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ORGANOSOLV PRETREATMENT AS A MAJOR STEP OF LIGNOCELLULOSIC BIOMASS REFINING

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Introduction

• The conversion of biomass within biorefineries is seen as a potential alternative to current reliance on non-renewable resources.

• The transition from a traditional “oil-refinery” to a “bio-refinery”, based on renewable lignocellulosic biomass, is crucial if we are to move to a more environmentally friendly economy.

• Lignocellulosic biomass receives more attention because it does not compete as a food resource, and it can reduce carbon dioxide in the atmosphere by up to 75–100%.
• The key components of lignocellulosic biomass, i.e., cellulose, hemicelluloses and lignin, are closely associated with each other at the plant cell level.
• This close association, together with the partly crystalline nature of cellulose, reduces cellulose reactivity towards acid and enzymatic hydrolysis in native biomass.
• Thus, organosolv pretreatment is necessary to render the carbohydrate fraction to acid, enzymatic and microbial action.
• Biorefining is the sustainable processing of biomass into a spectrum of marketable products (food and feed, materials, and chemicals) and energy (fuels, power, and heat).

• In biorefinery appropriate fractionation of the complex lignocellulose material, into its constituents, is of most importance.
Lignocellulosic biorefinery scheme

Primary Biorefinery

Organic solvent Pretreatment

Lignocellulosic biomass

Cellulose

Heat / Power

Processing

Secondary Biorefinery

Pulp/Paper

Hemicelluloses’ sugars

Acid hydrolysis

Conversion & synthesis

Fermentation

Ethanol

Butanol

Lactic acid

Chemical derivatives e.g. Furfural, HMF

Phenolics

Fuel additives

Electricity

Heat

Enzymatic Hydrolysis

Lignin
• This study focused on the organosolv pretreatment process of wheat straw which facilitates hydrolysis and fermentation processes.

• Ethanol (CH$_3$CH$_2$OH), Methanol (CH$_3$OH), Diethylene glycol (C$_4$H$_{10}$O$_3$), Acetone (C$_3$H$_6$O) and Butanol (C$_4$H$_9$OH) were evaluated as solvents.

• Sulfuric acid was the pretreatments’ catalyst.

• The effect of the five organic solvents on pretreatment results was analyzed.
Experimental

Raw material

• The wheat straw used was obtained from Kapareli Village of Thebes, Greece, as a suitable source for full-scale industrial applications.

• The moisture content of the material when received was 9% w/w; after screening, the fraction with particle sizes between 10 and 20 mm was isolated.
## Composition of wheat straw

<table>
<thead>
<tr>
<th>Component</th>
<th>% w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>33.7</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>24.1</td>
</tr>
<tr>
<td>• Xylose</td>
<td>18.9</td>
</tr>
<tr>
<td>• Arabinose</td>
<td>2.7</td>
</tr>
<tr>
<td>• Acetyl groups</td>
<td>2.5</td>
</tr>
<tr>
<td>Klason lignin (acid insoluble)</td>
<td>17.0</td>
</tr>
<tr>
<td>Ash</td>
<td>4.7</td>
</tr>
<tr>
<td>Extractives</td>
<td>6.2</td>
</tr>
<tr>
<td>Other components</td>
<td>14.4</td>
</tr>
</tbody>
</table>
Experimental equipment and procedures

- A 3.75-L batch reactor PARR 4843 was used for the organosolv fractionation.
- Reaction ending temperature was 160 ºC whereas the reaction time was 20 min (not including the preheating time).
- The reaction was catalyzed by H₂SO₄, 0.045 N, in a 50% v/v aqueous/organic solvent solution; the liquid/solid ratio was 20/1.
- The organic solvents used were: ethanol, methanol, diethylene glycol, acetone and butanol.
Organosolv pretreatment’s (a) temperature and (b) pressure profile vs. time
(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1).
Effect of organic solvent on Solid Residue Yield.

Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1.
Effect of organic solvent on (a) lignin composition and (b) removed lignin percentage

(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)
Removed lignin vs. Solid Residue Yield
(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)

\[ y = -5.5899x + 2.9154 \]

\[ R^2 = 0.9569 \]

- Methanol
- Ethanol
- Acetone
- Butanol

Removed lignin%

SRY%
Effect of organic solvent on (a) cellulose composition and (b) removed cellulose percentage
(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)
Effect of organic solvent on (a) xylan composition and (b) removed xylan percentage

(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)
Removed xylan vs. Solid Residue Yield

(Sulfuric acid 0.045N; temperature 160°C; time 20 min;
liquid: solid ratio = 20:1)

\[
y = -1.2949x + 1.4788
\]

\[
R^2 = 0.9717
\]
Effect of organic solvent on (a) glucose and (b) xylose concentration, before and after post-hydrolysis

(Sulfuric acid 0.045N; temperature 160°C; time 20 min; liquid: solid ratio = 20:1)
Conclusions

• Within the Biorefinery concept, from the five solvents (ethanol, methanol, diethylene glycol, acetone, butanol) examined herein as regards organosolv pretreatment (sulfuric acid 0.045 N, 160 °C, 20 min) of wheat straw, butanol gave the highest delignification effect, i.e., 60% lignin removal.

• Maximum cellulose concentration was 72% w/w (on pretreatment’s solid residue) using acetone while delignification was 59% and 95% of xylan of the initial straw was hydrolyzed to 88% w/w xylose (expressed on initial xylan).