Recent Progress in Biocrude Upgrading and Co-processing

David C. Dayton, Ph. D.
RTI Senior Fellow and Biofuels Director

RTI is an independent, nonprofit institute that provides research, development, and technical services to government and commercial clients worldwide.

Our mission is to improve the human condition by turning knowledge into practice.

tcbiomass plus 2019

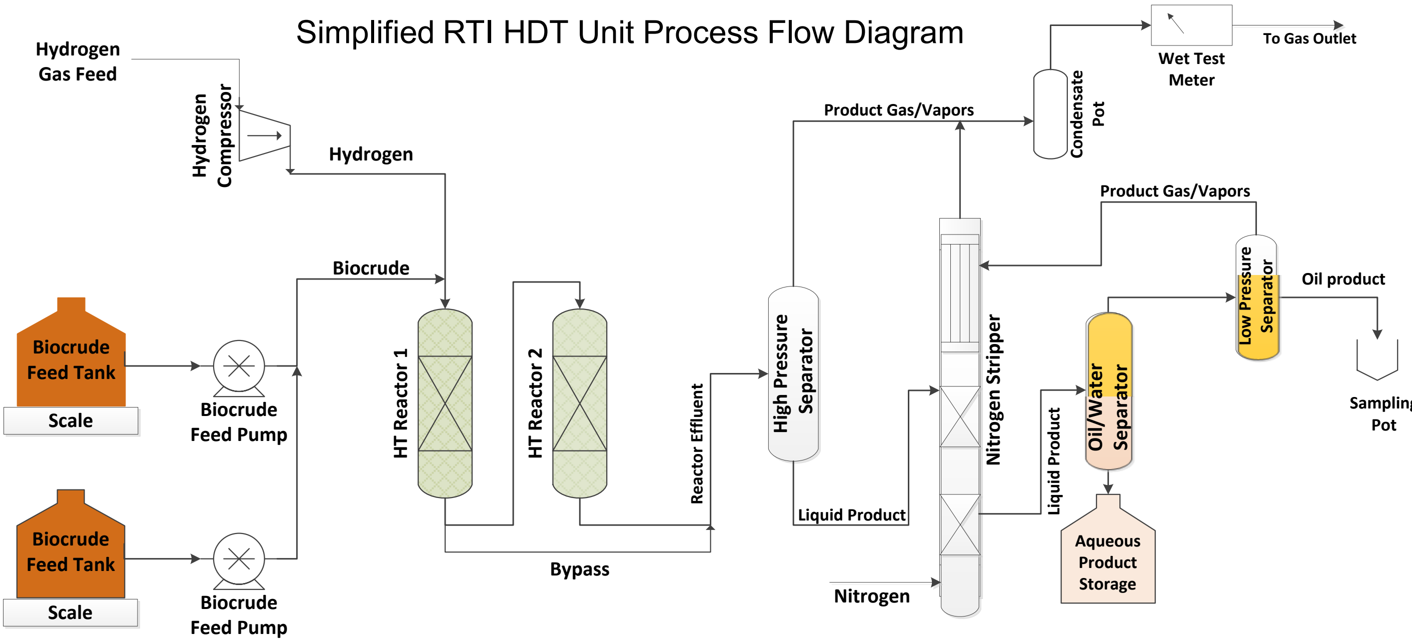
THE INTERNATIONAL CONFERENCE ON THERMOCHEMICAL CONVERSION SCIENCE: *BIOMASS & MUNICIPAL SOLID WASTE TO RNG, BIOFUELS & CHEMICALS*

Bio-crude Upgrading Overview

Investigate the impact of bio-crude quality in the hydroprocessing step

- Steady-state deoxygenation activity, hydrogen demand, and process severity with bio-crude of various quality (wt%O and chemical composition)
- Long-term operation to determine upgrading catalyst stability and lifetime (500-1000 hrs)
- Refinery integration and co-processing strategies

Simplified RTI HDT Unit Process Flow Diagram



Reactor volume: 350 mL
Catalyst volume: 20 - 250 mL

LHSV - 0.1 to 1.0
Flow rates - 50 to 250 mL/h

Max. design pressure - 3000 psig
Max. design temperature - 450 C

Bio-crude Upgrading Overview

Catalyst Loading, Sulfidation, and HDT Process Conditions

- HDT Catalyst: HaldorTopsøe Bio-Cat
- Catalyst Sulfidation: In-situ with H_2S in H_2 balance.
- Bio-crude flow rate: 50-250 ml/h
- Mass Balance Protocol: Allow at least 48 hours of run time prior to performing mass balance.
- Experiments continue until pressure drop across reactor > 60-100 psig or feed runs out

Parameters	Typical Test Conditions
Temperature	290 – 350 °C
Pressure	1450-2000 psig
LHSV	0.125 - 0.5 1/h
H_2/oil	2000-3300 Nl/l

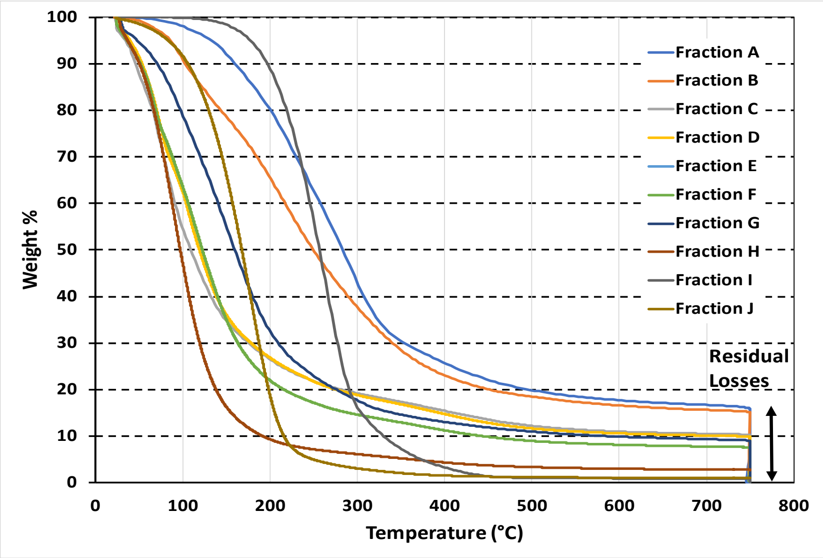
<u>Analysis of Bio-crude and HDT products include:</u>

Elemental Analysis(CHNSO), GC-MS, FTIR, NMR, Carbon Number Distribution, Distillation by ASTM D1160, SG 60/60 by ASTM D4052, Kinematic Viscosity by D445, and Karl Fischer Titration.

Bio-crude Upgrading Overview

Challenges:

- High process severity (T, P, LHSV) is required for bio-crude upgrading
- Bio-crude upgrading is limited by catalyst deactivation
- Poor bio-crude thermal stability (reactivity) causes reactor fouling/plugging.



Bio-crude quality beyond wt% O.

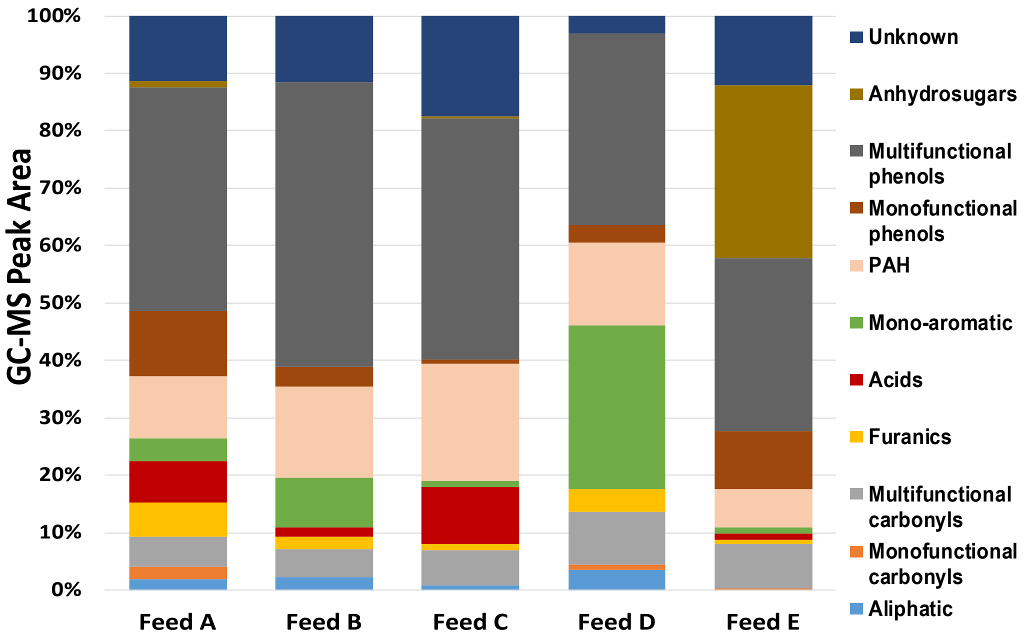
How does bio-crude chemical composition impact upgrading?

Strategies for Bio-oil/Bio-crude Upgrading

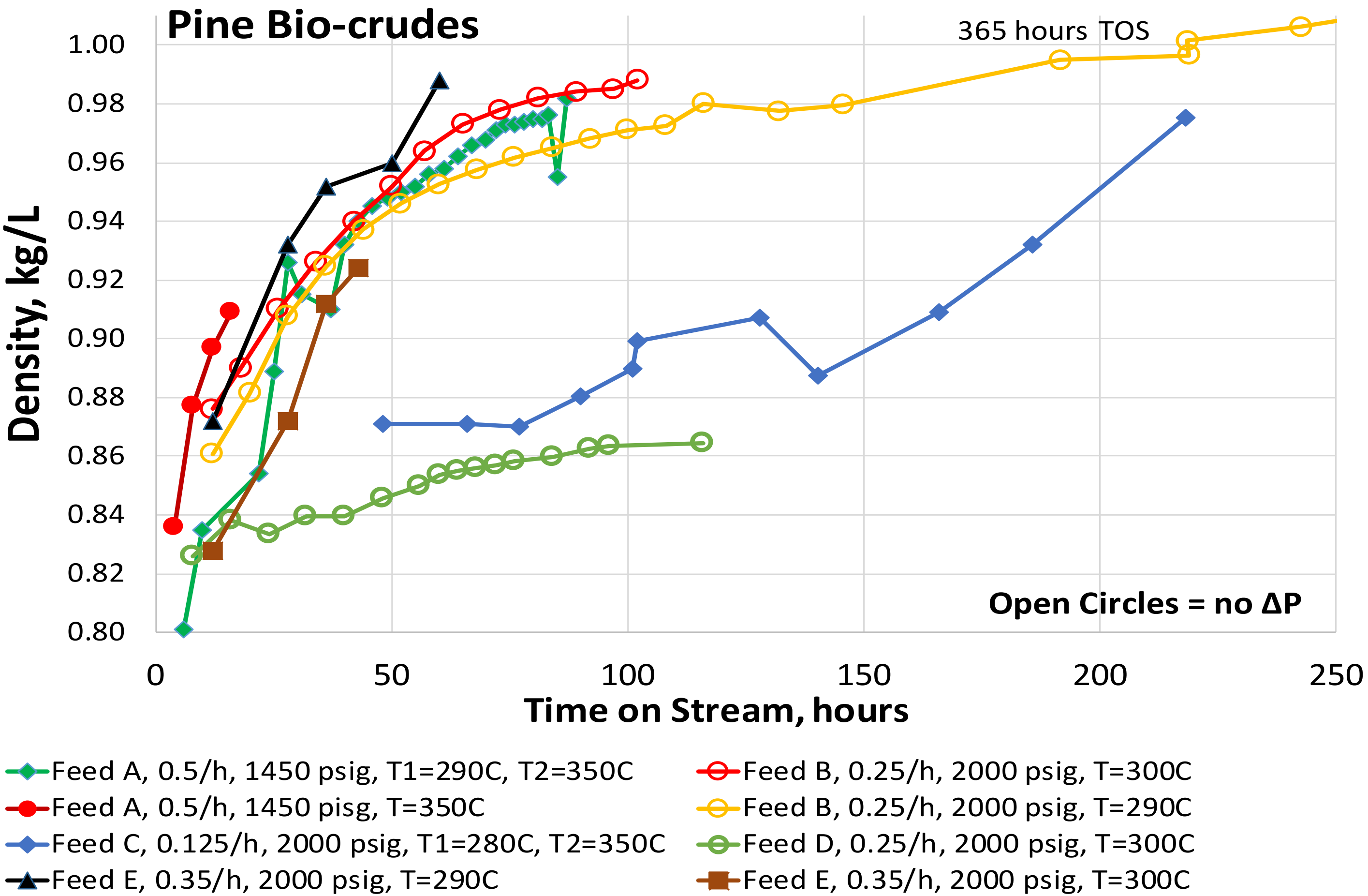
Strategy	Process
Pre-processing	• Ultrafiltration • Ion exchange • Chemical modification (esterification, etherification, neutralization)
Stabilization	• Mild hydrotreating • 200°C, 1500 psig, Ru/C
Fractionation	• Separations (Liquid-Liquid Extraction) • Distillation (Thermal Stability)
Pyrolysis process	• Catalysts, process conditions, and feedstocks to control chemical composition. Target: ~15 wt% oxygen
Co-processing	• Hydrotreat blends of petroleum refining intermediates and bio-crude (5-50 vol%) to control oxygen and sulfur content

Pine CFP Bio-crude Compositions

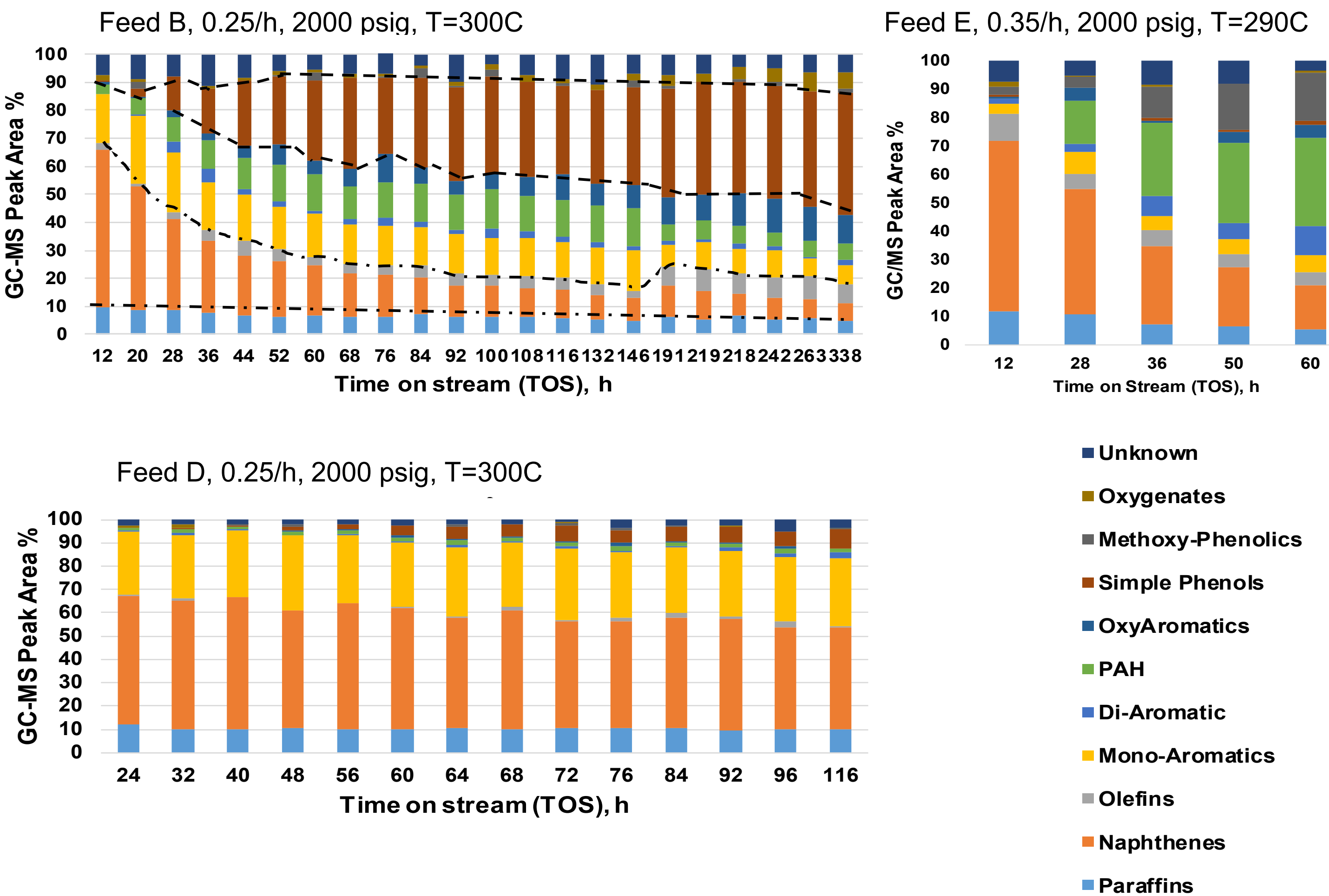
wt.% dry basis	A	B	C	D*	E
C	72.7	73.1	69.7	76.6	63.7
H	7.1	7.1	7.2	7.9	6.7
N	0.6	0.3	0.3	0.5	0.5
O	19.6	19.5	22.8	15.0	29.6
H/C	1.17	1.17	1.24	1.24	1.26



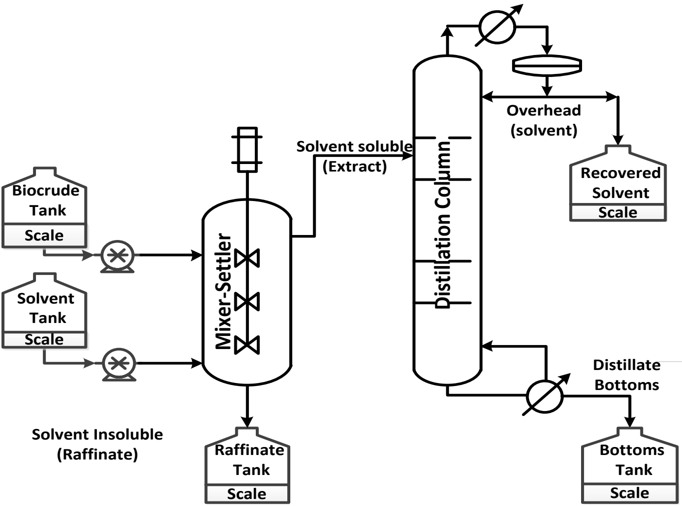
Pine Bio-crude Hydrotreating: Feedstock and Process Conditions



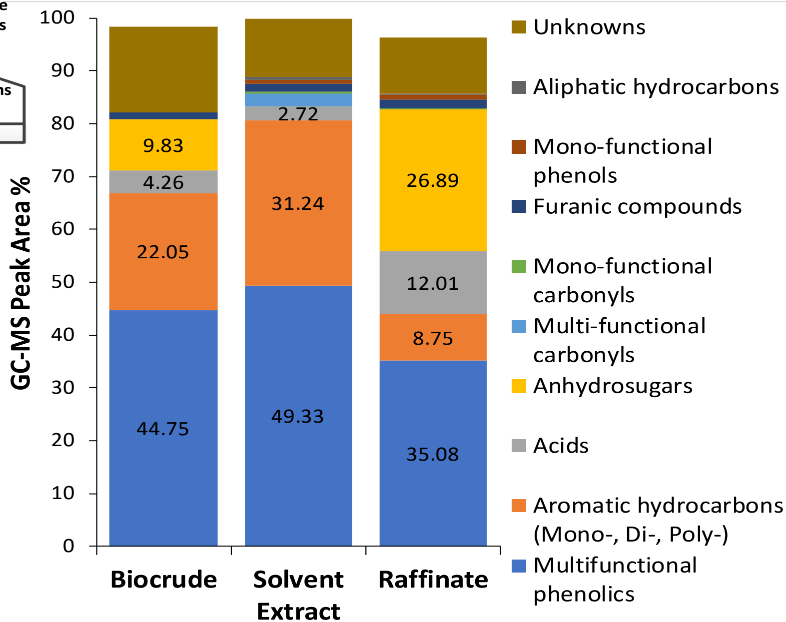
Pine Bio-crude Hydrotreated Products



Bio-crude Separations

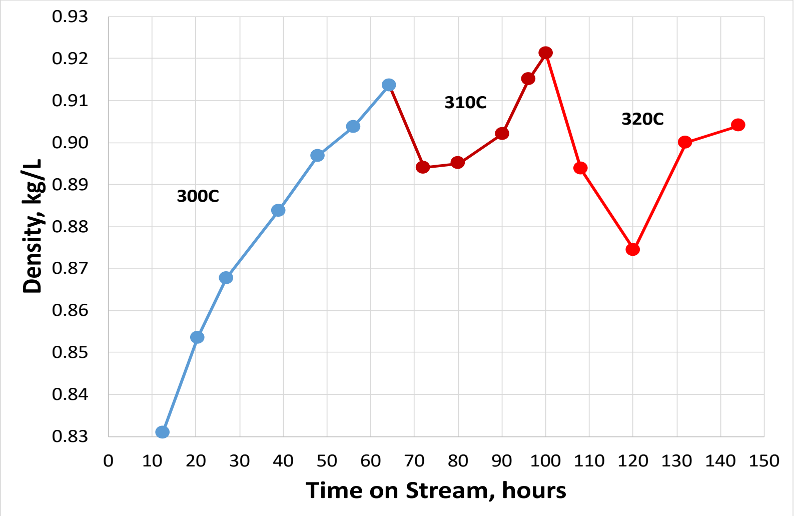


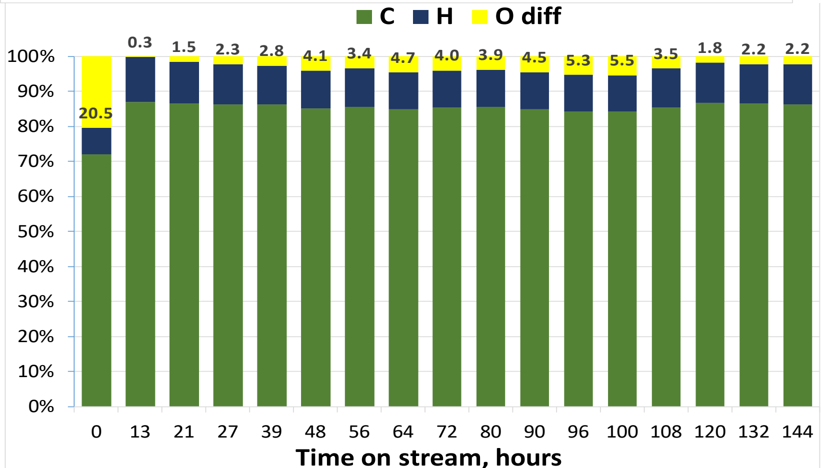
Solvent Extraction		Distillation	
INPUT	Mass (kg)	INPUT	Mass (kg)
Bio-crude	26.1	Extract	31.4
Solvent	29.3		
OUTPUT	Mass (kg)	OUTPUT	Mass (kg)
Raffinate	22.6	Solvent	24.3
Extract	32.6	Bottoms	6.3



- Solvent extraction separates out acids and anhydrosugars
- Although not detected with GC-MS, oligomers likely end up in the raffinate

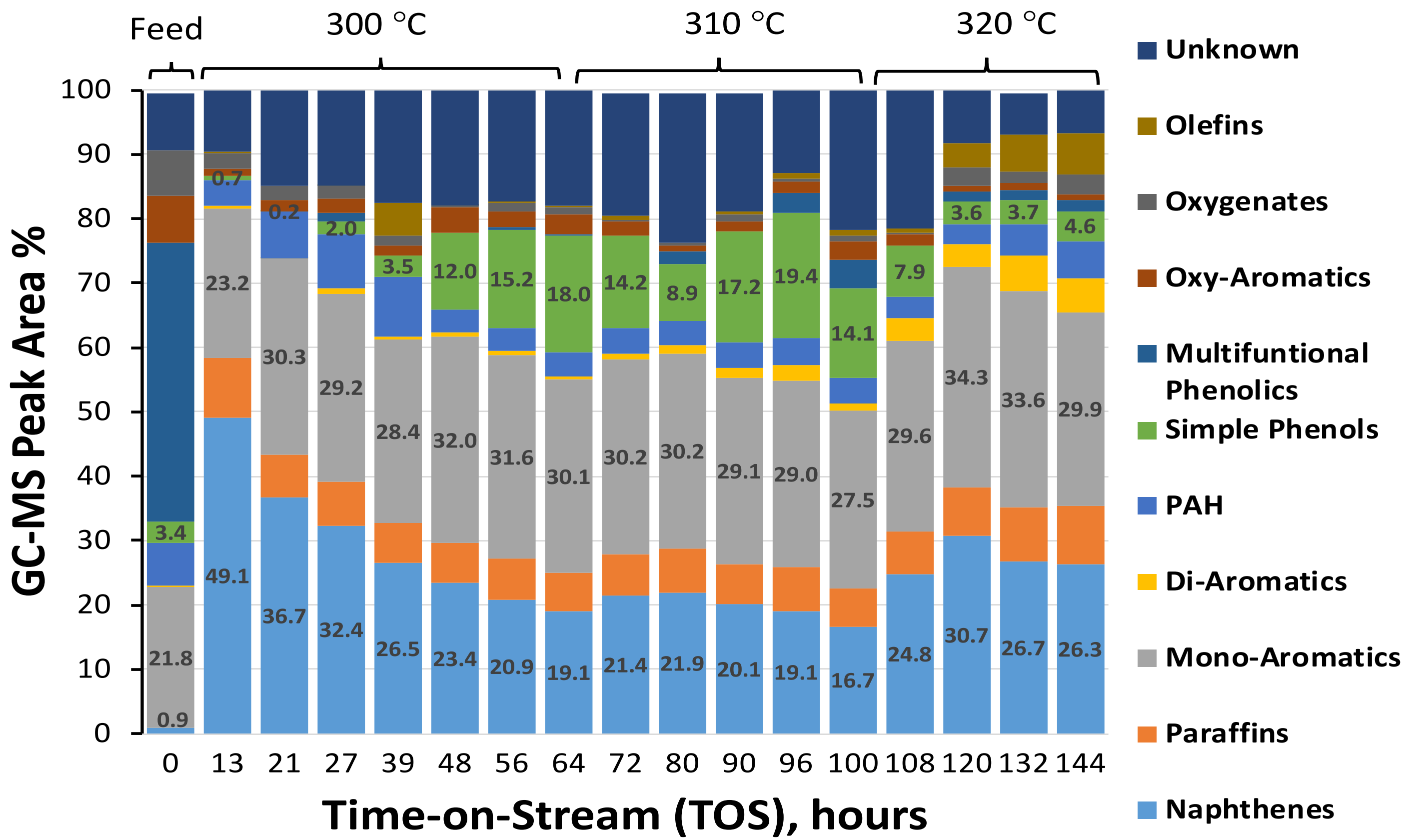
Solvent Extracted Bio-crude Hydrotreating: Physico-chemical Properties





Catalyst	TK-341
H_2 Flow Rate (sccm)	400
Feed Rate (g/h)	70-77
Pressure (psig)	2000
Average Temperature (^oC)	300
LHSV (h^{-1})	0.35
H_2/oil ratio (Nl/l)	3300

Hydrotreated Product Compositions



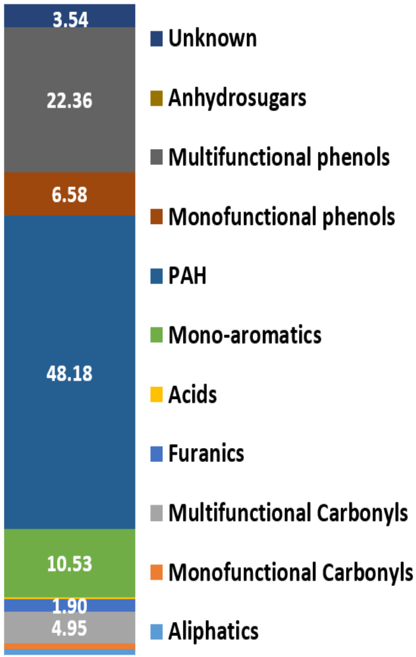
RCFP Bio-crude Production and Upgrading

12-L RCFP bio-crude produced in 2"FBR over 10 months
Average Hydrogen Consumption: 2.3 wt% Biomass

Reaction Conditions
Catalyst: Mo/Al_2O_3
Hydrogen: 80 vol%
Temperature: 460° C

	Carbon Balance*	Mass Balance
Aqueous	2.5	27.4
Organic (C_4^+)	43.0	19.6
Liquid Bio-crude	*26.4*	*15.9*
C4-C6	*16.6*	*3.7*
Gas	26.8	13.1
Char+Coke	30.1	35.9
Total	102.4	96.0

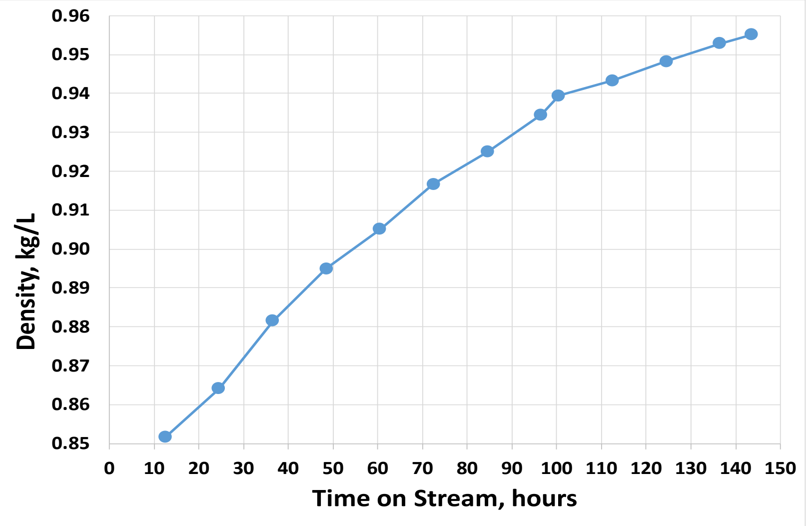
RCFP Bio-crude Composition
(GC-MS Area%)

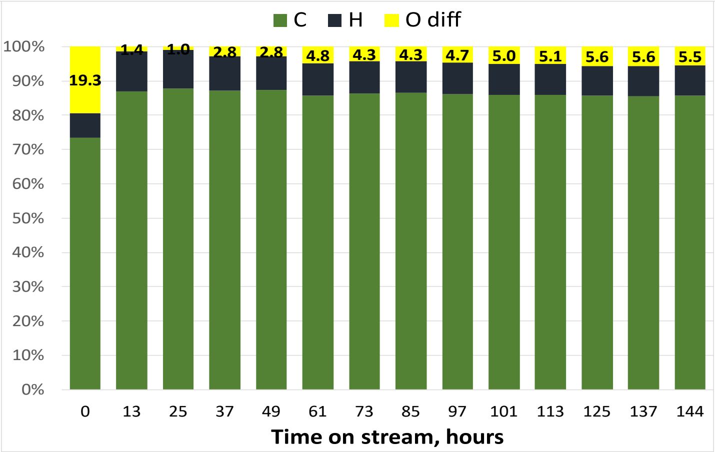


Elemental

Properties	
Moisture, wt%	8.5
C wt%, dry	73.2
H wt%, dry	7.3
N wt%, dry	0.2
O (by diff)	19.3

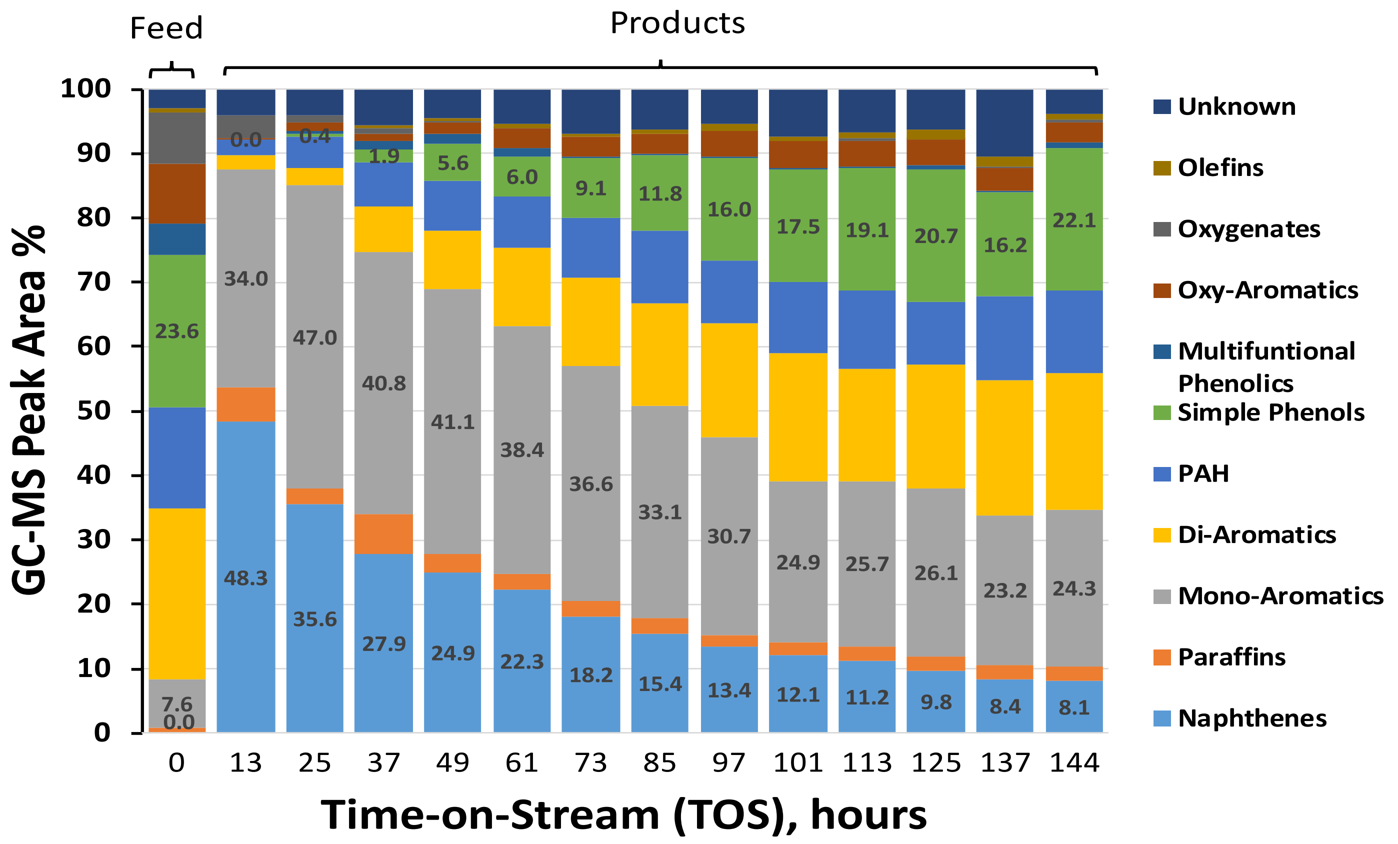
RCFP Bio-crude Upgrading: Physico-chemical Properties





Catalyst	TK-341
H_2 Flow Rate (sccm)	3300
Feed Rate (g/h)	62
Pressure (psig)	2000
Average Temperature (^oC)	300
LHSV (h^{-1})	0.31
H_2/oil ratio (Nl/l)	3300

RCFP Bio-crude Upgrading: Hydrotreated Product Compositions

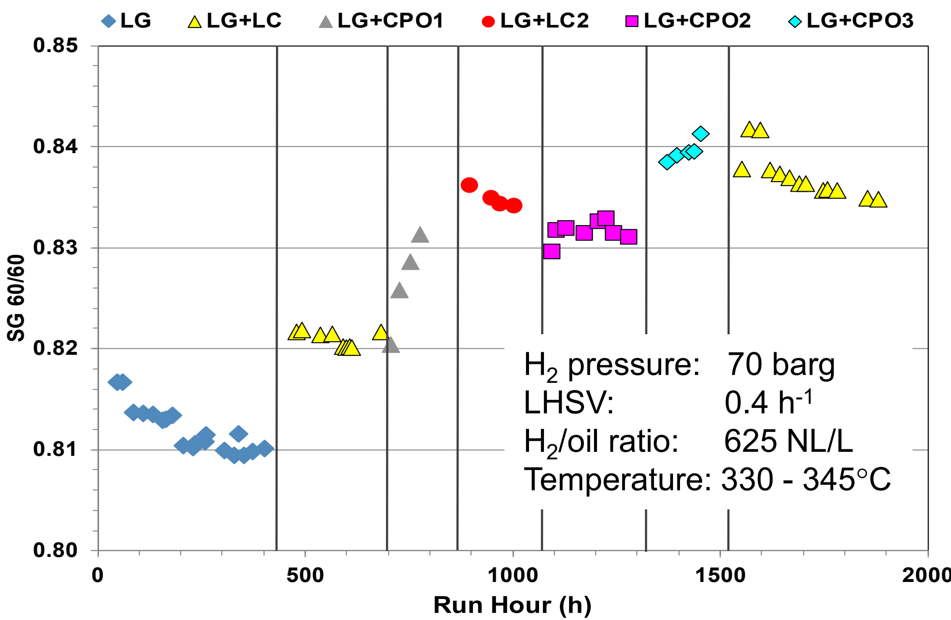


Co-processing Bio-crude with Refinery Intermediates

30% Light Cycle Oil (LC) or Partially Upgraded Bio-crude (CPO) blended with 70% straight run diesel

Property	30/70 LC1/LG	30/70 LC2/LG	30/70 CPO1/LG	30/70 CPO2/LG	30/70 CPO3/LG
H, wt %	12.46	12.14	12.80	12.58	12.31
O, wt %	-	-	1.26	1.84	2.47
S, wt %	1.19	1.00	0.828	0.903	0.717
N, ppm	213	433	258	327	377
SG	0.863	0.873	0.861	0.867	0.882

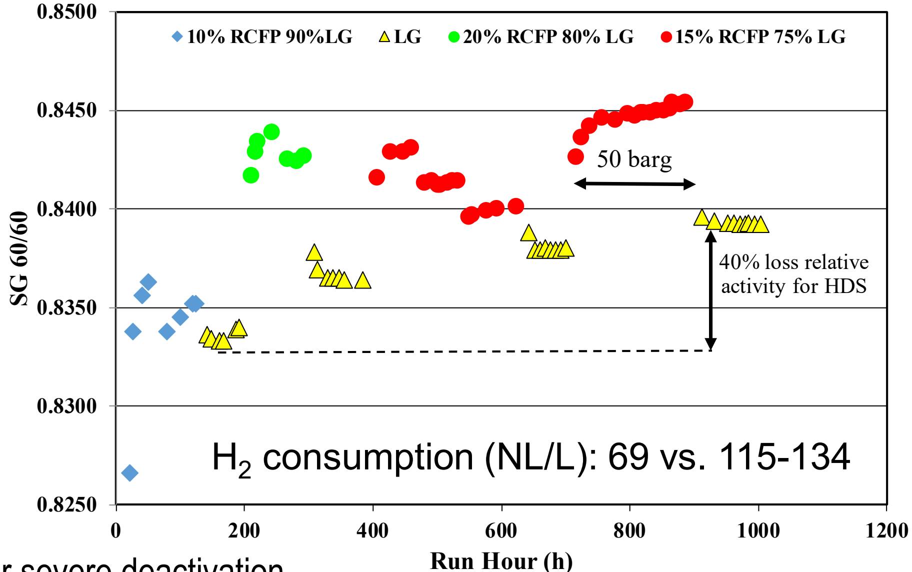
- No additional pressure drop with CPO
- 6% lower diesel yield from CPO ([O] in feedstock and light and a heavy fractions outside diesel range)
- Lower H_2 consumption for CPO compared to the LCO (HDS vs. HDO)



RCFP Bio-crude Co-processing with Light GasOil

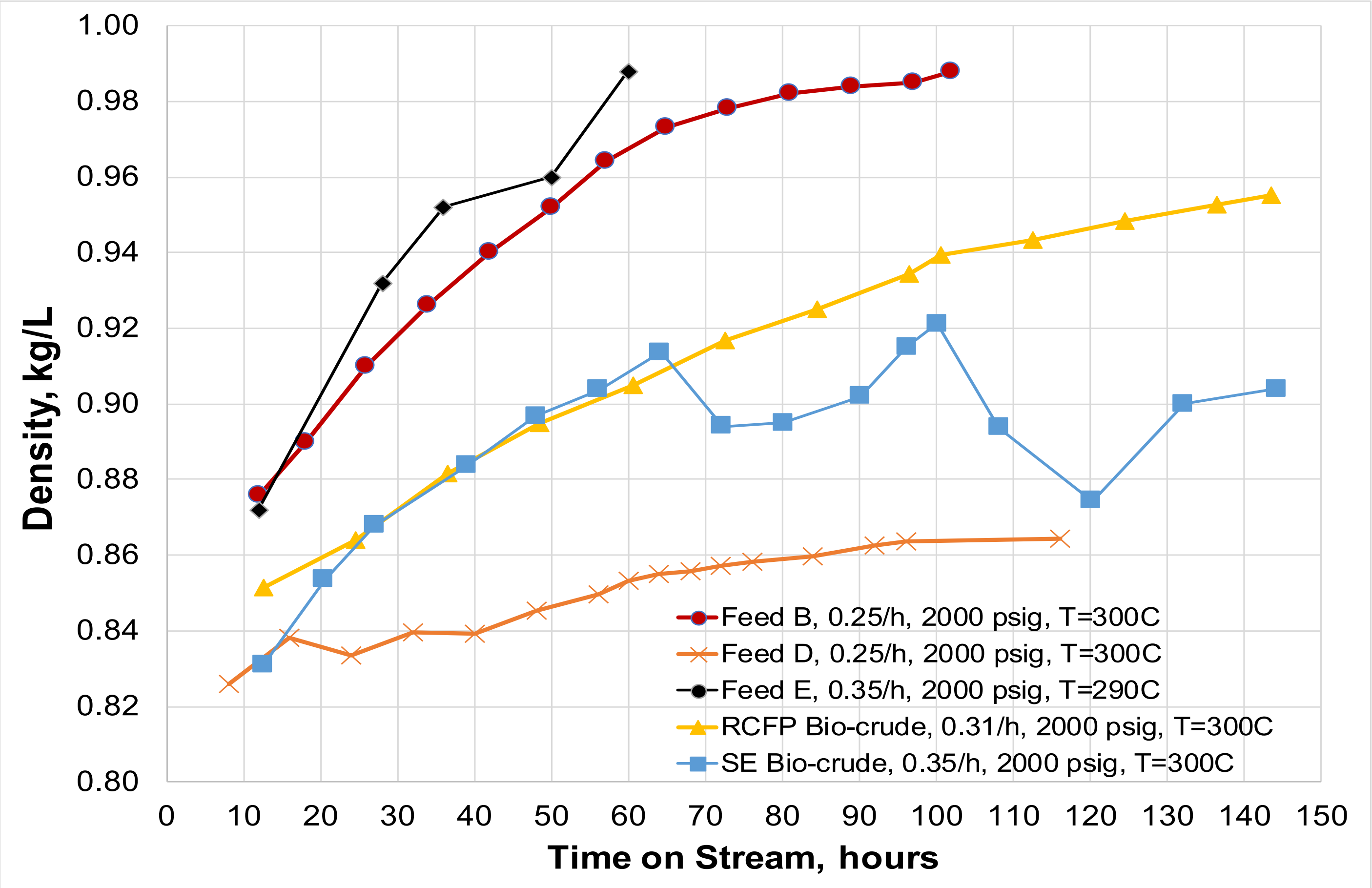
Analysis	Unit	LG	RCFP	10/90 RCFP/LG	15/85 RCFP/LG	20/80 RCFP/LG
SG at 60/60°F		0.8541	1.005	*0.8667*	0.8726	*0.8782*
O	wt %	-	9.65	-	-	-
S	wt %	1.30	0.001	*1.14*	1.04	*1.01*
N	wt ppm	148	425	*165*	180	*201*
H	wt %	13.09	8.28	*12.59*	12.43	*12.18*

Pressure (Inlet pH_2)	50 – 70 barg (725-1015 psig)
Temperature	340 – 360°C
LSHV	2 h^{-1}
H_2/oil ratio	500 Nl/l



- > 1000 hours without shut-downs or severe deactivation
- Blended feed oxygen in the range 0.9 – 1.9 %wt
- Product oxygen ≤6 ppmw
- Approximately 89 % of RCFP bio-crude converted to hydrocarbons on weight basis

Summary



1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
Density, kg/L
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Time on Stream, hours
Feed B, 0.25/h, 2000 psig, T=300C
Feed D, 0.25/h, 2000 psig, T=300C
Feed E, 0.35/h, 2000 psig, T=290C
RCFP Bio-crude, 0.31/h, 2000 psig, T=300C
SE Bio-crude, 0.35/h, 2000 psig, T=300C

Conclusions

Commercially-relevant steady-state hydrotreating

- More anyhdrosugars and acids = faster reactor plugging
- Pyrolysis processes for minimizing thermally unstable components
- Separations for removing undesirable components
- Co-processing (50% lower pressure) to minimize impacts of bio-crude composition

Hydrotreating catalyst deactivation

- Mechanism
- Sulfur loss
- Recovery by increasing temperature

Total oxygen content for hydrogen demand
Oxygen speciation for upgrading process performance

Caution: What is not identified with GC/MS that causes additional problems?

Acknowledgements

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

RTI Biomass Team

- Dr. Ofei Mante
- Dr. Phil Cross
- Joseph Weiner
- Jonathan Peters
- Gary Howe
- Kelly Amato

Haldor Topsøe A/S

- Jostein Gabrielsen
- Nadia Luciw Ammitzboll
- Sylvain Verdier
- Christian Ejersbo Strebel

HALDOR TOPSØE

CATALYSING YOUR BUSINESS

RTI Bio-crude Production Capabilities

Pilot-scale (1TPD) *in situ* Catalytic Fast Pyrolysis

- Continuous feed circulating fluidized bed reactor/regenerator
- Pyrolysis temperature: 350-500 ºC
- Regenerator Temperature: 560-640 ºC
- Residence time: 0.5-1.0 s
- Biomass Feed Rate: 35-70 kg/h
- Bio-crude production rate: 20-50 gal/hr

Laboratory Fluidized Bed Reactor System

- 2.5" fluidized bed reactor with 4" disengagement zone
- Biomass feeding rate: 2-5 g/min
- Liquid collection: 3 condensers and 1 ESP
- Non-condensable gases analyzed by micro GC
- Liquid product analyzed by Karl Fischer titration, elemental analysis, GC/MS