U.S., Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

# Building Blocks from Biocrude: High Value Methoxyphenols

(WBS 2.5.5.406)

March 9, 2017

Thermochemical Conversion


Ofei D. Mante, PI

RTI International


This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Goal Statement

**Goal**: Develop and optimize a hybrid separation method to recover high-value methoxyphenols(MPs) to improve the process economics and environmental impact for the production of advanced biofuels from catalytic pyrolysis integrated with hydroprocessing.

| Separation Optimization | Product Development | Upgrading | Techno-economic and Life cycle Analysis |
|---|---|---|---|
| ➢ Develop a separation strategy to efficiently & economically recover MPs with >90% purity. | ➢ Perform market and business opportunity assessment for MPs.<br>➢ Establish market price for mixed MPs and co-products | ➢ Evaluate the impact of removing MPs from biocrude in the hydro-processing step. | ➢ Demonstrate reduction in cost of biofuel production (< $3/gge)<br>➢ Demonstrate 50% GHG emissions reduction for the integrated process compared to petroleum. |

- Expanding the biofuels value chain to secure paths to existing and new markets reduces economic risks.
- Provides the U.S chemical industry with a straightforward technology for the production of methoxyphenols as chemical building blocks from biomass.

# Quad Chart Overview

## Timeline

Project start date: 10/01/2016

- BP1: 10/01/2016 to 12/31/2016
- BP2: 01/01/2017 to 09/30/2017
- BP3: 10/01/2017 to 09/30/2019

Project end date: 09/30/2019

- ~8% completed

## Barriers

- Ct-G. Efficient Intermediate Cleanup and Conditioning.
- Ct-H. Efficient Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals.
- Ct-I. Product Finishing Acceptability and Performance

## Partners

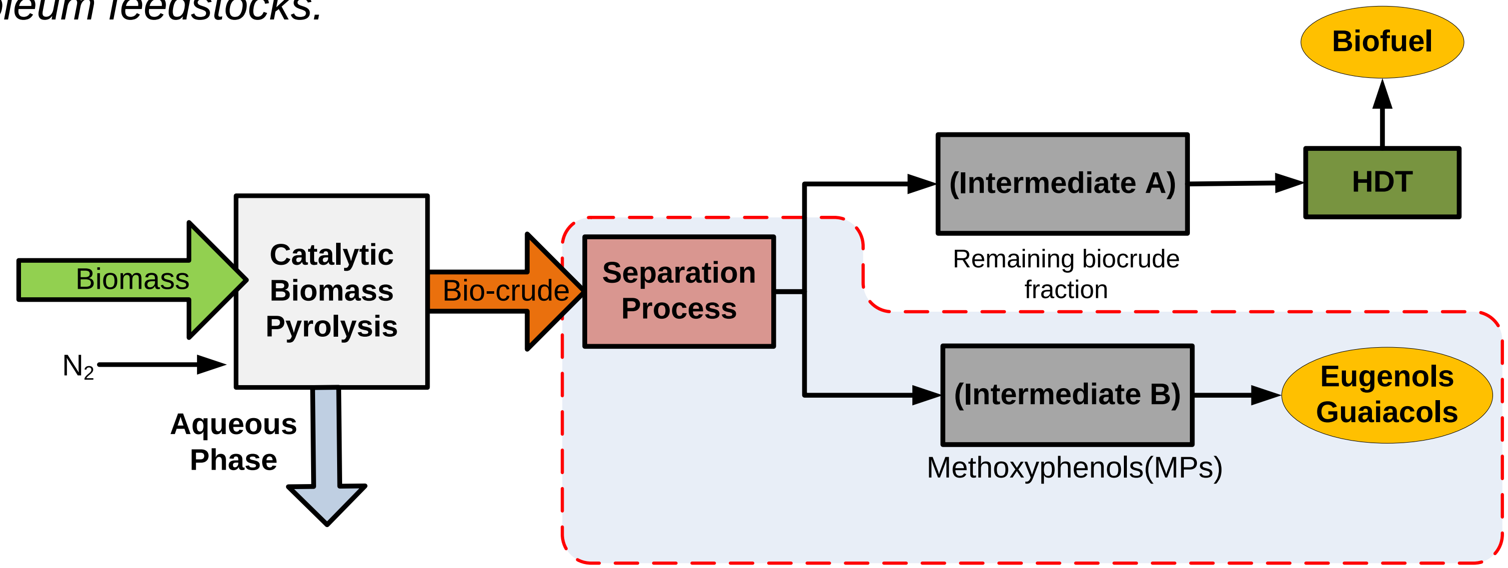
- RTI – Project Lead, Separation Technology Development, Hydroprocessing, Project Management
- Arkema- Market Feasibility and Co-product Development
- AECOM- Techno-economic and Life Cycle Analyses

| | Total Costs FY 12 –FY 16 | Total Planned Funding (FY 17-Project End Date) |
|---|---|---|
| **DOE Funded** | 0 | $1,987,148 |
| **Project Cost Share** | 0 | $220,794 |
| **Arkema** | 0 | $80,000 |
| **State of NC** | 0 | $140,794 |

# 1- Project Overview

**History**: *RTI CFP Technology produces partially deoxygenated, thermally stable biocrude that contains useful methoxyphenols (MPs) such as eugenol, isoeugenol, dihydroeugenol, and guaiacols (methyl-, and ethyl-).*

**Context**: *Inherent functionalized nature of biomass offers unique opportunity for the production of bio-based oxygen-containing chemicals that are not easily synthesized from petroleum feedstocks.*




- ➢ Evaluate commercial viability of mixed phenolic fraction as a feedstock for value-added bioproducts. Establish price point for MPs based on current markets ($3-$5/kg).
- ➢ Investigate key separations and chemistries to expand recovered intermediates into multiple markets.
- ➢ Define technical requirements for product quality and purity.
- ➢ Demonstrate that remaining biocrude fractions can be upgraded into biofuels.

# 2 – Management Approach

**Approach:** *Detailed project plan with quarterly milestones and deliverables; validations; annual Go/NoGo decision points; and monthly project meetings.*

**Budget Period 1(BP1)**
**Task 1.0**: Initial Validation of Project (**RTI**)

**BP1 Go/No Go Decision Point**: The criteria for success will be:

- Demonstration of biocrude production from loblolly pine in 1 TPD catalytic biomass pyrolysis unit
- Use laboratory PiloDist Unit for bio-crude distillation (ASTM 1160) into four (4) fractions with residue formation < 25wt%.
- At least 75% recovery of the initial concentration of MPs in the biocrude by fractional distillation in 2 steps.

**Budget Period 2 (BP2)**
**Task 2.0**: Development of a Separation Strategy to Recover MPs (**RTI**)

**Task 3.0:** Market Assessment and Initial Techno-Economic and Life-cycle Analyses **(Arkema & AECOM)**

**Intermediate Validation of Project (RTI, Arkema, AECOM)**

**BP2 Go/No Go Decision Point: The criteria for success will be:**
- TEA shows that recovery of MPs reduces the cost of biofuel production by 30%.
- LCA shows that biocrude derived MPs have lower GHG emission compared to fossil-derived pathways.

# 2 – Management Approach

**Approach:** *Detailed project plan with quarterly milestones and deliverables; validations; annual Go/NoGo decision points; and monthly project meetings*

**Budget Period 3 (BP3)**
**Task 4.0:** Laboratory Separations for Co-product Recovery **(RTI)**
**Task 5.0:** Market Feasibility of Co-Product Pathways (**Arkema**)
**Task 6.0:** Evaluation of one Product Pathway (**RTI & Arkema**)
**Task 7.0:** Techno-Economic Analysis and Life Cycle Assessment (**AECOM**)
**Task 8.0:** Project Management and Reporting (**RTI**)
**Final Validation of Project.**

**Key Milestones and Deliverables**

| | |
|---|---|
| FY17 | • Achieve ≥ 85 separation efficiency for mixed MPs with >90% purity.<br>• Complete market and business opportunity assessment of mixed MPs |
| FY18 | • TEA, and LCA demonstrating \$3/gge and a minimum of 50% GHG emissions reduction.<br>• Complete design, fabrication, installation, and commissioning of laboratory scale separation system. |
| FY19 | • Achieve at least 90% of the recovery efficiency of the small scale separation at the laboratory scale.<br>• Complete product development assessment (PDA).<br>• TEA and LCA demonstrating < \$3/gge and > 50% GHG emissions |

# 2 - Technical Approach – Recovery of MPs

PILODIST
ASTM D1160


*Enhanced thermal stability of biocrude makes it technically feasible to optimize solvent extraction and distillation methods to concentrate and purify methoxyphenols (MPs).The two techniques will be examined individually and then as a hybrid.*

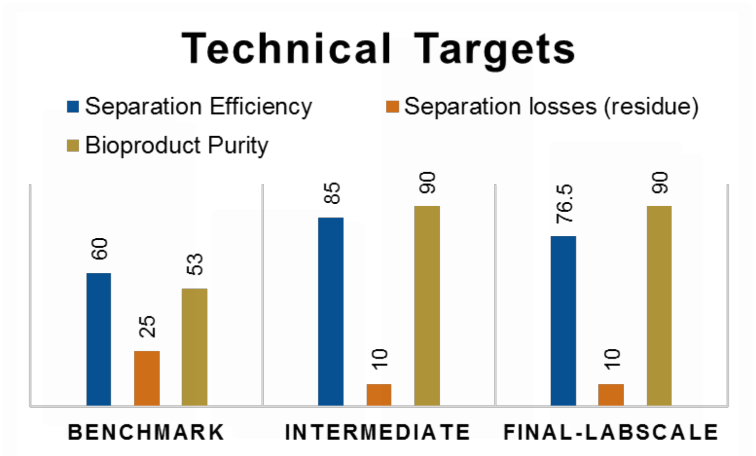
## Approach:

- Identify the efficient technique for concentration and purification of MPs at the bench-scale.
- Develop a hybrid separation strategy by integrating the two techniques to maximize separation efficiency (≥ 85wt%) and product purity (≥ 90%) at the bench-scale.
- Design and build a lab-scale separation system.
- Produce 60 gallons of biocrude for separation and upgrading studies.
- Operate and optimize lab-scale separation unit to achieve 90% of the separation efficiency at the bench-scale and produce MPs bioproduct with ≥ 90% purity.

**Challenges**: biocrude complexity, separation efficiency, final product purity, residue formation, energy demand, and solvent recovery and re-use

## Critical Technical Goals

- Development and demonstration of efficient and cost competitive separation strategy to obtain MPs products with ≥ 90% purity.
- Identification of key biocrude components that negatively impact the separation.



# 2-Technical Approach- Product Development & Hydrotreating

## Approach: Product Development Assessment

- Conduct market analysis to determine the potential value for mixed MPs as well as technical and nontechnical barriers to entry.
- Identify three key chemistries to develop co-product pathways to expand MPs into other market (e.g., vanillin, polymers)

**Challenges**: Value of mixture of MPs; targeted co-product may require single chemical reactants.

**Existing MPs market Price**

| Methoxyphenol product | Average Price ($/kg) |
|---|---|
| Eugenol | 3.4 – 4.5 [1,2] |
| Eugenol (Clove oil) | 15 – 86 [3,4] |
| Vanillin (synthetic) | 12 – 15 [5] |
| Vanillin (lignin) | 100-200 [5] |

## Approach: Hydrotreating of Fractionated Biocrude

- Perform hydrotreating studies on the fractionated biocrude to evaluate the impact of removing MPs on performance metrics (process stability, hydrogen demand, and product yields/quality)

**Challenges**: Reactor plugging, catalyst deactivation, and hydrogen demand.

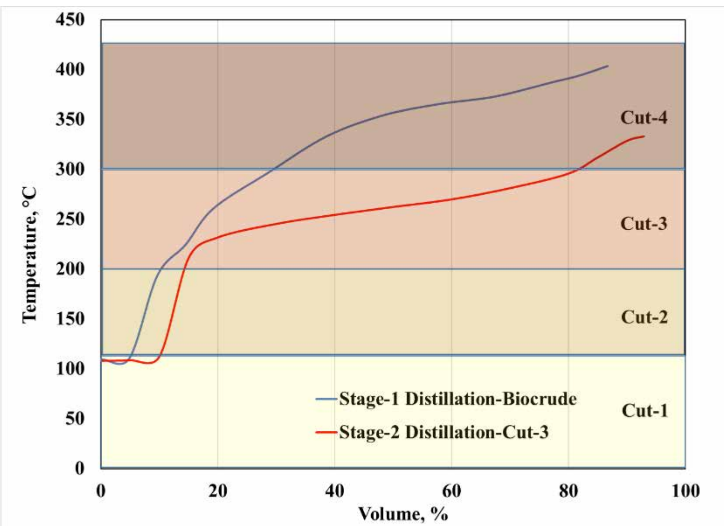
## Critical Technical Goals

- Development of a high-value product pathway using MPs as a chemical feedstock.
- TEA and LCA demonstrating the positive economic impact and environmental benefit of recovering MPs from biocrude.

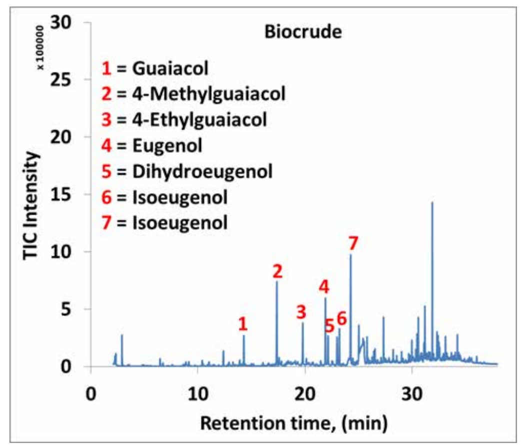
**[1].** A. V. Bridgwater, *Identification and market analysis of most promising added-value products to be co-produced with the fuels*, 2010. **[2].**P. Varanasi, P. Singh, M. Auer, P. D. Adams, B. A. Simmons and S. Singh, *Biotechnology for Biofuels*, 2013, 6, 1-9. ; **[3].**C. G. Pereira, J. M. Prado and M. A. A. Meireles, in *Natural Product Extraction: Principles and Applications*, The Royal Society of Chemistry, 2013, DOI: 10.1039/9781849737579-00442, pp. 442-471; **[4]** .International Trade Centre, *US Imports of Essential Oils, 2009 to 2013–Part One*, 2014.; **[5]** Wong, J. T. (2012). Technological, Commercial, Organizational, and Social Uncertainties of a Novel Process for Vanillin Production from Lignin, Simon Fraser University.

# 3 – Technical Accomplishments/Progress/Results

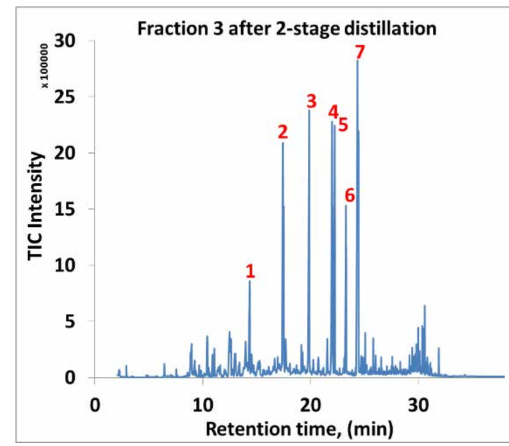
- **Initial validation of proposed concept has been completed and Go/No-Go decision milestones were met.**
- The criteria for success:
  - Use laboratory PiloDist Unit for biocrude distillation into four (4) fractions with residue formation < 25wt%.
  - At least 75% recovery of the initial concentration of MPs in the biocrude by fractional distillation in 2 steps



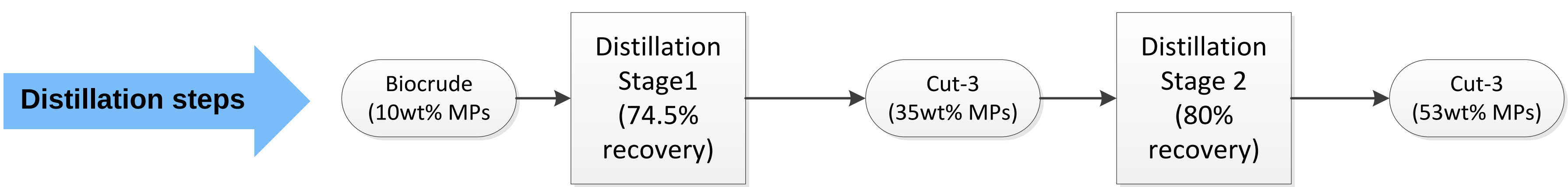

Distillation curves for biocrude oil and cut-3




GC-MS Chromatogram showing MPs in biocrude




GC-MS Chromatogram showing MPs in cut-3 fraction after 2-stage distillation



# 4 - Relevance

MEGA-BIO FOA (DE-FOA-0001433) Objective: To develop biomass to hydrocarbon biofuels conversion pathways that can produce variable amounts of fuels and bioproducts based on external factors such as market demand. More specifically, the FOA's aim is to examine strategies that capitalizes on revenue from bioproducts as part of cost-competitive biofuel production.

This project supports the strategic goal of Conversion R&D to develop commercially viable technologies for converting feedstocks into energy-dense, fungible, finished liquid transportation fuels and bioproducts or chemical intermediates.

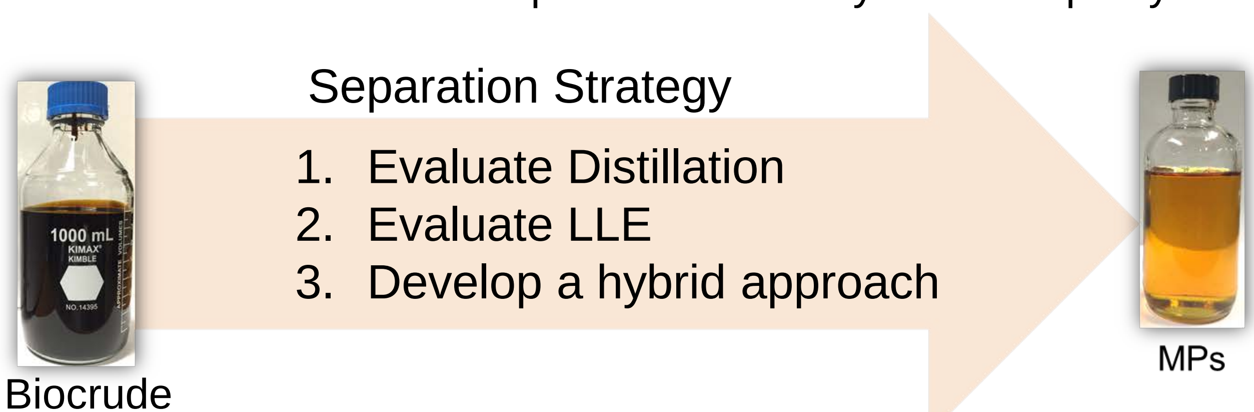
- Supports the development of efficient and low-cost separation and purification techniques critical to the manufacturing of bio-based chemicals and biofuels from biocrude.
- Provides alternative to the state-of-the-art oxygen removal strategies and enables understanding of the impact of bio-oil chemical composition on hydrotreating with respect to catalyst stability, hydrogen demand, and product quality.
- Enables reactive chemistries to be explored to expand the mixture of MPs into bioproducts that efficiently integrate into current markets.

***Achieving technical success in recovering high-value MPs from direct biomass catalytic pyrolysis products prior to upgrading to biofuels could provide a significant source of revenue to improve overall process economics and help meet the mission of EERE's Bioenergy Technologies Office (BETO) of $3/gge for the production of renewable hydrocarbon fuels from lignocellulosic biomass by 2022.***

# 5 - Future Work : Separations for MPs Recovery

**Bench-scale separations**

- Evaluate distillation for the recovery of MPs from biocrude.
  - Determine optimum process conditions.
  - Identify the minimum number of stages.
  - Determine separation efficiency and energy requirement.
  - Detailed characterization of biocrude, fractions, and residues to ascertain the impact of biocrude composition.
- Evaluate liquid-liquid extraction for the recovery of MPs from biocrude.
  - Determine appropriate solvents (e.g., switchable solvents and alkali solution).
  - Evaluate solvent recovery and re-use as well as energy requirements.
  - Detailed characterization of biocrude, fractions, and residues to ascertain the impact of biocrude composition.
- Develop a hybrid separation strategy
  - Based on the identification of the efficient approach for concentration and for purification; a separation strategy will be developed to maximize the benefits of LLE and distillation to achieve 85% separation efficiency and MPs purity of at least 90%.



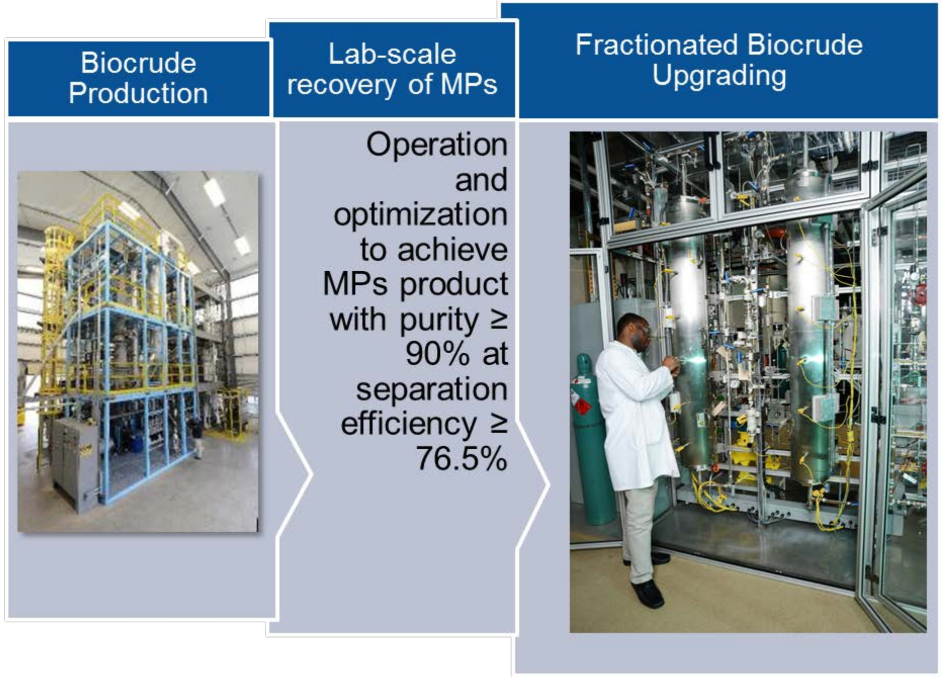
# 5 - Future Work : Separations for MPs Recovery

**Laboratory-scale distillation**

- Design, fabricate, and commission a lab-scale separation system based on the developed hybrid strategy.
- Produce a minimum of 60 gallons of loblolly pine biocrude for separation.
- Operate and optimize process conditions for the lab-scale system to achieve 76.5% separation efficiency and at least 90% purity.

**Upgrade the remaining bio-crude fraction**

- Perform upgrading studies on the remaining fraction of biocrude after MPs removal.
- Compare the hydrotreating studies to evaluate the impact of MPs removal on performance (hydrogen demand, process stability, product quality).



# 5 – Future Work - Product Development Assessment

## Business Opportunity for MPs

- Market assessment: characteristics, size, demand, and cost
- Traditional and emerging business opportunities.
- Value chain analysis to identify markets
- Technical and nontechnical barriers to entry

## Feasibility of Co-Product Development

- Opportunities for the MPs and derivatives as building blocks.
- Identification of three co-product pathways.
- Identify technical requirements: quality, purity, properties, performance, and market entrance challenges.
- Evaluate one of the identified pathway(s) to expand the MPs into higher margin markets.
- Develop a commercialization strategy.

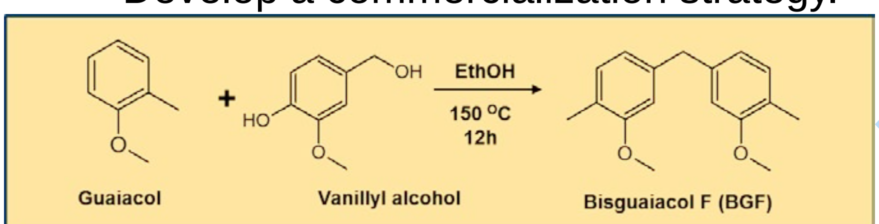

Leveraging Arkema's Biorefinery Options

Single source of raw materials

- Castor Oil-based plants/Pine Wood-based plants
- Multiple Products linked by the stoichiometry of chemical reactions
- Optimize best value for all co-products
- Simultaneous growth of several markets to satisfy all coproducts

Multiple sourcing of starting materials

- Epoxidized oils plant/Fatty Nitriles & Amines plant
- Multiple biomass inputs possible
- Flexibility
- Several markets for products can grow independently
- Opportunities for new products with new raw materials




*Example of potential chemistries that could be considered to expand the MPs into other building blocks.*

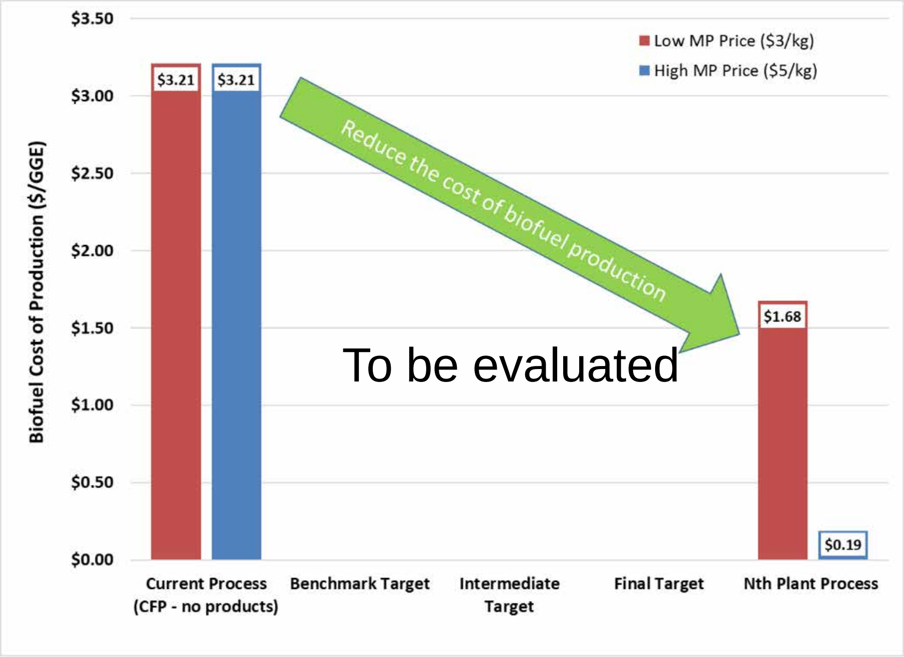
# 5 - Future Work-Techno-economic and Life Cycle Analyses

**TEA and LCA**

- Perform process modeling and preliminary economic assessment based on the intermediate key performance parameters(kpp) for the bench-scale separation.
  - Preliminary heat and material balance for the separation step.
  - Update capital and operating cost
  - Revise the cost of fuel production
- Evaluate the initial greenhouse gas (GHG) emissions reduction potential of the integrated biofuel and bioproduct process.
  - Overall material and energy flows
  - GHG emissions
  - Other impacts (e.g., water consumption)

- Finalize TEA and LCA for the integrated process based on the final kpp data obtained from the lab-scale hybrid separation system and the upgrading step.

- Model an Nth Plant Process considering 20% MPs in biocrude; recovery efficiency of 85%; 10% residual losses; and the remaining 70% of the initial biocrude is upgraded to biofuel.



# Summary

- **Approach**
  - Develop a hybrid separation approach tailored to the physicochemical properties of biocrude to maximize the benefits of distillation and LLE to achieve 90% purity of recovered MPs.
  - Perform market and business opportunity assessment for mixed MPs.
  - Develop co-product pathways focusing on exploiting the functionality of the recovered MPs.
  - Evaluate the economic and sustainability impact.
- **Technical Accomplishments/Progress/Results**
  - Initial validation task completed and Go/No-Go decision milestones met.
- **Relevance**
  - Supports BETO's Conversion R&D Objectives in 2016 MYPP.
  - Concept increases the economic and environmental impact for the production of advanced biofuels.
- **Future Work**
  - Development of a Separation Strategy to Recover MPs at the bench-scale.
  - Market Assessment of MPs and Product Development Analysis.
  - Laboratory Separations for Co-product Recovery and Upgrading for biofuels.
  - Complete TEA and LCA for the integrated biorefinery for biofuel and bioproduct.

# Acknowldegments


**BETO Project Officer: Liz Moore**

**RTI Contributors**

- Ofei D. Mante (PI)
- David C. Dayton
- Mustapha Soukri
- Kaige Wang
- Kelly Amato
- David Barbee
- Jonathan Peters

**Arkema**

- Jean-Luc Dubois

**AECOM**

- Pamela Spath

# Additional Slides

# Responses to Previous Reviewer's Comments

New Project – Started in FY17

# Publications, Patents, Presentations, Awards & Comm

## Publications

- Mante, O. D.; Dayton, D. C.; Soukri, M., Production and distillative recovery of valuable lignin-derived products from biocrude. RSC Advances 2016, 6 (96), 94247-94255.

## Presentation

- O.D. Mante, “Lignin-Derived Products from Biocrude as Building Block Chemicals” Oral Presentation, 2016 AIChE Annual Meeting, November 13-18, 2016San Francisco, CA.