Investigating the insecticidal activity of lignin, cellulose and hemicellulose bio-oil

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Introduction

• Agricultural and forestry residues are primarily composed of:
  • lignin (L)
  • cellulose (C)
  • hemicellulose (H)

• C and H have industrial use (e.g., in paper production)

• 40-50 million tons of L per annum produced worldwide, currently a waste product

• Biomass conversion to produce high value pesticides
# Introduction

<table>
<thead>
<tr>
<th>Biomass</th>
<th>L</th>
<th>C</th>
<th>H</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eucalyptus</td>
<td>29</td>
<td>48</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>11</td>
<td>22</td>
<td>15</td>
<td>52</td>
</tr>
<tr>
<td>Corn stover</td>
<td>17</td>
<td>36</td>
<td>23</td>
<td>24</td>
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</tbody>
</table>

- Biomass contains varying proportions of lignin, cellulose and hemicellulose
- Bio-oils from a range of biomass have varying insecticidal activity
Objectives

• Compare the insecticidal activity of bio-oils produced from L, C and H biomass components

• Compare the insecticidal activity of the mixture of bio-oils \((L_{oil}+C_{oil}+H_{oil})\) and mixture of biomass \((L+C+H)\)

• Synergy?
  – Greater than additive effects
  – Lower concentrations can be used:
    • Smaller environmental impact
    • Cheaper

Definitions:

*Mixture of Bio-oils* = bio-oils produced from individual biomass components were combined on the basis of their yield

*Mixture of Biomass* = bio-oil produced from combination of biomass components in equal parts
Experimental Biomass

Lignin
- particle size < 200 µm
- derived from wood
- Organosolv lignin

Cellulose
- particle size < 500 µm
- derived from plant source

Hemicellulose
- particle size < 800 µm
- obtained from birch wood
Experimental

- Fluidized bubbling bed of sand
- Pyrolysis at 550°C
- Vapor Residence Time: 2.3 s
Experimental
CPB 2nd instar larvae bioassay

- Potato leaf (*Solanum tuberosum* var. Kennebec) discs were treated with control or bio-oil (150 µl)
- Five Colorado potato beetle 2nd instar larvae (*Leptinotarsa decemlineata* (Say)) were placed on each treated disc
- Mortality of larvae was recorded after 48 h
- All insect bioassays were held in an environmental chamber at 25° C, 50% RH
Experimental Determination of LC$_{50}$

Example: LC$_{50}$ (mg/ml) of the lignin bio-oil
Experimental Synergism Determination

\[ S = M \left[ \frac{X_L}{L} + \frac{X_C}{C} + \frac{X_H}{H} \right] \]

M, L, C and H : LC\(_{50}\)s of the mixture of bio-oils, and L, C, and H oils

\(X_L, X_C, X_H\) : weight fractions of L, C, and H oils in the mixture of bio-oils

- S > 1 (Antagonistic toxicity)
- S = 1 (Additive toxicity)
- S < 1 (Synergistic toxicity)

Results

Bio-oil yield (%) from L, C and H and mixture of biomass

![Graph showing bio-oil yield from L, C, and H and their mixtures.](chart.png)
Results

L more effective insecticide than C and H bio-oil

48 h LC$_{50}$ (95% C.I.) values for L, C and H bio-oil with 2nd instar Colorado potato beetle
Results

L, C and H bio-oil combination produced antagonistic effect (S= 1.36)

48 h LC$_{50}$ (95% C.I.) values for L, C, H, mixture of bio-oil and mixture of biomass with 2nd instar Colorado potato beetle
Results
Combination of C and H bio-oil produced synergistic effect ($S = 0.82$)

48 h $LC_{50}$ (95% C.I.) values for C, H and Coil + Hoil with 2nd instar Colorado potato beetle
Results
No interaction between L bio-oil fractions (additive toxicity, $S = 0.98 \approx 1$)

$48 \text{ h } \text{LC}_50$ (95% C.I.) values for L, Lc-aq, Lc-tar, and Lesp with 2nd instar Colorado potato beetle
Conclusion

• To maximize the insecticidal activity:
  (1) Separate lignin fraction and pyrolyze it
  (2) Use only the lignin ESP bio-oil fraction

• Further research is recommended to investigate the toxicity of the *mixture of bio-oils* in which the L content is higher than the other two principal components
Future Projects

Separation and identification of active lignin ESP bio-oil components

HPLC chromatograph for lignin bio-oil sample

<table>
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<th>2</th>
<th>20</th>
<th>25</th>
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<th>31</th>
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</thead>
<tbody>
<tr>
<td>Water</td>
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<td>25</td>
<td>0</td>
<td>0</td>
<td>90</td>
<td>90</td>
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<tr>
<td>Acetonitrile</td>
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<td>25</td>
<td>75</td>
<td>100</td>
<td>100</td>
<td>10</td>
<td>10</td>
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