VALORIZATION OF BREWER'S SPENT GRAIN BY FURFURAL RECOVERY/REMOVAL FROM SUBCRITICAL WATER HYDROLYSATES BY PERVAPORATION

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BREWER´S SPENT GRAIN (BSG)

BSG is a **lignocellulosic biomass** with a valuable protein and carbohydrates composition.

After **beer production**, BSG is generated, being the **85% of the total by-products** of this industry.

BSG chemical composition[1]

Component	g/100g dry-BSG
Protein	**22.1 ± 0.5**
Cellulose	14.0 ± 0.2
Hemicellulose	**32.0 ± 0.6**
Lipids	6.2 ± 0.3
Total lignin	20.8 ± 0.2
Ash	3.32 ± 0.06

FURFURAL FROM HEMICELLULOSE

- ✓ **Furfural** is considered one of the **top value-added chemicals** derived from biomass.
- ✓ It´s conventional production involves the use of strong acids.
- ✓ The **recovery processes** are energy-consuming and use harmful solvents.

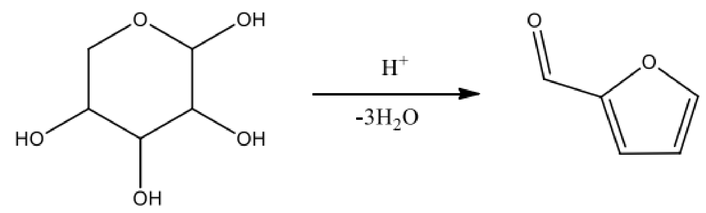

Figure 1. Acid catalyzed pentose dehydration process[2].

LABORATORY SCALE SubW SYSTEM

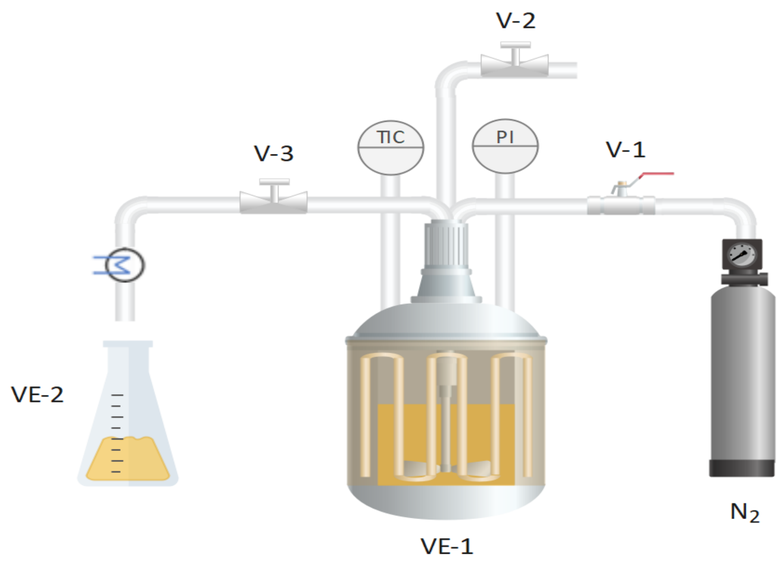

Figure 2. Diagram of the laboratory-scale subcritical water equipment. VE-1: extractor; VE-2: sample collector; V-1: pressurization valve; V-2: pressure relief valve; V-3: needle valve.

This work proposes the **furfural production** from the **hemicellulose fraction of the BSG** by subW, withouth the addition of any catalyst, and further recovery by organophilic pervaporation.

SWE SYSTEM	
Reactor volume	**500 mL**
Pressure	**50 bar**
Temperature	**175 °C**
Time	**60 minutes**
Biomass load	**5% (w/w)**

PERVAPORATION	
Temperature	**55 °C**
Pressure	**300 Pa**
Time	**180 °C**

PERVAPORATION SYSTEM

2 types of membranes:
PDMS: Polydimethyl siloxane
POMS: Polyoctylmethyl siloxane

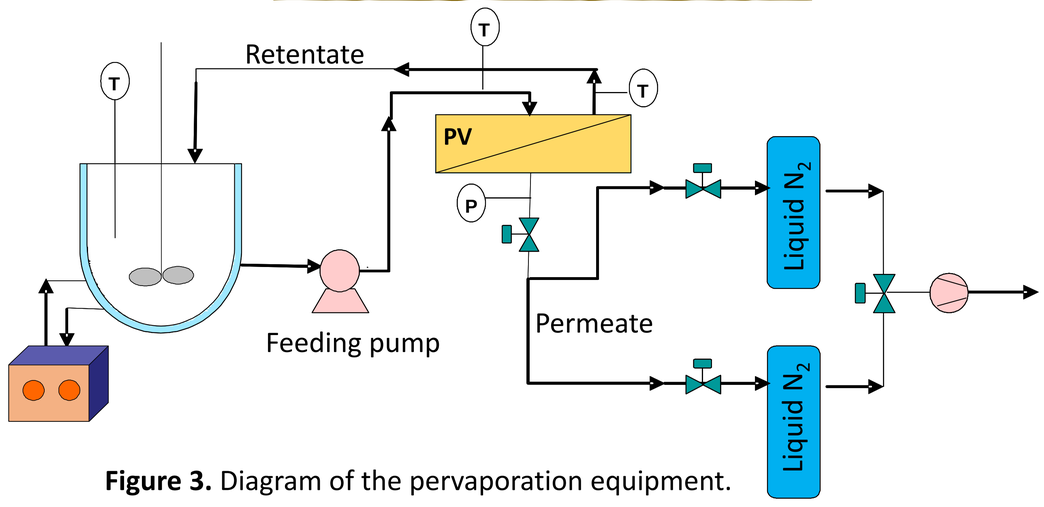

Figure 3. Diagram of the pervaporation equipment.

SubW (Subcritical water) was proposed for the **hydrolysis of BSG.**

Hydrolysis products included sugar monomers such as **xylose, glucose and arabinose and degradation products.**

Furfural is the main **degradation product** from the **pentoses.**

Compound	$C_{0,\ PDMS}$	$C_{PV\text{-}PDMS}$	$C_{0,\ POMS}$	$C_{PV\text{-}POMS}$
Furfural	1.7	0.35	1.3	0.17
HMF	0.18	0.20	0.15	0.16
Formic acid	0.46	0.55	0.36	0.41
Acetic acid	0.85	0.89	0.79	1.0
Lactic acid	0.27	0.32	0.30	0.31

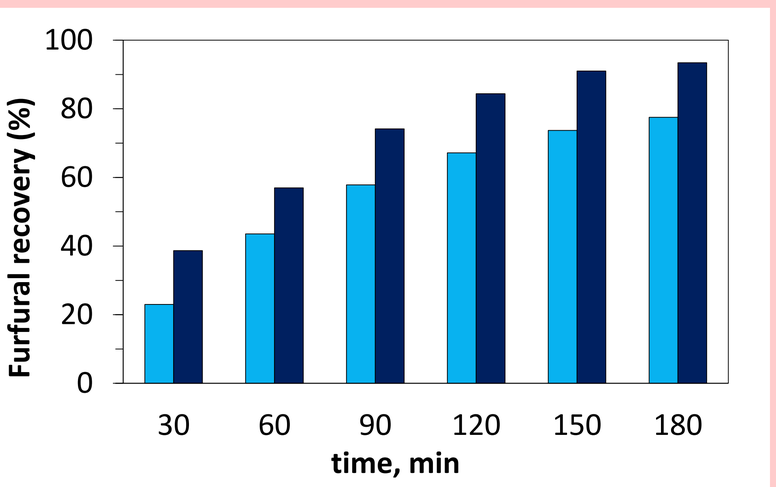

Figure 4. Furfural recovery in the permeate for PV of BSG hydrolysates for each membrane (PDMS POMS) over PV time.[3]

The **enrichment factor (β)** is the relationship between the concentration in the permeate and the feed for a specific component

$$\beta = w_{i,p} / w_{i,f}$$

β	PDMS	POMS
Furfural	48	**63**
Formic acid	0.82	0.16
Acetic acid	0.77	0.18

Furfural recovery increased gradually during **pervaporation time** for both **PDMS and POMS** membranes.

CONCLUSIONS

- Both membranes showed a great selectivity to furfural.
- **POMS** membrane produced the **highest furfural recovery (93%).**
- The **highest enrichment factor** for both membranes was towards **furfural.**

Subcritical water and pervaporation showed to be an effective combination for the production and recovery of biomass-derived furfural.

References

[1] P. Alonso-Riaño, M.T. Sanz, Ó. Benito-Román, S. Beltrán, E. Trigueros, Subcritical water as hydrolytic medium to recover and fractionate the protein fraction and phenolic compounds from craft brewer´s spent grain, *Food Chemistry*, **2021**, 351, 129264.
[2] M. Celman, L. Gutiérrez, C. Ormachea, C. Ferretti, Evaluation of the recovery of furfural from wood scraps, *Chemistry Proceedings*, **2022**, 8, 8.
[3] P. Alonso-Riaño, A.E. Illera, M.S.T. Amandio, A.M.R.B. Xavier, S. Beltrán, M.T. Sanz, Valorization of brewer´s spent grain by furfural recovery/removal from subcritical water hydrolysates by pervaporation, *Separation and Purification Technology*, **2023**, 309, 123008.

Acknowledgements

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