The reason we need sustainable third generation gaseous algae biofuels

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Foz do Iguaçu, Brazil, April 4, 2014

Bioenergy and Biofuels Research Group (B^{2}RG)

- B2RG founded in 2007:
- Funding of €3 M from :
  - SFI, Ecoventi, EPA, DAFF, IRCSET, BGE, BGN, HEA PRTLI, Marie Curie ITN
- Present team11 PhD students and 2 post-doctorates
- Published
  - 61 peer review journal papers
  - 30 peer review conference papers

Policy on Biofuels

Directive 2009/28/EC (Renewable Energy Directive)

•Share of renewable energy sources in transport (RES-T) by 2020 at least 10%
•Biofuels must achieve a 60% reduction in GHG as opposed to fossil fuel displaced.
•Biofuels from lignocellulosic material shall be considered at twice energy content.

***EC, Proposal for a DIRECTIVE OF THE EUROPEAN PARLIMENT* Brussels 2012**.
In : http://ec.europa.eu/clima/policies/transport/fuel/docs/com_2012_595_en.pdf

•The share of biofuels from cereal and other starch rich crops, sugar and oil crops limited to consumption in 2011 (5%)

•Biofuels (from algae, municipal solid waste, manures and residues) and gaseous fuels from non biological origin shall be considered at 4 times energy content

•In September 2013 this limit on food biofuel was proposed to be raised to 6% with a requirement that 2.5% energy in transport to come from advanced biofuels (such as those sourced from sea weeds) with no weightings applied. More arduous!!

What will fuel transport systems of the future?

This paper seeks to decry the notion of a single solution or "silver bullet" to replace petroleum products with renewable transport fuel. At different times, different technological developments have been *in vogue* as the panacea for future transport needs: for quite some time hydrogen has been perceived as a transport fuel that would be all encompassing when the technology was mature. Liquid biofuels have gone from exalted to unsustainable in the last ten years. The present flavor of the month is the electric vehicle. This paper examines renewable transport fuels through a review of the literature and attempts to place an analytical perspective on a number of technologies.

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Electric Vehicles

•10% of cars proposed to be EV in 2020;ca. 300,000 vehicles required

•Freight (HGV’s) and public service vehicles account for over 50% of energy in transport

•Maximum of 40% of electricity “green” in 2020

•Renewable energy supply in transport (RES-T) from EV limited to 10% of 50% of 40% = 2%

•EV’s not used for long distance.

•Expected 1.6% RES-T from 10% EV’s

•What is source of other 8.4% RES-T to meet 2020 target?

Hydrogen?

	Hydrogen	Methane
Energy value	142 MJ/kg	55.6 MJ/kg
Molecular weight	2.016	16.042
Density	0.085 kg/m_n^3	0.677 kg/m_n^3
Energy value	12.1 MJ/m_n^3	37.6 MJ/m_n^3
Compression	700 bar	220 bar
Energy per unit compressed storage	8.47 MJ/L	8.27 MJ/L
Energy to compress	13 %	3.3 %

Steam reforming of methane to hydrogen: 39 – 49% losses:
20-30% in steam reforming; 6% in pipelines; 13% in compression.

Water Hydrolysis: 49 – 53% losses:
26% in electrolysis; 4-8% in transmission; 6% in pipelines; 13% in compression.

EV v's hydrogen: EV 3 times as efficient as hydrogen
100 kWeh = 69 kWeh in an EV compared to 23 kWeh in a hydrogen vehicle.

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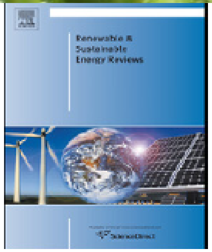

A roadmap for the introduction of gaseous transport fuel: A case study for renewable natural gas in Ireland

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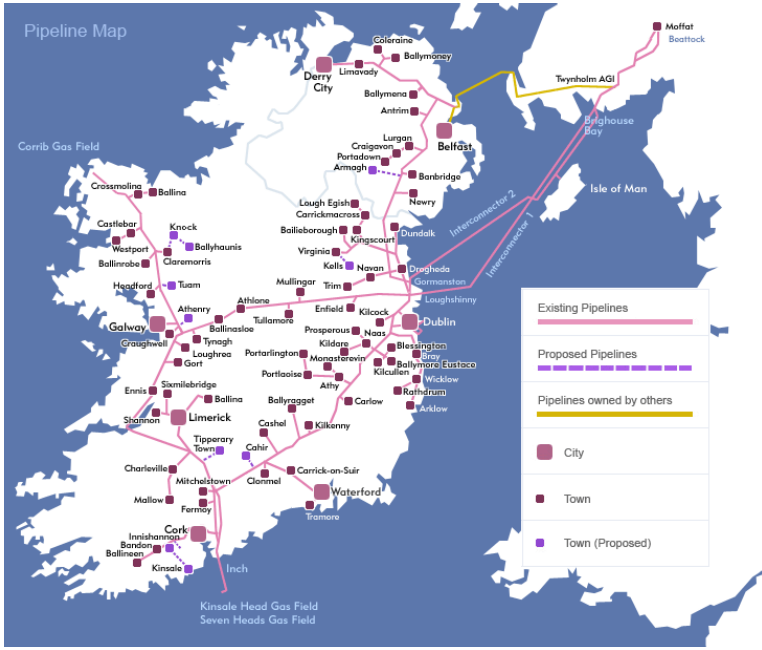
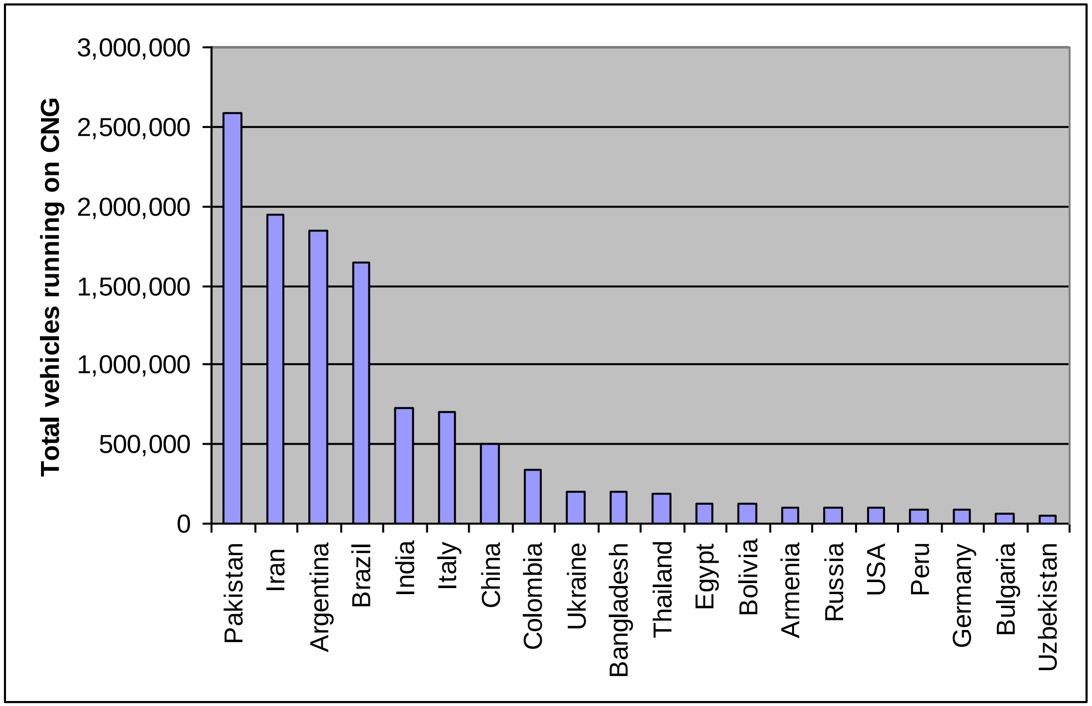
Irish Gas Grid

Serves:
153 towns
19 counties (26 counties in Ireland)
619,000 houses (ca. 45% of houses)
24,000 industrial and commercial



Number of vehicles running on CNG worldwide



Alternative Transport Fuel Infrastructure Directive

http://www.europarl.europa.eu/RegData/bibliotheque/briefing/2013/130647/LDM_BRI(2013)130647_REV1_EN.pdf

Gas supply (LNG and CNG)

LNG should be available for navigation along the Trans-European Transport (TEN-T) core network in all maritime ports by 2020 and inland ports by 2025.

LNG refuelling points should be developed to sustain heavy-duty road transport along the TEN-T core network (refuelling points at less than 400 km apart).

By the end of 2020, Member States should also ensure the setting up of a sufficient number of CNG refuelling points (at least every 150 km) to sustain circulation of all CNG vehicles across the Union.

This should entail at least 25 filling stations in Ireland by 2020.

Waste Management xxx (2013) xxx–xxx

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The potential of algae blooms to produce renewable gaseous fuel

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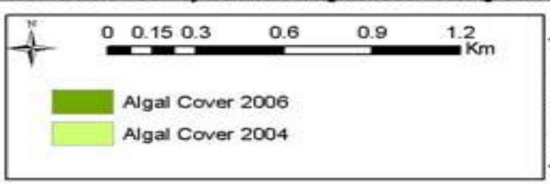
Algae bloom in West Cork

Argideen Estuary



Metric	EQR 2004	EQR 2006
Total % cover	0.30	0.37
Total affected area (ha)	0.37	0.39
Avg biomass AIH (gm^{-2})	0.24	0.39
Avg biomass affected area (gm^{-2})	0.13	0.21
% entrained	nr	nr
Final Score	**0.26**	**0.34**
WFD Classification	POOR	POOR

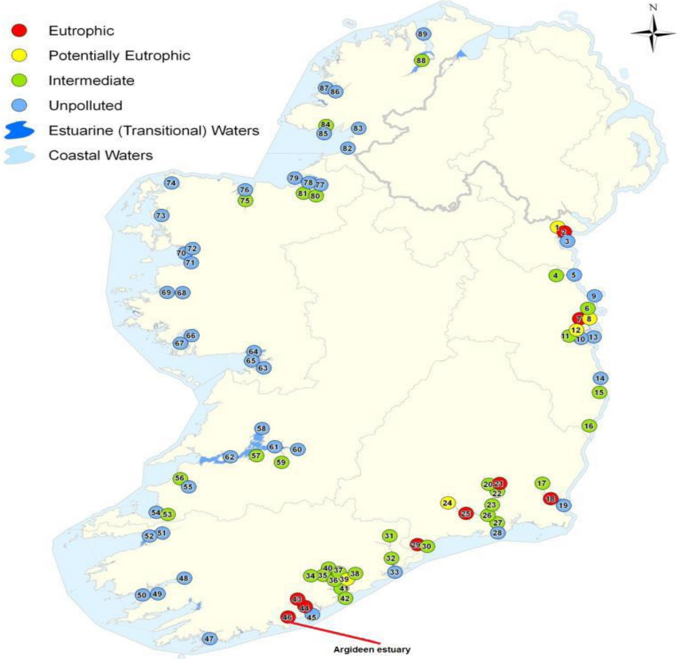
Provisional WFD classification for the Argideen Estuary using opportunistic algae growth.

epa Environmental Protection Agency

Macro-algae: source of 3rd generation biofuel

- Green tides in eutrophic estuaries
- 10,000 tonnes of sea lettuce arise in West Cork annually
- Sufficient to power 264 cars per annum

20m3 CH4 /t wet vs 100 m3 CH4/t dry



Ultimate Analysis of Ulva

Table 1 Ultimate analysis of seaweed samples

Ulva Lactuca	C	H	N	C:N ratio	DS %	VS %
1. Fresh	25.4	3.7	3.3	7.7	19	11
2. Wilted & unwashed	27.2	4	3.1	8.7	20	11
3. Washed & dried	22.3	3.3	2.3	9.6	72	40
4. Washed & wilted	23.3	3.2	2.6	8.8	32	16

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 \quad (1)$$

Table 4. Theoretical methane yields of all pre-treated samples of Ulva collected.

Ulva Lactuca	CH_4 L / kg VS	Biogas L / kg VS	CH_4 %
1. Fresh	431	838	51.5
2. Wilted & unwashed	460	864	53.3
3. Washed & dried	394	793	50.4
4. Washed & wilted	402	816	49.6

Biomethane Potential BMP of Ulva

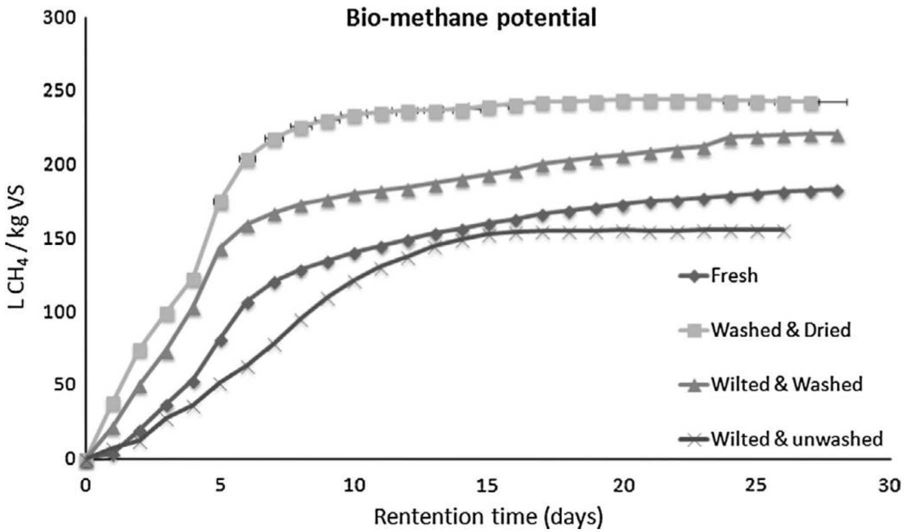


Table 6
BMP results compared to theoretical yield.

Sample	BMP result L CH_4/ kg VS	Standard deviation	Max potential L CH_4/kg VS from Buswell, (Table 5)	Yield m^3 CH_4/t wet based on BMP	C:N ratio
Year 1					
1 Fresh	183.2	5.83	431	20.2	7.7
2 Wilted and unwashed	165.0	9.47	460	18.2	8.7
3 Washed and dried	250.2	13.32	394	100.1	9.6
4 Wilted and washed	221.1	22.74	402	35.4	8.8

Literature on BMPs from Ulva

Ulva Lactuca	Pre-treatment	SMY ($L\ CH_4/kg\ VS$)	Country	Reference
No pre-treatment				
Fresh		183	Ireland	Allen et al., 2013
Fresh		174	Denmark	Bruhn et al., 2011
Fresh		128	France	Peu et al., 2011
Unwashed				
Unwashed	Wilted	165	Ireland	Allen et al., 2013
Unwashed	Macerated	271	Denmark	Bruhn et al., 2011
Washed not dried				
Washed	Chopped	171	Denmark	Bruhn et al., 2011
Washed	Milled	191	Ireland	Vanegas and Bartlett 2013
Washed	Macerated	200	Denmark	Bruhn et al., 2011
Washed	Wilted	221	Ireland	Allen et al., 2013
Dried with size reduction				
Washed and dried	Chopped	241	France	Jard et al., 2013
Washed and dried	Macerated	250	Ireland	Allen et al., 2013

Increased BMP yields with co-digestion

Sample	BMP result L CH_4/ kg VS	Standard deviation	Max potential L CH_4/kg VS from Buswell, (Table 5)	Yield m^3 CH_4/t wet based on BMP	C:N ratio	Increased yield in co-digestion (%)
Slurry	136	2.99	382	7.00	19.8	
Dried Ulva	226	6.66	401	104.86	7.1	
Fresh Ulva	205	5.01	412	21.32	9.1	
Co-digestion						
Yield based on mono-digestion						
75% Fresh	220	4.91	188	20.11	11.77	+17.0
50% Fresh	200	11.2	171	15.88	14.45	+17.0
25% Fresh	183	7.85	153	12.30	17.12	+19.6
75% Dried	210	6.31	203	75.915	10.275	+3.4
50% Dried	193	5.42	181	50.064	13.45	+6.7
25% Dried	186	8.81	158	29.24	16.62	+17.7

What is an optimum percentage of Ulva that may be co-digested with dairy slurry in a stable anaerobic process producing third generation gaseous biofuel?

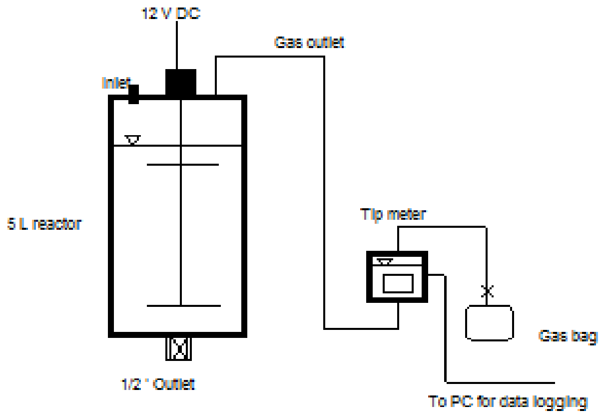
E. Allen, D. Wall, C. Herrmann and J.D. Murphy

Substrate	TS	VS	C:N	Specific Methane Yield		
	%	%		L/kg VS	L /kg TS	m^3/kg wwt
Fresh Ulva	17.75	10.35	7.7	205	120	21.2
Dried Ulva	77.94	46.36	9.6	226	134	104.7
Dairy slurry	8.65	5.75	19.8	136	90	7.8
Inoculum	2.43	1.40	18.4	53	30.5	0.7

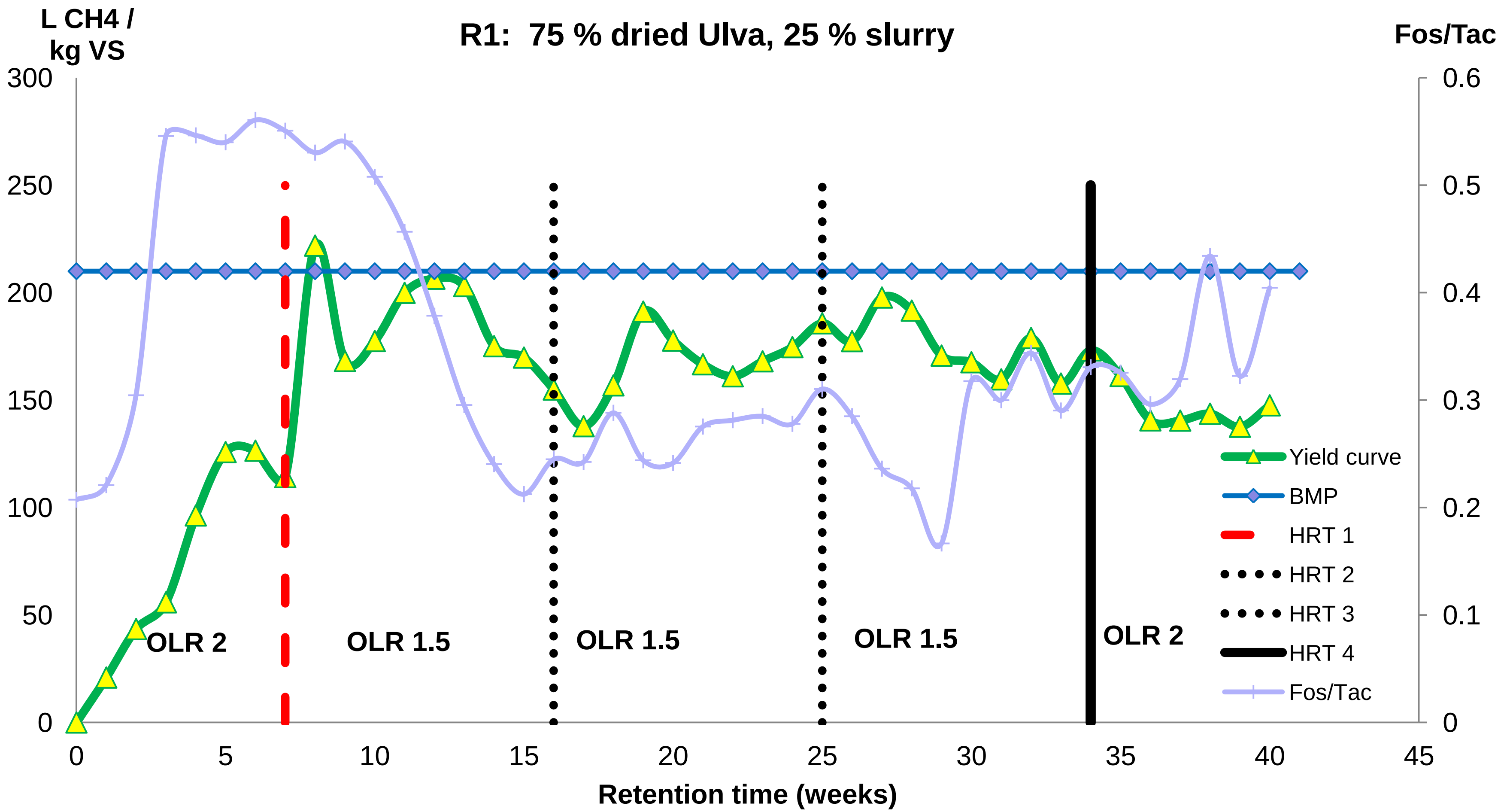
Table 1: Characteristisation of substrates and inoculum (from Allen et al., 2013)

Experimental design

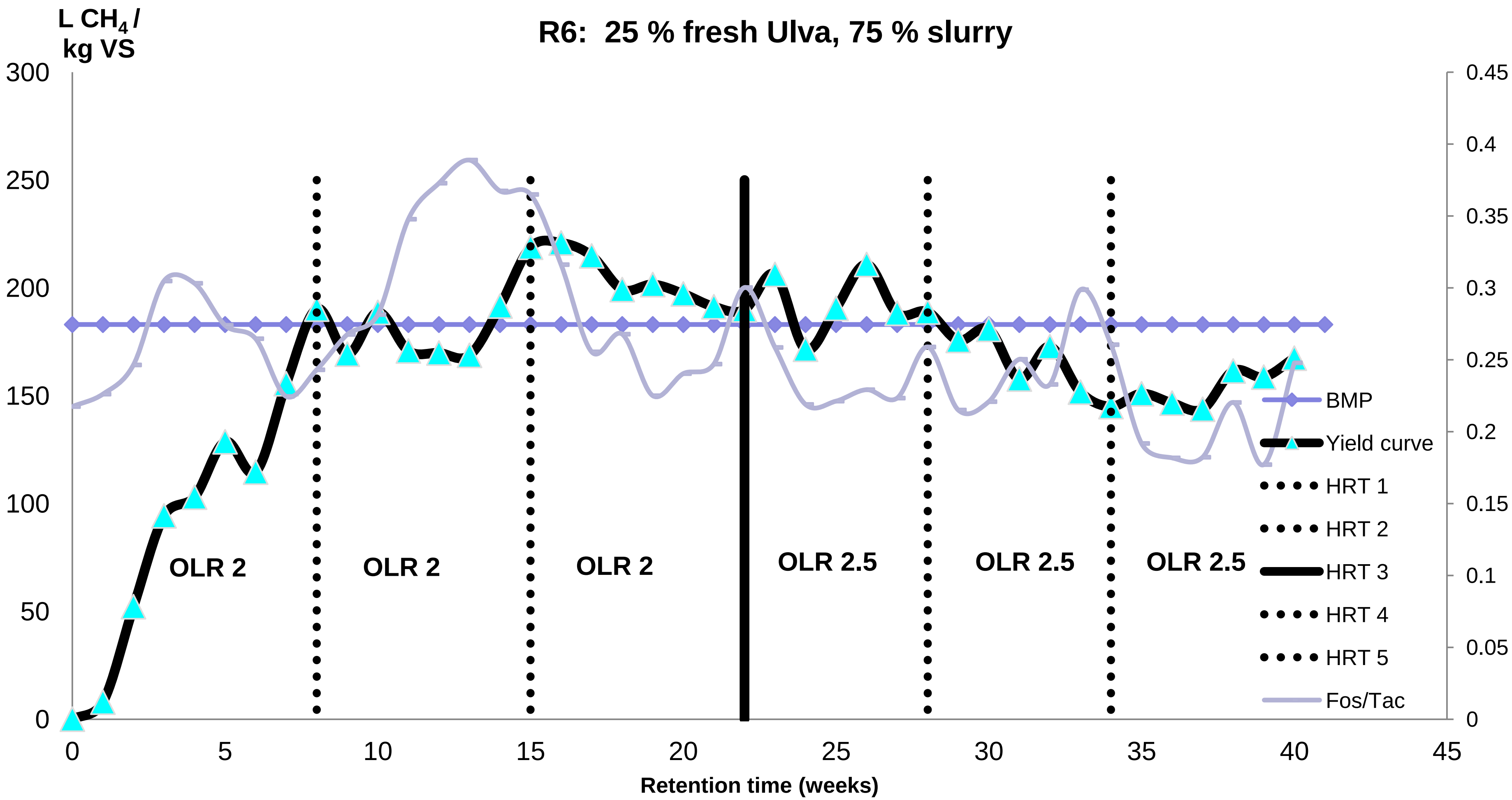
Reactor Number	Dairy slurry (%)	Dried Ulva (%)	Fresh Ulva (%)	C:N ratio	BMP L CH_4/kg VS	Biodegradability Index
R1	25	75		10.3	210 (6.3)	0.53
R2	50	50		13.5	193 (5.4)	0.49
R3	75	25		16.6	186 (8.8)	0.48
R4	25		75	11.8	220 (4.9)	0.54
R5	50		50	14.5	200 (11.2)	0.50
R6	75		25	17.1	183 (7.8)	0.47



It is not recommended to use 75% Ulva in co-digestion



Optimum Mix was 25% fresh Ulva

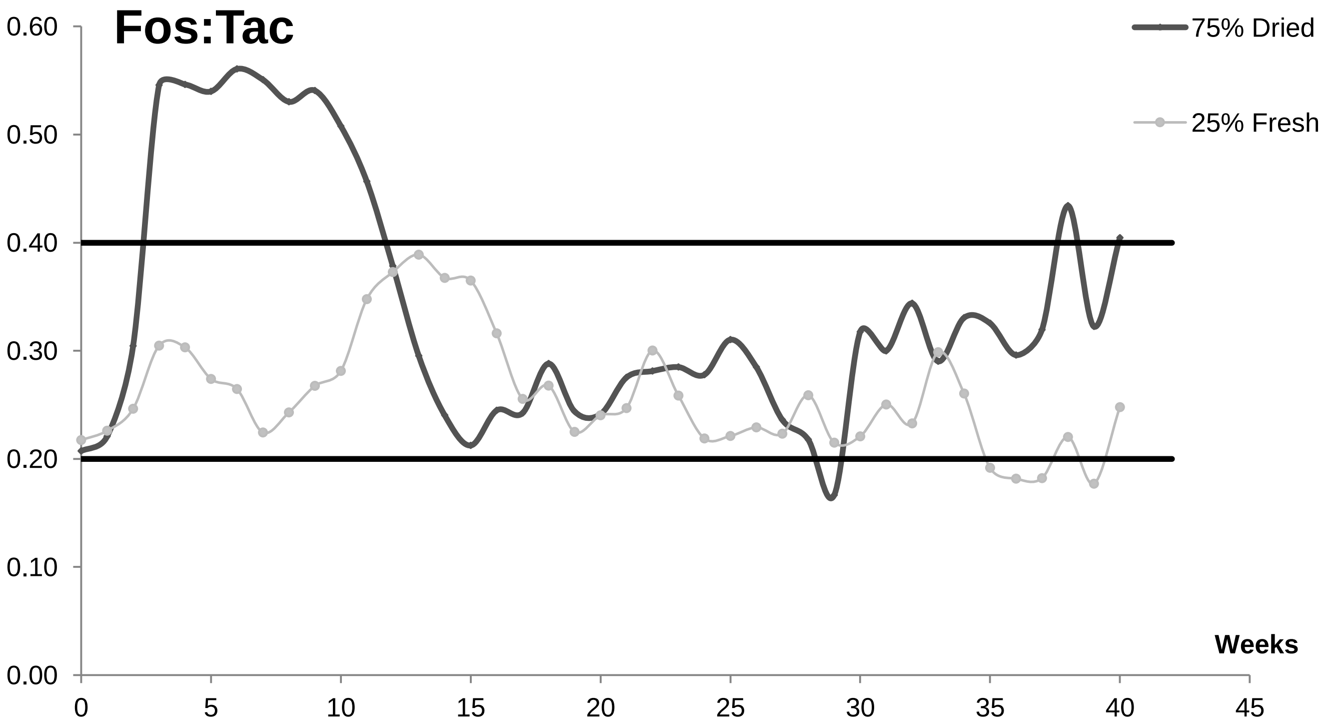


Comparison of worst and best

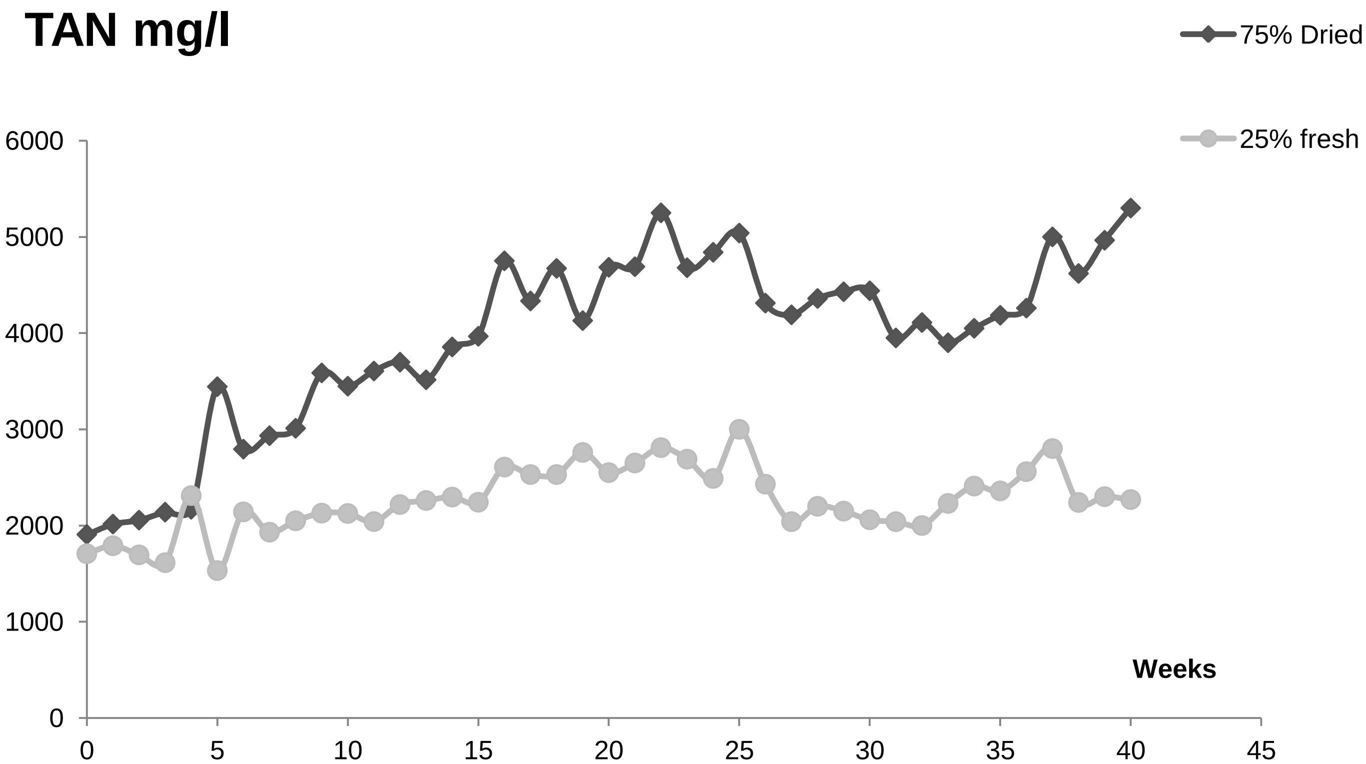
Efficiency = SMY/BMP

Continuous Results	BMP L CH_4 kg VS^{-1}	SMY L CH_4 kg VS^{-1}	Efficiency factor	CH_4 %	HRT days	Fos:Tac (Max)	tVFA mg/l	TAN mg/l
R1 75% Dried Ulva	**210**							
OLR 2 kg VS/m3/d		83	0.40	33	49	0.56		3,443
OLR 1 kg VS/m3/d		177	0.84	47	63	0.34		5,250
OLR 1.5 kg VS/m3/d		145	0.69	47	56	0.43		5,300
R6 25% Fresh Ulva	**183**							
OLR 2 kg VS/m3/d		178	0.95	51	49	0.39		2,760
OLR 2.5 kg VS/m3/d		170	0.93	52	42	0.30		3,000

Fos:Tac ratio

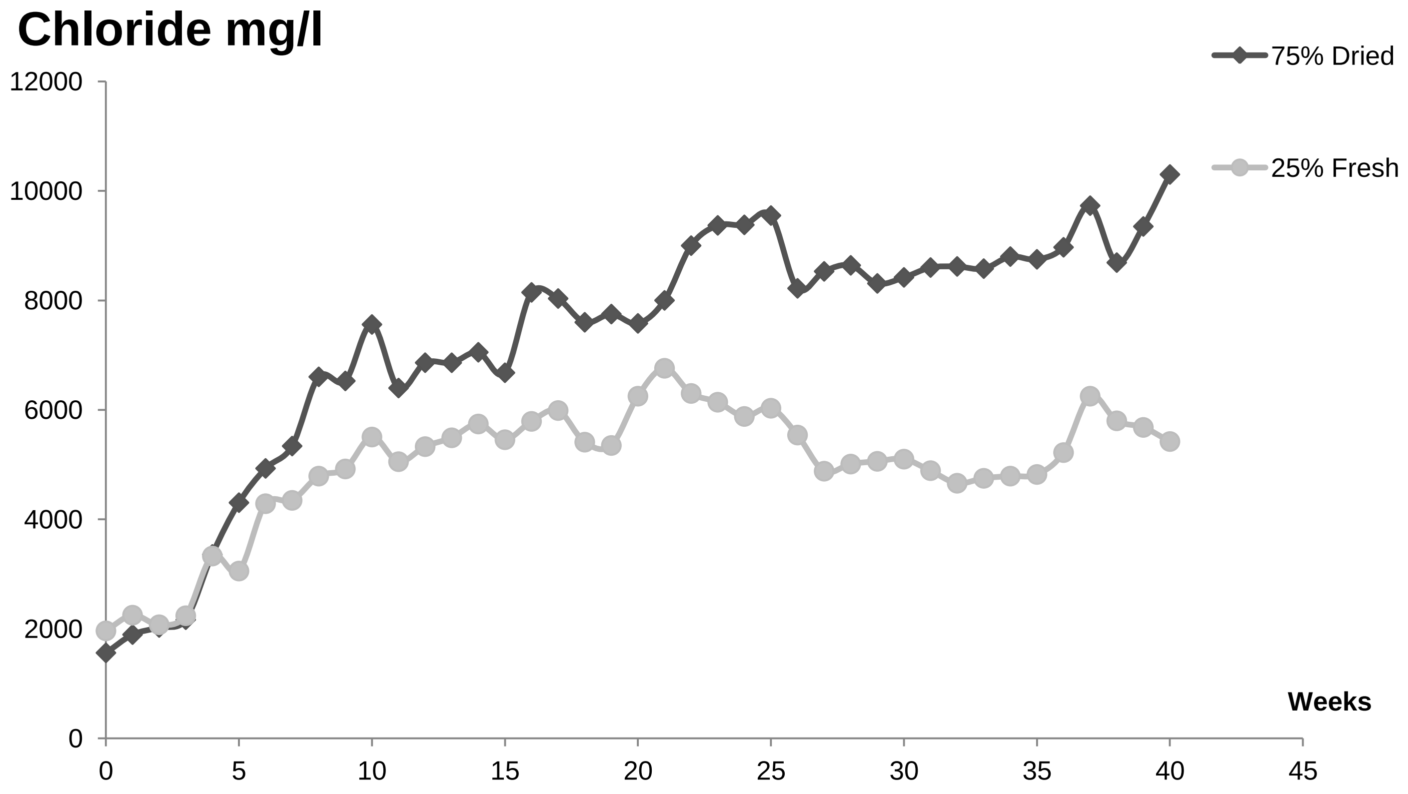


TAN



TAN mg/l
75% Dried
25% fresh
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
30
35
40
45
Weeks

Chloride


Chloride mg/l
12000
10000
8000
6000
4000
2000
0
0
5
10
15
20
25
30
35
40
45
Weeks
75% Dried
25% Fresh

Brown Seaweeds

Himanthalia elongate

Laminaria Digitata

Fucus Serratus

Saccharina Latissima

Ascophylum Nodosum

Sea weed	BMP Yield	Country	Reference
Brown Seaweeds			
H. elongate	261	West Cork, Ireland	Allen et al. 2014
	202	Brittany, France	Gard et al., 2013
L. digitata	218	West Cork, Ireland	Allen et al. 2014
	246	Sligo, Ireland	Vanegas and Bartlett 2013
F. serratus	236	West Cork, Ireland	Allen et al. 2014
S. latissima	342	West Cork, Ireland	Allen et al. 2014
	335	Sligo, Ireland	Vanegas and Bartlett 2013
	223	Trondheim, Norway	Vivekanand et al, 2011
	220	Norway	Østgaard et al.
	209	Brittany, France	Gard et al., 2013
A. nodosum	166	West Cork, Ireland	Allen et al. 2014
U. pinnatifida	242	Brittany, France	Gard et al., 2013
S. polyschides	225	Sligo, Ireland	Vanegas and Bartlett 2013
	216	Brittany, France	Gard et al., 2013
S. muticum	130	Brittany, France	
Red Seaweeds			
P. palmata	279	Brittany, France	Gard et al., 2013
G. verrucosa	144	Brittany, France	Gard et al., 2013

Resource of Macro-algae

A 1 ha farm could yield 130 wet tonnes of kelp per annum (Christiansen, 2008).

15% Volatile Solids = 19.5 tVS/ha/a @ 330 L CH_4/kg VS

6,500 L diesel equivalent /ha/a or **234 GJ/ha/a**

(compare with rapeseed 1350 biodiesel L /ha/a or 44 GJ/ha/a)

Ryan C. Christiansen (2008) British report: Use kelp to produce energy Available In:http://www.biomassmagazine.com/articles/2166/british-report-use-kelp-to-produce-energy/

Table 6. Best and worst case energy balances for grass and willow biomethane (values expressed in GJ/ha/a).

	Worst case		Best Case	
	Gross	Net	Gross	Net
Willow biomethane	95.3	82.7	130.6	116.7
Grass biomethane	122	77	163	122

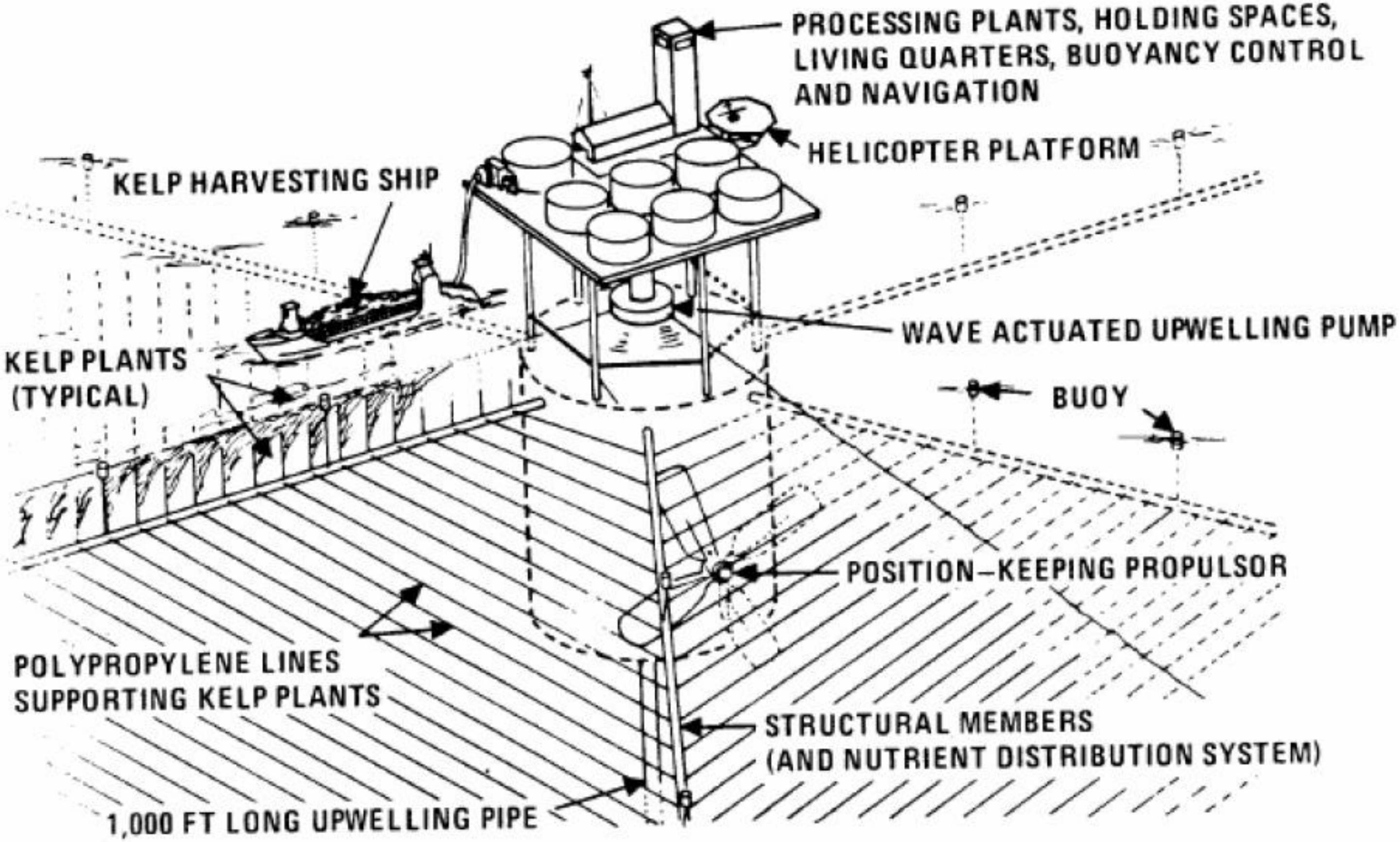
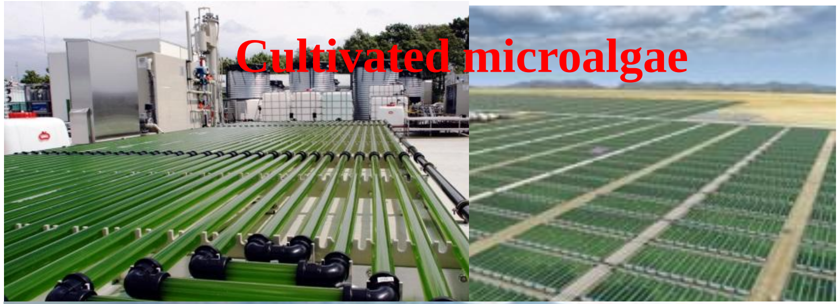
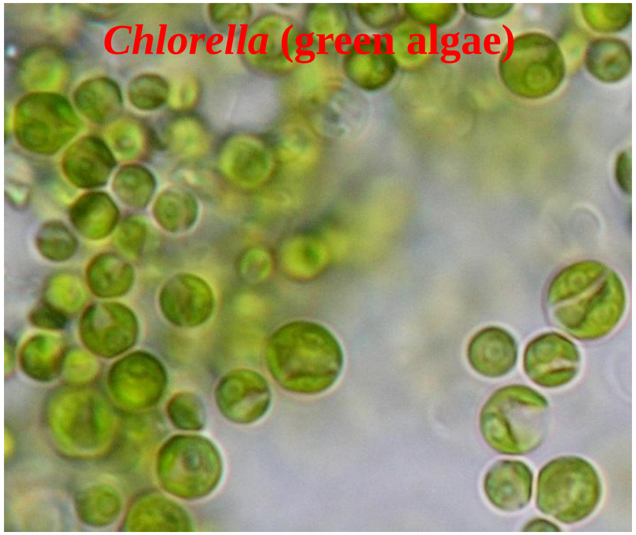


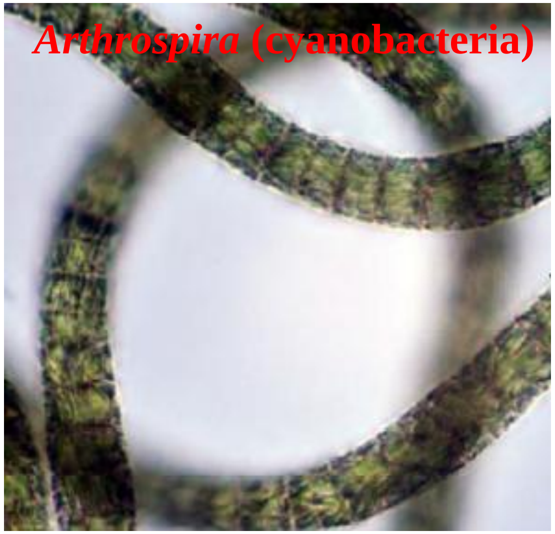
Figure 1. Conceptual design of 405 ha (1,000 acre) ocean food and energy farm unit. (Leese 1976) Source: David Chynoweth.

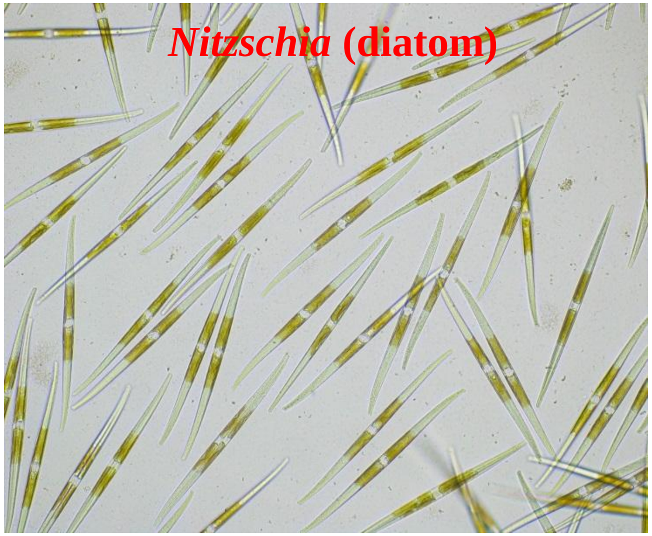
Description of Microalgae

- **Microscopic algae**, typically found in freshwater and marine systems
- **Unicellular species** which exist individually, or in chains or groups
- Produce approximately **half of the atmospheric oxygen** and simultaneously use carbon dioxide to grow photo-autotrophically
- **Main classes**: green algae (*Chlorophyceae*), blue-green algae (*Cyanophyceae*), and diatom (*Bacillariophyceae*)









Typical components and potential

Main chemical components: **20–60%** carbohydrates **30–70%** proteins, and **10–40%** lipids

Species of sample	Proteins	Carbohydrates	Lipids
Scenedesmus obliquus	50–56	10–17	12–14
Scenedesmus quadricauda	47	–	1.9
Scenedesmus dimorphus	8–18	21–52	16–40
Chlamydomonas rheinhardii	48	17	21
Chlorella vulgaris	51–58	12–17	14–22
Chlorella pyrenoidosa	57	26	2
Spirogyra sp.	6–20	33–64	11–21
Dunaliella bioculata	49	4	8
Dunaliella salina	57	32	6
Euglena gracilis	39–61	14–18	14–20
Prymnesium parvum	28–45	25–33	22–38
Tetraselmis maculata	52	15	3
Porphyridium cruentum	28–39	40–57	9–14
Spirulina platensis	46–63	8–14	4–9
Spirulina maxima	60–71	13–16	6–7
Synechoccus sp.	63	15	11
Anabaena cylindrica	43–56	25–30	4–7

A. Demirbas, *Energy Conversion and Management*, 2010, 51, 2738-2749

Methane production from micro-algae via anaerobic digestion

Buswell Equation: $$C_aH_bN_cO_d + (a + \frac{3}{4}c - \frac{b}{4} - \frac{d}{2})H_2O \rightarrow (\frac{a}{2} + \frac{3}{8}c + \frac{d}{4} - \frac{b}{8}b)CO_2 + cNH_3 + (\frac{a}{2} + \frac{b}{8} - \frac{3}{8}c - \frac{d}{4})CH_4$$

Theoretical methane yield for three types of organic compounds in microalgae

Substrate	Composition	L CH_4 g VS^{-1}
Proteins	$C_6H_{13.1}O_1N_{0.6}$	0.851
Lipids	$C_{57}H_{104}O_6$	1.014
Carbohydrates	$(C_6H_{10}O_5)n$	0.415

B. Sialve, N. Bernet and O. Bernard, *Biotechnology Advances*, 2009, 27, 409-416

- Theoretical methane yield for micro-algae: 500–800 L CH_4/kgVS
- Experimental methane yield from micro-algae: 200–400 L CH_4/kgVS
- High lipid content results in high methane yield
- Challenges: ammonium toxicity, sodium toxicity, and low accessibility due to cell wall
- Enhancement strategies: co-digestion to optimise C/N ratio, optimisation of growth condition to reduce protein content, and efficient pre-treatment to disrupt cell wall

Methane production from micro-algae via anaerobic digestion

Feedstock	Feedstock pretreatment	Reactor type	Temp (°C)	CH_4 yield (mL g^{-1})
Cyanobacterium *Arthrospira maxima*[a]	None	Digester flasks, continuous operation	35	160–310
Cyanobacterium *Arthrospira maxima*[a]	Ultrasonication	Digester flasks, continuous operation	35	170
Cyanobacterium *Arthrospira maxima*[a]	Heat treatment (50 °C, pH 11)	Digester flasks, continuous operation	35	210
Cyanobacterium *Arthrospira maxima*[a]	Heat treatment (100 °C, pH 11)	Digester flasks, continuous operation	35	220
Cyanobacterium *Arthrospira maxima*[a]	Heat treatment (150 °C, pH 11)	Digester flasks, continuous operation	35	240
Cyanobacterium *Arthrospira maxima*[a] with domestic sewage sludge	None	Digester flasks, continuous operation	35	360
Cyanobacterium *Arthrospira maxima*[a] with peat hydrolyzate	None	Digester flasks, continuous operation	35	280
Cyanobacterium *Arthrospira maxima*[a] with spent sulfite liquor	None	Digester flasks, continuous operation	35	250
Cyanobacterium *Arthrospira platensis*[a]	None	Batch fermenter	38	293
Microalga *Chlamydomonas reinhardtii*	None	Batch fermenter	38	387
Microalga *Chlorella kessleri*	None	Batch fermenter	38	218
Microalga *Chlorella* spp.	Drying and grinding	Batch bottle	37	>400
Microalga *Chlorella* spp.	Lipid extraction with 1-butanol[e]	Batch bottle	37	268
Microalga *Chlorella* spp.	*In situ* transesterification[e]	Batch bottle	37	222
Microalga *Chlorella vulgaris*	None	Batch bottle	37	286
Microalga *Chlorella vulgaris*	None	Continuous reactor	35	147–240
Microalga *Dunaliella salina*	None	Batch fermenter	38	323
Microalga *Dunaliella tertiolecta*	None	Batch bottle	37	24
Microalga *Euglena gracilis*	None	Batch fermenter	38	325
Microalga *Phaeodactylum tricornutum*	None	Batch bottle	33	350
Microalga *Phaeodactylum tricornutum*	None	Hybrid flow-through reactor	33	270
Microalga *Phaeodactylum tricornutum*	None	Hybrid flow-through reactor	54	290
Microalga *Scenedesmus obliquus*	None	Batch bottle	33	210
Microalga *Scenedesmus obliquus*	None	Hybrid flow-through reactor	33	130
Microalga *Scenedesmus obliquus*	None	Hybrid flow-through reactor	54	170
Microalga *Scenedesmus obliquus*	None	Batch fermenter	38	178
Microalga *Scenedesmus* spp.	Lipid extraction and alkaline heat treatment (100 °C 8 h)	Batch bottle	37	323
Mixed microalgal culture with *Scenedesmus* and *Chlorella* spp.	None	Fed-batch operated digester	35	248
Mixed microalgal culture with *Scenedesmus* and *Chlorella* spp.	None	Fed-batch operated digester	50	314
Mixed microalgal culture	None	Fed-batch operated digester	38	240
Mixed microalgal culture	Heat treatment (100 °C 8 h)	Fed-batch operated digester	38	320
Mixed microalgal culture[b]	Heat treatment (70 °C 60 h)	Semi-continuous plug-flow type sequential digester setup	40	335[f]
Mixed microalgal culture[c]	None	Fed-batch operated digester	45	402
Mixed microalgal culture[d]	None	Semi-continuous digester	35	143
Mixed microalgal culture[d] with waste paper (1:1)	None	Semi-continuous digester	35	293

A.-M. Lakaniemi, O. H. Tuovinen and J. A. Puhakka, *Bioresource Technology*, 2013, 135, 222-231

Biohydrogen production from micro-algae via dark fermentation

Glucose (carbohydrates): $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 \ + 4H_2$ **500 mL H_2/g VS**

Glutamic acid (proteins): $C_5H_9NO_4 + 1.5H_2O \rightarrow 2.25CH_3COOH + NH_3 + 0.5CO_2$ **0 mL H_2/g VS**

A. Xia, J. Cheng, R. Lin, H. Lu, J. Zhou and K. Cen, *Bioresource Technology*, 2013, 138, 204-213

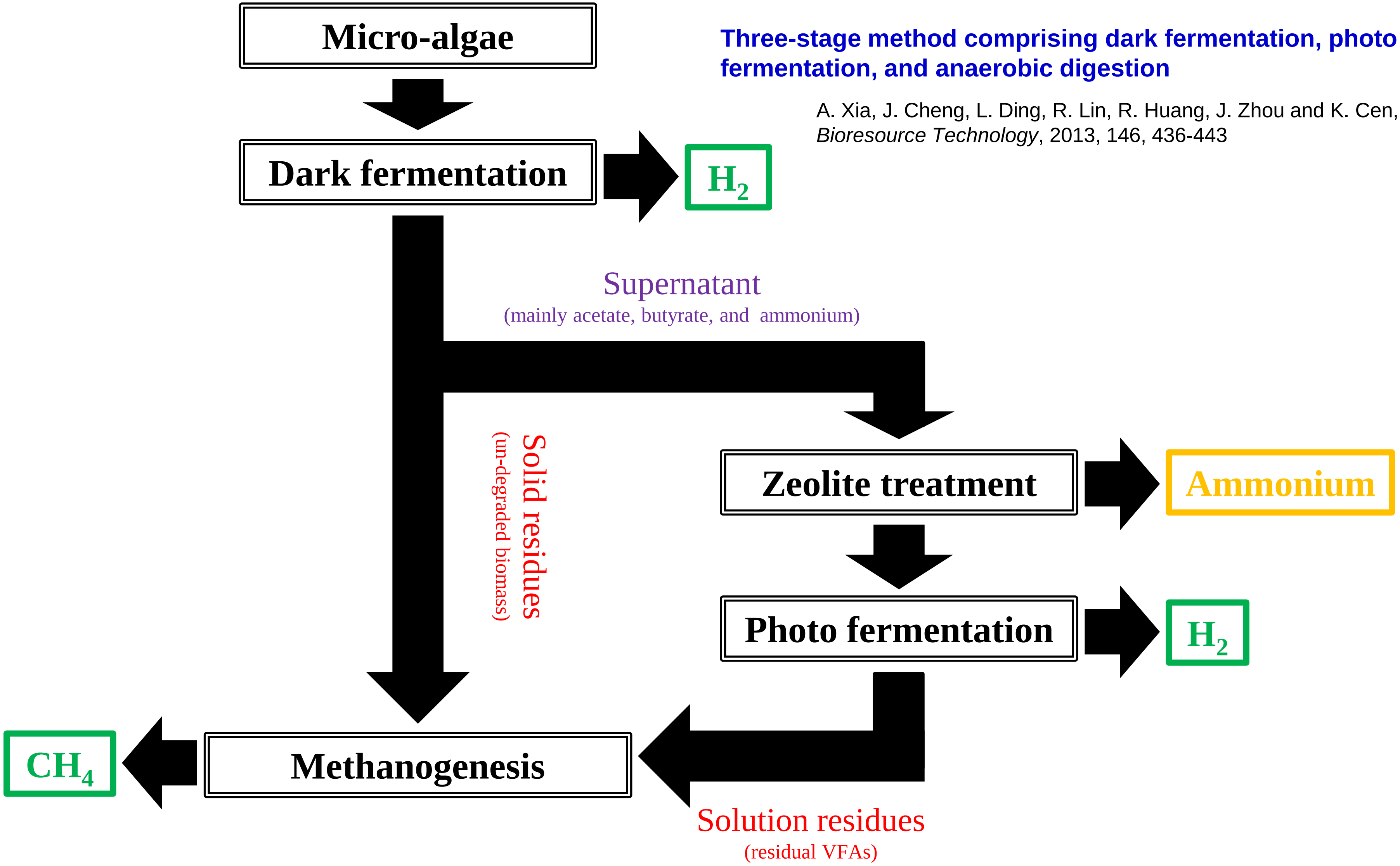
- Theoretical hydrogen yield of micro-algae: 200–450 mL H_2/g VS
- Experimental hydrogen yield of micro-algae: 50–120 mL H_2/g VS
- High carbohydrate content results in high hydrogen yield
- Challenges: low accessibility due to cell wall, low C/N ratio, energy in effluent
- Enhancement strategies: co-fermentation to optimise C/N ratio, optimisation of microalgae growth condition to reduce protein content, and efficient pre-treatment to disrupt cell wall, subsequent hydrogen fermentation and anaerobic digestion

Biohydrogen production from microalgae via dark fermentation

Microalga	Pre-treatment	Innocula	Yields and productivities[a]
Scenedesmus obliquus	Autoclave (15 min)	*Clostridium butyricum*	113.1 mL H_2/g VS 90.3 mL H_2/g (dw) 84.6 mL H_2/L_{FM}/h
Scenedesmus obliquus (wet)	Autoclave (15 min)	*Enterobacter aerogenes*	57.6 mL H_2/g VS 45.1 mL H_2/g (dw) 22.6 mL H_2/L_{FM}/h
Scenedesmus obliquus	Autoclave (30 min)	*Clostridium butyricum*	2.9 mol/$mol_{total\ sugars}$
Chlorella vulgaris	Acid; alkaline; autoclave; enzymatic	*Clostridium butyricum*	81 mL H_2/g (dw)
Chlamydomonas reinhardtii		*Clostridium butyricum*	17.29 mL H_2/L_{FM}/h
Nannochloropsis	Thermal + acid + pressure	*Clostridium acetobutylicum*	3.39 mL H_2/L_{FM}/h
Anabaena sp.	Autoclave (15 min)	*Enterobacter aerogenes*	15.2 mL H_2/g (dw)
Nannochloropsis sp.	Autoclave (15 min)	*Enterobacter aerogenes*	60.6 mL H_2/g (dw)
Thalassiosira weissflogii	Mechanical pressing; sonication; French press; freeze–thaw; stirring + sonication	*Thermotoga neapolitana*	36.2 mL H_2/L_{EXT}/h
Chlamydomonas reinhardtii	Sonication; methanol; autoclave + acid; enzymatic	*Termotoga neapolitana*	35.83–53.3 mL H_2/L_{FM}/h
Arthrospira maxima	Enzymatic	Anaerobic activated sludge	49.7–78.7 mL H_2/g (dw)
Arthrospira maxima (wet)	Boiling; bead milling; ultrasonication; enzymatic	Anaerobic activated sludge	38.5–92 mL H_2/g (dw)
Chlorella vulgaris and *Dunaliella tertiolecta*		Anaerobic digested sludge	10.8 and 12.6 mL H_2/g VS
Scenedesmus	Alkaline; thermal; alkaline + thermal	Anaerobic digested sludge	16.89–45.54 mL/g VS
Scenedesmus	Thermal	Anaerobic digested sludge	25.64–40.27 mL/g VS
Scenedesmus obliquus	Ultrasonication	Anaerobic consortia	7.06–8.40 mL H_2/L_{FM}/h

A. P. Batista, P. Moura, P. A. S. S. Marques, J. Ortigueira, L. Alves and L. Gouveia, *Fuel*, 2014, 117, 537-543

Subsequent photo fermentation and anaerobic digestion



Three-stage method comprising dark fermentation, photo fermentation, and anaerobic digestion

A. Xia, J. Cheng, L. Ding, R. Lin, R. Huang, J. Zhou and K. Cen, *Bioresource Technology*, 2013, 146, 436-443

Subsequent photo fermentation and anaerobic digestion

Acetate (photo fermentation): $$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Acetate (anaerobic digestion): $$CH_3COOH \rightarrow CO_2 + CH_4$$

Energy yields of micro-algae via combined hydrogen fermentation and anaerobic digestion are **significantly** higher than those via single stage dark anaerobic fermentation

Fermentation type	Substrate	Dark Anaerobic (DA) fermentation		Photo-fermentation (PF)		Anaerobic Digestion (AD)		Total
		H_2 yield (mL H_2/g VS)	Energy yield (kJ/g VS)	H_2 yield (mLH_2/g VS)	Energy yield (kJ/g VS)	CH_4 yield (mLCH_4/g VS)	Energy yield (kJ/g VS)	Total energy yield (kJ/g VS)
DA + PF	*Arthrospira platensis*	98.5	1.3	256.2	3.3	/	/	4.5
DA + PF + AD	*Nannochloropsis oceanica*	39.0	0.5	144.9	1.9	161.3	6.4	8.7
DA + PF + AD	*Chlorella pyrenoidosa*	75.6	1.0	122.7	1.6	186.2	7.4	9.9
DA + PF + AD	*Chlorella pyrenoidosa* and starch	276.2	3.5	388.0	5.0	126.0	5.0	13.5
DA + AD	*Arthrospira maxima*	82.8	1.1	/	/	115.3	4.6	5.6

Biofuels: Gross Energy Production per hectare per annum

1st G Ethanol from:	l/ha/a	GJ/ha/a
Sugar cane	**6400**	**135**
Sugar beet	5500	117
Wheat	3150	84

1st G Biodiesel from:	l/ha/a	GJ/ha/a
Oil palm	**5000**	**165**
Coconut	2260	75
Jatropha	1590	52
Rape seed	1355	46
Pea nut	890	29
Sun flower	800	26
Soyabean	375	12

2nd G biomethane from:	GJ/ha/a
Grass	**160**
Willow	130

3rd G biomethane from:	tVS/ha/a	m^3CH_4/kg VS	m^3CH_4/ha/a	GJ/ha/a
Micro-algae	**140**	**340**	**47,600**	**1713**
Sugar kelp	20	330	6,600	238

3rd G bioH_2 & bioCH_4 from:	tVS/ha/a	GJ H_2/ha/a	GJ CH_4/ha/a	GJ/ha/a
Micro-algae	**140**	**364**	**1036**	**1400**

Dark fermentation + photo fermentation + anaerobic digestion *Chlorella pyrenoidosa*

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