





DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Hybrid HEFA-HDCJ Process for the Production of Jet Fuel Blendstocks

March 26, 2021, (12:00:00 PM)

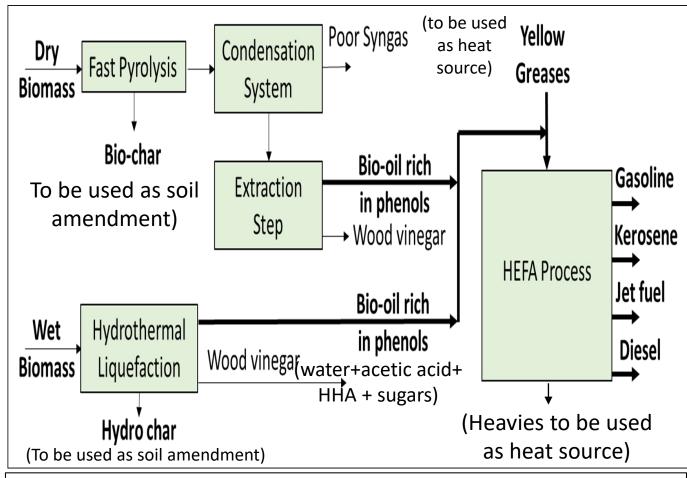
System Development and Integration (SDI) Technology

Area

Manuel Garcia-Perez Washington State University

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Project Overview



Target: Production of 100 gallons of jet fuel and study of its fuel and combustion properties. The information collected will allow using existing HEFA plants for the processing of Pyrolysis and HTL oils

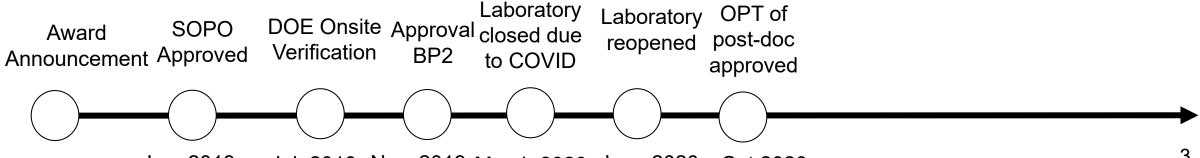
Project Goal: Evaluate the technical and feasibility of economic usina hvdroprocessed esters and fatty acids (HEFA) facilities for refined co-processing oils pyrolysis hydrothermal or (HTL) oils with yellow greases. Techno-economic analyses will be used to develop technical targets for commercialization. A replicable methodology for the design and evaluation of a supply chain for the Hybrid HEFA-HDCJ concept will be developed and used for the conditions Washington state. The fuel and combustion properties of resulting jet fuel cuts will be studied. In our techno-economic analysis we will evaluate several strategies for using the wood vinegar (separation of chemicals, wet oxidation to produce acetic acid, commercialization as pesticide).

Project Overview

Project Importance: Although HEFA is the most promising technology for jet fuel production, the construction of new units is limited by the availability of triglycerides in the form of used cooking oil, yellow greases, oil seeds and tallow. Co-processing triglycerides with the phenolic rich fraction of pyrolysis oils and yellow greases could help to increase feedstock availability.

Main Technical challenge: Phenolic rich oils from biomass pyrolysis and HTL have a hydrodeoxygenation behavior different to triglycerides. Pyrolysis and HTL oils are very reactive and tend to cross react to make heavy products. The presence of yellow greases can act as a diluent to prevent coke formation. In this project we will study: (1) strategies to co-feed Pyrolysis oils and triglycerides in HEFA units, (2) conditions maximizing jet fuel yield and minimize coke formation and (3) fuel and combustion performance of jet fuel cut (4) Supply chains configurations in Washington State.

Project History:



1. Management

PI: Dr. Garcia-Perez (Responsible for Project coordination, weekly meeting and Reporting)

Task 1: DOE verification (Responsible: Dr. Garcia-Perez, Status: Completed)

Task 2: Production of bio-crudes rich in phenolic compounds (Responsible: Drs. Garcia-Perez and Han Status: Completed)

- Study 2.1. Pyrolysis oil and yellow greases collection Responsible: Dr. Garcia-Perez and Han (Completed) (100 %)
- Study 2.2. Hydrothermal liquefaction of two woody biomass feedstock Responsible: Andy Smith (Completed) (100 %)
- Study 2.3. Production of a phenolic rich oil and wood vinegar Responsible: Drs. Garcia-Perez and Han (Completed) (100 %)

Task 3: Bio-oil Chemical Characterization (Responsible: Dr. Garcia-Perez, Ms. PaivaStatus: On-going)

Study 3.1. Characterization of bio-oil fractions Responsible: Dr. Garcia-Perez and Ms. Paiva (On going) (40 %)

Task 4: Co-hydrotreatment studies (Responsible: Drs. Olarte, Garcia-Perez and Han, Ms. Paiva Status: On-going)

- Study 4.1. Miscibility and emulsion stability of PRPO and PRHTL and yellow greases (Responsible Dr. Han and Ms. Paiva) (On going) (70 %)
- Study 4.2 Bench scale batch co-hydrotreatment studies of pyrolysis and HTL phenolic rich oils with yellow greases and distillation of products (Pesponsible: Dr. Han) (On going) (80 %)
- Study 4.3 Co-hydrotreatment of pyrolysis oils phenols rich in phenols with yellow greases in a continuous hydrotreatment unit to produce 100 gallons of jet fuels (Responsible: Dr. Olarte) (Not started yet) (0 %)
- Study 4.4 Blend limits for novel alternative fuels (Responsible: Dr. Stouffer) (Not started yet) (0 %)

Task 5: Techno-economic, LCA and Supply Chain Analysis (Responsible: Dr. Zhang and Dr. Wolcott, Status: On-going)

- Study 5.1. Mass and energy balances of all the HEFA/HDCJ design cases (Responsible: Dr. Zhang) (On going) (15 %)
- Study 5.2 Techno-economic Analysis and LCA (Responsible: Dr. Zhang) (On going) (20 %)
- Study 5.3 Supply chain analysis in Washington State (Responsible: Dr. Wolcott) (on going) (20 %)

Task 6: Fuel properties and Combustion studies (Responsible: Dr. Stouffer, Ms. Paiva)

- Study 6.1. Chemical composition and fuel properties of transportation fuel cuts (Responsible: Ms. Paiva) ((Not started yet)
- Study 6.2. Combustion studies using Referee Rig at AFRL and operated by UDRI: (Responsible: Dr. Souuffer) (Not started yet)

Management - Team:

WSU: Manuel Garcia-Perez, Anamaria Paiva, Yinglei Han (Bio-oil collection and characterization, phase equilibrium, emulsion stability, batch hydrotreatment studies, fuel properties)

PNNL: Andrew Schmidt (HTL Studies)

PNNL: Mariefel Olarte (Continuous hydrotreatment studies)

WSU: Xiao Zhang (TEA and LCA of technologies)

WSU: Michael Wolcott (Supply chain)

University of Dayton: Scott Stouffer (Combustion studies)

Communication within team: Weekly meetings, quarterly meetings with project manager, annual group meeting

1. Management

RISKS	MITIGATION STRATEGY
Failure to identify conditions to achieve jet fuel yield over 30 wt. %	Purchase of additional quantities of waste cooking oil to ensure the production of 100 gallons of jet fuel.
Content of oxygen in the resulting jet fuel cut higher than 0.1 wt. %. High content of O reduces jet fuel thermal stability.	The oxygenated molecules will be removed with the aid of a silica-gel column
Emulsion stability achieved lower than required to ensure stable feeding	Modification of feeding system with the addition of a second pump
Identification of potential toller for production of 100 gallons of jet fuel.	Identification of 2-4 toller to ensure 1 will be successful.

2. Approach

Part 1: (Tasks 2 and 3) Production, collection and characterization of yellow greases, phenolic rich fraction from pyrolysis oil and HTL oil for jet fuel production. We studied the equilibrium of bio-oils and different solvents. The extraction with butanol seems to be a promising path (**Status: completed**)

Part 2: (Tasks 4) Production of emulsion: Identify conditions to produce a stable emulsion to feed the hydrodexygenation reactor. This task is needed to allow the co-feeding in systems with a single feeding pump. (1) Batch hydrotreatment: Screen different hydrotreatment conditions and identify suitable catalysts to reach 30 wt. % jet fuel and less than 1 wt. % coke level. (Status: Tests at batch conditions almost completed) (2) Continuous tests at bench scale. These tests will be conducted with sulfide-Ni-Mo catalyst. The continuous tests are designed to confirm the hydrotreatment conditions and yields for the 100 gallons test. 3) Continuous scale for the production of 100 gallons of oil (Status: Tests at batch conditions almost completed, bench continuous tests will start shortly) Target: Production of 100 gallons of jet fuel! Main Challenge: Identification of potential toller and production of 100 gallons of jet fuel from yellow greases / Bio-oil blends.

Go/No Go: PRODUCTION OF 100 GALLONS OF JET FUEL

Part 4: (Tasks 5) (1) Techno-economic analysis, Life Cycle Assessment and Supply Chain analysis. Needed to confirm the economic and environmental viability of the concept proposed (Status: on progress)

Part 5: (Tasks 6) Fuel properties and Combustion studies. Needed to conform the quality of the final product (Status: Not started yet).

3. Impact

HEFA (Hydroprocessed Esters and Fatty Acids): The only option for short term deployment of jet fuel uses the HEFA technology. Fuel received ASTM approval thanks to the work of Honeywell UOP, Dynamics Fuels, Neste Oil, and the Environment and Energy Research Center (EERC). The resulting jet fuel has low content of aromatics, so it is subjected to 50 % blend limit. The main limitation of this technology is feedstock (triglyceride and fatty acids) availability.

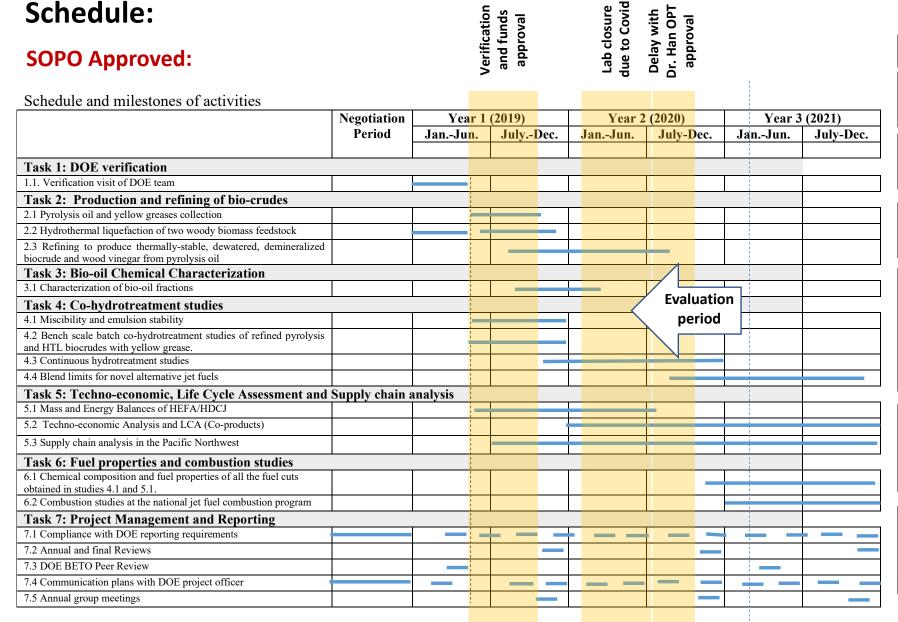
Impact: As of 2018, United States had four commercial renewable diesel plants with a combined capacity of **356 million gallons** and **one renewable jet fuel plant** with a capacity of **42 million gallons**. Another **68 million gallons** will be added by **one plant under expansion** and **two under construction**.

Our project will allow the co-processing of lignin rich fractions from pyrolysis oil in HEFA units and the identification of appropriate conditions for co-processing.

4. Progress and Outcomes

Current status of the project and highlight accomplishments:

- Task 1: DOE verification (Responsible: Dr. Garcia-Perez, Status: Completed)
- Task 2: Production of bio-crudes rich in phenolic compounds (Responsible: Drs. Garcia-Perez and Han Status: Completed)
- Task 3: Bio-oil Chemical Characterization (Responsible: Dr. Garcia-Perez, Ms. PaivaStatus: On-going)
- Task 4: Co-hydrotreatment studies (Responsible: Drs. Olarte, Garcia-Perez and Han, Ms. Paiva Status: On-going)
 - Study 4.2 Bench scale batch co-hydrotreatment studies of pyrolysis and HTL phenolic rich oils with yellow greases and distillation of products (Pesponsible: Dr. Han) (On going) (80 %)
 - Study 4.3 Co-hydrotreatment of pyrolysis oils phenols rich in phenols with yellow greases in a continuous hydrotreatment unit to produce 100 gallons of jet fuels (Responsible: Dr. Olarte) (Not started yet) (0 %)
 - Study 4.4 Blend limits for novel alternative fuels (Responsible: Dr. Stouffer) (Not started yet) (0 %)
- Task 5: Techno-economic, LCA and Supply Chain Analysis (Responsible: Dr. Zhang and Dr. Wolcott, Status: Ongoing)
 - Study 5.1. Mass and energy balances of all the HEFA/HDCJ design cases (Responsible: Dr. Zhang) (On going) (15 %)
 - Study 5.2 Techno-economic Analysis and LCA (Responsible: Dr. Zhang) (On going) (20 %)
 - Study 5.3 Supply chain analysis in Washington State (Responsible: Dr. Wolcott) (on going) (20 %)
- Task 6: Fuel properties and Combustion studies (Responsible: Dr. Stouffer, Ms. Paiva)
 - Study 6.1. Chemical composition and fuel properties of transportation fuel cuts (Responsible: Ms. Paiva) ((Not started yet)
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Verification visit: July 28-31, 2019.

Approval of Funds to start working in period 2: November 18, 2019.

Laboratory closed due to COVID: March 15, 2020

Laboratory partially re-opened: June 15, 2020

PhD defense Yinglei Han: July 24, 2020 (Although the lab was closed till June our PhD student working in several papers and defended his PhD dissertation). This student stayed in the group as post-doc.

PhD defense Evan Terrell: September 24, 2020. The student left the group. But part of his research is used as foundation to understand the chemical make up of lignin oligomers.

Our former PhD student Yinglei Han stayed with us as Post-doc working in this project. However he was not allowed to work till his OPT was received and approval on: Oct 5, 2020

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From the moment we received the funds to work in budget period 2 until February 1st, 2021 our team has been working in the lab for this project for seven months.

4. Progress and Outcomes

Task 2.1. Collection of Pyrolysis oil and yellow greases collection.

Oils received from BTG



BTG (Netherlands) produced 1 ton (230 gallons of pyrolysis oil.

Vegetable Oils received from Baker Commodities Inc.

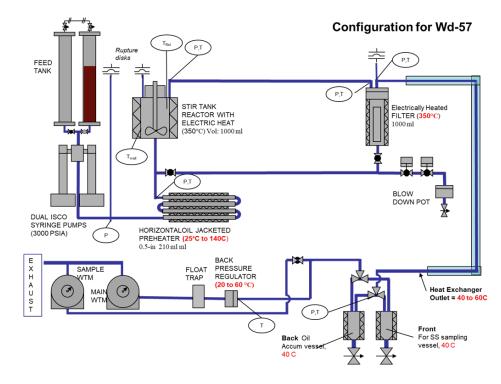


Baker Commodities Inc supplied 330 gallons of yellow greases.

Importance: The pyrolysis oil and the waste cooking oil for the production of 100 gallons of jet fuel is now stored at WSU. Getting access to these volumes was a major challenge now successfully completed.

Task 2.2. Hydrothermal liquefaction of two woody biomass feedstock (Douglas fir and Hybrid Poplar) for the production of HTL oils.

HTL System Configuration and Operational Highlights (Run Wd-57)



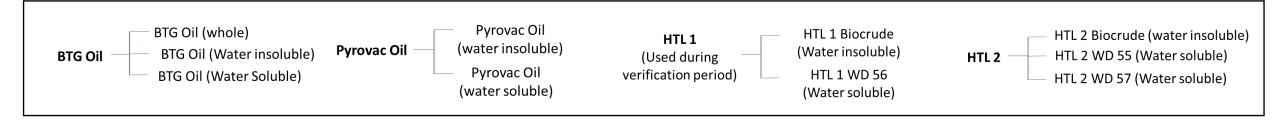
Importance: The HTL oil to be used in the project was produced and characterized. This oil will be used in the batch hydrotreatment test to compare the performance of pyrolysis and HTL oils

- Run completed on February 12, 2020
- 11.2 h time on stream with feed
- 22.3 L slurry processed
- 7 steady state samples use for data analysis
- 690 g biocrude recovered
- Run terminated after objectives were satisfied.
- 630 g biocrude provided to WSU

Parameter	Unit	Value
Rxt Configuration		CSTR
HOS	hour	12
Reactor Temperature	С	346
Pressure	psig	2760
Vol at Temp	mL	1000
Feed Rate	mL/h	2006
LHSV	L/L/h	2.0

Study 3.1. Characterization of bio-oil fractions.

Identification of Samples Received



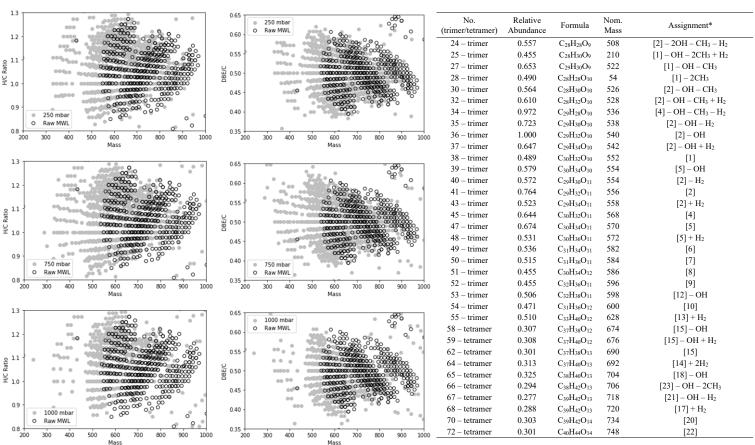
	UV Fluorescence	FTIR	HHV	HPLC	TOC	COD	Elemental analysis	TGA
HTL 1 Biocrude	N	N	Υ	-	-	-	Υ	N
HTL 1 WD 56 (WS)	N	N	-	Υ	Υ	Υ	Υ	N
HTL 2 Biocrude	Υ	Υ	Υ	-	-	-	Υ	Υ
HTL 2 WD 55	Υ	Υ	-	Υ	Υ	Υ	Υ	-
HTL 2 WD 57	Υ	Υ	-	Υ	Υ	Υ	Υ	-
Pyrovac WIS	N	N	N	-	-	-	N	N
Pyrovac WS	N	N	-	N	N	N	N	N
BTG oil	Υ	Υ	Υ	-	-	-	Υ	Υ
BTG WIS	Υ	Υ	-	Υ	Υ	Υ	Υ	-
BTG WS	Υ	Υ	-	Υ	Υ	Υ	Υ	-

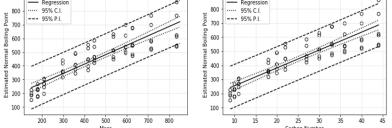
Importance: We have made progress in the characterization of all the pyrolysis and HTL oils to be used in this proposal.

Study 3.1. Characterization of bio-oil fractions. (Oils will be sent shortly to

PNNL for ICR-MS analysis)

Pyrolytic lignin formation mechanism

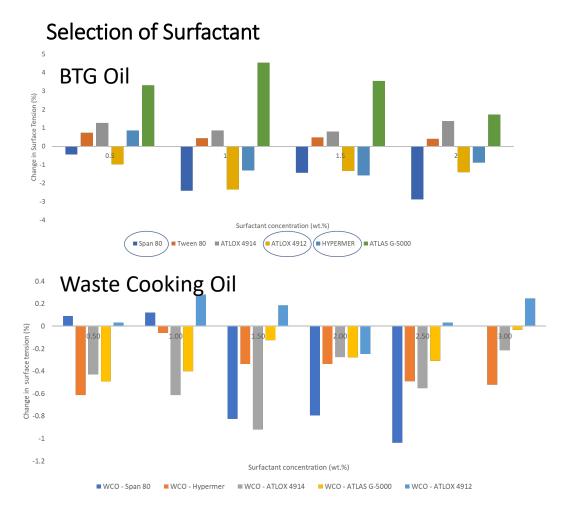




Our group has made major contributions proposing chemical structures for the lignin oligomers used in this project. This work is really important because it clearly shows that our pyrolytic lignin rich fraction is formed by modified lignin fragments. The level of modification is controlled by the need to reach the boiling point needed to scape the liquid intermediate inside the particle.

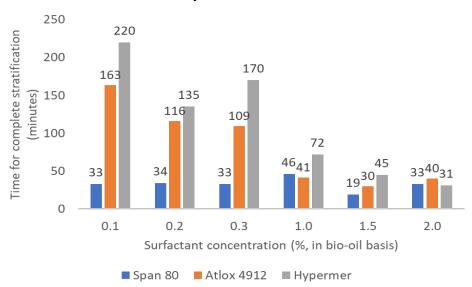
Importance: Progress in the understanding of formation mechanism and chemical make-up of pyrolysis derived lignin dimers and trimers.

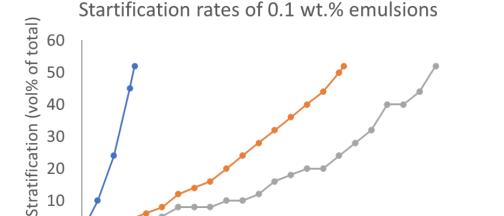
Study 4.1. Emulsion Stability



Importance: We have identified conditions for the production of Pyrolysis oil in waste cooking oil (WCO) emulsions stable > 3 hours. This time is suitable to ensure stability of the blend in single pump feeding hydrotreater. The production of stable emulsion will allow us to operate hydrotreaters with a single pump.

Emulsion stability tests





100

150

Minutes

200

250

50

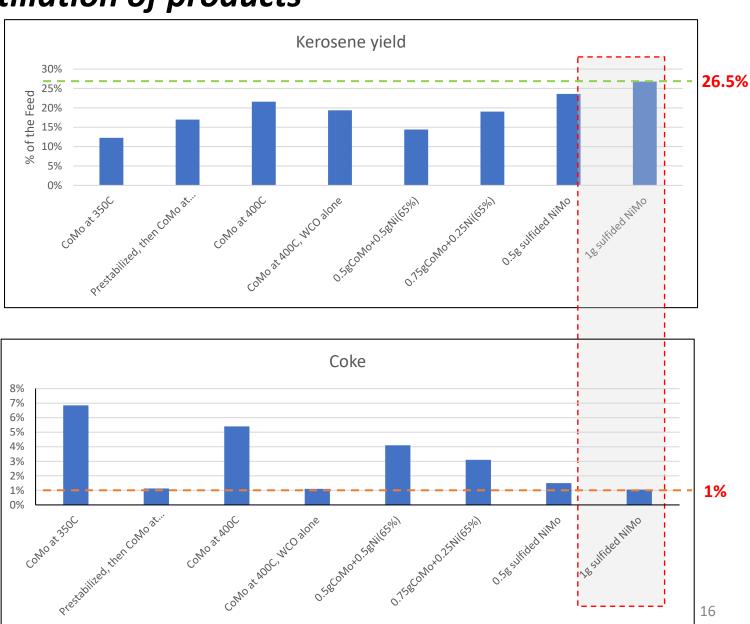
Study 4.2. Bench scale batch co-hydrotreatment studies of BTG phenolic rich oils with yellow greases and distillation of products

Sulfided NiMo/Al₂O₃ works the best

Kerosene yield= 26.5 wt.% Coke yield = 1.0 wt.%

Importance: In our batch hydrodeoxygenation studies we have identified suitable conditions for the cohydrotreatment of BTG phenolic rich phase/WCO blends into kerosene. The yield of kerosene obtained is close to the yield needed to produce the 100 gallons of jet fuel required in this project. Coke formation was lower than 1 wt. %.

Han Y, Pires A, Garcia-Perez M: Co-hydrotreatment of Bio-oil lignin-rich fraction and Vegetable oil. *Energy & Fuels*, **2020**, 34, 516-529



Study 4.3 Co-hydrotreatment of pyrolysis oils phenols rich in phenols with yellow greases in a continuous hydrotreatment unit to produce 100 gallons of jet fuels

- Two main purposes:
 - Validate batch-scale system data from WSU
 - Generate data package as basis for Request for Proposal (RFP) for tollers to produce
- Planned experiments: Consist of 2 to 3-week cumulative continuous flow campaign
- Proposed timeframe: FY2021 Q3 Q4

Request for Information (RFI)

- WSU, and PNNL path forward to produce 100 gallons of jet range fuels is through contracting a 3rd-party contract manufacturer (toller).
- June 2020 December 2020: A Request for Information (RFI) was posted (574700-RFI Hydroprocessing and Distillation Opportunity).
- Potential tollers: 3
 - PNNL identified one during late 2019 path forward planning
 - Two responses to the RFI



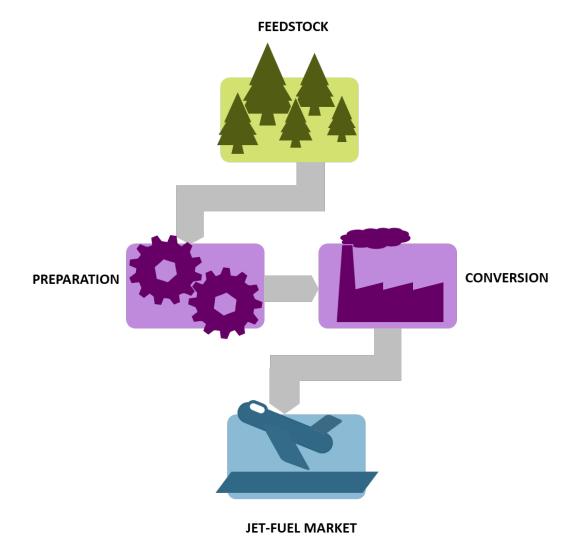
Task 5.3. Supply Chain Analysis

Techno-Economic Analysis

- ✓ Process Model
- ✓ Financial Analysis
- Mass and Energy Balance
- **Geospatially Specific Operational Expenses**

Supply Chain Analysis

- ✓ Siting Model
- ✓ Logistics Optimization Model
- ✓ Geospatial Layers
 - Transportation
 - Feedstock
 - Energy
 - Market Demand Centers



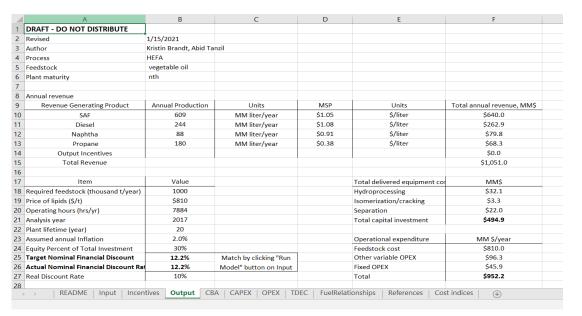
Importance: Our team has been developing some of the tools needed for the design of suitable supply chains for the co-processing of bio-oil and vegetable oil in HEFA units for jet fuel production.

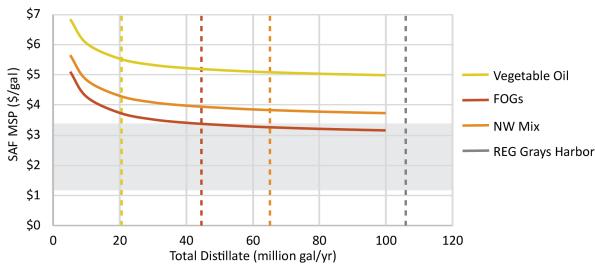
Task 5.3. Supply Chain Analysis Harmonized Techno-Economic Analysis

Technology	Status
HTL	In Construction
Pyrolysis	Harmonization
HEFA	Harmonized



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Importance: We have developed harmonized techno-economic analyses for the standalone pyrolysis and HEFA technologies. We are currently developing a harmonized TEA for the HTL technology. We made an effort to use standardized financial and economy assumptions. These Harmonized TEA are available for the public to use,

Summary

- Overview: Although HEFA is the most promising technology for jet fuel production, the construction of new units is limited by the availability of triglycerides in the form of used cooking oil, yellow greases, oil seeds and tallow. Coprocessing triglycerides with the phenolic rich fraction of pyrolysis oils and yellow greases could help to increase feedstock availability.
- **Goal:** Evaluate the technical and economic feasibility of using hydro-processed esters and fatty acids (HEFA) facilities for co-processing of refined pyrolysis oils or hydrothermal liquefaction (HTL) oils with yellow greases. Design and evaluation of a supply chain for the Hybrid HEFA-HDCJ concept for the conditions of Washington state. Fuel and combustion properties of resulting jet fuel cuts.
- **Management:** Among all the risks identified our main challenge is the identification of a potential toller for production of 100 gallons of jet fuel. To mitigate this risk we are working to identify between 2 and 4 tollers to ensure one will be successful.
- Approach: Production and characterization of waste cooking oil and pyrolysis and HTL derived oils. Co-Hydrotreatment at bench scale (batch and continuous conditions) to identify suitable processing conditions. 100 gallons of jet fuel will be produced in a Toller. The fuel and combustion behavior of the resulting jet fuel cut will be studied. TEA and LCA will be conducted for the new technology proposed as part of supply chains for the conditions of Washington State.
- Impact:Our project will allow the co-processing of lignin rich fractions from pyrolysis oil in HEFA units and the
 identification of appropriate conditions for co-processing.
- Progress & Outcomes: We have completed the collection of all the oils and are working in the characterization, phase equilibrium, emulsion stability and batch hydrotreatment tasks.
- **Future Work:** Continuous hydrotreatment, production of 100 gallons, fuel and combustion characterization, TEA, LCA and supply chain analysis.

Thank you ©

Questions?



Additional Slides

Quad Chart Overview

Timeline

Funds Approved :5/2019

Project end: 10/2022 (To be re-negotiated)

	FY19-Present Costed	Total Award
DOE Funding	WSU: \$ 395,333 PNNL: \$ 169,735 Total: \$ 565,068	WSU: \$ 1,453,637 PNNL:\$ 1,308,847 Total: \$ 2,762,484
Project Cost Share	WSU: \$ 287,546	WSU: \$ 710.420

Project Partners*

- Washington State University
- Pacific Northwest National Laboratory
- University of Dayton

Project Goal:

To identify suitable conditions to produce AJF by co-processing cooking oils and bio-crudes rich in phenols from the pyrolysis and hydrothermal liquefaction (HTL) thermochemical pathways.

End of Project Milestone:

- (1) A report with the analytical information on all the pyrolysis oils and the oils rich in phenols studied
- (2) The yield of gases, coke, oil and watery phase. The yield of naphtha, kerosene, diesel and gas oil for each of the reaction conditions
- (3) 100 gallons of jet fuel
- (4) Mass and Energy balances of a Hybrid HEFA-HDCJ Process
- (5) Break-even price of transportation fuels, sensibility analysis and carbon footprint
- (6) Supply chain for the conditions of Washington State
- (7) Generate data on fuel properties and combustion behavior of the HEFA/HDCJ jet fuel needed for ASTM certification

Funding Mechanism

FOA: DE-FOA-0001926

CFDA: 81.087

Topic Area: No 1. Drop-In Renewable Jet Fuel Blendstocks

Publications, Patents, Presentations, Awards, and Commercialization

Mechanisms of Pyrolytic Lignin Formation:

- Terrell E, Dellon LD, Dufour A, Bartolomei E, Broadbelt LJ, Garcia-Perez M: A Review on Lignin Liquefaction: Advanced Characterization of Structure and Micro-kinetic Modeling. *Industrial and Engineering Chemistry Research*, **2020**, 59, 526-555
- Terrell E, Carre V, Dufour A, Aubriet F, Le Brench Y, Garcia-Perez M: Contributions to Lignomics: Stochastic Generation of Oligomeric Lignin Structures for interpretation of MALDI-FT-ICR-MS ChemSusChem, **2020**, Vol. 13, 17
- Terrell E, Garcia-Perez M: Novel Strategy to Analyze Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Data of Biomass Pyrolysis Oil Oligomeric Structure Assignment. Energy & Fuels, 2020, 34, 7, 8466-8481
- Terrell E, Garcia-Perez M: Vacuum Pyrolysis of Hybrid Poplar Milled Wood Lignin with FT-ICR-MS analysis of feedstock and products for the Elucidation of Pyrolytic Lignin formation Mechanism and Chemistry, Accepted Energy and Fuel, **2020**, 34, 11, 14249-14263

Bio-oil Refinery strategies:

Publications

- Pinheiro-Pires AP, Arauzo J, Fonts I, Domine ME, Fernandez-Arroyo A, Garcia-Perez ME, Montoya J, Jene FC, Pfromm P, Garcia-Perez M: Challenges and Opportunities for Bio-oil Upgrading and Refining: A review. *Energy and Fuels*, **2019**, 33, 6, 4683-4720
- Han Y, Pinheiro-Pires A, Denson M, McDonald, A, Garcia-Perez M: Ternary Phase Diagram of Water / Bio-oil / Organic Solvent for Bio-oil Fractionation, Energy and Fuels, **2020**, 34, 12, 16250-16264

Bio-oil Hydrotreatment:

- Han Y, Gholizadeh M, Tran C-C, Kaliaguine S, Li C-Z, Olarte M, Garcia-Perez M: Hydrotreatment of pyroysis bio-oil: A review. *Fuel Processing Technology*, 195, **2019**, 106140
- Han Y, Pires A, Garcia-Perez M: Co-hydrotreatment of Bio-oil lignin-rich fraction and Vegetable oil. Energy & Fuels, 2020, 34, 516-529

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.

Key Model Assumptions

- Mass and Energy Balance: A Basic Engineering Package (BEP) which includes: preliminary design and process description, process flow diagram and mass and energy balances
- **TEA**: Determine the break-even price of transportation fuels for the HEFA/HDCJ process proposed. Assumptions as those used in Tanzi el at (2021).
- LCA:Complete the life-cycle analysis to determine environmental impact effects of the process and determine the appropriate classification for the fuel as a low-carbon alternative
- Resource Assessment: Complete a supply chain that use geographically-explicit information for the conditions at Washington State