ASCENT 1
Alternative Jet Fuel:
Co-Processing Bioliquids in Petroleum Refining Processes

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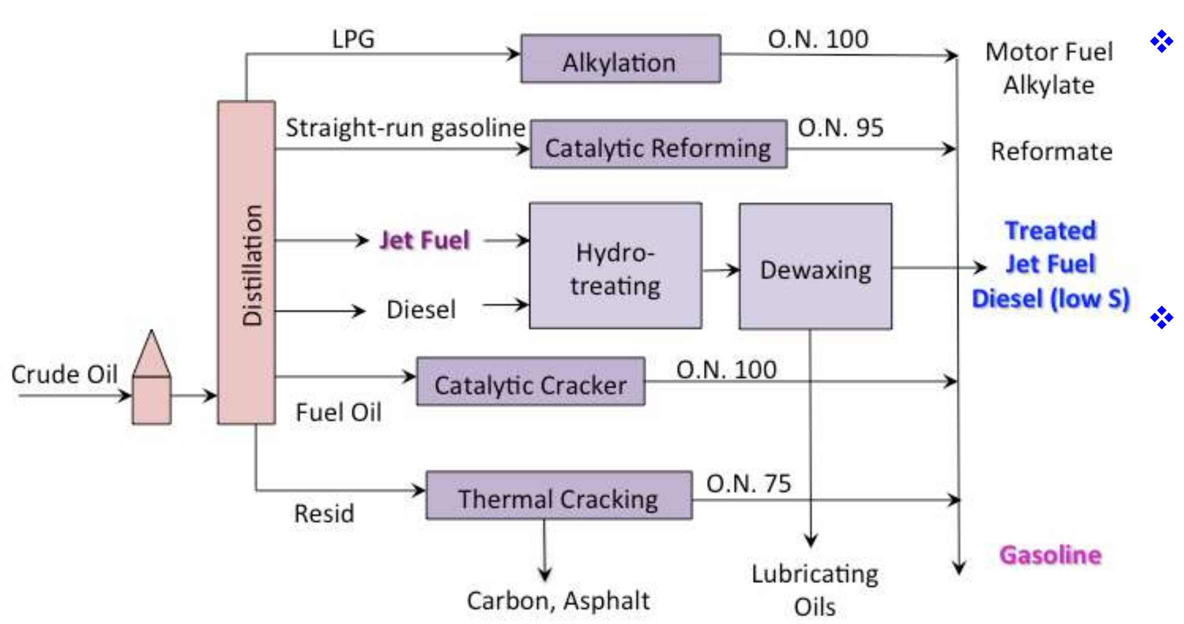
Motivation and Objectives

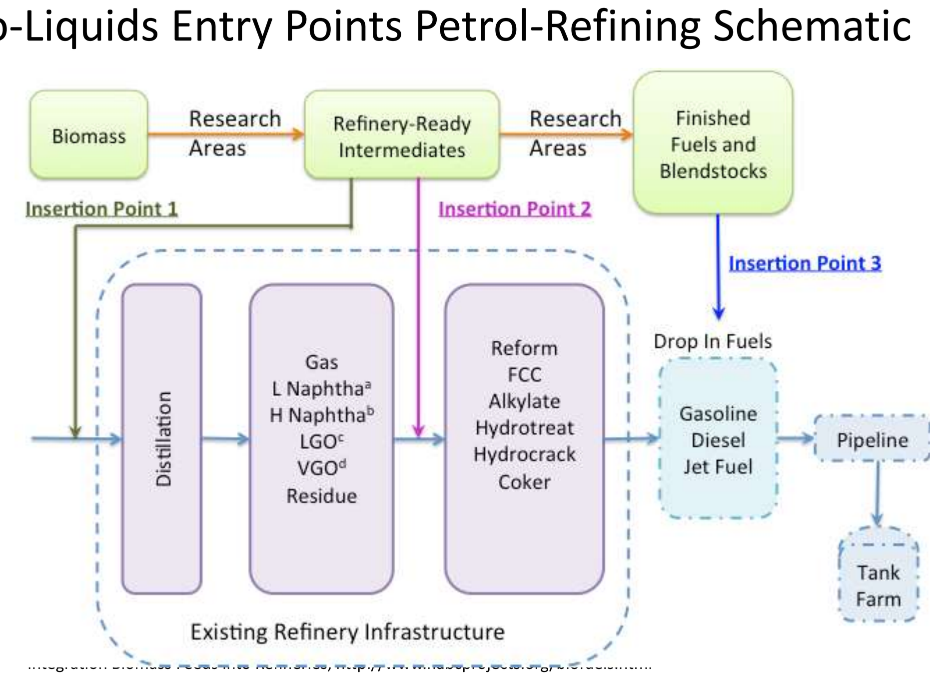
- The Federal Aviation Administration (FAA) – supporting development of alternative jet fuels (AJF) derived from biomass
- Military and commercial aviation sectors have set greenhouse gas (GHG) emission reduction targets and are entering into contracts and offtake agreements with biofuel producers.
- Scale-up of new, stand-alone AJF technologies has been slower than anticipated. Petroleum refineries supply transportation fuels and have distribution systems to airports in place
- Therefore, incorporating biomass-derived liquids (bio-liquids) into petroleum refineries can make producing and blending alternative fuels more practical and incentivize petroleum companies to invest in production of AJF and other biofuels.

Simple Petroleum Refining Schematic



- Primary product in refinery
  - Gasoline
  - By Alkylation and Cat Reforming
  - To increase yield and octane # gasoline
- Main processes to make jet fuel and diesel
  - Hydrotreating
  - Fluid Catalytic Cracking
  - Processes good for larger molecules

Bio-Liquids Entry Points Petrol-Refining Schematic



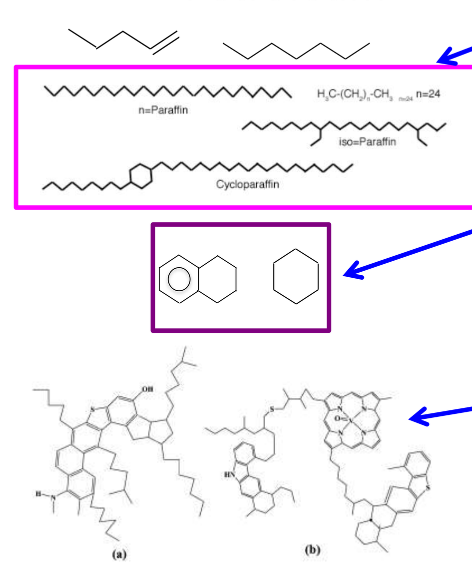
- Three probable entry points for bio-based liquids into a refinery
- **Insertion point 1**: least desirable insertion point. Bio-based liquids contain oxygen and olefins, and could cause problems for jet fuel production and quality, as many refineries produce jet fuel directly from the crude unit. These and any other contaminants within the bio-crude would also be spread throughout the refinery if introduced here.
- **Insertion point 3:** more desirable insertion point for bio-based liquids; bio-based liquid must be converted to a near-finished fuel. Component blended must meet the ASTM standards for fuel. In the case of jet fuel, the product must also meet certification standards as a blend. Some renewable fuels can enhance properties of fuel compared to traditional petroleum-derived.
- **Insertion point 2:** more desirable insertion point for bio-based intermediates. Several refining processes can be utilized to convert the bio-based liquid into fuels. Conversion processes will alter the size, shape, and hydrogen content of molecules; these include hydrocrackers, fluid catalytic crackers (FCC), and cokers. The main factors that must be taken into account are 1) bio-based liquids must not harm or reduce the life of catalysts and reactors, 2) product yield cannot be reduced, and 3) product quality cannot be compromised.

Conclusions and Next Steps

- Focusing on two main processes for refinery integration
  - **FCC**
  - **Hydrogenation**
- Easier to process vegetable oils in both processes compared to pyrolysis oils
- Pyrolysis oils easiest to process using hydrogenation, products tend to be mainly aromatic (which causes coking of catalyst in FCC) – can be used in low blends with hydrogenated pyrolysis oils
- This review expanded on types of catalysis used or potential of use
- Oxygenated functional groups may need to be removed using catalysts not well-known in the petroleum industry.

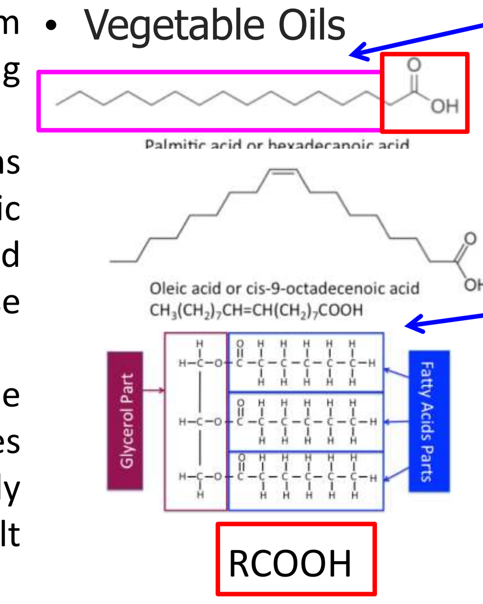
Insertion Point 2: Bio-liquid Intermediate in a Petroleum Refinery – Chemical Structures

Petroleum



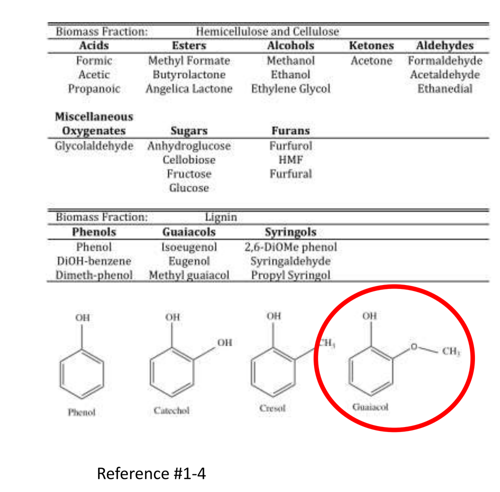
- Primary petroleum compounds are long alkane chains
- Petroleum contains some hydroaromatic components and cycloalkanes (these good for jet fuel)
- Large molecule called asphaltenes are removed early on to make asphalt or carbon materials

Vegetable Oils

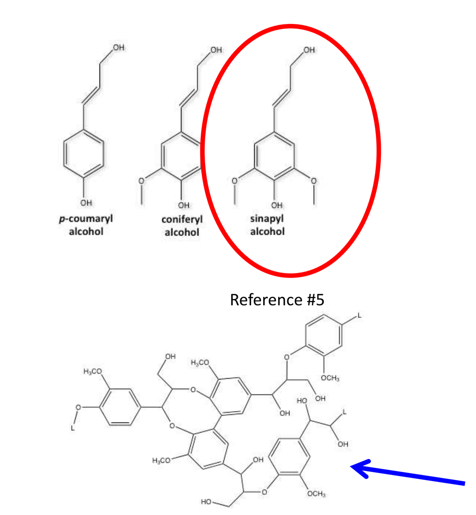


- Primary component of vegetable oils is long chain alkanes, but with carboxylic acids and esters
- Original structure of vegetable oil is triglyceride
- Must break triglyceride down into fatty acids, then remove acid groups

Pyrolysis Tars

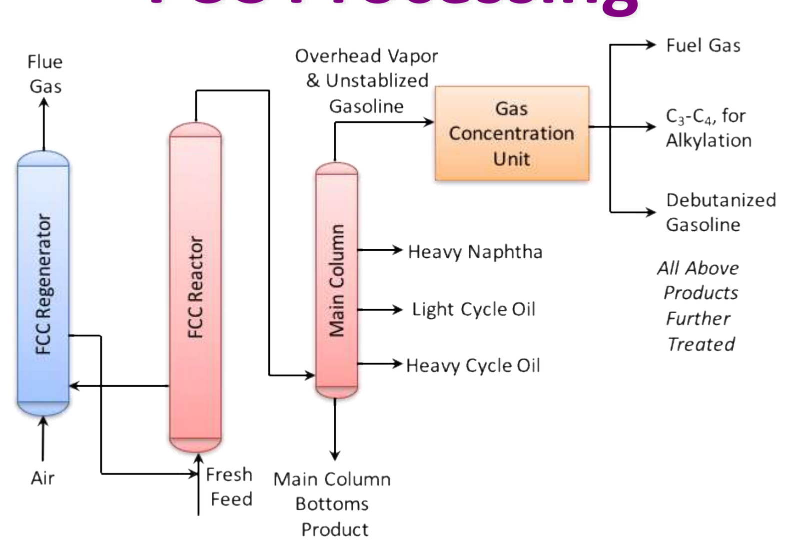


Lignin By-Product



- Primary component of pyrolysis tars and lignin is aromatic components, but with hydroxy (OH) groups and esters
- Any process must remove oxygenated components
- Original structure of lignin is made up of building blocks of alcohols with methoxy groups (circled in red)
- Possible lignin molecule

FCC Processing



- Typical feed to FCC unit: heavy gas oils – unit breaks larger molecules into smaller components. Coke deposited on catalyst, so constant regeneration as well as new added catalyst when needed.
- Schematic of typical unit shown to the left. Several feeds have been considered: treated microalgae bio-crude, microalgae oil, vegetable oils, and pyrolysis oils.
- Catalysts: Typical catalysts used in FCC: zeolites, such as H-Y and HZSM-5 (aluminosilicate catalysts with various cations depending on the application or substrate).

Table 1: PNNL Pyrolysis Oil Hydrotreating for FCC

Degree Catalytic Hydrotreating	Max VGO Feed Preheat Temperature	Percentage of pyrolysis oil	Yield observation
(O wt %, dry)	(without nozzle plugging)	(co-processed)	(while co-processing)
None (38 %)	93 °C (~200 °F)	Up to 5 wt %	↑ Coke, ↓ Gasoline
Mild (22 %)	93 °C (~200 °F)	Up to 3 wt %	↑ Coke, ↓ Gasoline
Medium (11 %)	370 °C (Up to 700 °F)	10 %	Similar to VGO
Severe (2 %)	370 °C) (Up to 700 °F	10 %	Similar to VGO

- Study by PNNL on pyrolysis oils blended with petroleum feeds in FCC. Holladay, J., "Refinery Integration of Renewable Feedstocks," Presentation, *CAAFI R&D*, SOAP-Jet webinar series, **November 14, 2014.**
- For FCC processing of pyrolysis oils, even low oxygen percentage feeds of pyrolysis oils caused significant shifts in yields. PNNL concluded that pyrolysis oil feeds would need to be hydrotreated to reduce oxygen content to ≤ 11% - see results in Table 1.

Vegetable Oils FCC Catalysts

- HZSM-5 main catalyst used
  - Lower coke formation
  - Main products hydrocarbons
- Other catalysts include:
  - MCM-41 (better for kerosene production)
  - $ZnCl_2$
  - Silica-alumina
  - Al_2O_3, MgO
  - K-HZSM-5 , Pt-HZSM-5 and additional catalysts

Vegetable Oils FCC Processing Outcomes

- Primary product gasoline
- Relatively easy to process vegetable oils
- Higher conversion than other bio-liquids
- Affect on product distribution
  - Increased water, oxides, LPG, gas
  - Decreasing yields of gasoline and middle distillates

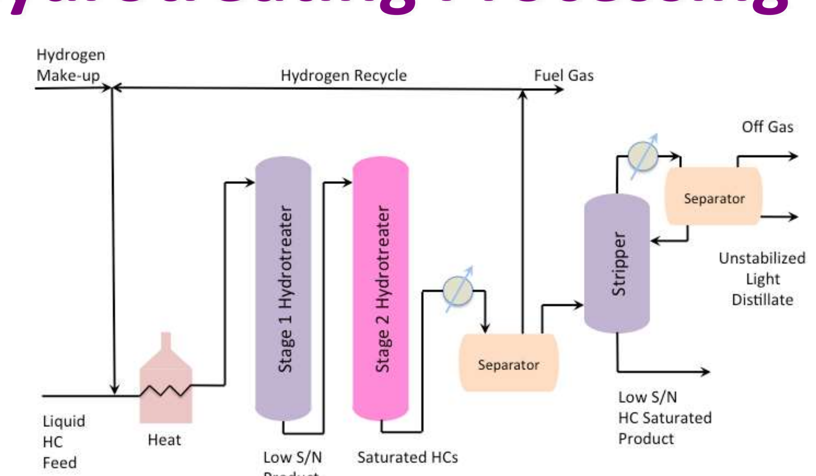
Pyrolysis Oils Catalysts

- Zeolites (cracking catalysts)
  - HZSM-5**, ZSM-5, H – Y*
  - H– mordenite, silicate, and silica– alumina catalysts
- HZSM-5 most effective catalyst on pyrolysis oils
  - Yielded organic distillates, overall hydrocarbons, and aromatics
  - Yielded the least amount of coke

Pyrolysis Oils Processing

- Pyrolysis bio-oils major problems during FCC operation – very dependent on conditions
- Problems mainly related to reactor plugging due to formation of significant amounts of coke, tar, and char.
- Irreversible catalyst deactivation (loss alumina)
- Gasoline higher aromatic content, ↑ ON #

Hydrotreating Processing



- Common hydrotreating schematic is shown to the left.
- Hydrotreating is highly utilized in petroleum refining. In a first stage, often sulfur and nitrogen are removed using catalyst specifically for that – CoMo and NiMo metals on carbon and silicon supports. Hydrogenation of double bonds and aromatic compounds is incomplete with these catalysts, so a second stage is utilized using Pt and Pd supported catalysts.
- Based on study by Chevron and BP, the maximum amount of 5% vegetable oil co-processed with petroleum feeds because the water generated would cause problems for catalysts commonly used in refining. Similar catalyst to removing sulfur and nitrogen can be used for deoxygenation, but other potential catalysts include metal phosphides and $Pt/Nb_2O_5/SiO_2$ (Pd can be used as well) are being designed specifically to remove bio-based oxygen components. A future review will discuss this in greater detail.
- The HEFA process, below, which has been through the jet fuel certification process, is primarily a hydrotreating process for vegetable oils.
- Common catalysts used in various processes shown for each type of feed.

Vegetable Oils Hydrotreating Catalysts

- Co-MoS_2, Ni-MoS_2
  - Metal Sulfides
  - Support α-Al_2O_3
  - Can be deactivated processing oxygen to water (lose S or will coke)
  - Main catalyst used in industrial case
- Ru, Rh, Pd and Pt (can saturate double bonds)
  - Noble metals
  - Can have some hydrocracking, which shortens HC chain length, selective decarboxylation/decarbonylation
  - Support ZrO_2
  - Support Nb_2O_5-modified silica
  - Keep saturation to minimum
- MoO_3, Cr_2O_3, WO_3, Nb_2O_5, and V_2O_5
  - Metal oxides

HEFA Schematic

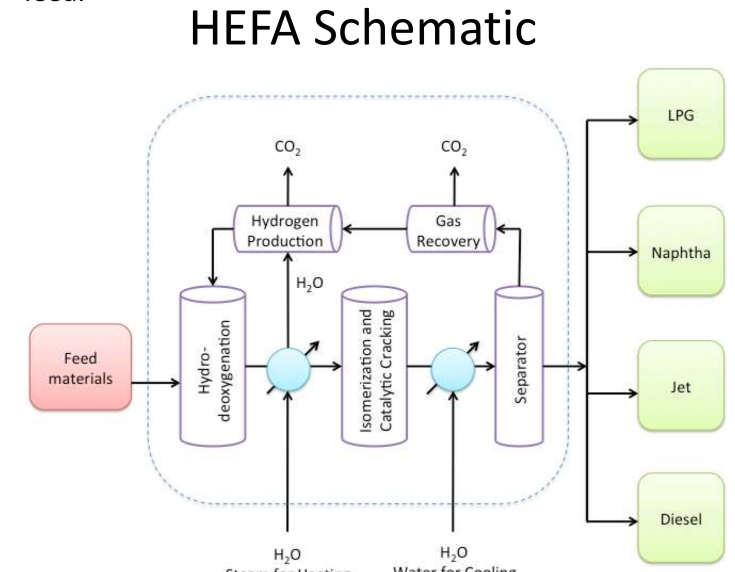
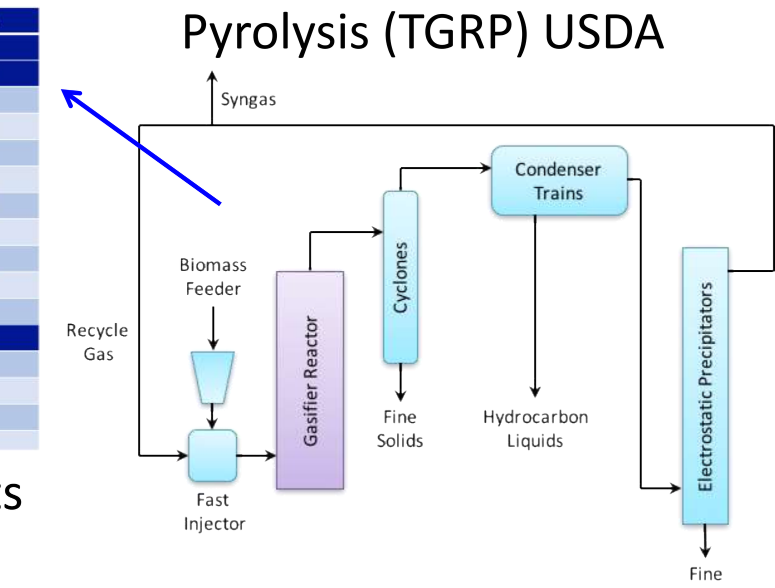


Table 2: Comparison of Oils from TGRP

Properties of Bio-oil	Oak Pyrolysis Oils		Switchgrass Pyrolysis Oils		Pennycress Pyrolysis Oils	
Recycle Percent	70		65-80	0	65-80	0
Catalyst	None	Beta-Zeolite	None	HZSM-5	None	None
Water (wt %)	4.79	7.7	3.2	5.1	10.2	7.7
Carbon (wt %, db)	80.24	76.5	80.29	68.55	68.37	69.01
Hydrogen (wt %, db)	5.88	5.63	5.67	5.74	8.3	8.35
Nitrogen (wt %, db)	2.07	0.28	1.5	0.74	8.1	7.14
Oxygen (wt %, db)	11.81	17.4	12.54	24.97	14.65	14.75
C/O	9.06	5.9	8.53	3.67	6.2	6.2
H/C	0.88	0.9	0.84	1	1.45	1.5
HHV (MJ/kg, db)	34	32.3	33.2	29.7	33.2	31.4
TAN (mg KOH/g)	55.8	68	24	51	76	84
Yields Products						
Bio-oil Organics	32	0	32	59	35	38
Water	27	10	23	11	16	14
Bio-Char	19	21	15	15	31	37
Non-condensable gases	22	15	30	15	17	11

Tail Gas Reactive Pyrolysis (TGRP) USDA



Pyrolysis Oils Hydrogenation Catalysts

- Co-MoS_2, Ni-MoS_2
  - Metal Sulfides
  - Support α-Al_2O_3
  - Directly to benzene w/out hydrogenating to cyclohexane
  - Can be deactivated processing oxygen to water (lose S or will coke)
- MoO_3, Cr_2O_3, WO_3, Nb_2O_5, and V_2O_5
  - Metal Oxides
- Ru, Rh, Pd and Pt (can saturate ring to cyclohexane)
  - Noble metals
  - Support ZrO_2
  - Support Nb_2O_5-modified silica
  - Keep saturation to minimum
- Ni_2P
  - Metal Phosphides
  - Supported on Al_2O_3, ZrO_2, and SiO_2
- W_2C and Mo_2C
  - Metal carbides

Hydrogenation Reaction Pathway Phenol to Benzene or Cyclohexane