Study of the synergistic effect of a green pressurized reaction media (subW-CO_2) with homogeneous and heterogeneous catalysts for furfural production from sugar-derived biomass

Alba E. Illera

H. Candela, A. Bermejo-López, P. Barea, Ó. Benito-Román, R. Melgosa, S. Beltrán, M.T. Sanz

5th CIAB
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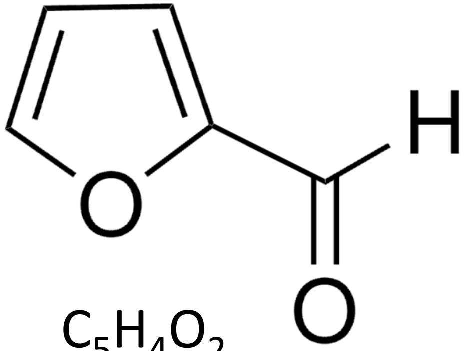
Furfural

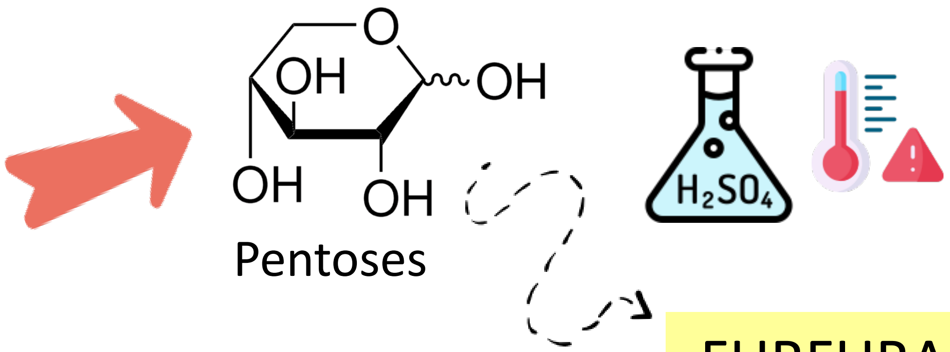


$C_5H_4O_2$

- Aromatic aldehyde
- Obtained from dehydration of pentoses
- Used for solvents, resins and chemicals production
- Intermediate for plastics, fuel and lubricants

Agricultural residues

Cellulose
Hemicellulose
Lignin



Pentoses

FURFURAL

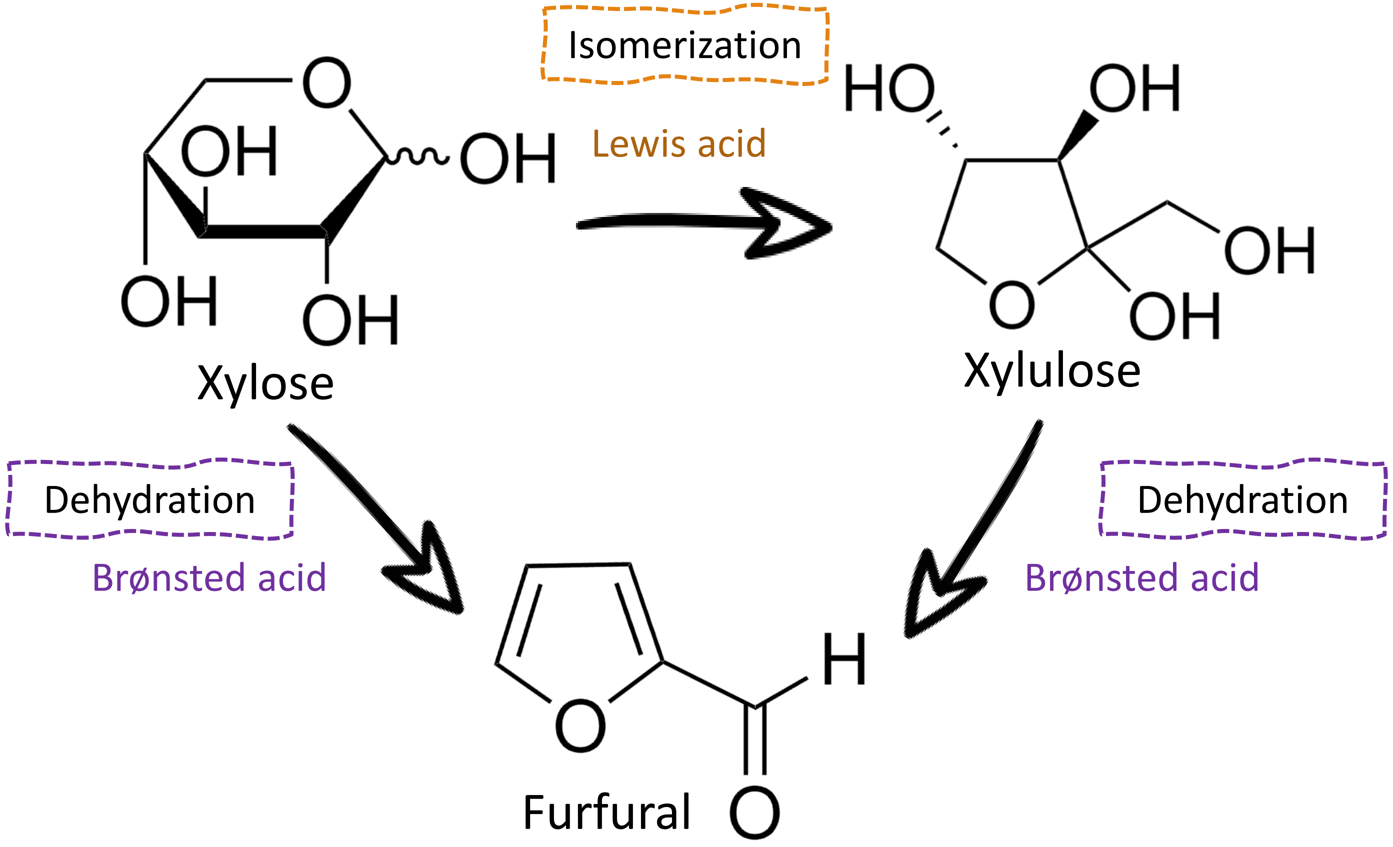
Furfural from xylose

Xylose

- Main pentose in hemicellulose
- Functional isomer: xylulose
- Furfural produced from their dehydration

To increase furfural production:

- Catalysts
- Organic solvents



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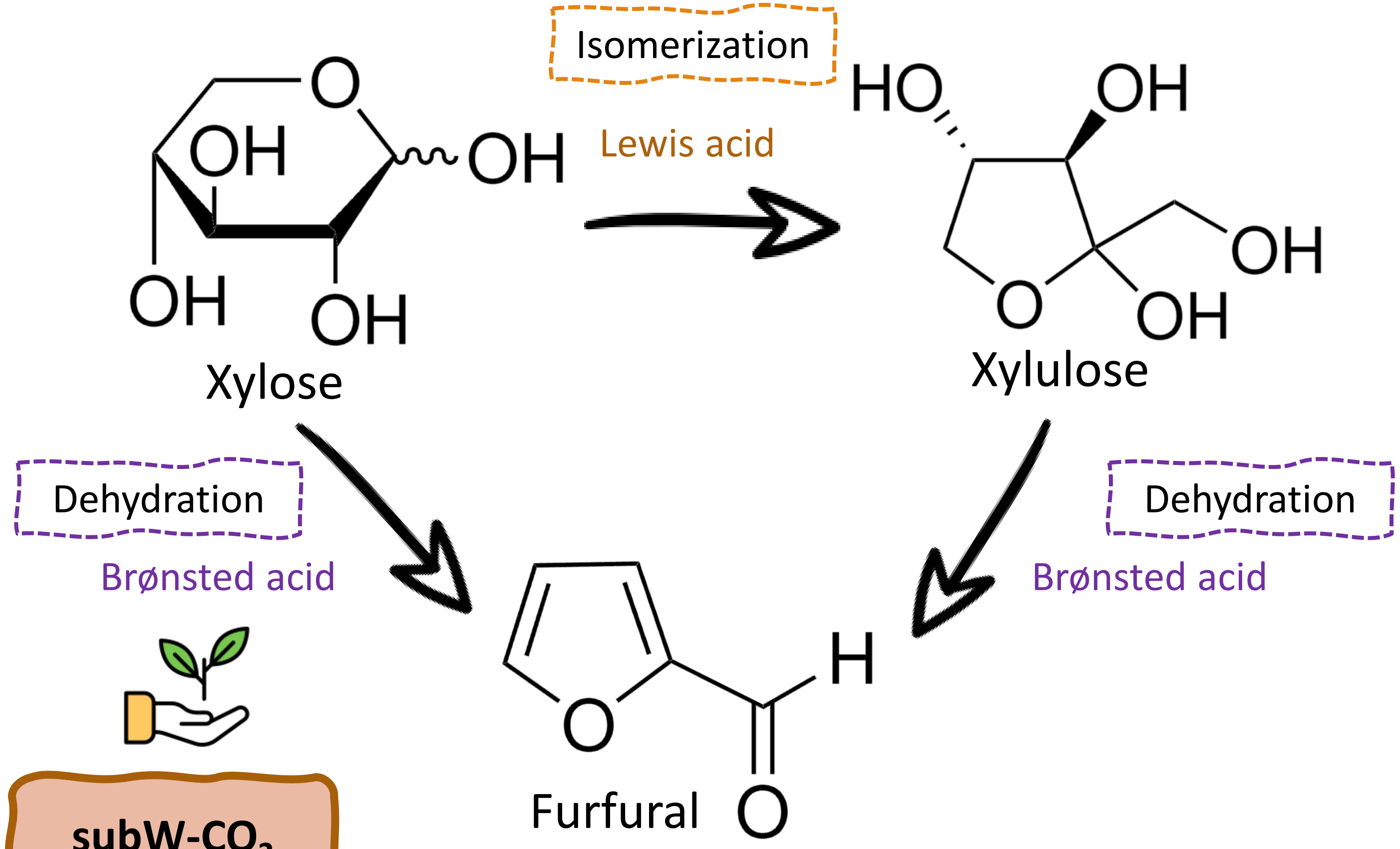


subW-CO_2

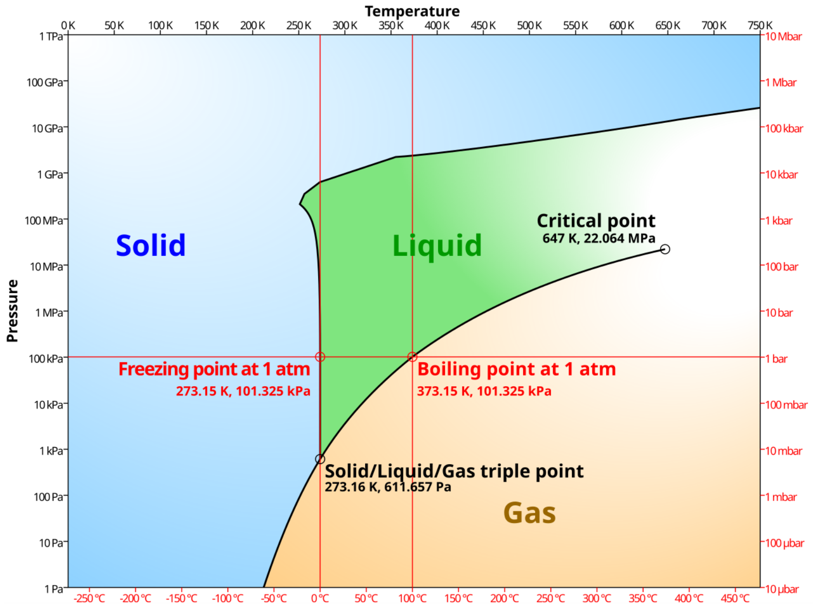
subW-CO_2 for furfural production

Subcritical water (subW)

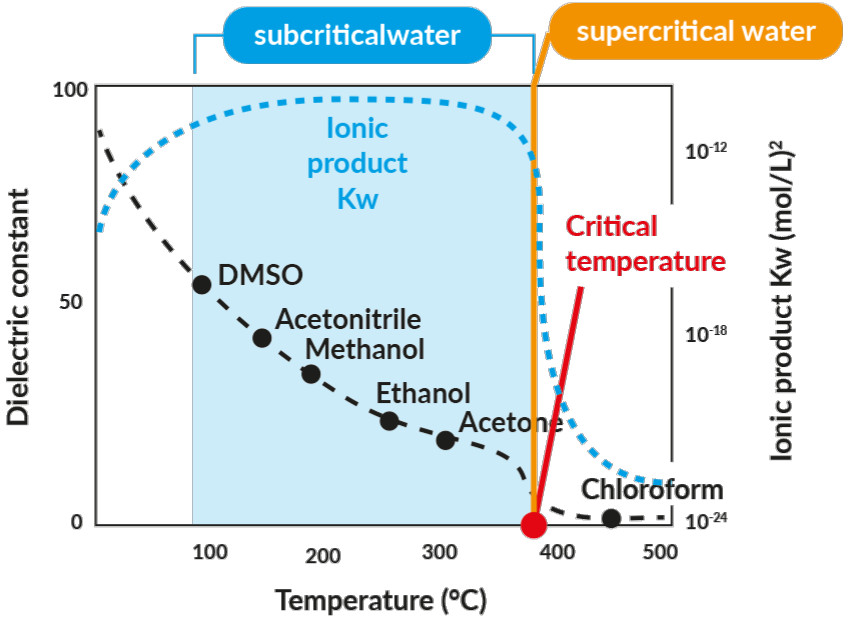
Water above 100°C in the **liquid state** due to the effect of **pressure**

Below critical p and T

Water phase diagram [1]



Ionic product- dielectric constant [2]



[1] http://www1.lsbu.ac.uk/water/water_phase_diagram.html
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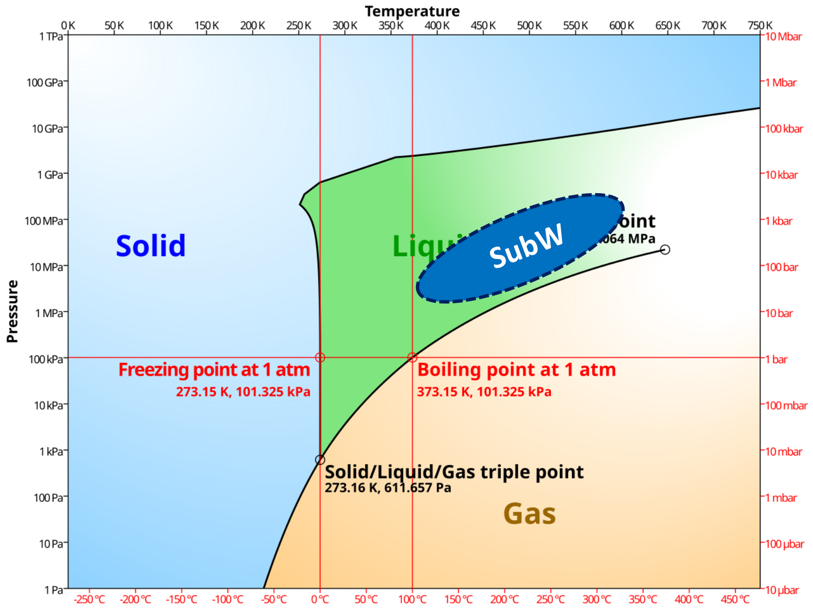

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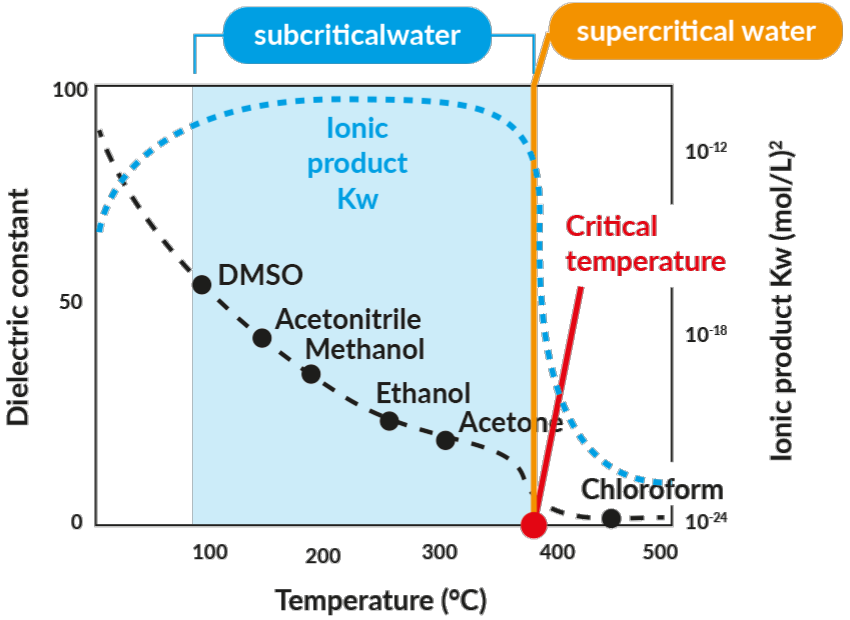

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Water ionic product (mol/L)²:

$K_w = [H^+][OH^-]$

25 °C → 1×10^{-14}

200 °C (10 bar) → $\mathbf{1 \times 10^{-9}}$

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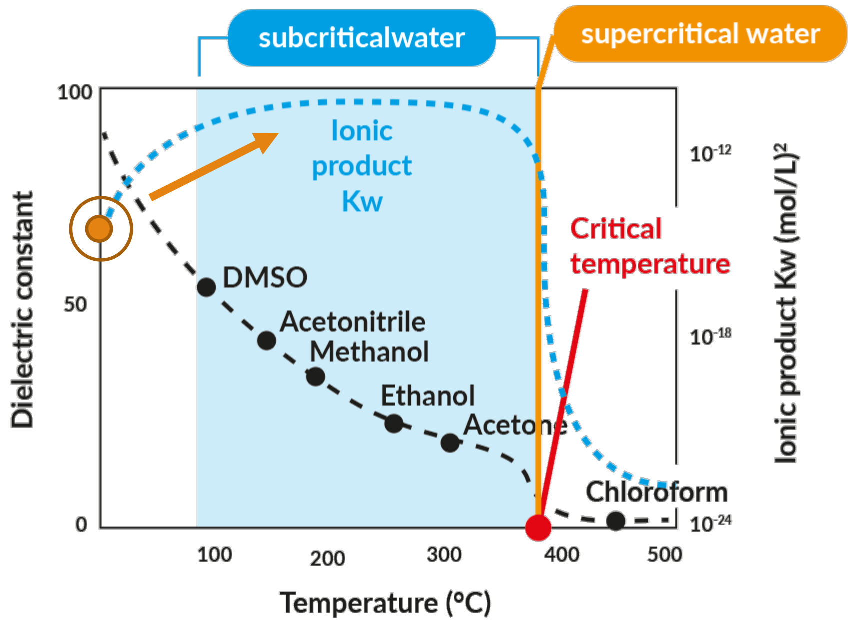

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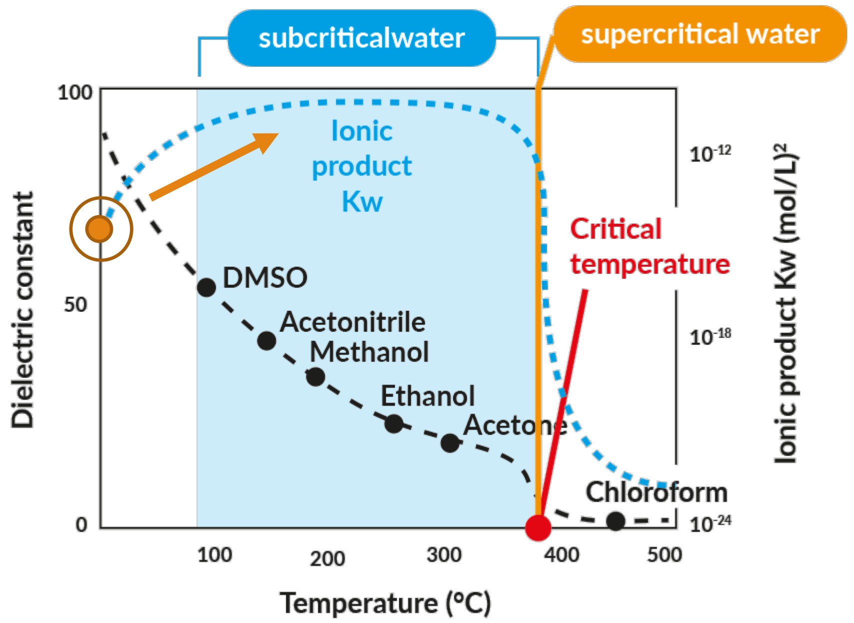
Acidic and basic catalyst properties

Ionic product- dielectric constant [2]



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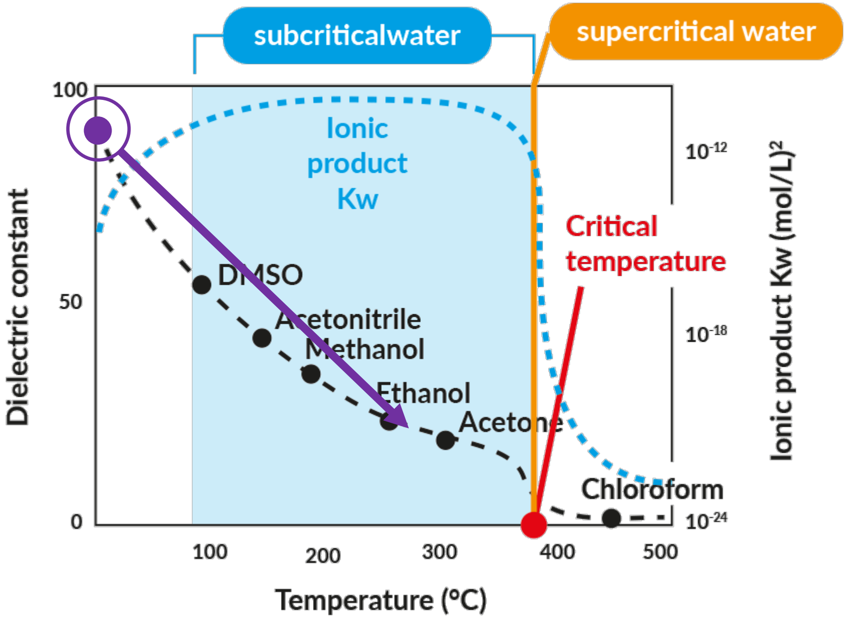
Water dielectric constant:

25 °C → 78.4

200 °C (10 bar) → **35**

Ionic product- dielectric constant [2]



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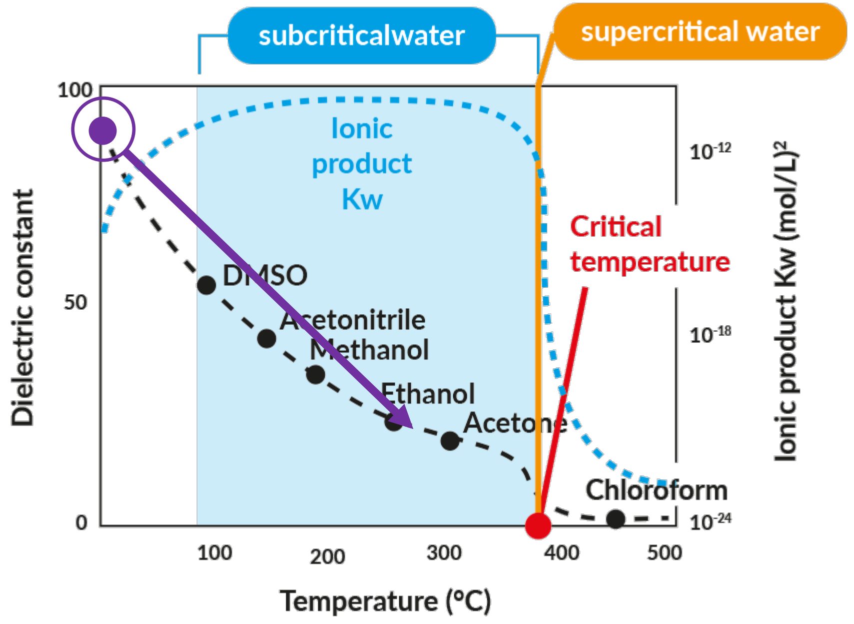
Similar to ethanol and acetone solvent properties

Ionic product- dielectric constant [2]



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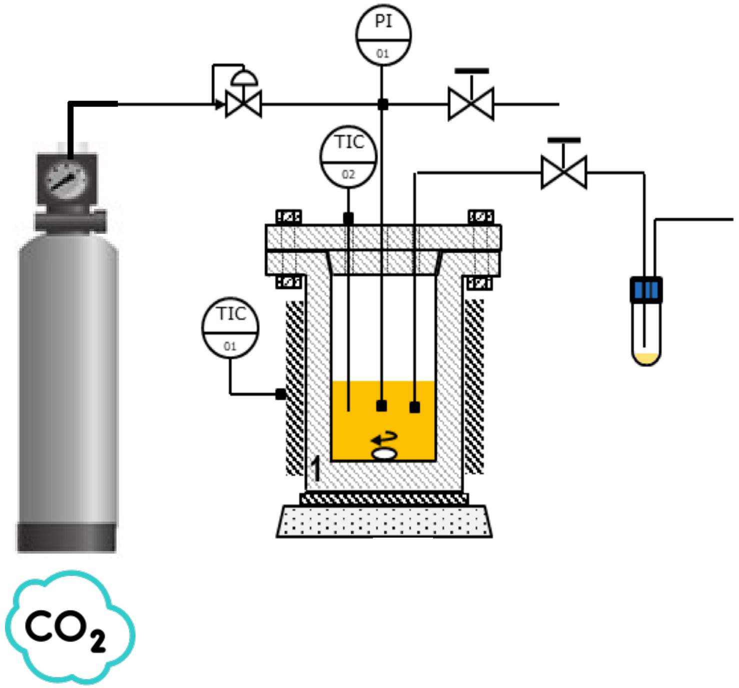
subW-CO_2 for furfural production

Subcritical water (subW) + CO_2

- **Pressurizing agent** for **subW**
- **Solvent-free** biphasic system
- Only **water** and **carbon dioxide**
- **CO_2** acting as a **Brønsted acid**

$$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_{3\,(aq)}$$



- 200 ml
- 50 bar
- 180 °C
- 4 hours

subW-CO_2 for furfural production

Subcritical water (subW) + CO_2

No catalyst

Homogeneous catalysts:

Lewis acids | $AlCl_3$, $CrCl_3$, $FeCl_3$

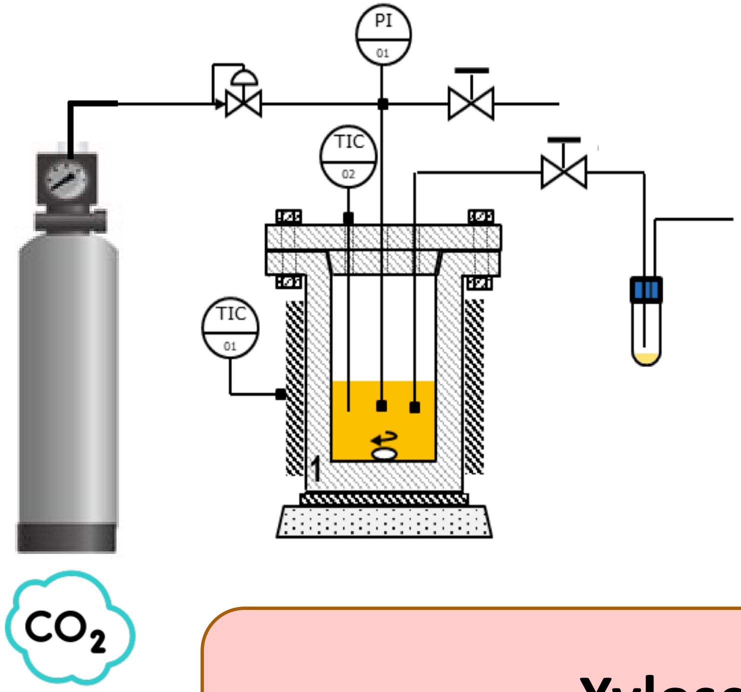
Aluminum sulfates | $Al_2(SO_4)_3$, $KAl(SO_4)_3$

Heterogeneous catalysts:

Zeolites | Ferrierite, ammonium β, hydrogen

Clay — Montmorillonite K10

Resin — *Nafion NR50*



- 200 ml
- 50 bar
- 180 °C
- 4 hours

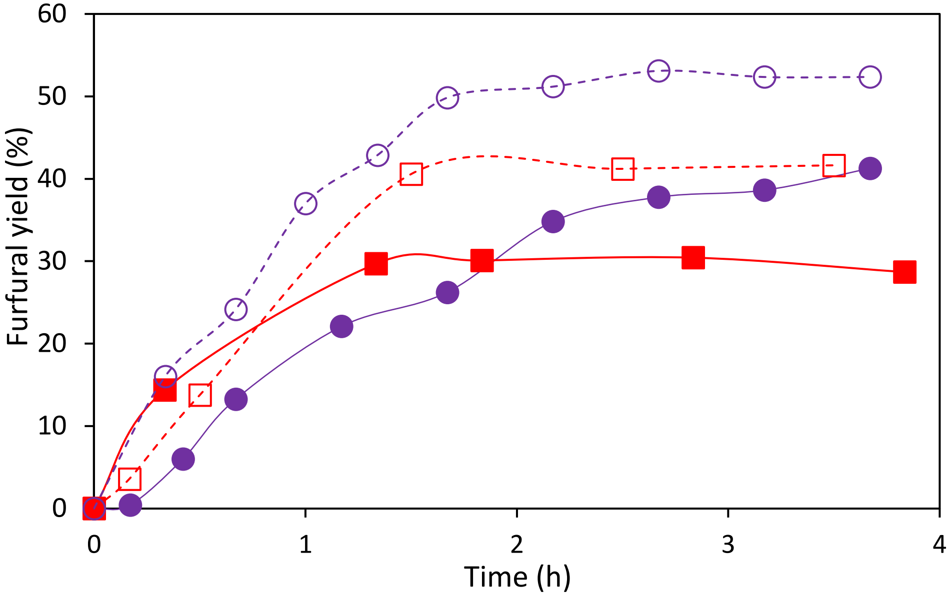
Xylose: 11g/L

Catalyst: (2% weight/xylose weight)

subW-CO_2 with no catalyst added

Subcritical water (subW) + CO_2

No catalyst



$$Furfural\ yield\ (\%) = \frac{moles\ of\ furfural_{(t)}}{moles\ of\ sugar\ monomer_{(0)}} * 100$$

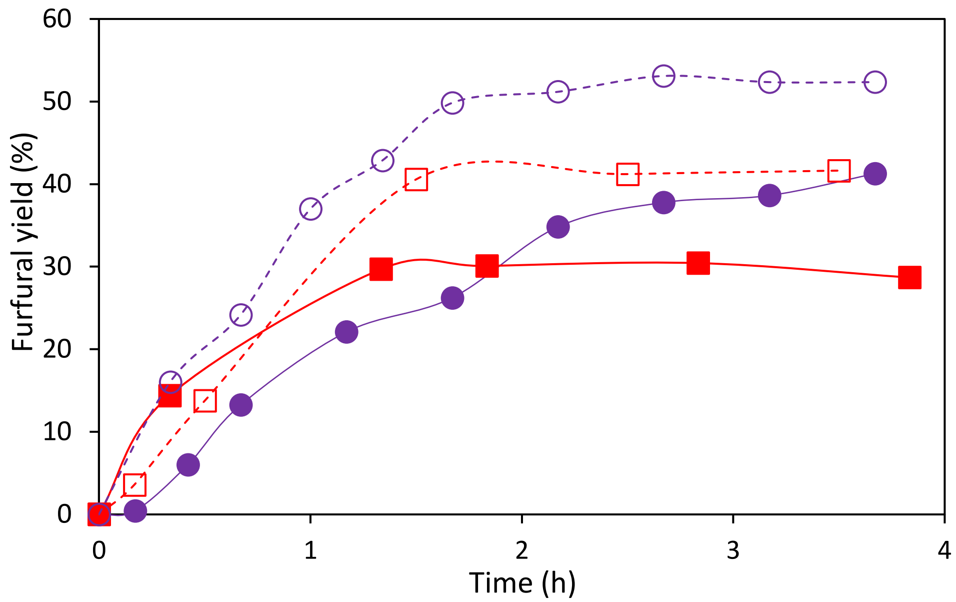
subW-CO_2 + $AlCl_3$
subW-CO_2
subW-N_2 + $AlCl_3$
subW-N_2

	With no catalyst	With $AlCl_3$
subW-N_2	30 %	41 %
subW-CO_2	41 %	53 %

$subW\text{-}CO_2$ with no catalyst added

Subcritical water (subW) + CO_2

No catalyst



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$subW\text{-}CO_2$
$subW\text{-}CO_2 + AlCl_3$
$subW\text{-}N_2$
$subW\text{-}N_2 + AlCl_3$

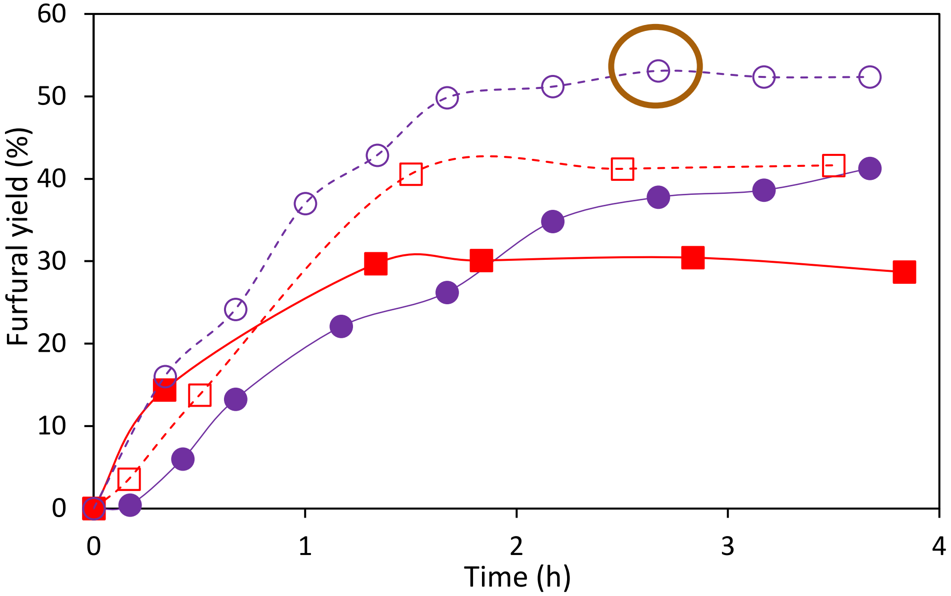
	With no catalyst	With $AlCl_3$
$subW\text{-}N_2$	30 %	41 %
$subW\text{-}CO_2$	41 %	53 %

$subW\text{-}CO_2$ → same furfural yield ← **$subW\text{-}N_2$**

$subW\text{-}CO_2$ with no catalyst added

Subcritical water (subW) + CO_2

No catalyst



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- $subW\text{-}CO_2$
- $subW\text{-}N_2 + AlCl_3$
- $subW\text{-}N_2$

	With no catalyst	With $AlCl_3$
$subW\text{-}N_2$	30 %	41 %
$subW\text{-}CO_2$	41 %	**53 %**

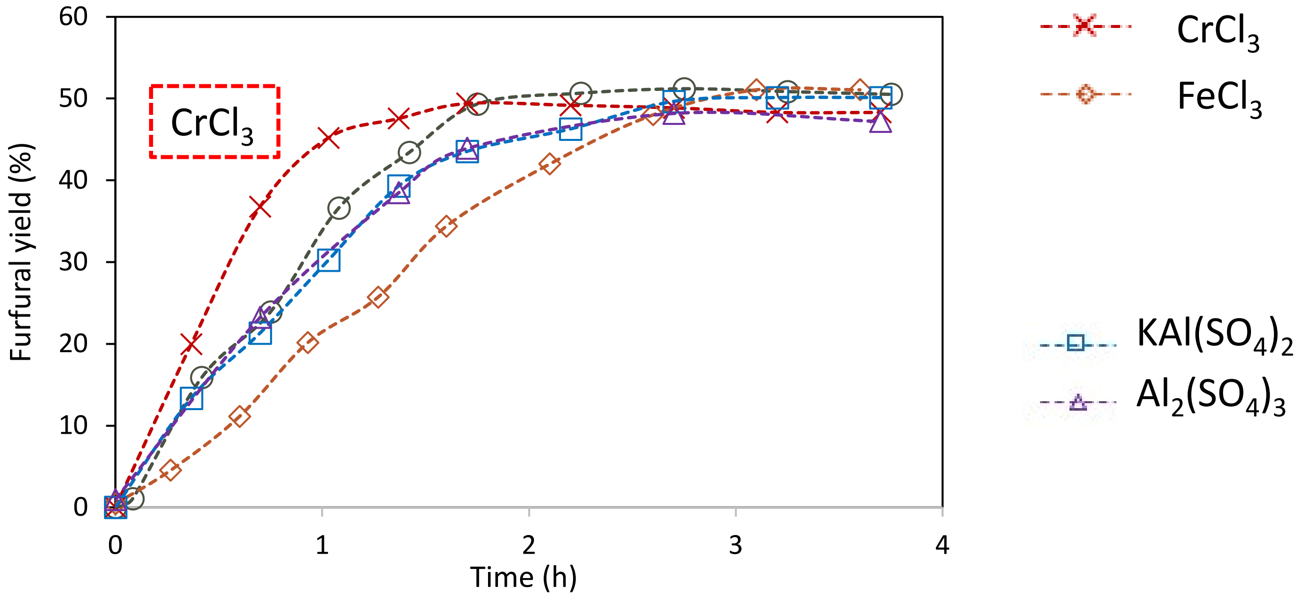
$subW\text{-}CO_2$ → same furfural yield ← **$subW\text{-}N_2$**

With or without catalyst, **$subW\text{-}CO_2$** → **Higher furfural yield**

subW-CO_2 + homogeneous catalysts

Subcritical water (subW) + CO_2

Homogeneous catalysts



Lewis acids

Maximum furfural yield: **50-53%**

$CrCl_3$ was the **fastest catalyst**

$FeCl_3$ showed the **slowliest furfural formation**

Aluminum sulfates

Maximum furfural yield: **50%**

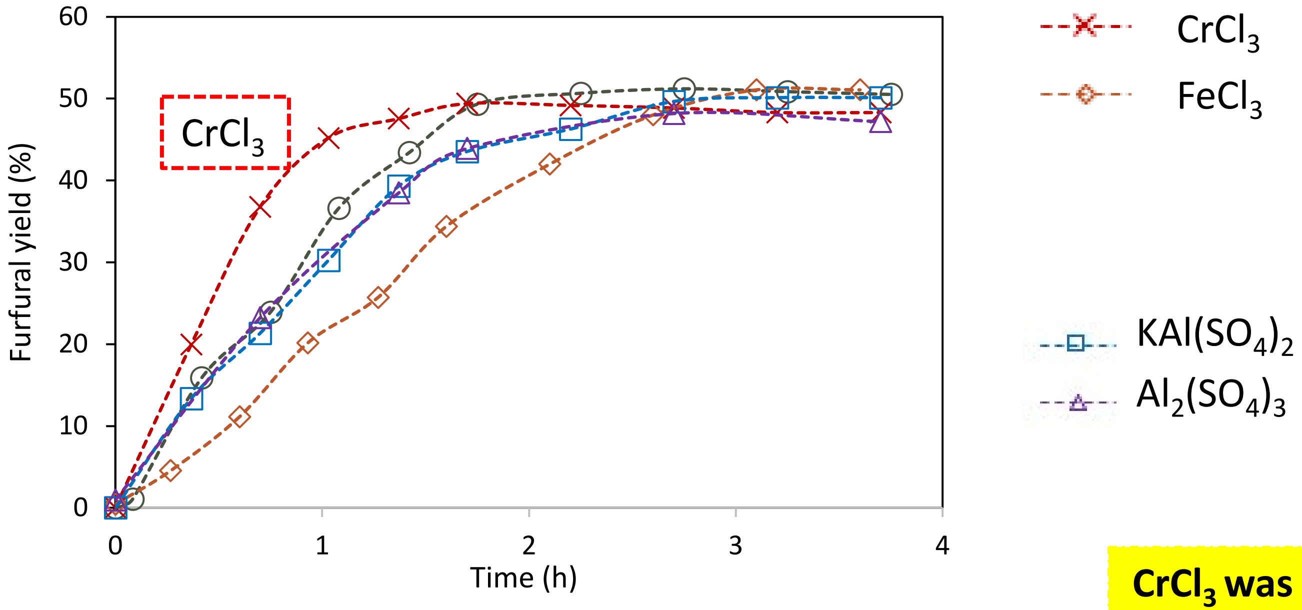
No difference between the catalysts

(SO_4^{-2}) group did not improve furfural yield

$subW\text{-}CO_2$ + homogeneous catalysts

Subcritical water (subW) + CO_2

Homogeneous catalysts



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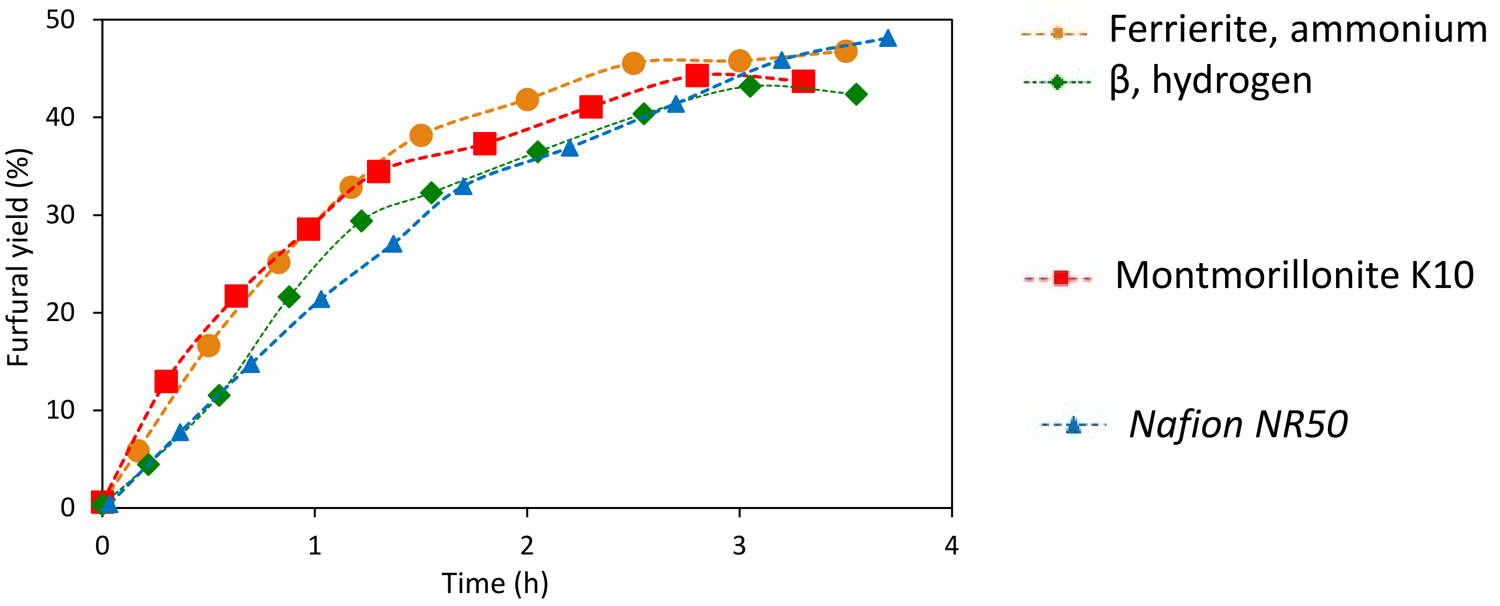
$CrCl_3$ was selected as the best catalyst of this group

subW-CO_2 + heterogeneous catalysts

Subcritical water (subW) + CO_2

Heterogeneous catalysts



Zeolites

Maximum furfural yield: **43-48%**
Ferrierite ammonium showed **higher furfural yield**

Clay

Maximum furfural yield: **44%**

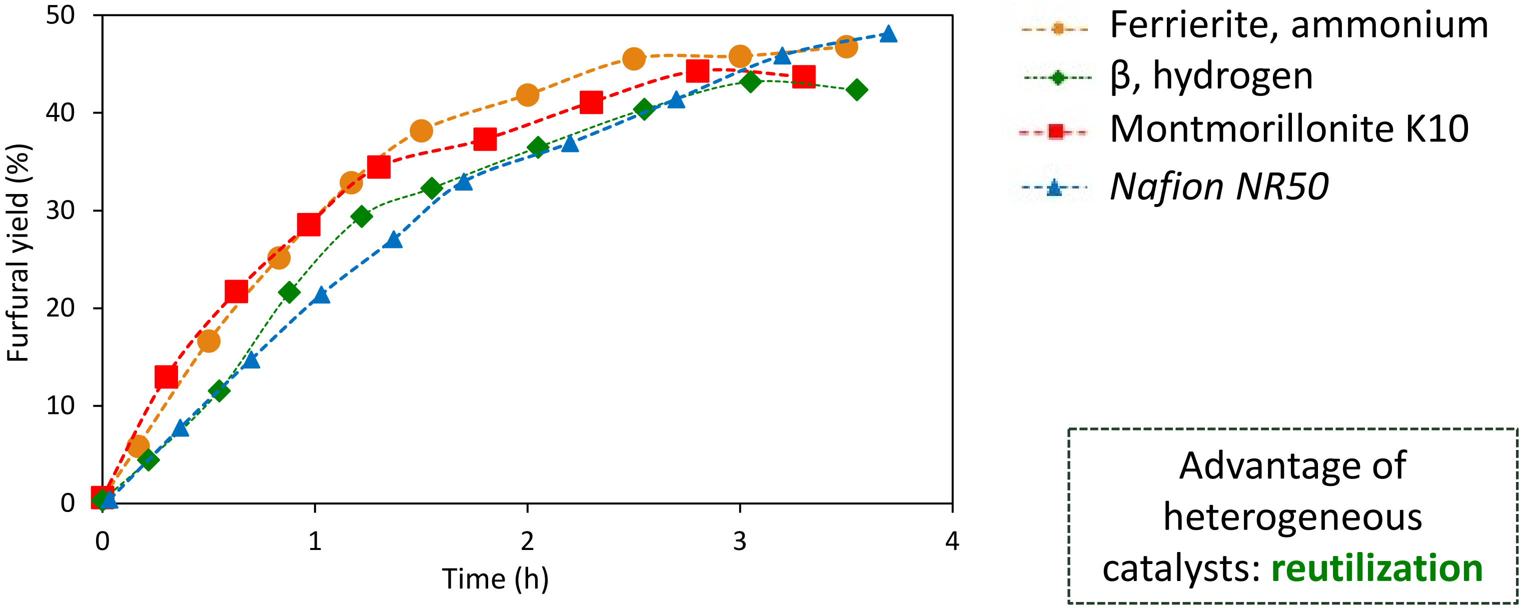
Resin

Slowliest conversion
Highest furfural yield: **48%**

subW-CO_2 + heterogeneous catalysts

Subcritical water (subW) + CO_2

Heterogeneous catalysts



- Lower furfural yield than homogeneous catalysts
- Slowlier furfural production
- Dissolved in the water, except *Nafion NR50*

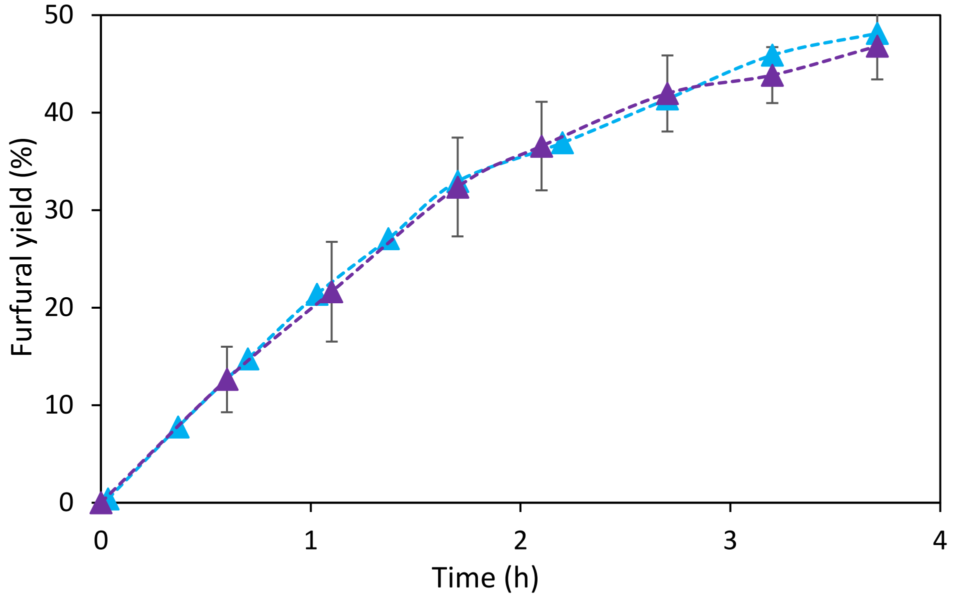
Advantage of heterogeneous catalysts: **reutilization**

→ ***Nafion NR50***

subW-CO_2 + *Nafion NR50*

Subcritical water (subW) + CO_2

Reutilization of Nafion NR50



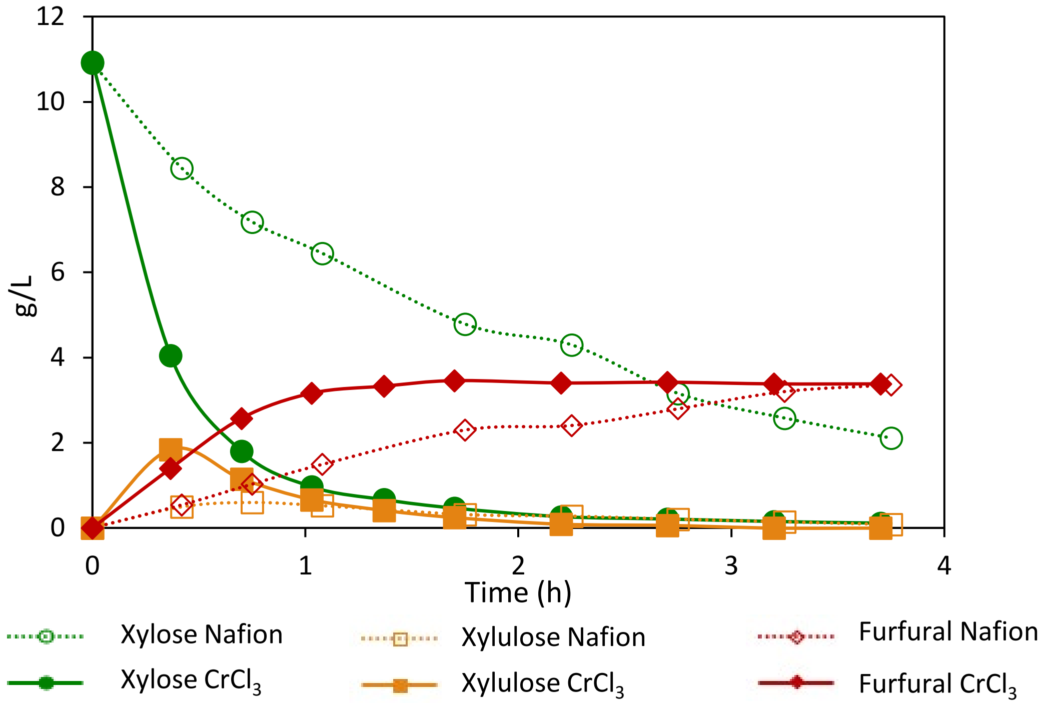
Nafion NR50

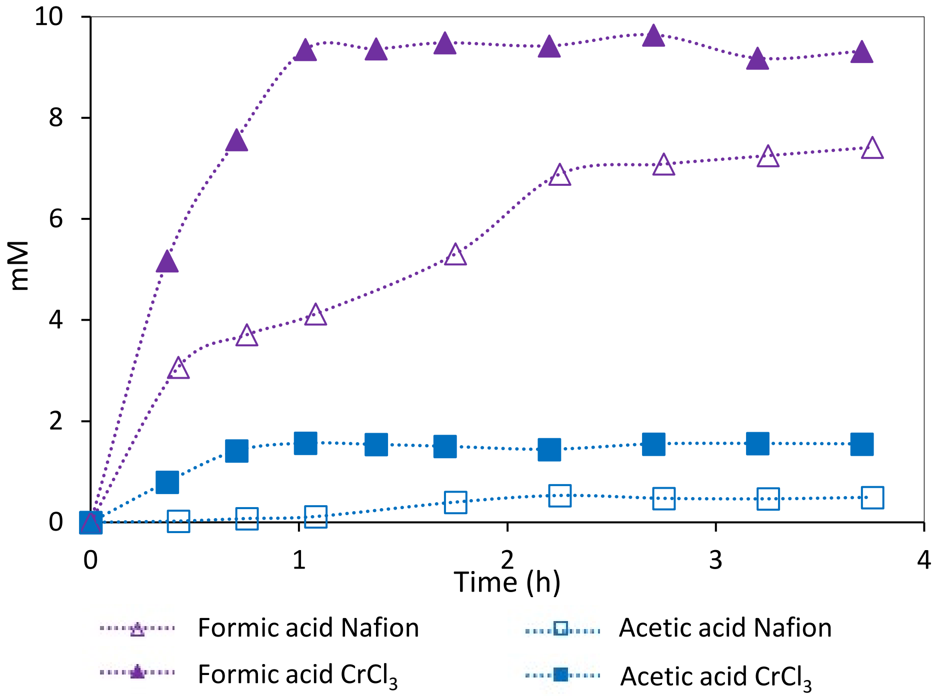
Nafion NR50 (average 10 times used)

- Resin did not lose effectiveness towards furfural production
- Easy reutilization process
- No catalyst residue in the final solution

Nafion NR50 **was selected as the best catalyst of this group**

Selectivity/degradation products

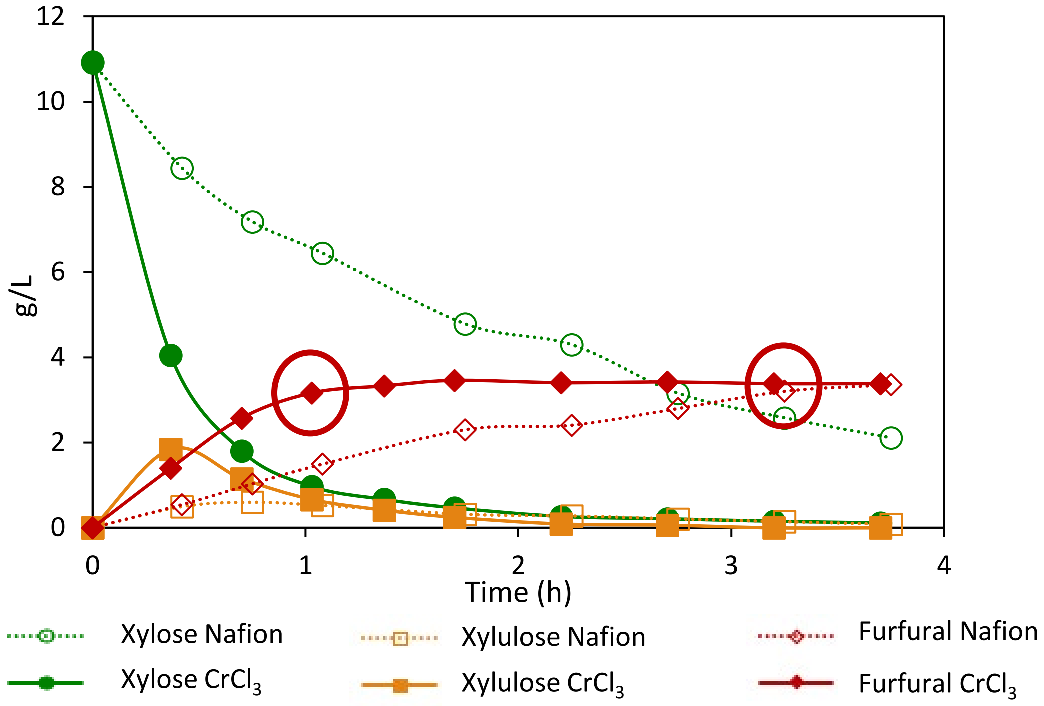


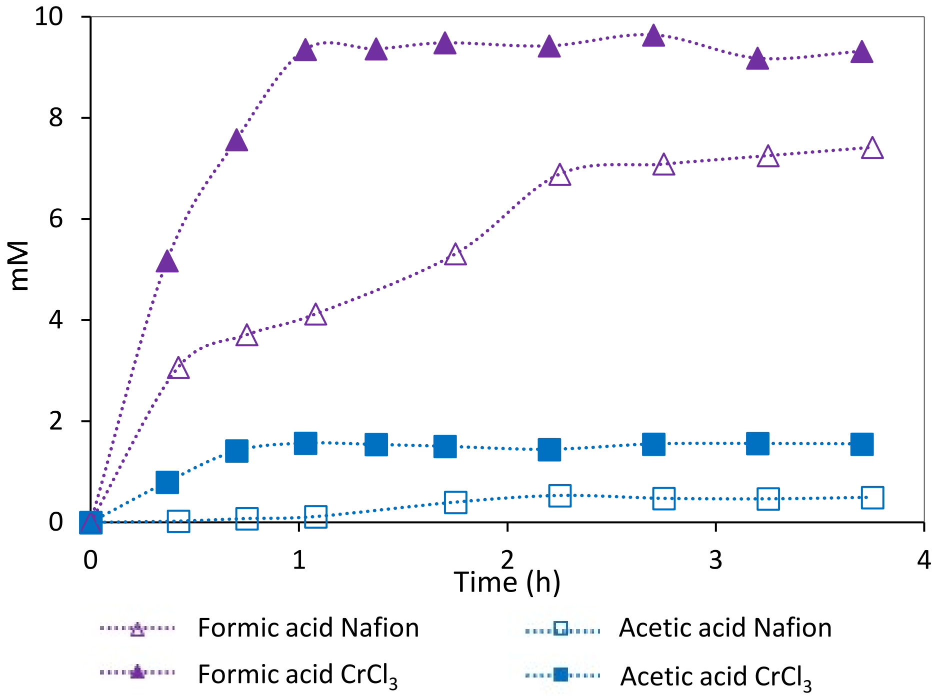


- Xylose conversion was lower when using Nafion
- Furfural production was faster with $CrCl_3$

- Nafion produced less degradation products
- Nafion showed **higher selectivity** towards furfural (60.9% vs. 50.1%)

Selectivity/degradation products





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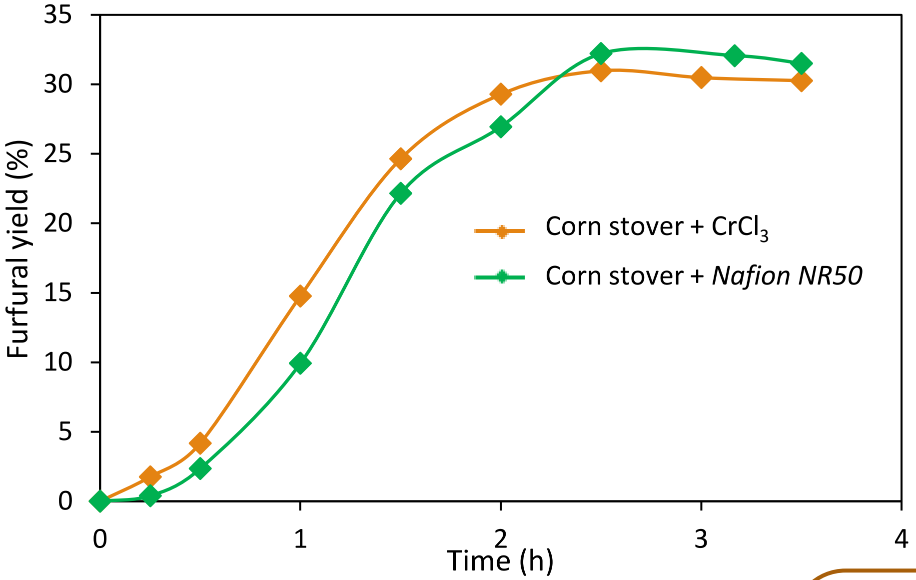
subW-CO_2 and corn stover

Corn stover: leaves, stems and corn cobs

	Composition (%)	Corn stover
	Extractives	8.7 ± 0.6
Hemicellulose	Xylans	**25 ± 3**
	Arabinans	**4.1 ± 0.5**
	Acetyl	4.2 ± 0.2
Cellulose	Glucans	41.4 ± 4
Lignin	Soluble	1.7 ± 0.5
	Insoluble	18 ± 3
	Ash	2.7 ± 0.4
	Protein	3.2 ± 0.2



	Xylose	Corn stover
subW-CO_2 + *$CrCl_3$*	**50 %** (1.7 h)	**31 %** (2.5 h)
subW-CO_2 + *Nafion NR50*	**48 %** (3.7 h)	**32 %** (2.5 h)

- **Lower furfural yield than** when using **xylose**
- **Similar furfural yield** from corn stover with both catalysts.
- **Reaction time** was the **same** for **both catalysts.**

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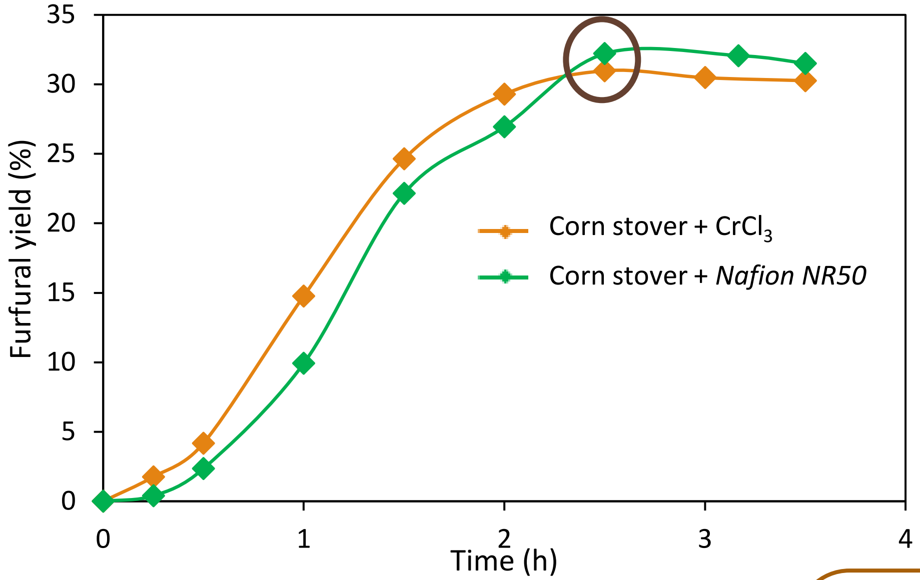

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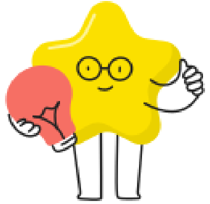
Conclusions



- **subW** showed **catalytic effect** for **furfural production** from xylose
- **subW-CO_2** improved furfural yield due to its Brønsted acid effect
- **subW-CO_2** + homogeneous and heterogeneous catalysts further improved furfural yield
- **$CrCl_3$** was the fastest catalyst, while **Nafion resin** was the most selective towards furfural
- **Nafion resin** could be reused at least 10 times without losing effectivity with xylose
- **$CrCl_3$** and **Nafion resin** produced > 30 % furfural yield from corn stover
- **subW-CO_2** is a promising **solvent-free biphasic system**, greener than traditional ones

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THANK YOU!

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