

# Sustainable Integrated Process towards a Complete Exploitation of Brewer's Spent Grain

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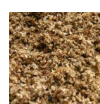
## Abstract

Brewer's Spent Grain (BSG) is the most abundant by-product generated during the first steps of the brewing process and represents about 85% of the total waste. It is usually disposed of due to its complex composition and the high level of moisture, which makes it difficult to store and transport. Up to now, its main exploitation is the use as animal feed. From an economic point of view, the handling or disposal of BSG often represents a cost in the brewery balance, especially when the waste production exceeds the farmers demand and it is necessary to pay specialized disposal companies for transportation and treatment. One of the major challenges in biomass valorization is the efficient biomass fractionation because the complex structure of the plant cell wall and the high crystallinity of cellulose make the feedstock recalcitrant to separation into its components.

In the present work, BSG was recovered from a local brewery and processed with a new approach in order to obtain the most complete valorization. In particular, the whole process has been divided in two main parts. A first pretreatment with hot water in autoclave allowed the separation of a solution containing the soluble proteins and sugars which accounted for 25% of the total starting biomass. This first step permitted the preparation of a valuable growing medium which was successfully employed for different microbial fermentations leading to valuable fungal biomass as well as triglycerides with a high content of linear or branched fatty acids, depending on the microorganism used. The water-insoluble residue was then submitted to a lignocellulose deep-eutectic-solvent-mediated fractionation which allowed the recovery of two main fractions: BSG<sub>2</sub> Cellulose and BSG<sub>2</sub> Lignin. The latter was tested as potential precursor for the development of cement water reducers with encouraging results. This combined multistep strategy for the treatment of the waste biomass appears to be a promising sustainable strategy for the development of a full exploitation of BSG from a circular economy perspective.

## Materials

### Starting Biomass



1. Wet BSG: Susceptible to microbial deterioration

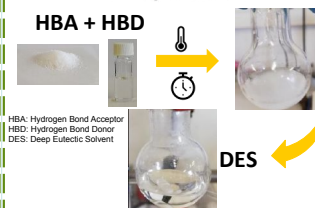


2. Dry BSG: Moisture content < 10%



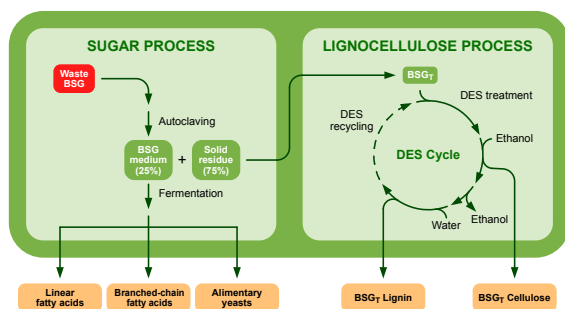
3. Shredded BSG: Easier to store and to valorize

### DES Preparation



## Results

### Integrated process



### 1. SUGAR PROCESS

Microbial strain	Growth conditions	Biomass productivity	Fatty acid productivity	Branched chain FAs (%)			Linear FAs (%)		
				iso	anteiso	others	Saturated fatty acids	Mono-unsaturated fatty acids	Poly-unsaturated fatty acids
<i>Phaffia rhodozyma</i> (DSM 5626)	6 days 22°C, pH 6.5	3.6 g/L (135 g/Kg BSG)	-	-	-	-	-	-	-
<i>Yarrowia lipolytica</i> (DSM 8218)	4 days 25°C, pH 6.5	1.5 g/L (55 g/Kg BSG)	200 mg/L (7.5 g/Kg BSG)	-	-	-	-	-	-
<i>Yarrowia lipolytica</i> (DSM 70562)	4 days 25°C, pH 6.5	1.6 g/L (61 g/Kg BSG)	220 mg/L (8.2 g/Kg BSG)	-	-	-	16.5	9.00	72.0
<i>Rhodococcus opacus</i> (DSM 43205)	4 days 28°C, pH 7.0	2.4 g/L (89 g/Kg BSG)	547 mg/L (20.5 g/Kg BSG)	-	-	19.1	44.6	21.7	9.10
<i>Streptomyces cavourensii</i> (DSM 112466)	4 days 28°C, pH 7.0	2.1 g/L (80 g/Kg BSG)	220 mg/L (8.2 g/Kg BSG)	28.4	37.7	6.80	15.0	3.70	7.50
<i>Streptomyces albidoflavus</i> (DSM 112467)	4 days 28°C, pH 7.0	1.7 g/L (64 g/Kg BSG)	180 mg/L (6.7 g/Kg BSG)	18.6	39.1	8.10	15.2	7.00	5.80

### 2. LIGNOCELLULOSE PROCESS

#### Quantitative Data

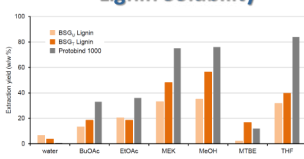
Composition DES HBA/HBD	Molar ratio (HBA/HBD)	Density of pure DES (g/cm <sup>3</sup> , 38 °C)	BSG <sub>2</sub> Cellulose recovery (%/w/w biomass)	BSG <sub>2</sub> Lignin recovery (%/w/w biomass)
Choline chloride/Formic acid	1/2	1.147	ns	ns
Choline chloride/Acetic acid	1/2	1.103	39	7
Choline chloride/L-Lactic acid	1/5	1.184	25	10
Betaine Glycine/Formic acid	1/2	1.161	55	9
Betaine Glycine/Acetic acid	1/2	1.107	32	8
Betaine Glycine/L-Lactic acid	1/5	1.203	53	7

### 3. LIGNIN CHARACTERIZATION

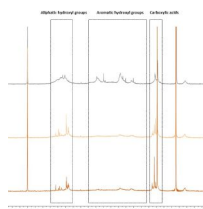
#### GPC

Sample	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	D
BSG <sub>2</sub> Lignin	820	1580	1.93
BSG <sub>1</sub> Lignin	670	1630	2.43
Protobind 1000	830	2800	3.37

#### Lignin Solubility

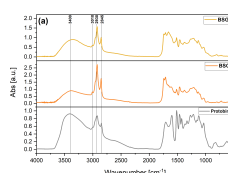
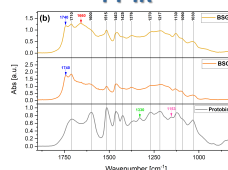


#### <sup>31</sup>P NMR

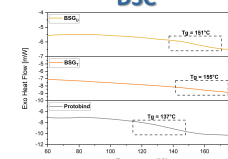


Sample	-OH, aliphatic (mmol/g)	-OH, aromatic (mmol/g)	-COOH (mmol/g)
BSG <sub>2</sub> Lignin	2.27	2.77	2.3
BSG <sub>1</sub> Lignin	1.78	3.21	3.99
Protobind 1000	3	4.67	1.42

#### FT-IR



#### DSC

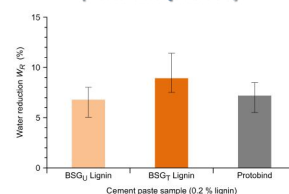


### 4. LIGNIN EXPLOITATION

A possible lignin application is the production of cement water reducers, a key component for most concrete formulations. Lignins can be directly used as low performance water reducer or derivatized in order to obtain high-performance products comparable to modern synthetic formulations.

The obtained BSG<sub>2</sub> Lignin demonstrates a water reduction capability for cement pastes comparable to Protobind, a well known commercial soda Lignin, indicating that it can constitute a promising starting point for the development of high performance sustainable cement water reducers.

#### Water reduction capability (cement pastes)



## Conclusions

- Almost complete transformation and exploitation of starting BSG waste
- A comprehensive approach combining biomass hot water treatment with successive deep eutectic solvent-mediated fractionation
- BSG<sub>2</sub> Lignin tested as water reducer in cement paste with comparable results as technical commercial lignin
- 75-80% of the mass of the latter important agro-food waste transformed into high value-added products of industrial relevance

## Our References

C. Allegretti, E. Bellinetto, P. D'Arrigo, G. Griffini, S. Marzorati, L.A.M. Rossato, E. Ruffini, L. Schiavi, S. Serra, A. Strini, D. Tessaro, S. Turri  
Towards a Complete Exploitation of Brewer's Spent Grain from a Circular Economy Perspective  
Fermentation (2022) 8, 151, doi: 10.3390/fermentation8040151

Chiara Allegretti, Francesco G. Gatti, Stefano Marzorati, Letizia Anna Maria Rossato, Stefano Serra, Alberto Strini, Paola D'Arrigo  
Reactive Deep Eutectic Solvents (RDES): A New Tool for Phospholipase D-Catalyzed Preparation of Phospholipids  
Catalysts (2021) 11, 655, doi: 10.3390/catal11060655

Chiara Allegretti, Simon Fontanay, Klaus Rischka, Alberto Strini, Julien Trouquet, Stefano Turri, Gianmarco Griffini, Paola D'Arrigo  
Two-Step Fractionation of a Model Technical Lignin by Combined Organic-Solvent Extraction and Membrane Ultrafiltration  
ACS Omega (2019) 4, 4615-4626, doi: 10.1021/acsomega.8b02851

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