Valorization of hemicellulose-biomass side streams via catalytic hydrogenation into value added chemicals and fuels

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Utilization of Biomass

FOSSIL FUELS

BIO-BASED

Fuels
- Bioethanol
- Biodiesel
- Green Diesel

Platform Chemicals
- Furfural
- Levulinic acid
- HMF
- Biooil

Plastics
- Poly(3-hydroxybutyrate) biodegradable plastic

BIOMASS

Sustainability
(Bio)Catalysis
A successful commercial example of biomass derived plastic replacing PET

YXY Technology

Dehydration  Oxidation  Polymerization

Glucose → MMF (5-methoxy methyl furfural) → FDCA → PEF

Methyl Levulinate

Plant based Feedstock

https://www.avantium.com/yxy/yxy-technology/
Lignocellulosic Biomass

**Structure**
- **Cellulose:**
  - General formula: \( (C_6H_{10}O_5)_n \)
  - MW: 300,000-500,000

- **Hemicellulose:**
  - General formula: \( (C_5H_8O_4)_n \)
  - Consists of \( C_5 \) & \( C_6 \) sugars, uronic acids, acetyl units

- **Lignin:**
  - Phenolic monomers

**Composition**

- **Cellulose:**

- **Hemicellulose:**
  - General formula: \( (C_5H_8O_4)_n \)

- **Lignin:**
  - Phenolic monomers

- **Cellulose:** 30-50%, **Hemicellulose:** 20-40%, **Lignin:** 15-25%

- Others, 5-35% - Ash 3-10% (Si,Al,Ca,Mg,K,Na), Extractives: Resins, Phenols, Sterols, etc
Lignocellulosic biomass raw materials

- Agricultural and forestry residues/waste (wheat straw, trimmings, tree branches)
- Industrial wood processing residues (e.g. sawdust)
- Food industry waste (e.g. kernels, shells)
- Municipal solid waste (e.g. waste paper)
- Perennial or annual crops with high yield 1-4 ton/1000m² year (e.g. eucalyptus, pseudoacacia, willow, miscanthus, switch grass, cellulosic sorghum,..)

**Cereals** (328.52Mt)
- *Wheat* (148.83Mt)
- *Maize* (80.37Mt)
- *Barley* (50.10Mt)
- ***+ others*** (49.22Mt)

**Oil-bearing crops** (73.10Mt)
- *Rapeseed* (53.99Mt)
- *Sunflower* (14.63Mt)
- ***+ others*** (4.48Mt)

**Permanent Crops** (21.86Mt)
- *Olive trees* (17.11Mt)
- *Vineyards* (4.08Mt)
- ***+ others*** (0.68 Mt)

**Sugar-starchy crops** (13.41Mt)
- *Sugar beet* (9.23Mt)
- *Potatoes* (4.18Mt)

*European Commission Report, 2018*
Biomass (agricultural) residues in Greece


Center for Renewable Energy Sources & Saving, Greece, 2010
Integrated lignocellulosic biomass valorization (Bio-refinery)

Lignocellulosic biomass → Hydrothermal Pretreatment Neat + H₂O → Cellulose + Lignin

Cellulose

Hemicellulose (xylan/xylose, furfural, acetic acid)

- Catalytic “transfer” hydrogenation → Furfural, furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran
  - Platform chemicals, Fuel additives, Resins

Lignin

- Enzymatic hydrolysis
- Catalytic hydrogenolysis → Alkoxy-phenols, Alkyl-phenols
  - Aliphatic, esters
  - BTX, PAHs
- Catalytic fast pyrolysis
  - Platform chemicals, Resins, Polymers

- Sugar Alcohols
  - Catalysts, Platform chemicals, Fuel additives, Polymers

平台化学品、燃料添加剂、聚合物

- Ethanol Fuels, Platform chemicals, fuel additives, polymers
Hydrothermal pre-treatment (in pure H₂O)

**Biomass**

**Autoclave reactor**

**Solid product**
Cellulose + Lignin

**Enzymatic Hydrolysis**

**Liquid product**
Hemicellulose monomers and oligomers, xylose, furfural, acetic, formic acid, etc.

**Experimental conditions:**
- Temperature: 130-220°C
- Time: 15-180 min
- LSR: 15
- Stirring: 400 rpm

Severity factor (logRo)

\[ R_0 = t \cdot \exp \left( \frac{T-100}{14.75} \right) \]

Generalized reaction scheme

**Hemicellulose hydrolysis at subcritical water**

- Self-catalyzed hydrolysis (pH 5 → 2.5)
- The catalyst (acetic acid) is a biomass component

**Cellulose hydrolysis at subcritical water**

**Sugars dehydration products**

- Furfural
- 2-Furoic acid
- Formic acid
- Levulinic acid
- Formic acid
Evolution of main structural components in hydrothermally treated solids
Xylose and furfural concentration vs. % hemicellulose removal

Mostly as xylan oligomers
Dominant pathways/products depend on catalyst type, reaction parameters and solvent (acting or not as H-donor for inducing transfer hydrogenation)

Furfural derived chemicals and fuels

Catalytic hydrogenation experiments of hemicellulose stream

Solvent, $\text{H}_2$ source

T, Catalyst

Furfural + Solvent

Furanic compounds: Furfuryl alcohol, 2-MF, 2-MTHF, etc.

- **Solvent:** Ethyl acetate, $\text{H}_2\text{O}$, EtOH & IPA (as $\text{H}_2$ donor - transfer hydrogenation)
- **$\text{H}_2$ gas:** 30 bar at room temp.
- **Temperature:** 180 °C
- **Catalyst:** Ru, Pd, Pt, Cu, Ni supported on Micro/mesoporous Activated Carbon
## Catalysts for furfural hydrogenation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total SSA (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Micropore area (m²/g) / volume (cc/g)</th>
<th>Meso/macro-pore &amp; external area (m²/g) / volume (cc/g)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon (AC)</td>
<td>1281</td>
<td>0.946</td>
<td>841 / 0.343</td>
<td>440 / 0.603</td>
<td>-</td>
</tr>
<tr>
<td>3%Pt/AC</td>
<td>1180</td>
<td>0.847</td>
<td>759 / 0.309</td>
<td>421 / 0.538</td>
<td>13.6</td>
</tr>
<tr>
<td>3%Pd/AC</td>
<td>1338</td>
<td>0.947</td>
<td>886 / 0.362</td>
<td>452 / 0.585</td>
<td>16.6</td>
</tr>
<tr>
<td>5%Ni/AC</td>
<td>1251</td>
<td>0.884</td>
<td>831 / 0.343</td>
<td>420 / 0.541</td>
<td>6.8</td>
</tr>
<tr>
<td>10%Ni/AC</td>
<td>1246</td>
<td>0.895</td>
<td>806 / 0.329</td>
<td>440 / 0.566</td>
<td>Ni(0) 23.5- NiO 6.1</td>
</tr>
<tr>
<td>10%Cu/AC</td>
<td>1172</td>
<td>0.828</td>
<td>768 / 0.313</td>
<td>403 / 0.515</td>
<td>Cu(0) 23.2 - Cu₂O 16.6</td>
</tr>
<tr>
<td>5%Ni-15%W/AC</td>
<td>1025</td>
<td>0.720</td>
<td>678 / 0.276</td>
<td>347 / 0.444</td>
<td>Ni(0) 7.8 - WO₂ 9.9 - NiWO₄ 15.5</td>
</tr>
</tbody>
</table>

![Adsorbed N₂ (cc/g, STP) vs. P/P₀](image1.png)

(a) 5%Ni/AC, (b) 3%Pt/AC, (c) 3%Pd/AC, (d) 10%Cu/AC
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>H₂ (bars)</th>
<th>X (%)</th>
<th>FAL</th>
<th>THFAL</th>
<th>2-MF</th>
<th>2-MTHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>1</td>
<td>180</td>
<td>30</td>
<td>15.6</td>
<td>10.1</td>
<td>0.0</td>
<td>43.4</td>
<td>0.0</td>
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<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>3</td>
<td>180</td>
<td>30</td>
<td>19.6</td>
<td>6.0</td>
<td>0.0</td>
<td>58.4</td>
<td>0.0</td>
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<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>6</td>
<td>180</td>
<td>30</td>
<td>29.3</td>
<td>3.6</td>
<td>0.0</td>
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<td>0.0</td>
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<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>9</td>
<td>180</td>
<td>30</td>
<td>34.8</td>
<td>5.8</td>
<td>1.1</td>
<td>74.6</td>
<td>11.5</td>
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<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>6</td>
<td>180</td>
<td>30</td>
<td>19.6</td>
<td>6.0</td>
<td>0.0</td>
<td>58.4</td>
<td>0.0</td>
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<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>6</td>
<td>220</td>
<td>30</td>
<td>43.4</td>
<td>4.4</td>
<td>3.8</td>
<td>69.4</td>
<td>13.2</td>
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</table>

**Effect of reaction time & temperature**

![Furfural conversion diagram](image-url)
## Effect of catalyst type

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>H₂ (bars)</th>
<th>X (%)</th>
<th>FAL</th>
<th>THFAL</th>
<th>2-MF</th>
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<tbody>
<tr>
<td>3%Pd/AC</td>
<td>EtOAc</td>
<td>3</td>
<td>180</td>
<td>30</td>
<td>19.6</td>
<td>6.0</td>
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<tr>
<td>3%Pt/AC</td>
<td>EtOAc</td>
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<td>180</td>
<td>30</td>
<td>72.9</td>
<td>3.5</td>
<td>1.5</td>
<td>74.3</td>
<td>0.0</td>
</tr>
<tr>
<td>10% Ni/AC</td>
<td>EtOAc</td>
<td>3</td>
<td>180</td>
<td>30</td>
<td>19.3</td>
<td>21.7</td>
<td>1.3</td>
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<tr>
<td>10%Ni/15%W-AC</td>
<td>EtOAc</td>
<td>3</td>
<td>180</td>
<td>30</td>
<td>53.7</td>
<td>18.0</td>
<td>5.4</td>
<td>42.1</td>
<td>0.0</td>
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</tbody>
</table>

- Pt based catalyst were very reactive and selective towards 2-MF (polar, aprotic solvent)
- Ni based catalysts exhibit also high selectivity to 2-MF but activity improvement is needed
Catalytic transfer hydrogenation of furfural (solvent acting as hydrogen donor)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>FA</th>
<th>THFA</th>
<th>MF</th>
<th>MTHF</th>
<th>iPrOMF</th>
<th>Mass balance (%)</th>
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<tr>
<td>1</td>
<td>-</td>
<td>2</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>104</td>
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<tr>
<td>2</td>
<td>10%Cu/AC</td>
<td>24</td>
<td>22</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>103</td>
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<tr>
<td>3</td>
<td>3%Pd/AC</td>
<td>47</td>
<td>21</td>
<td>1</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td>87</td>
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<tr>
<td>4</td>
<td>3%Pt/AC</td>
<td>93</td>
<td>47</td>
<td>1</td>
<td>24</td>
<td>3</td>
<td>5</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>5%Ni/AC</td>
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<td>6</td>
<td>1</td>
<td>66</td>
<td>2</td>
<td>3</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>5%Ni/AC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>102</td>
</tr>
<tr>
<td>7</td>
<td>5%Ni/AC&lt;sup&gt;c&lt;/sup&gt;</td>
<td>95</td>
<td>20</td>
<td>1</td>
<td>50</td>
<td>1</td>
<td>1</td>
<td>78</td>
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<tr>
<td>8</td>
<td>5%Ni/AC&lt;sup&gt;d&lt;/sup&gt;</td>
<td>87</td>
<td>13</td>
<td>1</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>38&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>5%Ni/AC&lt;sup&gt;f&lt;/sup&gt;</td>
<td>67</td>
<td>38</td>
<td>1</td>
<td>17</td>
<td>1</td>
<td>13</td>
<td>103</td>
</tr>
</tbody>
</table>

<sup>a</sup> 200 °C, 5 h, 0.35 M furfural in 60 mL isopropanol, 30 bars H<sub>2</sub>; <sup>b</sup> 0 bar H<sub>2</sub>/200 °C; <sup>c</sup> 0 bar H<sub>2</sub>/260 °C; <sup>d</sup> In methanol; <sup>e</sup> Unknown compound eluting at 3.8 min in GC analysis, not included (48 % of total peak area); <sup>f</sup> Spent catalyst recovered after the experiment in entry 5

Ni, Cu, Pt, Pd on micro/mesoporous carbon

An example of the successful collaboration between Greece, France and Spain, involving training/exchange of young scientists within the frame of European COST Action “LIGNOVAL”


Catalytic hydrogenation experiments of “real” hemicellulose stream

Aqueous side-stream from Hydrothermal Pretreatment of biomass (beech wood)

H₂ (30 bar) → 3%Pd/AC

80% FF conversion > 95% selectivity to:

Furfuryl alcohol
Tetrahydrofurfuryl alcohol
Enzymatic hydrolysis optimization (beech sawdust)

Hydrothermal Pretreatment 220 °C, 15 min

Beech wood (Lignocel) Cellulose 42,1%

→ Pretreated solid Cellulose 63,2%

→ Extracted solid Cellulose 77,0%

→ Liquid hydrolyzate Glucose 99,3%

Xylose Furfural Acetic acid

FAL, 2-MF, 2-MTHF

A synergy between thermochemical pretreatment, chemo- and bio-catalysis is necessary for more efficient biomass valorization.
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