# DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

# Building Blocks from Biocrude: High Value Methoxyphenols

(WBS 2.5.5.406)

March 5, 2019

Advanced Development & Optimization (ADO)

Ofei D. Mante, PI

RTI International

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

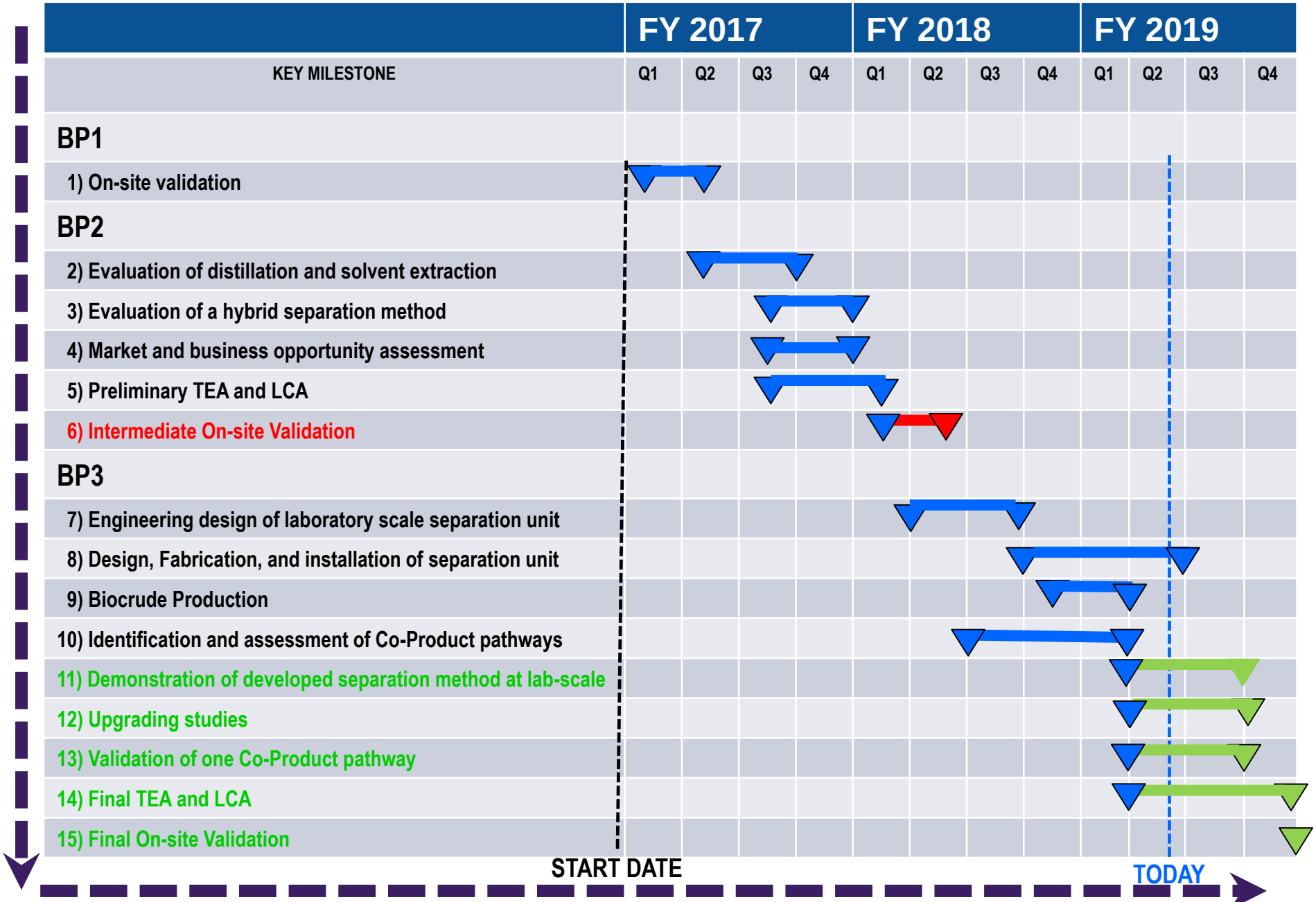
# Goal Statement

**Goal**: Develop and optimize a separation strategy to recover high-value bioproducts to improve the process economics and environmental impact for the production of advanced biofuels from catalytic pyrolysis integrated with hydroprocessing.


**Outcome**:

- Experimental data, Market Analysis, TEA, and LCA for recovery of methoxyphenols as bioproducts alongside biofuel production.
- Reduce economic risks by expanding biofuels value chain to existing and new bioproduct markets.
- Provide the U.S chemical industry with scalable technology for producing an alternative biobased building blocks useful in making ingredients for applications like flavor & fragrance(f&f), pharmaceutical, natural essential oils, and specialty polymers.

# Key Milestones



# Project Budget Table

| | Original Project Cost (Estimated) | | Project Spending and Balance | | Final Project Costs |
|---|---|---|---|---|---|
| **Budget Periods** | **DOE Funding** | **Project Team Cost Shared Funding** | **Spending to Date** | **Remaining Balance** | **What funding is needed to complete the project.** |
| **BP1** | $190,019 | $21,113 | $192,997 | $0 | |
| Task 1- On-site Validation | $190,019 | $21,113 | $192,997 | $0 | |
| **BP2** | $460,308 | $49,130 | $521,763 | $0 | |
| Task 2- Separation Development | $268,839 | $20,867 | $318,103 | $0 | |
| Task 3 -Market Assessment and Initial TEA & LCA | $117,092 | $20,000 | $139,119 | $0 | |
| Task 8 - Project Management | $74,376 | $8,264 | $64,541 | $0 | |
| **BP3** | $1,336,821 | $150,551 | $665,856 | $821,515 | |
| Task 4 - Laboratory Separations | $519,703 | $45,523 | $461,724 | $103.502 | |
| Task 5 - Market Feasibility | $126,686 | $30,000 | $116,382 | $40,304 | |
| Task 6 – Co-Product Validation | $255,550 | $30,000 | $0 | $285,550 | |
| Task 7 - Final TEA & LCA | $277,289 | $27,517 | $30,783 | $274,023 | |
| Task 8 - Project Management | $157,593 | $17,510 | $56,967 | $118,136 | |

# 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

- ~60% 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

## Budget

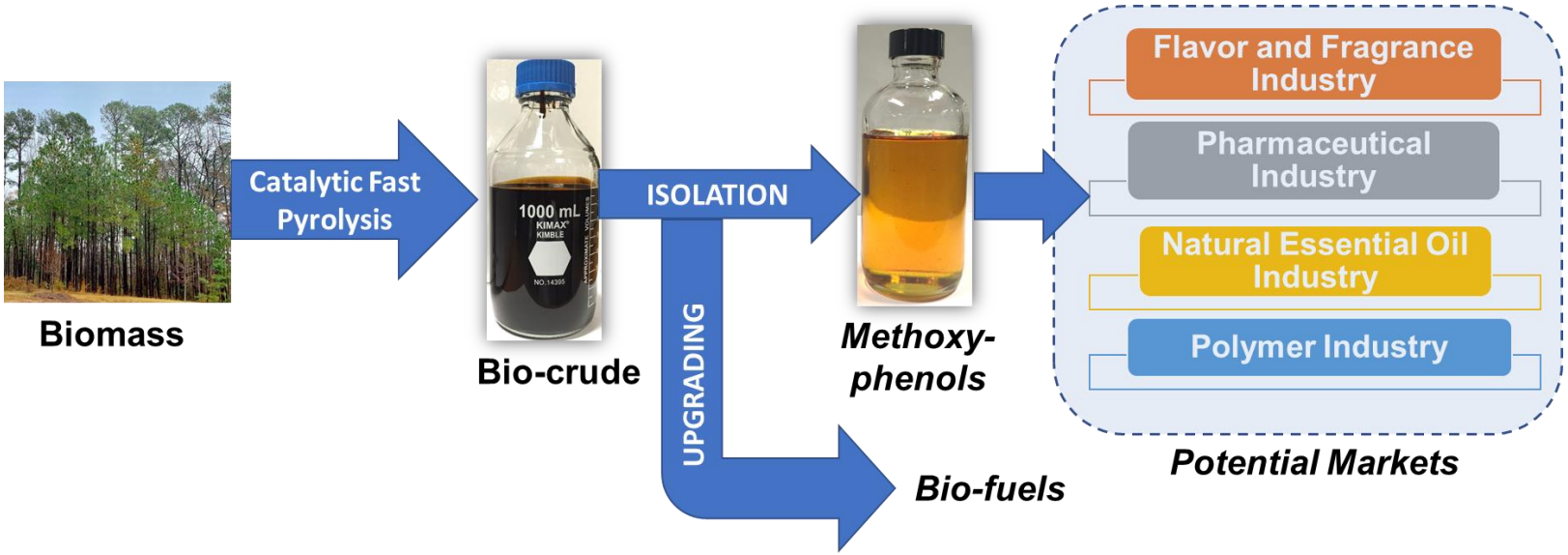
| | Total Costs Pre FY17 | FY 17 Costs | FY 18 Costs | Total Planned Funding (FY 19-Project End Date |
|---|---|---|---|---|
| **DOE Funded** | $0 | $556,420 | $462,807 | $967,921 |
| **Project Cost Share** | | | | |
| **Arkema** | $0 | $0 | $20,000 | $60,000 |
| **State of NC** | $0 | $70,243 | $70,551 | $0 |

# 1- Project Overview

MEGA-BIO: Bioproducts to Enable Biofuels (DE-FOA-0001433). *The FOA's aim is to examine strategies that capitalizes on revenue from bioproducts as part of cost-competitive biofuel production.*

**Project High-Level Objectives**

- Develop and optimize a separation strategy for recovery of MPs from biocrude.
- Evaluate commercial viability of the MPs as a feedstock for value-added bioproducts.
- Demonstrate that remaining biocrude fractions can be upgraded into biofuels.
- Perform TEA and LCA to demonstrate that recovery of MPs as bioproducts can reduce the cost of biofuel production by 30% and GHG emissions by 50%.

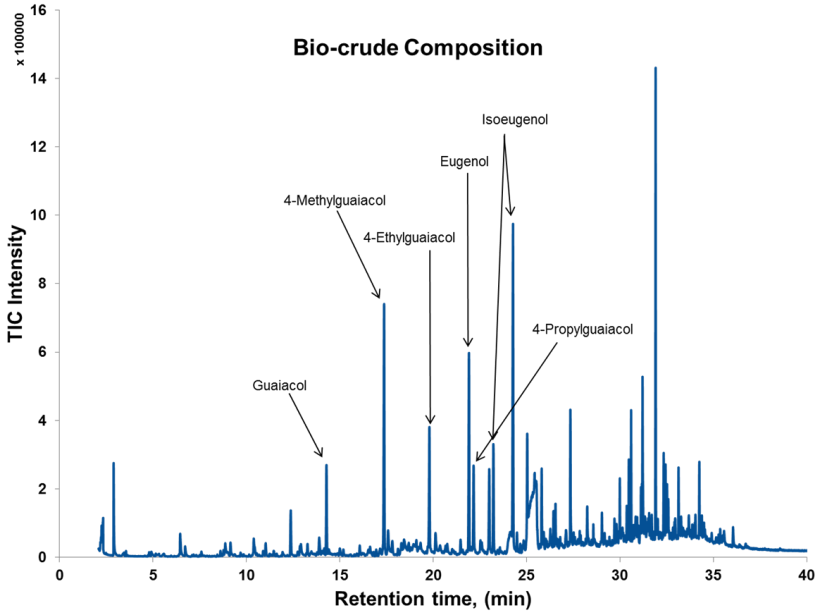



***Completed 2 on-site validations (BP1 and BP2)***
***Milestones are on track***
***About 38% of the budget is available to complete the project.***

# 1- Project Overview- Why Methoxyphenols?

**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-).*

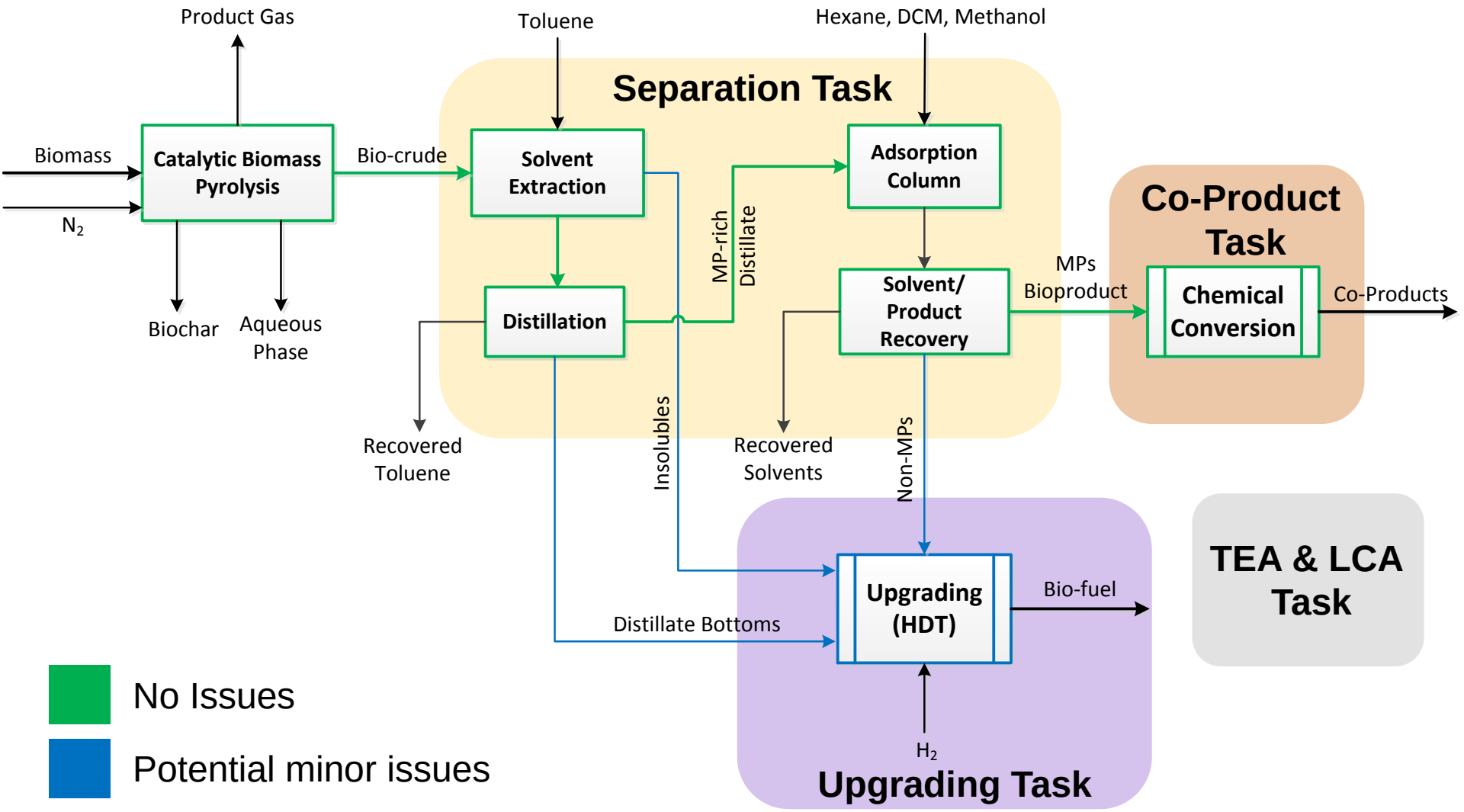
## Yield/Selectivity of Chemicals of Interest



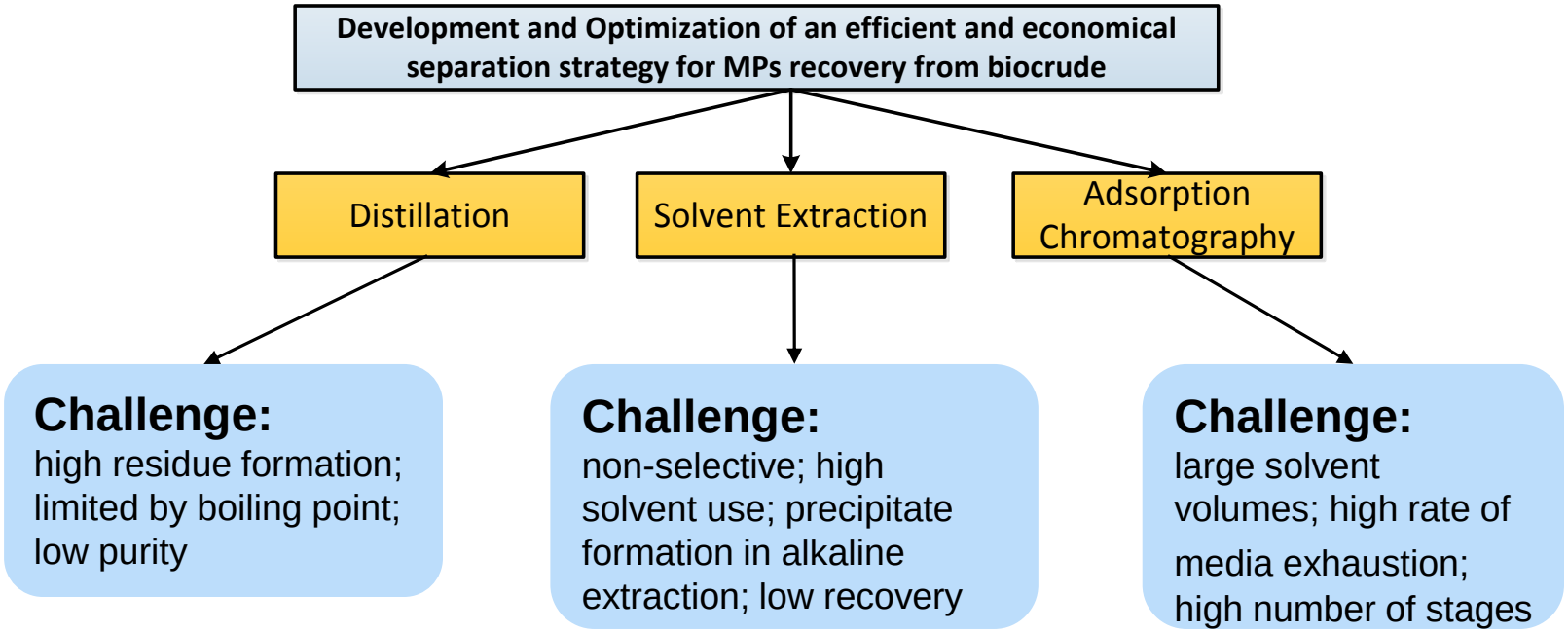

| Partially deoxygenated biocrude | |
|---|---|
| Major Chemical Components | GC-MS Analysis (wt.% dry basis) |
| Levoglucosan | 11.40 |
| Isoeugenols | 10.55 |
| Furfural | 6.94 |
| Hydroxy Ketones | 4.00 |
| Guaiacols | 3.75 |
| Acetic Acid | 2.18 |
| Benzenediols, alkylated | 1.72 |
| Phenols, mono | 1.37 |
| Vanillin and phenolic aldehydes | 0.82 |
| Cyclopentanones, Hydroxy | 0.74 |
| Benzenediols | 0.72 |
| Eugenol | 0.68 |
| 2(5H) Furanone | 0.63 |
| Propanoic acid, 2-oxo-, methyl ester | 0.48 |
| Furans | 0.41 |
| Cyclopentanones | 0.36 |

- Methoxyphenols are of relatively high concentration in the biocrude (9-15 wt%). CFP process conditions and feedstock can be adjusted to maximize MP production.
- MPs are oxygenated and attract higher market price (>$2/kg) than hydrocarbons (BTX) made from biomass
- MPs can act as building blocks for other products and fuels in synthetic routes that are more straightforward and economical compared to using petroleum feedstocks.

# 2 - Technical Approach – Process Operations Block Diagram



# 2 - Technical Approach – Separations




**Approach**:

- Evaluate distillation, solvent extraction, and adsorption chromatography
- Modify selected methods to address biocrude separation challenges
- Identify a hybrid strategy to enhance separation efficiency and bioproduct purity.

**Critical Technical Goals**

- Develop and demonstrate efficient and cost competitive separation strategy to obtain MPs products with efficiency (≥ 75wt%) and product purity (≥ 90%) at the bench-scale.
- Demonstrate scalability of the process. Design and fabricate a lab-scale separation system to achieve 90% of the separation efficiency at the bench-scale.

# 2-Technical Approach- Product Development & Hydrotreating

## Product Development Assessment

- Conduct market analysis to determine the potential value for mixed MPs as well as technical and nontechnical barriers to entry.
- Investigate three key co-product chemistries to expand MPs into other market (e.g., vanillin, flame retardants, biocides, carprolatone)

**Challenge:**
Value of mixture of MPs; co-products may require single chemical reactants; barriers to market entry

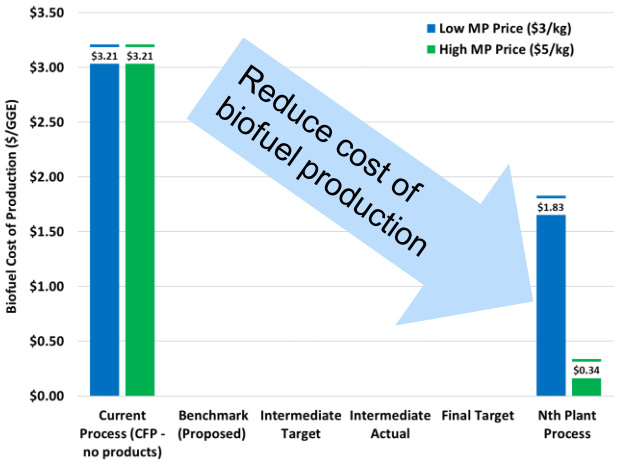
## Hydrotreating Fractionated Biocrude

- 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)

**Challenge:**
different feedstock; 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.



# 2 – Management Approach

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

## Budget Period 1(Complete)

Task 1.0: Initial Validation of Project (RTI)
***BP1 Go/No Go Decision Point (Achieved)***

## Budget Period 2 (Complete)

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 (Achieved)
***BP2 Go/No Go Decision Point Criteria Met: Bio-products reduce biofuel production cost by 30%***

## Budget Period 3 (On-going)

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

## Key Milestones and Deliverables

| FY17 | FY18 | FY19 |
|---|---|---|
| • ≥ 85 separation efficiency for mixed MPs with >90% purity.<br>• Complete market and business opportunity assessment of mixed MPs | • Design, fabrication, installation, and commissioning of laboratory scale separation system.<br>• TEA and LCA demonstrate $3/gge and a minimum of 50% GHG emissions reduction. | • Maintain 80% of the recovery efficiency at the laboratory scale.<br>• Complete product development assessment (PDA).<br>• TEA and LCA demonstrating < $3/gge and > 50% GHG emissions reduction |

# 3 – Technical Accomplishments/Progress/Results

## Separations

- Successfully developed three scalable strategies for recovery of MPs from biocrude by modification and integration of solvent extraction, distillation and chromatography techniques.
- Addressed challenges such as residue formation, non-selectivity, and low recovery typically associated with the selected techniques for biocrude separation.

***Key Milestone : Developed approach achieves 75% recovery efficiency, over 90wt% purity, and no residual losses.***

***Key Milestone : Designed, fabricated, and installed a 7-gallon per day lab-scale separation unit***

## Product Development

- A market assessment of the MPs was completed. Demand and prices were determined based on import-export flows for the US.
- Identified four potential application of MPs and chemistries for synthesis of vanillin, flame-retardant additive, and caprolactone.

***Key Milestone : Completed market and business opportunity assessment for the MPs.***

***Key Milestone : Developed chemistries for synthesis of vanillin, flame-retardant additive, and caprolatone.***

- ***Developed ozonolysis synthesis route from the MPs to vanillin at an overall yield of 83 wt% with purity of 99%.***
- ***Demonstrated the potential use of the mixed MPs as a biocidal product.***
- ***Developed a flame retardant additive with a V-0 rating from the MPs bioproduct***

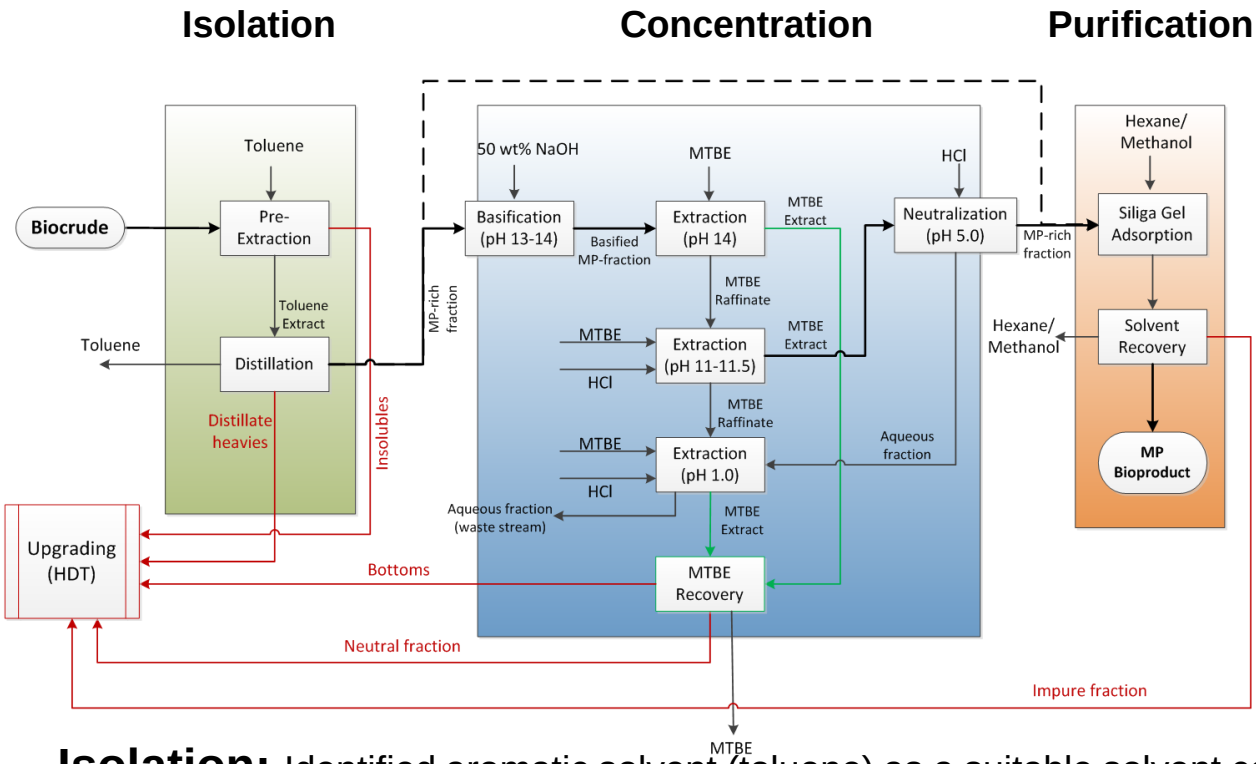
## TEA & LCA

- Updated process model to reflect experimental operation and results and performed preliminary capital cost estimation. Preliminary LCA of the integrated pathway to fuels and chemicals.

***Key Milestone : Preliminary TEA shows that recovery of the MPs as bioproduct has the potential to reduce biofuels selling price by at least 30%. Preliminary GREET LCA results demonstrate that the pathways have at least 50% GHG emissions reduction compared to petroleum gasoline***

# 3 – Technical Accomplishments/Bench-top Separation

## Developed Separation Strategies




### *Three Separation Strategies*

- **Isolation-Concentration**
- **Isolation-Purification**
- **Isolation-Concentration-Purification**

### Intermediate Validation Targets

| Separation Metrics | Proposed Target | Achieved Target |
|---|---|---|
| **Overall Efficiency, %** | 85 | 75 |
| **Product Purity, wt%** | 90 | 95 |
| **Residual Losses, wt%** | 15 | 0 |

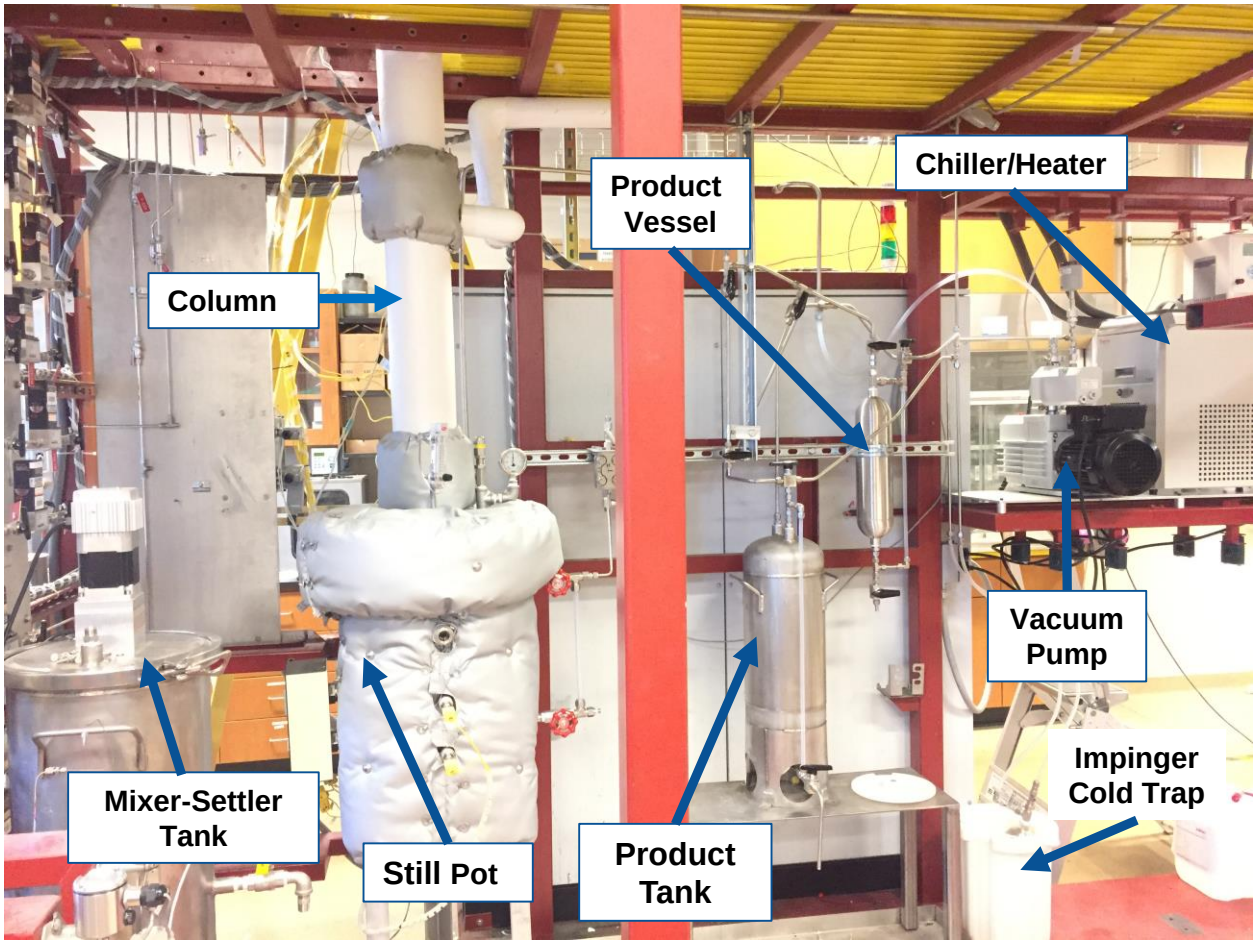
**Isolation:** Identified aromatic solvent (toluene) as a suitable solvent capable of selectively extracting the MPs from biocrude. Distillation was used after extraction to obtain a fraction boiling within180 and 320 °C with about **45-50 wt%** concentration of the MPs at overall recovery efficiencies of 78-99 %.

**Concentration:** Achieved by exploiting differences in pKa of the various phenolics and compounds in the isolated MP-rich fraction. Alkaline extraction at pH 11.5 was identified as optimal to concentrate the MP-fraction at more than 90% efficiency. A product containing up to **86 wt% MPs** can be achieved.

**Purification:** Identified a gradient elution method over silica gel that separates targeted MPs from other components. The process can yield a bio-product with purity up to **97 wt% MPs** with 85-97% efficiency.

# 3 – Technical Accomplishments/Lab-scale Separation Unit

A laboratory separation system that can process up to 7 gallons of biocrude per day has been designed, fabricated, installed, and commissioned.





The developed lab-separation capability will allow large quantities of MPs-bioproduct to be separated for co-product development and enough fractionated-biocrude for extensive hydrotreating studies.

# 3 – Technical Accomplishments/Market Assessment and Product Development

**Approach:** Arkema used industry standard assessment of bio-based products.

- There is market demand for guaiacol, ethylguaiacol, eugenol and isoeugenol.
- The price of guaiacol is approximately **$5/kg**. The price for eugenol and isoeugenol in today's market varies from **$12 to $30/kg**.
- Eugenol is available at various purities in the market ranging from 73% to 99.5%.

**Market Strategy:**

- Separation of individual MPs to attract different methoxyphenol markets.
- Utilization of the mixed MP bioproduct as a feedstock for other applications with large market size.

**Business Opportunity Assessment: Potential Applications of the MPs bioproduct**

- **Flavor & Fragrance: Vanillin Synthesis (**400 million/**18,000 tons per year**; 85% from petroleum ($10 – 20/kg))
- **Flame Retardants:** Global consumption of flame retardants (RF) is estimated to be more than **2.25 million tons per year**.
- **Biocidal Application:** More than **400,000 tonnes** of biocidal active ingredients are produced or imported annually in Europe. Global biocides market is expected to be at USD 13.9 billion by 2025.
- **BPA substitute** (**bisguaiacol-F**): Market size over **6.5 million tonnes per year.**
- **Caprolactone:** More than **10, 000 tonnes** per year produced in Europe.

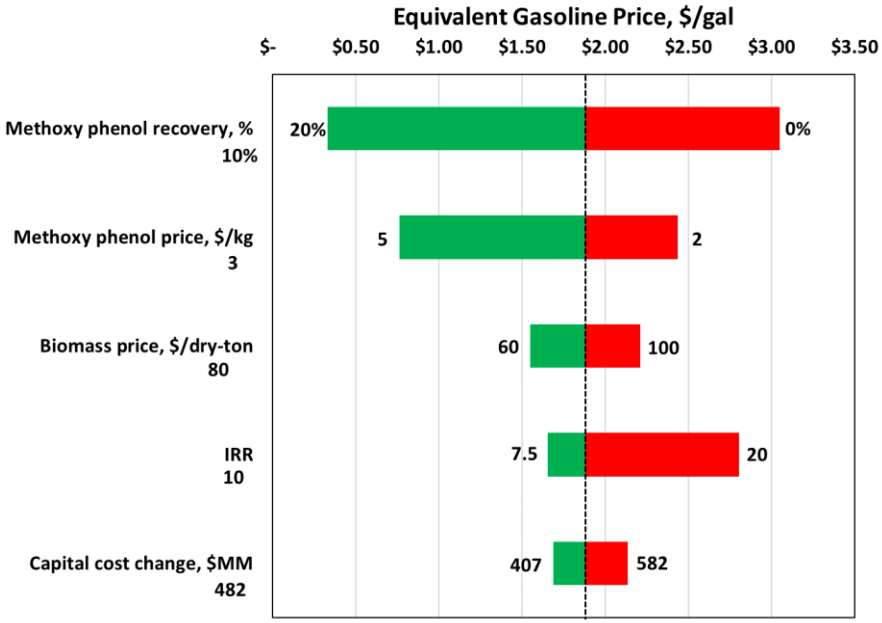
# 3 – Technical Accomplishments/ Preliminary Process Design

**Approach:** *Update previous process model and economic analysis to include bioproduct separation in the biofuel process design for a 2000 bone dry ton/day plant.*

- Major design changes are as follows:
  - Whole logs vs wood chips (wood chips only)
  - Steam Reformer (Changed feedstock to natural gas)
  - Changed hydrogen purification system from amine system to PSA.
- Capital cost estimates were performed for the construction of four plant options.
- Cost estimate approach was by factoring/parametric estimating methodology and vendor quotes.

Preliminary analysis indicates that the MFSP decreases by 20% if the MP bioproduct sells for $2/kg and by 40% if the MP bioproduct sells for $3/kg.

The preliminary sensitivity analysis shows the impact of MP recovery and price point, biomass feedstock cost, IRR, and capital cost.

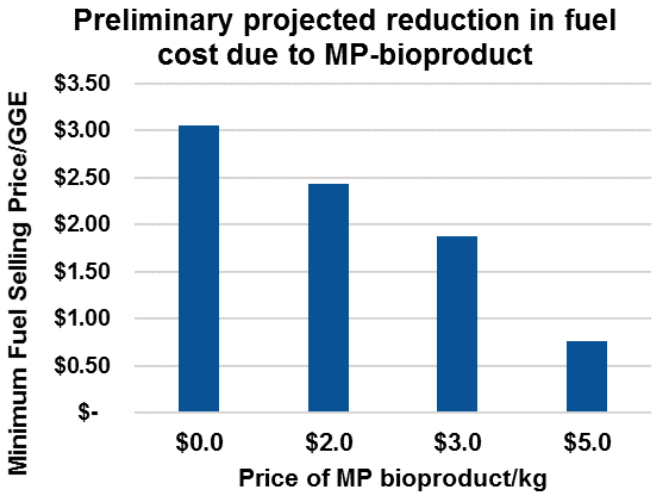


# 4 - Relevance

Supports the mission of EERE's Bioenergy Technologies Office (BETO) to recover high-value bio-products to enable $3/gge production of renewable hydrocarbon fuels from lignocellulosic biomass by 2022.

- 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 marketable MPs and co-products from direct biomass catalytic pyrolysis products prior to upgrading to biofuels could provide a significant source of revenue to improve overall process economics.



# 5 - Future Work : BP3 Tasks

**Laboratory-scale Separation**

- 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).

**Co-Product Development**

- Identify technical requirements: quality, purity, properties, performance, and market entrance challenges of co-products.
- Validation of the identified pathway(s) to expand the MPs into higher margin markets.
- Develop a commercialization strategy.

**TEA and LCA**

- 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 75%; no residual losses; and the remaining of the initial biocrude upgraded to biofuel.

# Summary

- **Approach**
  - Separation strategy development and optimization for MPs recovery.
  - Design, fabrication, and installation of a lab-scale separation unit.
  - Market assessment of MPs and product development analysis.
  - Upgrading of fractionated biocrude to biofuels.
  - TEA and LCA
- **Technical Accomplishments/Progress/Results**
  - Developed separation strategy achieves 75% recovery efficiency, over 90wt% purity, and no residual losses.
  - Designed, fabricated, and installed a 7-gallons of biocrude per day lab-scale separation unit to support co-product development and upgrading studies.
  - Completed market and business opportunity assessment for the MPs.
  - Developed chemistries for synthesis of vanillin, flame-retardant additive, and caprolactone.
  - Preliminary TEA shows that recovery of the MPs as bioproduct has the potential to reduce biofuels selling price by at least 30%.
- **Relevance**
  - Supports BETO's Conversion R&D Objectives in 2016 MYPP.
  - The project demonstrates how revenue from bioproducts could be used as part of cost-competitive biofuel production strategy.
- **Future Work**
  - Laboratory Separations for Co-product Recovery and Upgrading for biofuels.
  - Complete TEA and LCA for the integrated biorefinery for biofuel and bioproduct.

# Acknowldegments


U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE




**BETO Project Officer: Liz Moore**

**RTI Contributors**

- Ofei D. Mante (PI)
- David C. Dayton
- Mustapha Soukri
- Samuel J. Thompson
- Jonathan Peters
- Kaige Wang
- Kelly Amato
- Michael Carpenter
- David Barbee
- Philip Cross
- Joseph Weiner

**Arkema**

- Jean-Luc Dubois

**AECOM**

- Pamela Spath

# Additional Slides

# Responses to Previous Reviewer's Comments

## Overall Impressions

**Reviewer Comments**

Producing higher value chemicals to support the development and use of renewable fuels is become a major theme in the BETO development efforts. The hope is that these could supplement or replace renewable energy credits. Until now the justifications for this program for biooils has not been based on a rigorous TEA with participation of a chemical manufacturer. This project address this need. The program levarages RTI's ability to produce large quantities of cata-pyrolysis and pyrolysis liquids. This is a key enabler of many related projects involving upgrading of the liquids and aqueous vapor products and should be funded if possible.

The difficulty with this project is that proposed experimental work is weak. There is no evidence of a deep understanding of the problems associated with separation of bio oil relative other types of chemical feedstocks. Information from prior efforts to separate biooil in the open literature and patents are not included in the planning and used as a kickoff. There are processes for separating chemicals from coal gasification, coal tar and low temperature coal pyrolysis in the past that include commercial process design and economics.

**PI Response**

With respect to the separation work, solvent extraction using alkaline and switchable hydrophilic solvents (e.g., N,N-dimethylcyclohexylamine) and fractional distillation under vacuum will be evaluated in the development of a hybrid approach for isolation, concentration, and purification on the MPs bioproduct. The research plan and the project execution strategy have been designed to be flexible enough to accommodate possible technical challenges. For example, formation of an azeotropic composition below the target concertation (>90%) of MPs is unknown but such an occurrence will limit the use of distillation as a purification step. The evaluation of adsorption separation (e.g., using an acrylic ester sorbent XAD-7 or a strongly basic anion exchange resin) could be considered as a mitigation strategy to ensure that the target concentration of MPs is achieved. Also, the solvents to be explored in the extraction study could be expanded to other potential solvents if those to be initially evaluated are found not to meet the recovery efficiency targets. The challenge with final product quality/purity will be addressed in the project work and cost of additional separation processes will be captured in the TEA.

**Reviewer Comments**

One of the few projects where I feel that the targets are not relevant to the goals of BETO. The current market for Eugenol etc is in the few thousand tons range, very specialized and very sensitive to minor odor components and thus reason for cost as they often require further purification (Thus high cost due to low market volume, purity and end use is low in products so can afford the price).
Billion ton feed use is mismatched with thousand ton market and as such cannot impact BETO fuel cost long term. I applaud the teams results which were outstanding but relevance out ways the solid work results on the program. I am not sure that the Technoeconomic analysis would provide any different result if market impact is taken into account. Any substantial volume production of the material targets would totally disrupt the current market price. Again, team did nice job working the program and accomplishments on goals but program is not a fit with BETO needs.

**PI Response**

This project is responsive to the MEGA-BIO FOA (DE-FOA-0001433) which has the 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. This means there is flexibility with the project's hydrocarbon biofuels conversion pathways such that it can be modified to produce more/less advanced fuels versus the MPs bioproducts based on external factors. The market assessment to be performed by Arkema will provided valuable information of the potential of the methoxyphenols with respect to their current market and potential applications. Technical requirements (quality, purity, properties, and performance) and market entrance challenges will be evaluated. Value chain analysis will be conducted to identify three key chemistries to expand MPs into other market .

# Responses to Previous Reviewer's Comments

## Overall Impressions

**Reviewer Comments**

Producing higher value chemicals to support the development and use of renewable fuels is become a major theme in the BETO development efforts. The hope is that these could supplement or replace renewable energy credits. Until now the justifications for this program for biooils has not been based on a rigorous TEA with participation of a chemical manufacturer. This project address this need. The program levarages RTI's ability to produce large quantities of cata-pyrolysis and pyrolysis liquids. This is a key enabler of many related projects involving upgrading of the liquids and aqueous vapor products and should be funded if possible.

The difficulty with this project is that proposed experimental work is weak. There is no evidence of a deep understanding of the problems associated with separation of bio oil relative other types of chemical feedstocks. Information from prior efforts to separate biooil in the open literature and patents are not included in the planning and used as a kickoff. There are processes for separating chemicals from coal gasification, coal tar and low temperature coal pyrolysis in the past that include commercial process design and economics.

**PI Response**

With respect to the separation work, solvent extraction using alkaline and switchable hydrophilic solvents (e.g., N,N-dimethylcyclohexylamine) and fractional distillation under vacuum will be evaluated in the development of a hybrid approach for isolation, concentration, and purification on the MPs bioproduct. The research plan and the project execution strategy have been designed to be flexible enough to accommodate possible technical challenges. For example, formation of an azeotropic composition below the target concertation (>90%) of MPs is unknown but such an occurrence will limit the use of distillation as a purification step. The evaluation of adsorption separation (e.g., using an acrylic ester sorbent XAD-7 or a strongly basic anion exchange resin) could be considered as a mitigation strategy to ensure that the target concentration of MPs is achieved. Also, the solvents to be explored in the extraction study could be expanded to other potential solvents if those to be initially evaluated are found not to meet the recovery efficiency targets. The challenge with final product quality/purity will be addressed in the project work and cost of additional separation processes will be captured in the TEA.

**Reviewer Comments**

One of the few projects where I feel that the targets are not relevant to the goals of BETO. The current market for Eugenol etc is in the few thousand tons range, very specialized and very sensitive to minor odor components and thus reason for cost as they often require further purification (Thus high cost due to low market volume, purity and end use is low in products so can afford the price).
Billion ton feed use is mismatched with thousand ton market and as such cannot impact BETO fuel cost long term. I applaud the teams results which were outstanding but relevance out ways the solid work results on the program. I am not sure that the Technoeconomic analysis would provide any different result if market impact is taken into account. Any substantial volume production of the material targets would totally disrupt the current market price. Again, team did nice job working the program and accomplishments on goals but program is not a fit with BETO needs.

**PI Response**

This project is responsive to the MEGA-BIO FOA (DE-FOA-0001433) which has the 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. This means there is flexibility with the project's hydrocarbon biofuels conversion pathways such that it can be modified to produce more/less advanced fuels versus the MPs bioproducts based on external factors. The market assessment to be performed by Arkema will provided valuable information of the potential of the methoxyphenols with respect to their current market and potential applications. Technical requirements (quality, purity, properties, and performance) and market entrance challenges will be evaluated. Value chain analysis will be conducted to identify three key chemistries to expand MPs into other market .

# Responses to Previous Reviewer's Comments

## Relevance

**Reviewer Comments**

Current TEA analysis of catalytic pyrolysis suggest that the value of the fuel produce cannot alone support the process. Experimental evaluation extracting chemicals from pyrolysis products is needed to determine if it can increase the value of the biooil. The value of many of the products is significantly lower than the RIN value for fuels. Obtaining products with the required chemical purity for use as chemical intermediates may require additional purification steps that add to the costs. It is not clear that the volumes of the chemicals that could be obtained would be significant enough to have a major impact on development of fuel processes.

**PI Response**

A quick analysis suggests that the targeted MPs have more value than RIN value for fuel based on the prices of MPs at $3-5/kg, fuel selling prices of $3/gge and selling price of RINs at $0.77.The existing market size of methoxyphenols is about 142,000 tonnes/yr. The mixed MPs are potential feedstocks for the synthesis of other chemical ingredients as BsiphenolA with a market size of 6.5 million tonnes/yr and the alkylphenols with a market size of 540, 00 tonnes/yr. As part of the market assessment of the MPs by Arkema, there will be an evaluation of other potential products that the MPs could serve as a chemical building block.

## Project Approach

**Reviewer Comments**

Project objectives need to be better aligned with technical approach. Project proposes to pyrolyze whole biomass and then perform a liquid-liquid extraction on the highly mixed, multi-phase, unstable pyrolysis liquids. This extraction will only target some of the species generated from the lignin fraction which is likely only 30% of the incoming biomass. An upstream biomass separation to fractionate the lignin from the cellulose and hemis/extractives, followed by lignin suspension in a solvent and then pyrolysis is much more logical if the target is methoxyphenols. It might even be reasonable to suspend the lignin in methoxyphenols if the pyrolysis conditions are mild enough to avoid degradation (comes with the added benefit of in-situ solvent production). .

**PI Response**

The technical focus of this project is not on the production of MPs; but rather on the separation of MPs present in biocrude produced from the biomass catalytic pyrolysis technology. Even though the targeted MPs could be produced from an isolated lignin stream; the concept of converting lignin solely to bioproducts doesn't meet the biofuels requirements set forth in the FOA and ultimately the project milestones.

**Reviewer Comments**

Project just started in October 2016. The work is split in three budget periods and will include bench-scale separation; laboratory-scale distillation; upgrade the remaining bio-crude fraction; business evaluation; TEA and LCA.. The methoxyphenol objective is sound and the equipment is proven and makes sense, but the project must consider efficiencies more seriously for the results to have any commercial relevance. Moving to a lignin only, solvent liquefaction pyrolysis is logical.

**PI Response**

High separation efficiency of 85 wt% with residual losses of 10wt% is the final technical target to be achieved and demonstrated on a bench-scale during the intermediate validation of the project. The use of lignin only for production of MPs is beyond the scope of this project which is focusing on the separations of MPs.

# Publications, Patents, Presentations, Awards & Comm

## Publications

- Mante, O.D.; Thompson, S.J.; Soukri, M. and Dayton, D.C. “A Selective Extraction Method for Recovery of Monofunctional Methoxyphenols from Biomass Pyrolysis Liquids.” Submitted to Green Chemistry
- Thompson, S.J.; Mante, O.D.; Soukri, M. and Dayton, D.C. “Vanillin Production from Biomass-Derived Methoxyphenols.” Submitted to Green Chemistry
- Mante, O.D.; Thompson, S.J.; Soukri, M.; and Dayton, D.C. “Isolation and Purification of monofunctional methoxyphenols from loblolly pine biocrude” ACS Sustainable Chemistry & Engineering Manuscript. Accepted 12/18/2018
- Luebeck, J. S., G. Tomasi, K. G. Poulsen, O. D. Mante, D. C. Dayton, S. Verdier and J. H. Christensen . Non-target analysis of oxygenates in catalytic fast pyrolysis biocrudes by supercritical fluid chromatography-high resolution mass spectrometry. Energy & Fuels. Accepted 12/11/2018
- Kristensen, M.; Hansen, A. B.; Mante, O. D.; Dayton, D. C.; Verdier, S.; Christensen, P.; Christensen, J. H., Complementary Analysis of the Water-Soluble and Water-Insoluble Fraction of Catalytic Fast Pyrolysis Biocrudes by Two-Dimensional Gas Chromatography. Energy & Fuels 2018, 32 (5), 5960-5968.
- Mante, O. D., Dayton, D. C., & Soukri, M. (2016). Production and distillative recovery of valuable lignin-derived products from biocrude. *RSC Advances*, *6*(96), 94247–94255.

## Patents

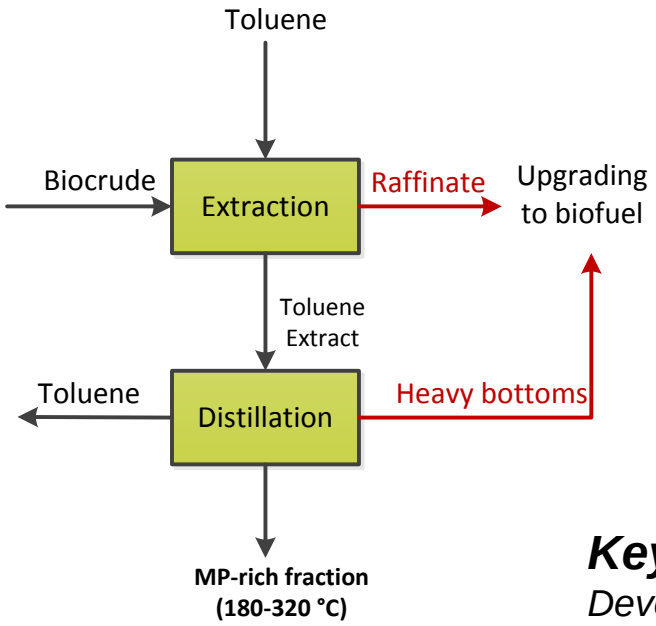
- Mante, O. D.; Soukri, M.; Thompson, S.J and Dayton, D.C “Process for Selectively Recovering a Phenolic Compound from Feedstock Comprising Biocrude and/or Bio-oil." US provisional patent application filled, July 2018. US application 62/695,904.

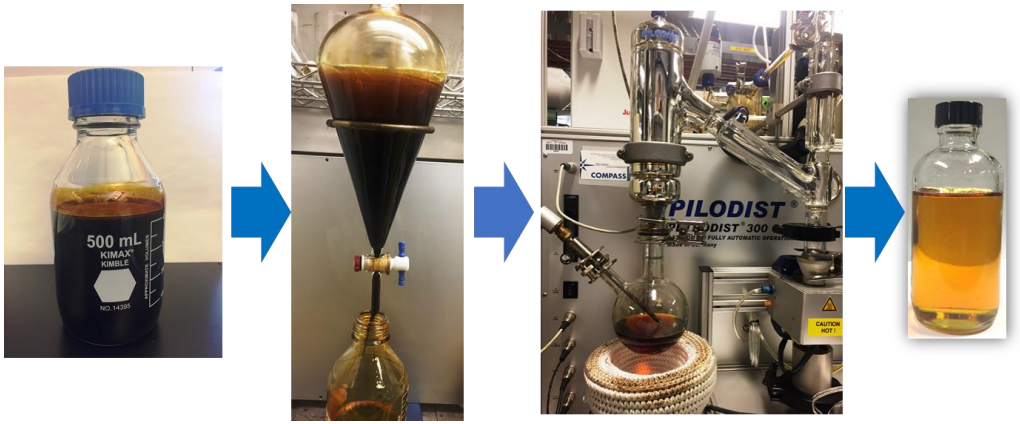
# 3 – Technical Accomplishments/Separations

**Step 1** : *Isolation of a crude mixture of MPs from biocrude*

## Approach: Solvent extraction and Distillation

- Established a selective method for isolating a crude MP mixture boiling between **180 and 320 °C**.
- Identified **aromatic solvent (toluene)** as a suitable solvent capable of selectively extracting the MPs and other thermally stable components from biocrude.
- Distillation of the toluene extract results in a phenolic fraction with **45-50 wt% concentration** of the MPs.
- Overall **recovery efficiencies** for the targeted MPs are between **78-99 wt%.**




***Key Technical Accomplishment:***

*Development of a method* ***that prevents residue formation*** *during distillation of biocrude chemicals. Identified solvent selectively removes thermally unstable components such as anhydrosugars (e.g., levoglucosan), polyphenolic compounds and oligomers (pyrolytic lignin), acids, aldehydes and hydroxy ketones.*

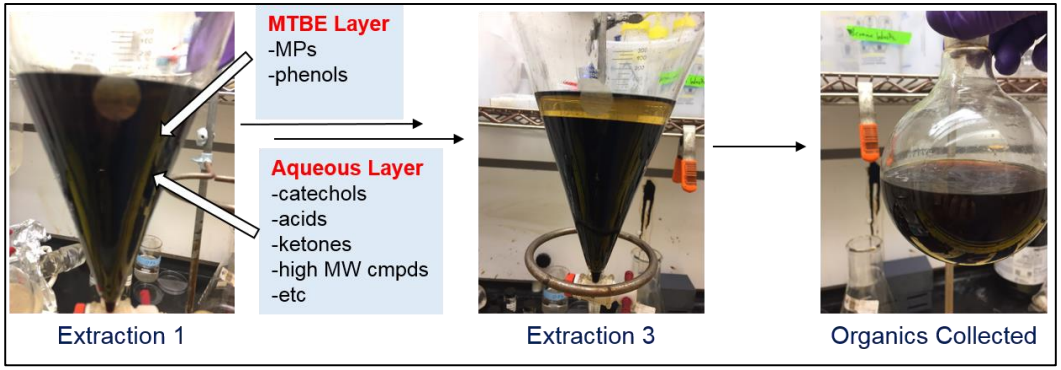
# 3 – Technical Accomplishments/Separations

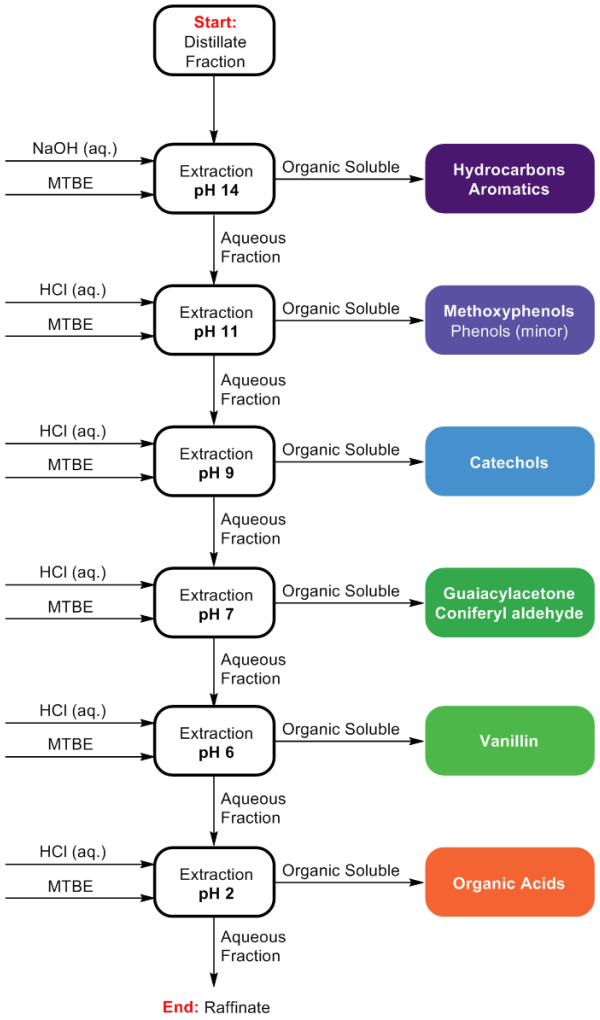
**Step 2** : *Concentration of the isolated MP fraction by alkaline extraction*

## Approach: Selective Alkaline Extraction

- Modified conventional alkaline extraction to selectively separate out MPs from other phenolic compounds with similar boiling points.
- Exploited minor differences in ***pKa*** of the different phenolics in the isolated MP-rich fraction.
- Identified a narrow **pH (10-12) range** where the MPs can be selectively separated with high efficiency.
- The MPs of interest can be recovered at pH 11.5 with more than **90%** efficiency. A bio-product containing up to **86 wt%** eugenols and guaiacols was recovered.

**Recovery of MPs at pH 11-11.5)**




## *Key Technical Accomplishment:*

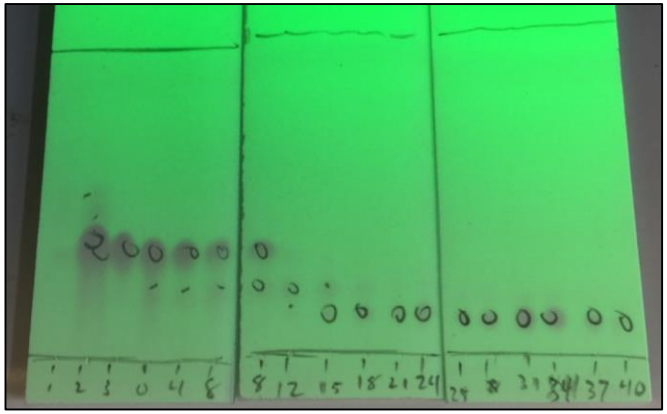
*The modified alkaline extraction method enables **selective separation of different functional phenolics***

# 3 – Technical Accomplishments/Separations

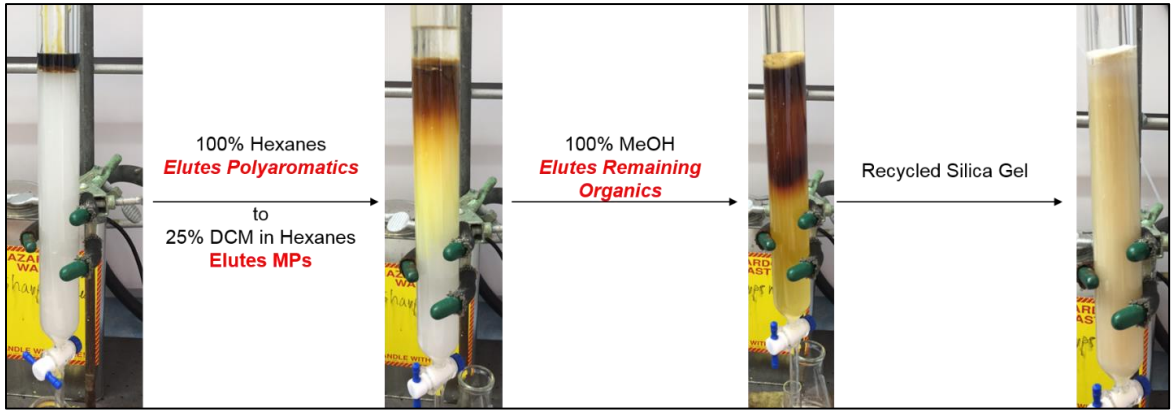
**Step 3** : *Purification*

## Approach: Adsorption chromatography

- Identified a gradient elution method over silica gel that enables purification of the MP bioproduct.
- Hexane solvent separates out non-polar impurities
- 25% DCM in hexane allows exclusive elution of the MPs
- 100% DCM enables elution of non-MP phenolic impurities
- 100% Methanol elutes all other polar impurities.
- The purification process can yield a bio-product with purity up to **97 wt% (eugenols and guaiacols)** with **85-97%** efficiency.



TLC of MP elution from silica gel column.



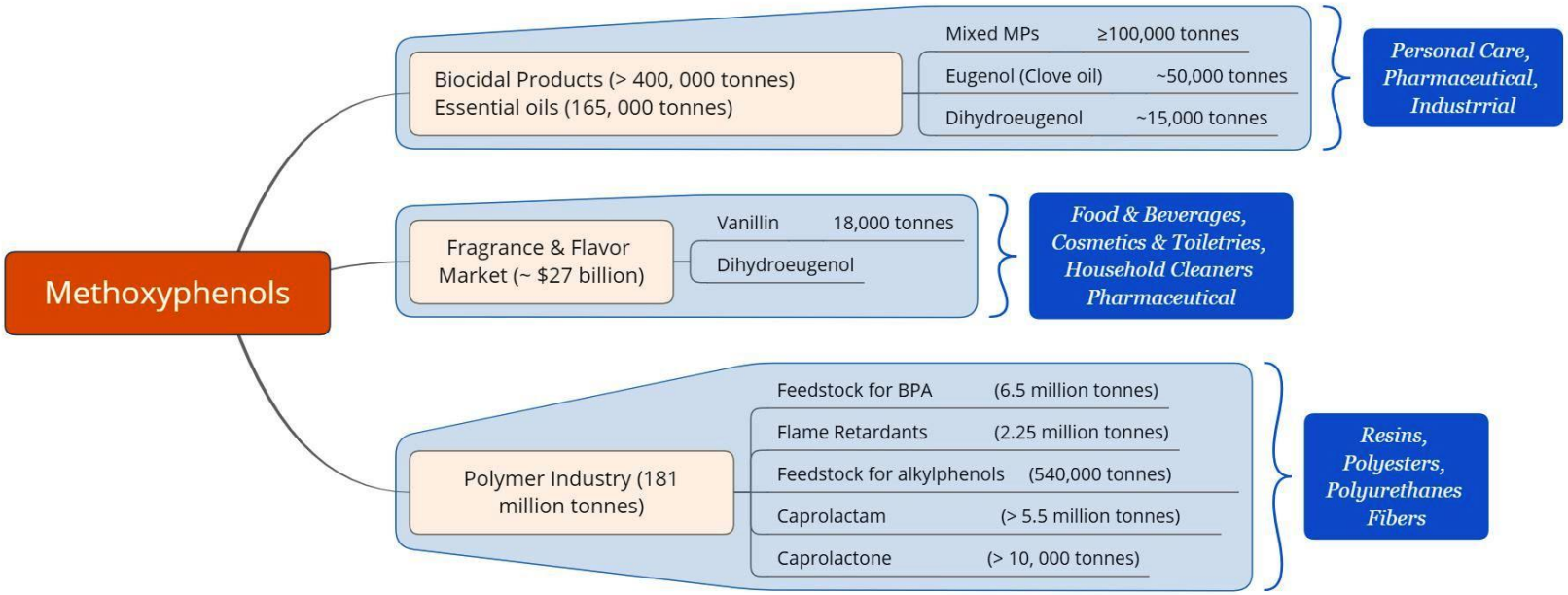

**Methoxyphenols bioproduct**
(*A potential essential oil*)

## *Key Technical Accomplishment:*

*Establishment of a purification process that allows an MP bio-product with >90% purity to be achieved.*

# 3 – Technical Accomplishments/Market Assessment and Product Development

**The MP bioproduct is a feedstock for many applications with large market sizes.**
**The MP bioproduct purity and quality requirement can be tailored to end use applications.**




## ➢ Existing Market Opportunity

| Methoxyphenol | Market Volume (tonne per year) | Average Price (USD per tonne) | Major U.S. Producers/Suppliers |
|---|---|---|---|
| **Eugenol** | 5,000-22,000 | 12,000-30,000 | Universal Presev-A-Chem Inc |
| **Guaiacol** | >25,000 | ~2,000-5,000 | Solvay-Rhodia |
| **4-Methylguaiacol** | ~80,000 | >3,000 | Advanced Biotech, TREATT |
| **4-Propylguaiacol** | 15, 000 | | Firmenich |
| **Clove oil** | 2,000-50,000 | 15,000-86,000 | |