Test presentation

Max Kochanski, CBI

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How to speed up the R&D implementation – use of high-pressure fluid in the production of pivot compounds from biomass

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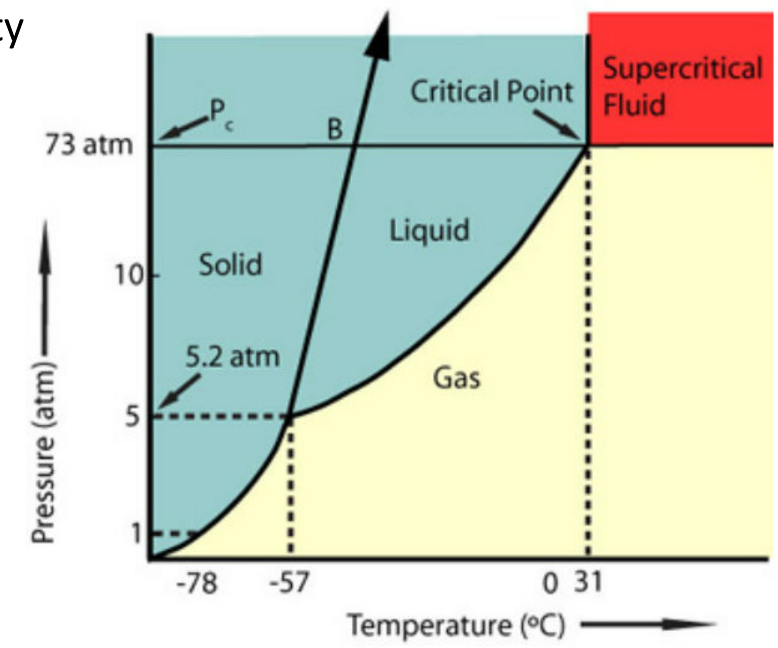
Supercritical Fluids

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

- Unique physicochemical properties such as liquid-like density and gas-like diffusivity
- Tunable properties
- Environmentally sustainable



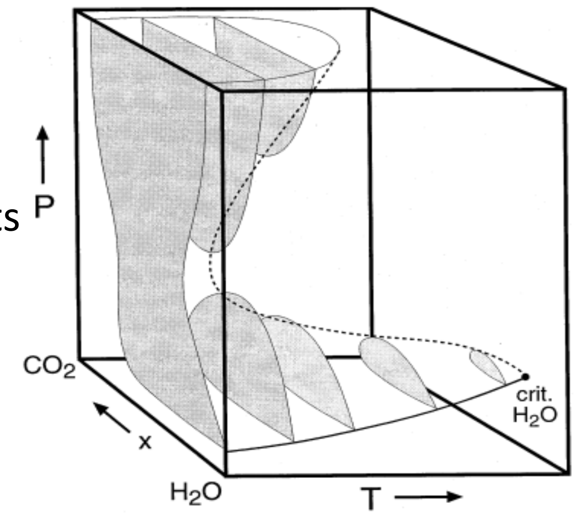
Typical fluids: CO_2, H_2O, propane

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

Why high-pressure CO_2/H_2O biphasic system?

Main advantages

- ❑ Green solvents
- ❑ Nontoxic, nonflammable and inexpensive reagents
- ❑ Easy to scale-up
- ❑ ↓Temperatures and ↓ degradation products
- ❑ It can act as a detoxification methodology



Phase diagram of CO_2/H_2O mixture
(Geochim Cosmochim AC, 2000, 64, 1753-1764)

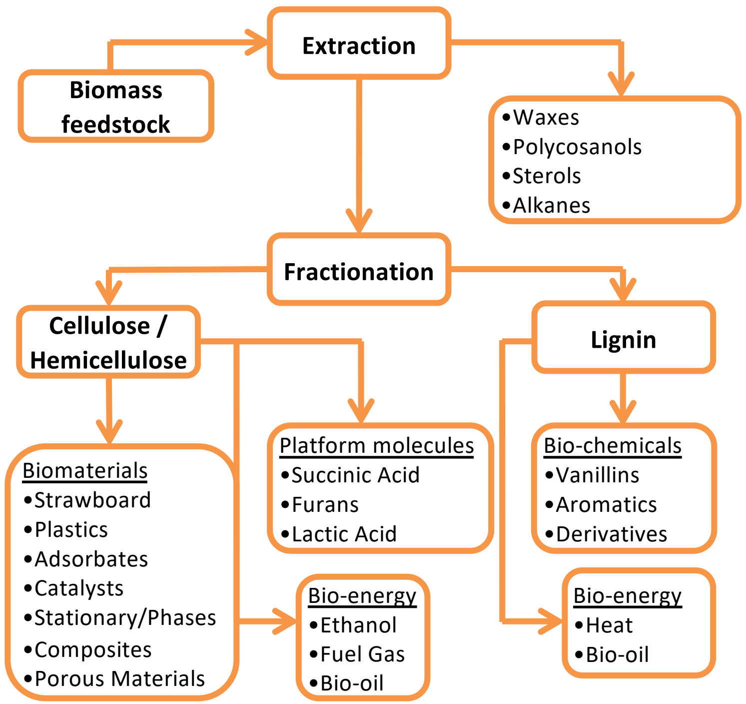
CHEMICAL REVIEWS
Review
pubs.acs.org/CR

Carbon Dioxide in Biomass Processing: Contributions to the Green Biorefinery Concept

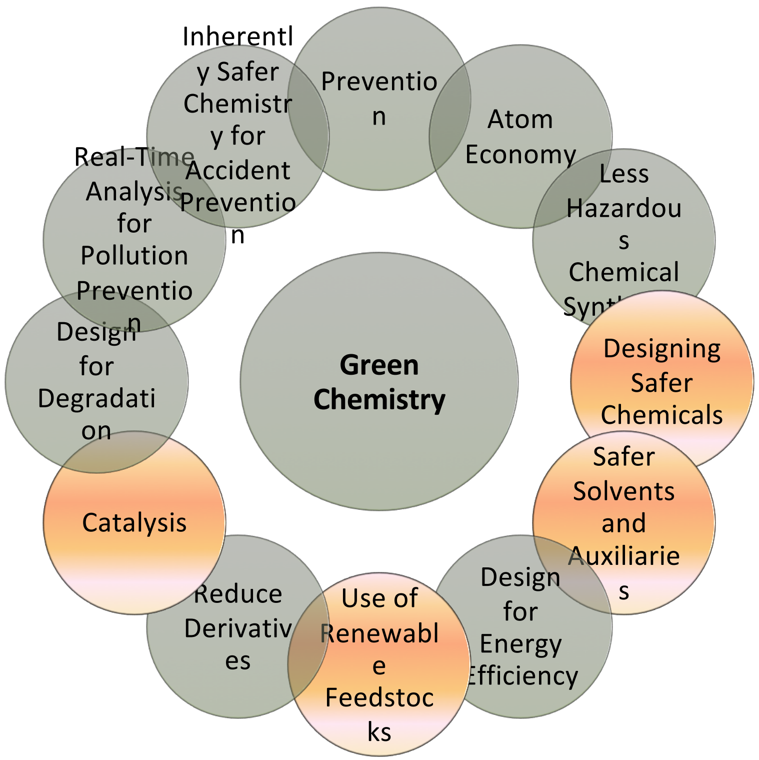
Ana R. C. Morais, Andre M. da Costa Lopes, and Rafał Bogel-Łukasik*

LNEG

Integration of Green Chemistry into Biorefinery

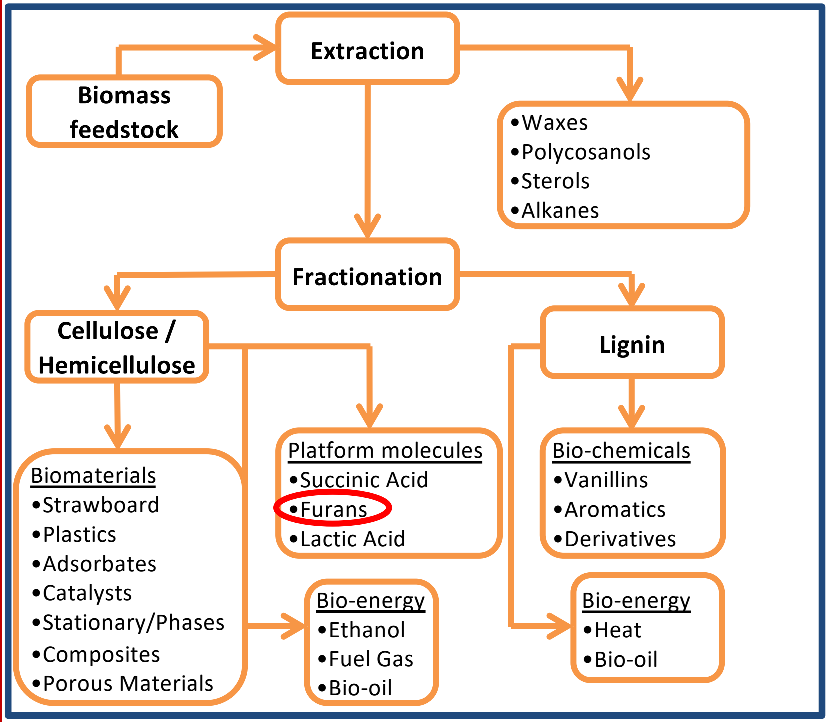


Biorefinery concept scheme.
Adapted from Kamm et al. Biorefineries – Industrial Processes and Products. Ullmann's Encyclopedia of Industrial Chemistry, 2007.



Twelve principles of Green Chemistry.
Adapted from Anastas and Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.

Most promising chemicals produced from biomass



Top 10 added-value chemicals

1. Ethanol
2. **<u>Furans (FURFURAL)</u>**
3. Glycerol and derivatives
4. Biohydrocarbons
5. Lactic acid
6. Succinic acid
7. Hydroxypropionic acid/aldehyde
8. Levulinic acid
9. Sorbitol
10. Xylitol

Biorefinery concept scheme.
Adapted from Kamm et al. Biorefineries – Industrial Processes and Products. Ullmann's Encyclopedia of Industrial Chemistry, 2007.

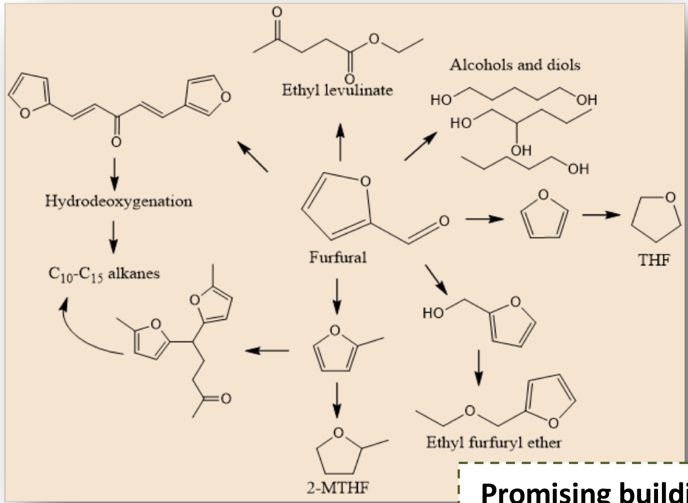
Top 10 added-value chemicals produced from biorefinery carbohydrates.
Bozell and Petersen, Green Chemistry. 2010, **12**, 539-554.

Problems, Challenges & Proposed solution

FURFURAL

✓ Versatile biomass-based platform chemical

Potential:



Promising building-block

Outline of potential chemical and fuel derivatives produced from furfural.

Adapted from Lange et al., ChemSusChem. 2012, **5**, 150–166

PROBLEM

I S ıction:

- X mineral acid-based
- X corrosion problems
- X low yield and selectivity
- X waste streams

CHALLENGES

NOVEL AND CLEANER TECHNOLOGY

It would be characterised by:

- ✓ no need of mineral acids/halides and heterogeneous catalysts addition
- ✓ green solvents (e.g. H_2O and CO_2)
- ✓ biphasic system → no need of salts

PROPOSED SOLUTION

High-pressure CO_2 as:

- ❑ promoter of *in-situ* **acid catalyst** formation & **phase separation inducer**

Furfural production – approach concept

Water processes

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

CO_2 + H_2O biphasic system

- ❑ Mixture becomes more acidic (pH ≈ 3)

$$\boldsymbol{CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+}$$

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

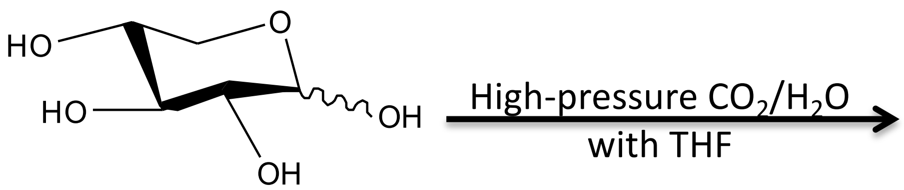
➡ *In-situ* formation of carbonic acid

50 bar of CO_2	20/35 bar of CO_2	Water process
3.72	3.78	5.5

T = 200 ^oC

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

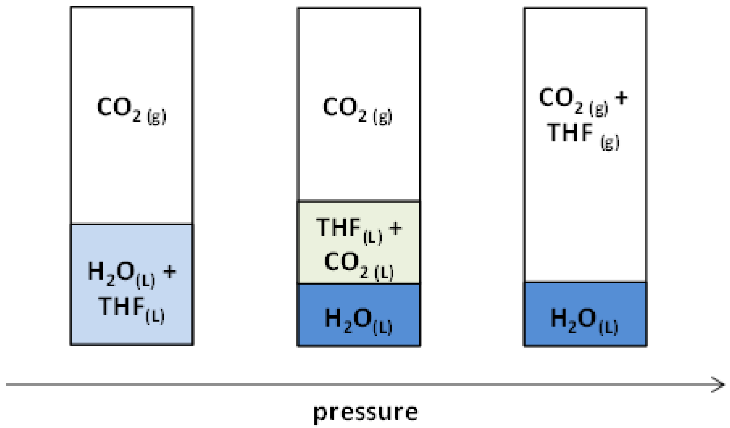
Furfural production – approach concept



C_5-sugars rich-liquor

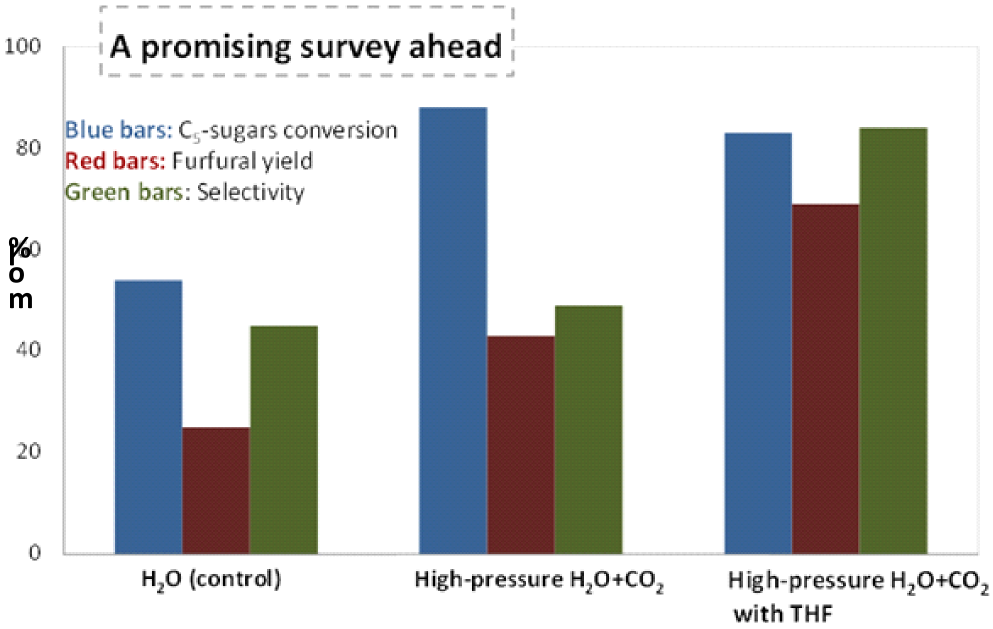
↑ **furfural yield**
↑ **reaction selectivity**

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.

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

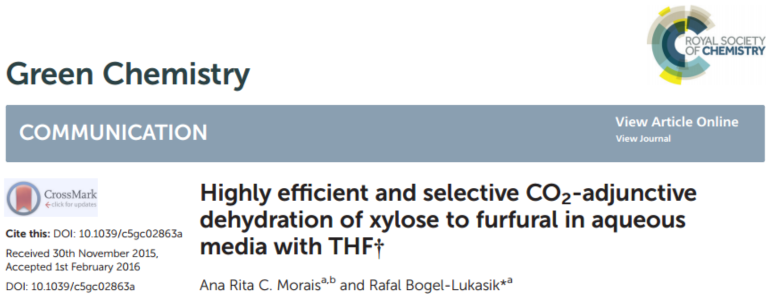
[Xylose]$_{feed}$ = 12.5 g/L

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**


Green Chemistry

COMMUNICATION

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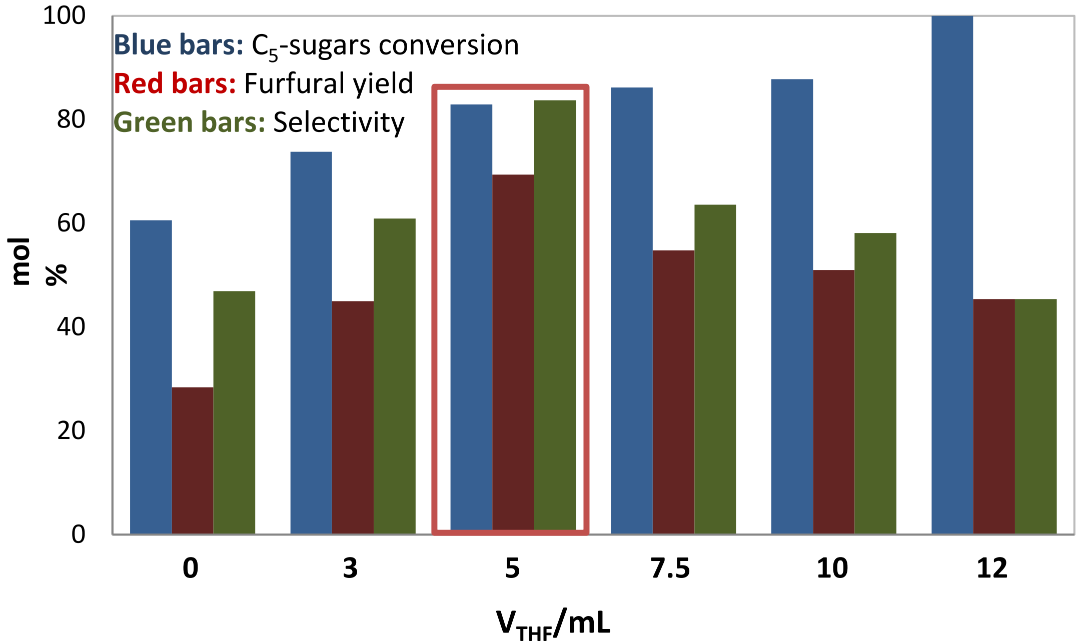
Highly efficient and selective CO_2-adjunctive dehydration of xylose to furfural in aqueous media with THF†

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

Does quantity of THF influence the furfural production?



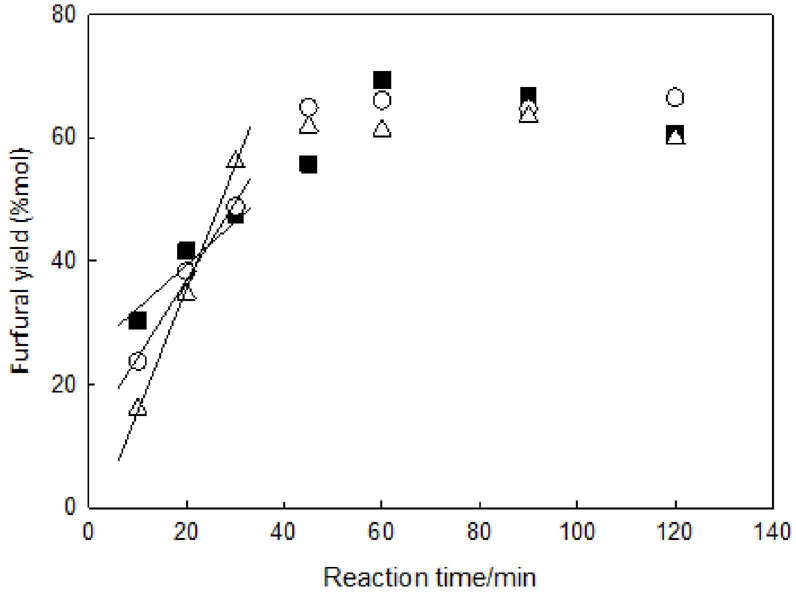
Reaction conditions:
T = 180 ^oC
t = 60 min
p_{CO_2} = 50 bar
[Xylose]$_{feed}$ = 12.5 g/L
Total volume = 15 mL

Benefits

- Higher V_{THF} in reactive system adjuncts to achieve higher xylose conversion
- Excessive amount of THF has negative effect on furfural yield and reaction selectivity

Influence of other parameters

- Holding time and initial xylose feed



The evolution of furfural yield for various initial xylose concentrations achieved over time (■ –12.5 g/L, ○ – 9.4 g/L, △ – 6.3 g/L)

Reaction condition:
T = 180 °C
t = 60 min
p_{CO_2} = 50 bar
V_{H_2O} / V_{THF} **ratio** = 10/5, mL/mL

Results

- Furfural production was the fastest for the lowest xylose concentration
- Prolonged reaction times have negative effect on the furfural yield

Production of furfural from lignocellulosic residue

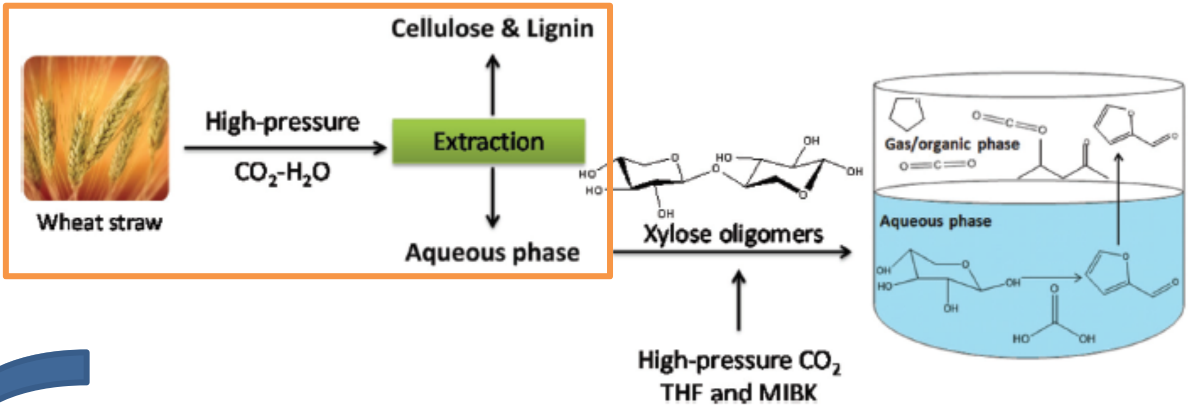


Table 2 Composition of hemicellulose hydrolysates (g L^{-1}) and yield of each product (g per 100 g of initial amount of polymer present in wheat straw) obtained in the high-pressure CO_2–H_2O experiments

	T (°C)	200								210		220	
	t (min)	0		5		10		15		0		0	
	$pCO_{2\ initial}$ (bar)	50		50		50		50		50		50	
Reaction conditions	Final pH[a]	3.91		3.52		3.31		3.20		3.68		3.29	
Composition/yield		g L^{-1}	g per 100 g	g L^{-1}	g per 100 g	g L^{-1}	g per 100 g	g L^{-1}	g per 100 g	g L^{-1}	g per 100 g	g L^{-1}	g per 100 g
XOS		12.9	71.7	7.4	41.4	1.8	10.4	—	—	11.0	61.4	3.5	20.2
Xylose		2.3	11.4	5.1	24.7	6.5	31.9	4.1	19.9	3.8	18.5	5.5	28.5
AOS		1.0	21.3	0.1	2.0	0.2	5.4	—	—	0.1	2.0	0.2	4.3
Arabinose		1.9	36.9	1.8	35.2	1.2	22.4	0.8	14.9	2.1	40.9	1.1	22.0
Furfural		0.6	4.4	2.5	19.5	5.1	39.1	6.1	46.6	1.3	9.7	3.3	26.8
Formic acid		1.2	—	2.4	—	3.3	—	3.6	—	2.1	—	3.0	—
AcOS		1.7	—	0.6	—	—	—	—	—	0.7	—	0.2	—
Acetic acid		2.1	—	3.5	—	5.0	—	5.6	—	3.1	—	4.3	—
GlcOS		5.5	12.7	5.3	12.3	3.1	7.4	1.7	3.9	4.6	10.8	3.4	8.3
Glucose		0.7	1.5	1.1	2.2	1.9	3.9	2.0	4.2	1.1	2.2	1.5	3.3
5-HMF		—	—	0.2	0.6	0.5	1.6	1.0	2.9	0.1	0.3	0.3	1.0

[a] Measured pH of hydrolysate after hemicellulose extraction reactions; XOS – xylooligosaccharides; AOS – arabinooligosaccharides; AcOS – acetyl groups linked to oligosaccharides; GlcOS – glucooligosaccharides; 5-HMF – 5-hydroxymethylfurfural.

Production of furfural from lignocellulosic residue

Table 3 Chemical composition of hemicellulose hydrolysate from high-pressure CO_2–H_2O process and aqueous and organic phases produced after dehydration of hemicellulose hydrolysate performed under high pressure CO_2 as a catalyst in a water/THF system with MIBK

	Concentration ($g\ L^{-1}$)			
		After dehydration to furfural[b]		
Components	After hemicellulose extraction[a]	Aqueous phase	Organic phase	Σ
Xylose				
Monomers	2.3	0.3	—	0.3
Oligomers	12.9	—	—	—
Arabinose				
Monomers	1.9	—	—	—
Oligomers	1	—	—	—
ΣC_5-sugars	18.1	0.3	—	0.3
Glucose				
Monomers	0.7	0.5	—	0.5
Oligomers	5.5	—	—	—
ΣC_6-sugars	6.2	0.5	—	0.5
Aliphatic acids				
Acetic	2.1	1.3	1.4	2.7
Formic	1.2	2.1	0.9	3.1
Furans				
Furfural	0.6	0.2	2.9	3.1
5-HMF	—	0.5	0.6	1.1

[a] Reaction conditions: 200 °C, 50 bar of initial CO_2 pressure, mixture loading of 10 (75 g of H_2O/7.5 g of dry wheat straw). [b] Reaction conditions: 180 °C, 50 bar of initial CO_2 pressure within 60 min of holding time.

- Total C_5-sugars conversion… lower furfural yield and reaction selectivity

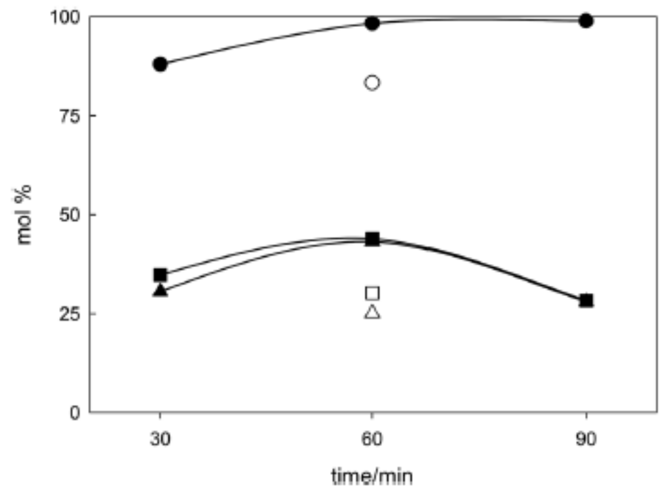


Fig. 7 The reaction selectivity (triangle up), furfural yield (square) and C_5-sugars conversion (circles) dependence on holding time and temperature (180 °C – closed symbols, 160 °C – open symbols).

- **Formic and acetic acids** can act as additional homogeneous catalysts leading also to its further degradation.

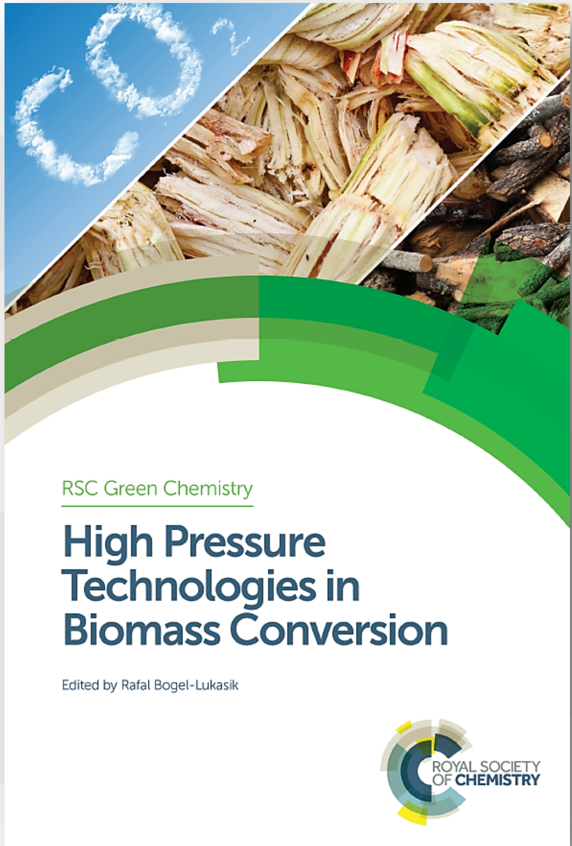
Final remarks

- The combined adjunctive character of **CO_2 as either promoter of *in-situ* acid catalyst or phase splitting inducer** in aqueous media and **THF as *in-situ* an extracting solvent** enabled a simple operational procedure for xylose dehydration into furfural;

- The conversion of D-xylose into furfural above **83 mol% with furfural yield of 70 mol% and the selectivity of 84 %** was achieved with only 50 bar of CO_2 pressure and in presence of THF.

- The total conversion of C_5-sugars into furfural using wheat straw hydrolysates was obtained, however quite low furfural yields and reaction selectivity of **43 mol%** and **44 %** were achieved.

Acknowledgments



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Max Kochanski, CBI

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