



Università di Foggia



GAL
Gargano
agenzia di sviluppo

**LA DIVERSIFICAZIONE DELLE PRODUZIONI PER ACCRESCERE IL
REDDITO PER GLI OPERATORI DELLA FILIERA ITTICA**

Ischitella-Foce Varano 25th October 2019

**“La produzione di macroalghe in ambienti
marino costieri: bioraffineria e produzione
di interesse economico”**

M. Francavilla ^{a,b}

^aUniversity of Foggia, Department of Agriculture, Food and Environmental Science, Foggia (Italy)

^bInstitute of Marine Science - National Research Council, Venice (Italy)

email: matteo.francavilla@unifg.it

Biorefinery

“Biorefining is the sustainable synergetic processing of biomass into a spectrum of marketable food & feed ingredients, products (chemicals, materials) and energy (fuels, power, heat)”

International Energy Agency (IEA) – TASK 42

Biorefinery

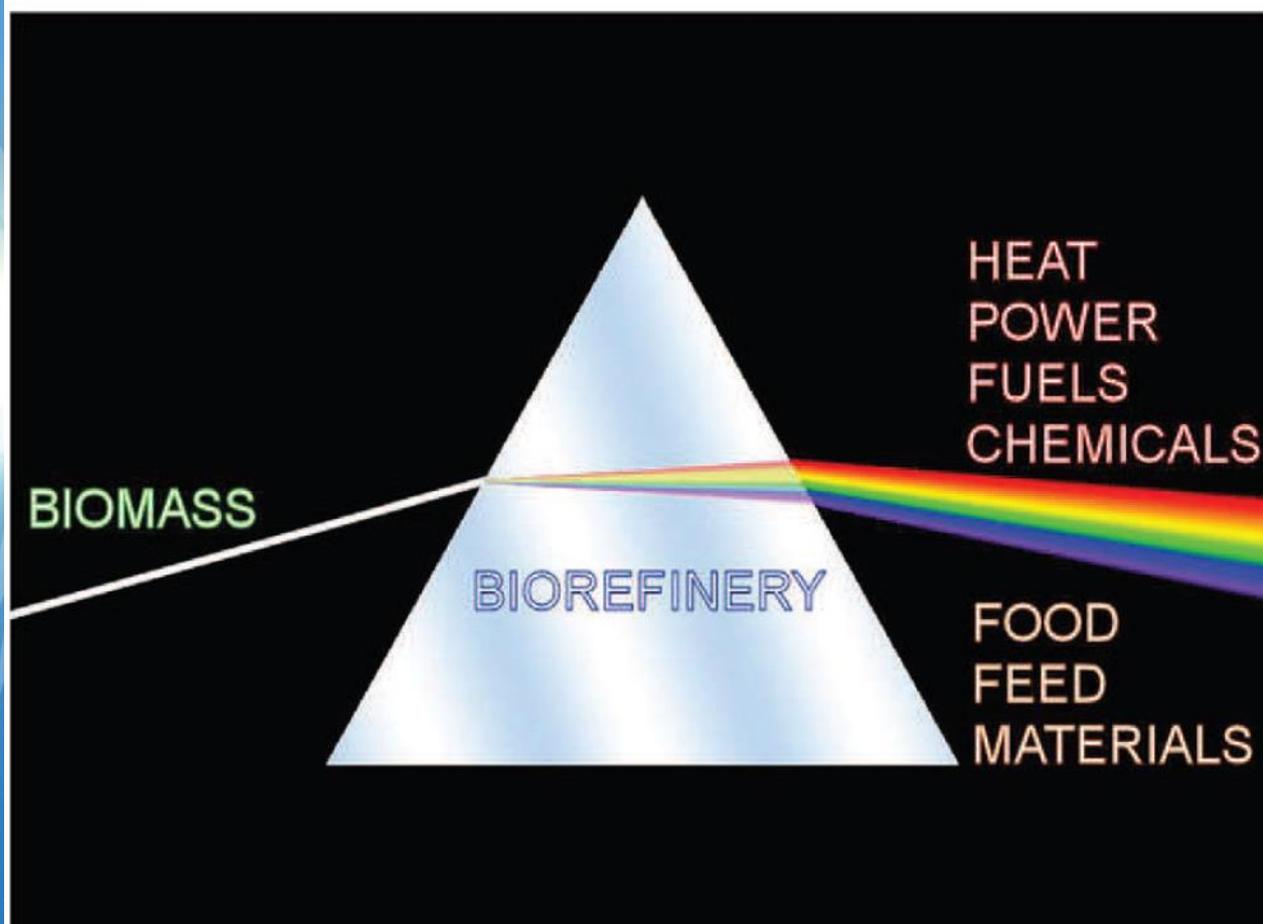
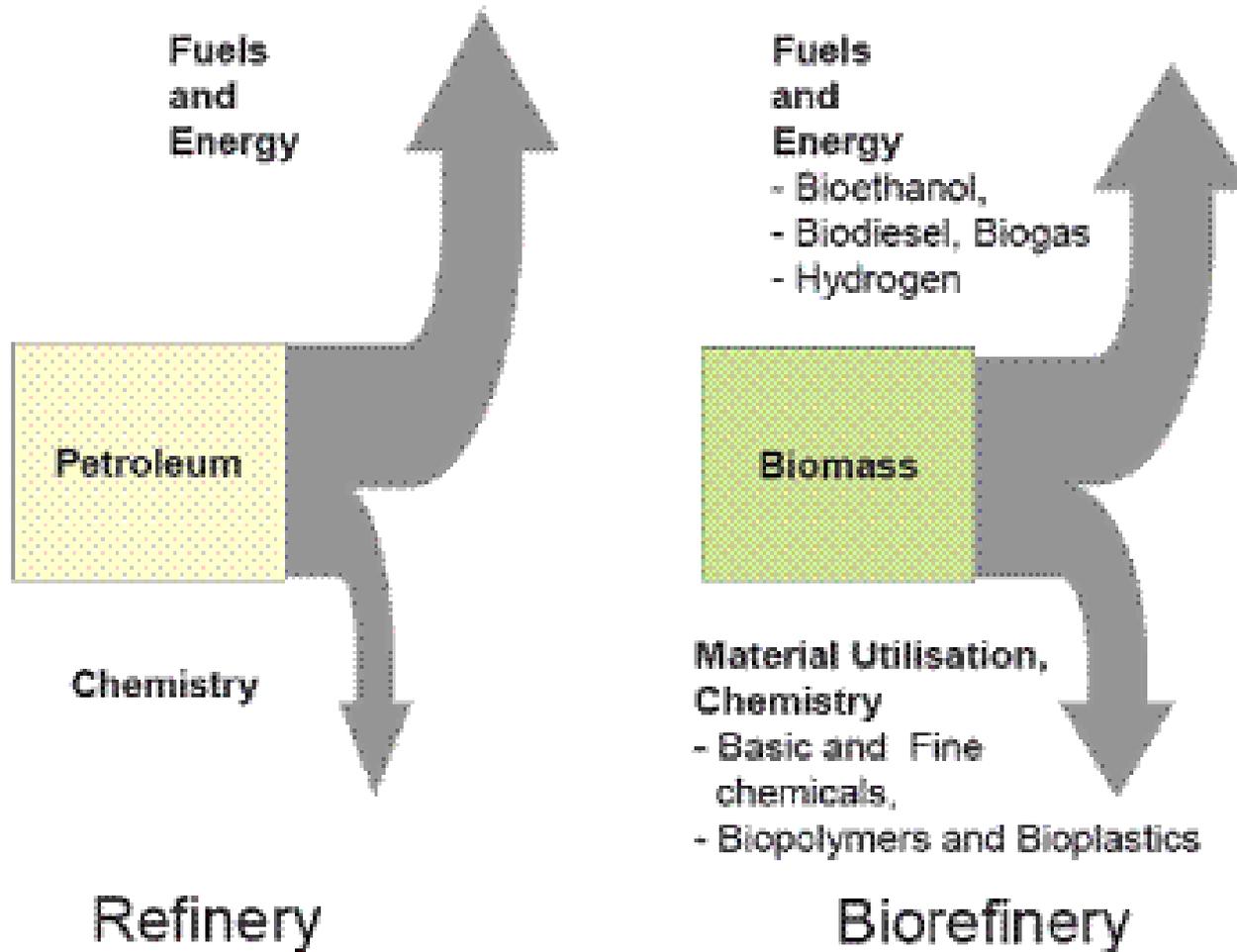
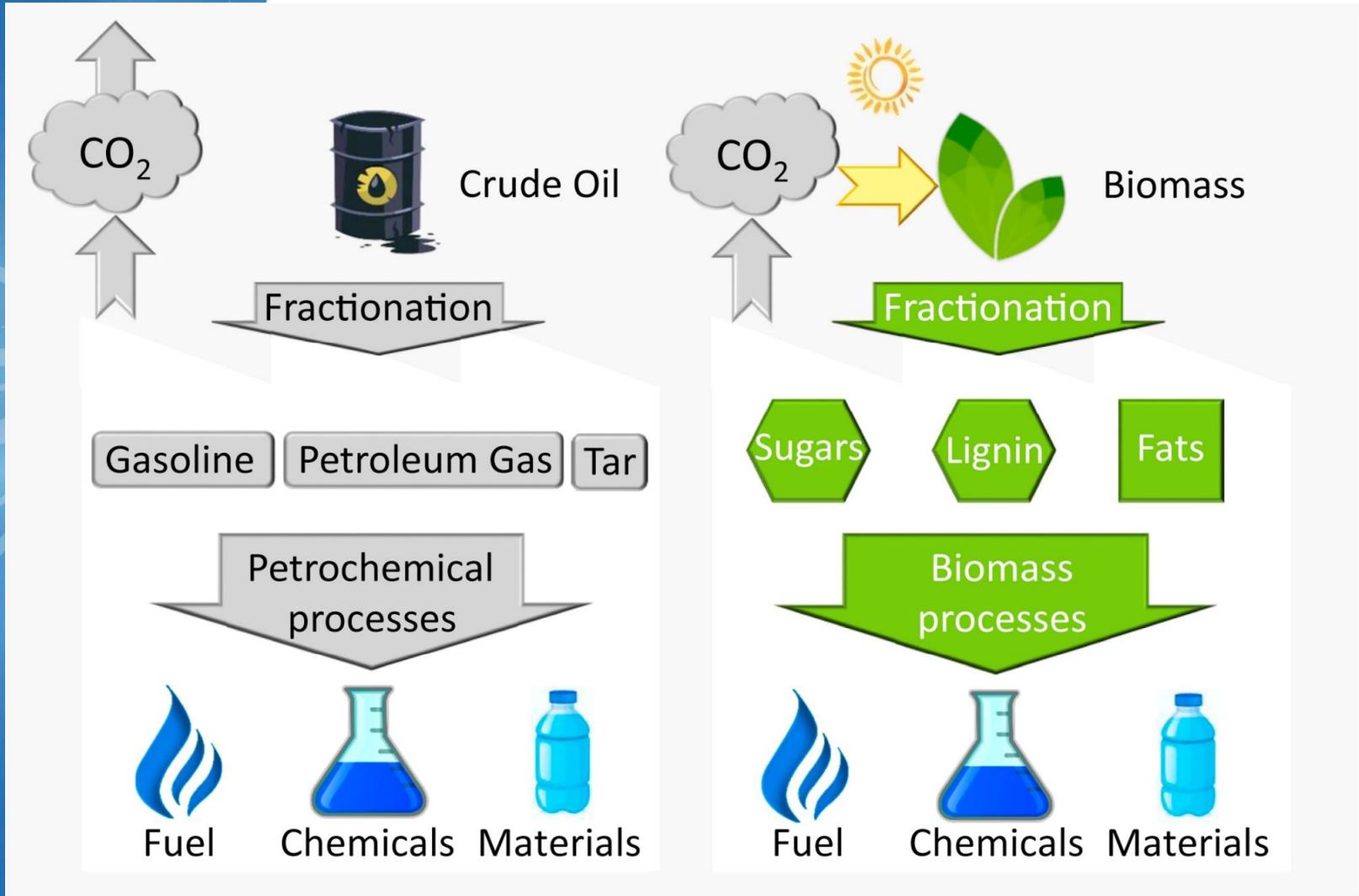


Figure 1.1 Biorefinery and its role in the transformation of biomass.

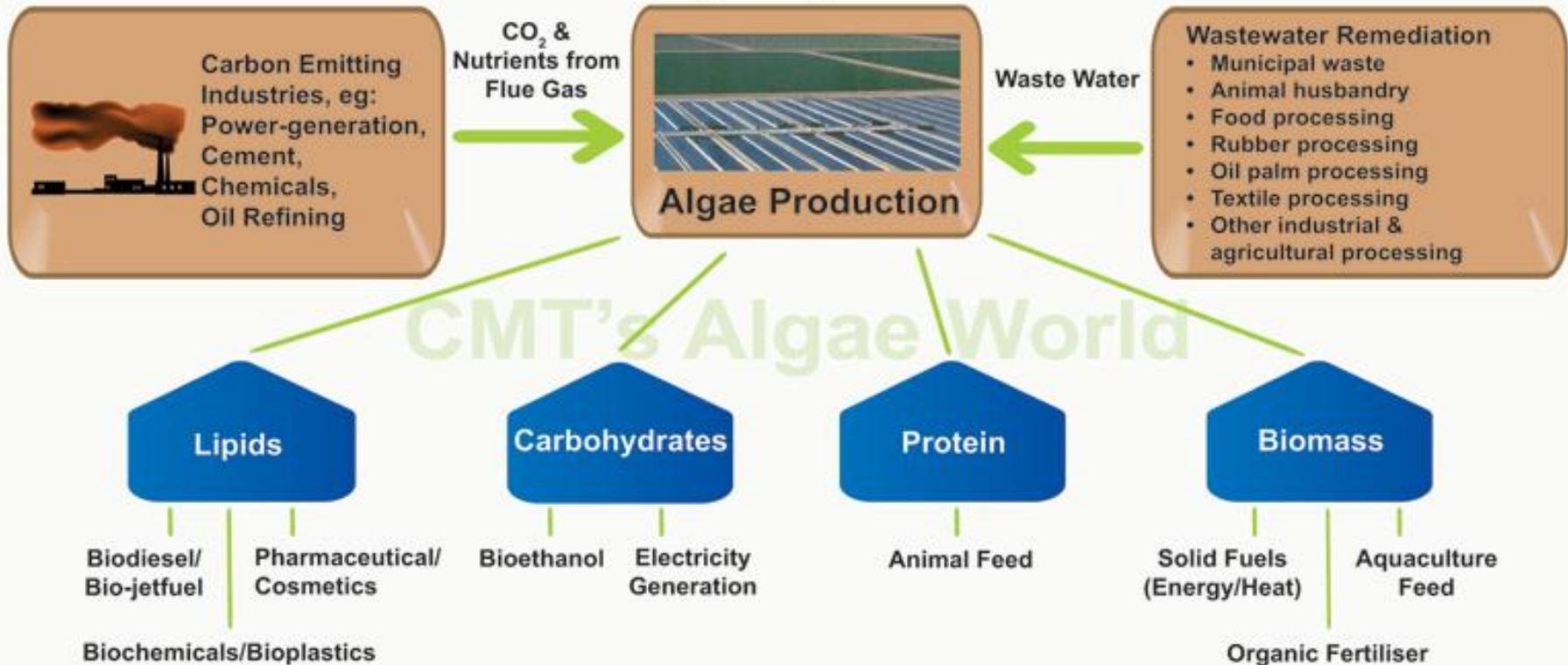




The BioRefinery Approach:

Generate multiple products from any biomass resource

Flow Chart of Algae Inputs to End-Products



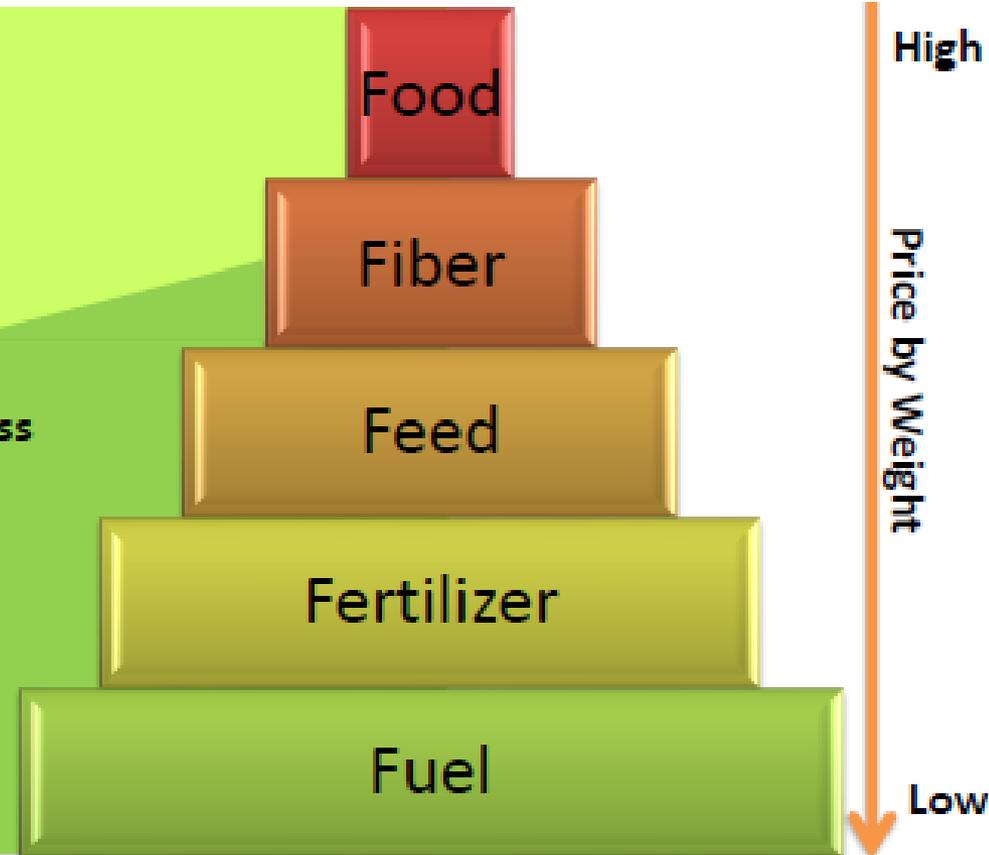
5 Fs of Biomass

Specialties = Health Care Business

- *Functional Foods
- *Cosmetic Materials
- *Medical Products Materials

Commodities = Energy, Environment Business

- *Chemical Products
- *Compound Feed Materials
- *Fertilizer Materials
- *Industrial Use Oils
- *Bio-Jet Fuels



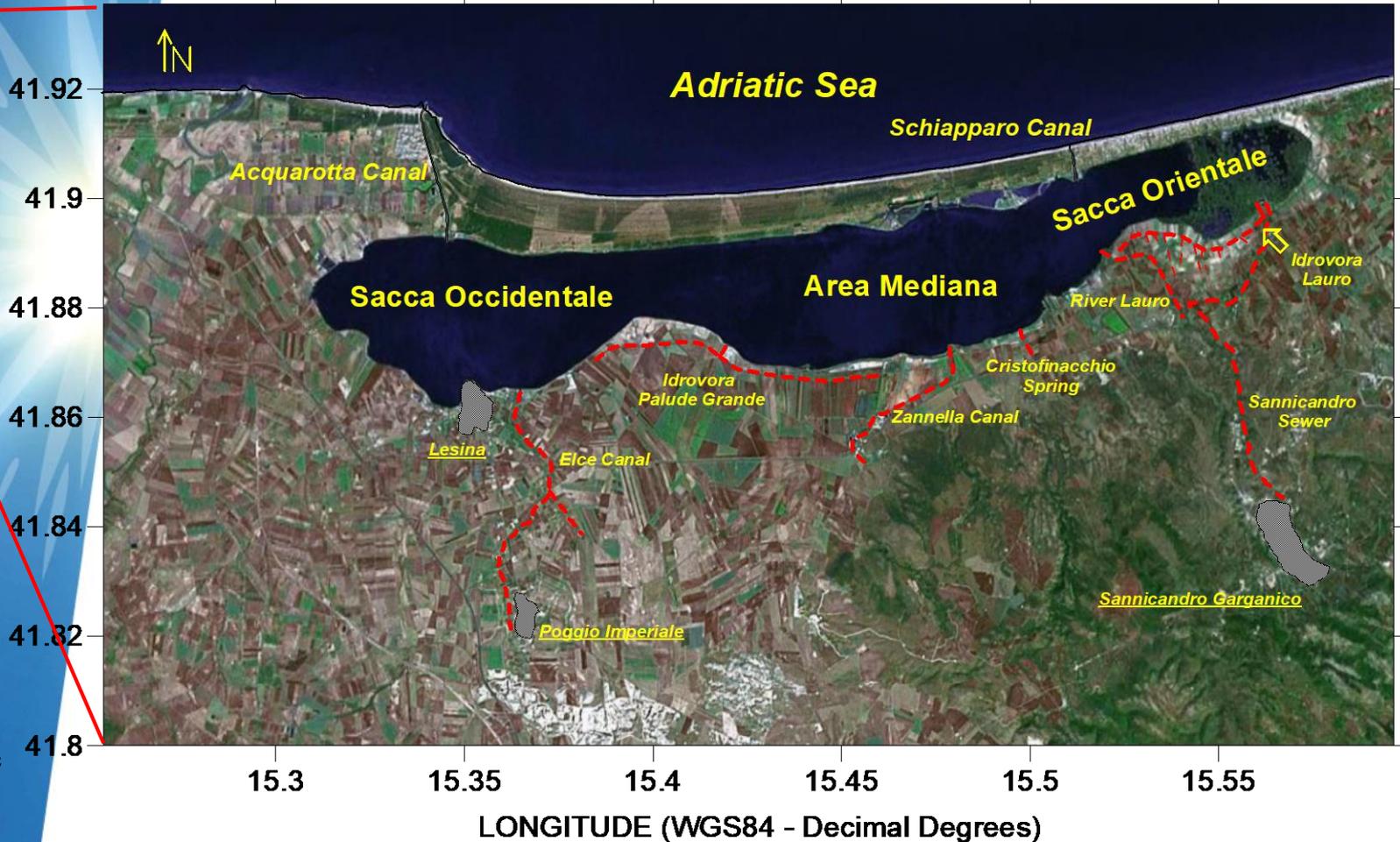
Gracilaria gracilis as nutrient remover (bioremediation)



The Lesina lagoon (Italy)



LATITUDE (WGS84 - Decimal Degree)



Mean Depth: ≈ 1 m

Surface Area: ≈ 50 Km²



Foggia



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Il sviluppo



Longline plants

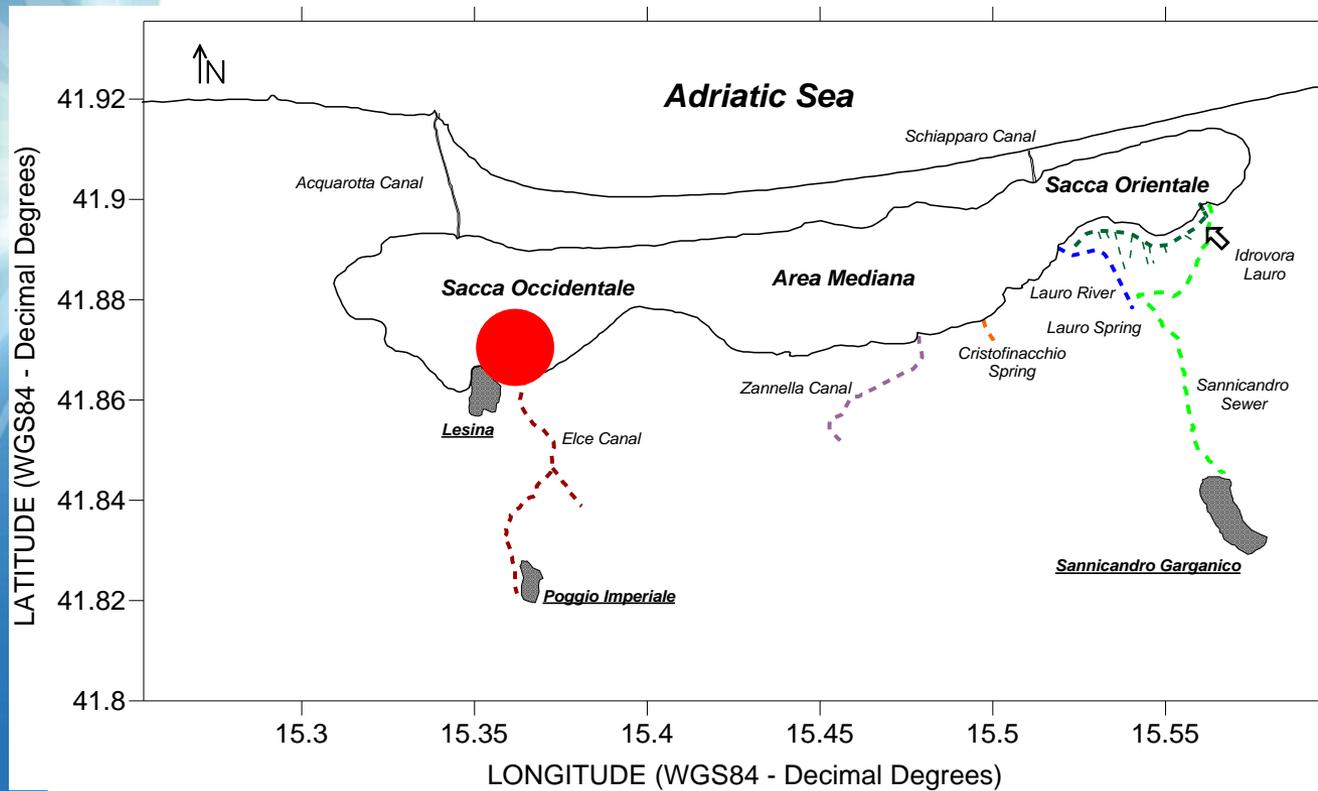


Longline



Gracilaria gracilis

Installation of a longline plants in Orti-Cammarata site in order to produce and spread *Gracilaria gracilis* into Sacca Occidentale.

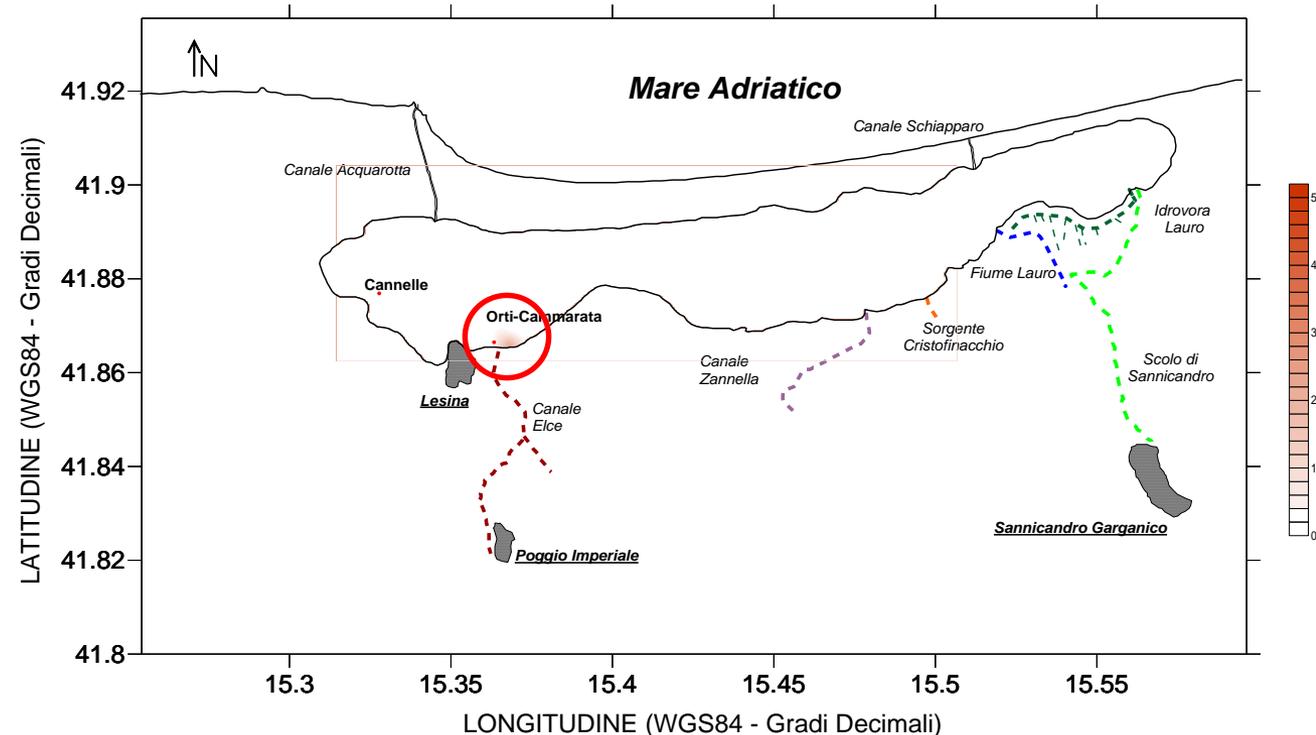


Standing crop of *Gracilaria gracilis* at beginning of test

Table 1
Rules used for the quali-quantitative analysis of *Gracilaria verrucosa* (ex) meadow.

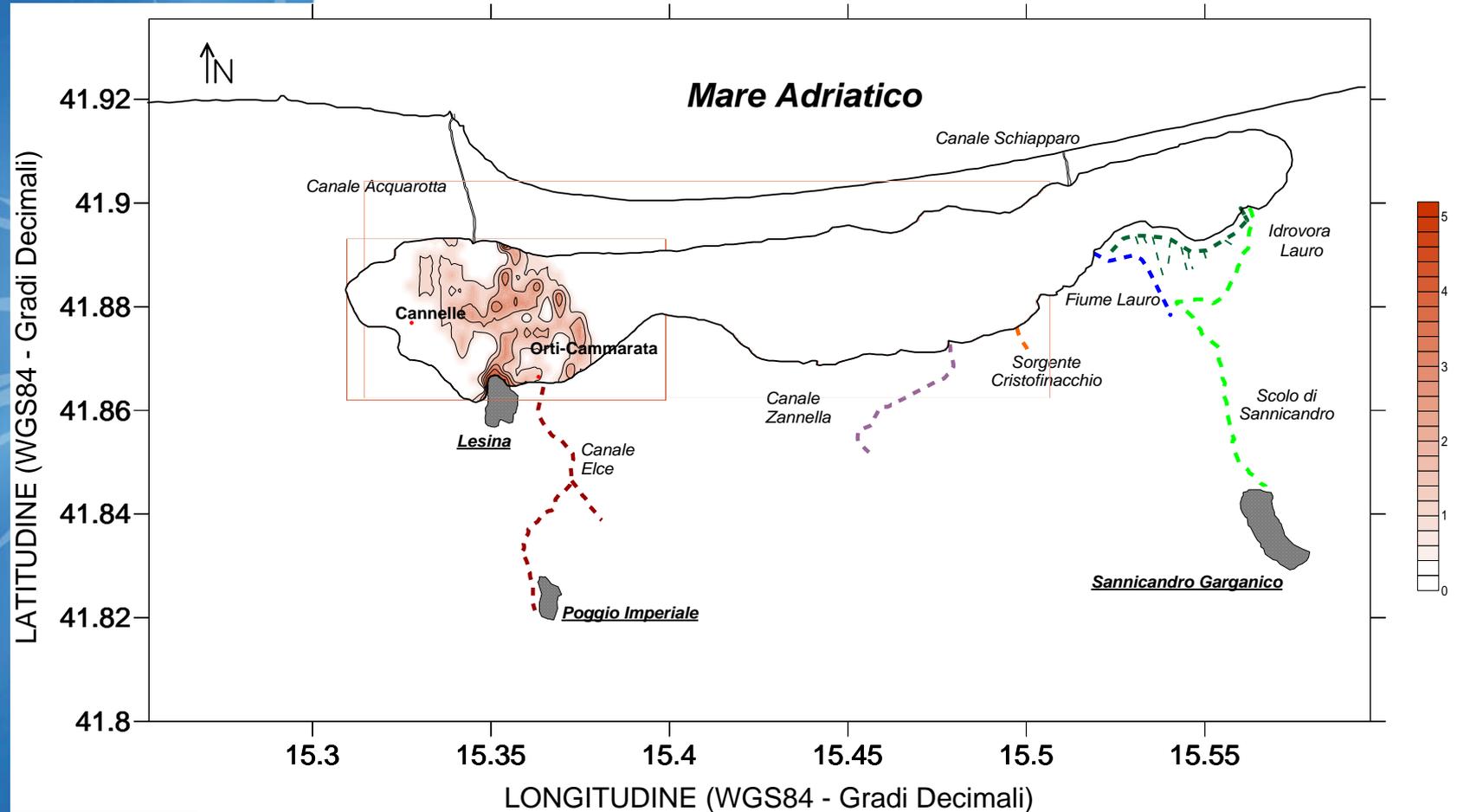
Value	Covering percentage	Density (kg w.w./mq) (mean±std error)
0	0 %	0
1	1% <> 25%	0.07±0.02
2	25% <> 50%	0.45±0.12
3	50% <> 75%	0.9±0.31
4	75% <> 100%	1.82±0.5
5	*Accumulation	6±2

*The accumulation is a macroalga standing crop with thickness higher than 20 cm.



The area covered was of 1 Ha with an estimated biomass of 0.2 metric tons w.w.

Standing crop of *Gracilaria gracilis* at the end of test



The area covered was of 615 Ha with an estimated biomass of 1224 metric tons w.w..

Commercial applications of *Gracilaria gracilis*

1. Agar-agar production

- Used as stabiliser for emulsions and suspensions and as gelling agent in food, pharmaceutical and cosmetic industry.
- Anti-tumoral activity (it induces apoptosis of tumor cells)

2. It could be an excellent substrate for biomethane generation

- 30% of dry weight consists of Carbon.
- macroalga consists of polysaccharides, with zero lignin and low cellulose content, which makes it an easy material to convert to methane by anaerobic digestion processes.

Yield of methane produced from different feedstocks.

Biomass	Methane yield (m ³ kg ⁻¹)	Reference
<i>Laminaria sp.</i>	0.26 – 0.28	Chynoweth et al. (1993)
<i>Gracilaria sp.</i>	0.28 – 0.4	Bird et al. (1990)
<i>Sargassum sp.</i>	0.12 – 0.19	Bird et al. (1990)
<i>Macrocystis</i>	0.39 – 0.41	Chynoweth et al. (1993)
Water hyacinth	0.13- 0.21	Chynoweth et al. (1993)
Sorghum	0.26 – 0.39	Chynoweth et al. (1993)
Poplar	0.23- 0.32	Chynoweth et al. (1993)
Food waste	0.54	Chynoweth et al. (1993)

“Thinking Gracilaria of Lesina lagoon as a *multi product source*”

*Macroalghe della laguna di Lesina: potenziali sorgenti di
prodotti naturali di uso farmaceutico e alimentare
(MADLENA)*



A project funded by



Agar

Lipids

Fatty Acids

Carbohydrates

Sterols

Antioxidant
activity

Proteins



Phenolic content

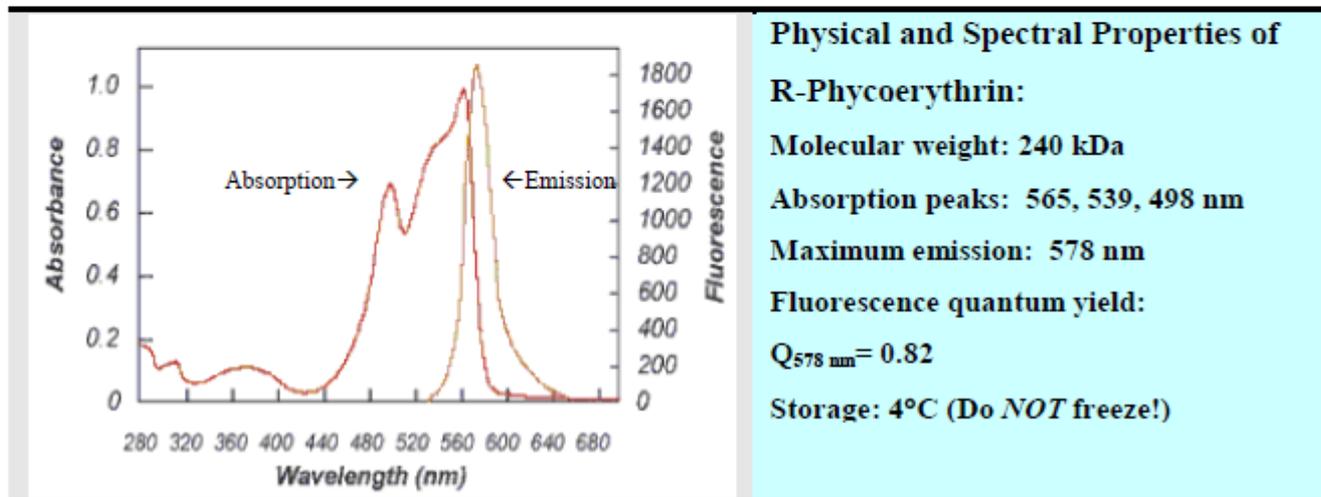
*FrancaVilla et al.,
Marine Drugs 2013.*

Phycobiliproteins

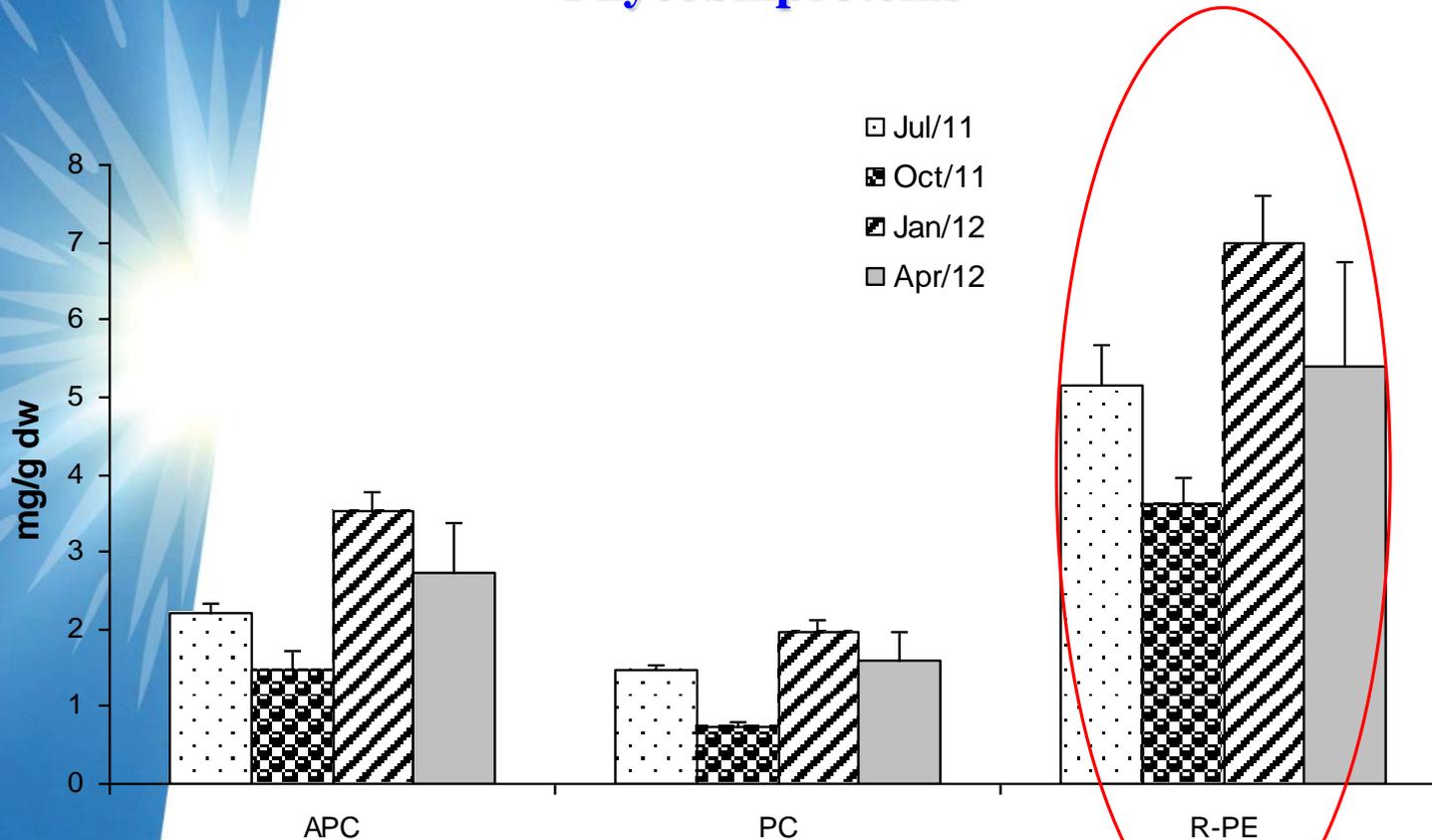
Phycobiliproteins

Phycobiliproteins can be used as very useful fluorescent probes because of their excellent spectroscopic properties (Vernon et al., 1982; Ayyagari et al., 1995), stability, high absorption coefficients, and high quantum yields. Phycobiliproteins are also widely used as natural colorants for food and cosmetic. Phycobiliproteins have wide usage and great economic potential (Niu et al. 2006; Bermejo et al., 2007).

R-Phycoerythrin



Phycobiliproteins



R-PE: R-phycoerythrin

PC: phycocyanin

APC: Allophycocyanin



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52412 Sigma-Aldrich

R-Phycoerythrin

BioReagent, passes test for gel electrophoresis

CAS Number 11016-17-4 | MDL number MFCD00081950



SDS

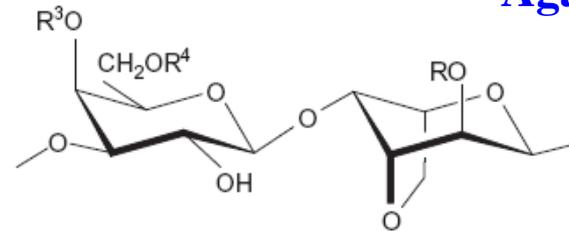
SKU-Confezionamento	Disponibilità	Confezionamento	Prezzi (EUR)	Quantita'
52412-1MG-F	✓ Disponibile per la spedizione il 24.10.19 - D&A	1 MG	146.00	0 ★ i
52412-5MG-F	✓ Solo 4 a stock (altri in arrivo) - DA	5 MG	497.00	0 ★ i

Ordini Bulk?

AGGIUNGI AL CARRELLO

Product Recommendations

Agar



R = H, or Me
 R¹ = H, Me, or β -D-Xylp

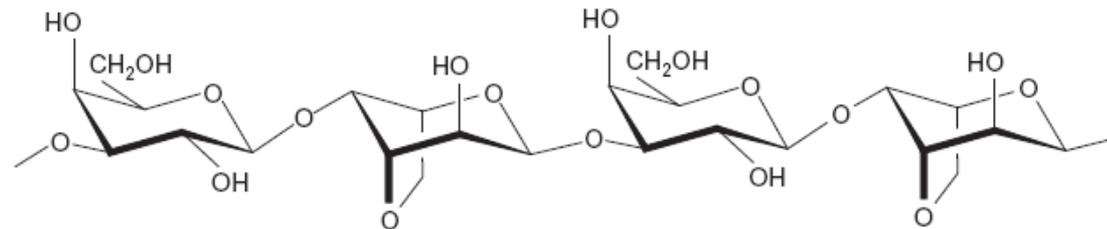
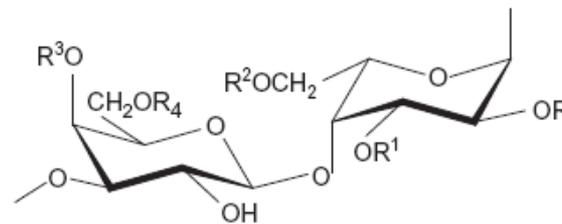
R² = H, or SO₃⁻

R³ = H, or SO₃⁻

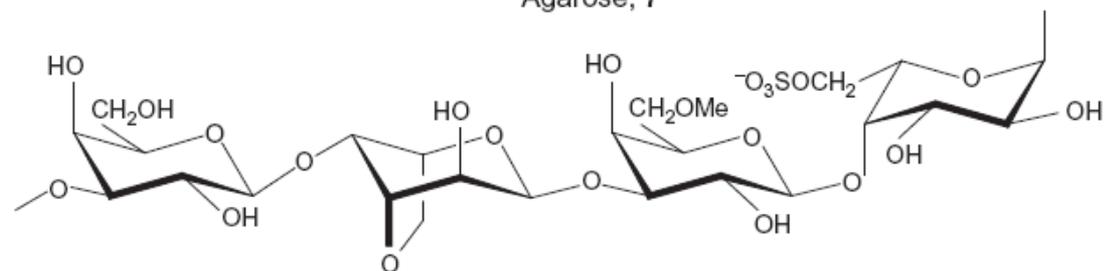
R⁴ = H, Me, SO₃⁻, β -D-Xylp, or

4-O-Me- α -L-Galp

R³, R⁴ = HOOC-C(Me)-



Agarose, 7



Porphyran, 10

SCHEME 2. Structural diversity in the polysaccharides of the agar group.

Extraction methods

Classic:

Water 120°C, 1.5h

Microwave assisted extraction:

Water 100°C, 10 min

Water 110°C, 20 min

Water 140°C, 15 min

Classic Extraction

Microwave Assisted Ectraction

Sample	Agar Yield (%)	Sample	Agar Yield (%)
NA (Jun/11)	21.3	NA - 100°C (Jun/11)	25.72
ATA (Jun/11)	14.2	NA - 110°C (Jun/11)	25.4
		NA - 140°C (Jun/11)	0
		ATA - 100°C (Jun/11)	2.07
		ATA - 110°C (Jun/11)	6.62
		ATA - 140°C (Jun/11)	15.95

Notes:

NA = Native Agar

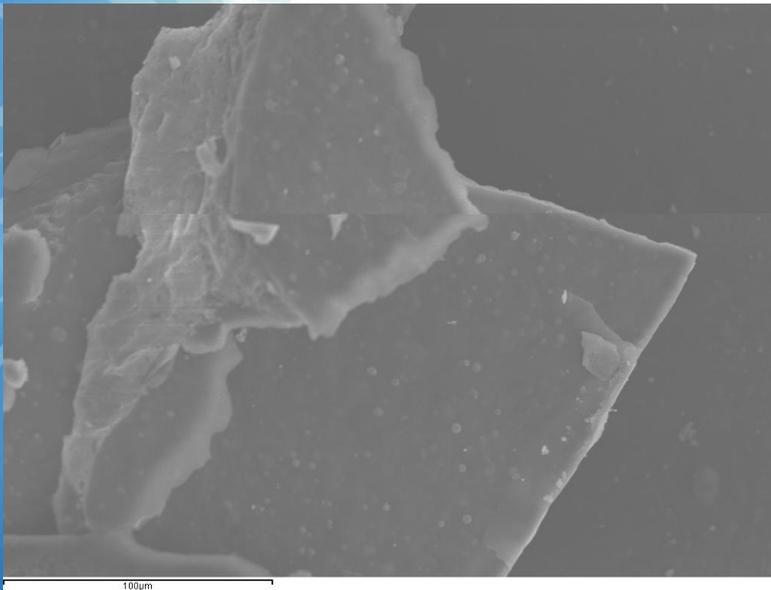
ATA = Alkali-Treated Agar

Temperature (100, 110 and 140°C) is the value used in MAE programme

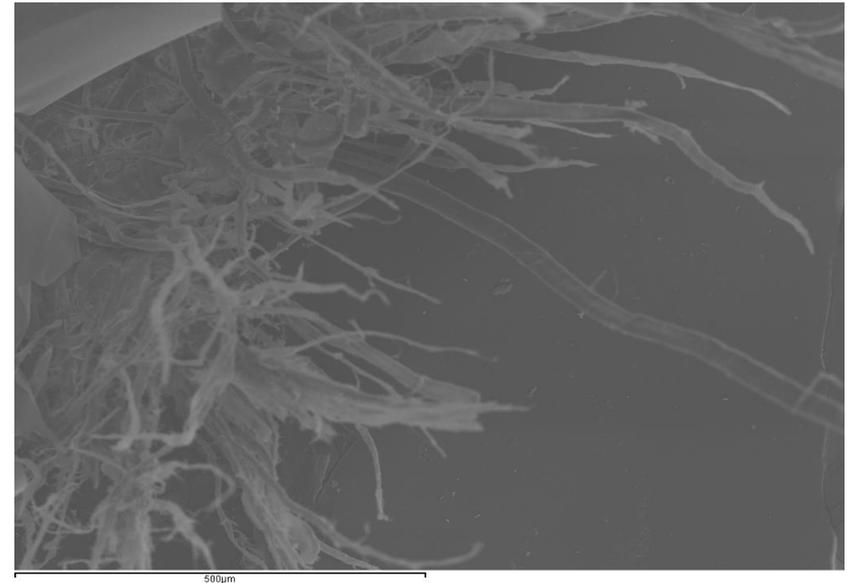
FrancaVilla et al., Carbohydrate Polymer 2013.

The differences observed between non-treated and alkali-treated materials were also noticeable in SEM micrographs of both types of materials

Mesoporous agar materials



Non-treated



Alkali-treated

Francavilla et al., Carbohydrate Polymer 2013.

Preparation of mesoporous agar materials

- **Microwave extracted (then dried)**

- Untreated samples

S_{BET} 5 m² g⁻¹
Pore Diameter 2.3 nm
Pore volume 0.05 mLg⁻¹

- Treated samples (NaOH)

S_{BET} 25-40 m² g⁻¹
Pore Diameter 2.2-2.8 nm
Pore volume 0.57-0.65 mL g⁻¹

- **Microwave extracted + Solvent exchanged (then dried)**

- Untreated samples

S_{BET} 12 m² g⁻¹
Pore Diameter >20 nm
Pore volume 1.06 mLg⁻¹

- Treated samples (NaOH)

S_{BET} 15-23 m² g⁻¹
Pore Diameter 2.1 nm
Pore volume 0.68-0.24 mLg⁻¹

FrancaVilla et al., Carbohydrate Polymer 2013.

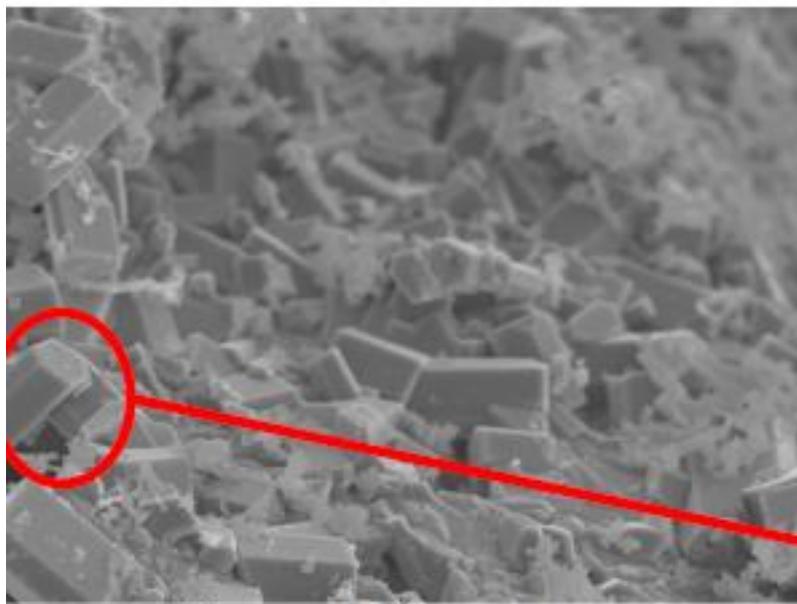


ScCO₂ dried untreated Agar extracted
from macroalgae (*Gracillaria Verrucosa*)

Applications:
Highly porous and consistent
Antimicrobial foams (Ag NPs)



MACROALGAL VALORISATION: NATURAL BIO-TEMPLATES AND BIOPOLYMERS



MW-assisted extraction of
biotemplates/biopolymers

Nanocrystals of
metal oxides

ZnO
TiO₂
Fe₃O₄

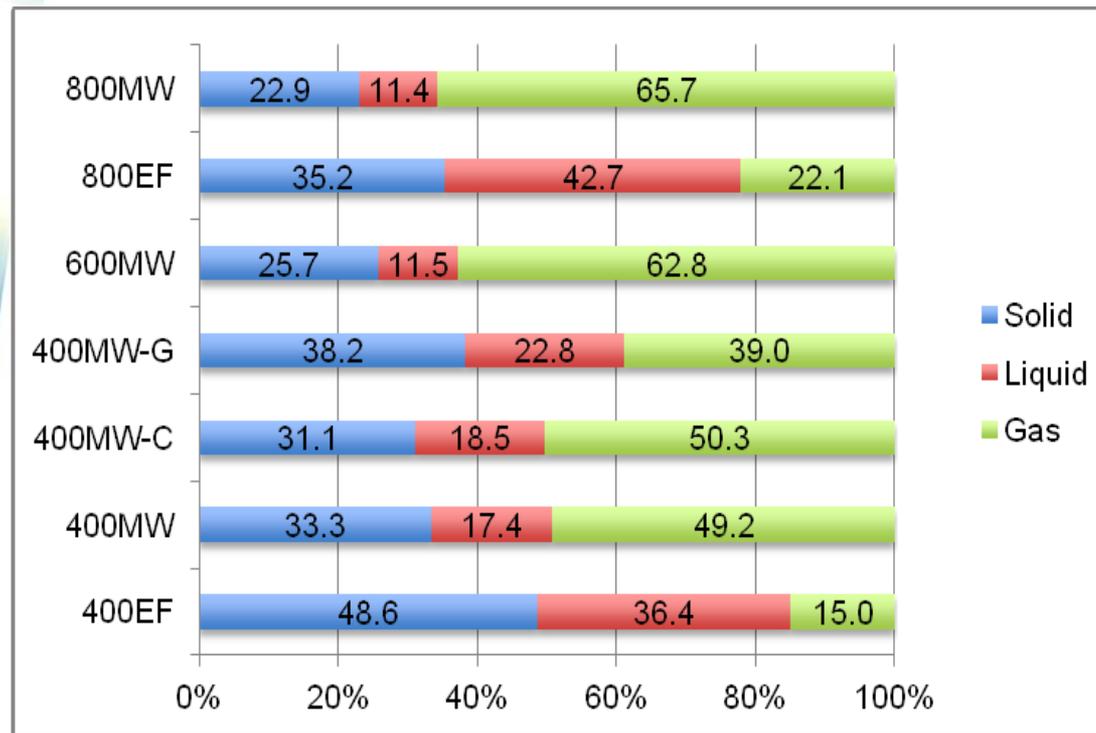
Applications:

Sunscreen formulations
Heterogeneous catalysis
Dye-sensitised solar cells

FrancaVilla et al., Green Chemistry 2014.

Microwave-induced pyrolysis of *Gracilaria gracilis*

Two different heating devices were used: a conventional electric furnace (EF) and a microwave oven (MW).



Bermúdez, Francavilla, Calvo, Arenillas, Franchi, Menéndez, Luque, RSC Advances 2014

Gas compositions (vol.%) of the gaseous fractions obtained in the pyrolysis

	400EF	400MW	400MW- G	400MW- C	600MW	800 EF	800 MW
H ₂	0.0	56.7	49.7	57.5	48.2	33.2	49.2
CH ₄	4.3	1.5	4.6	1.5	1.5	11.1	1.3
CO ₂	78.2	22.0	34.0	24.8	8.8	18.0	5.7
C ₂ H ₄	1.0	0.9	0.7	0.2	0.25	1.0	0.9
C ₂ H ₆	1.7	0.1	0.6	0.3	0.14	1.2	0.1
CO	14.9	18.9	10.3	15.7	41.1	35.6	42.9
Syngas (H ₂ +CO)	14.9	75.5	60.1	73.2	88.3	68.8	92.1
H ₂ /CO	0	3.01	4.80	3.66	1.17	0.93	1.15

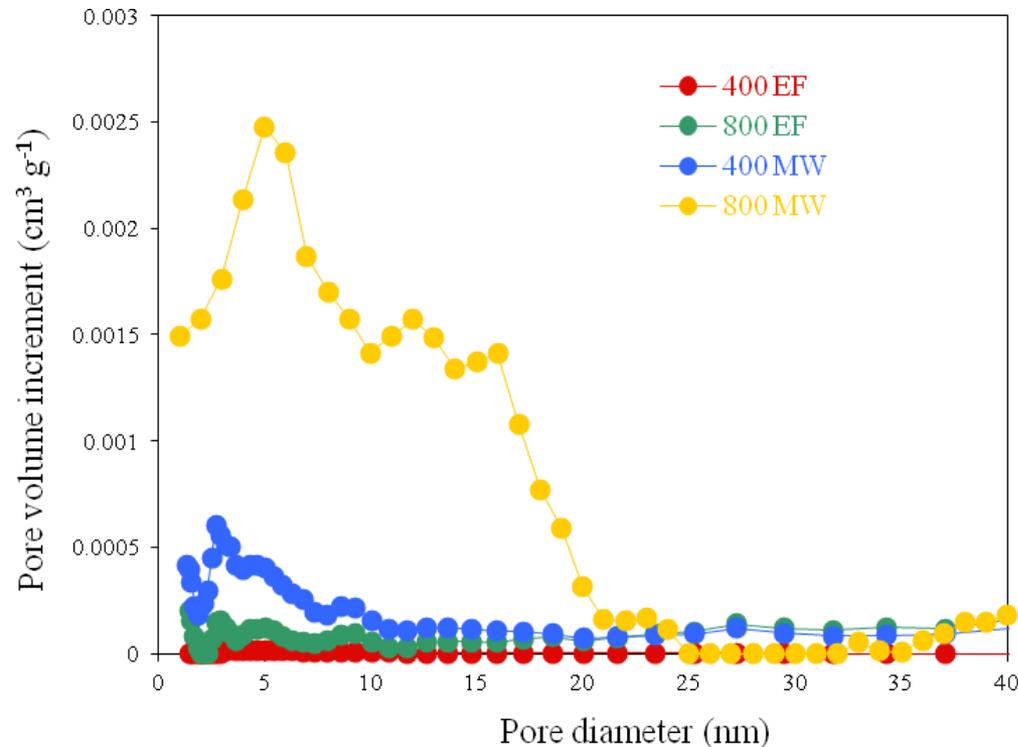
Bermúdez, Francavilla, Calvo, Arenillas, Franchi, Menéndez, Luque, RSC Advances 2014

Gas production ($l_{n.c.}/g$ of algae) of the different components of the gaseous fractions obtained in the pyrolysis

	400EF	400MW	400MW- G	400MW- C	600M W	800 EF	800 MW
H ₂	0.00	0.38	0.21	0.38	0.39	0.08	0.45
CH ₄	0.00	0.01	0.02	0.01	0.01	0.03	0.01
CO ₂	0.07	0.15	0.15	0.17	0.08	0.04	0.05
C ₂ H ₄	0.00	0.01	0.00	0.00	0.00	0.00	0.01
C ₂ H ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.01	0.13	0.05	0.10	0.34	0.08	0.40
Syngas	0.01	0.51	0.26	0.48	0.73	0.16	0.85

Bermúdez, Francavilla, Calvo, Arenillas, Franchi, Menéndez, Luque, *RSC Advances* 2014

Pore size distribution from the N₂ isotherms of the solids obtained in the pyrolysis.



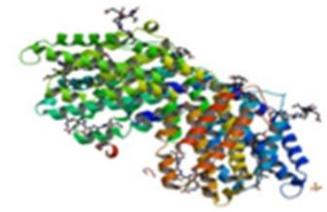
Bermúdez, Francavilla, Calvo, Arenillas, Franchi, Menéndez, Luque, RSC Advances 2014

Flash Pyrolysis valorization of residue of *Gracilaria gracilis* after phyobiliproteins extraction

Phycobiliproteins Extraction



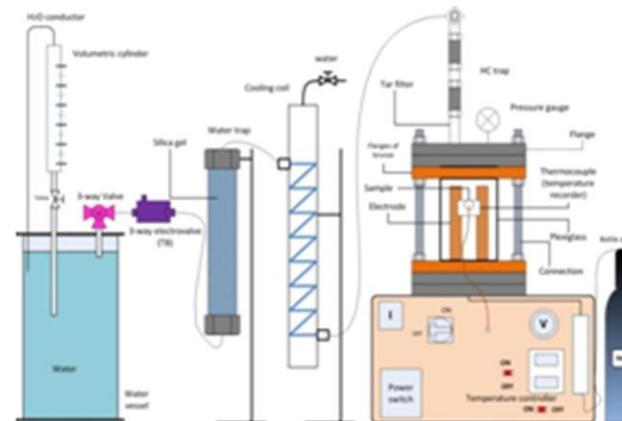
Gracilaria gracilis



R-Phycoerythrin

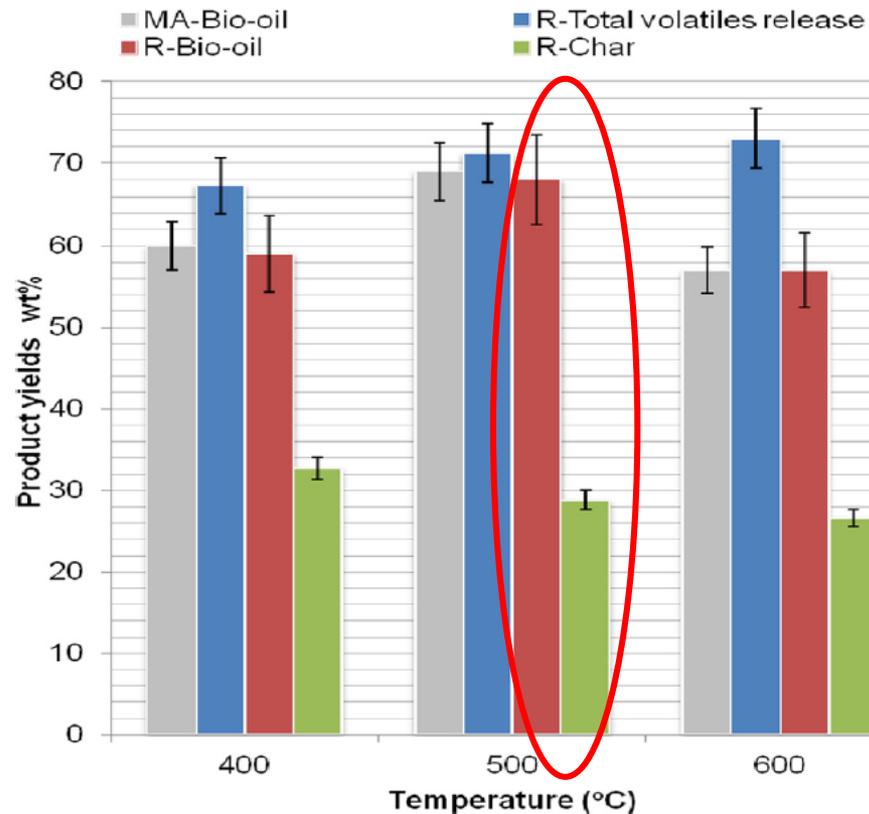


Solid residue pyrolysis



Francavilla et al., *Bioresource Technology*, 2015

Bio-oil and Bio-char yields from *Gracilaria gracilis* (MA) and its residue (R) after phycobiliproteins extraction.



At 500 °C

Bio-oil: 65%dw

Bio-char: 28% dw

Francavilla et al., Bioresource Technology, 2015

Elemental composition of bio-oil derived from *Gracilaria gracilis* (MA) and its residue (R) after phycobiliproteins extraction.

	C ^a	H ^a	N ^a	S ^a	O	H/C ^c	H/O ^c	References
<i>G. gracilis</i> (MA)	52.76	8.15	5.32	1.83	31.94 ^b	1.85	4.08	Present study
<i>G. gracilis</i> (R)	53.34	8.24	2.96	0.57	34.89 ^b	1.85	3.78	Present study
Algae meal	60.84	6.05	9.45	0.56	23.1	1.19	4.19	Ferrera-Lorenzo et al. (2014)
Mix of Macroalgae	59.7	7.2	4.2	0.1		1.45		Yanik et al. (2013)
<i>Fucus serratus</i>	68.4	8.9	2.7	0.1		1.56		Yanik et al. (2013)
<i>Laminaria digitata</i>	55.6	7.1	2.2	0.1		1.53		Yanik et al. (2013)
<i>Enteromorpha clathrata</i>	57.8	7.887	9.27		25.03	1.64	5.04	Wang et al. (2013)
<i>Sargassum natans</i>	53.82	8.174	6.54		31.45	1.82	4.16	Wang et al. (2013)

^a wt%, dry.

^b wt%, by difference.

^c Molar ratio.

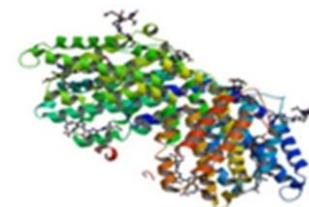
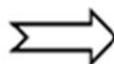
Francavilla et al., *Bioresource Technology*, 2015

Production of *platform compounds* from residue of *Gracilaria gracilis* by microwave assisted catalysis

Phycobiliproteins Extraction



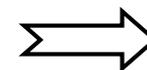
Gracilaria gracilis



R-Phycocerythrin



Microwave Assisted Catalysis



Levulinic Acid

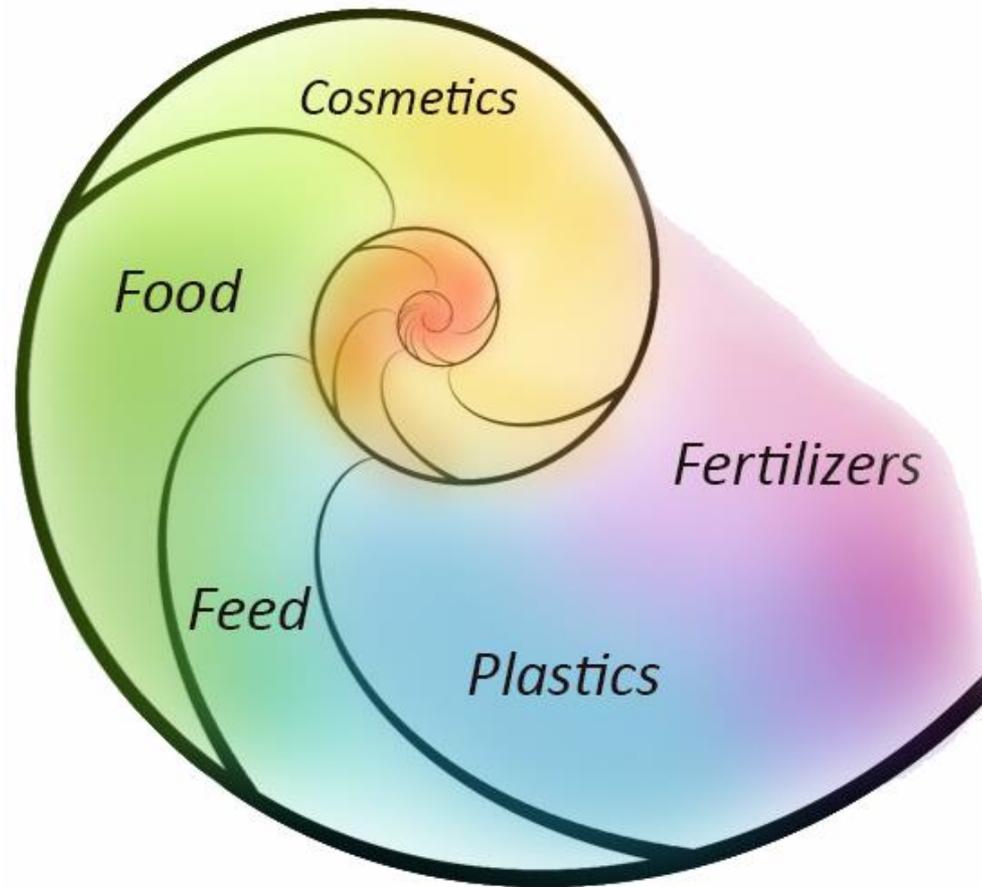
Lactic Acid

5-HMF

Furfural

Francavilla et al., in preparation

Algae for High-value Products, Food and Feed



Pilot Plants



 **STAR**
FacilityCentre
For a brighter green

Photobioreactors Plant

Anaerobic Digestion Plant

Pyrolysis/Gasification Plant

An “integrated biorefinery platform”

Silage crop
Organic wastes

Agro & Food residues
and byproducts

Ligno-cellulosic feedstock
- Straws
- Prunings & Trimmings from fruit trees

Microalgae



Anaerobic Digestion



Photo bioreactor



Pyrolysis

Methane

Fine-chemicals

Digestate

Compost, fertilizer,
soil conditioner

Bio-oil

Biochar

Solid and Liquid
biofuels

LABORATORY



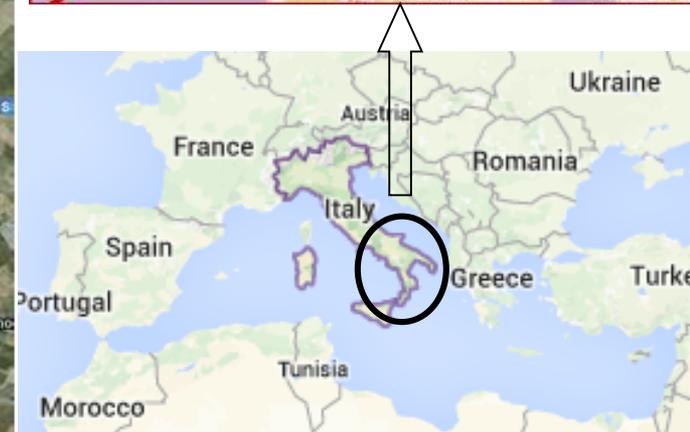
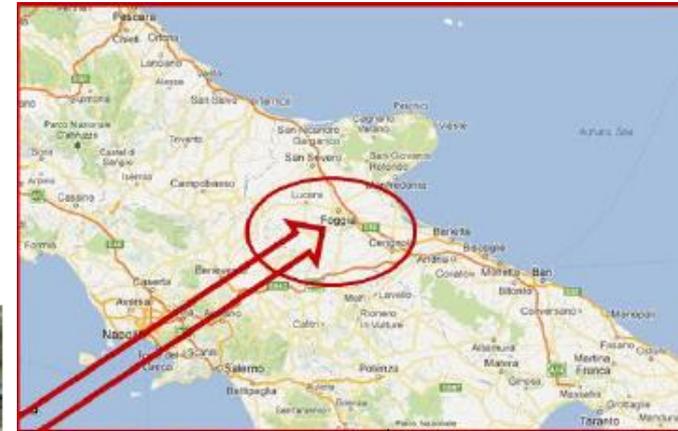


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Laboratory,
March 2014



WHERE WE ARE



STAR* FACILITY CENTRE

SS 16, Km 687

Zona ASI, FOGGIA

Figure A22.
Geographical location
of the STAR Facility
Centre



Università di Foggia



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Thank you for your attention

CONTACT:

Matteo FRANCAVILLA, PhD
Email: matteo.francavilla@unifg.it
Mobile: +393403927680