Biorefinery concept: Greener approach of integration of biofuels and bioproducts delivery

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LNEG Investigação para a Sustentabilidade

Labóratorio Nacional de Energia e Geologia, I.P.

UB-Unit of Bioenergy

gathering together skills in **4 Thematic Areas**

Head: *Francisco Gírio, PhD* (francisco.girio@lneg.pt)

Co-coordinator: *Alberto Reis, PhD* (alberto.reis@lneg.pt)

1. ENDOGENOUS BIOMASS RESOURCE

Contact: Filomena Pinto, PhD

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2. BIOFUELS & BIOPRODUCTS

Contact: Rafal Łukasik, PhD

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4. SUSTAINABILITY FOR BIOENERGY

Contact: Francisco Gírio, PhD

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3. MICROORGANISMS, MICROALGAE & ENZYMES TOWARDS BIOECONOMY

Contact: Susana Marques, PhD

(susana.marques@lneg.pt)

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Staff= 30 researchers + 35 grantees and students

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1. ENDOGENOUS BIOMASS RESOURCE

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2. BIOFUELS & BIOPRODUCTS

Contact: Rafał Łukasik, PhD

for 2017-2021

TOTAL **EU** FUNDING in **H2020** = **3.4 M€**

TOTAL **NATIONAL** FUNDING = **2.6 M€**

(francisco.girio@lneg.pt)

3. MICROORGANISMS, MICROALGAE & ENZYMES TOWARDS BIOECONOMY

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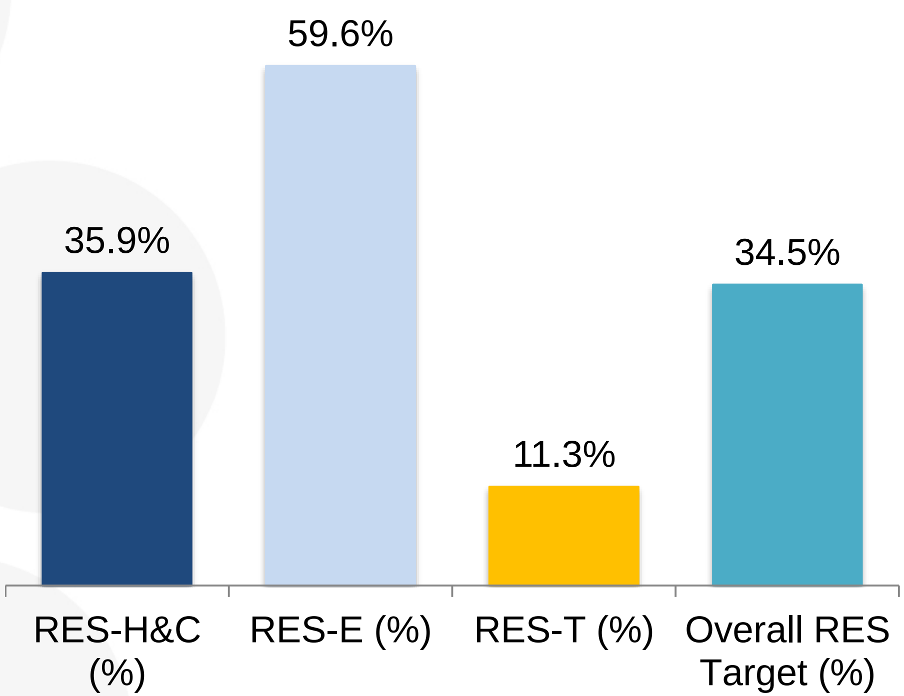
- Biomass is natural renewable and abundant feedstock in Portugal
- Contribution of Biomass for national targets

Biomass contributes to 93% for heat & cooling and to 87% for transport[(1)]

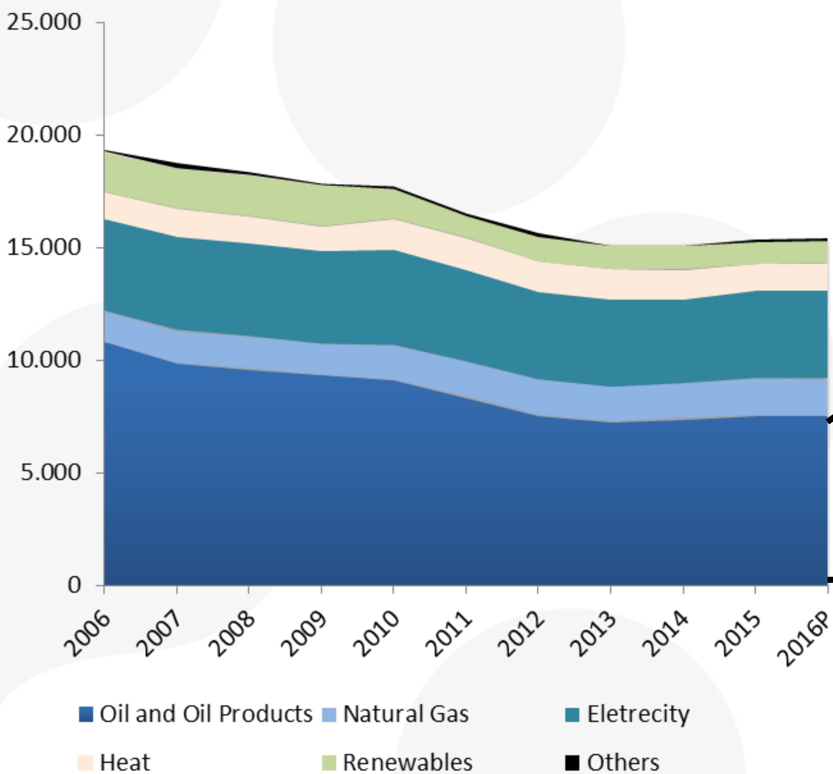
Targets for 2020 [(1)]



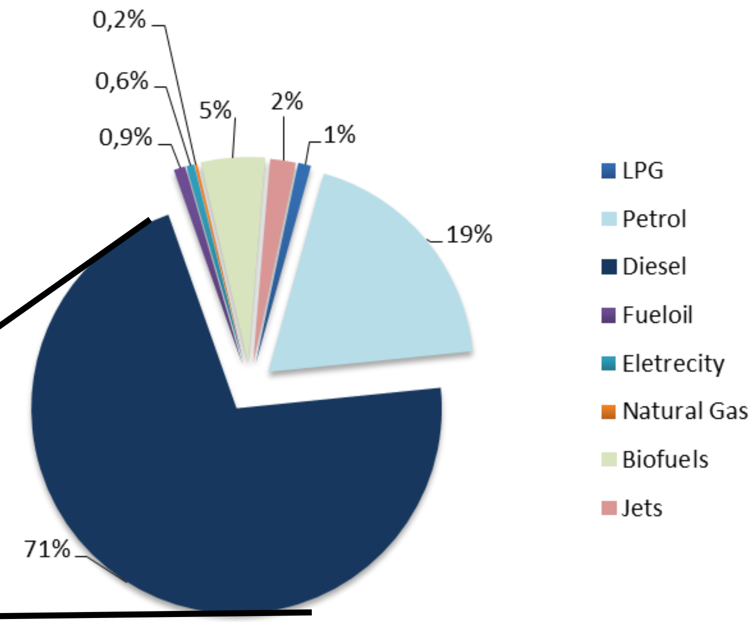
(1) PNAER (2013)

➢ **Transport** – the main sector of primary energy (37%)

Diesel (71%), Gasoline (19%), Jet-A1 (2%),...



Source: DGEG



~ 95 % Fossil!

The GHG emission per economy sector

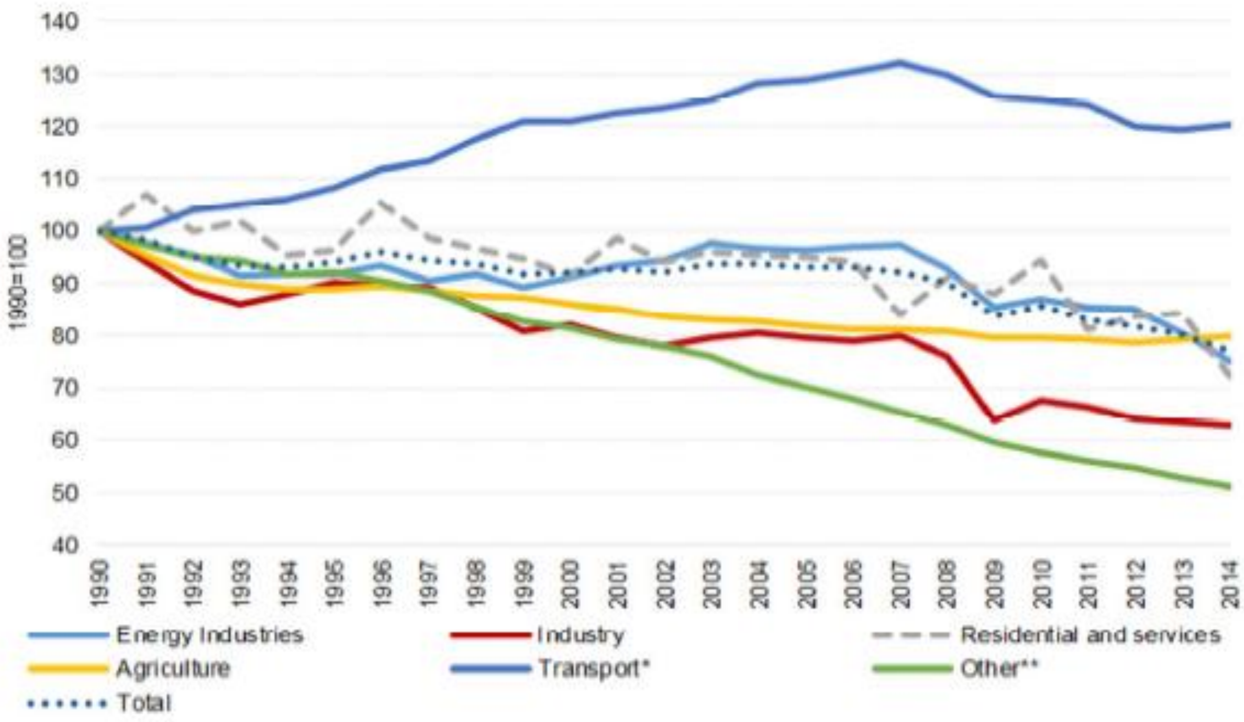


Figure 7: Evolution of GHG emissions by sector (1990=100), EU[16]

Status of Advanced Biofuels – implementation to the market

Type	Fuel	Time to deployment after REDII, years
Commercial	Crop based, HVO, Anaerobic Digestion to Biomethane	0
1st of a kind, ready for commercialisation	Cellulosic ethanol, Methanol, DME Synthetic Biomethane	3
Innovation ready for 1st of a kind	Other Lignocellulosic Synthetic fuels	4-8
Advanced innovation stage	Pyrolysis oils, Synthetic and Low Carbon Fossil Fuels	5-10
Early innovation stage	e-fuels, algae, etc.	5-8

Source: STF, SGAB Report, 2017

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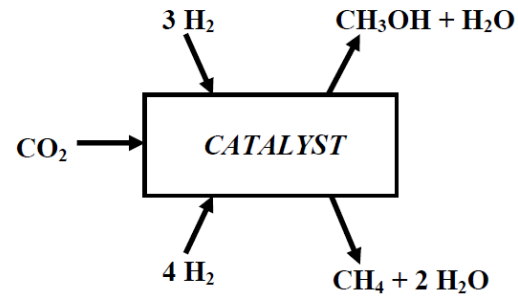
Some exemples of (European) implementation of advanced biofuels in the industrial scale

➢ **Transport** – Advanced biofuels



Toyota to supply its hydrogen technology to Caetanobus SA (Portugal) Europe

- Toyota's fuel cell system to be used in Caetanobus' first FCEV[*] city buses

- Caetanobus to launch first hydrogen demonstration city bus in autumn 2019

Lisbon, Portugal—September 26th, 2018—Toyota today took another important step towards a broader hydrogen society by announcing that it will provide its hydrogen fuel cell technology to Caetanobus SA in Portugal.

+ 9.2 %

The increase of biofuels consumption for transport in the European Union between 2016 and 2017 (in energy content)

Groundbreaking for Clariant's sunliquid® cellulosic ethanol plant in Romania

- **Investment represents biggest industrial commitment by an international corporation in the region of Craiova**
- **Location chosen for combination of feedstock supply and infrastructure**
- **Annual production capacity of 50 000 tons of cellulosic ethanol**

Muttenz, September 12, 2018 – Clariant, a world leader in specialty chemicals, toda started construction of the first large-scale commercial sunliquid plant for the prod cellulosic ethanol made from agricultural residues. At the flagship facility, the sunli developed by the company is being used on an industrial scale for the first time. The

SCANIA – first Scania Bioethanol truck (**ED95**) sold to a customer (Lantmannen Agroetanol) - 29.10.2018 (source: www.scania.com)

Sustainability: ED95- Bioethanol blended with an ignition improver, reduces 90% GHG emmissions.

Technology: The 13-litres bioethanol engine delivers 2,150 Nm, equal to that of its diesel sibling, and the fuel consumption is also on pair with a conventional diesel engine.

Most significant engine changes: Modification of the fuel injection system and the cylinders, for increase the compression.

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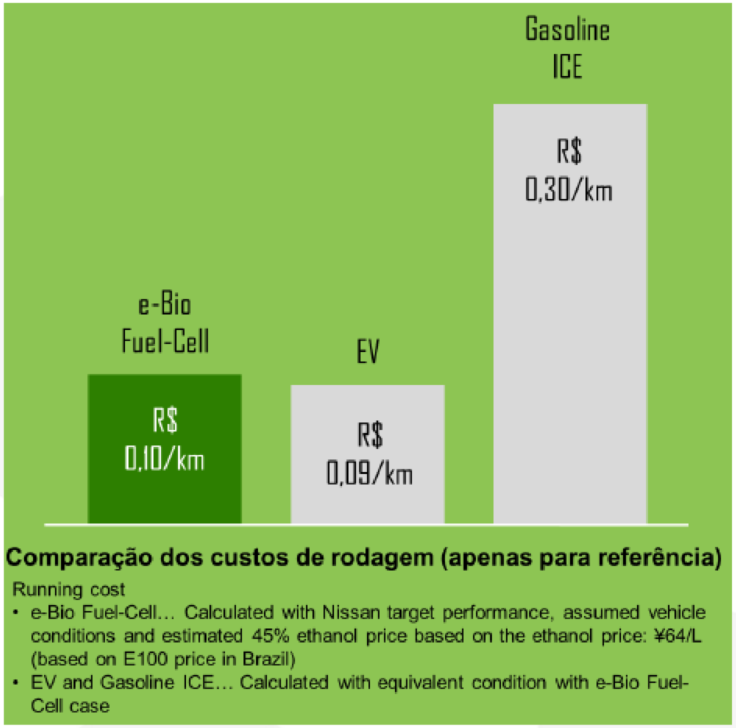
NISSAN – Pioneer in technology bringing together bioethanol, hydrogen and electricity to power automotive vehicles



Sustainability:Carbon-free technology (W-T-W) – CO_2 emmissions = CO_2 uptake.

Technology: A SOFC (solid oxide fuel cell) using bioethanol as fuel.

Performance: Combining the SOFC-powered ethanol (either 100% ethanol or 45% etanol and 55% water) with motor and 24 kWh electric battery Nissan SOFC achieves an autonomy of 600 kms (2017) .

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Energy efficiency and GHG emissions

Vehicle	Fuel consumption (L gasoline eq./100 km)		GHG emissions (g CO_2 eq./km)	
	WTW	TTW	WTW	TTW
Gasoline	6,00	5,10	144,00	121,00
Diesel	4,70	3,90	113,00	93,00
***Fuel Cell* H_2**	4,53	2,21	83,66	0,00
***Fuel Cell* Ethanol (100%)**	4,70	2,45	14,07	56,34
Electricity (BEV)	3,87	1,38	50,43	0,00

Source: Well to wheel analysis of low carbon alternatives for road traffic. *Energy and Environmental Science*. 8, 3313 (2015)

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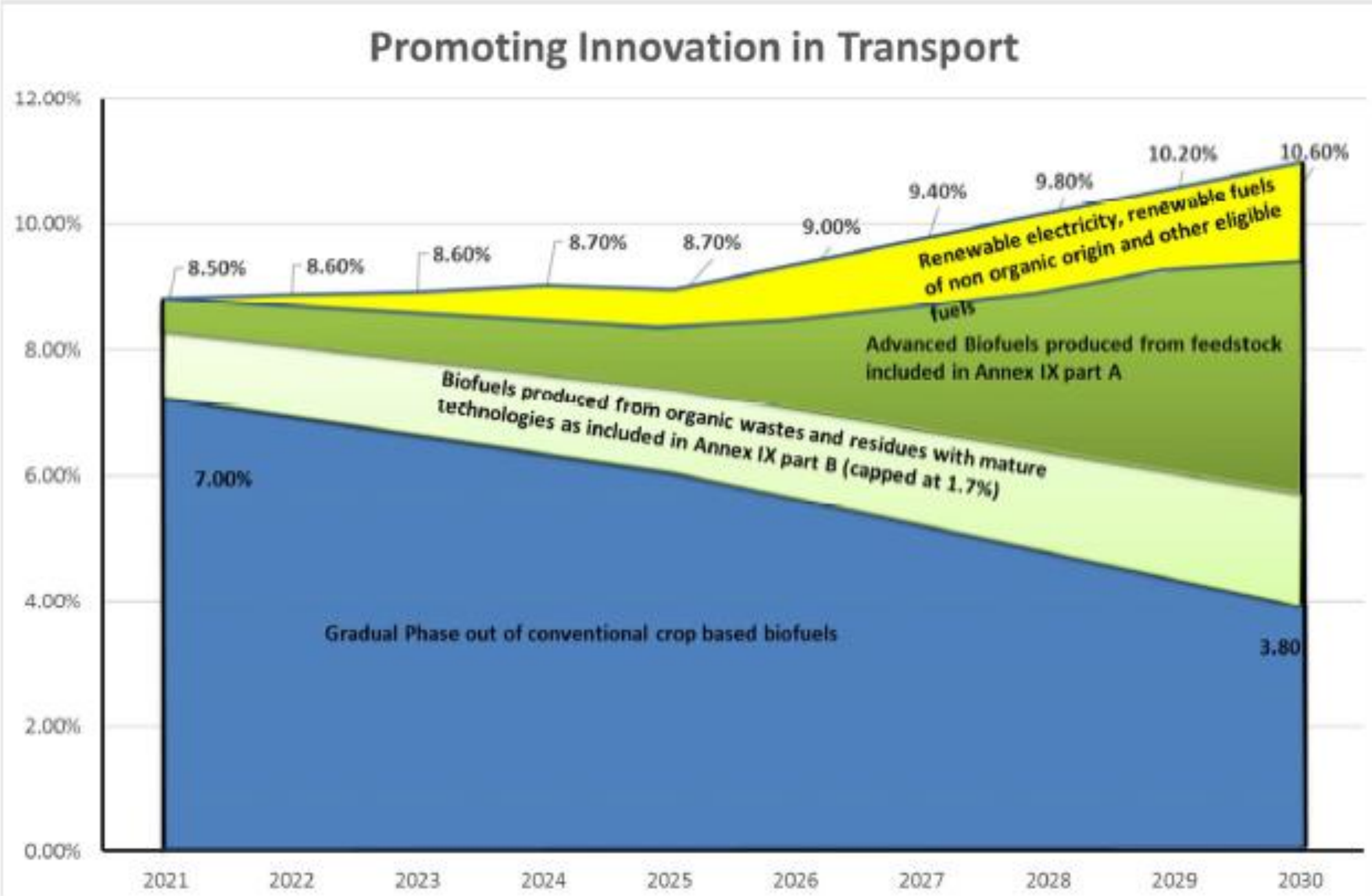


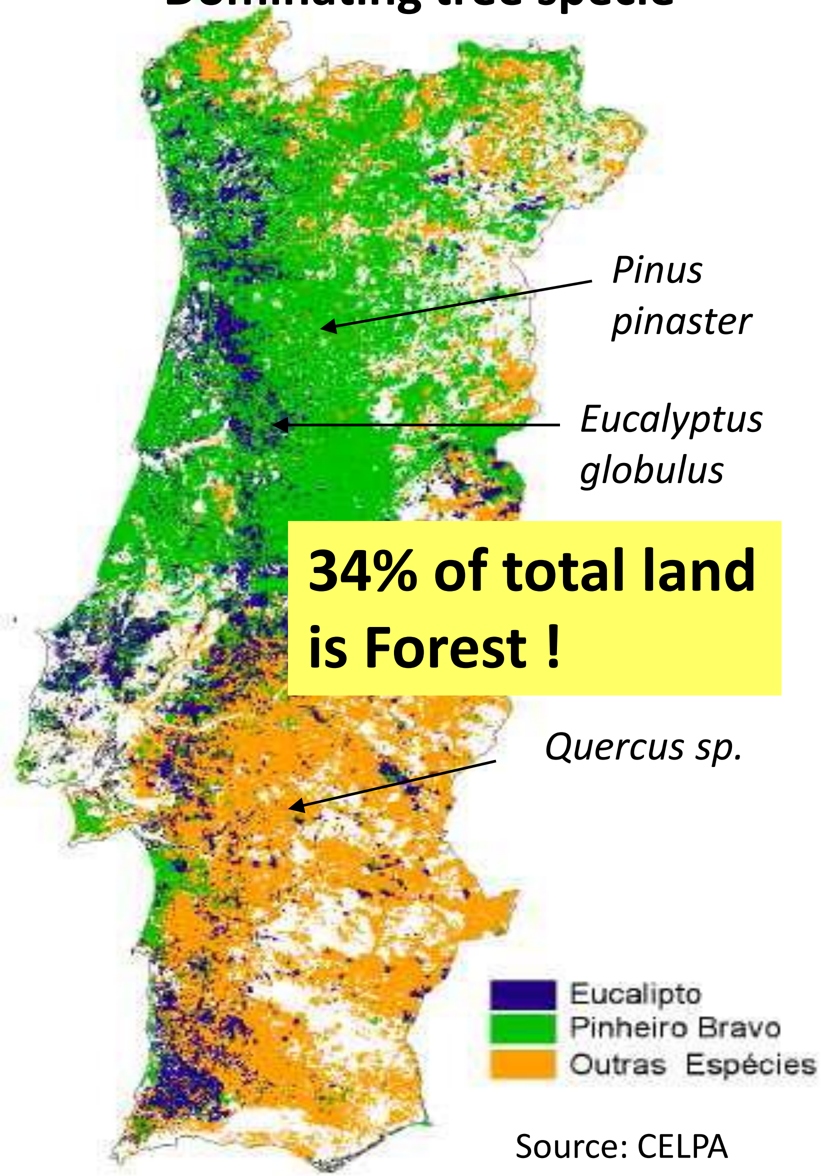
Figure 10: RED II proposed structure of caps and minimum shares for the various fuels[30]

[30] K. Maniatis, "The role of Advanced Biofuels in Decarbonising Transport RED II", Lignofuels 2017, Helsinki, adapted from an EC package presentation on RED II.

Source: STF, SGAB Report, 2017

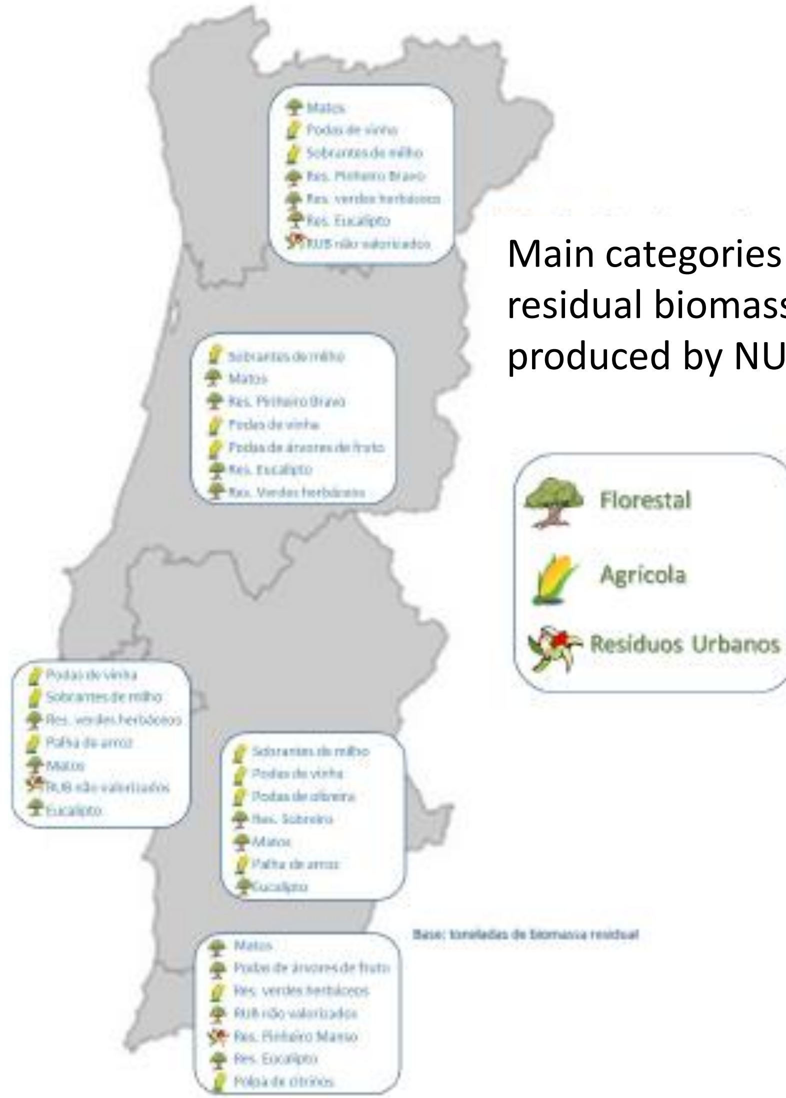
The Forest Biomass Resources

Dominating tree specie



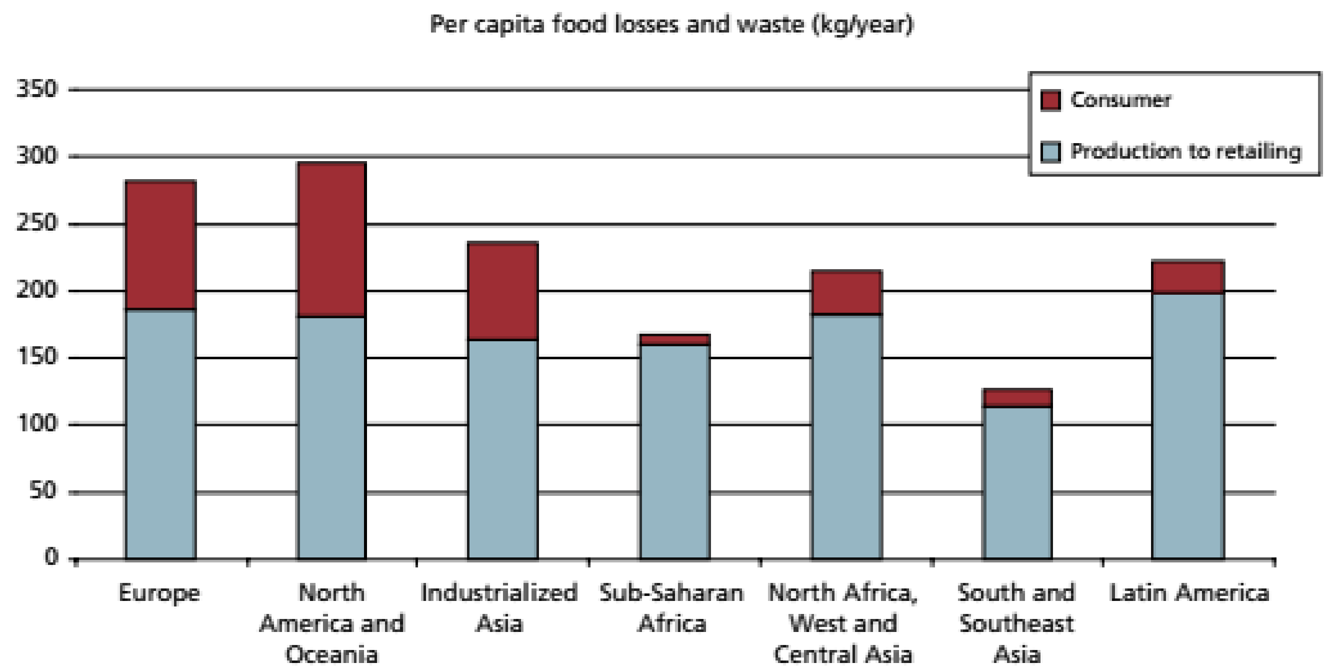
34% of total land is Forest !

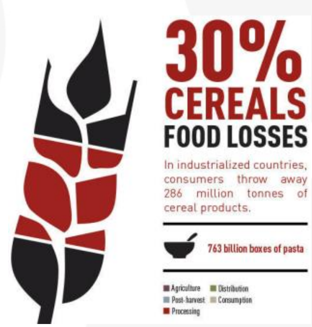
Source: CELPA

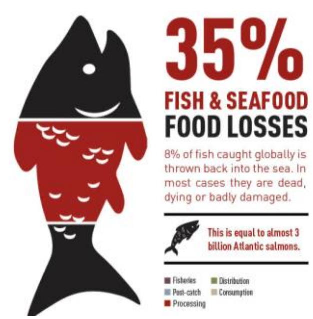


Main categories of residual biomass produced by NUTS2

Food waste vs. Food lost







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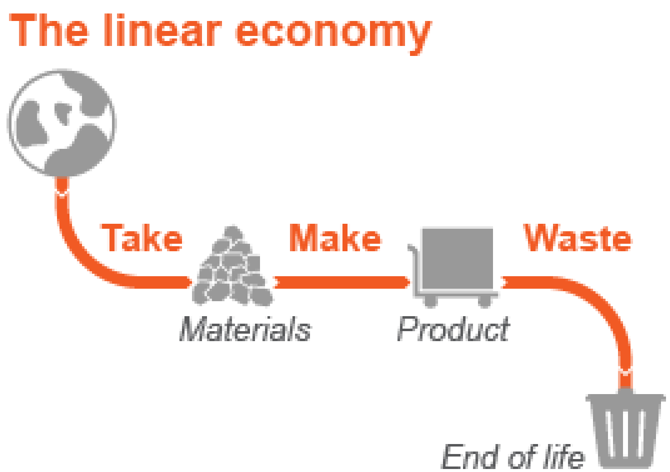
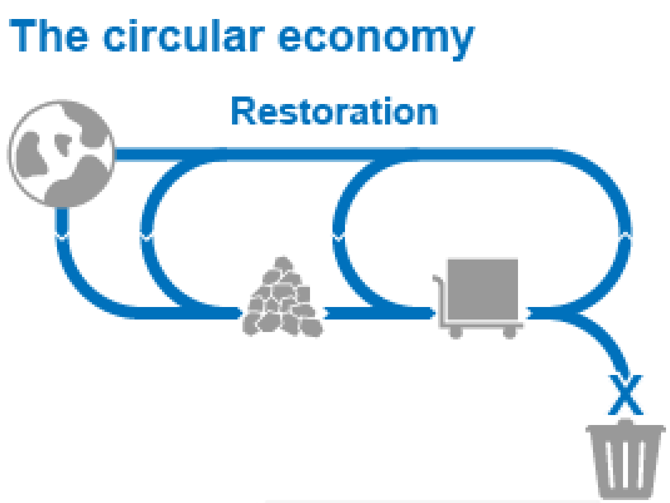
http://www.fao.org

Broader concept of "Biomass" – Circular Economy





http://desso-thegreatindoors.com/ce-c2c/what-is-the-circular-economy/

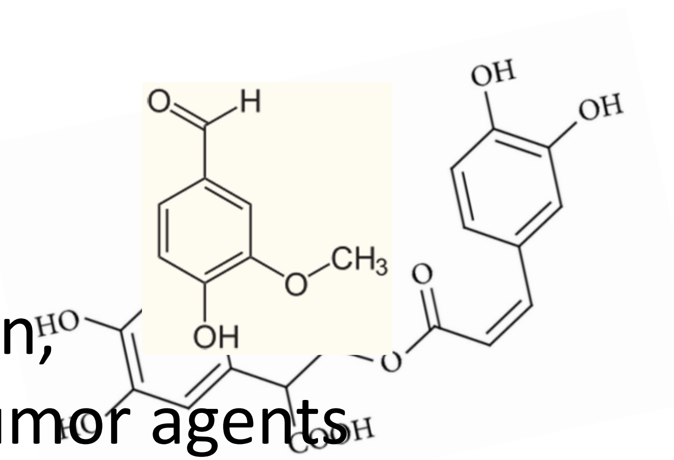
The Economics of the Coming Spaceship Earth
By Kenneth E. Boulding, 1966

Biomass – source of valuable products

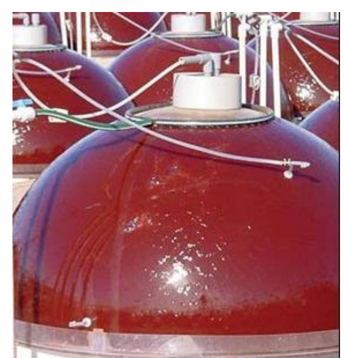
Polyunsaturated fatty acids (omega-3, omega-6)

Oligosaccharides

Phenolics (e.g. vanillin, catechol, tricin, rosmarinic acid) - antioxidants, antitumor agents



Natural carotenoids (*astaxanthin*)



Biomass deconstruction pre-treatments

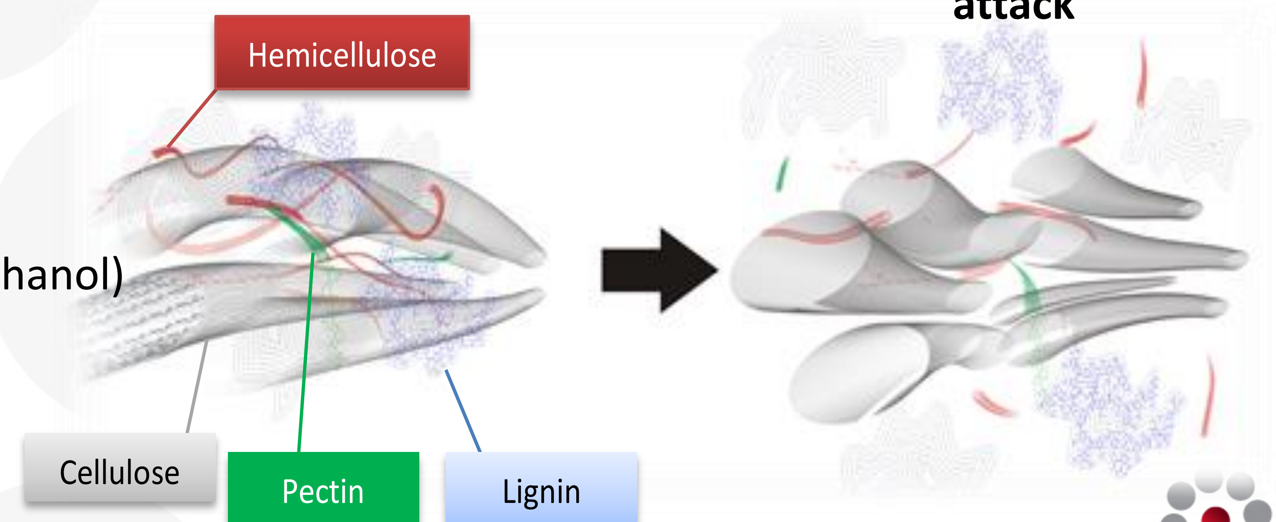
Pretreatments → **Essential to disrupt the complex structure of lignocellulosic biomass** → **↑ Extraction of lignin**
↓ Crystallinity of cellulose

↓

↑ Surface area for enzyme binding and attack

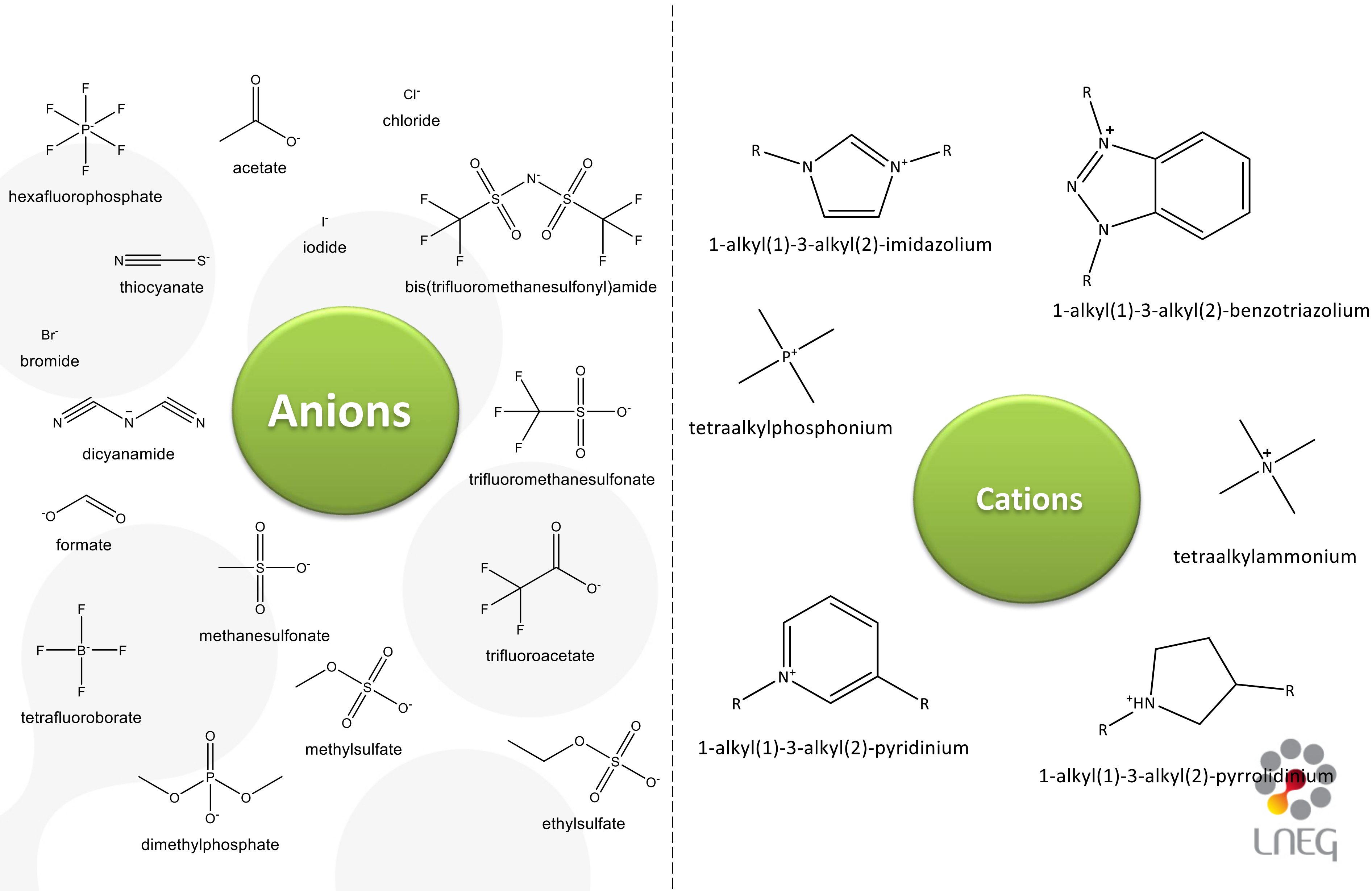
Conventional pretreatments

- Natural pulping
- Hydrothermal
- Dilute acid hydrolysis
- Organosolv (acetone, ethanol)
- Alkaline
- Amonia-like
- **Novel systems**



M. H. L. Silveira, A. R. C. Morais, A. M. da Costa Lopes, D. N. Olekszyszen, R. Bogel-Łukasik, J. Andreaus, L. P. Ramos, ChemSusChem, 2015, 8, 3366 – 3390

Ionic liquids



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3-step biomass fractionation with ILs

Bioresource Technology 142 (2013) 198–208

Contents lists available at SciVerse ScienceDirect

ELSEVIER

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Pre-treatment of lignocellulosic biomass using ionic liquids: Wheat straw fractionation

André M. da Costa Lopes[a], Karen G. João[a], Djonatam F. Rubik[a,b], Ewa Bogel-Łukasik[c], Luís C. Duarte[a], Jürgen Andreaus[b], Rafał Bogel-Łukasik[a,*]

[a] Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia, 1649-038 Lisboa, Portugal
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RSC Advances

RSC Publishing

PAPER

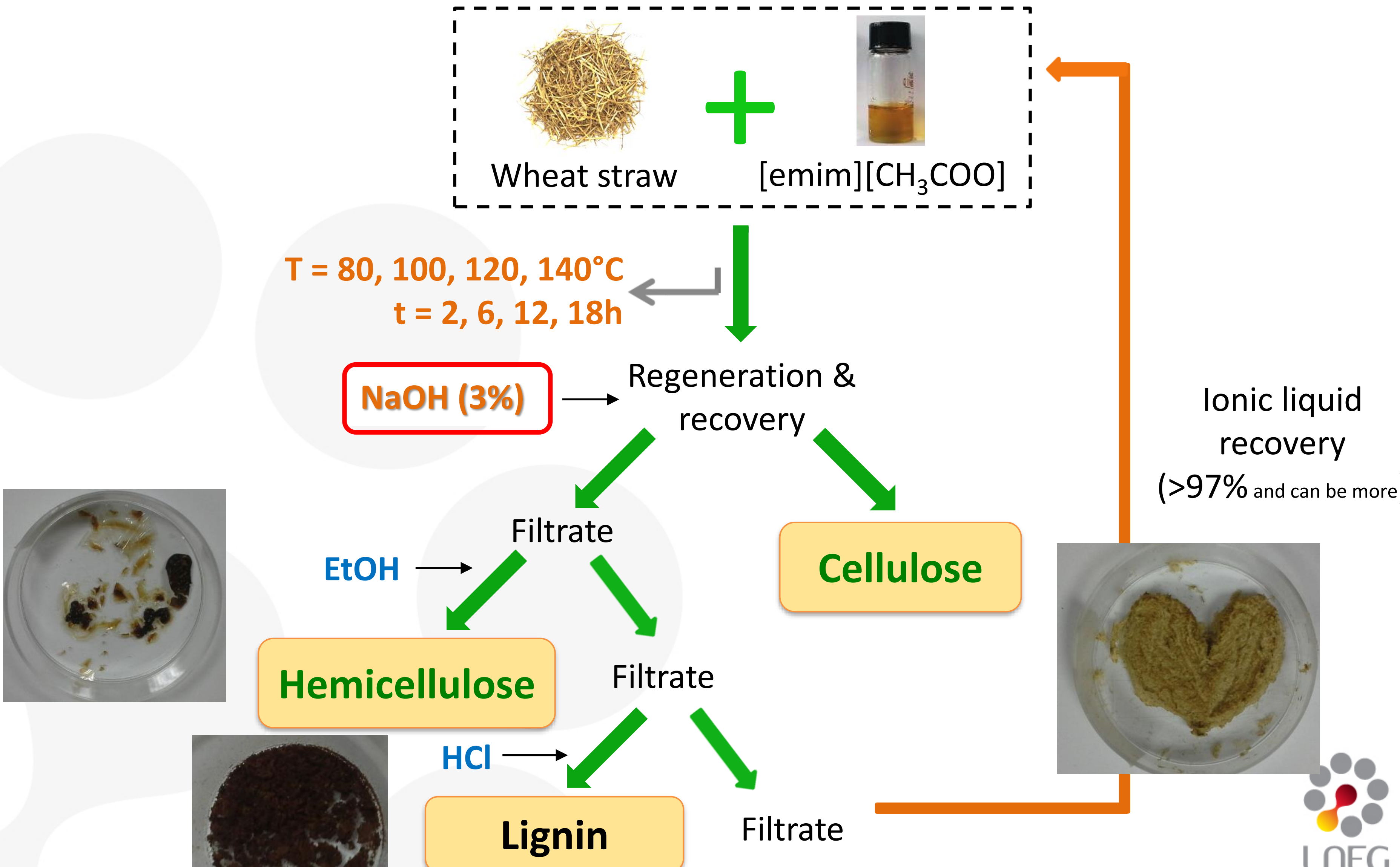
Cite this: *RSC Advances*, 2013, **3**, 16040

Novel pre-treatment and fractionation method for lignocellulosic biomass using ionic liquids

Sara P. Magalhães da Silva,[ab] André M. da Costa Lopes,[a] Luisa B. Roseiro[a] and Rafał Bogel-Łukasik*[a]

LNEG

3-step biomass fractionation with ILs



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. Bogeł-Łukasik, PT106947, 2013.

Enzymatic hydrolysis

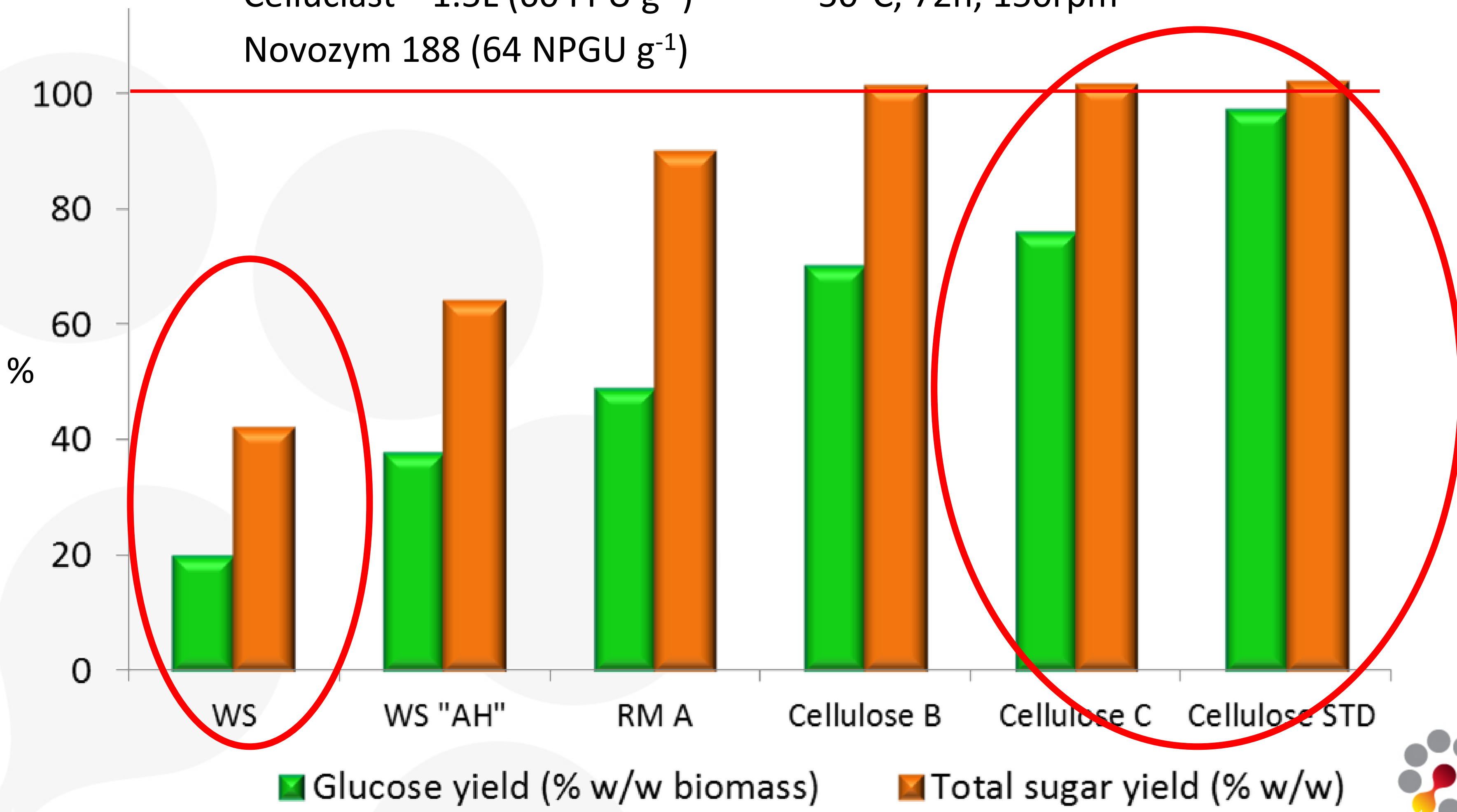
Enzymes:

Celluclast® 1.5L (60 FPU g^{-1})

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

Conditions:

$50^{o}C$, 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

Phenolic extraction from recovered IL

ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Extraction and Purification of Phenolic Compounds from Lignocellulosic Biomass Assisted by Ionic Liquid, Polymeric Resins, and Supercritical CO_2

André M. da Costa Lopes,[†,‡] Miriam Brenner,[†] Pedro Falé,[§] Luísa B. Roseiro,[†] and Rafał Bogel-Łukasik[*,†]

[†]Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia, 1649-038 Lisboa, Portugal

[‡]LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

[§]Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

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Phenolic extraction from recovered IL

Recovered
$[emim][CH_3COO]$

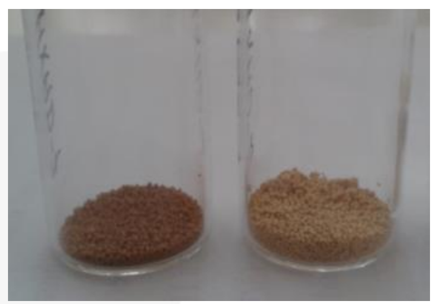
+

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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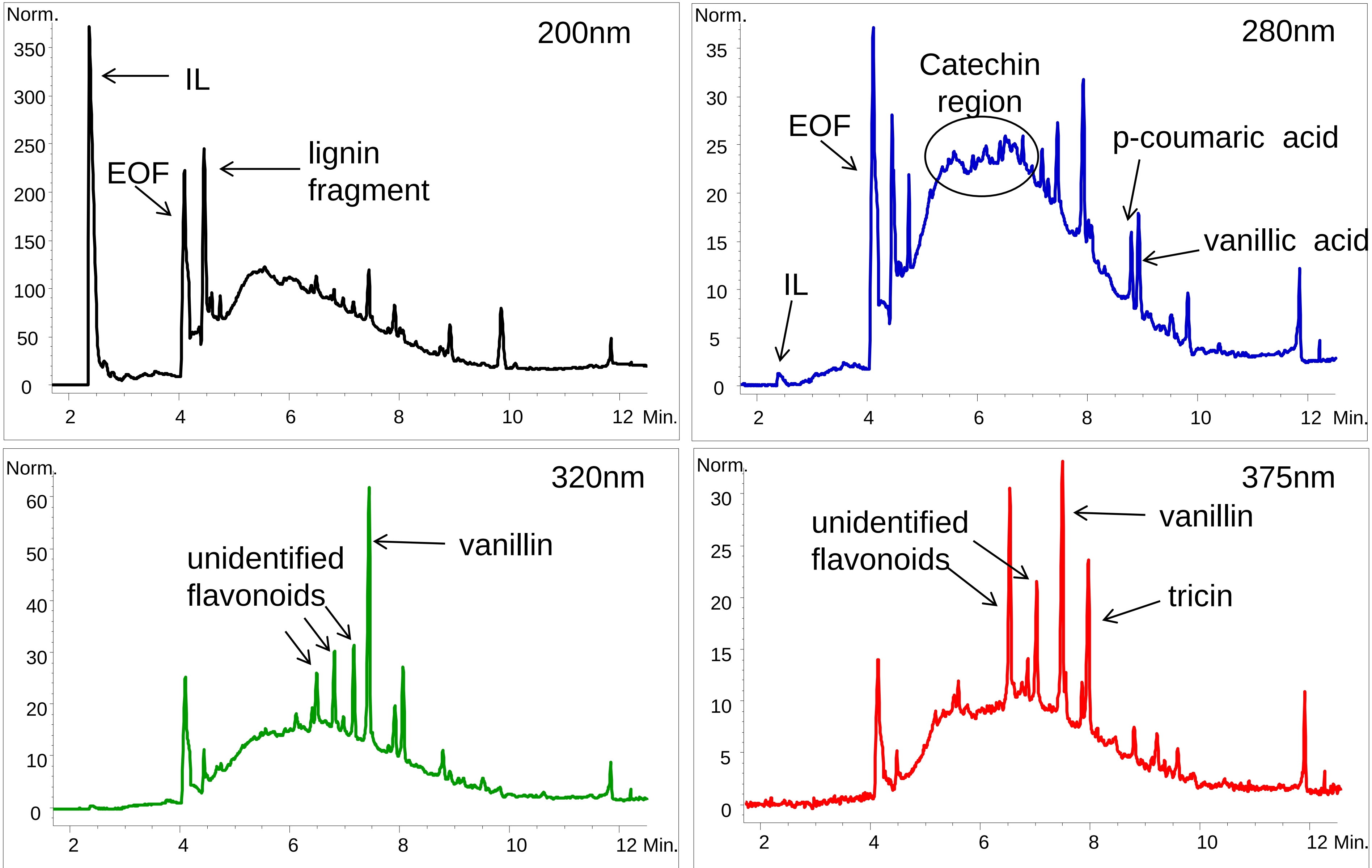
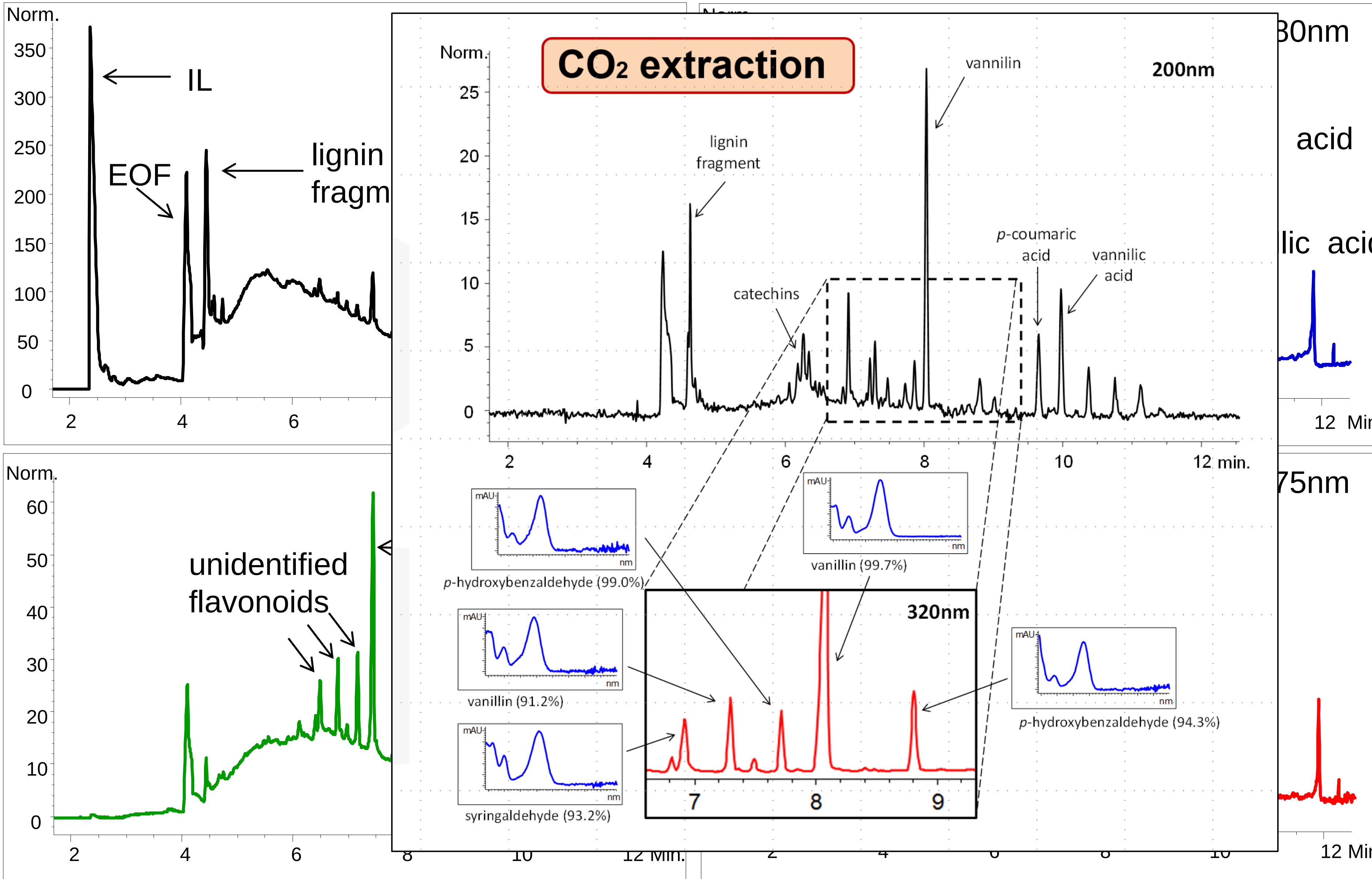
Phenolic profile with Amberlite XAD-7 resin



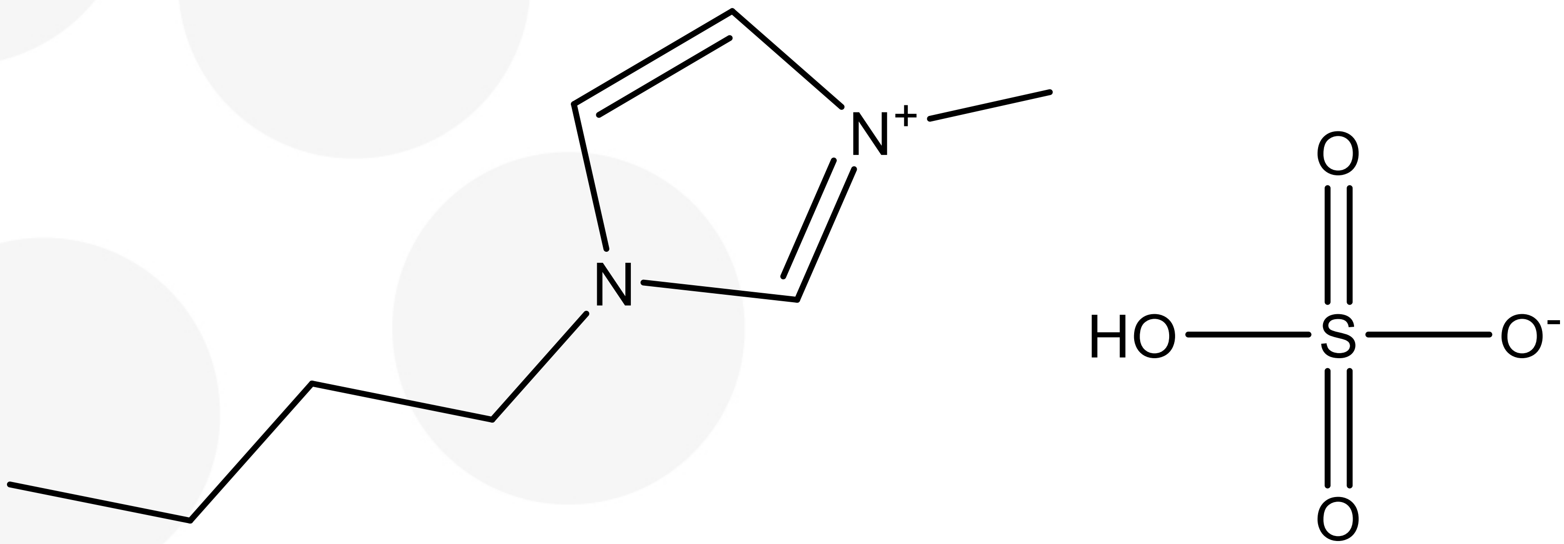
A. M. da Costa Lopes, M. Brenner, P. Fale, L. B. Roseiro and R. Bogel-Lukasik, *ACS Sustain. Chem. Eng.*, 2016, **4**, 3357

Phenolic profile with Amberlite XAD-7 resin



A. M. da Costa Lopes, M. Brenner, P. Fale, L. B. Roseiro and R. Bogel-Lukasik, *ACS Sustain. Chem. Eng.*, 2016, **4**, 3357

[bmim][HSO_4] solvent and catalyst for biomass



1-butyl-3-methylimidazolium hydrogen sulphate

Pre-treatment conditions for pentose production

Green Chemistry

PAPER

Check for updates

Cite this: *Green Chem.*, 2018, **20**, 4043

Biorefinery approach for lignocellulosic biomass valorisation with an acidic ionic liquid†

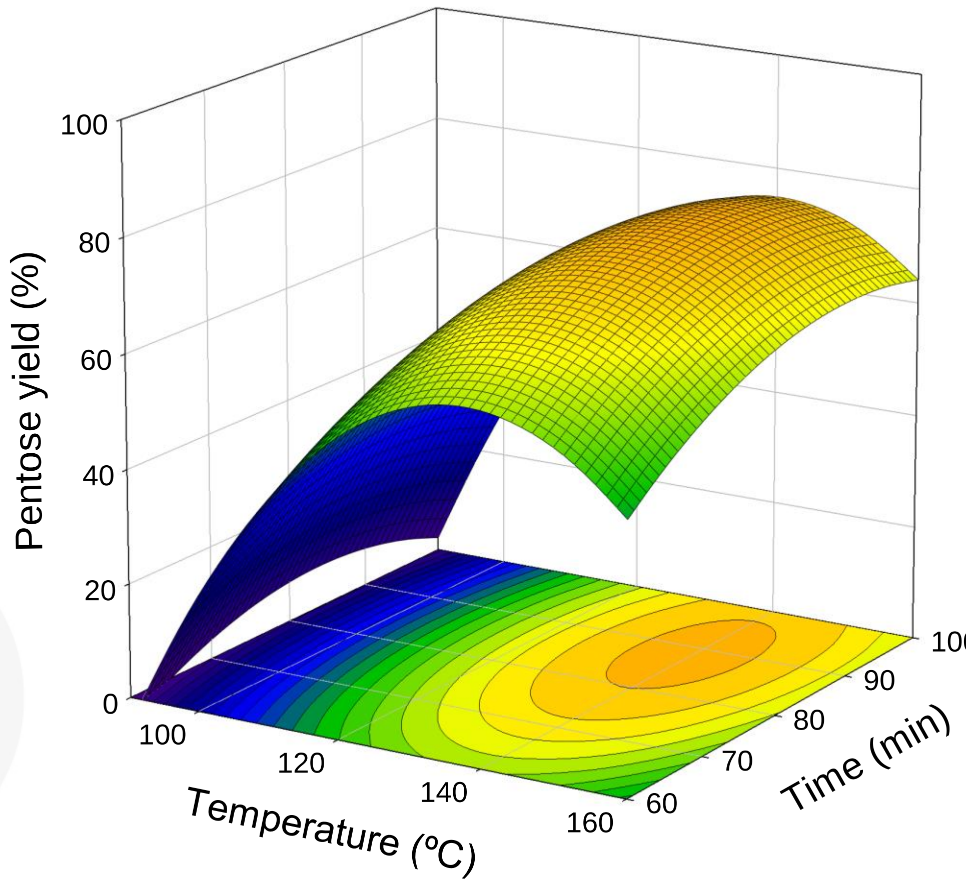
André M. da Costa Lopes, [a,b] Roberto M. G. Lins, [a,c] Ricardo A. Rebelo [c] and Rafał M. Łukasik *[a]

Pre-treatment conditions for pentose production

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2$$

Model parameters (MP)	*Y_1*	
	MP	*p*
β_0	70.36	0.001
β_1	28.33	0.004
β_2	2.59	0.72
β_3	5.95	0.45
B_{11}	-34.95	0.012
β_{22}	-8.43	0.44
β_{33}	-8.20	0.42
β_{12}	5.76	0.74
β_{13}	2.59	0.14
β_{23}	2.69	0.20
F-test		
Effectiveness of the parameters	5.90	
Significance level	0.03	
R^2	0.91	

$$Y_1 = 13.82 + 19.77X_1 + 7.04X_2 - 18.29X_1X_2 - 32.00{X_1}^2$$



Pentoses %mol	
Expected	Obtained
78.8	81.9

141 °C
90.0 min

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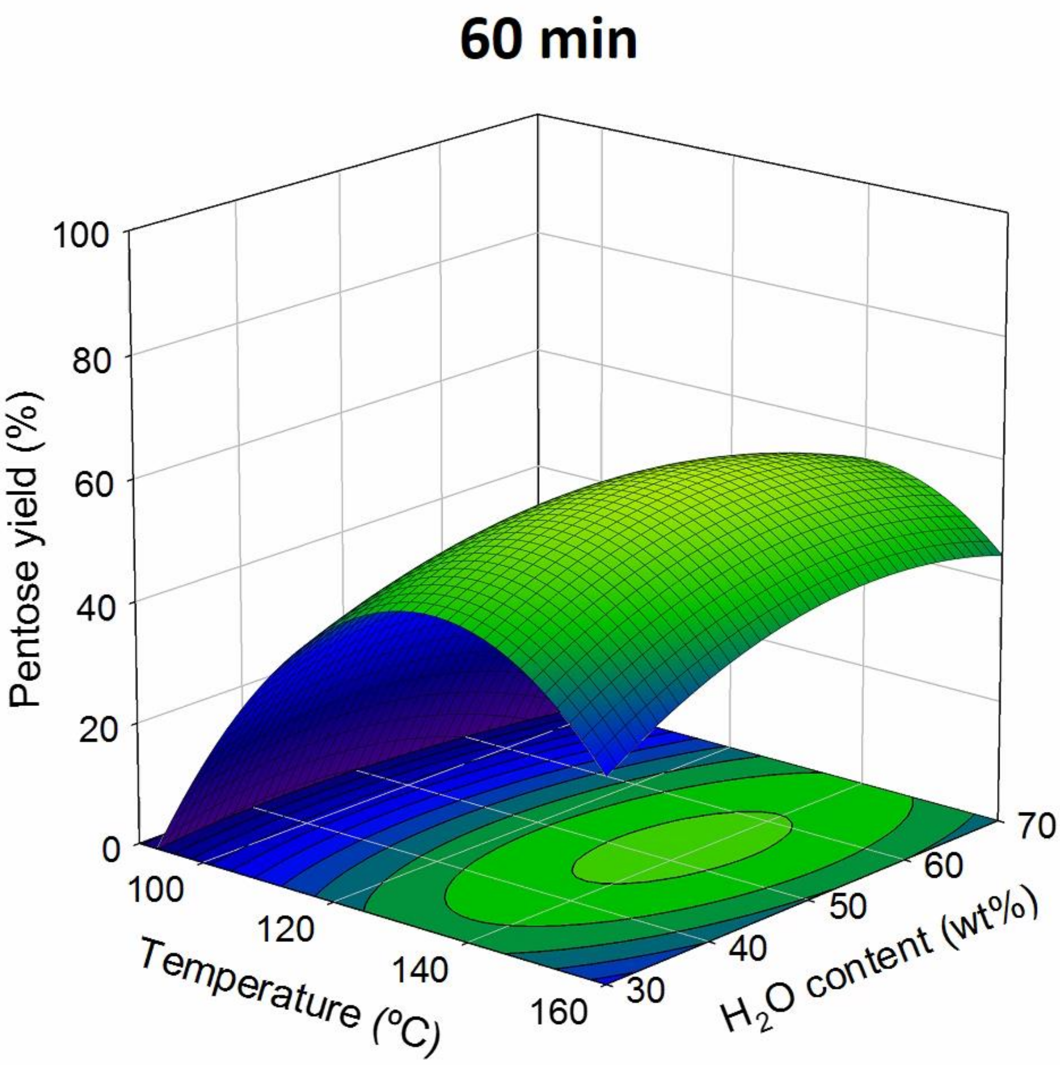
Maximisation of pentose production



Do we have cheaper alternative to ILs?

YES! It is imidazole!

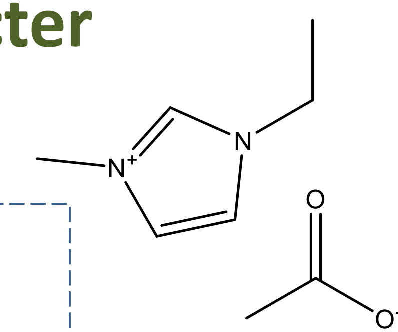
Proprieties

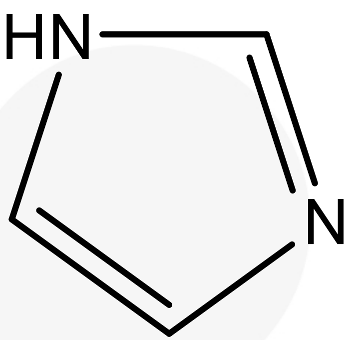
- High boiling-point
- Negligible vapor-pressure
- Low toxicity
- Easy to handle and to recycle
- Amphoteric

Broadly use:

❑ Precursor of imidazolium-based ILs

✓ **Alkaline character**





Imidazole

Alternative to:

- Ionic liquids

(*e.g.* 1-ethyl-3-methylimidazolium acetate)

- Traditional solvents

(*e.g.* ethanol, NaOH…)

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Imidazole – new alternative for IL

ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Imidazole: Prospect Solvent for Lignocellulosic Biomass Fractionation and Delignification

Ana Rita C. Morais,[†,‡] Joana Vaz Pinto,[§] Daniela Nunes,[§] Luísa B. Roseiro,[†] Maria Conceição Oliveira,[∥] Elvira Fortunato,[§] and Rafał Bogel-Łukasik*[,†]

[†]Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

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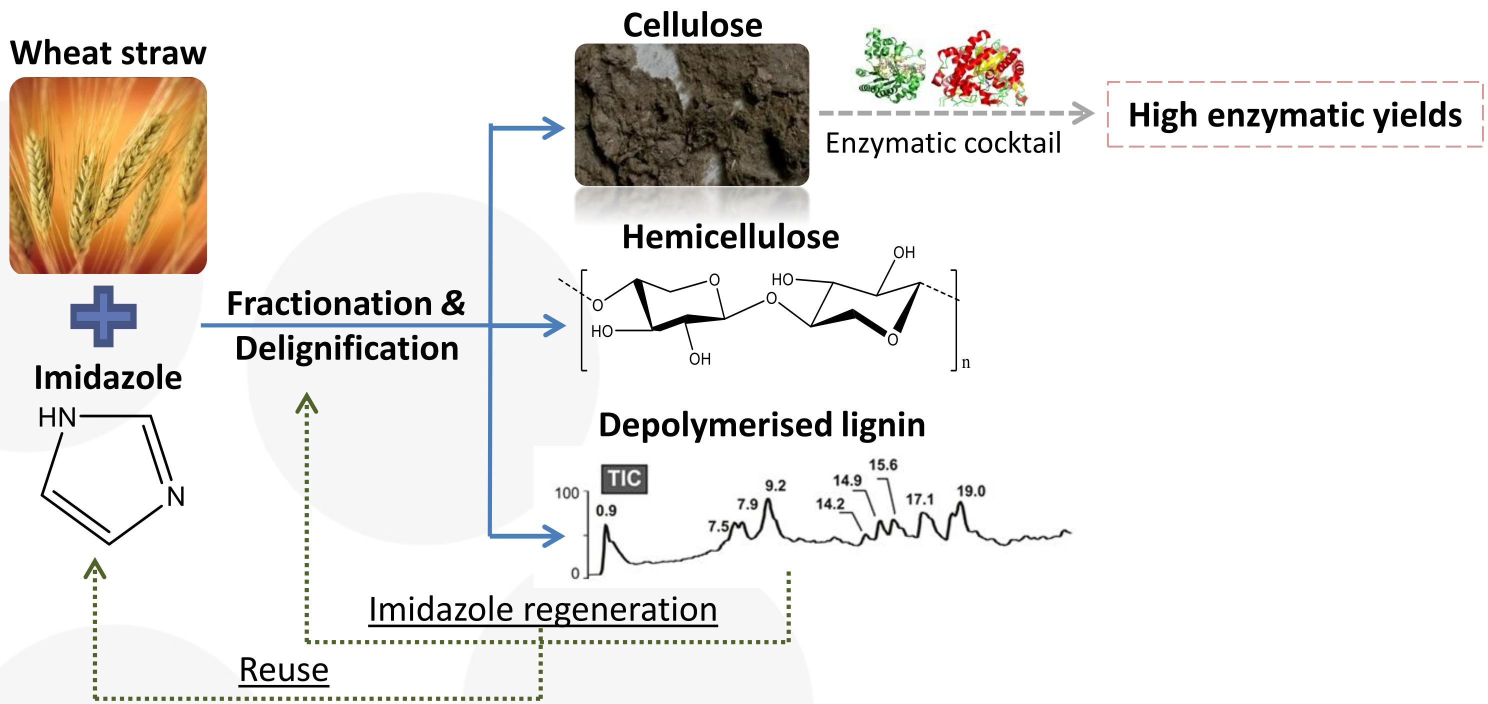
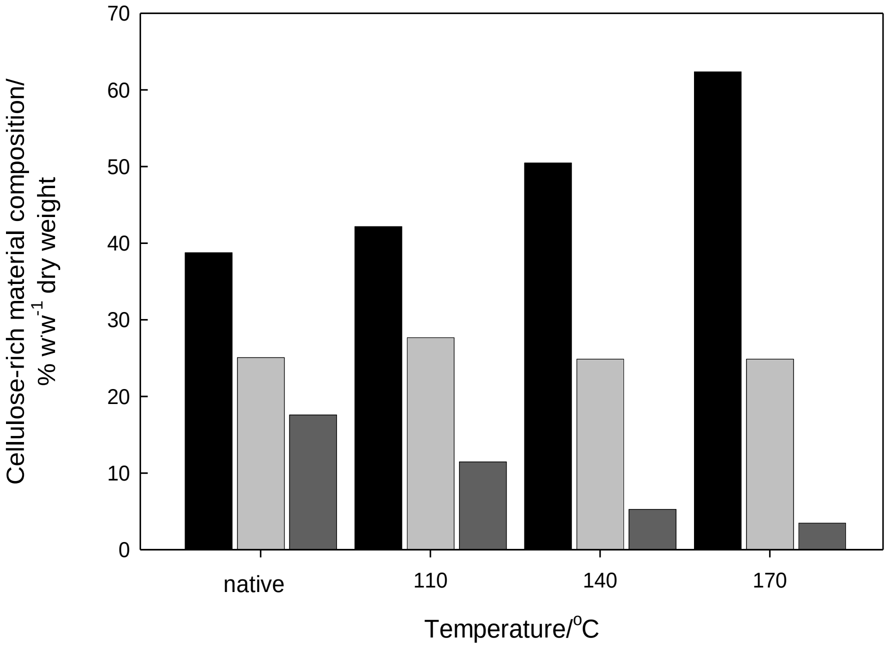
Imidazole – new alternative for IL

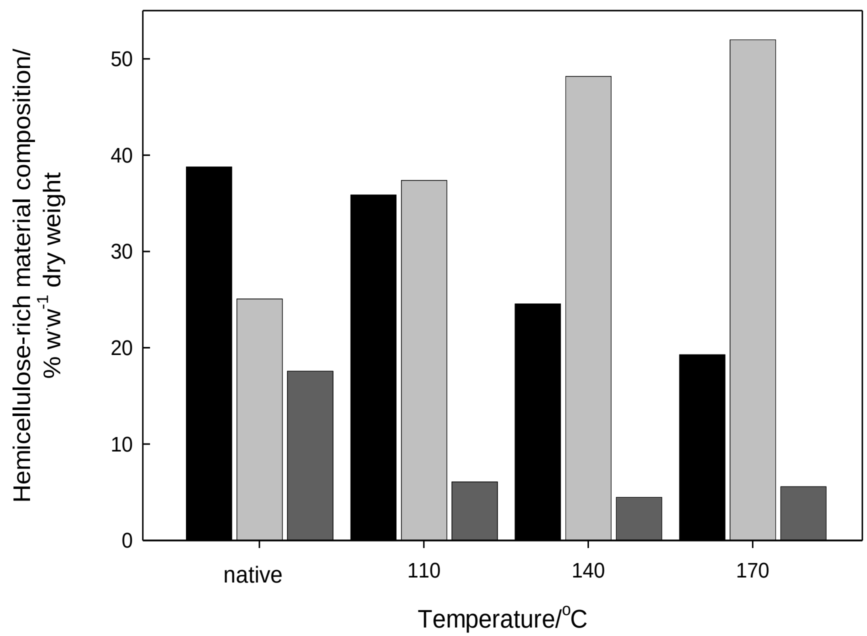


Ana Rita C. Morais, Joana Vaz Pinto, Daniela Nunes, Luísa B. Roseiro, Maria Conceição Oliveira, Elvira Fortunato, Rafał Bogel-Łukasik, *ACS Sustainable Chem. Eng.*, 2016, 4, 1643-1652

Fractionation with imidazole

Temperature effect





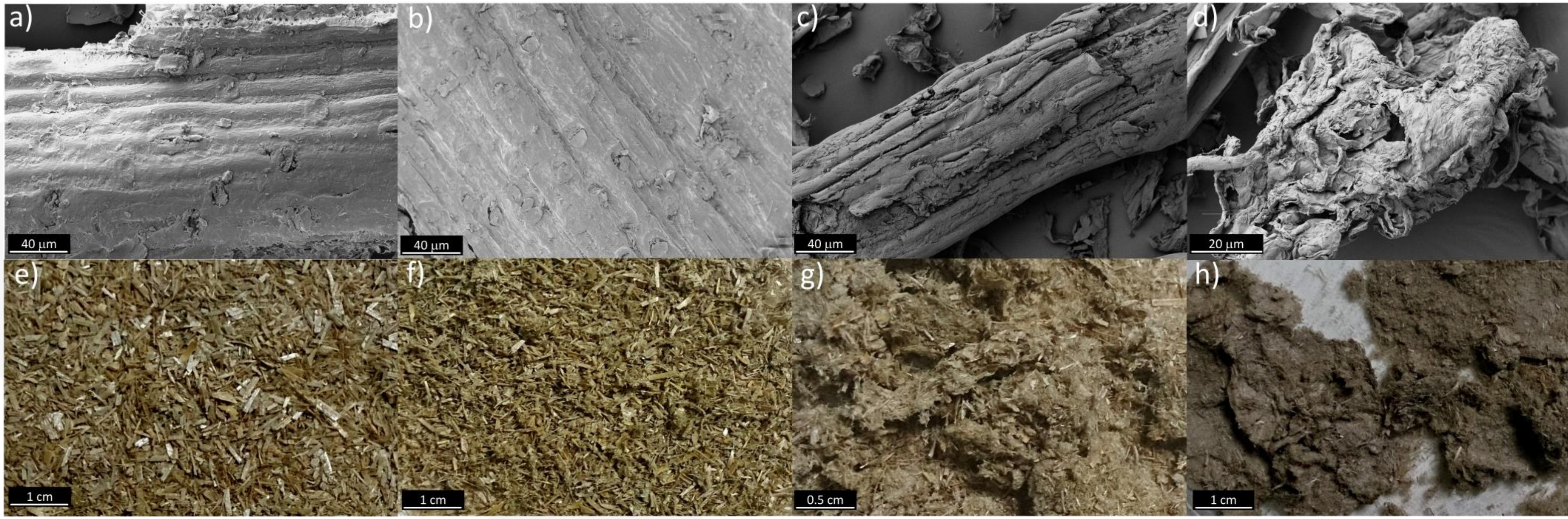
- Cellulose and hemicellulose-rich materials were achieved
- 91.4% w·w^{-1} of lignin present in wheat straw was extracted at 170 ^{o}C for 2 h

ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Imidazole: Prospect Solvent for Lignocellulosic Biomass Fractionation and Delignification

Ana Rita C. Morais,[†,‡] Joana Vaz Pinto,[§] Daniela Nunes,[§] Luísa B. Roseiro,[†] Maria Conceição Oliveira,[∥] Elvira Fortunato,[§] and Rafał Bogel-Łukasik*[,†]

Imidazole – new alternative for IL



Scanning electron microscopy images and pictures of native wheat straw (a, e) and regenerated cellulose samples produced at 110 °C (b, f), 140 °C (c, g) and 170 °C (d, h) for 2 h reaction

Ana Rita C. Morais, Joana Vaz Pinto, Daniela Nunes, Luísa B. Roseiro, Maria Conceição Oliveira, Elvira Fortunato, Rafał Bogel-Łukasik, *ACS Sustainable Chem. Eng.*, 2016, 4, 1643-1652

Fractionation with imidazole

Enzymatic hydrolysis

Pre-treatment reaction conditions		Glucan conversion	Xylan conversion
Temperature (ºC)	Time (h)	yield (w·w^{-1})	yield (% w·w^{-1})
110	2	55.3±2.3	40.3±3.1
140	2	81.9±2.4	68.9±3.3
170	2	99.3±1.7	80.9±3.8
170	1	99.8±1.5	80.3±2.8
170	4	92.8±1.3	67.3±1.6
Native wheat straw		34.3±2.1[a]	12.9±1.9[b]

- Pre-treatment with imidazole plays an important role in improving the enzymatic hydrolysis yields

ACS Sustainable Chemistry & Engineering
Research Article
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Imidazole: Prospect Solvent for Lignocellulosic Biomass Fractionation and Delignification

Ana Rita C. Morais,[†,‡] Joana Vaz Pinto,[§] Daniela Nunes,[§] Luísa B. Roseiro,[†] Maria Conceição Oliveira,[∥] Elvira Fortunato,[§] and Rafał Bogel-Łukasik*[,†]

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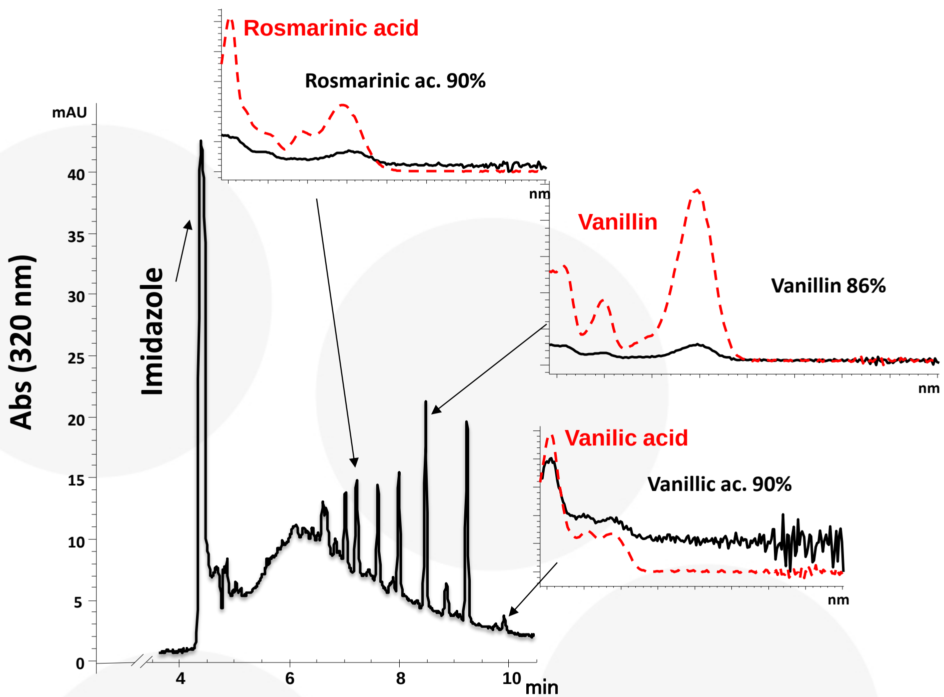
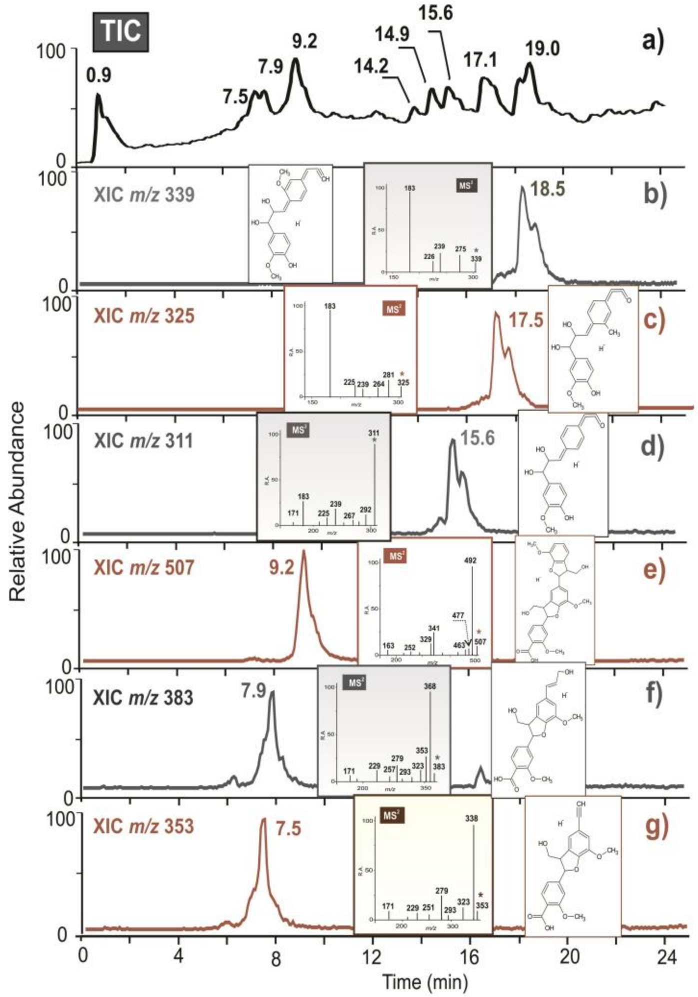
Ana Rita C. Morais, Joana Vaz Pinto, Daniela Nunes, Luísa B. Roseiro, Maria Conceição Oliveira, Elvira Fortunato, Rafał Bogel-Łukasik, *ACS Sustainable Chem. Eng.*, 2016, 4, 1643-1652

Imidazole – new alternative for IL



Electropherogram recorded at 320 nm showing the CE separations of methanolic SPE fraction. Matching percentages with authentic standards are indicated.



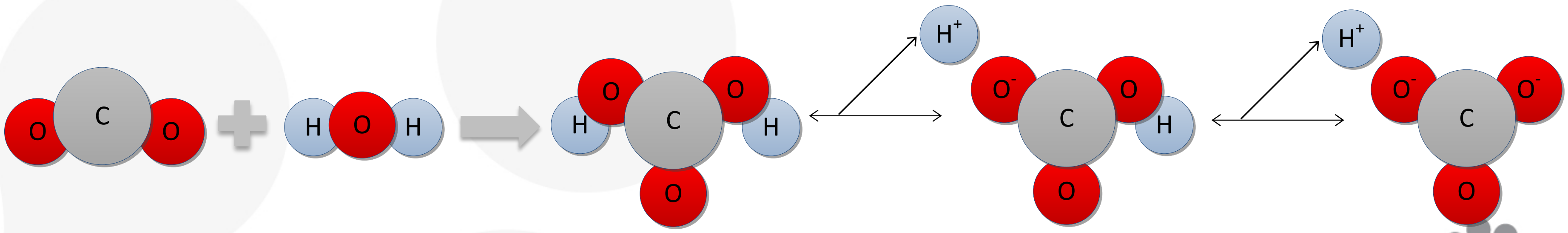
HPLC-MS/MS analysis of a sample of lignocellulosic biomass degradation products

Ana Rita C. Morais, Joana Vaz Pinto, Daniela Nunes, Luísa B. Roseiro, Maria Conceição Oliveira, Elvira Fortunato, Rafał Bogel-Łukasik, *ACS Sustainable Chem. Eng.*, 2016, 4, 1643-1652

Alternative technology

Sub-/Supercritical Fluids

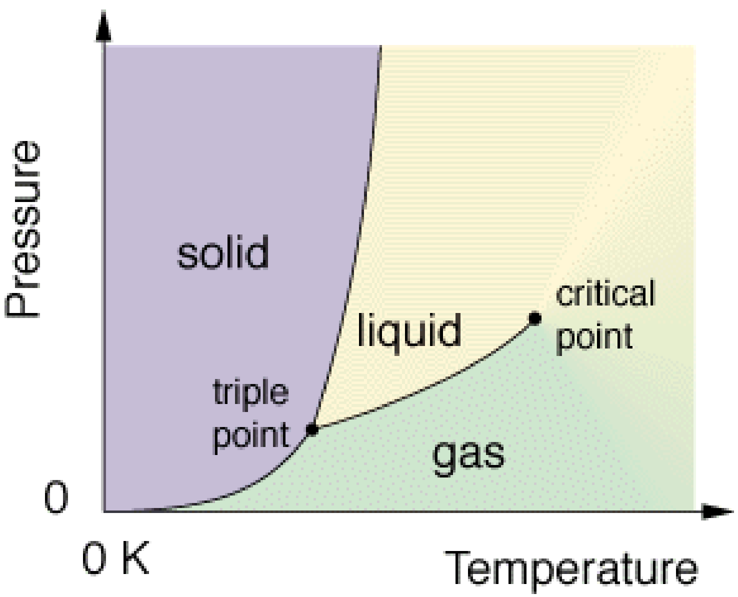
High-pressure CO_2-H_2O biphasic system

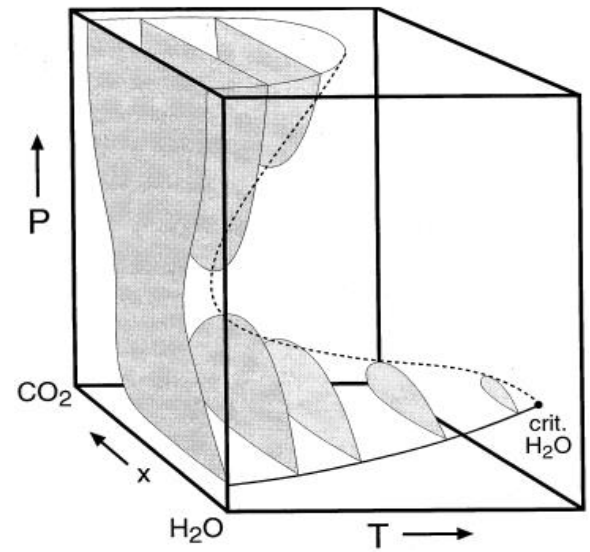


Properties of supercritical fluids

Typical supercritical solvents: CO_2, H_2O, propane, butane

- GRAS - generally regardes as safe (scCO_2 and water)
- cheap, non-toxic (scH_2O, scCO_2)
- chemically inert, odourless, testeless
- non-flammable, non-explosive
- reaction gases (H_2, O_2) totally miscible
- reaction and separation step integrated



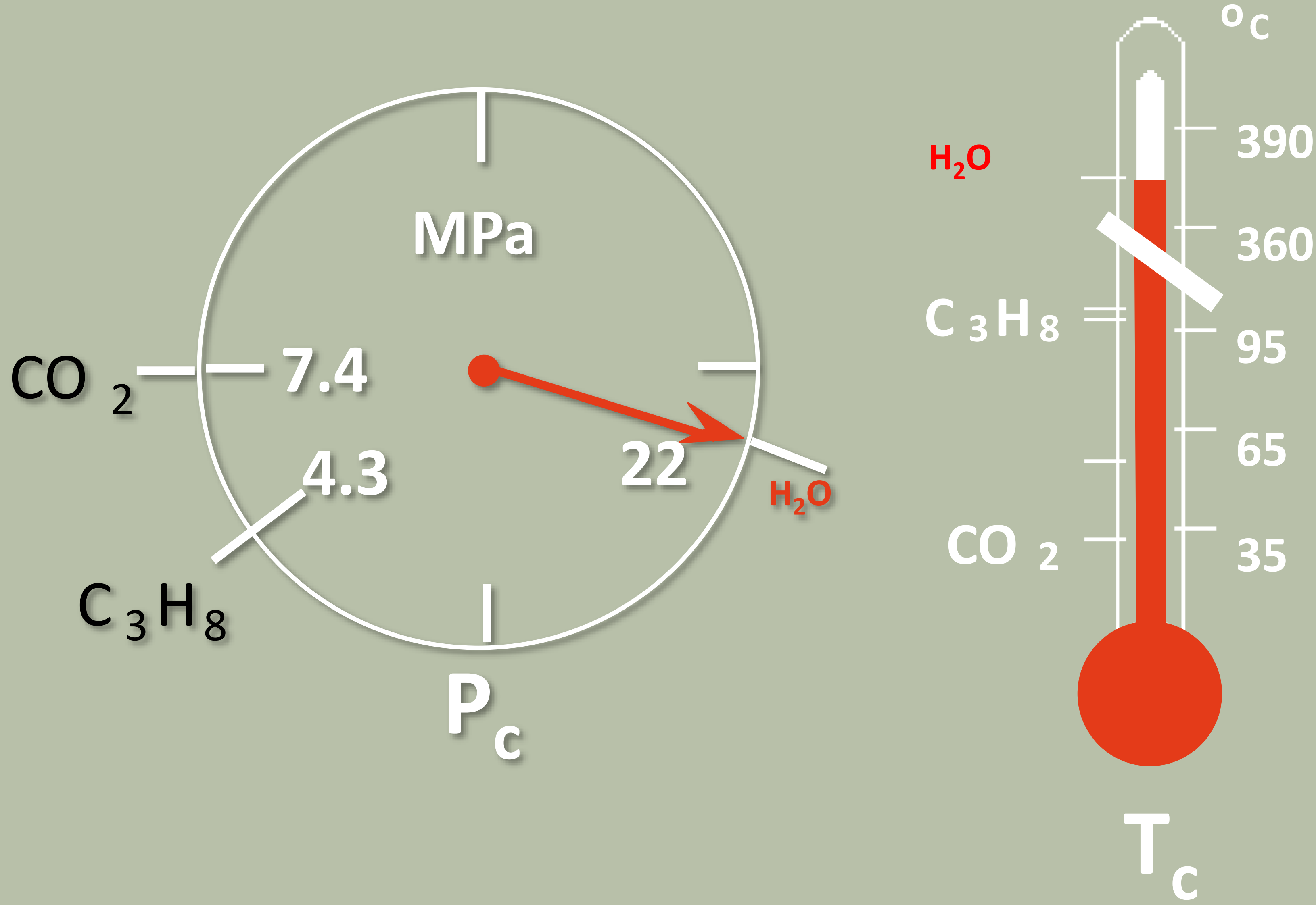


Phase diagram of CO_2 + H_2O mixture

(Geochim Cosmochim AC, 2000, 64, 1753-1764)

	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	$0.3\text{-}2.4\cdot10^{-2}$

Properties of supercritical fluids



Hydrothermal *vs.* High Pressure CO_2-H_2O mixture?

Hydrothermal

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

CO_2 + H_2O biphasic system

- Mixture becomes more acidic

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

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

↑ Hydrolysis of hemicellulose

↑ Enzymatic digestibility of cellulose

Estimated pH

$$\mathrm{pH} = 8.00 \times 10^{-6} \times \mathrm{T}^2 + 0.00209 \times \mathrm{T} - 0.216 \times \ln(\mathrm{P}_{CO_2}) + 3.92^*$$

50 bar of CO_2	20/35 bar of CO_2	Hydrothermal
3.72	3.78	5.5

pH @ T = 200 ^{o}C

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

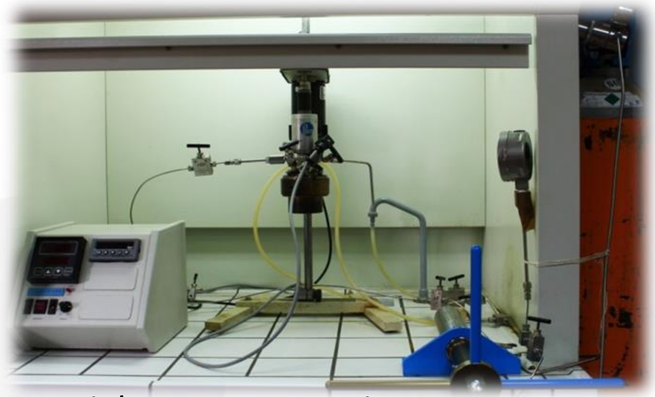
High-pressure CO_2-H_2O biphasic system

Experimental set-up

Biomass (loose, pellets)

+

H_2O & **CO_2**



High-pressure reaction system

Gas fraction

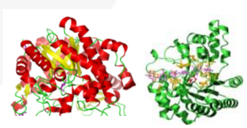
Volatile furfural

Liquid fraction

C_5-sugars-rich liquor

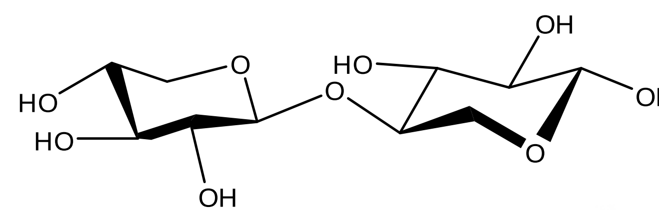
Solid fraction

Cellulose and Klason lignin



Cellulase and β-glucosidase

High saccharification yields



Xylose oligomers

Studied experimental conditions:

T = 160-220 ^{o}C
Initial pCO_2 = 20-50 bar
t = 0 to 90 min
LSR = 10 g/g

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Effect of CO_2 addition to autohydrolysis

Hydrothermal*

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

Green Chemistry

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The CO_2-assisted autohydrolysis of wheat straw

Cite this: *Green Chem.*, 2014, **16**, 238

Sara P. Magalhães da Silva,[a,b] Ana Rita C. Morais[a] and Rafał Bogel-Łukasik*[a]

*Carvalheiro et al. Appl. Biochem. Biotechnol., 2009, **153**, 84-93

Effect of CO_2 addition on the morphology of residue

- **Scanning electron microscopy**

Untreated | **Hydrothermal[a]** | **High-pressure CO_2/H_2O[a,b]**

[a]T = 225°C; [b]initial CO_2 pressure of 60 bar

Addition of CO_2 to water promotes **advanced disruption of structure** of processed solids in comparison to autohydrolysis.

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Cite this: *Green Chem.*, 2014, **16**, 4312

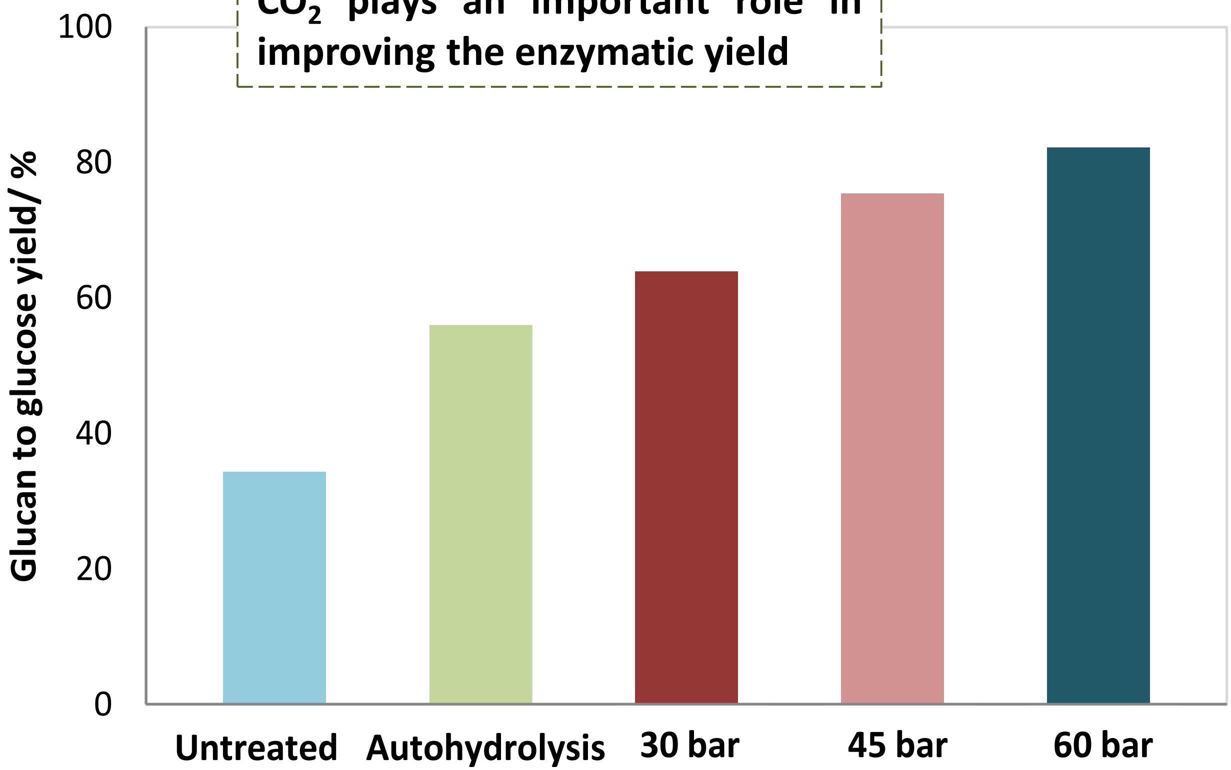
Integrated conversion of agroindustrial residue with high pressure CO_2 within the biorefinery concept

Ana R. C. Morais, Ana C. Mata and Rafal Bogel-Lukasik*

Effect of CO_2 addition and pressure

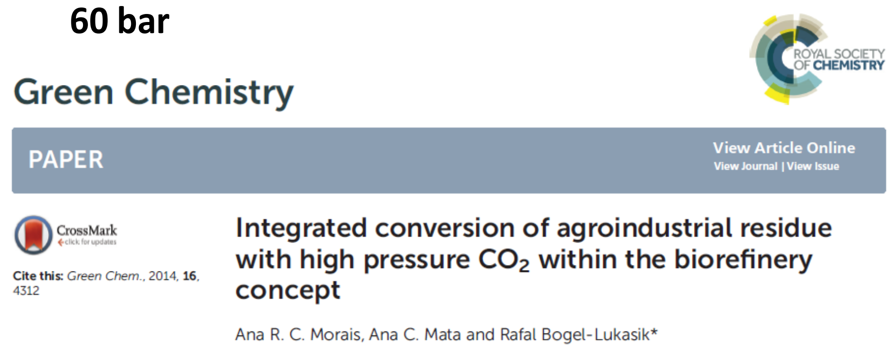
- **Enzymatic hydrolysis**

CO_2 plays an important role in improving the enzymatic yield



Reaction conditions:
T = 225 ^{o}C
t = non-isothermal conditions
p_{CO_2} = 50 bar
LSR = 10 g/g

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 ^{o}C



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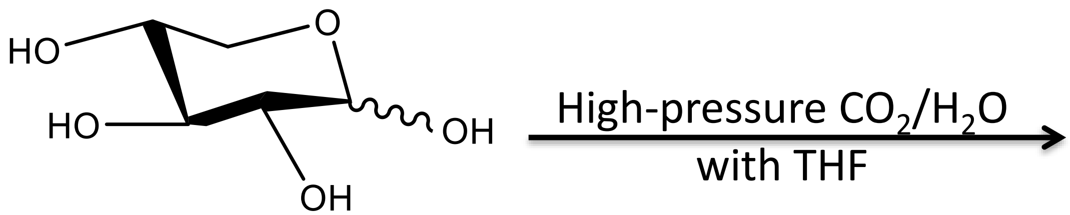
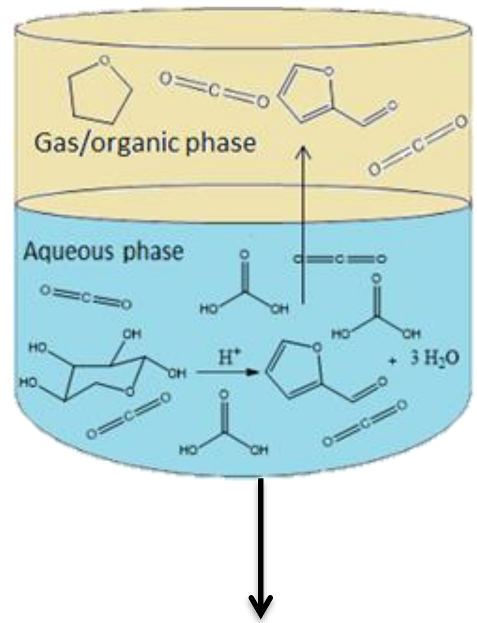
Furfural production – approach concept

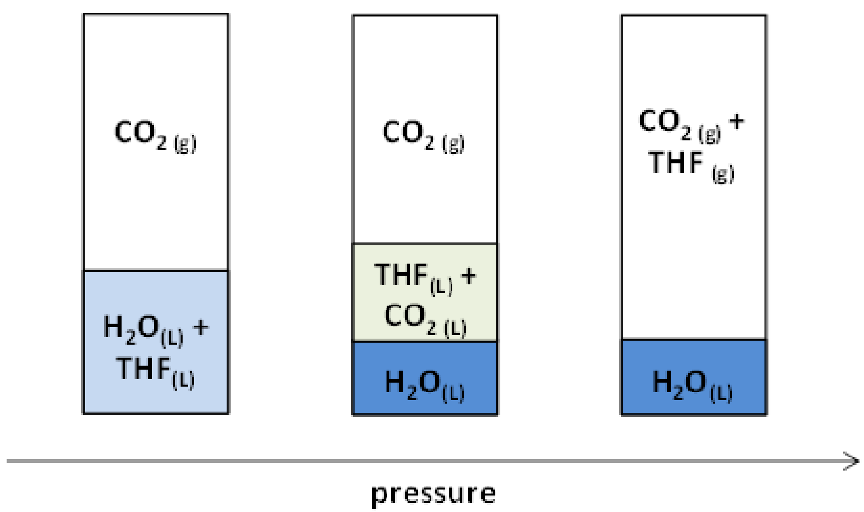


C_5-sugars rich-liquor

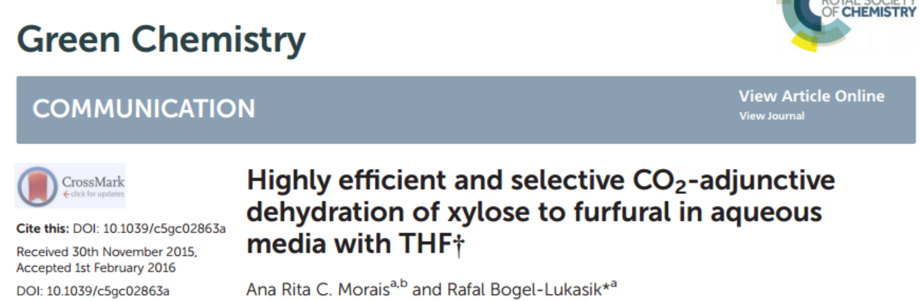


↑ **furfural yield**
↑ **reaction selectivity**

Theory beyond this approach:



Phase splitting of water/THF mixture in the presence of CO_2.
Adapted from Pollet et al., Green Chemistry, 2014, **16**, 1034–1055.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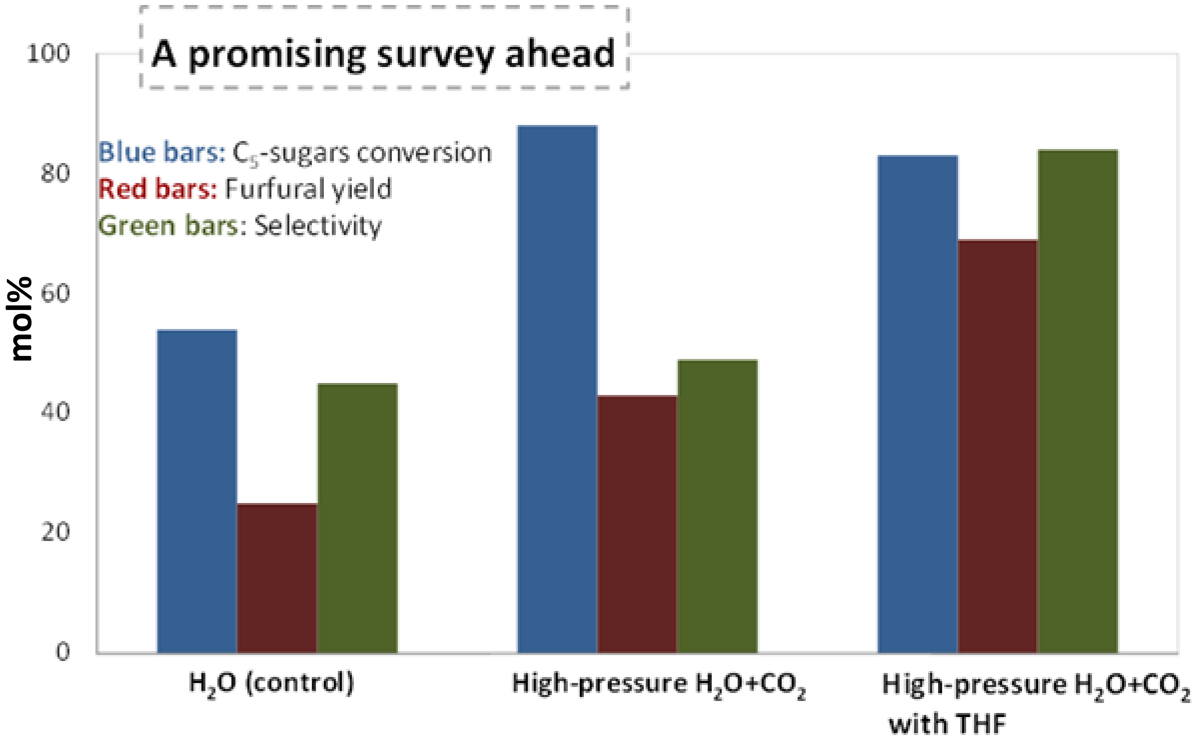
Highly efficient and selective CO_2-adjunctive dehydration of xylose to furfural in aqueous media with THF†

Ana Rita C. Morais[a,b] and Rafal Bogel-Lukasik*[a]

CO_2 as catalyst and phase splitting inductor



Best reaction conditions:

T = 180 ^oC
t = 60 min
p_{CO_2} = 50 bar
V_{H_2O}/V_{THF} **ratio** = 10/5, mL/mL
[Xylose]$_{feed}$ = 12.5 g/L

Main results

- High-pressure CO_2 acts as acidic **catalyst** and **phase splitting inductor**
- THF acts as *in-situ* furfural **extracting solvent**

Benefits

- Acidic medium **does not** represent a problem
- **No need of salts** → biphasic system
- CO_2 and THF are easily **recycled** and **reused**

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Take Home Message

Every action we take influences the entire value chain and because of this to achieve a **breakthrough** needed to address the challenges of nowadays society collaboration between technology, social sciences & humanities are strongly needed!

„I understand that international cooperation is a very hard task. However, it must be undertaken even at the cost of many efforts and true dedication"

Maria Skłodowska-Curie

LNEG

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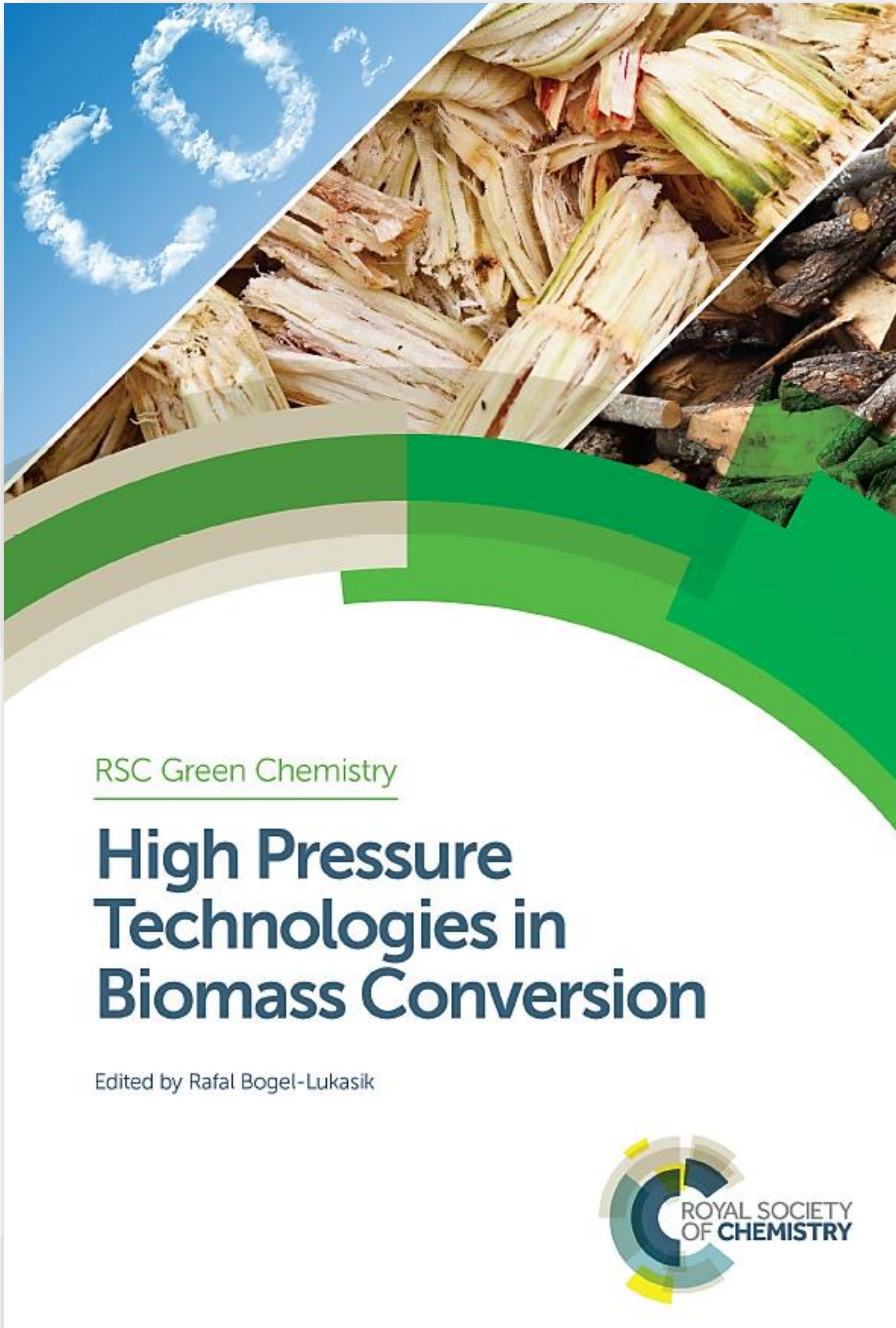
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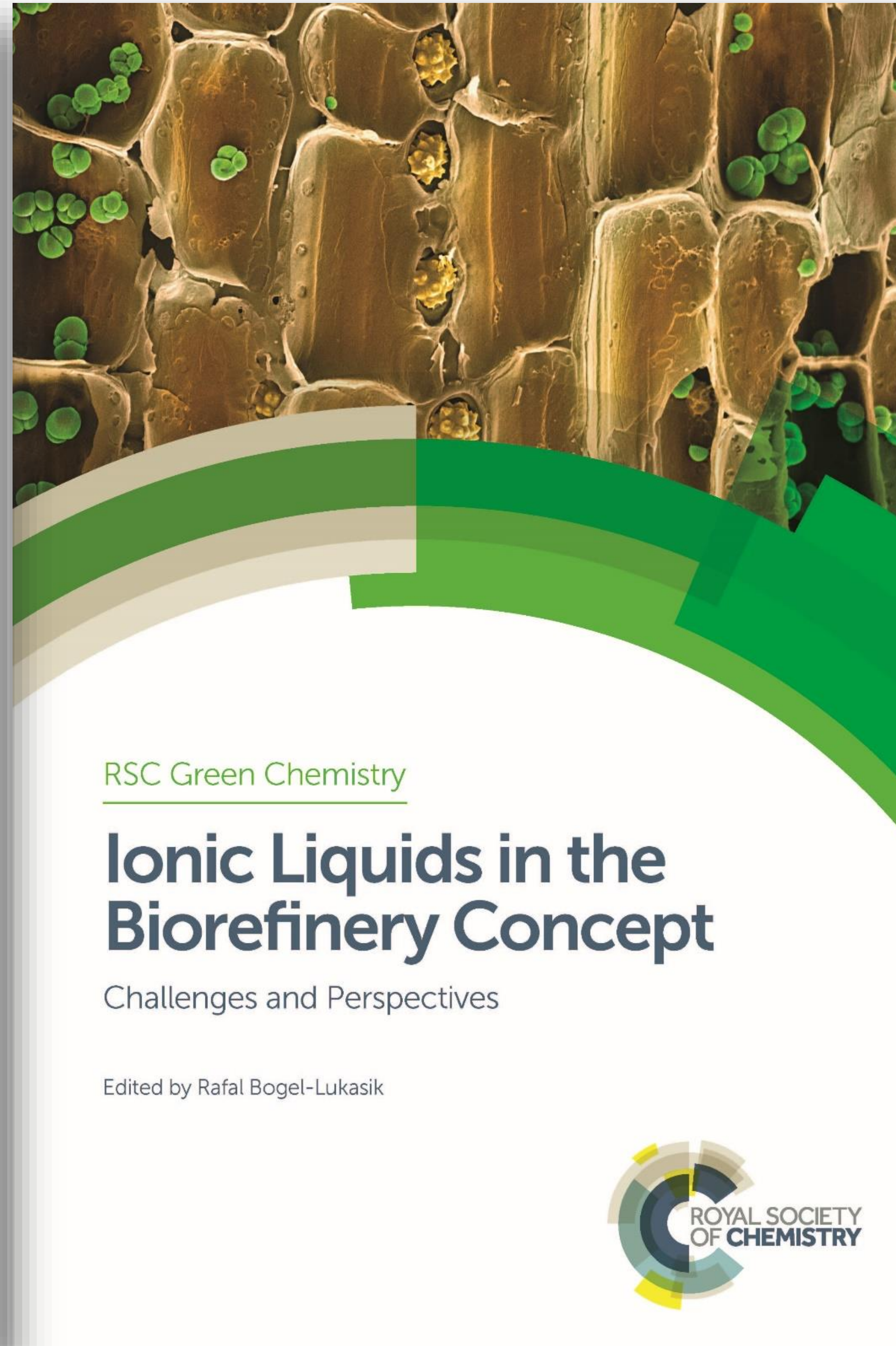
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