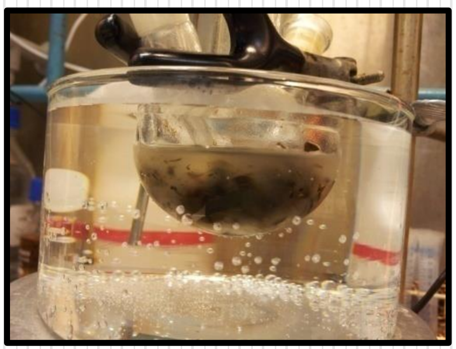
Mass balance of algae biomass treatment with ionic liquids

Ricardo Pezoa Conte



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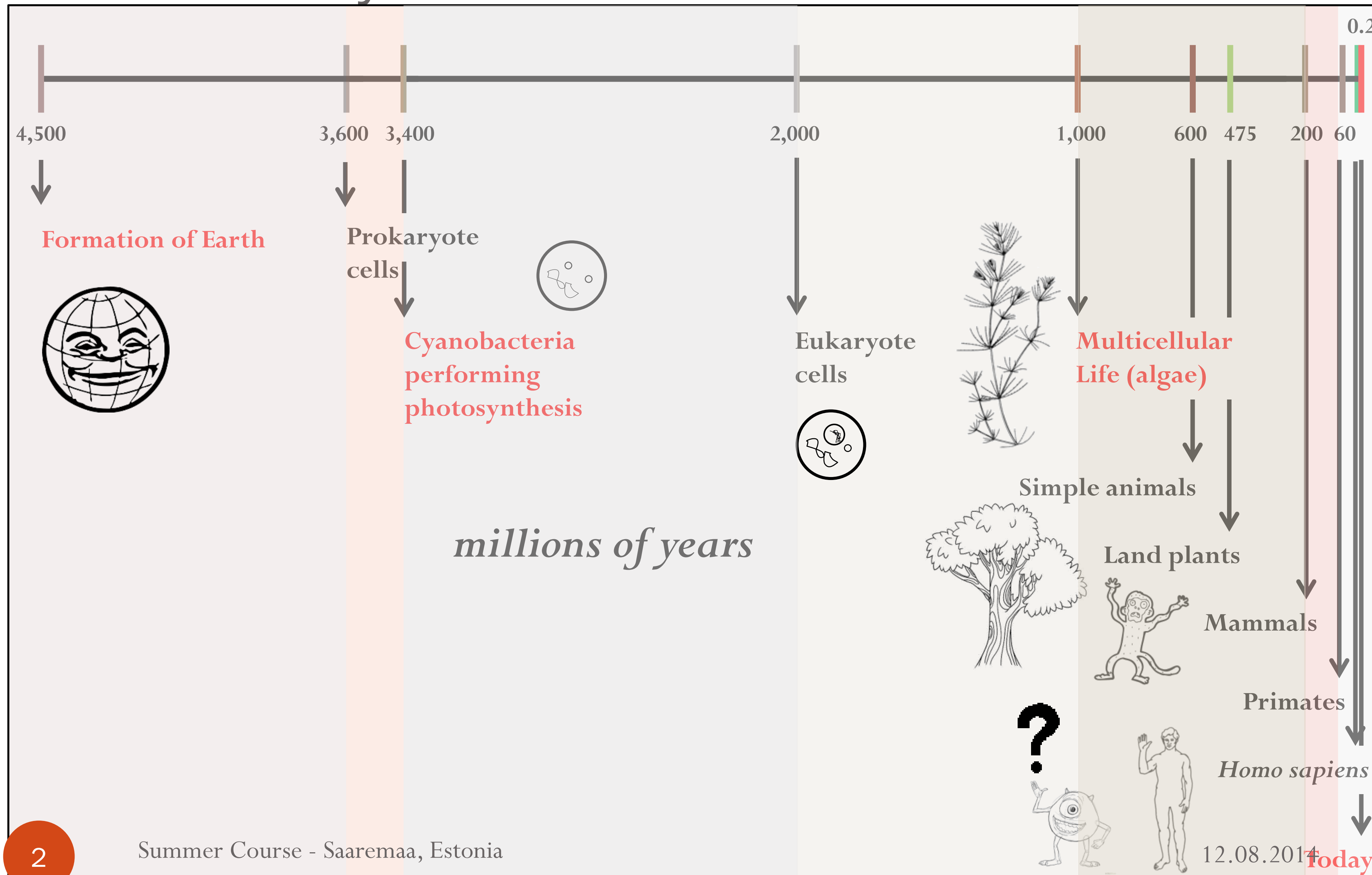
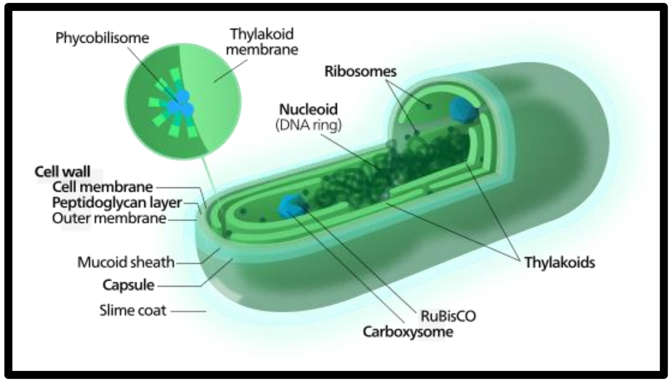
12.08.2014

Millions of years of evolution



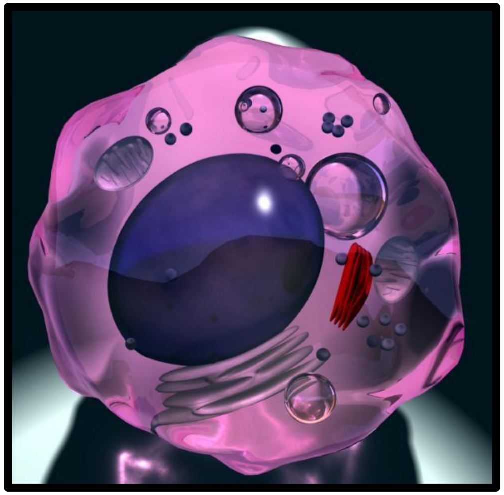
Cyanobacteria

- Cyanobacteria are prokaryotic organisms.
- They use photosynthesis to produce oxygen from water and take carbon dioxide to produce carbohydrates.
- Sun light is caught by pigments such as phycocyanin, which gives them their bluish color.

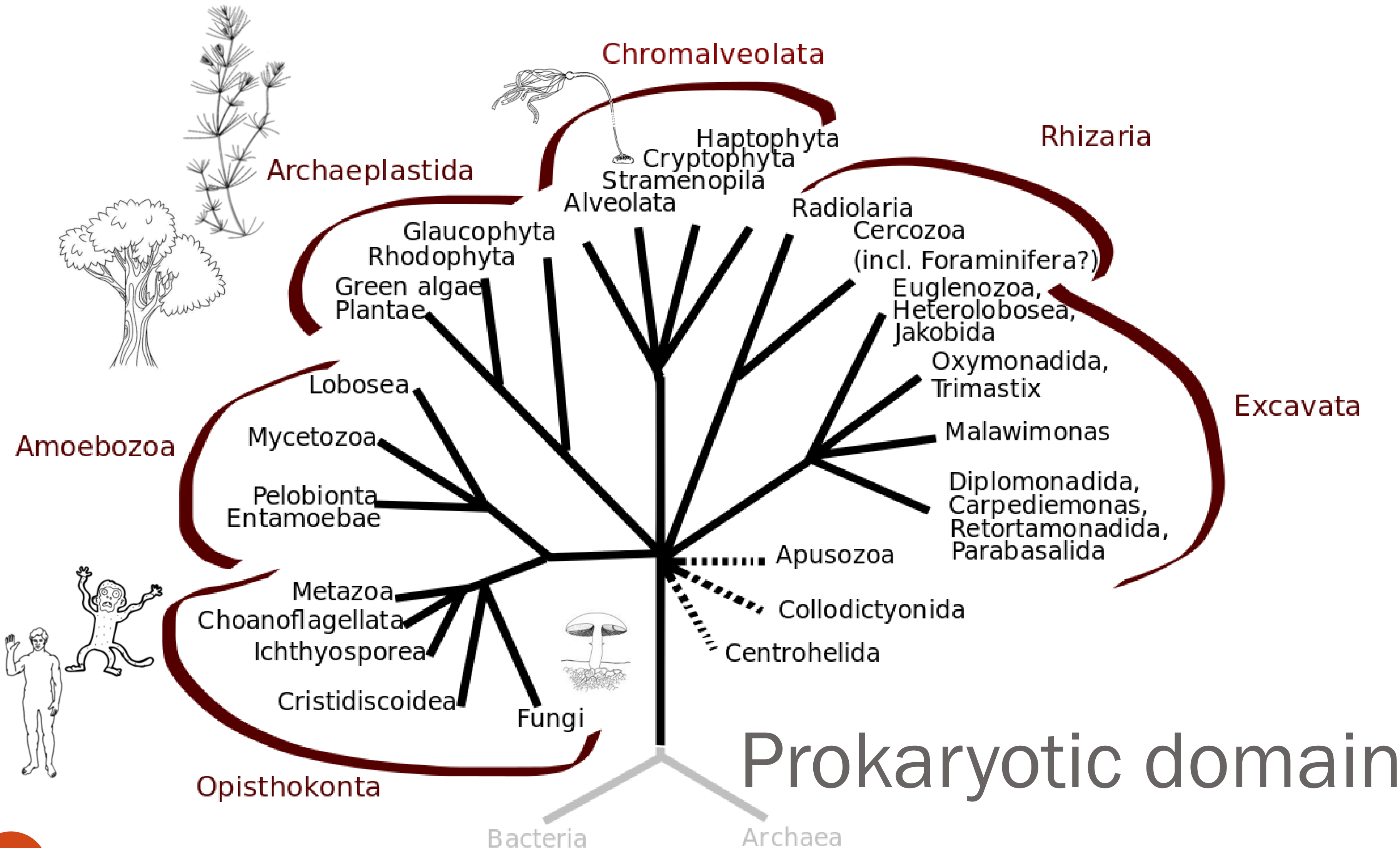


New atmosphere

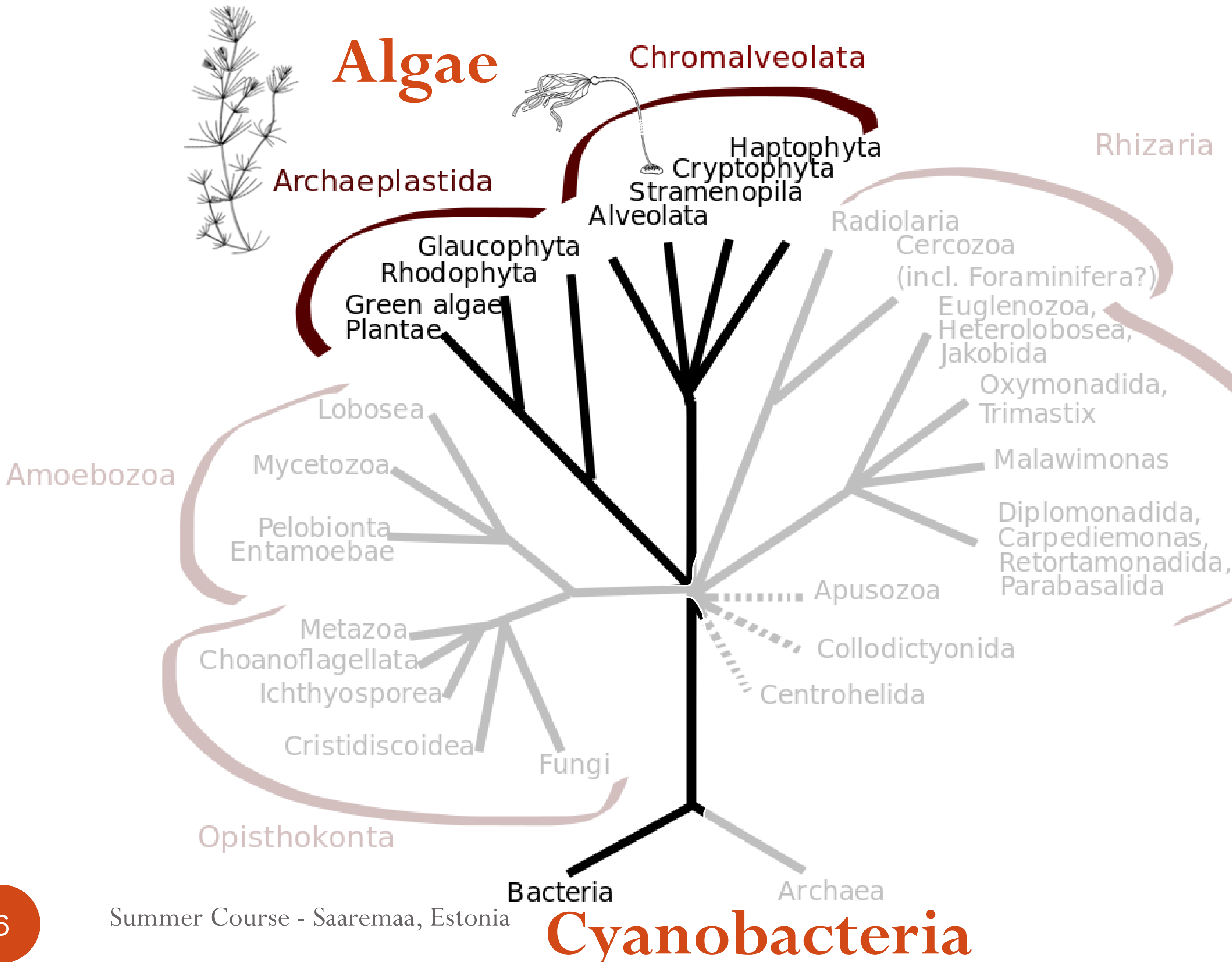
- Prokaryote organisms are mainly anaerobic, thus they do not require oxygen to live.
- New atmosphere rich in oxygen, due to photosynthetic organisms, led the formation of more evolved and complex microorganisms known as eukaryotic.



Eukaryotic domain



Eukaryotic domain



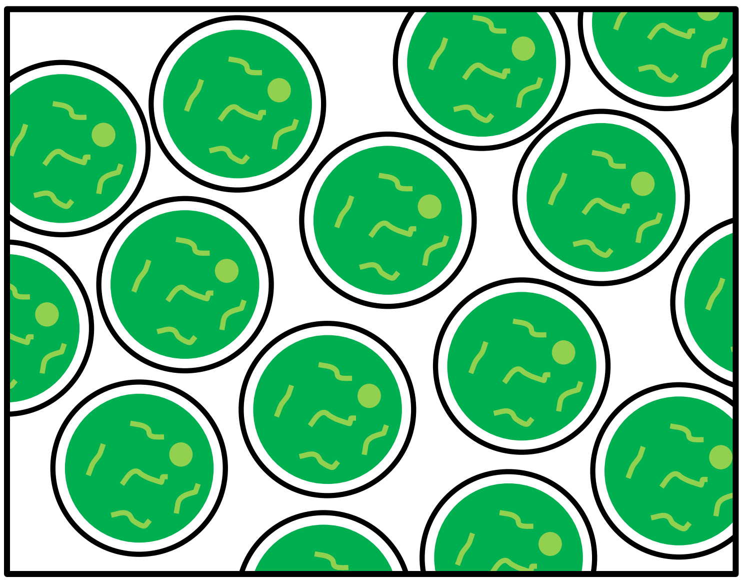
Algae

- They use sunlight to capture inorganic and organic carbon and store it as food source via photosynthesis.
- Approximately 50 % of biomass is believed to be grown up in marine environments.
- Algae has a high production rate between 20 – 50 dry ton/ha/year, meanwhile forest biomass is between 10 – 25 dry ton/ha/year

Algal subdivision

Microalgae

- Most of them are unicellular.
- Reach in lipids, protein and carbohydrates.



Macroalgae

- They are more like plants on earth
- Carbohydrates content is up to 70 %.

Seaweed Peter®

Macroalgae

Brown algae

Green algae

Red algae

Carbohydrates in algae

Brown algae

- Laminarin
- Mannitol
- Alginate
- Fucoidin
- Cellulose

Red algae

- Carrageenan
- Agar
- Cellulose
- Lignin

Green algae

- Starch
- Cellulose
- Sulphated polysaccharides
  - Containing:
    - Gluc. acid
    - Arabogalactans

Aim of this work

- Use photo-chemo and enzymatic processes in order to obtain bioethanol from agae.
- Investigate new processes to obtain different products from algae under a biorefinery concept.

Algae used in this work

Macrocystis pyrifera

- Brown algae
- Main carbohydrate: alginate
- Biomass yield: 50 dry ton/ha/year

Ulva rigida

- Green algae
- Main monosaccharide: glucose
- Biomass yield: 23 dry ton/ha/year

Macrocystis pyrifera

Ulva rigida


Lima
Rondonia
Mato Grosso
Bahia
State of
Goias
Nuestra Señora
de La Paz
Bolivia
Minas Gerais
Belo Horizonte
Mato Grosso
do Sul
São Paulo
Rio de Janeiro
Paraguay
Asuncion
Parana
Curitiba
Chile
Santa
Catarina
Rio Grande
do Sul
Santiago
Uruguay
Buenos Aires
Argentina
Montevideo
Google


La Serena,
Chile
Coquimbo
5
La Herradura Bay

World production in 2006 of wild stock harvested and cultured algae

Harvest of wild stock			Aquaculture		
Source	Production [wet Mton]	% of total	Source	Production [wet Mton]	% of total
World total	**1,143,273**	**100.00**	**World total**	**15,075,612**	**100.00**
China	**323,810**	**28.32**	**China**	**10,867,410**	**72.09**
Chile	**305,748**	**26.74**	Philippines	1,468,905	9.74
Norway	145,429	12.72	Indonesia	910,636	6.04
Japan	113,665	9.94	South Korea	765,595	5.08
Russian Federation	65,554	5.73	Japan	490,062	3.25
Ireland	29,500	2.58	North Korea	444,300	2.95
Mexico	27,000	2.36	**Chile**	**33,586**	**0.22**
Iceland	20,964	1.83	Malaysia	30,000	0.20
France	19,160	1.68	Vietnam	30,000	0.20
Australia	15,504	1.36	Cambodia	16,000	0.11
Morocco	14,870	1.30	Taiwan	5,949	0.04
South Korea	13,754	1.20	India	4,668	0.03
Canada	11,313	0.99	Kiribati	3,900	0.03
Indonesia	9,830	0.86	South Africa	3,000	0.02
South Africa	6,600	0.58	South Africa	818	0.01
United States	6,238	0.55	Russian Federation	320	0.00
Madagascar	5,300	0.46	Tanzania	120	0.00
Peru	3,434	0.30	Solomon Islands	119	0.00
Italy	1,400	0.12	Fiji Islands	90	0.00
Ukraine	1,121	0.10	Mali	70	0.00
Others	3,079	0.27	Others	64	0.00

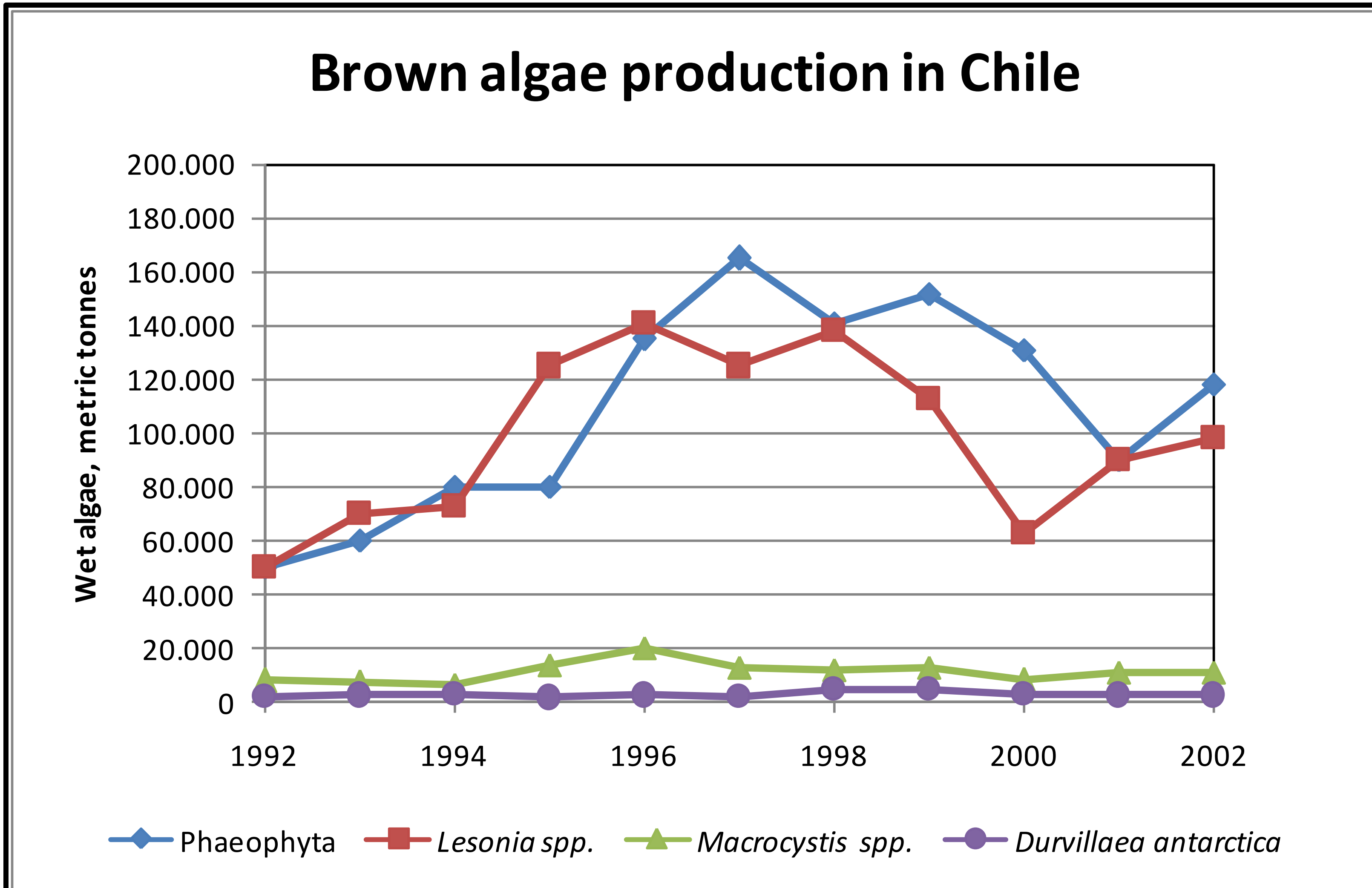
Roesijadi, G. et al. Macroalgae as a Biomass Feedstock: A Preliminary Analisis. US Department of Energy, September 2010

World wide farmed seaweed production in 2004

Taxa	Common name	Wet metric tons
Laminaria japonica	Japanese kelp	4,519,701
Plantae aquaticae	Aquatic plant	2,605,107
Undaria pinnatifida	Ealkame	2,519,880
Porphyra tenera	Laver (Nori)	1,397,660
Eucheuma spp.	Eucheuma seaweeds	1,264,438
Gracilaria spp.	Gracilaria seaweeds	948,292
Rhodophyceae	Red seaweeds	410,570
Sargassum fusiforme	Fusiform sargassum	131,680
Kappaphycus alvarezii	Elkhorn sea moss	44,906
Phaeophyceae	Brown seaweeds	23,030
Monostroma nitidum	Green laver	11,514
Caulera spp.	Caulerpa seaweeds	4,252
Enteromorpha prolifera	Dark green nori	3,280
Gelidium amansii	Japanese isinglass	1,150
Asparagopsis spp.	Harpoon seaweeds	12
Total		**13,885,472**

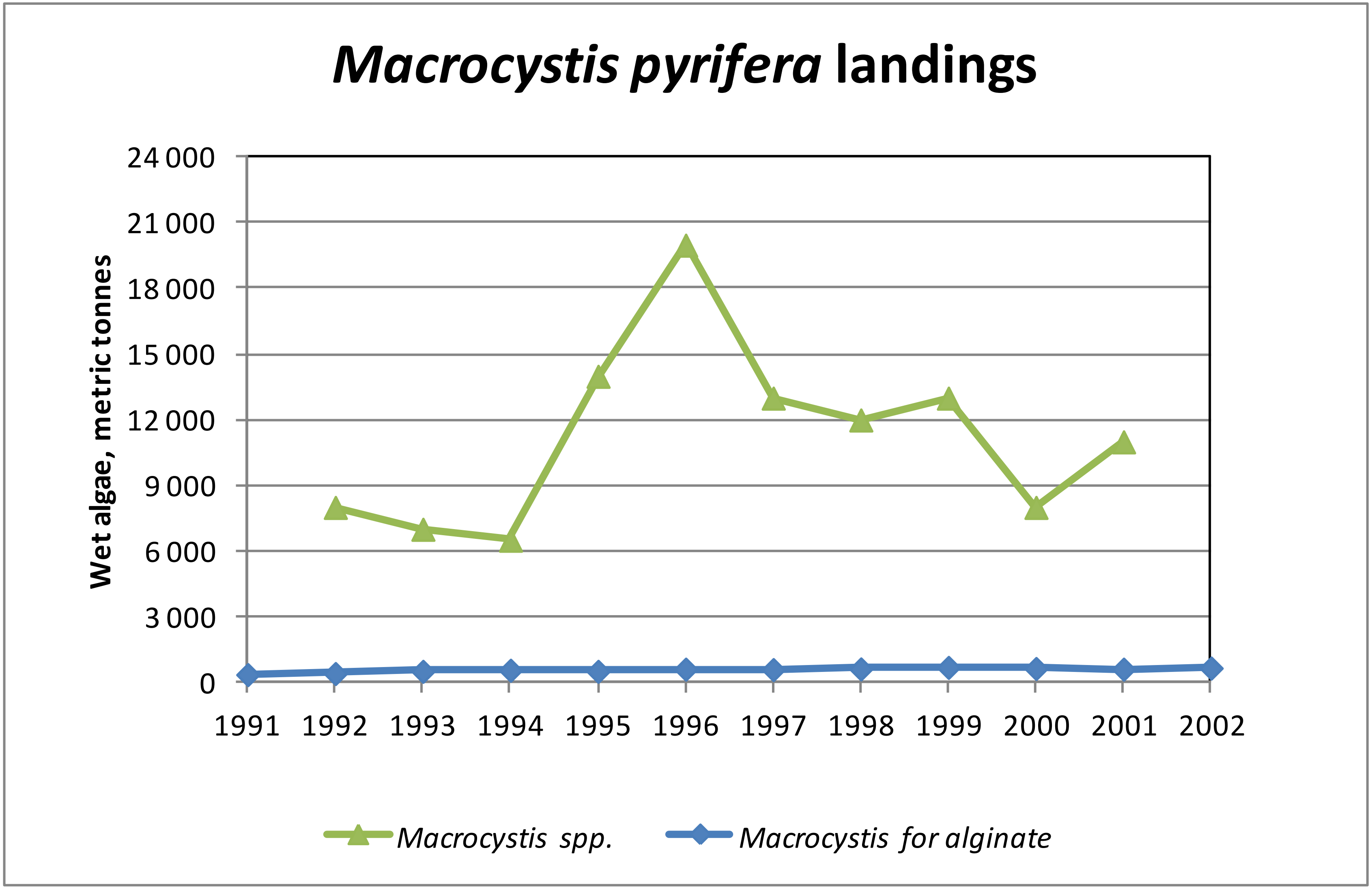
Roesijadi, G. et al. Macroalgae as a Biomass Feedstock: A Preliminary Analisis. US Department of Energy, September 2010

Brown algae



Buschmann, A.H. et al. Int. J. Environment and Pollution, Vol. 33, No. 4, 2008

Macrocystis pyrifera landings



Buschmann, A.H. et al. Int. J. Environment and Pollution, Vol. 33, No. 4, 2008

Commercial uses

Macrocystis pyrifera

- Alginate for use in human food and as aditives.
- Feed for abalon cultures (seafood).
- For bioremediation
- New products
  - Organic fertiliziers.
  - Compounds with health activity, such us anticoagulant and anti-inflamatory.
  - Bioethanol

Ulva rigida

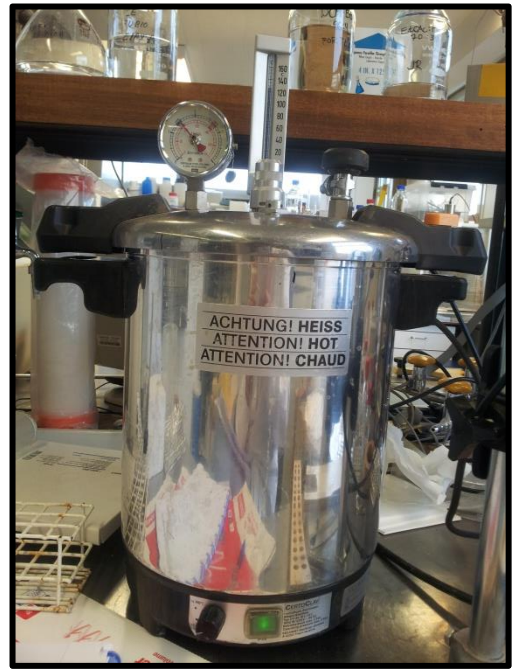
- Food in Asia.
- New products
  - Formation of gels
  - Bioethanol

Experimental

Experiments

Dilute acid hydrolysis treatment

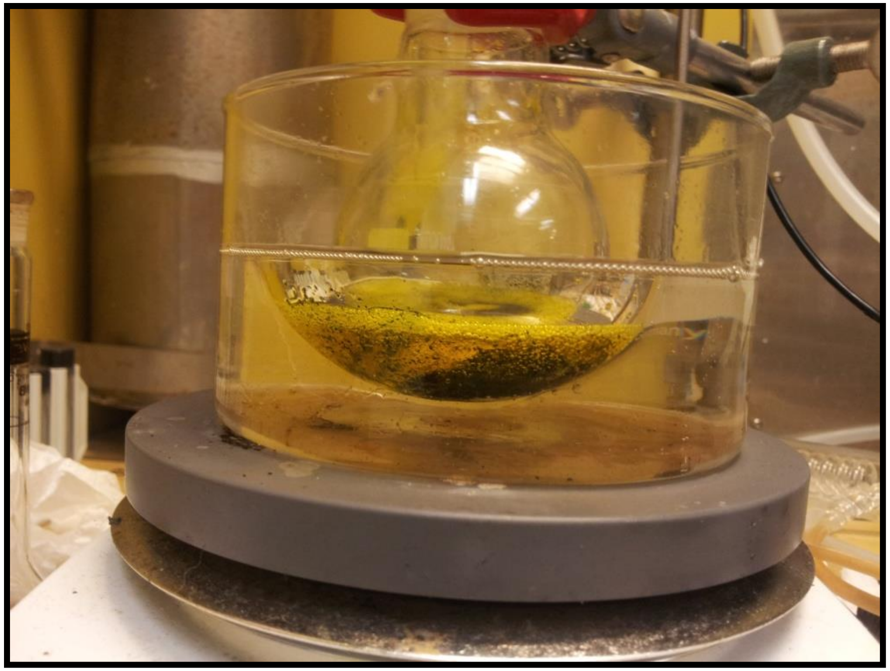
- Reagent
  - Acid H_2SO_4 1.0 % v/v
  - Water   distilled water
- Biomass loading   10 % w/w
- Temperature   125°C
- Pressure   1.5 atm
- Time   60 min
- Samples   duplicate



Experiments

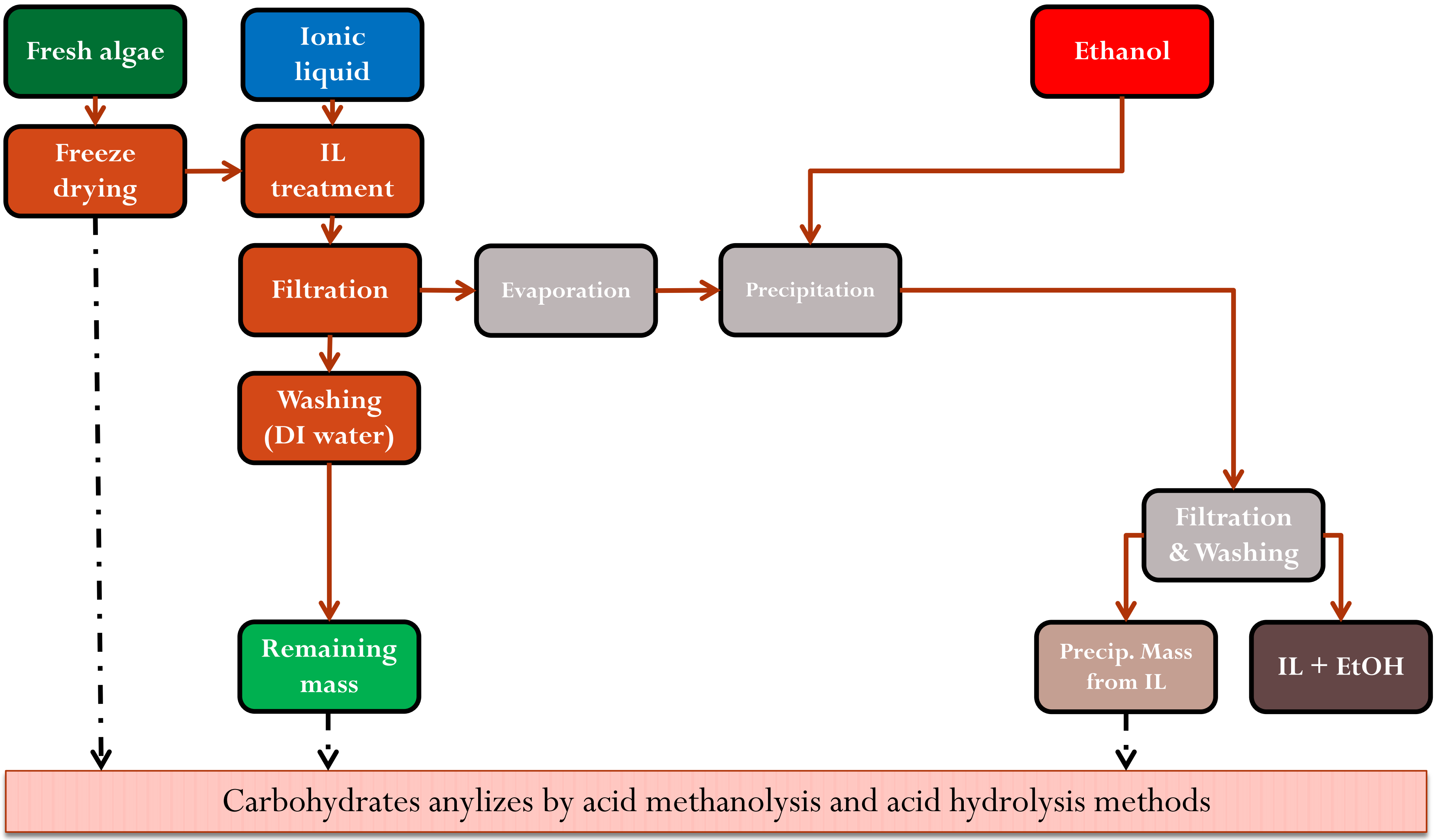
Ionic liquids treatment

- Reagent
  - SIL — DBU/MEA/SO_2
  - IL — TMG-CO2Et
- Biomass loading — 10,% w/w
- Temperature — 100 - 130°C
- Pressure — atmospheric
- Stirring — magnetic
- Time — 6 – 20 h
- Samples — duplicate

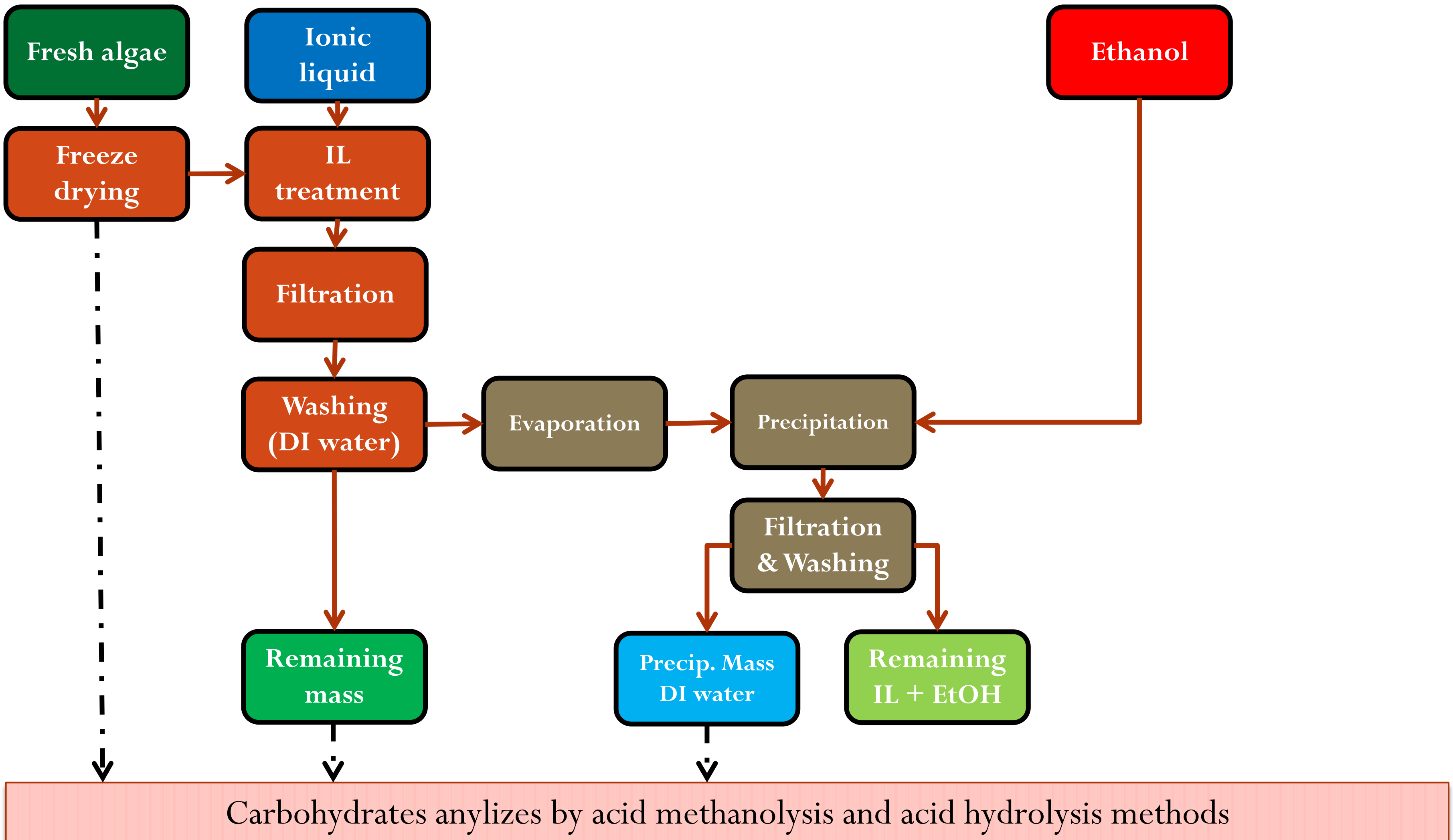


TMG : 1,1,3,3-tetramethylguanidine
CO_2Et : propionic acid

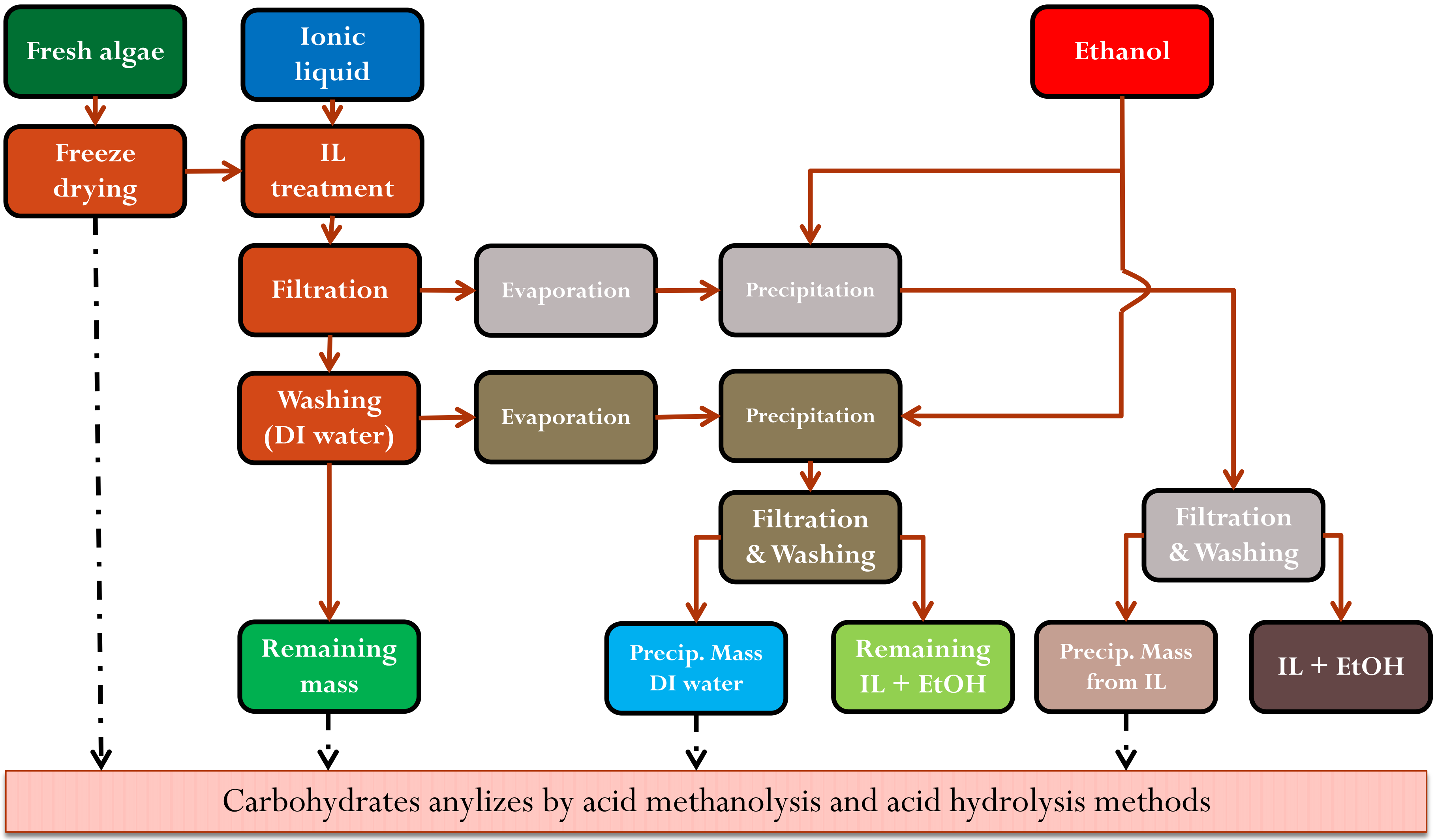
Methodology for ILs



Methodology for ILs



Methodology for ILs

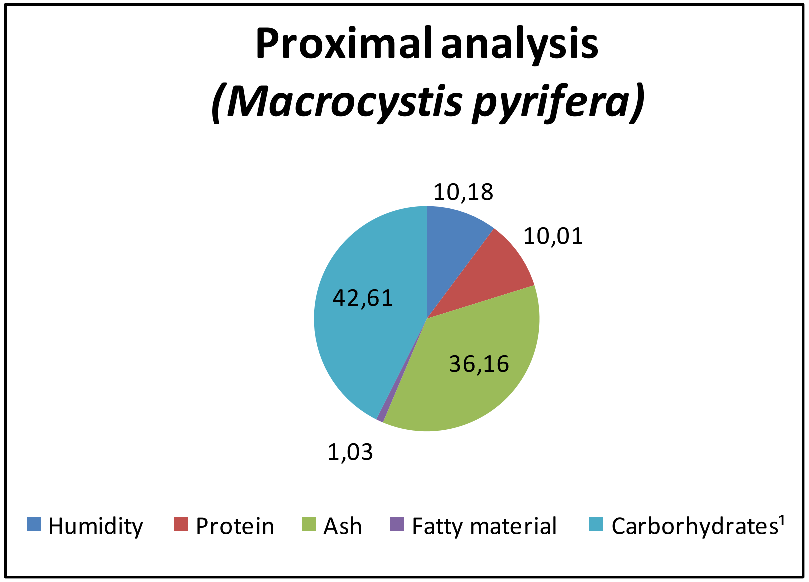


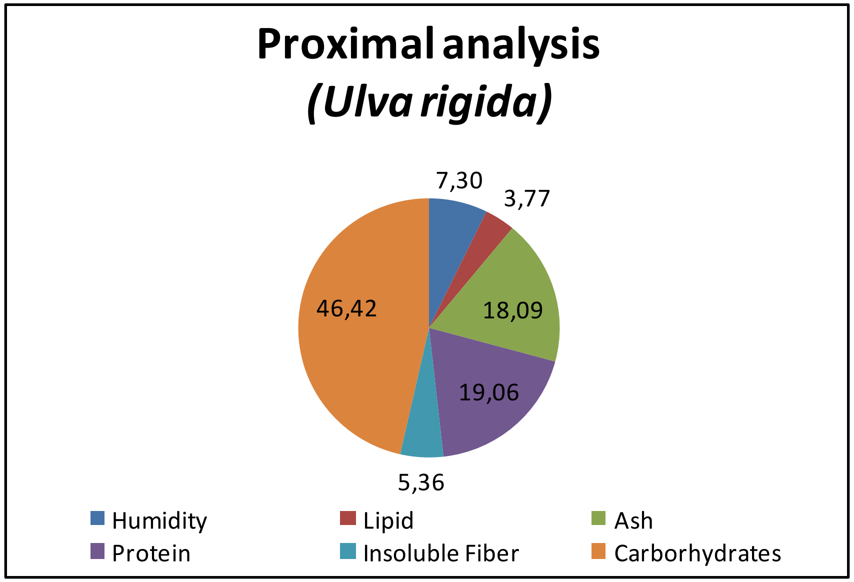
Methods

- Acid methanolysis for determination of hemicelluloses, pectins and alginate.
- Acid hydrolysis for determination of cellulose.
- FTIR for qualitative analyzis of relevant picks.
- TEM pictures of treated and untreated samples.

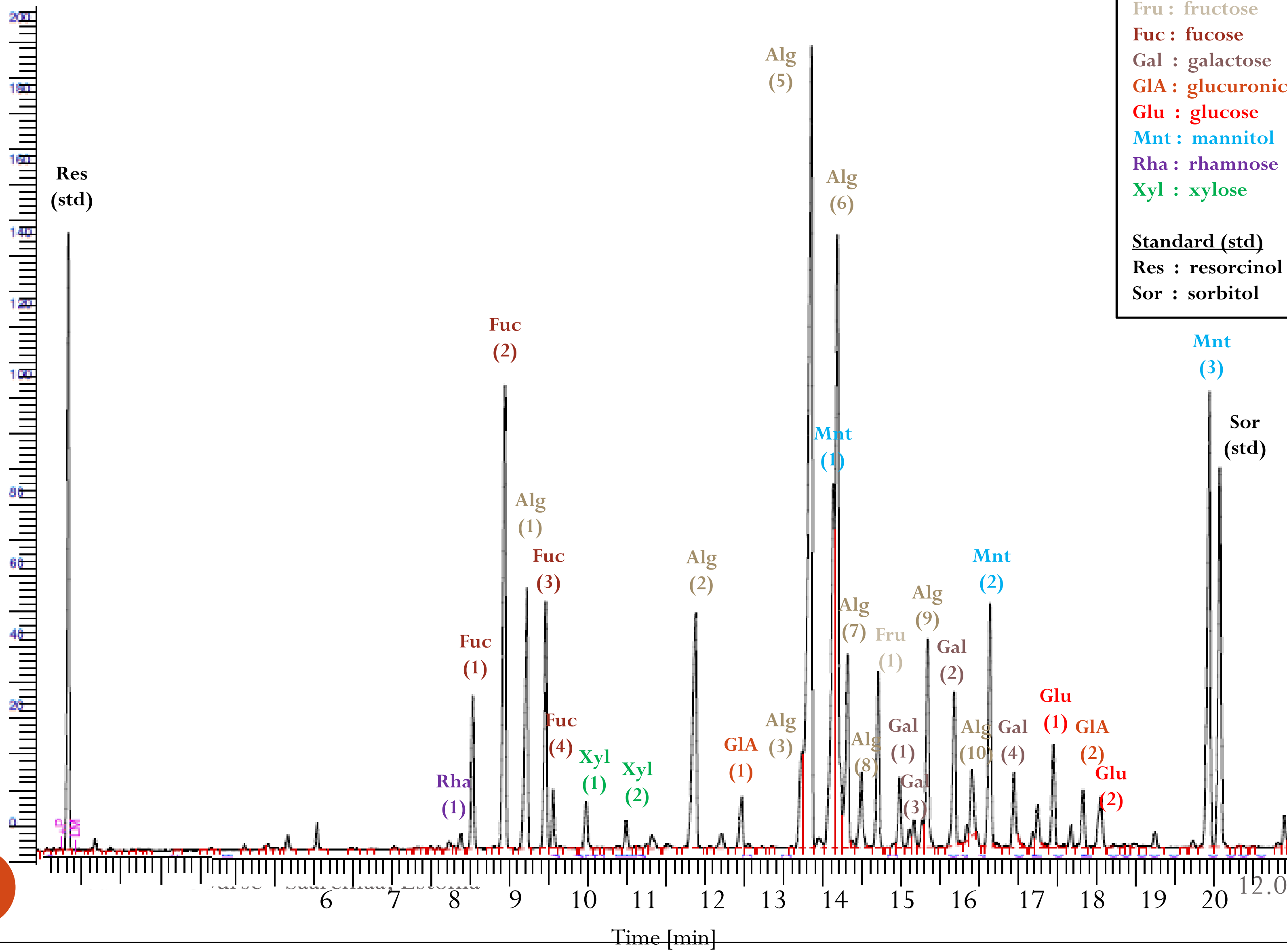
Results

Proximal analysis





Carbohydrates in *M. pyrifera*



Monosaccharides

Alg : alginic acid
Fru : fructose
Fuc : fucose
Gal : galactose
GlA : glucuronic acid
Glu : glucose
Mnt : mannitol
Rha : rhamnose
Xyl : xylose

Standard (std)

Res : resorcinol
Sor : sorbitol

Carbohydrates in *M. pyrifera*

Component (mg/g of dry algae)	*Macrocystis pyrifera*
Alginic acid	275.74 ± 4.03
Arabinose	0.15 ± 0.02
Fucose	19.08 ± 0.95
Galactose	11.03 ± 0.13
Galacturonic Acid	0.34 ± 0.02
Glucose	40.64 ± 7.85
from acid hydrolysis[1]	40.64 ± 7.85
from acid methanolysis[2]	4.67 ± 1.43
Glucuronic Acid	9.03 ± 0.18
Fructose	6.61 ± 0.01
Mannose	< 0,1
Mannitol	36.30 ± 2.12
Rhamnose	0.50 ± 0.02
Xylose	2.80 ± 0.01

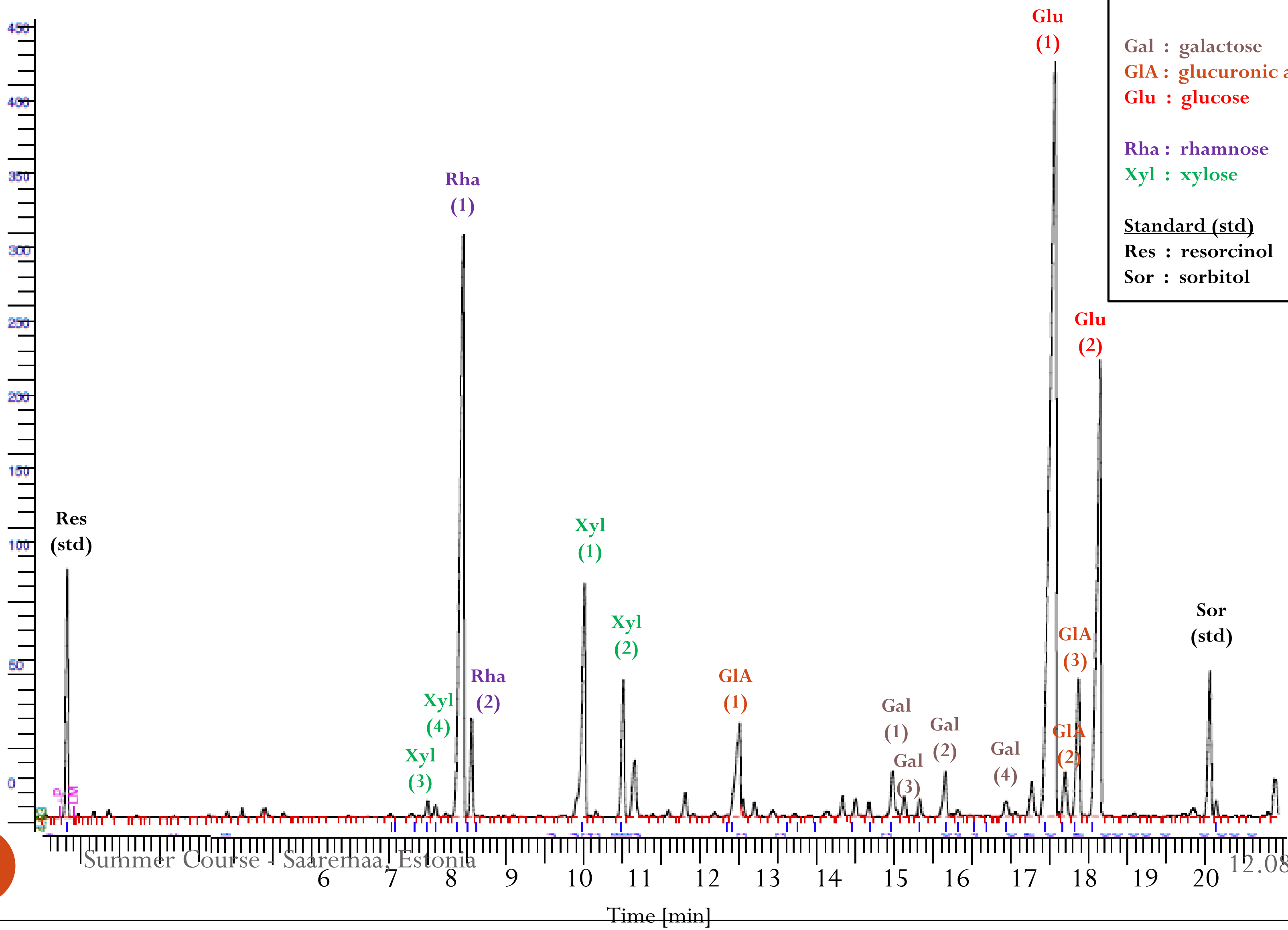
AVG ± STD

[1] acid hydrolysis method is meant to release all glucose in biomass, included from cellulose.

[2] acid methanolysis method method is meant to atack hemicelluloses and pectins, leaving free cellulose fraction.

Difference in glucose amount reported for these two methods suggests some cellulose content in this alga.

Carbohydrates in *U. rigida*



Monosaccharides

Gal : galactose
GlA : glucuronic acid
Glu : glucose

Rha : rhamnose
Xyl : xylose

Standard (std)
Res : resorcinol
Sor : sorbitol

Carbohydrates in *U. rigida*

Component (mg/g of dry algae)	*Ulva rigida*
Alginic acid	18.05 ± 6.11
Arabinose	0.69 ± 0.03
Fucose	< 0,1
Galactose	11.73 ± 0.14
Galacturonic Acid	1.38 ± 1.50
Glucose	182,75 ± 7,76
from acid hydrolysis[1]	182,75 ± 7,76
from acid methanolysis	184,22 ± 1,09
Glucuronic Acid	62.28 ± 0.88
Fructose	1.36 ± 0.10
Mannitol	0.93 ± 0.77
Rhamnose	81.15 ± 2.46
Xylose	38.53 ± 1.06

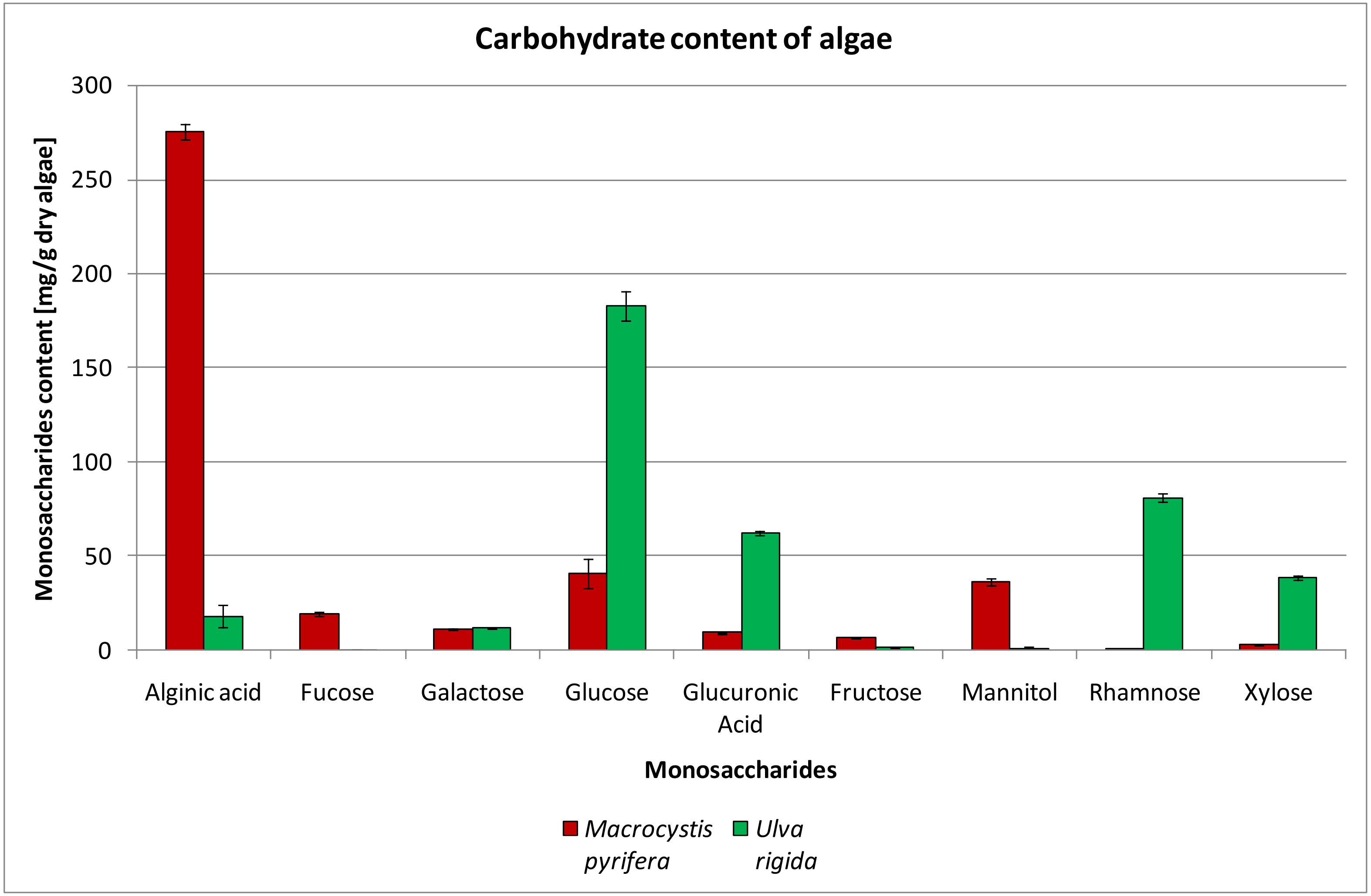
AVG ± STD

[1] acid hydrolysis method is meant to release all glucose in biomass, included from cellulose.

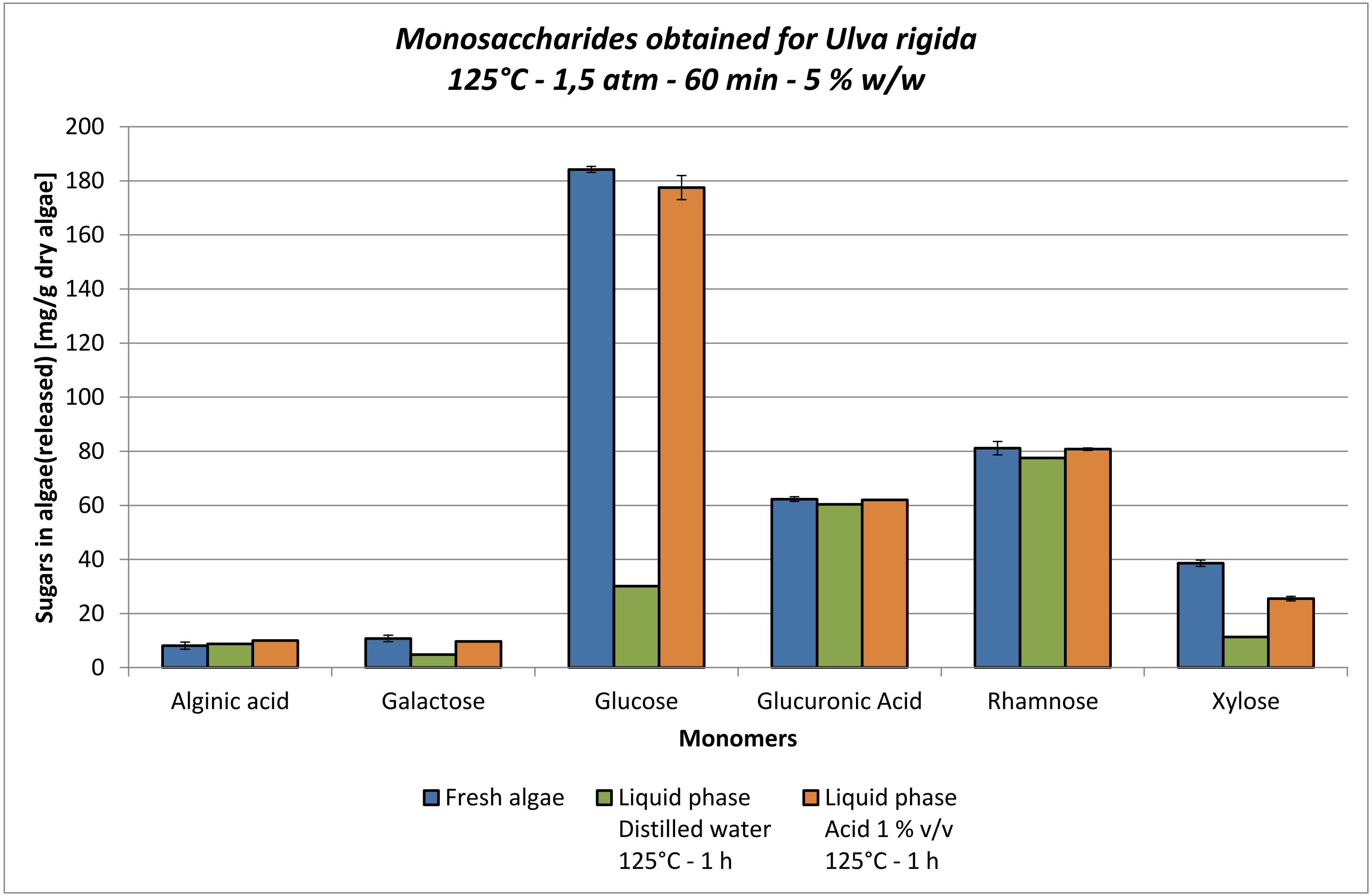
[1] acid methanolysis method method is meant to atack hemicelluloses and pectins, leaving free

No difference in glucose amount reported for these two methods suggest there is no cellulose content in this alga.

Carbohydrate content in Algae



Dilute sulfuric acid treatment *U. rigida*



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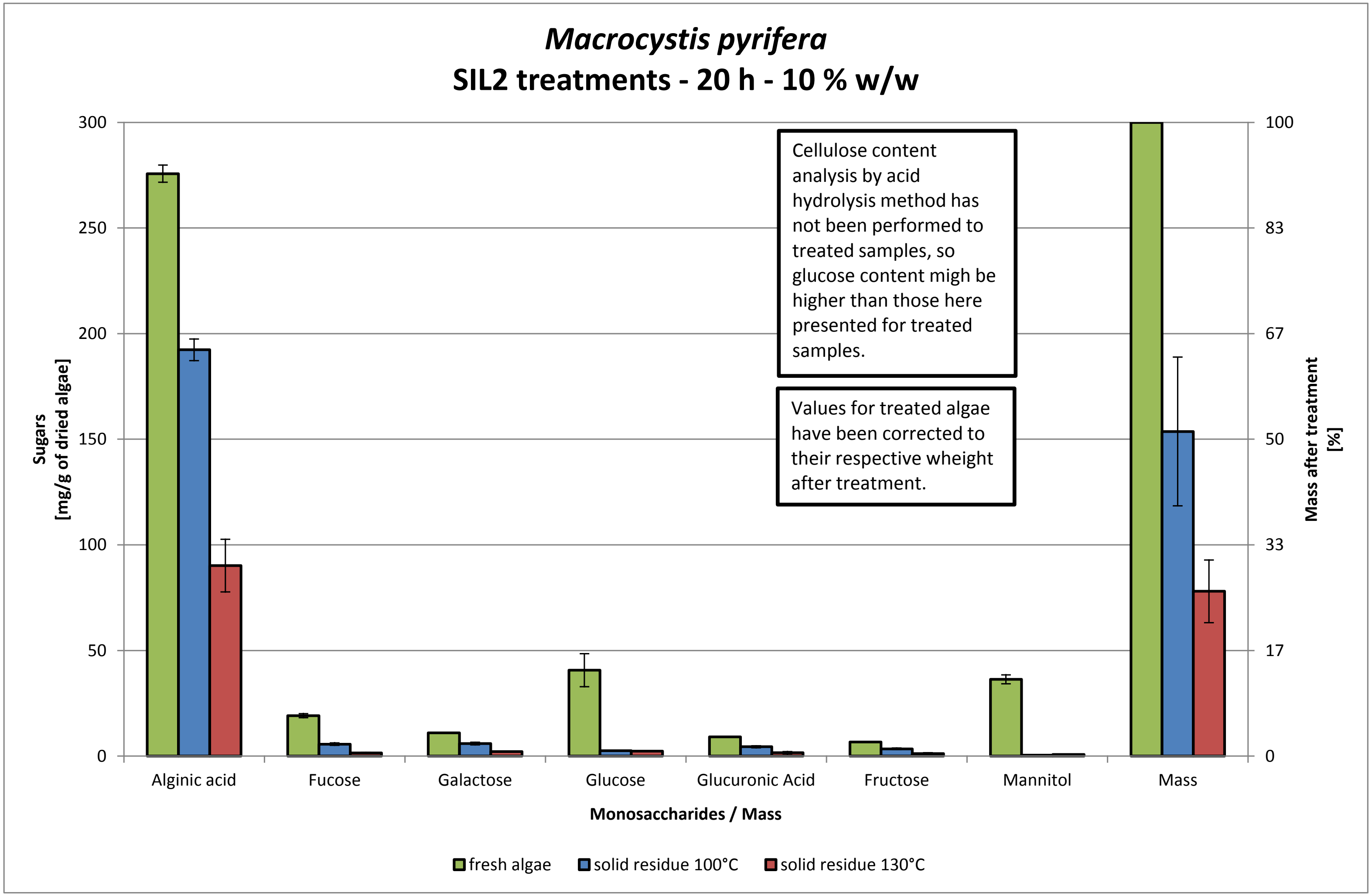
IL treatments
M. pyrifera



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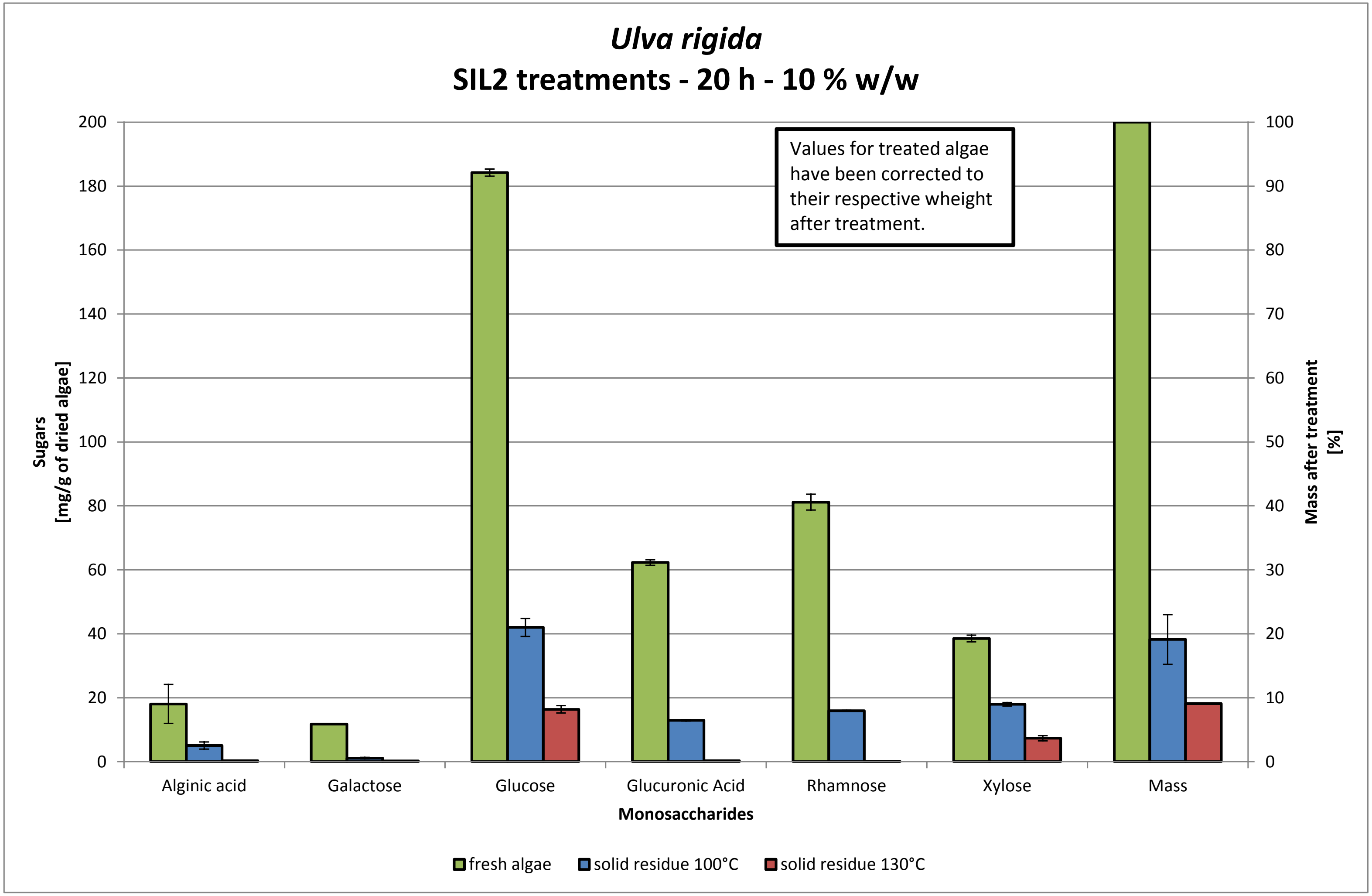
SIL2 treatments
U. rigida



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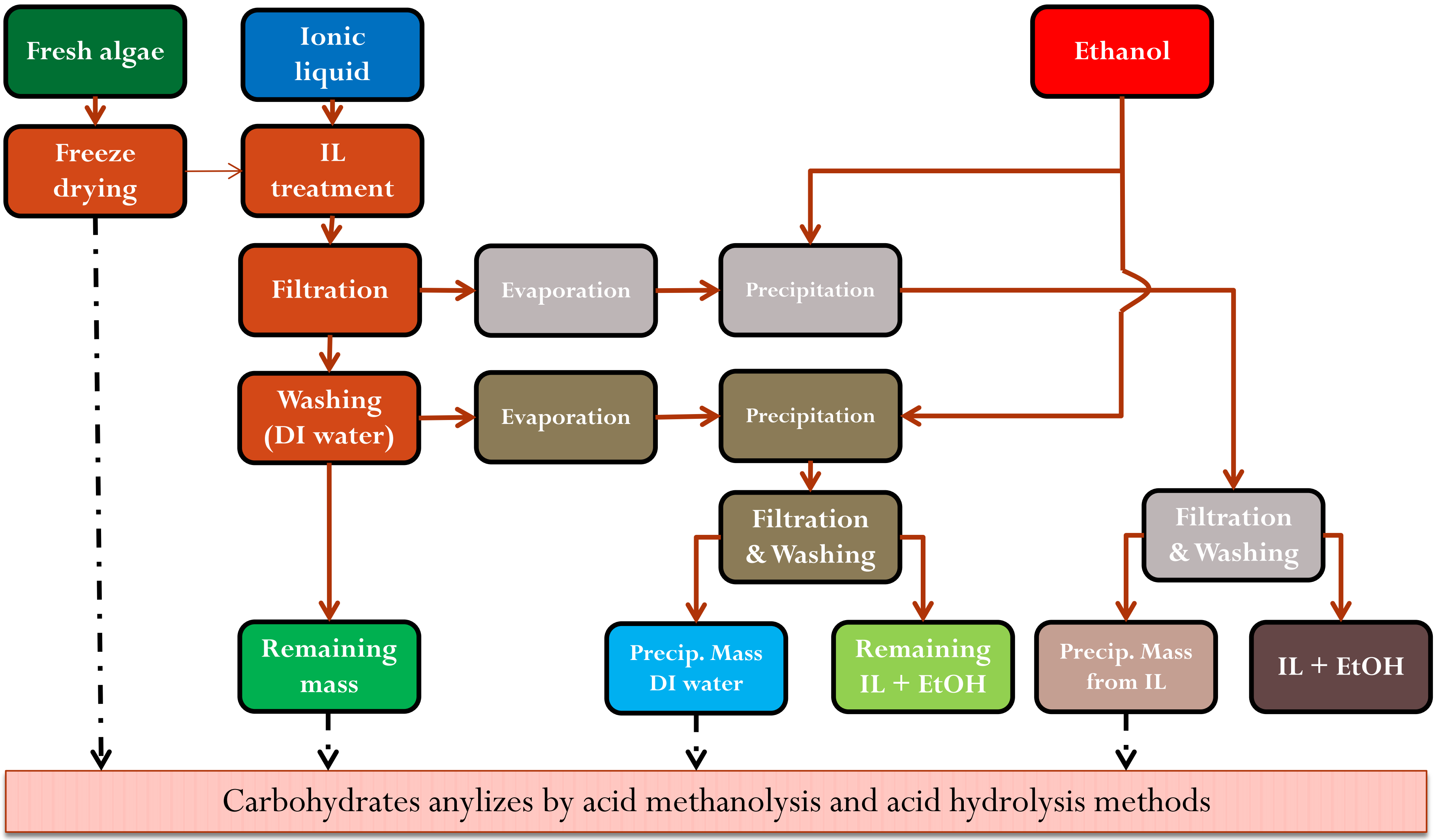
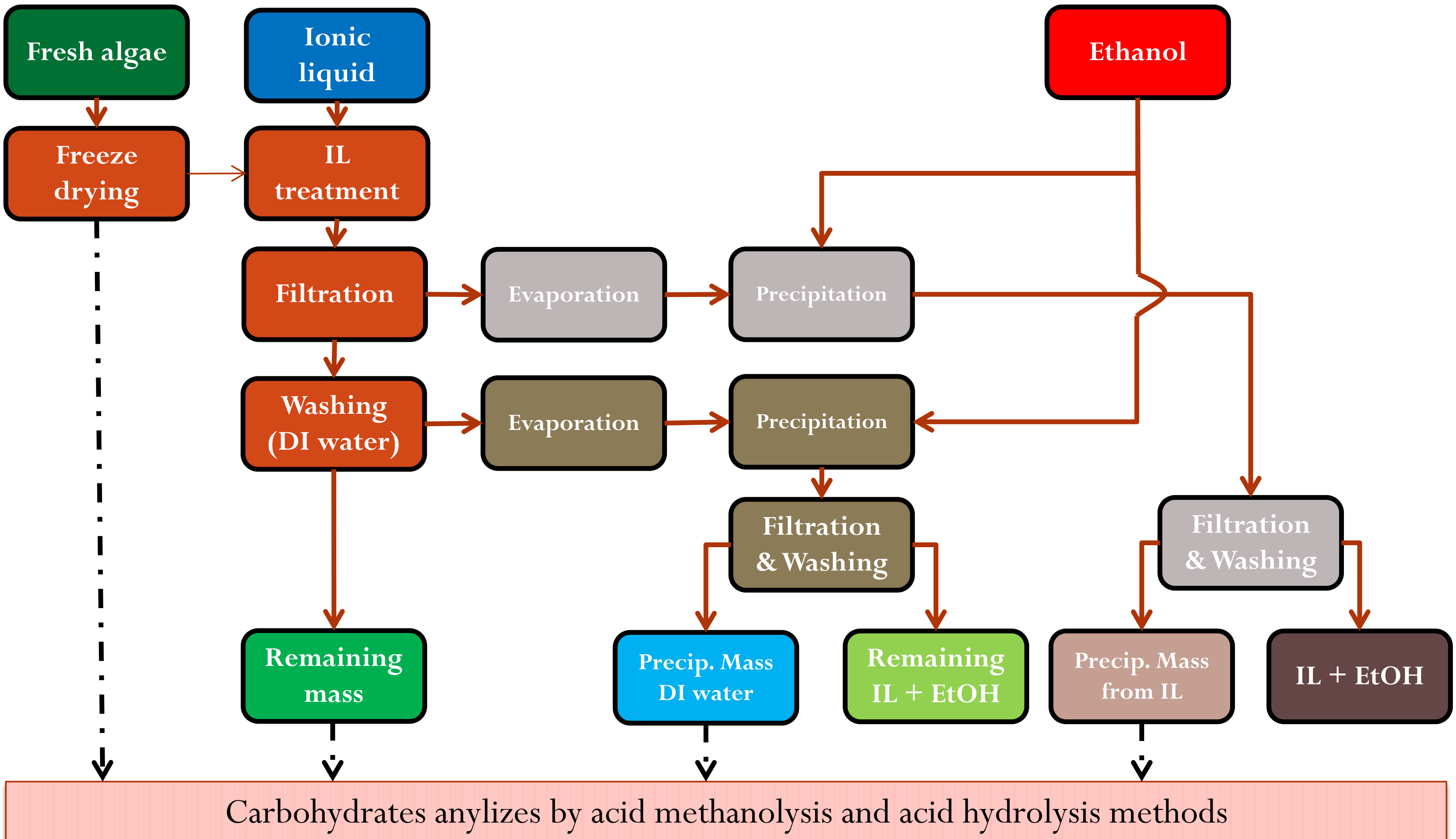
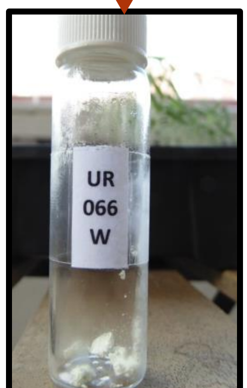
Methodology for ILs

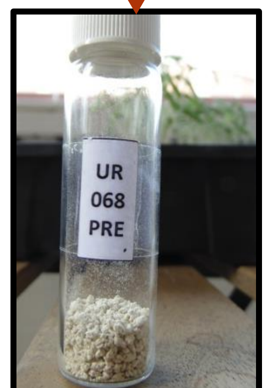


Methodology for ILs



Untreated algae



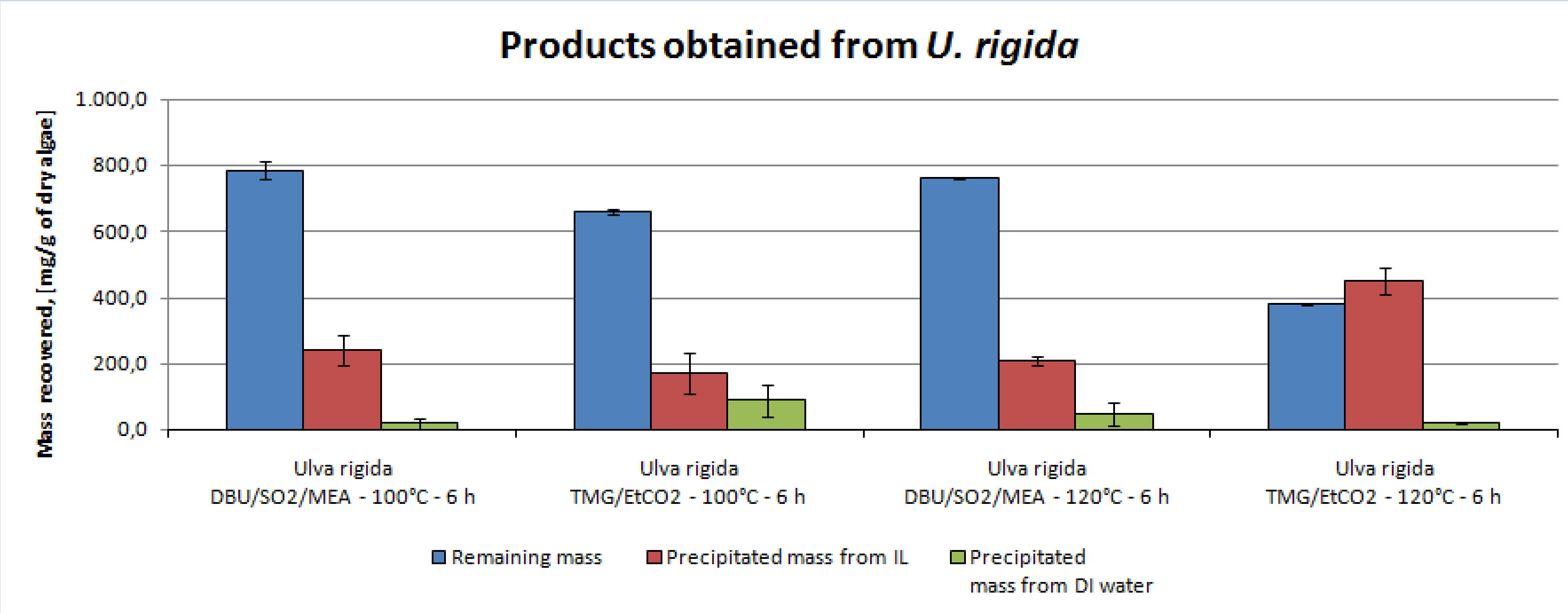


Treated algae

Precipitated from wash water

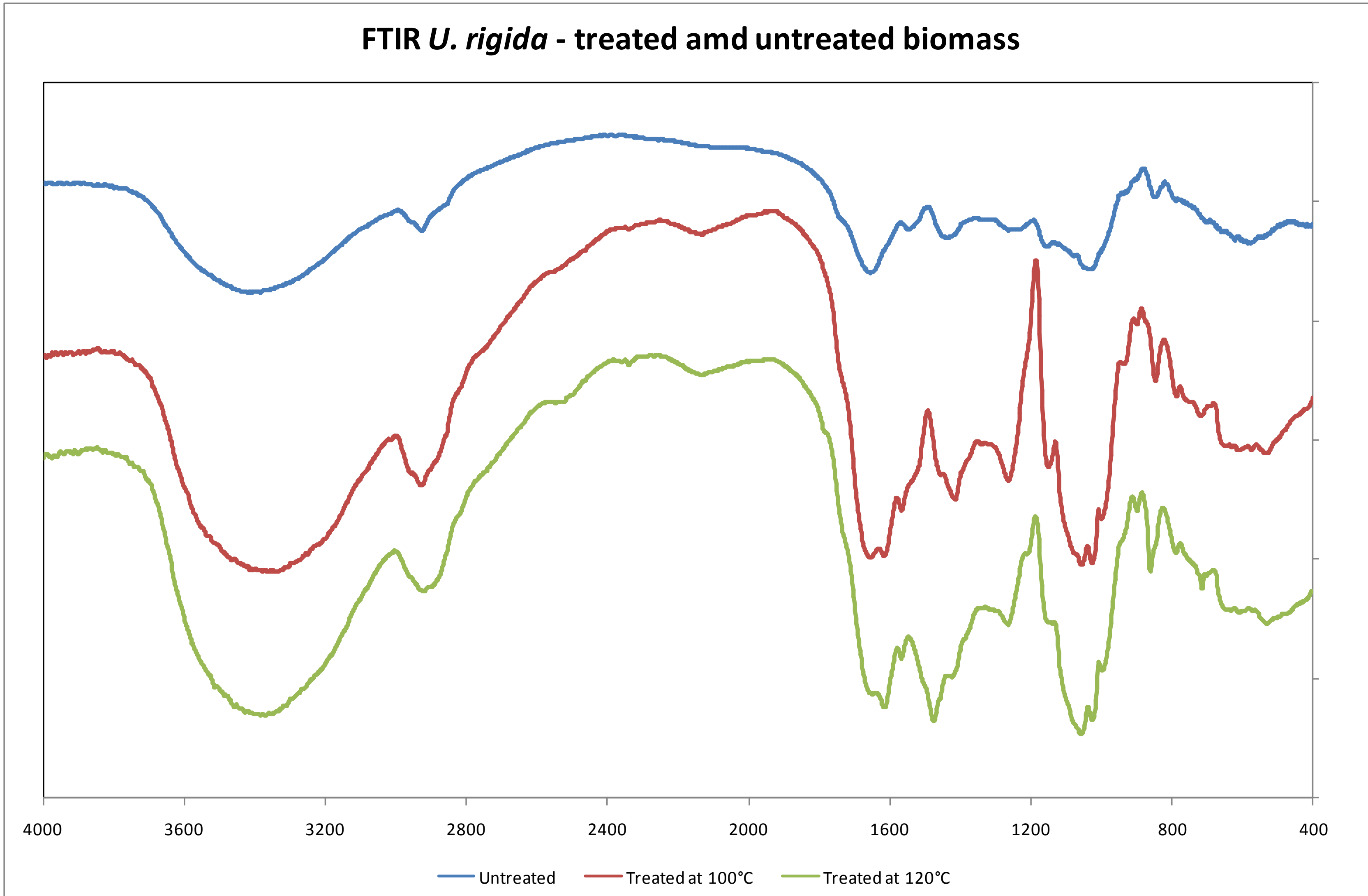
Precipitated from IL

Results mass balance



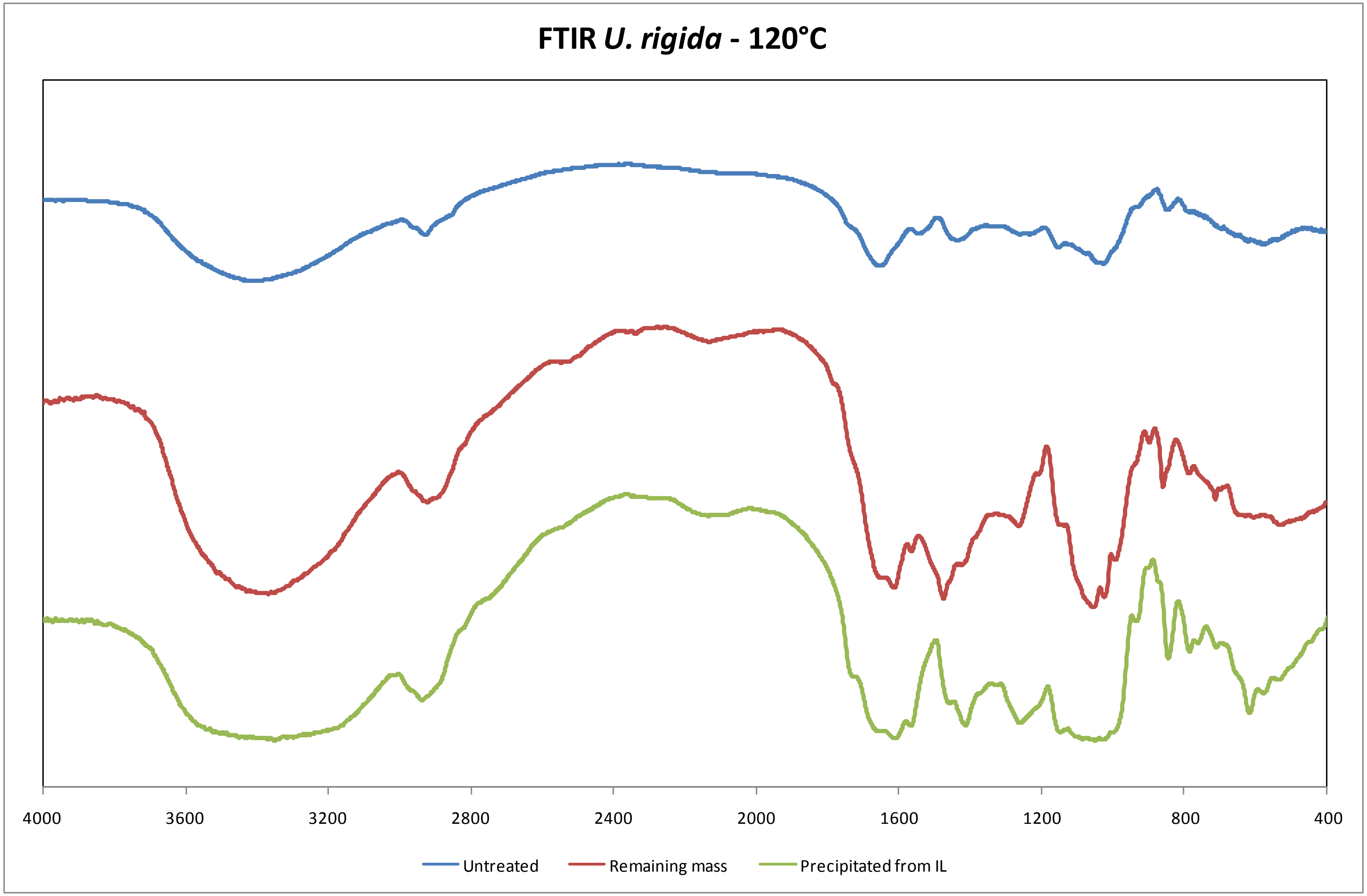
Experiments		Initial mass [mg]	Remaining mass [mg]			Precipitated mass from IL [mg]			Precipitated mass from DI water [mg]			Total recovered mass [mg]		
DBU/SO_2/MEA	100°C	1,000.00	785.37	±	27.70	239.33	±	44.12	18.23	±	17.66	1,042.93	±	1.24
TMG-$EtCO_2$	100°C	1,000.00	659.89	±	8.27	170.39	±	59.47	88.25	±	47.94	918.53	±	99.14
DBU/SO_2/MEA	120°C	1,000.00	761.37	±	1.18	208.19	±	15.36	48.43	±	35.91	1,017.99	±	19.37
TMG-$EtCO_2$	120°C	1,000.00	379.58	±	0.42	450.32	±	41.85	18.46	±	1.65	848.36	±	39.78

FTIR



FTIR *U. rigida* - treated amd untreated biomass
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Untreated
Treated at 100°C
Treated at 120°C

FTIR



FTIR *U. rigida* - 120°C
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Untreated
Remaining mass
Precipitated from IL

Conclusions

Conclusions

- Algae have high potential for biofuels production, due to high presence of carbohydrates, which can also lead to obtaining byproducts under a biorefinery concept.
- *M. pyrifera* has high content of alginic acid which results a challenge how to obtain this carbohydrate for the food industry and even use remaining sugars for bioethanol production.
- *U. rigida* has a high content of glucose (18 %), probably coming from starch. Also it has high amounts of rhamnose (9 %) and xylose (6 %) which can lead bioethanol production or e.g. production of polyols (sugar hydrogenation).

Conclusions

- Sulfuric acid treatment for *U. rigida* shows high hydrolysis of carbohydrates. Furfural compounds must be quantified in order to see how techno-economically feasible this treatment really is.
- Mass have been obtain for Ils treatments for U. rigida. Nevertheless characterization of products, principally remaining biomass and precipitated mass from Ils must be performed.

Acknowledgements

- This works is part of the project 'Optimal production of bioethanol from macroalgae via photo-chemo-enzymatic processing – OPTIFU'.
- Akademi of Finland – AKA – and Comisión Nacional de Investigación, Ciencia y Tecnología de Chile – CONICYT – are greatfully acknowledged for funding this project.

Thank you for your attention