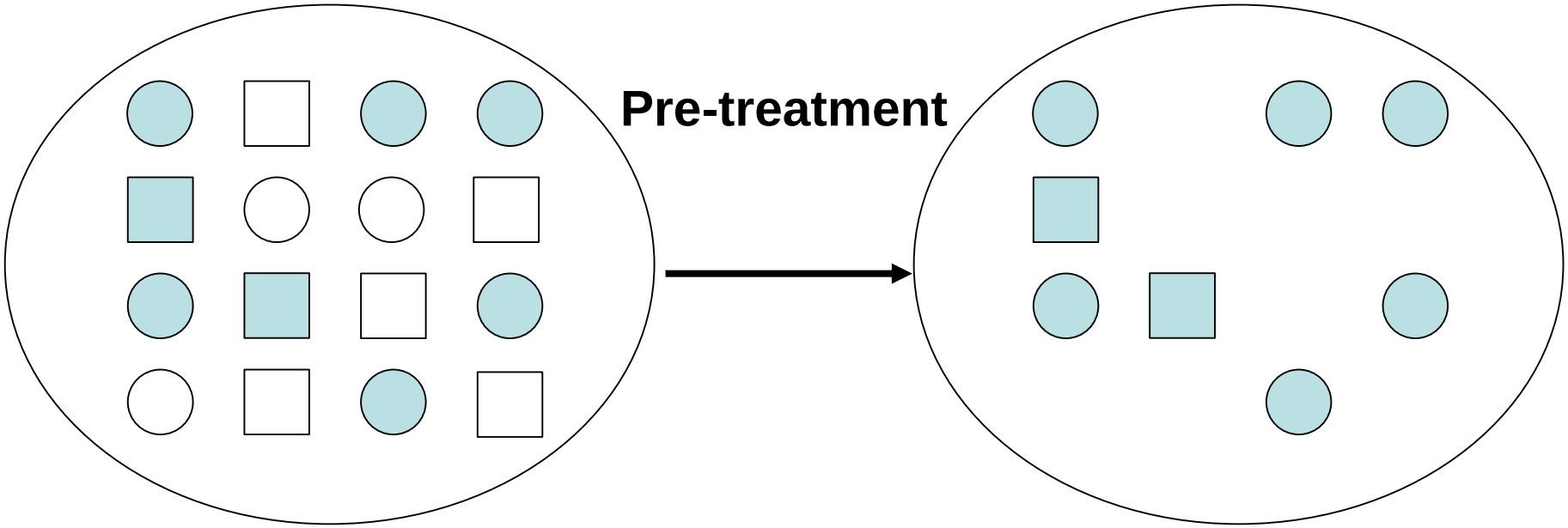
Pre-treatment methods



Physical, chemical, physicochemical, biological technologies

* Bundhoo et al. (2015), Effects of pre-treatment technologies on dark fermentative biohydrogen production: A review

Inoculum pre-treatment



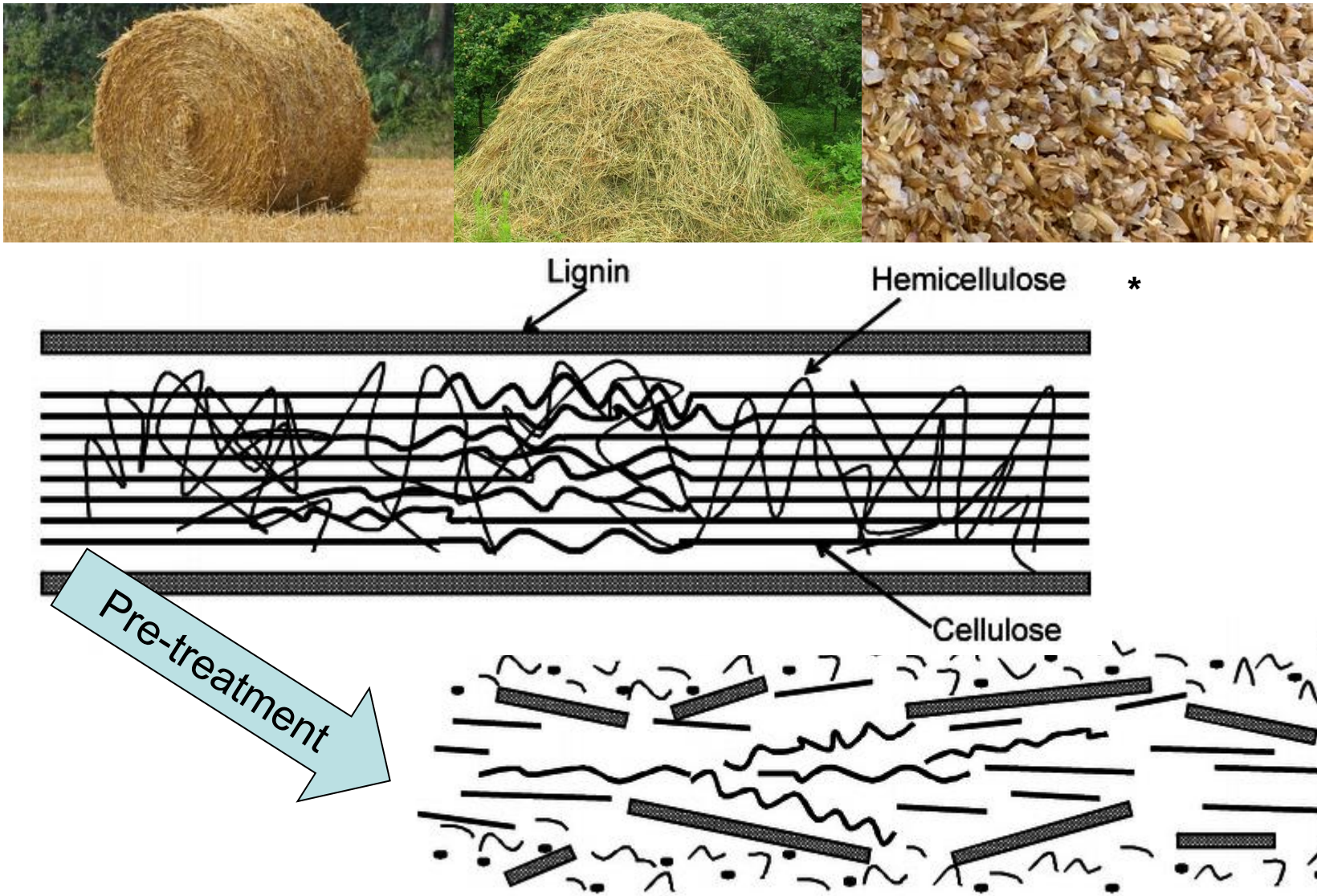
Sporulating H_2-producers

Non-Sporulating H_2-producers

Sporulating H_2-consumers

Non-Sporulating H_2-consumers

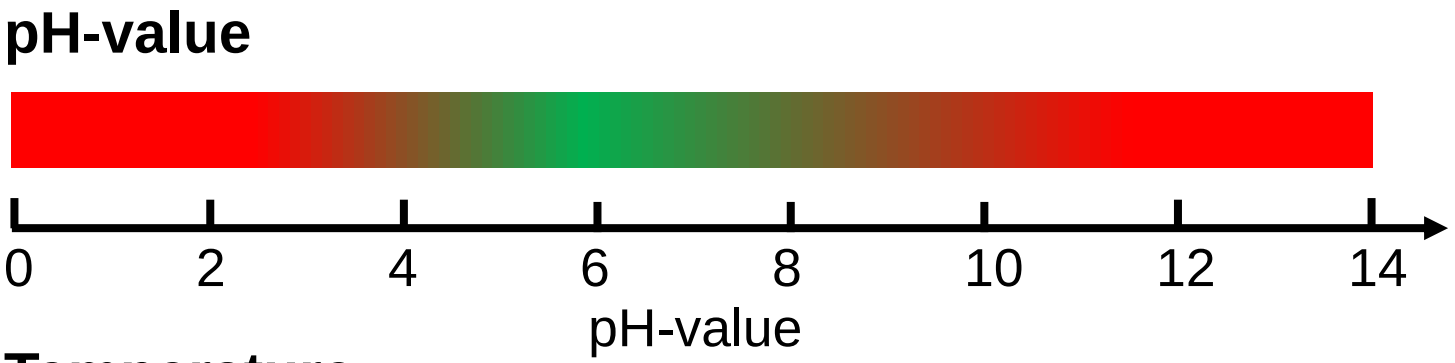
Substrate pre-treatment



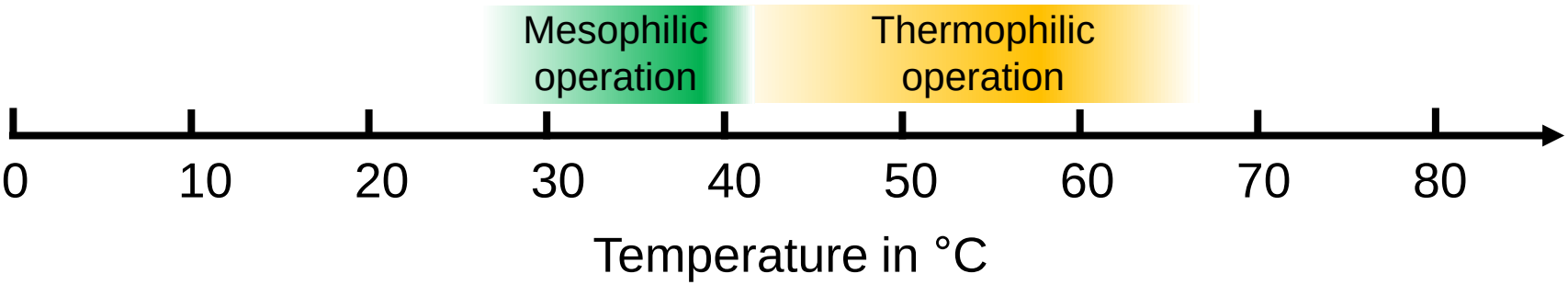
* Chaturvedi et al. (2013); An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products

Important parameters in dark fermentation

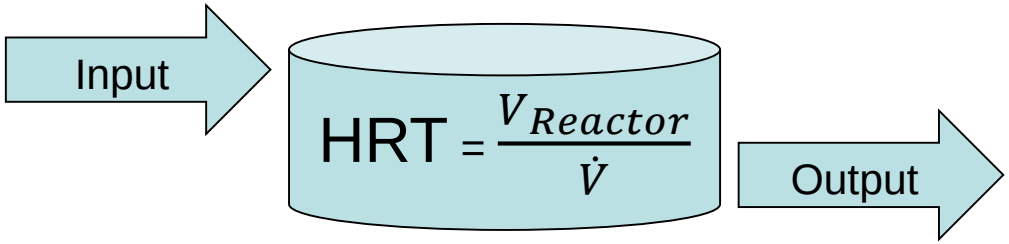
pH-value



Temperature



Hydraulic retention time



Dark fermentation:
HRT ≤ 24 h

Biogas production:
HRT ≥ 24 h

Potential substrates

Agricultural substrates		
Livestock farming	Energy crops	Herbal residues
		
Industrial substrates		
Meat processing	Fruit processing	Sugar industry
		
Municipal substrates		
Collected organic waste	Landscape conservation	
		

Theoretical energy yield

H_2
Molar mass: 2 g / mole
Energy value: 142 kJ / g

Dark fermentation

Theoretical optimum:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$$ → **3.41 MJ**

≙ 5.26 kWh/ $kg_{glucose}$

Formation of acetic acid:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CO_2 + 2CH_3COOH + 4H_2$$ → **1.13 MJ**

≙ 1.74 kWh/ $kg_{glucose}$

Formation of butyric acid:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CO_2 + CH_3CH_2CH_2COOH + 2H_2$$ → **0.57 MJ**

≙ 0.88 kWh/ $kg_{glucose}$

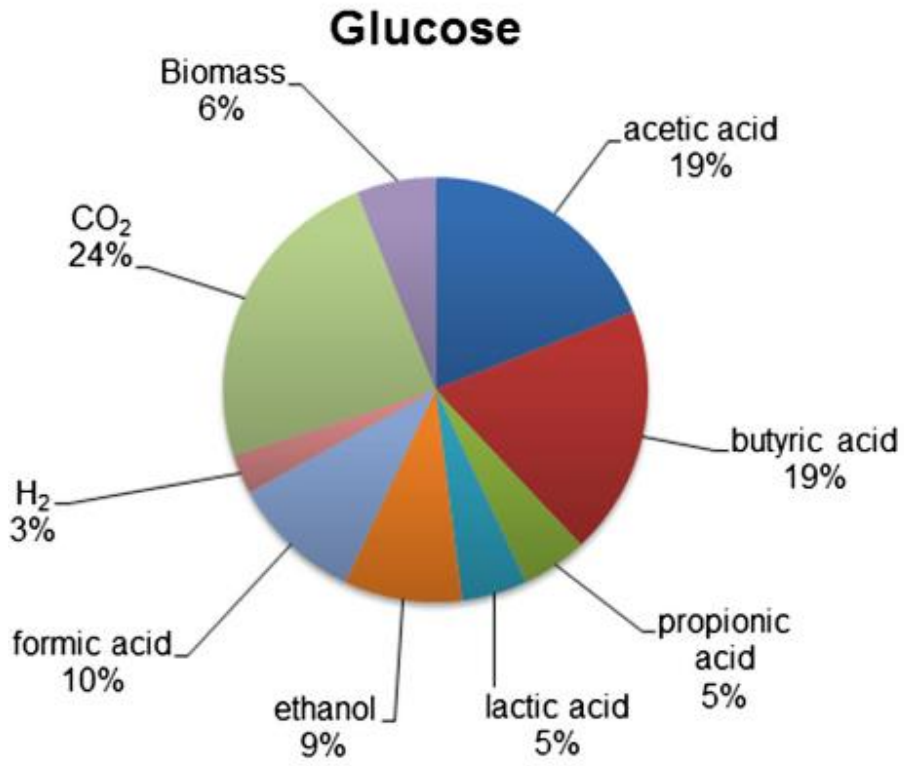
Biogas production

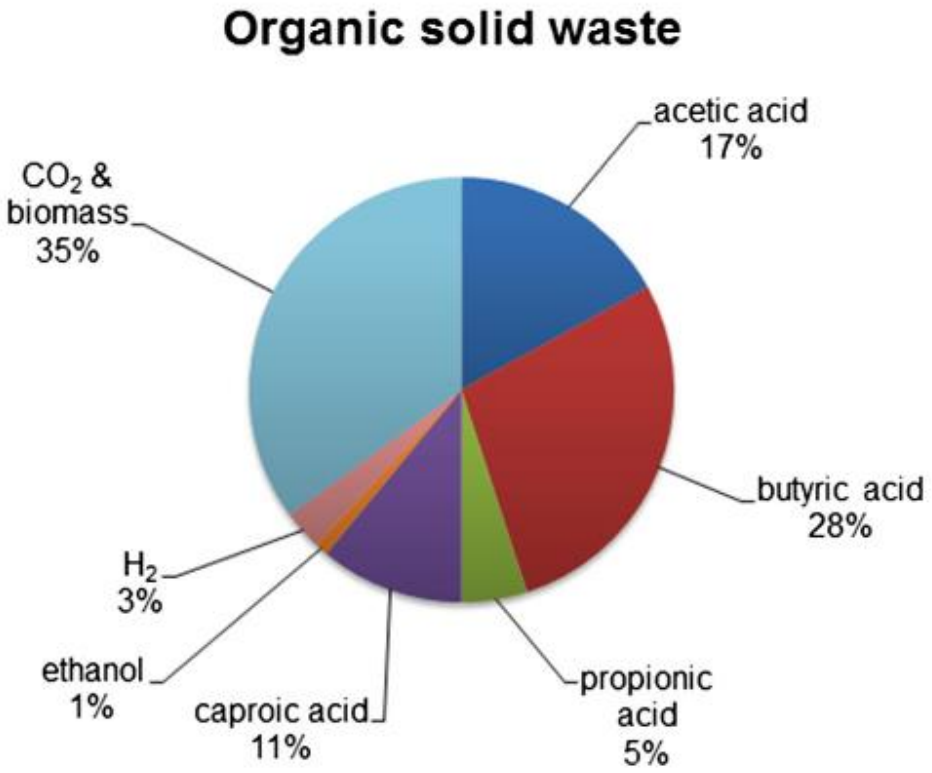
$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$$ → **2.7 MJ**

≙ 4.16 kWh/ $kg_{glucose}$

CH_4
Molar mass: 16 g / mole
Energy value: 55.6 kJ / g

Product distribution during dark fermentation



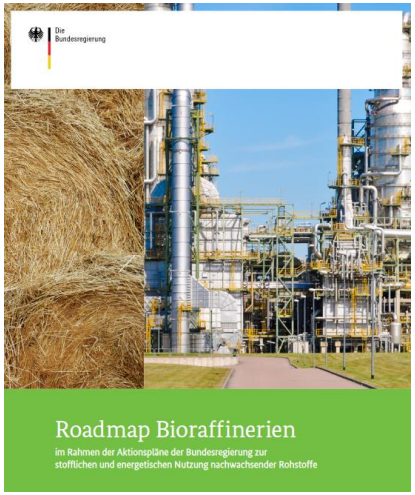


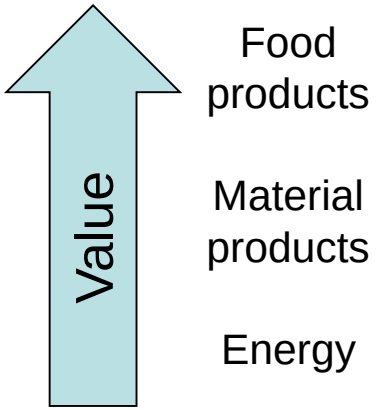
Yields are expressed as mass percentage of substrate consumed (i.e. glucose and organic solid waste)

* Bastidas-Oyanedel et al. (2015), Dark fermentation biorefinery in the present and future (bio)chemical industry

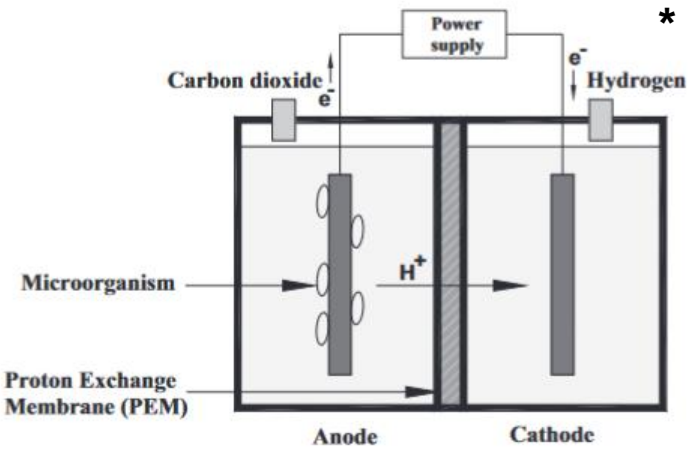
Concepts for dark fermentation

- Only little parts of the used organic substrates are converted to H_2 via dark fermentation, but significant amounts of other carbonaceous products emerge.
- It is expected that biogenic carbon will gain importance with increasing de-fossilization.
- Dark fermentation as a stand-alone option for hydrogen production therefore does not seem to be a viable concept, as the (valuable) carbon would be lost in the process.
- However, by coupling dark fermentation with other biobased processes as part of a biorefinery, it could gain relevance in the future.





Concepts for dark fermentation



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H_2 cleaning

H_2

H_2

Photo-fermentation

Organic acids

(Waste) biomass

Pre-treatment

Dark fermentation

Microbial electrolysis cell

Organic acids

Anaerobic digestion:

$CH_3COOH \rightarrow CH_4 + CO_2$

$8e^- + 8e^+$

Cathode: $8H^+ + 8e^- \rightarrow 4H_2$

Anaerobic digestion

CH_4

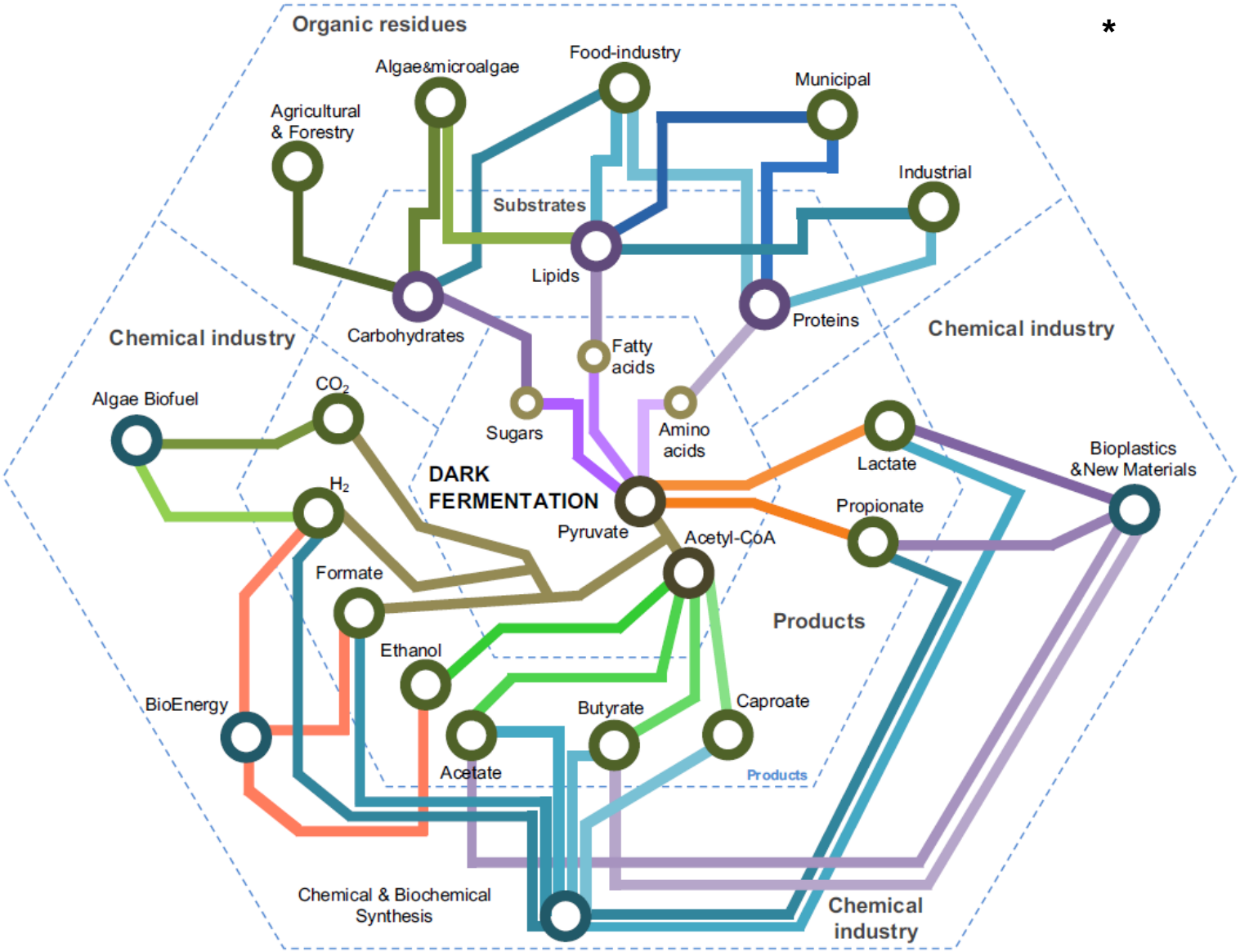
* Ghimire et al. (2015), A review on dark fermentative biohydrogen production from organic biomass

Concepts for dark fermentation

Remarks:

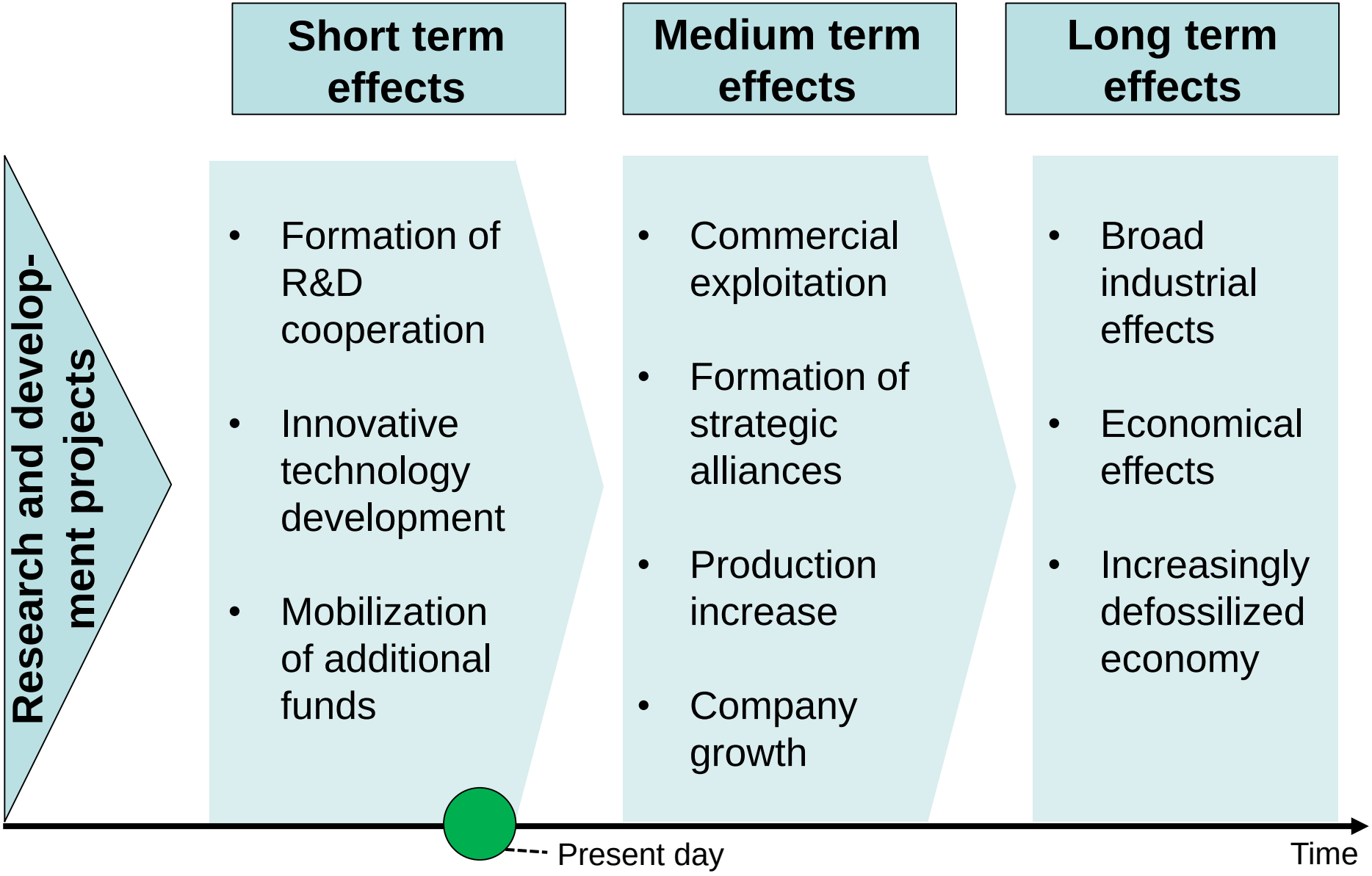
- The processes presented are not yet market ready (with the exception of anaerobic digestion).
- The integration of dark fermentation is relatively complex (e.g. due to the need for special expertise regarding the microorganisms involved, need for additional reactors, etc.).
- Economies of scale could compensate for the high costs, but there must be enough biomass at the plant's location for this to succeed (transport over long distances usually leads to high costs).
- By increasing the value of the products (e.g. use of the resulting acids in the chemical industry), the processes could be economically viable in some places.

Classification in the biorefinery sector



* Bastidas-Oyanedel et al. (2015), Dark fermentation biorefinery in the present and future (bio)chemical industry

Time horizon



Conclusion

- Hydrogen production from biomass via the dark fermentation route can be useful under certain conditions, but only if resulting co-products can be used.
- There are still questions about the classification of hydrogen produced in this way (so far it is not considered "green").
- In many areas, the process is too complex and thus will not be able to compete with other concepts (e. g. biogas production, hydrogen) in the long term.

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