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

October 2025

Manuel Garcia-Perez
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Michael P. Wolcott
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U.S. DEPARTMENT of ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Final Technical Report (FTR)

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2. Disclaimer:

3. Executive Summary:

The hydrotreatment of bio-oil derived from the pyrolysis and biocrude from hydrothermal liquefaction of lignocellulosic materials to produce hydrocarbons faces significant technological challenges, mainly due to the high reactivity and poor thermal stability of bio-oil, resulting in the formation of large quantities of coke. This problem has been addressed by existing PNNL patents with a two-step hydrotreatment technology in which the bio-oil is first stabilized with a noble hydrogenation metal (often Pt or Ru). Then, in the second step, the bio-oil is deoxygenated with a Ni-Mo or Co-Mo sulfide catalyst. The main problem with this approach is that the Pt/Ru catalysts deactivate easily in the presence of S or other impurities, which are commonly present in pyrolysis oils. In this project, we explored technological solutions to mitigate coke formation, avoiding the use of Pt/Ru catalysts. Our strategy is based on three actions: (1) Bio-oil stabilization in the presence of alcohols. In this project, we studied the stabilization with butanol. (2) the use of a cosolvent to solubilize the bio-oil. Because coke formation reactions are second-order reactions a reduction in the concentration of reactive bio-oil molecules. In this case, we used yellow greases as a co-solvent. (3) Separation of bio-oil reactive fractions. In this project, we studied the removal of water-soluble fractions. Our batch co-hydrotreatment studies confirmed that the addition of butanol and methanol and the blend with lipids effectively contributed to mitigating coke formation (reducing coke yield to about 1 wt.% %). The removal of sugars did not have a noticeable effect on the overall coke yield, suggesting that coke precursors are present in all bio-oil fractions. Our analytical work suggests that they may be concentrated in the water-insoluble/CH_2Cl_2 insoluble fractions of pyrolysis oils. Although the technological strategies tested resulted in significant coke

reductions, the levels achieved were not sufficiently low to ensure a reliable operation in continuous, fixed-bed trickle-bed reactors. Long runs of more than 100 hours (maximum: 255 h) of co-processing time on stream were achieved in a continuous 40 mL reactor. When the same test was conducted in a larger 400 mL reactor, pressure drop increases associated with coke formation were observed. This increase in coke formation could be due to larger temperature gradients in the bed. Hydrodeoxygenation tests in moving bed reactors and using more active hydrogenation catalysts (for example Ni) could lead to more reliable operations. Unfortunately, our team did not have access to such experimental setups. The technoeconomic analysis suggests that although alcohol use is an effective means to reduce coke formation, the use of alcohol increases production cost. Thus, its use needs to be minimized. A delicate balance needs to be found between the use of technological solutions that allow the reliable operation of the system (stabilization with Ni catalysts, use of small quantities of solvents, processing in moving bed reactors) with a tolerable level of coke formation for the hydrodeoxygenation reactor used and that result in minimum production costs.

4. Background:

Introduction: Several pathways for the production of alternative jet fuel (AJF)have been reported (IATA 2011, Hileman et al. 2013, David et al. 2015, Klein-Marcuschamer et al. 2013, Pearlson et al. 2013, Swanson et al. 2010, de Jong et al. 2015). Five of these pathways (Hileman et al. 2013) have received ASTM certification for up to 50 vol. % blends with commercial petroleum-based jet fuels (Zschocke et al. 2012). One of the major challenges for the wide adoption of AJF is its non-competitive price ($3-10 per gallon) compared to jet fuel derived from petroleum (close to $2 per gallon). Thus, it is *critical to develop technology/strategies to reduce fuel production costs*. Integration with existing industrial infrastructure and commercialization of co-products are the two cost-reduction strategies that will be studied in this project.

Technology challenges and opportunities:

- **HEFA is the best current option for jet fuel production.**
- **HTL and fast pyrolysis are the most promising short term pathways for jet fuel production.**
- **HTL and fast pyrolysis companies cannot move towards commercialization due to lack of bio-crude refineries.**

De Jong et al. (2017) compared the short-term techno-economic feasibility of six of the conversion pathways for alternative jet fuel production. His analysis concluded that *hydroprocessed esters and fatty acids (HEFA) is the best current option for jet fuel production*. HEFA is the most developed alternative jet fuel technology with a Fuel Readiness Level (FRL) of 9 (Mawhood et al. 2016). The economic analysis conducted by Pearlson et al. (2013) estimated HEFA minimum fuel selling prices (MFSP) between $ 3.8 and $ 4.4 per gasoline gallon equivalent (gge). The other technologies being developed have lower readiness levels. These includes Fischer-Tropsch (FRL: 7-8), direct sugar to hydrocarbons (Amyris) (FRL: 5-7), Alcohol to jet (FRL: 4-6), Hydrotreated depolymerized cellulosic jet (HDCJ) (FRL: 6) and aqueous phase reforming (FRL: 6) (Mawhood et al. 2016). De Jong et al.. (2015)

also concluded that *in the short term, the hydrotreated depolymerized cellulosic jet (obtained from hydrothermal liquefaction (HTL) and pyrolysis) is the most promising pathway for jet fuel production*. However, companies commercializing technologies for biomass pyrolysis and HTL cannot move to commercialization due to the lack of technologies for bio-crude refining. In this project we studied the co-hydrotreatment of pyrolysis oil and hydrothermal liquefaction biocrude and their fractions from lignocellulosic materials. The hydrotreatment operational conditions studied are similar to those used in HEFA units. The strategies studied are shown in Figure 1. Basically we studied the co-hydrotreatment of the lignin rich fraction and the whole pyrolysis oils with lipids.

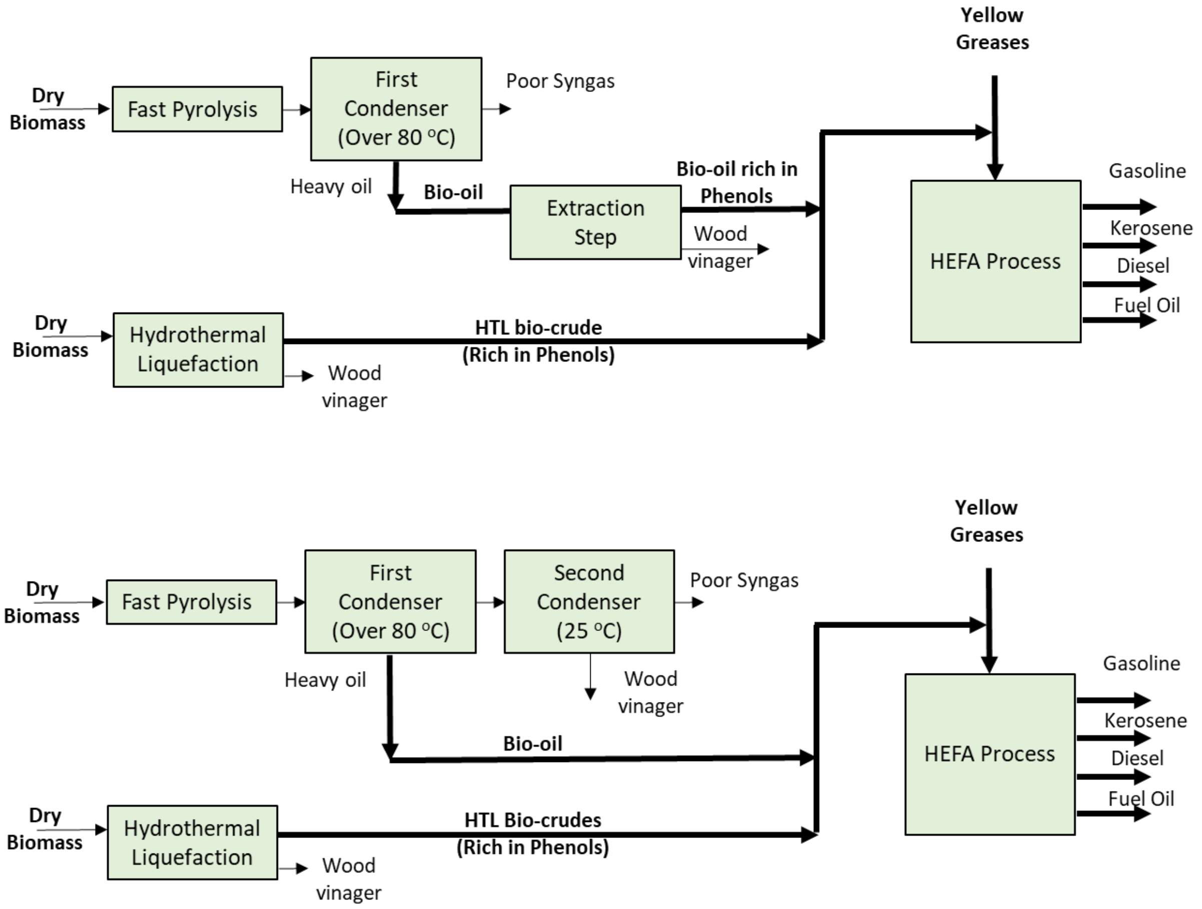


Figure 1. Scheme of the hybrid HEFA/HDCJ system proposed

State of the Art:

Biomass pyrolysis reactors: Fast pyrolysis has been studied for more than 30 years. Pyrolysis can be conducted using a range of temperatures (typically between 350 and 600 °C) and residence times (less than 2 s in the case of fast pyrolysis) to optimize the desired product (Bridgwater et al. 2001, Liaw et al. 2012, 2013, Westerhof et al. 2012, Mourant et al. 2011, Shen et al. 2009, Garcia-Perez et al. 2002, 2008).). There are many types of pyrolysis reactor configurations (bubbling fluidized bed, ablative, auger, circulating bed, etc.) each with advantages and disadvantages (Garcia-Nunez et al. 2017). In this study, we used a bio-oil produced by BTG in an industrial scale ablative reactor. Fast pyrolysis of woody biomass yields between 55 and 70 wt. % crude bio-oil, between 10 and 20 wt. % char and also between 10 and 20 wt.% gases (Garcia-Nunez et al. 2017). This technology was preferred to process materials with less than 20 wt. % moisture.

Hydrothermal liquefaction: In the 1970's, a biomass HTL process was developed at the Pittsburg Energy Research Center (PERC). A 18 kg/h pilot plant was tested in Albany, Oregon, between 1970 and 1980 (Zhu et al. 2014). Between 1970's and 2011, other two more HTL pilot plants were built and operated by the Lawrence Berkeley Laboratory (LBL) (10 kg/h) and Shell Laboratory (10 kg/h) (Zhu et al.. 2014). Hydrothermal liquefaction converts biomass into bio-crudes and an aqueous phase by processing in a hot (250-374 ^{o}C), pressurized (4-22 MPa) water environment (Gollakota and Savage 2018, Elliott et al. 2015). Compressed hot water (subcritical water) has enhanced solvent properties that facilitate the formation of liquid oil products from biomass. Biomass was dissolved and liquefied in this process, and the major products are biocrude, water with dissolved organics, gas, and solids (primarily minerals). HTL reactions involve depolymerization and condensation coupled with dehydration, decarbonylation, and decarboxylation. Between 20 and 50 wt. % of the original biomass is typically collected as organics soluble in the aqueous phase (Cao et al. 2017). With woody feedstocks, the crudes from hydrothermal liquefaction are typically composed of lignin-derived phenolic compounds which represent between 17 and 40 wt. % (Cao et al. 2017). Gases account for between 5 and 10 wt. % of the original organic compounds present in the feedstock (Cao et al. 2017). The yield of hydro-char is between 5 and 10 wt. % (Nie et al. 2018). For lignocellulosic feedstocks, buffering agents such as sodium carbonate are normally employed to reduce acid-catalyzed degradation reactions that lead to excess polymer/char formation. As part of the National Advanced Biofuels Consortium (NABC), the HTL team, led by PNNL studied the effect of process conditions (temperatures and residence time) on the processing of loblolly pine and corn stover. A very important variable studied was the recycling of aqueous phase products to increase bio-crude yield and reduce aqueous phase generation (Nie et al. 2018). These results confirmed that the water recycling led to improved biocrude quality. Carbon yields improved, and the bio-crude produced was more stable. Bio-oil yield used for carbon balance was 32 wt. %. PNNL is one of the leaders in hydrothermal liquefaction research with many publications in this area (Marrone et al.. 2018, Edmundson et al. 2017, Elliott et al. 2017, Snowden-Swan et al. 2017).

Bio-oil Chemistry: Crude bio-oils from fast pyrolysis are multi-phase, dark-brown liquids with an elemental composition that is very similar to those of biomass (Garcia-Perez et al. 2006). Excellent reviews on bio-oil characterization and the

Differences in composition between HTL, slow pyrolysis and fast pyrolysis oils:

- **HTL and slow pyrolysis decanted oils are rich in phenolic compounds derived from lignin.**
- **In addition to phenols, fast pyrolysis oils also contain highly oxygenated sugars and fragmentation products from cellulose and hemicellulose which can be easily removed by water addition.**

influence of feedstock and pyrolysis technologies on bio-oil chemical composition are also available (Czernik and Bridgwater 2004, Bridgwater and Peacocke 1994, Meier and Faix 1999, Evans and Milne 1987). Because fast pyrolysis oil is formed by hundreds of compounds it is desirable to express their chemical composition in term of a few chemical groups or families (Hallet and Clark 2006, Garcia-Perez et al. 2007). The idea of describing bio-oil composition in terms of chemical families was first proposed by Hallet and Clark (Halle and Clark 2006). They described bio-oil as a mixture of four fractions (organic acids, aldehydes/ketones, water, and pyrolytic lignin). Other studies describing bio-oil in terms of chemical families have been published (Garcia-Perez et al. 2007, Stankovikj et al. 2017). Stankovikj et al. (2017) described bio-oil composition in seven main groups or families based on their chemical composition and origins. Water formed by dehydration reactions is the most abundant bio-oil molecule, making up between 15 and 30 wt. % (Stankovikj et al. 2016, Pecha et al. 2017). The *second major fraction* is C2-C4 molecules (mainly hydroxyacetaldehyde, acetol, and acetic acid) quantified by GC/MS (Czernik and Bridgwater 2004, Stankovikj et al. 2016, Bridgwater 1996). This fraction, formed from carbohydrate fragmentation reactions represent between 8 and 26 wt. % (Stankovikj et al. 2016). Mono-phenols with small quantities of furans forms the third major bio-oil fraction (between 2 and 7 wt.%). These molecules are also typically quantified by GC/MS and are formed from the depolymerization of lignin or its oligomeric products (Stankovikj et al. 2016, 2013). The *fourth fraction* is lignin-derived oligomers, also known as “pyrolytic lignins”, which are quantified by cold water precipitation (Scholze and Meier 2001). This fraction is collected in the form of a water-insoluble powder that typically accounts for between 7 and 24 wt. % (Stankovikj et al.. 2016) and is formed from lignin depolymerization. This fraction has been thoroughly characterized elsewhere (Scholze and Meier 2001 a,b, Bayerbach et al. 2006, 2009). The water-soluble fraction (fifth fraction) contains carbohydrates (mono and oligo anhydrosugars) and other poorly known oligomers (Garcia-Perez et al. 2007, Stankovikj et al. 2016). This fraction has carbohydrates derived from the depolymerization of cellulose and hemicellulose and is quantified by the sulfuric acid assay (Stankovikj er al 2016, Pecha et al. 2017). Levoglucosan, cellobiosan and cellotriosan are the main carbohydrates found in pyrolysis oils (Westerhof et al. 2016). This fraction typically accounts for between 12 and 17 wt. % (Stankovikj et al. 2016). Studies by ICR-MS and UV-Fluorescence of the water-soluble fractions and the whole pyrolysis oil (Stankovikj et al. 2017, 2016) point to the existence of another two oligomeric fractions soluble in water. ICR-MS studies clearly show the presence of highly dehydrated pyrolytic sugars, but we lack standards and analytical strategies to separate, quantify and characterize this fraction (Stankovikj et al. 2016). Bio-crude derived from lignocellulosic biomass through HTL and decanted oil obtained after water addition to fast pyrolysis oils, are mostly formed by mono-phenols and lignin oligomers. In this project we made major contributions to the understanding of the chemistry of bio-oil oligomeric fractions.

Bio-crude hydrotreatment: One of the most promising areas to fully utilize bio-oils is the production of drop-in fuels via hydrotreatment. In the now classic review, Douglas Elliott (2007) clearly indicated that compared with hydrotreating fast pyrolysis oils, the hydrotreatment of slow pyrolysis oil and HTL biocrude is relatively easy. The two-stage method was patented by PNNL for the processing of fast pyrolysis oils (Elliott 2007, Elliott and Baker 1989). In the first stage, called stabilization, aldehyde and ketones are converted to alcohols (stabilization). Typical conditions for stabilization use a cobalt-molybdenum catalyst, temperatures between 250 and 350 °C, a pressure of 69-98 atm. and a hydrogen rich environment (about 95%). During the stabilization parallel reactions take place including: decarboxylation (limited CO_2 production), re-polymerization (water production), and hydrotreating. For the hydrotreatment of bio-oils, noble metal catalysts (Ruthenium (Ru)/Carbon (C), Ru/Titanium Oxide (TiO_2), Ru/Aluminium oxide (Al_2O_3), Platinum (Pt)/C, and Palladium (Pd)/C) have also been studied along with the sulfided NiMo /Al_2O_3 and CoMo/ Al_2O_3 catalysis (Wildschut et al. 2009, Elliott et al.. 2015). In the second step, most of the deoxygenation and cracking occur with a nickel-molybdenum catalyst and temperature ranging from 400 to 500 °C, and pressure from 98 to 138 atm and residence time between 2 and 20 hours. The products of the hydro-deoxygenation step are distilled and commercialized as heavy fuel, diesel, jet fuel, and gasoline. The pyrolytic bio-oil has been mixed up to 10-20 wt. % with heavy petroleum fractions (i.e. gas oil, vacuum gas oil, (VGO)) and then co-processed via a catalytic cracking process in lab-scale reactors using fluid catalytic cracking (FCC) and zeolite-type catalysts (Fogassy et al. 2011), and also in a demonstration FCC refinery unit (De Rezende Pinho et al. 2015). In general, the amounts of valuable products obtained, such as gasoline, naphtha and light cycle-oil (LCO), do not differ much from those achieved when only a petroleum fraction is processed, and the same could be stressed for other products, such as light gases and olefins. Nevertheless, the production of aromatics (including phenolic compounds) is strongly increased (De Rezende Pinho et al. 2015) as well as the amount of char and coke formed on the catalyst surface, leading to the deactivation of the catalyst (Fogassy et al. 2011, 2012). Studies of catalytic cracking of hydrocarbon fractions with the addition of model oxygenated compounds, representative of the bio-oil composition, revealed that their presence leads to the rapid formation of carbonaceous deposits (via oxygenated compounds deoxygenation) onto the zeolitic acid active sites of the FCC catalyst (Fogassy et al. 2011). The formed bio-carbon (and/or bio-char) is mainly responsible for blocking the pores in the zeolitic structures, thus deactivating the catalyst and making its regeneration and re-use difficult.

HEFA hydrotreatment operational conditions are similar to those used for the hydro-deoxygenation of bio-crudes from HTL and slow pyrolysis (T: 300-450 °C, P: 19-92 atm, Catalysts: NiMo, Pd, ZSM-5, Res. time 2-5 h)

HEFA: The hydro-processed esters and fatty acids (HEFA) process is a commercially deployed technology that converts vegetable oils and animal fats from triglycerides into hydrocarbons suitable for use in diesel and jet fuels (Pearlson et al. 2013). Since 2008, several airlines have been successfully using this fuel (Seber et al. 2014). HEFA fuels are produced around the world using technologies provided by Neste Oil, UOP, ENI and Galp Energia. In 2007, Tyson and Syntroleum formed Dynamic Fuels in Louisiana (this plant was acquired in 2014 by Renewable Energy Group). Altair Fuels is another example of a HEFA technology with UOP technology (Pearlson et al. 2013, Seber et al. 2014). This plant was recently acquired by World Energy for 72 million dollars. Seber et al. (2014) calculated the lifecycle greenhouse gas emissions and production costs of producing HEFA jet and diesel fuels from tallow, and yellow greases. Tallow and used cooking oil-derived yellow greases account for 68% of the total triglycerides available. Typically, with this technology, between 1.5 and 3.8 kg of H_2 is consumed per 100 kg of oil processed to yield 4-5 kg of propane, 1-8 kg of naphtha, and 75-85 kg of diesel (Rispoli et al. 2015). CO_2 and H_2O are also produced. The authors found GHG emission reductions compared with petroleum between 75 and 85% and a fuel production cost between $3.57 and $ 3.99 per gallon (Seber et al. 2014). The authors concluded that a price support of at least $ 0.38 per gallon will be necessary to make this full-on average price competitive. The co-processing of yellow greases with bio-crudes rich in phenols could be an effective way to reduce HEFA production cost. Both PNNL and WSU have publications in the hydrotreatment of vegetable oil (Botella et al. 2018, Tran et al. 2017, Zhu et al. 2013).

Jet fuel Characterization: Jet fuel is a generic name for aviation fuels used in gas turbine engine powered aircraft, composed of a mixture of C_8-C_{16} n and iso paraffins (35-45 vol. %), cycloparaffins (30-35 vol. %), aromatics (20-25 vol. %) and olefins (less than 5 vol. %). The paraffins are the most stable components and do not readily react with materials in which they come into contact with such as elastomers, paints, and various metals. Generally, they are clean-burning compared to other hydrocarbons and have a high heat release per unit weight. The aromatics are needed to swell rubber seals. Several papers have been published on properties of alternative jet fuels (Starck et al. 2016, Pires et al. 2018, Corporan 2011, Zhang 2016, Hui et al. 2012). Most of the ASTM-approved jet fuels production technologies (HEFA, FT, direct sugars to hydrocarbons, alcohol to jet (ATJ)), except FT-SPK, only produce the paraffinic fraction of jet fuel (Pires et al. 2018). The hydrotreatment of bio-oils rich in phenols derived from pyrolysis and hydrothermal liquefaction of lignocellulosic materials mostly results in the production of aromatics. Thus, co-hydrotreatment of 20 wt. % of bio-oils rich in phenols with yellow greases in HEFA units should result in a bio-oil with composition within ASTM specifications.

Techno-economic analysis: Fast pyrolysis followed by the two-step hydrotreatment process could result in a transportation fuels minimum selling price between $ 1.50 and 4.70 per gallon gasoline equivalent (Wright et al. 2010, Jones et al. 2013). A techno-economic analysis of a 2,000 dry metric ton per day HTL-Bio-crude refinery (Zhu et al. 2014) estimated a minimum selling price (MSP) of $ 4.44/gallon for the state-of-the-art case and $ 2.52 / gallon for the goal case. The minimum selling price in the case of hydrothermal liquefaction was also between $2.20 and 4.50 per gallon (Zhu et al. 2014, Nie et al. 2018, Pedersen et al. 2018). Snowden-Swan et al. (2016) conducted a similar techno-economic analysis for the hydrothermal liquefaction and upgrading of municipal wastewater treatment plant sludge. The authors (Snowden-Swan et al. 2016) estimated a minimum selling price of $ 4.90 per gallon of gasoline equivalent. Cost reductions could be achieved if co-products are developed from the organic molecules soluble in the aqueous phases. To further mature HTL and pyrolysis, development efforts should focus on process integration along the entire production chain encompassing pre-treatment, processing, hydrotreatment, distillation, and utilization of process water resulting from transportation fuels (Biller et al. 2017). PNNL is without any doubt a leader in techno-economic analyses for pyrolysis and hydrothermal liquefaction (Zhu et al. 2014, 2013).

Cost reduction challenges: Although several fast pyrolysis plants were built and are currently operated around the world, the lack of bio-oil refining capabilities is the major hurdle for the deployment of this technology (Stankovikj et al. 2016). The high concentration of oxygen in bio-oil – up to 40 wt. % (Karatzos et al. 2014) – associated with the reactivity of these compounds, affects the thermal stability of these oils during storage, handling, and upgrading (Zacher et al. 2014). Due to the presence of water and the large number of molecules covering a wide range of molecular weights and functionalities, bio-oil refining will require more separation steps than conventional petroleum refining. Consequently, bio-oil refining costs are likely to be higher than for competing sources of organics (sugars and petroleum) (Lange 2016). To ensure economic competitiveness, bio-oil price need to be a fraction of those of sugar (typically: $ 300-400 t^{-1}) and petroleum (typically: $ 206-687 t^{-1}). As a first approximation, we will target a bio-crude minimum selling price below $ 150 t^{-1}.

Significant cost reductions towards achieving BETO-targeted transportation fuel costs are possible if the aqueous phase is separated and commercialized as a wood vinegar, the oil rich in phenol is co-processed in HEFA units and if the HEFA unit is built in a repurposed refinery.

The main bio-oil refinery concept under study today is based on the two-step hydrotreatment bio-oil refinery concept initially proposed by PNNL (de Jong et al. 2015, Zacher et al. 2014, Elliott et al. 2012). With this technology 33 wt. % of this oil can be converted into hydrocarbons (Jones et al. 2013, 2009). The published techno-economic analyses of this technology estimated minimum selling prices of resulting transportation fuels between $ 694 and 1,455/t ($ 2.10 and 4.40 per gallon) (Wright et al. 2010, Jones et al. 2013, Jones 2009, Arbogast et al. 2013). In order to explore cost reduction alternatives for the two-step bio-oil refinery concept, we used the fast calculation strategy recommended by Lange et al. (2016). In the chemical industry, typical conversion costs are between $ 100-300 per ton of feed (Lange et al. 2016). Conversion costs depend on complexity and scale and correlate well with the energy transfer duty applied and the number of separation segments (Lange et al. 2016). A simple calculation supposing an optimistic bio-oil cost of $150 t^{-1}, an optimistic conversion cost of $ 200 tfeed^{-1} (Lang et al. 2016), and a fuel product yield of 33 wt. %, suggests that a refinery with these characteristics will only be only viable if the resulting products can be commercialized at a minimum selling price of $ 1,060/t (within the range of the costs reported in the literature $694-1,455/t) (Wright er al 2010, Jones er al 2013, 2009, Arbogast et al.. 2013). This cost estimation suggests that the two-step bio-refinery concept proposed will result in products competitive with chemicals and solvents ($1,000 and 2,000/t) but will have problems competing with transportation fuels (gasoline market price: $700-800/t) (Lange et al. 2016). We conducted four bio-oil refining techno-economic studies to understand the landscape for improving the existing technologies. The properties of the jet fuel cut that will result from the co-processing of yellow greases, PRPO, and PRHTL will likely depend on each feedstock weight fraction contribution. In this project we were initially planning to produce and test 100 gal (Tier 1 and 2 test of ASTM D4054). The scope of the work was changed due to the technical issues faced in operating the 400 mL hydrotreatment reactor. Our project focused on identifying strategies to reliably operate that unit. In one of our recent studies (Pires et al. 2018), we measured the high heating value (HHV) of three commercial jet fuels and obtained a HHV between 44.5 and 46.1 MJ/kg. The jet fuels from HEFA and HDCJ studied have HHV 47.2 and 44.3 MJ/kg, respectively. The jet fuel we plan to produce in this project is likely to have a HHV comparable to that of commercial jet fuels. Based on our results with the HEFA and HDCJ jet fuels (Pires et al. 2018), we are very confident that our fuel will meet or exceed ASTM D4054 and D7566 requirements. The lean blowout, atmospheric cold start ignition, and altitude relight behavior of this fuel will be studied. This information is needed for jet fuel ASTM approval.

5. Project Objectives:

The main objective of this project was to identify suitable processing conditions and technological solutions to produce AJF by co-processing cooking oils and bio-crudes, avoiding the use of precious metal catalysts in the hydrogenation step. The performance of the phenolic-rich fraction was compared with the performance of the whole pyrolysis oil. This project effectively contributed to testing a hybridized HDCJ/HEFA process. This project identified suitable pilot plant processing conditions for the co-processing of lipids and bio-oils from pyrolysis and HTL. Our main hypothesis was that stabilizing the bio-oils with alcohols, blending the oils with lipids, and removing bio-oil fractions with a tendency to form coke will result in reduction in substantial coke formation reductions that will allow us to avoid the use of Pt/Ru catalysts for bio-oil stabilization. The following (7) tasks were conducted to test our central hypothesis:

Task 1: Collection of bio-crudes and yellow greases to be studied: This task aims to collect pyrolysis oils and yellow greases (used cooking oils) and to produce the HTL liquids for use in this project.

Task 2: Bio-crude chemical characterization: The main goal of this task was to characterize the chemical composition of all the bio-crudes studied in this project. In this project, we will study two pyrolysis oils (BTG and Pyrovac) and two hydrothermal liquefaction oils produced by Pacific Northwest National Laboratory (PNNL).

Task 3: Co-hydrotreatment studies: The task aims to study at bench scale the effect of co-hydrotreatment on product yield and catalyst coke formation. Tests were conducted at under batch and continuous conditions.

Task 4: Techno-economic, life cycle assessment and supply chain analysis: This task compared the technical-, economic-, and environmental performance of the HEFA/HDCJ proposed with the standalone pyrolysis-two-step hydrotreatment, HTL/hydrotreatment and HEFA, and to design and analyze a supply chain for the conditions of Washington State.

Task 5: Fuel properties of resulting fuels: The main goal of this task was to study Tier 1 fuel properties of all the fuel cuts obtained.

This project is innovative because it tested under batch and continuous conditions the co-processing of pyrolysis oils with lipids. The effect of bio-oil composition on catalyst coke formation tendency was studied for Ni-Mo and Co-Mo catalysts. The chemical composition and fuel properties of the resulting fuels were thoroughly tested. Techno-economic and supply chain analyses were conducted for the conditions of Washington State.

Innovation and Impacts

Can HEFA units become the nucleation seed for the deployment of new bio-refineries for jet fuel production?

- **All the jet fuel production technologies end up with a hydro-deoxygenation step similar to HEFA.**
- **Several companies are studying hybridized concepts with HEFA.**

HEFA is a commercially available feedstock. However, the quantities of yellow greases available for jet fuel production are limited. To grow, HEFA units need to diversify the feedstocks they can process (used tire oil, pyrolysis and HTL oil) (Han et al. 2017). The hybridization of HEFA with other jet fuel production technologies make sense because all the pathways approved or under study by ASTM require a hydrotreatment step operated at conditions (temperature, pressure, type of catalyst) similar to the one used by HEFA. The advantages of hybridizing alternative jet fuel technologies to take advantage of each other's strengths have been recognized by other researchers. For example, Emerging Fuels Technology (EFT) from Oklahoma is licensing a hybridized FT/HEFA technology, which also offers significant advantages compared with standalone concepts (http://emergingfuels.com/). Chevron, Phillips66 and BP studied the co-processing of HEFA feedstocks with petroleum hydrocarbons (http://www.caafi.org/information/pdf/CoProcessing_of_HEFA_Feedstocks_with_Petroleum_Hydrocarbons_for_Jet_Production_June192015.pdf). Several petroleum companies are co-processing lipids and pyrolysis oils in fluid catalytic crackers. However, before a HEFA operator starts to co-process other oils in their unit, it is critical to know the best hydrotreatment conditions to obtain a product with the desired quality. The impact of new oils on catalytic activity also needs to be known. Furthermore, the resulting fuel cuts need to be ASTM certified otherwise, they cannot be commercialized.

Companies commercializing technologies for biomass pyrolysis and HTL cannot move to commercialization due to the lack of technologies for bio-crude refining. The two step hydrotreatment concept patented by PNNL has some weaknesses: need to use expensive precious metal catalysts for the stabilization of pyrolysis oils, high hydrogen consumption (5.8 g of H_2/100 g of oil) (Jones er al 2013), the lack of high value products, coke formation and reactors plugging (Zacher et al. 2014). Bio-oil deoxygenation is fundamentally an emerging, poorly known, and very expensive unit operation (Lange 2016). In this step, the oxygen purchased as part of the bio-oil is converted into water with high hydrogen and energy consumption (Lange 2016). Although, in principle, we could reduce production cost by increasing the yield of products, there are fundamental technical challenges to increasing hydrocarbons yield. If a fully deoxygenated molecule is the main targeted product (let's suppose benzene), to achieve a 33 wt. % bio-oil conversion (C content: 43 wt. %), overall carbon conversion efficiencies need to be higher than 70%. Achieving higher efficiencies in a biorefinery concept with several unit operations is challenging (Lange 2016). The separation of products from lignin and products from cellulose and hemicellulose and their separate upgrading offers opportunities for cost reduction. The co-processing of yellow greases and pyrolysis and

HTL derived oils in HEFA units and the commercialization of the wood vinegar could result in significant cost reductions (from $ 4.42 per gallon to $ 1.94 per gallon).

6. Project Results and Discussion:

In this project, we procured purified bio-oils rich in phenols from fast pyrolysis and HTL of woody biomass. In order to reduce capital and operational costs, we co-processed these bio-crudes rich in phenols with non-edible vegetable oils under conditions comparable with those used in existing commercial HEFA units. The hybridized HEFA-HDCJ process proposed will result in reduced production costs (from $4.42 per gallon with the two-step hydrotreatment concept to $2.05 per gallon with the concept proposed) and a product with chemical composition similar to commercial jet fuels. Our project will specifically advance the state of the technology for the co-hydrotreatment of yellow greases and pyrolysis and HTL oils. Techno-economic analyses and Life cycle assessments of the hybrid technology proposed for transportation fuels production with co-products from the aqueous phase will be conducted to estimate jet fuel cut minimum selling price and its environmental footprint. We will evaluate the impact of co-products on the overall economic and social performance of the proposed hybrid bio-refinery. Our central hypothesis is that the commercialization of co-products from the water-soluble fraction and the co-hydrotreatment in the HEFA unit could reduce the breakeven price of transportation and jet fuels that are generated close to $2/gallon, and that the GHG will be 50% compared to the petroleum baseline. The resulting fuels will be characterized and the combustion behavior of the jet fuel studied.

Task 1: Collection of bio-crudes and yellow greases to be studied (PI Responsible: Dr. Manuel Garcia-Perez):

Study 2.1. Pyrolysis oil and yellow greases collection: BTG (Netherlands) produced 1 ton (230 gallons of pyrolysis oil), these oils were separated into a water-soluble and a water insoluble-fraction (See Figure 2). Briefly, the oil was produced from a clean softwood mix using a rotating cone reactor (https://www.btg-bioliquids.com/). The average particle size was 3 mm; the average reactor temperature was 500 °C, ambient pressure was used, and the gas residence time was less than 2 s. The condensation temperature was 40 °C (one-step condensation). The yield of bio-oil was approximately 65 wt. %. The FP oil was partitioned into WS_{BTG} and WIS_{BTG} fractions as described elsewhere (Heeres et al. 2019). Briefly, solvent-hexane was first used to separate the extractives from the oil. Next, the aqueous and nonaqueous phases were separated by water extraction, with a bio-oil to water ratio of 2:1, at 60 °C. The yields of WIS_{BTG} and WS_{BTG} were 24 and 43 wt. % in an extractive-free biomass basis (Heeres et al. 2019) and 35.3 and 63.2 wt. % in pyrolysis oil basis (1.5 wt. % of extractives), respectively.

We also received 42 gallons of Pyrovac oil. Pyrovac oil was produced from almond shells in November 2020 at the Pyrovac facility in Saint-Lambert-de-Lauzon, QC, Canada (www.pyrovac.com). Briefly, the pyrolysis temperature was 475 °C, and the feed rate was 400 kg/h. The reactor was operated under reduced pressure conditions using a well-stirred continuous feed reactor and indirectly heated with a molten salt heat carrier. Such a reactor configuration enables reasonable control of the product quality and consistency. The cooled biochar is collected at the bottom of the reactor, while the organic vapors, steam, and non condensable gases are driven out of the reactor using a blower. The condensing column was operated at a temperature of 73 °C under reduced pressure. The condensing system is run, so the water-lean bio-oil and aqueous phases are separately collected. The aqueous and nonaqueous phases are separated by water extraction. Briefly, 15 g of the Pyrovac oil was dispersed in 30 g of water in a centrifuge tube. The aqueous and nonaqueous fractions were separated by centrifugation (4200 rpm, 30 min). The yields of $WIS_{Pyrovac}$ and $WS_{Pyrovac}$ were 28 and 72 wt %, respectively.

Figure 2. Oils received from BTG

Our team purchased 330 gallons of vegetable oil from Baker Commodities Inc (See Figure 3). The 8 drums (55 gallons) were pumped and filtered with a 200 mesh filter.

Figure 3. Vegetable Oils received from Baker Commodities Inc

Study 2.2. Hydrothermal liquefaction of two woody biomass feedstock (Douglas fir and Hybrid Poplar) for the production of HTL oils: The hydrothermal liquefaction of two woody biomass feedstock was completed and the oil and aqueous phase samples were transported to WSU. (PI Responsible: Andy Schmidt)

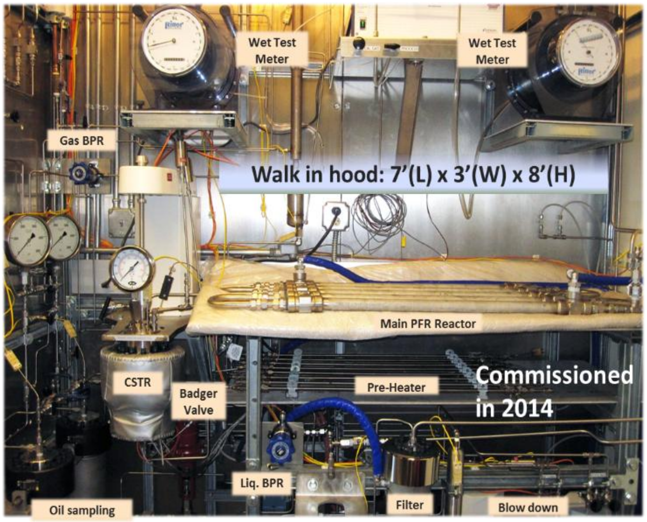


Figure 4. Photo of Bench Scale HTL System

The biocrude ($\text{WIS}_{\text{WD-57}}$) and aqueous phase ($\text{WS}_{\text{WD-57}}$) studied were produced at the PNNL from Douglas-fir (*Pseudotsuga menziesii*) wood flour provided by the Idaho National Laboratory (INL), with 3.6 wt % moisture and 0.17 wt % ash (dry feed). The HTL system configuration included a tubular preheater and a 1 L continuous stirred tank reactor (See Figure 4). Before the experiment, Douglas-fir particles were used to prepare a feed slurry, essential to enable pumping at the bench scale. Briefly, HTL byproduct water from a previous test was blended with the wood flour, and the mixture was ground in an immersion mill, creating a 13 wt. % solid slurry with ~98% of the particles <0.4 mm. After that, 1 wt. % of sodium carbonate (total slurry basis) was mixed into the slurry as a pH buffering agent to control pH excursion, reducing acid-catalyzed decomposition reactions that lead to char formation. In the HTL system, the slurry was brought to operating pressure (20.7 MPa) using a continuous flow dual-barrel Teledyne Isco syringe pump. After pressurization, the slurry was heated in a tubular heat exchanger and then brought to the HTL reactor temperature (350 °C) in a continuously stirred tank reactor (CSTR). Rapid mixing in the CSTR facilitates heat transfer and accommodates product slurry swelling. The liquid hourly space velocity used was 2.0 L/L/h. Downstream of the reactors, solids were removed from the product stream by settling and with a stainless-steel filter. After solids removal, the product was collected in one of two alternating oil jacketed separators/collection vessels. The product was retrieved and cooled. The HTL biocrude was obtained from gravity separation from the aqueous phase. The mass and carbon yields to biocrude were 32 and 49 wt. %, respectively. The carbon yield to the aqueous fraction was 27 wt. %.

Study 2.3. Production of a phenolic-rich oil and wood vinegar from the pyrolysis oil: (PI Responsible: Manuel Garcia-Perez): The 60 gallons of pyrolysis oil from BTG was separated into a phenolic-rich oil and a wood vinegar. We used the method described by Steele et al. (2013), which found that the optimal conditions for levoglucosan extraction were 1.3:1 (water: bio-oil) at 25 ^{o}C for 20 min. The 20 gallons of oil will be gently dropped into a 55-gallon container containing 26 gallons of stirred water. The aqueous phase formed will be removed with a peristaltic pump.

Task 3: Bio-oil Chemical Characterization: The main goal of this task is to characterize the chemical composition of all the oils to be studied in this project. (PI Responsible: Manuel Garcia-Perez)

Study 3.1. Characterization of bio-oil fractions: The chemical composition of each of the fractions will be evaluated by GC/FID, Karl Fischer titration, GC/MS, IEC, HPLC, and UV-fluorescence.

The results of this task were published in four manuscripts:

Pinheiro-Pires PP, Garcia-Perez M, Olarte M, William K, Schmidt A, Kevin Z, Denson M, Terrell E, McDonald A, Ha Y: Comparison of the Chemical Composition of Liquids from Pyrolysis and hydrothermal liquefaction of lignocellulosic materials, Energy & Fuels, **2023,** 37, 10, 7221-7236

Terrell E, Garcia-Perez M: Novel Strategy to Analyze Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Data of Data of Biomass Pyrolysis Products for Oligomeric Structure Assignment. Energy and Fuels, **2020,** 34, 7, 8466-8481

Manrique-Waldo 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. Energy & Fuels, **2023**, 37, 7, 5189-5205

Domes-Denson M, Terell E, Kostetskyy, P, Olarte M, Broadbelt L, Garcia-Perez M: Theoretical Insights on the Fragmentation Reaction of Oligomeric Sugars to Remove Acetol and Glycoaldehyde. Energy & Fuels, **2023**, 37, 18, 13997-14005

Domes-Denson M, Terell E, Kostetskyy P, Olarte M, Broadbelt L, Garcia-Perez M: Elucidation of Structure and Physical Properties of Pyrolytic Sugar Oligomers driveded from Cellulose Depolymerization/Dehydration reactions: A Density Functional Theory Study. *Energy & Fuels*, **2023**, 37, 11, 7834-7847

The paper of Pinheiro-Pires et al. (2023) studied the differences in the chemical composition of BTG, Pyrovac, and HTL oils. Although major differences in thermal stability and hydrotreatment behavior of hydrothermal liquefaction (HTL) and pyrolysis oils have been reported, little is known about the variations in the chemical composition of these oils that could explain such differences. The samples were characterized by GC−MS, Karl Fischer titration, carbonyl content, total acid number, elemental composition, calorific value, proximate analysis, Fourier transform infrared spectroscopy, Folin−Ciocalteu (FC), and UV fluorescence. Fourier transform ion cyclotron resonance mass spectrometry (ICR-MS) and electrospray ionization mass spectrometry (ESI-MS) were also used to analyze the fractions. The most prevalent class of compounds in the water-insoluble phases was phenols. Water-soluble phases contained mainly oxygenated compounds derived from cellulose and hemicellulose and were richer in the carbonyl functional group. The water content of the resulting aqueous phases was 65 (W_{BTG}) and 96 ($WS_{Pyrovac}$) wt. %. The bio-oil from BTG has higher water content and lower high heating value compared to Pyrovac oil. According to the GC−MS results, BTG oil contained more acetic acid and higher TAN number than the Pyrovac oil, while Pyrovac oil was mainly composed of monophenols. The higher number of monophenols in the Pyrovac oil was also confirmed by the FC method. Although the UV fluorescence spectra, ICR-MS, and the ESI-MS analyses showed some minor differences in the molecular weight and chemical make-up of the oligomers soluble and insoluble in water from pyrolysis and HTL, the differences observed were not significant enough to justify the differences in hydrotreatment behavior between these oils reported in the literature.

The paper of Terrell and Garcia-Perez (2020) addresses one of the most prominent challenges for the analysis of biomass pyrolysis products: the characterization of the abundant oligomer fraction of bio-oil. This fraction is principally made up of pyrolytic lignins and dehydrated, highly modified sugar oligomers, called humins, in the liquid phase and is mainly responsible for coke formation. In this paper we used high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) which is an emerging technique for analysis of this oligomer fraction. This technique allows an accurate determination of $C_xH_yO_z$ formulas for detected oligomers. Using simple dehydration and fragmentation reaction schemes, formulas were developed to describe the structures of oligomers derived from cellulose, hemicellulose, and lignin. In this study, FT-ICR MS analysis was coupled with combinatoric dehydration and fragmentation modeling to match experimentally detected bio-oil oligomers with hypothetical pathways for their formation during pyrolysis. This paper presents a novel strategy by which oligomeric structures can be proposed for bio-oils. Using this approach, it becomes possible to advance the understanding of both the molecular structures comprising the bio-oil oligomer fraction and the pathways by which these structures form during biomass pyrolysis reactions.

The paper of Manrique et al. (2023) for the first time attempted to describe the structure of pyrolytic lignin based on density functional theory (DFT) calculations. This study proposes dimer, trimer, and tetramer structures based on their relative thermodynamic stability for a hardwood lignin model in pyrolysis. Different configurations of oligomers were evaluated by varying the positions of the guaiacyl (G) and syringyl (S) units and the bonds βO4 and β5 in the hardwood model lignin through electronic structure calculations. The homolytic cleavage of βO4 bonds is assumed to occur and generate two free radical fragments. These can stabilize by taking hydrogen radicals that may be in solution during the intermediate liquid (pathway 1) formation before the thermal ejection. An alternative pathway (pathway 2) could occur when the radicals use intramolecular hydrogen, turning themselves into stable products. Subsequently, a demethylation reaction can take place, thus generating a methane molecule and new oligomeric lignin-derived molecules. The most probable resulting structures were studied. We used FTIR and NMR spectra of selected model compounds to evaluate our calculation approach. Thermophysical properties were calculated using group contribution methods. The results give insights into the lignin oligomer structures and how these molecules are formed. They also provide helpful information for the design of pyrolysis oil separation and upgrading equipment.

The papers of Domes-Denson et al. (2023 a, b) focused on the use of DFT calculations to propose a probable structure for oligomers derived from cellulose. Dehydration is known to be among the most important reaction families during cellulose pyrolysis; water is the most important product. Together with water, dehydration reactions also form a range of poorly known oligomer species of varying molecular sizes, often collected as part of the bio-oil water-soluble (WS) fraction. In this work, we used electronic structure calculations to evaluate the relative thermodynamic stabilities of several oligomer species from cellulose depolymerization intermediates undergoing three consecutive dehydration events. A library of the thermodynamically favored candidate molecular structures was compiled. Results revealed that most of the water molecules are eliminated from the non-reducing end, forming thermodynamically more stable conjugated compounds. This is consistent with results reported in literature where dehydration reactions occur preferably at the non-reducing ends of oligomers. The theoretical Fourier-Transform Infrared Spectroscopy and NMR spectra of these proposed sugar oligomers qualitatively conform to the experimental result of pyrolytic sugars. Understanding their chemical structure could help to develop rational strategies to mitigate coke formation as sugars are often blamed to cause coke formation during bio-oil refining. The estimated physical–chemical properties (boiling point, melting point, Gibbs free energy of formation, enthalpy of formation, and solubility parameters, among others) are also fundamental to conducting first-principles engineering calculations to design and analyze new pyrolysis reactors and bio-oil up-grading units. In the second paper, Domes-Denson studied the fragmentation reactions yielding hydroxyacetone and hydroxyacetaldehyde from oligomeric sugars, following previous work on dehydration reactions to propose structures of these oligomers. Hydroxyacetone and hydroxyacetaldehyde are primary products of cellulose fast pyrolysis, but the fragmentation reaction mechanism of these compounds from oligomers merits further study. The density functional theory approach was employed to study this reaction. Results revealed that hydroxyacetone and hydroxyacetaldehyde fragments are more favorably removed from the nonreducing end based on their thermodynamic stabilities. As a result of this study, we proposed new potential structures of unknown oligomeric sugars. Theoretical FTIR and NMR spectra were calculated so that in the future, when these molecules are separated, their experimental spectra and the theoretical ones herein reported can be used to confirm the structures of these oligomeric sugars. Also, the thermodynamics and physical properties of these compounds were estimated by using the group contribution method. These properties are essential in the design of technologies for bio-oil refining.

Our group is currently working on three other manuscripts aiming to better understand the chemical composition of the oligomeric fractions of BTG oils. These are the main fractions responsible for coke formation. The papers will be submitted within the next three months.

Mora M, Garcia A, Manrique R, Sierra-Jimenez V, Fabregas E, Puy N, Clingenpee A, Garcia-Perez M: Separation and in-depth characterization of biomass fast pyrolysis oil oligomeric fractions: Part 1 – Water-insoluble dichloromethane-soluble fraction. Paper to be submitted to Energy & Fuels, **2025**

Manrique R, Denson M, Afrin A, Gagaa MH, Garcia A, Haghighi-Mood S, Alsbou E, Sierra-Jimenez V, Carvalho Carregosa J, Wisniewski A, Mora M, Clingenpeel A, Rojas M, Chejne F, Olarte M, Garcia-Perez M: Separation and in-depth characterization of biomass fast pyrolysis oil oligomeric fractions: Part 2 – Water-insoluble, dichlorimethane-insoluble fraction. Paper to be submitted to Energy & Fuels, **2025**

Domes Denson M, Gaaga MH, Carvalho Carregosa J, Garcia A, Alsbou E, Menezes Santos R, Wisnieski A, Sierra Jimenez V, Li W, Clingenpee A, Olarte M, Mora M, Afrin A, Garcia-Perez M: Separation and in-depth characterization of biomass fast pyrolysis oils oligomeric fractions: Part 3 Water-soluble fraction. Paper to be submitted to Energy & Fuels, **2025**

These three papers separated and characterized in detail BTG oligomeric fractions (water soluble, water insoluble/CH_2Cl_2 soluble and water insoluble/CH_2Cl_2 insoluble). The bio-oil was initially fractionated via cold water precipitation, yielding a water-soluble fraction representing 51.5 wt.% of the original oil. Subsequent chromatography using Sepabeads resin separated this fraction into sugars (55.6 wt.%) and phenols (44.4 wt.%). The water-insoluble fraction was then separated depending on its solubility in CH_2Cl_2.

The sugars were concentrated through rotary evaporation and further fractionated using silica gel open column following an increasing polarity of solvents (dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EA), methanol (MeOH), and water (H_2O)). Each fraction underwent comprehensive analysis via FTIR, UV-Fluorescence, Py-GC/MS, NMR, ESI-MS, and H-ESI-FT Orbitrap MS. Generated chemical formula representations indicated that fractions had average O/C ratios between 0.69 and 0.84 and H/C ratios between 1.41 and 1.76, comparable to cellulose (O/C = 0.833, H/C = 1.66). Increased solvent polarity correlated with higher O/C and H/C values, suggesting higher content of phenols in the DCM and THF soluble fractions. EA, MeOH, and H_2O fractions were rich in sugars with a low degree of dehydration and fragmentation. Sugars eluted with H_2O had higher molecular weights than those eluted with EA and MeOH. Molecular representations for each fraction were proposed to enhance the understanding of the chemistry of pyrolytic sugars. The water-insoluble CH_2Cl_2-soluble fraction, constituting 15.5 wt.% of the BO, was further separated using a novel open-column chromatography method into three distinct subfractions: ethyl ether (56 wt.%), ethyl acetate (23 wt.%), and methanol (20 wt.%). Comprehensive characterization using UV fluorescence, FT-IR, ^1H, ^{13}C, and 2D HSQC NMR, and FT-ICR MS revealed significant compositional differences among the fractions. The sub-fractions obtained exhibited elemental ratios in the following range (H/C: 1.20–1.26; O/C: 0.26–0.38; DBE: 9.15–9.46), positioning them between the subfractions from the water-soluble fraction (H/C: 1.41–1.73; O/C: 0.69–0.81; DBE: 4–8) and the subfractions from the water-DCM insoluble fraction (part 2) (H/C: 0.82–1.02; O/C: 0.26–0.36; DBE: 14–20). Phenolic dimers dominated all DCM-soluble PL but differed in associated compound types: the ethyl ether fraction was enriched in terpenoids and lipids, the ethyl acetate fraction featured hybrid carbohydrate-lignin and larger lignin oligomers, and moderately dehydrated sugars (humins), and the methanol fraction contained hybrid carbohydrate-lignin oligomers and moderately dehydrated sugars. Representative structures proposed for each fraction illustrate their diverse chemical compositions. The water-insoluble CH_2Cl_2-insoluble fraction, known as high molecular weight pyrolytic lignin (HMW-PL) accounts for 9.2 wt.% of the original oil, increases upon aging, and is associated with coke formation during bio-oil upgrading. Understanding its composition is crucial for controlling the behavior of pyrolysis oil during processing. HMW-PL was fractionated using a silica gel column with solvents of increasing polarity (ethyl acetate (EA), acetone (AC), isopropanol (ISO), and methanol (MeOH)). The majority (49.2 wt.%) eluted with EA, followed by AC (19.9 wt.%), ISO (8.2 wt.%), and MeOH (8.1 wt.%), while 14.1 wt.% remained in the column. The resulting subfractions were characterized by UV-fluorescence, FTIR, NMR (^{13}C, ^1H), and (–)APCI-FT-Orbitrap MS. Subfractions showed decreasing molecular weights and DBE (double bond equivalence) values (20 to 14) with increasing solvent polarity and had average H/C ratios (0.82-1.02) lower than the water–insoluble–CH_2Cl_2 soluble fraction (1.20-1.26), but comparable O/C ratios (0.26-0.36). Compared to the water-soluble fraction (on average, H/C: 1.41-1.73, O/C: 0.69-0.81), the water-insoluble fractions were lower in oxygen and hydrogen, indicating the H/C ratio's usefulness in predicting bio-oil oligomer solubility. UV-fluorescence revealed conjugated ring systems in all fractions. The EA fraction contained predominantly lignin-derived dimers and trimers, while the AC, ISO, and MeOH fractions had fewer aromatics but more humins and hybrid oligomers. FTIR supported significant compositional differences among different fractions, and NMR confirmed methyl-aromatic structures consistent with lignin derivatives. (–)APCI-FT-Orbitrap MS detected dimers and trimers (C#: 13~20, O#: 5), mostly with 180-400 Da molecular weights. This fractionation approach enabled the definition of four distinct subfractions and the proposal of surrogate molecular structures for each, enhancing the understanding of HMW-PL composition. Summarizing this series, an expanded analytical method was proposed, categorizing bio-oil oligomers into nine sub-groups based on solubility and solvent polarity. These groups ranged from sugars with varying dehydration levels to lignin-derived oligomers, terpenoids, lipids, monophenols, and volatile compounds. This comprehensive separation scheme significantly advances the characterization and understanding of pyrolysis oil fractions.

Task 4: Batch Co-hydrotreatment studies: The main goal of this task was to study the effect of co-hydrotreatment on product yield and catalyst coke formation. (PI Responsible: Manuel Garcia-Perez)

Study 4.1. Miscibility and emulsion stability of pyrolysis oils and lipids. We have conducted miscibility studies with different solvents. A paper was published in Energy and Fuels.

Han Y, Paiva-Pires A, 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

Separating bio-oil by fractionation with different chemical compositions is a critical step to refine these oils and obtain high-value products. Cold water precipitation of pyrolytic lignin from bio-oil is the most common approach used. However, the obtained aqueous phase from this method still contains phenols and is diluted and difficult to use. In this study, the use of liquid–liquid extraction with different solvents (1-butanol, ethyl acetate, 1-octanol, dichloromethane, toluene, and hexane) for the separation of targeted molecules (lignin oligomers, sugars, acetic acid) is explored. Ternary phase diagrams for the organic solvent/water/bio-oil are reported. The partition coefficient of compounds of interest (both light and heavy fractions) is reported for the liquid–liquid equilibrium zone. When using butanol as the solvent, the highest separation factor of total phenols over total sugars was observed. Our results provide information to design L–L separation units with the capacity to selectively recover targeted molecules from pyrolysis oils. Figure 5 shows some of the phase diagrams developed in this project (Han et al. 2020).

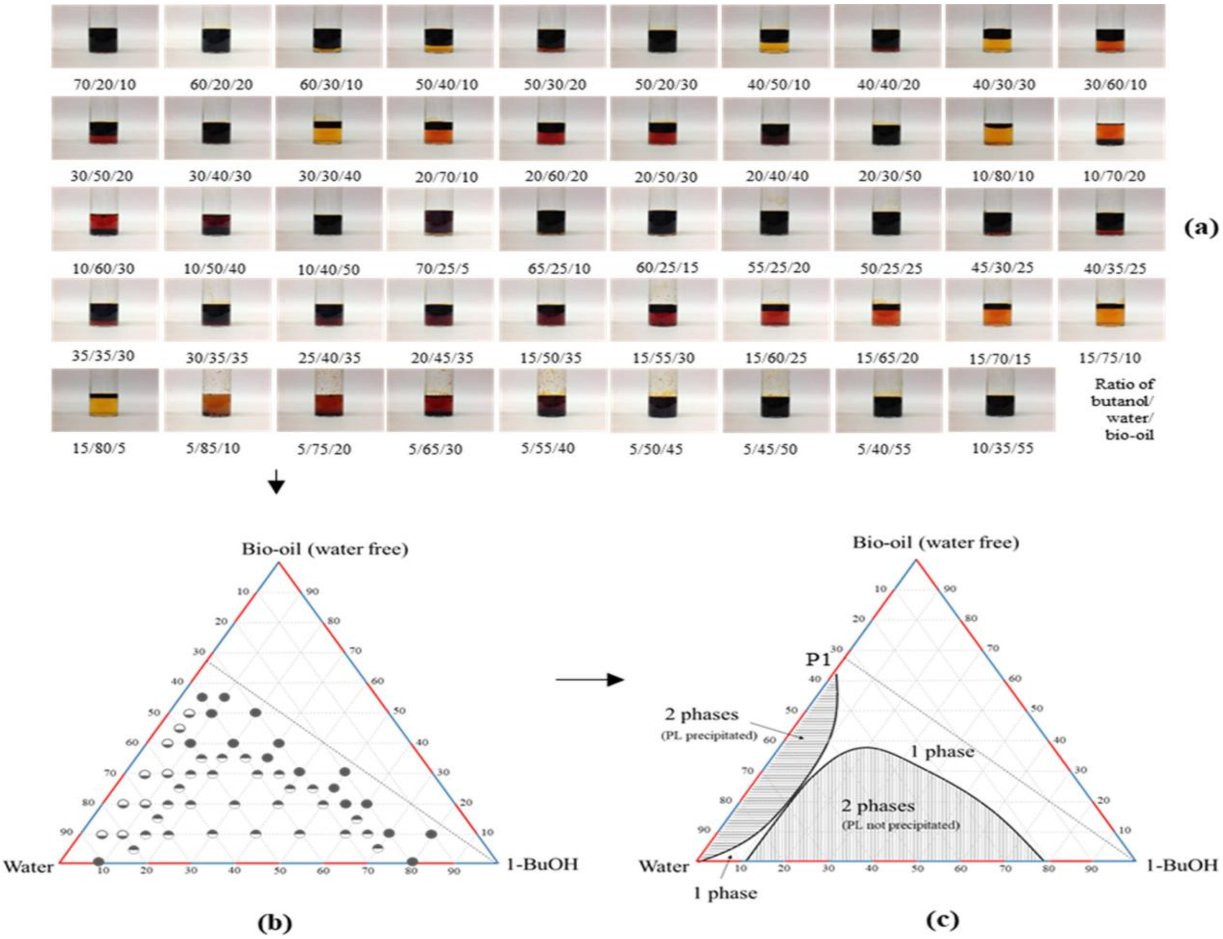


Figure 5. Phase diagram describing the miscibility of pyrolysis oil fractions in the presence of water and 1-buthanol.

Figure 6 shows the phase equilibrium data used to estimate the constants of equilibrium.

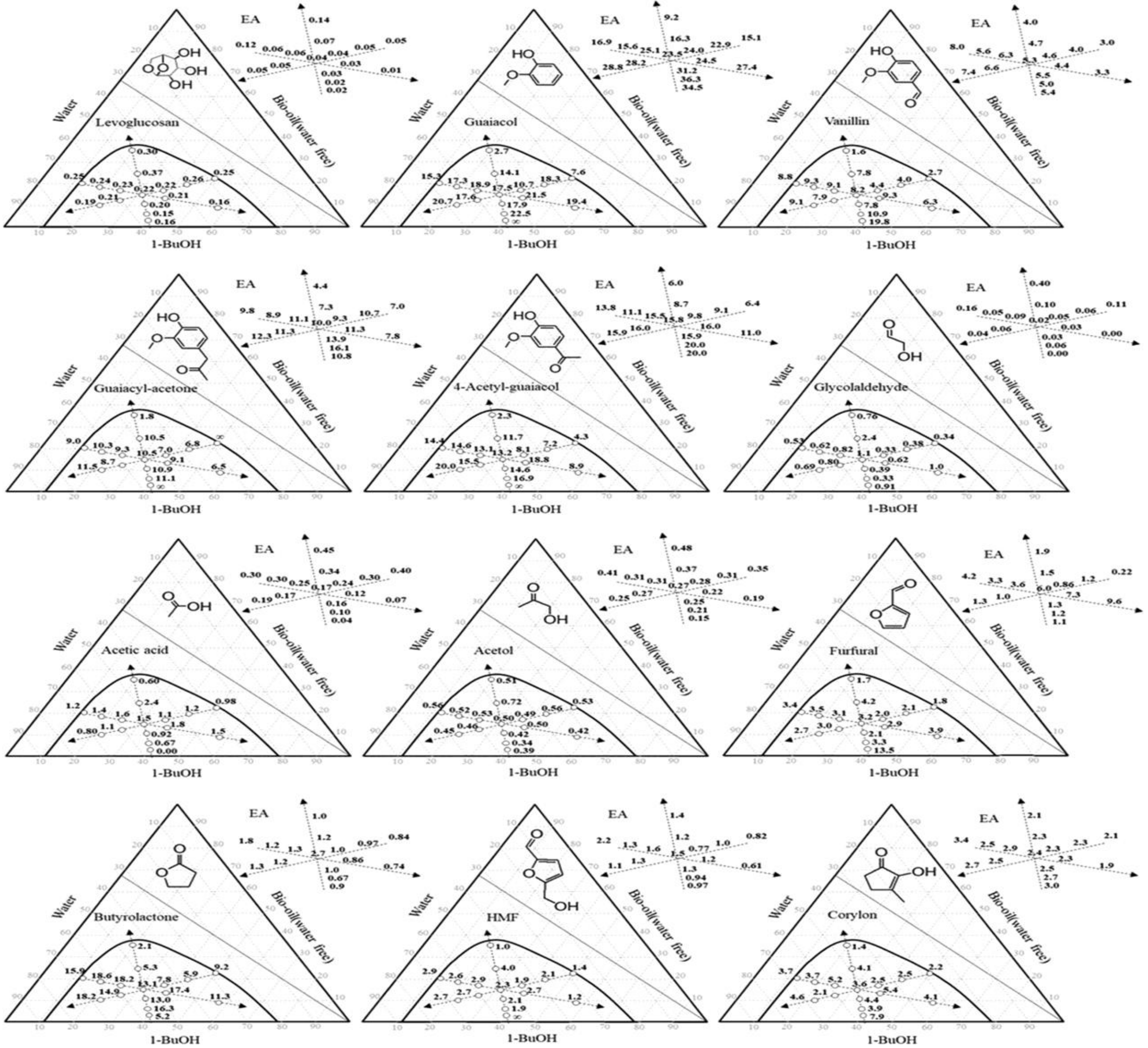


Figure 6. Phase diagram and data used to calculate the constants of phase equilibrium for targeted compounds

The data generated by this project was used to validate phase equilibrium models developed by the German Karlsruhe Institute of Technology.

Rojas Salas M, Fonseca F, Araujo A, Garcia-Perez M, Funke A: Liquid-liquid equilibrium prediction in fast pyrolysis bio-oil systems: A framework for incorporating bio-oil complexity. *Energy & Fuels*, **2024**, 38, 19, 18769-18780

Liquid−liquid extraction, a cornerstone technique for bio-oil refining, suffers from a critical data gap: the lack of reliable partition coefficients (K_{ow}) for key fast pyrolysis bio-oil (FPBO) components. This absence hinders the application of established modeling strategies for the optimization of these processes. To address this challenge, the model developed by the Karlsruhe Institute of Technology employed simulations to calculate K_{ow} values for crucial FPBO components based on a bio-oil surrogate mixture and activity coefficients calculated with UNIFAC Dortmund. This study focused on the unresolved structure of pyrolytic lignin ('pyrolignin'), whose chemical composition is largely unknown. Consequently, there is a large variety of representatives proposed for pyrolignin in the literature. To account for the uncertainty of how to best represent pyrolignin, 20 possible structures (phenolic dimers to tetramers) are tested to determine which describes the experimental data best. Also, two different approaches to quantifying the pyrolignin fraction in surrogate FPBO were investigated. Interestingly, the best K_{ow} predictions for levoglucosan are obtained without including any modeled pyrolignin and modeling it with large molecules or molecule mixture. Several specific pyrolignin structures (dimer D2, trimer F1, and tetramers I1 and I3) demonstrate promising agreement with experimental data. This work establishes a framework for incorporating bio-oil complexity into process modeling, particularly the influence of diverse pyrolignin structures. This paves the way for more accurate simulations and ultimately the design of efficient and effective bio-oil refining processes.

We also studied the stability of bio-oil/vegetable oil emulsions with 6 sufactants: Span 80, Tween 80, Atlas G5000, Atlox 4912, Atlox 4914, and Hypermer B261. Among the surfactants studied Span 80, Atlox 4912, and Hypermer B261 were able to reduce the surface tension of the bio-oil. They were all able to reduce the surface tension of the yellow greases studied, at different concentrations. Surfactants Span 80, Atlox 4912, and Hypermer B261, resulted in emulsions with stability up to 33 min, 2 h 43 min, and 3 h 40 min, respectively.

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

A review paper on bio-oil hydrotreatment catalysts was published:

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

The first studies were conducted with Co-Mo and the second group of studied with Ni-Mo. The results with Co-Mo were published the following one papers:

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

The studies with sulfide Ni-Mo catalysts were published in three manuscripts:

Pires APP, 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

Marique RJW, Chejne F, Olarte M, Garcia-Perez M: Co-hydrotreatment of Pyrolytic Lignin and Cooking oil to Produce Hydrocarbons. Energy & Fuels, **2024**, 38, 9, 7917-7928

Domes-Denson M, Manrique-Waldo RJ, Olarte M, Garcia-Perez M: Co-hydrotreatment of Bio-oil and Waste Cooking Oil to Produce Aviation Fuels. Energy & Fuels, **2024**, 38, 6982-6991

Figure 7 shows the experimental set up used in these studies.

Figure 7. Lab hydrotreatment experimental set-up.

Han et al. (2020) studied blends of lignin-rich oil (LRO) and vegetable oil (1:8, 1:4, 1:2, and 1:1). These blends were prepared and hydrotreated over $CoMo/Al_2O_3$ (catalyst liquid ratio of 1:50) at 623 K and 500 rpm, with 9.3 MPa of cold initial H_2 pressure for 4 h. The yield of liquid, gas, and solid products was reported. The yield of coke obtained was in all of the cases very high (between 25 and 50 wt % of the LRO processed, depending upon the LRO/vegetable oil ratio used). Most of the product from the lignin-rich fraction remained in the heavy fractions. To mitigate coke formation, blends containing 0.5 g of butanol/g of LRO studied were co-hydrotreated with vegetable oils maintaining the

LRO/vegetable oil ratios. The presence of 1-butanol mitigated coke formation, but it did not translate in the production of distillable fractions; the LRO contributed to the formation of a heavy oil. The LRO needs to be stabilized and cracked before co-deoxygenation. Cracking/stabilization studies in the presence of butanol and methanol were conducted over Ni/SiO_2–Al_2O_3 at 473 K with 9.3 MPa of cold H_2 pressure for 24 h. The best results were obtained with the oils stabilized in the presence of butanol. The yield of coke formed decreased from 34.7 wt. % on LRO basis to 6.65 wt. %. The behavior of the stabilized/cracked LRO/vegetable oil blends (1:4) in terms of the product yield was comparable to the yields obtained when vegetable oil was deoxygenated alone. The solid residue (coke) increased from 0.04 wt. % when vegetable oil was processed alone to 1.13 wt. % when a 1:4 blend of stabilized/cracked lignin/vegetable oil was co-processed.

This paper, published by Pires et al. (2023) reports the co-hydrotreatment of Biomass Technology Group commercial pyrolysis oil water-insoluble (WIS) phase (also known as pyrolytic lignin) and yellow greases (waste cooking oil), aiming to produce sustainable aviation fuels (SAFs). We used a sulfided NiMo/Al_2O_3 blend with 16 wt. % WIS and a central composite experimental design to identify processing conditions increasing kerosene yield and reducing coke formation. The input variables were: (1) reaction temperature (320, 350, and 380 °C), (2) initial hydrogen pressure (5, 6, and 7 MPa), and (3) amount of catalyst (0.7, 1.0, and 1.3 g). The hydrotreated oily phases were distilled to obtain gasoline (<150 °C), kerosene (150−250 °C), diesel (250−350 °C), and residual oil (>350 °C). The reaction temperature is the main factor affecting the yield of gaseous, solid, and liquid products. Meanwhile, a higher initial hydrogen pressure and catalyst loading increased the yield of kerosene and other distillates and decreased the coke formation. A high temperature correlated with a lower content of oxygenates in kerosene cuts. Based on our experimental results, we propose to conduct hydrotreatment studies at 380 °C, an initial H_2 pressure of 7 MPa, and 1.3 g of catalyst. Under the identified conditions, it was possible to improve the kerosene yield to more than 20 wt % and reduce the yield of coke to close to 2.0 wt %. The chemical composition and fuel properties of the gasoline, kerosene, and diesel cuts were thoroughly analyzed. The content of aromatics and phenols in the kerosene fraction produced at the conditions identified in this project exceeded the recommended values for SAFs. New strategies (such as blending and more intense hydrotreatment to remove oxygenated compounds) need to be implemented to reduce the content of these molecules in our final product.

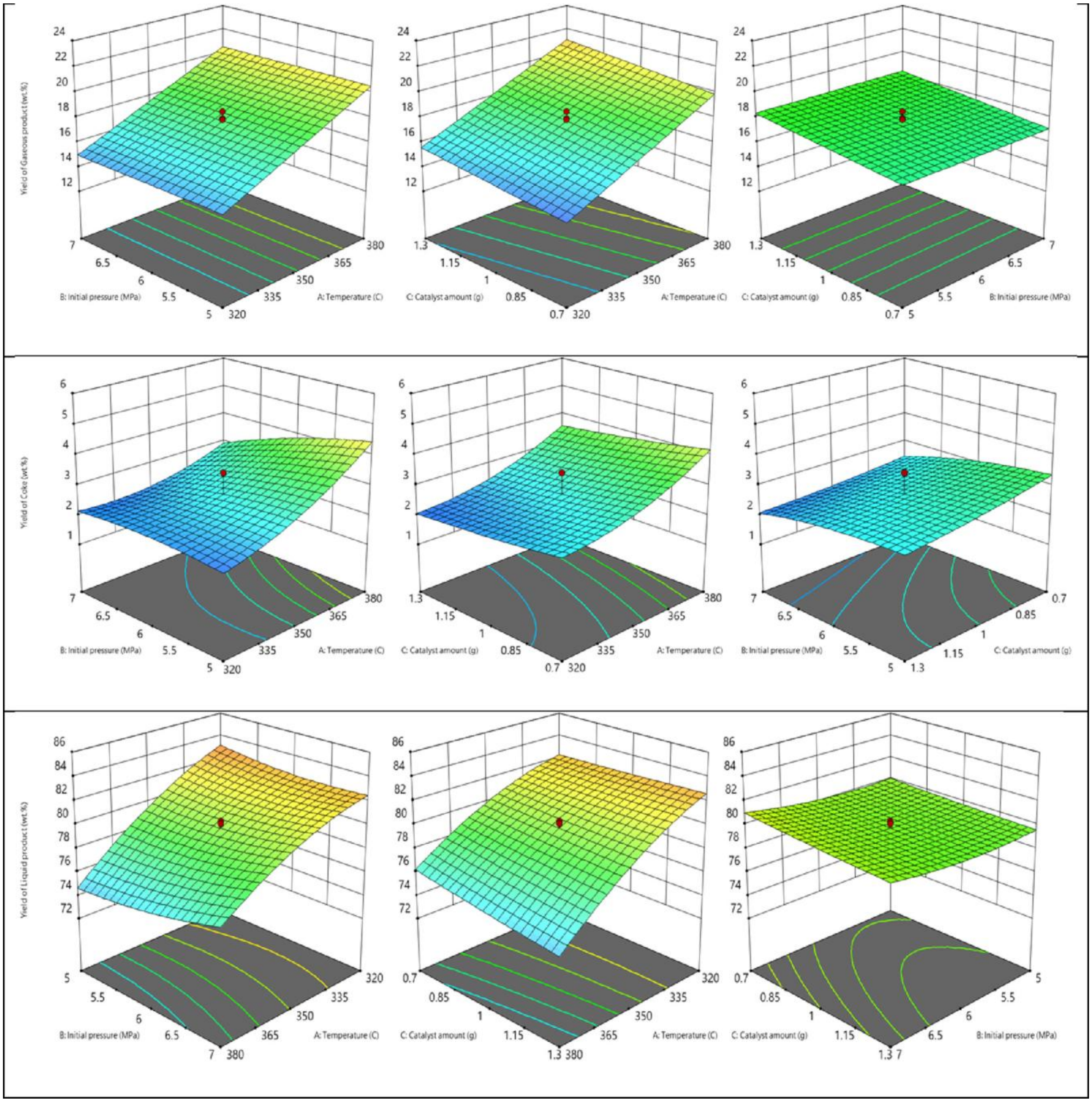


Figure 8. (a) Yield of gas products over temperature, initial pressure, and catalyst amount; (b) Yield of coke over temperature, initial pressure, and catalyst amount; (c) Yield of liquid products over temperature, initial pressure, and catalyst amount.

The paper published by Manrique et al. (2024) reported the results of co-hydrotreatment with different PL/WCO blend ratios (0, 10, 20, 30, and 40 wt %) over the NiMo/γ-Al_2O_3 catalyst. The coke formation value for WCO was 0.7 wt % and ranged between 1.5 and 2.5 wt % with the increase of pyrolytic lignin in the blend. The data suggest that coke is formed from both the sugar- and lignin-derived oligomers since the coke yield reported in this study is comparable with the coke yield obtained by coprocessing the bio-oil fraction without light oxygenate compounds, based on previous studies. All blends are recommended for co-hydrotreatment based on coke yield. The yield of products as a function of lend ratios is shown in Figure 9. The resulting organic phase was distilled into hydrocarbons at <150 °C, 150 to 250 °C, and 250 to 350 °C. The organic product's overall hydrocarbon distribution was strongly dependent on the pyrolytic lignin concentration. The yield of the distillation cut with a boiling point range between 250 and 350 °C was higher in the hydrotreated samples, with more than 20% during distillation. Two-dimensional GC×GC was used to determine carbon distribution on the combustibles. FTIR and UV fluorescence spectra showed that most feedstocks were converted to potential combustibles for transportation applications after hydrotreatment. The distillation cuts properties, such as density, viscosity, and surface tension, were reported and compared to transportation fuel properties. Hydrocarbon yields reveal the potential of cohydrotreatment to upgrade pyrolytic lignin into valuable products. These findings provide useful insights into utilizing pyrolytic lignin to produce promising combustibles suitable for transportation applications.

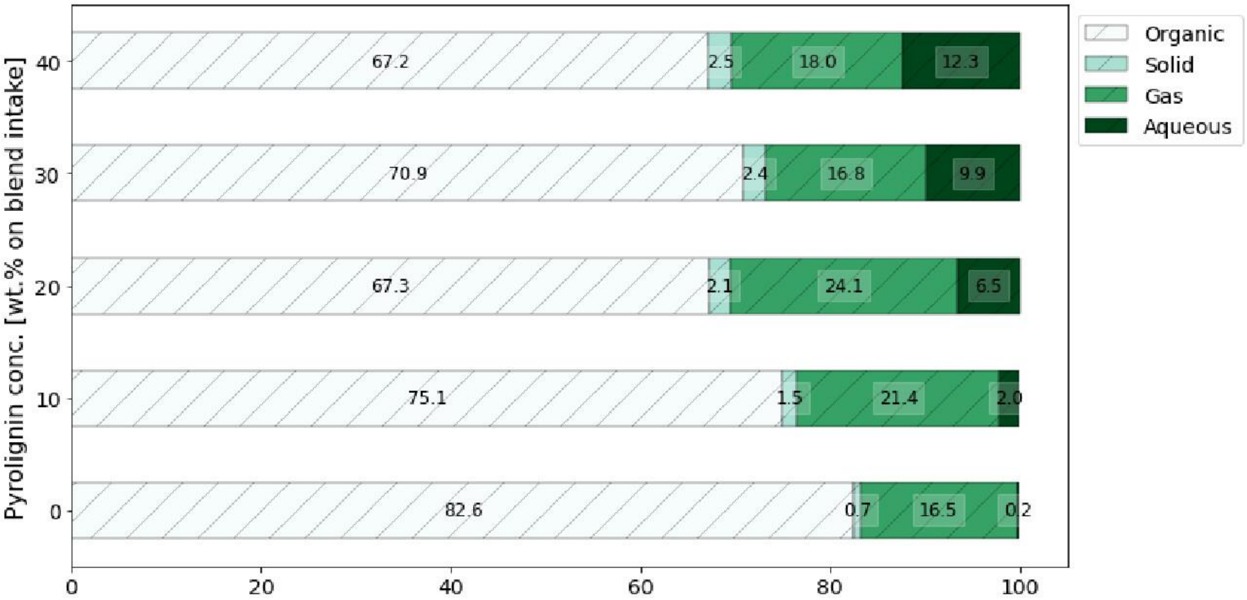


Figure 9. Product Yield (wt. %) as a function of pyrolytic lignin content in the blend (Manrique et al.. 2024)

Domes-Denson et al. (2014) reported the co-hydrotreatment of the heavy bio-oil fraction with waste cooking oil (WCO) using the NiMo/γ-Al_2O_3 catalyst, followed by the distillation of the resulting deoxygenated oil and the characterization of the resulting fuel cuts. The heavy Biomass Technology Group (BTG) bio-oil fraction was obtained by removing the very reactive light-oxygenated compounds via rotary evaporation and subsequently mixed with 1-butanol. The resulting oil was blended with WCO and subjected to a two-step co-hydrotreatment process. The first step, called "stabilization," was aimed at saturating highly reactive hydrogen-deficient compounds. The second step, called "deoxygenation," aimed to remove bio-oil oxygen, primarily as H_2O. This study examined the impact of varying bio-oil concentrations (0, 10, 20, 30, 40 wt % of WCO) on the upgraded oil's yield, composition, and fuel properties. The yield of products obtained with the whole pyrolysis oil is shown in Figure 10. The resulting hydrotreated oil was distilled into gasoline-range, kerosene-range, and diesel-range hydrocarbons at <150, 150–250, and 250–350 °C, respectively. The yield of the hydrotreated oil indicated that as the bio-oil concentration increased, the amounts of coke (0.7–2.4%) and water (2–10 wt %) increased, while the organic layer yields decreased (80–63%). The coke yield was comparable to the coke yield obtained when co-processing the pyrolytic lignin fraction. This suggested that coke was formed from both the sugar oligomers and the lignin-derived oligomers. The UV fluorescence analysis on the hydrotreated oil showed that more polycondensed and conjugated ring compounds formed as the bio-oil concentration was increased. These compounds are precursors of coke. Fourier transform infrared spectroscopy (FTIR) results showed that most raw materials were converted to biofuels after the hydrotreatment. To achieve less than 1 wt % of coke yield, blends with up to 20 wt % pyrolysis oil should be used. An increase in the bio-oil concentration led to a slight increase in the gasoline yield and a decrease in kerosene and diesel yields. The identified carbon species found in the fuel cuts included *n*-paraffin, iso-paraffin, cycloparaffin, and aromatics. Further, the jet fuel cut (kerosene) was characterized by density, surface tension, and viscosity. Our product conforms to the standard specifications for sustainable aviation fuels (Jet A-1). Further research is suggested to fine-tune the operating parameters for achieving reduced coke yield and enhanced kerosene yield.

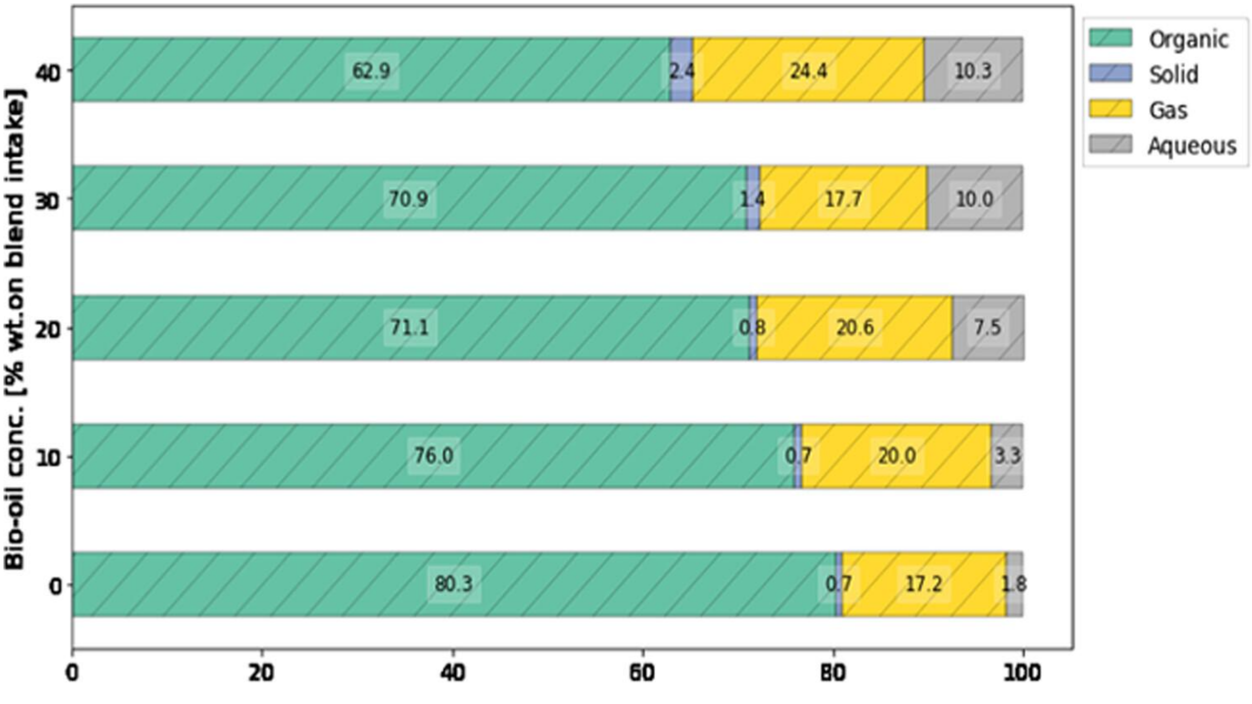


Figure 10. Yield of Products obtained from the co-hydrotreatment of yellow greas and BTG oil.

Task 5: Continuous Co-hydrotreatment studies: The main goal of this task was to explore the performance of co-hydrotreatment in continuous conditions. (PI Responsible: Mariefel V. Olarte).

PNNL used two scales of continuous flow, trickle bed systems to support this project. The feedstocks, yellow grease and pyrolytic lignin with butanol, were provided by WSU. Characterization of these feeds are shown in Tables 5.1 and 5.2. The hydrotreating catalyst (NiMo on alumina) was obtained from a commercial partner (Co A). Three hydrocracking catalysts were used: (1) a zeolite extrudate purchased from a commercial entity for use in a previous project (Co B), and (2) two engineered catalysts from a catalyst vendor (Co C).

Table 5.1 Analysis of Pyrolytic Lignin + BuOH

Property	Concentration (µg/g)
Aluminum, µg/g	9.33
Calcium, µg/g	5.88 (single sample)
Silica, µg/g	14.44 (single sample)
Sulfur, µg/g	308.5
Carboxylic Acid Number (CAN), mg KOH/g	33.8
Phenolic Acid Number (PhAN), mg KOH/g	119.3
Total Acid Number (TAN), mg KOH/g	153.1
Carbonyl, mmol/g	2.79 (before)
	2.69 (after)

Table 5.2 Analysis of Yellow Grease

Property	Concentration (µg/g)
Chromium, µg/g	6.19 (single sample)
Iron, µg/g	24.0 (single sample)
Potassium, µg/g	16.34
Sodium, µg/g	10.70
Sulfur, µg/g	58.46
Carboxylic Acid Number (CAN), mg KOH/g	30.6
Phenolic Acid Number (PhAN), mg KOH/g	0
Total Acid Number (TAN), mg KOH/g	30.6
Carbonyl, mmol/g	0.33 (before)
	0.29 (after)

The objective of this task is to produce enough AJF for testing. (A change of scope changed the goal from production of 100 gallons). The results of the batch hydrotreating studies done at WSU were used to inform the continuous flow studies. However, several changes needed to be accomplished to produce jet fuel range hydrocarbons in the trickle bed reactors. These include the additional use of cracking and hydrocracking catalysts aside from the hydrotreating catalyst from Co A to enable jet fraction production. Both the lab (40-60 mL) and bench scale (400 mL) continuous flow systems were used.

Tests in the 40-60 mL continuous hydrotreatment system: PNNL initially used the two bed hydrotreating configuration: stabilization/guard bed followed by the main bed configuration with the sulfided NiMo catalyst used in the batch tests (Olarte et al. 2016). The size of the stabilization bed was based on the stabilization step developed during the batch tests (Task 4). Aside from this modification to the previous size of the stabilization bed, additional modifications were implemented. Typical experiments consisted of priming the sulfided catalyst bed with only yellow grease as feed, followed by co-processing with pyrolytic lignin with butanol.

The initial run resulted in a process shutdown within 30 hours (including yellow grease priming) due to plugging at the top of the stabilization bed, suggesting that a much lower temperature was needed to prevent the acceleration of the thermal reactions that result to coke formation. As such, the upper bed temperature was controlled to temperatures less than 100°C, even though the batch stabilization set point temperature was 250°C. Another early hydrotreating test resulted in post-reactor plugging due to the formation of gelatinous solid, which GC-MS result suggest as long-chain alkanes starting at C_{20}. Most of the product (>90%) had boiling points higher than 275°C (Figure 5.1). This result suggested that further cracking of the organics was required to prevent this from happening again. As such, a cracking catalyst (HCK-1) was added. The additional catalyst allowed the production of more hydrocarbons within the jet fuel boiling point range (Figure 5.2). Butane was found at the highest concentration in the effluent gas stream, barring the unused H_2 and the residual N_2 used for re-pressurizing the collection pots. This small alkane is likely a by-product of the added butanol for reducing the pyrolytic lignin viscosity.

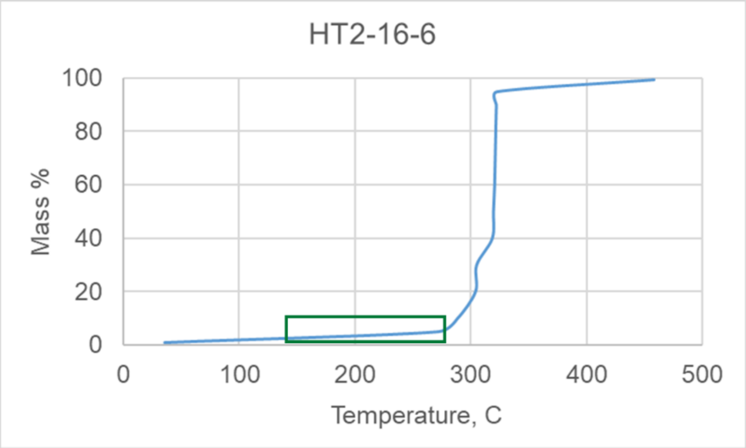


Figure 5.1. Simulated distillation of initial pyrolytic lignin-yellow grease organic product

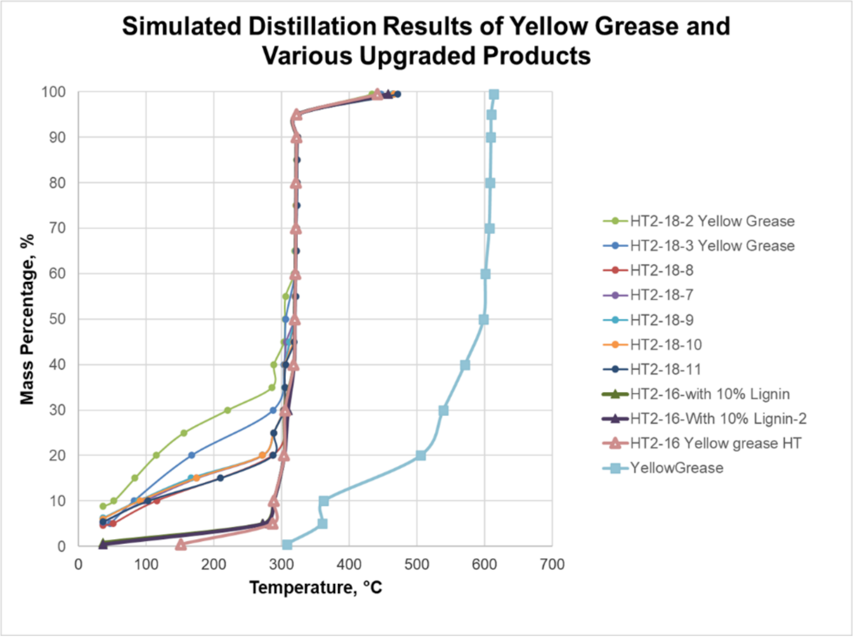


Figure 5.2. Simulated distillation of products formed with additional hydrocracking

The goals of the following continuous reactor tests focused on improving the yield of the jet fraction, while allowing for longer continued operation without pressure build-up/plugging.

Other hydrocracking catalysts were used to reduce the fraction of heavy components and improve the yield of the jet fuel fraction. As shown in Figure 5.3, three types of hydrocracking catalysts resulted in different amounts of heavy fractions. The use of either HCK-2 and HCK-3 lowered the amount of heavy fractions (>338°C), while HCK-3 provided slightly higher expected jet fuel fraction (orange bars) compared to either HCK-1 or HCK-2 by simulated distillation.

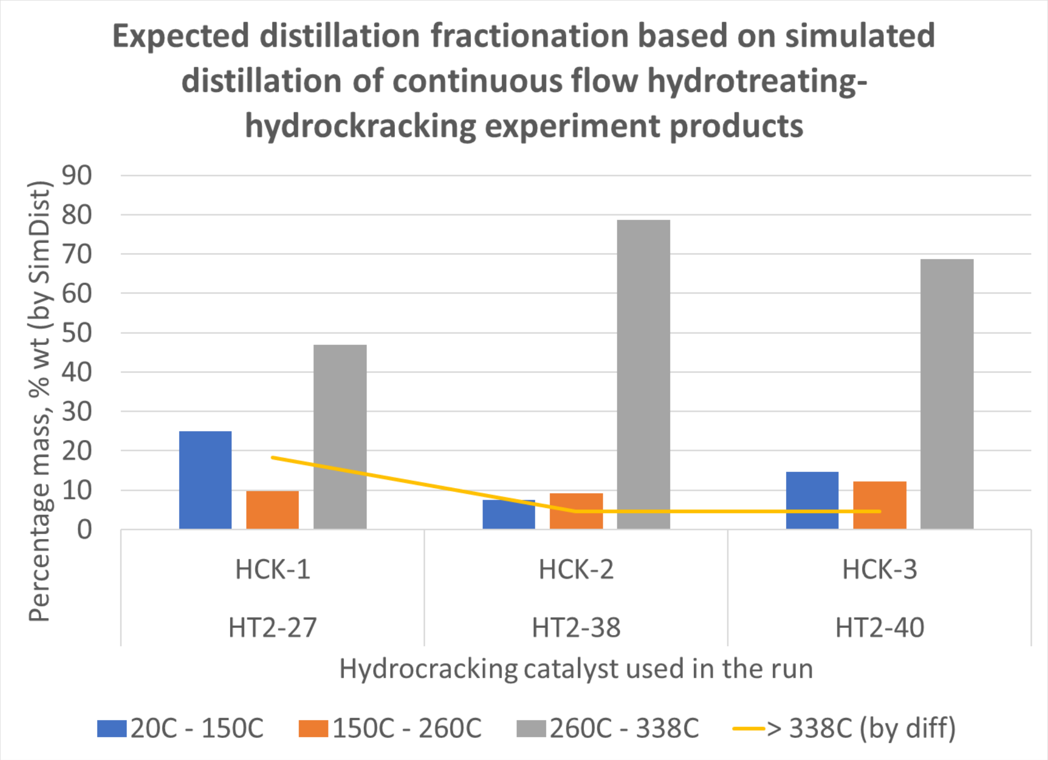
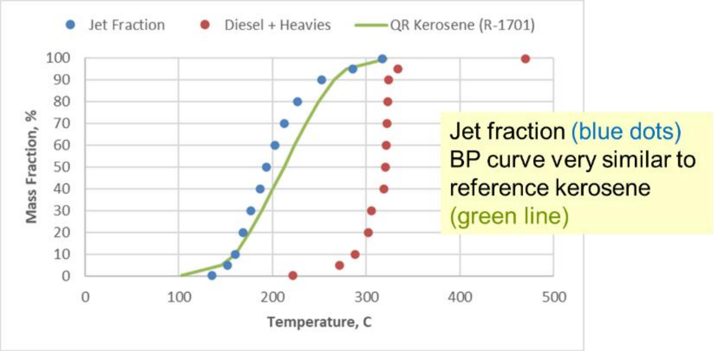


Figure 5.3 Simulated distillations of co-processing products using three different cracking/hydrocracking catalysts.

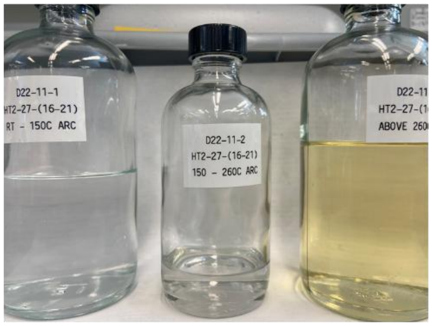
The longest campaign achieved for co-processing was 255 hours.

An invention disclosure was submitted for this: A process to co-process waste greases and pyrolytic lignin (iEdison No. 0685901-23-0146).

Figure 5.4 shows the distilled products for one campaign, with fractions divided to light gasoline (RT to 150°C), jet (150°C to 260°C) and heavy diesel + heavies (> 260°C). The associated table compares the amounts based on simulated distillation and batch distillation.



Jet fraction (blue dots) BP curve very similar to reference kerosene (green line)



	Temperature Range	Simulated Distillation Amounts	Batch Distillation Amounts	Color
Light Gasoline	RT to 150 C	25.8	35.7	Colorless
Jet	150 C to 260 C	10.7	7.7	Colorless
Heavy diesel + Heavies	> 260 C	74.5	54.6	Pale yellow

Figure 5.4 Summary of the distillation of HT2-27 co-processed upgraded oil

Additional analyses of distilled fractions are shown in Figure 5.5. As shown, oxygen was only found in heavier fractions. The jet fraction pour point temperature was measured at -36°C, which was still higher than the target -40°C, likely due to the larger molecular weight compounds found in the GC-MS analysis of this fraction (Figure 5.5, lower right corner). As will be shown below, adjusting the boiling point cuts to maximize the jet fuel yield will be necessary.

	C	H	N*	S*	O*
Light Gasoline	83.55 ± 1.07	16.55 ± 0.18	*0.34 ± 0.52*	*0.02 ± 0*	*0.02 ± 0*
Jet	85.28 ± 0.11	15.78 ± 0.03	*0.17 ± 0.04*	*0.01 ± 0*	
Heavy diesel + Heavies	85.29 ± 0.14	15.68 ± 0.02	*0.30 ± 0.18*	*0.01 ± 0*	

* Below calibration (negligible)

	Density, g/cc**	API-D	Viscosity, cST**
Light Gasoline	0.6727 ± 0.00	0.6744	0.4877
Jet	0.7564 ± 0.00	0.7609	1.6407
Heavy diesel + Heavies	0.7836 ± 0.00	0.7875	5.9295

** at 20C

	Cloud Point, C	Pour Point, C
Jet	-31.5	-36.0
Heavy diesel + Heavies	< 21	18

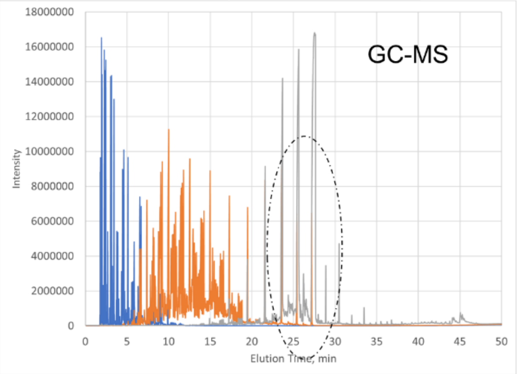


Figure 5.5 Analyses of the various distilled fractions

Tests in the 400 mL continuous co-hydrotreatment system: To produce larger amounts of jet fuel for analysis and testing, the 400 mL reactor was used at PNNL. For several years, the reactor was heated using a heater jacket filled with hot oil. More recently, it was heated to target reactor temperatures using four (4) zones heated electrically.

Based on Table 5.3, hydrocarbons produced from the 400 mL reactor could have the same elemental analysis as 40-60 mL reactor. Distillation cuts can also be better optimized from the typical range of 150°C – 250/260°C.

Table 5.3 Comparison of the elemental analyses from products produced in the lab scale (40-60 mL) and in the bench (400 mL) scales

		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

Table 5.4 Cloud point and pour point properties from products produced in the lab scale (40-60 mL) and in the bench (400 mL) scales

	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

One challenge encountered was the very brief co-processing time at the larger reaction system. The longest time on stream before a run was stopped due to plug formation was 32 hours of co-processing yellow grease and pyrolytic lignin + butanol. It is possible that heat and mass transfer played a role in the scaled up results. Analysis of the jet fraction during this campaign showed that 50:50 mix of co-processed jet fuel and petroleum Jet A can satisfy expected jet fuel properties, as shown in Figure 5.6. Properties tested included surface tension, density, viscosity, lower heating value, flash point, derived cetane number and freeze point.

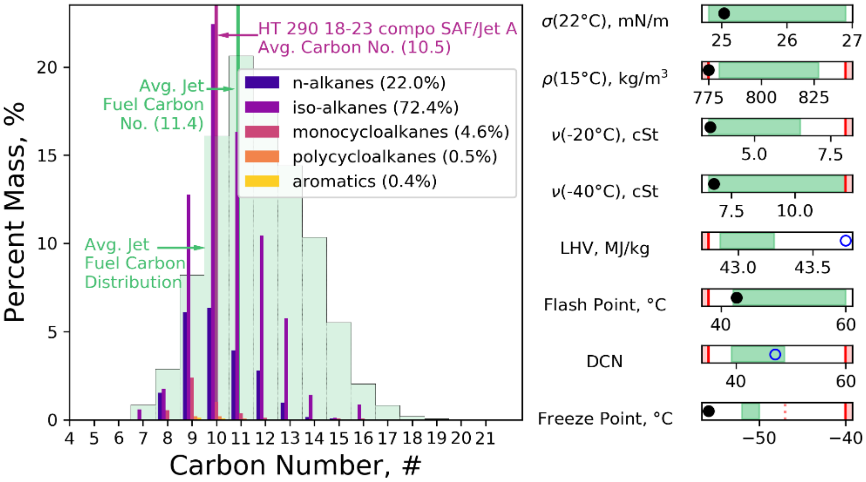


Figure 5.6 Analysis of 50:50 HT290 SAF cut: Jet A blend

Test in the 20 L hydro treatment unit. Due to safety concerns, PNNL management did not allow the operation of the 20 L hydrotreatment unit. This unit is now transferred to a private company and is currently in service as of the author's knowledge.

Task 6: Techno-economic, Life cycle Assessment and Supply Chain Analysis: This task is needed to compare the technical-, economic- and environmental performance of the HEFA/HDCJ proposed and to design a supply chain in Washington. Two papers were published with the initial results of this task. PI Responsible:

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

Pinheiro Pires AP, Martinez-Valencia LM, Tanzil AH, Garcia-Perez M, Garcia-Ojeda JC, Bertok B, Heckl I, Argoti A, Friedler F: Synthesis and Techno-Economic Analysis of Pyrolysis Ooil Based Refineries Using P-Graph, Energy & Fuels, **2021**, 35, 16, 13159-13169

Study 5.1. Mass balances of all the HEFA/HDCJ design cases. The yield of products obtained in batch hydrotreatment conditions were used as starting point to conduct the mass balances of the different schemes studied. (PI Responsible: Manuel Garcia-Perez and Xiao Zhang)

Case 1: Bio-oil Blend with Yellow Greases

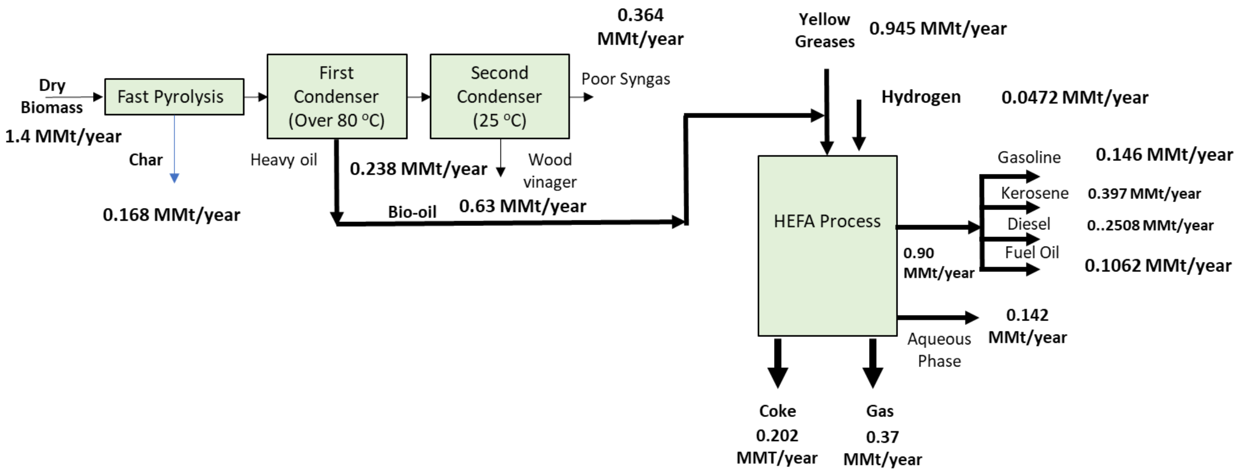


Figure 11. Mass Balances for the case Bio-oil is co-processed with fellow greases

Case 2: Bio-oil Blend with Yellow Greases but Adding Butanol (Denson et al. 2024)

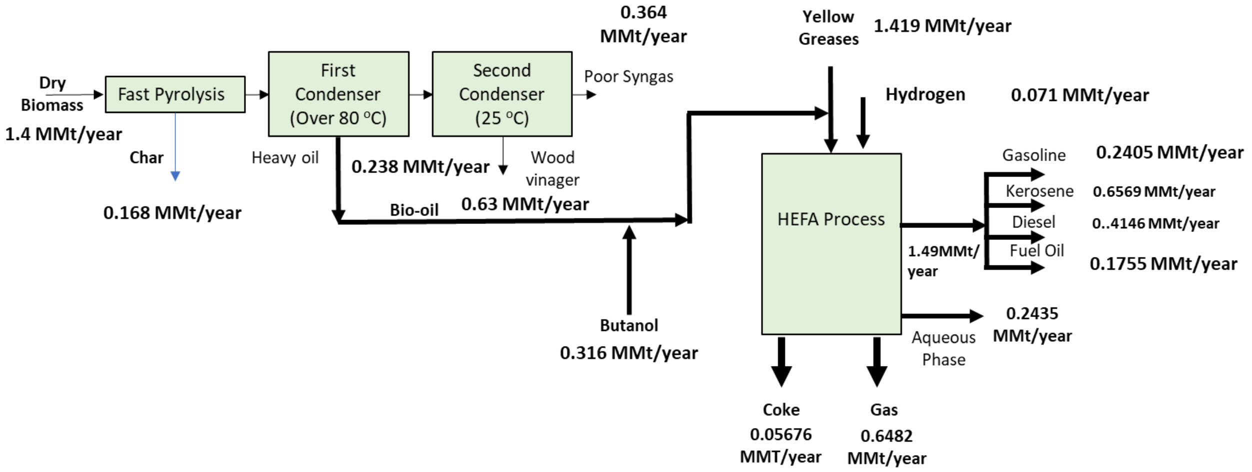


Figure 12. Mass Balances for the case Bio-oil stabilized with butanol is co-processed with yellow greases

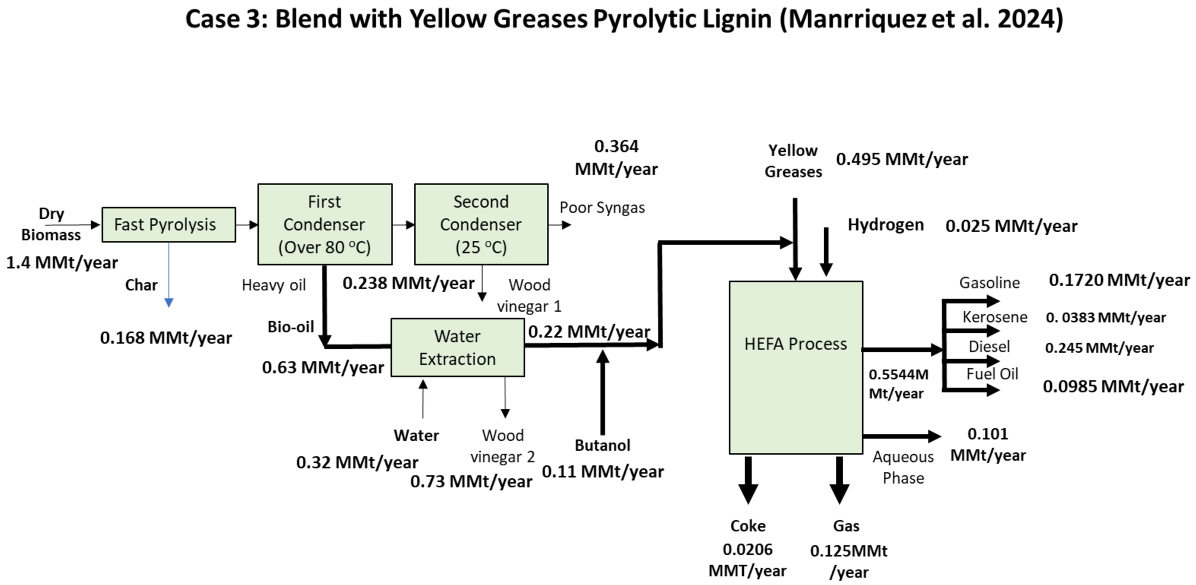

Case 3: Blend with Yellow Greases Pyrolytic Lignin (Manrriquez et al. 2024)

Figure 13. Mass Balance for the case in which the pyrolytic lignin stabilized with butanol is co-processed with yellow greases

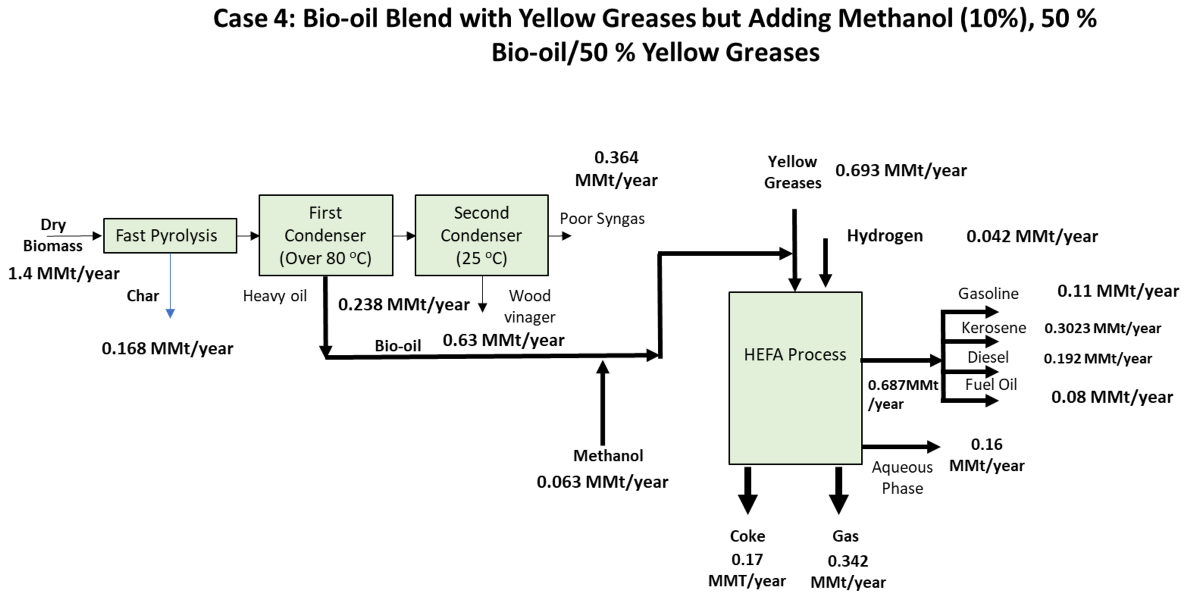

Case 4: Bio-oil Blend with Yellow Greases but Adding Methanol (10%), 50 % Bio-oil/50 % Yellow Greases

Figure 14. Mass Balance for the case in which the Bio-oil was stabilized with 10 wt. % methanol is co-processed with yellow greases (1 Bio-oil :1 Yellow Greases).

Study 6.2 Techno-economic Analysis: We conducted TEAs of the concepts shown in Figures 11, 12 and 13 for an nth plant with a depreciation schedule of 7 years double declining balance to straight line. Straight line duration: 10 years. All the estimations were made for 2021. The char produced was commercialized at $ 400/ton and the wood vinegar at $ 200/ton. We used the following design and financial indicators:

Table 1. Design and Financial indicators used in our TEA.

Parameter	Value	Unit
Real cost of equity	%	10
Corporate Tax Rate	%	17.3
Inflation	% / year	2
Equity share	%	30
Loan Interest rate	% / year	8
Loan Term	years	10
Property Insurance	% FCI	1
Local Taxes	% FCI	1.5
Feedstock		Forest Residues
Feedstock price	$/dry ton	60
Facility scale	MMt/year	1.4

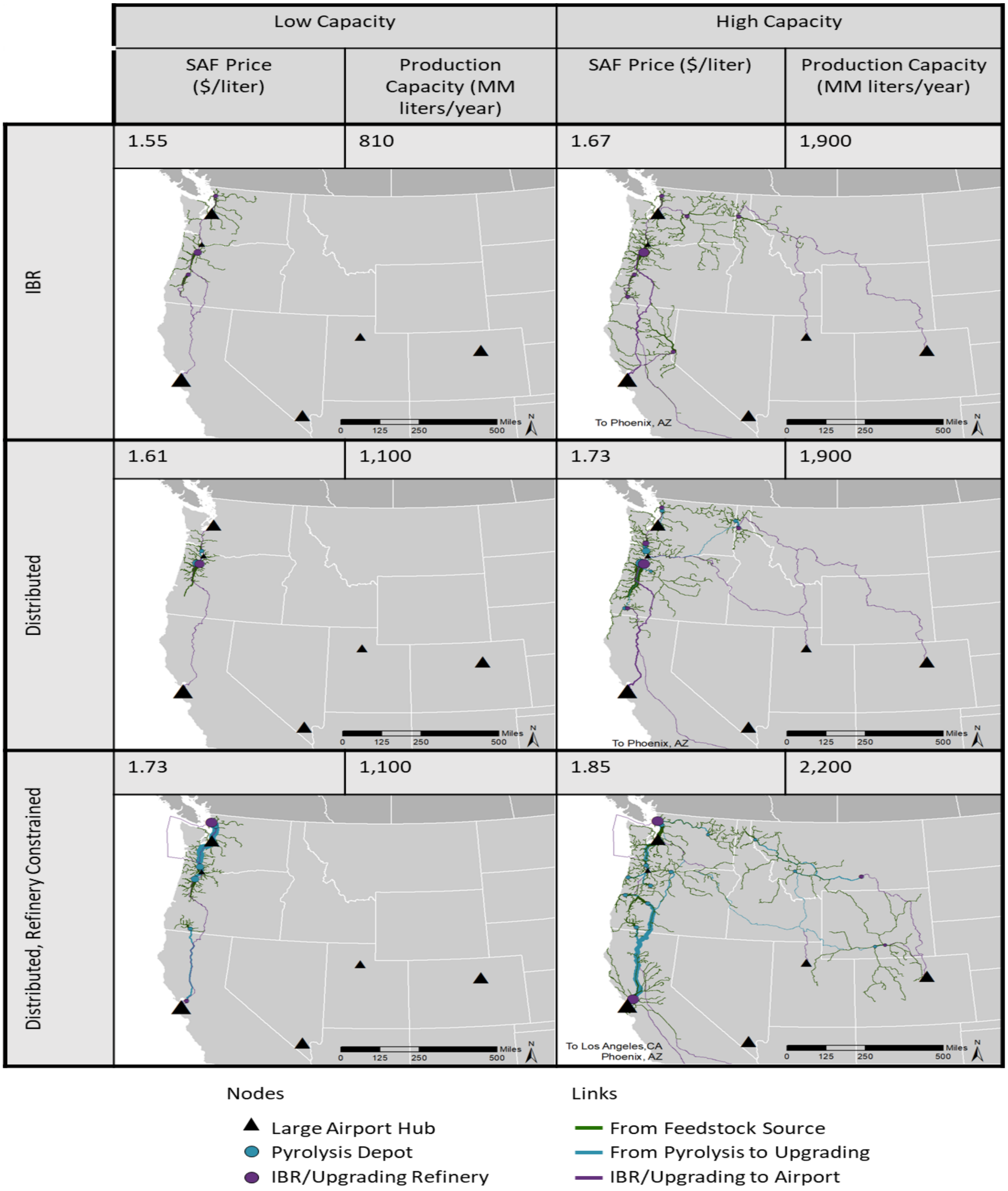
The minimum fuel selling price for the fuels produced is presented in table 2. Although the minimum fuel selling price obtained when the bio-oil was co-processed with yellow greases was lowest, the fixed bed hydrotreatment reactors cannot operate reliably with such levels of coke formation. More coke tolerant reactors such as the moving beds need to be tested.

Table 2. Minimum fuel selling price of the fuels produced ($/L)

Fraction	Case 1: Whole Bio-oil co-processed with Yellow greases	Case 2: Whole Bio-oil with butanol co-processed with Yellow greases.	Case 3: Pyrolytic lignin and butanol co-processed with Yellow greases	Case 4: Bio-oil stabilized with 10 % methanol and co-processed with Yellow greases
Kerosine (SAF)	0.68	0.86	0.95	0.88
Diesel	0.69	0.87	0.97	0.90
Gasoline	0.65	0.81	0.90	0.83
Bunker Fuel	0.66	0.84	0.93	0.86

Study 6.3 Supply chain analysis in Washington State: In this task we will use geographically-explicit information to design jet fuel supply chains (PI Responsible: Michael Wolcott)

Our supply chain analysis used Many-Step Transshipment Solver (MASTRS), an optimization-based supply chain management tool that was developed to provide detailed analyses of regional-scale supply chains with a focus on bioproducts. MASTRS provides options to create models with varying configurations, multiple methods to create and add facility candidates, and the ability to complete batch modeling. In this manuscript, a supply chain that produces sustainable aviation fuel (SAF) from three sources of woody biomass produced within the western United States was modeled as a case study. Performance of three production scenarios is considered: (1) a greenfield integrated pyrolysis biorefinery scenario that converts biomass into fuel at a single location; (2) a distributed scenario that converts biomass to bio-oil at one or more greenfield pyrolysis depots, which is subsequently converted into finished distillates at a greenfield upgrading refinery; and (3) a distributed model that constrains upgrading refinery locations to existing petroleum refineries. Greenfield facility candidates were sited by the MASTRS candidate generation procedure. It was found that an integrated biorefinery model was the lowest cost scenario, producing SAF at a minimum selling price. This demonstration illustrates how MASTRS can be used to determine where and at what price fuel becomes economically feasible, how the supply chain scales with new capacity and the performance of different supply chain configurations. Figure 14 shows capacity production configurations for different models.



	Low Capacity		High Capacity	
	SAF Price ($/liter)	Production Capacity (MM liters/year)	SAF Price ($/liter)	Production Capacity (MM liters/year)
IBR	1.55	810	1.67	1,900
Distributed	1.61	1,100	1.73	1,900
Distributed, Refinery Constrained	1.73	1,100	1.85	2,200

Figure 14. Low (left) and high (right) capacity production for the three configurations.

Task 7: Fuel properties: The main goal of this task is to study the fuel properties of all the fuel cut obtained. (PI Responsible: Manuel Garcia-Perez)

Study 7.1. Chemical composition and fuel properties of transportation fuel cuts. All the fuel cuts were thoroughly analyzed. The results of the analysis were reported in the following papers.

(1) 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

(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

(3) Marique RJW, Chejne F, Olarte M, Garcia-Perez M: Co-hydrotreatment of Pyrolytic Lignin and Cooking oil to Produce Hydrocarbons. Energy & Fuels, **2024**, 38, 9, 7917-7928

(4) Domes-Denson M, Manrique-Waldo RJ, Olarte M, Garcia-Perez M: Co-hydrotreatment of Bio-oil and Waste Cooking Oil to Produce Aviation Fuels. Energy & Fuels, **2024**, 38, 6982-6991

7. Significant Accomplishments and Conclusions:

The main challenge to process pyrolysis oils is its tendency to form coke. When using precious metal catalysts it is possible to use fixed bed reactor. However, these catalysts tend to deactivate in the presence of S and are very expensive. The other option available today is to use hydrocracking units that are tolerant to very high levels of coke in which most of the bio-oil is converted to coke without significantly affecting the operation of these units but resulting in the production of very low yield of oils. Our project proved that it is possible to reduce the tendency of the oils to form coke using technological solutions. Oils stabilized with alcohols and co-processed with lipids result in lower coke formation. Although we were able to operate a 100 mL fixed bed unit satisfactorily for 136 hours, the levels of coke formed in a 400 mL fixed bed unit did not allow us to operate reliable that unit. Still we believe that a more tolerant moving bed unit would have allowed our team to achieve satisfactory operation without using precious metal stabilization catalysts. Unfortunately, our team did not have a moving bed unit to conduct this study.

8. Path Forward:

Based on the experience acquired in this project, the PIs believe that it is possible to reliably hydro deoxygenate pyrolysis oils without using precious metal catalysts. However, a combination of technological solutions that we could not study in this project is needed to achieve reliable operation. We recommend to study in more details stabilization with Ni, in conjunction with the use of alcohols to stabilize the oil. The co-processing with lipids seems to be a promising option to reduce coke formation. However, we need to study technological solutions in which the lipid or other more stable liquid is also used as a heat carrier. The lipid can be heated and blended hot with the pyrolysis oil to achieve very high heating rates and reduce coke formation. More studies are needed to identify the main fractions responsible for coke formation. The removal of these fractions could result in lower coke yields. Because the tolerance of fixed beds to coke formation is very low, it is critical to create experimental facilities where hydrotreatment studies can be conducted in moving beds.

9. Products:

Peer-reviewed Publications:

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. Han Y, Pires A, Garcia-Perez M: Co-hydrotreatment of Bio-oil lignin-rich fraction and Vegetable oil. *Energy & **Fuels***, **2020,** 34, 516-529
3. Pinheiro-Pires AP, Arauzo J, Fonts I, Domine ME, Fernandez-Arroyo A, Garcia-Perez ME, Montoya J, Chejne F, Pfromm P, Garcia-Perez M: Challenges and Opportunities for Bio-oil Upgrading and Refining: A review. *Energy and Fuels*, **2019**, 33, 6, 4683-4720
4. 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
5. 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 Results. ChemSusChem, **2020**, 4428-4445
6. 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
7. Terrell E, Garcia-Perez M: Novel Strategy to Analyze FT-ICR MS Data of Biomass Pyrolysis Products for Oligomeric Structure Assignment. Energy and Fuels, **2020,** 34, 7, 8466-8481
8. Han Y, Paiva-Pires A, 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
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10. 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. Energy & Fuels, **2023**, 37, 7, 5189-5205
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12. 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
13. Domes-Denson M, Terell E, Kostetskyy, P, Olarte M, Broadbelt L, Garcia-Perez M: Theoretical Insights on the Fragmentation Reaction of Oligomeric Sugars to Remove Acetol and Glycoaldehyde. Energy & Fuels, **2023**, 37, 18, 13997-14005
14. Manrique R, Chejne F, Olarte M, Garcia-Perez M: Co-hydrotreatment of Pyrolytic Lignin and Waste Cooking Oil to Produce Hydrocarbons. Energy & Fuels, **2024,** 38, 9, 7917-7928
15. Rojas-Salas M, Gomez-Fonseca F, Correa de Araujo AC, Garcia-Perez M, Funke A: Liquid-Liquid Equilibrium Prediction in Fast Pyrolysis Bio-oil Systems; A Framework for Incorporating Bio-oil Complexity. Energy Fuels, **2024**, 38, 19, 18769-18780
16. Domes-Denson M, Manrique-Waldo RJ, Olarte M, Garcia-Perez M: Co-hydrotreatment of Bio-oil and Waste Cooking Oil to Produce Aviation Fuels. Energy & Fuels, **2024**, 38, 6982-6991

Presentations:

1. Garcia-Perez M: Co-hydrotreatment Tcbiomassplus 2019, Chicago, Oct 7-9, **2019**
2. Terrell E: Stochastic modeling and experimental analysis of lignin pyrolysis to estimate the effects of direct oligomer vaporization. Virtual TCS 2020, Richland Oct 5-7, **2020**
3. Terrell E: Proposed structures for the ologomeric fraction of bio-oil through fragmentation modelling coupled with FT-ICR-MS analysis. Virtual TCS 2020, Richland, Oct 5-7, **2020**
4. Han Y: Ternary phase diagram of water/ bio-oil/organic solvents for bio-oil fractionation. Virtual TCS 2020, Oct. 5-7, **2020**
5. Pinheiro-Pires AP: P-graph as a tool to select viable biorefineries. Virtual TCS 2020, Oct 5-7, **2020**
6. Garcia-Perez M, Elucidating pyrolysis oil oligomeric Chemical structures: Experimental studies and DFT calculations. Pyroliq II, Viena Austria, May 9 **2023**
7. Denson M, Olarte M, Garcia-Perez M: Co-hydrotreatment of bio-oi and yellow greases using NiMo catalyst. Pyroliq II, Viena Austria, May 10, **2023**

10. Project Team and Roles:

Dr. Garcia-Perez acted as the PI for the project. Dr. Garcia-Perez and his team have been working on projects related to the pyrolysis of forest and agricultural biomass into bio-fuels, co-products and char.

Dr. Michael Wolcott is Regents Professor and LP Distinguished Professor in Washington State University's Department of Civil and Environmental Engineering. He is also a member of the interdisciplinary Materials Science and Engineering faculty and a researcher in the Composite Materials and Engineering Center. Wolcott led the supply chain analysis study.

Dr. Xiao Zhang is a professor at the Bio-products, Sciences & Engineering laboratory at the Washington State University Tri-cities campus. Dr. Zhang is known for his contributions to advance the science and technology of lignin depolymerization and pulp and paper chemistry. He led the TEA studies.

Dr. Mariefel Olarte is a Senior Research Chemical Engineer at PNNL*,* Dr. Olarte developed expertise in catalytic aqueous phase reforming of woody biomass, acid hydrolysis in aqueous and ionic liquid systems, base-catalyzed depolymerization of lignin, and catalyst development for hydrodeoxygenation of biomass-derived compounds using supported nickel and phosphide catalysts. She led the continuous hydrotreatment studies

Mr. Andrew Schmidt acted as the manager for Hydrothermal Liquefaction activities. Mr. Schmidt (M.S. ChE) has been with the PNNL since 1988. His project management and research experiences at PNNL over the past 30 years have been focused on biomass conversion, hydrothermal processing, separations processing, and radioactive waste management.

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