Athens 2014

2nd INTERNATIONAL CONFERENCE on
Sustainable Solid Waste Management

"Thermogravimetric characteristics and pyrolysis of red seaweed Gracilaria gracilis residues"

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Goal of Biomass Group: Research Activities

Biomass Group
LABORATORY OF CHEMICAL PROCESS AND PLANT DESIGN

Development of new processes & products for valorisation of biomass and waste

Thermochemical Conversion of recyclable and renewable materials

→ Research & Development

→ ENERGY
→ BIOFUELS
→ MATERIALS
→ H2

INNOVATION

← GREEN TECHNOLOGY | GREEN PRODUCTS →

Biomass and Waste Group

Main Research Activities

Laboratory of Chemical Processes and Plant Design
Department of Chemical Engineering
Aristotle University of Thessaloniki.

- **Applied & basic research** concerning **the thermochemical conversion** of **biomass** and **wastes** into **energy** and **high added value materials.**
- **Thermochemical Valorization of Biomass and Waste both by pyrolysis and gasification: Lab and Pilot scale Experiments & Modeling and simulation of such processes using commercial softwares.**
- **Assessment of bio-energy plants** and renewable energy sources units **through detailed techno-economic studies**
- **Design of integrated energy systems of conjunct thermochemical processes with ICEs and fuel cells.**

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Sources of Biofuels

Using fossil fuels as energy is unsustainable due to:

Depleting resources | **Greenhouse effect**

<u>Necessity to find new clean sources</u>

⇓

BIOMASS

1st Generation

- ✓ *Conventional technology*
- ✗ *Influence in food market*

Ej: Corn,cane,maize

2nd Generation

- ✓ *No competition with food market*
- ✗ *Insufficient resources*

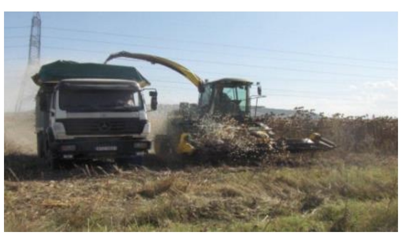
Agricultural and forest residues

3rd generation

- ✓ *Fastest growing industry*
- ✗ *Further research required*

Algae






Algal Biomass

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Macroalgae

a) *blue algae (Cyanophyta),*
b) *green algae (Chlorophyta),*
c) *brown algae (Phaeophyta) and*
d) *the red algae (Rhodophyta)*

Microalgae

Diatoms

Green algae

Golden algae

Main components of Algae

Algae

- **Proteins**
- **Carbohydrates**
- **Lipids**
- **Valuable compounds**

algae: High content of proteins, carbohydrates and lipids

⇩

Best suitable option as source of biofuel production

Marine Macroalgae

A potentially important source of **renewable energy** and biofuel production

- ❖ Average photosynthetic efficiency in comparison with terrestrial biomass

  aquatic biomass ~ 6–8% , whereas

  terrestrial biomass ~1.8–2.2%.

Massively cultivated in the Far East, ***BUT*** on a smaller scale in Europe

Challenges:

❖growing fast rate macroalgae in the open ocean

❖***reducing collection costs***

RECOVERY

OF HIGH ADDED VALUE COMPOUNDS

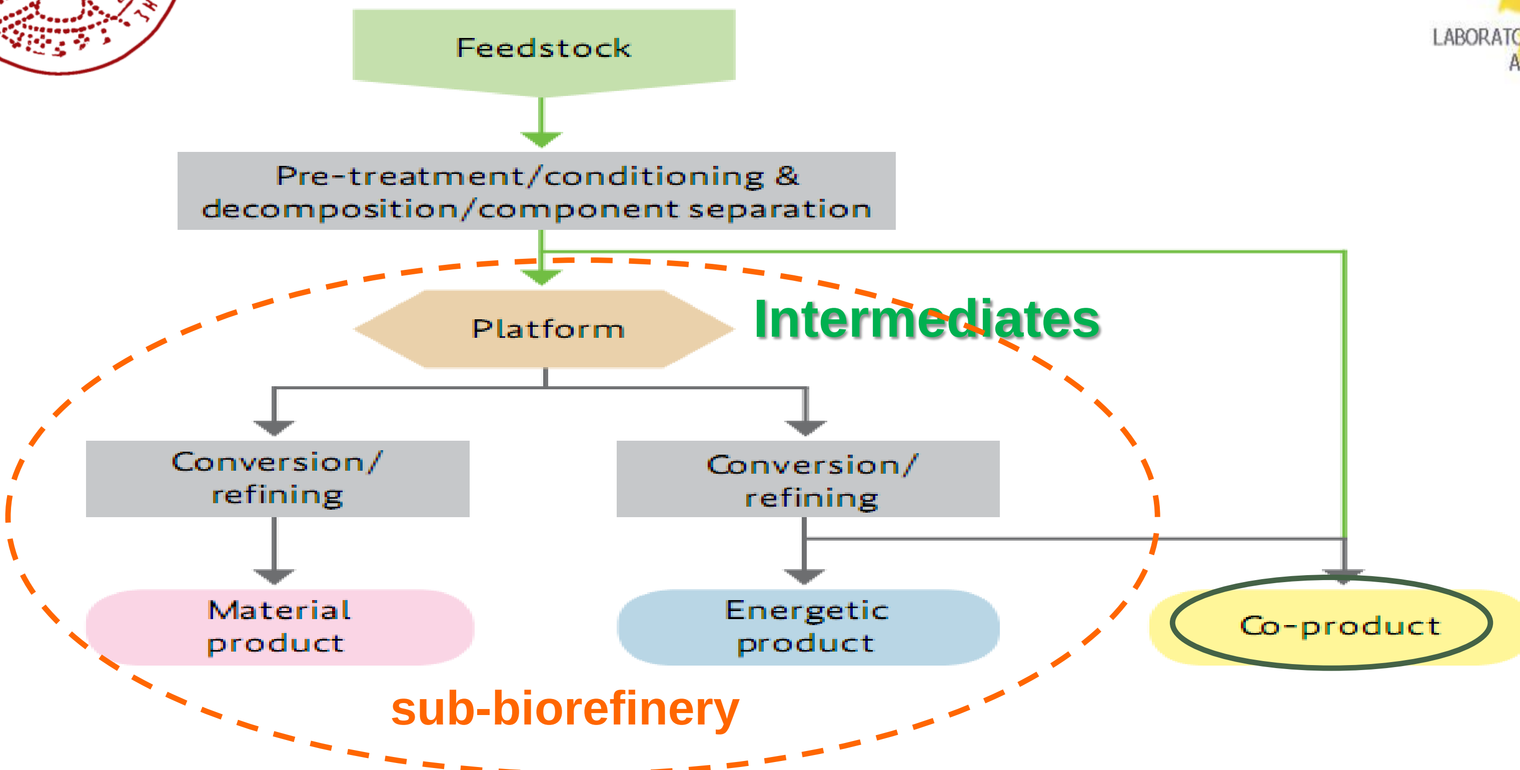
❖**Algae have been studied intensively last years for biofuel production**

❖**commercial-scale production is currently economically not viable.**

a key way to increase revenue & reduce the net cost of fuel production

Extracting other valuable chemicals

Algal Biorefinery



HIGH ADDED VALUE COMPOUNDS EXTRACTION
ALGAL RESIDUE VALORIZATION

TO ENHANCE ALGAL BIOREFINERY SUSTAINABILITY

Algal waste sub-biorefinery

- Not only the algal biomass but also the **residues from algal processing**, in the context of a biorefinery, **represent a renewable source of energy (biorefinery residues and wastes).**

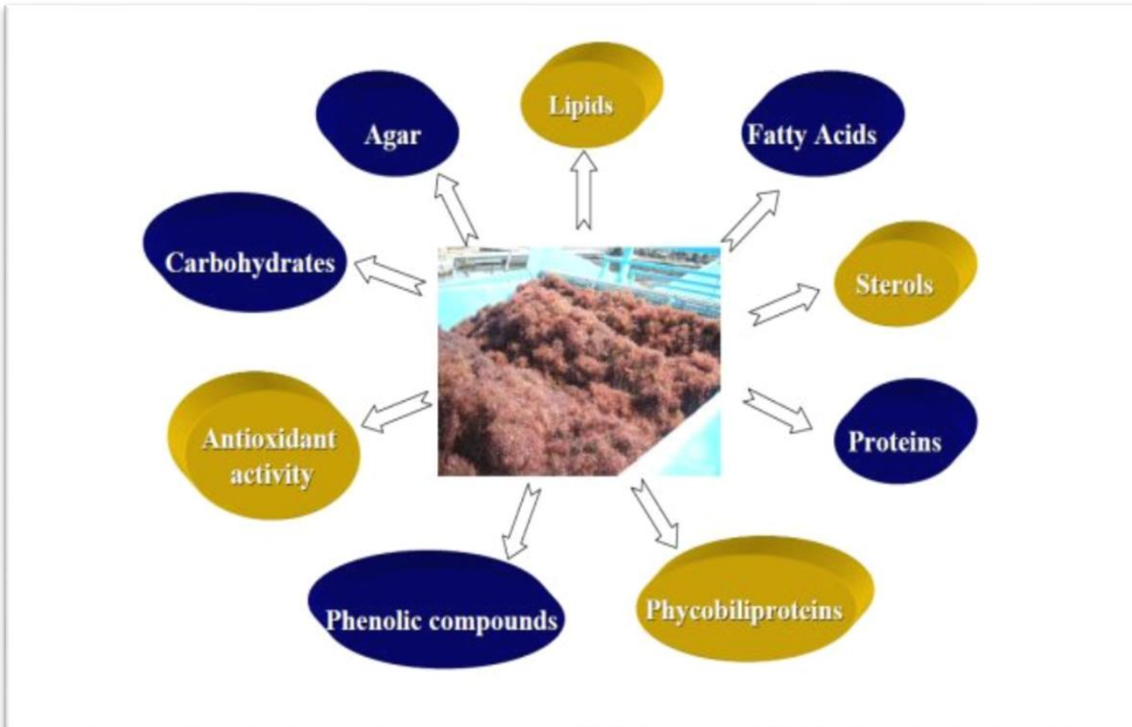
- Algal residues can be treated **(gasified or pyrolysed) for further valorisation.**

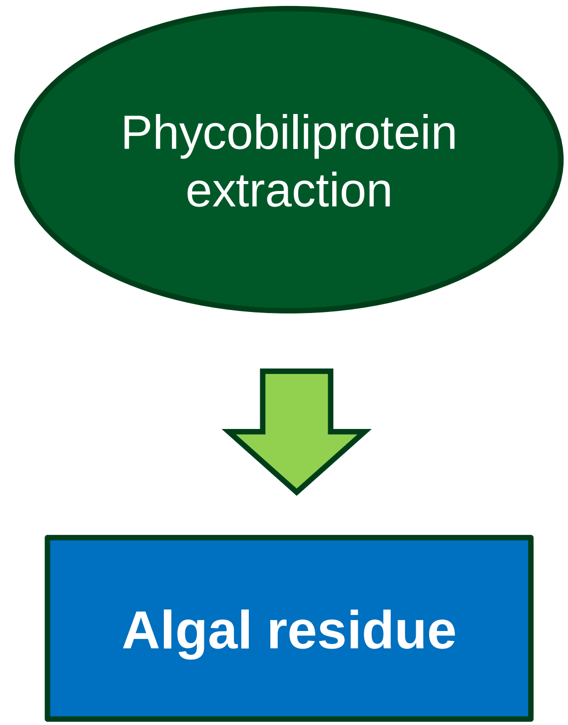
- In such a **theromochemical algal waste sub-biorefinery, residues can be converted into biofuels and other bioproducts**

Red Seaweed Gracilaria gracilis

“A Multi Products Source”

Collected in Lesina Lagoon (Southern Adriatic Sea, Italy), a stable coverage found.





Ref: Francavilla M, Franchi M, Monteleone M, Caroppo C. The Red Seaweed *Gracilaria gracilis* as a Multi Products Source. *Marine Drugs*. 2013; 11(10):3754-3776.

Phycobiliprotein extraction

from red seaweed Gracilaria gracilis

These proteins are found in:

❖ cyanobacteria (blue-green algae),

❖in a class of biflagellate unicellular eukaryotic algae (cryptomonads),

❖**and in Rhodophyta (red algae).**

Phycobiliproteins act as photosynthetic accessory pigments

HIGH ADDED VALUE COMPOUNDS

TO ENHANCE ALGAL BIOREFINERY SUSTAINABILITY

Fuel characteristics

of Gracilaria Gracilis & Gracilaria residue as a by-product of phycobiliproteins extraction

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Proximate analysis

Sample	Moisture %	Volatile Dry %	Ash Dry %	Fixed Carb Dry %
Gracilaria Raw	9.13	67.32	19.98	12.70
Gracilaria Extracted	1.32	74.99	20.88	4.14

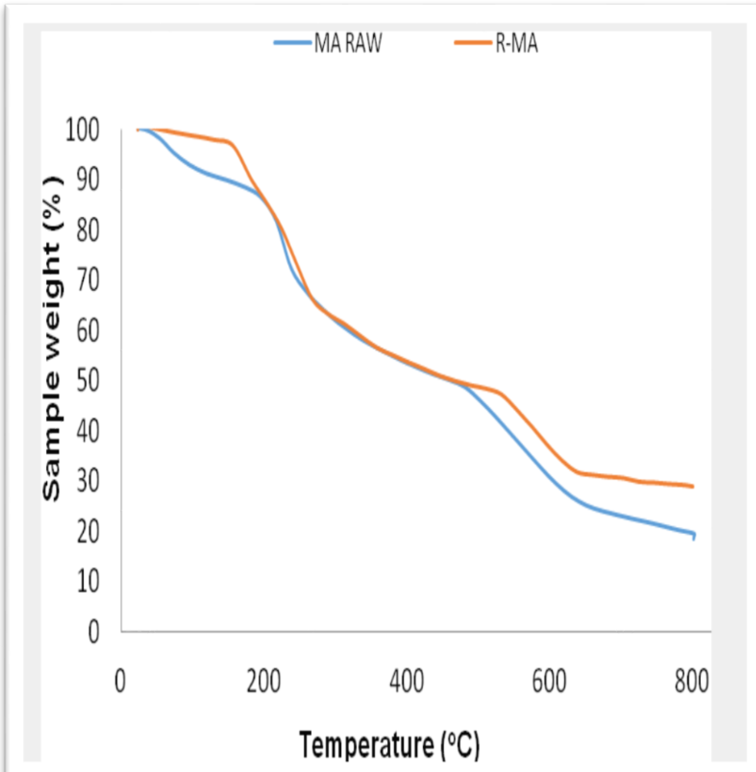
Ultimate analysis

	Carbon %	Hydrogen %	Nitrogen %	Sulfur %	***Protein %***
Gracilaria Raw	31.53	5.13	4.07	1.61	***25.43***
Gracilaria Extracted	31.67	5.17	3.98	1.58	***24.88***

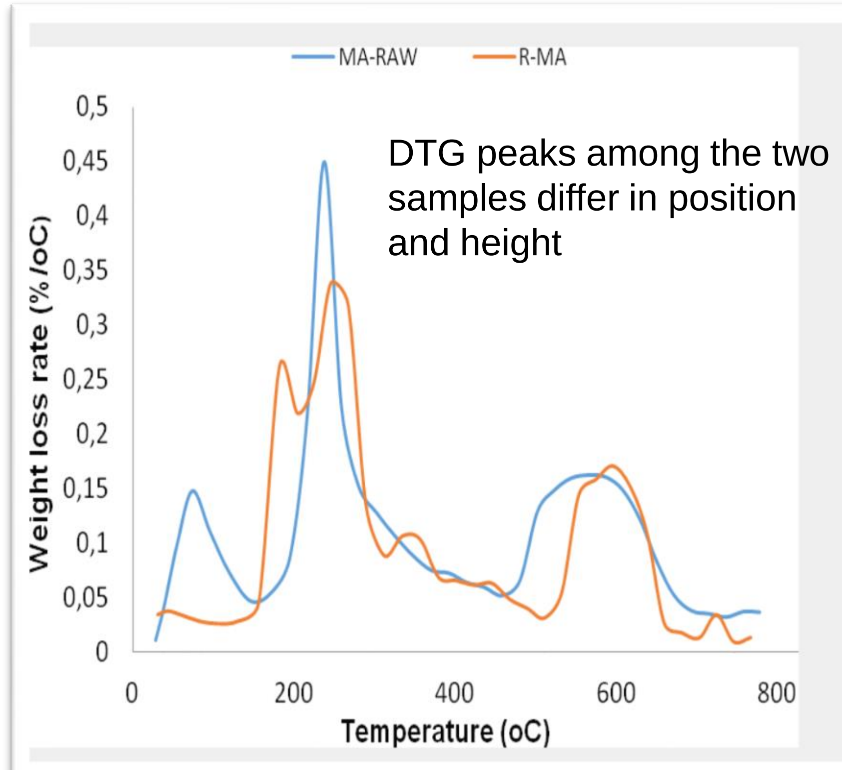
The residue after the extraction of high added value compounds as phycobiliproteins can be potentially further valorized via pyrolysis for liquid fuel and solid material production.

TG pyrolysis

Heating rate of 10°C/min (nitrogen atmosphere)



TG pyrolysis profiles of Gracilaria gracilis residue after phycolibiprotein extraction (R-MA) and raw Gracilaria gracilis.



DTG curves of Gracilaria gracilis residue after phycolibiprotein extraction (R-MA) and raw Gracilaria gracilis

TG Analysis (I)

The different thermal degradation behaviour is attributed to the differences in the inherent structural and chemical characteristics between the two samples

❖the first decomposition regime represents the decomposition of hemicellulose (most reactive compound decomposes between the range of 200 and 350 ^{o}C)

❖the second corresponds to the decomposition of cellulose.

❖For the flat tailing section lignin is responsible, which is known to decompose slowly over a broader temperature range.

TG Analysis (II)

Raw macroalgae

❖mass loss between the range of 180– 270^{o}C is attributed to the decomposition of carbohydrate while,

❖ the degradation of proteins takes place between 320–450^{o}C.

Macroalgae residue after phycobiliprotein extraction,

❖the main weight loss appears to be in the region of 250 ^{o}C. DTGmax is shifted to the right comparing with the temperature (~230^{o}C) that major weight loss of raw macroalgae occurs.

❖T> 500^{o}C, weight loss might be attributed to carbonate decomposition.

TG Analysis results (III)

in comparison with terrestrial lignocellulosic biomass materials

The thermal degradation onset temperature of algal biomass occurs at a lower temperature in comparison with terrestrial lignocellulosic biomass materials; e.g

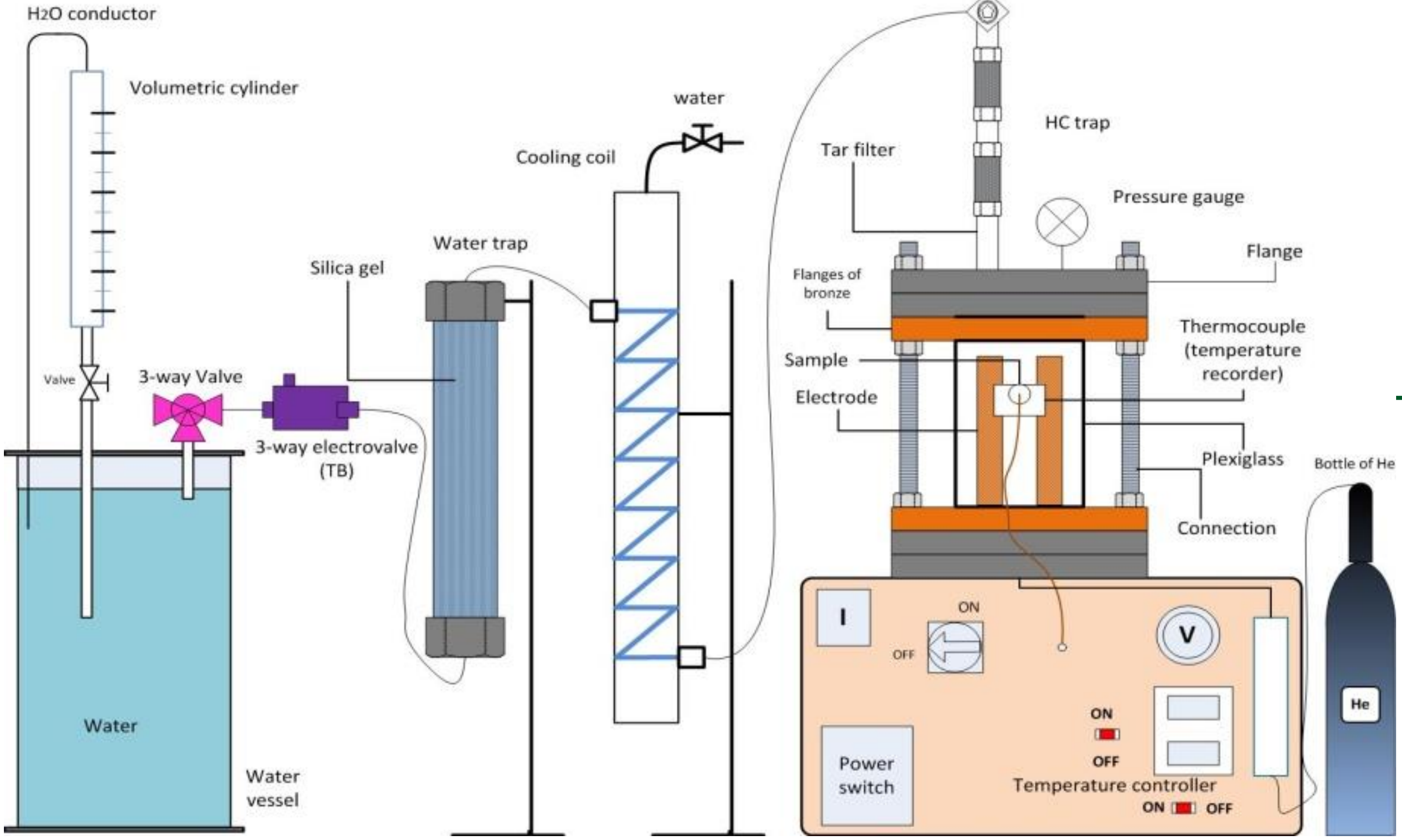
- ✓straws and grasses of high cellulosic content,
- ✓woody biomass of high lignin content,
- ✓different agro-residues and agri-food industrial solid residues as well as
- ✓biomass pretreatment materials such as lignin and pulp.

The behavior of algal biomass could be attributed to high carbohydrate and protein content as well as to the catalytic influence of the inherent metals

Pyrolysis Reactor

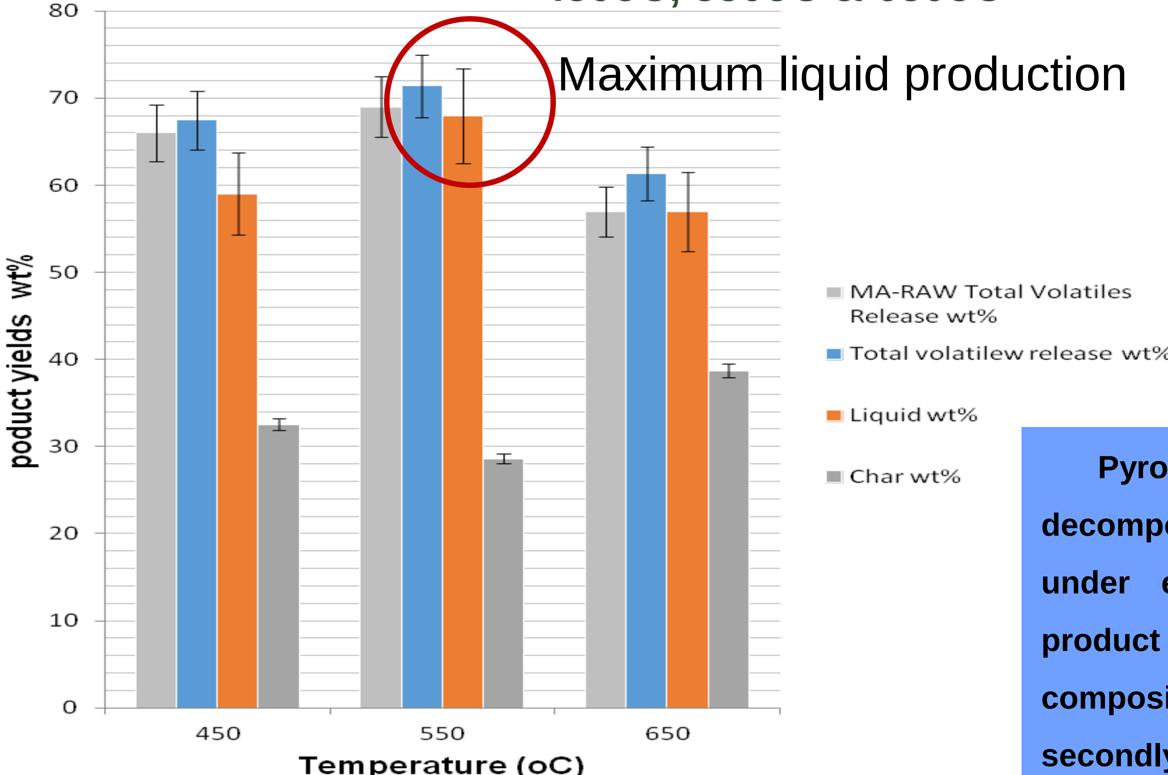
Laboratory captive sample reactor (High Heating rates).

It is mostly used for <u>kinetic parameter determination</u>



Fast pyrolysis product yield distribution

Macroalgae residue after phycobiliprotein extraction
450oC, 550oC & 650oC



Pyrolysis refers to the thermal decomposition of organic compounds under exclusion of air. The liquid product yield is dictated, firstly, by the composition of the feedstock and, secondly, by the pyrolysis conditions

Macroalgae residue releases during fast pyrolysis experiments higher amount of volatiles comparing with the raw material, which is attributed to the pretreatment process

Pyrolysis process

Effect of *pyrolysis process on bio-oil yield*

- **Slow pyrolysis ⇨ Lower yields of bio-oil**
- **Fast pyrolysis ⇨ Highest yields of bio-oil**
- **Catalytic pyrolysis ⇨ To improve bio-oil characteristics**

CONCLUSIONS (I)

- Algae are considered a future feedstock for **biorefinery** and also for **3rd generation biofuels.**

- Most critical point, **harvesting and extraction costs**

- Pyrolysis characteristics of red seaweed residues are investigated by means of a **thermogravimetric analyzer** and a **fast pyrolysis captive sample reactor.**

CONCLUSIONS (II)

- The different thermal degradation behaviour between **macroalgae and the residue after extraction** is attributed to the **differences in the inherent structural and chemical characteristics of the samples.**

- **Fast pyrolysis leads to the highest bio-oil yields**

- Pyrolysis' product yield distribution is a function **of the feedstock (macroalgae or residue after extraction)** and the **temperature.**

- At medium temperature, **550oC**, pyrolysis of the residue **gives higher oil** (**reaching values of ~70wt**%) yields and **lower char yields**.

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Thank you for your attention!

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