DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

A Catalytic Process to Convert Municipal Solid Waste Components to Energy

11.30AM-12 PM EST, 4/7/2023

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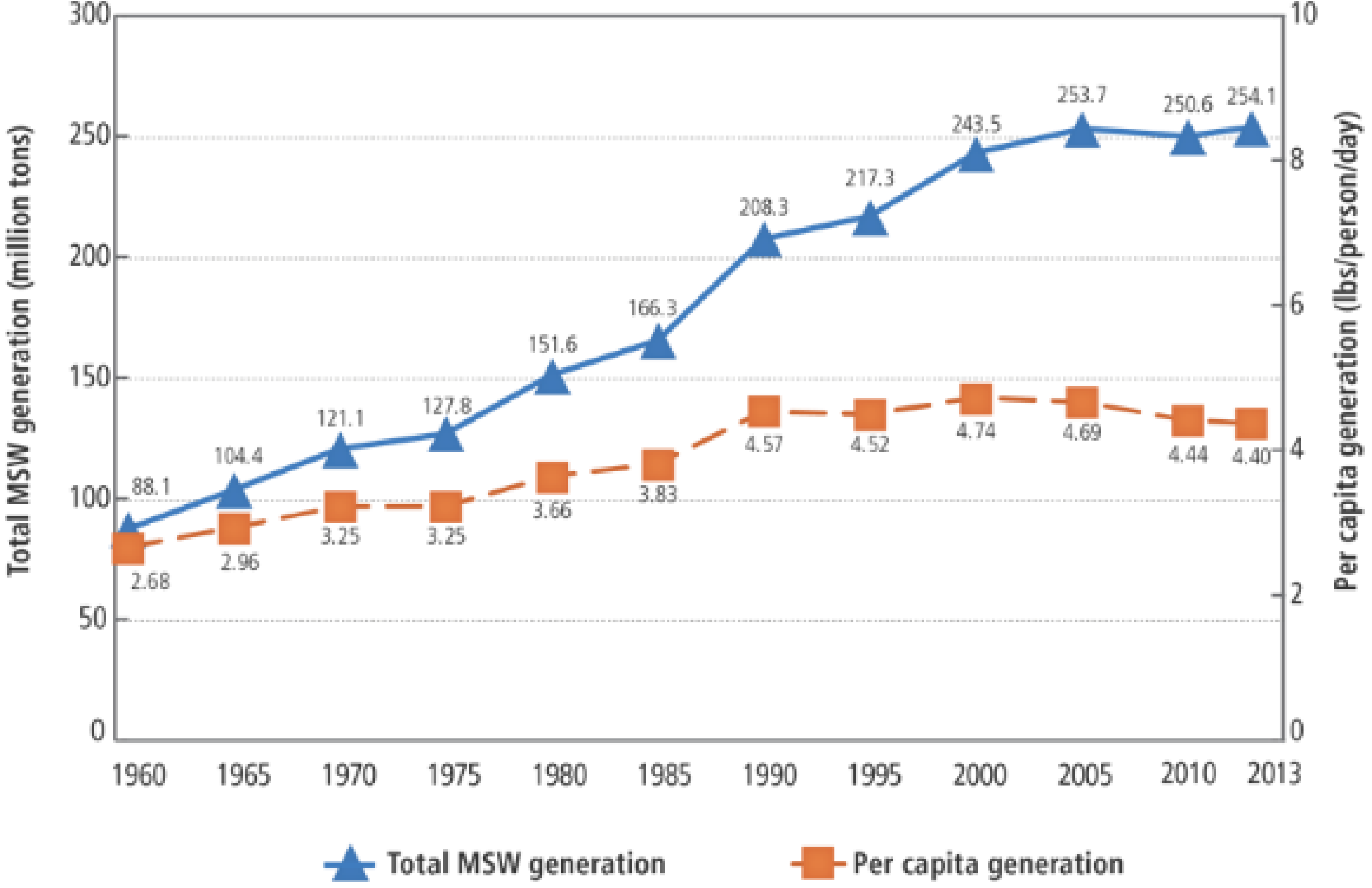
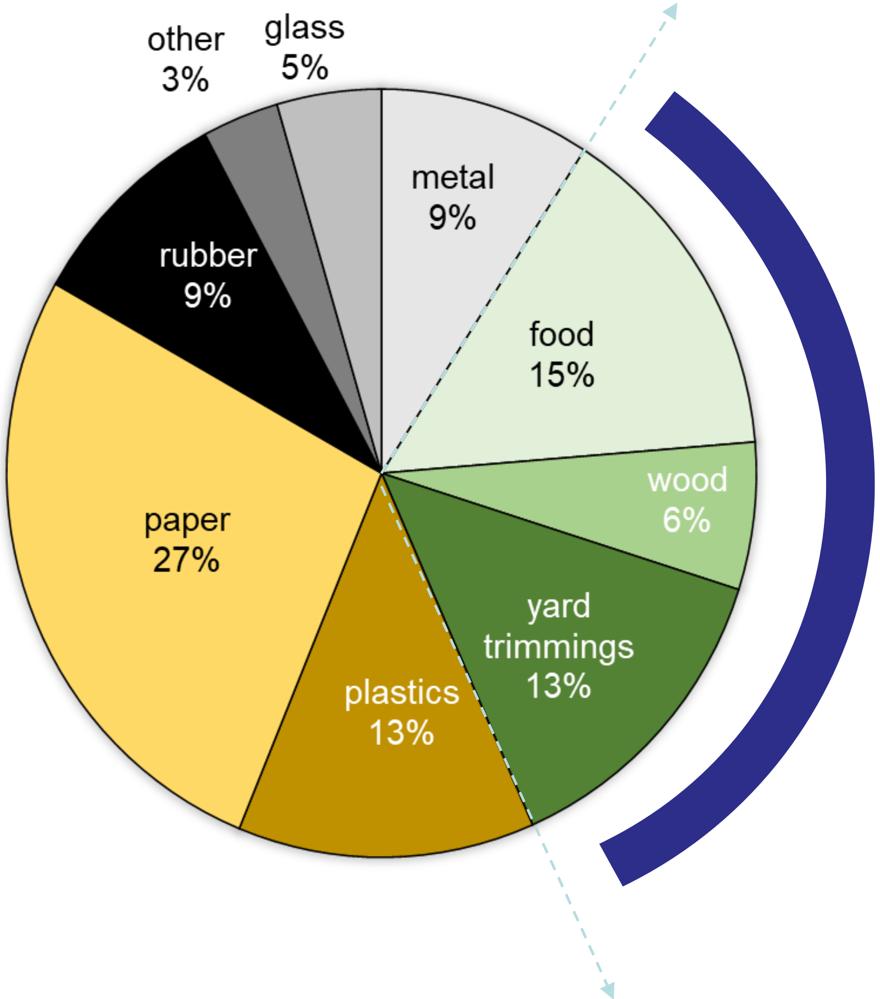
Project Overview: Background

https://archive.epa.gov/epawaste/nonhaz/municipal/web/html/





Focus of this project

https://greenbeston.com/what-is-municipal-solid-waste/

Food and other organic wastes are abundant, how do we increase biocrude yield enough to make it economical?

Project Overview: Background

- **Obstacles to using the organic fraction of MSW**
  - Complex mixture with high water content
  - Composition depends on source and varies seasonally
  - Collection and sorting of widely distributed waste materials
  - Unfavorable energetically for pyrolysis or gasification

- **Possible/competing technologies for MSW-to-Energy**
  - Anaerobic Digestion
    - Inefficient use of carbon
    - Slow process – days to weeks
    - Product biogas contains impurities with costly removal
    - Large reactors require lots of space
  - **Hydrothermal liquefaction**
    - Efficient use of carbon
    - Compatible with wet and complex/variable feeds
    - Produces an energy dense liquid oil product
    - Fast process – minutes to hours
    - Compact technology for distributed deployment


Wet, compositionally complex


PNNL HTL process development unit

Project Overall Goals

- Generation of bench-scale and pilot-scale data and models to de-risk commercialization of a process to convert a combined stream consisting of the food waste and green waste components of municipal solid waste (MSW) into an energy-dense biocrude and refined lignin stream

- Development of a robust strategy to improve processibility and conversion of MSW to energy dense liquid product as a biopower intermediate by integrating green waste fractionation with HTL and catalytic upgrading

Technical Goals

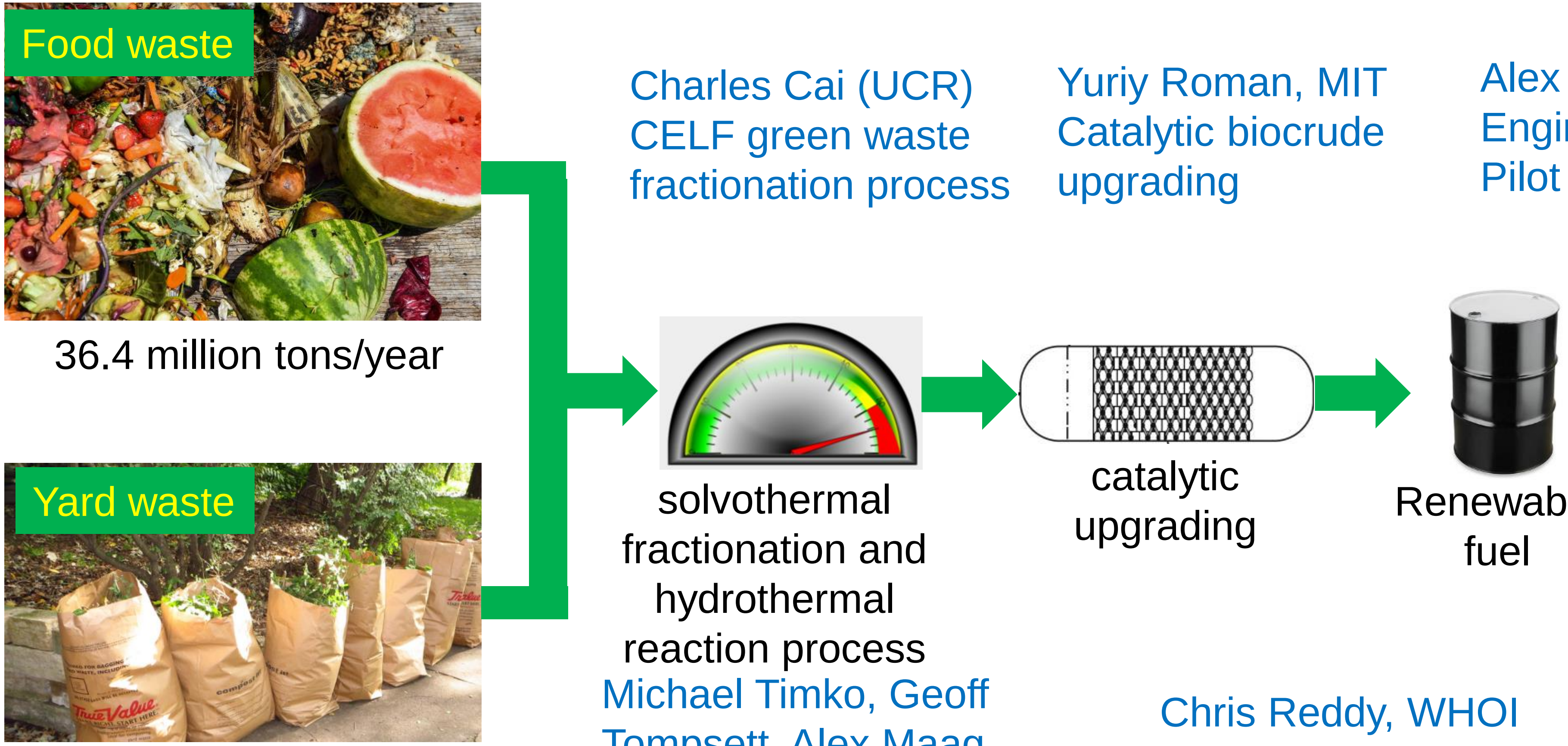
- 1) demonstration of co-solvent separation of municipal green waste to produce isolated lignin-rich (>80 wt% lignin), lignin-free (>20 wt%), and minerals/ash-rich streams (95 wt%);

- 2) >40% energy recovery as HTL bio-oil product, based on the lower heating value of the product stream compared to the feed, by a combination of HTL and catalytic upgrading of a food waste surrogate;

- 3) production of a product stream with <2 wt% nitrogen and <7 wt% oxygen content, as determined by elemental analysis, using a model compound or surrogate feed stream as achieved by any combination of HTL, catalytic upgrading, and HDO/HDN upgrading.

- >100 hrs (cumulative) operation of the pilot-scale HTL reactor;
- >100 hrs (cumulative) use of the C-C coupling catalyst;
- >100 hrs (cumulative) use of the HDO/HDN catalyst;
- LCOE of $3.64/gge ($31.9/mmBTU) – an 26% reduction.
- EROI of 5

Project Overview and Team



36.4 million tons/year

35.4 million tons/year

Charles Cai (UCR)
CELF green waste
fractionation process

Yuriy Roman, MIT
Catalytic biocrude
upgrading

Alex Paulsen, Mainstream
Engineering
Pilot Scale operation

solvothermal fractionation and hydrothermal reaction process

catalytic upgrading

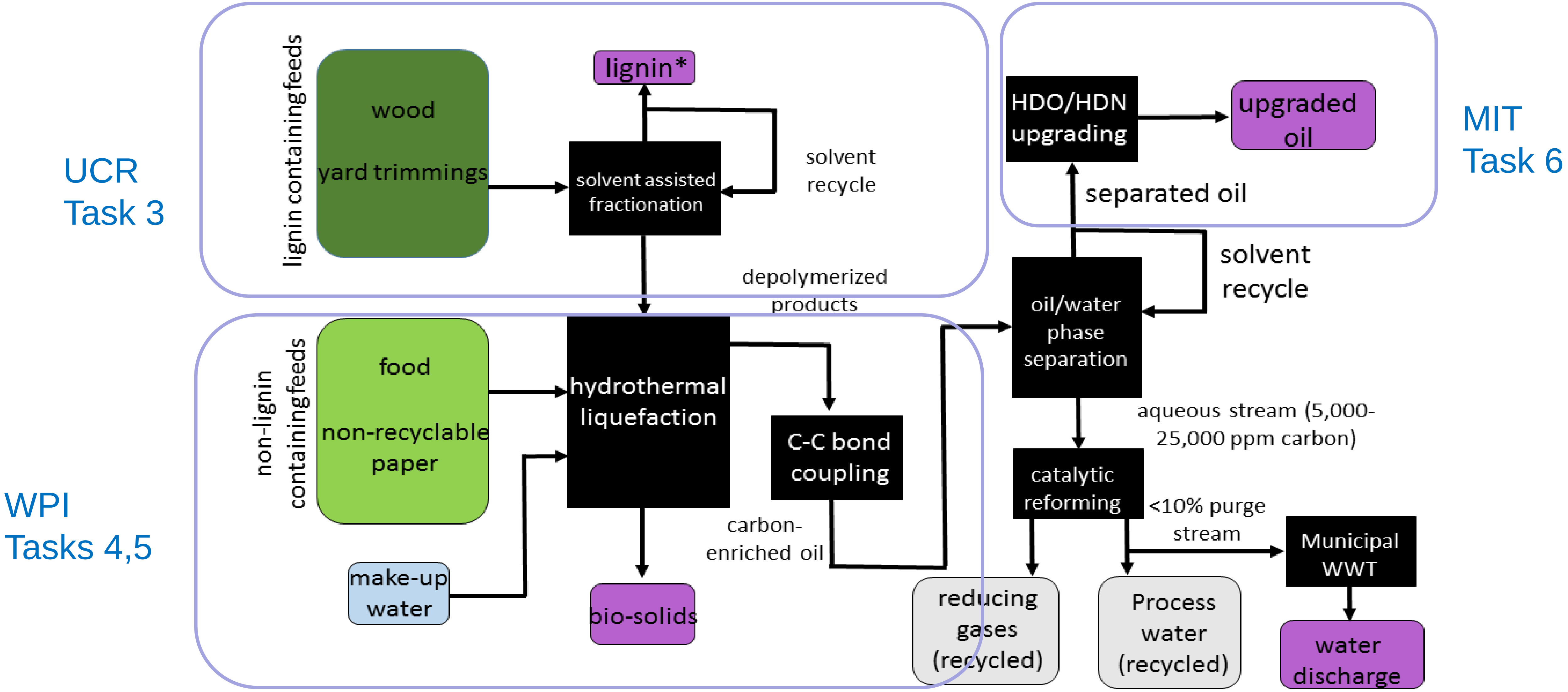
Renewable fuel

Michael Timko, Geoff Tompsett, Alex Maag (WPI) HTL, CHTL

Chris Reddy, WHOI
analytical

- Food waste and yard waste are abundant, inexpensive organic-rich feed streams (compare with algae)
- Co-processing can increase process scale, improve economics
- Combined hydrothermal and solvothermal fractionation and reaction process can optimize bio-crude yields, minimize wastes
- Upgrading with inexpensive catalysts can minimize hydrogen use for renewable fuel production

2-Approach: The Process



Simplified process flow diagram of the catalytic hydrothermal liquefaction (HTL) process. The organic fraction of the MSW is feed (green). Process steps are black. Products are purple.

2-Approach: Technical Approach (Detailed) -1

- **Task 1: Initial Verification**
- **Task 2: Intermediate Verification**
- **Task 3: Co-solvent lignin fractionation of green waste (UC-Riverside)**
  - Improving lignin extraction from green waste.
  - Increasing the fraction of MSW treated in the HTL process by evaluating HTL of Lignin-free and lignin-rich feed streams
  - Performance objective - production of a lignin-free stream, containing <10% lignin, and a lignin-rich stream, containing >90% lignin.
  - **Equipment**: 1 liter "Parr" batch reactor, 1 gal steam-assisted reactor, 1 gal steam-injected reactor, Outdoor ventilated green waste storage
  - **Feedstock**s: Athens (California) green waste and BDP Industries green waste (supplied from WPI)

- **Task 4 and 5: Non-catalytic and Catalytic hydrothermal liquefaction of food waste and green waste - Heterogeneous Base Catalysts (WPI)**
  - **Catalysts:** Inexpensive heterogeneous base catalysts, mixed metal oxides, metals supported on oxides, hydroxyapatite
  - **Equipment:** Parr batch reactors, semi-continuous fed batch reactor systems, Continuous packed bed reactor of biocrude aqueous phase hydrothermal processing
  - **Feedstocks:** Food waste mixture, Dehydrated food waste from VA hospital and Mt Holyoke College, Green waste from BDP Industries(NY) and Athens(CA)

2-Approach: Technical (detailed) -2

- **Task 6: Catalytic hydrogenation of biocrude upgrading to fuel products (MIT)**
  - Batch and Continuous packed bed reactors, Catalysts: Molybdenum carbide, supported MoCo, for removal of oxygen and nitrogen from biocrude compounds, Solvent diluted biocrude or separated hydrothermal biocrude feeds
  - Reduce HTL biocrude will contain <7 wt% oxygen and <2 wt% nitrogen
  - Require stable catalyst operation profiles >100 h on stream (cumulative) that maintain >50% conversion

- **Task 7: Technoeconomic Analysis (Mainstream Engineering/WPI)**
  - Utilize PNNL spreadsheets based on sewage sludge hydrothermal liquefaction adapted for economic analysis of the overall process
    - Calculate the energy return on investment and levelized cost of energy
  - Use @Risk software for regression coefficient analysis for the sensitivity of net present value
  - GREET analysis for calculating the life cycle analysis (LCA) of the overall process

- **Task 8: Pilot Scale Continuous Operation (Mainstream Engineering)**
  - Continuous catalytic hydrothermal reactor: Max. 350˚C, 35 MPa, 1.3 L, 0-120 mL/min, Collect oil, water, gas, and char is hot filtered, Catalyst cage holds catalyst in reactor, use catalyst pellets

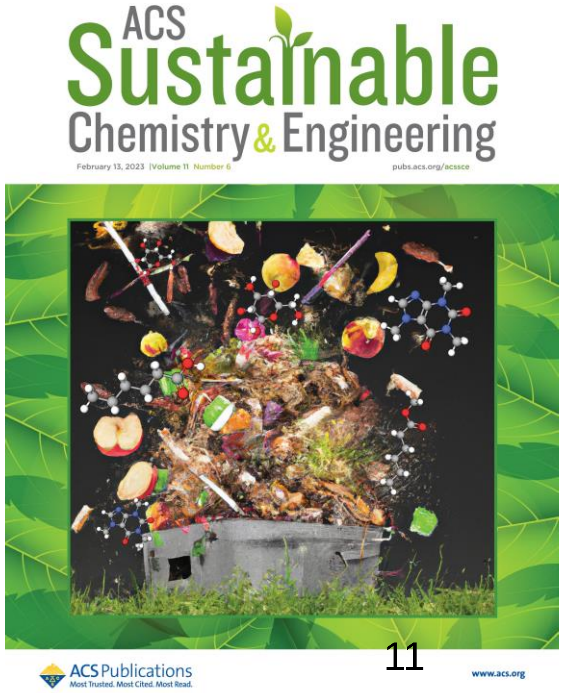
3-Impact:

- **Target 1**: US Fuel Diesel Market
  - U.S. generates over 250 million tons of MSW per year
  - HTL process targets approximately 40% of this waste stream (organic fraction)
  - the US consumes 140 billion gallons of gasoline per year, represents billion-dollar opportunities
  - proposed technology can produce 10-15% of the annual domestic gasoline usage (assuming 100% material efficiency) in energy dense oil product or 3-5% with 25% efficiency
  - Market options include **transportation o**r use in **stationary** power generation
  - TAB (Phillips66) will guide *market* decision
  - Renewable fuel company (River Otter Renewables) interested in developing the technology

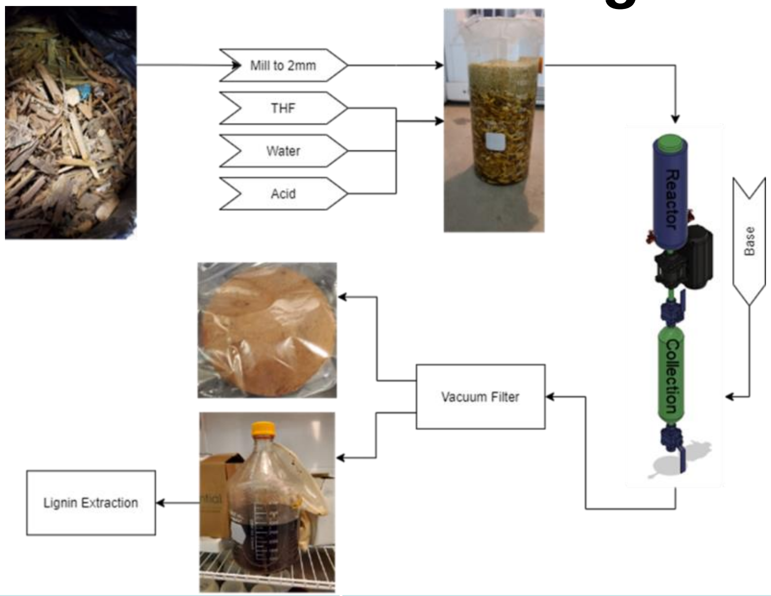
- **Other Products**
  - co-products of char-based Class A bio solids and lignin ($200/ton)
  - have substantial potential markets in ground covering, fertilizer, water purification, energy storage, and power generation

3-Impact

- **Dissemination of Results**
  - Patent application accepted
  - Published 8 papers in high impact journals (e.g. *Sustainable Energy and Fuels*, IF 5.5; *ACS Sustainable Chemistry & Engineering*, IF 7.6), 4 more in preparation
  - Conference presentations: AIChE, ACS
  - Media coverage: Biofuels Digest, Telegram & Gazette, Biofuels News, Spectrum News, ChemicalProcessing.com
  - Collaborating companies Mainstream Engineering, MG Fuels and River Otter Renewables assessing the technology
  - 8 Awards won by students
  - 2 Masters and 1 PhD Thesis, 11 undergraduate projects



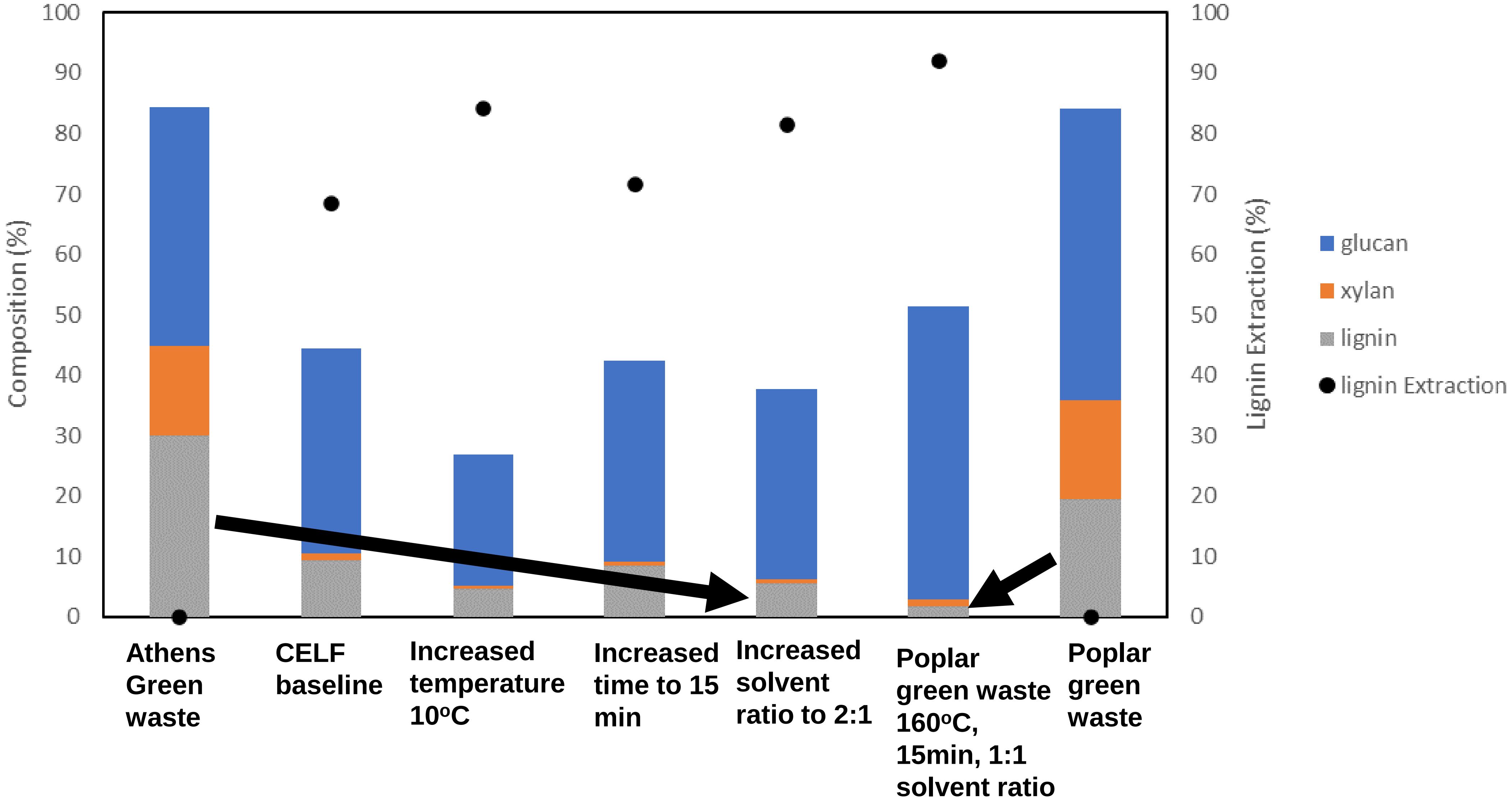
4-Progress and Outcomes
Task 3 – Fractionation of lignin and carbohydrates from green waste (UC-Riverside)



Milestones achieved	Benchmark
>90% lignin-free fraction from real green waste, (Atlas green waste, 170^{o}C, 1% acid, 15 min) <20% carbohydrate in lignin phase Produced 1 kg of CELF lignin form green waste. For continuous HTL Quantified solvent loss Reused solvent in process	80% lignin free with ethanol organosolv from biomass >90% lignin free from CELF of woody biomass

- **Milestones Complete**
  - Produced lignin rich (>90% lignin) and lignin-free streams (<10% lignin) using real green waste feed
  - ***Benchmark: 80% lignin free with ethanol organosolv from biomass And >90% lignin free from CELF of woody biomass***
  - Produced 1 kg of lignin from biomass for continuous HTL processing
  - Quantified the solvent losses and solvent reuse. The total recovered THF is 87% from the feed stream and 98% from the CELF liquor stream
- **Milestones in Progress**
  - All milestones met
- **Challenges and Delays to Milestones**
  - Removal of ash content from green waste
  - Pandemic restrictions to labs and worker illness (delay ~6 months)
- **Future Work to Complete**
  - Work complete

Task 3- CELF Lignin and Carbohydrate Fractionation Optimization



4 - Progress and Outcomes

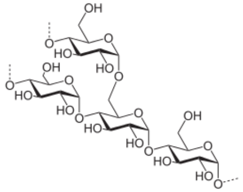
Task 4 – HTL of food waste and green waste fractions (WPI)

BDP green waste trimmings

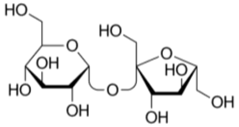
Food mixture

Food waste (UConn cafeteria)

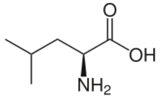
Food Waste VA Hospital



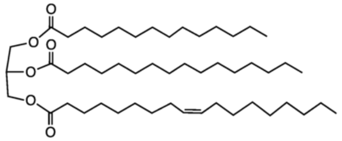
Carbohydrates



Sugars



Amino Acids



Fats (Triglycerides)

HTL Oil

Batch Reactor
Wet Feed: 15 wt%
T = 300 °C
P = 150 – 200 atm

4 - Progress and Outcomes
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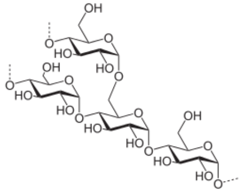

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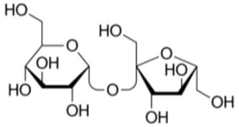

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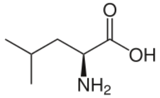

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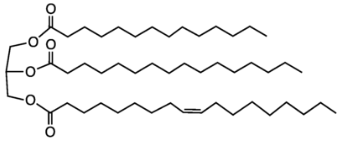

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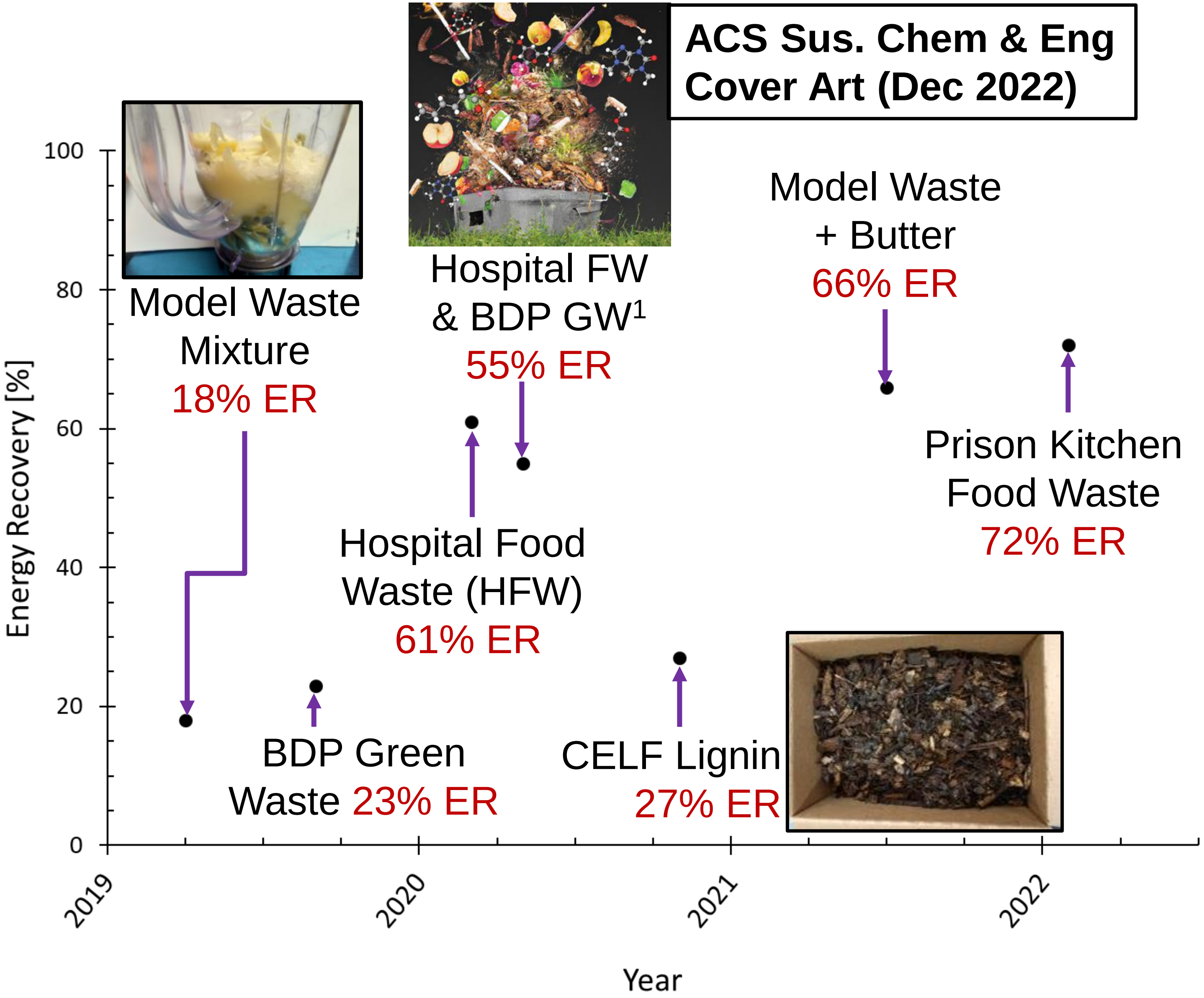

ACS Sus. Chem & Eng Cover Art (Dec 2022)

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[1] LeClerc, et al. "Emergent chemical behavior in mixed food and lignocellulosic green waste hydrothermal liquefaction." *ACS Sus Chem & Eng* (2022).

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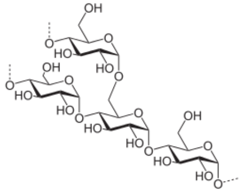

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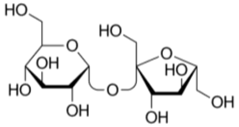

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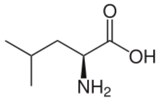

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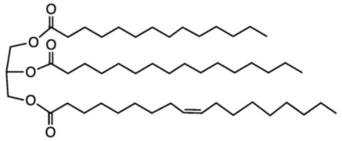


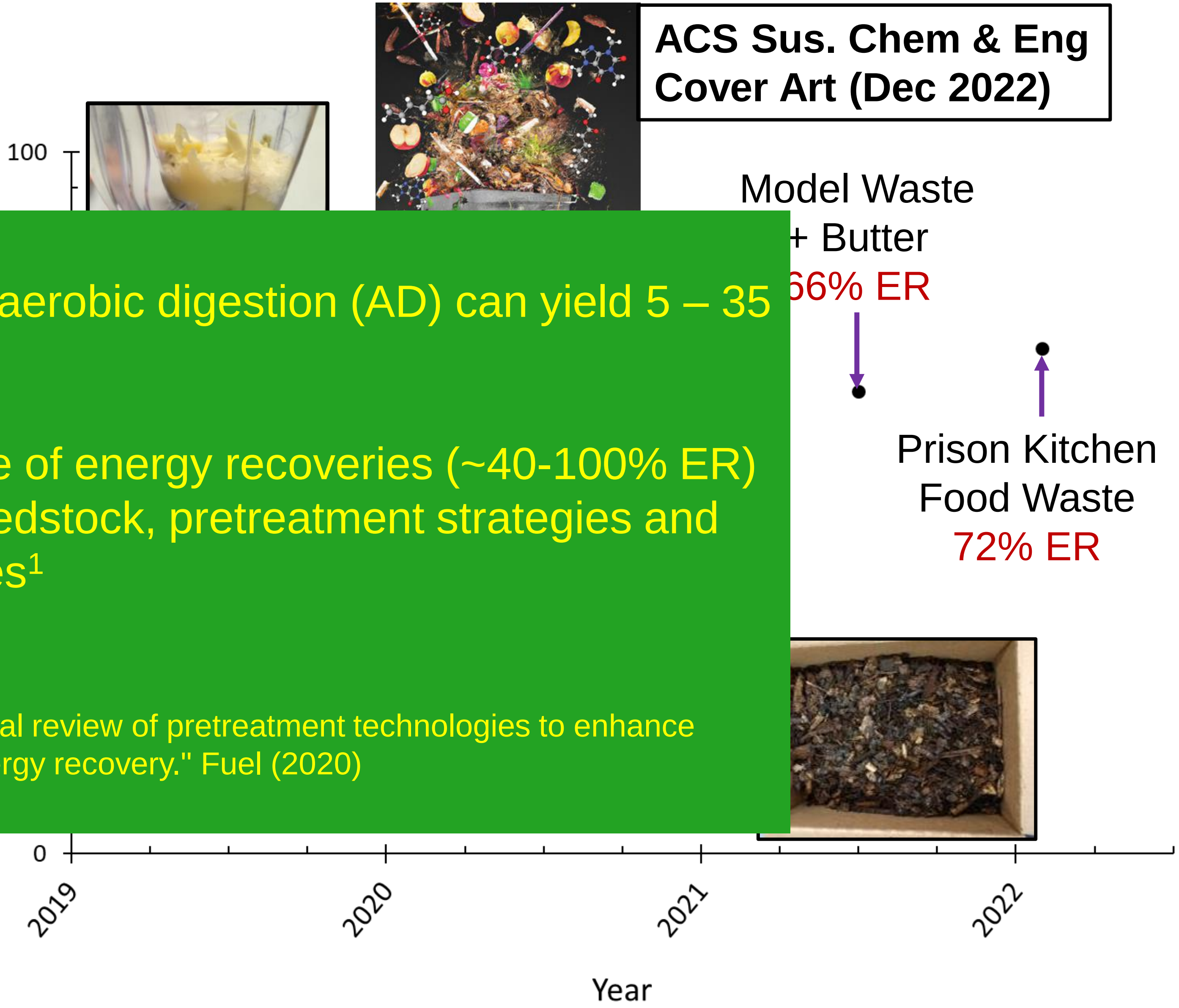
Fats (Triglyceride

HTL Oil

For comparison, Anaerobic digestion (AD) can yield 5 – 35 MJ biogas/kg solids

- AD has wide range of energy recoveries (~40-100% ER) → dependent on feedstock, pretreatment strategies and number of AD stages[1]

[1] Atelge, M. R., et al. "A critical review of pretreatment technologies to enhance anaerobic digestion and energy recovery." Fuel (2020)



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4 - Progress and Outcomes
Task 4 – HTL of food waste and green waste fractions (WPI)

- **Milestones on target**
  - Evaluated HTL performance of mixture and real food waste feed streams, green waste and food waste-green waste mixtures plus additional lignin-free green waste stream
  - Optimization of reaction time, temperature and solids loading
  - Used machine learning to model relation between feedstock and biocrude yield

- **Milestones in Progress**
  - Started kinetic studies on the effects of reaction temperature and time for different feed stocks

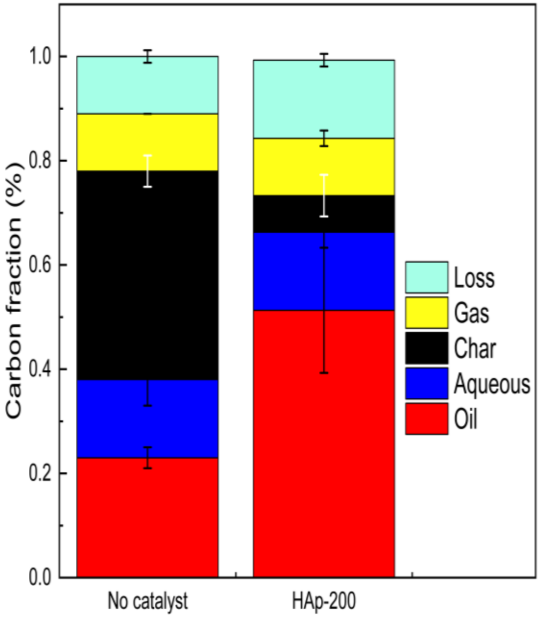
- **Challenges and Delays to Milestones**
  - Low oil yield from carbohydrate-rich feeds
  - Pandemic restrictions to labs and worker illness.
  - Delayed project milestones by ~6 months

- **Future Work to Complete**
  - kinetic studies on the effects of reaction temperature and time for different feed stocks

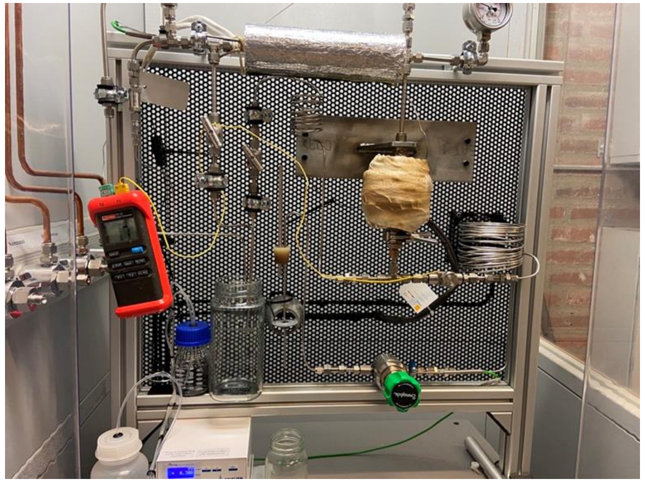
HTL evaluation	Oil Yield and ER
food surrogate mixture	20%, 18% ER
Lignin from green waste	50%, 27% ER
food waste/lignin	34%, 42% ER
green waste/food waste	34%, 50% ER
real food waste	42%, 72% ER

4-Progress and Outcomes

Task 5 – Catalytic Carbon-carbon coupling reactions – Catalytic HTL (WPI)



Hydroxyapatite catalyst with food waste feed, batch reactor



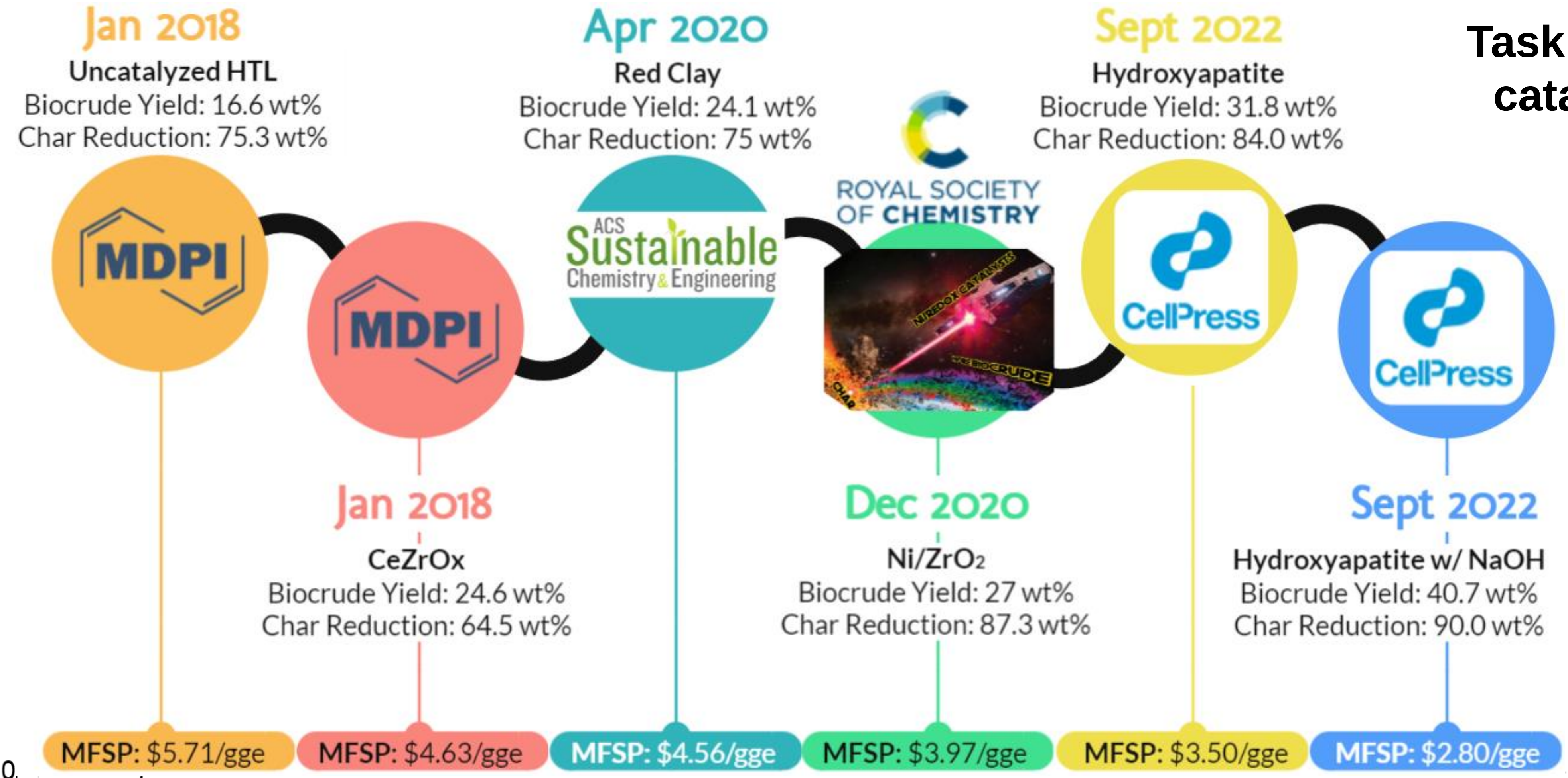
Continuous reactor built for aqueous phase upgrading

Milestones achieved	Benchmark
>45% energy recovery from food waste mixture and real food waste, 300 ºC, 20 MPa batch 52 h continuous CHTL of Hydrothermal aqueous phase	18% ER for food waste HTL (no catalyst) up to 89% ER for algae

- **Milestones on target**
  - ***>45% energy recovery with CHTL of food waste***
  - ***Benchmark: 18% ER for food waste HTL (no catalyst)***

    76% ER from sludge (PNNL), up to 89% ER for algae
  - ***Completed 52 hours continuous catalytic HTL of HTL aqueous phase using zeolite catalyst***
  - showed significant reductions in aqueous phase organic carbon (70%) and production of BTEX chemicals.
- **Milestones in Progress**
  - Completing >100 hours continuous CHTL
- **Challenges and Delays to Milestones**
  - Low conversion using hydroxyapatite, switched to ZSM-5 catalyst for continuous reactor
  - Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months
- **Future Work to Complete**
  - 48 hours (cumulative) stability of catalyst under actual reaction conditions while retaining >80% of original activity

Task 5 – HTL with catalyst timeline



Jan 2018
Uncatalyzed HTL
Biocrude Yield: 16.6 wt%
Char Reduction: 75.3 wt%
MFSP: $5.71/gge

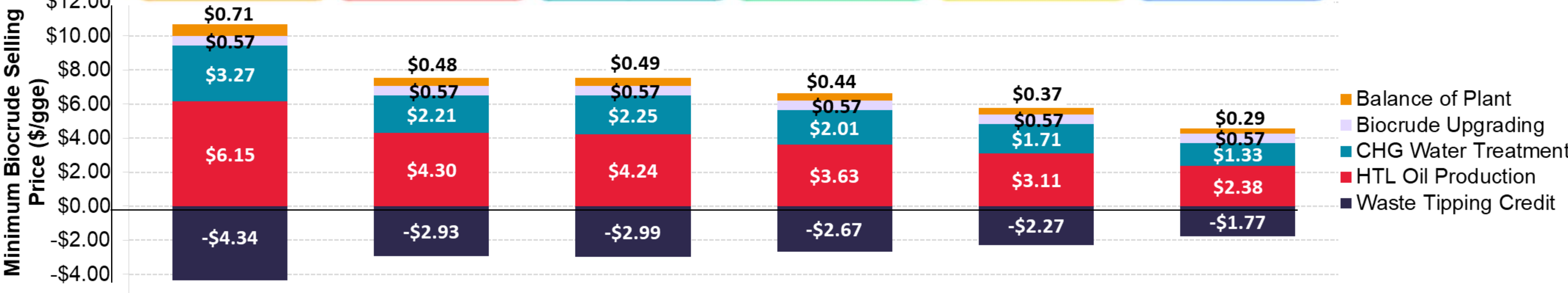
Jan 2018
CeZrOx
Biocrude Yield: 24.6 wt%
Char Reduction: 64.5 wt%
MFSP: $4.63/gge

Apr 2020
Red Clay
Biocrude Yield: 24.1 wt%
Char Reduction: 75 wt%
MFSP: $4.56/gge

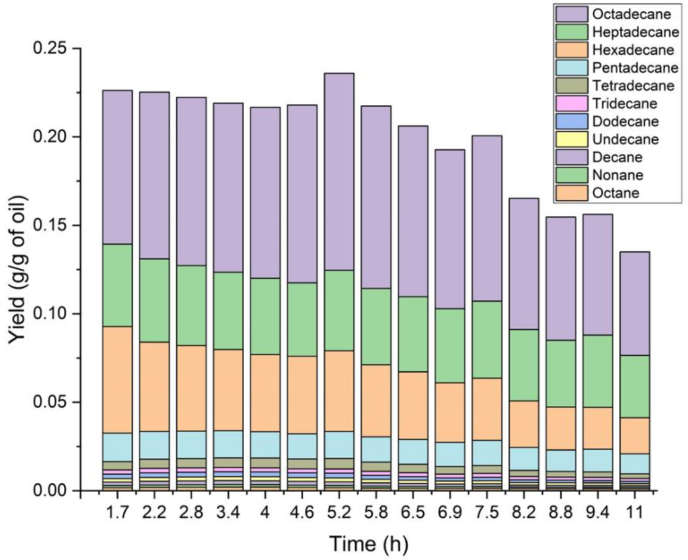
Dec 2020
Ni/ZrO_2
Biocrude Yield: 27 wt%
Char Reduction: 87.3 wt%
MFSP: $3.97/gge

Sept 2022
Hydroxyapatite
Biocrude Yield: 31.8 wt%
Char Reduction: 84.0 wt%
MFSP: $3.50/gge

Sept 2022
Hydroxyapatite w/ NaOH
Biocrude Yield: 40.7 wt%
Char Reduction: 90.0 wt%
MFSP: $2.80/gge



4-Progress and Outcomes
Task 6 – Hydrodeoxygenation/hydrodenitrogenation Upgrading of Biocrude (MIT)



NiMoS-Al_2O_3 catalyst. Conditions: 350°C, 80 bar H_2, 5wt% biocrude in toluene feed, 0.3 mL/min flow rate

=> Alkane products

Milestones achieved	Benchmark
Production of upgraded oil with **<1 wt% O and <1 wt% N** from biocrude dilute in toluene Catalyst operation >100 hours on stream (cumulative) that maintain >50% conversion ***NiMoS/Al_2O_3 best to date***	upgrading algae oil standard <3%O, <1%N, sewage sludge HTL oil <1%O, <23%N, feedstock dependent

- **Milestones on target**
  - Catalyst synthesis and evaluation completed
  - Production of HTL oil with **<1 wt% oxygen content and <1 wt% nitrogen content** from hydrothermal biocrude achieved using dilute solution in toluene solvent
  - ***Benchmark: upgrading algae oil standard <3%O, <1%N, sewage sludge HTL oil <1%O, <23%N, feedstock dependent***
  - catalyst operation time-on-stream >100 hours (cumulative) with differing catalysts and dilutions
- **Milestones in Progress**
  - Stable catalyst operation profiles >100 hours on stream (cumulative) that maintain >50% conversion
  - Catalyst stability study

Challenges and Delays to Milestones

- Catalyst stability at high biocrude concentration
- Pandemic restrictions to labs and worker illness ~6 months delay)

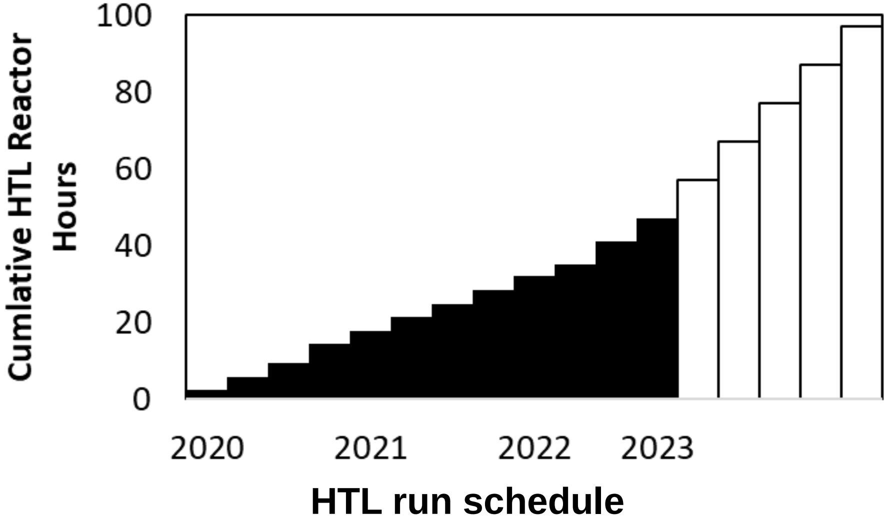
Future Work to Complete

- Stable catalyst operation profiles >100 hours on stream

(cumulative) that maintain >50% conversion

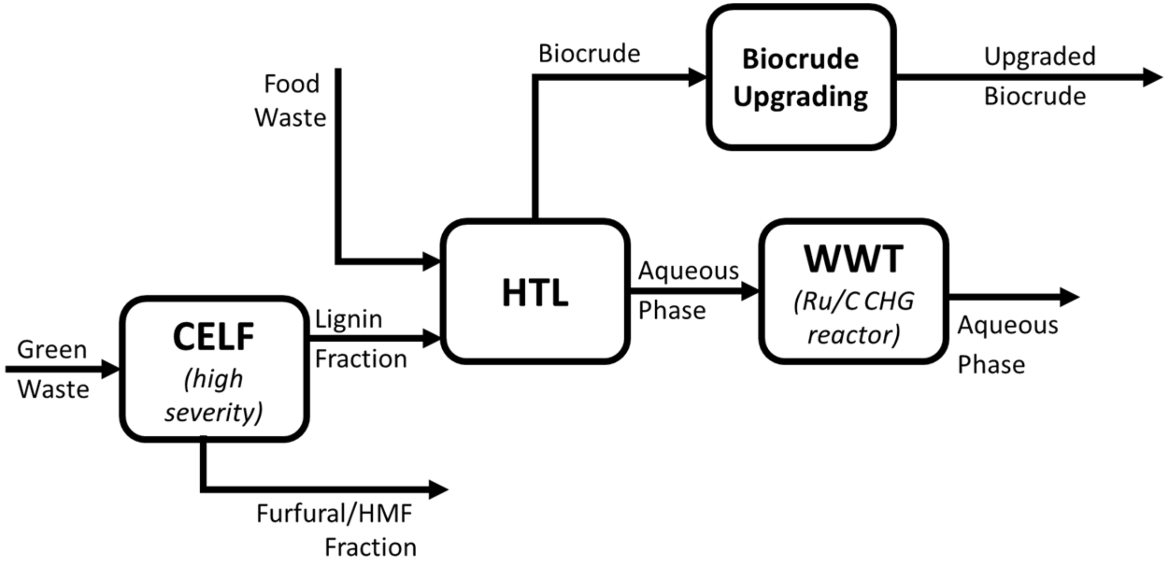
4-Progress and Outcomes

Task 7 – Continuous Hydrothermal Liquefaction Pilot Plant Operation (Mainstream)



- **Milestones on target**
  - Pilot scale continuous hydrothermal reactor system constructed and operated for >45 hours with surrogate and real feeds
  - Scale-up quantities of Biocrude supplied to MIT and WPI
- **Milestones in Progress**
  - Continuous reactor operation with catalysts and real food waste feed, toward >100 h operation
- **Challenges and Delays to Milestones**
  - Pumping real feedstocks
- **Future Work to Complete**
  - 55 hours (cumulative) operation of the HTL pilot plant, with combined >40% energy recovery as HTL oil and lignin products

4-Progress and Outcomes
Task 8 – Technoeconomic analysis and Life Cycle Analysis (Mainstream/WPI)



TEA Inputs

Feedstock	Yield (%)	HHV (MJ/kg)
HFW: AGWL (75:25)	31.5	30.2

TEA outputs

Feedstock	Parameter	Calculated Metrics
HFW:AGWL (75:25)	MFSP	$2.74/gge
	ER (HTL Only)	39.1%
	ER (HTL/CELF)	38.7%
	EROI	1.73

- **Milestones on target**
  - Completed Milestone of initial TEA/LCA on 100 dry ton per day scale
  - TEA completed for combined lignin-food waste process
  - We calculate **$2.74/gge** (including $1.1/gge upgrading, $0 tipping fee, no transportation costs, 30 min catalyst lifetime and for a 100 ton/year plant) for food waste and lignin
  - ***Benchmark: price that state-of-the-art $3.46/gge for upgraded oil form HTL of sewage (PNNL 2017)***
  - ***Benchmark: market value of diesel fuel ($2.7***)

- **Milestones in Progress**
  - Final Updates to TEA/LCA
- **Challenges and Delays to Milestones**
  - No delays to date

- **Future Work to Complete**
  - Update final TEA and LCA of CELF-HTL process with continuous HTL data

4-Progress and Outcomes
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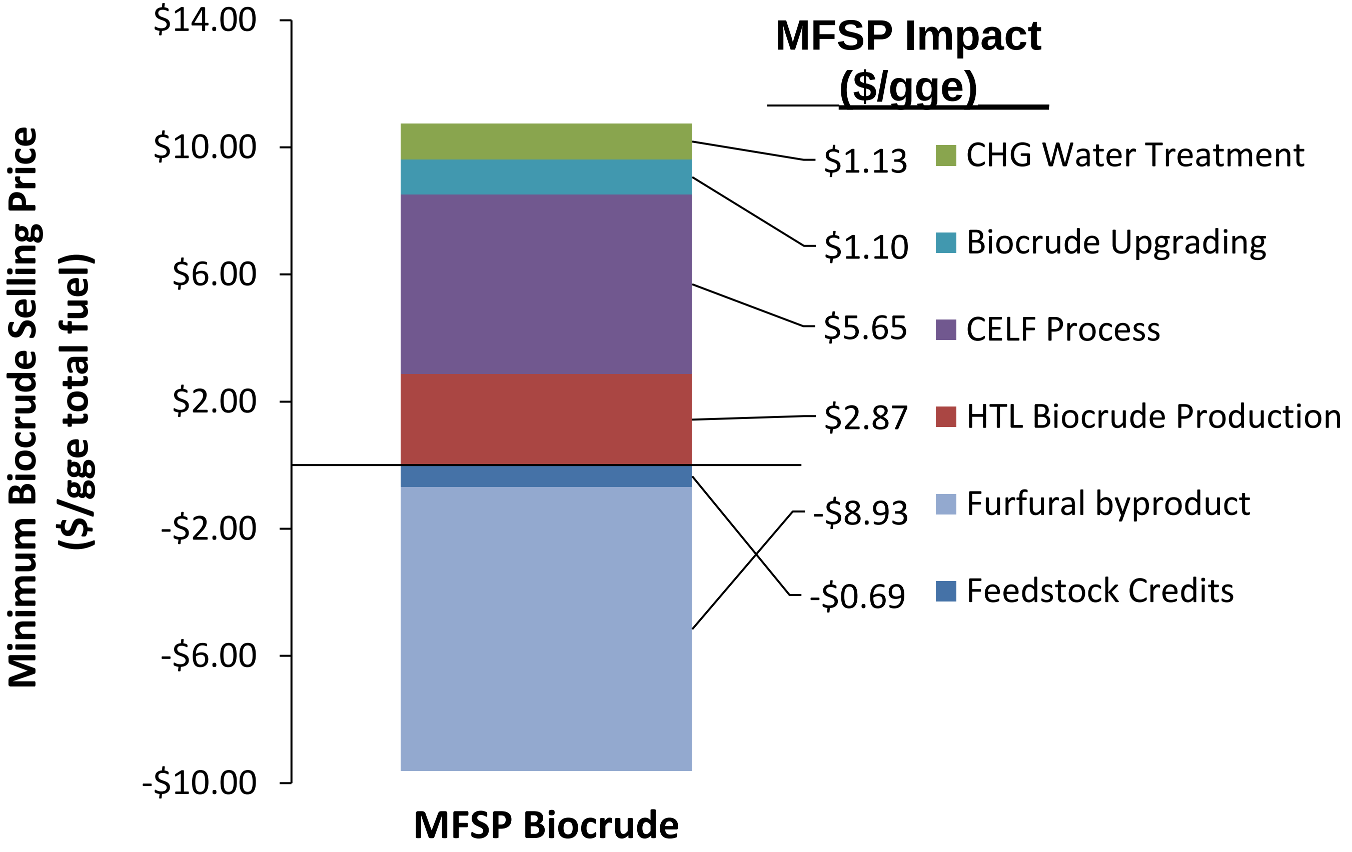

<u>Net Bio-oil MFSP:</u> $2.74/gge

Figure: Itemized costs associated with bio-oil selling price

4-Progress and Outcomes
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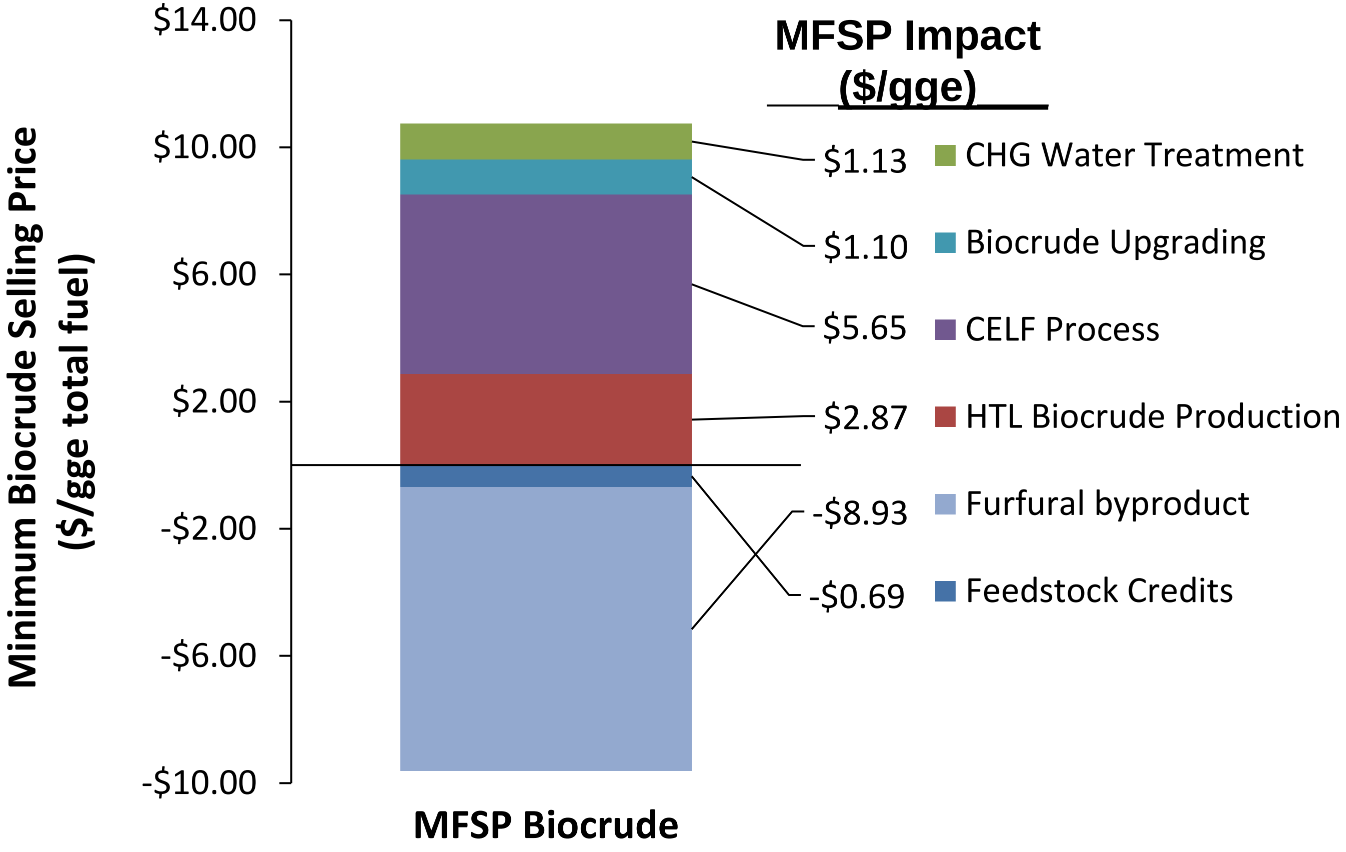


Net Bio-oil MFSP: $2.74/gge

Figure: Itemized costs associated with bio-oil selling price

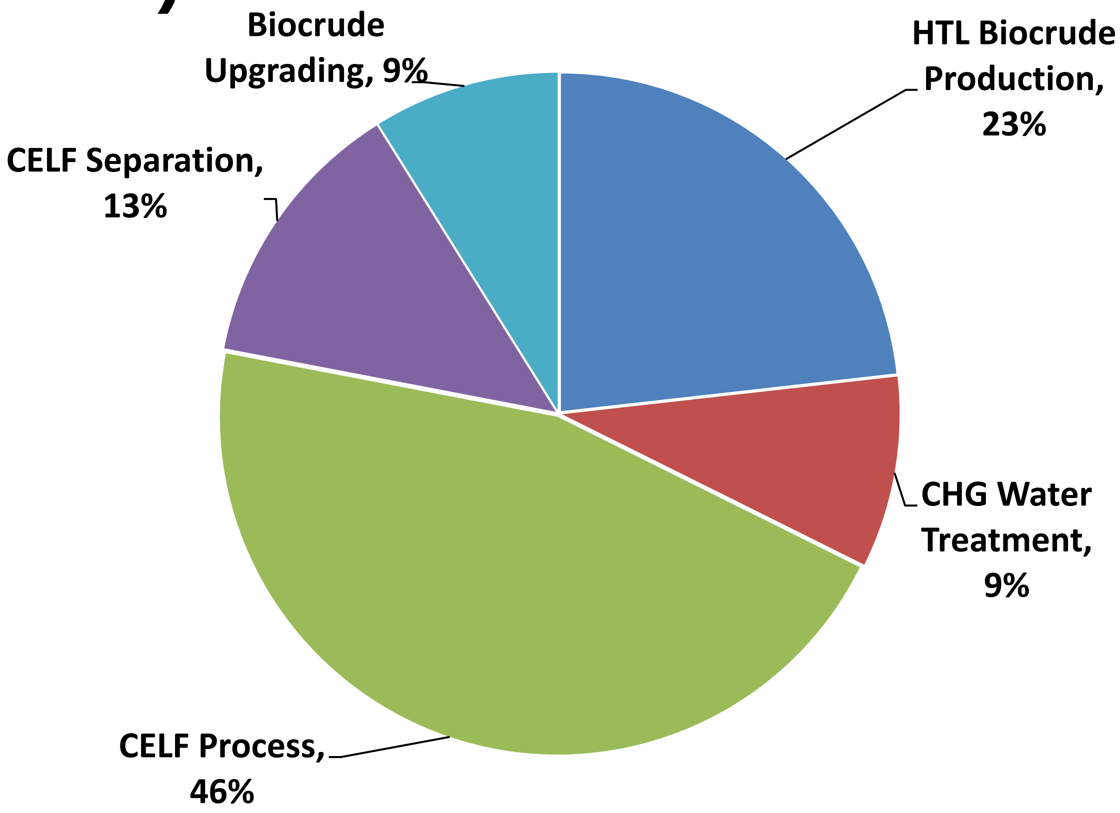


Figure: Fraction of MFSP cost associated with each process unit (includes CAPEX & OPEX)

- CELF process requires the most expenditure, but also produces a valuable furfural coproduct stream
- MFSP largely driven by CELF process costs

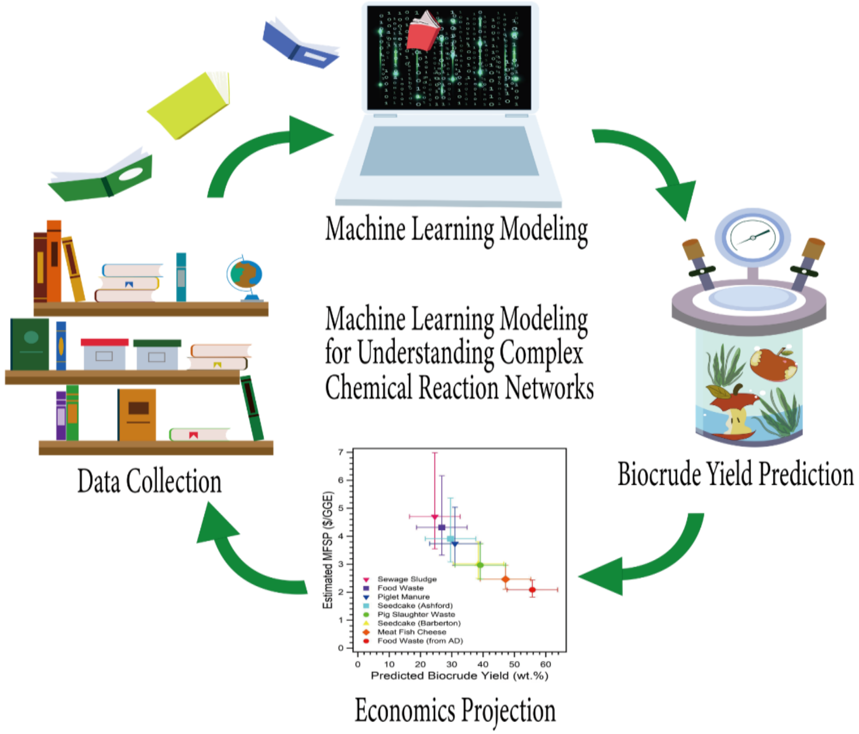
HTL Biocrude Upgrading

- PNNL
  - CoMo, NiMo catalysts
  - 2000 h steady state, time on stream using food waste and sludge feedstock biocrudes
  - Ref,. ACS Sustainable Chem. Eng. 2021, 9, 12825−12832

- Aarborg University, Denmark
  - NiMo catalysts
  - 2000 h continuous operation
  - Refs. Aalborg Linkedin and Renewable Energy,141, 2019, 420-430.

- WPI/MIT
  - Concentrated on Mo_2C catalyst for HDO/HDN to reduce hydrogen usage

Task 8 -Evaluating HTL Process Design Predictive MFSP using Machine Learning



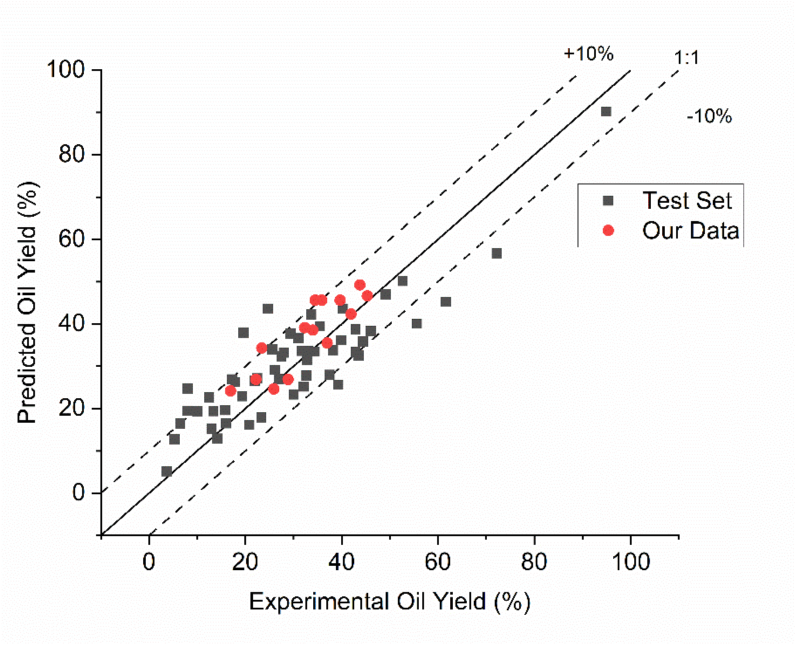
Machine Learning Modeling

Machine Learning Modeling for Understanding Complex Chemical Reaction Networks

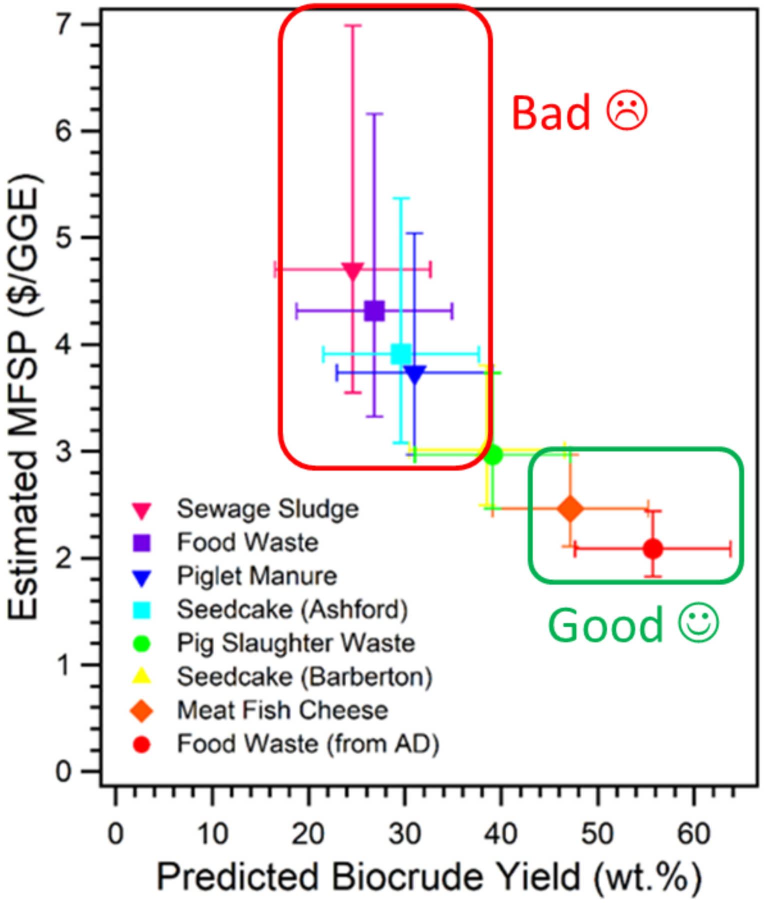
Biocrude Yield Prediction

Economics Projection

Data Collection



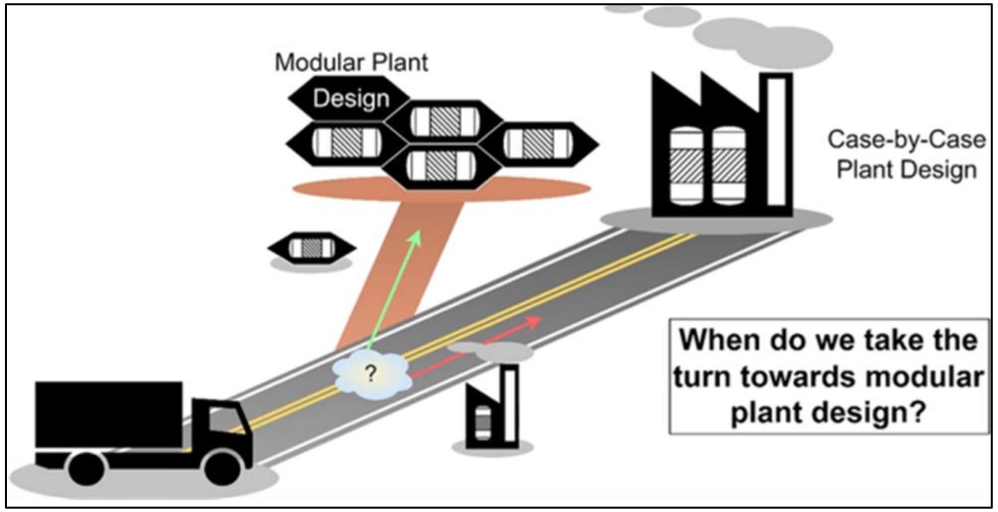
Our Random Forrest model outperforms other models
Can predict the biocrude yield for specific feeds with error ~8%



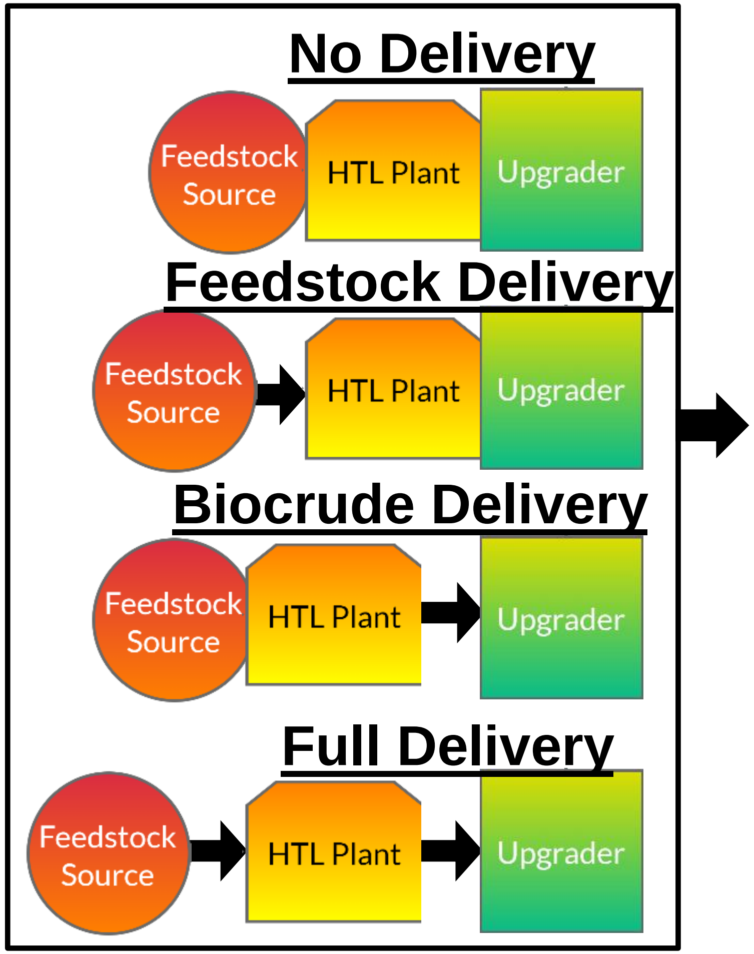
Estimated MFSP in $ per gallon of gasoline equivalent (GGE) as a function of predicted biocrude yield
Accurate enough to distinguish between “good” and “bad” feeds

Cheng et al., *Chemical Engineering Journal*, **2022**

Task 8 - Evaluating HTL Process Design - Modularized Plants



- Modularization of HTL near feedstock source can improve process economics
- Optimal scale shown for the model to be 60 DTPD
- After HTL, delivering a carbon dense biocrude for upgrading can minimize transportation costs



No Delivery

Feedstock Source
HTL Plant
Upgrader

Feedstock Delivery

Feedstock Source
HTL Plant
Upgrader

Biocrude Delivery

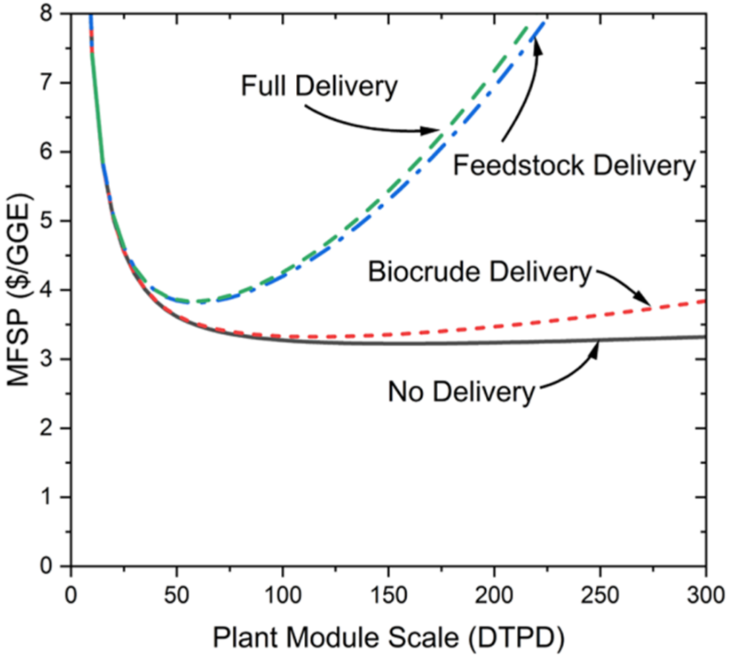
Feedstock Source
HTL Plant
Upgrader

Full Delivery

Feedstock Source
HTL Plant
Upgrader

Considered
4 Delivery Scenarios

Scenario Comparison
TEA Model



Published: ACS Sustainable Chemistry & Engineering 2023 11 (2), 733-743

Summary - 1

All milestones met or to be met before project completion

- Task 1: Initial Verification – Completed
- Task 2: Intermediate Verification - Completed
- Task 3 – CELF green waste fractionation
  - Produced lignin rich **(>90% lignin) and lignin-free streams (<10% lignin) using real green waste feed**, <20% carbohydrate in lignin phase
  - produced **1 kg of lignin from green waste**
- Task 4 – HTL
  - Evaluated three different food wastes, two different green wastes, lignin fractions, and their mixtures
  - Modeled HTL reaction pathways and biocrude yields
  - Achieved **>70% ER with food waste feed**
- Task 5- Catalytic HTL
  - Evaluated five generations of catalysts to improve biocrude yields
  - Optimal performance achieved using hydroxyapatite (HAp)
  - 55 h continuous ex situ upgrading of aqueous phase
- Task 6 – HDO/HDN
  - Exceeded oxygen and nitrogen removal milestones
  - Working on catalyst stability for Mo_2C

Summary - 2

Task 7 – Continuous HTL

- Completed 45 h out of 100 h required continuous operation using pilot scale reactor

Task 8 – TEA/LCA

- New economic modelling methods developed
- Combined CELF-HTL process optimized at 75% food waste and 25% lignin feed
- Projected **MFSP $2.74/gge, EROI 1.73**
- LCA :
  - HTL food waste: **-0.98 ton CO_2/ ton food waste**
  - CELF lignin HTL: **6.7 ton CO_2/ ton food waste**
  - CELF lignin + food waste HTL: **-0.65 ton CO_2/ ton food waste**

Quad Chart Overview

Timeline

- Project start date: 10/1/19
- Project end date: 9/30/22, 6/30/23 NCE

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 –* (10/01/2018 – 4/30/2020) BP1 $219,212	(negotiated total federal share) $1,995,199
Project Cost Share *	$54,861	$502,620

TRL at Project Start: 3

TRL at Project End: 5

Project Goal

Generation of bench-scale and pilot-scale data and models to de-risk commercialization of a process to convert a combined stream consisting of the food waste and green waste components of municipal solid waste (MSW) into an energy-dense bio-oil and refined lignin stream

To develop a robust strategy to improve processibility and conversion of MSW to energy dense liquid product as a biopower intermediate by integrating green waste fractionation with HTL and catalytic upgrading

End of Project Milestone

>100 hrs (cumulative) operation of the pilot-scale HTL reactor;

>100 hrs (cumulative) use of the C-C coupling catalyst; >100 hrs (cumulative) use of the HDO/HDN catalyst; LCOE of $3.72/gge ($32.6/mmBTU) – an 26% reduction. EROI of 5

Funding Mechanism

FOA: BETO/DOE 1926-1564

Award Number: DE-EE0008513, 2019

Project Partners*

- MG Fuels

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments

2021 BETO Project Reviewer Comments:

Comments: Might avoid using the term biosolids for the solid inert material that falls out of HTL. Just less rules/concerns than if it is called a biosolid. Extensive use of milestones and quantitative goals. Doing a great job of tracking progress against these values. Are going to miss some of the intermediate targets, eg MFSP, but will have made substantial progress on many others Seem to have hit some stretch milestones early with some good research choices. Team seems to be communicating well, and clearly articulated the challenges that COVID-19 has placed on the team. Team accurately communicated the level of risk/uncertainty, as well as presented reasonable mitigation plans. The project is still a bit early relative to others in the commercialization process, and may have a bit of trouble bridging the valley of death Scale, and runtime are accurate for the scale, but are still well removed from commercial relevancy This team is engaging with critical commercial partners including an oil company Phillips 66 Have assembled a strong advisory board Are using the PNNL HTL work/TEA to help better position this work with the other work that has been done in the HTL space, particularly the work that has been funded by BETO. Team is engaging with other DOE funded work, and with the larger scientific enterprise.

Comments: STRENGTHS - Strong multi-industry partnerships from research organizations and commercial partners - Structured engagement of commercial partners from each stage of the value chain - Clear research approach. Differentiated from other HTL research projects and influenced by industry advisors - strong understanding of regional needs and evidence of adapting research efforts to match these needs (e.g. identification of aviation gas needs) - Valuable progress on commercially viable catalyst (Hydroxyapatite) WEAKNESSES - Currently not included tipping or transportation fee. Will be critical to include this in model (there appears to be plans to adapt the model to include this) - It was difficult to determine what scale the catalyst work was being performed at and the scale-up challenges that would arise as the technology transitioned to more commercially relevant scales -In light of COVID-19, t would be valuable to explore the health and safety risk of transporting and handling large volumes of waste at commercial scale - Understanding the cost of processing waste with high soil content, or the cost of treating the feedstock to remove soil will be required

Comments: The project results to date are encouraging and they are meeting most of their milestones. They have a very diverse advisory team which is a benefit on this type of project. One concern is the problem they encountered with the food waste slurry and having to use dried waste. As the scale increases, using a dried feedstock may be impractical. I think it is important to understand why there was a problem with the waste slurry and how that can be changed moving towards full-scale processes. Would like to see a mass balance and a discussion on the waste streams produced and how they can be disposed or issues with disposal. Also a discussion on the potential impacts of recycle streams to the WRRF relative to nutrient removal or other permit or operational effects.

Comments: The management appears to be fine. The advisory board is particularly strong. The presentation was very unclear. There were aspects of the flow chart that was presented that were unclear and appeared to be undecided at the present time (for example, whether the upgrading was in situ or ex situ, how the green waste entered into the overall process). The presence and characteristics of waste streams that come from the proposed process are not clear, nor are the challenges that they may present. This should be incorporated into the TEA/LCA and into the flow chart. The most progress appears to have been made in the area of the catalyst use, which appeared to be strong. The scaling up of the system earlier than expected is also very good. The ultimate goals regarding mixing the yard waste and food waste were unclear. It seems that "pure" feeds are being used at this point, but again, that was not clear.

Comments: This project looks to improve overall performance of hydrothermal liquefaction (HTL) technology to convert a specific fraction of municipal solid waste (the food and yard waste portion) to liquid hydrocarbon fuels. The project management appears sound and the use of and composition of the Advisory Board is outstanding. These companies representing all of the key areas that intersect in this project (e.g., food waste source, waste management, refinery, HTL commercial company) should help guide the research and ensure that the project remains focused on real world issues and constraints. The approach concentrates on certain parts of the overall proposed process and is generally reasonable, though not all tasks appear to be of equal value. It is not clear what the innovation is in the lignin fraction portion of the project or how it has been successful, but it is also not clear why it is needed. HTL has been successfully demonstrated on wood feeds in the past without having to remove lignin and it is not obvious from the results presented that lignin removal is worth the additional steps and process complexity. While the use of catalysts in HTL tests adds to the process complexity, the ability to grow carbon chains to ensure that more carbon stays in the oil phase instead of the aqueous phase and the resulting higher biocrude carbon yields is impressive. This may signify a key advantage to catalyst use and possibly be a game changer, especially when the target feed is mostly six carbon carbohydrate species as opposed to longer chain lipids that are more likely to stay in the product oil phase on their own. The upgrading results presented are not that impressive to date. The milestone of demonstrating less than 9% oxygen in the upgraded oil sets the bar much too low. Current hydrogenation technology can easily achieve the required target of less than 1% oxygen for acceptance by a refinery, so it is not clear what exactly has been accomplished in this task to date. The construction of a continuous HTL pilot plant will be useful if it represents a fully integrated version of the proposed process. The technoeconomic assessment (TEA) is modeled after that developed by PNNL and the results presented with respect to minimum fuel selling price (MFSP) of the fuel product appears to be comparable to that presented by PNNL. While this is encouraging on the one hand, it is not clear how this project's TEA distinguishes itself from that of PNNL and whether this is an unnecessary duplication of effort. Some of the stated TEA assumptions (e.g., no tipping fees or transportation costs) are not realistic and a base case non-zero value should be included in the model. The impact of this project in advancing HTL technology and the development of liquid hydrocarbon fuels is significant and entirely consistent with BETO's objectives.

Note: This slide is for the use of the Peer Reviewers only – it is not to be presented as part of your oral presentation. These Additional Slides will be included in the copy of your presentation that will be made available to the Reviewers.

Publications, Patents, Presentations, Awards, and Commercialization

- **Publications**

1. Patent application on Hydroxyapatite HTL catalysis, approved by USPTO patent examiner, 2022.
2. LeClerc, Heather O., Jeffrey R. Page, Geoffrey A. Tompsett, Sydney F. Niles, Amy M. McKenna, Julia A. Valla, Michael T. Timko, and Andrew R. Teixeira. "Emergent chemical behavior in mixed food and lignocellulosic green waste hydrothermal liquefaction." *ACS Sustainable Chemistry & Engineering* (2022).
3. Cheng, Feng, Geoffrey A. Tompsett, Caroline M. Murphy, Alex R. Maag, Nicholas Carabillo, Marianna Bailey, Jeremy J. Hemingway et al. "Synergistic effects of inexpensive mixed metal oxides for catalytic hydrothermal liquefaction of food wastes." *ACS Sustainable Chemistry & Engineering* 8, no. 17 (2020): 6877-6886.
4. Maag, A. R., Paulsen, A. D., Amundsen, T. J., Yelvington, P. E., Tompsett, G. A., & Timko, M. T. (2018). Catalytic hydrothermal liquefaction of food waste using CeZrOx. *Energies*, *11*(3), 564.
5. Cheng, F., Tompsett, G. A., Alvarez, D. V. F., Romo, C. I., McKenna, A. M., Niles, S. F., ... & Timko, M. T. (2021). Metal oxide supported Ni-impregnated bifunctional catalysts for controlling char formation and maximizing energy recovery during catalytic hydrothermal liquefaction of food waste. *Sustainable Energy & Fuels*, *5*(4), 941-955.
6. Hydroxyapatite catalyzed hydrothermal liquefaction transforms food waste from an environmental liability to renewable fuel, LeClerc, H.O., Tompsett, G.A., Paulsen, A.D., ...Teixeira, A.R., Timko, M.T., iScience, 2022, 25(9), 104916.
7. Accuracy of predictions made by machine learned models for biocrude yields obtained from hydrothermal liquefaction of organic wastes, Cheng, F., Belden, E.R., Li, W., Shahabuddin, M., Paffenroth, R.C., Timko, M.T., Chemical Engineering Journal, 2022, 442, 136013.
8. Elucidating the role of reactive nitrogen intermediates in hetero-cyclization during hydrothermal liquefaction of food waste, H. LeClerc, L. Mateo, G. A. Tompsett, M. T. Timko and A. Teixeira. Green Chemistry, 2022, 24(13), pp. 5125–5141.
9. Roadmap for Deployment of Modularized Hydrothermal Liquefaction: Understanding the Impacts of Industry Learning, Optimal Plant Scale, and Delivery Costs on Biofuel Pricing, Muntasir Shahabuddin, Eduardo Italiani, Andrew R. Teixeira, Nikolaos Kazantzis, and Michael T. Timko, ACS Sustainable Chemistry & Engineering 2023 11 (2), 733-743
10. In preparation. Scheidemantle, Tompsett, Timko, Cai. 2022. “Evaluation of novel co-solvent pulping reactor for one-pot pretreatment and fractionation municipal green waste for the production of bio-oil”. *ChemSusChem*.
11. In preparation. “Molecular tracking of lignin obtained from co-solvent enhanced fractionation and processed under HTL conditions.”, Ronish Shrestha, Feng Cheng, Geoffrey Tompsett, Brent S, Charles Cai and Michael T. Timko. An invited submission at RSC Sustainable Energy and Fuels before the end of the calendar year
12. In preparation 2022. Catalytic Strategies for Hydrotreating of HTL bio-crude: A potential application on liquefaction of food waste feedstocks, Andres Granados-Focil, Meshack Audu, Geoffrey Tompsett and Michael Timko
13. In preparation: Waste refinery without waste: Cascade Circular Solvothermal Process Approach” For Energy & environmental Science, 2023.
14. Shahabuddin, M., & Italiani, E. (2021). Techno-Economic Analysis to Determine the Optimal Scale of Hydrothermal Liquefaction: Effects of Learning Rates, Transportation, and Catalysis. : Worcester Polytechnic Institute. MQP Project.
15. Shahabuddin, M. (2022). Economic Tools and Roadmaps for Widespread Deployment of Hydrothermal Liquefaction. : Worcester Polytechnic Institute. Master of Science Dissertation
16. Shrestha, R. (2022) Worcester Polytechnic Institute. Structure and thermal reactivity of kraft and co-solvent fractionated lignin processed under Hydrothermal Liquefaction, Master of Science Dissertation
17. LeClerc, H. (2023) Molecular pathway analysis of biocrude in hydrothermal liquefaction, Worcester Polytechnic Institute, PhD Dissertation.

- **Conference presentations**
- 255c Uncovering the Effect of Mechanochemical Pretreatment on Biocrude Yields and Chemical Mechanism of Lignocellulosic HTL, Heather LeClerc, Alex Maag, Geoffrey Tompsett, Michael T. Timko and Andrew R Teixeira, AIChE Annual Meeting Phoenix, AZ, November 2022.
- 25d Accuracy of Predictions Made By Machine Learned Models for Biocrude Yields Obtained from Hydrothermal Liquefaction of Organic Wastes, Feng Cheng, Elizabeth Belden, Wenjing Li, Muntasir Shabuddin, Randy Paffenroth and Michael T. Timko, AIChE Annual Meeting Phoenix, AZ, November 2022.
- 495c Predicting the Role of Reactive Nitrogen Intermediates during Hydrothermal Liquefaction of Food Waste, Heather LeClerc, Rasha Atwi, Amy M. McKenna, Michael T. Timko, Richard H. West and Andrew R Teixeira, AIChE Annual Meeting Phoenix, AZ, November 2022.
- 532a Continuous Carbon Recovery from HTL Aqueous Phase, Poster Session: Catalysis and Reaction Engineering (CRE) Division, Heather LeClerc, Geoffrey Tompsett, Daniele Castello, Michael T. Timko, Thomas H. Pedersen and Andrew R Teixeira, AIChE Annual Meeting Phoenix, AZ, November 2022.
- 66g Monomers and Biocrude from Hydrothermal Liquefaction of Solvent-Fractionated Lignin, Session: Efficient Processing of Lignin to Bioproducts and Biofuels, Ronish Shrestha, Feng Cheng, Geoffrey Tompsett, Brent Scheidemantle, Charles M. Cai, Klaus Schmidt-Rohr and Michael T. Timko, AIChE Annual Meeting Phoenix, AZ, November 2022.
- Shrestha, R. (2022). Structure and thermal reactivity of kraft and co-solvent fractionated lignin processed under Hydrothermal Liquefaction. Worcester Polytechnic Institute. Masters Thesis.

Publications, Patents, Presentations, Awards, and Commercialization

- **Undergraduate Projects**
- 5 Major Qualifying projects (WPI), 6 NSF REU undergraduate projects, >8 undergraduate research volunteers

- **Awards**:
- Heather LeClerc, Graduate Research Fellowship award 2020
- Muntasir Shahabuddin, Graduate Research Fellowship award 2022
- Heather LeClerc, Heh Won Chang Green Chemistry Fellowship 2021
- Heather LeClerc, WPI Women's Impact Network Grant, 2020
- Heather LeClerc, Fulbright Scholarship 2021
- Heather LeClerc, MIT Rising Star of Chemical Engineering 2022.
- Heather LeClerc, CRE poster award at AIChE, November 2022.
- Heather LeClerc, Gaylord Donnelley postdoctoral fellowship at Yale, Starting July 2023.

- **Commercialization:**
- River Otter Renewables company negotiating with WPI for technology

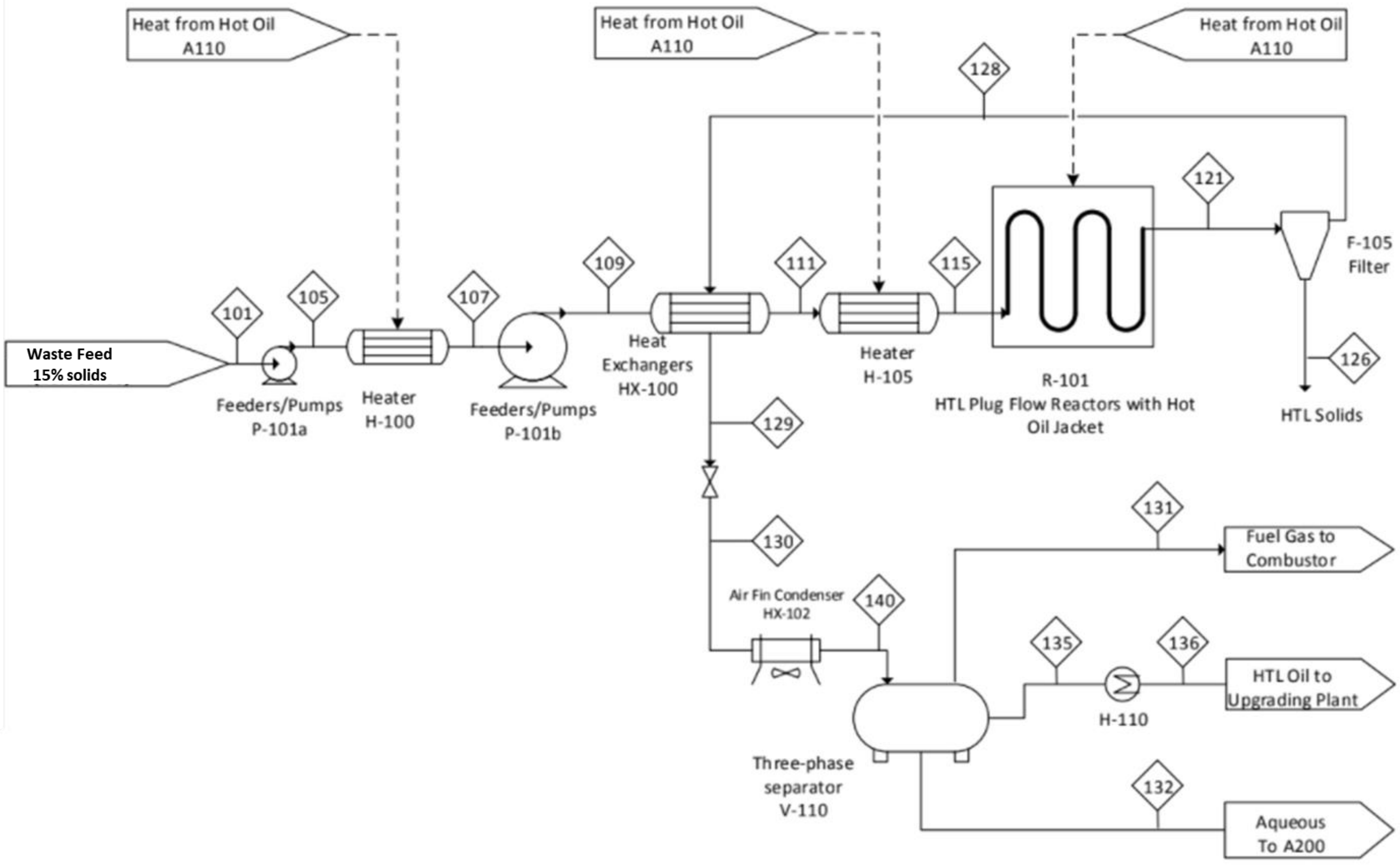
Supplemental Slides - TEA

Process Flow diagram of HTL Unit

Reaction Conditions

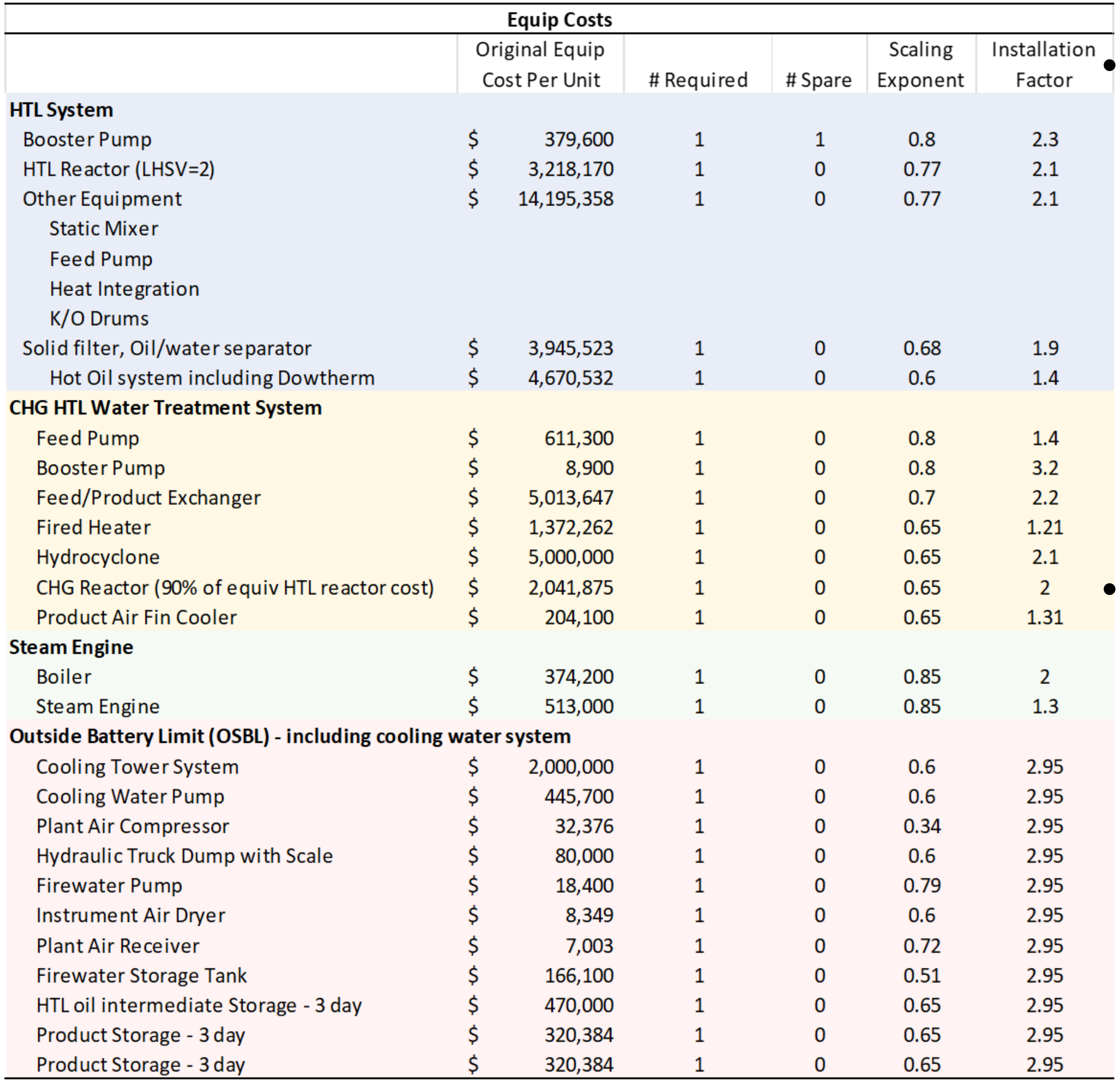
- Temperature: **300 °C**
- Residence Time: **30 min**
- Scale: **112 TPD**
  (Line 155 into HTL)
- **15% wt organic loading**

HTL Inflow Stream	**Flowrate** *(tons/day)*
Total Flowrate (#115)	755.5
Dry Biomass Basis	112
HTL Outflow Stream	
Filtered Solids (#126)	8.4
Aqueous Phase (#132)	680.0
HTL Oil (#136)	42.8
Fuel Gas (#131)	12.8



**Process flow diagram adopted from PNNL sludge model

TEA – HTL Equipment Costs



Equip Costs					
	Original Equip Cost Per Unit	# Required	# Spare	Scaling Exponent	Installation Factor
HTL System					
Booster Pump	$ 379,600	1	1	0.8	2.3
HTL Reactor (LHSV=2)	$ 3,218,170	1	0	0.77	2.1
Other Equipment	$ 14,195,358	1	0	0.77	2.1
Static Mixer					
Feed Pump					
Heat Integration					
K/O Drums					
Solid filter, Oil/water separator	$ 3,945,523	1	0	0.68	1.9
Hot Oil system including Dowtherm	$ 4,670,532	1	0	0.6	1.4
CHG HTL Water Treatment System					
Feed Pump	$ 611,300	1	0	0.8	1.4
Booster Pump	$ 8,900	1	0	0.8	3.2
Feed/Product Exchanger	$ 5,013,647	1	0	0.7	2.2
Fired Heater	$ 1,372,262	1	0	0.65	1.21
Hydrocyclone	$ 5,000,000	1	0	0.65	2.1
CHG Reactor (90% of equiv HTL reactor cost)	$ 2,041,875	1	0	0.65	2
Product Air Fin Cooler	$ 204,100	1	0	0.65	1.31
Steam Engine					
Boiler	$ 374,200	1	0	0.85	2
Steam Engine	$ 513,000	1	0	0.85	1.3
Outside Battery Limit (OSBL) - including cooling water system					
Cooling Tower System	$ 2,000,000	1	0	0.6	2.95
Cooling Water Pump	$ 445,700	1	0	0.6	2.95
Plant Air Compressor	$ 32,376	1	0	0.34	2.95
Hydraulic Truck Dump with Scale	$ 80,000	1	0	0.6	2.95
Firewater Pump	$ 18,400	1	0	0.79	2.95
Instrument Air Dryer	$ 8,349	1	0	0.6	2.95
Plant Air Receiver	$ 7,003	1	0	0.72	2.95
Firewater Storage Tank	$ 166,100	1	0	0.51	2.95
HTL oil intermediate Storage - 3 day	$ 470,000	1	0	0.65	2.95
Product Storage - 3 day	$ 320,384	1	0	0.65	2.95
Product Storage - 3 day	$ 320,384	1	0	0.65	2.95

- **Current estimates for equip costs for HTL, WWT, upgrading & OSBLs (see left)**
  - Incorporate any additional process units required into CELF model *(Piping, pumps, filters, mixers, heat exchangers, etc…)*
  - Include indirect cost estimate for CELF *(Can use similar estimations used in HTL model)*

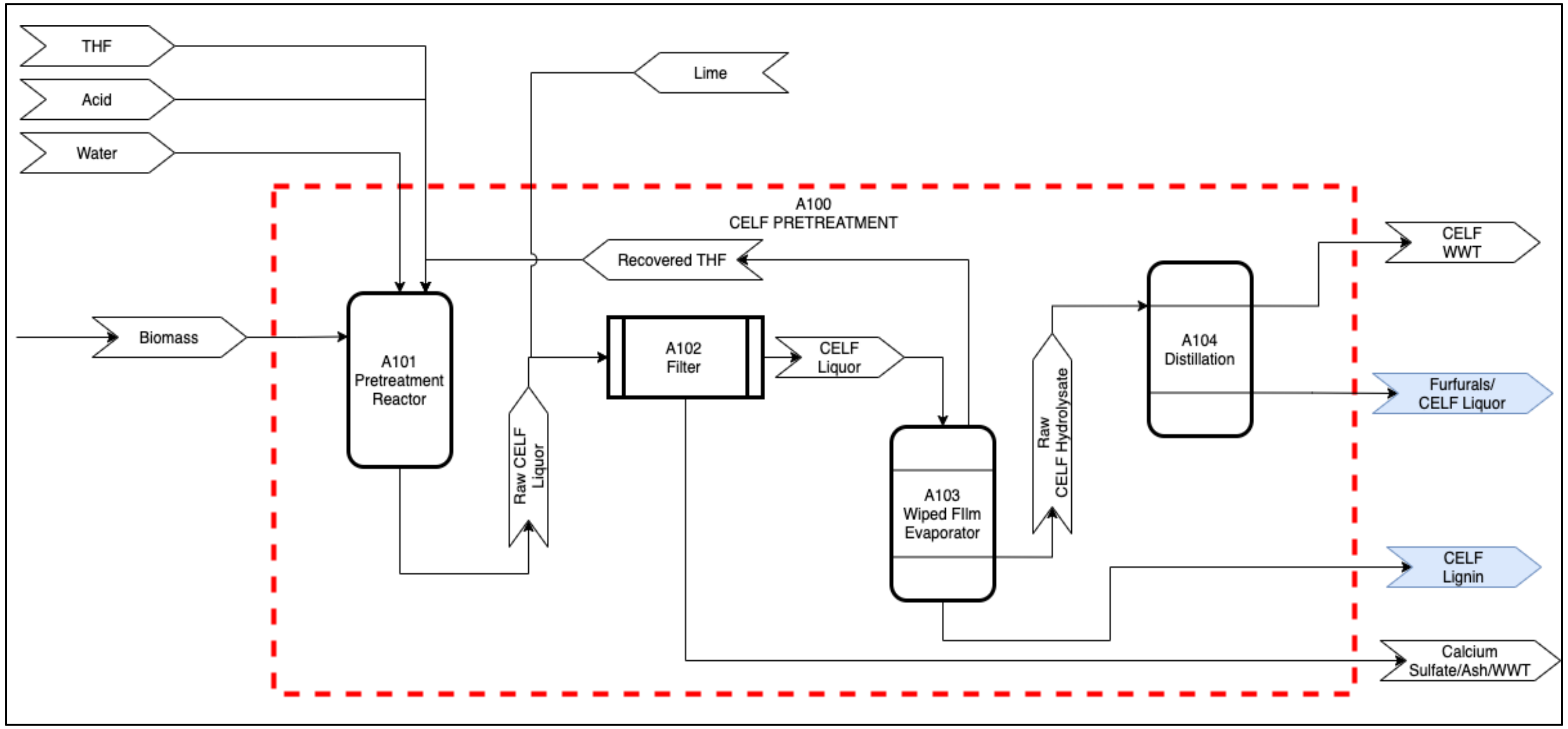
- **Operating expense estimates available for both CELF and HTL models *(labor costs, raw materials, & utilities)***
  - Consolidate labor costs between HTL & CELF models.
  - Consider heat integration between CELF and HTL

TEA – CELF Process Details

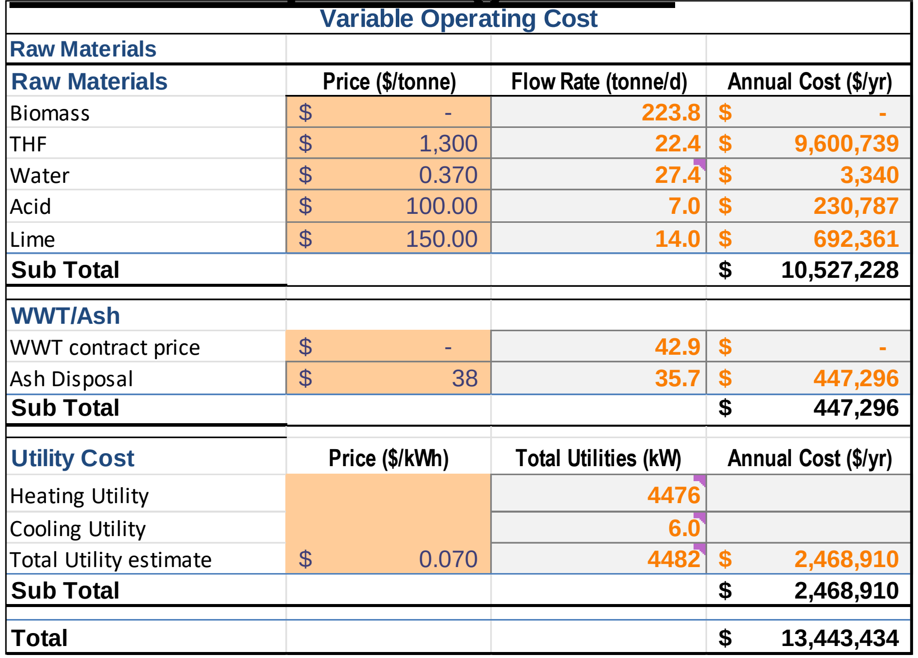
- CELF Process includes four CAPEX units with raw materials, waste disposal and utility costs included in the two tables (Right)
  - Biomass feed set to $0/ton – possibly could have a tipping fee ($89.37/ton in LA County[1])
  - THF large fraction of variable operating cost (~95% of costs)
  - Water effluent is sent to CHG reactor prior to WRRF

Equipment Costs

Unit Operation	Original Equip Cost per Unit	Scale Exponent	Installation Factor
Pretreatment Reactor	$ 22,000,000	0.6	1.5
Filter	$ 500,000	0.8	1.5
Wiped Film Evaporator	$ 2,000,000	0.9	2.5
Distillation	$ 1,000,000	0.6	2.5



Variable Operating Costs



Variable Operating Cost			
Raw Materials			
Raw Materials	**Price ($/tonne)**	**Flow Rate (tonne/d)**	**Annual Cost ($/yr)**
Biomass	$ -	223.8	$ -
THF	$ 1,300	22.4	$ 9,600,739
Water	$ 0.370	27.4	$ 3,340
Acid	$ 100.00	7.0	$ 230,787
Lime	$ 150.00	14.0	$ 692,361
Sub Total			**$ 10,527,228**
WWT/Ash			
WWT contract price	$ -	42.9	$ -
Ash Disposal	$ 38	35.7	$ 447,296
Sub Total			**$ 447,296**
Utility Cost	**Price ($/kWh)**	**Total Utilities (kW)**	**Annual Cost ($/yr)**
Heating Utility		4476	
Cooling Utility		6.0	
Total Utility estimate	$ 0.070	4482	$ 2,468,910
Sub Total			**$ 2,468,910**
Total			**$ 13,443,434**

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[1] **URL:** https://www.lacsd.org/services/solid-waste/tipping-fees-for-solid-waste-and-recyclables

TEA Discounted Cash Flow Assumptions

Assumptions	Value
Fixed Capital Investment	$116,214,230.67
Equity	40%
Loan Interest	8.0%
Loan Term, years	10
Annual Loan Payment	$10,391,608
General Plant	$114,868,455
Steam Plant	$1,345,776
Baghouse Bags (5 yr life, Ryton MOC)	$480,646
Working Capital (% of FCI)	5.00%
Salvage Value	
General Plant	0
Steam Plant	0
MACRS Depreciation	
Depreciation Period (Years)	
General Plant	7
Steam/Electricity System	20
Construction Period (Years)	3
% Spent in Year -3	8.00%
% Spent in Year -2	60.00%
% Spent in Year -1	32.00%
Start-up Time (Years)	0.5
Revenues (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
Internal Rate of Return	10.00%
Income Tax Rate	21.00%
System Bio-oil Production Rate (MM gge/yr)	3.133
CELF Byproduct Production Rate (dry ton/yr)	27,990
CELF Byproduct Selling price ($/ton)	1000
Operating Hours per Year	7,920
Cost Year for Analysis	2016
Cost Year Increment	0
Minimum Fuel Selling Price ($/gge)	**2.72**

- (Right) Discounted Cash flow estimates used to calculate MFSP at bottom
- Takes into account FCI, interest and depreciation when calculating a 30 yr NPV
- CELF byproduct (furfural or furans) are set to a value and taken into account when determining the biooil price
- MFSP is determined by adjusting the biooil selling price such that the 30 yr NPV is set to zero

Supplemental Slides – Bio-oil Market

Fuel Type, Market and Customers

Fuel Product:

- HTL Biocrude Fuels
  - Renewable diesel for transportation (marine/road), jet fuel, or for use in home heating
- CELF Byproducts
  - **Either** - furfurals as a commonly used platform chemical for industrial use
  - **Or** - Methyl furans for as a renewable diesel blend

Market:

- HTL Biocrude Fuels
  - Diesel/gasoil market consumption in US is 172 billion gallons per year in 2020[1]
  - Fuel oil market consumption in US is 12 billion gallons per year in 2020 *(includes marine fuel, industrial furnace oil and heavy oil)*[1]
  - Current TEA at a 110 DTPD waste throughput projects a production of 3.2 million gge/yr biocrude → 0.002% or 0.03% of diesel or fuel oil's US market demand, respectively
- CELF Byproducts
  - Global furfural market size projected to be 429 million tons/yr in 2020[2]
  - Current TEA at a 110 DTPD waste throughput projects a production of 28,000 tons/yr of furfural/HMF or 0.006% of the US market size
  - Methyl furans market size would be dictated by the corresponding fuel market and expected blending ratio

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[1] Statistical Review of World Energy 2021 | 70th edition

[2] GVR Report cover Furfural Market Size, Share & Trends Report Furfural Market Size, Share & Trends Analysis Report By Process, By Raw Material

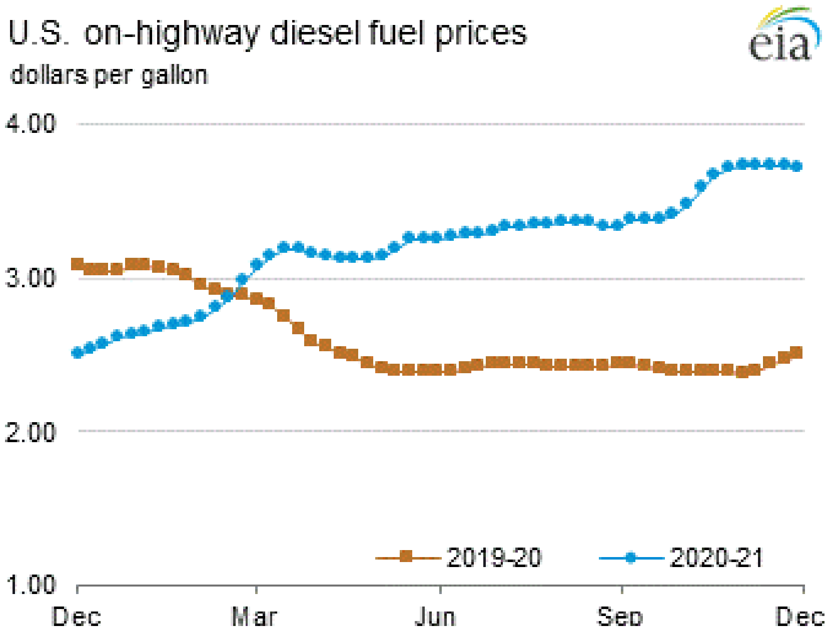
Fuel Type, Market and Customers

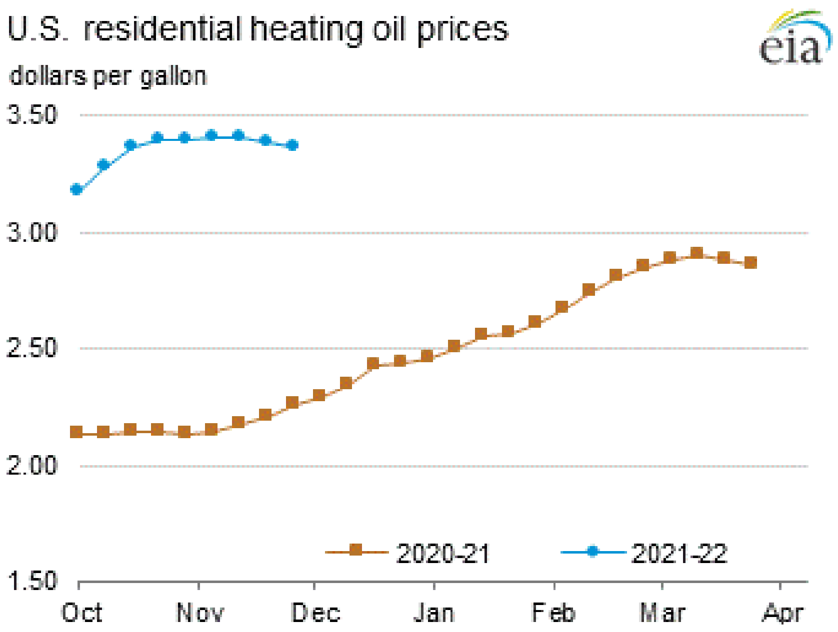
Product Price:

- Diesel & residential heating oil prices are at similar prices as of Oct 2021, ranging between $3.15 – $3.60/gal
- Marine diesel fuels is another alternative to target as a final product → price varies by state *($2.80/gal in Alaska to $3.40/gal in California)*
- Assuming a consumer price of $3/gge, the commercial value of the product is valued in billions of dollars
- Phillips 66 suggests that oil companies net $0.10 to $0.15 per gallon of gasoline, translating to projected profits of $300-500 MN/yr.

Customers:

- Phillips66, Fuels processing companies, MG Fuels for scale up and marketing for CELF products





Figures: EPA weekly index https://www.eia.gov/petroleum/weekly/index.php Marine Diesel reference:
http://www.psmfc.org/efin/data/fuel.html

Fuel Type, Market and Customers

- Some key fuel grades and metrics *(left table)*
  - Diesel Oil
    - Grade #2 most common grade at gas stations
  - Heating Oils
    - Grade #1 is a heavier version of kerosine → higher boiling point, more viscous → cheaper
    - Grade #2 heating oil is like grade 2 diesel, but with slightly different metrics

- Emission considerations
  - EPA federally regulates diesel fuel sulfur standards to ≤15 ppm$_w$ for highway and nonroad *(i.e marine)* grades
  - Sulfur is regulated to ≤10 ppm$_w$ in EU
  - International marine fuel regulated to 1000 ppm sulfur *(IMO 2020 limits)*

Properties	**No. 2 Road Diesel**	**No. 1 Heating Oil**	**No. 2 Heating Oil**	**No. 2 Marine Diesel**
Requirement	ASTM D975	ASTM D396-18a	ASTM D396-18a	ISO D2069
Flash Point *(°C)*, min	52	38	38	60
Water Sediment, *(%vol)*, max	0.05	0.05	0.05	0.1
Distillation Temp, °C				
10% vol, max	-	215	-	
90% vol, min	282	-	282	
90% vol, max	338	288	338	
Kinematic Viscosity *(40 °C, mm^2/s)*				
min	1.9	1.3	1.9	2
max	4.1	2.4	4.1	11
Ash, *(%mass)*, max	0.01	-	-	0.01
Sulfur, *(ppm)*, max	0.5 - 15	5 - 5000	5 - 5000	0.5-15
Density at 15 °C, *(kg/m^3)*, max		850	875	890
Lubricity at 60 °C, *(WSD in microns)*, max	520	520	520	520
Ramsbottom Carbon Residue, *(%mass on 10% distillation residue)*, max	0.35	0.15	0.35	0.3
Cetane Number, min	40	-	-	35