Biogas production

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Workshop –Seaweed for Biofuel

Contents:

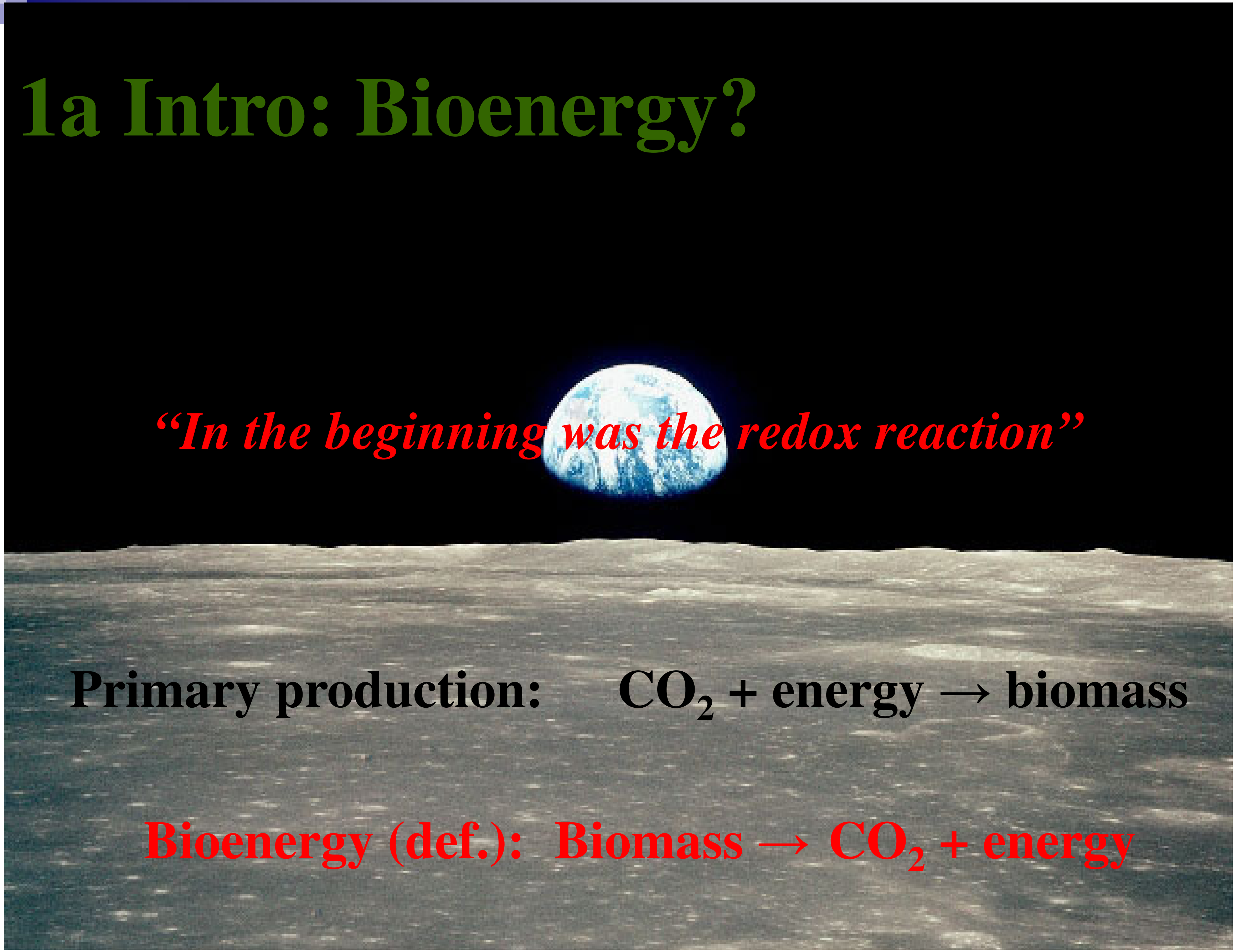
Basics of bio-energy & -gas

1. Intro; bioenergy? politics? ecomomy?
2. Biogas basics
3. Once upon a time
4. Process operation

Case seaweeds

5. Seaweeds?
6. The HRAD concept
7. Biogas for transport; LBG & CBG
8. Concluding remarks

1a Intro: Bioenergy?



"In the beginning was the redox reaction"

Primary production: CO_2 + energy → biomass

Bioenergy (def.): Biomass → CO_2 **+ energy**

COD?

1: Def.: COD is the amount of oxygen needed to oxidize some organic compound completely to CO_2.

2: Measure: Oxidize with potassium dichromate, yellow colour due to Cr^{6+}.

3: Calculate: Balance reaction eq. to find moles O_2 needed.

4: Estimate: Use average composition; ex. biomass $C_5H_7O_2N$.

5: COD balance: $COD_{substr.} + COD_{oxygen} = COD_{biomass} + COD_{prod.}$

(with by def. COD_{oxygen} / $Weight_{oxygen} = -1$)

"In the beginning was the redox reaction"

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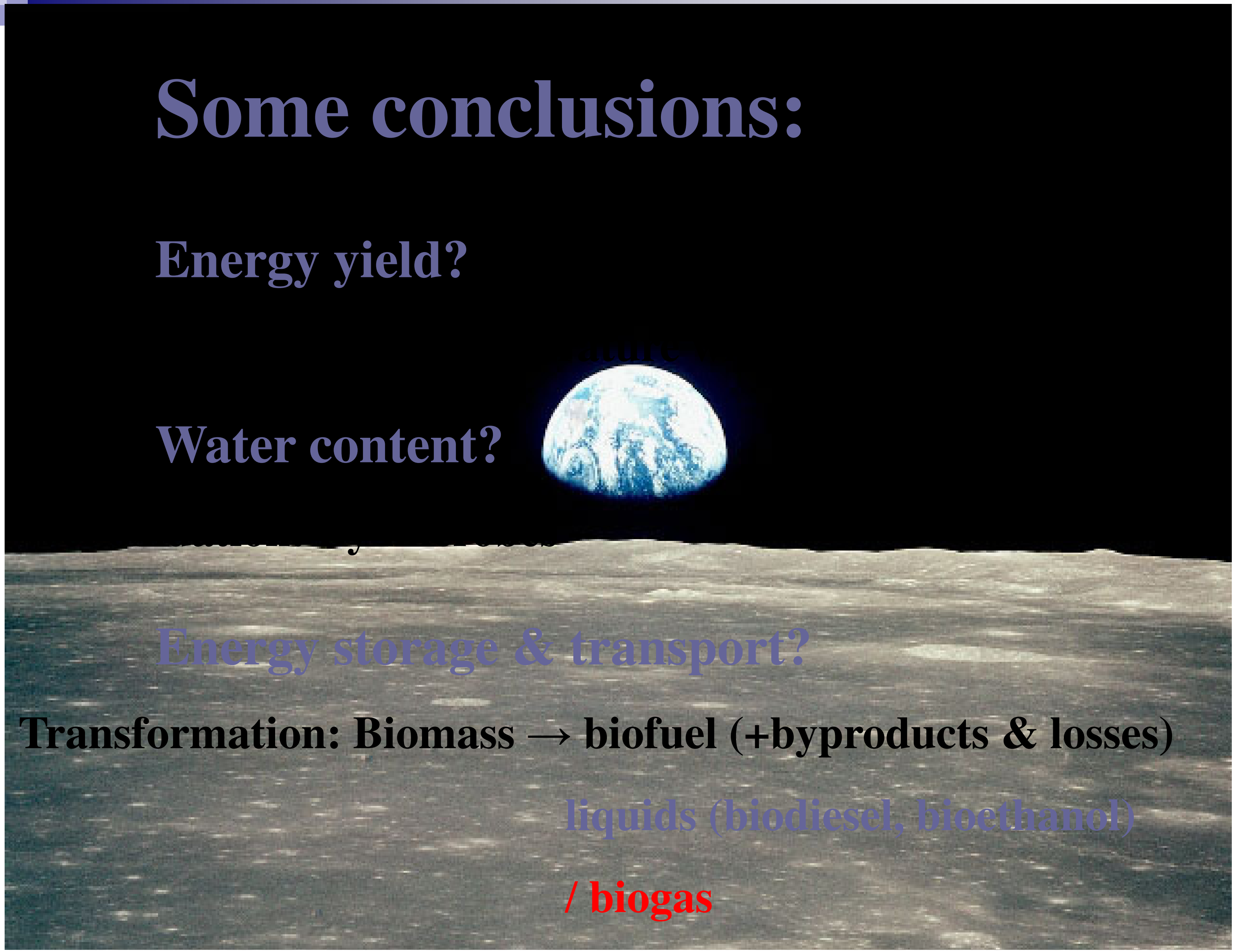

Some conclusions:
Energy yield?
Water content?
Energy storage & transport?
Transformation: Biomass → biofuel (+byproducts & losses)
liquids (biodiesel, bioethanol)
/ biogas

1b Intro: Politics?

The Swedish lessons 1980

1. There is no energy source without negative environmental impact.
2. The major energy source of the future will be: Stop wasting. Corresponding strategy: Diversify!
3. The key to successful economic developent is disconneting growth from energy demand.

1c Intro: Economy?

The economy is in the totality, stupid.

2. Total process

Hydrolysis

Acidogenesis

VFA

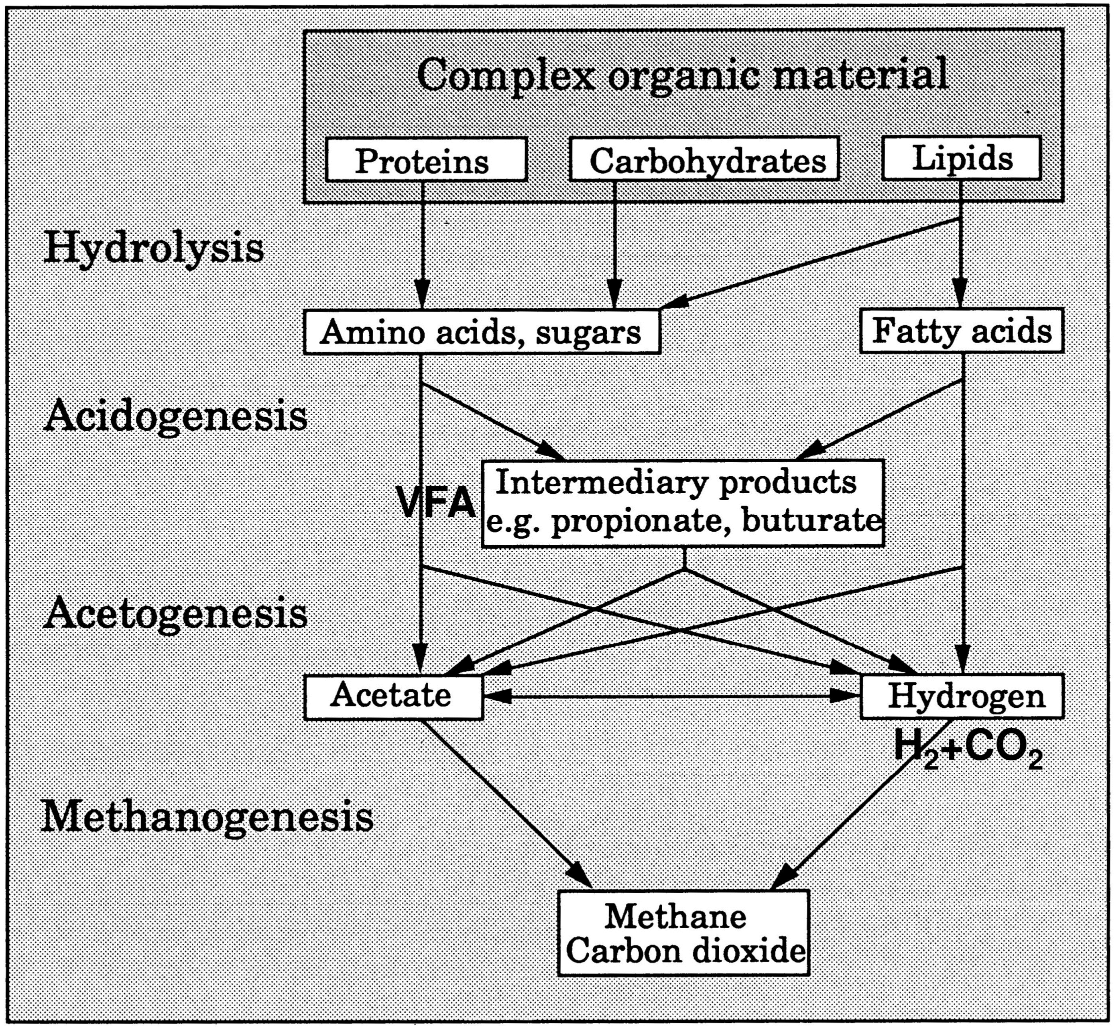
Acetogenesis

H_2+CO_2

Methanogenesis

CH_4/CO_2

$\approx 50\%/50\%$



Volatile fatty acids VFA:

H-COOH	formic acid	
CH_3-COOH	acetic ”	
CH_3-CH_2-COOH	propionic	
CH_3-CH_2-CH_2-COOH	butyric	
CH_3-CH_2-CH_2-CH_2-COOH	valeric	
CH_3-CH_2-CH_2-CH_2-CH_2-COOH	kaproic	etc.
-	- -	
CH_3-CHOH-COOH	lactic acid	
-	- -	
CH_3-OH	metanol	
H_3-CH_2-OH	ethanol	a.o. -

2. Total process

Hydrolysis

Acidogenesis

VFA

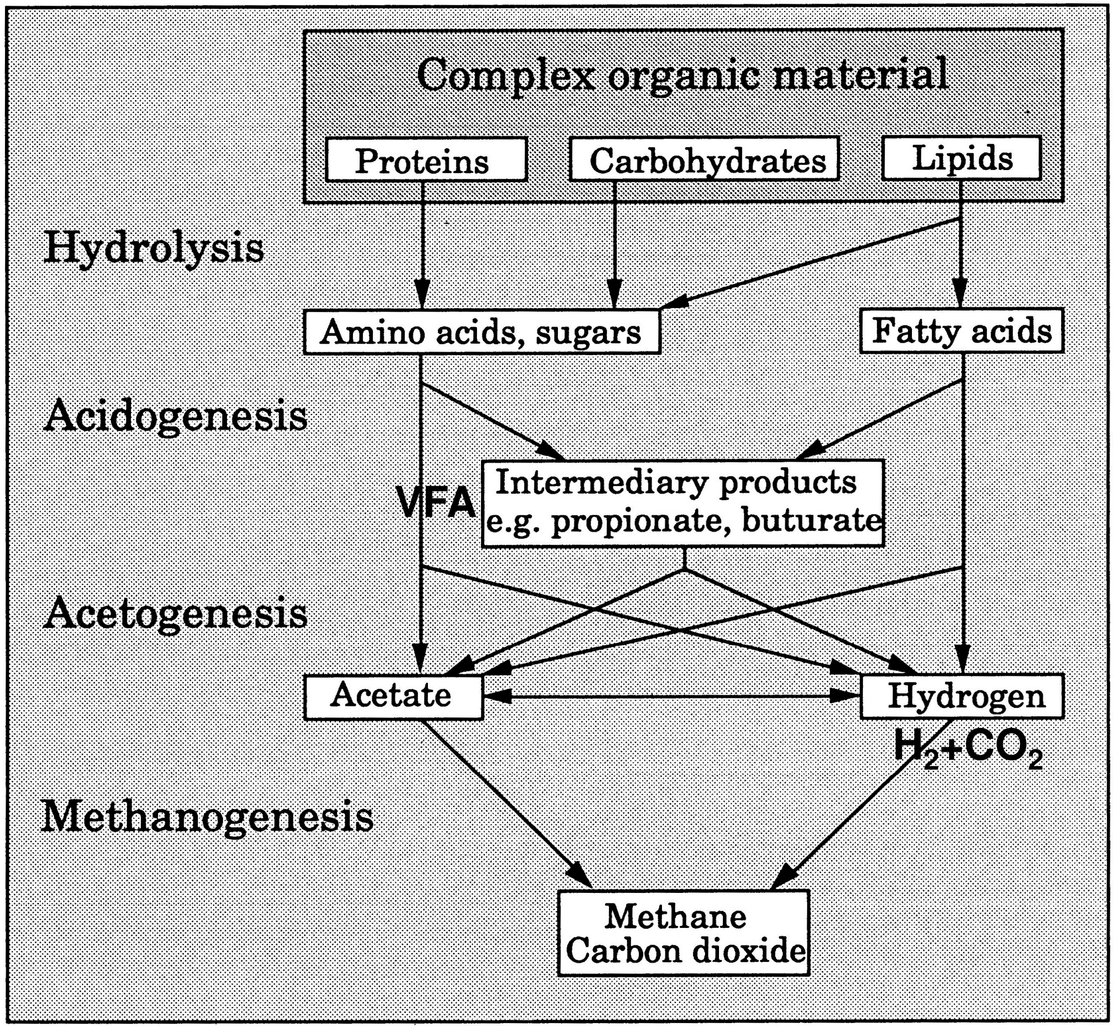
Acetogenesis

H_2+CO_2

Methanogenesis

CH_4/CO_2

≈ 50%/50%



VFA acetogenesis:

Case ethanol:

1. S-organism:

$2\ C_2H_5OH + 2\ H_2O \rightarrow 2\ CH_3COOH + 4\ H_2 \quad \Delta G^{0'} = +9.7 kJ$

$\Delta G' < 0$ at $P_{H2} < 10^{-4}$ atm

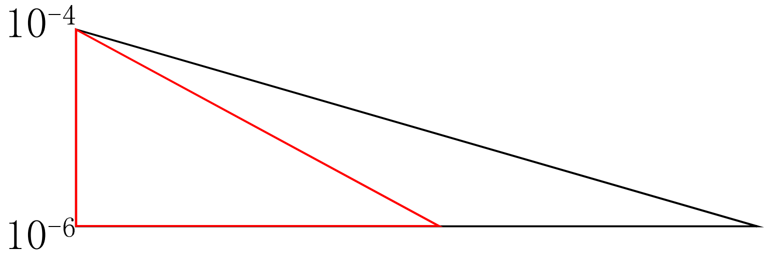
2. Methanobacterium bryantii:

$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O \quad \Delta G^{0'} = -131 kJ$

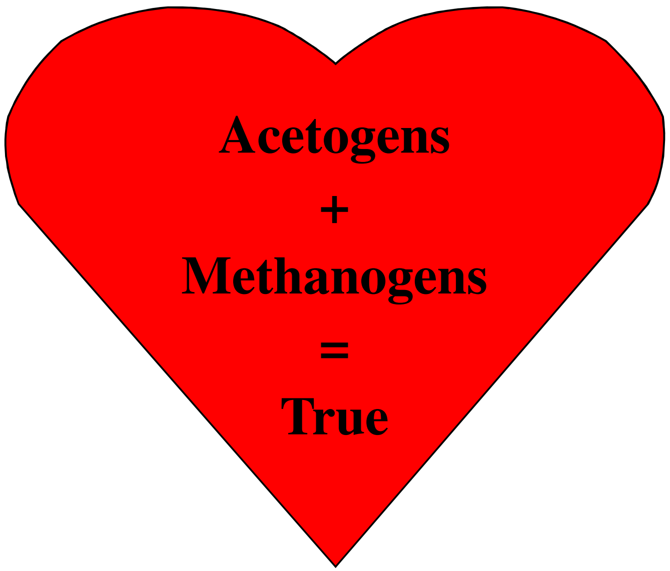
$\Delta G' < 0$ at $P_{H2} > 10^{-6}$ atm

Morale:

H_2 flux depends on gradient:



Stay close! →

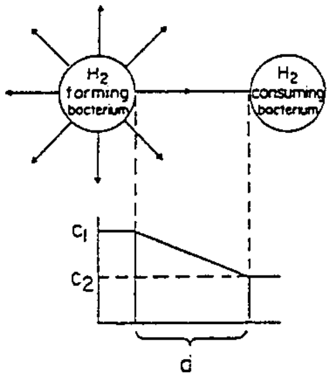


Interspecies hydrogen transfer

Stay close: →→

= Syntrophic consortia!

Clustering will also promote granule formation, c.f. UASB.



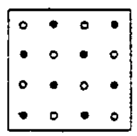
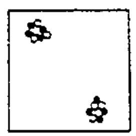
$$J_{H_2} = -A \cdot D \cdot \frac{c_2 - c_1}{d} \quad mol \cdot sec^{-1}$$

$D_{25°C}$ = Diffusion constant for H_2 = $4.9 \cdot 10^{-5} cm^2 \cdot sec^{-1}$

A = Surface area of H_2 forming bacterium = $4 \pi r^2$

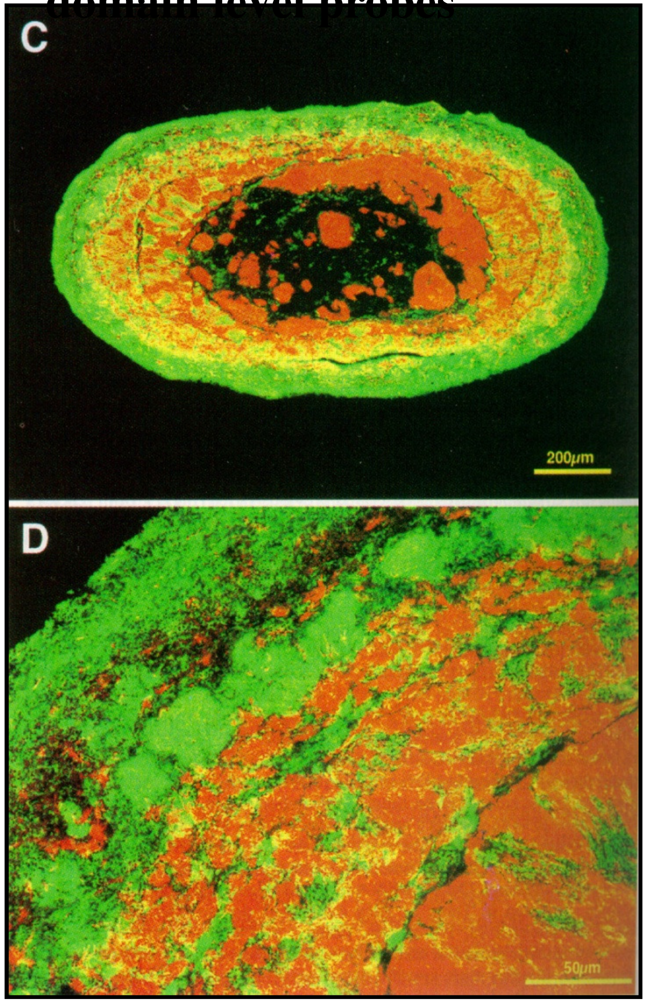
c = Concentration of H_2 in water

d = Distance between H_2-forming and H_2-consuming bacteria

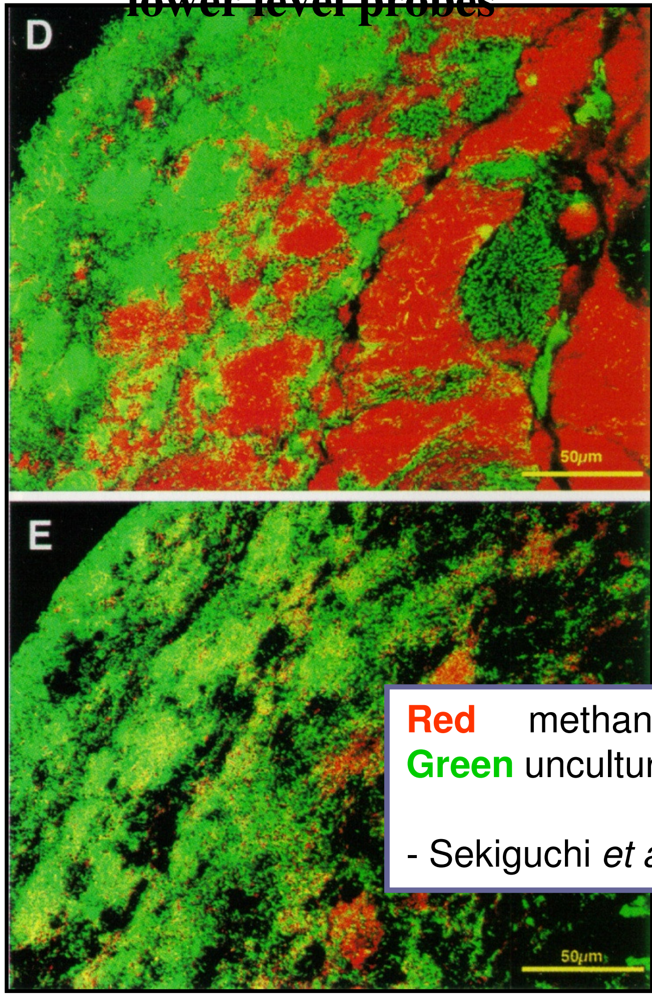
10^9 cells/ml	10^9 cells/ml
equal distribution	cluster formation
	
d = 8 µm	d = 0.08 µm
r = 1 µm	r = 1 µm
c_1 = 0.05 µM	c_1 = 0.05 µM
c_2 = 0.005 µM	c_2 = 0.005 µM
$J_{H_2} = \frac{10\ nmol\ H_2}{min \cdot ml}$	$J_{H_2} = \frac{1000\ nmol\ H_2}{min \cdot ml}$

Granule structure by FISH

domain level probes



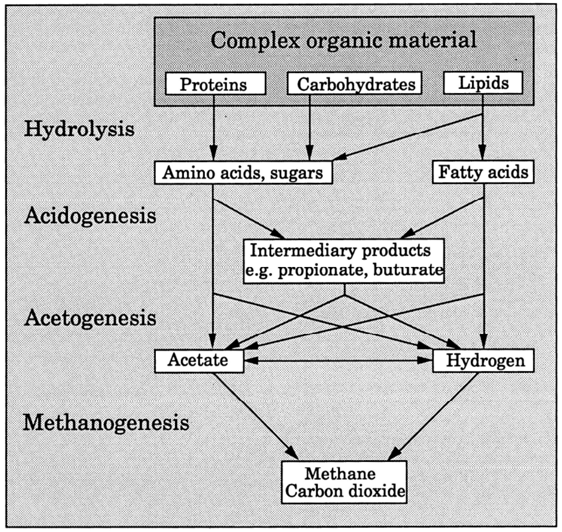
lower level probes



Red methanogens
Green uncultured bacteria

- Sekiguchi *et al.* (1999).

4. Process operation



	Process	*rate* limiting at
1	Hydrolysis	recalcitrant materials
2	Acidogenesis	- *never* -
3	Acetogenesis	overload; ”surgjæring” → low pH
4	Methanogenesis	short sludge age; low μ^{max}

Conclusion: Stabilize at steady state!

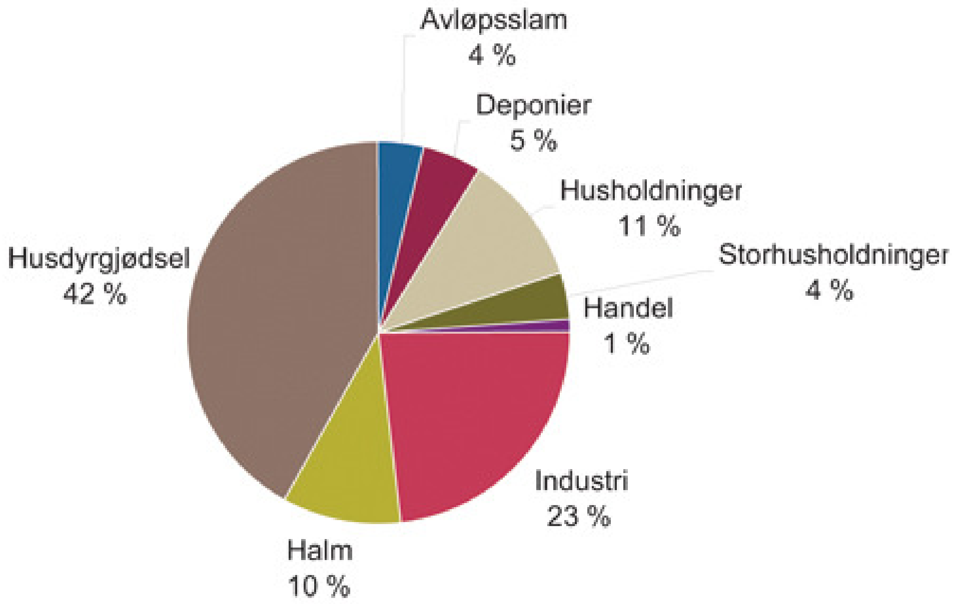
Local cases: Go see Ladehammeren or Høvringen ww treatment plants, or Heggstadmoen landfill

Biogas resources of Norway

Waste:

Price << 0

Potential 6 TWh



Cultivation??

Price ??

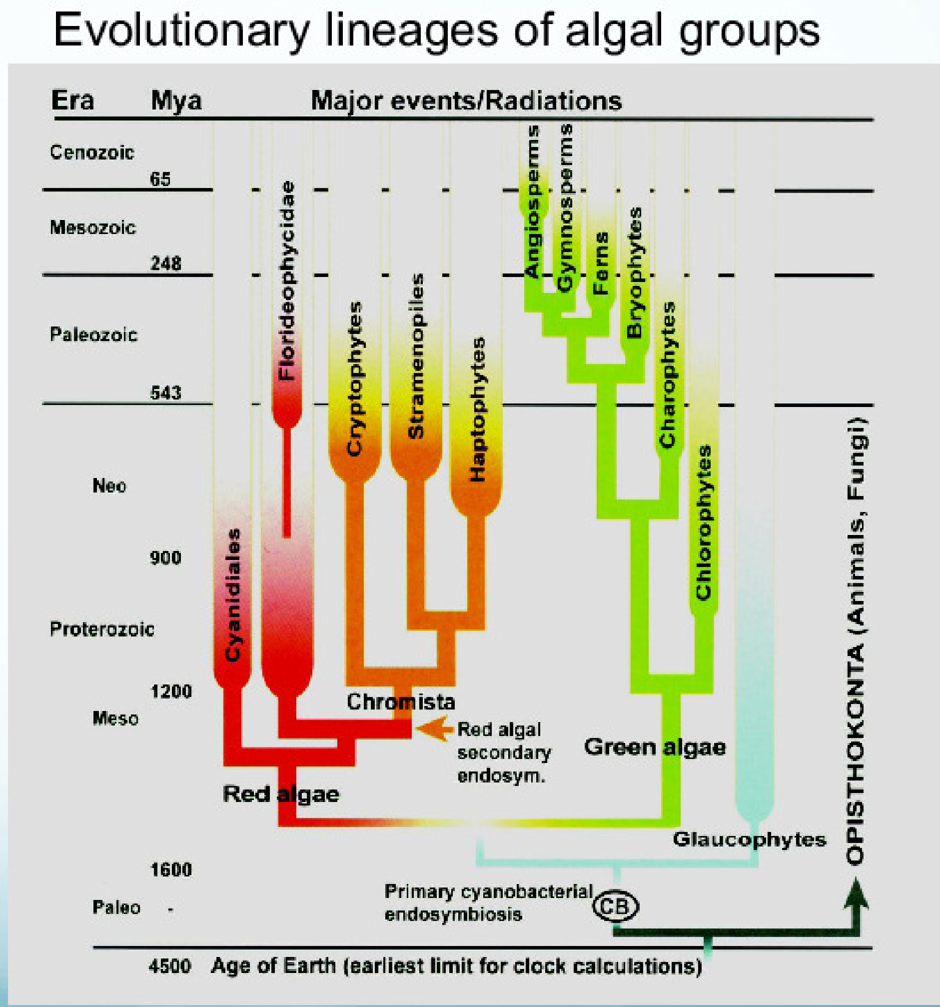
5. Seaweeds?

Red

Green

Brown

Time scale based on molecular clocks and fossil data



Battacharya & Medlin (2004)

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5. Seaweeds?

~~Red~~

~~Green~~

Brown

	Brown algae	Red algae	Green algae
pigments	chlorophyll a + c fucoxanthin o.a. carotenoids	chlorophyll a phycobilines div. carotenoids	chlorphyll a + b div. carotenoids
storage carbohydrates	laminaran (β-1,3 glucan) mannitol	floridéan starch (α-1,4 glucan) floridosid	starch (α-1,4 glucan)
structural polysaccharides	alginate fucoidan (cellulose)	galactanes (agar, carrageenan) (cellulose)	cellulose mannose ulvan
morphology size	no unicellular to 50 m	few unicellular to 1 m	many unicellular to 1 m
flagella	heterokont	absent	isokont
bioactive compounds	phlorotannines (polyphenols)	halogenated org. compounds	few known (Caulerpales, Ulvales)
number of species (% marine)	1800 (99 %)	6000 (90%)	9000 (10 %)

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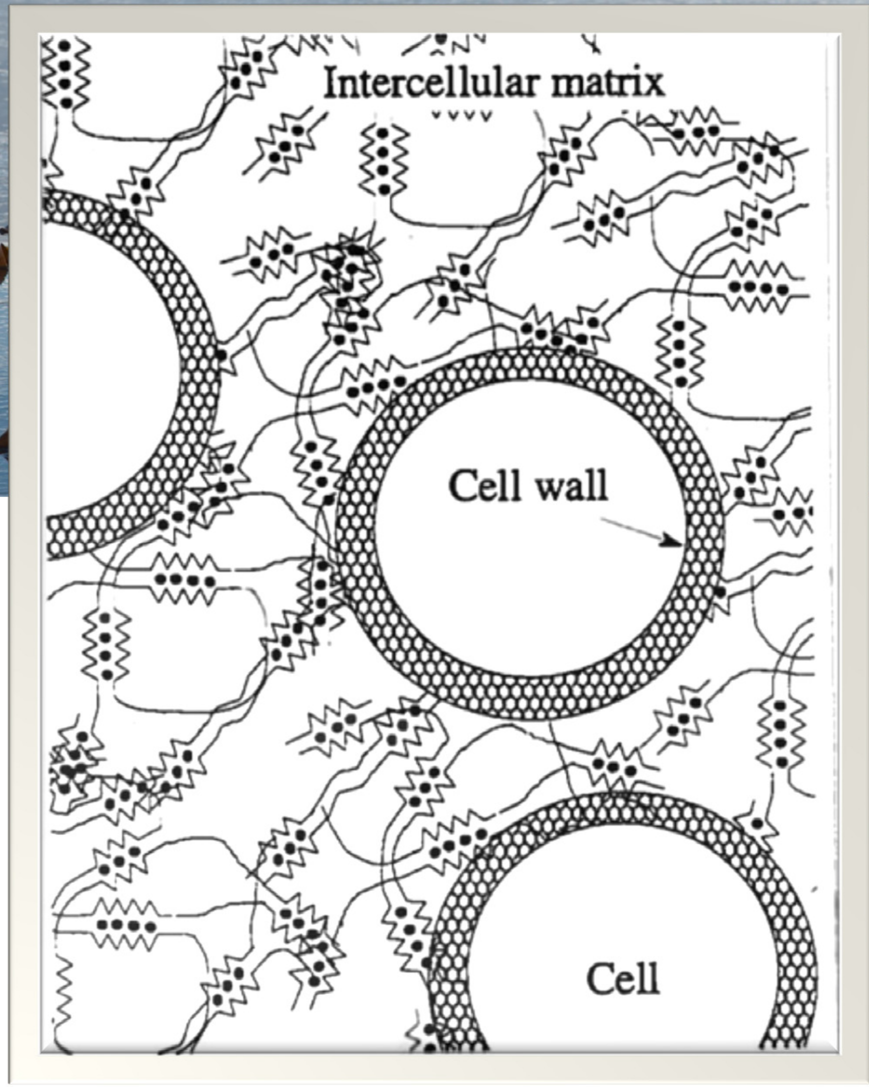
Brown seaweeds

Physical structure

Chemical composition

Alginate
Laminaran
Mannitol
Others: Fucoidan
Protein
Cellulose
Polyphenols («tannins»)



Brown seaweeds

Physical structure

Particle size by

grinding / milling

Gel matrix dissociation by

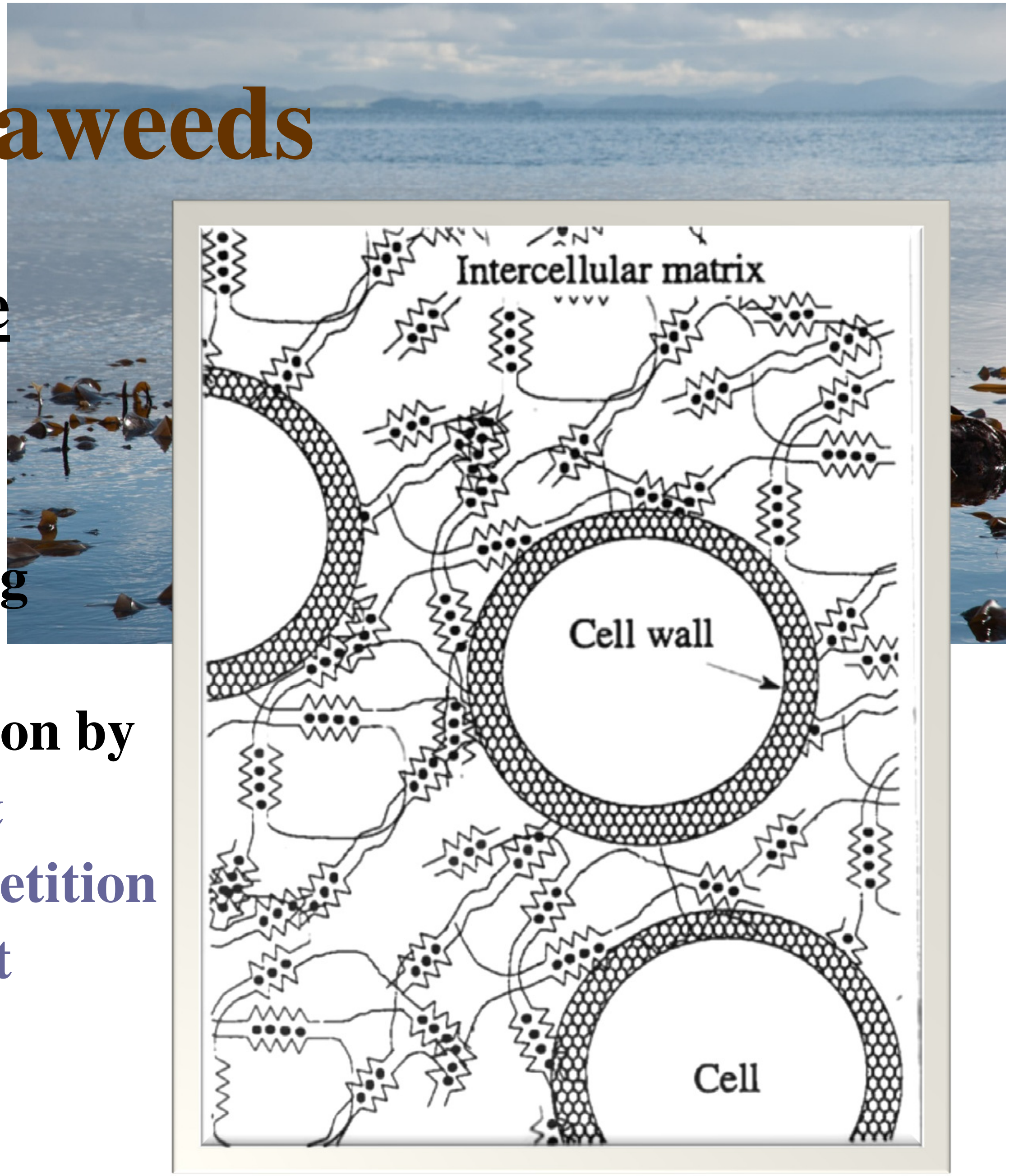
osmotic shock &

Na^{+} / Ca^{++} competition

EGTA treatment

Acid hydrolysis

etc.; ORD



Brown seaweeds

Fermentation of *Ascophyllum nodosum* :

Polyphenol content limited
alginate lyase activity
manniton consumption
methane production

Degradation stimulated by
fixation of polyphenols
by formaldehyde etc.

Brown seaweeds

Fermentation of

***Laminaria hyperborea* stipe:**

Polyphenols of peripheral tissu gave extended lag phase due to polyphenols compared to core

Crosslinking by polyphenols or Ca-guluronate residues apparently limited yield in batch systems

Brown seaweeds

Fermentation of
***Laminaria hyperborea* fronds:**

Easily degradable;
acetate + some propionate
as dominant VFAs

Diauxic pattern in batch («dessert first»)

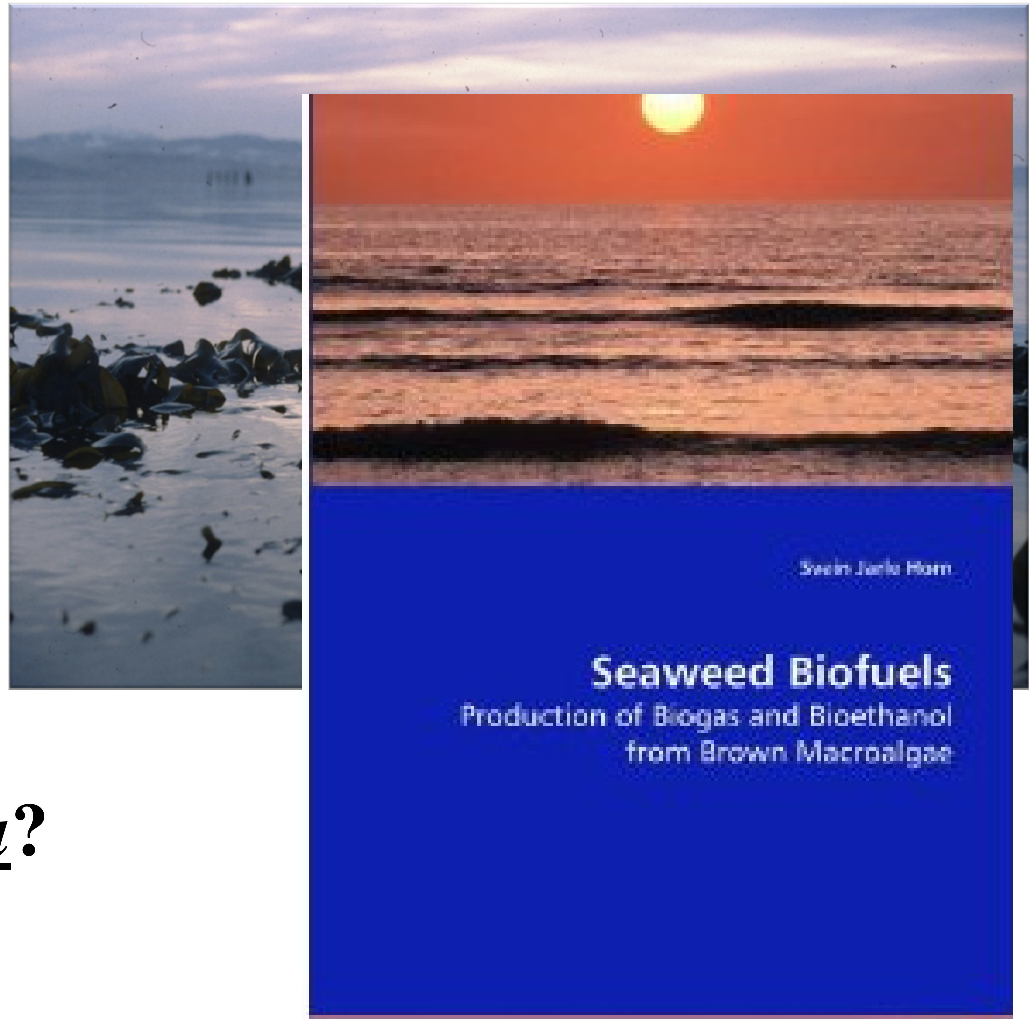
Successful methane production in
continuous reactor systems

Brown seaweeds

Fermentation of
***<u>Laminaria digitata</u>*:**

Easily degradable;
low in polyphenols,
low in high G alginate

Fermentation of
***<u>Saccharina latissima</u>*?**

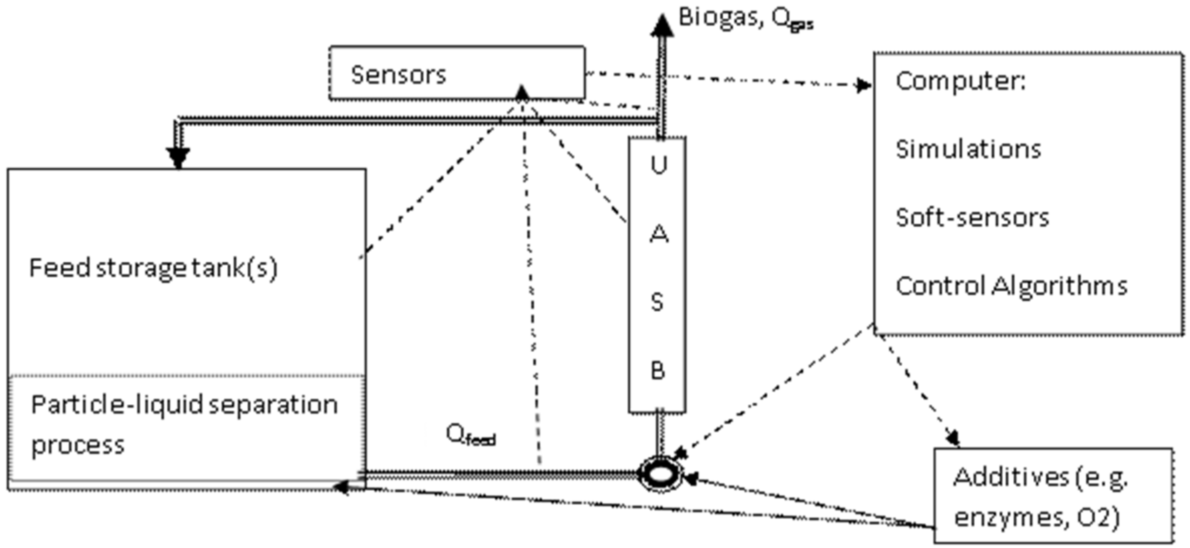


VDM Verlag Dr. Müller 2009

6. The HRAD concept

High Rate Anaerobic Digestion

Compact: In need of retention to keep biocatalyst stuck at high throughput flow = low HRT



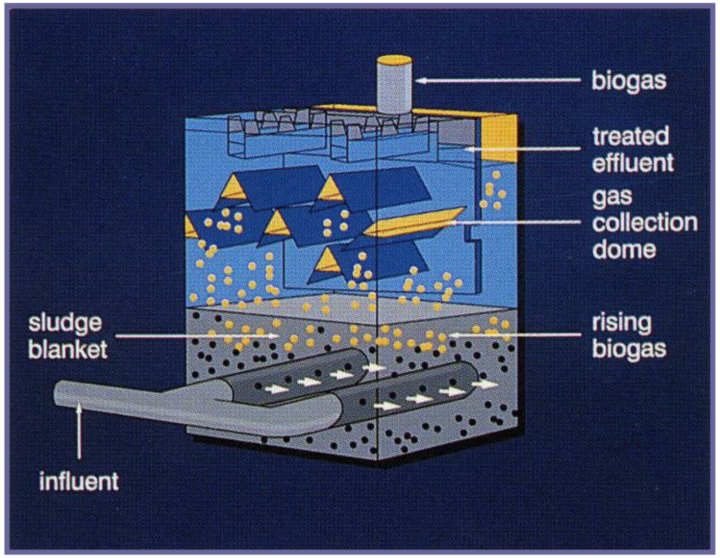
C.f. BIONA project

UASB

Developed by Lettinga, Wageningen.

Note sludge separation zone on top.

Biopaq→



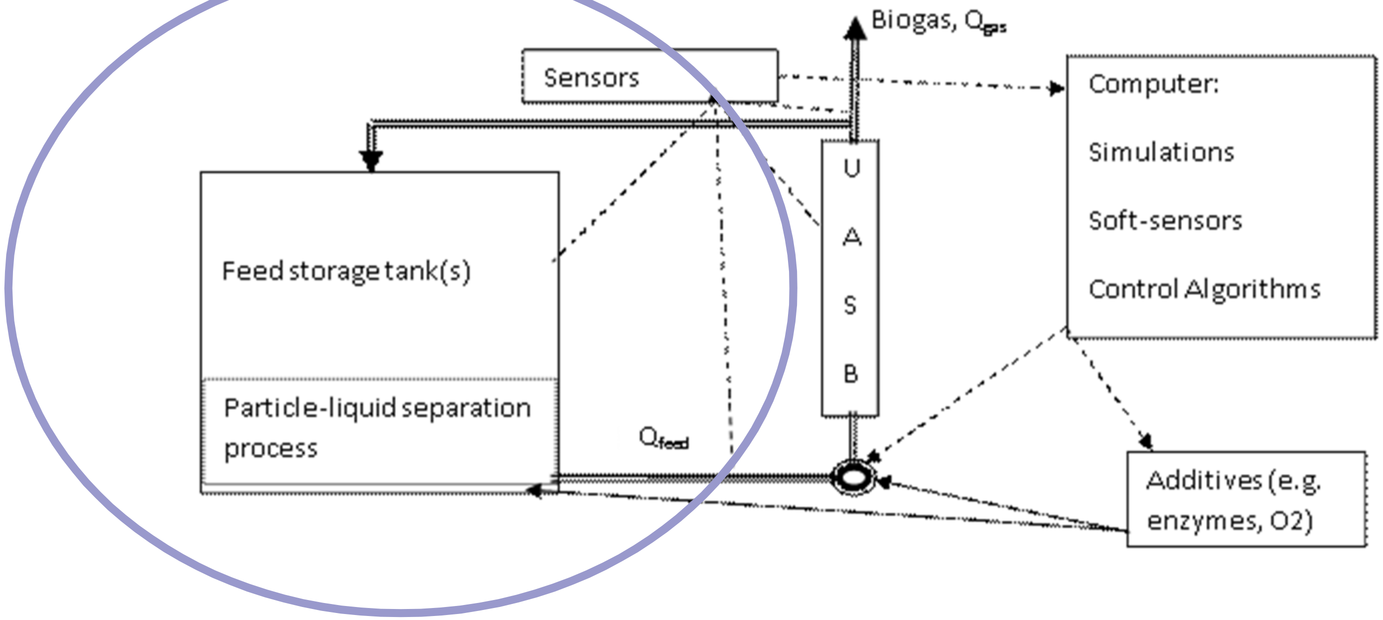
← Granules

Hydrolysis

in recycled pretreatment:

- washout of VFAs to avoid product inhibition

Retention?????????????



7. Biogas for transport

Biofuels:

Biodiesel ~ $C_8H_6O_2$ ~ vegetable oils and lipids
< B20 in standard diesel engines

Bioethanol C_2H_5OH by fermentation & destillation
E20 USA, E85 Sweden up to E98 Brazil

Biogas CH_4 (+ CO_2) by fermentation. Purified,
compressed CLG or liquified LBG (-163 ^oC)
standard combustion / 80 % in dual diesel

LBG

-163°C

Lidköping Biogas - opened summer 2012

60 GWh – corresponding to:
6 000 cars doing 17 000 km /year
16 000 ton CO_2 reduction / year

BIOGAS
MELLANNORRLAND
Mittnorden visar världen den gröna vägen
Green Highway
Trondheim
Stjørdal
Meråker
Storlien
Åre
Järpen
Krokom
Östersund
Brunflo
Gällö
Bräcke
Borgsjö
Vattjom
Sundsvall
Symbolförklaring
Biogas-pump
E85 Etanol
Laddstation
RME Biodiesel
E14
Mittbanan/Meråkerbanan
European route E14

8. Concluding remarks

1. Any industry generating organic waste has to consider local biogas production as a part of waste management.
2. This is also true for any seaweed based industry producing alginate, fertilizer, bioethanol or other products.
3. Thus; biogas will in any case be a major or minor product in any significant uilization of brown seaweed biomass.
4. Any cultivation for bioenergy has to compete with wastes priced at << 0 as raw materials. This is absolutely possible.
5. LBG is rapidly becoming a significant liquid fuel for the transport sector. Accordingly, LNG will follow.
6. A more direct price competition will thus be established between LBG/LNG and conventional liquid fuels.

8. Concluding remarks c.t.d.