Alternative Jet Fuel: Review of Current Viable Biomass-Based Sources and Technologies

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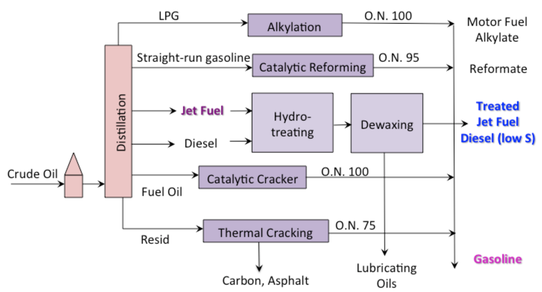
Introduction

- 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.

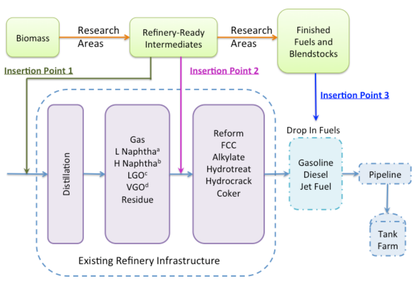
Figure 1: Simple Petro-Refining Schematic



- **Figure 2**. 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.

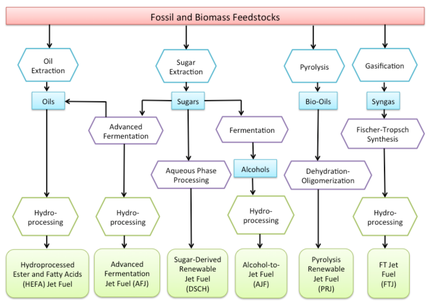
- **Figure 3** shows a schematic of the various bio-based AJF processes being developed for AJF production. All of these processes have been certified or in the process of being certified. More depth on each is shown on the poster.

Figure 2: Bio-Liquids Entry Points Petrol-Refining Schematic



Advanced Biofuels Processing and Integration, National Advanced Biofuels Consortium Integration Biomass Feeds into Refineries, http://www.nabcprojects.org/biofuels.html

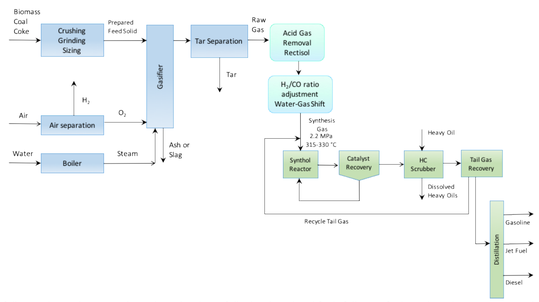
Figure 3: Bio-Liquid Processes Certified or in Certification Process



Malina, R., Pearlson, M., Carter, N., Bredehoeft, M., Wollersheim, C., Hakan, O., Hileman, J., and Barrett, S., "HEFA and F-T jet fuel cost analysis," *Laboratory for Aviation and the Environment, MIT, LAE.MIT.EDU,* **November 27, 2012.**

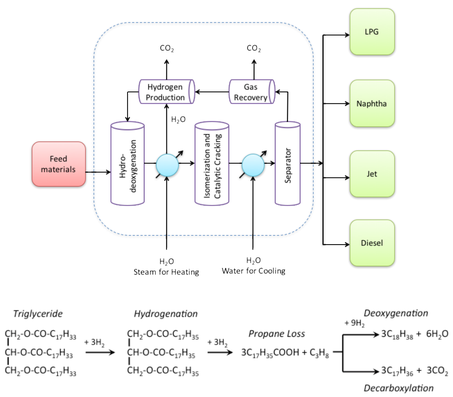
Insertion Point 3: Blend Ready Bio-Based Jet Fuel Processing

Figure 4: Gasification-FT



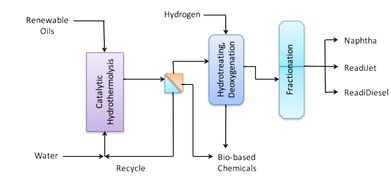
- Gasification following by Fischer-Tropsch synthesis has been fully developed and fuels fully certified. Bio-based sources are used as well as solid fossil fuels such as coal.
- One of the fuels that made it through the approval process is Synthetic Paraffinic Kerosene (SPK) made by Fischer-Tropsch synthesis (FTJ on Figure 3) (aka FT-SPK). An additional process has been developed to add aromatic compounds to the mix for jet fuel and uses the acronym FT-SPK/A. The main difference between FT-SPK and FT-SPK/A is in the process.
- Figure 4 shows the steps of gasification processing through FT synthesis from solid organic materials. **FT-SPK was certified in 2009 to be used in a 50% blend with traditional petroleum-derived jet fuel, and FT-SPK/A was certified in 2015 up to a 50% blend.**

Figure 5: HEFA



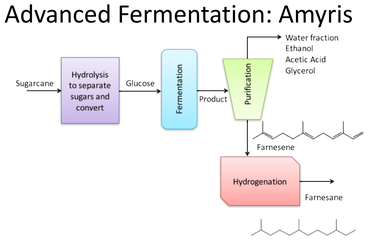
- The HEFA-SPK process has been developed for commercial production around the world to produce a drop-in jet fuel and diesel fuel in the middle distillate range (aka Green Jet Fuel, Green Diesel Fuel, and HRJ/HRD). Figure 5 shows process schematic and reaction chemistry.
- Companies currently producing HEFA-SPK fuels at commercial scales include Neste Oil in Europe and Asia and Syntroleum with Tyson Foods (Dynamic Fuels in Louisiana). **Jet fuel made from HEFA was certified for use in aircraft in 2011 up to a 50% blend.**
- In the first stage of the HEFA process, several chemical reactions occur; hydrogen is initially used to saturate carbon-carbon double bonds in the triacyl glyceride. Additional hydrogen is used in the second reaction, which removes the propane backbone of the triacyl glyceride; this leaves three free fatty acids per triacyl glyceride molecule. In the final stage, deoxygenation takes place using hydrogen, where the oxygen leaves as water, or with decarboxylation, where oxygen leaves as CO_2. The resulting product is alkyl hydrocarbon chains. The alkyl chains are preserved during hydrodeoxygenation (HDO), while the alkyl chains are shortened during decarboxylation (DCO).
- Pearlson, M. Wollersheim, C., and Hileman, J., *Biofuels, Bioproducts, and Biorefining,* **2013**, *7,* 89-96.
- Karatzos, S., McMillan, J., Saddler, J., "The potential and challenges of drop-in biofuels," *Task 39, IEA Bioenergy,* **July 2014,** *Report T39.*

Figure 8: Catalytic Hydrothermolysis Virent, ReadiJet



- Hydrothermal liquefaction (hydrothermolysis) is a process that utilizes water in the near supercritical to supercritical range. Process schematic shown in Figure 8.
- Several companies have developed processes related to subcritical water processing on a wide variety of biomass materials. For jet fuel processing, processes have been developed using vegetable, algae, and animal oils. Virent and Applied Research Associates (ARA), along with Battelle in Ohio, have produced ReadiJet Fuel (Renewable Aromatic Drop-In) using a pilot scale facility. While the front end is different than the HEFA process, it has also been called the HEFA-SKA process, as it has some aromatic material in it. **Advantage of this process: process utilizes water, so biomass does not need to be dewatered.**
- They are in partnership with Chevron Lummus Global, particularly for the upgrading of the biocrude. The benefit of their process is the production of a variety of compounds, including n-, iso-, and cycloparaffins, aromatics, olefins, and organic acids. Sapphire Energy/ConocoPhillips and PNNL have also developed catalytic hydrothermolysis processes, with interest in further processing in refining facilities. **The fuel from Virent is in the certification process.**
- Conkle, H.N., Marcum, G.M., Griesenbrock, E.W., Edwards, E.W., Chauhan, S.P., Morris, Jr., R.W., Robota, H.J., Thomas, D.K., "Development of Surrogates of Alternative Liquid Fuels Generated from Biomass," http://wbi-icc.com/wp-content/uploads/2012/06/paper - development of surrogates of alternative liquid fuels generated from biomass.pdf, accessed **June 17, 2014**

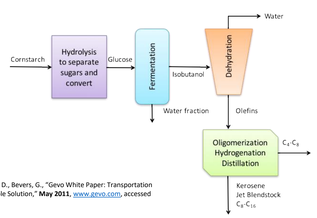
Figure 6: Direct Sugar to Hydrocarbon Advanced Fermentation: Amyris



Paris Air Show presentation, "Breaking the barriers with breakthrough jet fuel solutions," *Total/Amyris Renewable Aviation Fuel Joint Development Program,* Salon du Bourget, **June 2013**, http://www.alternativefuelsworldwide.com/presentations/TOTAL%20AMYRIS%20presentation%20Paris%20Air%20Show%2020-25%20min_v2.pdf, accessed **May 20, 2015.**

- Drop-in jet fuel pathway developed by Amyris, a company in San Francisco, CA with plants in Brazil, and Total, the global energy company operated out of France. Schematic is shown in Figure 6.
- Direct sugar to hydrocarbon (DSHC) method to produce a source of chemicals for jet fuel. Sugarcane is harvested and processed to produce sugar. Glucose from sugar is fermented to ethanol and additional products – farnesene, acetic acid and glycerol. This process maximizes the product farnesene, which is then hydrotreated to remove the double bond to produce farnesane; the structure of farnesane is a long chain isoparaffin molecule, $C_{15}H_{32}$.
- Currently the production is ~1 million liters of farnesane for diesel, but the process also produces jet fuel (~90,000 liters).
- It has been tested in a blend as high as 50% with conventional petroleum-based jet fuel, but it has been used in a 10% blend when tested in aircraft. **The jet fuel was certified and approved for commercial production, and to be blended with jet fuel at 10%, in 2014.** It is currently known by the acronym HFS-SIP, which stands for Hydroprocessed Fermented Sugar-Synthesized Iso-Paraffins (AFJ in Figure 3).

Figure 7: Alcohol-to-Jet: Gevo



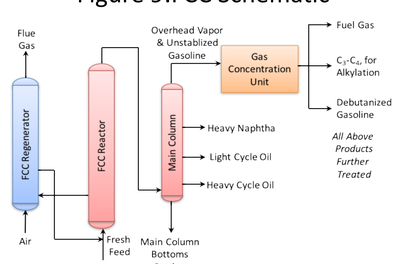
Ryan, C., Munz, D., Bevers, G., "Gevo White Paper: Transportation Fuels: Renewable Solution," **May 2011**, www.gevo.com, accessed **May 21, 2015**.

- In the current process for Alcohol-to-Jet-Fuel (AFJ, ATJ-SPK in CAAFI); main product is iso-butanol. Gevo developed a process to primarily produce iso-butanol due to genetic modification of yeasts. Process schematic shown in Figure 7.
- Iso-butanol can be used as a fuel itself, particularly for gasoline. However, the process developed specifically makes jet and diesel fuel. Once the iso-butanol is made, it is separated and dehydrated to produce olefins. Using oligomerization, hydrogenation, and distillation, a kerosene product is made containing C_8-C_{16}.
- The alternative jet fuel produced from this process is known as AFJ-SPK. **Certified for use in aircraft in April 2016, in a 50% blend with petroleum-derived jet fuel**.

Conclusions

- There are four processes that produce bio-jet fuel that have been qualified for use in aircraft: 1) the jet fuel from the gasification and Fischer-Tropsch processing (Sasol), 2) the jet fuel from HEFA processing (multiple companies), 3) production of farnesane produced directly from sugar (Amyris), and 4) alcohol-to-jet fuel (iso-butanol produced and further processed to produce C_{12}-C_{16} hydrocarbons, GEVO). Catalytic hydrothermolysis of microalgae is similar to HEFA processing and is being tested for qualification (ARA, Sapphire). These are bio-products that can be blended in with jet fuel feedstock and used as is. They would be blended directly with jet fuel (Insertion Point 3) and only a portion of the bio-jet fuel is blended with petroleum-derived jet fuel (10-50%); the amount of the bio-jet fuel blended depends on the process.
- There are several opportunities to incorporate bio-oils into various internal refinery processes, primarily the FCC unit, hydrotreating units, and delayed cokers. There has been research on bio-oils in the FCC unit and the hydrotreating units.
- Sapphire, PNNL, and several other researchers have tested microalgae bio-crude (hydrothermal liquefaction), vegetable oils, and pyrolysis bio-crude in typical FCC units. The microalgae bio-crude and vegetable oils are good candidates for processing in the FCC units. However, pyrolysis bio-crudes most often must be hydrotreated to remove oxygen before introduction into the FCC unit. PNNL found that bio-oils must have the oxygen content reduced to 11 % or lower before feeding into the FCC unit, otherwise significant changes in product concentrations occur.
- One group from the USDA has produced low-oxygen, low viscosity liquids from pyrolysis of biomass using recycle gases. They have been able to show a better quality liquid using a recycle gas (70-90 % of gas feed) than with nitrogen alone. However, when using this pyrolysis process, the yield of bio-oils decreases. The process is called tail gas reactive pyrolysis (TRRP)
- Some petroleum refining hydrotreating catalysts can be successfully used to deoxygenate bio-fuels. Future work will include more in-depth review study on deoxygenation of bio-based liquids, as functional groups in bio-based liquids may need to be removed using catalysts not well-known in the petroleum industry.

Figure 9:FCC Schematic



- 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.
- Figure 9 shows schematic of typical unit. Several feeds have been considered: Sapphire 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

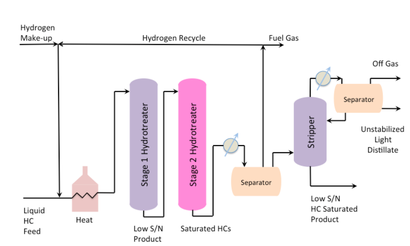
Degree Catalytic Hydrotreating	Max VGO Feed Preheat Temperature	Percentage of pyrolysis oil	Yield observation
(O wt %, dry)	(without nozzle plugging)	(co-processed)	(while co-processing)
None (38 %)	93 °C (~200 °F)	Up to 5 wt %	↑ Coke, ↓ Gasoline
Mild (22 %)	93 °C (~200 °F)	Up to 3 wt %	↑ Coke, ↓ Gasoline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

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

Vegetable Oils and Pyrolysis Oils as Intermediates

Figure 10: Hydrotreating Schematic

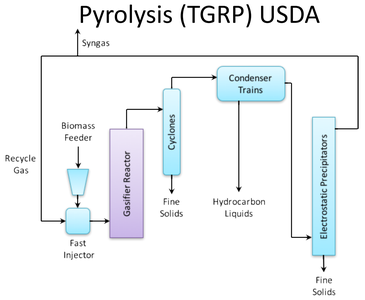


- Hydrotreating schematic is shown Figure 10.
- Hydrotreating is highly utilized in petroleum refining. In a first stage, often sulfur and nitrogen are removed using catalyst specifically for that – CoMo and NiMo metals on carbon and silicon supports. Hydrogenation of double bonds and aromatic compounds 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.

Table 2: Comparison of Oils

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

Figure 11: Tail Gas Reactive Pyrolysis (TGRP) USDA



- Oxygen in pyrolysis oils deters use in a petroleum refinery. This is a pyrolysis process to produce a low oxygen oil, developed at the USDA. Mullen, C.A., Boateng, A., and Goldberg, N., *Energy Fuels,* **2013**, *27* (7), 3867–3874.
- Process deoxygenates the biomass pyrolysis product using gas recycling. The gases provided a reducing environment for the pyrolysis process. Process schematic is shown in Figure 11.
- They have developed a portable processing unit that can be moved farm to farm in a particular geographic region.
- The reducing environment in the reactor provides gases that make a liquid product from pyrolysis that is much lower in oxygen than traditional fast pyrolysis units; the liquid product still contains some oxygen content, so it may need to be further processed. The overall yield is higher when using less product gas in the recycle, but the product oxygen content is higher.
- Table 2 shows the product properties of the oils with the lowest oxygen content compared to each other (pyrolysis oils from oak, switchgrass, and pennycress) and to products made with only nitrogen and upgraded using a catalyst.