Where are we with green biorefineries?

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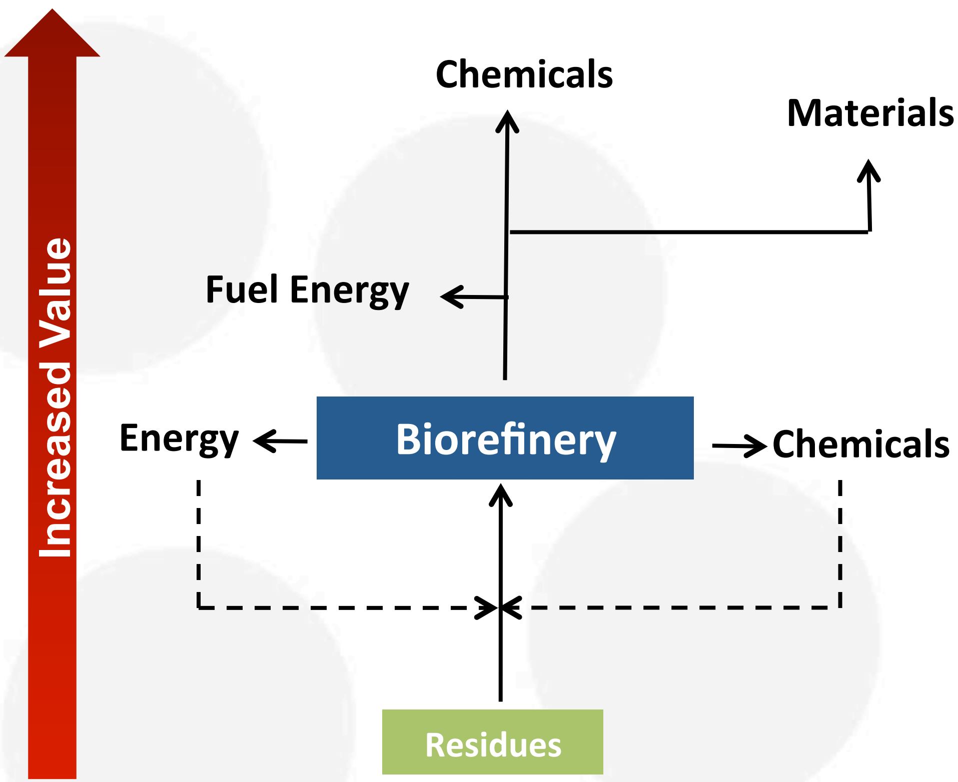
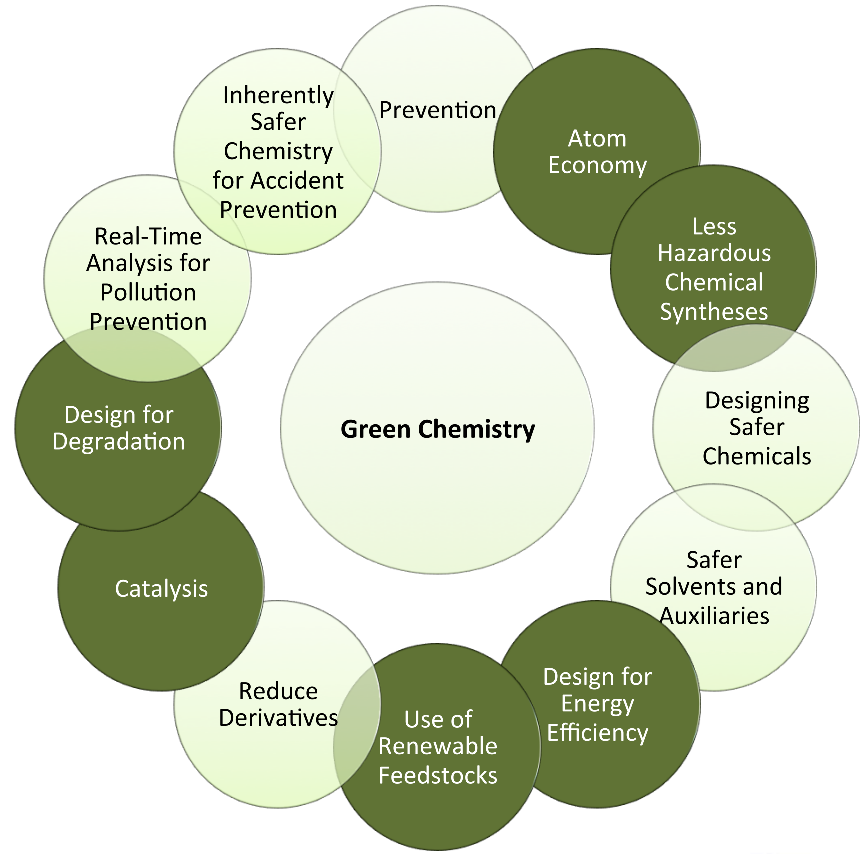
Biorefinery and the role of Green Chemistry



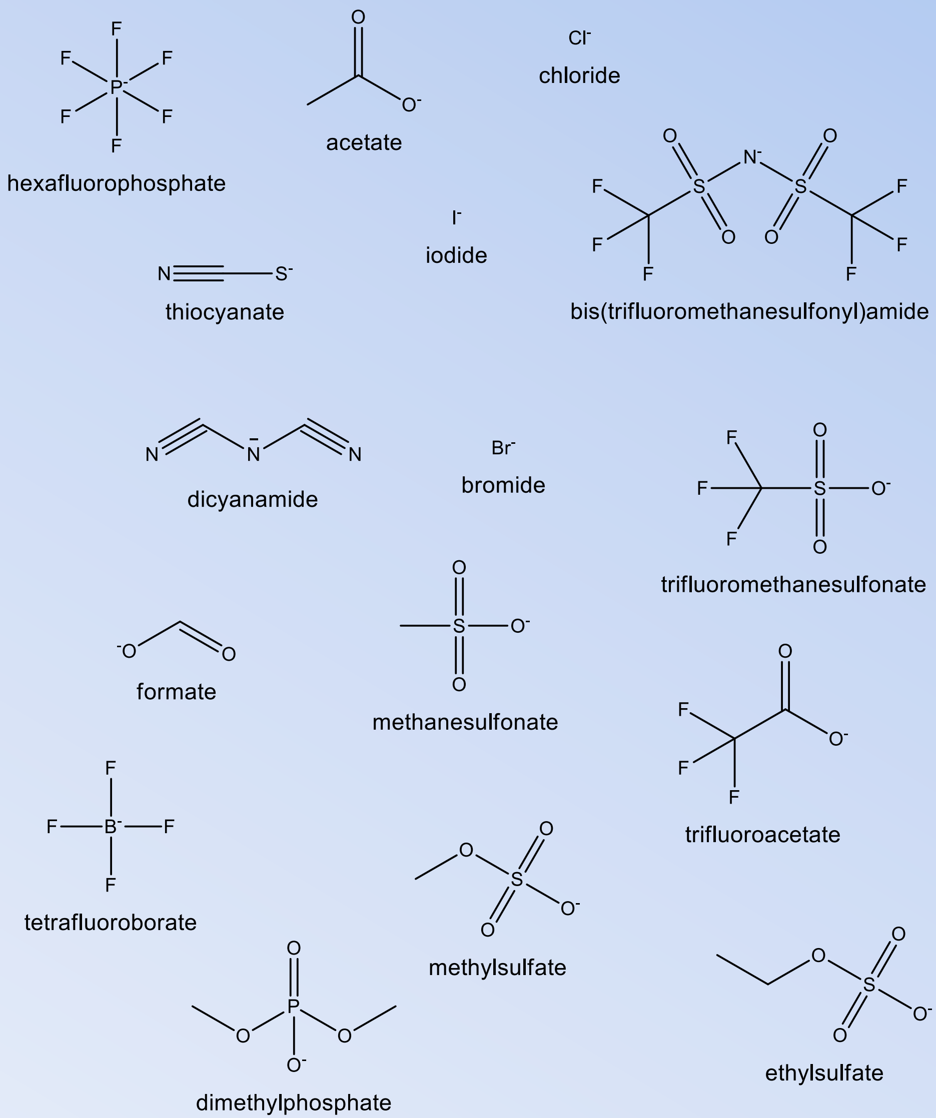
SIADEB www.siadeb.org (2014)



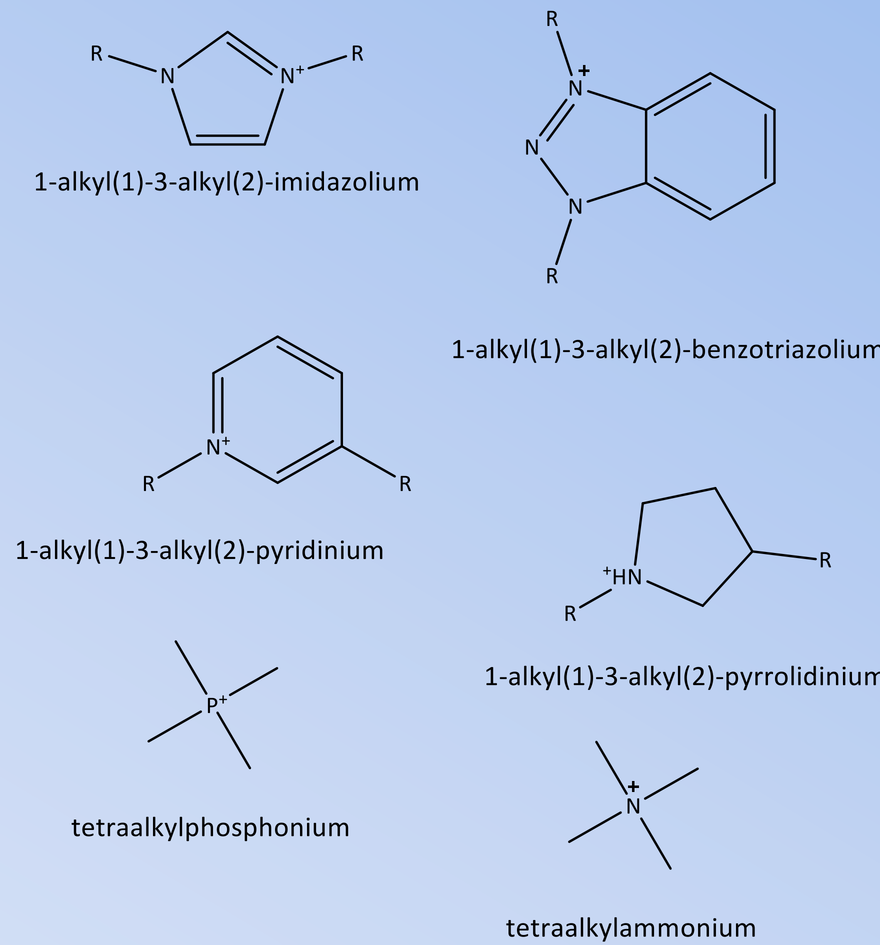
P.T. Anastas and J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.

What ionic liquids are?

Anions



Cations



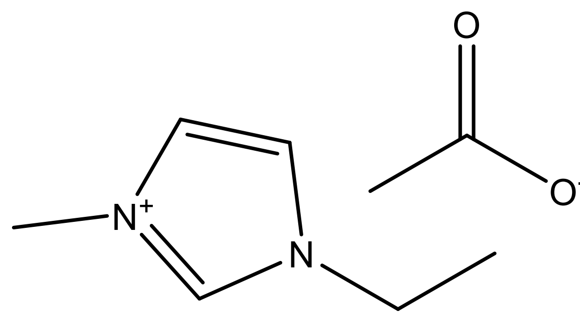
Properties of ILs

- **High polarity**
- **Negligible volatility**
- **Thermal stability**
- **High conductivity**
- **Large electrochemical window**

✓ **Solvent power**

Properties of ILs can be tailored, e.g.:

- **Density and Viscosity**
- **Solubility**
- **Lipophilicity and polarity**



1-ethyl-3-methylimidazolium acetate

The **toxicity** and **biodegradability** of ionic liquids are an issue

Pre-treatment of biomass with ILs

1) Alter the physicochemical properties of the biomass macromolecular components;
2) Extract a specific macromolecular fraction;
3) Perform different fractionation approaches after dissolution.

Advantages:

- ✓ ↓ Cellulose crystallinity;
- ✓ ↑ Extraction of lignin
- ✓ Less degradation of monosaccharides;
- ✓ Recyclability and reuse of ILs.

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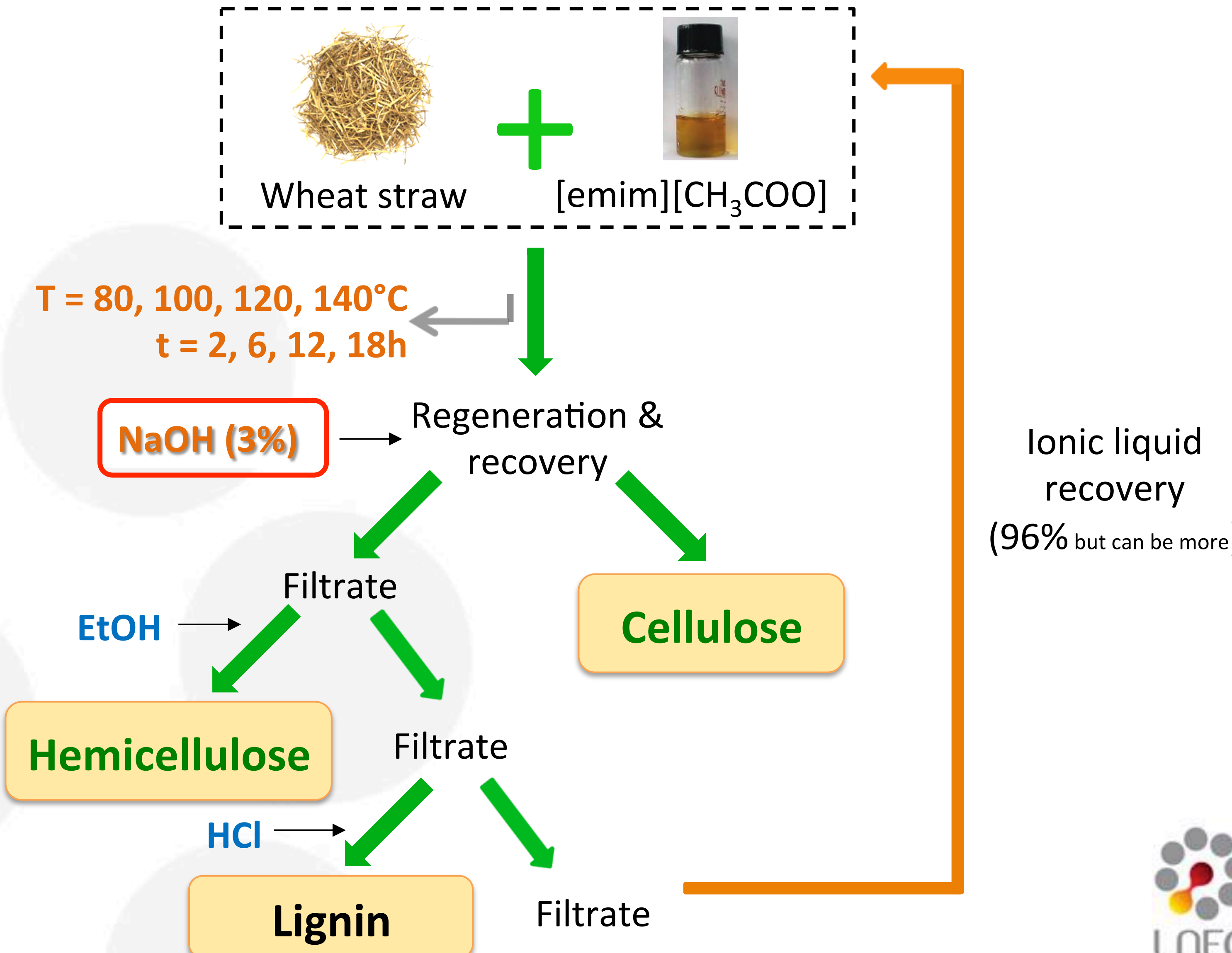
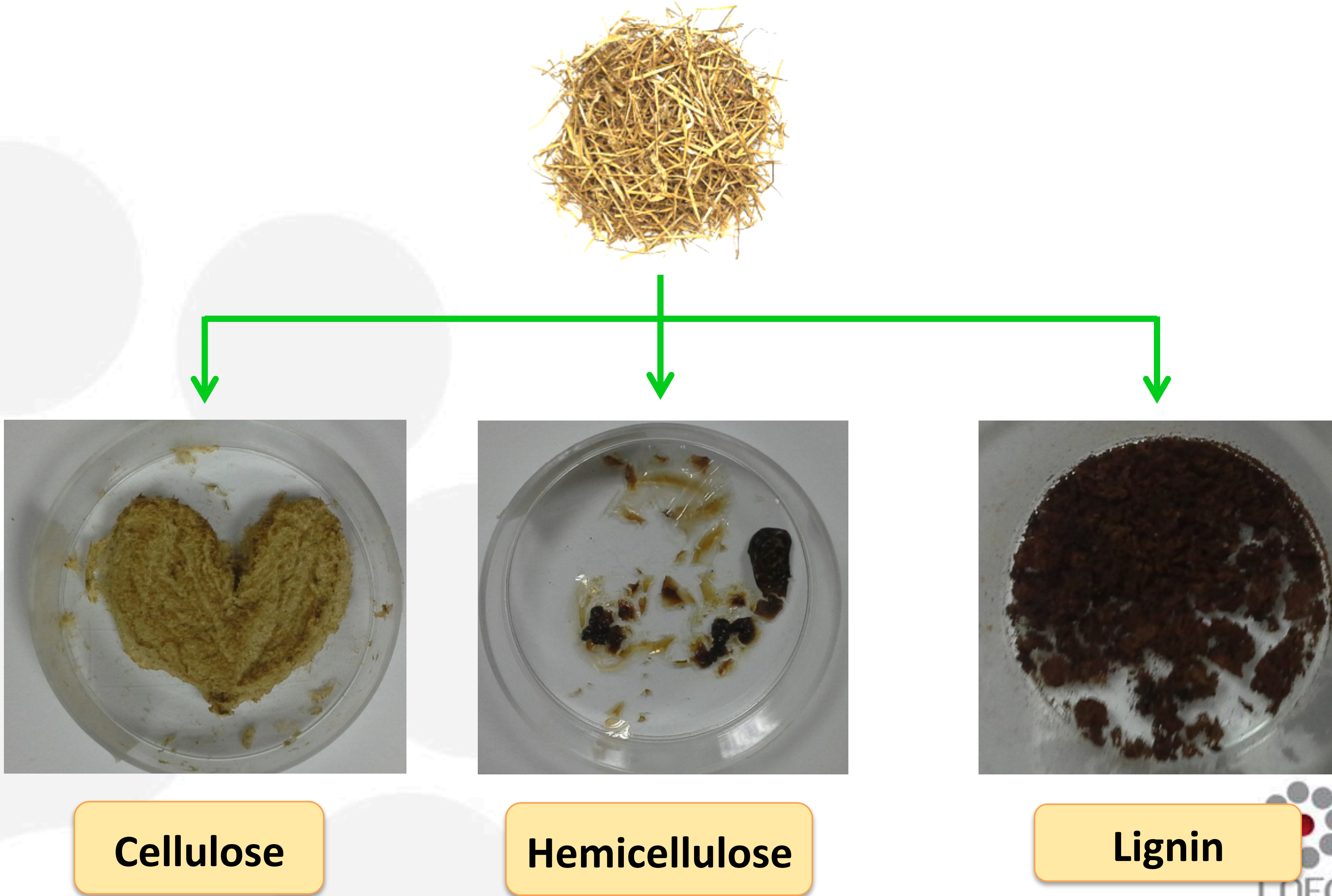
A. M. da Costa Lopes, K. João, A. R. C. Morais, E. Bogel-Lukasik and R. Bogel-Lukasik, *Sustain. Chem. Process.*, 2013, **1:3**

3-step fractionation

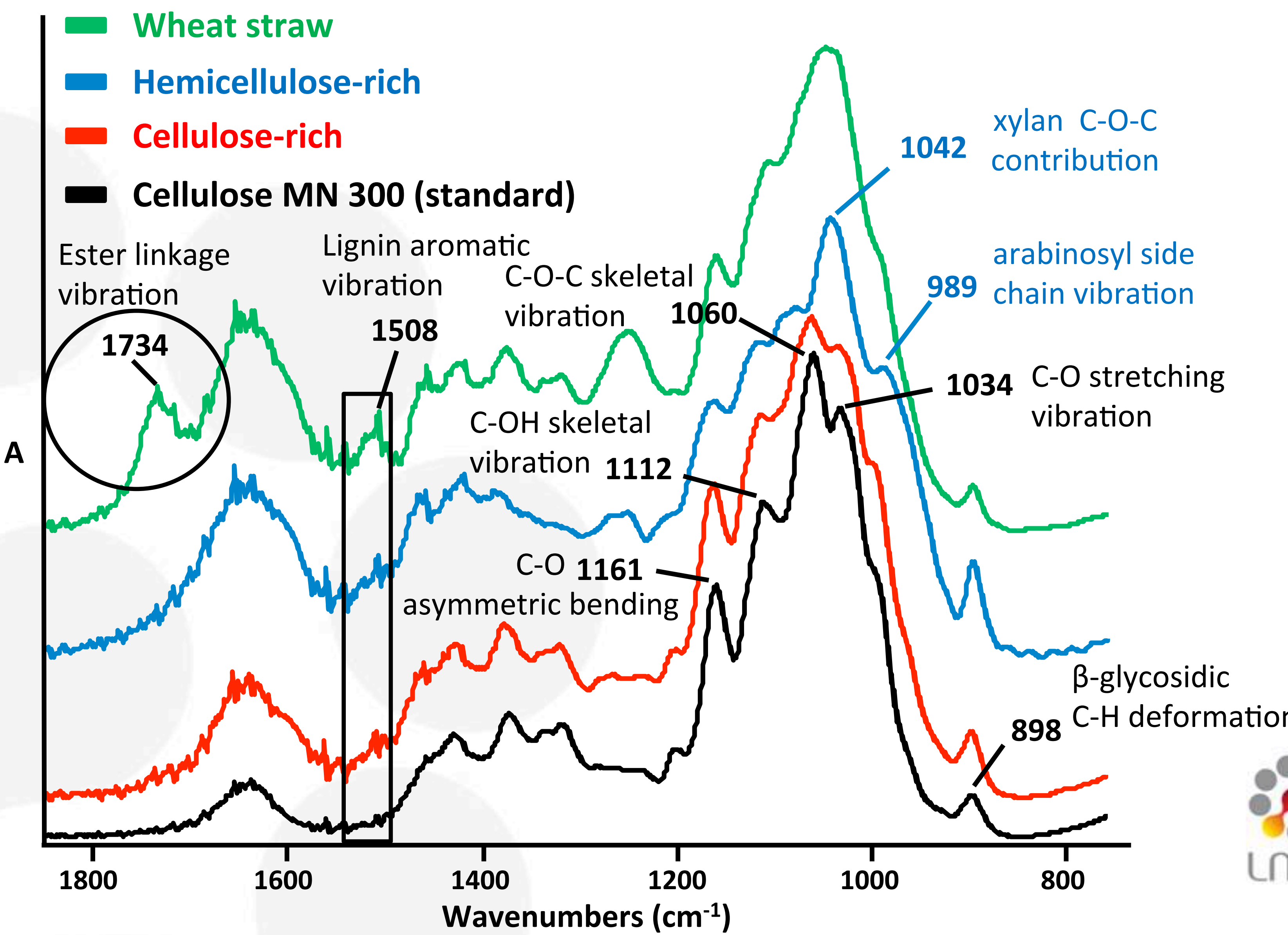


S. P. Magalhães da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Adv.*, 2013, **3**, 16040.
A. M. da Costa Lopes, R. Bogel-Łukasik, Portuguese Provisory Patent (106947), 2013.

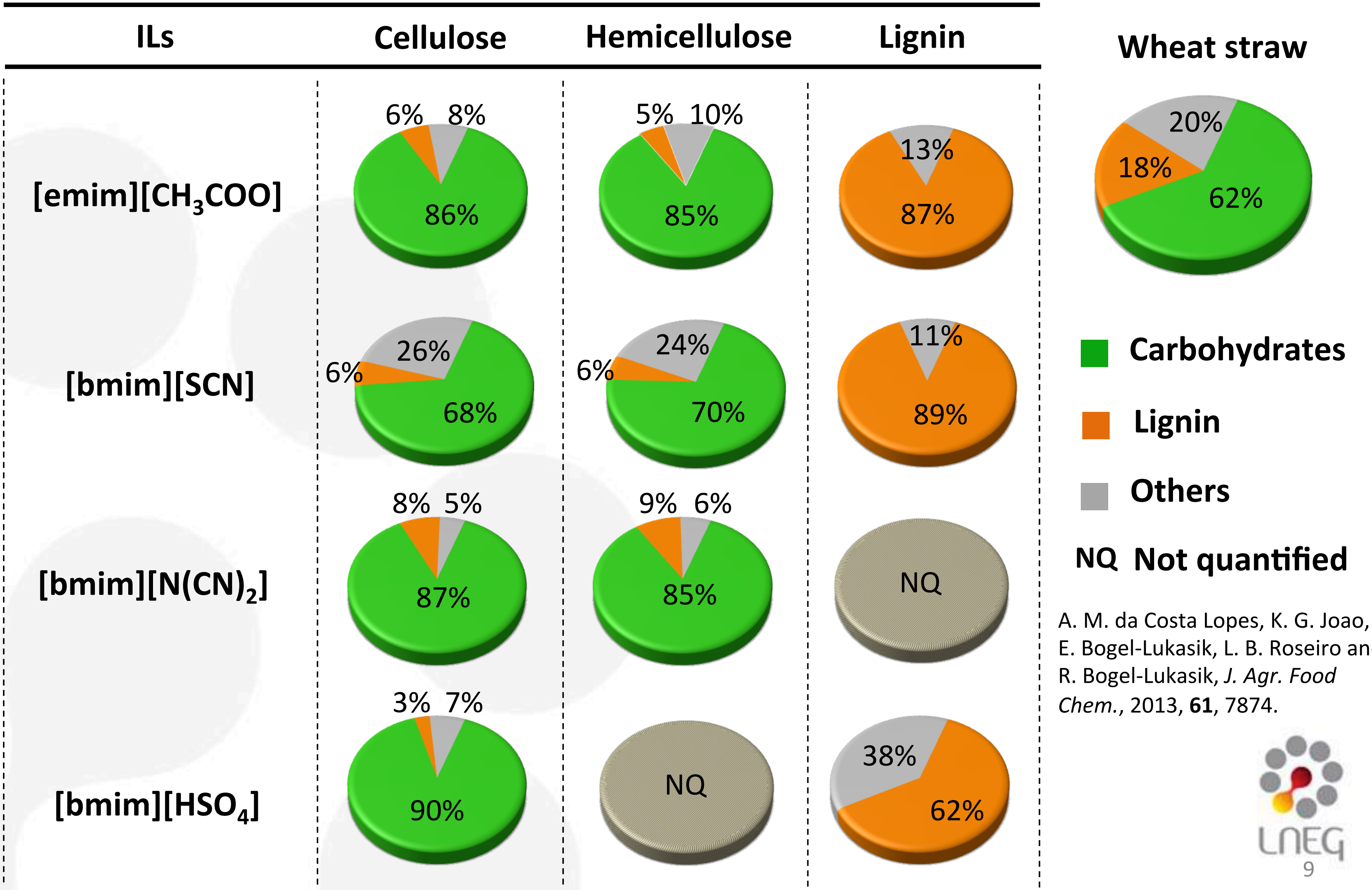
3-step fractionation



FTIR spectra of carbohydrate samples



Results with ILs



A. M. da Costa Lopes, K. G. Joao, E. Bogel-Lukasik, L. B. Roseiro and R. Bogel-Lukasik, *J. Agr. Food Chem.*, 2013, **61**, 7874.

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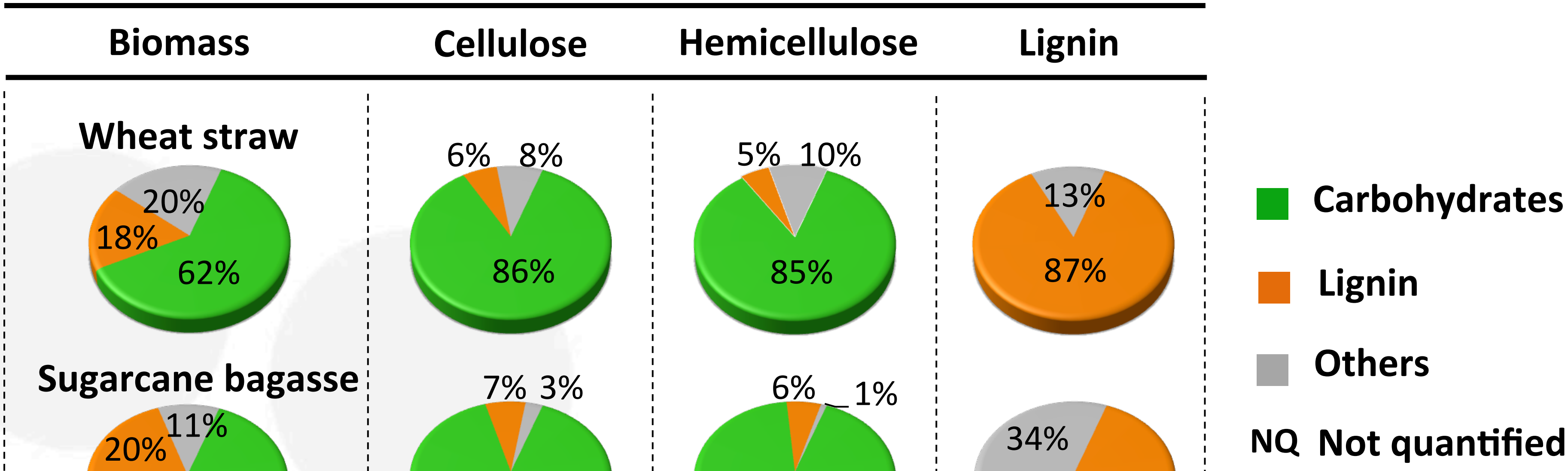
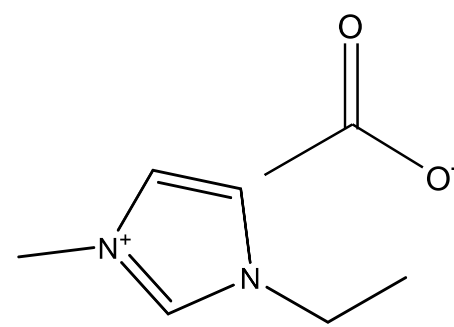
Results with different types of biomass





[emim][CH_3COO]

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Enzymatic hydrolysis

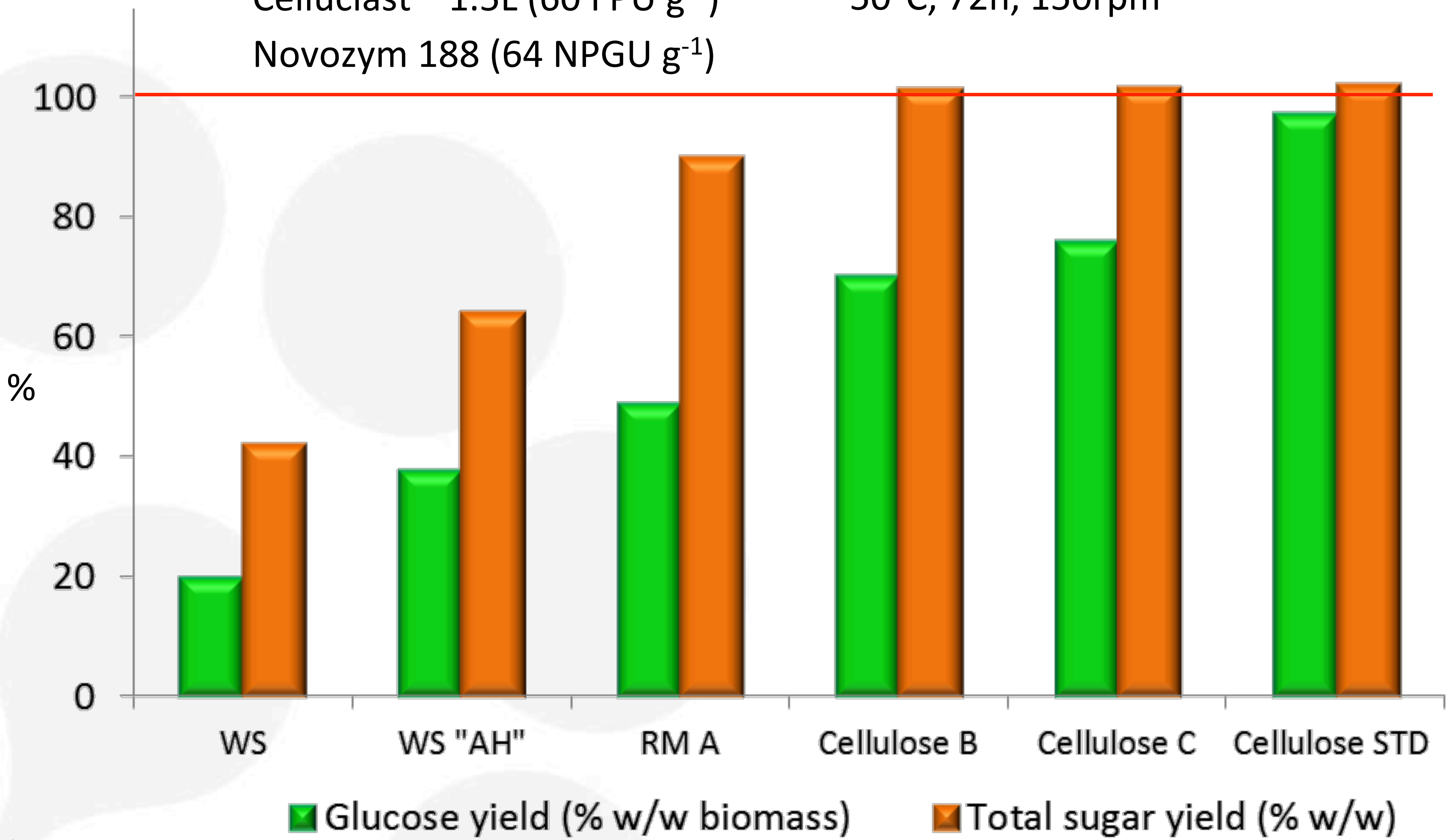
Enzymes:

Celluclast® 1.5L (60 FPU g^{-1})

Novozym 188 (64 NPGU g^{-1})

Conditions:

50°C, 72h, 150rpm

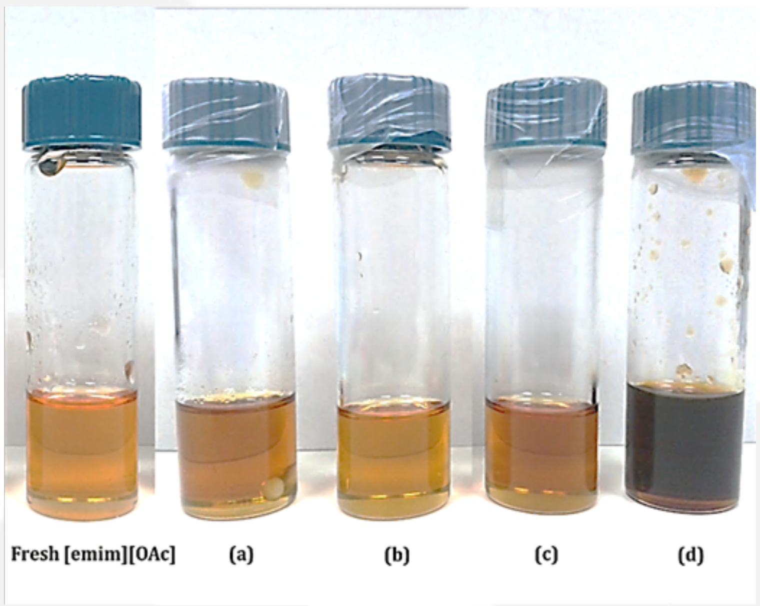


WS – wheat straw; AH – acid hydrolysed; RM – regenerated material; STD - standard

A. M. da Costa Lopes, K. João, D. Rubik, E. Bogel-Lukasik, L. C. Duarte, J. Andreaus and R. Bogel-Lukasik, *Bioresource Technol.*, 2013, **142**, 198-208

CE analysis of recovered [emim][CH_3COO]

✓ ILs **recovery yields** were generally **up** to **90% (w/w)**.



Colour of the fresh [emim][OAc] and recovered ILs after the wheat straw pre-treatment at different temperatures: **(a)** 80°C; **(b)** 100°C; **(C)** 120°C and **(d)** 140°C.

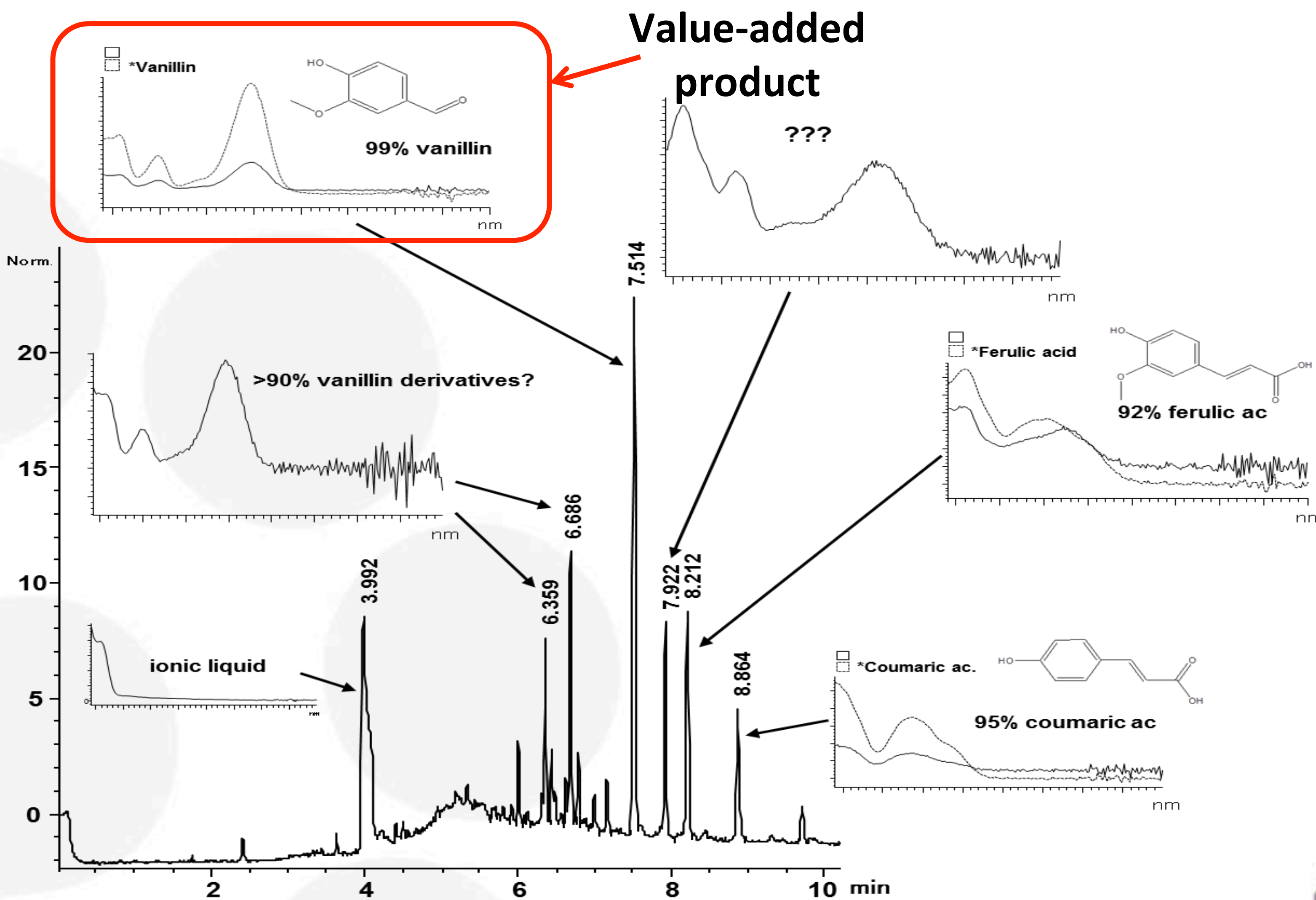
Solid Phase Extraction (SPE)

→

Capillary Electrophoresis (CE)

S. P. Magalhães da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Adv.*, 2013, **3**, 16040.

CE analysis of recovered [emim][CH_3COO]



Electropherogram recorded at 320 nm showing the phenolic profile of the recovered IL after pre-treatment at 100°C during 18h.

S. P. Magalhães da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Adv.*, 2013, **3**, 16040.

Phenolic extraction from recovered IL

Recovered [emim] $[CH_3COO]$

+

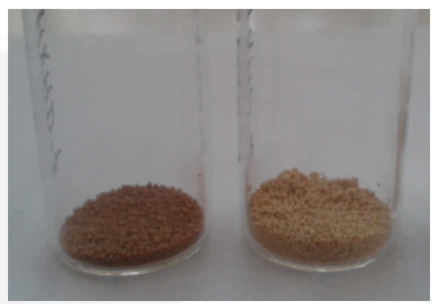
Adsorption Resin

- Small scale batch process

T = room temperature
t = 30 minutes

↓

- Filtration
- Washing (H_2O)



↓

- Extraction of phenolics (MeOH)

Identification and quantification of phenolics by capillary electrophoresis

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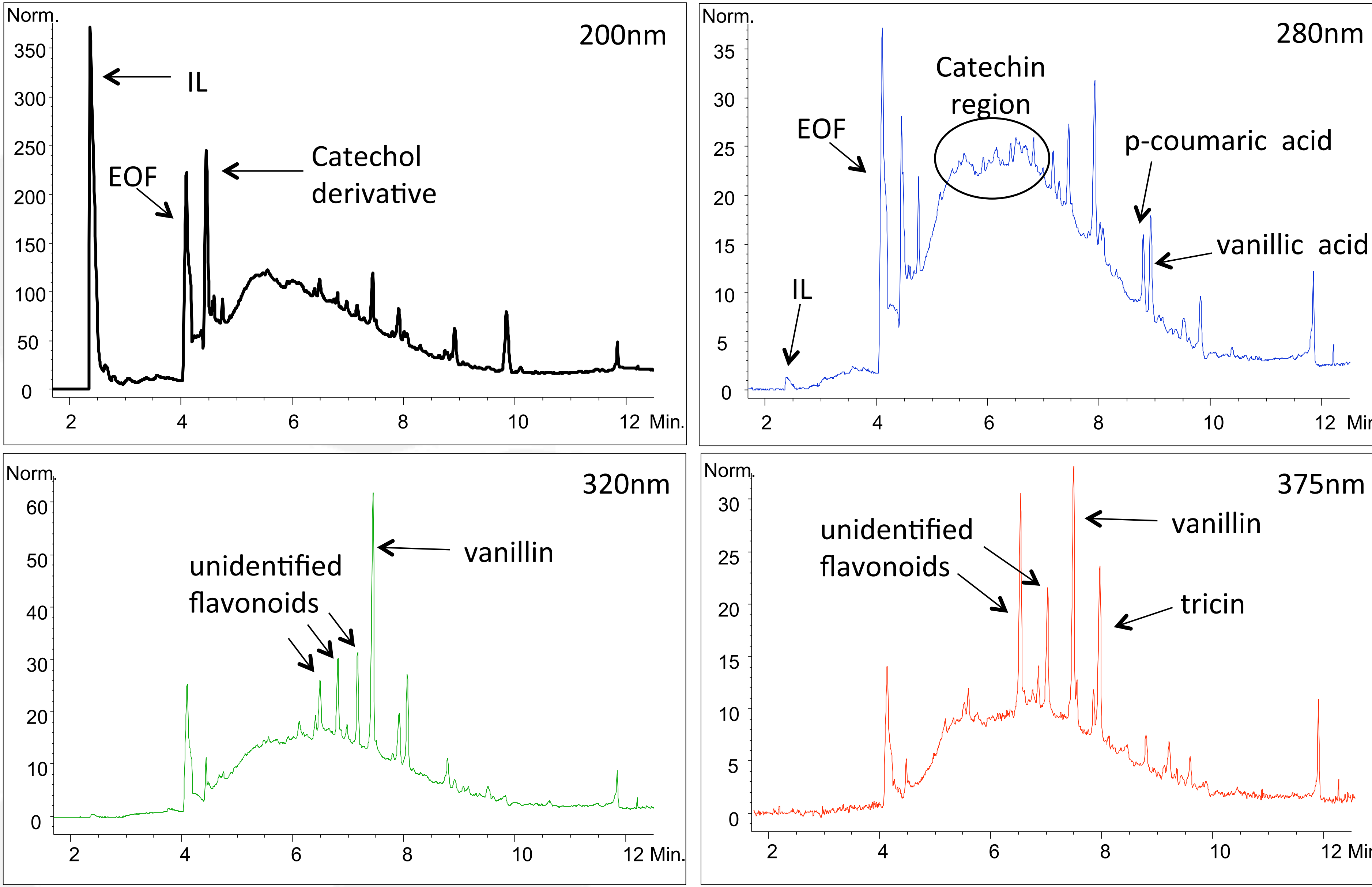
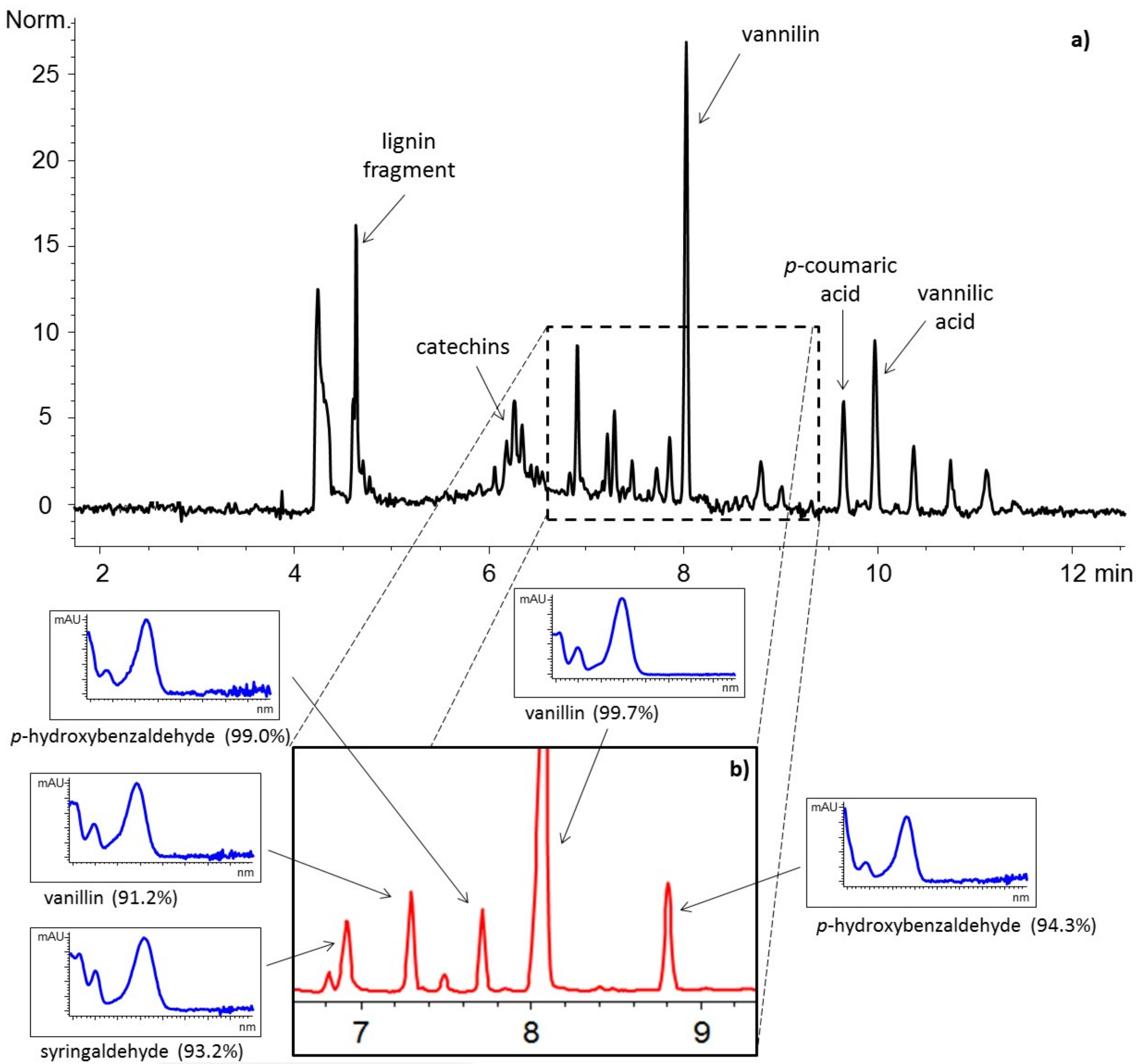
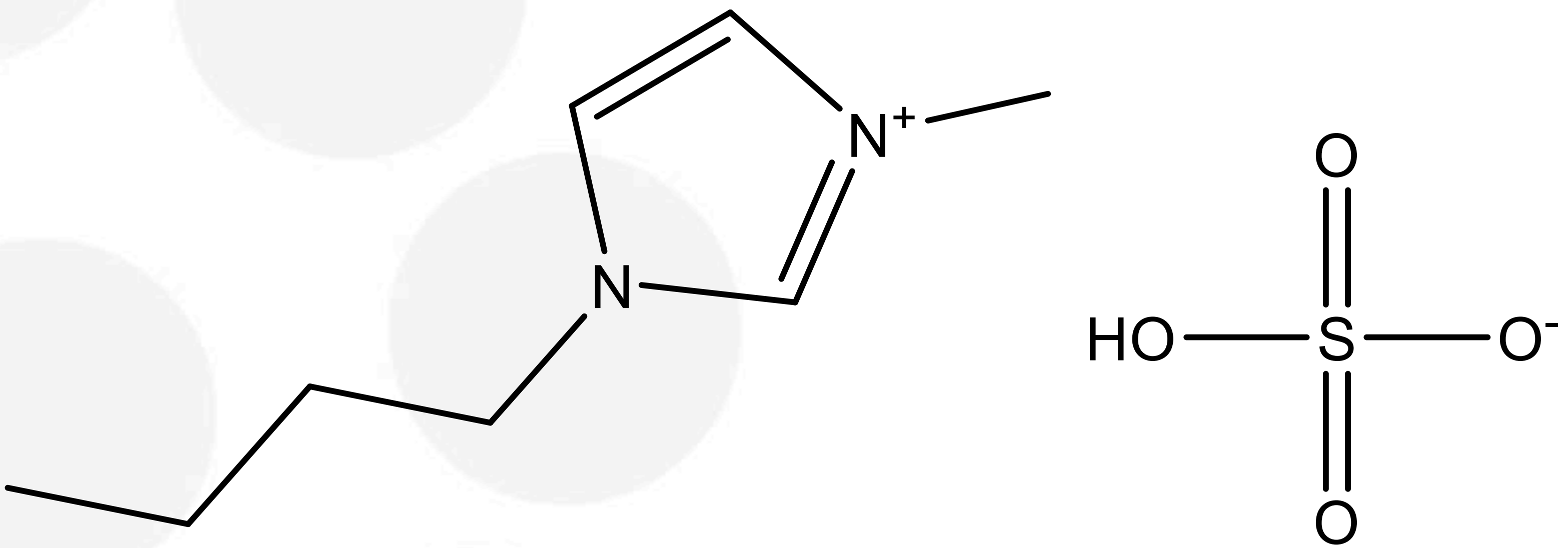
CE of extracted samples by Amberlite XAD-7



CE of extracted samples by resin and CO_2 treatment

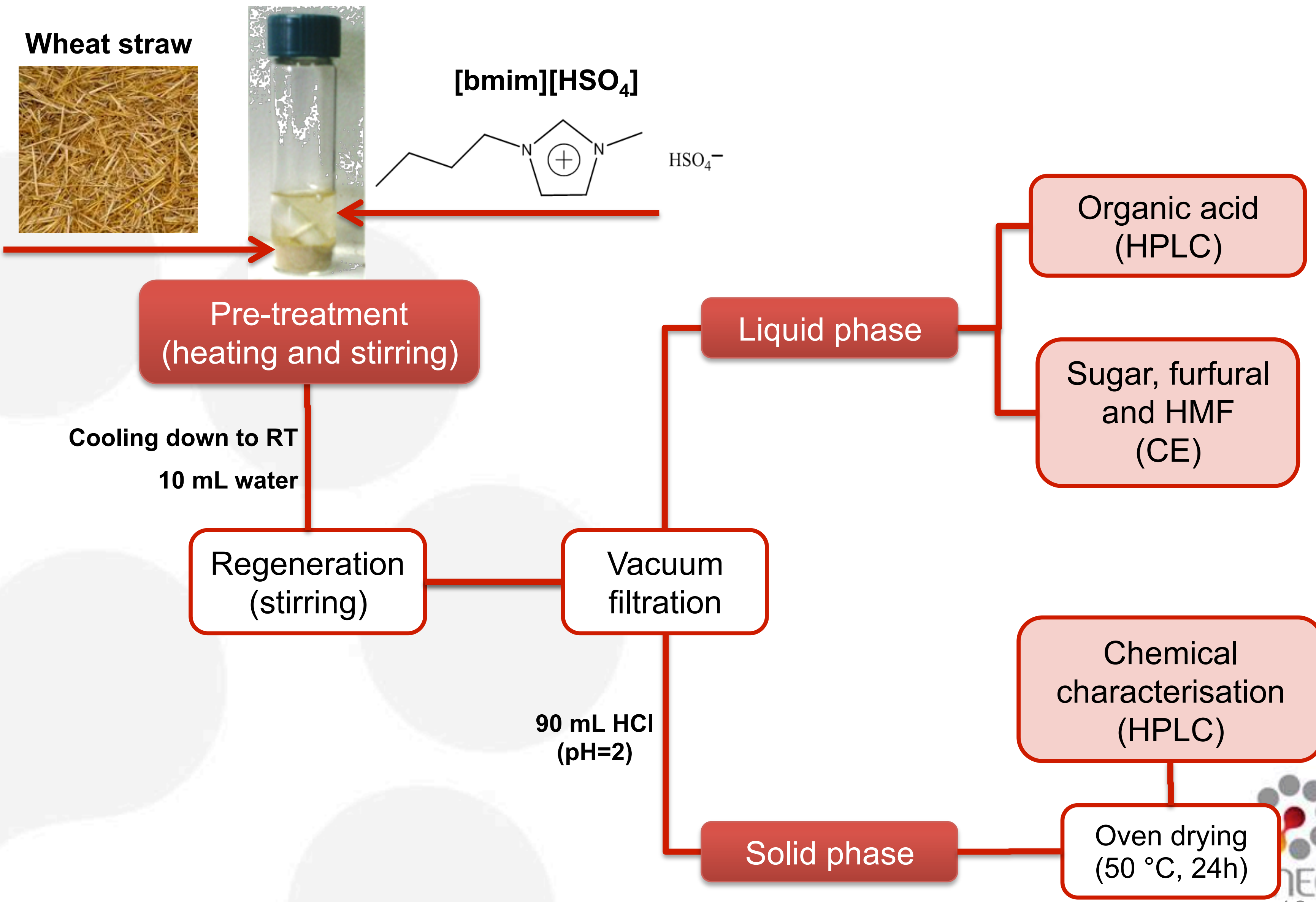


[bmim][HSO_4]
solvent and catalyst for biomass



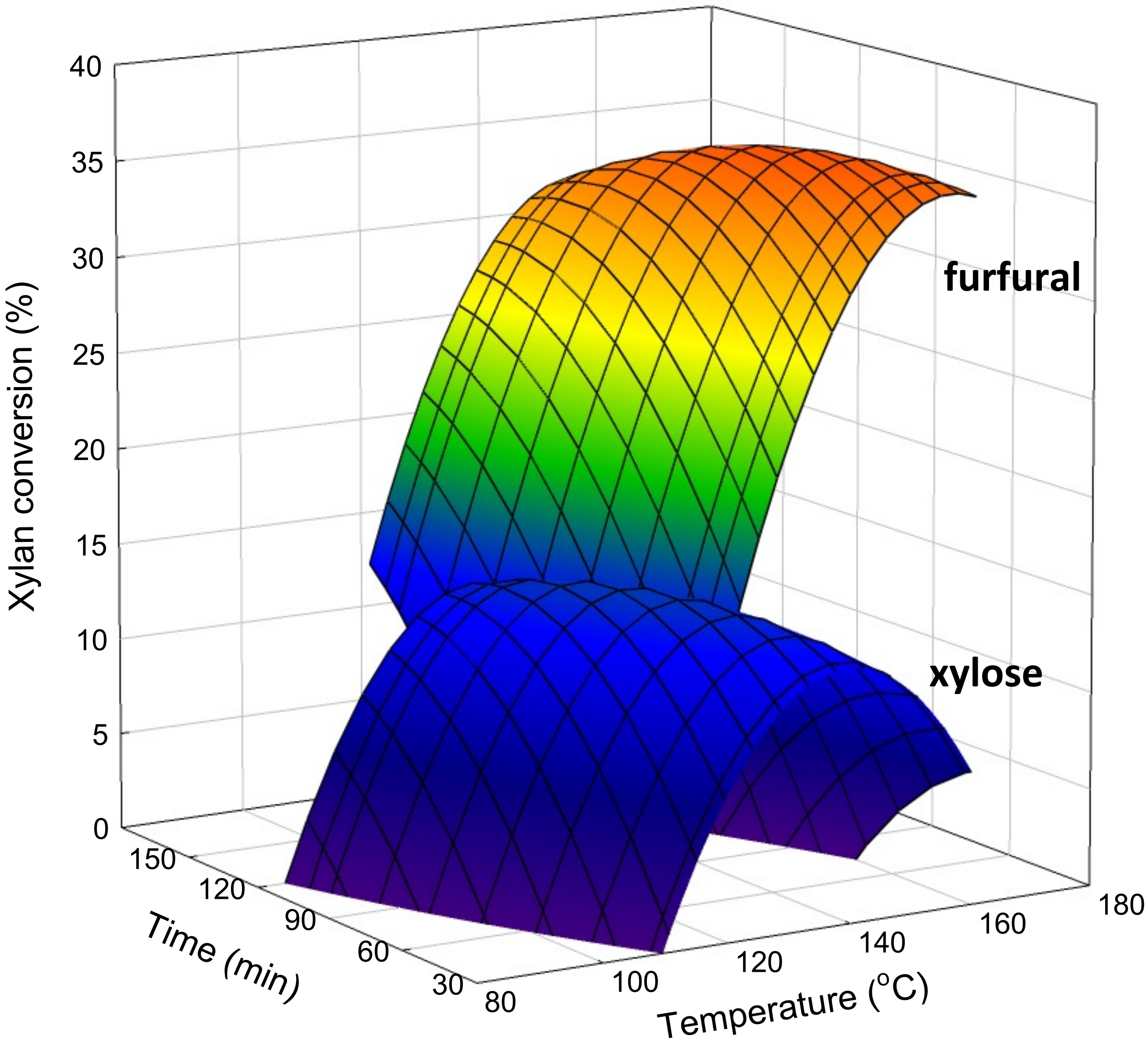
1-butyl-3-methylimidazolium hydrogen sulphate

Methodology for [bmim][HSO_4]



A. V. Carvalho, A. M. da Costa Lopes and R. Bogel-Lukasik, *RSC Adv.*, 2015, **5**, 47153.

Conversion of biomass with [bmim][HSO_4]



Conditions:

10% Biomass

1.2% humidity

A. V. Carvalho, A. M. da Costa Lopes and R. Bogel-Lukasik, *RSC Adv.*, 2015, **5**, 47153.

Fermentation in ILs

Possible products (at least up to now…)

1) Ethanol
2) Lipids
3) Organic acids (succinic acid)

ONLY 6 WORKS!

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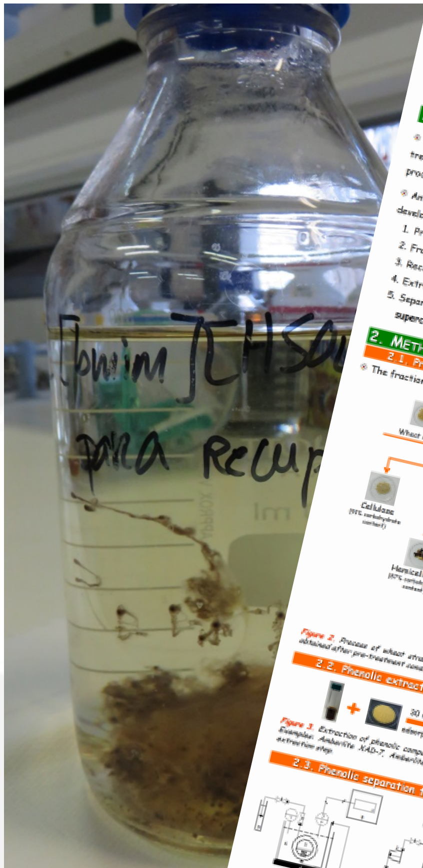
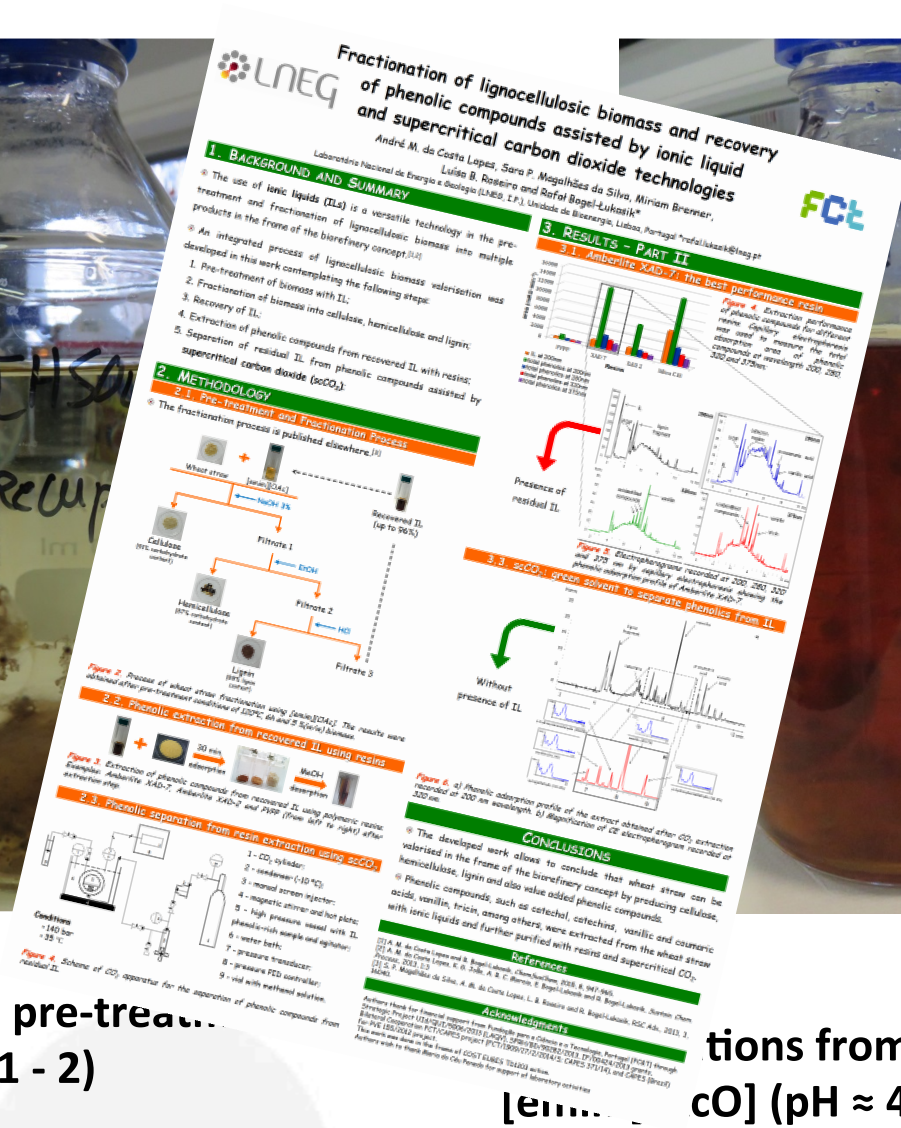
Fermentation in ILs

Microorganism		Ionic Liquid		Incubation conditions			Product		
Family	specie	Type	Concentration	T (°C)	t (h)	Substrate		Yield (%)	Ref.
Fungi	*Fusarium oxysporum* BN	[emim][H2PO2]	-	35	192	rice straw	ethanol	0.125g/g biomass (64.2% theoretical)	Xu, 2015
Yeast	*Rhodosporidium Toruloides*	[emim][Cl]	[30 - 60] mM	30	100	glucose	Lipids	~ [12 - 11] g.L-1	Huang, 2013
		[emim][DEP]	[30 - 60] mM	30	100	glucose		~ [10 -8] g.L-1	
		[emim][OAc]	[30 - 60] mM	30	100	glucose		~ [2 - 1] g.L-1	
	Saccharomyces Cerevisiae	[emim][Cl]	100 mM	30	6	glucose	ethanol	~ 18 g.L-1	Nakashima, 2011
		[emim][DEP]	100 mM	30	6	glucose		~ 17 g.L-1	
		[emim][DEP]	200 mM	34	170	cellulose		~ 1.5 g.L-1	
		[emim][OAc]	100 mM	30	6	glucose		~ 17 g.L-1	
		[emim][OAc]	[5.90 - 33.5] mM	30	72	glucose		~ [10 - 9] g.L-1	Ouellet, 2011
			[52.4 - 59.0] mM	30	72	glucose		~ 2 g.L-1	
Bacteria	*Actinobacillus succinogenes*	[amim][Cl]	0.01 %	37	12	glucose	Succinic acid	14.65 g.L-1	Wang, 2014
			0.1 %	37	12	glucose		16.00 g.L-1	
			1.0 %	37	12	glucose		12.41 g.L-1	
			-	37	12	Pinewood		0.24 g/gbiomass	
			-	37	12	corn stover		0.09 g/gbiomass	
			-	37	12	SE-corn stover		0.31 g/gbiomass	
			-	37	12	HCW-corn stover		0.27 g/gbiomass	

A. M. da Costa Lopes, R. Bogeł-Łukasik, in preparation, 2015.

Fermentation in ILs





Sugar solutions from pre-treat... [bmim][HSO_4] (pH ≈ 1 - 2)

...tions from pre-treatment with [em... ...cO] (pH ≈ 4)

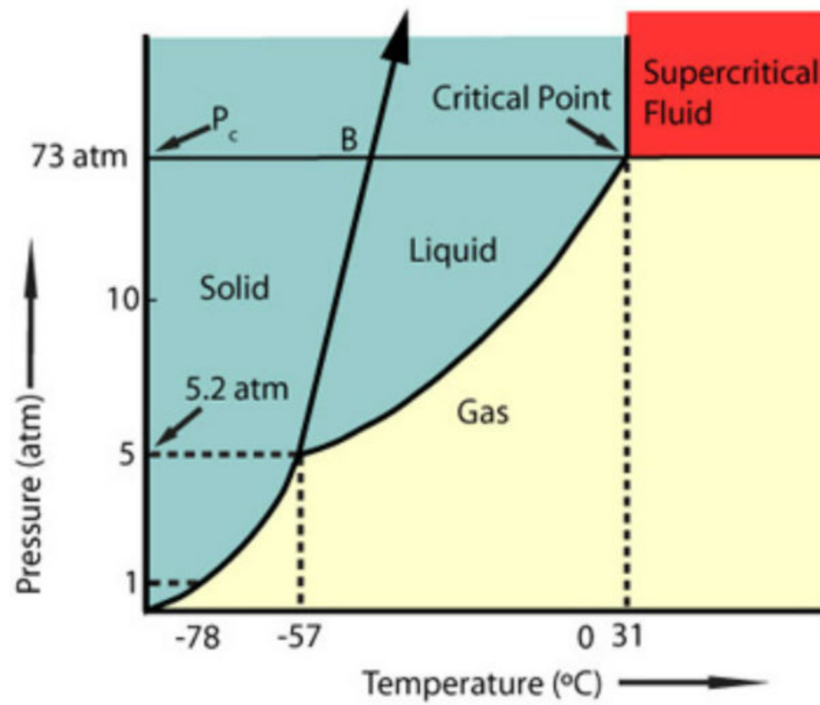
Supercritical fluids

Supercritical fluids (SCFs) are defined as substances above their critical temperature, T_c, and critical pressure, p_c.

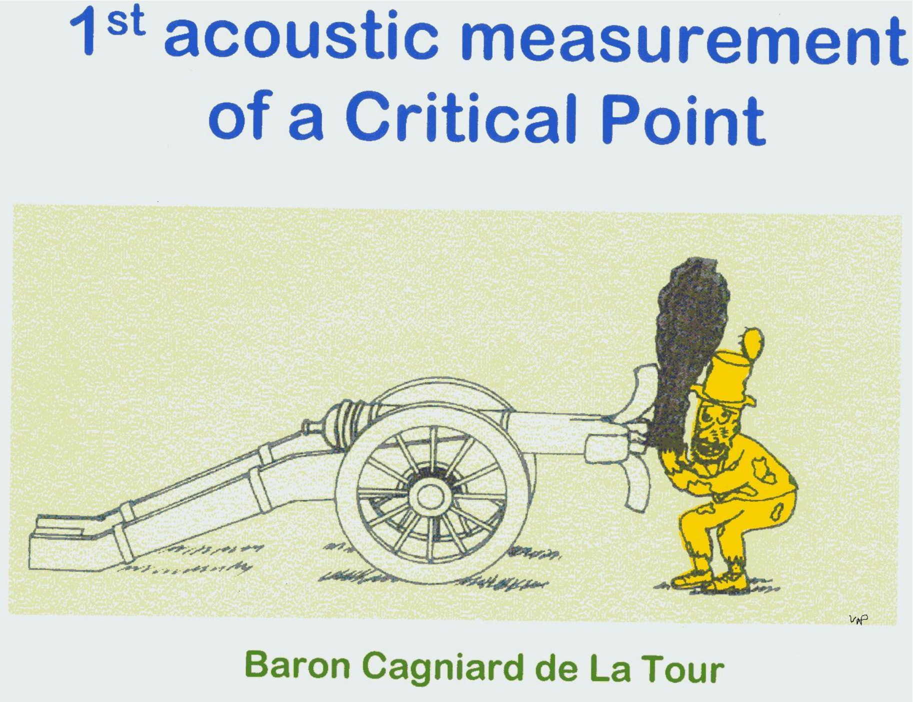
- Unique physicochemical properties such as liquidlike density and gaslike diffusivity
- Tunable properties
- Environmentally sustainable
- Easily to scale up

Typical fluids: CO_2, H_2O, propane, butane

	Density (g/mL)	Viscosity (P)
gas	~10^{-3}	$0.5\text{-}3.5\cdot10^{-4}$
ScF	0.2-0.9	$0.2\text{-}1.0\cdot10^{-3}$
liquid	0.8-1.2	$0.3\text{-}2.4\cdot10^{-4}$

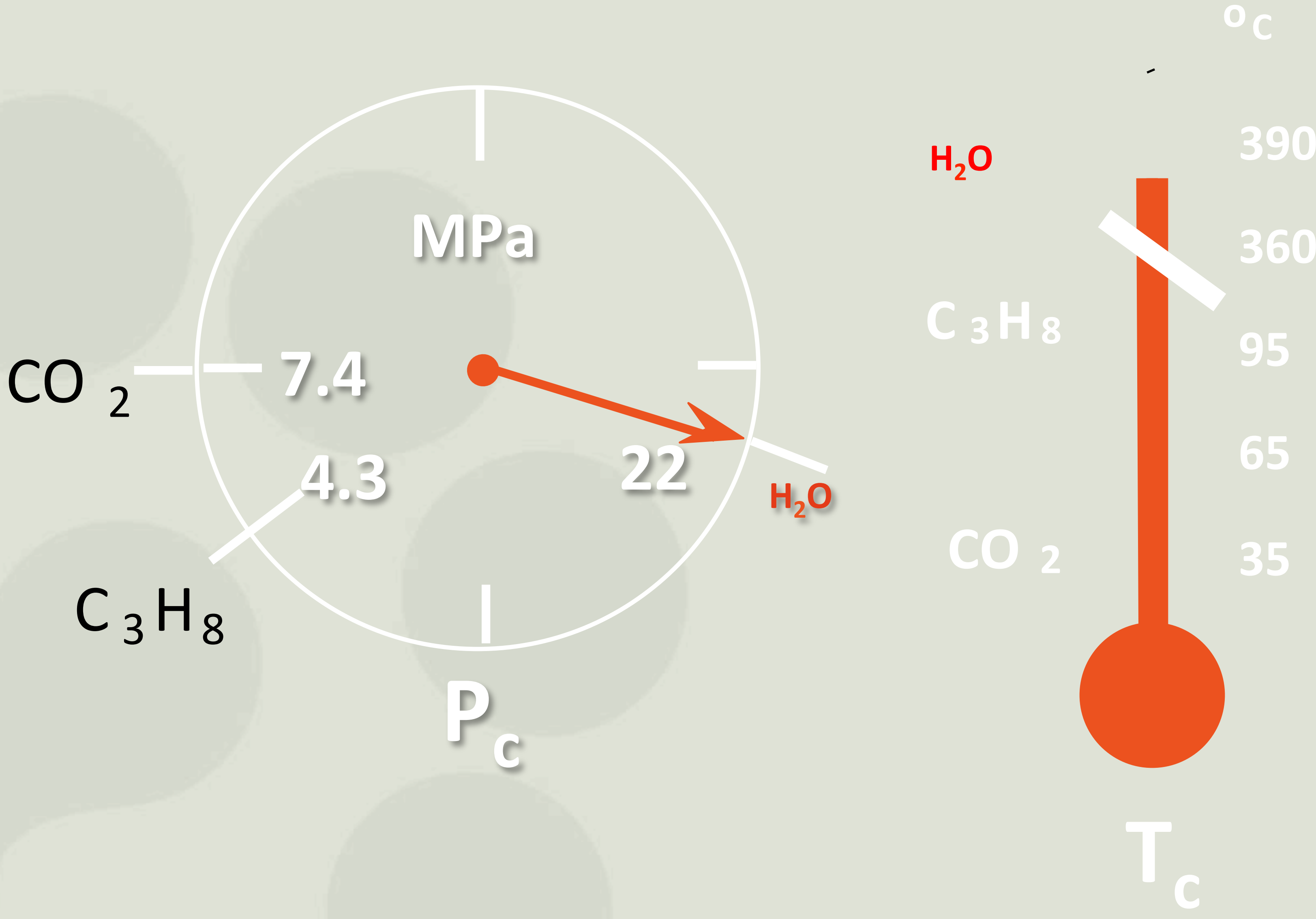


Supercritical fluids



Baron Charles Cagniard de La Tour discovered the critical point of a substance in his famous cannon barrel experiments. Listening to discontinuities in the sound of a rolling flint ball in a sealed cannon filled with fluids at various temperatures, he observed the critical temperature.

Proprieties of supercritical fluids



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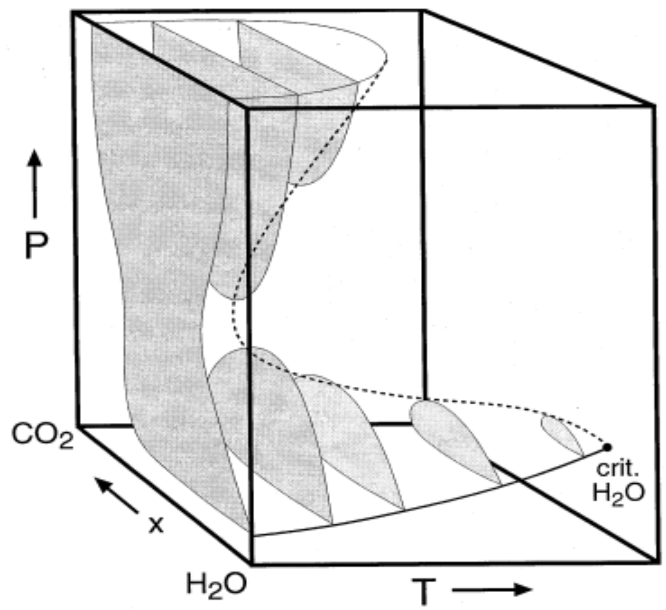
High pressure CO_2-H_2O binary system

CO_2-H_2O mixture advantages

- ❑ Sustainable and green solvent
- ❑ GRAS - generally recognized as safe
- ❑ Nontoxic, nonflammable and inexpensive reagent
- ❑ ↓Temperatures and ↓ degradation products
- ❑ It can act as a detoxification methodology



High pressure CO_2-H_2O binary system

Water-only reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

CO_2 + H_2O binary system

- ❑ Mixture becomes more acidic (pH ≈ 3) → ↑ dissolution of hemicellulose
↑ Enzymatic digestibility of cellulose

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$

Estimated pH $\quad \mathrm{pH} = 8.00\times10^{-6}\times T^2 + 0.00209\times T - 0.216\times\ln(P_{CO_2}) + 3.92$*

50 bar of CO_2	20 / 35 bar of CO_2	A.H
3.72	3.78	5.5 (at 220ºC)

*G.P. van Walsum, Appl. Biochem. Biotechnol., 91-3 (2001) 317.

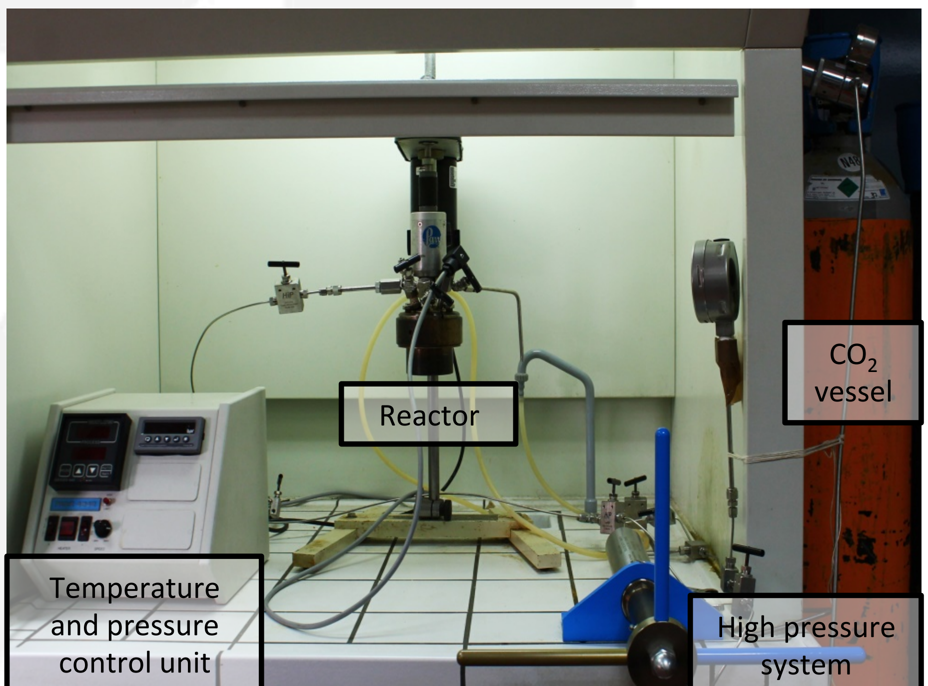
High pressure CO_2-H_2O binary system

$CO_2 + H_2O$

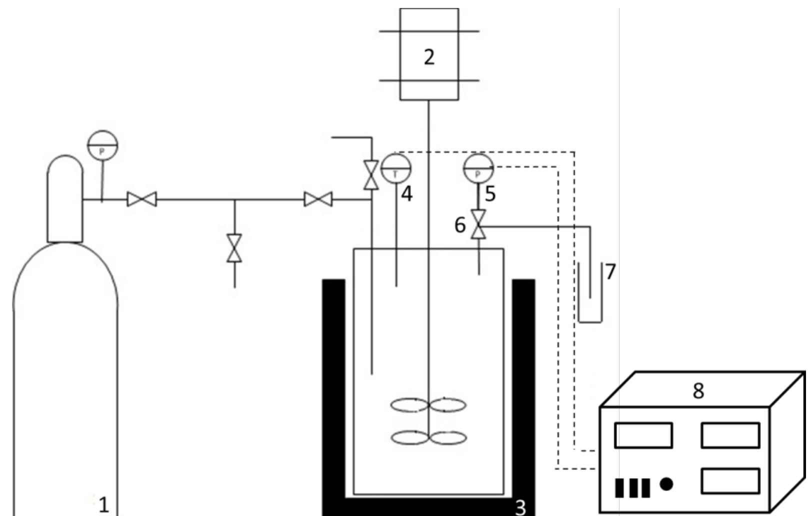
p_i CO_2 = 0, 15, 30, 45 and 60bar

Pretreatment
(180-225°C)

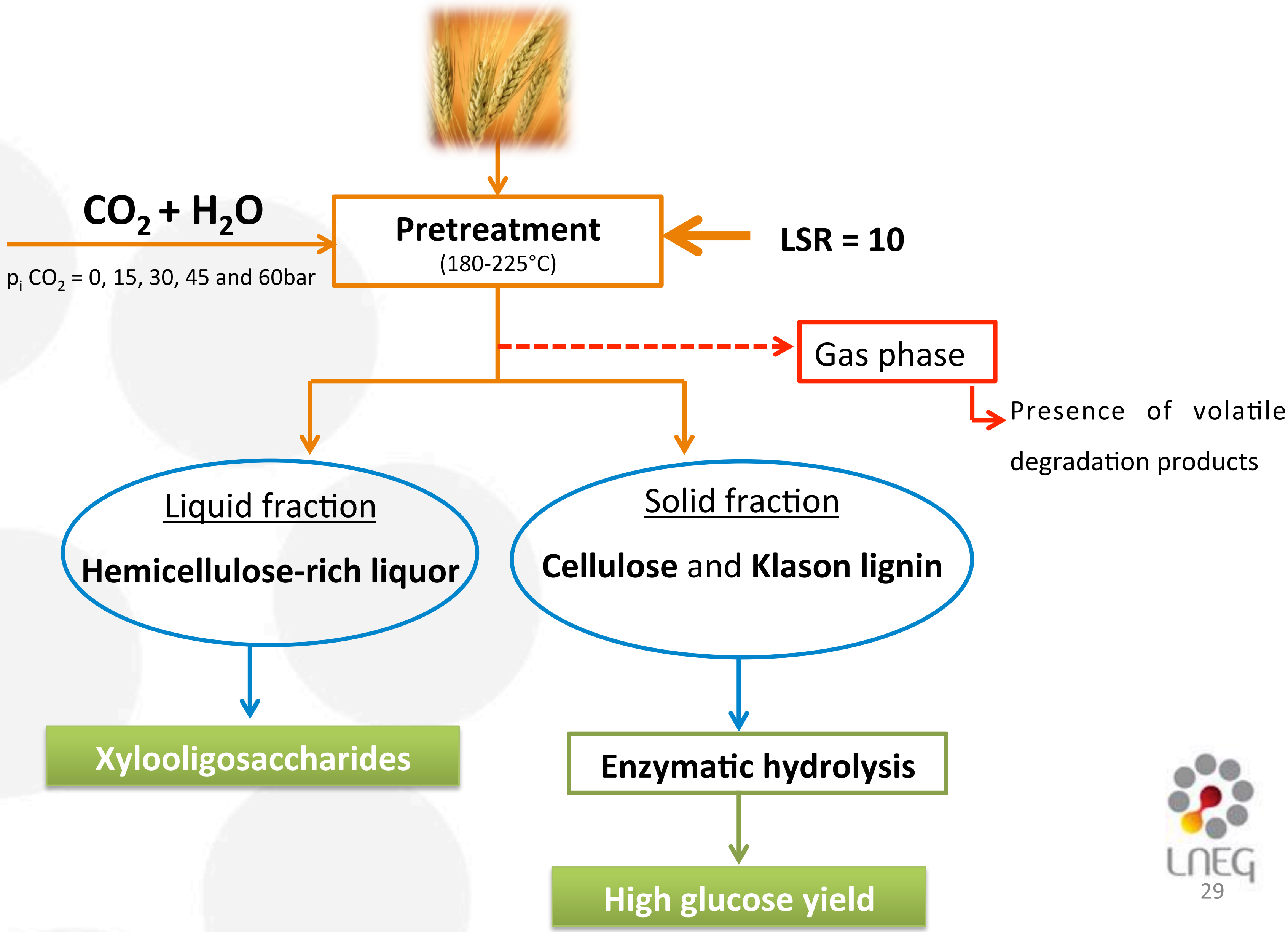
LSR = 10



Pre-treatment system.



High pressure CO_2-H_2O binary system



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Effect of CO_2 addition to water-only reaction

Water-only reaction*

High pressure CO_2-H_2O mixture

The same conditions:
- *Log R_0*
- 250g H_2O/ 25g wheat straw

Liquid fraction
- ↑ 65% of XOS concentration
- ↑ 100% of xylose concentration
- X More degradation of pentoses

Solid fraction
- ↑ Glucan
- ↑ Klason Lignin
- ✓ Lower xylan content
- Complete removal of arabinan

✓ The *in situ* formed **carbonic acid** enhances the **hydrolysis** of hemicellulose

*Carvalheiro, F., Silva-Talita, T., Duarte, L. and Gírio, F., Wheat Straw Autohydrolysis: Process Optimization and Products Characterization. *Applied Biochemistry and Biotechnology,* 2009. **153**(1-3). 84-93.

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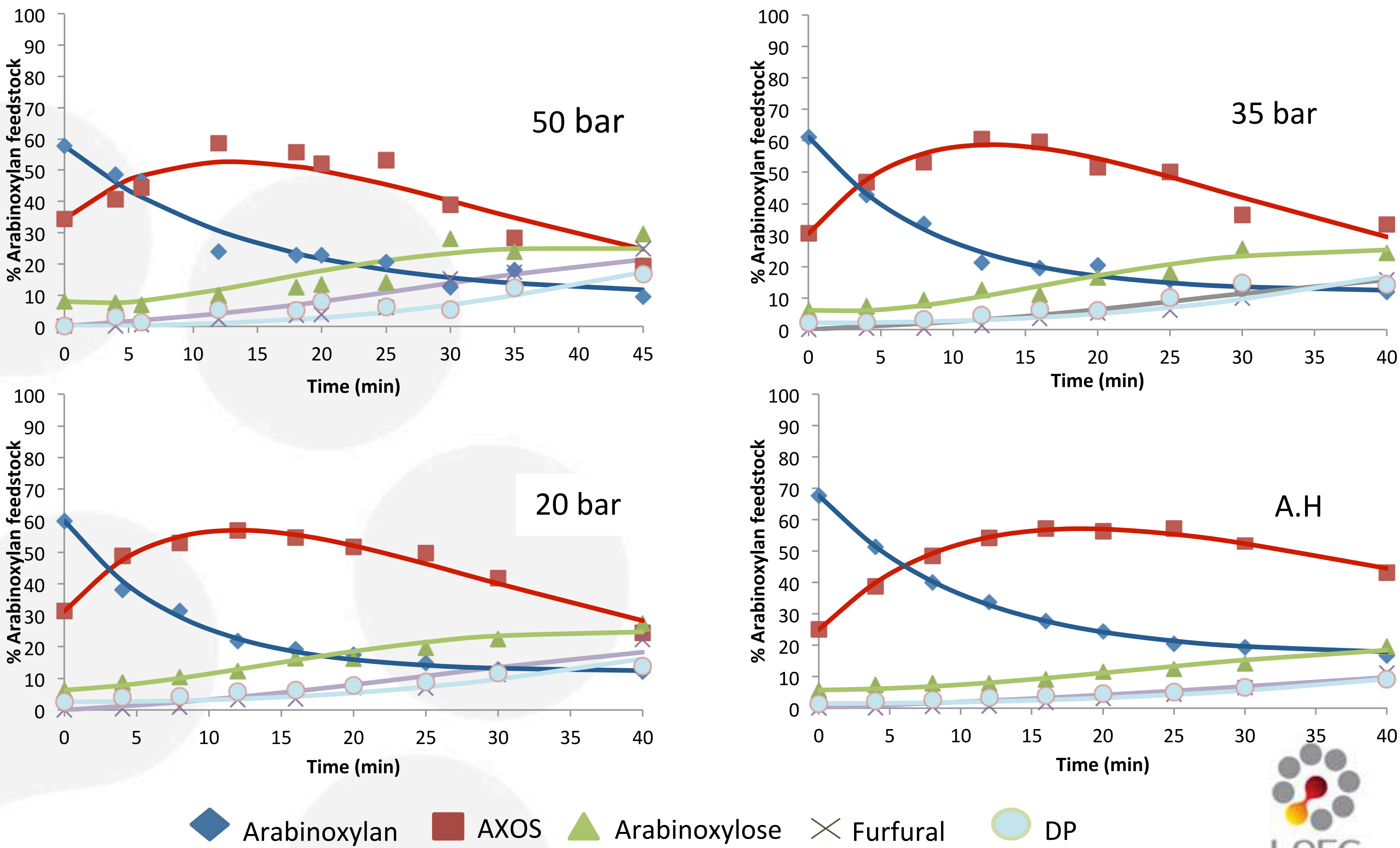
Effect of initial CO_2 pressure



Relvas, F. M., Morais, A. R. C., Bogel-Lukasik, R. (2015). Kinetic modeling of hemicellulose-derived biomass hydrolysis underhigh pressure CO2–H2O mixture technology. J. Supercrit. Fluid., 2015,**99**, 95-102.

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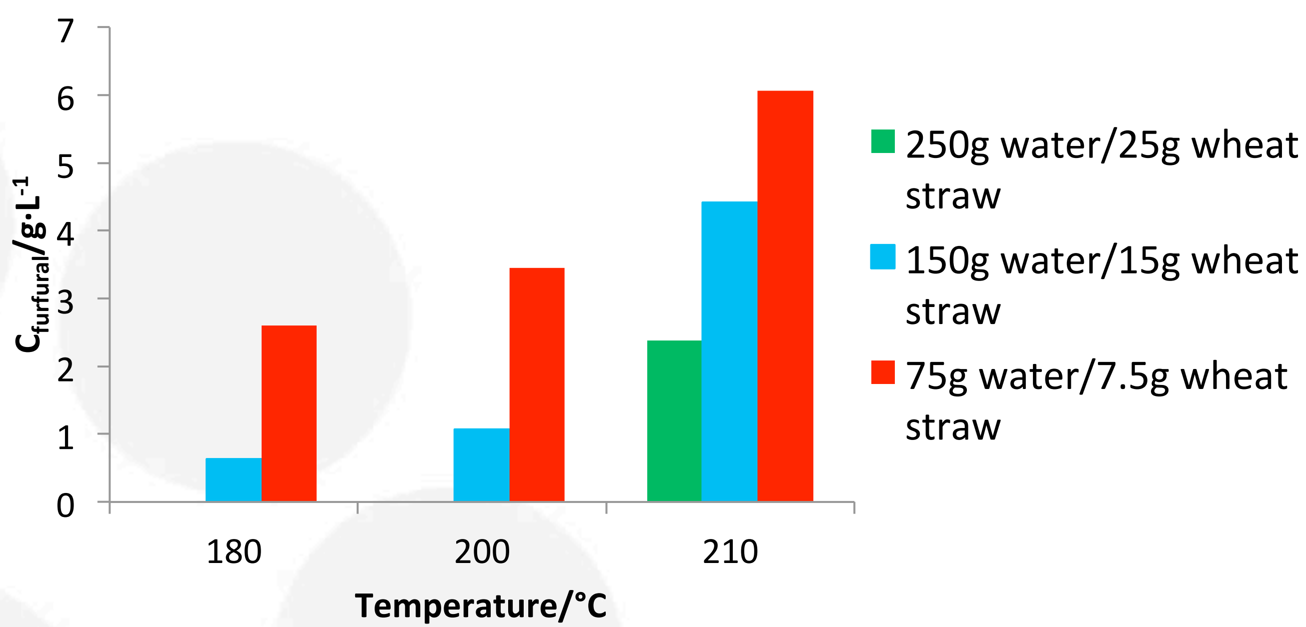
Production of volatile products

Gas phase



Furfural concentration in the recovered gas phase from depressurization for studied temperatures and biomass loading.

Detoxification effect during depressurization

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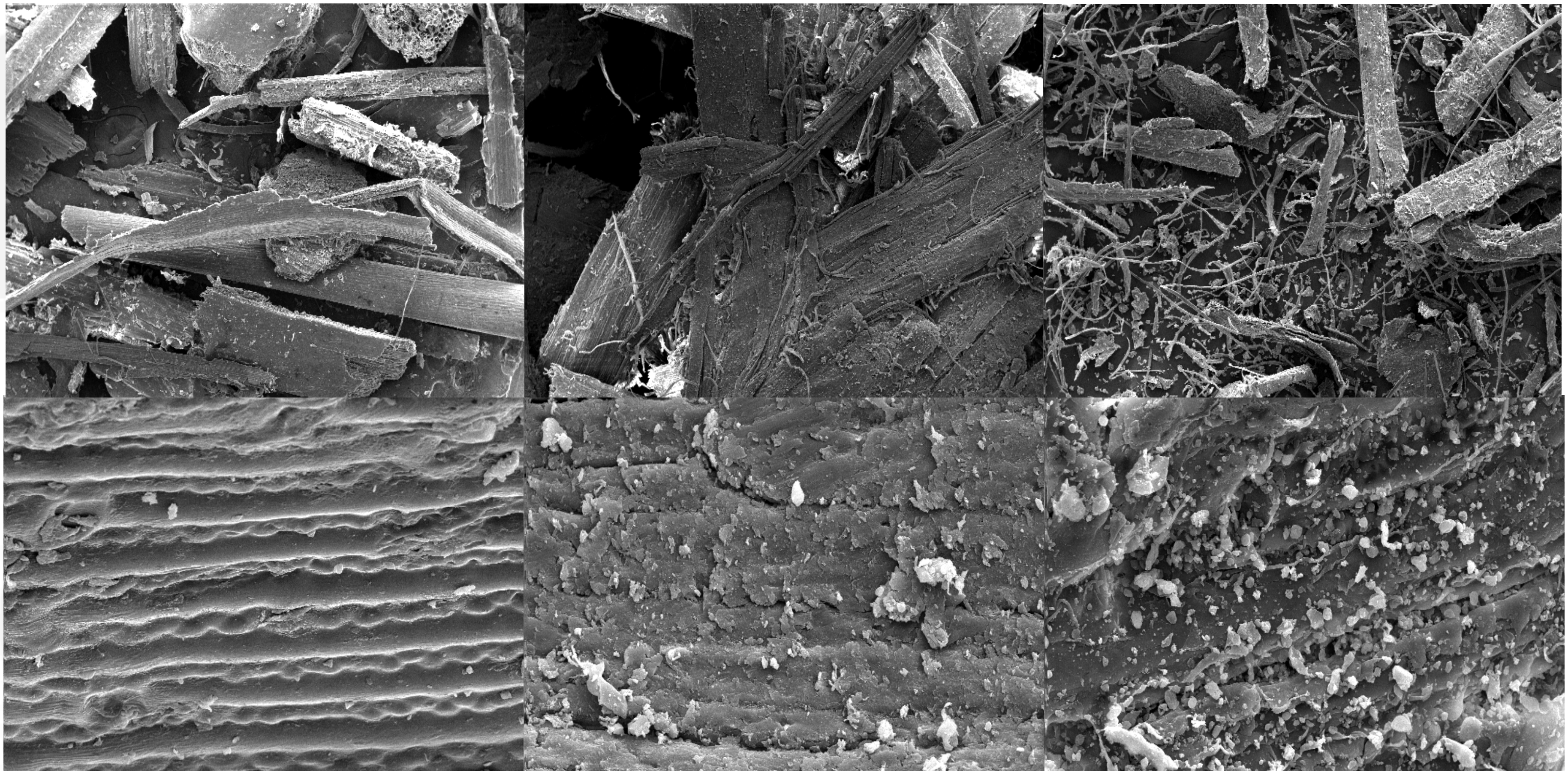
Magalhães da Silva, S. P., Morais, A. R. C., Bogel-Lukasik, R. (2015). The CO2-assisted autohydrolysis of wheat straw. Green Chem., 2014,**16**, 238-246.

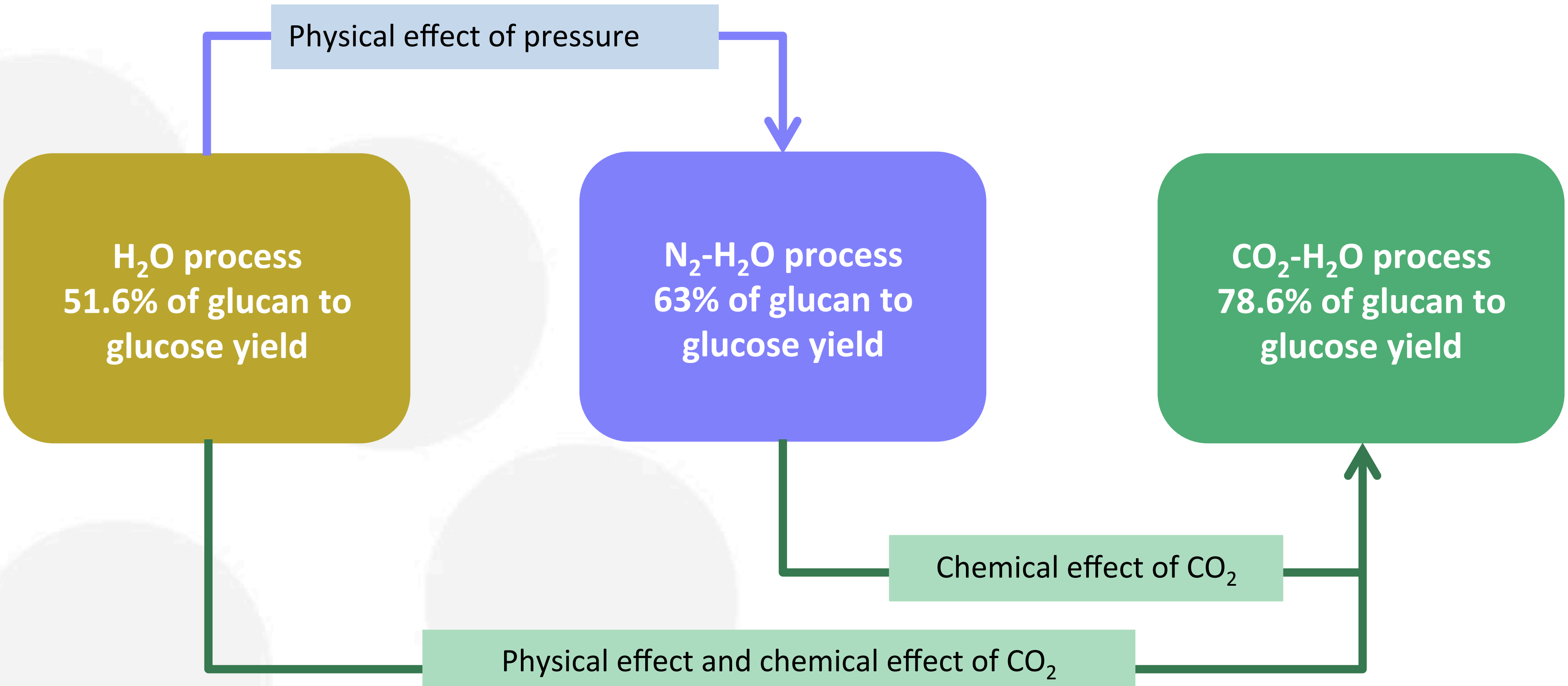
Effect of process on the ultrastructure of residue

Untreated | Treated at 225°C without CO_2 | Treated at 225°C with 45 bar of CO_2



Morais, A. R. C., Mata, A. C., Bogel-Lukasik, R. (2014). Integrated conversion of agroindustrial residue with high pressure CO_2 within biorefinery concept. Green Chem., 2014,**16**, 4312-4322

Effect of CO_2 pressure (chemical and physical)



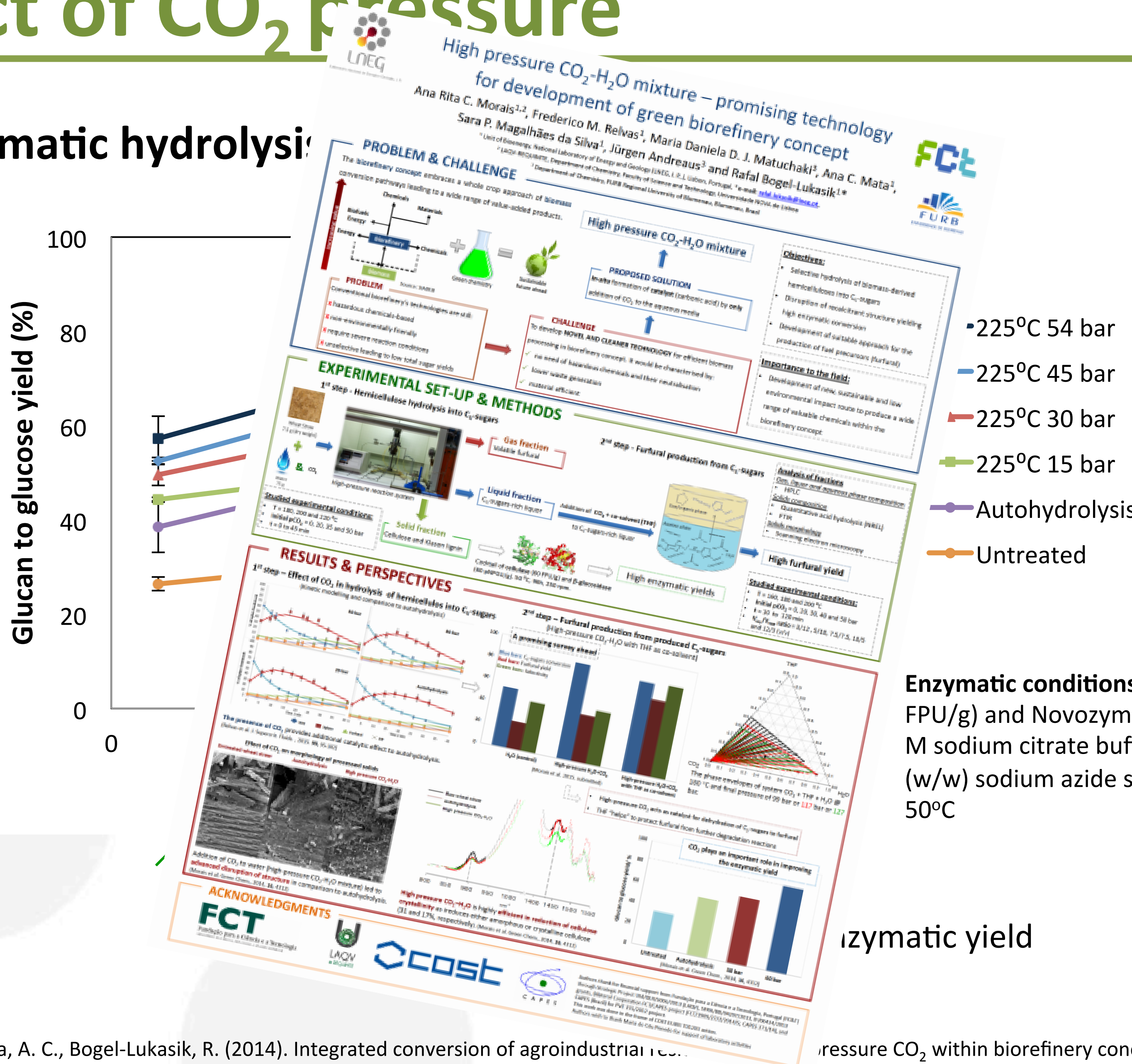
The glucan to glucose yield obtained after 72 h of hydrolysis.

Pre-treatment conditions:
Temperature: 225^{o}C
Initial pressure: 54 bar (when N_2 and CO_2 are present)

Morais, A. R. C., Mata, A. C., Bogel-Lukasik, R. (2014). Integrated conversion of agroindustrial residue with high pressure CO_2 within biorefinery concept. Green Chem., 2014,**16**, 4312-4322

Effect of CO_2 pressure

- **Enzymatic hydrolysi**



Enzymatic conditions: Celluclast® 1.5 L (64 FPU/g) and Novozym 188 (60 FPU/g); 0.1 M sodium citrate buffer (pH = 4.8) and 2 % (w/w) sodium azide solution, 250 rpm and 50°C

nzymatic yield

Morais, A. R. C., Mata, A. C., Bogel-Lukasik, R. (2014). Integrated conversion of agroindustrial res... ressure CO_2 within biorefinery concept. Green Chem., 2014,**16**, 4312-4322

Final remarks

With green solvents we can (up to now):

- Pre-treat and fractionate biomass to high purity fractions
- Produce sugars (C_5 and C_6 solutions selectively)
- Tune the process to obtain value-added compounds directly (e.g. oligosaccharides, vanillin) and selectively (xylose or furfural)
- Perform fermantation in green solvents

Acknowledgments

COST EUBiS TD1203 Food waste valorisation for sustainable chemicals, materials & fuels

Pesquisador Visitante Especial 155/2012

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Luisa B. Roseiro
Elvira Fortunato
Filipe Neves
Ewa Bogel-Lukasik
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1. Biorefinery and Green Chemistry by **J.-P. Mikkola**

2. The dissolution of biomass in ionic liquids towards pre-treatment approach by **C. Afonso**

3. Ionic Liquid Pre-treatment of Lignocellulosic Biomass for Biofuels and Chemicals by **S. Singh**

4. Biomass Hydrolysis in Ionic Liquids by **R. Martínez-Palou**

5. Relevance of Biomass Feedstocks for Ionic Liquid-assisted Extraction of Biomolecules by **R. Bogel-Lukasik**

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8. Ionic liquids as efficient tools for the purification of biomolecules and bioproducts from natural sources by **M. G. Freire**

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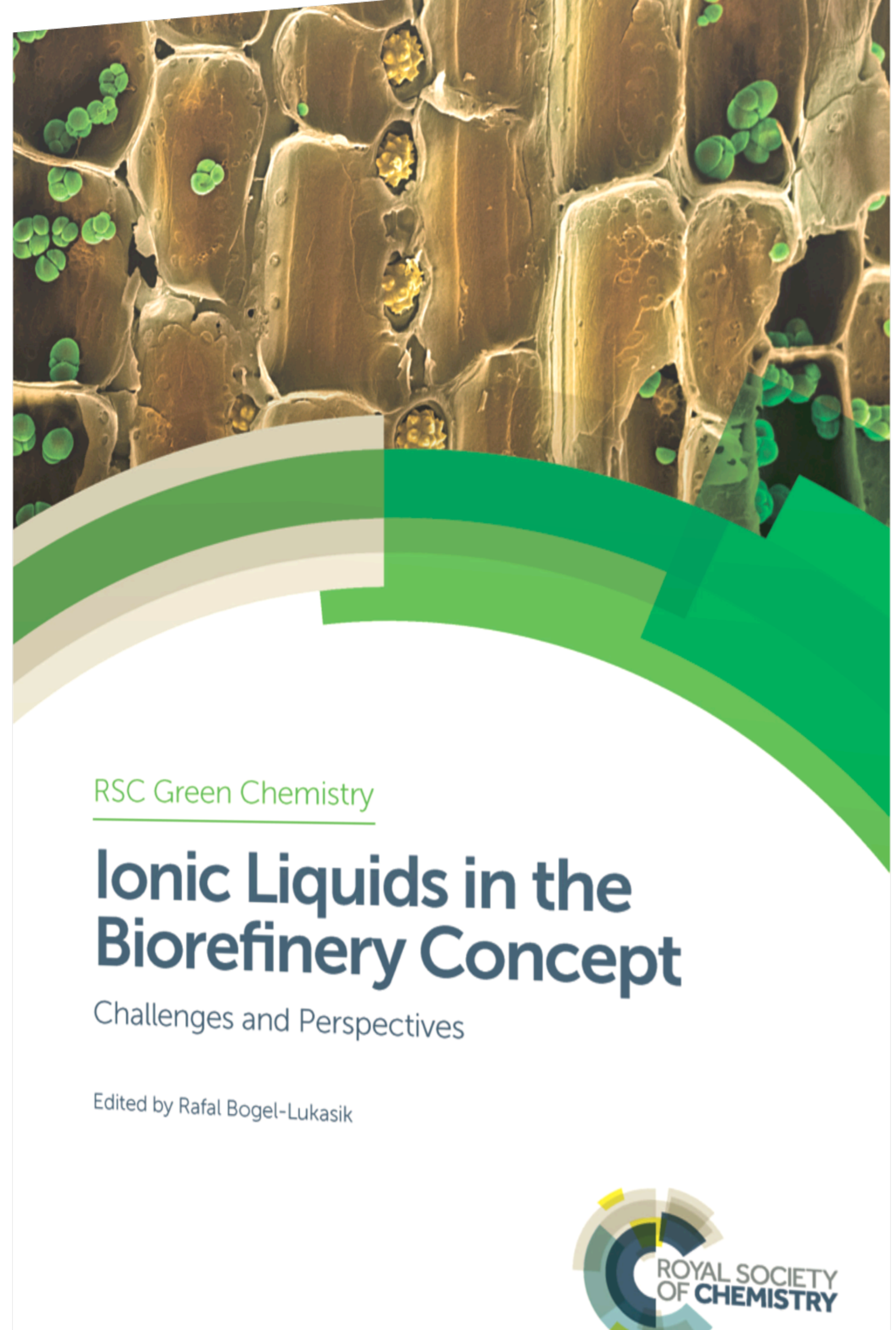

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