Developing a High Value Chemical Coproduct: Bio-base insecticides from Catalytic Fast Pyrolysis

A. Nolan Wilson*[1], Kylee Harris[1], Mark Nimlos[1], Matthew Grieshop[2]
[1]National Renewable Energy Lab, Golden, CO. [2]Michigan State University, East Lansing, MI.

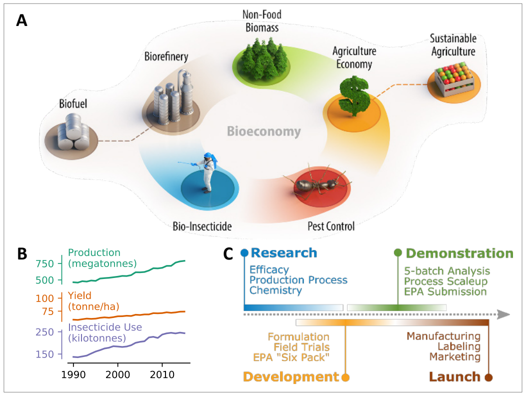

Figure 1: Bio-based insecticides can support a circular bio-economy through coproduction with biofuels.

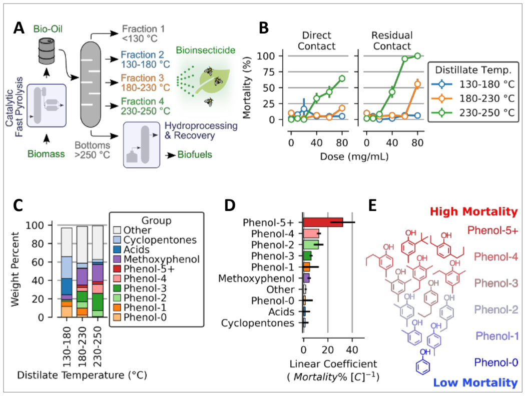

Figure 2: Both production and testing of bio-based insecticides were developed within this work.

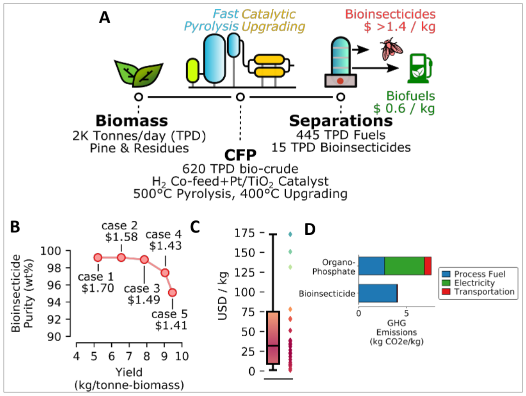

Figure 3: TEA and LCA demonstrate the potential for bio-based insecticides to reduce biofuel cost and reduce emissions.

Overview

Coproduction of biochemicals from the thermochemical conversion of biomass is a strategy to reduce biofuel costs and improve bio-oil quality in an integrated biorefinery.

(Challenge) Cost effective separations of coproducts from thermochemical conversion streams remains a challenge largely due to the heterogenous nature and stability of thermochemical conversion streams. **(Solution)** Bio-based insecticides isolated from catalytic fast pyrolysis (CFP) oils are a viable coproduct that can overcome the oil is more stable, they are a high value product, and they can remain a mixture of components. **(Approach)** This work focuses on the development of a bio-based insecticide coproduct that is distilled from a catalytic fast pyrolysis bio-oil produced using a platinum on titanium dioxide (Pt/TiO$_2$) catalyst to upgrade pyrolysis vapors.

Impact

Bioeconomy. Production of bio-based insecticides from the thermochemical conversion of biomass is a synergistic strategy that can impact both the transport and agriculture sectors, **Figure 1A**.The transport sector must reduce GHG emissions by 20 – 45% from 2010 levels by 2050 to meet targeted CO$_2$ levels. At the same time, agriculture production must increase by 25 – 70% from 2005 levels to meet food security for a projected 9.7 billion people in 2050.

Commercialization. Agricultural production, yield per unit of land, and insecticide use, **Figure 1B** (green, orange, and purple respectively), continue to increase with population growth, which creates a market pull for new, more sustainable pest management solutions. The commercialization of bio-based insecticides, **Figure 1C,** requires significant investments. This work has served to identify and mitigate risks along the pathway to market.

Process and Product

This work developed the process to separate bio-based insecticides from CFP oils and demonstrate the fractions had insecticidal activity dependent on composition.

Key Findings

- Due to increased stability of the CFP oil, the residual CFP oil after vacuum distillation remained viscous fluid, which indicated undesired coking reactions were sufficiently limited so the residual material could potentially be further processed into bio-fuels.
- The highest mortality was found for distillation fractions that were enriched in substituted phenols.
- Correlating composition with mortality showed increasing phenol alkylation correlated with increased activity.

Conversion and Separation Process. Woody biomass was pyrolyzed, and the subsequent vapors were upgraded over a fix bed of Pt/TiO$_2$ catalysts. The resulting bio-oil was distillated into fractions using a bench scale spinning band distillation column operated at 30 torr, **Figure 2A**.

Insecticidal Assays. Dose response curves using spotted winged drosophila, a relevant field-crop pest, for 3 of the fractions were developed to identify the most active fractions, **Figure 2B**. This was performed using both direct contact and residual exposure assays to measure the activity under different modes.

Compositional Analysis. Using GCxGCMS-FID coupled with a polyarc, compositional analysis of fractions was able to achieve > 99% analytical mass balance closure, **Figure 2C**. Multivariate linear coefficients were calculated by correlating activity with composition and show that increasing alkylation increases activity, **Figure 2D & E**. This can be used to further direct separations and co-optimize the process for biofuel and coproduct production.

Technoeconomics and Life Cycle Assessment

This work demonstrates the viability of using fractions from catalytic fast pyrolysis streams as bioinsecticides to reduce biofuel production costs and provide a chemical product that can positively impact agricultural sustainability.

Key Findings

- Technoeconomic modeling shows the bioinsecticide can be produce at a cost ≤ 1.7 $/kg. Fully formulated bioinsecticides typically sell for ≥ 6 $/kg.
- Bioinsecticides could reduce biofuel cost by 0.20 $/GGE, and there is opportunity for profitability across supply chai
- Supply chain analysis demonstrated the bioinsecticide can achieve a 46 – 88% reduction in green house gas emissions relative to petroleum incumbents.

Technoeconomic Analysis (TEA). TEA was used to determine the minimum product selling price (MPSP) for the bio-based insecticide fraction based on an existing process model and using a mass allocation approach, **Figure 3A**. The analysis showed the MPSP and product purity was a function of product yield from the separations, **Figure 3B**.

Bio-based Insecticide Market. Finished bioinsecticides formations can range from 6 – >100 $/kg with a median market price of 30 $/kg. The market is rapidly growing (8% CAGR) due to pressures from regulatory, customer, and evolved resistance for conventional insecticides.

Life Cycle Assessment (LCA). LCA used the material's through industry tool and showed both GHG, **Figure 3D**, and embodied energy can be significantly reduced relative to conventional insecticides.

References

1. Wilson, A. N. et al. Efficacy, economics, and sustainability of bio-based insecticides from thermochemical biorefineries. Green Chem. 23, 10145–10156 (2021).
2. Griffin, M. B. et al. Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration. Energy Environ. Sci. 11, 2904–2918 (2018).

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