DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Bio-crude Production and Upgrading to Renewable Diesel

WBS 3.5.1.301

April 4, 2023

System Development and Integration

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RTI International

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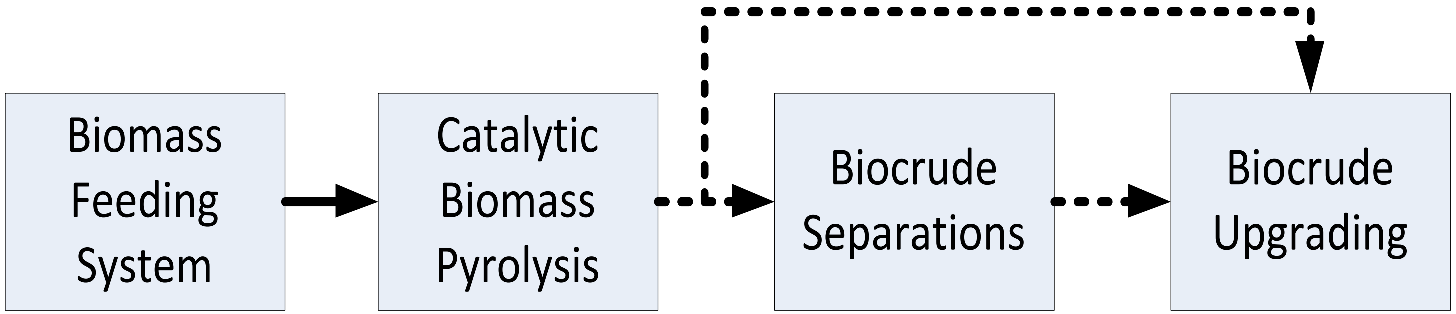
Project Overview

Project Goal

Explore synergies between innovative technology solutions for biomass feedstock preparation, pilot-scale catalytic pyrolysis, biocrude separations, and biocrude hydroprocessing to improve the carbon efficiency and process economics for making <u>100 gallons of drop-in renewable diesel</u>



Summary: Project will be executed in three budget periods separated by Go/NoGo decision points with a total of ten tasks.

The focus of the project is to:

1) Optimize the physical and chemical characteristics of biomass feedstock, in a commercially-viable manner, to maximize partially deoxygenated biocrude yields (independent of oxygen content) in catalytic biomass pyrolysis
2) Improve biocrude upgrading efficiency (reduce reactor fouling and increase time-on-stream) by fractionating the liquid intermediate and independently hydroprocessing each fraction to maximize biofuel production.

Targets

- Achieve 40% improvement of the current overall carbon efficiency of biofuel production in catalytic pyrolysis pathway
- Reduce the cost of biofuel production by at least 30%
- Demonstrate that the renewable diesel pathway has 50% less GHG emissions compared to fossil-derived diesel

Approach

BP1 - Initial Verification (award date October 2018, completed April 2020)

- Review and experimentally verify baseline data and project targets provided in the Block Flow Data.
  - Go/No-Go Decision: Validate technical data, performance metrics, and targets for the proposed research. Produce at least 10 gallons of biocrude (< 30 wt%O) with 20 wt% yield; separate biocrude into 3 fractions (solvent-soluble, water soluble, and pyrolytic lignin) with less than 5% residual losses; and upgrade biocrude in a pilot-scale hydroprocessing unit for at least 100 continuous hours.

BP2A – Biocrude production, separations and upgrading (completed October 2021)

- Prepare at least 250-kg of multiple biomass feedstocks and deliver to RTI for pilot CFP experiments to produce up 10 gallons of biocrude from each feedstock
- Fractionate biocrude and upgrade individual fractions
- Update TEA with experimental data for feedstock preparation, CFP, separations, and upgrading.
  - Go/No-Go Decision: Updated TEA shows improved biomass pyrolysis pathway reduces biofuel production cost by 30%. LCA shows that renewable diesel produced have 50% less GHG emission compared to fossil-derived diesel.

BP2B – Continued biocrude production and upgrading to renewable diesel blendstock (approved to continue August 2022)

- Feedstocks: Hardwood (Alder) Crumbles (1mm, 2mm, 4mm), Forest Residuals from INL
- Process Development: Increase residence time to improve conversion; optimize aqueous recycle for improved product recovery; complete100 hour run
- Separations and Upgrading: Alternate hydrotreating catalysts and catalyst loading; 500 hour run changing temperature to maintain catalyst activity; ASTM fuel testing
- Final TEA and LCA
  - Final Project Goal: Biocrude upgrading to produce up to 100 gallons of a diesel blendstock that meets ASTM D975 specifications. $3.00 MFSP from TEA and 50% GHG reduction from LCA

Feedstock Preparation Summary

Forest Concepts LLC

- Novel rotary shear Crumbler® technology
- 1mm, 2mm, and 4mm Douglas Fir Crumbles. ~1600 lbs of each
- Additional preparation of 1mm (1674 lbs) and 2mm (1860 lbs) Douglas Fir Crumbles
- 3880 lbs hardwood (Alder) 1mm and 2mm Crumbles
- Completed preliminary TEA for feedstock preparation

Idaho National Lab/Biomass Feedstock National User Facility

- Define quality metrics/variables for mechanical feedstock processing
- Forest Residues initial preparation and delivery – 2000 lbs received

Samples (~1 ton each)	Processing / Notes
Forest Residues	
Forest Residues	
Forest Residues	
50/50 Clean Pine / Residues	
50/50 Clean Pine / Residues	
75/25 Clean Pine / Residues	
25/75 Clean Pine / Residues	
50/50 Clean Pine / Residues	

1TPD CFP Biocrude Production Summary

Technical Accomplishments:

- 99.3 gallons of biocrude from CFP of 1mm (9.5 gal), 2mm (86.3 gal) , and 4mm (3.5 gal) Douglas Fir Crumbles (4856-kg) in the project
- Installed aqueous phase recycle to eliminate freshwater consumption and reduce volume of aqueous stream by 84%
- ~14 gallons of solvent extracted biocrude total

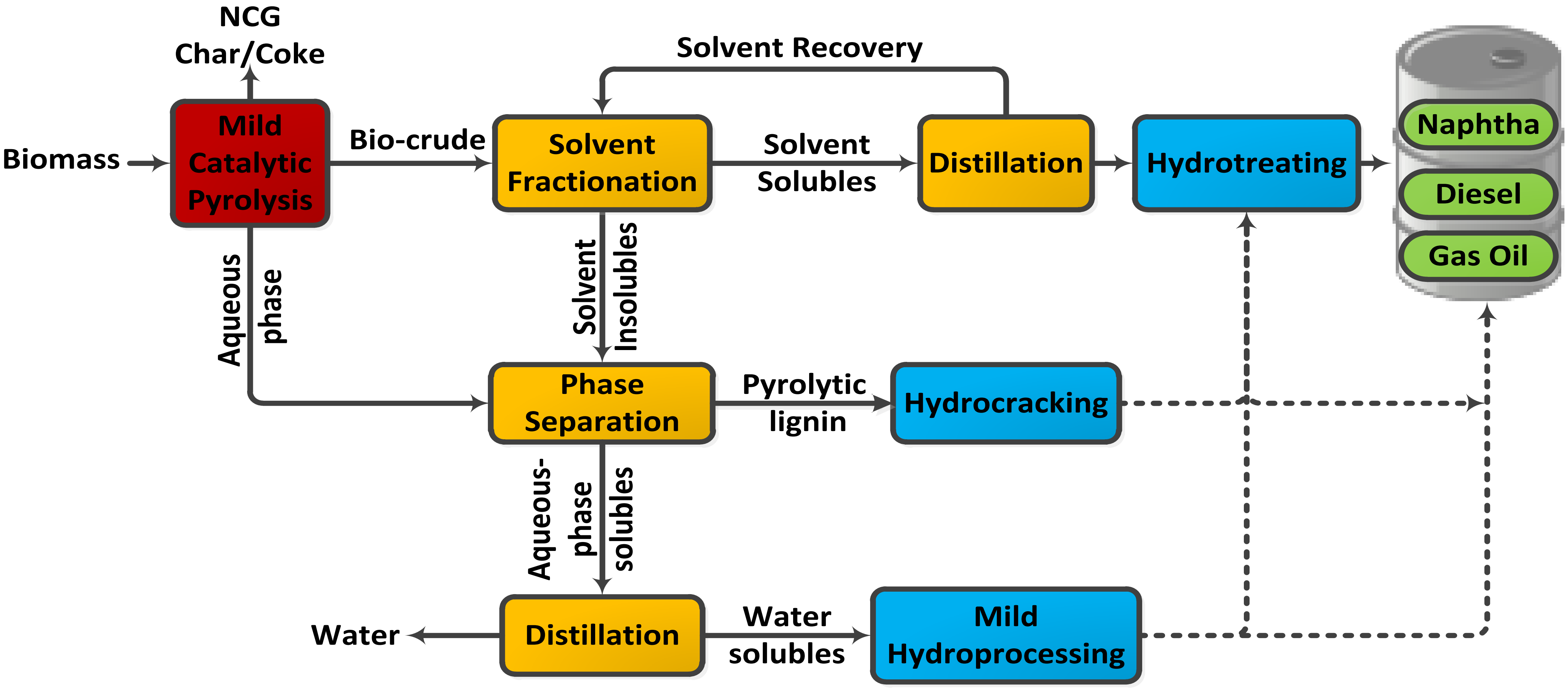
	1mm Douglas fir	2mm Douglas fir	4mm Douglas fir
Pyrolysis Temperature	***480***	***480***	***520***
Total Fed (kg)	527	603	403
Collection Point	Carbon Balance		
Total	96%	98%	96%
Ash pot	11%	12%	11%
Separator Solids	10%	13%	13%
Cold Filter Organic		1%	
Cold Filter Aqueous	5%	3%	8%
Hot Filter Organic	12%	10%	7%
Pyrolysis Gas	9%	9%	14%
Regen Gas	39%	43%	31%
Aqueous Recycle	10%	6%	12%
Liquid	27%	20%	27%
Solid	60%	68%	55%
Gas	9%	9%	14%

Aqueous Recycle Summary

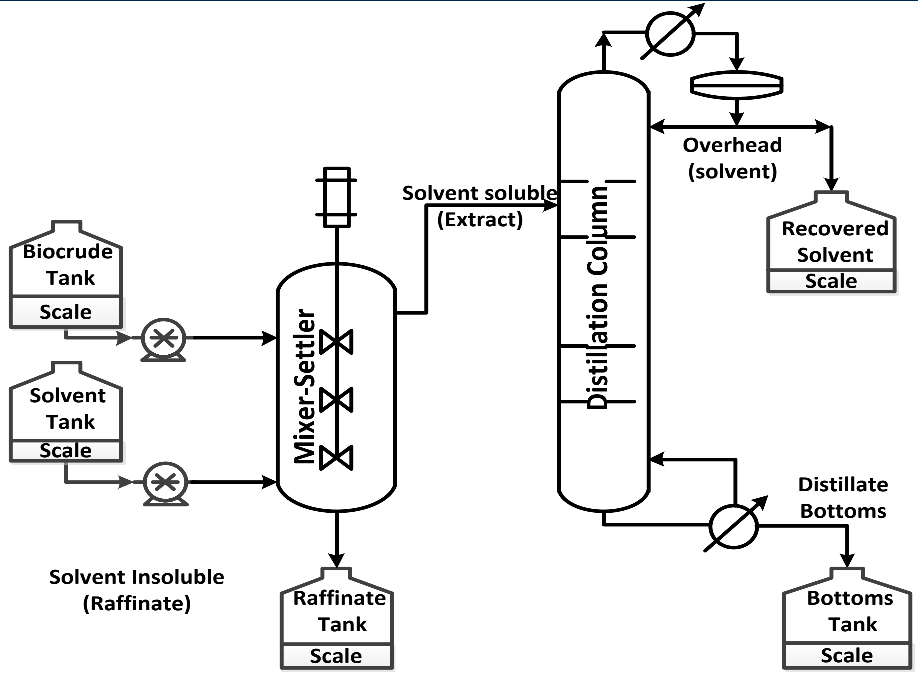
	2mm Douglas Fir Crumbles Average feeding rate – 103 lb/hr Total run time – 16.7 hr				2mm Douglas Fir Crumbles Average feeding rate – 127.3 lbs/hr Total run time – 6.4 hr			
	Mass Balance (kg)			Carbon balance	Mass Balance (kg)			Carbon balance
	Input	Output	Δ		Input	Output	Δ	
Totals	1635.8	1554.4	93%	99%	546.3	582.0	107%	98%
Catalyst		39.9						
Biomass	762.6				370.5			
Ash pot		56.1	3.4%	11%		31.7	5.8%	12%
Separator Solids		146.3	8.9%	12%		66.7	12.2%	13%
Cold Filter Organic		10.0	0.6%	2%		1.8	0.3%	1%
Cold Filter Aqueous		178.5	10.9%	4%		96.8	17.7%	3%
Hot Filter Organic		77.7	4.8%	12%		33.8	6.2%	10%
Day Tank		963.9	58.9%	3%		82.6	15.1%	6%
Pyrolysis Gas		82.0	5.0%	9%		40.2	7.4%	9%
Regen Gas			0.0%	47%		164	30.0%	43%
Water	873.2							
Regen Oxygen					119.0			
Aqueous Recycle					56.8	64.43	11.8%	0.3%

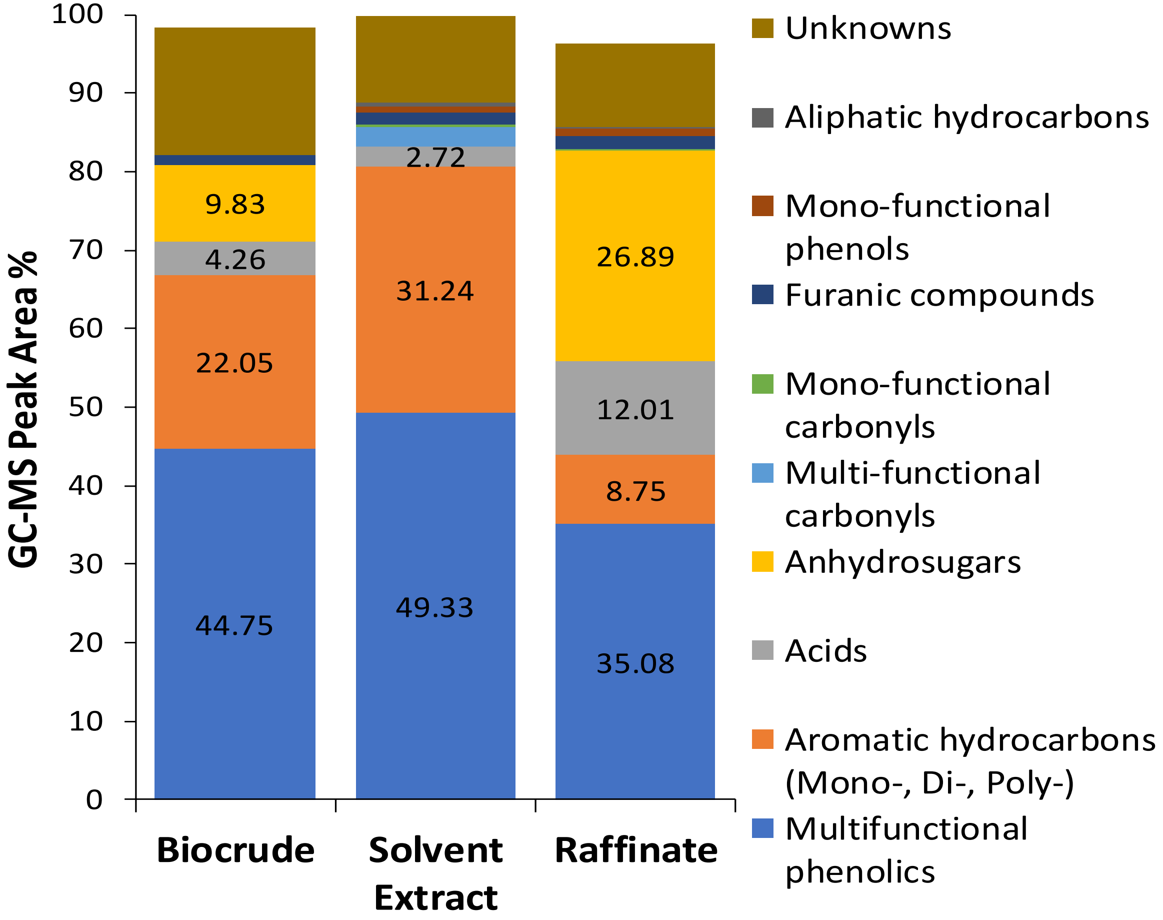
Separations and Upgrading

- Fractionate CFP liquid into different major functionality streams
- Utilize distinct suitable catalysts and process conditions to promote targeted hydroprocessing chemistries for efficient processing into biofuels.



Biocrude Separations





Solvent Extraction

INPUT	Mass (kg)
Biocrude	26.1
Solvent	29.3
OUTPUT	**Mass (kg)**
Raffinate	22.6
Extract	32.6

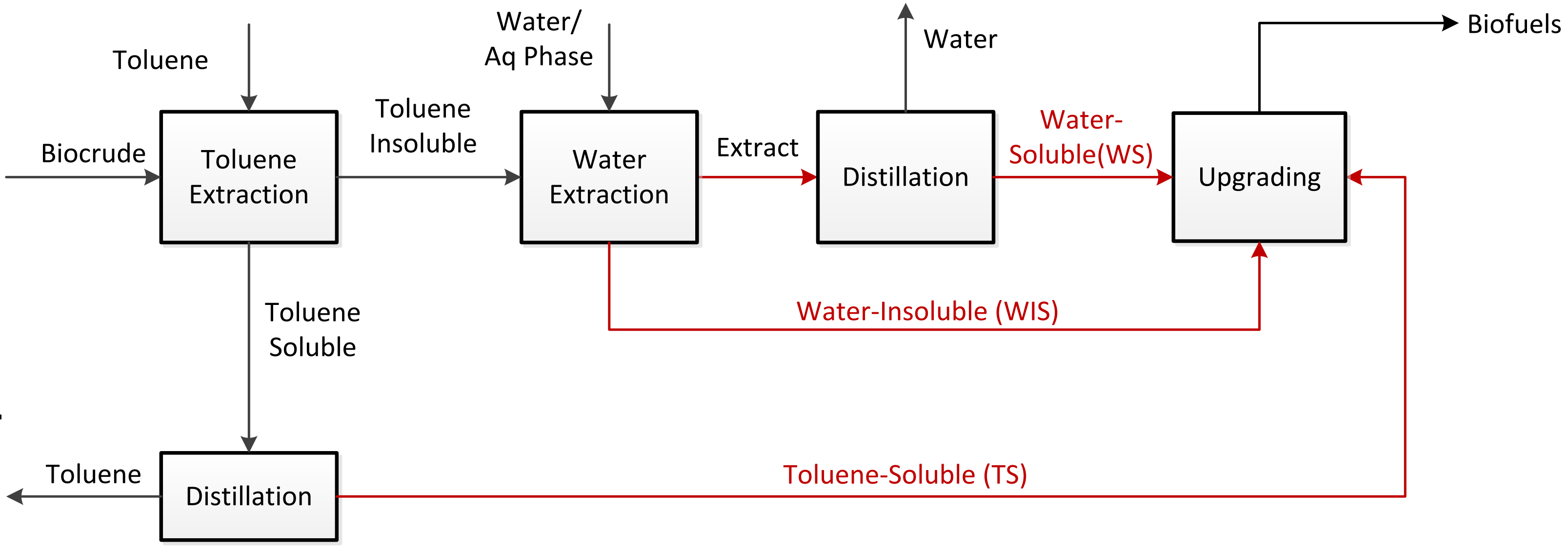
Distillation

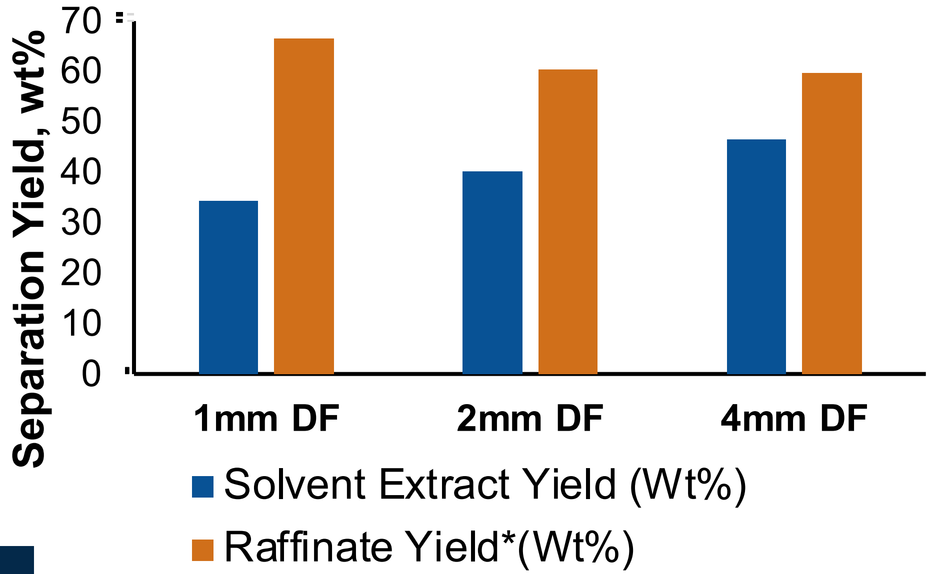
INPUT	Mass (kg)
Extract	31.4
OUTPUT	**Mass (kg)**
Solvent	24.3
Bottoms	6.3

- Solvent extraction separates out acids and anhydrosugars
- Although not detected with GC-MS, oligomers likely end up in the raffinate

Biocrude Fractionation Approach 1

- 1:1 volume ratio of solvent to biocrude.
- Two-stage extractions per batch of biocrude so raffinate from the first extraction was re-extracted.
- 2-hour extraction time
- Extracts distilled at 55-75°C under vacuum (74-201 torr) for solvent recovery.
- Water washing raffinate produced water-soluble (WS) and water-insoluble (WIS) fractions.

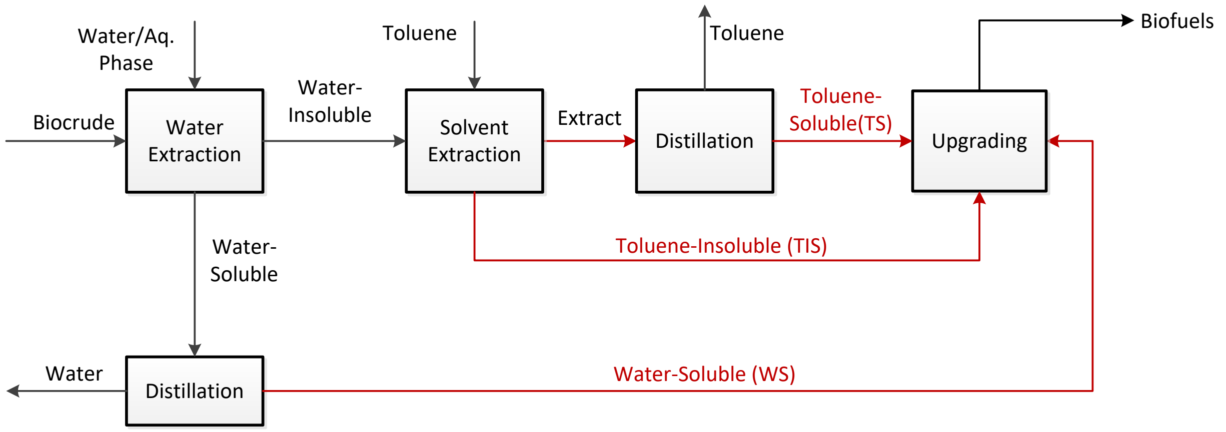


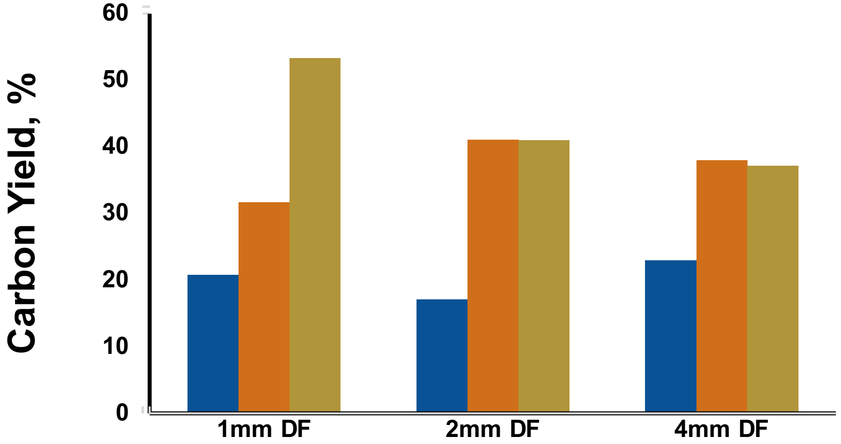


	1mm Douglas Fir	2mm Douglas Fir	4mm Douglas Fir
INPUT		Extraction Step Mass (kg)	
Biocrude	29.44	30.97	15.75
Toluene	43.49	50.83	36.94
OUTPUT			
Raffinate	19.62	18.67	9.39
Extract	51.01	60.40	42.62
Mass Closure	96.84%	96.65%	98.72%
INPUT		Distillation Step Mass (kg)	
Extract	50.72	59.75	42.59
OUTPUT			
Toluene	36.44	42.03	32.85
Product	10.18	12.46	7.32
Mass Closure	91.91%	91.20%	94.07%

Biocrude Fractionation Approach 2

- This separation strategy uses less volume of toluene solvent.
- Starts with water/aqueous extraction at 1:1 volume ratio.
- Biocrude is fractionated into water soluble and water-insoluble.
- The water-insoluble fraction is then fractionated into toluene soluble and toluene-insoluble.
- 2-hour extraction time
- Extracts distilled at under vacuum (100 torr) for water and solvent recovery.





	1mm DF	2mm DF	4mm DF
Water-soluble (WS)	20.80	17.09	22.95
Toluene-Soluble (TS)	31.66	41.02	38.02
Water/Toluene-Insoluble (TIS)	53.26	40.97	37.15

	1mm Douglas Fir	2mm Douglas Fir	4mm Douglas Fir
INPUT		Water Extraction Step Mass (g)	
Biocrude	237.8	237.1	234.8
Water	200.5	200.2	200.4
OUTPUT			
Water Soluble	285.3	254.7	299.1
Water-Insoluble	150.7	179.7	133.0
Mass Closure	99.48%	99.33%	99.29%
INPUT		Toluene Extraction Step Mass (g)	
Water-Insoluble	133.6	158.4	117.6
Toluene	151.6	125.1	172.9
OUTPUT			
Toluene Soluble	182.3	200.8	216.6
Toluene-Insoluble	98.1	79.2	68.4
Mass Closure	98.31	98.77	98.11
		Fractionated products (g)	
OUTPUT			
Water-soluble- Distilled	51.6	42.31	43.2
Toluene-Soluble Distilled	47.14	64.71	52.58
Water/Toluene-Insoluble	98.1	79.2	68.4

Biocrude Upgrading – Hydrotreating Fractions

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

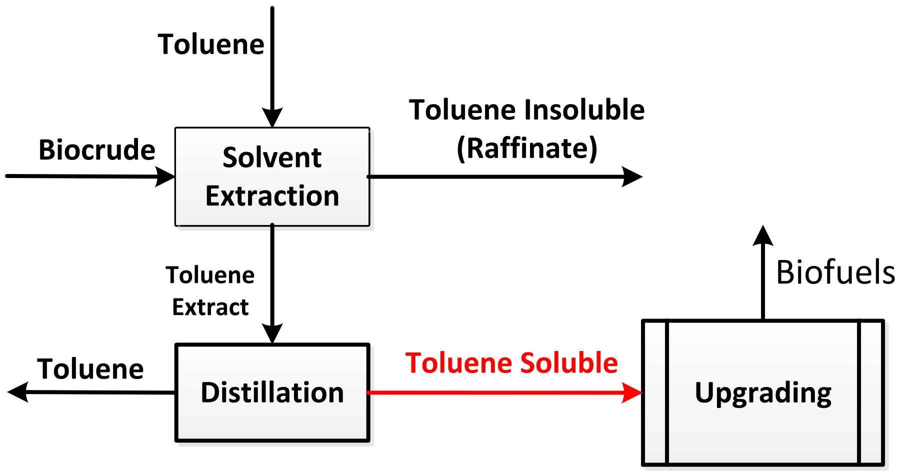
Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450C
Max. operating temperature: 430C
Max. operating pressure: 170 bar (2500 psig)

- Hydrotreat fractions independently
  - Solvent soluble
  - Solvent soluble distillate bottoms
  - Solvent insoluble (raffinate)
- Mass Balance Protocol: At least 48 hours of run time before mass balance
- Experiments continue until pressure drop across reactor > 60-100 psig or feed runs out

Operating Parameters	Input
HDT Catalyst*	TK-341 (Topsoe)
H_2 Flow Rate (sccm)	3000-4000
Feed Rate (g/h)	70-77
Pressure (psig)	2000
Average Temperature (°C)	250-350
LHSV (h-1)	0.18-0.35
H_2/oil ratio (Nl/l)	3300

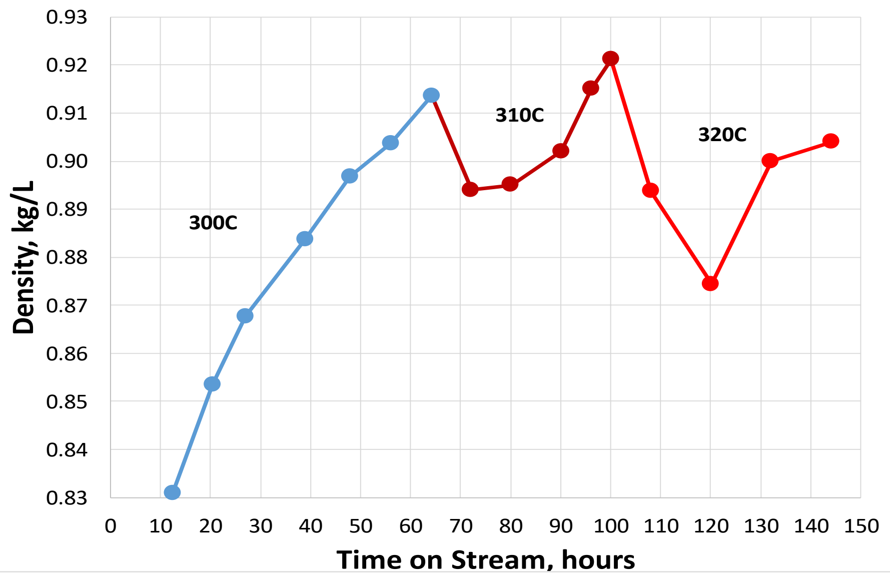
**In-situ sulfiding with H_2S in H_2 balance*

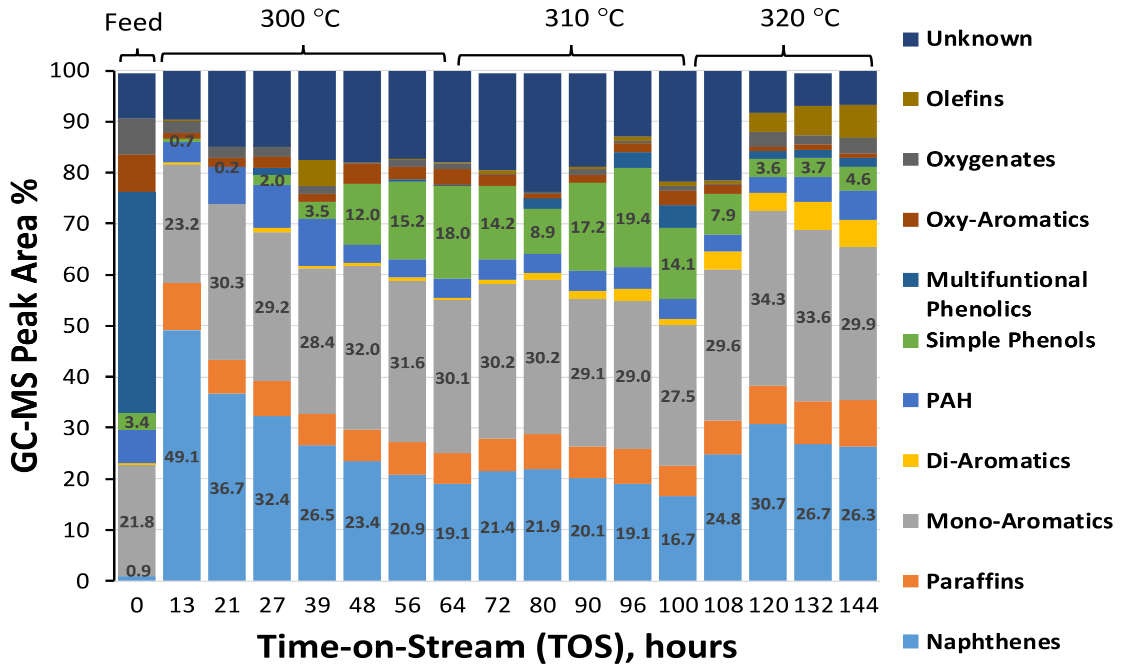
Summary of Toluene Extracted Biocrude Hydrotreating



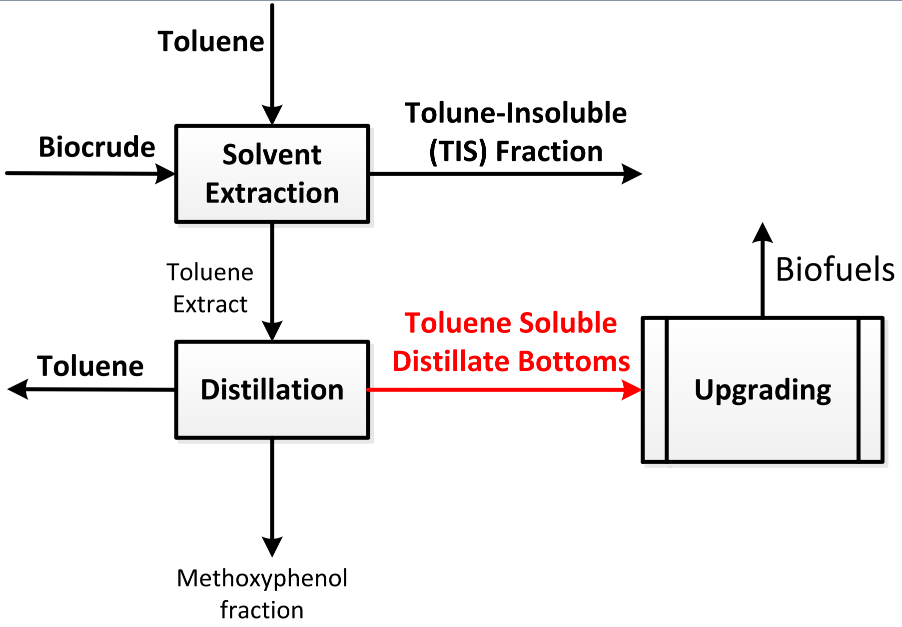
The toluene soluble fraction yield varies between 34-47wt%. The carbon yield also varies between 30-45%. The yields depend on the biocrude composition as dedicated by the process conditions and biomass feedstock.

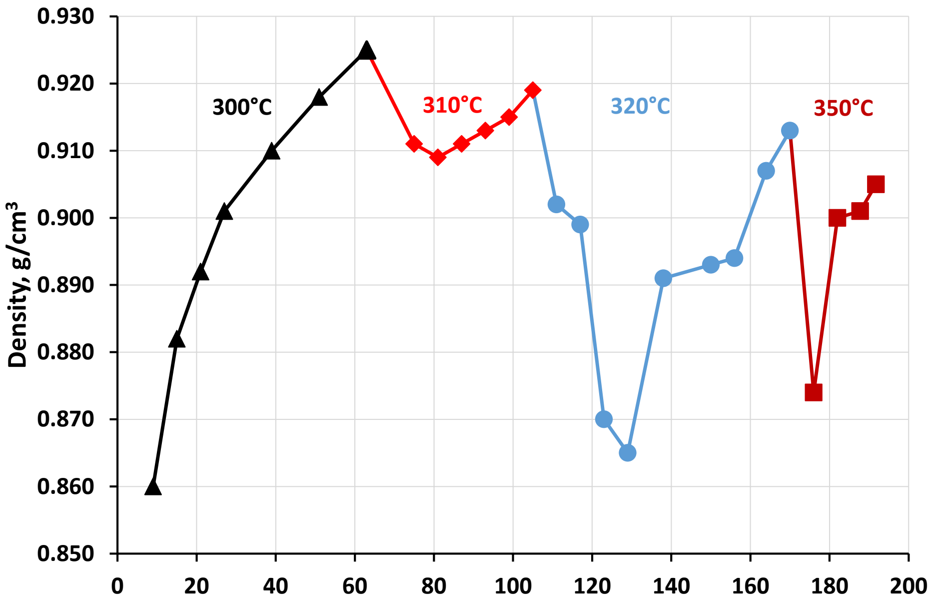
Parameters	Average MB
Mass yield of product oil, wt.%	77.10
Carbon yield of product oil, %	99.21
Mass yield of aqueous fraction, wt.%	18.10
Carbon yield of aqueous fraction, %	0.28
Product Gas yield, wt.%	1.88
Carbon yield of product gas, %	1.77
H_2 consumed, g of H_2/g of dry bio-oil	0.082
Mass Balance, %	96.46
Carbon Balance, %	101.25

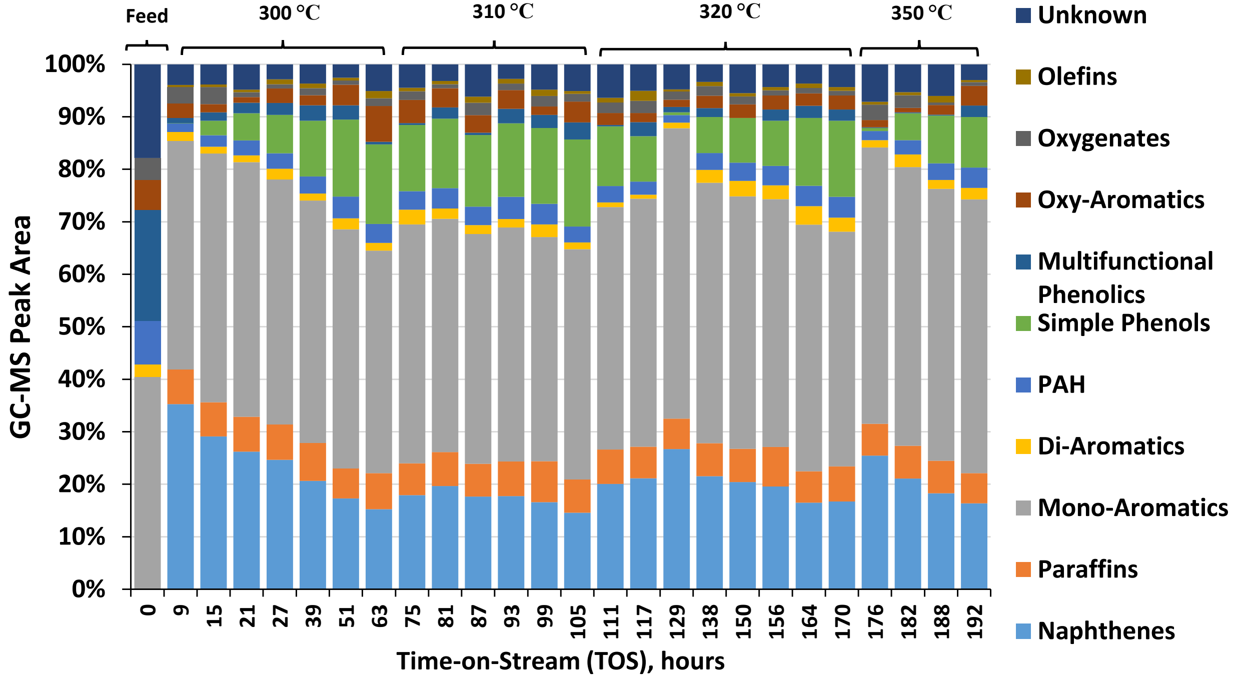




Extracted Biocrude Heavy Distillate Bottoms Upgrading



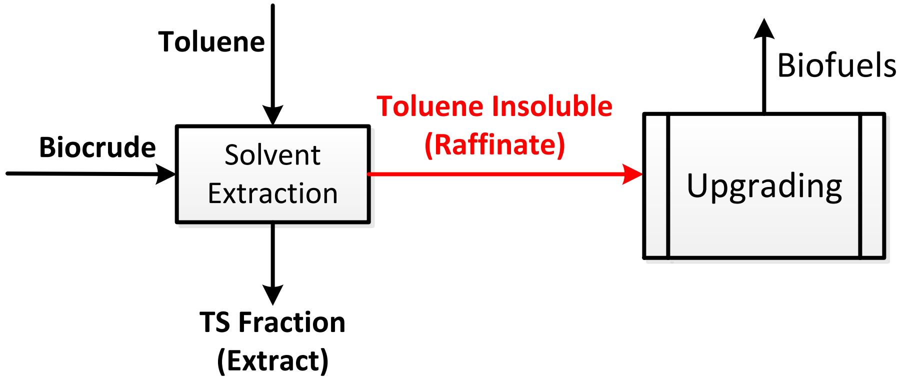


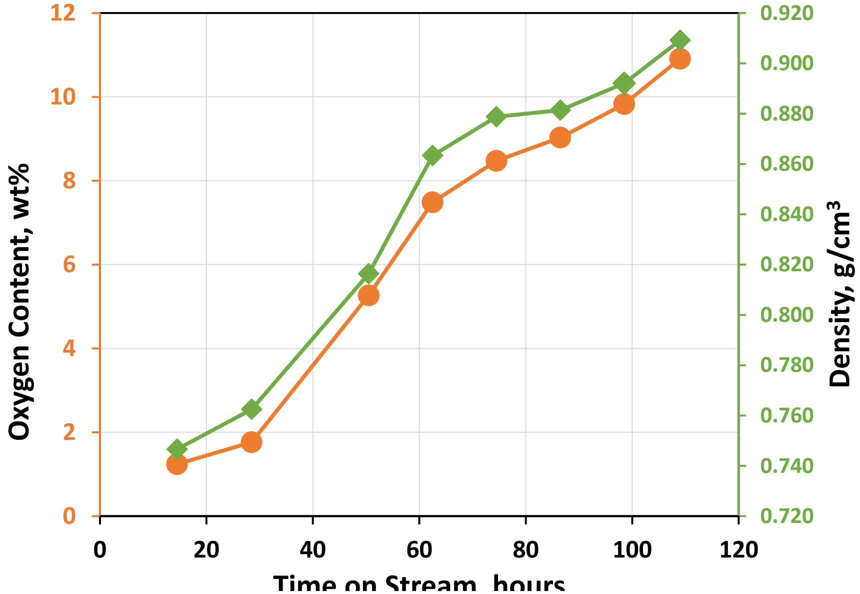


Very viscous fraction that behaves chemically like the toluene extracted fraction (low acids and sugars)

Parameters	Average MB (300°C)
Mass yield of product oil, wt.%	80.6
Carbon yield of product oil, %	97.15
Mass yield of aqueous fraction, wt.%	14.1
Carbon yield of aqueous fraction, %	0.2
Product Gas yield, wt.%	1.05
Carbon yield of product gas, %	0.85
H_2 consumed, g of H_2/g of dry bio-oil	0.0565
Mass Balance, %	95.7
Carbon Balance, %	98.15

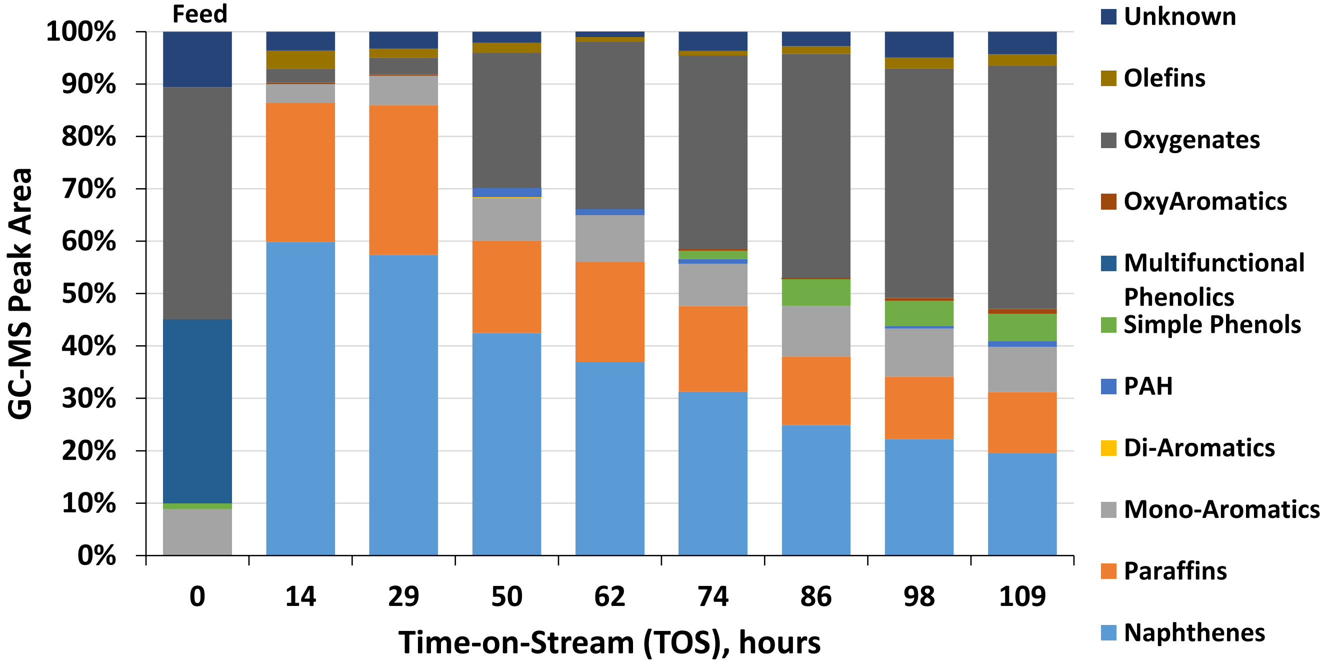
Summary of Raffinate Biocrude Hydrotreating





The raffinate is the toluene insoluble fraction of the biocrude. The yields is > 45wt%. The carbon yield is > 30 %. The yields depend on the biocrude composition as dictated by the process conditions and biomass feedstock.

Parameters	Average MB
Mass yield of product oil, wt.%	45.3
Carbon yield of product oil, %	73.9
Mass yield of aqueous fraction, wt.%	43.8
Carbon yield of aqueous fraction, %	7.4
Product Gas yield, wt.%	6.9
Carbon yield of product gas, %	7.6
H_2 consumed, g of H_2/g of dry bio-oil	0.063
Mass Balance, %	95.9
Carbon Balance, %	88.9



TEA Model – Revisions and Updates

Economic Parameters

- **Ash Disposal**: *The ash disposal cost was revised. In the base model, the ash disposal rate per year was very similar to the biomass consumption rate due to unit conversion error*.

- **Escalation Rate**: *In the previous model, 2% escalation per year was applied to the input prices (biomass, natural gas, etc.) but not applied to the output fuel. A 2% annual escalation on fuel price was applied in the updated model.*

- **Electricity Consumption**: *The electricity consumption was assumed to be zero in the previous model; the actual electricity consumed was applied.*

- **Catalyst makeup cost calculation**: *The catalyst:biomass ratio of 10 was updated to 5 based on pilot results; attrition rate of 185 ppm was updated to 55 ppm; and the catalyst cost was re-evaluated and changed from $19.5/kg to $10/kg.*

Process Parameters

- **CFP Yields and liquid Composition**: *The CFP product distribution and the chemical speciation of the liquid intermediates were updated based on recent pilot-scale results*

- **Hydrotreating Scenarios**: *Two different hydrotreating cases were considered to evaluate the tradeoff between biofuel yield and higher CAPEX and OPEX (hydrogen consumption)*
    - ***Case 1:*** *Both biocrude and aqueous organics are hydrotreated for fuel production*
    - ***Case 2:*** *Some aqueous organics (< C5) are diverted with wastewater and not used for fuel production*

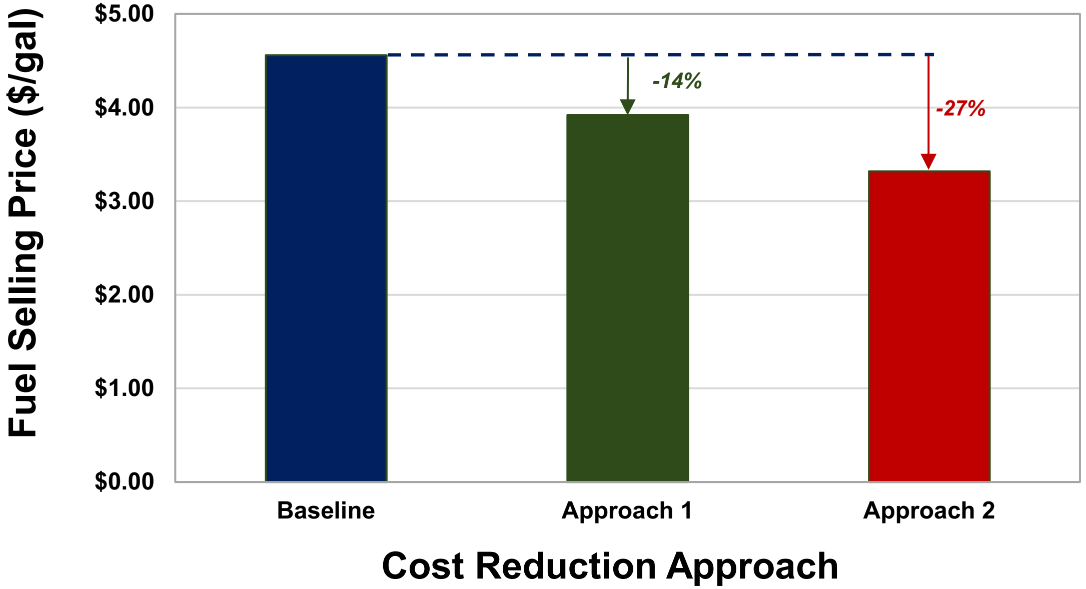
Updated TEA – Summary of Changes

Case 1 & 2 use the latest pilot scale testing data

- ❑ Case 1: Both biocrude and aqueous organics are hydrotreated for fuel production
- ❑ Case 2: Some aqueous organics (< C_5) are diverted with wastewater and not used for fuel production

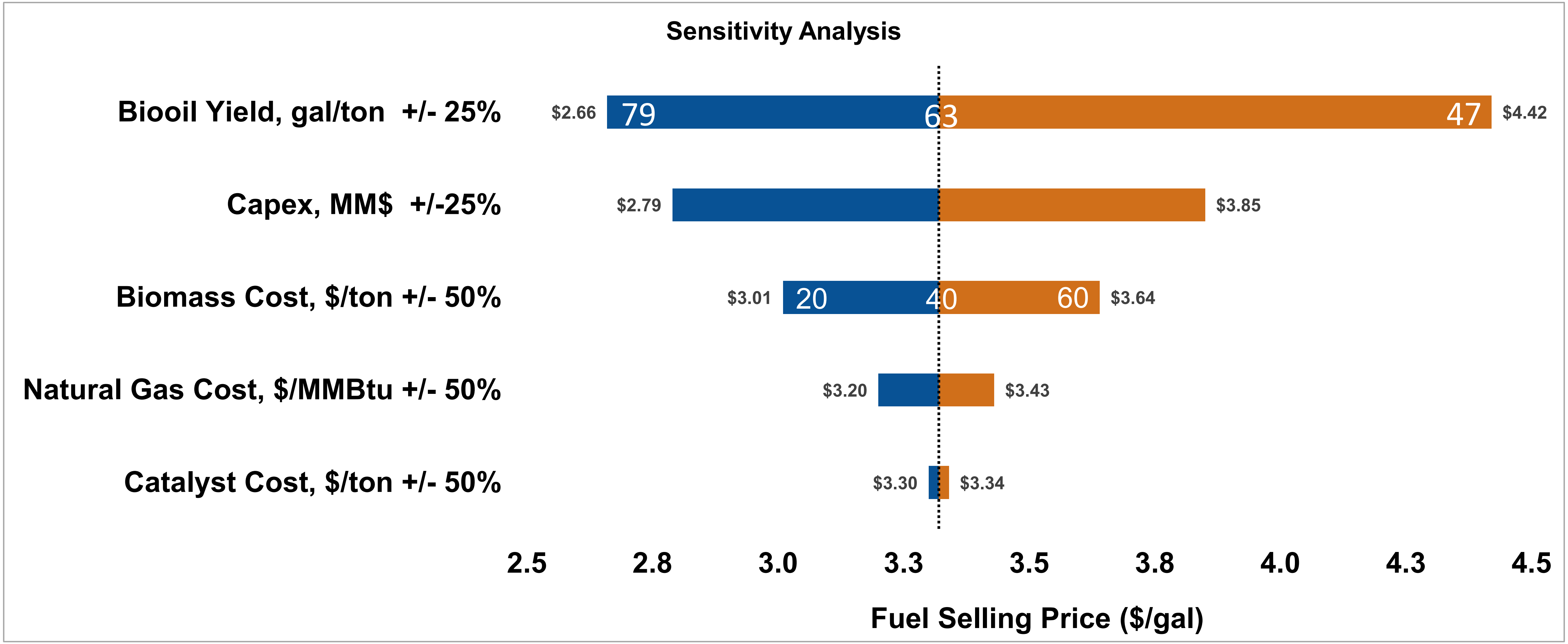
Gas	Mass Yield, %	25.0%		
	Mass Yield, %	21.4%	28.0%	
			27.6%	
Feedstock Consumption				
Biomass Daily Capacity	tons/day	2,000	2,000	
Fuel Production				
Biofuel Yield	gal/ton	62.54	63.14	60.01
Jet Fuel & Diesel, gal/hr	gal/hr	5,212	5,262	5,001
Utility Consumption				
Natural Gas	MMbtu/hr	349.2	312.2	269.0
	lb H_2/lb Oil		0.125	0.119
				707.0
Fuel Selling Price ($/gallon)				
Approach 2			$3.32	$3.33

- ❑ Approach 1: Reduction in ash disposal cost, electricity consumption and including fuel price escalation
- ❑ Approach 2: Improvement in pyrolysis product composition, and equipment and catalyst cost savings



27% reduction in fuel selling price achieved

Updated TEA – Sensitivity Analysis (Case 1)



- Biocrude yield has the highest impact on the FSP.
- CAPEX also has a large impact on the FSP. Important for refining the Feed Prep and Handling Costs and future refinery integration scenarios.

Cost of catalyst has minimal impact.

Remaining Scope – BP2B

Intermediate Verification resulted in a NoGo decision so the remainder of the project was re-scoped to demonstrate that additional streams can be prepared, separated and upgraded to similar products to achieve at least 25% carbon yield.

Feedstock Preparation

Forest Concepts LLC

- Process modeling of Crumbler® technology to improve energy and cost inputs for feed preparation and handling in TEA

Idaho National Lab

- Deliver additional forest residual feedstocks to RTI for conversion
- Compare feedstock preparation method with conversion process performance

Biocrude Production - RTI

- Produce biocrude from remaining feedstock (Alder, Forest Residuals)
- Demonstrate Approach 2 in laboratory-scale separation unit

Biocrude Separations and Upgrading

RTI

- Upgrade biocrude fractions to renewable diesel blendstock

Haldor Topsoe

- Evaluate catalyst activity and process conditions to evaluate upgrading strategy

Final TEA and LCA – RTI, Forest Concepts, LLC

Impact

Demonstrate a direct biomass liquefaction advanced biofuels pathway - Integrated, commercially-relevant pilot-scale unit operations for feedstock preparation, catalytic biomass pyrolysis (conversion), and biocrude separations and hydroprocessing (upgrading)

Technology Advancements:

- Reactor-ready feedstock that meets critical performance specifications
- Correlation between feedstock properties and conversion process performance
- Develop a strategy to improve biocrude upgrading efficiency (reduce reactor fouling and increase time-on-stream) by fractionating the liquid intermediate to separate chemical constituents best suited for bioproducts and biofuels, respectively, and processing different fractions independently, as warranted

This project directly supports the DOE/BETO Program goal to validate an nth plant modeled MFSP of \$3/GGE (2014\$) for a pathway to hydrocarbon biofuel with GHG emissions reduction of 50% or more compared to petroleum-derived fuel.

Summary

- Validate a commercially-relevant technology to produce reactor-ready feedstocks with specified critical performance factors
- Correlate feedstock properties with pilot-scale catalytic biomass pyrolysis process performance and achieve 40% higher biocrude yields
- Develop a novel separation strategy and a modified hydroprocessing strategy to improve biocrude upgrading performance
- Produce diesel blendstock that meets ASTM D975 specifications
- Validate an nth plant modeled MFSP of $3/GGE (2014$) for a pathway to hydrocarbon biofuel with GHG emissions reduction of 50% or more compared to petroleum-derived fuel.

Bio-crude Production and Upgrading to Renewable Diesel (DE-EE0008509)

Timeline

- Award Date: 10/1/2018 (Original End Date: 9/30/2021)
- Award Negotiations Concluded: 04/18/2019
- Initial Verification Meeting – July 19, 2019
- Proposed Budget Period 1 end date: 9/30/2019
- Actual Budget Period 1 end date: 3/30/2020
- Authorization to move into BP2: 4/29/2020
- Budget Period 2A: 4/1/2020 – 10/31/2021
- Intermediate Verification – June-October 2021
- Approval to continue: August 2022
- Budget Period 2B: 7/1/2021 – 9/30/2023

Project Goal

Improve the technical feasibility of renewable diesel production from cellulosic biomass by demonstrating the production of up to100 gallons of a renewable diesel blend stock that meets ASTM specifications

End of Project Milestones

Correlation between biocrude yields and feedstock PSD and other physical properties. Innovative biocrude fractionation strategy for upgrading, Pilot demonstration of an advanced biofuels technology that integrates catalytic biomass pyrolysis and hydrotreating to produce up to 100 gallons of renewable diesel blendstock that meets ASTM D975 specifications

Project Start: TRL-4 **Project End: TRL-6**

Partners

RTI International: Project lead, CFP, separations, and upgrading technology development, project management
INL: Feedstock modelling
NREL: CFD reactor modeling, process modeling and TEA, LCA
Forest Concepts, LLC: Innovative feedstock preparation, primary feedstock provider, modeling
Topsoe: Develop a new strategy (catalyst and process conditions) to upgrade biocrude.

Budget	Federal	Cost Share	Total Costs	FY19-FY23Q1 Actuals	
				Federal	Cost Share
BP1	$253,996	$63,499	$317,496	$157,714	$86,190
BP2A	$1,020,679	$255,170	$1,275,849	$1,212,770	$272,826
BP2B	$1,279,248	$319,812	$1,599,060	$39,656	$6065
[illegible]	$2,553,924	$638,481	$3,192,405	$1,410,140	$365,081

Process Development for Advanced Biofuels and Biopower (DE-FOA-0001926 issued May 3, 2018)
Topic Area 2: Drop-in Renewable Diesel Fuel Blendstocks

Bridge technologies from research to engineering, to integrate unit operations, and to engage in the R&D of integrated processes designed to produce drop-in renewable jet fuel or diesel blendstocks, or biopower.

Additional Slides

Responses to Previous Reviewers' Comments

- The go/no-go decision criteria seem to be far short of reasonable. A 30% oxygen product at 20 wt % yield is terrible—it has an approximate 25% yield of carbon in the product, and with significant oxygen yet to be removed. Much will leave as H2O, but there will also be carbon losses. How can this be close enough to commercially viable even to be worth testing? This is confirmed on slide 10—the yield of solid is 55%–68%, with a further 9%–14% lost as gas. Only 20%–27% liquid yield is achieved. What is the point in doing further work with such yields? The table on slide 10 is also confusing. Which numbers are supposed to add up? Liquid, solid, gas = total, but how the other numbers relate is unclear. There is simply no point in the downstream processing of a liquid that does not represent a commercially viable yield. The catalyst's stability (slide 18) was not achieved in 144 hours, so there is no telling what the product is going to be. Why are data presented for a catalyst that clearly has not yet stabilized?
- This is a well-organized and well-managed project with a sound approach to a difficult set of constraints of improving costs, improving carbon efficiency and decreasing GHG emissions. It is unclear if the overall goals of this project make sense—i.e., should BETO be pursuing this? Combining the three ambitious goals into a single process/project results in a flow sheet with dilute aqueous streams that could be very expensive to upgrade/recover products. The flow sheet does not look commercially achievable due to its complexity. The program may be over-constraining this project. Due to the technical issues (e.g., plugging), it is unclear if the overall goals of the project will be met. This reviewer would have liked to have seen an updated plan for addressing the technical issues that were found.

There are several goals to be achieved during this project. First, evaluate the impact of feedstock preparation on biocrude yields in the CFP process and revisit the CFP process conditions to maximize biocrude yield. Second, improve upgrading efficiency by fractionating biocrude using selected separations techniques and developing strategies to independently hydroprocess each fraction to maximize biofuel production. Fractionating the biocrude puts less emphasis on hydrodeoxygenation during CFP while that led to the design, fabrication, installation, and operation of pilot-scale unit operations for (1) CFP in a 1-ton/day unit and (2) biocrude upgrading in a hydroprocessing reactor system.

The impact of feedstock and feedstock preparation on CFP performance has been a focus in the project until this point and is an ongoing effort in budget period two. We have evaluated the biocrude yields and quality produced from a softwood feedstock (Douglas fir) prepared to three different particle sizes (1 mm, 2 mm, and 4 mm). We will repeat this activity with a hardwood feedstock (alder) that has already been prepared and delivered to RTI.

The second emphasis of this project is to develop new strategies for upgrading the biocrude intermediate into renewable diesel blendstocks. A primary driver of this effort is to segregate biocrude components that cause fouling in the hydrotreating reactor and expand the duration of upgrading experiments. The impact of process conditions on the steady-state hydrotreating catalyst activity can then be determined. Additionally, each fraction can be independently hydroprocessed to manage process severity and H2 demand while maximizing biofuel production. Biocrude fractionation performed to date has produced a solvent extracted fraction and a raffinate (solvent-insoluble fraction). The raffinate was extracted with water to produce water-soluble and water-insoluble fractions. Upgrading the solvent soluble fraction was very successful—after 144 hours TOS, no increase in pressure drop across the reactor was measured. The hydrotreating catalyst activity was also partially recovered by increasing the average hydrotreating temperature during this experiment. Fourteen gallons of solvent-extracted biocrude has already been produced to build on this preliminary study. Upgrading studies with the water-soluble and water-insoluble fraction were not as successful; however, we are investigating hydrocracking as an alternative to hydrotreating and opportunities for bioproduct recovery from the water-soluble raffinate fraction.

The existing process model of the integrated catalytic biomass pyrolysis biocrude upgrading process includes an option for separations for bioproduct recovery. This model will be updated with a modified configuration for biocrude upgrading that represents the new strategy based on the experimental results collected during this project. This model will form the basis of an updated TEA for the integrated process to document the impact of feedstock preparation on biocrude yield and quality as separations are used to achieve commercially relevant upgrading to biofuel. The end-of-project goal is to produce 100 gallons of renewable diesel from this pilot-scale integrated biofuel pathway to inform a TEA for an nth plant pathway to hydrocarbon biofuel with a target modeled MFSP of $3/GGE and a 50% reduction in GHG emissions compared to petroleum diesel. putting a greater focus on increasing biocrude yield. This study builds on past projects

Initial Verification- Independent Engineers Review*

Overview of Initial Verification Test Data					
Unit Operation	**Key Performance Parameter**	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
Feedstock	Forest Concepts to produce 1-2 mm Crumbles	none	No	yes	Produce Crumbles for Task 2
CFP	Produce 10 gallons of biocrude with 20% yield	Yield was not achieved	Yes - yield	yes	Generate plan to achieve desired yield
Separation	Separate biocrude into 3 fractions	none		Yes	Proceed to Task 2 activities
Upgrading	Upgrade oil fraction from separation to be compliant with ASTM D975	Yes – uncertainty around compliance with ASTM D975	ASTM D975 Analysis not completed	yes	If biocrude material is available from testing, further analyze diesel to establish baseline, then proceed to Task 2

Following our visit to the site July 10, 2019, the test data made available for our review, it is our opinion that;

- The that the maturity of the technology is a level that justifies that it be allowed to proceed to the activities as outlined in Task 2.0 of the Recipient's Statement of Project Objectives.
- We recommend that RTI develop a plan to improve bio-crude yield with their CFP process.
- If upgraded bio-crude product is still available from verification testing, we recommend that it be analyzed to the extent possible to determine how it compares to ASTM D975 criteria and to establish a baseline for future work and that results be shared with DOE.

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Intermediate Verification- Independent Engineers Review*

Overview of Intermediate Verification Test Results and SOPO Tasks					
Unit Operation	**Key Performance Parameter**	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
Verification Test Results					
Product Yield	Demonstrate the improved catalytic pyrolysis pathway for conversion of biomass to biofuel with an overall carbon efficiency of greater than or equal to 25%.	Calculations for the biocrude conversion were based on the carbon yield of streams that were not collected during the pilot trial, and processed (aqueous recycle, cold filter and separation solids). The CFP process was only set up to collect hot filter biocrude during the pilot trial. Only hot filter biocrude was used for fractionation and upgrading pilot trial.	If only the hot filter biocrude is used to calculate the overall carbon efficiency, the CFP process does not meet 25% overall carbon yield. The overall carbon yield did not meet 25% for the 2 mm when all streams were included.	No	Demonstrate that additional streams can be prepared, separated and upgraded to similar products and apply the data to the carbon yield.

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Intermediate Verification- Independent Engineers Review* (continued)

Overview of Intermediate Verification SOPO Tasks					
Unit Operation	**Key Performance Parameter**	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
Feedstock	Forest Concepts produced 3 sizes of Douglas fir Crumbles™ feedstock	none	No	yes	OK to proceed to BP3 when all task/targets completed
Pyrolysis Catalyst Evaluation	Prepare Catalyst performance evaluation	Did not occur	Did not occur	No	Complete Task
CFP	Produce 10 gallons of biocrude for each feedstock	Calculations for the biocrude produced were based on various streams that were not available to be processed. Effects of Catalyst properties were not evaluated.	Less than 10 gallons of biocrude (hot oil filter) for the 1mm and 4 mm feedstock	Yes, material appeared to be sufficient for Separation Step.	OK to proceed to BP3 when all tasks/targets are completed
	Measure Effects of catalyst properties, coke and alkali accumulation for catalyst performance and economic impact	Did not occur	Did not occur	No	Complete Task

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Intermediate Verification- Independent Engineers Review* (continued)

Overview of Intermediate Verification SOPO Tasks					
Unit Operation	**Key Performance Parameter**	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
Separation	Separate 5 gallons of each biocrude into 3 fractions with less than 1% carbon loss	none	Less than 5 gallons of 4 mm feedstock was available for separation. Data was not provided on the carbon loss.	No	Provide carbon loss data for material produced in Approach 1 and data showing the carbon yields are similar for streams generated in Approach 1 and Approach 2.
Upgrading	Upgrade the separated biocrude fractions with biofuel carbon yield > 90%	1) Had difficulty upgrading pyrolytic/toluene insoluble fractions, and used an assumption for calculating this fraction. 2) Assumption was made that the toluene insoluble raffinate would upgrade the same as the water soluble distillate bottoms. 3) Assumption is made that collected biocrude from the aqueous, cold filter and separated CFP will upgrade the same as the hot filter biocrude.	Not all separated products were upgraded. Overall carbon yields calculated for 2 mm and 4 mm feedstock were less than 90%.	No	Upgrade the pyrolytic fraction, and water soluble fractions. Provide data showing upgrade yields for separately sized feedstock. Upgrade aqueous material.

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Publications, Patents, Presentations, Awards, and Commercialization

- Publications:
  - Verdier, S.; Mante, O. D.; Hansen, A. B.; Poulsen, K. G.; Christensen, J. H.; Ammtizboll, N.; Gabrielsen, J.; Dayton, D. C. (2021). Pilot-scale hydrotreating of catalytic fast pyrolysis biocrudes: process performance and product analysis. Sustainable Energy and Fuels 2021, 5, 4668-4679. https://dx.doi.org/10.1039/d1se00540e
  - Garcia-Montoto, V.; Verdier, S.; Dayton, D. C.; Mante, O.; Arnaudguilhem, C.; Christensen, J. H.; Bouyssiere, B. (2021). Phosphorus speciation analysis of fatty-acid-based feedstocks and fast pyrolysis biocrudes via gel permeation chromatography inductively coupled plasma high-resolution mass spectrometry. RSC Advances 2021, 11 (43), 26732-26738. https://dx.doi.org/10.1039/d1ra03470g
  - Dayton, D. C.; Mante, O. D.; Weiner, J. (2021). Effect of Temperature on the Pilot-Scale Catalytic Pyrolysis of Loblolly Pine. Energy & Fuels. https://dx.doi.org/10.1021/acs.energyfuels.1c01685
- Patents: none
- Presentations:
  - On-site Verification Meeting - Bio-crude Production and Upgrading to Renewable Diesel (DE-EE0008509), RTI International, RTP, NC. July 10, 2019.
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – “Pilot-scale Catalytic Fast Pyrolysis of Douglas Fir Crumbles.” P. Cross.
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – “Upgrading Strategies for Fractionated Biocrude.” D.C. Dayton
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – “Impact of Naphthenic Bio-blendstocks on Diesel Fuel Properties.” O. Mante.
  - DOE Bioenergy Technologies Office 2021 Project Peer Review, March 25, 2021, System Development and Integration. “Biocrude Production and Upgrading to Renewable Diesel.” D.C. Dayton
  - D.C. Dayton, Invited Presentation at The Topsoe Advanced Biofuels Seminar September 8, 2022, in Lyngby, Denmark entitled “Catalytic Biomass Pyrolysis and Biocrude Upgrading.”
  - D.C. Dayton, Invited Presentation at the 2022 AFPM Summit in San Antonio, TX October 17-20, 2022, entitled “Biomass Pyrolysis: Bio-oil may look like oil….”