Ionic liquid treatment for algal biomass

OPTIFU Project

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CONTENT

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  - Biofuel
  - Types of algae
  - Carbohydrates on algae
  - Algae treatments
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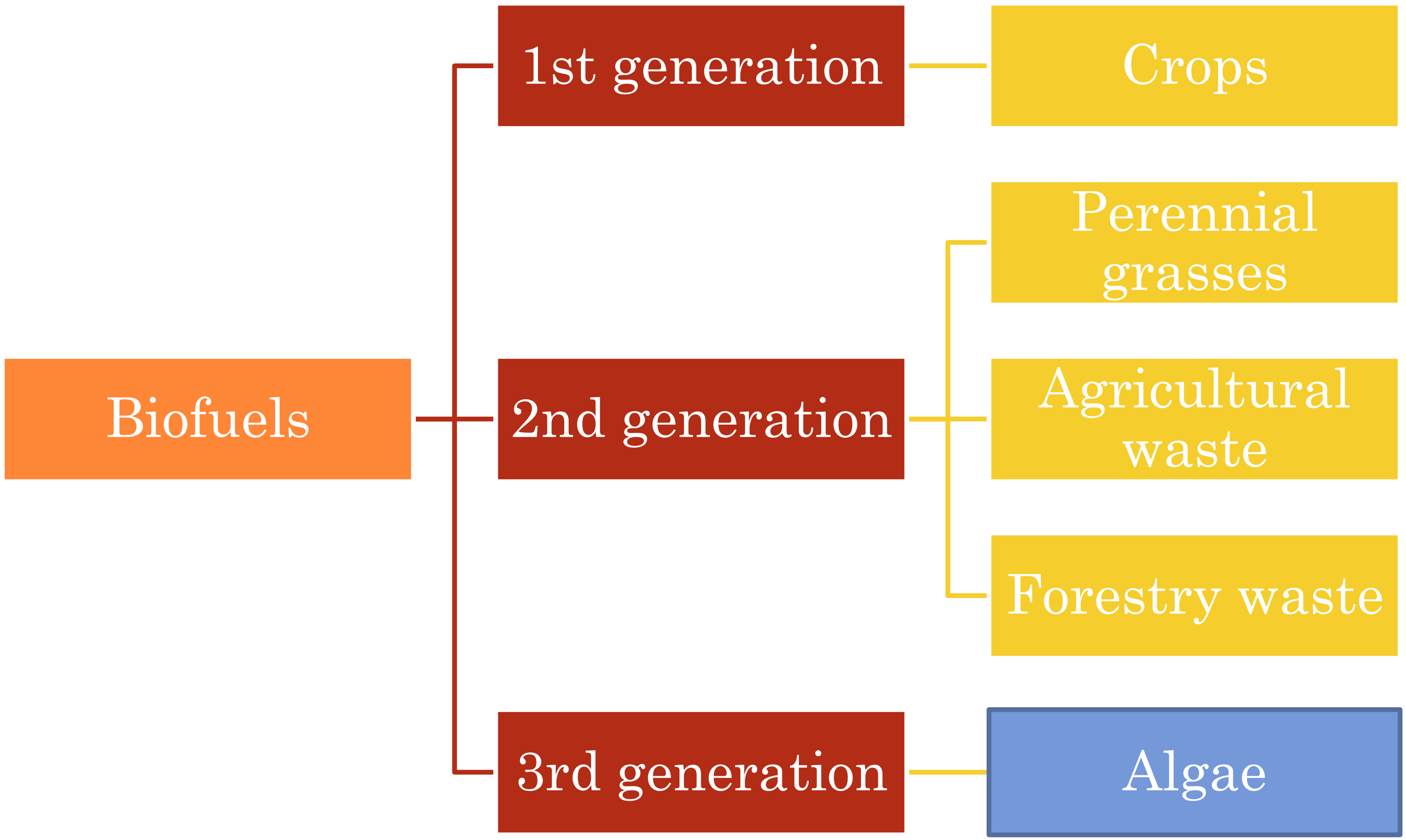
Biofuels


Biofuels
1st generation
2nd generation
3rd generation
Crops
Perennial grasses
Agricultural waste
Forestry waste
Algae

ALGAL CHARACTERISTICS

Microalgae

- Microscopic photosynthetic organisms.
- Many of them are unicellular

Macroalgae

- Composed by multiple cells.
- Their structures are composed by roots, stems and leaves.

Seaweed Peter®

Macroalgae

Brown algae

- Laminarin
- Mannitol
- Alginate
- Fucoidin
- Cellulose

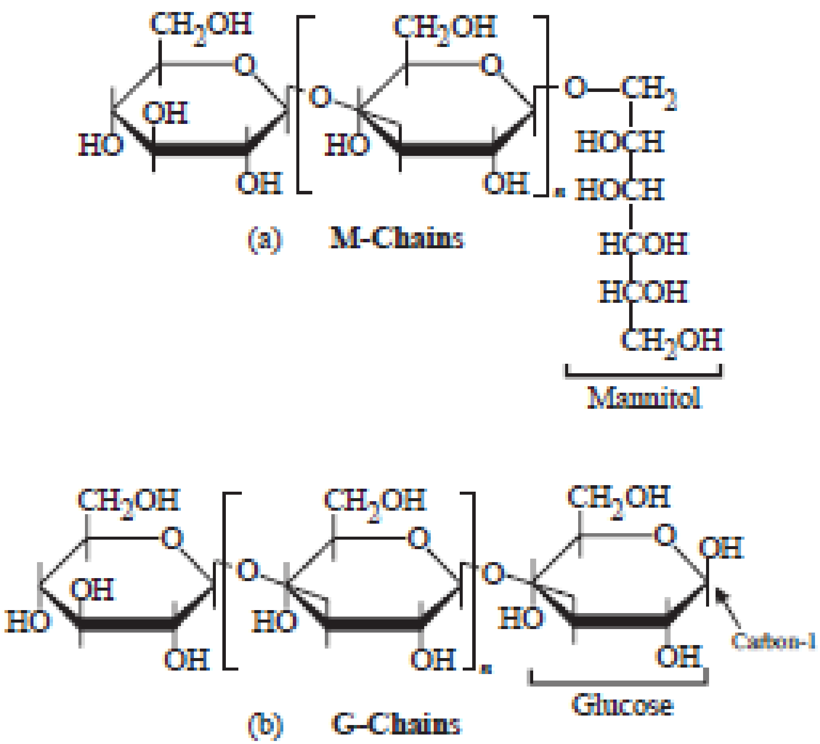
Red algae

- Carrageenan
- Agar
- Cellulose
- Lignin

Green algae

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

Carbohydrates of brown algae



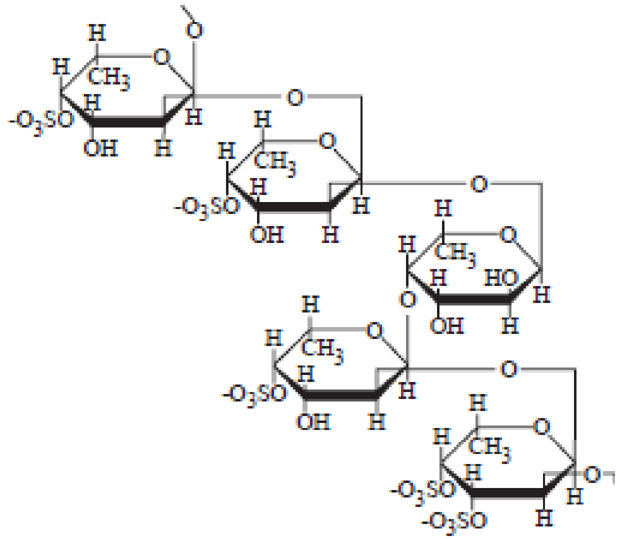
Laminarin

Mannitol: at the reducing end of laminarin.

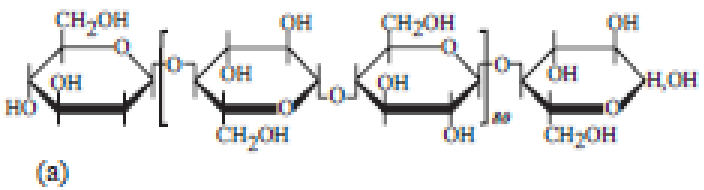
ß-1,3 and ß-1,6 branches

Picture taken from: T.A. Davis et al, Water Research 37 (2003) 4311-4330.

Carbohydrates of brown algae



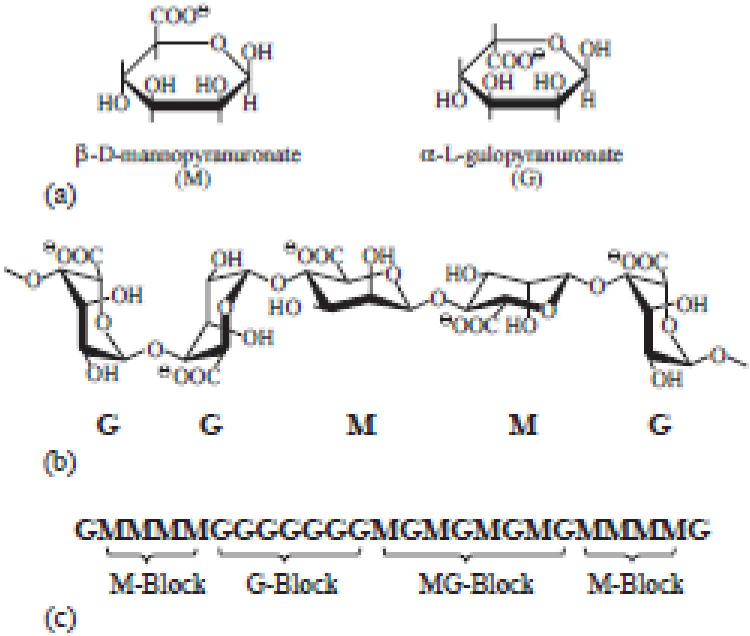
Fucoidin



Cellulose

Picture taken from: T.A. Davis et al, Water Research 37 (2003) 4311-4330.

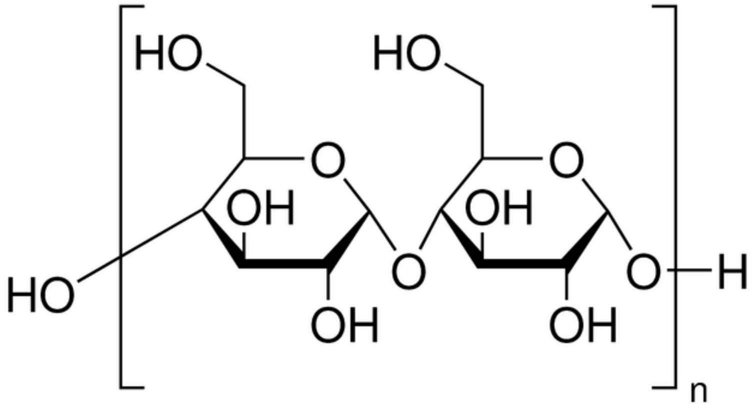
Carbohydrates of brown algae



Alginic acid

Picture taken from: T.A. Davis et al, Water Research 37 (2003) 4311-4330.

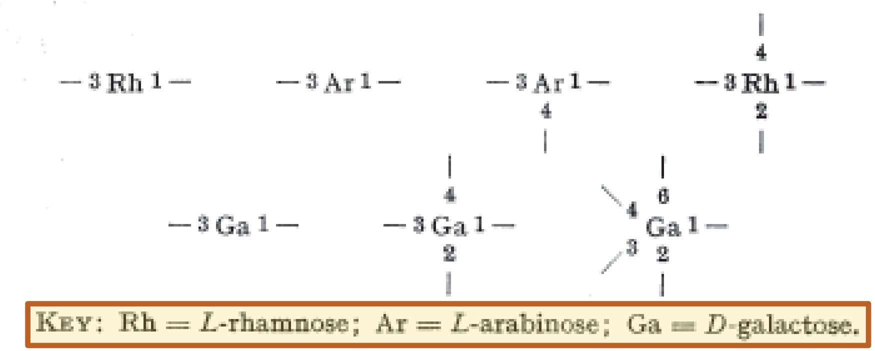
CARBOHYDRATES OF GREEN ALGAE



Starch

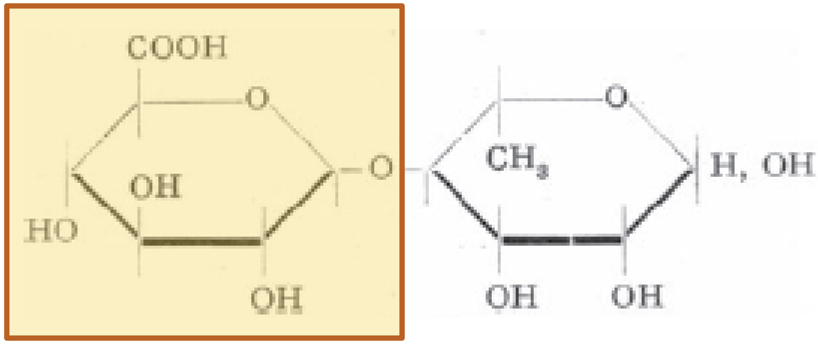
http://www.sigmaaldrich.com/catalog/product/sial/33615?lang=fi&region=FI

Carbohydrates of green algae



Sulfated arabinogalactans

Polysaccharides of marine algae, Progress in the Chemistry of Organic Natural Products XXIII



Glucuronic acid

Polysaccharides containing glucuronic acid

Polysaccharides of marine algae, Progress in the Chemistry of Organic Natural Products XXIII

Carbohydrates
Macrocystis pyrifera: Reported data

Macrocystis pyrifera	A.B. Ross et al [i]	A.B. Ross et al [ii]	F. Bobadilla et al [iii]	H. Zhao et al [iv]	A. Mansilla & M. Ávila [v]	W.L. White et al. [vi]	R. Westermeier et al. (vii)	D.P. Chynoweth et al. (viii), (ix)	A. Vergara-Fernández (x)
Composition									
Protein	n/r -	n/r -	n/r -	n/r -	9,2 - 17,5 % w/w [a]	n/r -	7,00 - 14,0 % w/w	n/r -	n/r -
Lipid	n/r -	n/r -	n/r -	n/r -	0,40 - 0,84 % w/w [a]	n/r -	0,05 - 0,50 % w/w	n/r -	n/r -
Ash	38.4 % w/w	26 % w/w	n/r -	59.2 % w/w	29,9 - 37,2 % w/w [a]	n/r -	35,0 - 50,0 % w/w	36,1 - 46,2 % w/w	n/r -
Total nitrogen	2.0 % w/w	3.1 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	1,70 - 2,20 % w/w	1,58 % w/w
Organic substance	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Total sugars	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Carbohydrates	n/r -	n/r -	n/r -	n/r -	3,3 - 8,5 % w/w [a]	n/r -	n/r -	n/r -	n/r -
Polysaccharides									
Alginic acid	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	20,0 - 50,0 % w/w	14,2 % w/w	n/r -
Laminarin	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	0,7 % w/w	n/r -
Cellulose	n/r -	n/r -	n/r -	35.9 % w/w	n/r -	n/r -	n/r -	4,8 % w/w	n/r -
Fucoidan	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	0,2 % w/w	n/r -
Mannitol	n/r -	n/r -	n/r -	n/r -	n/r -	13,0 - 14,4 % w/w	1,00 - 5,00 % w/w	8,30 - 21,4 % w/w	n/r -
Hemicellulose	n/r -	n/r -	n/r -	15.2 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -
Lignin	n/r -	n/r -	n/r -	9.9 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -
Monosaccharides									
Glucose	n/r -	n/r -	7.6 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Fucose	n/r -	n/r -	4.0 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Mannose	n/r -	n/r -	1.4 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Galactose	n/r -	n/r -	0.8 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Uronic acids	n/r -	n/r -	12.6 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -

(i) A.B. Ross et al., Bioresource Technology 99 (2008) 6494–6504.
(ii) A.B. Ross et al., J. Anal. Appl. Pyrolysis 85 (2009) 3–10.
(iii) F. Bobadilla et al, Carbohydrate Polymers 92 (2013) 241-248.
(iv) H. Zhao et al., J. Therm. Anal. Calorim. 111 (2013) 1685-1690.
(v) A. Mansilla & M. Ávila, Braz. J Pharmacogn. 21(2) (2011) 262-267.
(vi) W.L. White et al., J. Exp. Marine Bio. Eco. 391 (2010) 50-56.
(vii) R. Westermeier et al., J. Appl. Phycol. 24 (2012) 1191-1201.
(viii) D.P. Chynoweth et al., Chapter 11: Biological Gasification of Marine Algae, (1987) 285-303.
(ix) D.P. Chynoweth, Anaerobic Digestion of Marine Algae, Int. Gas Technology, Illinois.
(x) A. Vergara-Fernández et al., Biomass and Bioenergy 32 (2008) 338-344.

(a) Values measured in Summer, Fall, Winter and Spring.
n/r not reported

Carbohydrates
Ulva rigida: reported data

Ulva rigida	F. Frikha et al [(i)]	B. Negreanu-Pîrjol et al. [(ii)]	B. Queremer et al. [(iii)]	A.K. Siddahata et al. [(iv)]	A.K. Siddahata et al. [(v)]	B. Ray & M. Lahaye [(vi)]	B. Ray & M. Lahaye [(vii)]	W.L. Zemke-White, K.D. Clements [(viii)]	N. Zavodnik [(ix)]	L.M.P Valente et al. [(x)]
Composition										
Protein	7.3 % w/w	14.6 % w/w	n/r -	n/r -	10.0 % w/w [(a)]	n/r -	13.9 % w/w [(d)]	5.9 % w/w	15.7 % w/w	29.5 % w/w
Lipid	0.8 % w/w	0.7 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	1.1 % w/w	1.7 % w/w	1.4 % w/w
Ash	25.7 % w/w	18.4 % w/w	n/r -	n/r -	18.1 % w/w [(a)]	n/r -	25.0 % w/w [(d)]	14.6 % w/w	20.2 % w/w	n/r -
Total nitrogen	n/r -	2.32 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Organic substance	n/r -	68.9 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Total sugars	16.7 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	30.3 % w/w [(d)]	n/r -	n/r -	n/r -
Carbohydrates	n/r -	59.0 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Polysaccharides										
Starch	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	3.5 % w/w	n/r -	n/r -
Cellulose	n/r -	n/r -	n/r -	7.5 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -
Monosaccharides										
Glucose	n/r -	n/r (v)	0.4 % w/w	n/r -	0.04 rat.HWE [(b)]	3.00 % mol [(c)]	3.0 % mol [(d)]	n/r -	n/r -	n/r -
Rhamnose	n/r -	n/r (v)	10.1 % w/w	n/r -	1.00 rat.HWE [(b)]	25.30 % mol [(c)]	23.3 % mol [(d)]	n/r -	n/r -	n/r -
Arabinose	n/r -	n/r (v)	n/r -	n/r -	0.01 rat.HWE [(b)]	trace -	n/r -	n/r -	n/r -	n/r -
Xylose	n/r -	n/r (v)	2.8 % w/w	n/r -	0.09 rat.HWE [(b)]	10.90 % mol [(c)]	10.9 % mol [(d)]	n/r -	n/r -	n/r -
Galactose	n/r -	n/r -	n/r -	n/r -	0.02 rat.HWE [(b)]	0.40 % mol [(c)]	0.4 % mol [(d)]	n/r -	n/r -	n/r -
Mannose	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	trace -	n/r -	n/r -	n/r -
Uronic acids	n/r -	n/r -	n/r -	n/r -	n/r -	24.90 % mol [(c)]	20.9 % w/w [(d)]	n/r -	n/r -	n/r -
Glucuronic acid	n/r -	n/r (v)	6.1 % w/w	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -	n/r -

(i) F. Frikha et al., Ciencias Marinas 37(2) (2011) 113-124.
(ii) B. Negreanu-Pîrjol et al., St. Cerc. St. CICBIA 12(2) (2011) 173-184.
(iii) B. Quemener et al., Journal of Applied Phycology 9 (1997) 179–188.
(iv) A.K. Siddahanta et al., J. Appl Phycol 23 (2011) 919–923
(v) A.K. Siddahanta et al, Indian J. Mar. Sci 30 (2001) 166-172
(vi) B. Ray, M. Lahaye, Carbohydrate Research 274 (1995) 313-318
(vii) B. Ray, M. Lahaye, Carbohydrate Research 274 (1995) 251-261
(viii) W.L. Zemke-White, K.D. Clements, J. Exp. Mar. Biol. Ecol. 240 (1999) 137 –149
(ix) N. Zadvonik, Botanica Marina 30 (1987) 71-82.
(x) L.M.P. Valente et al., Aquaculture 252 (2006) 85–91

(a) Content in cold water extract.
(b) Ratio of sugars contenied in hot water extract.
(c) Fraction of ulvan extracted from algae.
(d) Fraction of sugars extracted from algae.

Algae Treatments

TREATMENTS FOR BROWN ALGAE

- Most experiments of brown algae have been done to *Laminaria japonica* species.
- B. Malihan et al., were able to achieve yields near 100 % of total reducing sugars, when using [BMIM][Cl]/HCl.
- Purity of total reducing sugars was around 95 %, accounting presence of furfural compounds at temperatures above 120°C.

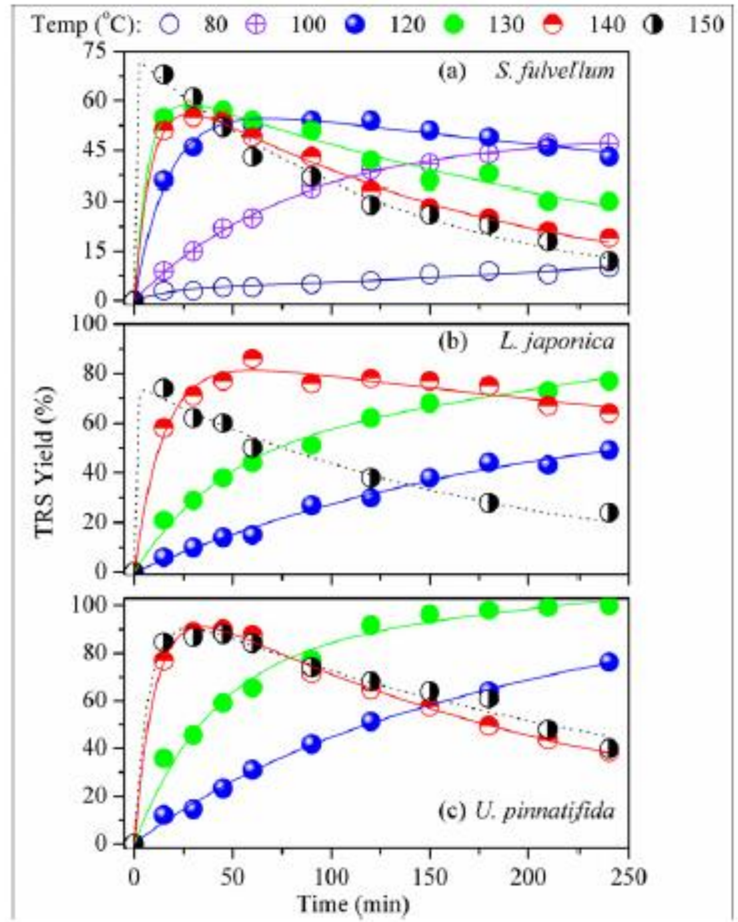
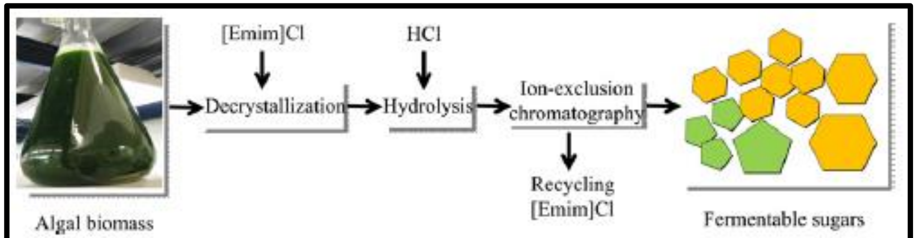


Fig. 3. TRS yields from the hydrolysis of (a) *S. fulvellum* (b) *L. japonica* (c) *U. pinnatifida* in [BMIM]Cl/HCl (30 wt.% acid loading with respect to biomass amount) at different reaction temperatures and time.

L.B Malihan et al. Bioresource Technology 118 (2012) 545-552

TREATMENTS FOR GREEN ALGAE

- Chlorella was dissolved on [EMIM][Cl] and 7 % w/w HCl (relative to biomass).
- Total sugars yield reached 90 % at 105°C for 3 h.
- At 120°C and at longer exposure times, content of furfural in hydrolizate increased.



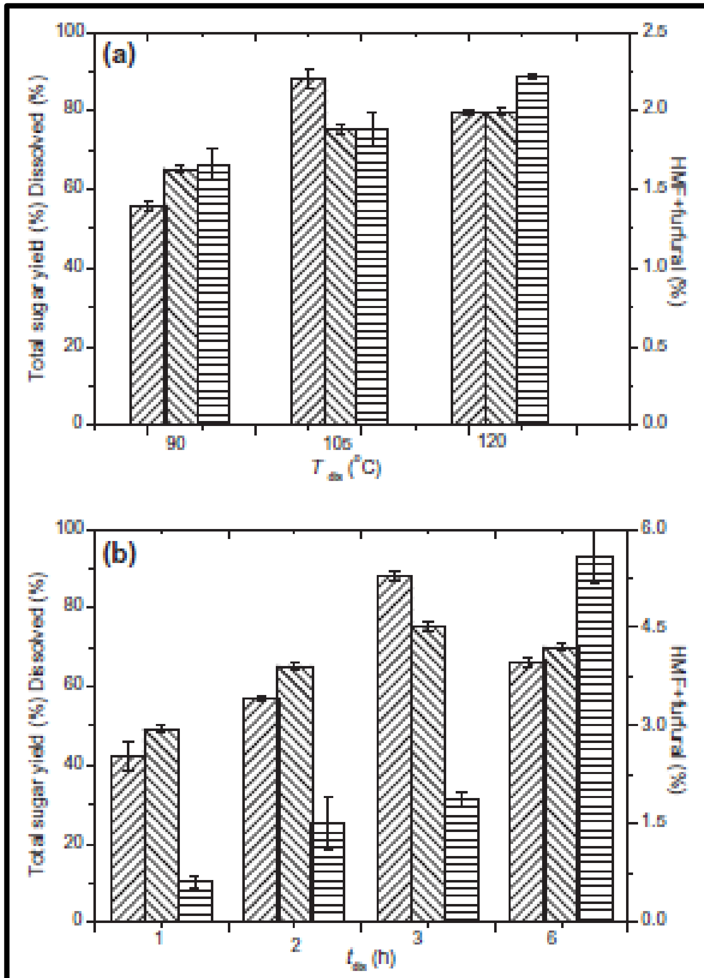


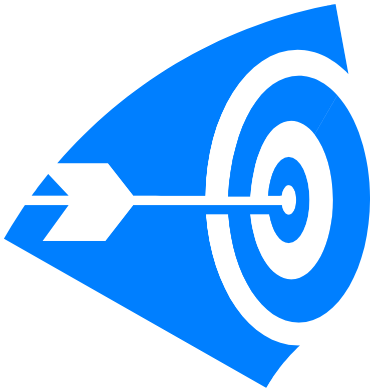
Fig. 1. Effect of dissolution temperature (a) and dissolution time (b) on [Emim]Cl hydrolysis of *Chlorella* biomass. ▨: Total sugar yield (calculated in the form of reducing sugar yield); ▨: dissolved percent of *Chlorella* biomass; ▤: (HMF + furfural)%. (For dissolution temperature test, other experimental conditions were: dissolved in [Emim]Cl for 3 h and then hydrolyzed at 105 °C and 7 wt.% HCl loading for 3 h; for dissolution time test, other conditions were: dissolved in [Emim]Cl at 105 °C, and then hydrolyzed at 105 °C and 7 wt.% HCl loading for 3 h).

N.Zhao, Y.Zhang, X.Gong, Q.Wang, Y.Ma. Bioresource Technology 118 (2012) 512-517.

Aim of this work

AIM

- The main target of this work is to determine carbohydrates composition of algae biomass, as well as to study the dissolution of these carbohydrates contained on algae biomass when treated with ionic liquids at different conditions.

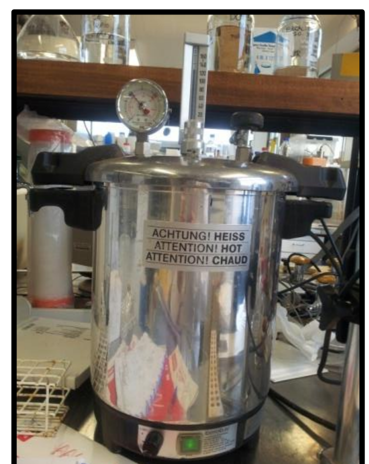


Determination of carbohydrates content in algae

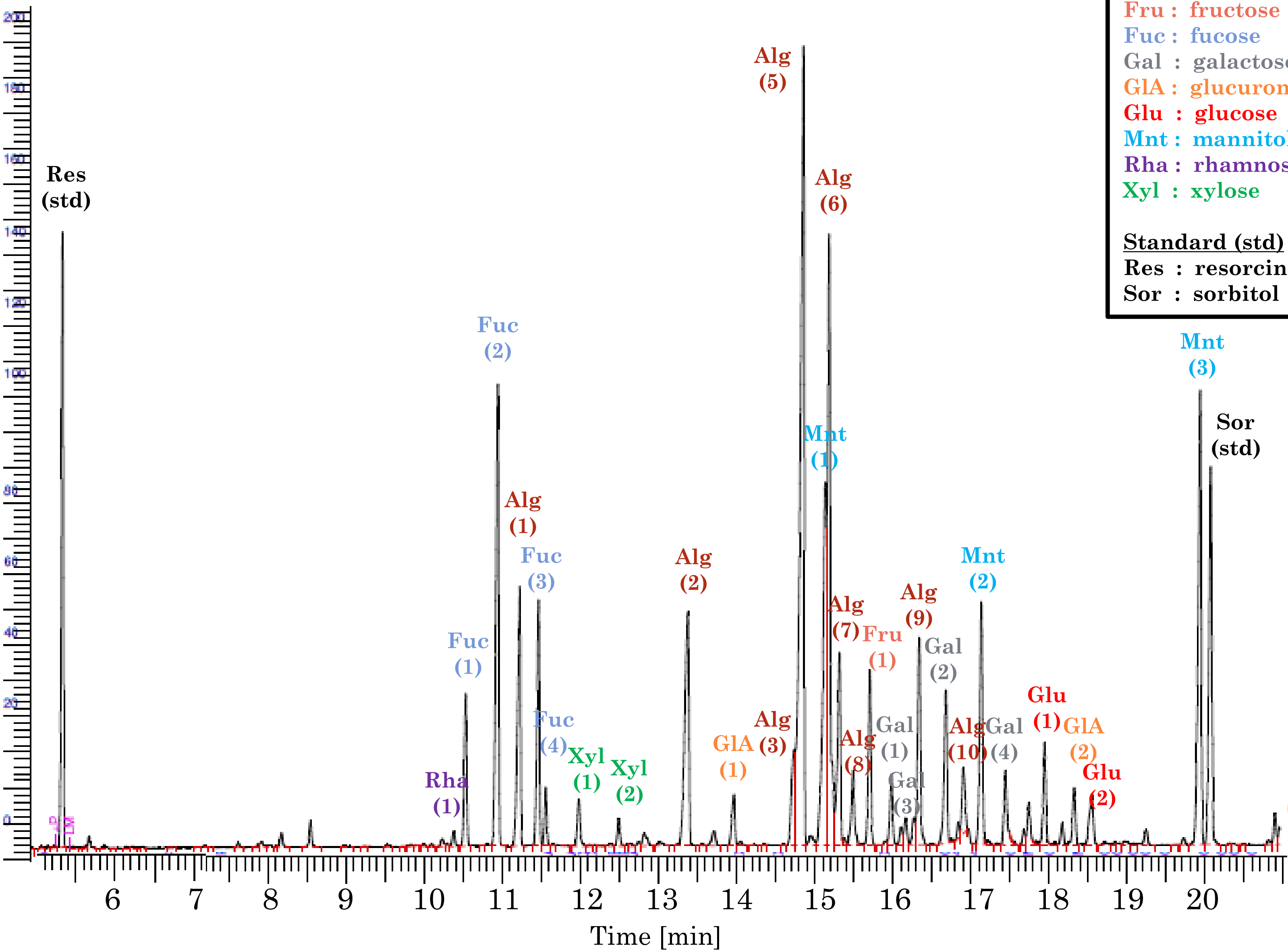
Experimental: Analysis of carbohydrates

Sugars analyzing methods (Sundberg et al, 1996)

- Acid methanolysis method (Sundberg et al, 1996)
  - Methanolysis
    - Reagent — Methanol 2M HCl
    - Conditions — 100°C/3 h
- Acid hydrolysis method (Sundberg et al., 1996)
  - Acid hydrolysis
    - Reagent — sulfuric acid
    - Conditions — autoclave & room T
- Silylation for GC analysis
    - Hexamethyldisilazane (HMDS)
    - Chlorotrimethylsilane
    - Pyridine
    - Conditions — 70°C/45 min
Room T°/overnight



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

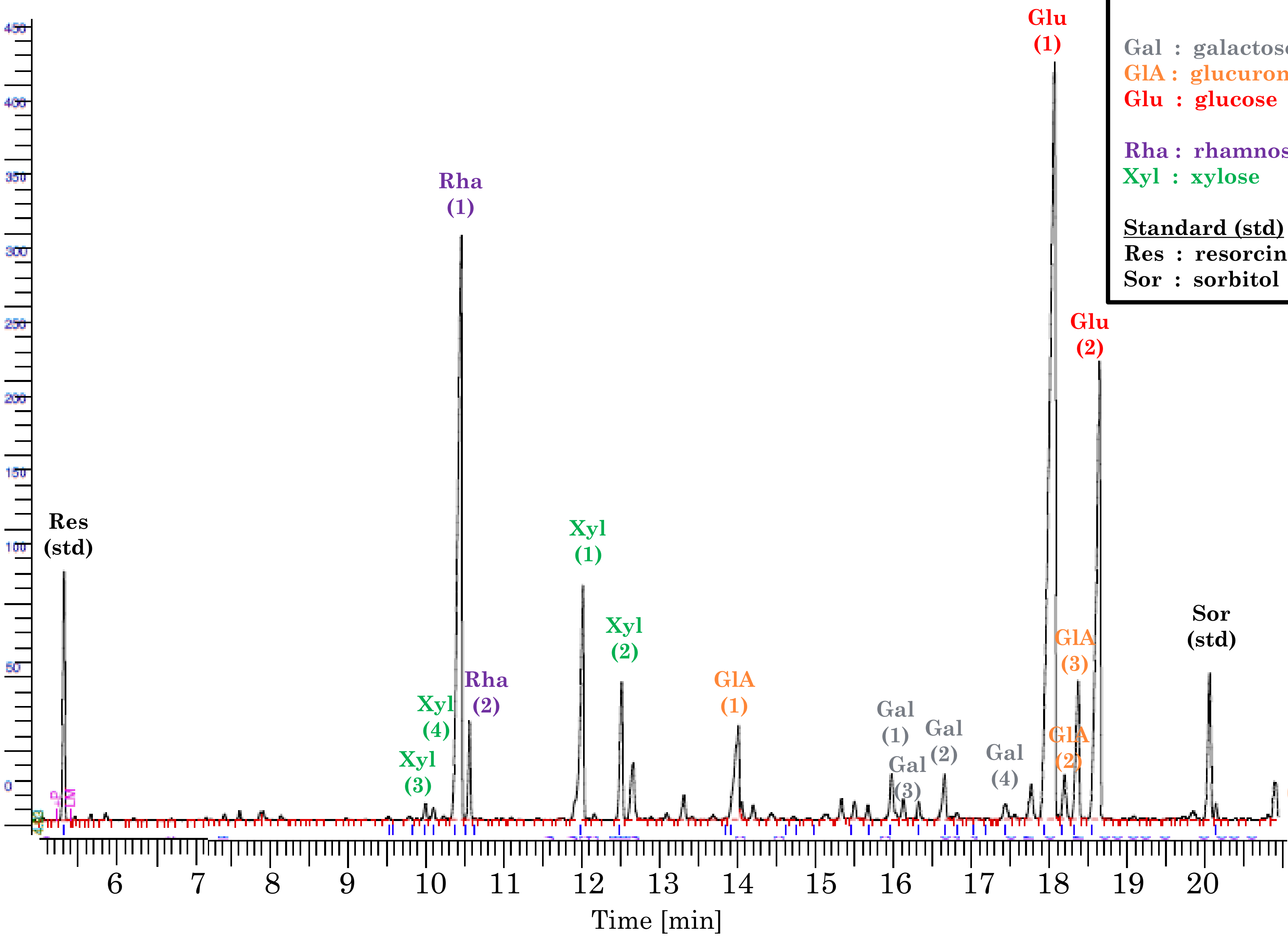
AVG ± STD

[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

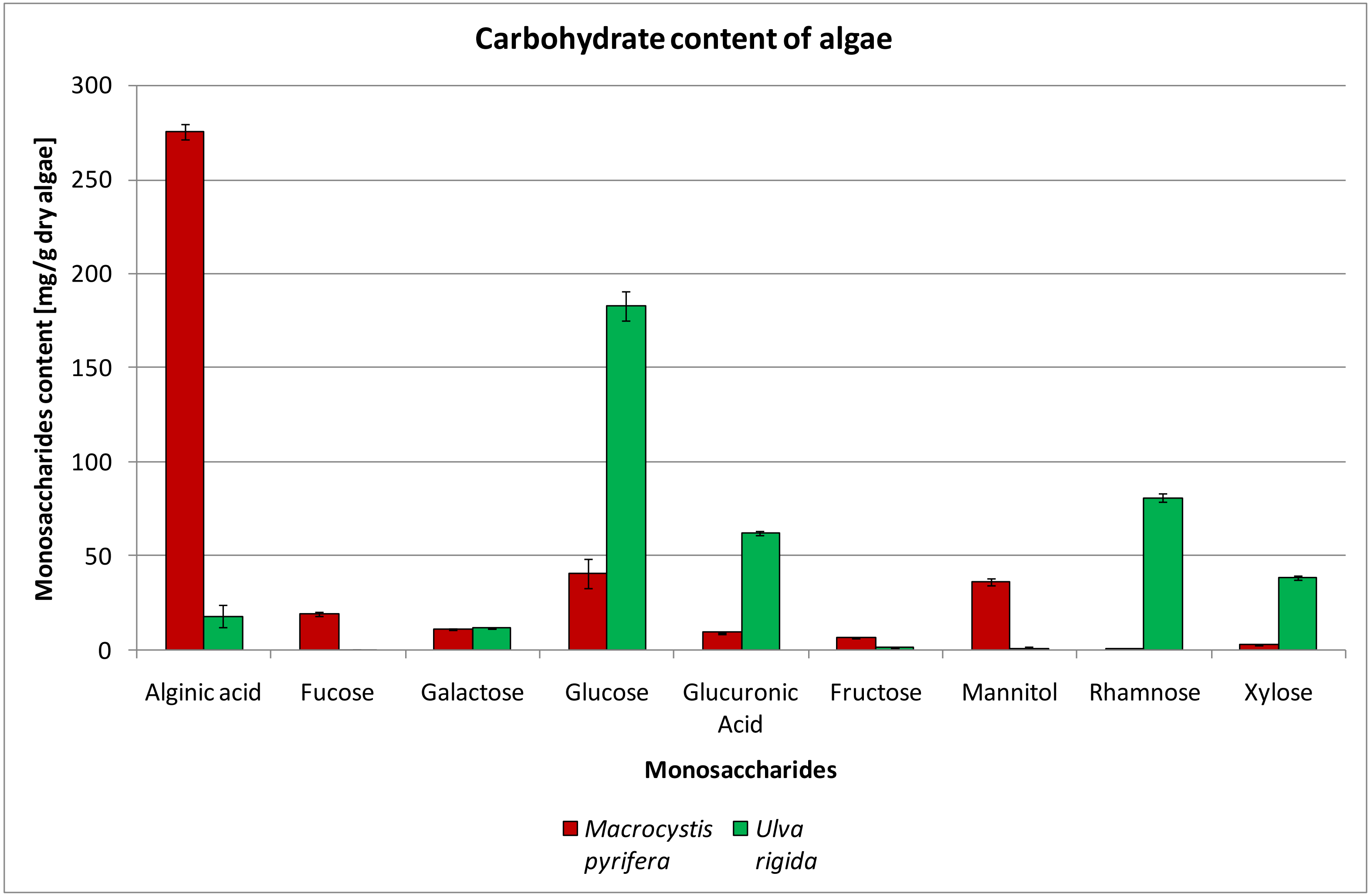
AVG ± STD

[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



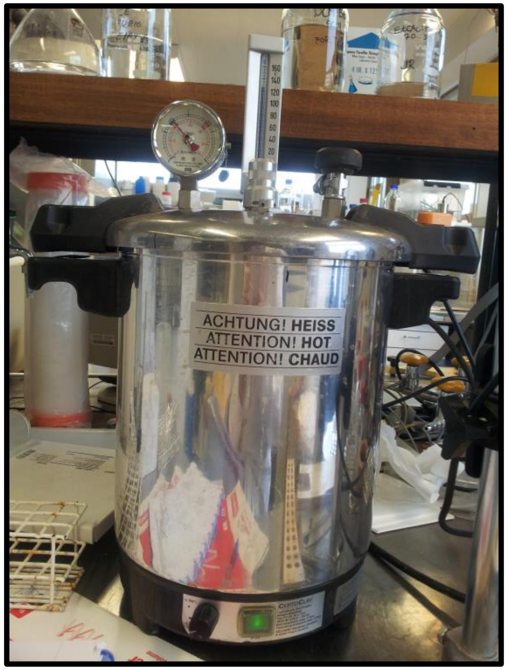
Laboratory meeting

Algae Treatments Experimental

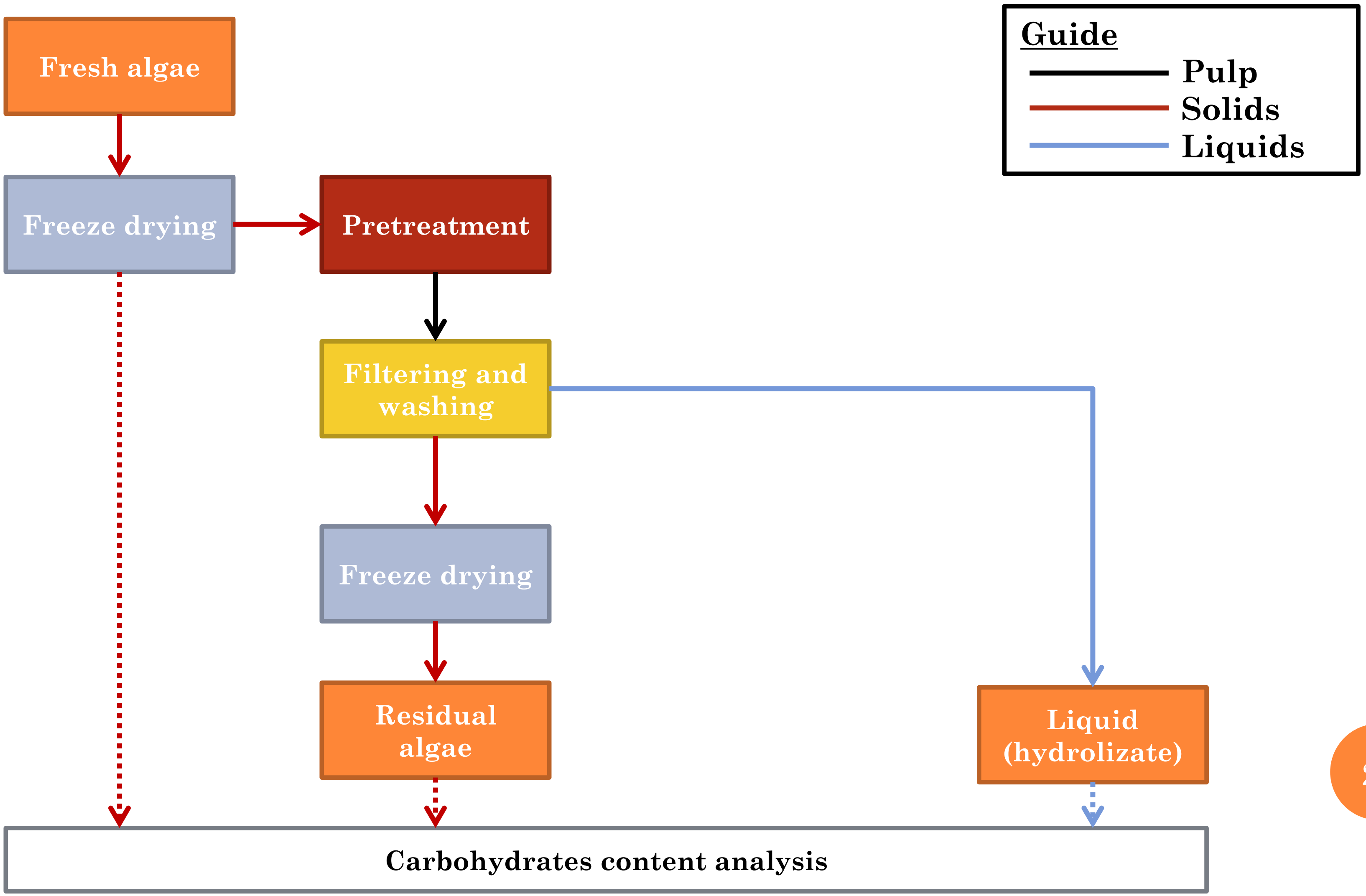
EXPERIMENTAL: ACID PRETREATMENT

Acid / water 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



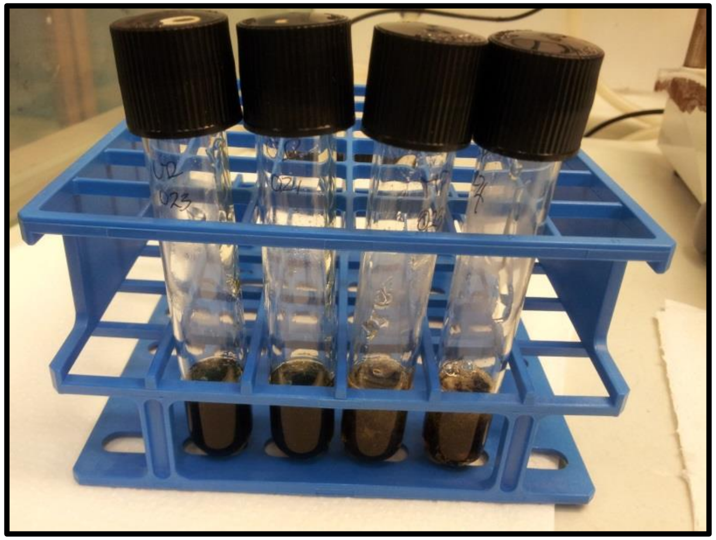
Experimental procedure: Acid treatment



Experimental: Ionic liquid treatment

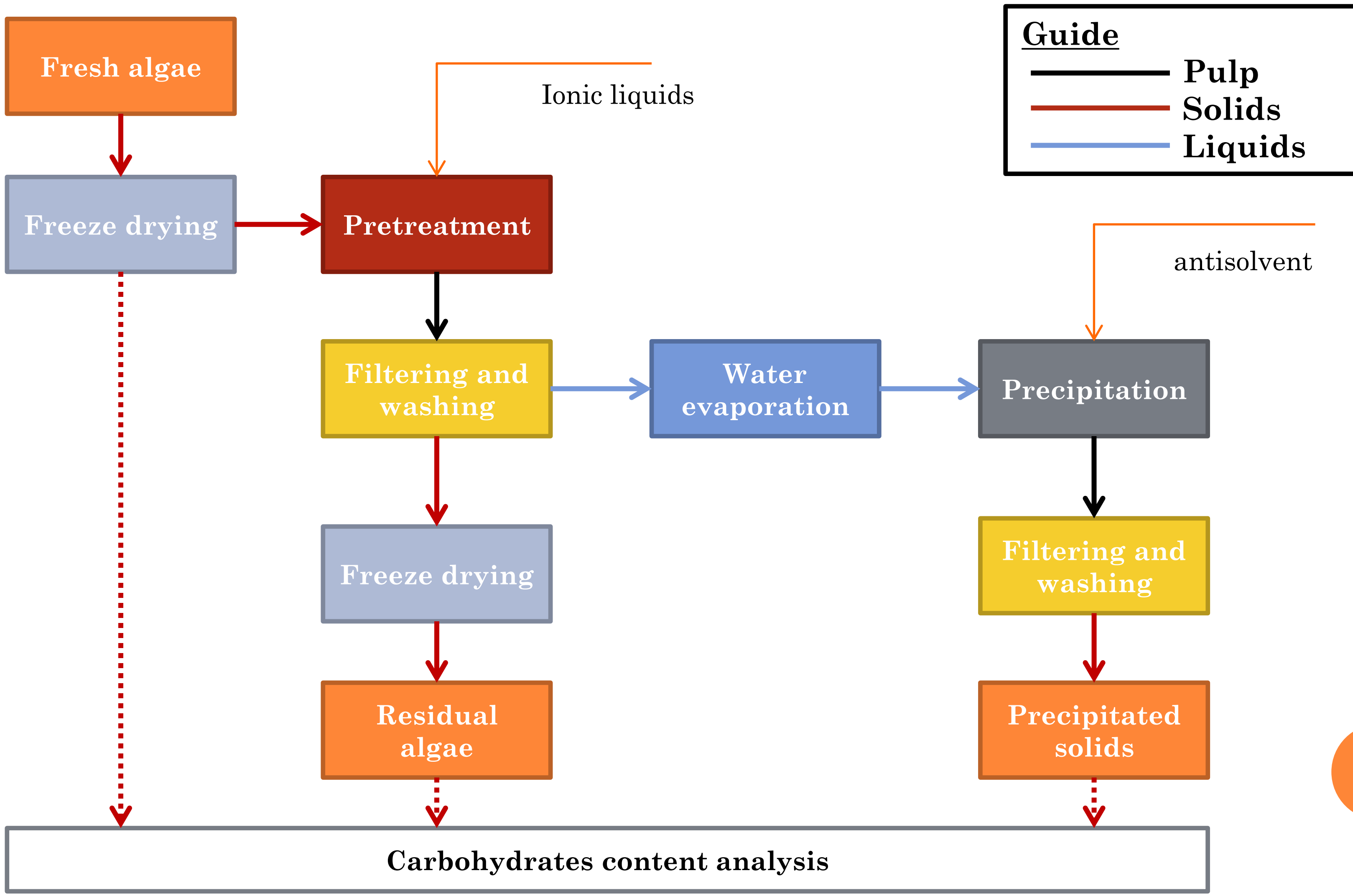
Ionic liquid treatment

- Reagent
  - SIL1 — DBU/MEA/SO_2
  - SIL2 — TMG-CO2Et
- Biomass loading — 10,% w/w
- Temperature — 100 - 130°C
- Pressure — atmospheric
- Stirring — magnetic
- Time — 20 h
- Samples — duplicate



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

EXPERIMENTAL PROCEDURE: IONIC LIQUIDS



Treatment results

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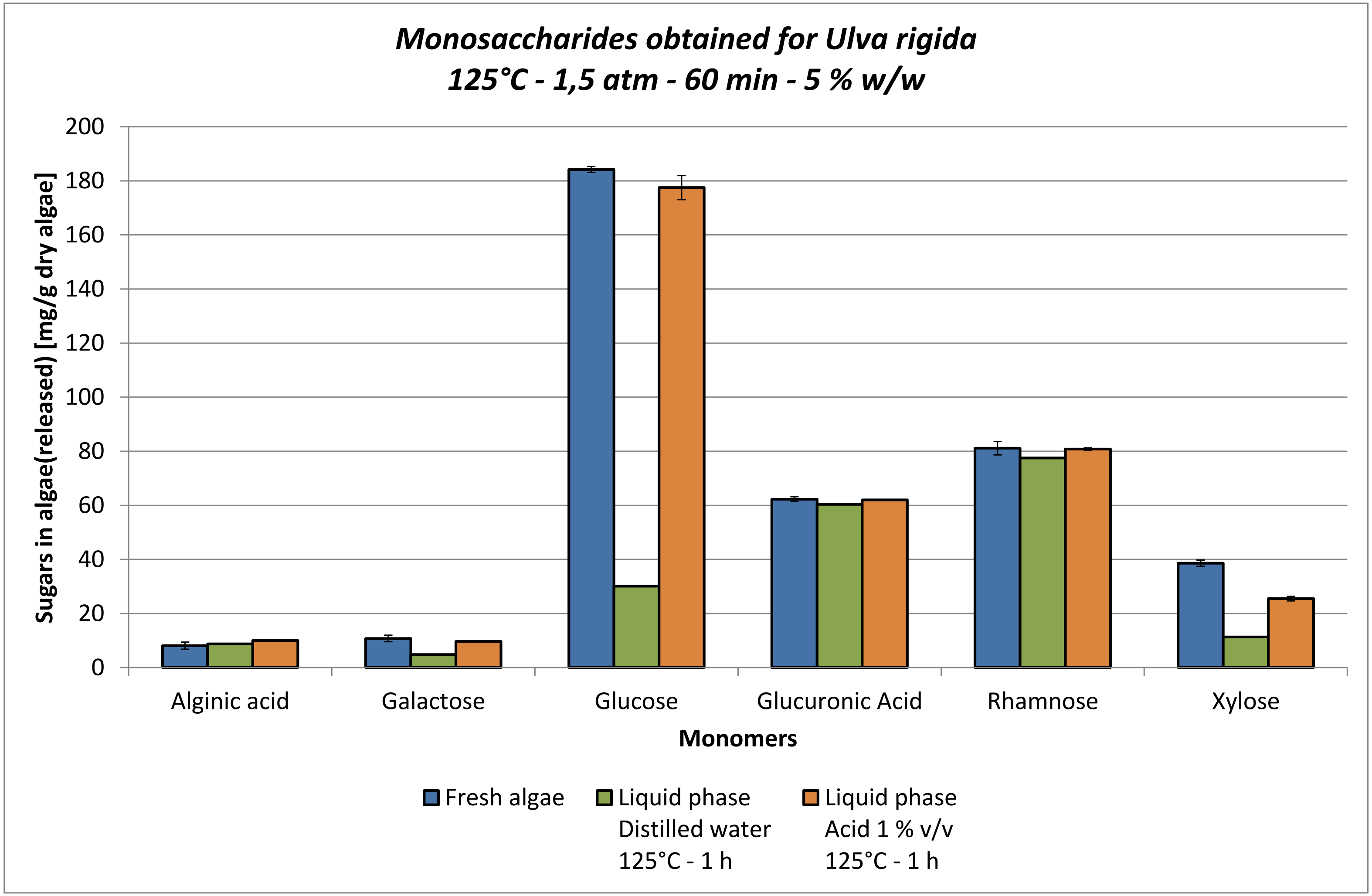
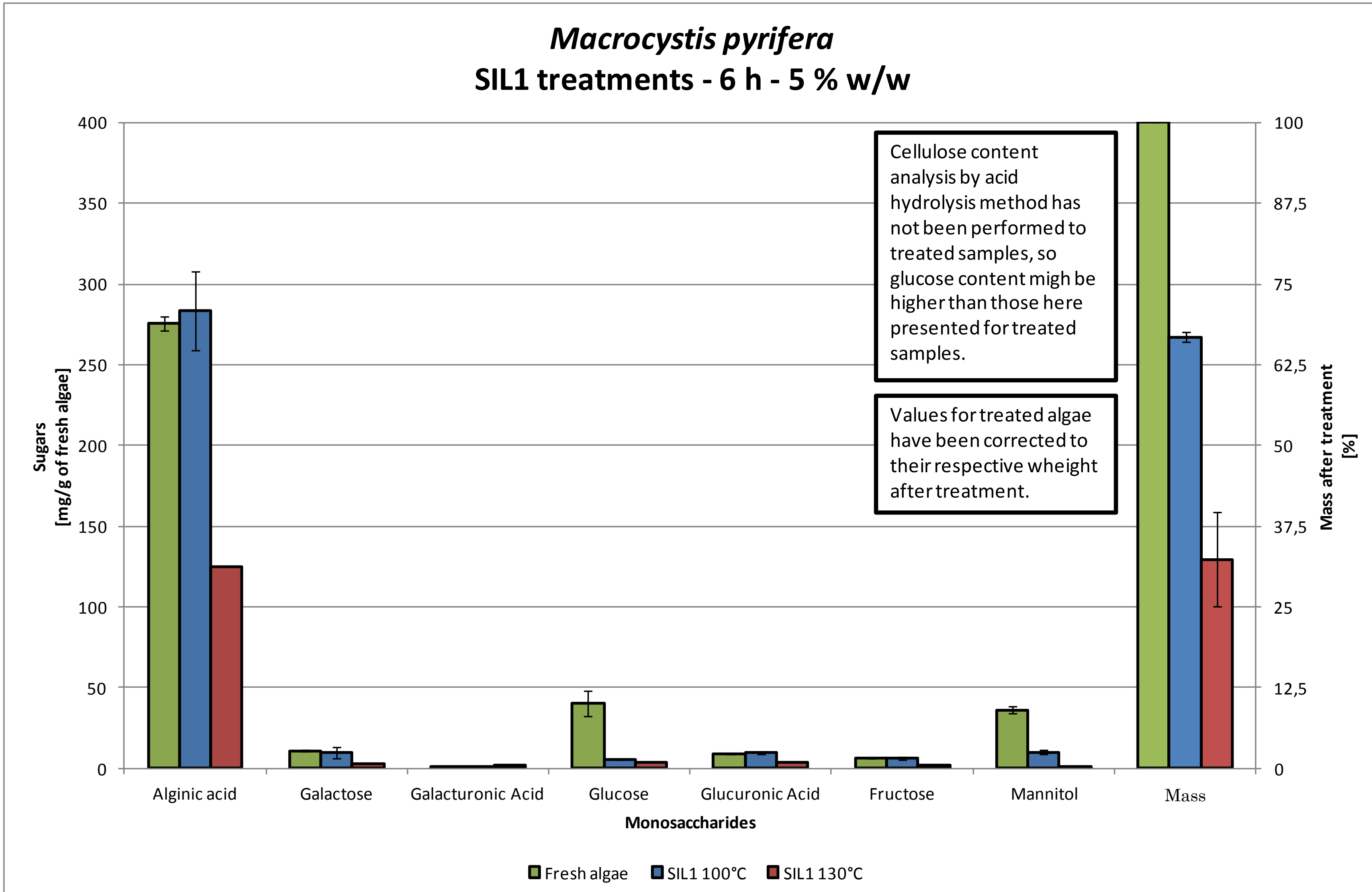
Dilute sulfuric acid treatment *U. rigida*

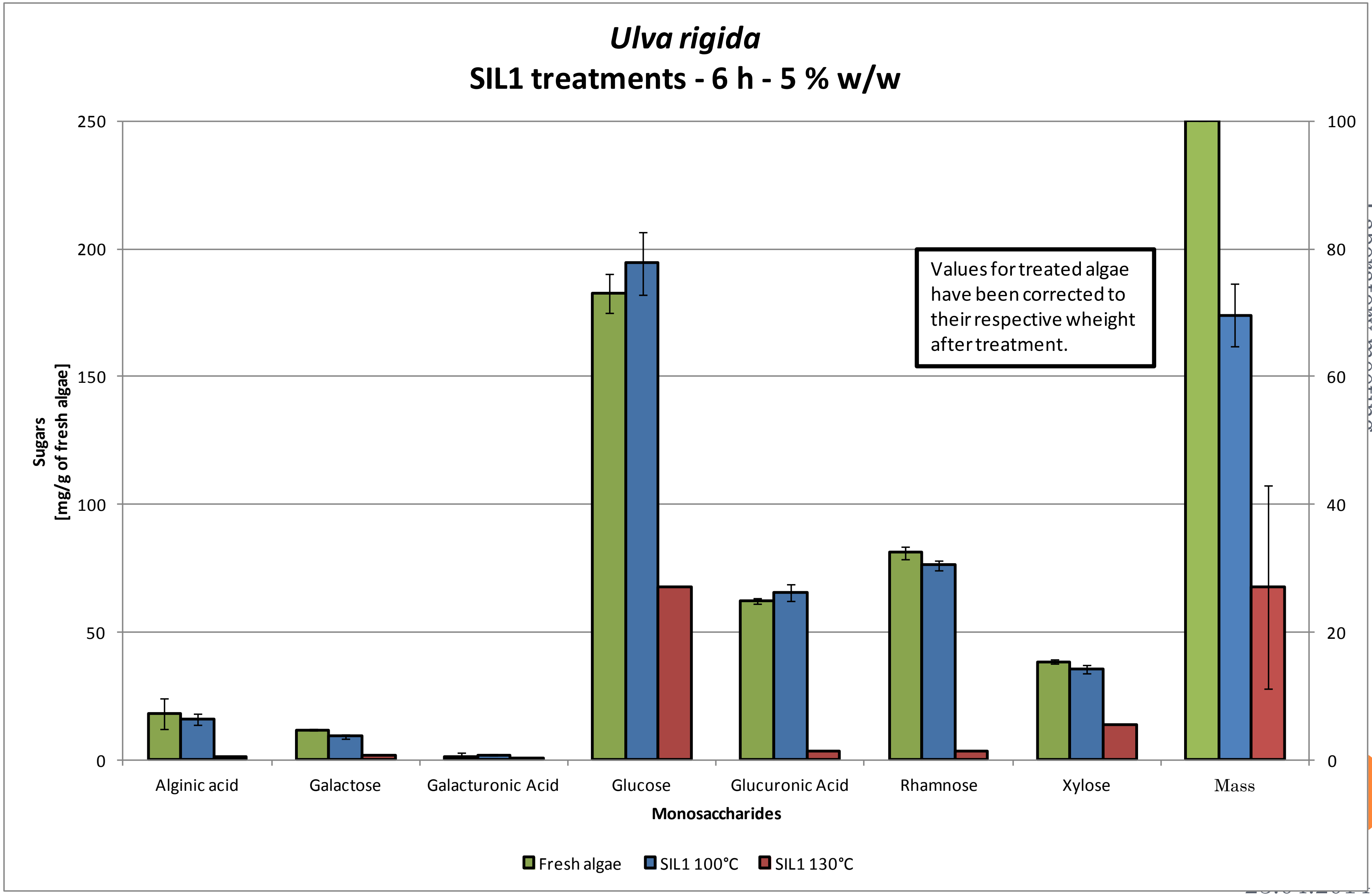


Laboratory meeting

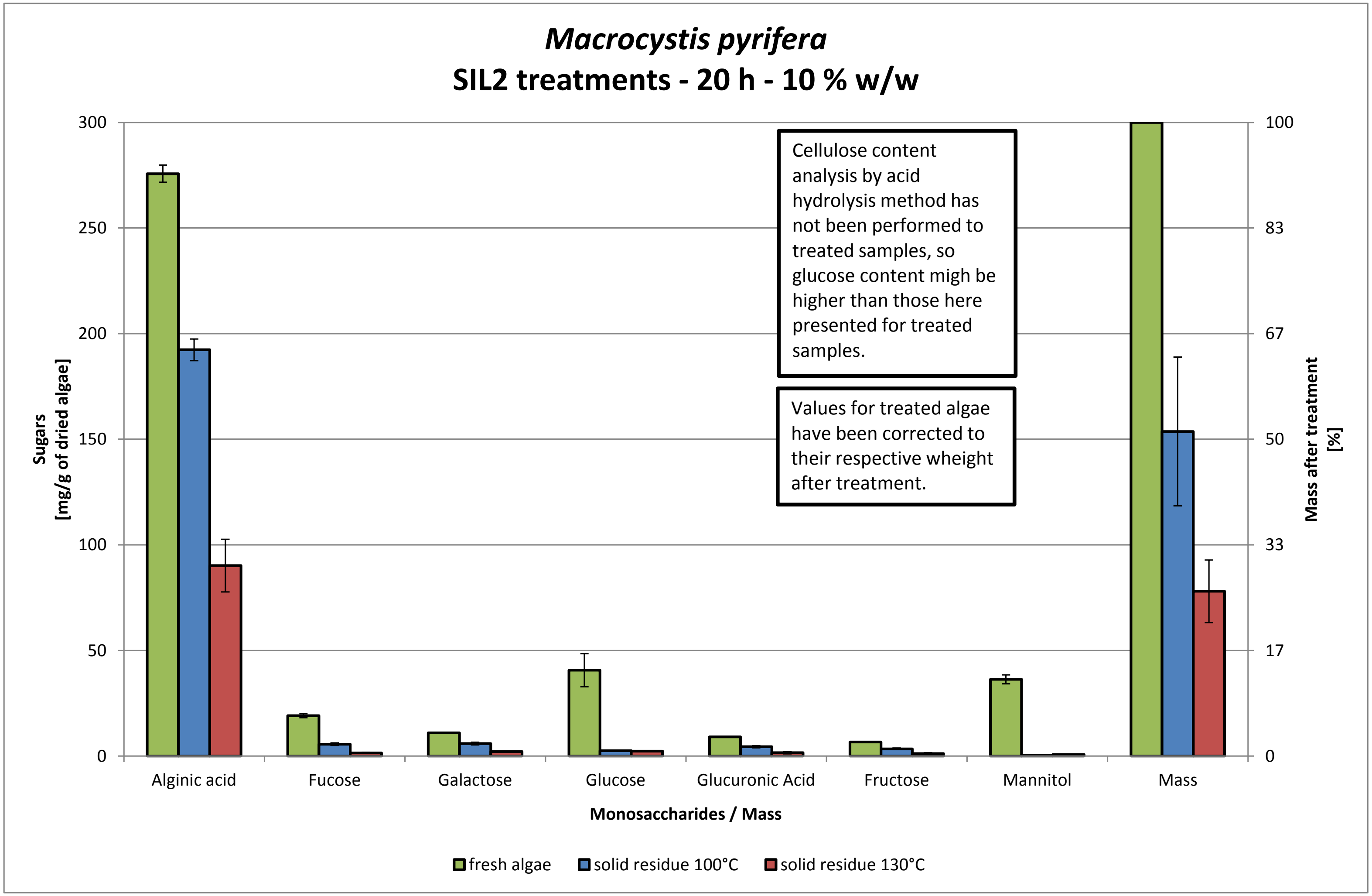
SIL1 TREATMENTS
M. PYRIFERA



SIL1 TREATMENTS
U. RIGIDA



SIL2 TREATMENTS *M. PYRIFERA*



Laboratory meeting

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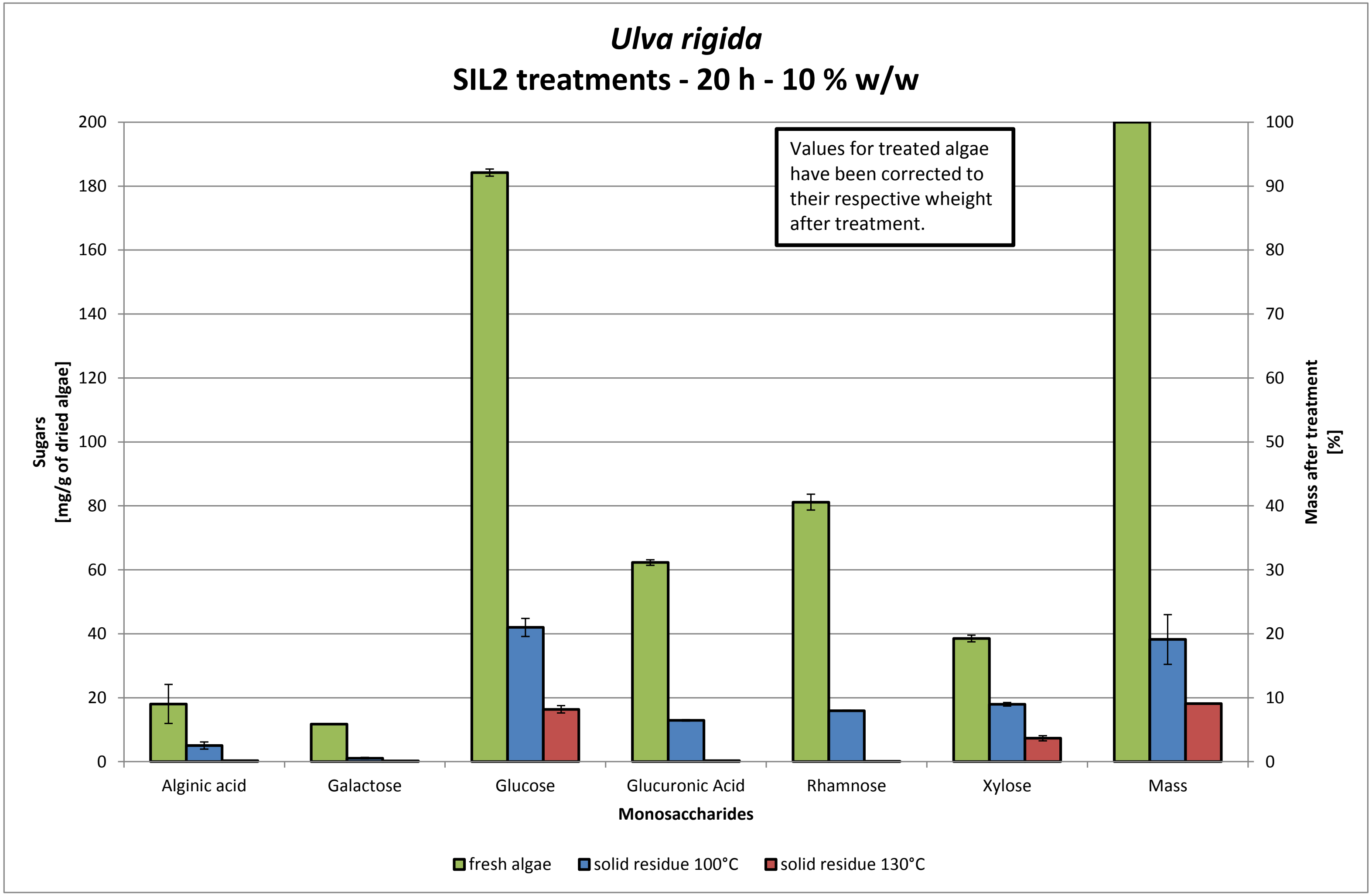
SIL2 TREATMENTS
U. RIGIDA



Laboratory meeting

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.
- IL treatments show high solubility of sugars at 130°C. Nevertheless characterization of liquid fraction is a big challenge to quantify sugars present in this fraction.

ACKNOWLEDGEMENTS

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