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PNNL-SA-xxx

Steam reforming and Liquefaction

Technical update and challenges

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Industrial steam reforming

Challenges:

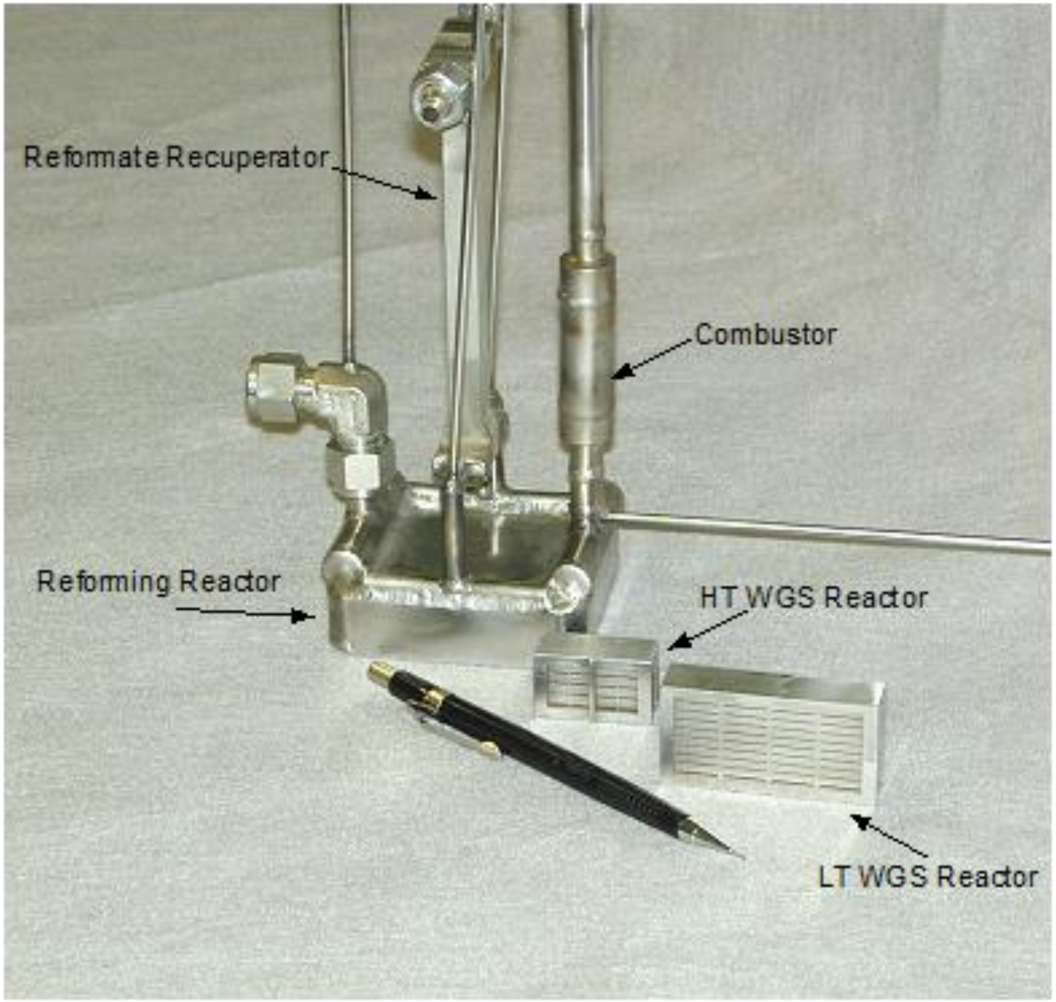
- Catalyst
  - Low cost
  - High Activity
  - Loading
- Reactor Design
  - Headers
  - Hot/cold points
- Fabrication
  - High volume
  - Catalyst
  - High P operation

Coupling process intensification with modular design

Courtesy of Velocys®

Small modular steam reforming

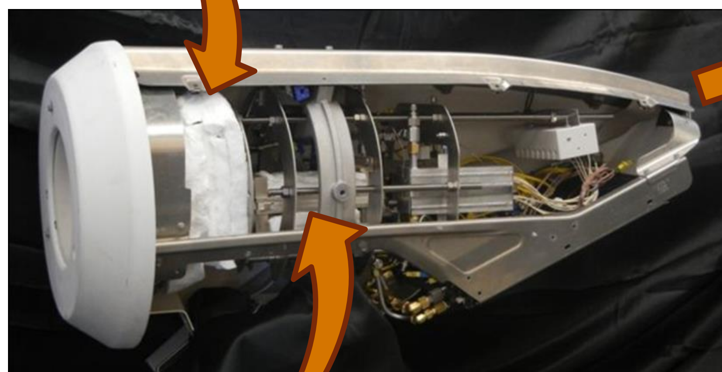
- Advantages
  - 10-100x volume reduction
  - 10x improvement in heat and mass transfer
  - Improved reactor control
  - High integration
  - Modular/reconfigurable
- Challenges
  - Catalyst
  - Reactor design
  - Fabrication



1-2 kW methane Steam Reformer

Portable, distributed power, easily moved

Applying in solar energy- storing energy in chemical bonds



Micro-channel heat exchanger technology

Low cost solar energy —
69% solar energy conversion efficiency

R&D 100 WINNER

Hydrothermal Liquefaction

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- Water assisted slow pyrolysis
- Highly efficient
- Simple in design to handle wet waste
- Several variants

FLC NATIONAL AWARDS

2015 R&D 100 WINNER

Wet waste: hydrothermal processing

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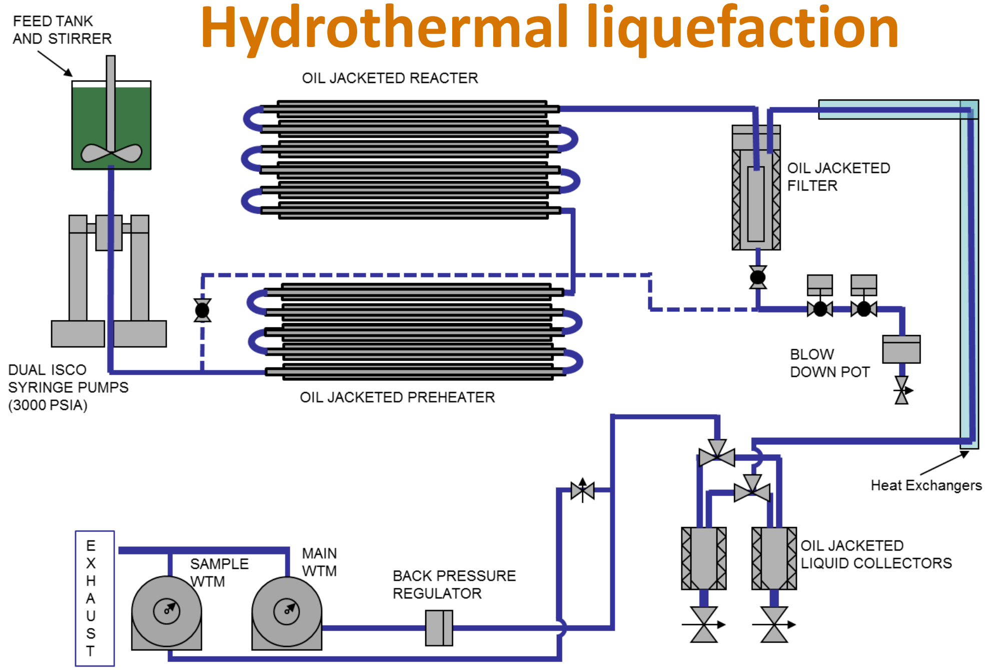
Hydrothermal liquefaction



Typical HTL operation at 350°C, 200 bar

Chemistry

- Water assisted pyrolysis
- Subcritical H_2O

Reactor

- Plug flow (pipes)

Advancements

- No reactive gas
- Solids/liquid and liquid/liquid separations
- No solvent (phase separation of water and biocrude oil
- Processing water sludge

Chemistry of hydrothermal liquefaction

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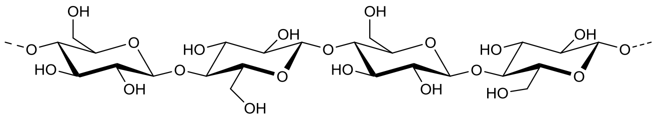
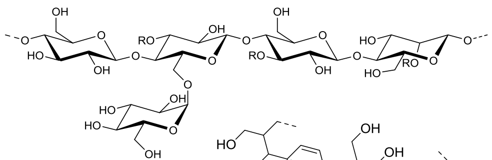
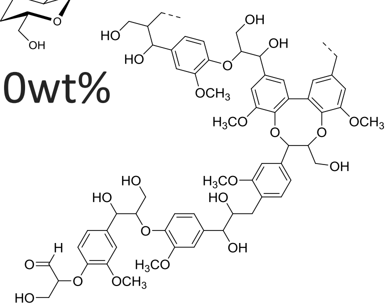
Cellulose = 0 - 45 wt%



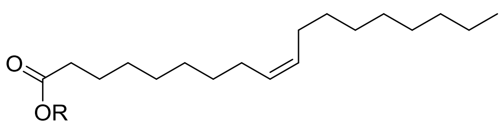
Hemicellulose = 0 - 30 wt%



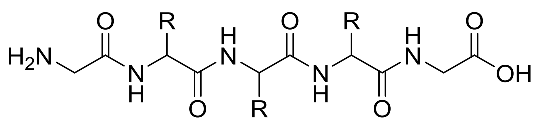
Lignin = 0 - 30wt%



Lipids/fats = 0 – 20%



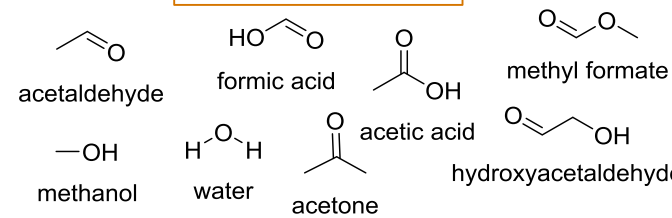
Proteins = 0 – 50 wt%



Inorganic = 0.1 - 20 wt%

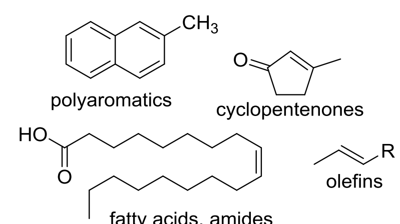
K, Na, Ca, P, Mg, Mn, Si, etc.

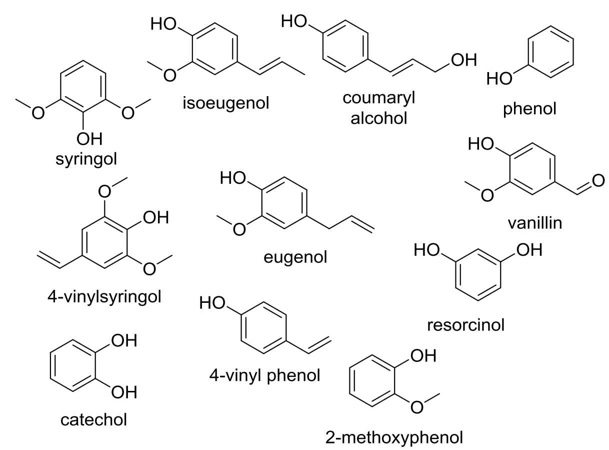
Water phase



Biocrude oil phase

No sugars
Few ketones,
Few aldehydes
Low alcohols
Few aliphatic ethers





Hydrothermal processing of wet waste

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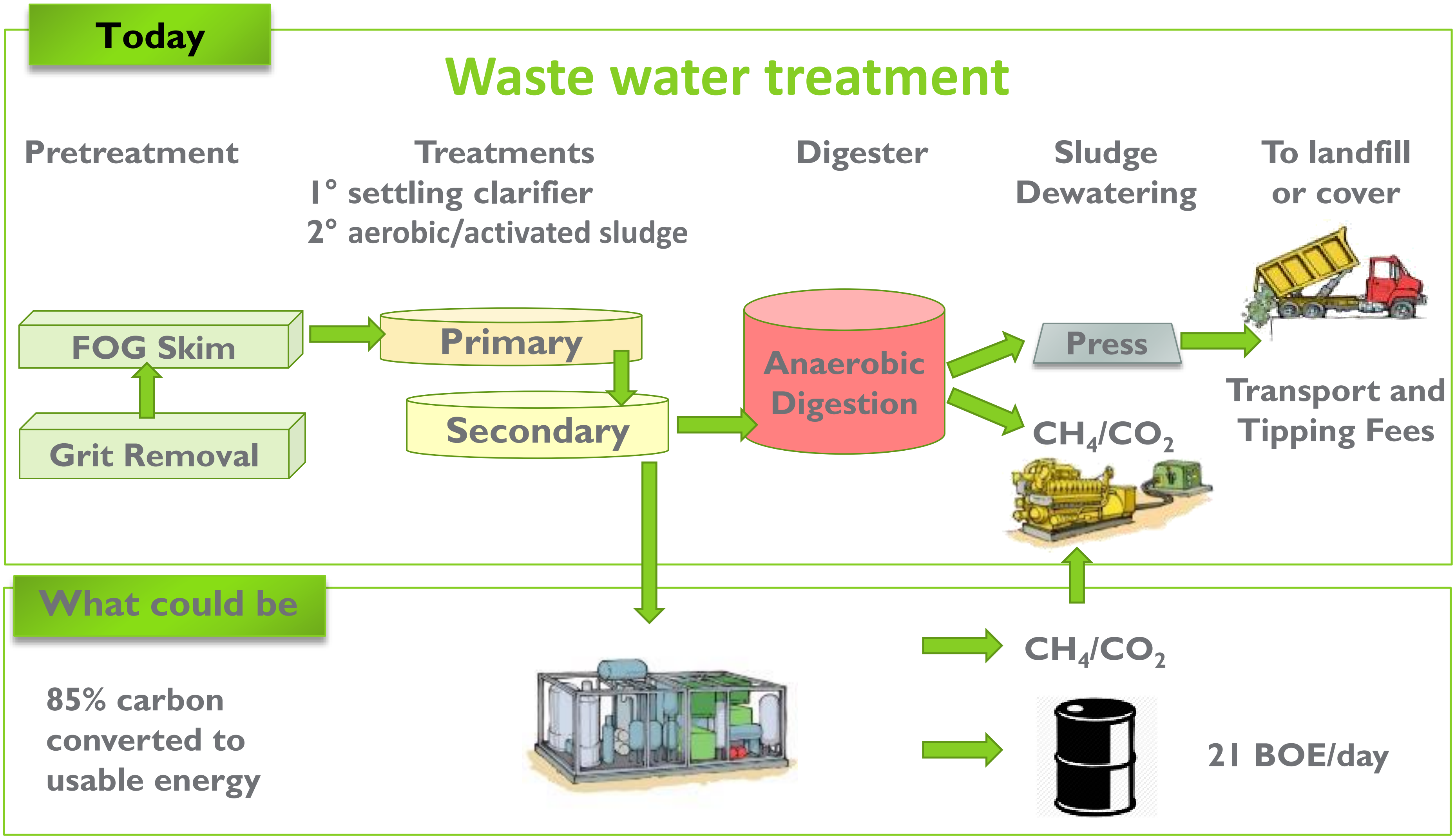
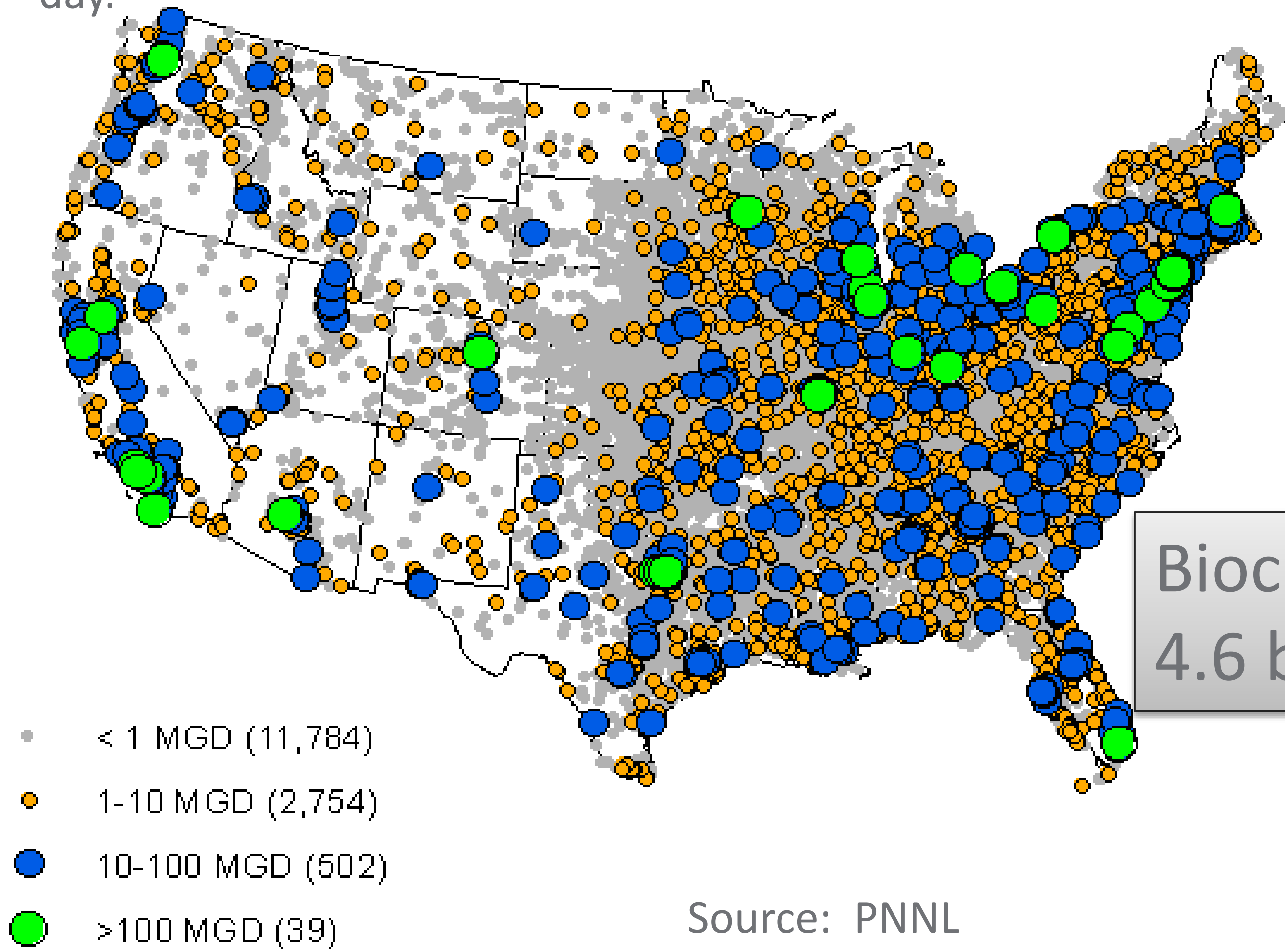


Feedstock supply Example
Waste water treatment plants

75% of the total US population is served by more than 16,000 publically owned treatment works (POTW), which treat nearly 32 billion gallons of wastewater every day.



Biocrude oil available
4.6 billion liters

Source: PNNL

Sewage sludge

- 16,000 publically owned treatment works (POTW)
- Serve 75% of US population
- Treat nearly 32 billion gallons of wastewater every day

- Size range of individual plants

Large > 10 mgd Medium: 1 - 10 mgd	89% of the volume 20% of the systems
Small: < 1 mgd	11% of the volume 80% of the systems

Annacis WWTP – Liquid Stream

Feedstock	Solids Conc. [wt%]	Ash [wt%, dry basis]	Density [g/mL]
Primary Sludge	11.9	7.5	1.04
Secondary Sludge	9.7	16.2	1.00
Class A Biosolids	15.9	28.0	1.05

Primary Sludge

Secondary Sludge

Class A biosolids

Partners

Genifuel

WERF
Water Environment Research Foundation
Collaboration. Innovation. Results.

metrovancouver

leidos

Experimental Conditions and Yields

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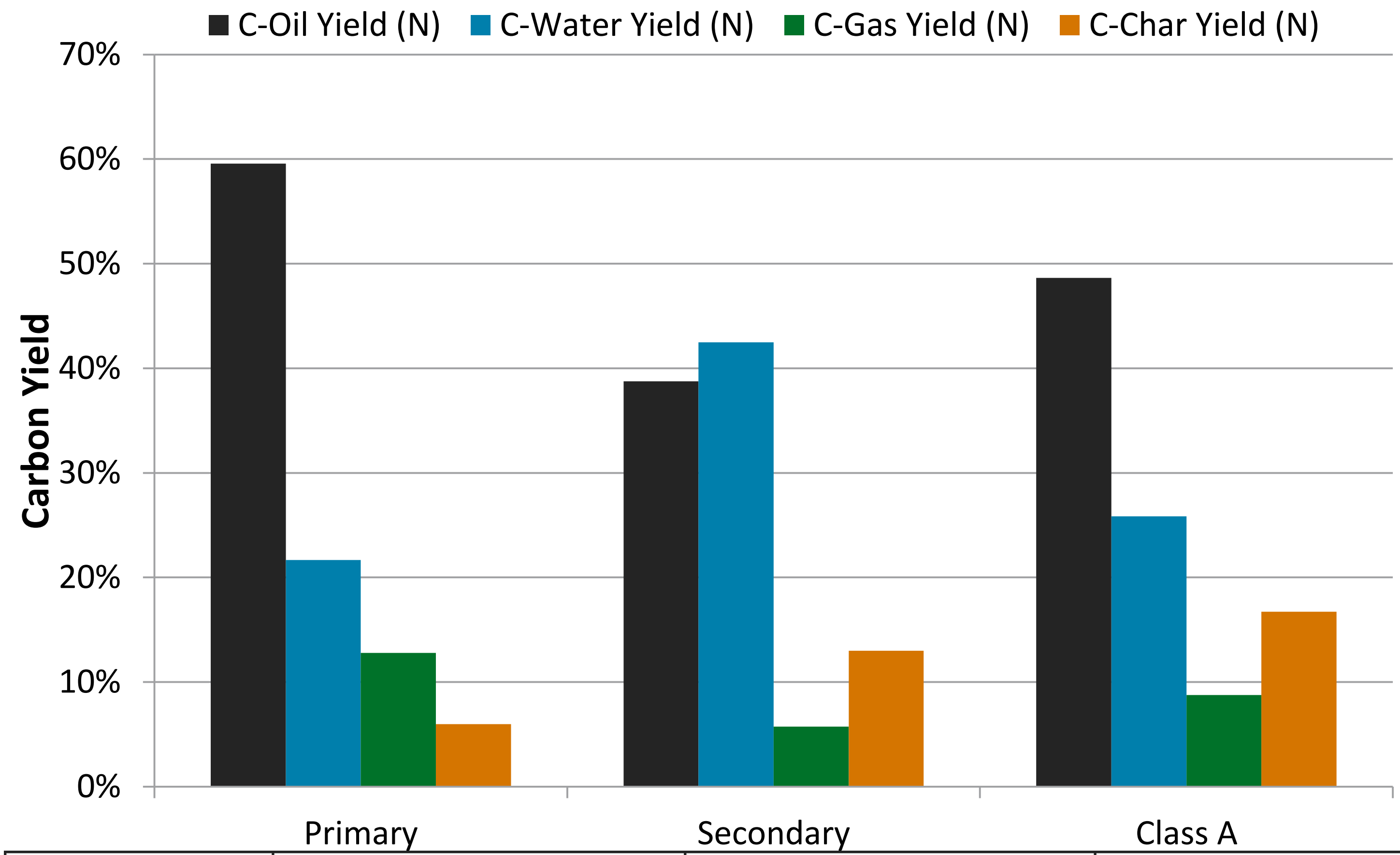
	Primary	Secondary	Class A
Overall Mass Balance	101%	103%	107%
Normalized Yields			
Oil Yield (dry basis) [g/g_{fd}]	37%	25%	35%
Solid Yield [g/g_{fd}]	4%	8%	12%
Gas Yield [g/g_{fd}]	22%	9%	15%
Aqueous Yield [g/g_{fd}]*	37%	58%	38%

*Aqueous yield calculated by difference

- Steady state window duration: 2 - 3 hours
- Average temperature: 330 - 350°C
- Average pressure: 2890 - 2925 psig
- Slurry feed rate: 1.5 L/h

Carbon balance and yield



	Primary	Secondary	Class A
C-Balance	94%	97%	111%
H-Balance	100%	111%	111%
O-Balance	102%	102%	107%

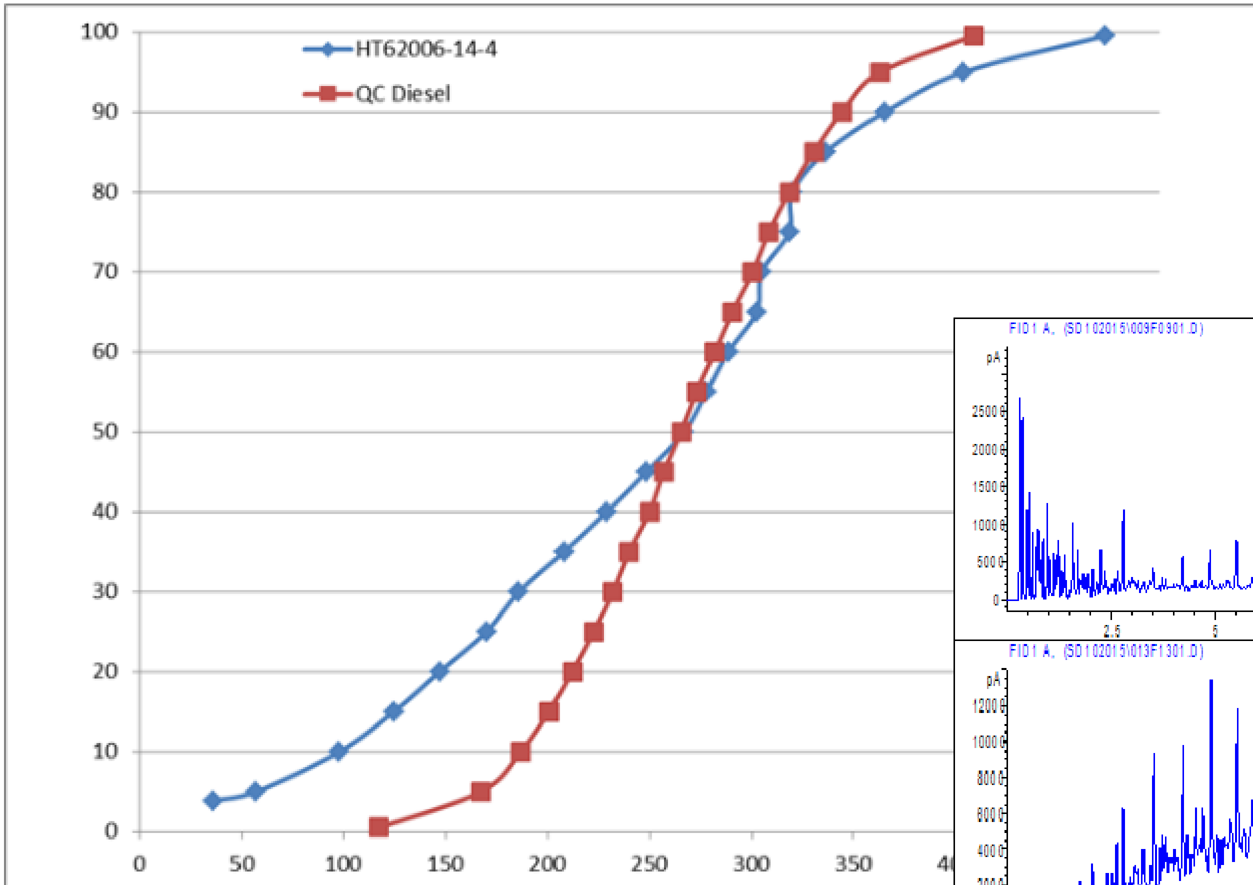
Biocrude oil Characterization

Biocrude	Primary	Secondary	Class A
Density [g/cm³, 40°C]	1.00	0.98	1.01
Viscosity [cSt, 40°C]	571	624	1088
HHV [MJ/kg, calc]	37.8	34.8	38.0
TAN [mg_{KOH}/g_{oil}]	65	38	36
Oxygen [wt%, dry basis]	8.1%	6.5%	6.2%
Nitrogen [wt%, dry basis]	4.3%	5.1%	4.5%
Moisture [wt%, KF]	13.0%	28.6%	13.5%
Ash [wt%]	0.33%	0.46%	0.18%

Biocrude from primary sludge

Aqueous Product	Primary	Secondary	Class A
Total Carbon [wt%]	1.3%	2.6%	1.9%
Sulfur [ppm]	260	160	280
pH	6.4	8.0	8.0

Upgraded HTL oil from waste water



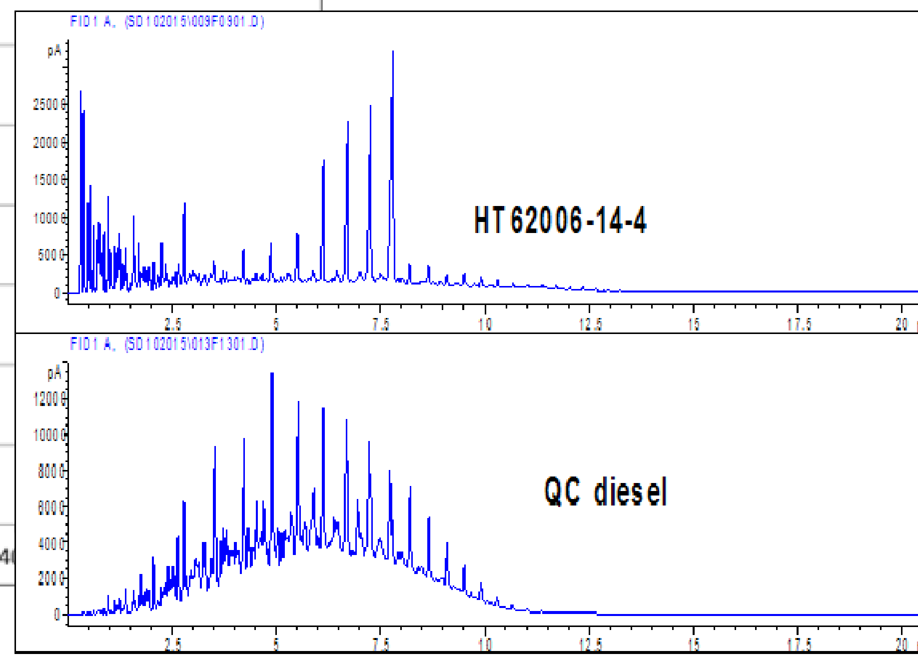
Single stage hydrotreatment

T = 400 °C

P = 1500 psig H_2

LHSV = 0.25 h^{-1}

Sulfided $CoMo/Al_2O_3$



HTL biocrude upgrading
Tetraselmis and forest residue

Upgrading the biocrude

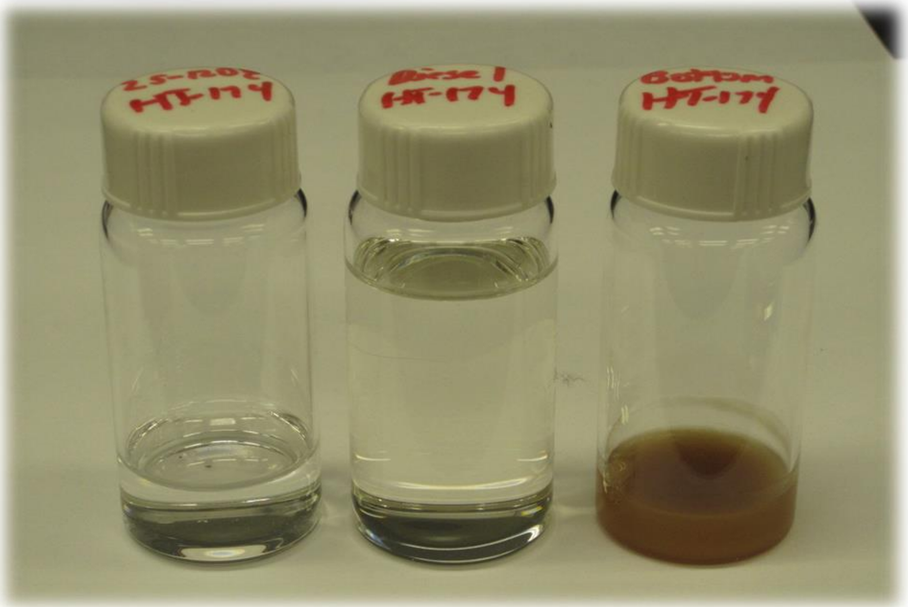
- Biocrude was filtered and acid washed
- Hydrotreating (24 cc bed)
  - 1500 psi and 400°C
  - Alfa Aesar $CoMo/Al_2O_3$ sulfided
  - LHSV: 0.25 cm^3/ cm^3-cat/h
  - WHSV tested: 0.34 g/g-cat/h
  - H_2 Flow = 125 scc/min
- Duration 103 and 210 h

Fractionating HTL derived hydrocarbons (algae)

- Hydrotreated Oil fractionated by simple distillation
- Majority of oil fractionates as a clear, white liquid
- Color bodies remain in the heavy fraction

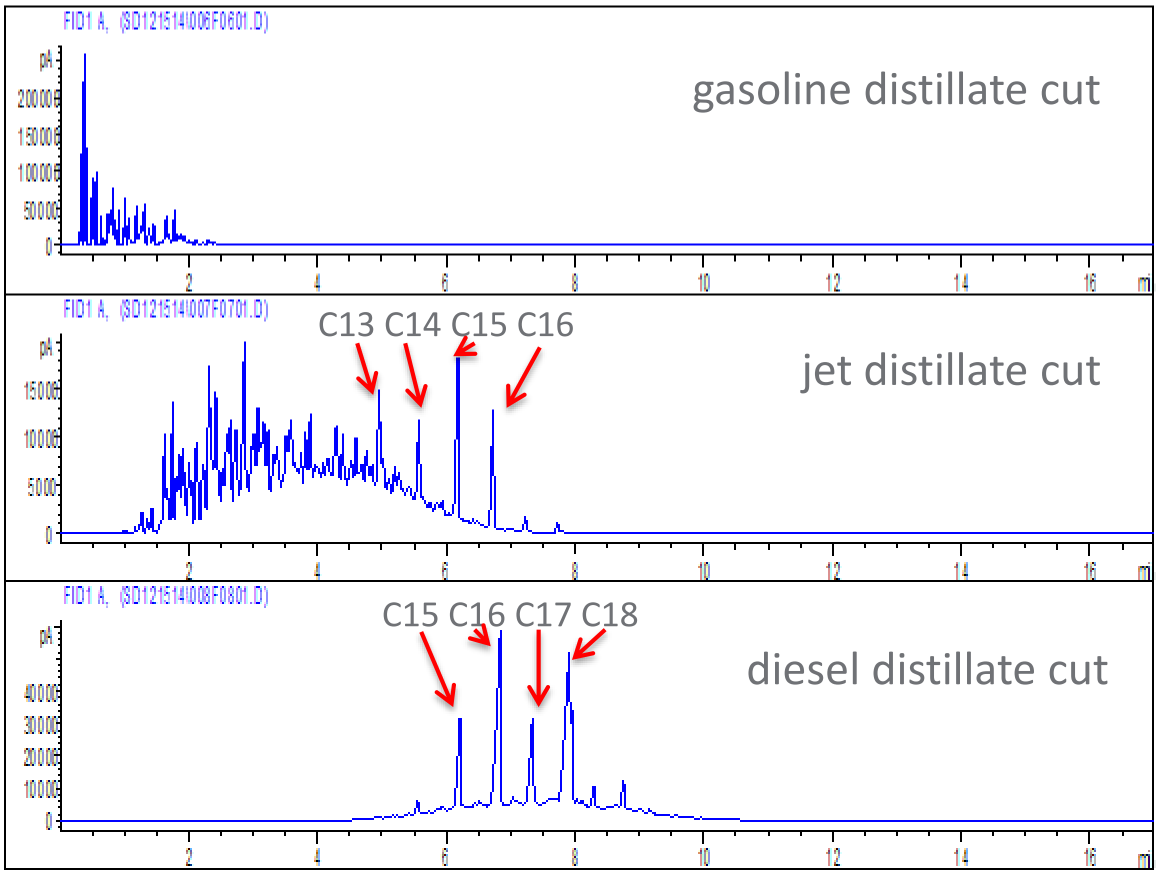
Hydrotreated (HT) biocrude

Fractionated HT biocrude



SimDis GC-FID (Tetraselmis)

The sim-dis GC-FID traces show the n-alkanes start at C13 and drop off after C18. Relatively high concentration of C15 and C16 n-alkanes are in the jet distillate sample which have a negative impact on freeze point.

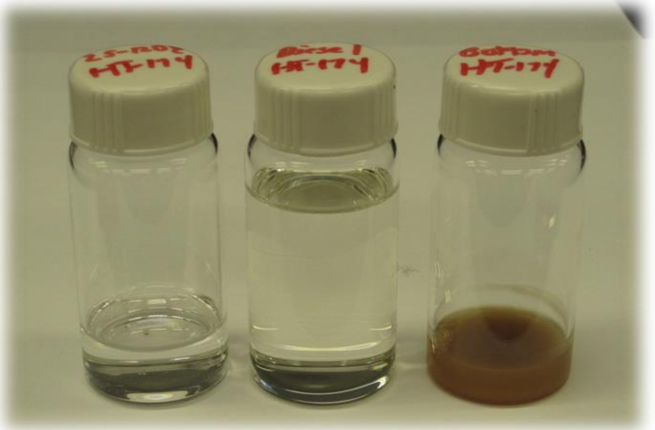


Fuel distribution

Source: HTL biocrude from Tetraselmis (algae)

	Temperature* Range, °C	fractions*, wt%	Diesel Yield*, wt%
Gasoline	20-150	24	24
Jet	150-250	27	
Diesel	250-390	45	72
Bottoms	>390	4	4

* Actual cuts were slightly different and sim-dis data used to project impact of changing cut point temperature



- Gasoline: high octane compounds, branched and cyclic alkanes with aromatics
- Jet: broad mixture of hydrocarbons with relatively low normal paraffin content
- Diesel: high in normal paraffins which contribute to a high cetane value fuel

Fuel property

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Source: HTL biocrude from Tetraselmis (algae)

Sample	Distillate Cut	Sulfur ASTM D5453 (ppm)	Flash Point (micro cup) °C	Cloud Pt ASTM D5773 (°C)	Pour Pt ASTM D5949 (°C)	Freezing Pt ASTM Dxxxx (°C)	Octane* (Cetane)
	naphtha/ gasoline	18					77
61573-62-D2	jet	13	50	-42	-48	-37	(40)
61573-62-D3	diesel	9		3	3	4	(59)

*Octane analyzer is a NIR instrument. Results are likely affected by matrices that vary from typical gasoline.

Comparing fuels from wood and algae

fuel	Range (°C)	Tetraselmis fractions	Forest residue fractions	Tetrselmis Cetane	Forest residue Cetane
Naphtha/ gasoline	20-150	24%	20%	(77)*	
jet	150-250	27%	26%	40	27
diesel	250-350	45%	35%	59	25
bottoms	>350	4%	19%		

*octane

Diesel + jet fraction is 72%

S content:

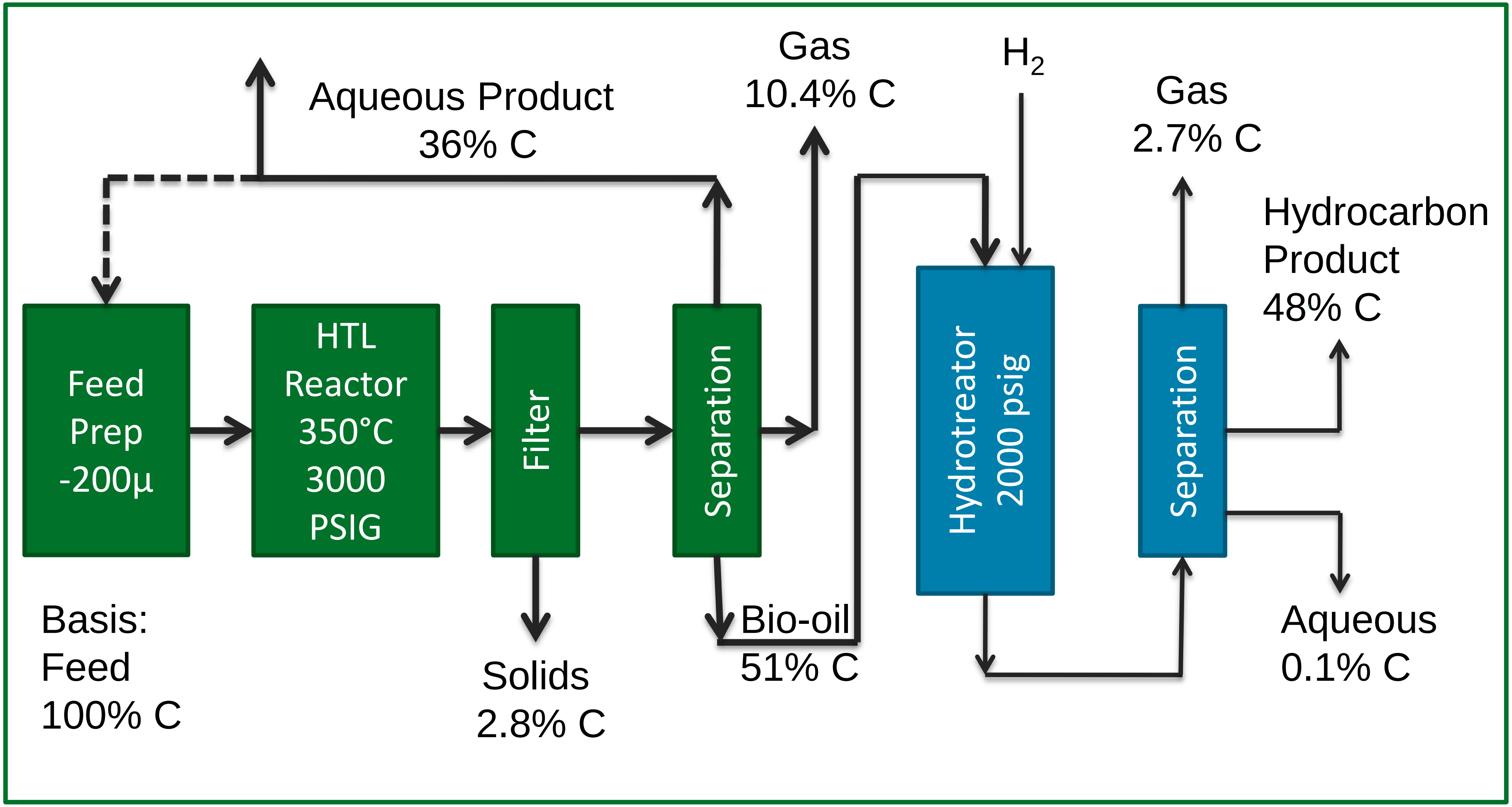
Tetraselmis	gasoline 18 ppm	jet 12 ppm	diesel 9 ppm
Forrest residue	gasoline 125 ppm	jet 20 ppm	diesel 8 ppm

Hydrogen demands

Petroleum hydrodesulfurization				Petroleum hydrocracking			Pyrolysis oil	HTL biocrude
Naptha HDS	Kerosene HDS	ATM resid HDS	Gas oil HDS	Mild HCK	Single STG HCK	Resid HCK	HDO	HDO
45	555	460	422	358	1150	660	~3400	~1800

H_2 chemical consumption, scf/bbl fd (standard cubic feet/barrel feed)

Typical HTL carbon flow (wood)
-- review technical challenges by stream--



Highest carbon efficient technology and highly energy efficient

Conclusions

Steam reforming

- Modularization coupled with process intensification
- Opens new opportunities

Liquefaction

- high quality biocrude oil from complex mixed waste

Technologies intersect

- Stable, low cost operation

Back upmaterial

Comparison

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	Current State	
	FP & HT	HTL & HT
Total energy efficiency to product, LHV	50	57
Fixed Capital Investment, $M	358	244
Product mass yield, % dry feed	24	27
Ratio of Product cost to value	1.17*	0.74*

* The equivalent values of the upgraded products for the present study were calculated on a weight averaged basis using the following values for products: gasoline = $986/ton, diesel = $916/ton, heavy hydrocarbon product = $698/ton.

Fuel distribution

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Source: HTL biocrude from Tetraselmis (algae)

	Distillation Temperature Range, °C	fractions, wt%	Proposed Temperature Range, °C	Projected fractions*, wt%	Projected Diesel Yield*, wt%
Gasoline	20-150	24	20-150	24	24
Jet	150-265	30	150-250	27	
Diesel	265-350	39	250-390	45	72
Bottoms	>350	8	>390	4	4

* sim-dis data used to project impact of changing cut point temperature

- Gasoline: high octane compounds, branched and cyclic alkanes with aromatics
- Jet: broad mixture of hydrocarbons with relatively low normal paraffin content
- Diesel: high in normal paraffins which contribute to a high cetane value fuel

Fuel property from wood biocrude

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Sample ID#	Distillate Cut	Sulfur ASTM D5453 (ppm)	Flash Point micro D93 (°C)	Cloud Pt ASTM D5773 (°C)	Pour Pt ASTM D5949 (°C)	Freezing Pt ASTM D5972 (°C)	Cetane
61573-63-D1	gasoline/naphtha	125					
61573-63-D2	jet	21	44	<-80	<-80	NA	27
6573-63-D13	diesel	8		-16	-24	-11.0	25
61573-63-D2+D3	jet+diesel	11	56	-25.	-33	-19.1	26

Feedstocks with lipids lead to higher cetane diesel fuels

Provided an example of each waste category and fuel type

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Class of stranded, dispersed carbon	Example sources	Barrels of Oil Equivalent	Reference processing approach
Dry wastes and residues	Sorted municipal solid waste, agriculture and forest residues	1.8 billion	Pyrolysis, hydrotreating
Wet wastes	Food processing waste, sludges, manures, etc.	1.2 billion	Hydrothermal liquefaction, hydrotreating
Gaseous	Flared gas, biogas, stranded gas, and CO_2	>0.4 billion	Partial oxidation; activation; reduction

Common challenge – upgrading oxygenated intermediates

Upgrading pyrolysis bio-oil and HTL biocrude

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❑ Fast Pyrolysis Oil Upgrading

→ **Pre-treatment** → **Low-Temp Stablization** → **High-Temp HT/HC** →

Pre-treatment	Low-Temp Stablization	High-Temp HT/HC
T = 60 – 160 °C	T = 120 – 160 °C	T = 390 – 410 °C
P = 200-1200 psig H_2	P = 1200 psig H_2	P = 2000 psig H_2
LHSV = 0.2-0.5 h^{-1}	LHSV = 0.2-0.4 h^{-1}	LHSV = 0.2-0.4 h^{-1}
Base metal catalysts	Supported Ru	Sulfided commercial catalyst

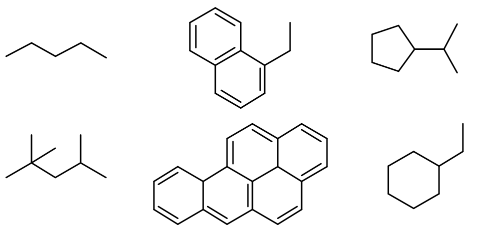
❑ Hydrothermal Liquefaction Oil Upgrading

→ **High-Temp HT/HC** →

T = 400 °C
P = 1500 psig H_2
LHSV = 0.25 h^{-1}
Sulfided $CoMo/Al_2O_3$

Crude oil hydrocarbons

ALIPHATICS	AROMATICS	NAPHTHENES
25%	17%	50%



Cost of hydrotreating for pyrolysis is high and is not amenable for small scale

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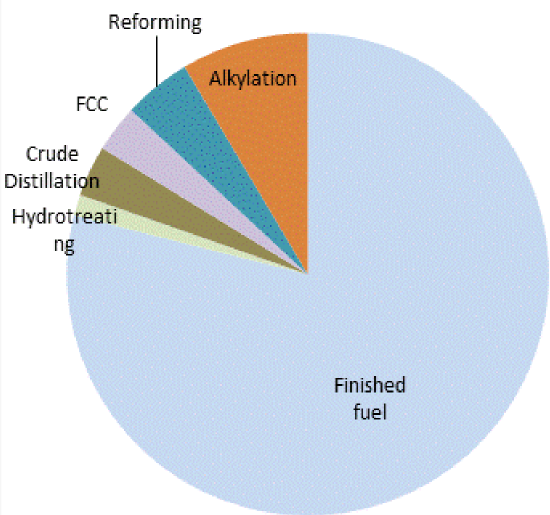
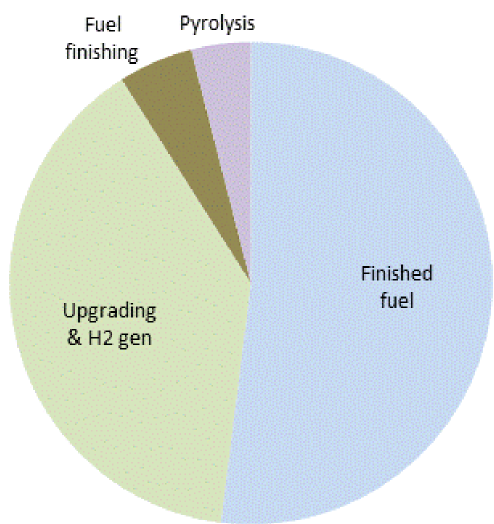
Energy Distributions:

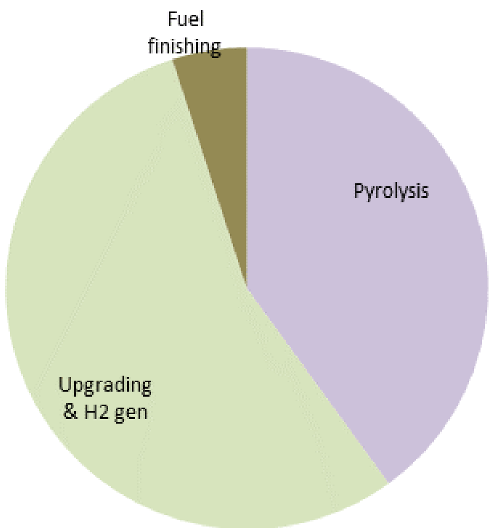


Typical petroleum refinery



Biorefinery – pyrolysis of wood

Capital Cost Distribution:



Biorefinery – pyrolysis of wood

Hydrotreating -- primary fraction of energy and capital (85% of operating cost)

Petroleum hydrodesulfurization				Petroleum hydrocracking			Pyrolysis oil	HTL biocrude
Naptha HDS	Kerosene HDS	ATM resid HDS	Gas oil HDS	Mild HCK	Single STG HCK	Resid HCK	HDO	HDO
45	555	460	422	358	1150	660	~3400	~1800

H_2 chemical consumption, scf/bbl fd (standard cubic feet/barrel feed)