Session XIII: Biofuels & Biobased Products

Sustainability assessment for the production of bio-based products using by-product streams derived from the pulp and paper industry

Anestis Vlysidis, D. Ladakis, M. Alexandri, I. Kookos, A. Koutinas

Department of Food Science and Human Nutrition
Agricultural University of Athens
Greece

23rd – 25th June 2016
Limassol, Cyprus
Our Research Group
Biorefinery development based on renewable resources

Valorisation of renewable resources

Agricultural crops and residues
Industrial wastes and by-product streams
Food waste and by-products

Biorefinery development

White biotechnology
Bioprocess / biorefinery engineering
Bioprocess / biorefinery design
Bioprocess optimisation

Added-value products

Food
Antioxidants
Chemicals

Feed
Biofuels
Heat

Agricultural crops and residues
Industrial wastes and by-product streams
Food waste and by-products

Food
Antioxidants
Chemicals

Feed
Biofuels
Heat

Agricultural University of Athens, Greece
Fermentation cases of Agricultural wastes integrated in biorefinery schemes


Agricultural University of Athens, Greece
Project: Valorising SSL from pulp and paper mills

Bioprocess optimisation
Techno-economic evaluation
Life Cycle Analysis

SSL

Fermentation

Phenolic Extract

Ultrafiltration

Phenolic Extraction with Ethyl acetate

LS

Fireproof biopolymers

Polybutylene succinate

Succinic acid production

Succinic acid Separation and Purification

Agricultural University of Athens, Greece
**SSL Production in Pulp and Paper Industry**

<table>
<thead>
<tr>
<th>SSL Characterisation</th>
<th>Value</th>
<th>St Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.277</td>
<td>0.007</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>552</td>
<td>167</td>
</tr>
<tr>
<td>Dry Matter (g-DM/L)</td>
<td>816.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Lignosulphonates (g/L)</td>
<td>458.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Ash % (g/g-DM)</td>
<td>8.62</td>
<td>0.55</td>
</tr>
<tr>
<td>Phenolics % (g/g-DM)</td>
<td>1.55</td>
<td>0.04</td>
</tr>
<tr>
<td>Carbohydrates (g/L)</td>
<td>176.41</td>
<td></td>
</tr>
<tr>
<td>Xylose (g/L)</td>
<td>128.08</td>
<td>0.59</td>
</tr>
<tr>
<td>Galactose (g/L)</td>
<td>21.47</td>
<td>5.50</td>
</tr>
<tr>
<td>Glucose (g/L)</td>
<td>19.27</td>
<td>0.39</td>
</tr>
<tr>
<td>Mannose (g/L)</td>
<td>7.41</td>
<td>1.30</td>
</tr>
<tr>
<td>Arabinose (g/L)</td>
<td>0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>Acetic Acid (g/L)</td>
<td>6.91</td>
<td>0.49</td>
</tr>
</tbody>
</table>

**Plasticizers for concrete production among others**

**Sugars are destroyed during precipitation after the addition of calcium or sodium hydroxide**

**Current uses**

**COOKING CHEMICALS**

SO₂/MeHSO₃

(Me: Ca, Mg, Na, NH₄)

**WOOD CHIPS**

**BLOW TANK**

+NaOH

+Ca(OH)₂

**WASHER**

**CELLULOSE FIBRES**

**MULTIPLE EVAPORATION PROCESSES**

**THICK LIQUOR**
Global annual production of bleached sulphite pulp: 3,570,476 t/yr (FAO, 2012) → 14% increase since 2009

- Annual production in United States of America: 989,074 t/yr (FAO, 2012) → 21% increase since 2009
- Annual production in South America: 211,000 t/yr (FAO, 2012) → 74% increase since 2009
- Annual production in European region: 2,056,902 t/yr (FAO, 2012) → 0.01% increase since 2009
Formation of Sugars & Inhibitors During the Process

Lignin

- Phenolic compounds
- Lignosulphonates

Cellulose

- glucose
- galactose
- mannose
- xylose
- arabinose

Hemicellulose

- Acetic acid
- Furfural
- 5-HMF
- Levulinic acid
- Formic acid

Agricultural University of Athens, Greece
Detoxification / Pretreatment and fermentation of SSL

SSL

- 0.63 g-SA/g yield
- Low by-product formation
- SA productivity 0.31 g/L/h (0.5 g/L/h @ 50 h)
- ~ 40 g/L final SA

Fermentations
A. succinogenes
B. succiniciproducens
Process Design of the SA production & purification of SA from SSL

Small scale plant
Annual Capacity of SSL: 15 kt
Hourly rate of 2.14 t/h

Agricultural University of Athens, Greece
Process Design of the SA production & purification of SA from SSL (cont’)

2 ktons of SA / year
Hourly rate: 300 kg/h
Using process simulation software UNISIM
Simulation of SA production & purification

Heat Integration
- Combine hot and cold stream
- Energy minimization
- 65% less consumption of steam
Techno-economic evaluation of SA bioprocess

Development of the Process Flow Diagrams

Sizing of the equipment and we find their characteristic values

Calculation of the equipment cost through empirical costing equations

Conversion to 2015 prices by using the CEPCI (CHEMICAL ENGINEERING PLANT COST INDEX)

Calculation of the installation cost ($C_{BM}$) via installation factors $F_{BM}$

Calculation of the fixed capital investment $FCl=1.6*C_{BM}$

$C_{BM}=M$ 9.7
- 47% Triple effect evaporator
- 37% the three fermenter together with their agitators
- FCI = M$ 15.6

Utility Cost was remarkable
- High requirements for steam
- M$ 0.85 per year

The Total Production Cost:

\[ TPC_{w,D} = 0.18 FCI + 2.73 C_{OL} + 1.23(C_{RM} + C_{UT} + C_{WT}) \]

TPC = M$ 11.1 per year
5.39 $/kg-SA produced

Current prices:
- 2.9 for biobased SA *
- 2.5 for petroleum derived SA *

* E4tech (UK) Ltd
LCA for the production and purification of SA

System boundaries
“Gate to gate” approach
LCA of SA bioprocess
Gabi software from PE International
Identification of “hot spots”: SA Production and Recovery

- **Environmental Impact**
  - **UNITS**
    - GWP 6.33 kg-CO2 Eq/kg of SA produced
    - ADP (MJ) 136.06 MJ/kg of SA produced
    - Energy Demand (MJ) 155.22 MJ/kg of SA produced

- **Abiotic resource depletion** includes depletion of nonrenewable resources, i.e. fossil fuels, metals and minerals.
- **Global warming potential (GWP)** is calculated as a sum of emissions of the greenhouse gases (CO2, N2O, CH4 and VOCs).
Main Conclusions & Future recommendations

• SSL is a by-product of the pulp and paper industry that can be used as a substrate in microbial fermentations
  – Needs to be pretreated first (remove the inhibitors)
  – Extract LS by nanofiltration
  – Extract phenolic compounds by solvent extraction
• Succinic acid can be produced in high yields and adequate productivities and final SA concentrations
• Techno-economic evaluation gave a higher TPC of SA from current SA costs
  – 5.3 instead of 2.9 $/kg
  – Under the same order of magnitude
  – Scale up designs (2→10→50 ktons) will significantly decrease the TPC
• The carbon footprint of the SA process showed a 6.3 kg-CO₂ Eq./kg-SA
  – Mainly due to the downstream process
  – The LCA results will be compared with petrochemical SA production
Thank you for your attention

The research leading to these results has received funding from the European Union’s Seventh Framework Program for research, technological development and demonstration under grant agreement nº 311935

Agricultural University of Athens, Greece
## Phenolic compounds

### Determination of the main phenolic compounds in the extracts by HPLC - DAD

<table>
<thead>
<tr>
<th>Phenolic compound (mg/L)</th>
<th>pH =2 ratio 1:3 v/v</th>
<th>pH =3.4 ratio 1:3 v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid</td>
<td>1038</td>
<td>525</td>
</tr>
<tr>
<td>Isorhamnetin</td>
<td>41</td>
<td>21</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>252</td>
<td>106</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>32</td>
<td>127</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>50</td>
<td>17.8</td>
</tr>
<tr>
<td>Acetosyringone</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Lariciresinol</td>
<td>142</td>
<td>-</td>
</tr>
<tr>
<td>Ellagic acid</td>
<td>1165.5</td>
<td>534</td>
</tr>
<tr>
<td>Caffeic acid</td>
<td>3.2</td>
<td>4</td>
</tr>
<tr>
<td>Vanillin</td>
<td>115</td>
<td>120</td>
</tr>
<tr>
<td>Catechin</td>
<td>127.6</td>
<td>53</td>
</tr>
</tbody>
</table>