Advanced Biofuels and Bio-Products from Catalytic Biomass Pyrolysis

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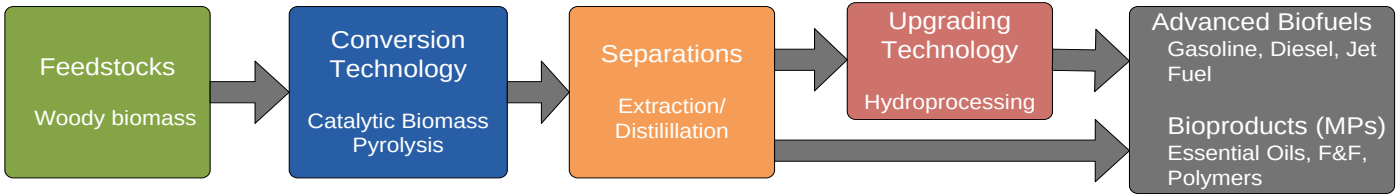
Overview

Demonstrate an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure compatible biofuels. Improve the economic viability of this process by recovering high-value bio-products.



Multiple feedstocks

- ***Continuous Process***
- ***Flexible Operating Conditions***
- ***Produce Bio-crude***

- ***Separation Efficiency***
- ***Quality and Purity***

- ***Bio-crude quality***
- ***Upgrading severity***

Scale-up CFP process to pilot-scale to validate catalyst performance and bio-crude yields and quality

1) Optimize the catalytic biomass pyrolysis process (1TPD) to maximize high-quality bio-crude production (< 20 wt% O and > 40% carbon recovery)
2) Improve bio-crude thermal stability

Design, build and operate a pilot-scale hydroprocessing unit to upgrade bio-crude intermediates

1) Evaluate the impact of bio-crude quality on the hydroprocessing step
2) Evaluate co-processing opportunities
3) Evaluate hydrogen demand of the integrated process
4) Maximize biofuels yield

Develop and optimize a hybrid separation method to recover high-value methoxyphenols(MPs) from biocrude.

1) Leverage catalytic biomass pyrolysis to produce a thermally stable biocrude with narrow product slate.
2) Tailor separation approach to the physicochemical properties of the biocrude.
3) Adapt a hybrid separation strategy for extraction, concentration and purification of MPs

Technical Capabilities

Pilot-scale (1TPD) *in situ* Catalytic Fast Pyrolysis

- Continuous feed circulating fluidized bed reactor/regenerator – scaleable design
- Maximize carbon efficiency and deoxygenation to control bio-crude properties
- Verify long-term deoxygenation activity and attrition resistance
- Maximize bio-crude yield

Challenges: char/coke formation reduces bio-crude yields, bio-crude recovery efficiency, steady-state bio-crude yields, obtaining pilot-scale quantities of catalyst and feedstock

Bio-crude Upgrading

- Design, fabrication, and installation of a pilot-scale (dual 350-mL reactors) hydroprocessing unit that provides data for scale-up
- Benchmark operation to verify system performance and data reliability
- Long-term unattended operation to determine upgrading catalyst stability and lifetime (500-1000 hrs)
- Refinery integration and co-processing strategies

Challenges: Reactor plugging, process severity correlated to bio-crude composition

Critical Technical Goals

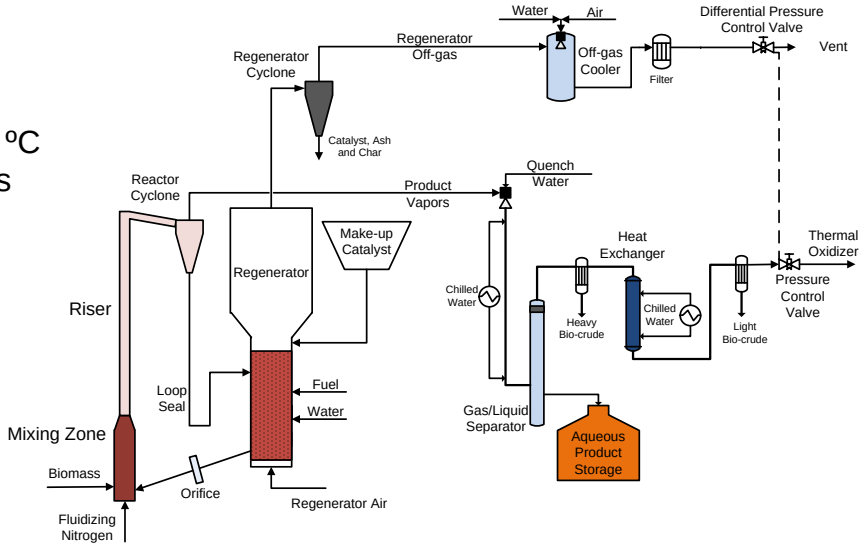
- Steady-state pilot plant operation to validate bio-crude yields
- Steady-state bio-crude upgrading to validate catalyst HDO activity
- Updated techno-economics to validate technology cost competitiveness

Pilot-Scale Studies: Methodology

Objective: Demonstrate steady-state operation to evaluate process conditions on biocrude yield and quality.

CFP Conditions:

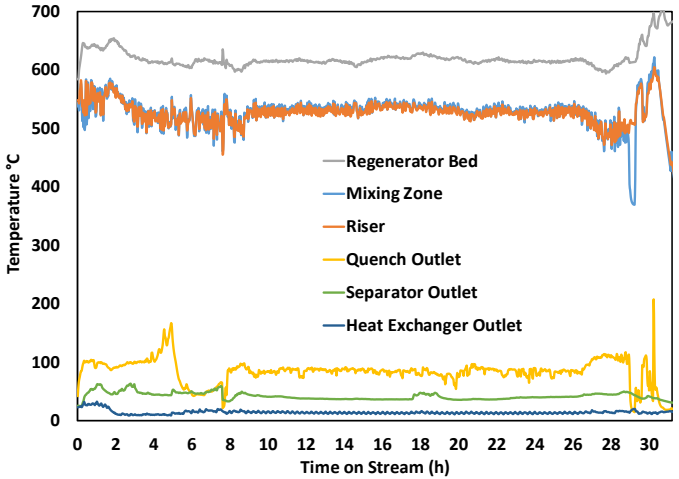
- Biomass Feed Rate: 35-70 kg/h
- Pyrolysis Temperature: 425-600 ºC
- Regenerator Temperature : 560-700 ºC
- Mixing Zone Residence time : 0.5-2 s
- Nominal 70 µm, non-zeolite alumina catalyst

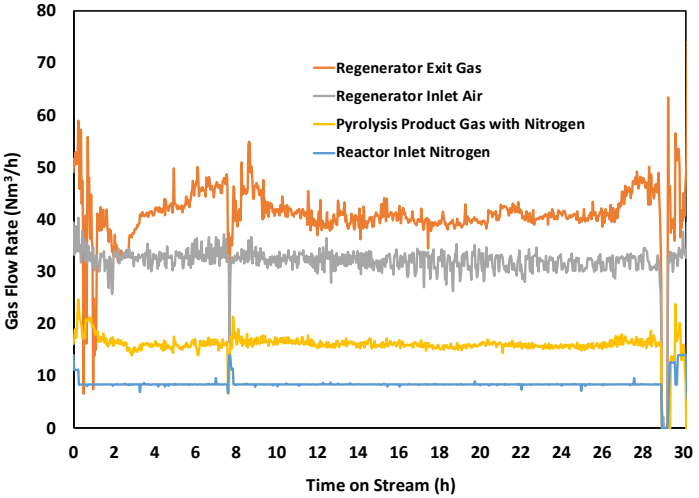


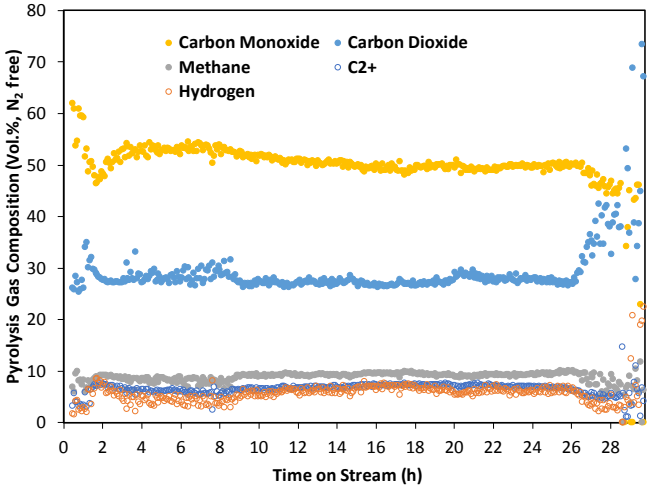
Biomass	Particle Size	Moisture wt%	Composition, wt% as-received			
			C	H	N	O
Loblolly pine	< 2 mm	15.0	47.4	6.5	0.1	46.2
Red Oak	< 2mm	10.0	45.5	6.4	0.4	47.7

Dayton, D. C.; Carpenter, J. R.; Kataria, A.; Peters, J. E.; Barbee, D.; Mante, O. D.; Gupta, R., Design and operation of a pilot-scale catalytic biomass pyrolysis unit. **Green Chemistry** 2015, 17 (9), 4680-4689

Loblolly Pine CFP Results Summary



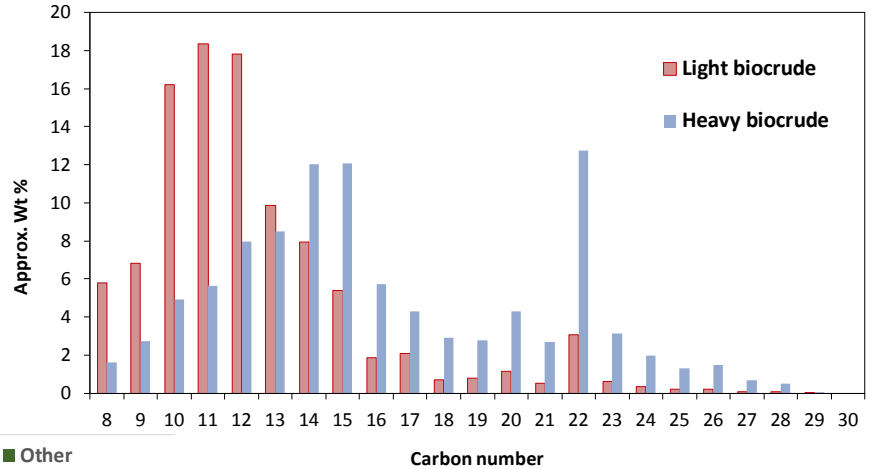


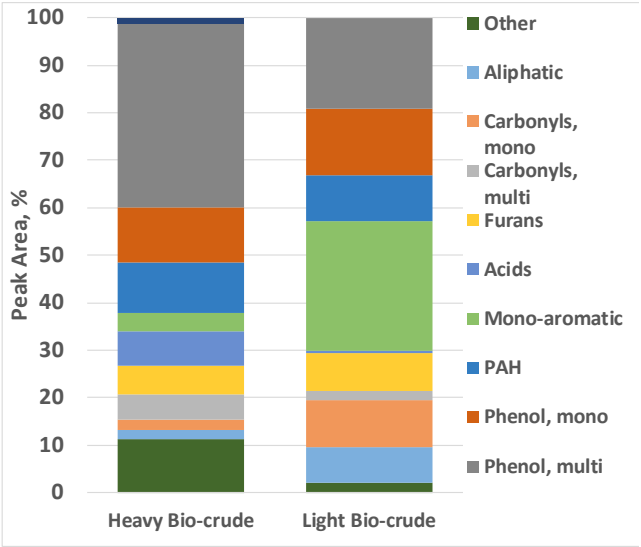


CFP Products	Yield (wt%)	Yield (Mole C%)
Organic liquid	10.9	11.5
Aqueous liquid	31.4	13.0
Total Liquid	42.3	24.5
Pyrolysis gas	25.0	21.8
Regenerator gas	13.6	28.7
Char	19.1	23.6

Bio-crude Physical and Chemical Properties

Properties	Biocrude	
	Light	Heavy
Moisture, wt%	4.9	11.4
Density, g/cm^3	1.018	1.162
Kinematic viscosity, cSt	4.1	154.0
Elemental Composition (dry basis)		
H, wt%	8.1	6.6
O, wt%	13.6	24.2
C, wt%	78.3	69.2





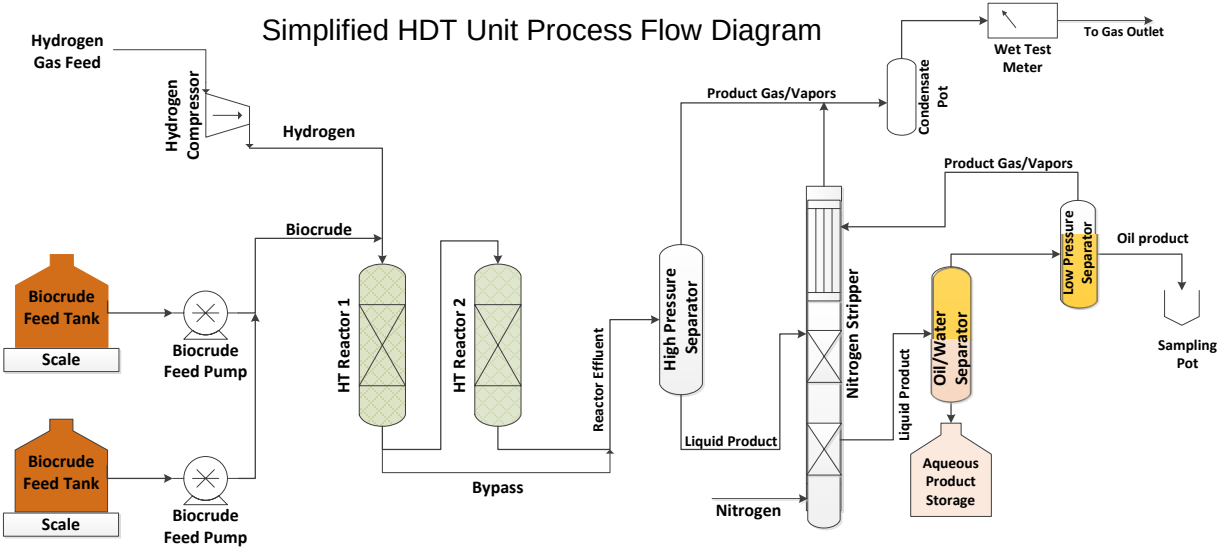
GC/MS Compound	Amount (wt%)	
	Light	Heavy
Acetic acid	0.14	0.45
2-propanone, 1-hydroxy-	0.24	0.77
2-butanone	1.38	0.44
2-pentanone	0.30	0.43
Furfural	1.99	0.34
Cyclopentanones	1.3	2.23
levoglucosan	ND	2.60
Phenol	0.90	0.44
Substituted phenols	4.22	6.12
Methoxyphenols	4.49	4.72
Toluene	0.82	0.01
o-Xylene	0.74	ND
Benzene, 1,2,3-trimethyl-	0.04	0.01
Indene	0.51	0.01
Benzene, 1,2-diethyl-	1.49	0.16
Alkanes (C7+)	1.18	0.24

Bio-crude Upgrading

Investigate the impact of bio-crude quality in the hydroprocessing step

- Steady-state deoxygenation activity, hydrogen demand, and process severity with bio-crude of various quality (wt%O)
- Long-term unattended operation to determine upgrading catalyst stability and lifetime (500-1000 hrs)
- Refinery integration and co-processing strategies

Challenges: Reactor plugging, process severity correlated to bio-crude composition



Reactor volume: 350 mL
Catalyst volume: 20 - 250 mL

LHSV - 0.1 to 1.0
Flow rates - 50 to 250 mL/h

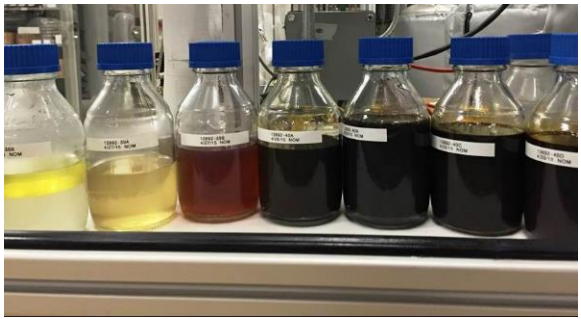
Max. design pressure - 3000 psig
Max. design temperature - 450 C

Bio-crude Hydrotreating

Catalyst Loading, Sulfidation, and HDT Process Conditions

- HDT Catalyst: HaldorTopsøe Bio-Cat
- Catalyst Sulfidation: In-situ with H_2S in H_2 balance.
- Bio-crude flow rate: 50-250 ml/h
- Mass Balance Protocol: Allow at least 48 hours of run time prior to performing mass balance.
- Experiments continue until pressure drop across reactor > 60-100 psig

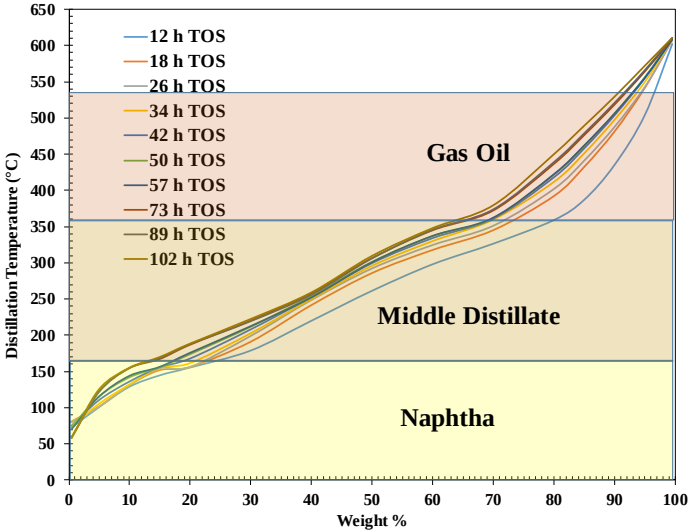
Parameters	Typical Test Conditions
Temperature	290 – 350 °C
Pressure	1450-2000 psig
LHSV	0.125 - 0.5 1/h
H_2/oil	2000-3300 Nl/l
TOS	16-396

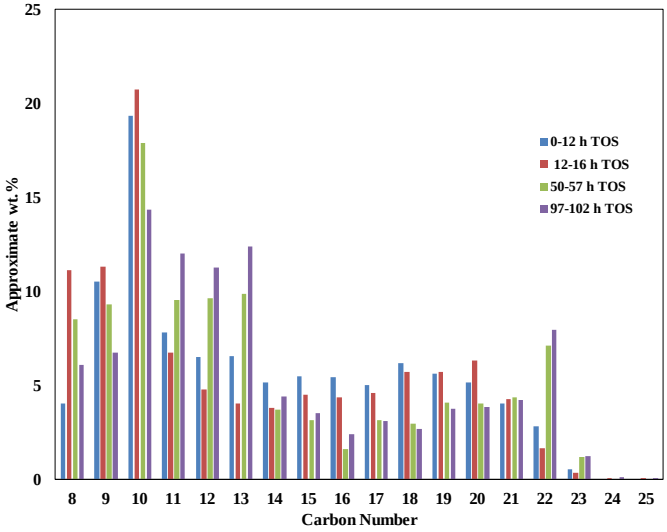


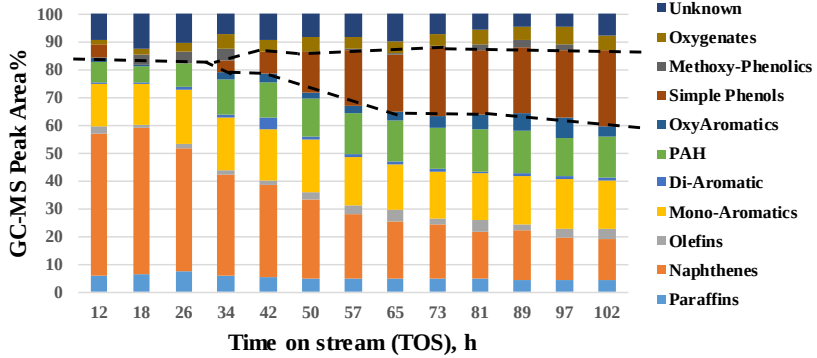
Analysis of Bio-crude and HDT products include:

Elemental Analysis(CHNSO), GC-MS, FTIR, NMR, Carbon Number Distribution, Distillation by ASTM D1160, SG 60/60 by ASTM D4052, Kinematic Viscosity by D445, and Karl Fischer Titration.

Hydrotreated Bio-crude Analyses

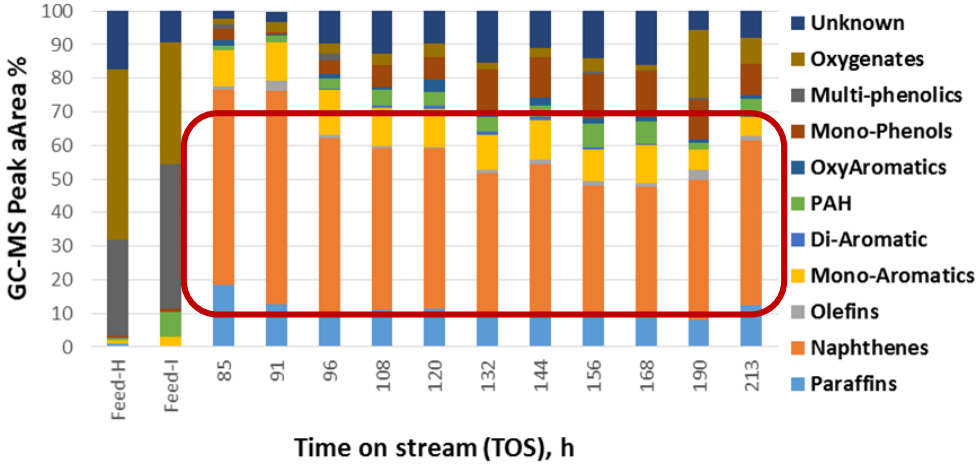






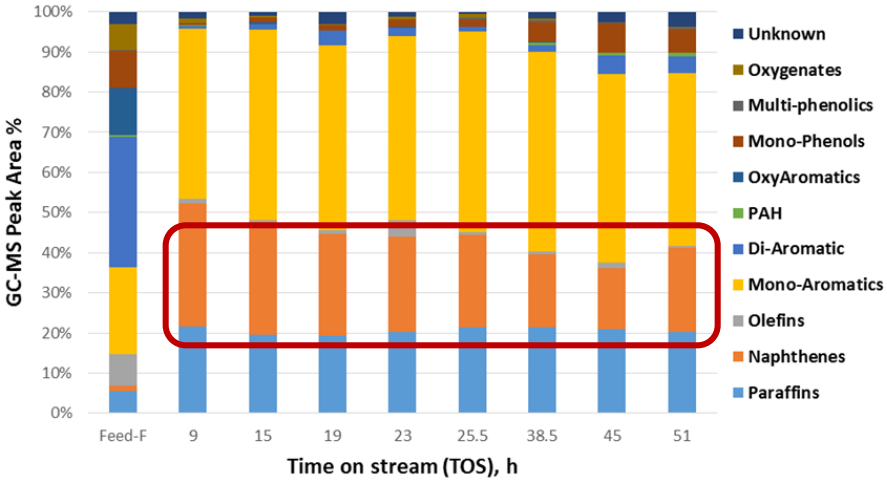
Mante, O. D.; Dayton, D. C.; Gabrielsen, J.; Ammitzboll, N. L.; Barbee, D.; Verdier, S.; Wang, K. G., Integration of catalytic fast pyrolysis and hydroprocessing: a pathway to refinery intermediates and "drop-in" fuels from biomass. **Green Chemistry** 2016, 18 (22), 6123-6135

Bio-crude Hydrotreating: Chemical Composition of HDT oils



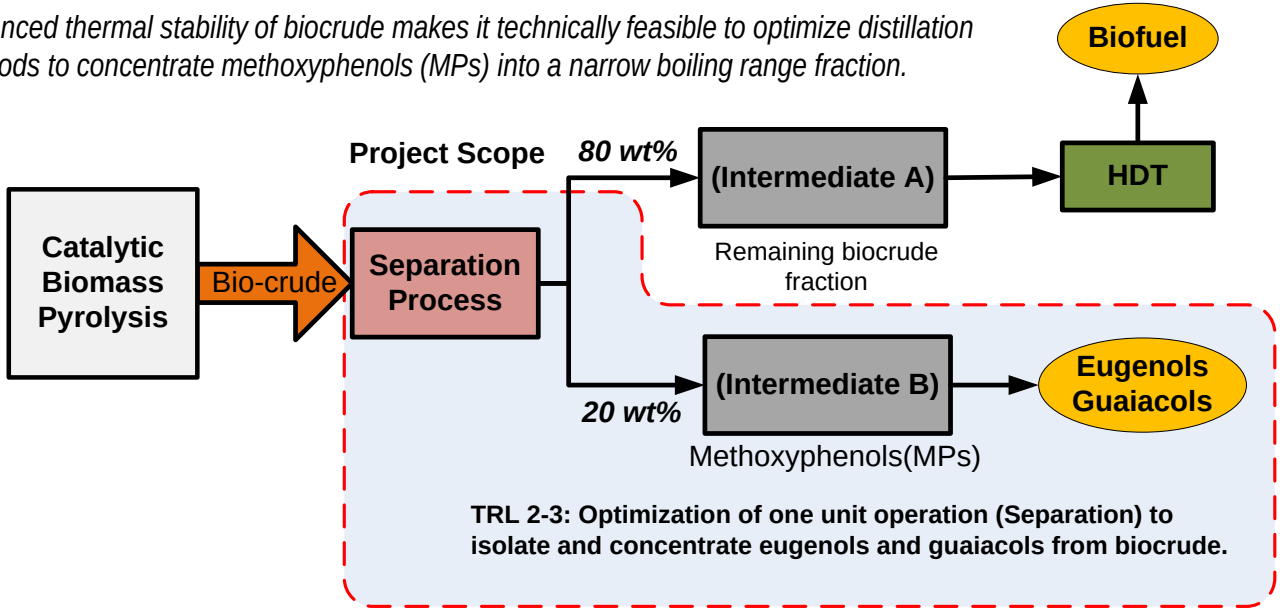
High yield of cyclic alkanes are produced from phenolic-rich feedstocks.

Less cyclic alkanes are produced from aromatic, hydrocarbon-rich feedstocks.



Bio-product Separations Concept

Enhanced thermal stability of biocrude makes it technically feasible to optimize distillation methods to concentrate methoxyphenols (MPs) into a narrow boiling range fraction.

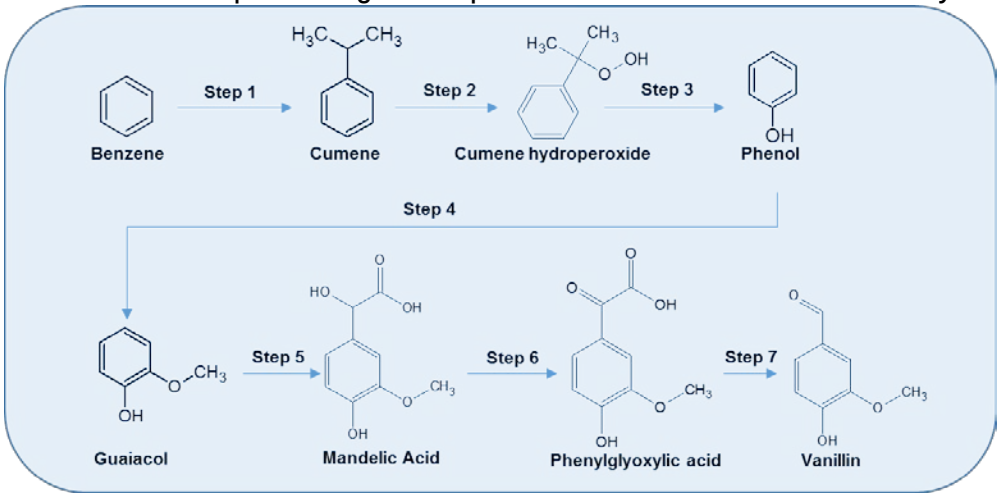


- **Evaluate commercial viability of mixed phenolic fraction as a feedstock for value-added bioproducts**
- **Investigate key separations and chemistries to expand recovered intermediates into multiple markets.**
- **Define technical requirements for product quality and purity.**
- **Demonstrate that remaining biocrude fractions can be upgraded into biofuels.**

Bio-Products Recovery

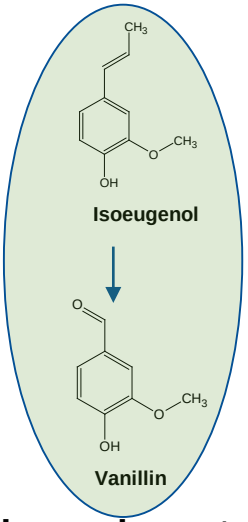
- Co-production of biofuels and methoxyphenols (MPs) in an integrated biorefinery to enhance the economic viability of advanced biofuels technologies
- The inherent structure of biomass contains oxygen and carbon that can be retained in the final products
- RTI CFP Technology produces partially deoxygenated, thermally stable biocrude with oxygen contents between 20 and 25 wt% and contains useful phenolic compounds such as eugenols (up to10 wt%) and guaiacols (up to 6.5 wt%)

Vanillin is an example of a high value product in the food and flavor industry



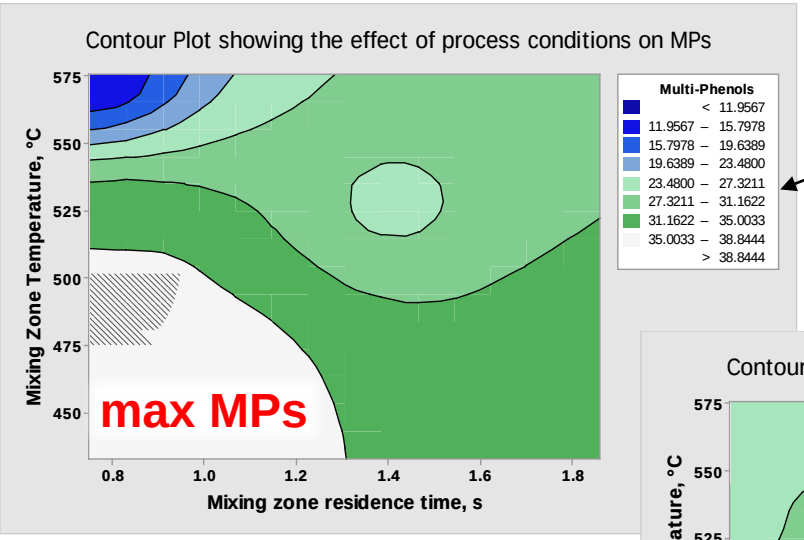
Petroleum route

OR

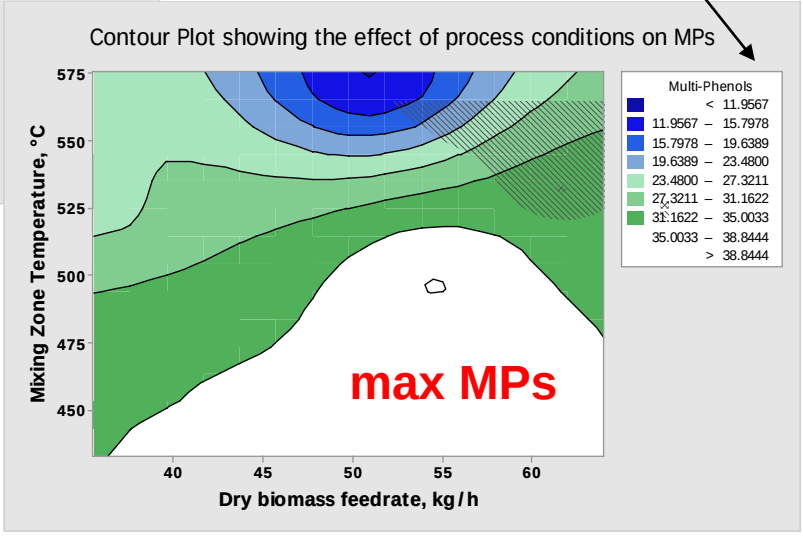


Bio-crude route

Process Conditions influence MPs Concentration



GC-MS
Peak Area %

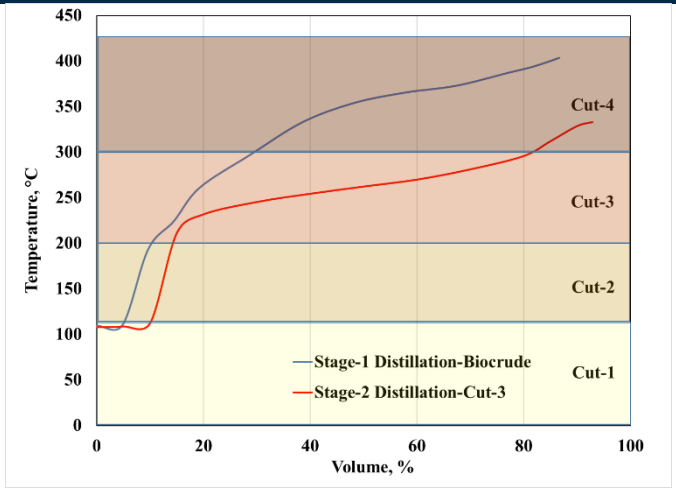


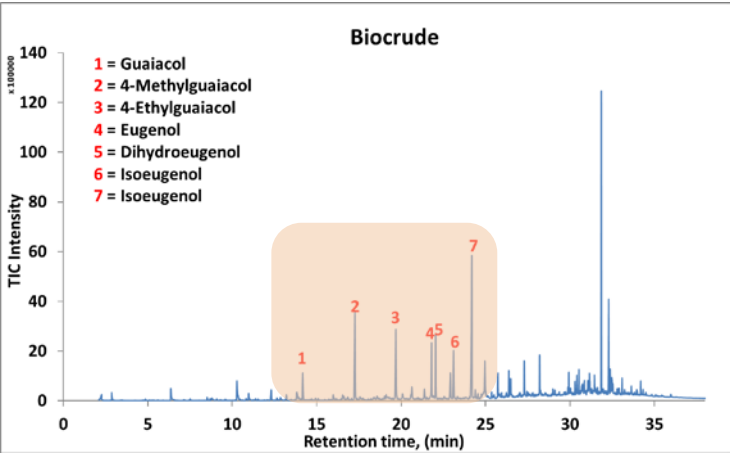
CFP process conditions can be adjusted to maximize MP production

Multi-stage Fractional Distillation

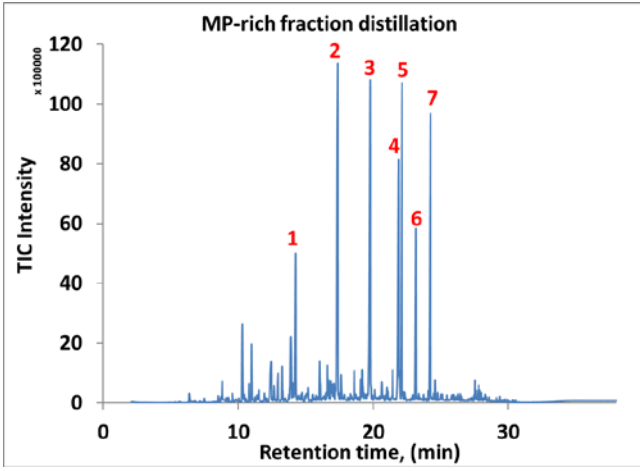
Stage-1 (175-310°C)

Stage-2 (229-285°C)

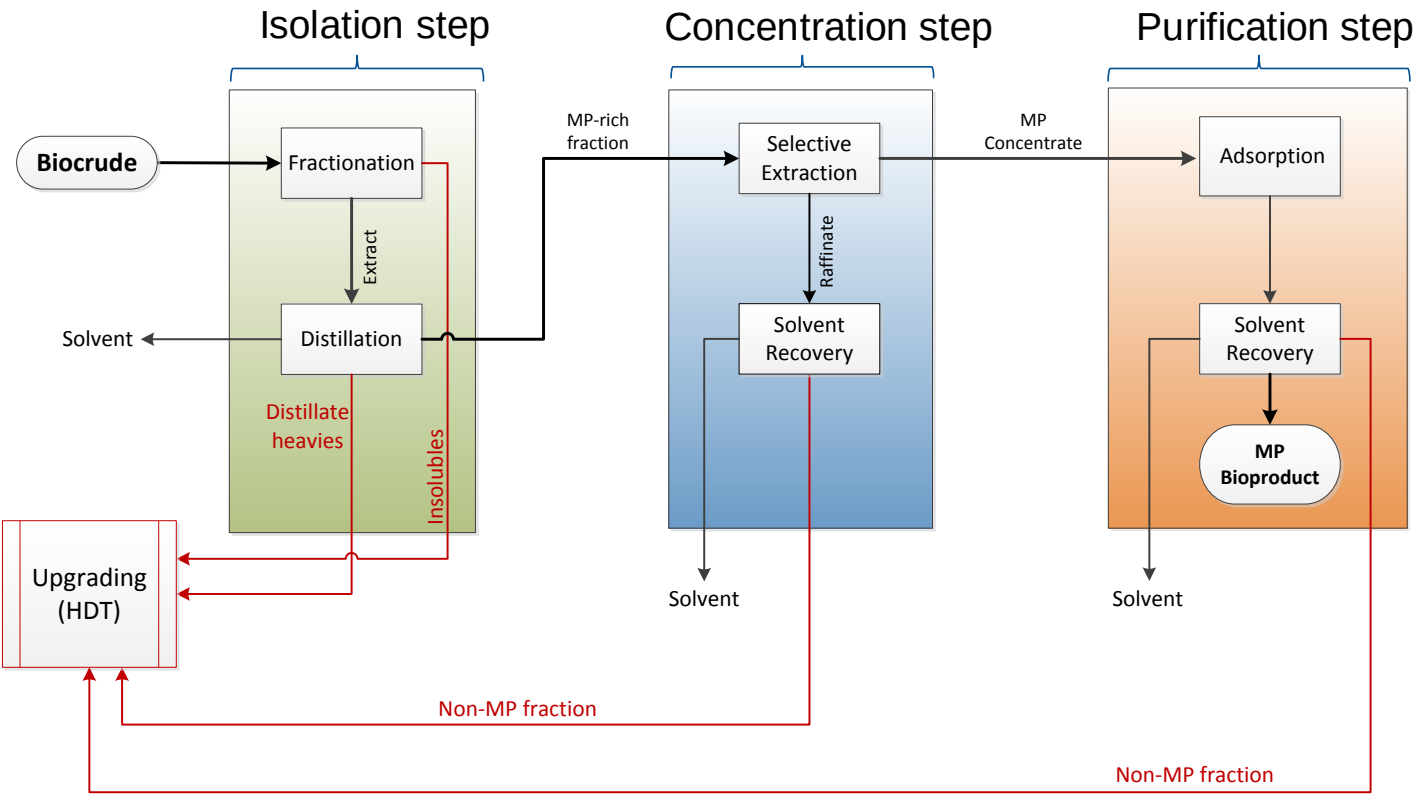




Distillation strategy not efficient for isoeugenol recovery

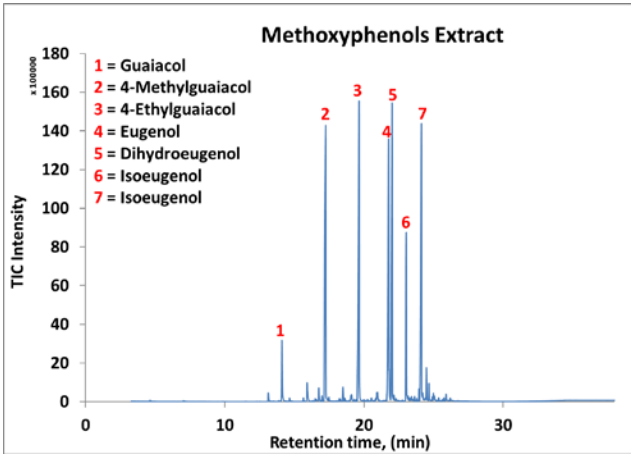


Current Separation Strategy

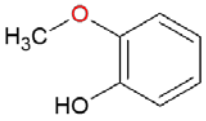


RTI Methoxyphenols Bioproduct

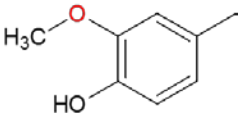
Methoxyphenols bioproduct
(*A potential essential oil*)



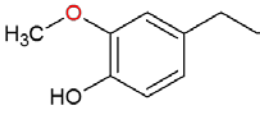
Guaiacols



Peak 1. Guaiacol

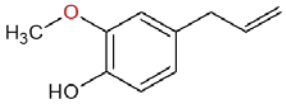


Peak 2. Methylguaiacol

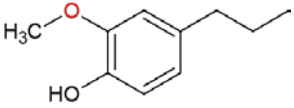


Peak 3. Ethylguaiacol

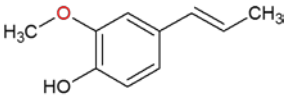
Eugenols



Peak 4. Eugenol



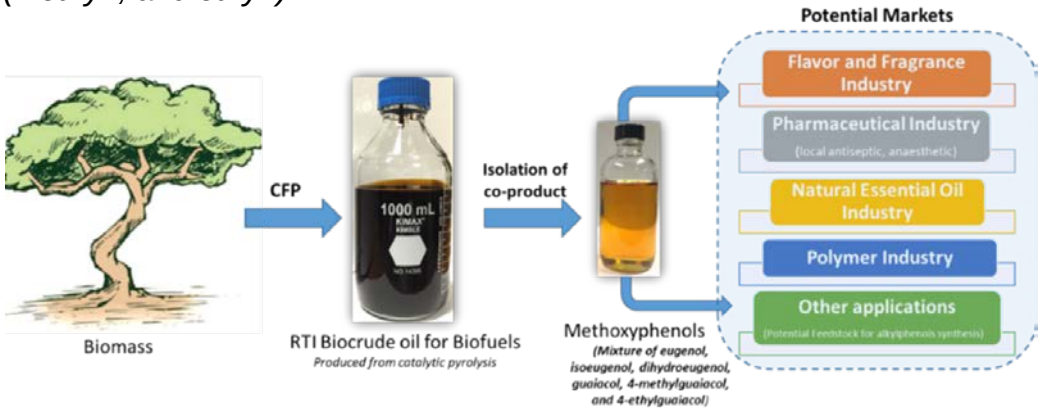
Peak 5. Dihydroeugenol



Peak 6&7. Isoeugenol

Biofuels and Bioproducts

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



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.

- Mixed phenolic fraction has commercial potential as a feedstock for value-added bioproducts with price points based on current markets.
- Preliminary TEA indicates MP yield and product price have largest economic impact. Biofuel production cost can be reduced by 30%.
- Strategic separations and chemistries can be used to expand into multiple markets with defined technical requirements for product quality and purity.
- Remaining biocrude fractions can be upgraded into biofuels.

Acknowledgements

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