Bio-Insecticidies from Thermochemical Biomass Conversion

March 10\textsuperscript{th}, 2021
Performance Advantaged BioProducts
Nolan Wilson
National Renewable Energy Lab
Goal: Create a sustainable, inexpensive bioinsecticide that leverages the inherent chemical functionality from thermochemical biomass conversion that can improve biofuel economics.

Objective: Identify and characterize at least one active ingredient for formulation & field trials.

Today’s Technology
Linear-supply-chain, synthetic insecticides are the incumbent product, but under growing public and regulatory scrutiny.

Importance
Agriculture production must expand 25-70% to feed of 9.7 billion people by 2050. Transportation must reduce carbon emissions by 20 – 45% to meet GHG 430 – 530 ppm CO$_2$eq

Risks
• Low insecticidal activity
• Inability to separations & characterization
• High toxicity or negative environmental impact
• High production costs
• CFP commercial maturity

Image Credit: Dennis Schroeder
Bioinsecticide Production using Catalytic Fast Pyrolysis (CFP). SOT 2019
1. CFP converts biomass into bio-oil.
2. Bioinsecticide is isolated from bio-oil.
3. Remaining bio-oil is further processed to biofuels.

Differentiators & Benefits
• Scalable & simple separations to a high-value mixed product
• Bioinsecticide can create market pull for CFP processes
NREL’s Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

**Value Proposition**
A high-value product that can support low-cost biofuels through catalytic fast pyrolysis

**Conventional Pesticide Market Trends**
- EPA delisting
- Evolved resistant (>500 species)
- Rising development costs and timelines ($250 million, 10 yrs)\(^1\)

**Bioinsecticide Market Trends**
- Low development costs & timelines ($10 million, 3 yrs)\(^1\)
- Significant market growth CAGR 8%

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1. Management

General Management Approach
Multi-institutional, multi-disciplinary team has expertise across range of technical areas for highest probability of success.

Co-funded by:
U.S. DEPARTMENT OF
ENERGY
USDA

Bioinsecticide development & commercialization
Economically viable tactics for pest management in field crop products
Integrated pest management for stored product insects
Coproduts and separations from catalytic fast pyrolysis streams

Bioinsecticides
(Tasks)

(1) Production & Characterization
NREL

(2) Field Crop Applications
MSU, Marrone

(3) Stored Product Applications
USDA

(4) Regulatory & Market Analysis
Marrone, NREL

Scientific Community
Publications, Conferences
Industry & Regulators
(Biorefiners, EPA-BPPD)
Solicted Feedback
Interviews, Proposals

DOE-BETO
Quarterly Meetings
Regular Reporting
CUPP (2.3.1.314)
Analysis (2.1.0.302)
Analytical (2.5.2.301)
Regular Meetings
Data Sharing
Project Planning

Separations & Characterization: Task 1
Insecticidal Activity: Tasks 2,3
Toxicity & Environmental Impact: Task 4
Process Economics: Task 4
1. Management

Addressing Project Management Risks
• Barrier-free transfer of materials
• Team meetings for coordination of efforts

Addressing Technical Risks
Tasks structured so each risk is addressed by a task and appropriate team members were responsible for task execution

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(1)

(2)

Production & Characterization
NREL

Field Crop
Applications
MSU, Marrone

(3)

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Regulatory & Market Analysis
Marrone, NREL

Stored Product
Applications
USDA

Separations & Characterization: Task 1
Insecticidal Activity: Tasks 2,3
Toxicity & Environmental Impact: Task 4
Process Economics: Task 4
1. Management

DOE-BETO Related Projects: Leveraged analytical methods from analysis project to close mass balance. **Related Risk: Inability to Characterize**

Regulators: Met with Biopesticides and Pollution Prevention Division (EPA-BPPD) to understand existing toxicological resources. **Related Risk: High toxicity or negative environmental impact**

Industry: Joint meeting with Ensyn (commercial bio-oil manufacturer) and Marrone to develop potential commercialization strategy and process. **Related Risk: CFP commercial maturity**
2. Approach

**Goal:** Create a sustainable, inexpensive bioinsecticide that leverages the inherent chemical functionality from thermochemical biomass conversion that can improve biofuel economics.

**Objective:** Identify and characterize at least one active ingredient for formulation & field trials.

### 2 year project plan

<table>
<thead>
<tr>
<th>Approach to Achieving Goal &amp; Objective</th>
<th>Metric</th>
<th>Key Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improve activity to commercial relevancy</td>
<td>Increase LC$_{50}$ &gt; 10%</td>
<td>FY20Q4, FY21Q2-GNG</td>
</tr>
<tr>
<td>Minimize phytotoxicity</td>
<td>&lt;10% leaf damage</td>
<td>FY21Q4</td>
</tr>
<tr>
<td>Identify hazardous components</td>
<td>&gt;25 compounds assessed</td>
<td>FY21Q1</td>
</tr>
</tbody>
</table>
2. Approach

**Technical Risks**
- Low Insecticidal Activity
- Ineffective Separations and Characterization
- High toxicity & Environmental Impact
- High production costs

**Research Approach**
- Screen many candidate fractions & highly active ones
- Model compound assays to identify source of activity
- Screen oils and separation conditions based on processibility
- Use advanced analytical methods to characterize fractions
- Perform toxicity and environmental risk assessment and use separations to remove problematic compounds
- Use phytotoxicity and soil persistence assays to determine if bioinsecticide assays fall within acceptable ranges
- Use sensitivity analysis to identify cost drivers and guide process development
3. Impact

**Impact to Biorefining**
Create market pull for biofuels through high-demand (CAGR 8%) coproduct. High-value coproduct from molecules that are difficult to convert to fuels (phenols).

**Impact to Agricultural Sustainability**
CFP is low-cost process with flexible feedstock for bioinsecticide production. CFP can lower insecticide supply chain emissions by ≥46%.
Industrial Engagement & Commercialization

- Marrone & Ensyn are developing near-term commercialization pathway
- FP (near term) commercialization will enable CFP commercialization pathway
- Marrone holds an option to exclusively license the technology
4. Progress and Outcomes

Insecticidal Activity

Through screening and model compound studies we have increased activity by 41% from start of project

- Screened 14 fractions from 2 bio-oils
- 7 insect models, 2 application spaces, & 3 assay modalities
- Used model compounds to identify alkylated phenols and methoxyphenols as active components.

Plot shows improvement in LC\textsubscript{50}, lethal concentration to achieve 50% mortality (lower is better), over the course of the project. Our bioinsecticide is approaching performance of commercial bioinsecticides, such as DiPel ®.
Economics
Bioinsecticides could reduce biofuel cost by 0.20 $/GGE, and there is opportunity for profitability across supply chain

- Our modeled breakeven price of active ingredient: 1.7 $/kg.
- Most insecticides sell for > 6 $/kg. Median market price is 30 $/kg

Market
Need for increased sustainability in agricultural. ≥46 % reduction in GHG emissions and ≥ 60 % reduction in embodied energy.
4. Progress and Outcomes

Toxicity & Environmental Impact
Through a risk assessment we identify 0/50 compounds to be highly hazardous but found 8 compounds which raised some concern.

• Carcinogenicity & mutagenicity are areas of concern
• Ames mutagenicity assays proposed for further analysis
• Bee toxicity identified as major data gap
4. Progress and Outcomes

Separations and Characterization
This project has made significant advances in characterizing thermochemical streams by closing mass balance from 39% to >99% for distillate fractions.

- Identification of oil and conditions for isolation of active fraction
- Carbonyl, CHNO, DSC, and metals analysis of distillate bottoms used to determine viability of downstream fuels processing

Plots shows analytical mass balance closure has been achieved through the course of the project. Alkylated phenols and methoxyphenols have been identified as active components of candidate fractions.
Timeline
- Oct 1st 2019
- Sept. 30th 2021

<table>
<thead>
<tr>
<th>Funding</th>
<th>FY20</th>
<th>Active Project (FY20-FY21)</th>
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<tbody>
<tr>
<td>DOE</td>
<td>$364,000</td>
<td>$728,000</td>
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<tr>
<td>USDA</td>
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<td>$194,000</td>
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Project Partners*
- USDA ARS Kansas, Marrone Bio Innovations, Michigan State University

Barriers addressed
(Ct-J) Identification and Evaluation of Potential Bioproducts
(Ct-K) Developing Methods for Bioproduct Production

Project Goal
Create a sustainable and inexpensive source for pest management that leverages the inherent chemical functionality from thermochemical biomass conversion and can improve biofuel economics.

End of Project Milestone
Demonstrate a balance between activity and phototoxicity can be achieved. Identify at least one bioinsecticide which does not exhibit prohibitive phototoxicity (<10% non-viable leaf tissue), maintains insecticidal activity, and has known regulatory risks identified in Q1.

Funding Mechanism
Bioenergy Technologies Office FY20 AOP Lab Call (DE-LC-000L071) – 2020

*Only fill out if applicable.*
### Summary

<table>
<thead>
<tr>
<th>Product</th>
<th>Anticipated decrease in gasoline/ethanol demand; diesel demand steady</th>
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<tbody>
<tr>
<td></td>
<td>Increasing demand for aviation and marine fuel</td>
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<tr>
<td></td>
<td>Demand for higher-performance products</td>
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<td></td>
<td>Increasing demand for renewable/recyclable materials</td>
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<tr>
<td>Feedstock</td>
<td>Sustained low oil prices</td>
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<td></td>
<td>Decreasing cost of renewable electricity</td>
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<td></td>
<td>Sustainable waste management</td>
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<td>Expanding availability of green H₂</td>
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<td>Closing the carbon cycle</td>
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<td>Risk of greenfield investments</td>
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<tr>
<td>Capital</td>
<td>Challenges and costs of biorefinery start-up</td>
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<td></td>
<td>Availability of depreciated and underutilized capital equipment</td>
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<tr>
<td>Social Responsibility</td>
<td>Carbon intensity reduction</td>
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<td>Access to clean air and water</td>
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<td>Environmental equity</td>
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### NREL’s Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

#### Management
Linked risks to tasks and team members

#### Approach
Aligned milestones to objective of identifying one active ingredient by end of project

#### Impact
Improvement to biorefining economics and agricultural sustainability
Near- and long-term commercialization path

#### Progress and Outcomes

- 20 ¢ biofuel selling price reduction (per GGE)
- 41 % improvement in activity
- 99 % characterization of fraction
- 0 highly hazardous compounds
- 2 candidates in project pipeline
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DOE Technology Manager Trevor Smith (and Nichole Fitzgerald formerly)

NREL Team:
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USDA ARS Kansas:
Robert Morrison, Arthur Frank, Alexander Bruce

MSU Team:
Matthew Grieshop, Juan Huang, Jackie Albert, John Dorgan

Marrone Team:
Amit Vasavada, Cole Pearson

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Additional Slides
Responses to Previous Reviewers’ Comments

Project has not been previously presented in BETO Peer Review.
Publications, Patents, Presentations, Awards, and Commercialization

**Patents**

**Licenses**
Marrone holds an option to exclusively license the technology.

**Manuscripts (In Preparation)**

**Presentations**