Anaerobic digestion of lignocellulosic wastes pre-treated with ionic liquids


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8th International Conference on Sustainable Solid Waste Management

[Graph and images related to CO2 emissions and sustainability metrics are shown, with annotations for China's targets and EU standards.]

[1] China's targets are higher than those for other regions. For other fuel types, the target will be lower.
[2] US and Canada's targets are even higher, with targets for commercial vehicles increasing.

Source: [Institutional logo and text]
Anaerobic digestion process
≈ 12000 biogas plants use crops and agricultural residues

Renewable Energy Directive (RED II)
Pretreatments

20 – 30%

CH₄ + CO₂
Pretreatments

- Chemical
- Biological
- Thermal
Ionic liquids (IL)
Ionic liquids (IL)

Chemical

Organic cations

Inorganic anions

VOLATILITY

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Objective

1-ethyl-3-methyl imidazolium acetate [Emim][Ac]

Wheat straw (WS)
Barley straw (BS)
Grape stem (GS)

CH₄
Wheat straw + Barley straw + Grape stem

Methods

1-ethyl-3-methyl imidazolium acetate
[Emim][Ac]

Different ratios
1:1, 1:3, 1:5 w:w biomass - [Emim][Ac]

120 °C - 120 min

Leachate
[Emim][Ac]

CH₄

IL1, IL3 and IL5
Methods

Wheat straw + Barley straw + Grape stem

With deionized water

120 °C - 120 min

IL1, IL3 and IL5

CH₄
INVESTIGATION results
### Wheat straw

<table>
<thead>
<tr>
<th></th>
<th>Wheat straw</th>
<th>Barley straw</th>
<th>Grape stem</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C (%)</strong></td>
<td>43.32 ± 0.02</td>
<td>43.89 ± 0.03</td>
<td>47.25 ± 0.09</td>
</tr>
<tr>
<td><strong>H (%)</strong></td>
<td>5.62 ± 0.03</td>
<td>5.75 ± 0.05</td>
<td>5.60 ± 0.07</td>
</tr>
<tr>
<td><strong>N (%)</strong></td>
<td>0.63 ± 0.01</td>
<td>0.56 ± 0.01</td>
<td>1.48 ± 0.01</td>
</tr>
<tr>
<td><strong>S (%)</strong></td>
<td>0.17 ± 0.01</td>
<td>0.11 ± 0.02</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td><em><em>O</em> (%)</em>*</td>
<td>20.58 ± 0.02</td>
<td>22.39 ± 0.01</td>
<td>11.35 ± 0.02</td>
</tr>
<tr>
<td><strong>VM (%)</strong></td>
<td>70.30 ± 0.03</td>
<td>72.70 ± 0.02</td>
<td>65.80 ± 0.01</td>
</tr>
</tbody>
</table>

*By difference: O = 100 – (C + H + N + ash)
Differential thermogravimetric (DTG) profiles

**Wheat straw**

- WS Raw
- WS IL3
- WS IL5

Volatiles matter, cellulose and hemicellulose

**Barley straw**

- BS Raw
- BS IL1
- BS IL3
- BS IL5

High molecular weight compounds, lignin and fixed carbon

**Grape stem**

- GS Raw
- GS IL1
- GS IL3
- GS IL5

Higher lignin content
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X-ray diffraction (XRD) profiles

Ionic liquid pretreatment

Reduction of cellulose crystallinity

Hydrothermal pretreatment

No significant variation
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Cellulose crystallinity index (CrI %)

\[ CrI (\%) = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \cdot 100 \]

- \( I_{002} \): maximum intensity above baseline at \( 2\theta = 22^\circ \)
- \( I_{am} \): minimum in intensity above baseline at \( 2\theta = 18^\circ \)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Raw</th>
<th>HT</th>
<th>IL1</th>
<th>IL3</th>
<th>IL5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>54.8</td>
<td>55.7</td>
<td>53.9</td>
<td>51.4</td>
<td>50</td>
</tr>
<tr>
<td>Barley straw</td>
<td>53.8</td>
<td>53.6</td>
<td>52.4</td>
<td>51.2</td>
<td>50.9</td>
</tr>
<tr>
<td>Grape stem</td>
<td>32.5</td>
<td>32.1</td>
<td>28.2</td>
<td>27.8</td>
<td>27.5</td>
</tr>
</tbody>
</table>

CrI %

5 - 16%
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Sugar yield in the leachates after HT and IL pre-treatments

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>WS (mg glucose g(^{-1}) biomass)</th>
<th>BS (mg glucose g(^{-1}) biomass)</th>
<th>GS (mg glucose g(^{-1}) biomass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>123.4 ± 1.1</td>
<td>41.2 ± 1.3</td>
<td>47.8 ± 0.6</td>
</tr>
<tr>
<td>IL1</td>
<td>127.6 ± 3.2</td>
<td>42.4 ± 0.8</td>
<td>50.0 ± 0.1</td>
</tr>
<tr>
<td>IL3</td>
<td>143.0 ± 4.8</td>
<td>45.5 ± 0.9</td>
<td>94.5 ± 0.7</td>
</tr>
<tr>
<td>IL5</td>
<td>158.2 ± 5.1</td>
<td>47.9 ± 1.6</td>
<td>188.1 ± 6.8</td>
</tr>
</tbody>
</table>

Sugar yield:
- Wheat straw: 28%
- Barley straw: 16%
- Grape stem: 293%
Biomethane potential test

15 g VS L\(^{-1}\) granular anaerobic sludge
ISR = 2
7.5 g VS L\(^{-1}\) substrate

Wheat straw
- WS Raw
- WS HT
- WS IL5

Grape stem
- GS Raw
- GS HT
- GS IL5

Biogas analysis
Vials to be sacrificed
Positive controls
Blanks
Cumulative methane yield along the anaerobic digestion
Cumulative methane yield: solid + leachate

Wheat straw

Grape stem

\( \text{CH}_4 \)
Cumulative methane yield: solid + leachate

- Wheat straw
- Grape stem

Cumulative methane yield (mL CH₄ g⁻¹ VS added)

- Raw
- HT + LF
- IL5 + LF

GS (black) and WS (red)

- 25 - 34% increase
- 56 - 61% increase
Conclusions

\[ \text{CH}_3 \text{N}^+ \text{O}_2 \text{CCH}_3 \]

\[ \text{CH}_3 \text{CH}_3 \]

\[ \text{CH}_4 \]
Acknowledgements

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Thanks

Never give up

R. P. Ipiales