DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

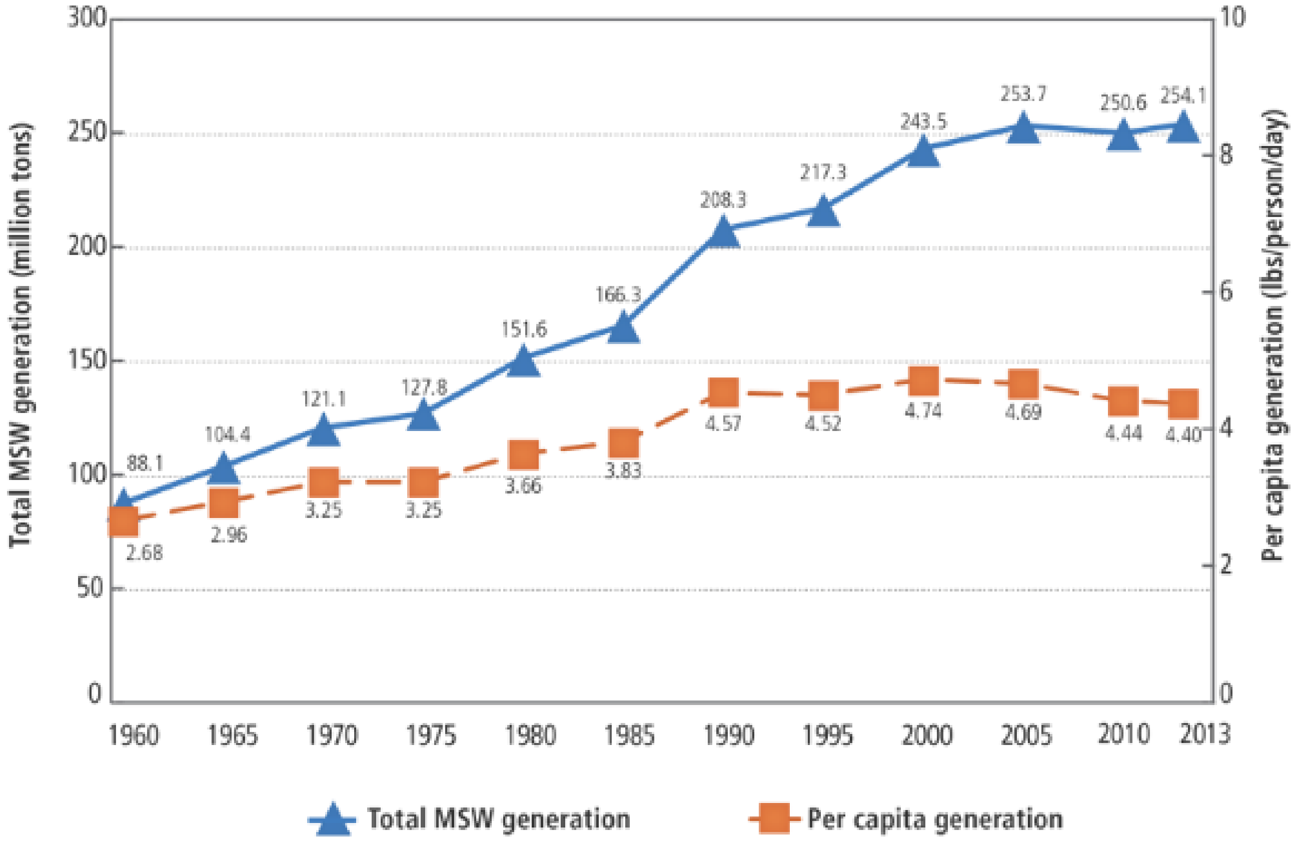
A Catalytic Process to Convert Municipal Solid Waste Components to Energy

12:35 PM EST, 3/9/2021
Technology Area Session: Organic Waste
WBS: 5.1.3.202

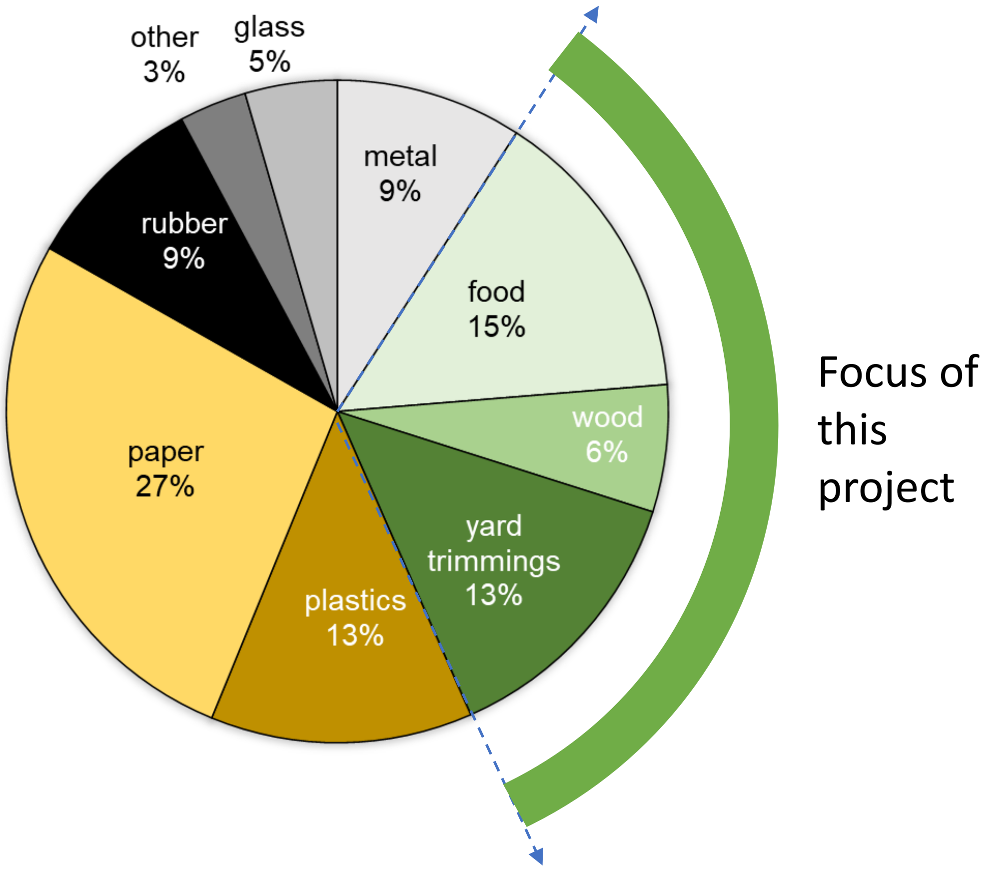
Michael Timko
Worcester Polytechnic Institute

Project Background

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



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 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
    - Slow process – days to weeks,
    - Product biogas contains impurities with costly removal
    - Large reactors not good for distribution and land use
  - **Hydrothermal liquefaction**
    - Compatible with wet and complex/variable feeds
    - Produces an energy dense liquid oil product
    - Fast process – minutes to hours
    - Compact technology for distributed power

Wet, compositionally complex

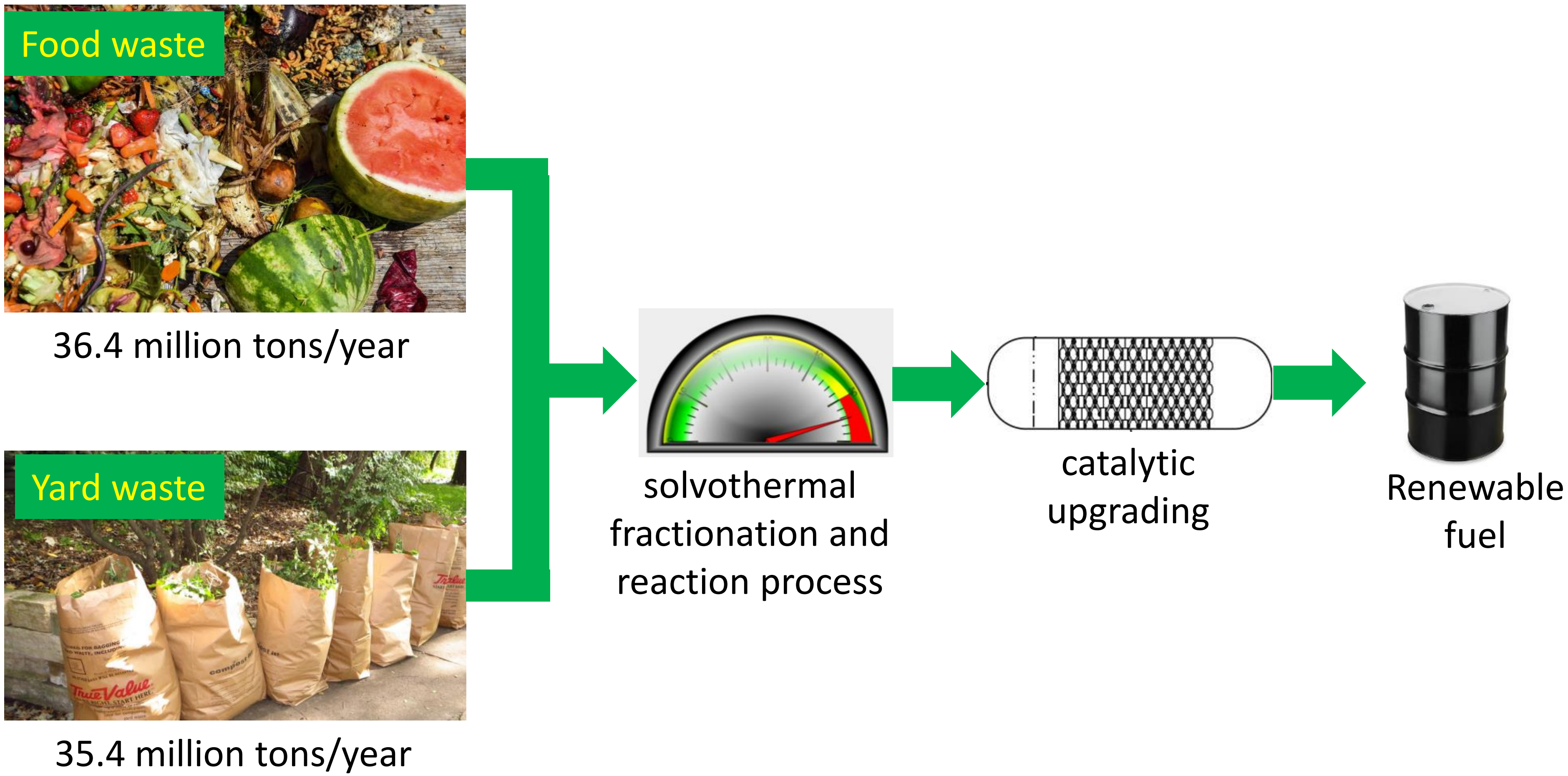
PNNL HTL process development unit

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 bio-oil 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

Project Overview



- 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

Technology Scale-up Strategy and Risks

- **Scale-Up strategy**
  - Mainstream Engineering – in collaboration with WPI – is constructing a pilot-scale process based on an HTL reactor which can be multi-purposed for the work we propose. (2 kg/h scale).
  - Technical Advisory board to help guide scale up and product/economics decisions

- **Risks**
  - Logistics of collection and securing waste streams
  - Challenge of handling of waste feedstocks
  - Risk of damage to reactor components due to exposure to corrosive liquids,
    - but HTL oils are neutral or weakly alkali so do not pose a serious corrosion risk,
    - acquired backup reactors and parts
  - Processing of complex bio-oil products for upgrading
    - Separations and solvent usage

1- Management

Primary Investigators

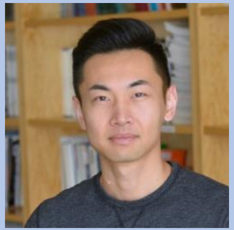
Prof. Michael Timko,
Overall PI, reporting
to DOE, Tasks 4,5,7,8

Prof. Andrew Teixeira
HTL models, Tasks 5

Prof. Geoff Tompsett
Lab work and
training, Tasks 4,5

WPI
Catalytic Hydrothermal Liquefaction of MSW

Sub-awards



Prof. Charles Cai,
UC-Riverside
Co-solvent extraction – green waste,
Task 3

Prof. Yuriy Roman,
MIT
Bio-oil upgrading
Task 6

Dr Alex Paulsen,
Mainstream Engineering
Technoeconomics, pilot plant
Tasks, 7,8

Dr Chris Reddy,
WHOI
Additional
Analytics

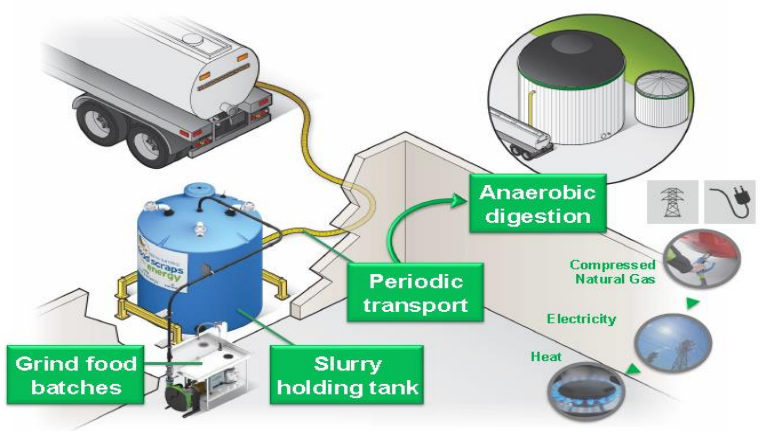
Supporting

Mr. Michael Gurin
MG Fuels
Tasks 1,7,8

Task 1 Initial Verification
Task 2 Intermediate Verification

1-Management

- **Advisory Board**:
  - Whole Foods Market - grocery chain known for its sustainable marketing
  - Phillips66 - a multi-national energy company
  - Agrivida - a successful bioenergy startup located in the greater Boston area
  - Republic Services - the second largest waste managing company in the U.S
  - Divert - a waste reduction company
  - Center for Sustainable Energy, Massachusetts
  - BDP Industries - a compositing company
  - Genifuel
  - Convened Feb-26-2021



Grind2Energy / Casella Waste food waste from Whole Foods Market

Green waste from BDP Industries

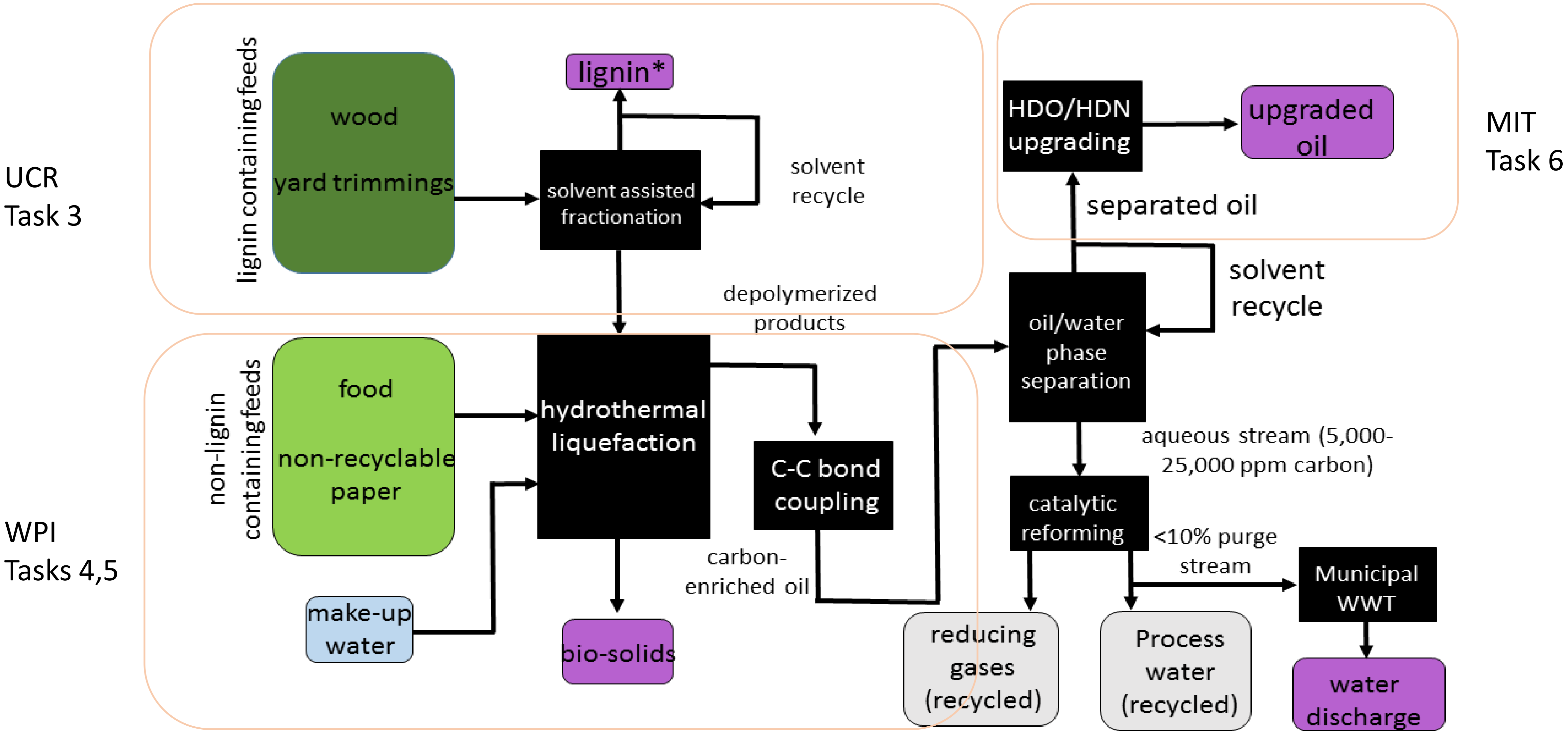
1-Management

TASK	TECHNOLOGICAL RISK	MITIGATION
3	Fractionation of mixed feed stream Effect of ash content of green waste material	Sieving and sorting mixed feed, Study acid concentration
5	Catalyst cost and stability	Screen inexpensive waste and natural materials as catalysts
5	Loss of carbon to aqueous phase in HTL	Ex-situ upgrading of aqueous phase, Modelling fate of nitrogen, phase separation study
4,5	Boosting biocrude yields	Evaluate 3 generations of catalyst types, Develop machine learning models to predict bio-oil yield
6	Processing of complex bio-oil products for upgrading	Solvent selection for product fractionation
6	developing a low-cost catalyst that performs both HDO/HDN	Perovskite and carbide catalysts already developed for lignin bio-oils
4,5,6	Risk of damage to reactor components due to exposure to corrosive liquids,	HTL oils are neutral or weakly alkali so do not pose a serious corrosion risk, catalysts buffer pH
7	Continuously pumping waste slurry	Initiated task early to mitigate problems
8	TEA uncertainty	Probabilistic TEA evaluation

1-Management

TASK	LOGISTICAL RISK	MITIGATION
1-8	Pandemic delays	Initiate complementary modelling studies Virtual meetings, lab space management Request no-cost extension
3,4	collection and securing waste streams	Sufficient green waste sourced and more easily available Food waste supplies sourced but hindered by Pandemic
3,4	Challenge of handling of waste feedstocks, storage, feeding	Handling and storage of large volumes of slurry food waste proved difficult. Alternative dried food waste sources were sourced
6	Production of sufficient feedstocks and oil products for testing	Sufficient materials transfer between Institutes Mainstream can operate scale-up system to supply sufficient oil products
3,4,5,6	Efficient Data throughput	Developed machine learning to maximize data analysis on hydrothermal processing and upgrading

2 Approach: The Process



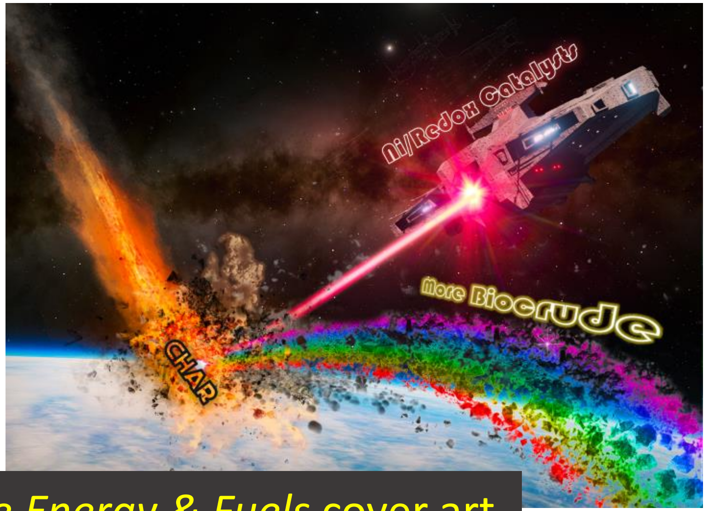
Simplified process flow diagram of the catalytic hydrothermal liquefaction (HTL) process. The organic fraction of the MSW is feed (green). Process steps are black. Products are purple.

2-Approach: Technical Approach (Detailed)

- **Co-solvent lignin fractionation of green waste (UC-Riverside Task 3)**
  - Improving lignin extraction from green waste and its separation from holocellulose and inorganic streams.
  - Increasing the fraction of MSW treated in the HTL process by evaluating HTL of Lignin-free and lignin-rich feed streams
  - Performance objective to be used in is the 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)
- **Non-catalytic and Catalytic hydrothermal liquefaction of food waste and green waste - Heterogeneous Base Catalysts (WPI Task 4 and 5)**
  - **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 bio-oil aqueous phase hydrothermal processing
  - **Feedstocks:** Food waste mixture, Dehydrated food waste from VA hospital, Green waste form BDP Industries
- **Catalytic hydrogenation of bio-oil upgrading to fuel products (MIT Task 6)**
  - Batch and Continuous packed bed reactors, Catalysts: Molybdenum carbide, perovskites, for removal of oxygen and nitrogen from bio-oil compounds, Solvent diluted bio-oil or separated hydrothermal bio-oil feeds
  - Reduce HTL bio-oil will contain <7 wt% oxygen and <2 wt% nitrogen
  - Require Stable catalyst operation profiles >100 h on stream (cumulative) that maintain >50% conversion
- **Technoeconomic Analysis (Mainstream Engineering, Task 7)**
  - 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
- **Pilot Scale Continuous Operation (Mainstream Engineering, Task 8)**
  - Continuous catalytic hydrothermal reactor: Max. 350˚C, 5000 PSI, 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

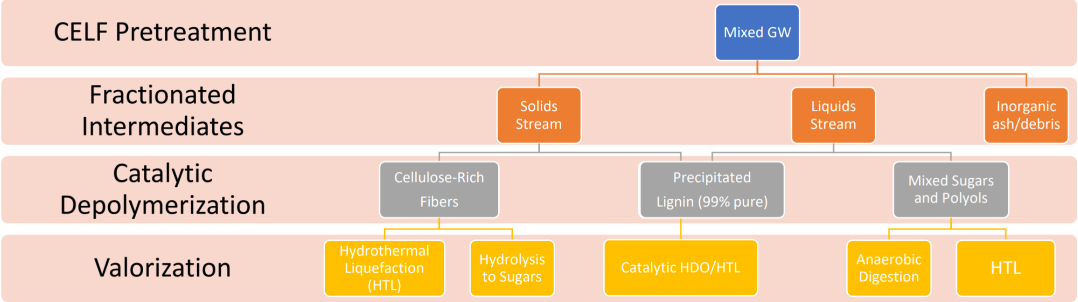
3-Impact:

- **If successful, this technology has significant markets for the products:**
- **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
  - 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
- **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
  - markets represent billion-dollar opportunities
- **Dissemination of Results**
  - Patent application submitted
  - Publishing in high impact journals (e.g. *Sustainable Energy and Fuels*, IF 5.5; *ACS Sustainable Chemistry & Engineering*, IF 7.6)
  - Conference presentations: AIChE
  - Achieving good media coverage: Biofuels Digest, Telegram & Gazette, Biofuels News, Spectrum News, ChemicalProcessing.com
  - Collaborating companies Mainstream Engineering and MG Fuels assessing the technology



Sustainable Energy & Fuels cover art

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



Milestones achieved	Benchmark
>80% lignin-free fraction from real green waste, (Atlas green waste, 170^{o}C, 1% acid, 15 min)	80% lignin free with ethanol organosolv from biomass >90% lignin free from CELF of woody biomass

- **Milestones Complete**
  - Initial verification passed with proven track record of fractionation from real feedstocks
  - Milestone of **>80% lignin-free** fraction achieved from real green waste feedstock
  - ***Benchmark: 80% lignin free with ethanol organosolv from biomass***

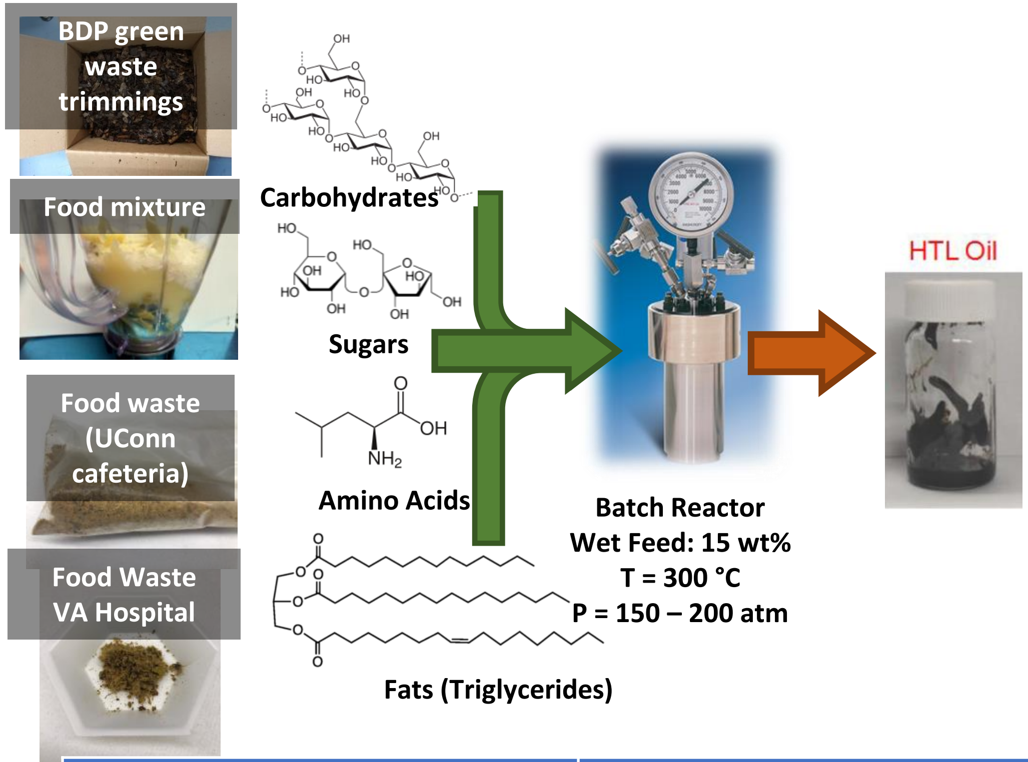
  And >90% lignin free from CELF of woody biomass

- **Milestones in Progress**
  - <20% carbohydrate in lignin phase
  - Produce lignin rich (>90% lignin) and lignin-free streams (<10% lignin) via further parameter optimization

- **Challenges and Delays to Milestones**
  - Removal of ash content form green waste
  - Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months

- **Future Work to Complete**
  - Intermediate Verification
  - Scale up processing to produce 2 kg of lignin-free biomass and calculate energy requirements with target of <2 MJ/kg
  - Quantify solvent losses and reuse solvent to produce >85% lignin-free streams

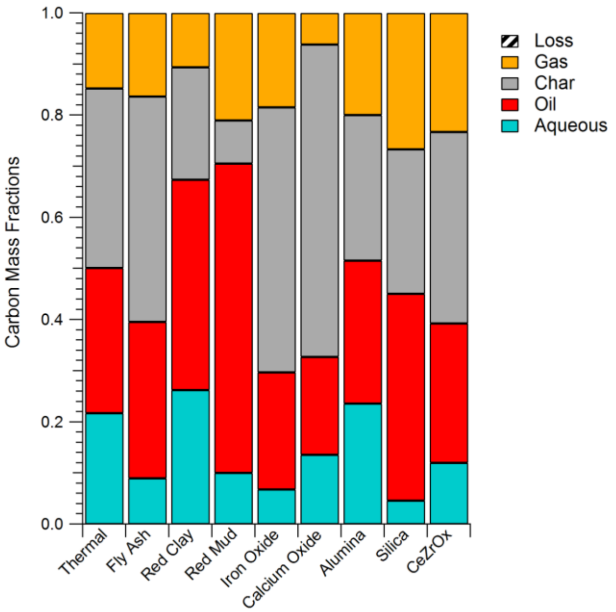
4-Progress and Outcomes
Task 4 – Hydrothermal liquefaction of food waste and green waste fractions (WPI)



HTL evaluation	Oil Yield and ER
HTL of food mixture	20%, 18% ER
HTL of real food wastes	35%, 39% ER
HTL of green waste/food waste	25%, 31% ER
HTL of lignin-free fraction	25%
HTL of lignin fraction	50%

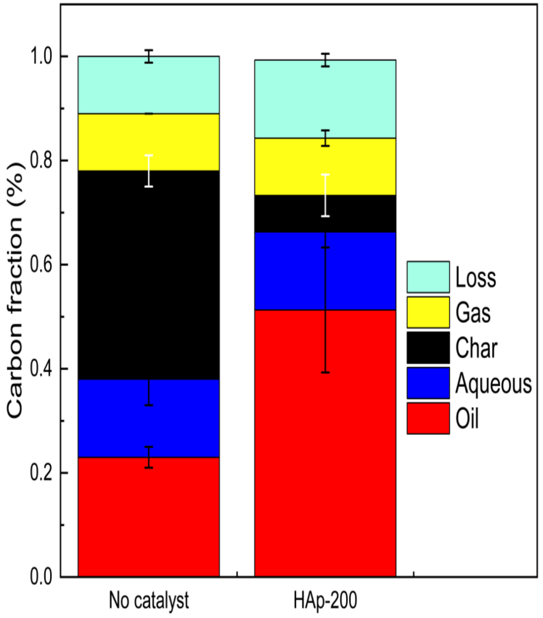
- **Milestones on target**
  - Initial verification passed with proven track record of fractionation from real feedstocks
  - Evaluated HTL performance of mixture and real food waste feed streams, green waste and food waste-green waste mixtures plus additional lignin-free green waste stream
  - Used 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
  - Construction of continuous stirred reactor system
- **Challenges and Delays to Milestones**
  - Low oil yield from carbohydrate-rich feeds
  - Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months
- **Future Work to Complete**
  - Intermediate Verification
  - Develop a lump kinetic model describing the chemical and transport processes that govern the conversion of feed to produce oil, gas and char products
  - Continuous operation of the lab-scale slurry reactor for >50 hours (cumulative)

4-Progress and Outcomes
Task 5 – Catalytic Carbon-carbon coupling reactions – Catalytic HTL (WPI)



Gen 2 inexpensive catalysts

Gen 1 catalysts



Gen 3 hydroxyapatite

Milestones achieved	Benchmark
>45% energy recovery from food waste mixture and real food waste, 300°C, 3000PSI batch	18% ER for food waste HTL (no catalyst) up to 89% ER for algae

- **Milestones on target**
  - Initial verification passed with proven track record of fractionation from real feedstocks
  - **Catalyst screening and >45% energy recovery, highest for non-algae feedstock**
  - ***Benchmark: 18% ER for food waste HTL (no catalyst)***

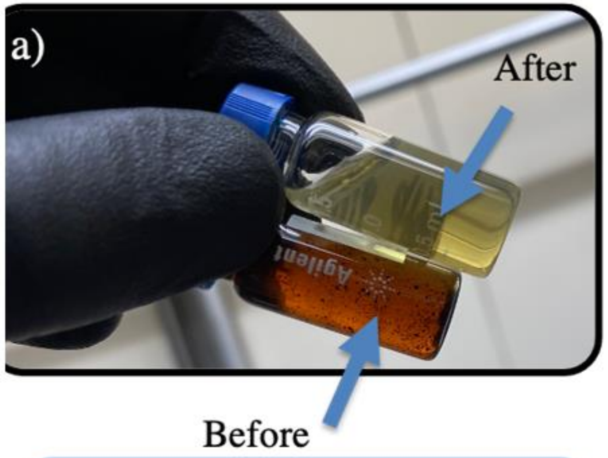
  76% ER from sludge (PNNL), up to 89% ER for algae

- **Milestones in Progress**
  - Optimization of conditions for >50% energy recovery from waste streams

- **Challenges and Delays to Milestones**
  - Optimization of conditions for >50% energy recovery from waste streams
  - Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months

- **Future Work to Complete**
  - Intermediate Verification
  - >100 hours (cumulative) stability of catalyst under actual reaction conditions while retaining >80% of original activity

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



$$C_nH_{2n+1}COOH \longrightarrow C_nH_{2n+2}$$

c)

	Before Reaction	After Reaction
C%	65.79	78.93
H%	8.77	9.77
N%	4.53	2.00
O%	20.82	8.46

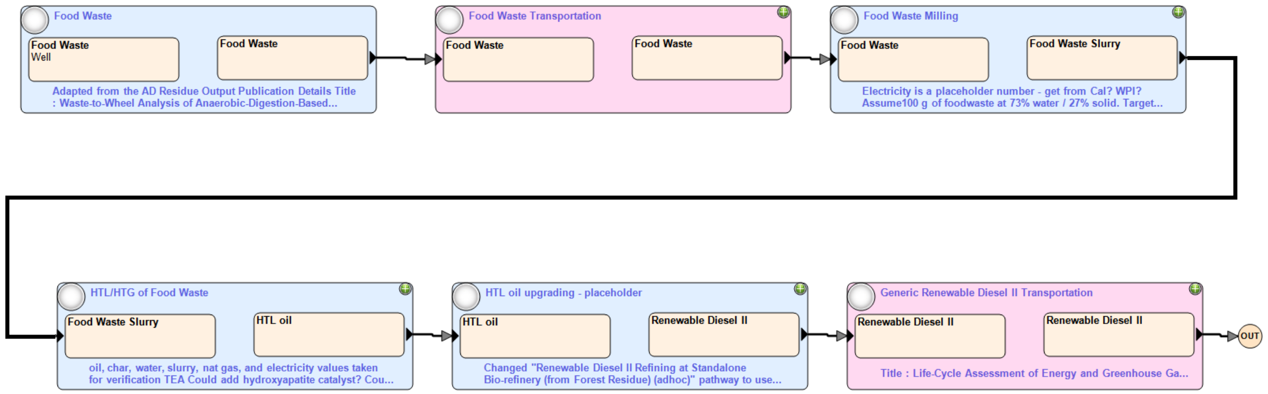
Milestones achieved	Benchmark
Production of HTL oil with **<9 wt% O and <2 wt% N** from hydrothermal bio-oil dilute in toluene	upgrading algae oil standard <3%O, <1%N, sewage sludge HTL oil <1%O, <23%N, feedstock dependent

- **Milestones on target**
  - Initial verification passed with model feed compounds
  - Catalyst synthesis and evaluation complete
  - Production of HTL oil with **<9 wt% oxygen content and <2 wt% nitrogen content** from hydrothermal bio-oil 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***
- **Milestones in Progress**
  - Production of HTL oil with <7 wt% oxygen content and <2 wt% nitrogen content of upgrading oil using higher concentration feed
- **Challenges and Delays to Milestones**
  - Handling of neat bio-oil and solvent selection
  - Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months
- **Future Work to Complete**
  - Intermediate Verification
  - Stable catalyst operation profiles >100 hours on stream (cumulative) that maintain >50% conversion

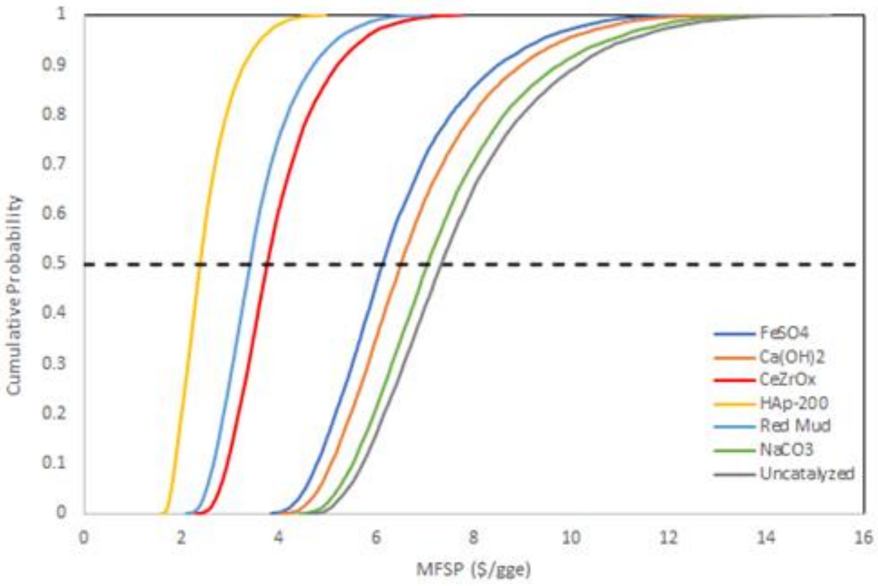
4-Progress and Outcomes
Task 7 – Continuous Hydrothermal Liquefaction Pilot Plant Operation (Mainstream)

- **Milestones on target**
  - Pilot scale continuous hydrothermal reactor system constructed and operated for >10 hours ahead of schedule
  - Scale-up quantities of Bio-oils supplied to MIT and WPI
- **Milestones in Progress**
  - Continuous reactor operation with catalysts and real food waste feed
- **Challenges and Delays to Milestones**
  - Preparation of catalyst pellets for catalytic hydrothermal liquefaction is has been achieved
  - No delays due to the Pandemic to date
- **Future Work to Complete**
  - Intermediate Verification
  - >100 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)



LCA Pathway for HTL of Food Waste to Renewable Diesel



Minimum fuel selling price vs scale with probability distribution curve. Increased catalytic performance results in a shift to lower cost.

- **Milestones on target**
  - Initial verification passed with us of adapted PNNL TEA spreadsheets
  - Completed Milestone of initial TEA/LCA on 100 dry ton per day scale
  - Completed Milestone for TEA/LCA, of LCOE equal to $4.83/gge,
  - We calculate **$3.1/gge** (including $1.1/gge upgrading, $0 tipping fee, no transportation costs, 30 min catalyst lifetime and for a 100 ton/year plant)
  - ***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**
  - Updates to TEA/LCA
- **Challenges and Delays to Milestones**
  - No delays to date

- **Future Work to Complete**
  - Intermediate Verification
  - Complete final TEA and LCA

Summary

- Steady progress towards all milestones has been achieved despite setbacks from the Pandemic
- **>80% lignin-free** fraction achieved from real green waste feedstock, comparable to 80% lignin free with ethanol organosolv from biomass and >90% lignin free from CELF of woody biomass
- 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. 39% energy recovery from real food waste. Used machine learning to model relation between feedstock and biocrude yield
- Catalyst hydrothermal liquefaction of food waste produces **>45% energy recovery**, highest for non-algae feedstock. Compare 18% ER for food waste HTL (no catalyst) and up to 89% ER for algae
- Production of upgraded oil with **<9 wt% oxygen content and <2 wt% nitrogen content** from hydrothermal bio-oil achieved using dilute solution in toluene solvent
- Pilot scale continuous hydrothermal reactor system constructed and operated for >10 hours ahead of schedule
- We estimate minimum fuel selling price of **$3.1/gge** (including $1.1/gge upgrading) compared to Milestone Target LCOE equal to $4.83/gge

Quad Chart Overview

Timeline

- Project start date: 10/1/19
- Project end date: 9/30/22

	FY20 Costed	Total Award
DOE Funding	(10/01/2018 – 4/30/2020) BP1 $219,212	(negotiated total federal share) $1,995,199
Project Cost Share	$54,861	$502,620

Project Partners*

- MG Fuels

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 Milestones

>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

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments

- If your project has been peer reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments which you have since addressed
- Also provide highlights from any Go/No-Go Reviews

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.

Process and Products

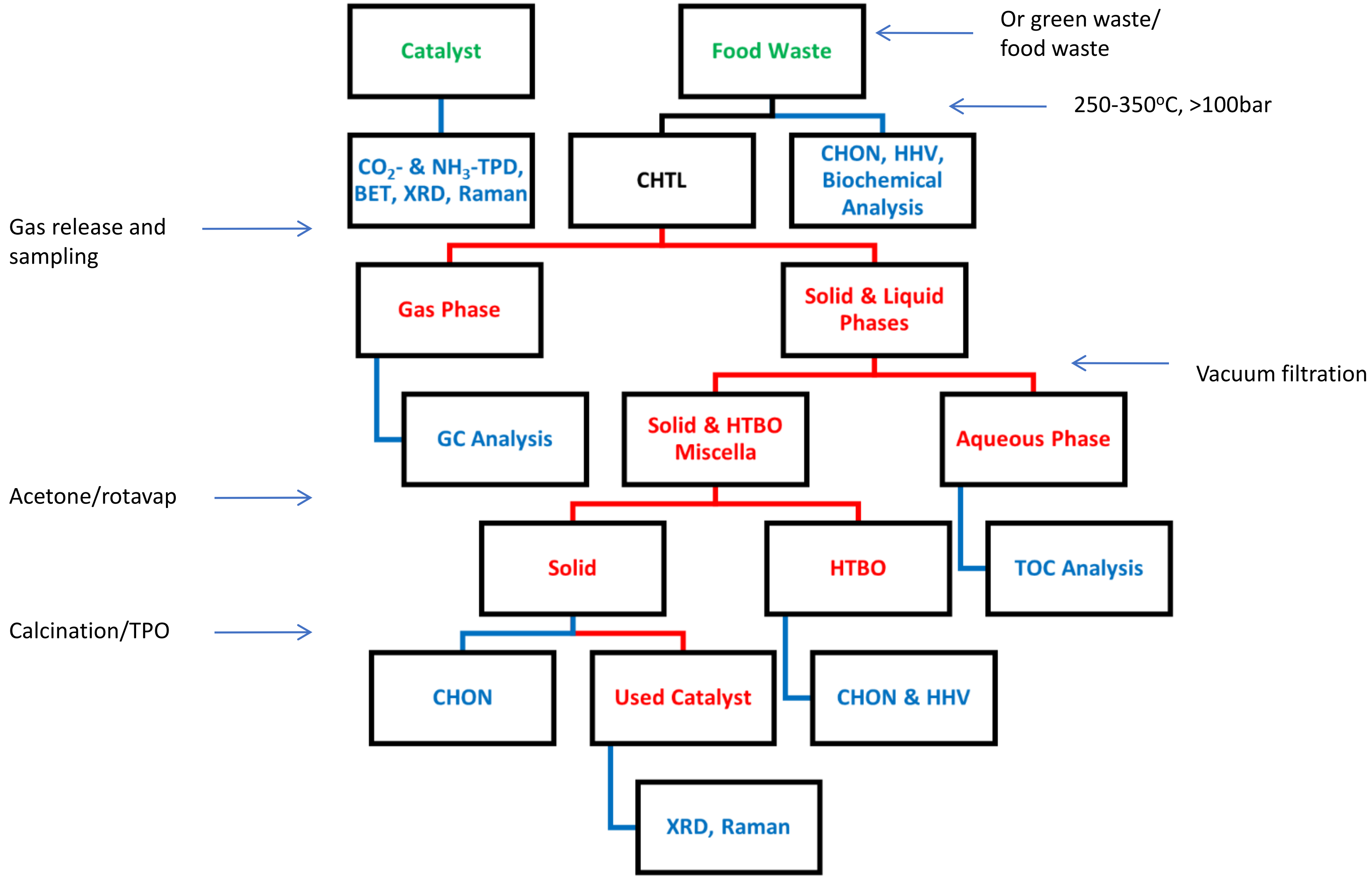
- **Process Includes**
  - a solvent separation step to remove lignin from the green waste stream to generate a delignified biomass stream;
  - a hydrothermal liquefaction (HTL) step to convert the food waste and holocellulose stream into a raw HTL bio-oil;
  - a catalytic upgrading step to increase HTL bio-oil yield and/or improve its composition; combined with/out HTL step;
  - a catalytic HDO/HDN step to reduce oxygen and nitrogen content of the HTL bio-oil to further improve its composition

1-Management

- **Team Roles and Responsibilities**
- WPI (Timko, Teixeira, Tompsett)
    - Project leader, (Task 3,4)
    - CHTL of food/green waste to bio-oil and hydrochar
    - Coordinate program, prepare reports, coordinate transfer of products
    - Operate pilot plant system at Mainstream in Final Verification
- MIT (Roman)
    - Subcontractor (Task 6)
    - Hydrogenation of model compounds (Initial) and HTL oil to remove oxygen and nitrogen and form upgraded oil fuel products
- UCR (Cai)
    - Subcontractor (Task 3)
    - Co-solvent extraction of lignin and holocellulose streams from green waste
- Mainstream Engineering (Paulsen)
    - Subcontractor (Task 7,8)
    - Technoeconomic Analysis/Life Cycle Assessment of overall process, pilot plant construction
- WHOI (Reddy)
    - Subcontractor
    - Additional analytical facilities for bio-oil characterization – GCxGC-MS, LC-MS
- MG Fuels (Gurin)
    - Technoeconomic Analysis/Life Cycle Assessment
    - Task 1 lignin extraction

2-Approach: Technical Approach

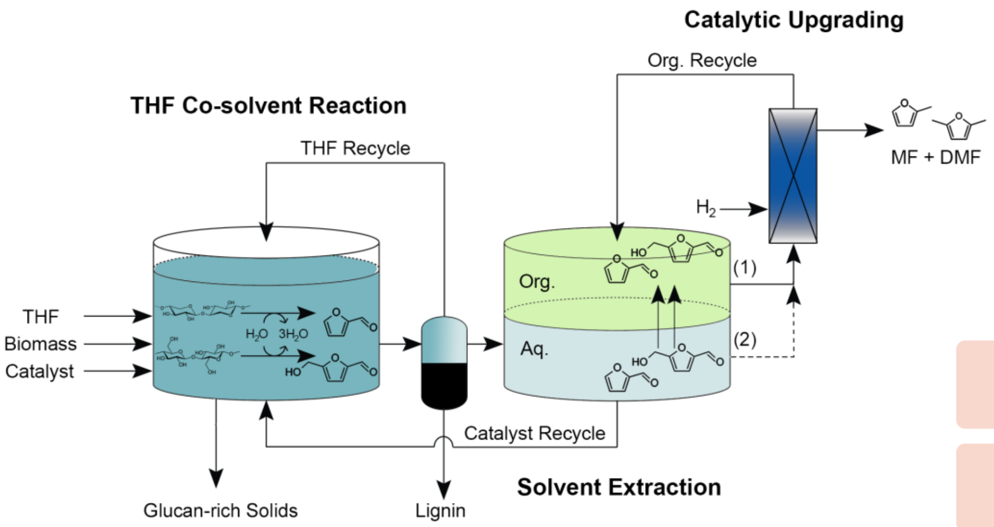
HTL and CHTL Batch Reaction and Bio-oil Extraction (WPI Task 4 and 5)



2 – Approach: Technical Approach

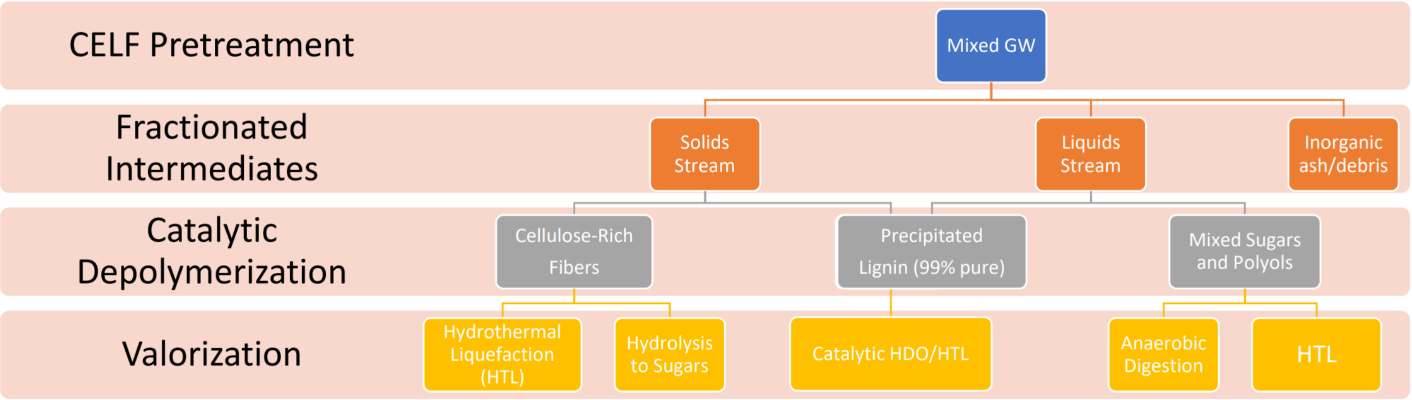
Co-solvent Enhanced Lignocellulosic Fractionation (CELF) of green waste (UCR, Task 3)

- One-pot fractionation of biomass followed by catalytic upgrading of sugars



Cai et al., 2013 ***Green Chemistry*** 15, 3140-3145
Cai et al., 2014 ***Green Chemistry*** 16, 3819-3829

Green waste (GW) form BDP Industries



2-Approach: Technical Approach:

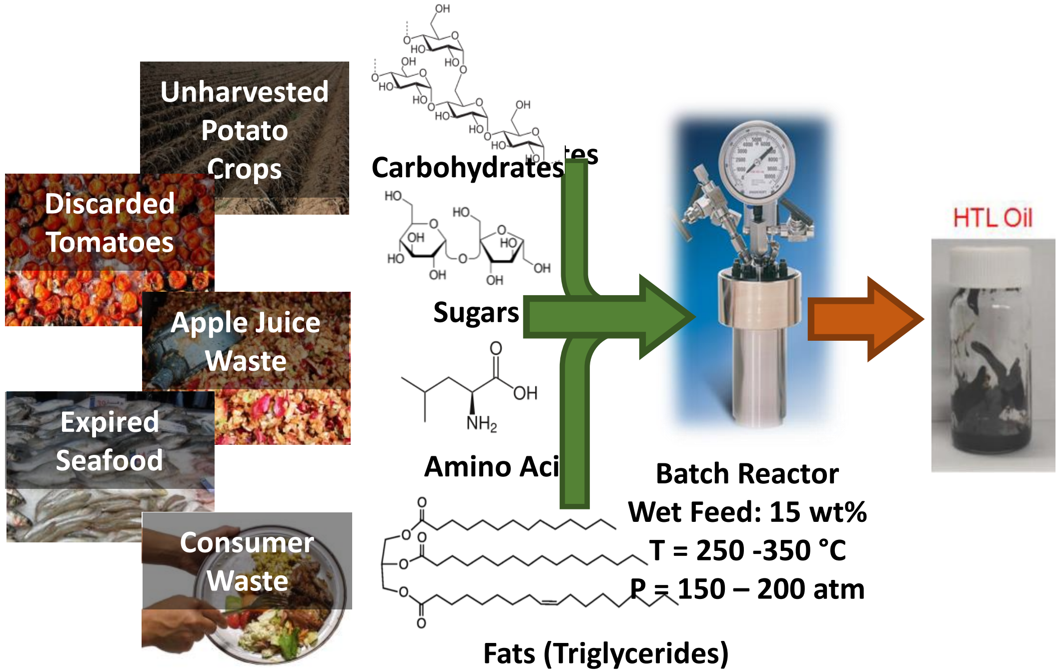
Non-catalytic and Catalytic hydrothermal liquefaction - Heterogeneous Base Catalysts (WPI Task 4 and 5)

- **Catalysts**
  - Metal oxides known to be hydrothermally stable
  - Inexpensive, reusable heterogeneous catalysts most desirable for HTL upgrading (see table right)

- Selection of inexpensive heterogeneous base catalysts:
  - Red Mud – Highly alkaline waste byproduct of Bayer Process
  - Red Clay – Commercial dry clay for use in ceramics
  - Fly Ash – inorganic residue from coal power stations
- Mixed metal oxides – ceria-zirconia
- Hydroxyapatite
  - Readily available, thermally stable, tunable acid and base sites

- **Equipment**
  - Parr batch reactors
  - semi-continuous fed batch reactor systems
  - Continuous packed bed reactor of bio-oil aqueous phase hydrothermal processing

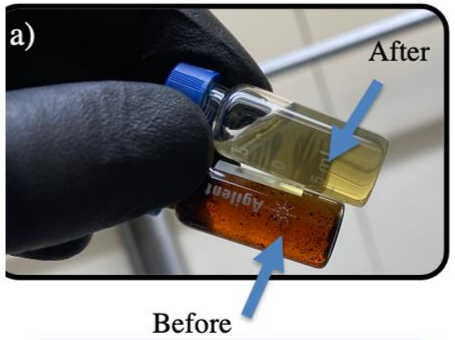
- **Feedstocks**
  - Food waste mixture
  - Dehydrated food waste from VA hospital
  - Green waste form BDP Industries



2-Approach: Technical Approach

- **Catalytic hydrogenation of bio-oil upgrading to fuel products (MIT Task 6)**
  - Batch and Continuous packed bed reactors
  - Catalysts: Molybdenum carbide, perovskites, for removal of oxygen and nitrogen from bio-oil compounds
  - Solvent diluted bio-oil or separated hydrothermal bio-oil feeds

  - Milestone: HTL bio-oil will contain <7 wt% oxygen and <2 wt% nitrogen
  - Milestone: Stable catalyst operation profiles >100 h on stream (cumulative) that maintain >50% conversion



$$C_nH_{2n+1}COOH \longrightarrow C_nH_{2n+2}$$

c)

	Before Reaction	After Reaction
C%	65.79	78.93
H%	8.77	9.77
N%	4.53	2.00
O%	20.82	8.46

2-Approach: Technical Approach

- **Technoeconomic Analysis (Mainstream Engineering, Task 7)**
  - 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
  - Used @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
    - to determine emissions required to produce a fuel
    - Created new resources, processes, and pathways to model food waste HTL

- **Pilot Scale Operation (Mainstream Engineering, Task 8)**
- Continuous catalytic hydrothermal reactor
  - Max. 350˚C, 5000 PSI, 1.3 L, 0-120 mL/min
  - Collect oil, water, gas, and char is hot filtered
  - Catalyst cage holds catalyst in reactor
  - Catalyst pellets formed with a press
  - Catalyst pellets are hydrothermally stable

2 –Approach: Challenges

- Transfer of sufficient oil products form WPI to MIT
  - Mainstream Engineering constructed and testing a continuous reactor system ahead of schedule
  - Managed sufficient bio-oil transfer by large scale processing by Mainstream Engineering
- Handling and thermal stability oil products during upgrading
  - Appropriate solvent usage and separations prior to processing were necessary
- Pandemic restrictions to labs and worker illness
  - Delay to project milestones by ~6 months
  - Access to real food waste sources during the Pandemic are extremely limited
  - Sufficient green waste was secured prior to the Pandemic

2-Approach: Go/No-Go Situations

Task	GNG 1 (3 months)	GNG (18 months)	GNG (33 months)
Task 3 Solvent fractionation	>70% extraction of lignin from green waste and solubilization of fugitive plastics Proven testing to date	>80% preservation of sugars from green waste	>90% accountability of all source components in green waste to independent process streams
Task 4 Hydrothermal liquefaction	>15% energy recovery for HTL without catalysts Published energy recoveries exceeding	Determination of HTL rates at one or more process conditions	Continuous flow operation demonstrated for >20 hours (cumulative)
Task 5 Hydrothermal liquefaction using a catalyst	>40% energy recovery for one or more catalysts Published energy recoveries exceeding GNG	>45% energy recovery for one or more catalysts, identification of catalysts which maximize EROI and LCOE irrespective of lifetime	>45% energy recovery for a catalyst with a lifetime >100 hours under hydrothermal HTL conditions
Task 6 Hydrogenation oil upgrading	>75% oxygen and nitrogen removal from model compounds for one or more catalysts Achieved >75% removal of oxygen and nitrogen from model compounds	>75% oxygen and nitrogen removal from HTL oil for one or more catalysts	>90% of energy recovery for catalysts with a lifetime >100 h on stream
Task 7 Pilot scale plant operation	n/a	n/a	>10 cumulative operating hours
Task 8 Technoeconomic Analysis and Life Cycle Assessment	Energy return on Investment (EROI) > 2.5, determination of most sensitive parameters, 10% reduction in Levelized Cost of Energy (LCOE)	EROI > 4, re-determination of parameter sensitivity, 15% reduction in LCOE	EROI > 5, re-determination of parameter sensitivity, 25% reduction in LCOE
Overall	Passed Initial Verification	Intermediate Verification due soon	Final Go/No-Go at end of project

2-Approach: Economic and Technical Metrics

Task	Metrics and Economic Measurements	Progress Evaluation
Task 3 Solvent fractionation of green waste	% extraction of lignin from green waste and solubilization of fugitive plastics	Weight percent of lignin removed and remaining in the carbohydrate fractions after co-solvent processing to optimize the reaction conditions for products with the highest bio-oil form HTL
Task 4 Hydrothermal liquefaction of food waste	% energy recovery for HTL without catalysts	Measure the weight yield and the calorific value of the bio-oils to calculate the energy recovery to assess the reaction kinetic and to evaluate green waste fractionation
Task 5 Hydrothermal liquefaction using a catalyst of food waste	% energy recovery for one or more catalysts	Measure the weight yield and the calorific value of the bio-oils to calculate the energy recovery to assess the activity of catalysts and reaction kinetics. Data used in economic analysis
Task 6 Hydrogenation bio-oil upgrading	% oxygen and nitrogen removal for one or more catalysts	Using Gas chromotography of product streams and elemental analysis to measure the reduction of oxygen and nitrogen content to assess the activity and stability of catalysts
Task 7 Pilot scale plant operation	Cumulative operating hours	Measure the catalyst stability and product yields with sum of time on stream
Task 8 Technoeconomic Analysis and Life Cycle Assessment	Energy return on Investment (EROI), Levelized Cost of Energy (LCOE)	Recalculate the EROI and LCOE based on the improved bio-oil yields and energy recovery to assess the feasibility of the overall process

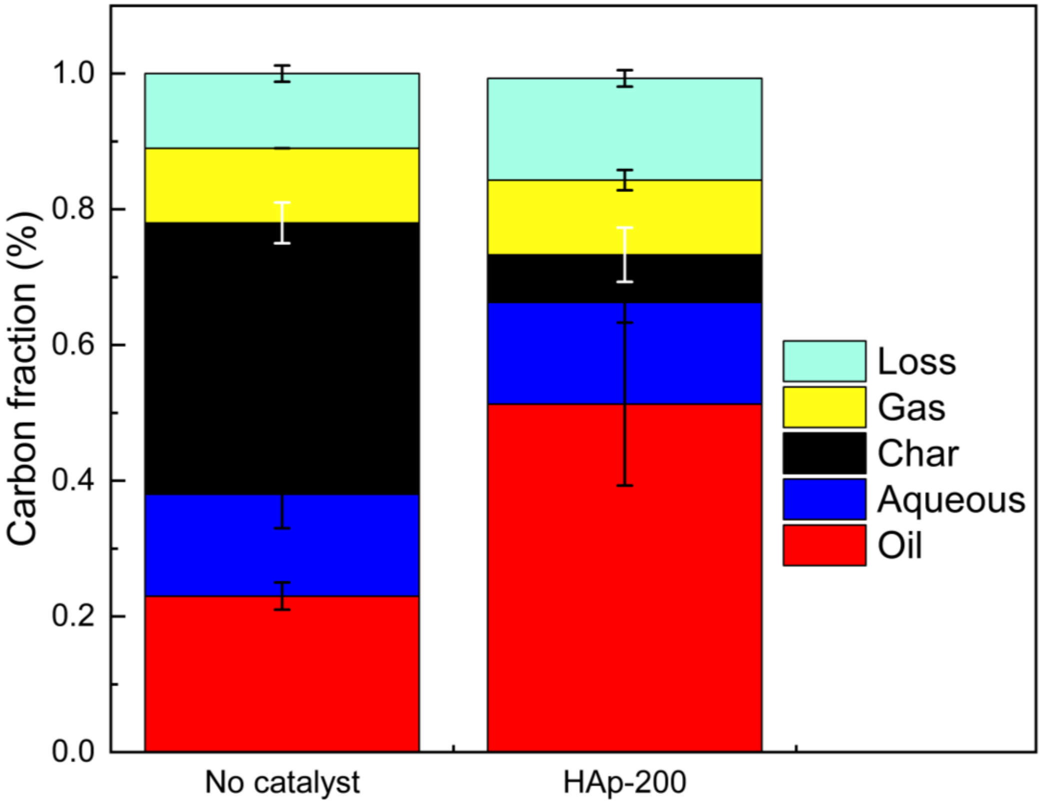
4-Progress and Outcomes

- Progress in meeting goals
  - Team successfully met the initial verification process to set baseline levels of fractionation, bio-oil yields, energy recovery, removal of heteroataoms and economics
  - Fractionation of green waste achieved >80% lignin free fraction meeting intermediate milestone, while the lignin fraction milestone requires further optimization with ash removal
  - New catalyst, hydroxyapatite, discovered giving significantly improved yields
  - Yield and energy recovery milestones for catalytic bio-oil from food waste have been met and the associated technoecomonics based on these yields
  - Hydrogenation upgrading of hydrothermal bio-oil has been successfully achieved using molybdenum carbide catalyst and dilution in toluene solvent
  - Continuous catalytic hydrothermal reactor has been constructed and operated by Mainstream Engineering, using food waste feed

4- Progress and Outcomes

Task	Initial Milestones	18 Month Milestones
Task 3 Solvent fractionation	>70% extraction of lignin from green waste and solubilization of fugitive plastics Proven testing to date	>80% preservation of sugars from green waste >80% achieved, lignin fraction requires further optimization
Task 4 Hydrothermal liquefaction	>15% energy recovery for HTL without catalysts Published energy recoveries exceeding	Determination of HTL rates at one or more process conditions Kinetic experiments in progress
Task 5 Hydrothermal liquefaction using a catalyst	>40% energy recovery for one or more catalysts Published energy recoveries exceeding	>45% energy recovery for one or more catalysts, identification of catalysts which maximize EROI and LCOE irrespective of lifetime >45% energy recovery achieved using hydroxyapatite catalyst
Task 6 Hydrogenation oil upgrading	>75% oxygen and nitrogen removal for one or more catalysts of model compounds >75% oxygen and nitrogen removal of model compound	>75% oxygen and nitrogen removal from HTL oils for one or more catalysts >75% oxygen and nitrogen removal from HTL oil using 1wt% dilution in toluene feed
Task 7 Pilot scale plant operation	n/a	Pilot scale reactor operated
Task 8 Technoeconomic Analysis and Life Cycle Assessment	Energy return on Investment (EROI) > 2.5, determination of most sensitive parameters, 10% reduction in Levelized Cost of Energy (LCOE) at $5.38 Baseline economics verified	EROI > 4, re-determination of parameter sensitivity, 15% reduction in LCOE at equal to $4.83/gge LCOE of $4.91 *(8.7% ↓)*
Overall	Passed Initial Verification	Intermediate Verification due soon

HTL Product Distribution



	C (wt%)	H (wt%)	O (wt%)[a]	N (wt%)	HHV (MJ kg^{-1})	Energy Recovery (%)	TOC in HTL Aqueous (ppm)
Food Waste	44.5	6.4	45.4	3.8	24.6	n/a	n/a
Thermal	69.0	8.4	19	3.7	36.1	18.1	24300
Hydroxyapatite	70.3	9	17.1	3.7	38.3	63.4	14500

- Non-catalytic HTL resulted in 2.04 ± 0.14g oil
- Hydroxyapatite-catalyzed HTL results in 6.1 ± .31g oil

Publications, Patents, Presentations, Awards, and Commercialization

Publications
Feng Cheng, Geoffrey Tompsett, Daniela Valeska Fraga Alvarez, Carla I. Romo, Amy M. McKenna, Sydney F. Niles, Robert K. Nelson, Christopher M. Redy, Segio Grandos-Focil, Alex D. Paulsen, Ruihan Zhang and Michael Timko, Sustainable Energy and Fuels, 2020. In Print.

Conference presentations:
1. Heather LeClerc, Understanding Molecular Fractionation of Food Waste Hydrothermal Bio-crude Products. *AIChE Annual Meeting.* Nov. 2020
2. Heather Leclerc, Bifunctional acid/base catalysis for improved biocrude recovery from food waste hydrothermal liquefaction. *AIChE Annual Meeting.* Nov. 2020
3. Michael Timko, PNNL Workshop on Hydrothermal liquefaction: Path to sustainable aviation fuel workshop, November 19, 2020.
4. Heather LeClerc, Molecular Fractionation and Description of Food Waste Hydrothermal Biocrudes. Poster, *AIChE Annual Meeting.* Nov. 2020.
5. Green conversion of food waste to energy through catalytic hydrothermal liquefaction. ACS Green Chemistry virtual Conference. June, 2020

Awards
Heather LeClerc, WPI. Won “Women in Chemical Engineering Travel Award” for AIChE attendance 2020.
Heather LeClerc, WPI. Won “Women’s Young Investigators Fellowship” through WPI, 2020, advised by Andrew Teixeira and Mike Timko
Heather LeClerc, WPI Sustainability competition graduate student winner, May, 2020. For Realizing a World without Waste through Catalytic Conversion of Food Waste, advised by Andrew Teixeira and Mike Timko
Heather LeClerc, awarded a grant from the National Science Foundation Graduate Research Fellowship Program, June 2020. For study on the catalytic hydrothermal liquefaction of food waste.
Heather LeClerc awarded $5,000 Heh-Won Chang, PhD, Fellowship in Green Chemistry from the American Chemical Society, June 2020. For study on the catalytic hydrothermal liquefaction of food waste.

Technology Transfer
None to date