DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

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

April 3, 2023, (4:20 PM)
System Development and Integration (SDI) Technology Area

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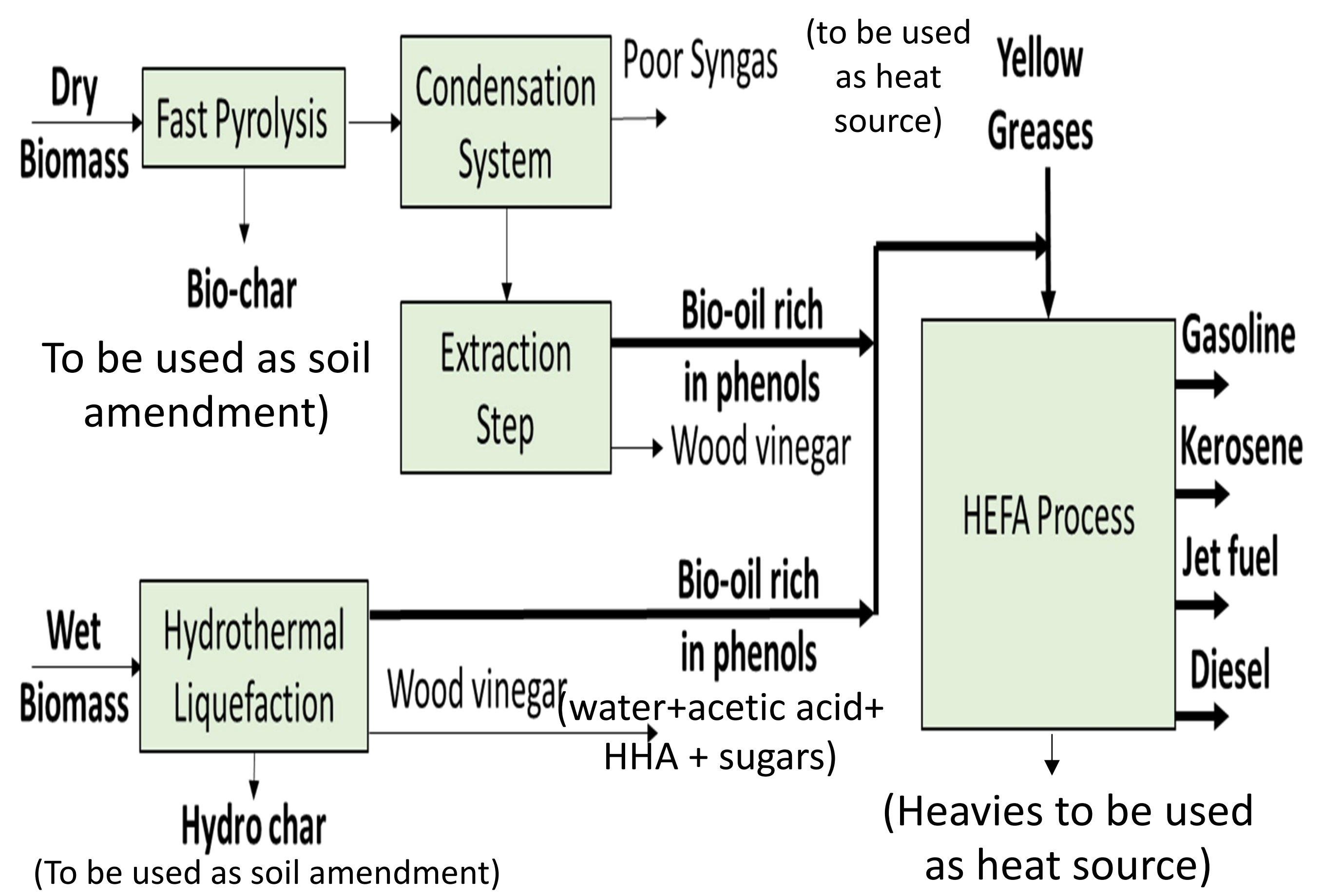
Washington State University

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

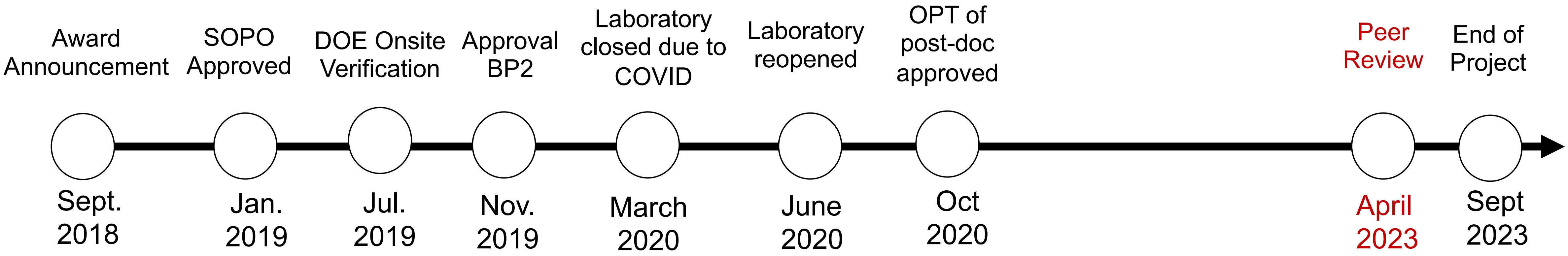
Project Goal: Evaluate the **technical and economic feasibility** of using hydro-processed esters and fatty acids (HEFA) facilities for the **co-processing of refined pyrolysis oils or hydrothermal liquefaction (HTL) oils with yellow greases**. **Techno-economic analyses** will be used to develop technical targets for commercialization. A replicable methodology for designing and evaluating **a supply chain for the Hybrid HEFA-HDCJ concept** will be developed and used for the conditions of Washington state. The **fuel and combustion properties of resulting jet fuel** cuts will be studied.

Project Overview

Project Importance: Although HEFA is the most promising technology for short term jet fuel production, the construction of new units is limited by the availability of triglycerides. **Co-processing triglycerides with the phenolic rich fraction of pyrolysis oils 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. This project studied: (1) strategies to co-feed Pyrolysis oils and triglycerides in HEFA units, (2) conditions maximizing jet fuel yield and minimizing coke formation, and (3) fuel and combustion performance of jet fuel cut (4) TEA and 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 **(Completed) (100 %)**

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) **(Completed) (100 %)**

Study 4.2 Bench scale batch co-hydrotreatment studies of pyrolysis and HTL phenolic rich oils with yellow greases and distillation of products (Responsible: Dr. Han) **(Completed) (100 %)**

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) **(In progress) (50 %)**

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) (90 %)**

Study 5.2 Techno-economic Analysis and LCA (Responsible: Dr. Zhang) **(On going) (90 %)**

Study 5.3 Supply chain analysis in Washington State (Responsible: Dr. Wolcott) **(on going) (90 %)**

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) (**(Completed) (100 %)**

Study 6.2. Combustion studies using Referee Rig at AFRL and operated by UDRI: (Responsible: Dr. Souffer) **(Not started yet)**

Management - Team:

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

PNNL: Andrew Schmidt (HTL Studies)

PNNL: Mariefel Olarte, Gary Neuenschwander, Miki Santosa, Igor Kutnyakov, Daniel Howe, Alan Cooper, Marie Swita an (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
Challenges to keep coke formation below 1 % in continuous conditions to avoid reactor clogging at the 400 mL reactor	Improve hydrogenation capacity. Testing of new operational conditions/catalyst
Yield of jet fuel lower than 30 %	Addition of hydrocracking step to increase fuel yield
Difficulties to achieve 100 gallons in the 400 mL system	Reduce fuel tests from tear β to α

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. Four papers were published/submitted with the results of this task. We found that the main difference between pyrolysis and HTL oils is the content of acids. We developed a new strategy based on ICR-MS characterization of pyrolysis oil and modeling to propose structural representation of pyrolytic lignin molecules (**Status: completed**)

Part 2: (Tasks 4) Production of emulsion and hydrotreatment studies: (1) Conditions to produce a stable emulsion to feed the hydrodeoxygenation reactor. This task will allow the co-feeding in systems with a single feeding pump (**Status: Completed**) (2) Batch hydrotreatment: Different hydrotreatment conditions and identify suitable catalysts to reach targeted jet fuel yield and less than 1 wt. % coke level. (**Status: Completed**) (3) 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. (**Status: Completed**). (4) Continuous scale for producing 100 gallons of oil (**Status: In Progress**) Target: Production of 100 gallons of jet fuel. **Main Challenge:** Impossibility of using the large bench scale PNNL hydrotreatment system. The production of 100 gallons will not be possible due to clogging issues in the 450 mL reactor. The team will be producing as much jet fuel as possible in the 450 mL continuous hydrodeoxygenation reactor.

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: In Progress)**

Part 5: (Tasks 6) Fuel properties and Combustion studies. Needed to confirm the quality of the final product (**Status: In Progress**).

3. Impact

HEFA (Hydroprocessed Esters and Fatty Acids): The only option for short term deployment of SAF. 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 2023, the United States has **five commercial renewable diesel plants** with a combined capacity of **590 million gallons** and **one sustainable aviation fuel (SAF) plant** with a capacity of **42 million gallons**. Production of renewable diesel is expected to grow in the near term to **2 billion gallons** with the construction of **six new plants and the expansion of three existing plants**. Production of SAF aims to reach 3 billion gallons a year by 2030.

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

https://afdc.energy.gov/fuels/emerging_hydrocarbon.html

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. Paiva, Denson and Manrique, Status: Completed)

Task 4: Co-hydrotreatment studies (Responsible: Drs. Olarte, Garcia-Perez and Han, Ms. Paiva, Denson and Manrique Status: In Progress)

Study 4.2 Bench scale batch co-hydrotreatment studies of pyrolysis and HTL phenolic rich oils with yellow greases and distillation of products (Responsible: Dr. Han) **(Completed)**

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) (**In Progress) (40 %)**

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: In Progress)

Study 5.1. Mass and energy balances of all the HEFA/HDCJ design cases (Responsible: Dr. Zhang) **(In Progress) (90 %)**

Study 5.2 Techno-economic Analysis and LCA (Responsible: Dr. Zhang) **(In Progress) (90 %)**

Study 5.3 Supply chain analysis in Washington State (Responsible: Dr. Wolcott) **(In Progress) (90 %)**

Task 6: Fuel properties and Combustion studies (Responsible: Dr. Stouffer, Ms. Paiva Denson and Manrique, Status: In Progress),

Study 6.1. Chemical composition and fuel properties of transportation fuel cuts (Responsible: Ms. Paiva, Denson, Manrique) **(Completed)**

Study 6.2. Combustion studies using Referee Rig at AFRL and operated by UDRI: (Responsible: Dr. Souuffer) **(Not started yet)**

Schedule:

SOPO Approved:

Verification and funds approval

Lab closure due to Covid

Delay with Dr. Han OPT approval

Schedule and milestones of activities

	Negotiation Period	Year 1 (2019)		Year 2 (2020)		Year 3 (2021)	
		Jan.-Jun.	July.-Dec.	Jan.-Jun.	July-Dec.	Jan.-Jun.	July-Dec.
Task 1: DOE verification							
1.1. Verification visit of DOE team							
Task 2: Production and refining of bio-crudes							
2.1 Pyrolysis oil and yellow greases collection							
2.2 Hydrothermal liquefaction of two woody biomass feedstock							
2.3 Refining to produce thermally-stable, dewatered, demineralized biocrude and wood vinegar from pyrolysis oil							
Task 3: Bio-oil Chemical Characterization							
3.1 Characterization of bio-oil fractions							
Task 4: Co-hydrotreatment studies							
4.1 Miscibility and emulsion stability							
4.2 Bench scale batch co-hydrotreatment studies of refined pyrolysis and HTL biocrudes with yellow grease.							
4.3 Continuous hydrotreatment studies							
4.4 Blend limits for novel alternative jet fuels							
Task 5: Techno-economic, Life Cycle Assessment and Supply chain analysis							
5.1 Mass and Energy Balances of HEFA/HDCJ							
5.2 Techno-economic Analysis and LCA (Co-products)							
5.3 Supply chain analysis in the Pacific Northwest							
Task 6: Fuel properties and combustion studies							
6.1 Chemical composition and fuel properties of all the fuel cuts obtained in studies 4.1 and 5.1.							
6.2 Combustion studies at the national jet fuel combustion program							
Task 7: Project Management and Reporting							
7.1 Compliance with DOE reporting requirements							
7.2 Annual and final Reviews							
7.3 DOE BETO Peer Review							
7.4 Communication plans with DOE project officer							
7.5 Annual group meetings							

Evaluation period

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.

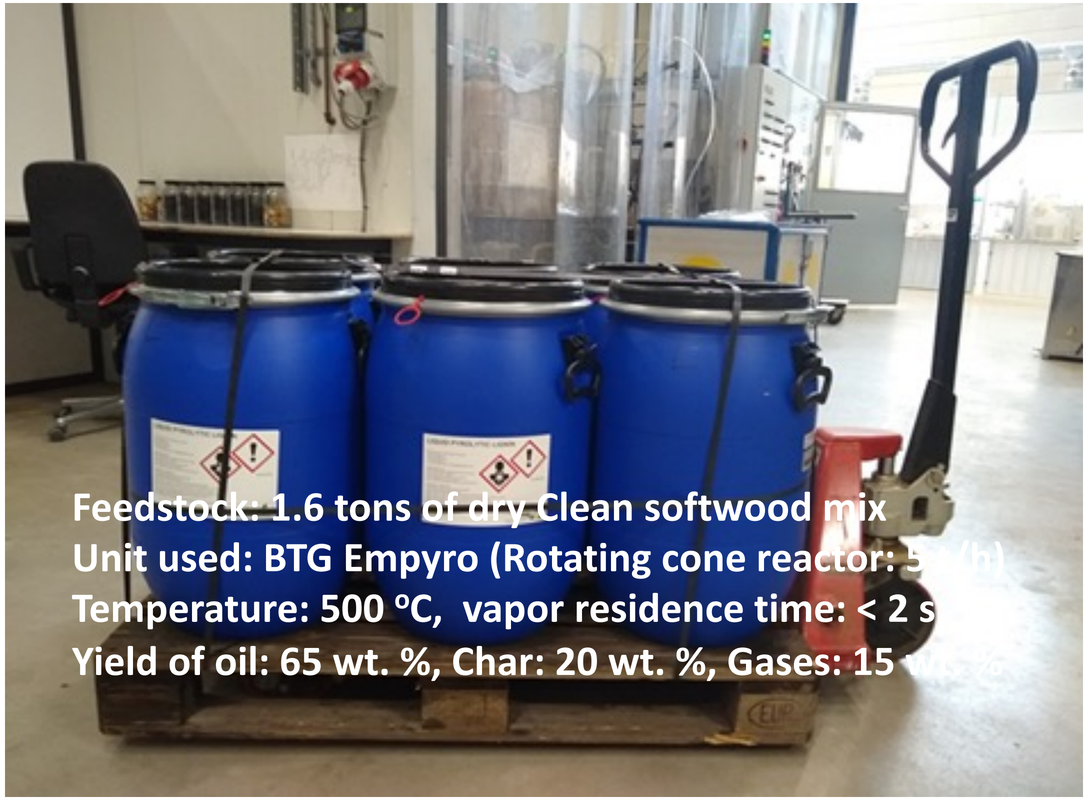
Our former PhD student Yinglei Han stayed with us as Post-doc working in this project. However he was not allowed to work till his OPT was received and approval on: Oct 5, 2020

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.

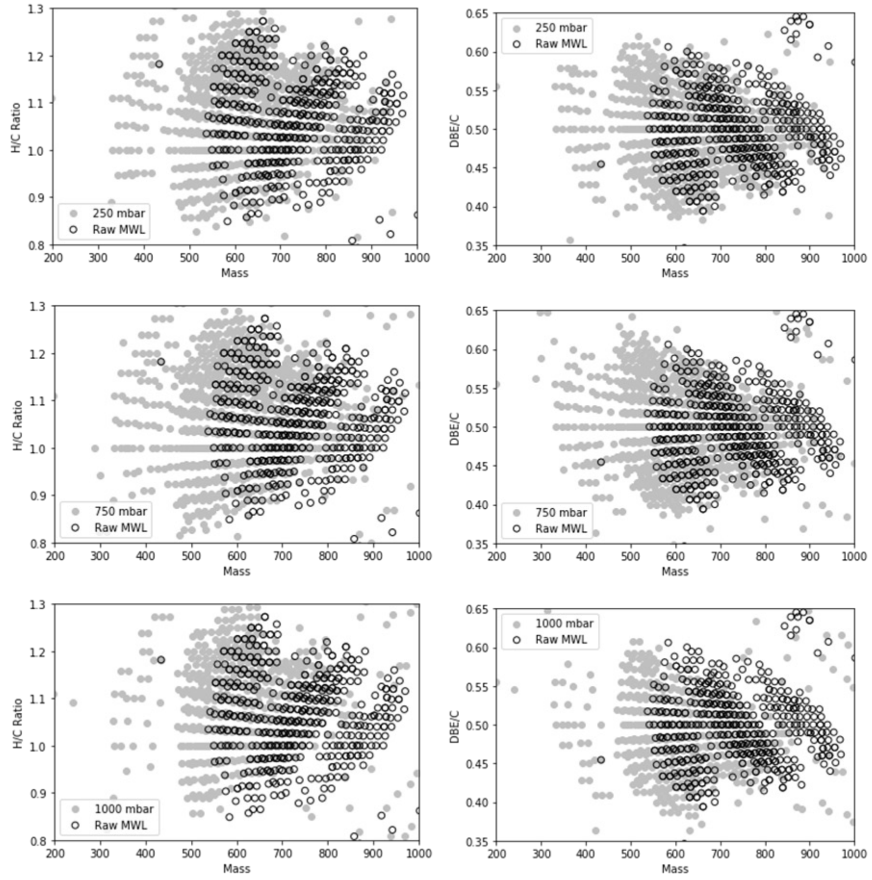
***Vegetable** Oils received from Baker Commodities Inc.*

Baker Commodities Inc supplied 330 gallons of yellow greases.

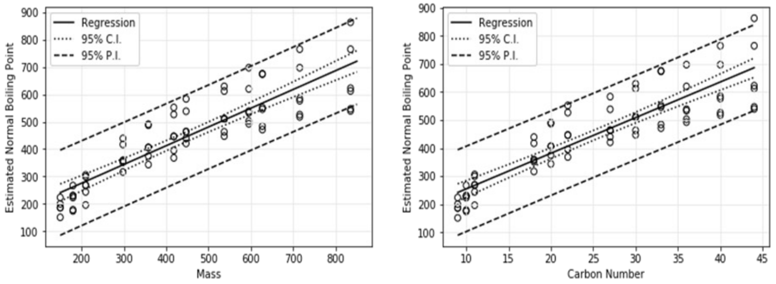
Importance: *The pyrolysis oil and the waste cooking oil for the production of 100 gallons of jet fuel is now stored at WSU.*

Study 3.1. Characterization of bio-oil fractions. (Oils will be sent shortly to PNNL for ICR-MS analysis)

Pyrolytic lignin formation mechanism



No. (trimer/tetramer)	Relative Abundance	Formula	Nom. Mass	Assignment*
24 – trimer	0.557	$C_{28}H_{28}O_9$	508	[2] – 2OH – CH_3 – H_2
25 – trimer	0.455	$C_{28}H_{30}O_9$	210	[1] – OH – 2CH_3 + H_2
27 – trimer	0.653	$C_{29}H_{30}O_9$	522	[1] – OH – CH_3
28 – trimer	0.490	$C_{28}H_{28}O_{10}$	54	[1] – 2CH_3
30 – trimer	0.564	$C_{28}H_{30}O_{10}$	526	[2] – OH – CH_3
32 – trimer	0.610	$C_{28}H_{32}O_{10}$	528	[2] – OH – CH_3 + H_2
34 – trimer	0.972	$C_{29}H_{28}O_{10}$	536	[4] – OH – CH_3 – H_2
35 – trimer	0.723	$C_{29}H_{30}O_{10}$	538	[2] – OH – H_2
36 – trimer	1.000	$C_{29}H_{32}O_{10}$	540	[2] – OH
37 – trimer	0.647	$C_{29}H_{34}O_{10}$	542	[2] – OH + H_2
38 – trimer	0.489	$C_{30}H_{32}O_{10}$	552	[1]
39 – trimer	0.579	$C_{30}H_{34}O_{10}$	554	[5] – OH
40 – trimer	0.572	$C_{29}H_{30}O_{11}$	554	[2] – H_2
41 – trimer	0.764	$C_{29}H_{32}O_{11}$	556	[2]
43 – trimer	0.523	$C_{29}H_{34}O_{11}$	558	[2] + H_2
45 – trimer	0.644	$C_{30}H_{32}O_{11}$	568	[4]
47 – trimer	0.674	$C_{30}H_{34}O_{11}$	570	[5]
48 – trimer	0.531	$C_{30}H_{36}O_{11}$	572	[5] + H_2
49 – trimer	0.536	$C_{31}H_{34}O_{11}$	582	[6]
50 – trimer	0.515	$C_{31}H_{36}O_{11}$	584	[7]
51 – trimer	0.455	$C_{30}H_{34}O_{12}$	586	[8]
52 – trimer	0.455	$C_{32}H_{36}O_{11}$	596	[9]
53 – trimer	0.506	$C_{32}H_{38}O_{11}$	598	[12] – OH
54 – trimer	0.471	$C_{31}H_{36}O_{12}$	600	[10]
55 – trimer	0.510	$C_{33}H_{40}O_{12}$	628	[13] + H_2
58 – tetramer	0.307	$C_{37}H_{38}O_{12}$	674	[15] – OH
59 – tetramer	0.308	$C_{37}H_{40}O_{12}$	676	[15] – OH + H_2
62 – tetramer	0.301	$C_{37}H_{38}O_{13}$	690	[15]
64 – tetramer	0.313	$C_{37}H_{40}O_{13}$	692	[14] + 2H_2
65 – tetramer	0.325	$C_{38}H_{40}O_{13}$	704	[18] – OH
66 – tetramer	0.294	$C_{38}H_{42}O_{13}$	706	[23] – OH – 2CH_3
67 – tetramer	0.277	$C_{39}H_{42}O_{13}$	718	[21] – OH – H_2
68 – tetramer	0.288	$C_{39}H_{42}O_{13}$	720	[17] + H_2
70 – tetramer	0.303	$C_{39}H_{42}O_{14}$	734	[20]
72 – tetramer	0.301	$C_{40}H_{44}O_{14}$	748	[22]



Major contributions proposing chemical structures for the lignin oligomers used in this project*. This work is 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.*

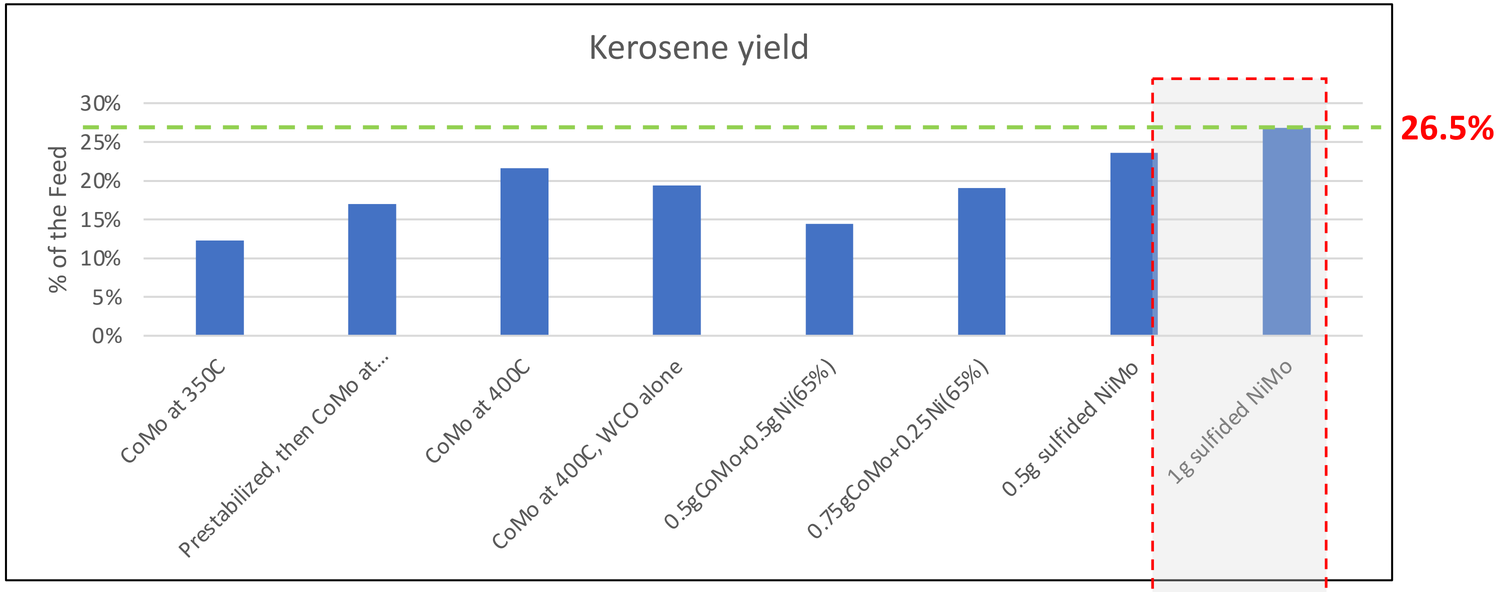
Terrell E, Garcia-Perez M: Vacuum Pyrolysis of Hybrid Poplar Milled Wood Lignin with FT-ICR-MS analysis of feedstock and products for the Elucidation of Pyrolytic Lignin formation Mechanism and Chemistry, Accepted Energy and Fuel, **2020,** 34, 11, 14249-14263

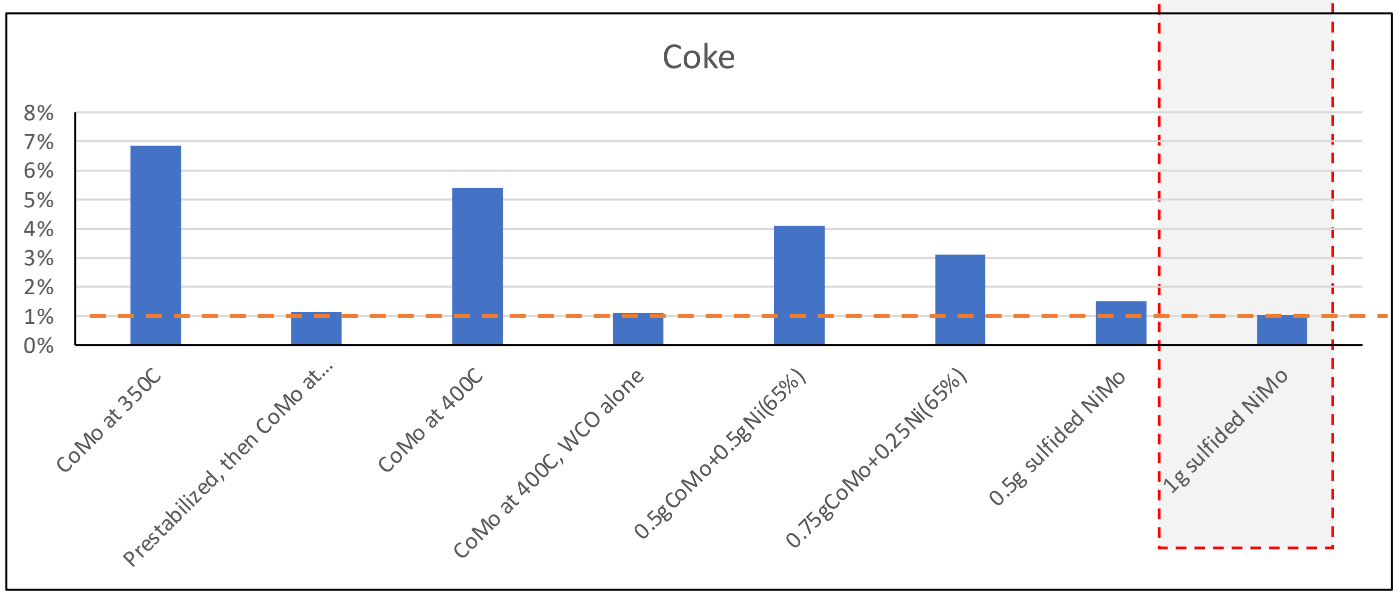
Study 4.2. Bench scale batch co-hydrotreatment studies of BTG phenolic rich oils with yellow greases and distillation of products

Sulfided NiMo/Al_2O_3 works the best

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

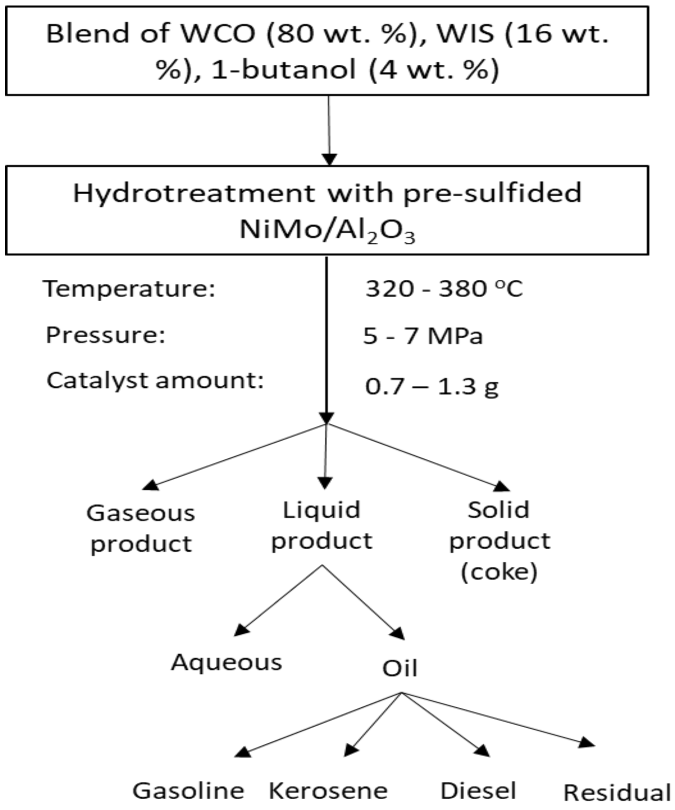
Importance: *In our batch hydrodeoxygenation studies we have identified suitable conditions for the co-hydrotreatment of BTG phenolic rich phase/WCO blends into kerosene. Coke formation was lower than 1 wt. %.*

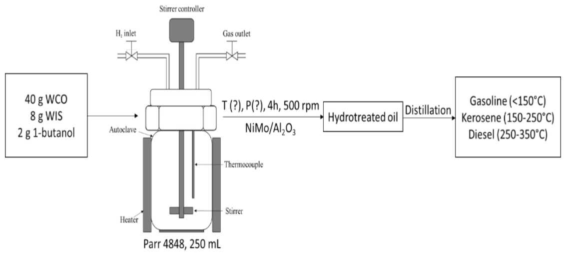


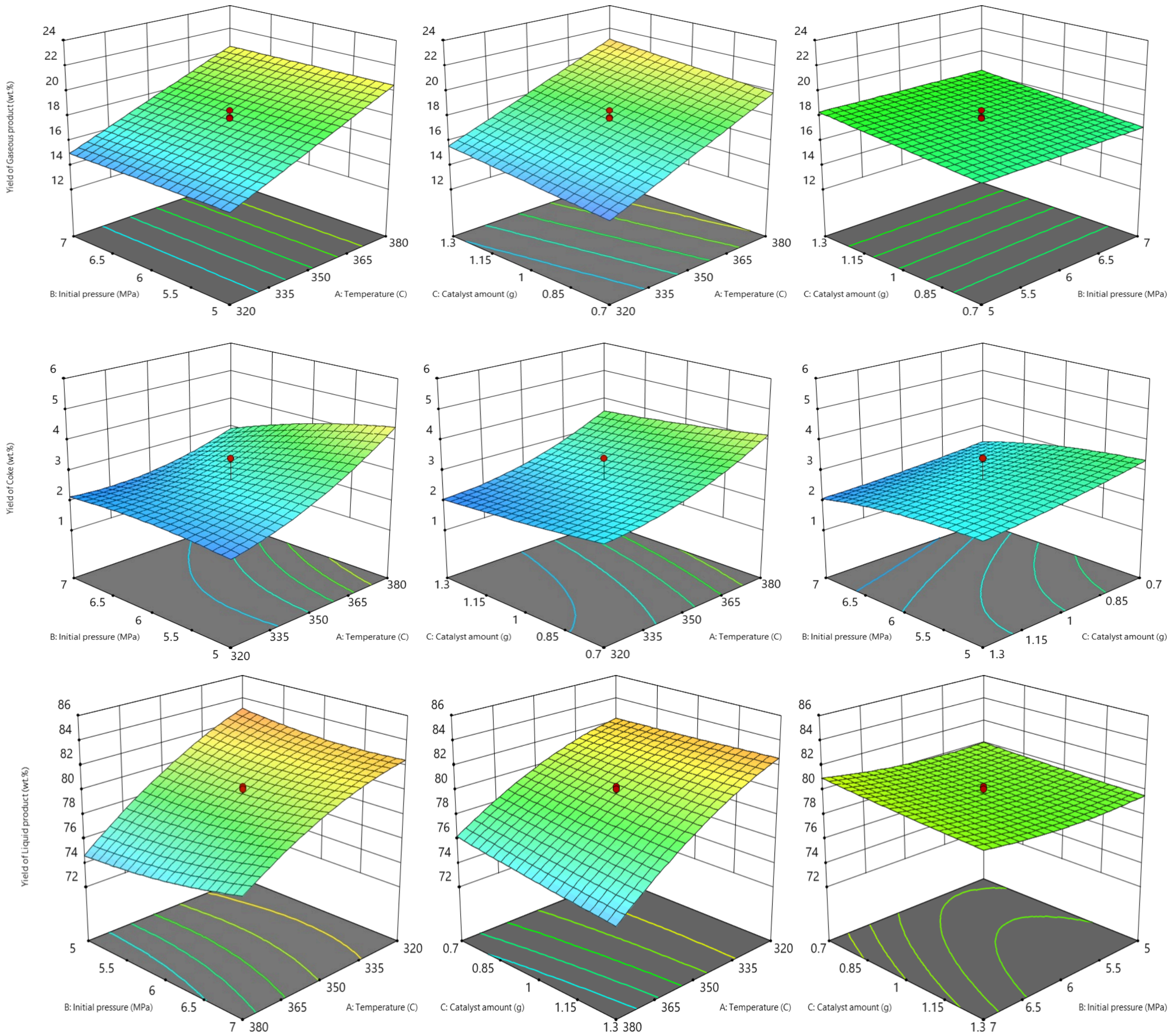


Han Y, Pires A, Garcia-Perez M: Co-hydrotreatment of Bio-oil lignin-rich fraction and Vegetable oil. *Energy & Fuels*, **2020,** 34, 516-529

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



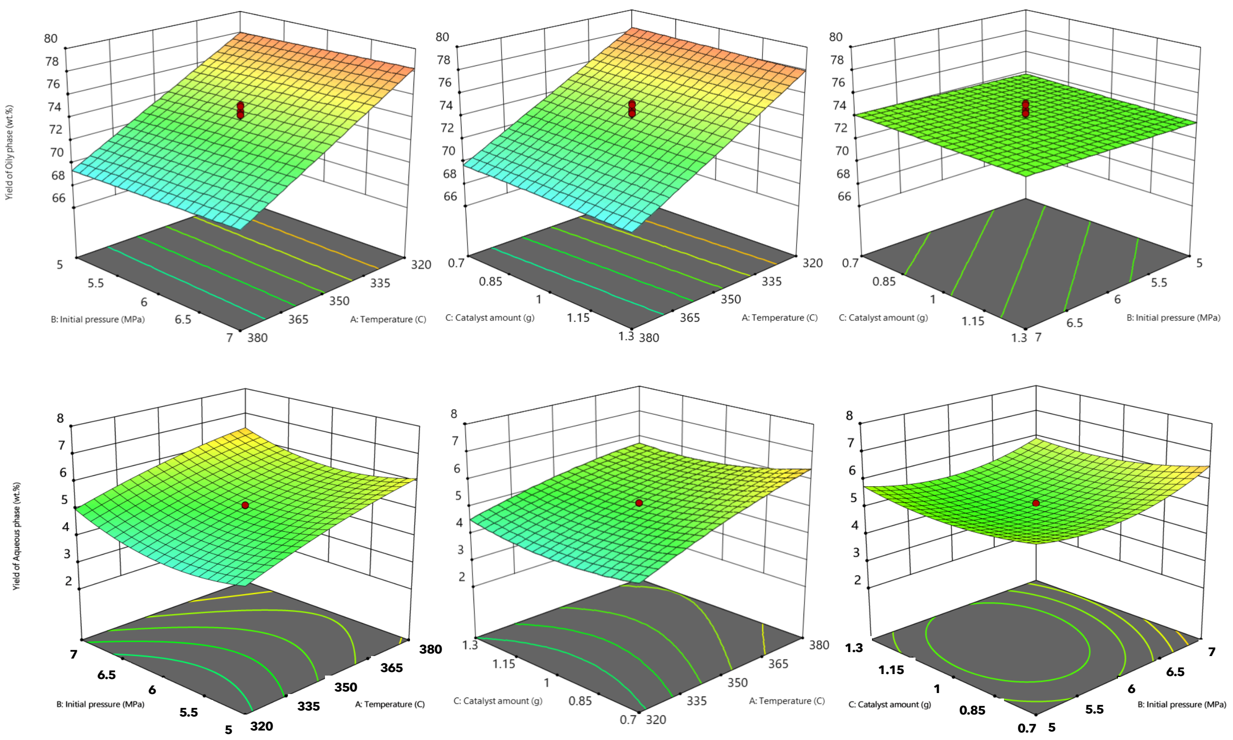


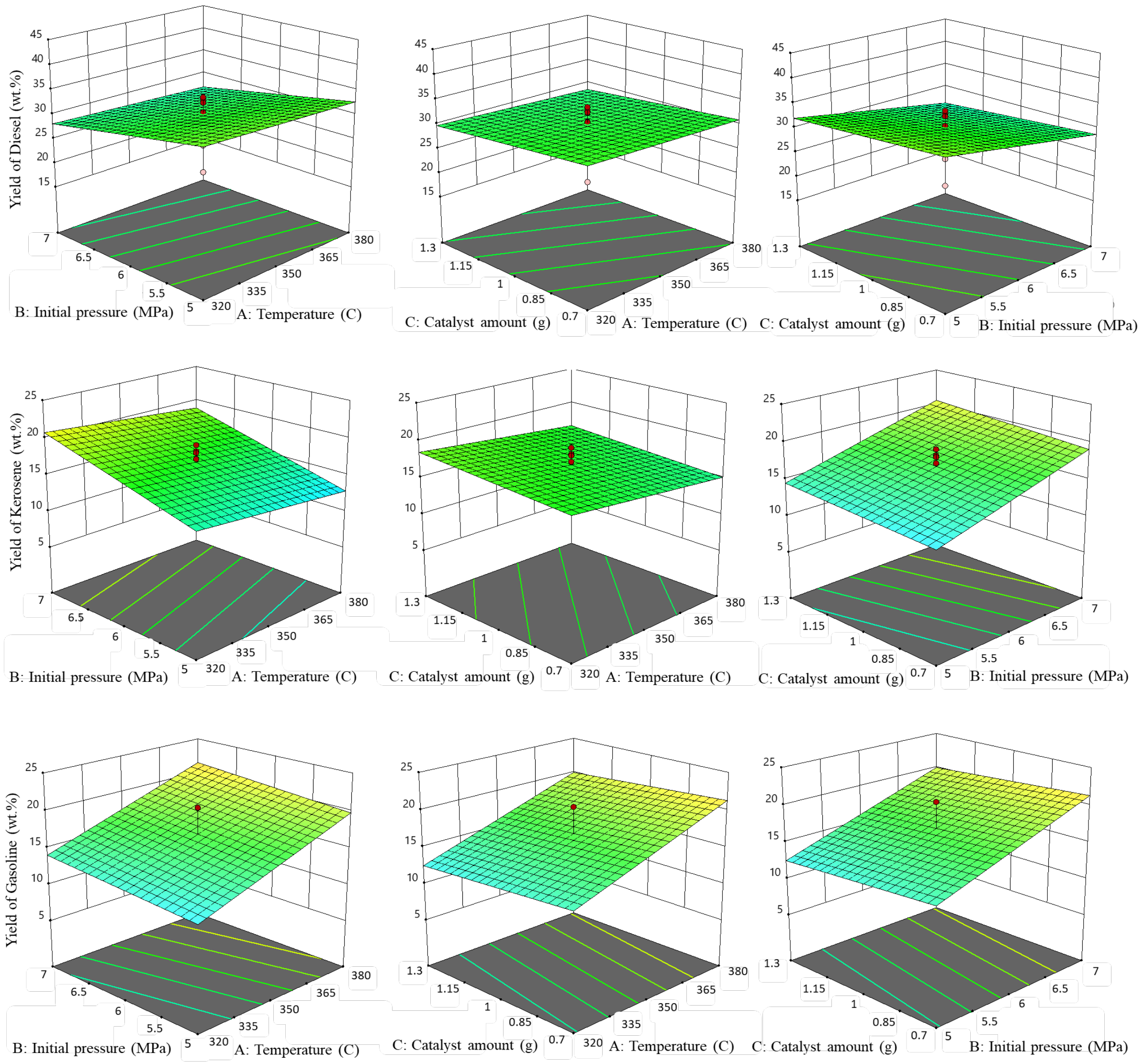


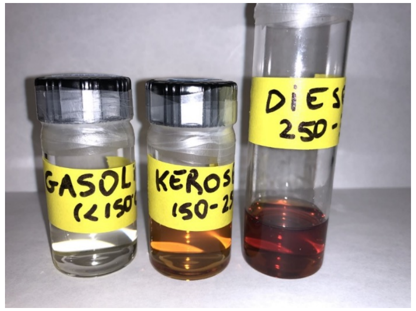
Importance: *Experimental design studies to identify the impact of processing conditions on the yield of pyrolysis products.*

Pinheiro-Pires AP, Olarte M, Garcia-Perez M, Han Y: Co-hydrotreatment of Yellow Greases and Pyrolysis Oil Water Insoluble Fraction: Part I: Experimental Design to Increase Kerosine Yield and Reduce Coke Formation. *Energy & Fuels*, **2023, 37**, 3, 2100-2114

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







Pinheiro-Pires AP, Olarte M, Garcia-Perez M, Han Y: Co-hydrotreatment of Yellow Greases and Pyrolysis Oil Water Insoluble Fraction: Part I: Experimental Design to Increase Kerosine Yield and Reduce Coke Formation. *Energy & Fuels*, **2023, 37**, 3, 2100-2114

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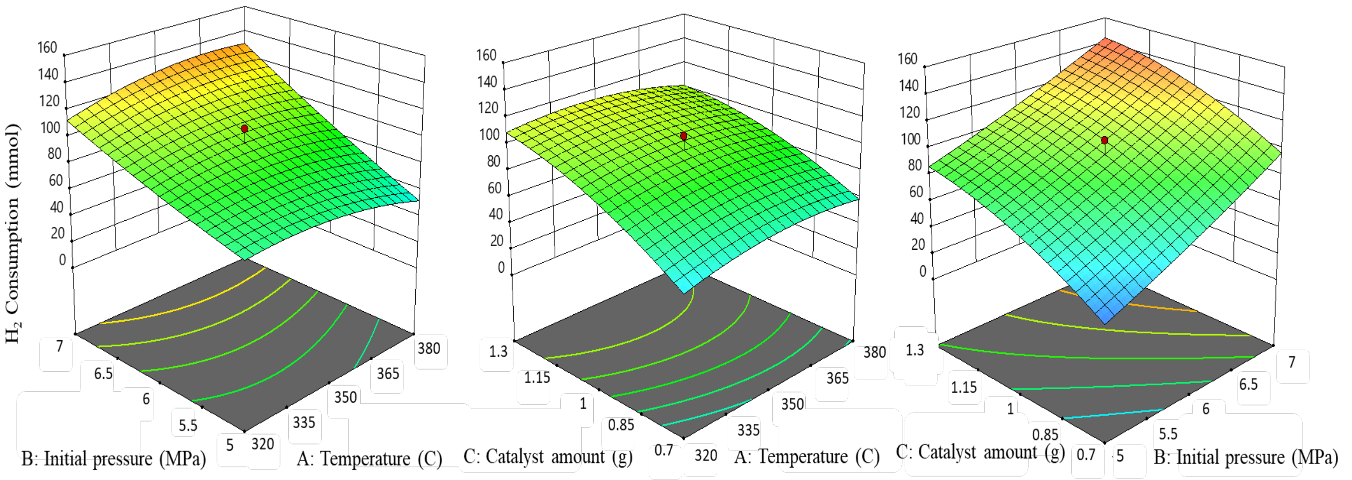
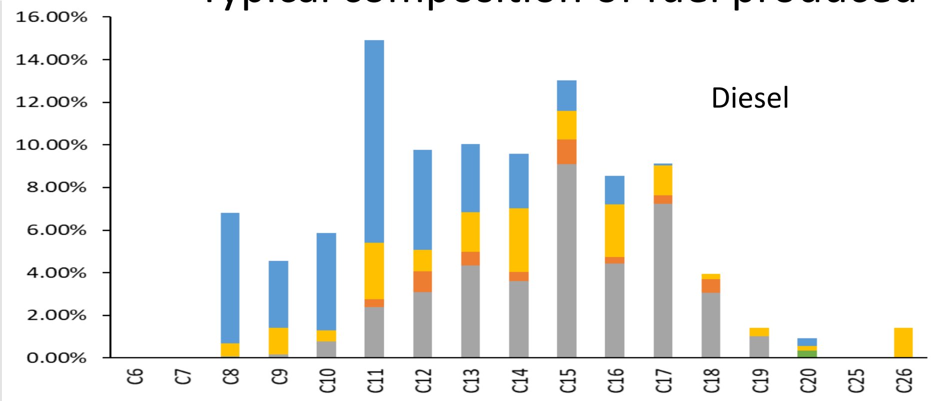
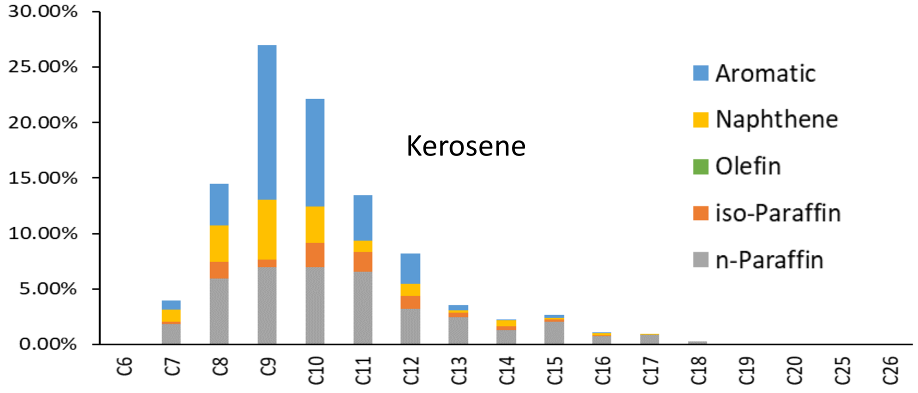
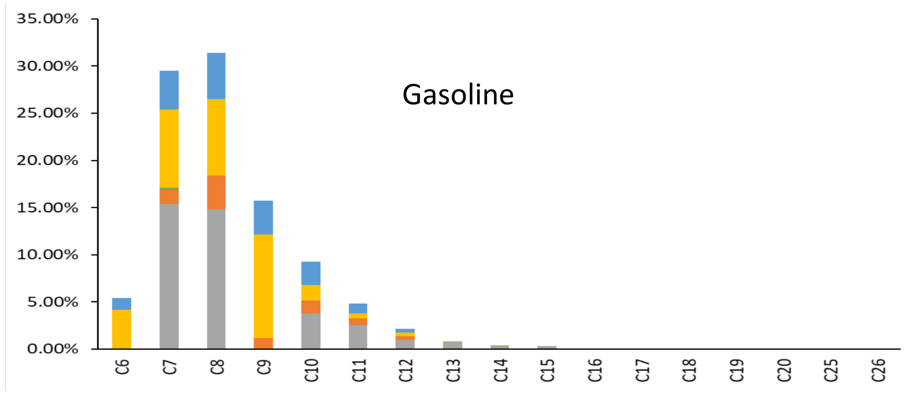


Typical composition of fuel produced







Overall fuel composition

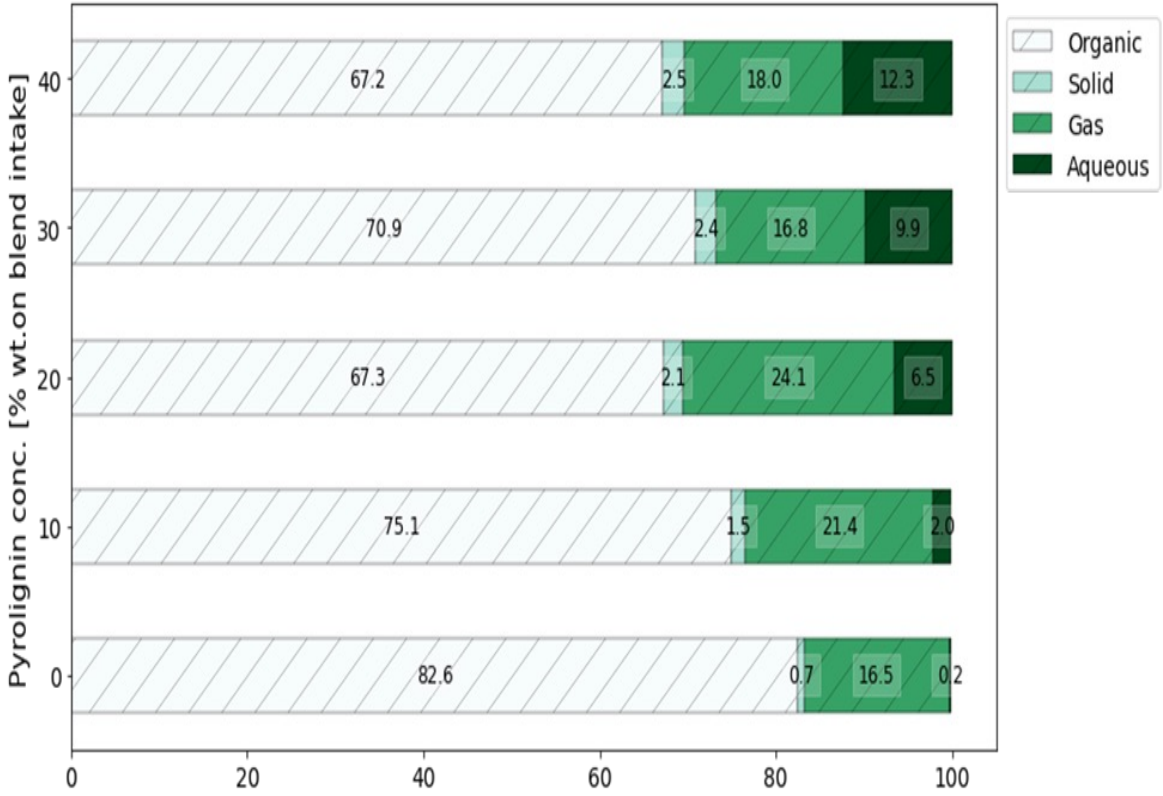
Fuel	n-Paraffin	Iso-Paraffin	Olefin	Naphthene	Aromatic
Gasoline	39.1	8.8	0.2	34.0	17.8
Kerosene	39.2	8.4	0.00	16.5	35.8
Diesel	39.3	4.9	0.3	18.4	37.0

	HHV (kJ/g)	Density (g/mL)	Water content (wt. %)	Surface Tension (mN/m)	Cloud Point (ºC)	Pouring Point (ºC)	Freezing Point (ºC)
Gasoline	44.1 ± 0.4	0.7	0.02	21.0 ± 0.1	NA	NA	NA
Kerosene	45.3 ± 0.0	0.8	0.06	24.2 ± 0.1	-39.6	-45.0	-33.7
Diesel	44.9 ± 0.1	0.9	0.03	23.6± 0.1	-5.7	-6.0	-5.2

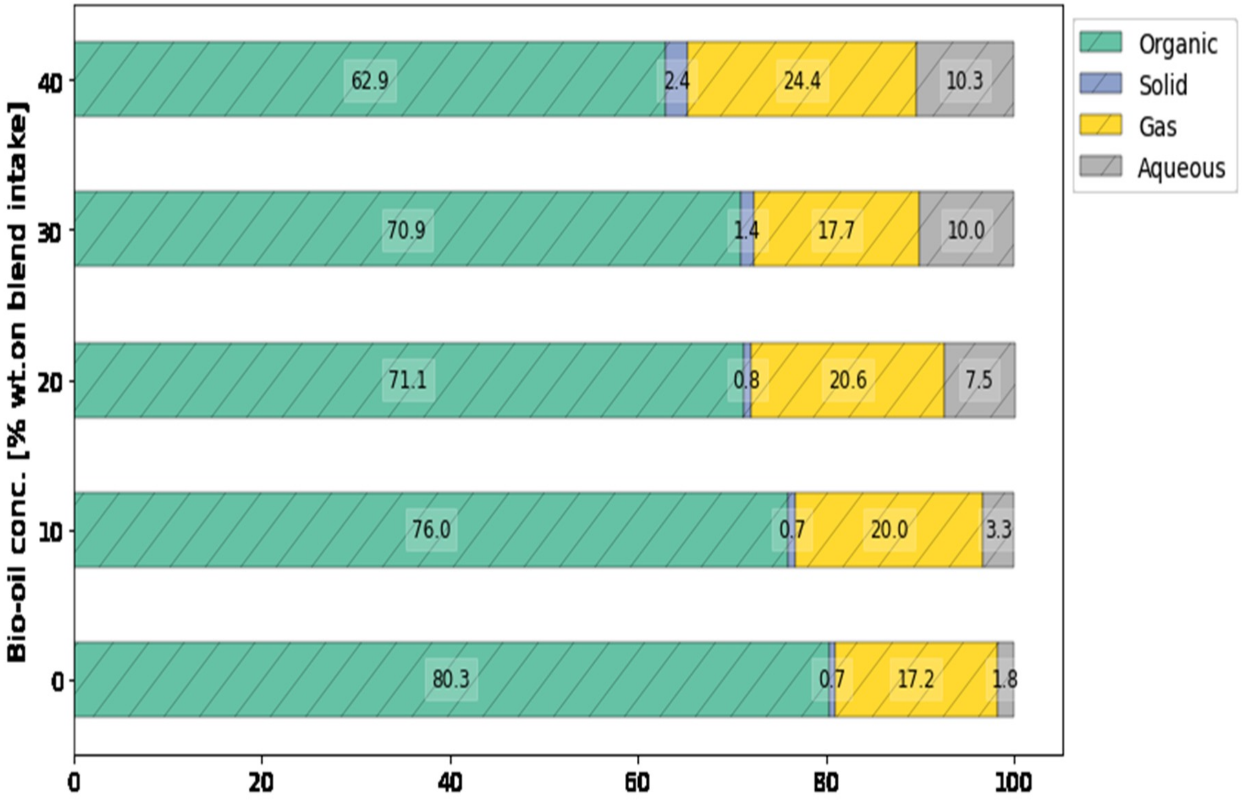
Pinheiro-Pires AP, Olarte M, Garcia-Perez M, Han Y: Co-hydrotreatment of Yellow Greases and Pyrolysis Oil Water Insoluble Fraction: Part I: Experimental Design to Increase Kerosine Yield and Reduce Coke Formation. *Energy & Fuels*, **2023, 37**, 3, 2100-2114

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

Yields from Pyrolytic lignin



Yield from Heavy Bio-oil fraction (Pyrolytic lignin + heavy sugars)



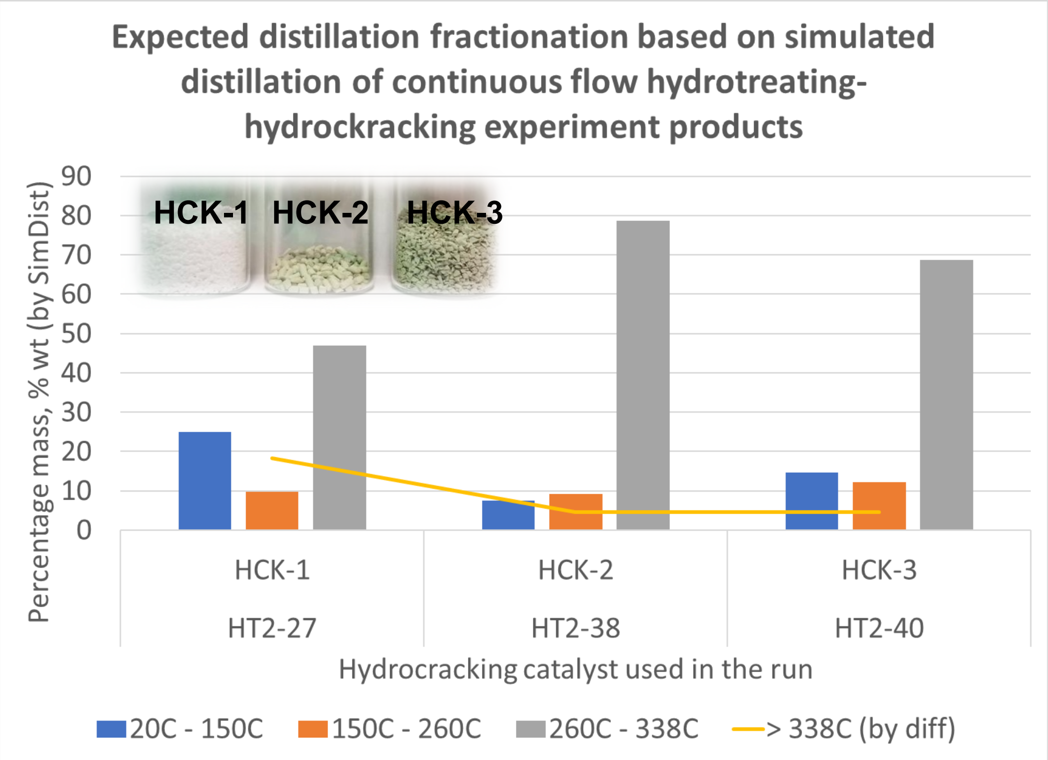
Importance: Pyrolytic lignin and the heavy bio-oil fraction result in similar overall organics, aqueous and coke yields. This result is important because opens the door to co-process all bio-oil oligomeric fractions.

Extrapolating the experimental values to 100 % bio-oil heavy fraction: **Organics: 42.5 wt. %**, **Aqueous: 26.5 wt. %**, **Gas: 23.4 wt. %**, **coke: 5.5 wt. %**)

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

- 100 gallons of jet fuels will not be produced.
  - Scope adjustment due to plugging during continuous co-processing
  - Longest TOS with co-processing: 255 h (lab scale); 26 h (bench scale)
- Experiments were tested in continuous lab (20 - 60 mL) and bench scale (400 mL) reactors.
  - Tested 3 hydrocracking catalysts in lab scale
  - Product profile different across various HCK catalysts

Jet fraction composition amount relatively consistent while gasoline and diesel fractions vary across HCK catalysts



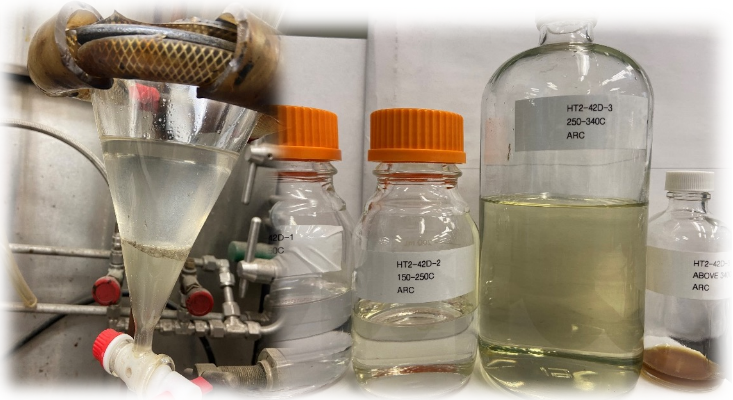
Lab scale

Bench scale

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

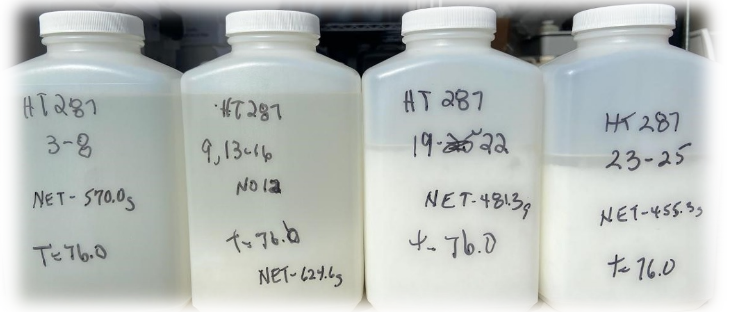
- Heteroatoms are negligible in the upgraded product.

		N [%]	C [%]	H [%]	S [%]	O(%)
HT2-42	Average	0.30	85.13	16.68	0.08	0.01
Lab Scale	St Dev	0.12	0.10	0.04	0.07	0.00
HT287	Average	0.20	85.22	17.21	0.04	0.04
Bench Scale	St Dev	0.07	0.23	0.19	0.03	0.00



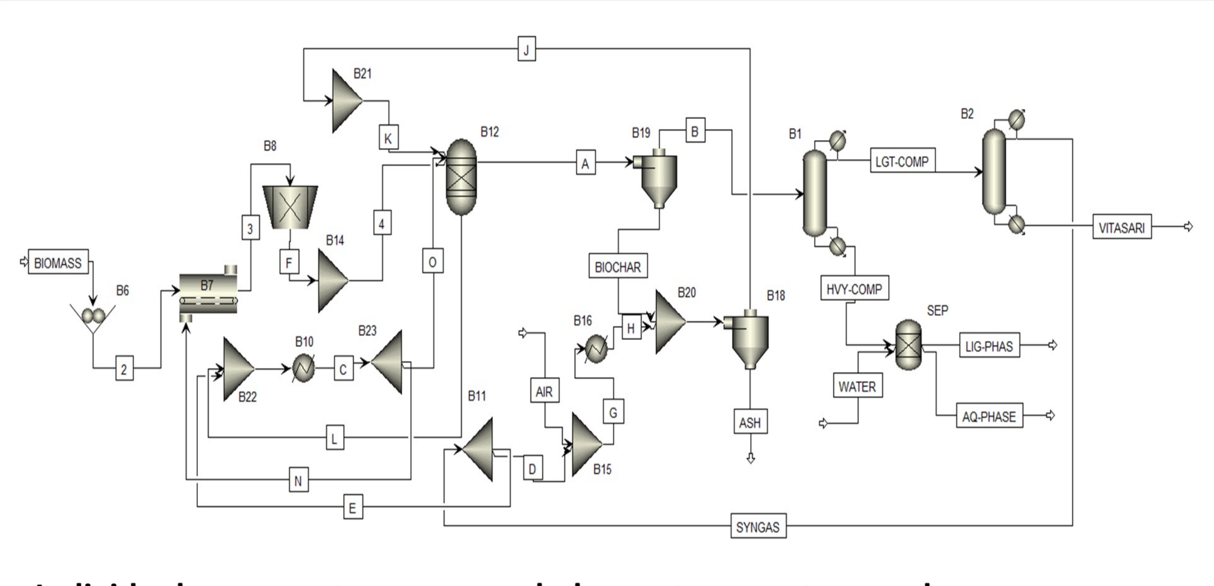
- Distillation cut could be better improved.

	Distillation Cut	Cloud Point, °C	Pour Point, °C
Bench Scale, HT2-27 composite	Jet (150C - 260C)	-31.5	-36
Lab Scale, HT287-D2	Jet (150C - 250C)	-35.4	-57



Study 5.1. Mass and energy balances of all the HEFA/HDCJ design cases

Simulation of Pyrolysis process in ASPEN Plus



Individual process streams mass balance, temperature and pressure

#	Stream name	m (kg/kg dry biomass)	T(°C)	P (bar)
1	Biomass	1.2	25	1.01
2	Chopped biomass	1.2	25	1.01
3	Dry, chopped biomass	1	90	1.01
4	Dry, grinded biomass	1	90	1.01
5	Biochar	0.15	480	1.01
6	Light compounds	0.40	105	1.01
7	Heavy compounds	0.45	N/A	N/A
8	Water	0.22	20	1
9	Aqueous phase	0.43	25	1.01
10	Lignin-rich phase	0.24	25	1.01
11	Syngas	0.21	38	1.01
12	Aqueous phase rich in C1-C4 compounds	0.19	N/A	N/A

- Preliminary ASPEN model simulating the Pyrolysis process of Biomass conversion to pyrolysis oil.
- Pilot scale data of the individual streams has been inferred from the dissertation “CONTRIBUTIONS TO THE DEVELOPMENT OF PYROLYSIS OIL BIOREFINERIES”.
- Scale up of the process to be done once the pilot scale simulation is revised with component level compositions.
- Integration of the Pyrolysis model with the HTL process to be done upon the completion of the scale up process

Task 5.3. Supply Chain Analysis

Harmonized Techno-Economic Analysis

Technology	Status	
HTL	🟠	In Construction
Pyrolysis	🟡	Harmonization
HEFA	🟢	Harmonized

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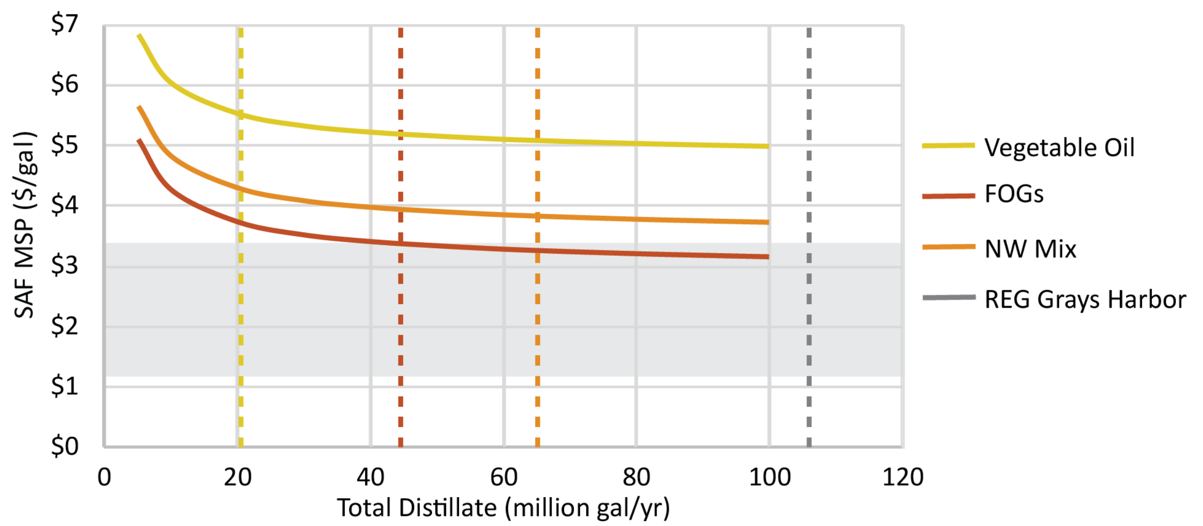
	A	B	C	D	E	F
1	**DRAFT - DO NOT DISTRIBUTE**					
2	Revised	1/15/2021				
3	Author	Kristin Brandt, Abid Tanzil				
4	Process	HEFA				
5	Feedstock	vegetable oil				
6	Plant maturity	nth				
7						
8	Annual revenue					
9	Revenue Generating Product	Annual Production	Units	MSP	Units	Total annual revenue, MM$
10	SAF	609	MM liter/year	$1.05	$/liter	$640.0
11	Diesel	244	MM liter/year	$1.08	$/liter	$262.9
12	Naphtha	88	MM liter/year	$0.91	$/liter	$79.8
13	Propane	180	MM liter/year	$0.38	$/liter	$68.3
14	Output Incentives					$0.0
15	Total Revenue					$1,051.0
16						
17	Item	Value			Total delivered equipment co	MM$
18	Required feedstock (thousand t/year)	1000			Hydroprocessing	$32.1
19	Price of lipids ($/t)	$810			Isomerization/cracking	$3.3
20	Operating hours (hrs/yr)	7884			Separation	$22.0
21	Analysis year	2017			Total capital investment	**$494.9**
22	Plant lifetime (year)	20				
23	Assumed annual Inflation	2.0%			Operational expenditure	MM $/year
24	Equity Percent of Total Investment	30%			Feedstock cost	$810.0
25	**Target Nominal Financial Discount**	**12.2%**	Match by clicking "Run		Other variable OPEX	$96.3
26	**Actual Nominal Financial Discount Rat**	**12.2%**	Model" button on Input		Fixed OPEX	$45.9
27	Real Discount Rate	10%			Total	**$952.2**
28						

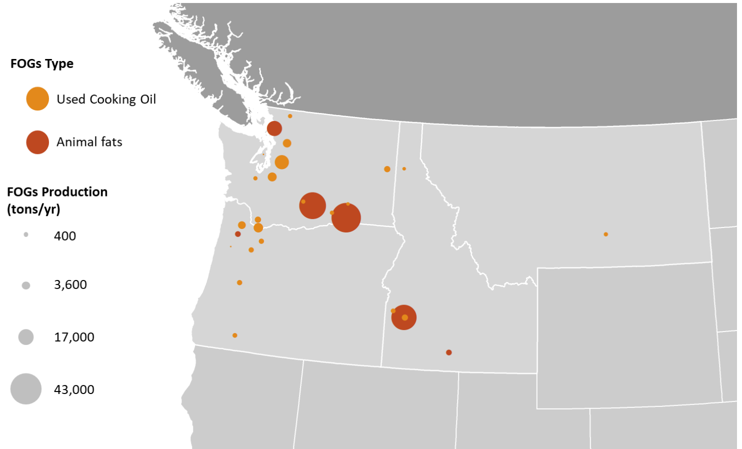
README | Input | Incentives | **Output** | CBA | CAPEX | OPEX | TDEC | FuelRelationships | References | Cost indices



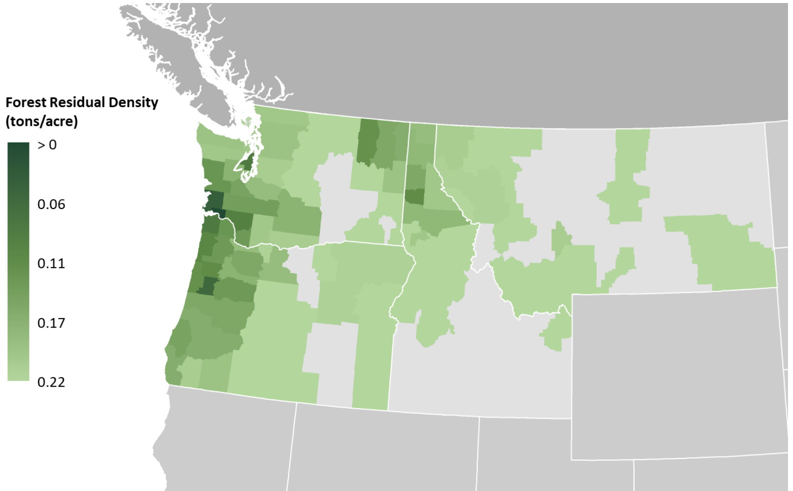
Importance: *We have developed harmonized techno-economic analyses for the standalone pyrolysis and HEFA technologies. We are currently developing a harmonized TEA for the HTL technology. We made an effort to use standardized financial and economy assumptions. These Harmonized TEA are available for the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

Task 5.3. Supply Chain Analysis

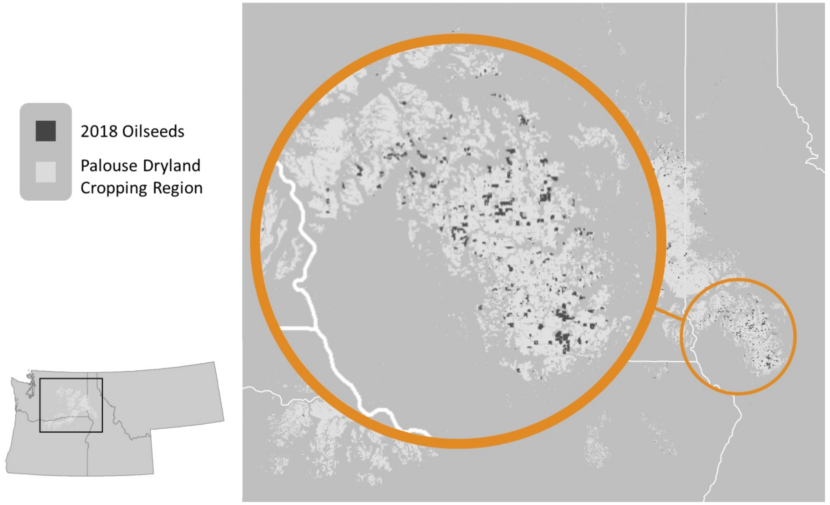
Northwest FOGs



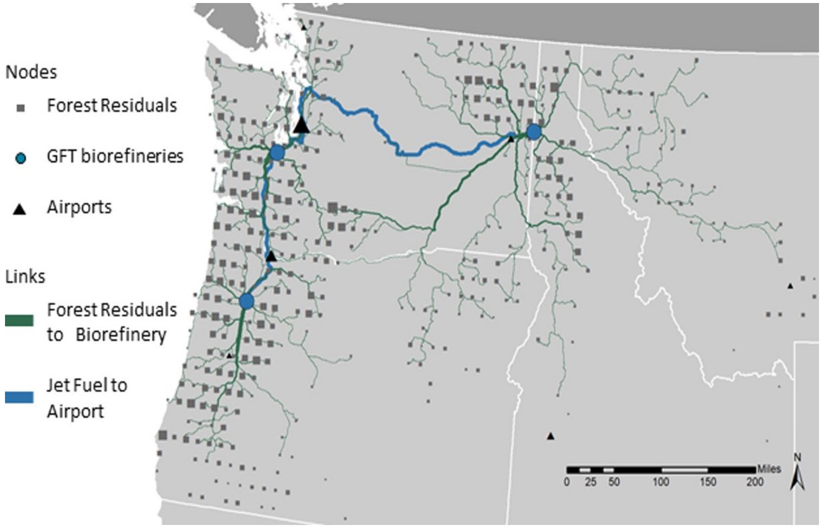
Northwest Forest Residuals



Northwest Oilseeds



Northwest Forest Residuals Supply chain



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. Co-processing 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 right now is to operate our 450 mL hydrotreatment reactor with reduced coke formation. This will reduce the shutdown time and will allow our team to increase the jet fuel produced for this project.
- **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. Larger quantities will be produced at the 450 mL hydrotreatment reactor. We will not be able to reach the 100 gallons of jet fuel but will produce as much SAF as funds allow. The fuel properties of the resulting fuels will be thoroughly characterized. The number of combustion tests will depend on the amount of jet fuel cut our team is able to produce. 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 and other heavy 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, batch and continuous hydrotreatment tasks. We are currently producing larger quantities of SAF at the 450 mL PNNL hydrotreatment unit.
- **Future Work:** Continuous hydrotreatment 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: $ 981,238* *PNNL: $ 884,607* *Total: $ 1,865,845*	*WSU: $ 1,453,637* *PNNL:$ 1,308,847* *Total: $ 2,762,484*
Project Cost Share	*WSU: $ 643,375*	*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

*Only fill out if applicable.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

Mechanisms of Pyrolytic Lignin Formation:

1 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

2 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

3 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

4 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, *Energy and Fuel*, **2020,** 34, 11, 14249-14263

Bio-oil Characterization:

5 Pinheiro-Pires AP, Garcia-Perez M, Olarte M, Denson M, Terrell E, Han Y: Comparison of the Chemical Composition of Liquids from the Pyrolysis and Hydrothermal Liquefaction of Lignocellulosic Materials, Paper Submitted to *Energy & Fuels*, **2022**

6 Manrique R, Terrell E, Kostetskyy P, Chejne F, Olarte M, Broadbelt L, Garcia-Perez M: Elucidating Biomass-Derived Pyrolytic Lignin Structures from Demethylation Reactions Through Density Functional Theory Calculations. Paper Accepted to *Energy & Fuels*, **2023**

Bio-oil Refinery strategies:

7 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

8 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:

9 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

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

11 Pinheiro-Pires AP, Olarte M, Garcia-Perez M, Han Y: Co-hydrotreatment of Yellow Greases and Pyrolysis Oil Water Insoluble Fraction: Part I: Experimental Design to Increase Kerosine Yield and Reduce Coke Formation. *Energy & Fuels*, **2023, 37**, 3, 2100-2114

TEA:

12 Pinheiro Pires AP, Martinez-Valencia LM, Tanzil AH, Garcia-Perez M, Garcia-Ojeda JC, Bertok B, Heckl I, Argoti A, Friedler F: Exploring new Pyrolysis Oil Based Biorefineries using p-graph. *Energy and Fuels*, **2021**, 35, 13159-13169

Responses to Previous Reviewers' Comments

Question 1: How much pyroil would saturate the market?

Answer 1: Our aim is to process yellow greases with 20-30 wt. % of pyrolysis oil fractions. Our study opens the possibility of processing between 175 and 200 million gallons of pyrolysis oil fractions per year.

Question 2: Availability of pyrolysis oil is big question (BTG in Netherlands and Ensyn unresponsive)

Answer 2: The main hurdle to catalyze pyrolysis oil production is the lack of refining technology. Although today only two companies produce pyrolysis oil, known-how for bio-oil production is very well known. With appropriate refining facilities the production of pyrolysis oil can grow exponentially.

Question 3: Why not to use TEA/LCA tools to decide where experimental need to be at?

Answer 3: We have developed simplified TEA/LCA to guide our experimental work. At this moment our main challenge is associated with the mitigation of coke formation to increase the number of hours we can operate continuously. Product yield is the most critical factor controlling fuel costs. In our processing conditions most of the oxygen is removed in the form of water. Some C is lost in the form of gases. We need to reduce gas formation or convert gaseous product into hydrogen.

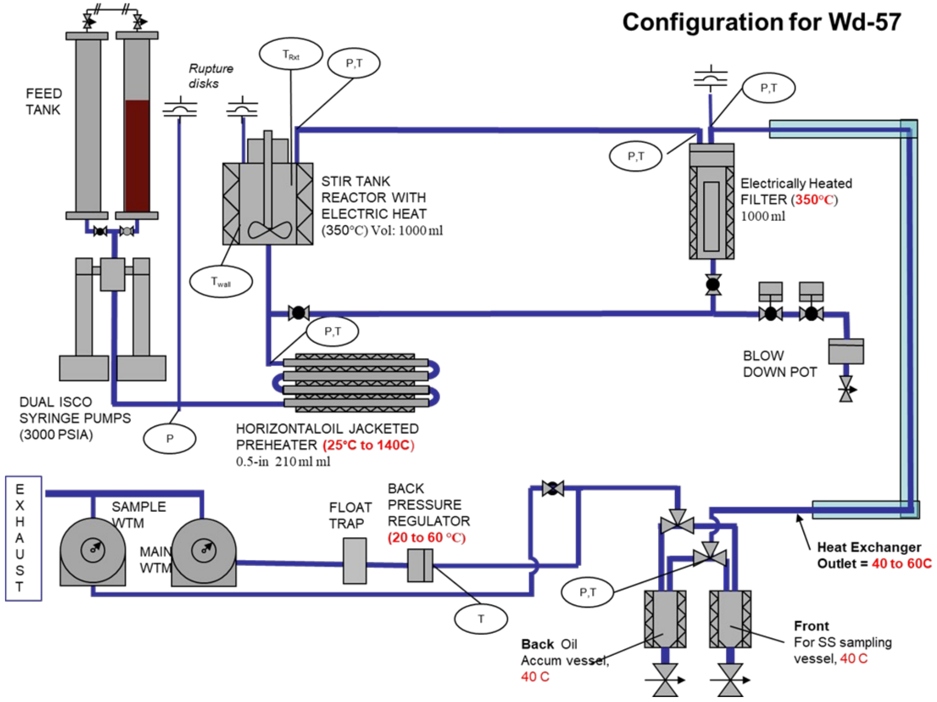
Key Model Assumptions

- **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

Tanzil AH, Brandt K, Wolcott M, Zhang X, Garcia-Perez M: Strategic Assessment of Sustainable aviation fuel production technologies: Yield improvement and cost reduction opportinites. Biomass and Bioenergy, 145, 2021, 105942

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)



- 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

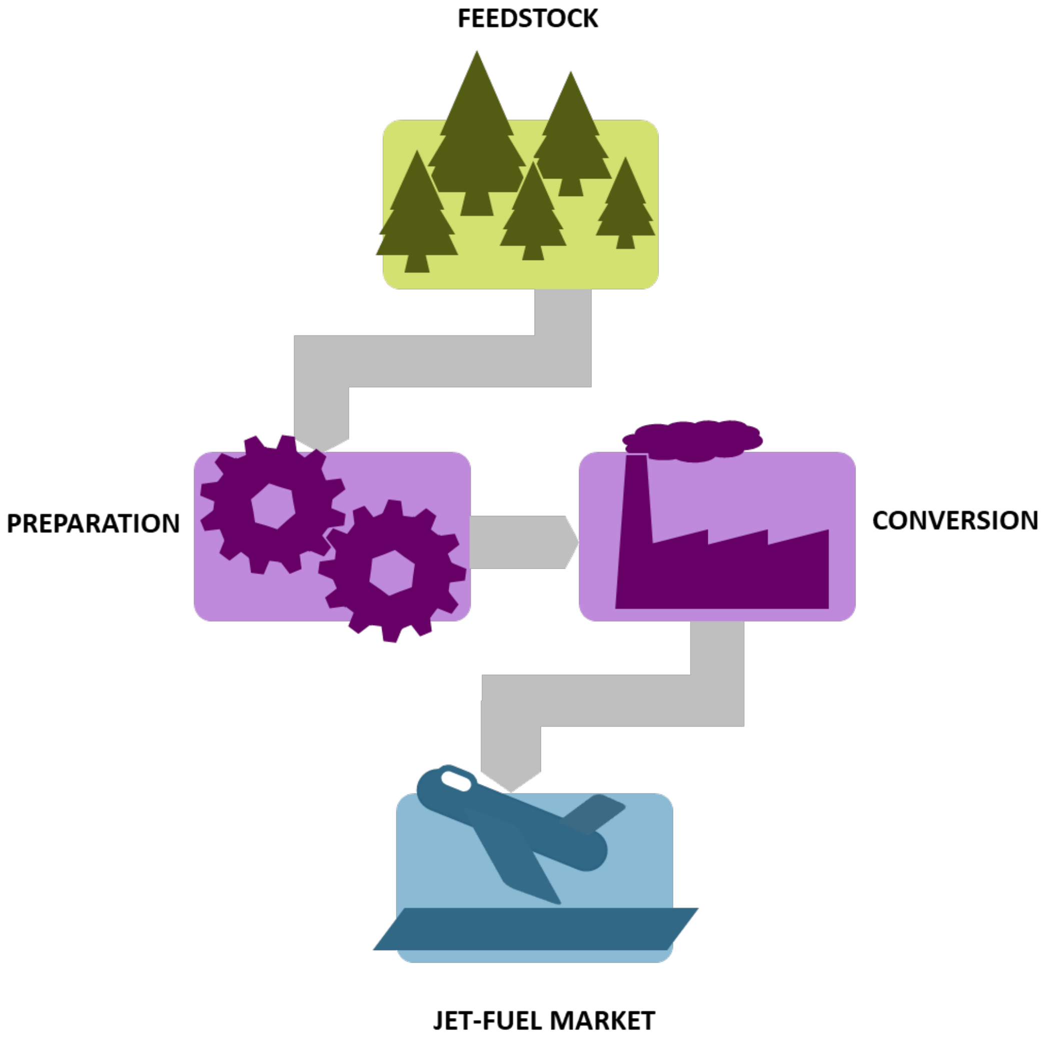
Parameter	Unit	Value
Rxt Configuration		CSTR
HOS	hour	12
Reactor Temperature	C	346
Pressure	psig	2760
Vol at Temp	mL	1000
Feed Rate	mL/h	2006
LHSV	L/L/h	2.0

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*

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.*