Biochemicals from Flax Shives/Straw
Extraction, purification and properties of selected compounds

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Total Flax Crop Utilization

**SEED**
- Oil → Industrial & Food
  (oil paints, varnishes and stains)
- Meal → Feed, Food & Industry
- Fiber → Industrial

**STRAW**
- Shive → Bio-Energy
  Bio-Chemicals
  Biomaterials

Feedstocks → Processing → Refining → Synthesis
## Chemical Composition of Flax Fiber and Shive

<table>
<thead>
<tr>
<th>Chemical composition (% total)</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Ash</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber</td>
<td>78</td>
<td>6</td>
<td>5</td>
<td>2</td>
<td>Sain &amp; Fortier, 2002</td>
</tr>
<tr>
<td>Shive</td>
<td>53</td>
<td>13</td>
<td>24</td>
<td>&gt;2</td>
<td>Cox et al., 1999</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>26</td>
<td>23</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>34</td>
<td>15</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>26</td>
<td>30</td>
<td>1.4</td>
<td>This study: Sun et al., 1995</td>
</tr>
</tbody>
</table>

National Renewable Energy Laboratory
Pressurized Low Polarity Water Extraction Technology

What is it?

- Pressurized low polarity water (PLPW) extraction is a promising extraction and fractionation technique that uses liquid water under pressure.

- PLPW extraction is based on the use of water as an extractant at temperatures between 100 and 374°C and a pressure high enough to maintain the water in liquid state (critical point of water, 221 bar and 374°C).

- PLPW also known as subcritical water, liquid hot water, pressurized hot water or superheated water is much less polar, less viscous, and with reduced surface tension than water at ambient conditions.
Pressure-enthalpy chart of water.

5.17 MPa (750 psi or 52 bar)

critical point of water: 221 bar and 374°C
Diagram of Pressurized Low Polarity Water Extractor

Factors that may affect PLPW extraction

- Temperature
- pH
- Particle size
- Flow rate
- Pressure
- Solvent to feed ratio
- Co-packing materials
- Bed depth
Optimization of Temperature, pH and Flow Rate of PLPW

for the Extraction of Hemicellulose, Cellulose,

Lignin and other Phenolic Compounds from Flax Shives
Experimental Design

- Central composite design 3 independent variables and 5 levels
  - Temperature (°C) 120 140 170 200 220
  - pH 1.8 4.0 7.0 10.0 13.1
  - Flow rate (mL/min) 0.3 1.0 2.0 3.0 3.7

- Particle size between 1 and 2 mm
- Pressure 750psi (5.2 MPa or 52 bar)

- Dependent variables
- Carbohydrates and phenolic compounds in extracts and residues
  - hemicellulose, cellulose, lignin and HBA: p-hydroxybenzaldehyde; VA: vanillic acid; SA: syringic acid; VN: vanillin; FA: ferulic acid; TP: total phenolic compounds (sum of concentration of HBA, VA, SA, VN and FA)
Effects of temperature and pH on PLPW extraction of polymers from ground dry flax shives
- C, H & L in PLPW flax shive residues

| Temp | pH | 140 | 200 | 140 | 200 | 140 | 200 | 140 | 200 | 140 | 200 | 140 | 200 | 140 | 200 | 140 | 200 |
|------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|      |    | 3.3 | 3.3 | 10  | 10  | 3.3 | 3.3 | 10  | 10  | 7   | 7   | 7   | 7   | 2   | 13  | 7   | 7   | 7   |

| Cellulose (%) | 34.3 | 34.7 | 29.4 | 28.3 | 36.9 | 28.4 | 30.1 | 28.4 | 32.2 | 23.0 | 34.3 | 28.7 | 34.7 | 34.3 | 33.1 | 32.6 | 32.5 |
| Hemicel (%)   | 25.9 | 19.8 | 10.8 | 4.6  | 4.9  | 3.2  | 11.5 | 5.4  | 19.8 | 1.2  | 2.4  | 8.1  | 8.0  | 15.1 | 11.5 | 11.2 | 11.1 |
| Lignin (%)    | 29.7 | 27.2 | 18.8 | 18.6 | 11.2 | 18.3 | 14.1 | 18.8 | 13.4 | 26.0 | 12.1 | 21.8 | 16.5 | 23.2 | 21.1 | 21.4 | 20.2 | 20.0 |

0 100 200 300 400 500 600 700 800 900 1000
Untreated flax shives

Cellulose Hemicellulose Lignin (AIS) ASL Ash
Experimental Model

The statistical software package Design-Expert ® 7.0 (Stat Ease, Inc, Minneapolis, USA) was used to generate a regression model in order to predict the effect of combined parameters on responses. To construct the response surface model, a second-order polynomial equation was fitted to the data using multiple regressions. The response of tested variables can be predicted by following second-order polynomial equation:

\[
Y_i = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j
\]

where \( Y_i \) = the predicted response; \( b_0, b_i, b_{ii} \) and \( b_{ij} \) are the intercept, the linear coefficient, squared coefficient and interaction coefficients, respectively.; \( \chi_i \) and \( \chi_j \) = the coded level of independent variables \( X_i \) and \( X_j \), \( n \) is the number of independent variables.
Effects of temperature and pH on PLPW extraction of cellulose from ground dry flax shives
- Cellulose in PLPW flax shive residues
Effects of temperature and pH on PLPW extraction of cellulose from ground dry flax shives

- Cellulose in PLPW flax shive residues
Effects of temperature and flow rate on PLPW extraction of lignin from ground dry flax shives

- Lignin in PLPW flax shive residues
Effects of temperature and pH on PLPW extraction of hemicellulose from ground dry flax shives.

**Hemicellulose in PLPW flax shive residues**
Effects of pH and flow rate on PLPW extraction of hemicellulose from ground dry flax shives.

Hemicellulose in PLPW flax shive residues
Effects of temperature and pH on PLPW extraction of vanillin from ground dry flax shives - in PLPW flax shive extracts
Effects of temperature and flow rate on PLPW extraction of vanillin from ground dry flax shives - in PLPW flax shive extracts
Effect of flow rate on the extraction of vanillin from flax shive with PLPW

- in PLPW flax shive extracts
## Total Phenolics and Antioxidant Activity of PLPW Flax Shive Extracts (C7 and C8)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Phenolics</th>
<th>Antioxidant activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g Gallic acid/kg sample</td>
<td>g Trolox/kg sample</td>
</tr>
<tr>
<td></td>
<td>Folin</td>
<td>HPLC</td>
</tr>
<tr>
<td><strong>C7</strong></td>
<td>65.5</td>
<td>66.1</td>
</tr>
<tr>
<td><strong>C8</strong></td>
<td>63.0</td>
<td>63.8</td>
</tr>
</tbody>
</table>

Particle size: 0.25 < < 1 mm; Pressure: 750 psi; Column: 40 cm*1.9 cm; Flow rate: 5 mL/min; Sample: 17.00 g flax shive; 0.47M NaOH-for C7, 0.67M NaOH-for C8.
PLPW Extraction -- Mode of Action

- PLPW has an unusually low dielectric constant that enables most of the hemicellulose to dissolve at 170-200°C and low pH.

- One half to two thirds of the lignin also dissolves from flax shives when this material is treated at 220°C and high pH.

- PLPW is suspected to cleave hemiacetal linkages and liberate acids during biomass hydrolysis. This facilitates the breakage of ether linkages in biomass.

- The chemical and physical changes caused to flax shives by PLPW extraction of hemicellulose should improve the accessibility of the enzymes to the cellulose fibrils.
Biochemicals from Flax/Linseed Shives/Straw
Conclusions

• Flax residues offer great potential for biochemicals and biomaterials; application of biorefinery concept at its best

• Enzymatic process coupled with green extraction processes can lead to promising industrial applications of flax shives

• Significant benefits from a sustainable process

• Next steps:
  – Enzyme selection
  – Extraction and purification of selected biochemicals
  – Scale up & full cycle
  – Economics of process

Reference:

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