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Prospects of pyrolysis of lignocellulosic biomass to produce marine biofuels

PNNL-ACT-SA-10195

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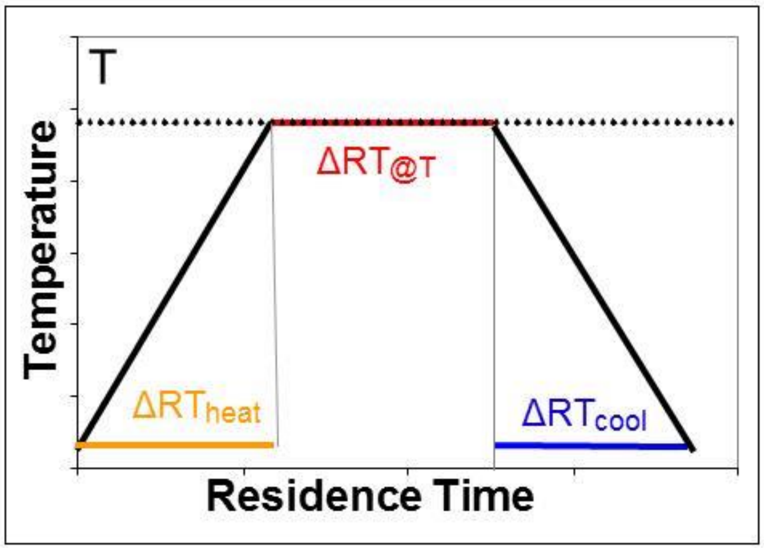
IEA Bioenergy ExCo78 workshop
Wednesday 9 November 2016, Rotorua, New Zealand

Outline

- What is pyrolysis?
- Bio-oil context as an energy carrier
- Characteristics of bio-oil
- Common upgrading approaches
- Upgrading considerations for marine fuel

What is Pyrolysis?
Direct Thermochemical Liquefaction (DTL)

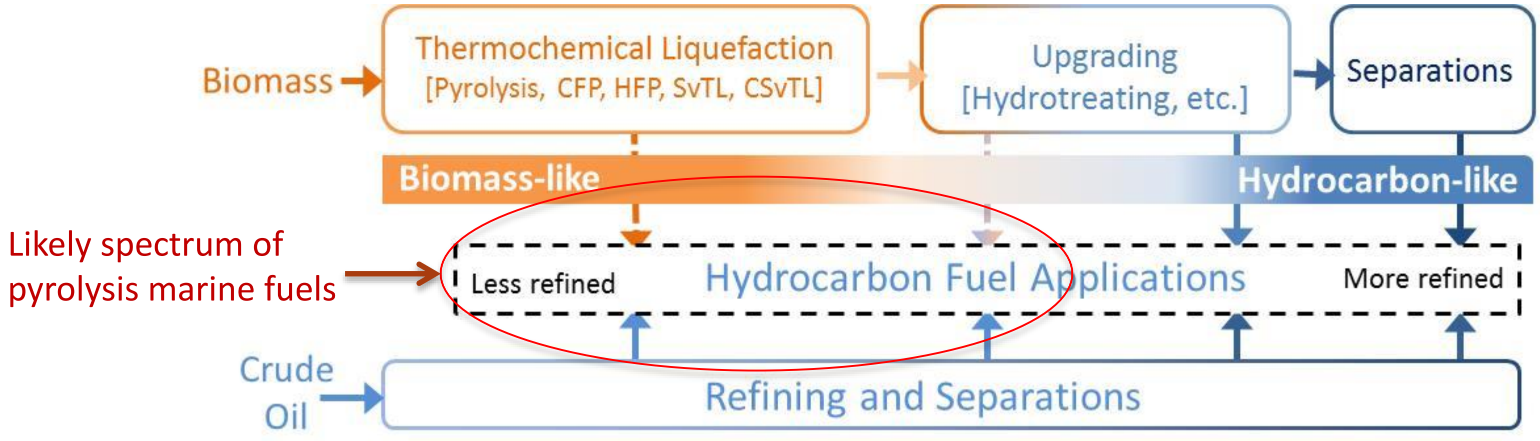
Pyrolysis: Thermochemical depolymerization of biomass in low oxygen environment to produce bio-oil or bio-crudes



Processes vary by equipment configuration, reaction media, reaction temperature (T), residence time (RT), heating/cooling rates (ΔRT), to determine product quality and yield

- Bio-oils: An energy carrier for end-use or as an intermediate
- Quality of bio-oil must be defined in context of an end-use
- DTL variations
  - Fast Pyrolysis (FP)
  - Catalytic Pyrolysis (CFP)
  - Hydropyrolysis (HFP)
  - Solvo-thermal Liquefaction (SvTL)
  - Catalytic SvTL (CSvTL)

Bio-oil context as an energy carrier



- Bio-oils are compositionally different than crude oils
- The spectrum of “raw to refined” bio-oils have been tested in engine and boiler applications
- Determine upgrading required for marine fuel applications

Pytec has tested Bio-oil in a modified 450 kWe diesel engine

BTG has tested a 1-cylinder CI-engine, adapted to run bio-liquids including pyrolysis oil

Comparison of Wood-Derived Bio-oils and Marine Fuel Specifications

Characteristic	FP Bio-oil	Marine Fuels* (ISO-F-DM_)	M. Resid Fuels* (ISO-F-RM_)
Water, wt%	15-25	<0.3	<0.3 – 0.5
Insol.solids, %	0.5-0.8	<0.1	<0.1
Sulfur, %	<0.05	<1 – 2	By statute
Ash	0.2-0.3	<0.01	0.04-0.15
HHV, MJ/kg	17	42	40
Density, g/ml	1.23	0.89-0.90	0.99-1.01
Viscosity, mm^2/s	30-85@40°C	1.4-11@40°C	10-700@50°C
Acid number, mg/KOH/g	80-120	<0.5	<2.5

- Undesired attributes include: Water content, energy density, solids, high viscosity, instability, miscibility, pH, combustion
- Desirable attributes include: Low sulfur
- Bio-oil is typically upgraded to address these characteristics in the end-use context

* Vermeire, M. B. (2007). Everything you need to know about marine fuels, Chevron Global Marine Products.

Common Upgrading Approaches

- Solvation: Diluents to improve characteristics or suppress chemical reactions
- Physical modifications: Separations, chemical treatment
- Catalytic Upgrading: Catalytic hydrogenation
  - Mild: Partial treatment to improve characteristics or reduce reactivity
  - Severe: Hydrodeoxygenation resulting in a hydrocarbon.
- Production modifications: DTL variations including CFP, HFP, SvTL, CSvTL
- End use modification: Changes to end-use engines, storage, handling

- All approaches add cost

Water Content

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Challenges

- Water Content: 15 to 25wt%

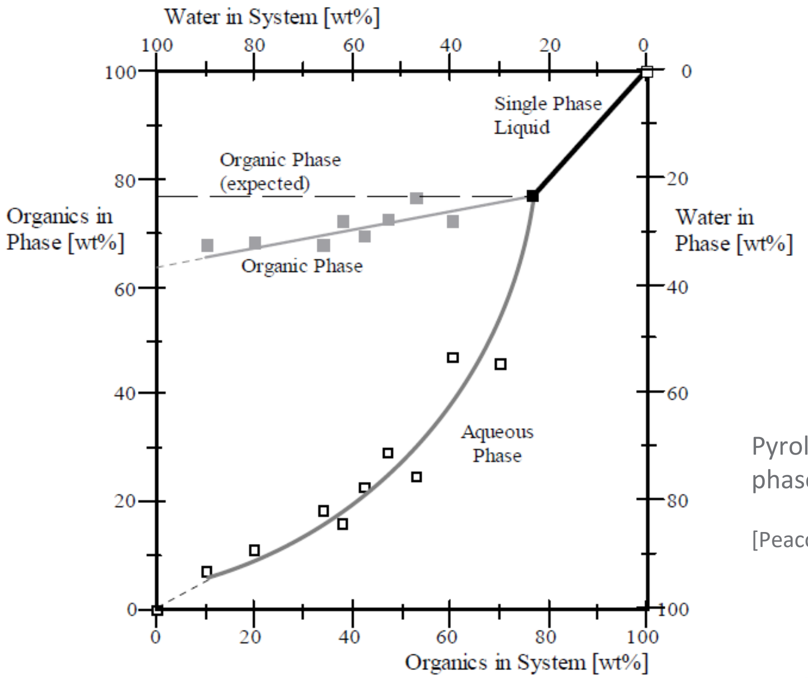
Considerations

- Water removal increases viscosity
- Additional water may induce phase separation

Example Research

Peacocke, G.V.C., Russell, P.A., Jenkins, J.D. and Bridgwater, A.V. 1994. Physical properties of flash pyrolysis bio-oils. Biomass & Bioenergy, Vol. 7, No. 16, pp. 169–177.

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M., and Chiaramonti, D., Fuel oil quality and combustion of fast pyrolysis bio-oils, Espoo 2013. VTT Technology 87. 79 p.



Pyrolysis liquid - water phase diagram

[Peacocke et al. 1994]

Solution		Impact	Add'l consequences
Solvation		Low	Low blend wall
Physical Mod.		High	- Viscosity
Catal	Mild	High	+ Cost, May increase viscosity
	Severe	High	++ Cost, + Viscosity
Prod. mod.		Low	- Viscosity, - Yield
End-use Mod.		?	+ Cost

[+] Positive [-] Negative

Energy Density

Challenges

- Oxygen: 40 to 50wt%
- Water: 15 to 25wt%
- Energy content low vs. petroleum

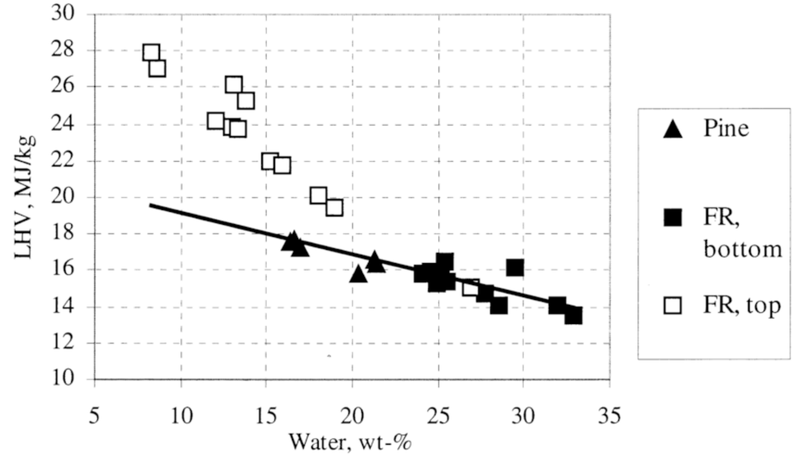
Considerations

- Impacted by water content
- Oxygen is removed as H_2O or by CO_2

Example Research

Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y., Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids Energy Fuels 2003, 17, 1-12.

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M., and Chiaramonti, D., Fuel oil quality and combustion of fast pyrolysis bio-oils, Espoo 2013. VTT Technology 87. 79 p.



Heating value of pine saw dust and brown forestry residue liquids (FR) as a function of water content. (Oasmaa et al. 2003)

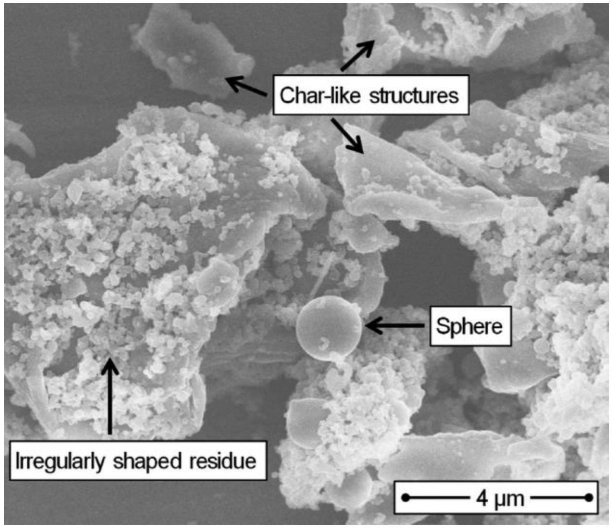
Solution		Impact	Add'l consequences
Solvation		None	n/a
Physical Mod.		Low	- Viscosity
Catal	Mild	High	+ Cost, May increase viscosity
	Severe	High	++ Cost, + Viscosity
Prod. mod.		Low	- Viscosity, - Yield
End-use Mod.		None	n/a

[+] Positive [-] Negative

Particulates

Challenge (carbon and alkali metals)

- Combustion efficiency
- Blockage
- Nozzle erosion
- Solids deposition



SEM image of particles filtered out of pyrolysis oil produced from forest residue displaying three types of morphology.

Molinder et al, **(2016)**

Considerations

- Filtration is uniformly positive

Solution		Impact	Add'l consequences
Solvation		None	n/a
Physical treat.		High	Can be difficult. Best done during production
Catal.	Mild	None	n/a
	Severe	None	n/a
Oil prod. Mod.		High	- Yield
End-use upgr.		None	n/a

[+] Positive [-] Negative

Example Research

Molinder, R., Sandström, L, and Wiinikka, H., (2016) Characteristics of Particles in Pyrolysis Oil, Energy & Fuels **DOI:** 10.1021/acs.energyfuels.6b01726

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M., and Chiaramonti, D., Fuel oil quality and combustion of fast pyrolysis bio-oils, Espoo 2013. VTT Technology 87. 79 p.

Viscosity

Challenges

- Handling and pumping
- Blending
- Combustion

Considerations

- Many factors increase viscosity

Example Research

Elliott, D., Oasmaa, A., Preto, F., Meier, D., and Bridgwater, A.V., Results of the IEA Round Robin on Viscosity and Stability of Fast Pyrolysis Bio-oils, *Energy Fuels*, 2012, 26 (6), pp 3769–3776.

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M., and Chiaramonti, D., Fuel oil quality and combustion of fast pyrolysis bio-oils, Espoo 2013. VTT Technology 87. 79 p.

lab	viscosity, initial cSt (avg)	moisture, initial wt% (avg)	viscosity after 24h@80C cSt	moisture after 24h@80C wt% (avg)	viscosity change %	moisture change %	mass loss
1	30.4	23.1	57.3	21.7	88	-6.06	0.088%
2	26.6	NA	37.2	NA	40	NA	0.034%
4	31.3	24.0	51.7	24.9	65	3.92	0.001%
7	31.0	23.6	53.8	25.2	74	6.60	0.003%
8	32.0	23.9	56.0	24.9	75	4.27	0.001%
11	29.9	25.1	50.2	26.0	68	3.79	0.068%
13	31.5	24.9	54.1	26.0	71	4.67	0.043%
16	30.6	24.2	51.7	26.2	69	8.26	0.016%
10	30.4	24.2	51.6	NA	70	NA	0.004%
15	26.7	23.7	phase separated during aging test, no results				
9	35.3	24.6	76.6	26.7	117	8.74	NA
5	69.7	24.8	102.5	26.2	47	5.52	0.11%
14	31.0	21.0	50.5	22.3	63	6.29	1.33%
6	101.9	25.1	101.4	24.9	-0.49	-0.84	0.082%
12	61.0	23.4	109	24.5	79	4.70	0.019%

[a]Avg of 3, when std dev is listed. NA = not analyzed.

Viscosity/Aging Measurements in Example Bio-oil #1

(Elliott et al. 2012)

Solution		Impact	Add'l consequences
Solvation		High	Effective
Physical treat.		Low	Can be difficult. Best done during production
Catal.	Mild	Low / -	+ Cost, May increase viscosity
	Severe	High	Effective, ++ Cost
Oil prod. Mod.		Low	Often increases viscosity
End-use upgr.		?	?

[+] Positive [-] Negative

Storage Stability

Challenge

- Viscosity increase
- Phase separation
- Inhomogeneity

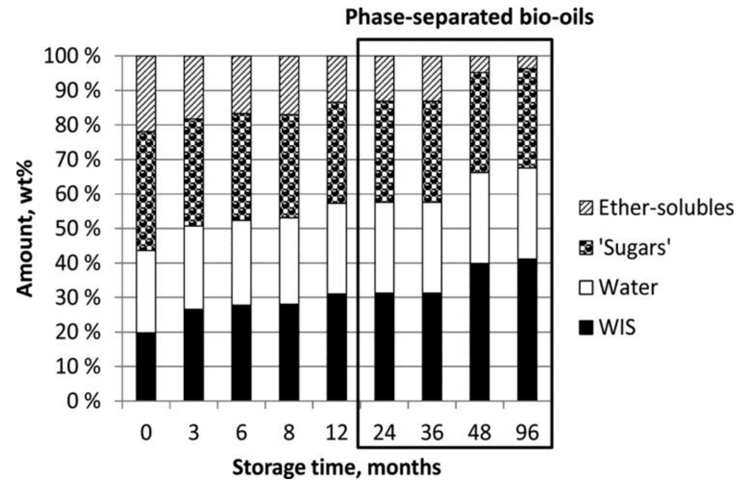
Considerations

- Also a factor of biomass source and technology

Example Research

Meier, D., van de Beld, B., Bridgwater, A.V., Elliott, D., Oasmaa, A., and Preto, F., State-of-the-art of fast pyrolysis in IEA bioenergy member countries Renewable Sustainable Energy Rev. 2013, 20, 619– 641

Oasmaa, A., Fonts, I., Pelaez-Samaniego, M.R., Garcia-Perez, M.E., and Garcia-Perez, M., Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review *Energy Fuels*, 2016, 30 (8), pp 6179–6200



Changes in compound groups of a pine bio-oil(1) during storage at room temperature. (Meier et al. 2013)

Solution		Impact	Add'l consequences
Solvation		High	May only slow polymerization
Physical treat.		Low	Slows polymerization
Catal.	Mild	High	+ Cost, May increase viscosity
	Severe	High	++ Cost
Oil prod. Mod.		varies	Potential for - Viscosity
End-use upgr.		None	n/a

[+] Positive [-] Negative

Miscibility/Blending

Challenge

- Combustion
- Solvent volume
- Blend ratio limitations
- Stability

Considerations

- Bio-oil requirements may vary by biomass and technology

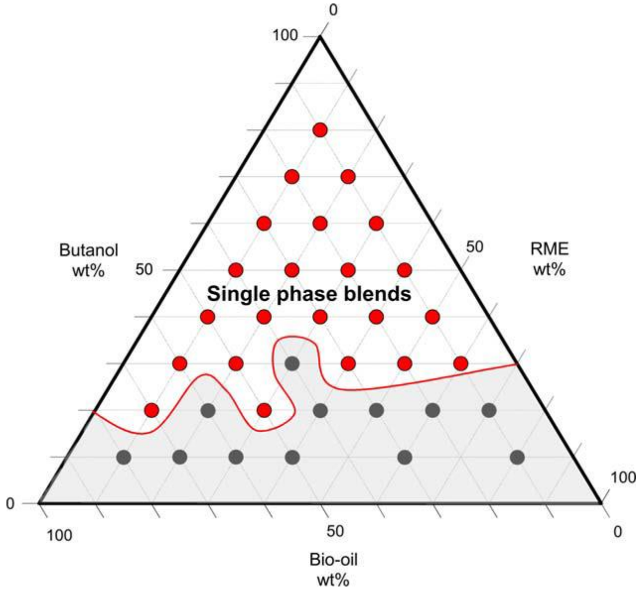
Example Research

Chong, K.J. and Bridgwater, A.V. (2016), Fast Pyrolysis Oil Fuel Blend for Marine Vessels. Environ. Prog. Sustainable Energy. doi:10.1002/ep.12402

Murugan, S., Ramaswamy, M.C., & Nagarajan, G. (2009). Assessment of pyrolysis oil as an energy source for diesel engines, Fuel Processing Technology, 90, 67–74.

Alcala, A. & Bridgwater, A.V. (2013). Upgrading fast pyrolysis liquids: Blends of biodiesel and pyrolysis oil, Fuel, 109, 417–426.

Nguyen, D. & Honnery, D. (2008). Combustion of bio-oil ethanol blends at elevated pressure, Fuel, 87, 232–243.



Phase diagram for three-component bio-oil, butanol, RME blends Chong et al. (2016), Fast Pyrolysis Oil Fuel Blend for Marine Vessels.

Chong et al. (2016)

Solution		Impact	Add'l consequences
Solvation		High	may still be unstable
Physical treat.		None	n/a
Catal.	Mild	High	+ Cost, May increase viscosity
	Severe	High	++ Cost
Oil prod. Mod.		Low	- Yield for Catalytic DTL
End-use upgr.		Low	Parallel injection

[+] Positive [-] Negative

Low pH

Challenges

- Corrosivity
- Storage material compatibility
- Combustion material compatibility

Exposure of brass nozzles to blends of upgraded bio-oil and heating oils. "Pyrolysis and Upgrading of Bio-oils Derived from US Northeast Hardwood for Application in Home Heating Oils", TCBiomass 2015.

Considerations

- Corrosivity high compared to typical petroleum fuels

Solution		Impact	Add'l consequences
Solvation		V. Low	Limited blend ratios
Physical treat.		None	+ Cost, other complications with titration
Catal.	Mild	None	n/a
	Severe	Varies	++ Cost, requires nearly complete HDO
Oil prod. Mod.		Low	Improved for solvo-liq.
End-use upgr.		Med	+ Cost

[+] Positive [-] Negative

Example Research

Keiser, J., Howell, M., Lewis, S., Connatser, R., Corrosion Studies of Raw and Treated Biomass-Derived Pyrolysis Oils. Proceedings of the NACE International Corrosion Conference, Salt Lake City, UT, March 11–15, 2012.

Haverly, M., Whitmer, L., and Brown, R., Evaluation of Polymer Compatibility with Bio-oil Produced from Thermochemical Conversion of Biomass, *Energy Fuels*, 2015, 29 (12), pp 7993–7997

Engine Combustion

Challenges

- Engine performance
- Longevity
- Emissions

Considerations

- Variable quality of oils

Pytec has tested Bio-oil in a modified 450 kWe diesel engine

BTG has tested a 1-cylinder CI-engine, adapted to run bio-liquids including pyrolysis oil

Solution		Impact	Add'l consequences
Solvation		High	may still be unstable
Physical treat.		None	n/a
Catal.	Mild	High	+ Cost, May increase viscosity
	Severe	High	++ Cost
Oil prod. Mod.		Low	- Yield for Catalytic DTL
End-use upgr.		Low	+ Cost

[+] Positive [-] Negative

Related Research

Hossain, A.K. & Davies, P.A. (2013). Pyrolysis liquids and gases as alternative fuels in internal combustion engines—A review, Renewable and Sustainable Energy Reviews, 21, 165–189

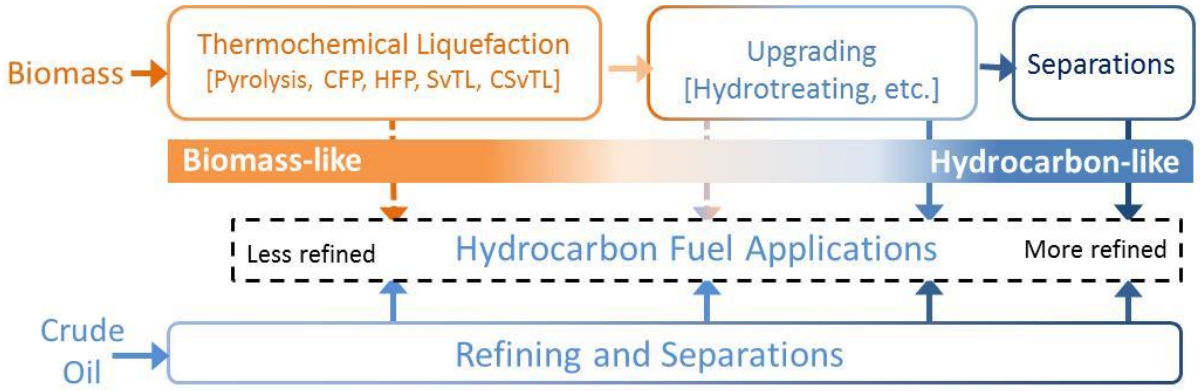
Solantausta, Y., Nylund, N.O., Westerholm, M., Koljonen, T., & Oasmaa, A. (1993). Wood -pyrolysis oil as a fuel in a diesel-power plant, Bioresource Technology, 46, 177–188.

Oasmaa, A., van de Beld, B., Saari, P., Elliott, D.C., & Solantausta, Y. (2015). Norms, Standards, and Legislation for Fast Pyrolysis Bio-oils from Lignocellulosic Biomass, Energy & Fuels, 29, 2471–2484.

Summary

- Bio-oils are compositionally different than crude oils
- Upgrading requirements for marine fuel are being researched
- Existing body of bio-oil research in boiler combustion, diesel engine use, and catalytic upgrading can be applied
- Modifications to end-use are likely

- Emissions and equipment longevity must be addressed



Thank You!

Acknowledgements:
Contributions and example research

Doug Elliott
Katie Chong
A.V. Bridgwater
Bert van de Beld
Dietrich Meier
Fernando Preto
Yrjö Solantausta
Anja Oasmaa
Kai Toven
Jim Keiser
Cordner Peacocke
PNNL Biomass Team