Advanced Thermochemical Conversion of Biomass to Biofuels and Bioproducts

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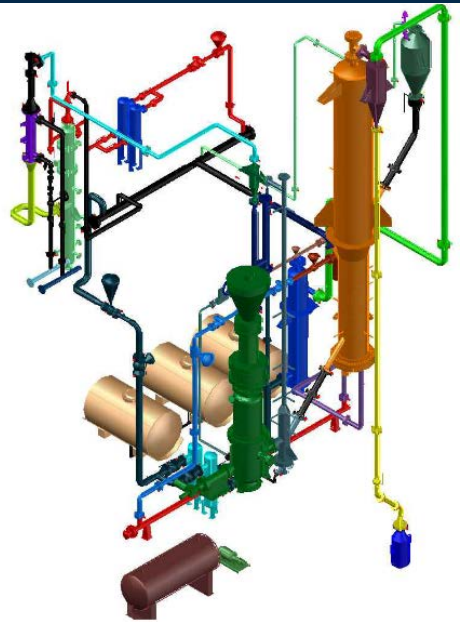
Outline



- Introduction
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  - Hydroprocessing for Biofuels
  - Separation and purification
- Bioproducts Development

delivering **the promise of science**
for global good

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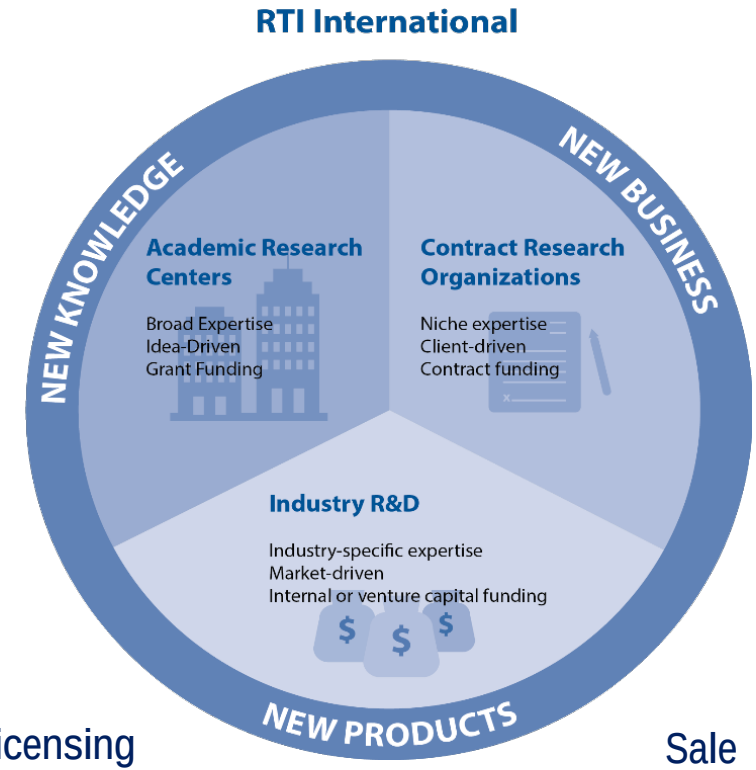
Flexible and Creative Business Relationships with Clients



Licensing

Joint Development

Cost Share Partnership

Sale

Spin-out

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Areas of Research

- Energy Research
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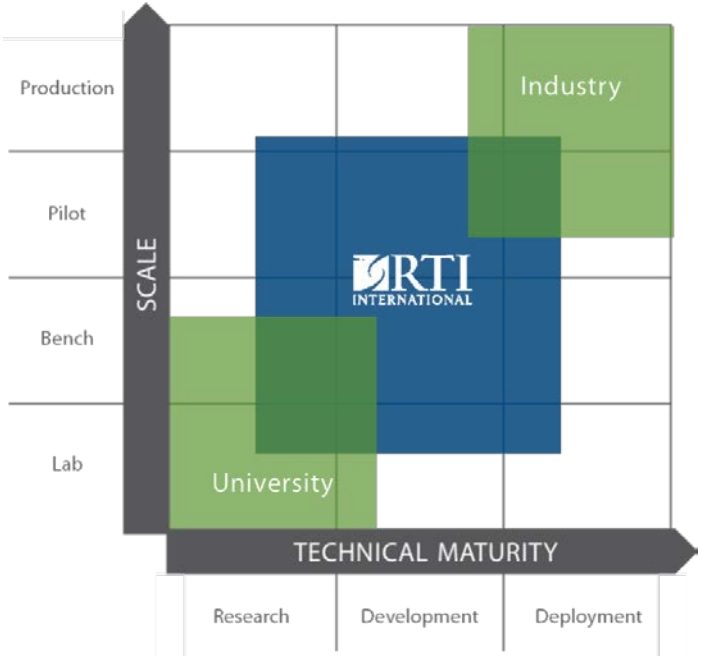
- Environmental Sciences
- International Development
- Social Policy
- Education & Workforce Development
- Health

Research to Impact, In Partnership with Leaders in Academia, Industry & Government



Development of step-out technologies requires **integration of process *and* materials innovation** with understanding of process scale-up

Research & Development

Materials Development
Computational Chemistry
Process Modeling, Simulation & Design
Lab and Bench Testing

Pilot Testing

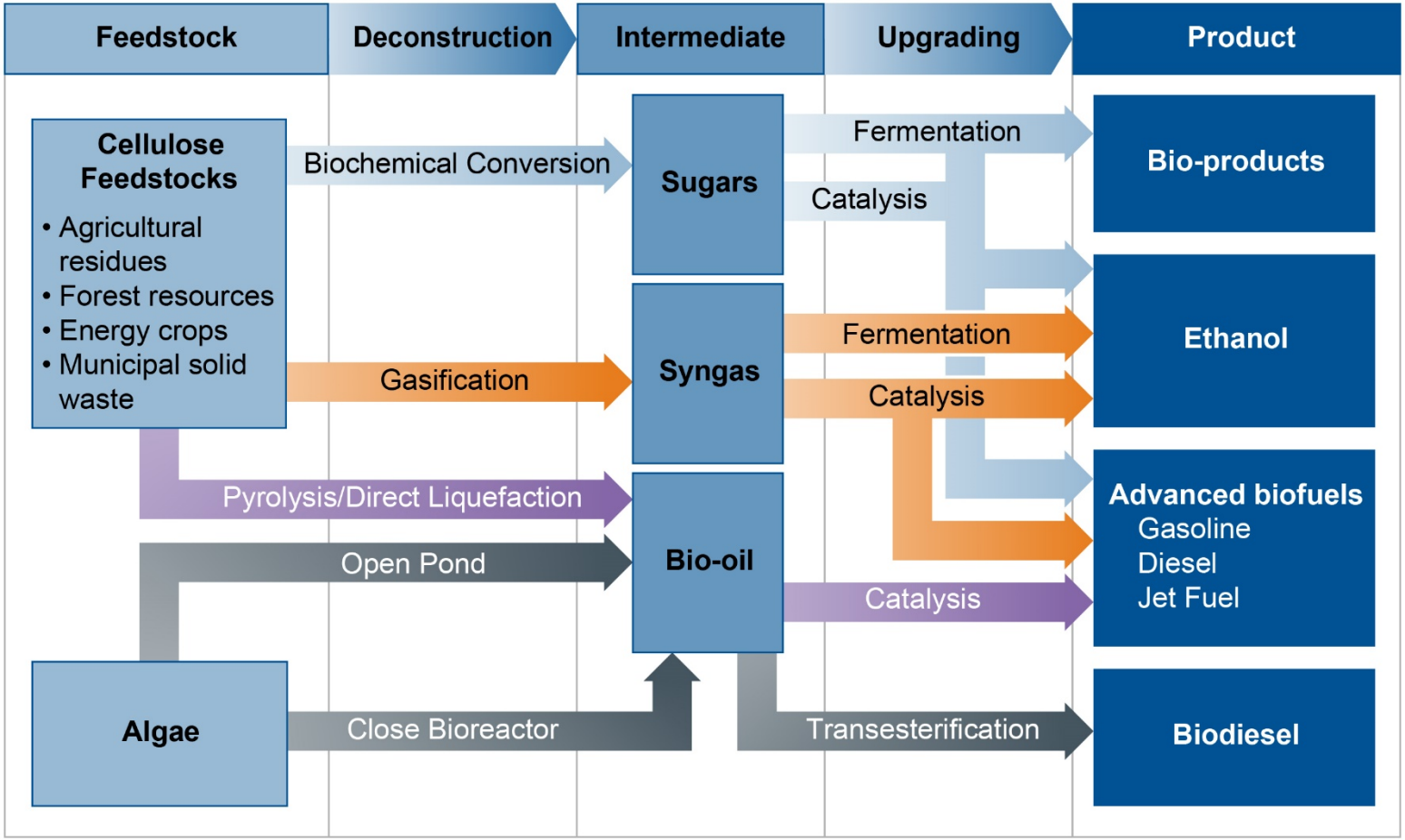
Integrated Process Development
Process Scale-Up

Demonstration & Deployment

Commercialization

Chemical Engineers | Environmental Engineers | Civil Engineers | Chemists

Biofuels Technology Options



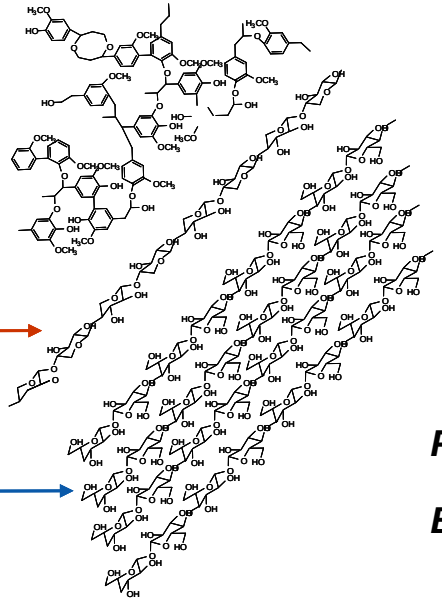
Thermochemical Conversion Process Severity

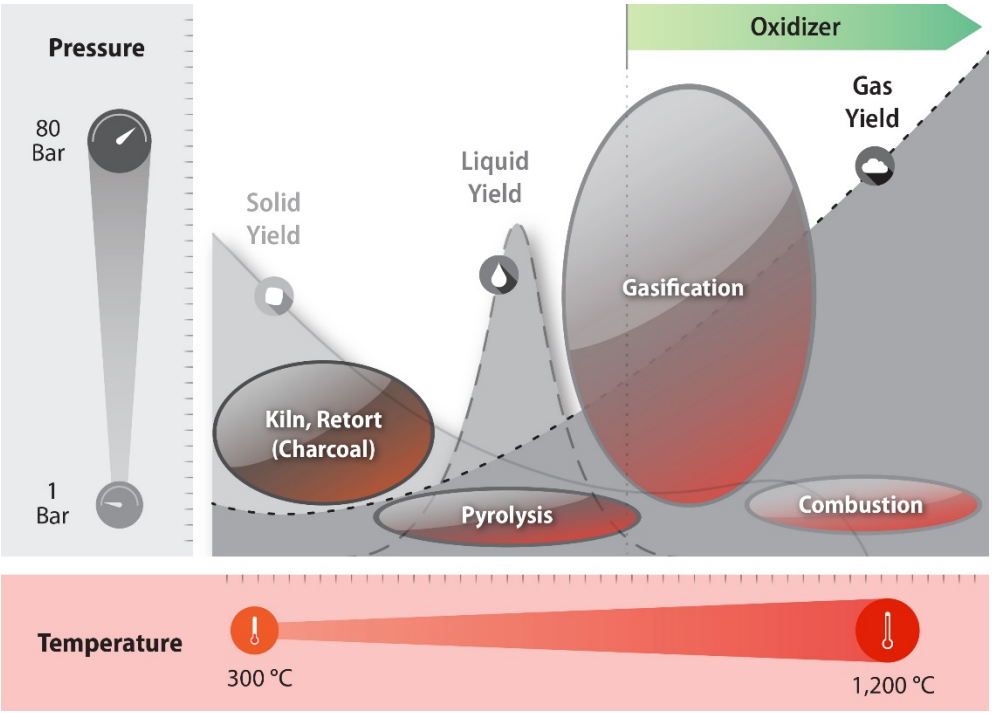
Gasification

- Thermal conversion (partial oxidation) of biomass at elevated temperature and reducing conditions to produce primarily CO, CO_2, and H_2 as products

Pyrolysis

- Thermal conversion (decomposition) of biomass in the absence of oxygen
- In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product

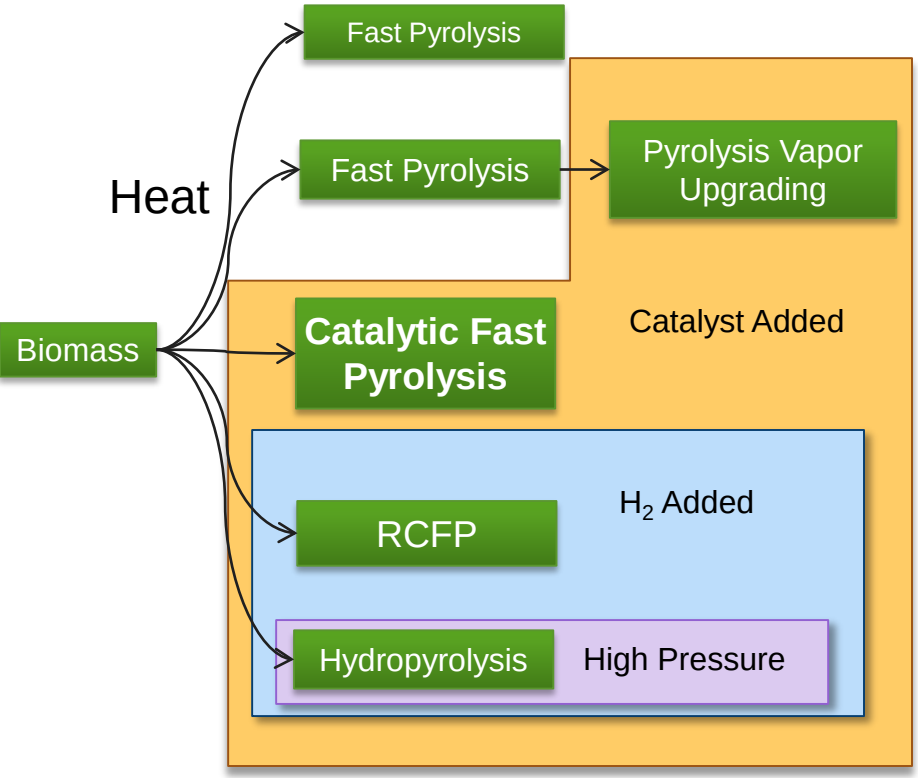


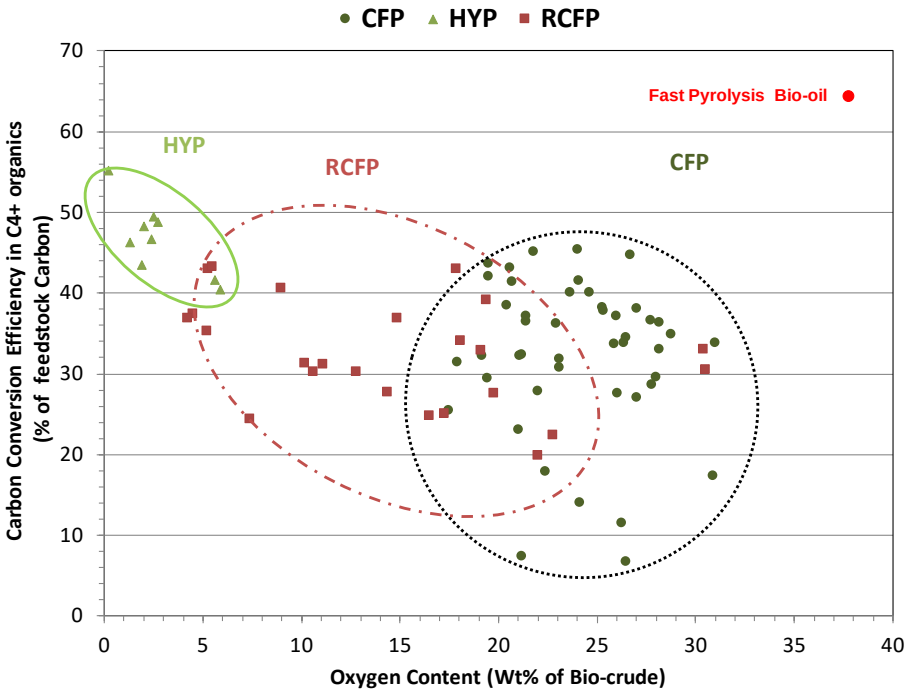


Primary technical challenge for renewable hydrocarbon fuels

Biomass – $CH_{1.8}O_{0.5}N_{0.2}$ ***Gasoline – CH_2***

Pyrolysis Pathways for Advanced Biofuels





Product Quality (wt% O) vs. Yield

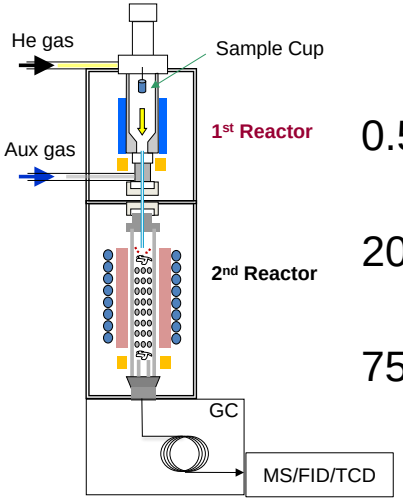
Biomass Pyrolysis Fundamentals - MicroPyrolyzer-GC/MS

Fundamental research to support technology development

- Dual microreactors for in situ or ex situ catalytic pyrolysis studies
- Fundamental chemical understanding of biomass pyrolysis processes

Efficiently screen catalysts and process conditions with real biomass

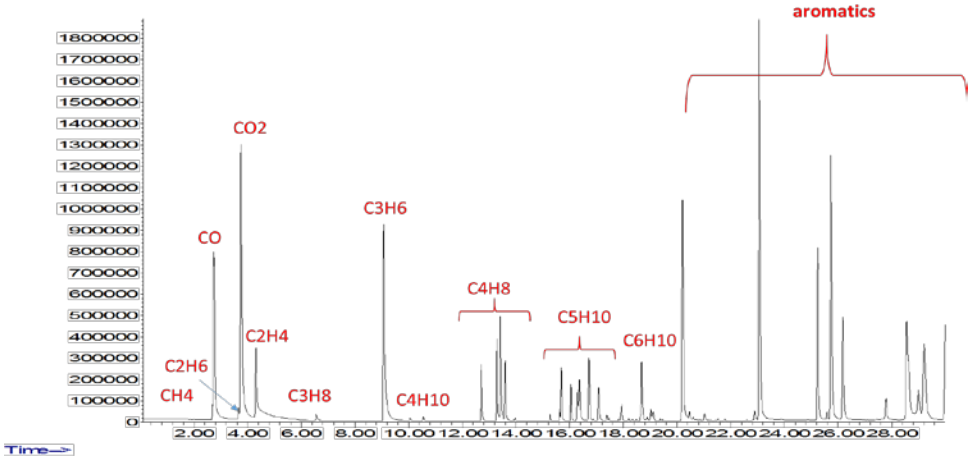
- Rapidly (30 min) characterize small (1 mg) samples
- Good mass balance (>90%)
- Excellent reproducibility (s.d.< 2~3%)



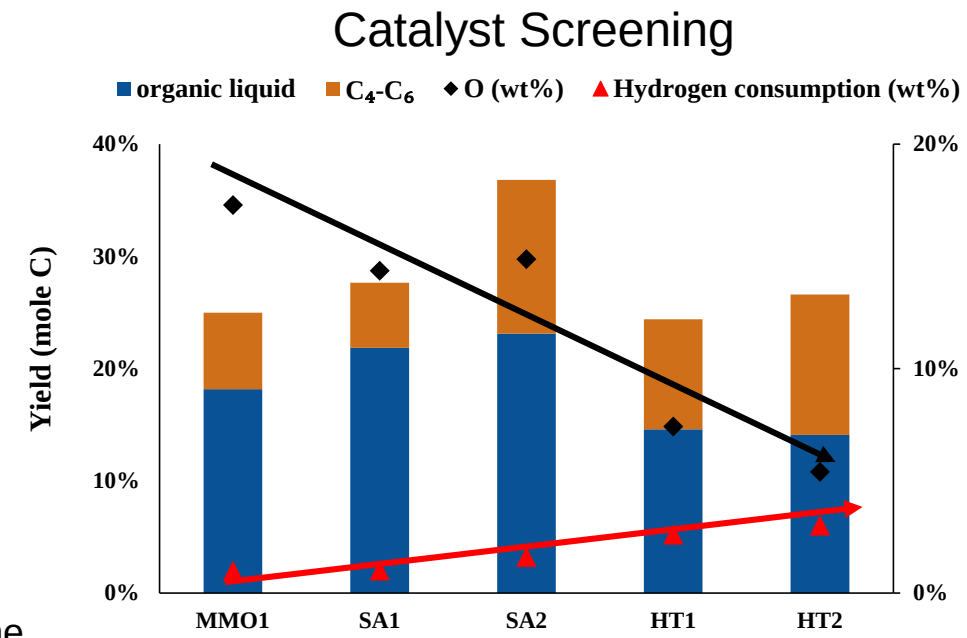
0.5mg pine - 500ºC pyrolysis

20mg MoO_3 catalyst - 450ºC

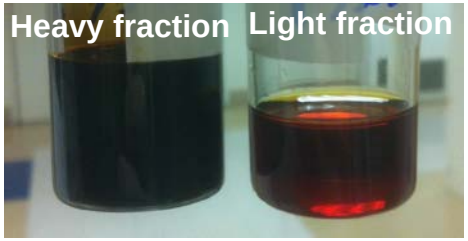
75 ml/min H_2 flow



Process Development and Biocrude Production



- 2.5" fluidized bed reactor with 4" disengagement zone
- Biomass feeding rate: 2-5 g/min
- Liquid collection: 3 condensers and 1 ESP
- Non-condensable gases analyzed by micro GC
- Liquid product analyzed by Karl Fischer titration, elemental analysis, GC/MS



Catalytic Biomass Pyrolysis Scale-up

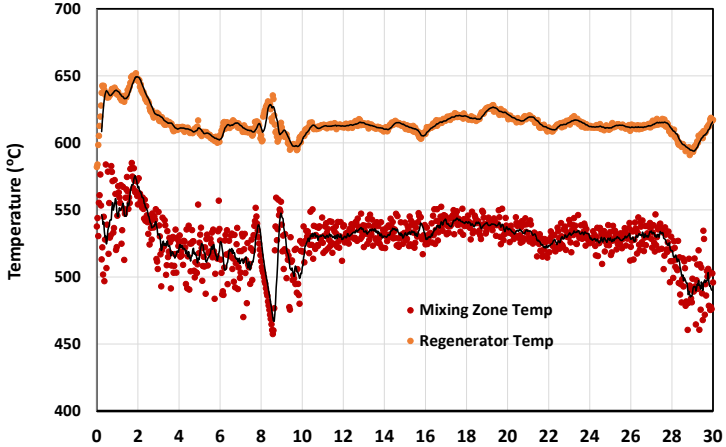
Understand the effect of operating parameters on product yields and quality

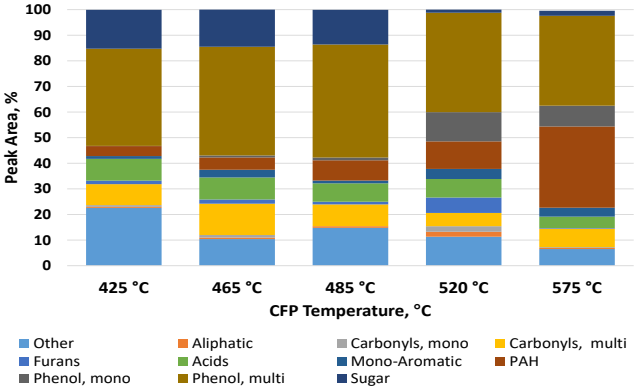
- Pyrolysis temperature (350-500 ºC); Regenerator Temperature (560-640 ºC)
- Residence time (0.5-1.0 s)
- Biomass Feed Rate: 35-70 kg/h
- Catalyst circulation rate (catalyst to biomass ratio)
- Type of biomass

Continuous, long-term operation

- Validate bio-crude yields and quality
- Demonstrate catalyst stability and durability
- Gain operational experience
- Collect engineering design data for scale-up

Produce bio-crude for Upgrading Technology Development and Bioproducts Separations





Waste to Energy - Biosolids Pyrolysis

Sample	Elemental Analysis*					Proximate Analysis*			
	C	H	N	O (diff)	Ash	Moisture	Volatiles	Fixed C	Ash
Milorganite	34.2	5.2	**5.7**	26.0	**28.8**	6.4	54.1	10.6	28.8
Dried Sewage Sludge**	36.9	5.7	**5.3**	26.2	**25.5**	4.0	56.9	13.6	25.5
Fecal sludge	47.5	6.8	**4.8**	25.9	**14.9**	1.7	69.6	13.8	14.9
Loblolly Pine	45.4	6.3	0.15	48.1	0.7	7.8	78.1	14.1	0.0
Corn Stover	44.0	5.9	0.5	47.1	2.5	4.4	77.8	17.8	2.5

*as received basis; ** secondary sludge after anaerobic digester in WWTP

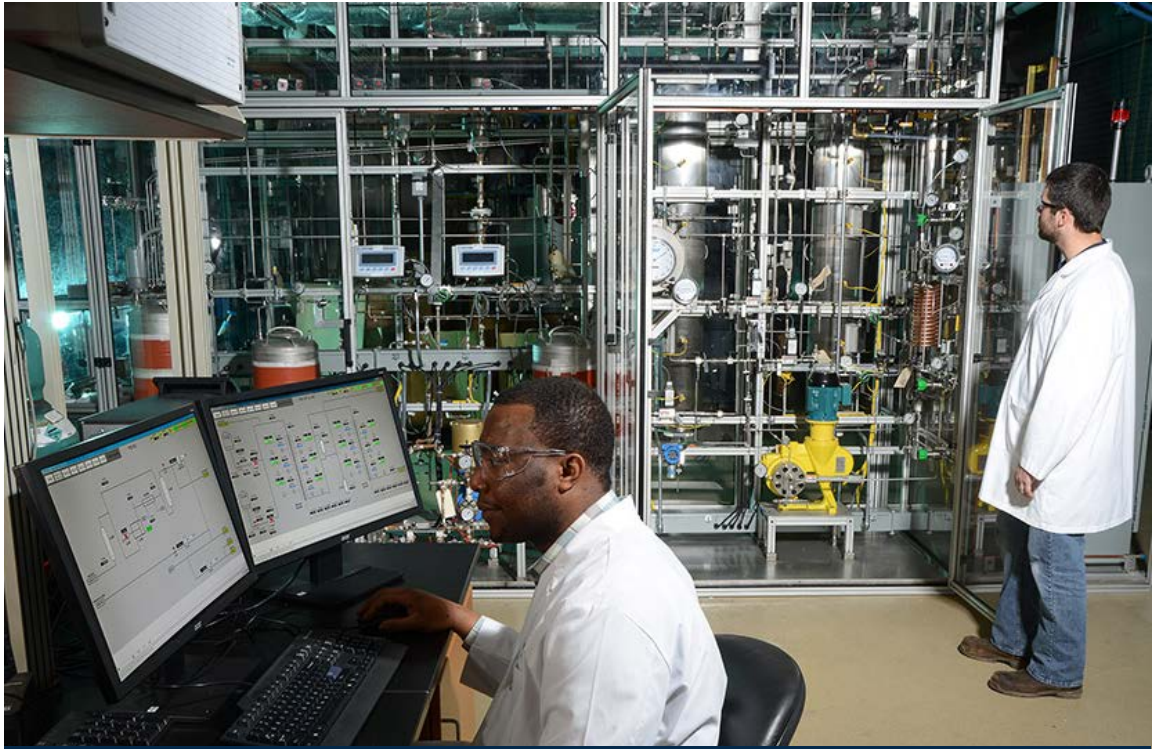
Milorganite™ is a commercial fertilizer produced by Milwaukee Metropolitan Sewage District

Biocrude composition from CFP of two sludge feedstocks

Feedstock	Milorganite	Sludge*
Elemental analysis (wt%)		
C	**69.5**	**73.0**
H	**8.5**	**8.8**
N	**10.0**	**11.1**
O	**12.0**	**7.0**
GC/MS analysis (peak area %)		
aliphatics	**9.1**	**15.3**
aldehydes/ketones	**1.7**	**3.9**
acids	**0.7**	**0.1**
Monoaromatics	**18.5**	**18.1**
PAHs	**22.2**	**8.8**
phenols	**9.0**	**3.5**
Nitrogen compounds	**38.0**	**48.4**

High nitrogen content is a challenge for biocrude upgrading but a potential for bioproduct recovery

Bio-crude Upgrading - Hydrotreating



UNIT OPERATIONS

- Oil feed system including pumps and flow control
- Gas feed system
- Reactor system
- Separator system
- Gas and liquid sampling system

Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450C
Max. operating temperature: 430C
Max. operating pressure: 170 bar (2500 psig)

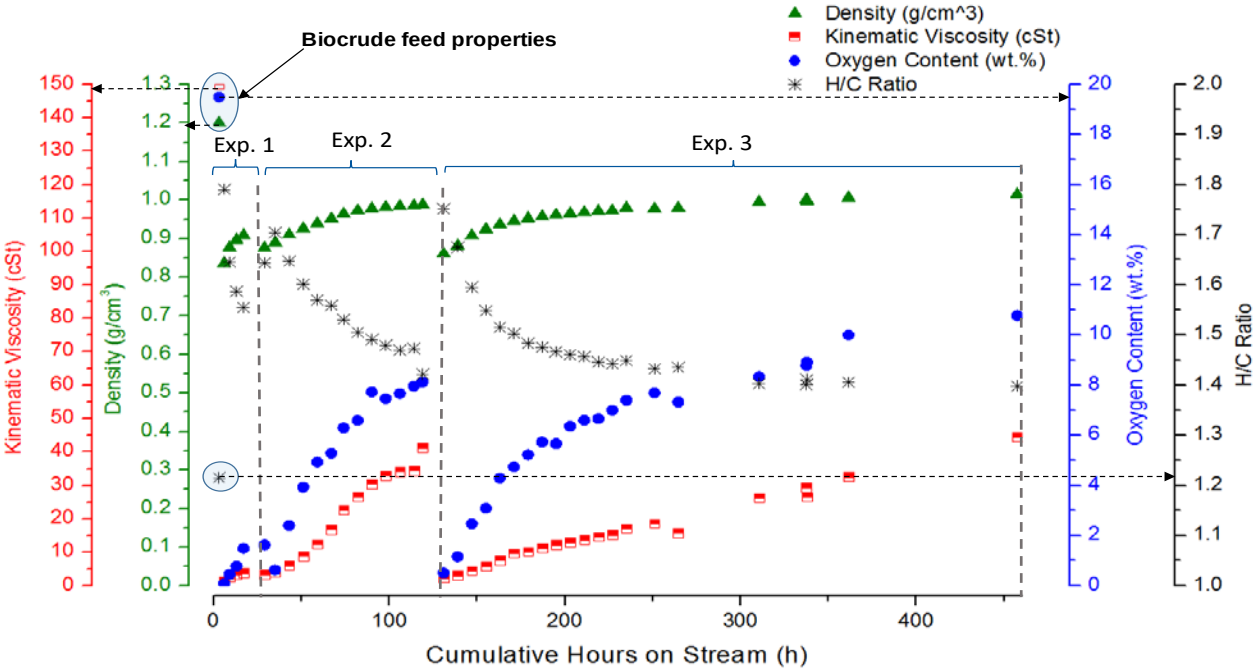
Investigate the impact of bio-crude quality in the hydroprocessing step

- 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

Effect of Hydrotreating Conditions

Condition	Experiment-1	Experiment-2	Experiment-3
Pressure (bar)	100	138	138
Average temperature (°C)	350	300	290
LHSV (h^{-1})	0.5	0.25	0.25
H_2/oil ratio (Nl/l)	2000	3000	3300
Catalyst dilution (Vol %)	40	60	60
TOS (h)	16	103	365

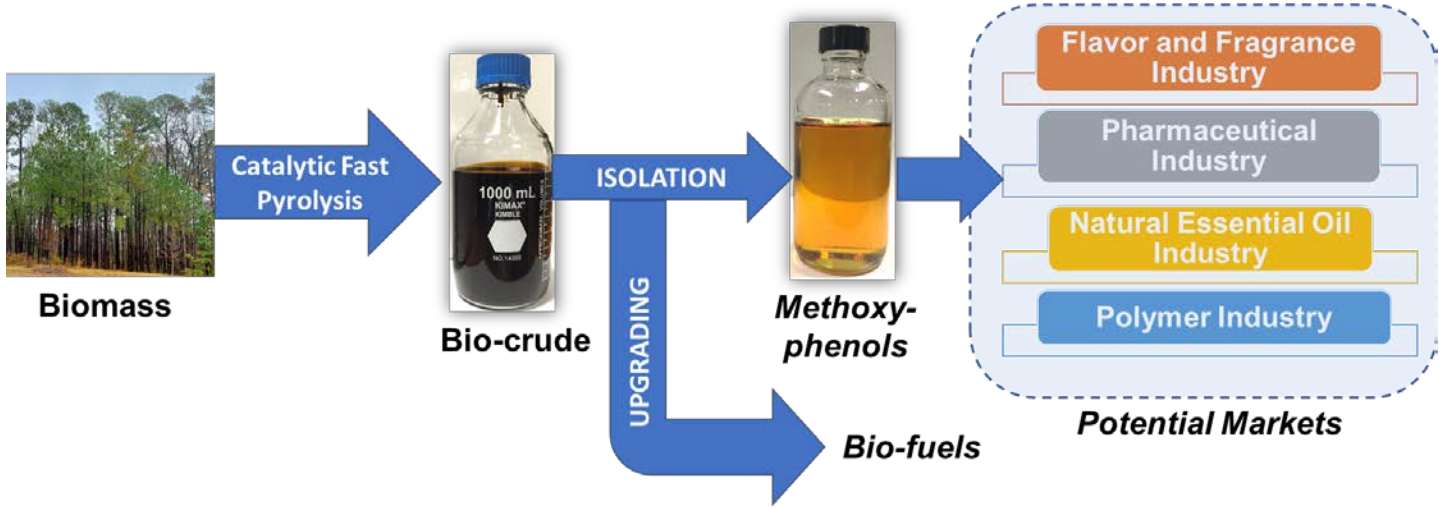


Mante, O. D.; Dayton, D. C.; Gabrielsen, J.; Ammitzboll, N. L.; Barbee, D.; Verdier, S.; Wang, K. G., Integration of catalytic fast pyrolysis and hydroprocessing: a pathway to refinery intermediates and "drop-in" fuels from biomass. **Green Chemistry** 2016, 18 (22), 6123-6135

Biofuels and Bioproducts

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.

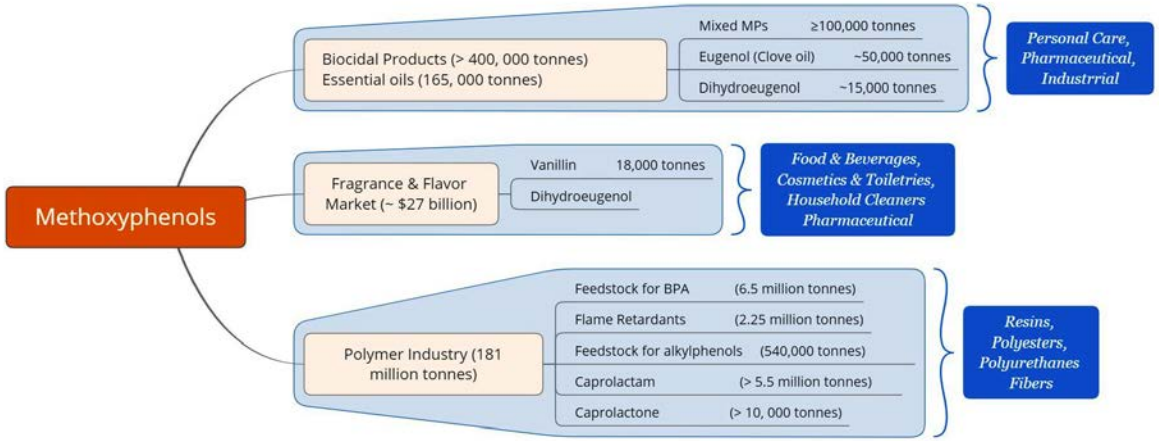


Methoxyphenols as Bioproducts

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

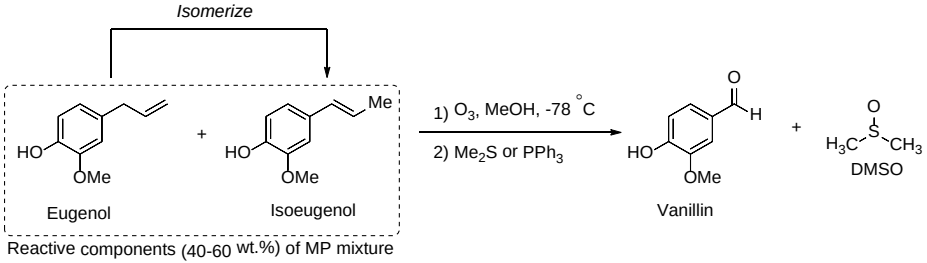
Yield/Selectivity of MPs

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



Feedstock for many applications with large market sizes.
Purity and quality can be tailored to end use applications.

- Relatively high methoxyphenol concentration in biocrude (9-15 wt%).
- Process conditions and feedstock can be adjusted to maximize MP production.
- Oxygenates attract higher market price (>$2/kg) than hydrocarbons (BTX) made from biomass
- Building blocks for other products with simpler and cheaper synthetic routes compared to using petroleum precursors.



Reactive components (40-60 wt.%) of MP mixture

Technical Approach for Separations

Development and Optimization of an efficient and economical separation strategy for MPs recovery from biocrude

Distillation

- High residue formation
- Limited by boiling point
- Low purity

Solvent Extraction

- Non-selective
- High solvent use
- Precipitate formation in alkaline extraction
- Low recovery

Adsorption Chromatography

- Large solvent volumes
- High rate of media exhaustion
- Many stages

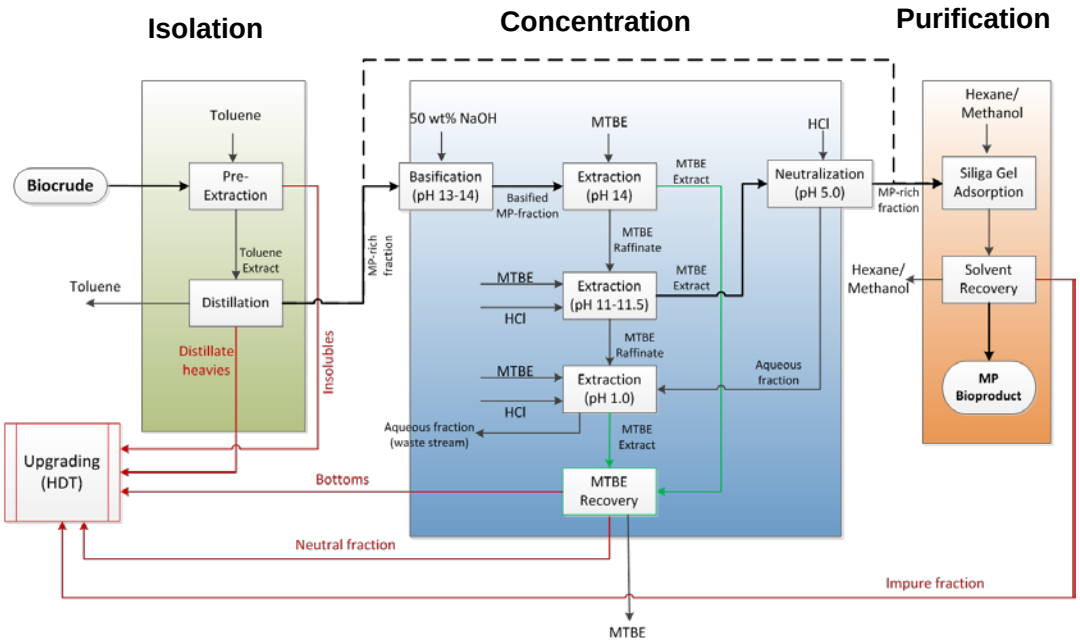
Approach

- 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 an efficient (≥ 75wt%), cost competitive separation strategy to obtain high purity (≥ 90%) MPs.
- Demonstrate process scalability

Bench-top Separation Strategy Development



Three Separation Strategies

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

Technical Targets

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

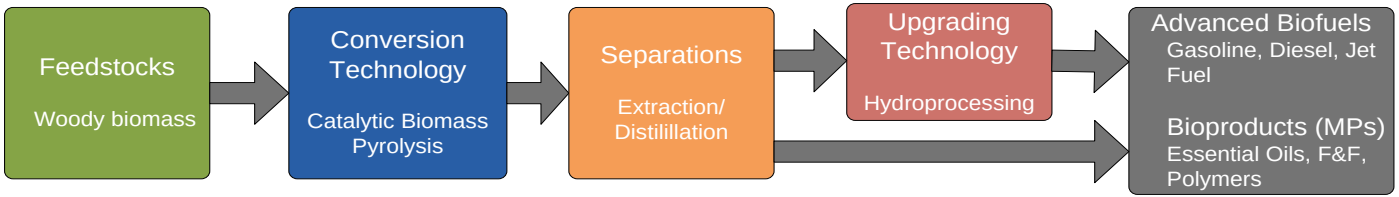
Isolation: Selective aromatic solvent (toluene) extraction for separating MPs from biocrude followed by distillation to obtain a fraction boiling within180 and 320 °C. **45-50 wt%** concentration of the MPs at overall recovery efficiency of 78-99 %.

Concentration: Alkaline extraction of recovered distillate exploiting differences in pKa of the various phenolics and compounds in the isolated MP-rich fraction. Alkaline extraction at pH 11.5 was optimal for concentrating the MP-fraction with more than 90% efficiency. A product containing up to **86 wt% MPs** can be recovered.

Purification: Gradient elution method over silica gel to separate targeted MPs from other phenolic components. Bio-product with **97 wt% MPs** with 85-97% recovery efficiency.

Summary of RTI R&D Activities

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

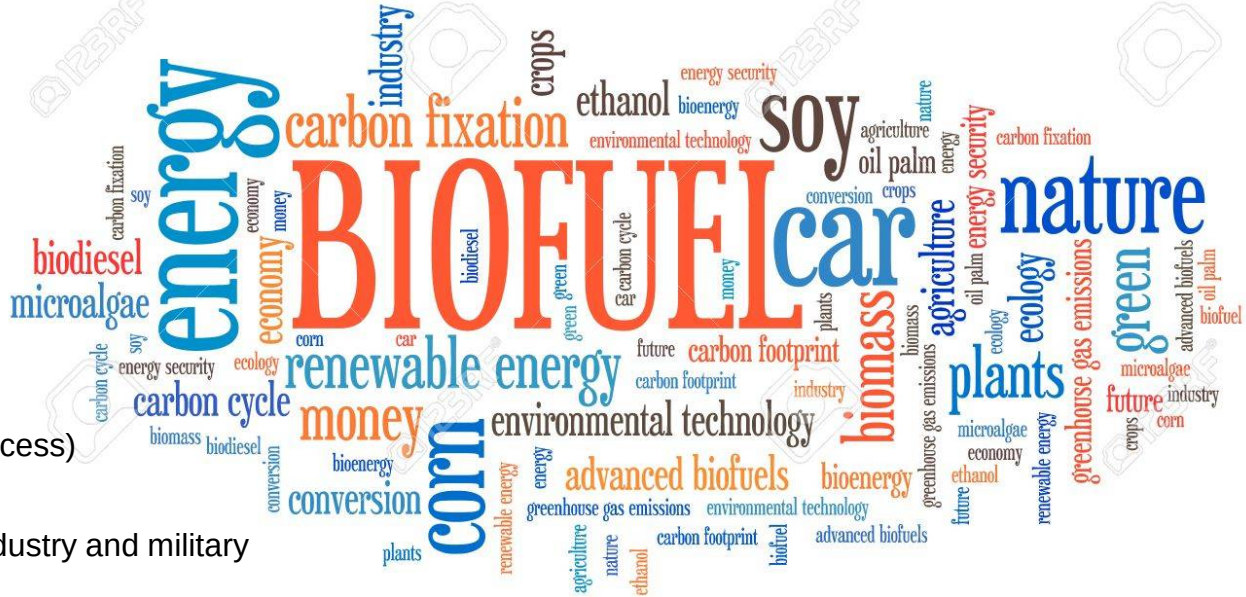
1) Evaluate the impact of bio-crude quality on the hydroprocessing step
2) Evaluate co-processing opportunities
3) Evaluate hydrogen demand of the integrated process
4) Maximize biofuels yield

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

Continuing Challenges

- Technical barriers
  - Improve biofuel yields
  - Maximize carbon efficiency
  - Minimize hydrogen consumption
  - Feedstock quality vs. technology robustness
- Economics: How do we become cost competitive? ($3/gge)
  - Tax credits and subsidies (short term)
  - Reduce CAPEX – optimize scale
  - Leverage integration opportunities
  - Reduce feedstock costs
  - High value co-products
- Sustainability
  - GHG emissions reduction
  - Waste-to-energy
  - Direct and indirect land use changes
  - Water consumption (feedstock and process)
- Market acceptance
  - Early adopters: commercial aviation industry and military
  - Blendstocks and fuel properties
  - Infrastructure compatibility



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Industry Partners

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- Kim Knudsen
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