UNIVERSIDAD DE BURGOS

Biotecnología Industrial y Medioambiental BIOIND www.ubu.es/bioind

Corn stover biorefinery based on hydrothermal and membrane processes

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3er Encuentro Ibérico de Fluidos Supercríticos

OURENSE, SPAIN

22-24 JULIO

Flucomp

1. Introduction

42,1 % cellulose
34,5 % hemicellulose
25,7 % lignin

- ❑ Abundant agricultural by-product
- ❑ Lignocellulosic biomass

↓ Use of fossil fuels

Sustainable processes

Valorization

Green technologies

Integral approach

Furfural

Ethanol

1. Introduction

Biomass hydrolysis

Break interaction between the three lignocellulosic components

Hydrothermal treatment: Subcritical water **(subW)**
Mild conditions (160- 210 °C)

- Hemicelluloses are solubilized in liquid fraction
- Insoluble solid presents a high concentration of cellulose

Dehydration

Pentoses → Furfural

- [ ] subW treatment

Consecutive saccharification and fermentation process

Cellulose → Ethanol

- [ ] Enzymatic hydrolysis
- [ ] Fermentation

1. Introduction

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Biomass hydrolysis

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Hydrothermal treatment: Subcritical water **(subW)**
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Pentoses → **Furfural**

- subW treatment

Cellulose → **Ethanol**

- Enzymatic hydrolysis
- Fermentation

Recovery by **PERVAPORATION**

- Membrane separation method
- Permeation + evaporation

2. SubW treatment

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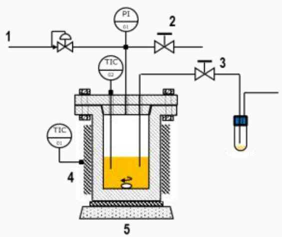
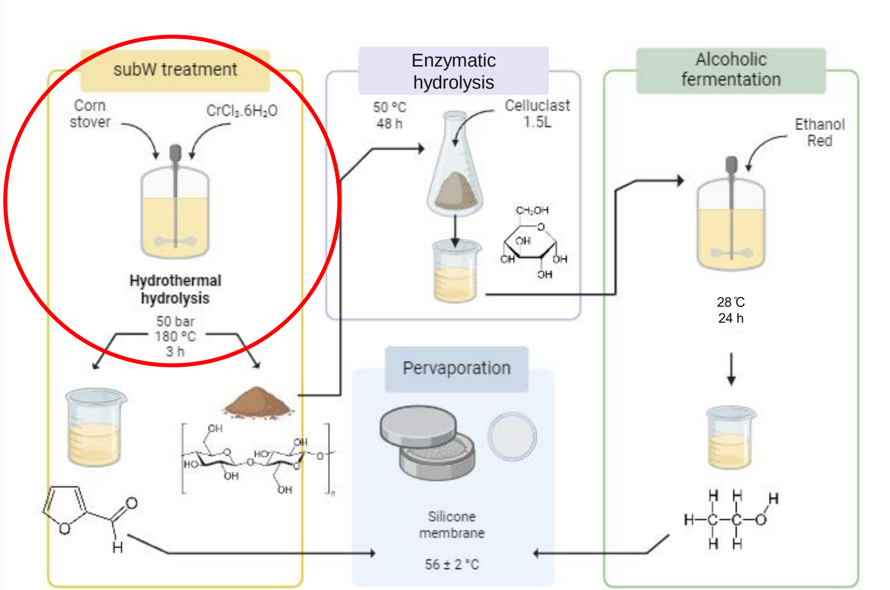
$CrCl_3$ as catalyst for ↑ furfural production

180 °C 3 h	50 bar (CO_2) V = 200 ml	Corn stover (5 % w/w) $CrCl_3$ (2 % w/w xylose)



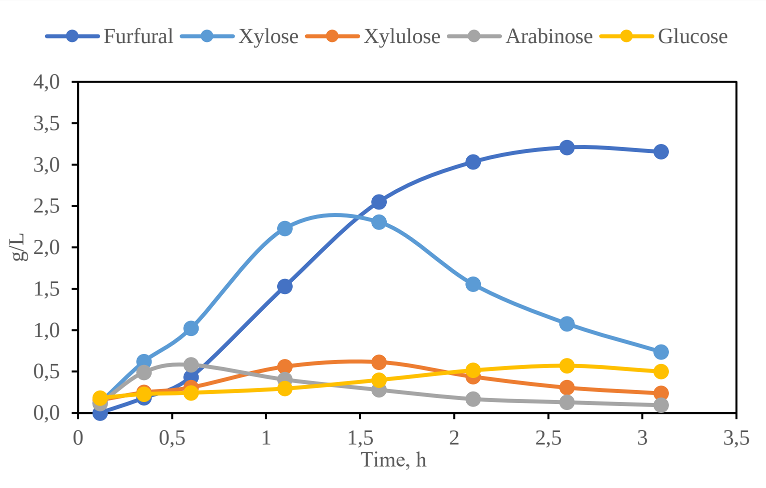
1. Gas inlet with pressure regulator
2. Gas outlet with a purge valve
3. Sample valve
4. Ceramic heating resistance
5. Magnetic stirrer

Components	Corn stover
Lignin	25,7
Soluble lignin	8,3
Insoluble lignin	17,4
Glucans	**42,1**
Hemicelluloses	**34,5**
Xylans	25,8
Arabinans	4,5
Acetyl	4,2



2. SubW treatment

180 °C **3 h**	**50 bar (CO_2)** **V = 200 ml**	Corn stover (5 % w/w) $CrCl_3$ (2 % w/w xylose)

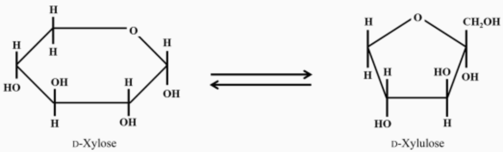


Xylose → Furfural
Maximum furfural concentration = 3,2 g/L

Small amounts of other sugars were solubilized

2. SubW treatment

Lewis acid catalyst contributes to faster xylulose formation from xylose



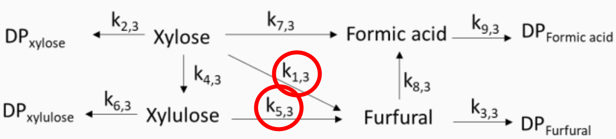
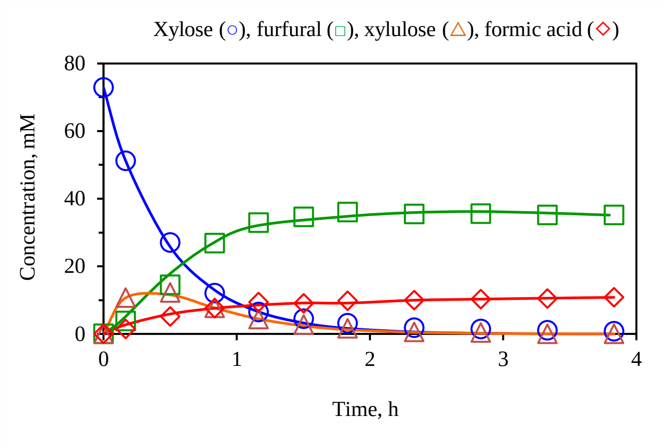


Table. Kinetic rate constants (h^{-1}) in subW/CO_2 system + $CrCl_3$ at 180 °C

$k_{1,3}$	0,0605
$k_{4,3}$	1,4298
$k_{5,3}$	2,8933
$k_{5,3}/k_{1,3}$	47,8

Ratio $k_{5,3}/k_{1,3}$ → Faster formation from xylulose as intermediate

180 °C 50 bar (CO_2) 4 h | Xylose study



2. SubW treatment

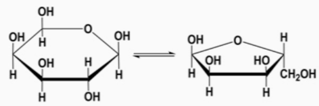
Arabinose study
Xylose-like mechanism

180 °C 50 bar
(CO_2) 4 h

Corn stover study

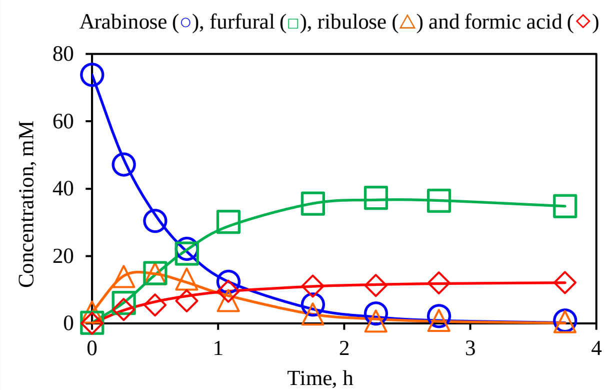
180 °C 50 bar
(CO_2) 3 h

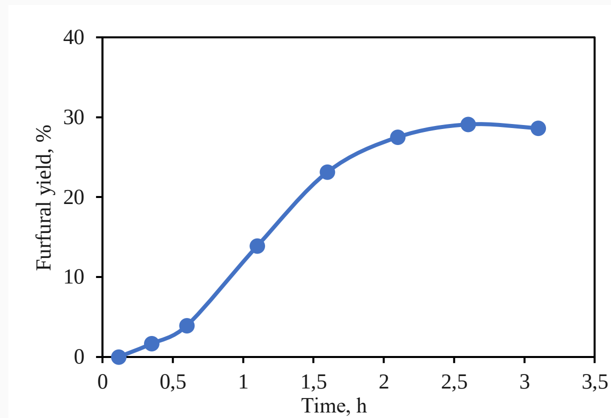
Fastest pathway is forming ribulose



Yield = 29,1 %

From pentoses





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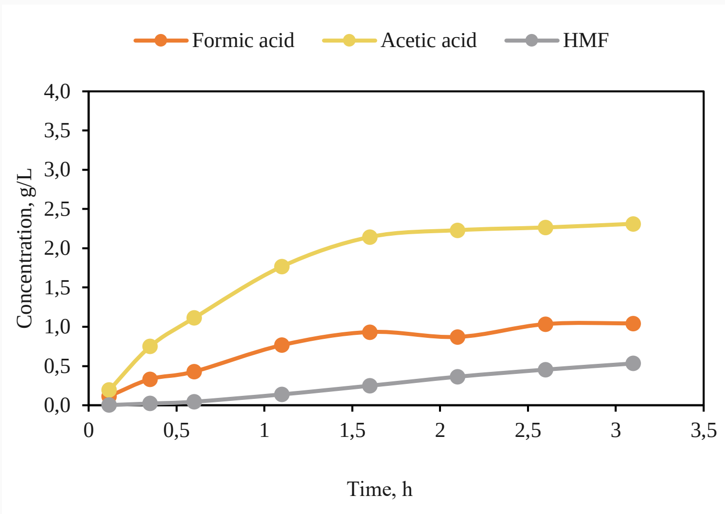
2. SubW treatment

180 °C 3 h	50 bar (CO_2) V = 200 ml	Corn stover (5 % w/w) $CrCl_3$ (2 % w/w xylose)

Glucose is converted into HMF



Hydrolysate	g/L
Xylose	0,7
Xylulose	0,2
Arabinose	0,1
Glucose	0,5
Furfural	3,2
HMF	0,5
Acetic acid	2,3
Formic acid	1,0

Degradation

Formic acid

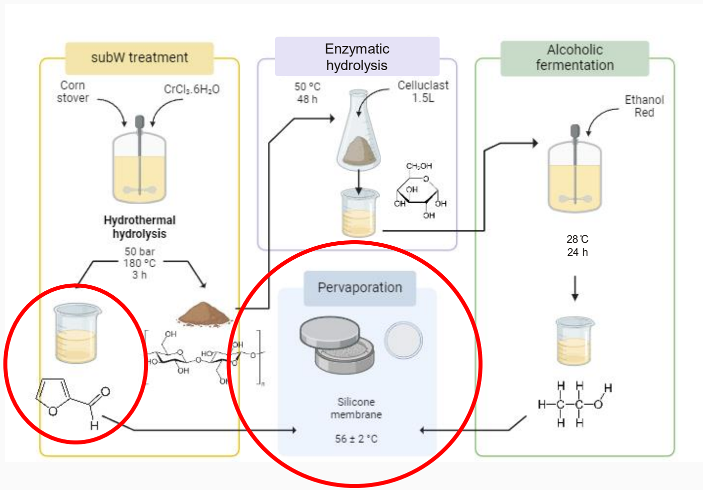
Acetic acid

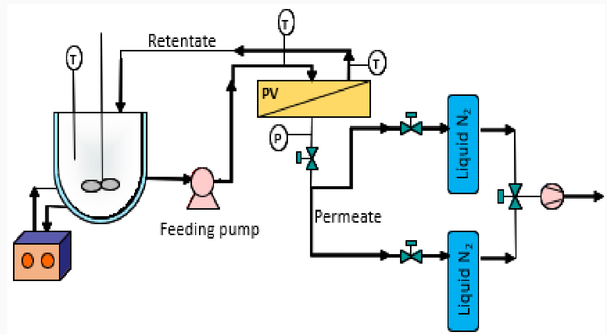
Acetyl groups from hemicellulose

3. Furfural recovery

Silicone hydrofobic membrane

One side of membrane: Feed
Other side of membrane: Vacuum → Vapor stream





N_2 to condense permeate vapor stream

3. Furfural recovery. Effect of T and C

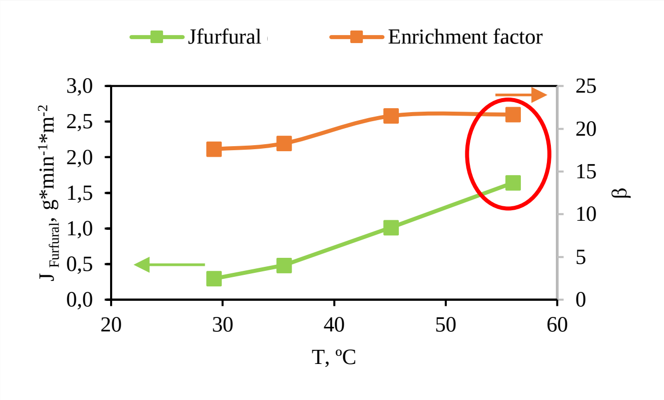
- ❑ If T ↑, J ↑
- ❑ If T ↑, β ↑ and remains constant

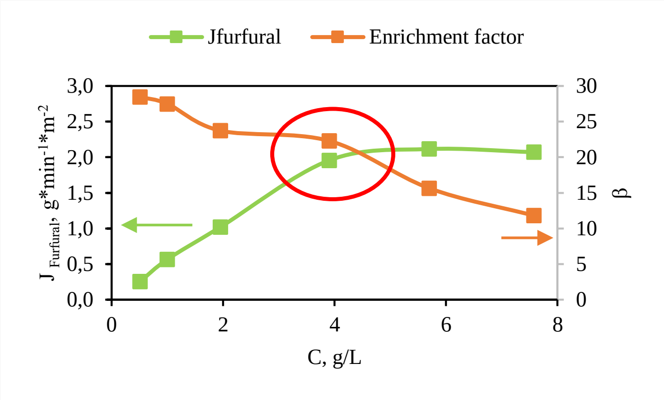
4 g/L Furfural solution

$$\beta = \frac{[Furfural]_{Permeate}}{[Furfural]_{Feed}}$$

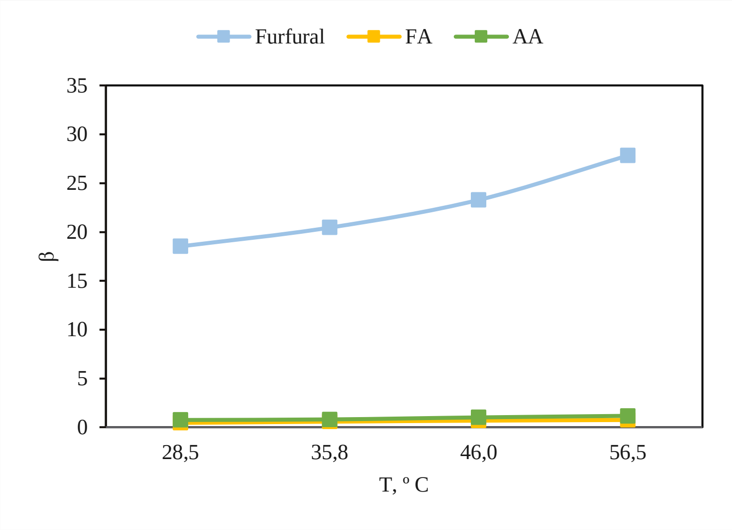
T = 56 ˚C

- ❑ If C ↑, J ↑
- ❑ If C ↑ , β ↓(Excessive membrane swelling)





3. Furfural recovery. Selectivity



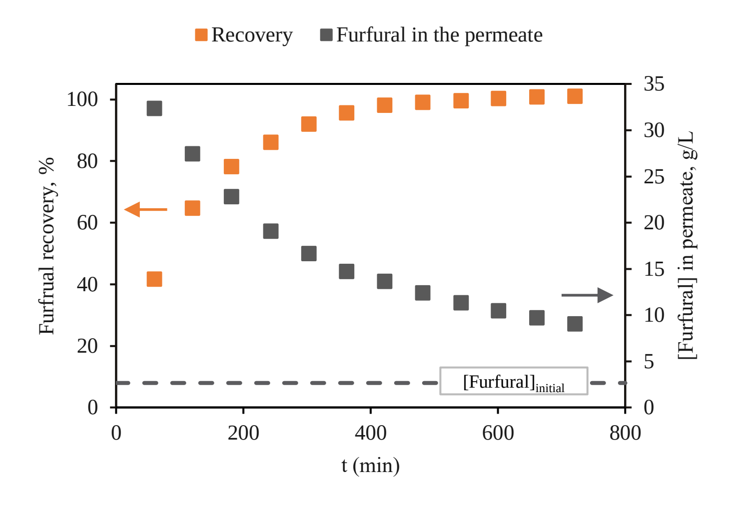
3 g/L Furfural
3 g/L Acetic acid (AA)
1,7 g/L Formic acid (FA)

$$\beta = \frac{[Furfural]_{Permeate}}{[Furfural]_{Feed}}$$

- ❑ If T ↑, $\beta_{Furfural}$ ↑
- ❑ β_{AA} and $\beta_{FA} \leq 1$
- ❑ $\beta_{Furfural}$ >>>> β_{AA} and β_{FA}

Working at higher T, the selectivity towards furfural increases over other compounds

3. Furfural recovery. Hydrolysate



100 % furfural recovery

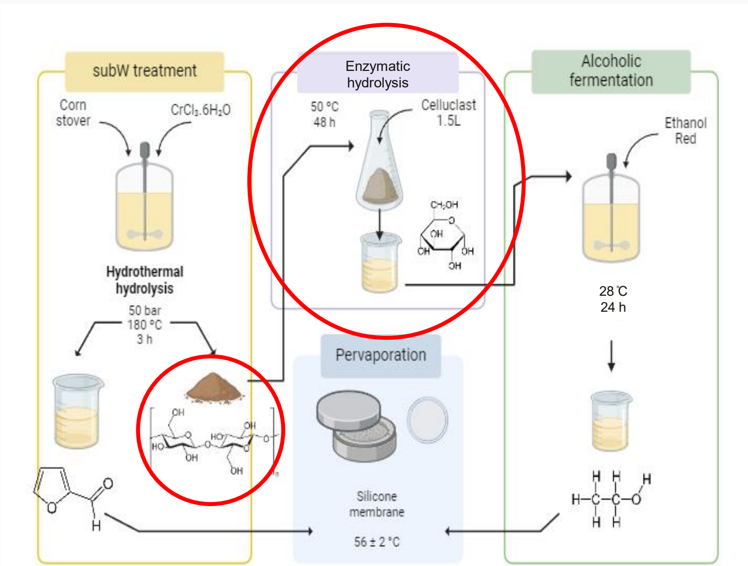
9 g/L furfural in the permeate

Establishing criteria to stop pervaporation:

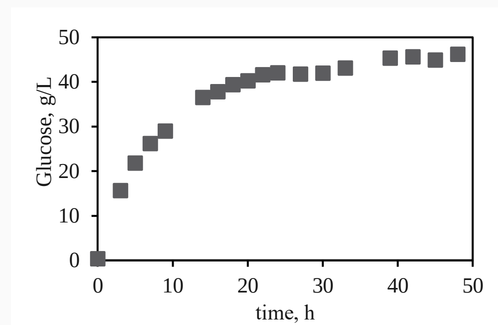
- At 245 min to recover **86 %** furfural with [19,08] g/L furfural in the permeate
- At 480 min to recover **99 %** furfural with [12,39] g/L furfural in the permeate

4. Enzymatic hydrolysis (HE)

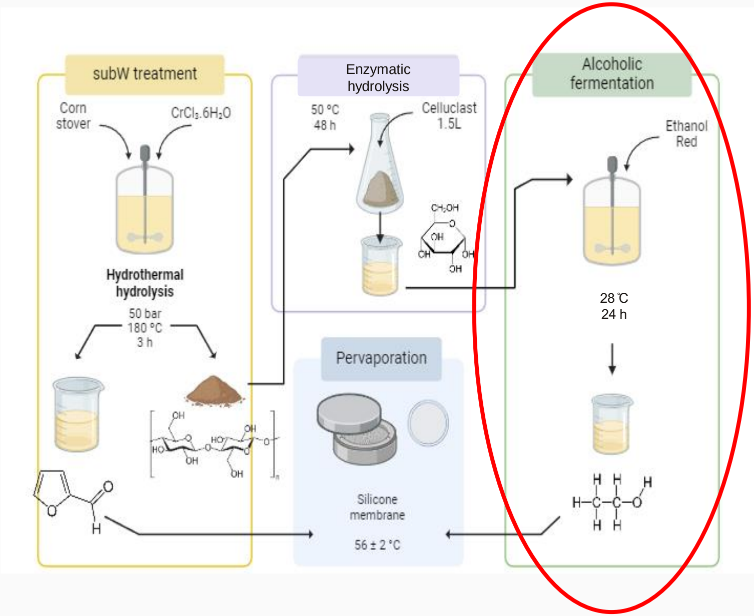
[Hydrolysate]final 46 g/L glucose	50 °C 48 h



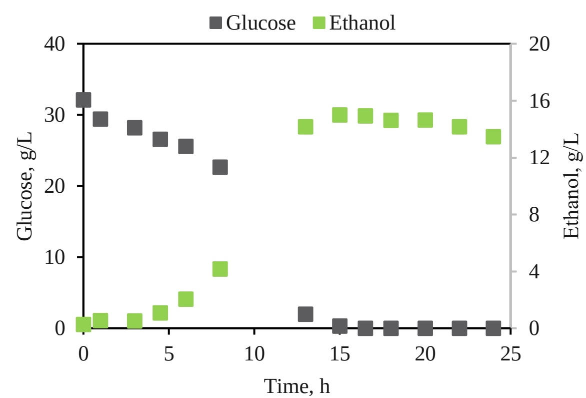
Components	Corn stover	PLE solid residue	HE solid residue
Lignin	25,7	36,54	57,5
Soluble lignin	8,3	0,84	1,1
Insoluble lignin	17,4	35,70	56,4
Glucans	**42,1**	**64,88**	**29,2**
Hemicelluloses	**34,5**	**2,31**	**5,4**
Xylans	25,8	2,13	4,9
Arabinans	4,5	0,18	0,5
Acetyl	4,2		



4. Enzymatic hydrolysis (HE)



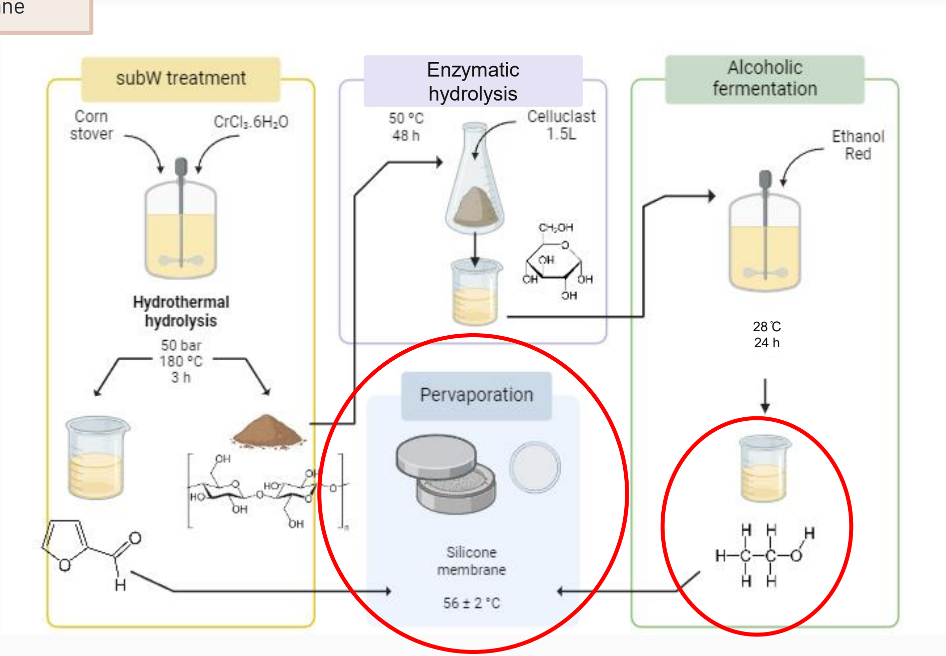
Fermentation by Ethanol Red (*Saccharomyces cerevisiae* strain)



28 °C	24 h	$[Ethanol]_{final}$ = 14 g/L

6. Ethanol recovery

Silicone hydrofobic membrane



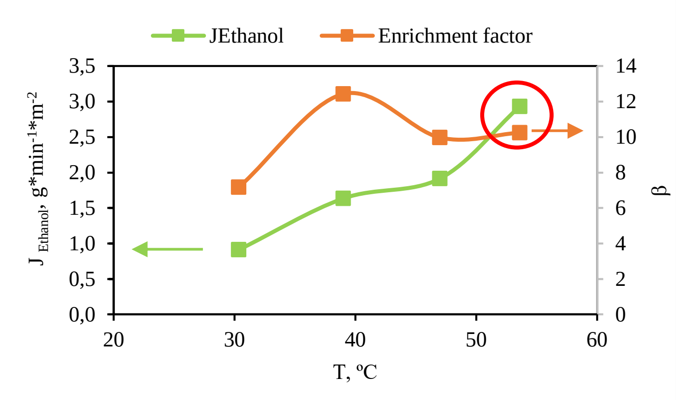
6. Ethanol recovery. Effect of T and C

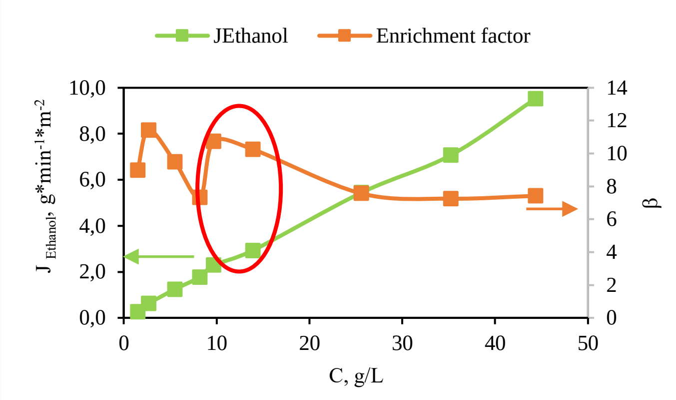
6 g/L Ethanol solution

- If T ↑, $J_{Ethanol}$ ↑
- If T ↑↑, β↓ and remains constant

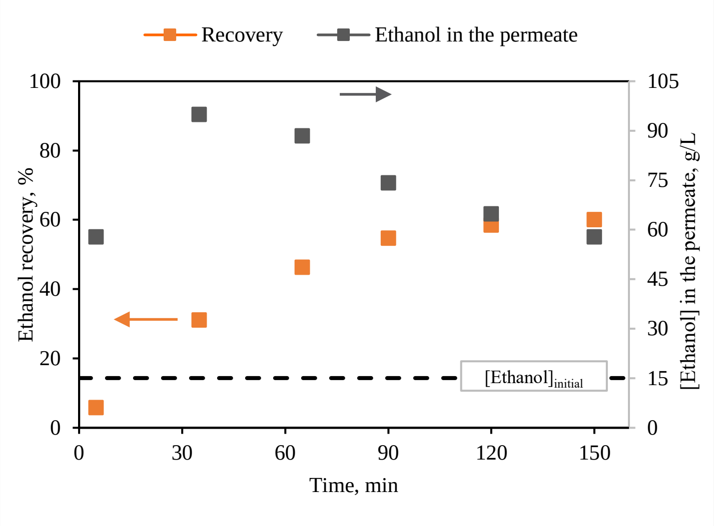
T = 56 ˚C

- If C ↑, $J_{Ethanol}$ ↑
- If C ≥ 25, β↓ and remains constant





6. Ethanol recovery. Fermentation broth



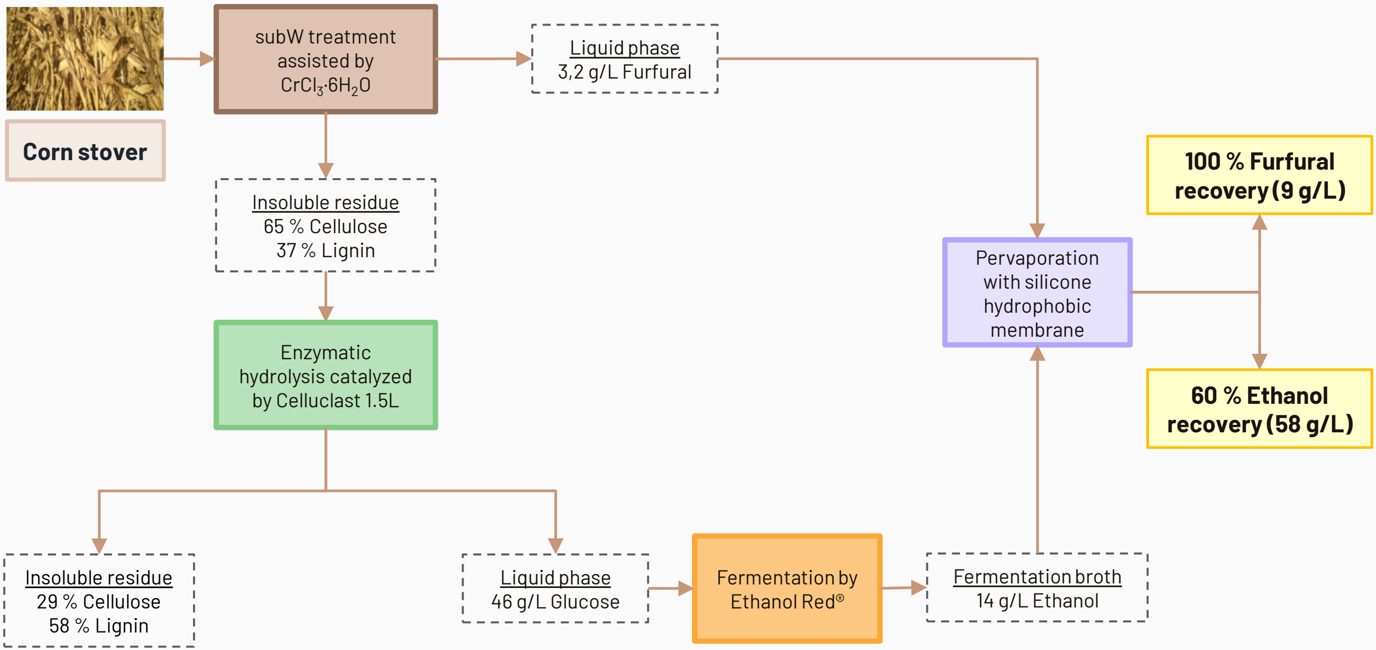
60 % ethanol recovery

57,77 g/L ethanol in the permeate

Establishing criteria to stop pervaporation:

- At 90 min to recover **54,70 %** ethanol [74,13] g/L ethanol in the permeate
- At 150 min to recover **60,03 %** ethanol [57,77] g/L ethanol in the permeate

7. Conclusions



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