



Bio-Insecticides from Thermochemical Biomass Conversion

March 10th, 2021 Performance Advantaged BioProducts Nolan Wilson National Renewable Energy Lab

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Project Overview

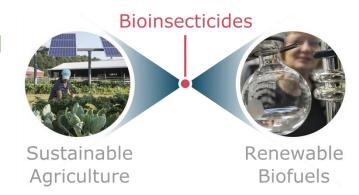
Goal: Create a sustainable, inexpensive
bioinsecticide that leverages the inherent chemical
functionality from thermochemical biomass
conversion that can improve biofuel economics.
Objective: Identify and characterize at least one
active ingredient for formulation & field trials.

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 CO₂eq

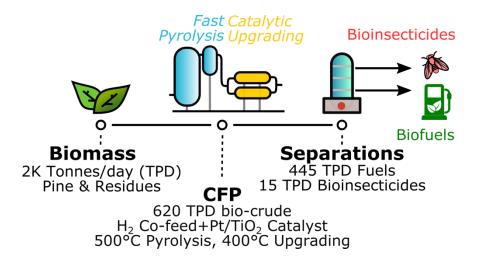


<u>Risks</u>

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

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

Market Trends



Gasoline/ethanol demand decreasing, diesel demand steady

Increasing demand for renewable/recyclable materials

Increasing demand for aviation and marine fuel

- Demand for higher-performance products
- A
 - Sustained low oil prices
- Feedstock
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H₂
- Closing the carbon cycle
- Risk of greenfield investments
- Line Challenges and costs of biorefinery start-up



Social Responsibility Availability of depreciated and underutilized capital equipment

Carbon intensity reduction

Access to clean air and water

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 lowcost 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%

¹ P. G. Marrone, *Pest Manag. Sci.* (2019)

1. Management

General Management Approach

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





arrone[•] Bioinsecticide development & commercialization



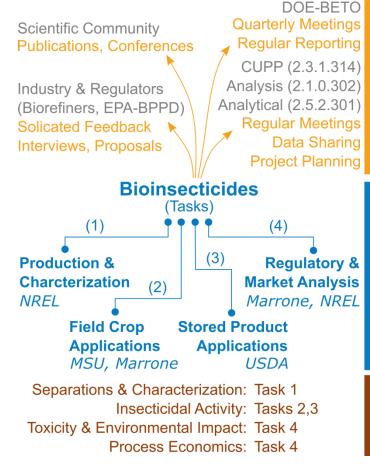
STATE SITY Economically viable tactics for pest management in field crop products



^{ral} Integrated pest management for stored product insects



Coproducts and separations from catalytic fast pyrolysis streams



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



Bioinsecticide development & commercialization



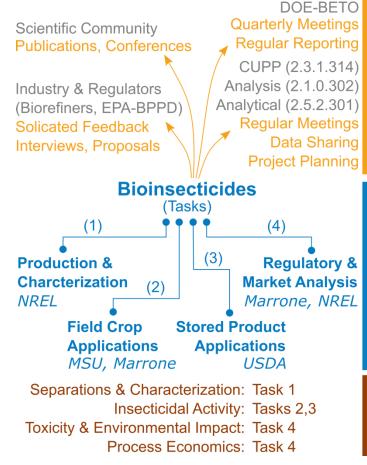
Economically viable tactics for pest management in field crop products



^{ral} Integrated pest management for stored product insects



Coproducts and separations from catalytic fast pyrolysis streams

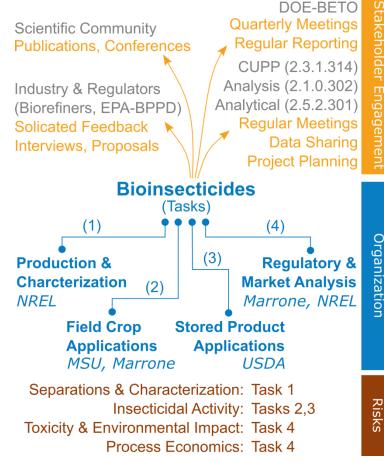


1. Management

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

Approach to Achieving Goal & Objective	Metric	Key Milestones
Improve activity to commercial relevancy	Increase LC ₅₀ > 10%	FY20Q4, FY21Q2-GNG
Minimize phytotoxicity	<10% leaf damage	FY21Q4
Identify hazardous components	>25 compounds assessed	FY21Q1

2. Approach

Technical Risks

Low Insecticidal Activity

Ineffective Separations and Characterization

High toxicity & Environmental Impact

High production costs

Research Approach

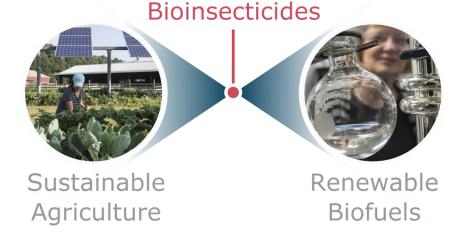
- Screen many candidate fractions & highly active ones
- Model compound assays to identify source of activity
- Screen oils and separation conditions based on processibility
- Use advanced analytical methods to characterize fractions
- Perform toxicity and environmental risk assessment and use separations 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

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

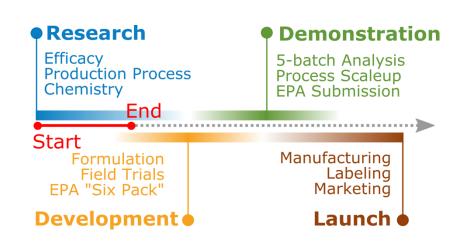
CFP is low-cost process with flexible feedstock for bioinsecticide production. CFP can lower insecticide supply chain emissions by ≥46%



3. Impact

Industrial Engagement & Commercialization

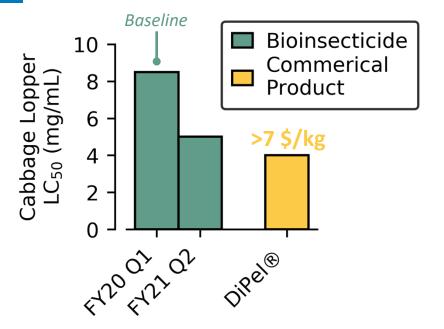
- Marrone & Ensyn are developing near-term commercialization pathway
- FP (near term) commercialization will enable CFP commercialization pathway
- Marrone holds an option to exclusively license the technology
- Pending International Patent Application (PCT). "Biomass-based pesticides and methods of making the same". (PCT/US20/66306)



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_{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 \mathbb{R} .

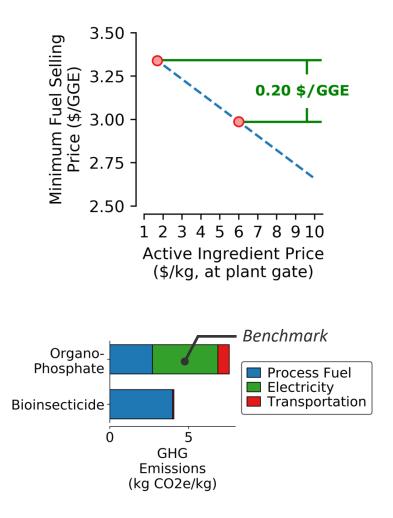
Economics

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.



Toxicity & Environmental Impact

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

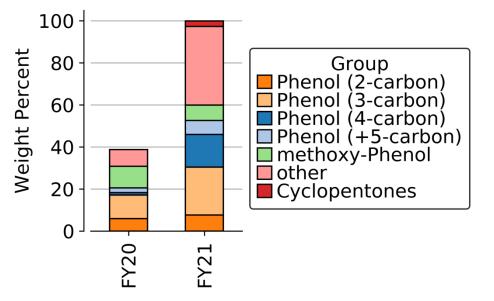
- Carcinogenicity & mutagenicity are areas of concern
- Ames mutagenicity assays proposed for further analysis
- Bee toxicity identified as major data gap



Image Credit: John De La Rosa

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.

Quad Chart Overview (for AOP Projects)

Timeline

- Oct 1st 2019
- Sept. 30th 2021

Funding	FY20	Active Project (FY20-FY21)
DOE	\$364,000	\$728,000
USDA	\$97,000	\$194,000

Project Partners*

- USDA ARS Kansas, Marrone Bio Innovations, Michigan State University
- **BETO Projects**: Catalytic Upgrading of Pyrolysis Products. Separations Consortium. Process Scaleup for Production Environments. Analytical Development and Standardization for Biomass-derived Thermochemical Liquids. Thermochemical Platform Analysis

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

Summary



Anticipated decrease in gasoline/ethanol demand; diesel demand steady

Increasing demand for aviation and marine fuel

Demand for higher-performance products



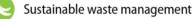
Increasing demand for renewable/recyclable materials



Sustained low oil prices



Decreasing cost of renewable electricity



Expanding availability of green H₂



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Closing the carbon cycle

Risk of greenfield investments

Challenges and costs of biorefinery start-up



Availability of depreciated and underutilized capital equipment

Carbon intensity reduction

Access to clean air and water

Environmental equity

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
 - candidates in project pipeline

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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.

Patents

Pending International (PCT) Patent Application (PCT/US20/66306)

Licenses

Marrone holds an option to exclusively license the technology.

Manuscripts (In Preparation)

- 1. Wilson et al. "Economics, Efficacy, and Sustainability of Bioinsecticides from Thermochemical Biorefineries". (2021)
- 2. Morrison et a. "A bio-oil Derived Insect Growth Regulator for a Variety of Stored Product Beetles". (2021)

Presentations

- 2. Montgomery, J.R., F.H. Arthur, A. Bruce, A.N. Wilson, and W.R. Morrison III. Characterizing composition and assessing byproducts from biofuel production as potential biorational insecticides to induce lethality in stored product insects. 68th Annual Meeting of the Entomological Society of America, Virtual.
- 3. Morrison, III W.R. Diversifying IPM programs for stored products. Upper Gulf Coast Grain Handlers Conference, Texas A&M University.
- 4. Grieshop, M.J., Huang J., Perkins, J., Fanning, P., Dorgan, J., Wilson, N. Evaluation of fast pyrolysis bio-oils as a potential source of novel biopesticides. Poster presented at: 2020 Entomological Society of America Virtual Annual Meeting. (November 11-25, 2020)
- Huang, J., Perkins J., Wilson N. and Grieshop, M.J., (December 8, 2020) Screening Biobased Chemicals for Their Insecticidal Activity against Spotted Wing Drosophila and Oriental Fruit Moth. Presented Virtual Poster at the 2020 Great Lakes Fruit and Vegetable Expo. Grand Rapids, MI