Opportunities and Challenges for Hydrotreating of Catalytic Fast Pyrolysis Oil to Fuels

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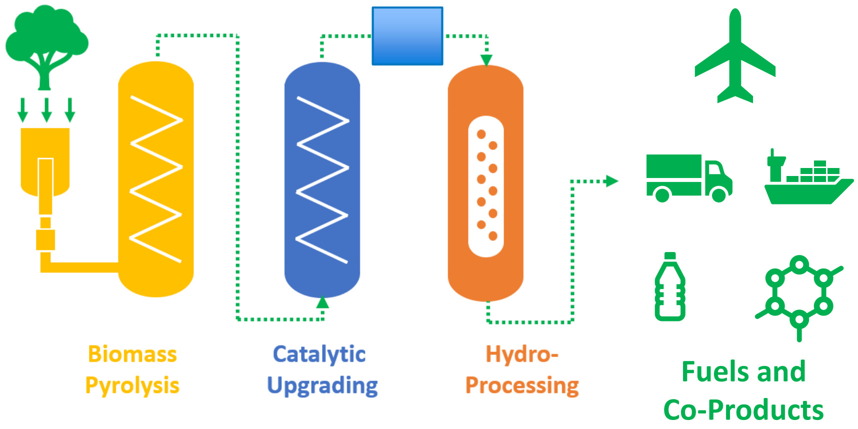
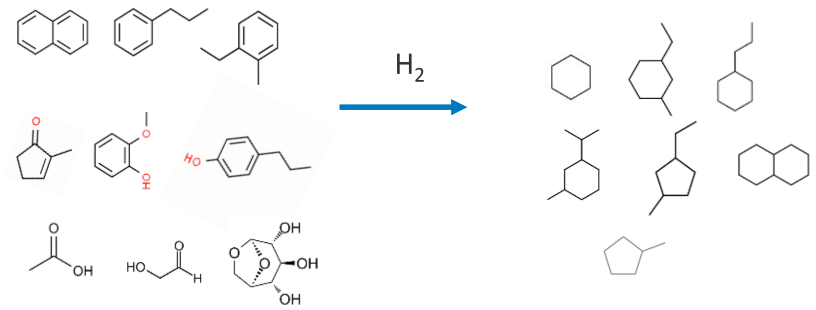
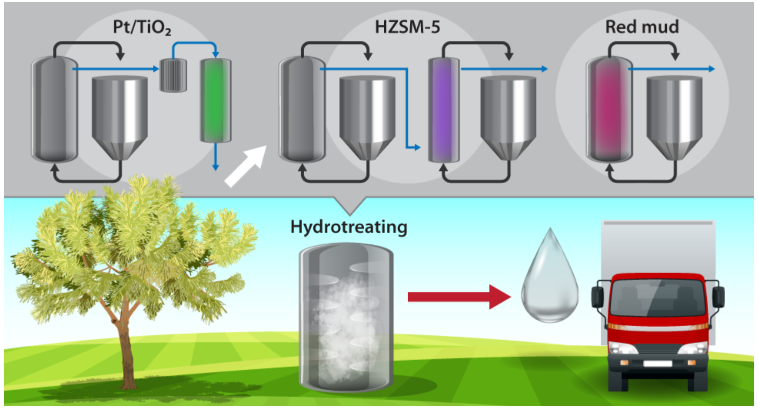
Fuel via Hydrotreating of Catalytic Fast Pyrolysis Oils





- Fast pyrolysis produces liquid oil at a high yield
  - Product has high oxygen content (~30% O dry basis) and is reactive
  - Requires several stages of hydrotreating to produce hydrocarbon fuels
- Catalytic fast pyrolysis (CFP)
  - Utilizes vapor phase upgrading over a catalyst to produce a more deoxygenated (15-22% O) and stable oil product
  - Lower concentrations of reactive components
  - CFP oils still require hydroprocessing for final deoxygenation
  - A valuable source of **cycloalkanes** that are not easily produced from other biomass sources

Hydrotreating of CFP Oils to Gasoline and Diesel



Catalyst	**Zeolite HZSM-5**	**HDO Pt/TiO_2**	**Red mud**
Mode	**Ex situ**	**Ex situ**	**In situ**
Pyrolysis reactor	Fluidized bed	Fluidized bed	Fluidized bed
Upgrading reactor	Fluidized bed	Fixed bed	-
Pyrolysis temperature, °C	500	500	400
Upgrading temperature, °C	500	400	-
Feed gas	100% N_2	85% H_2/15% N_2	15% N_2/85% recycle gas
Catalyst regeneration	no	yes	no

- Three CFP oils produced from pine
- Hydroprocessed under identical conditions
  - $NiMo/Al_2O_3$, 130 bar, 400°C, LHSV 0.2 h^{-1}
  - Distilled to gasoline and diesel cuts

Iisa et al., *Energy Fuels, 2023, 37, 19653*
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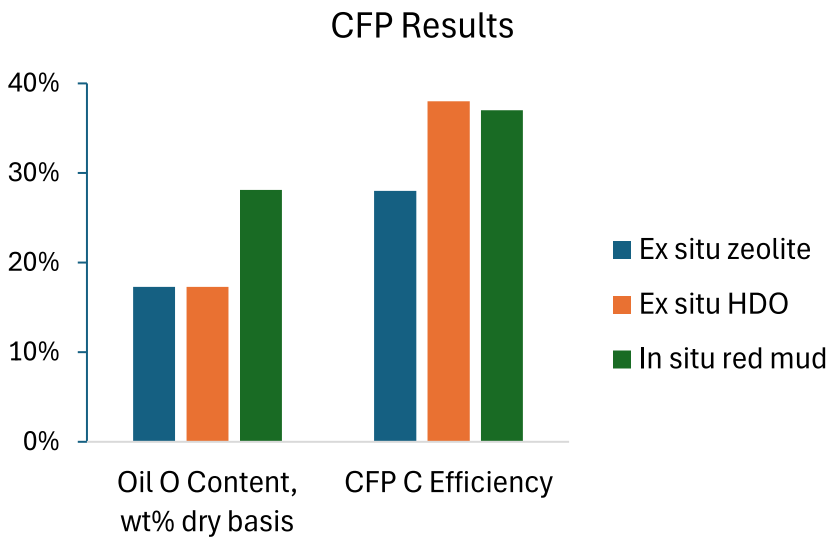
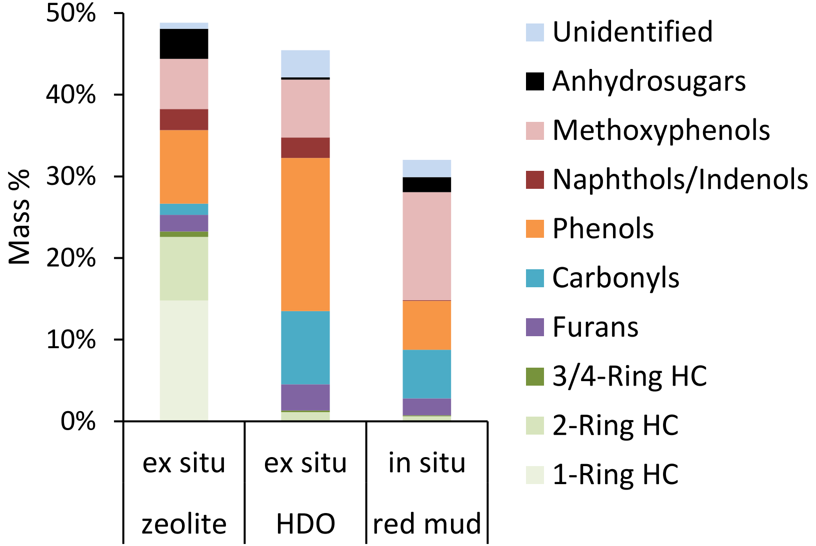
Hydrotreating of Three CFP Oils

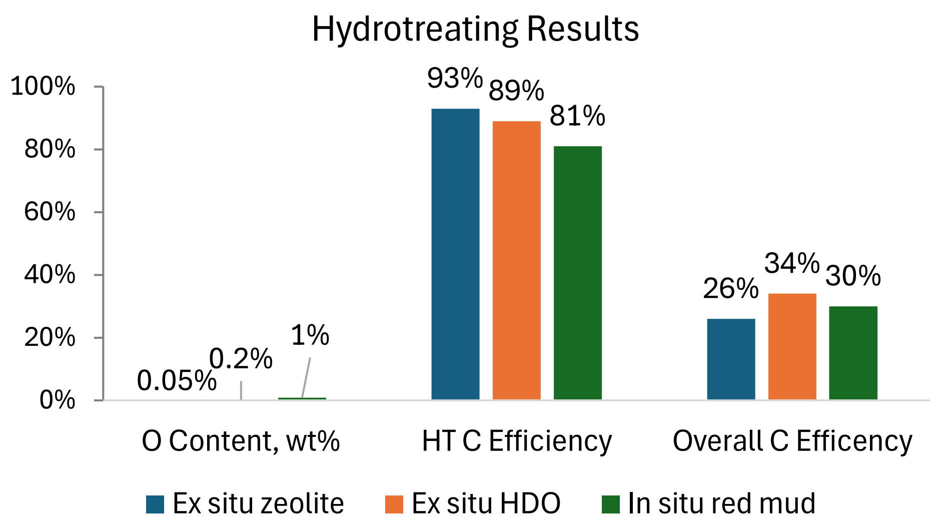


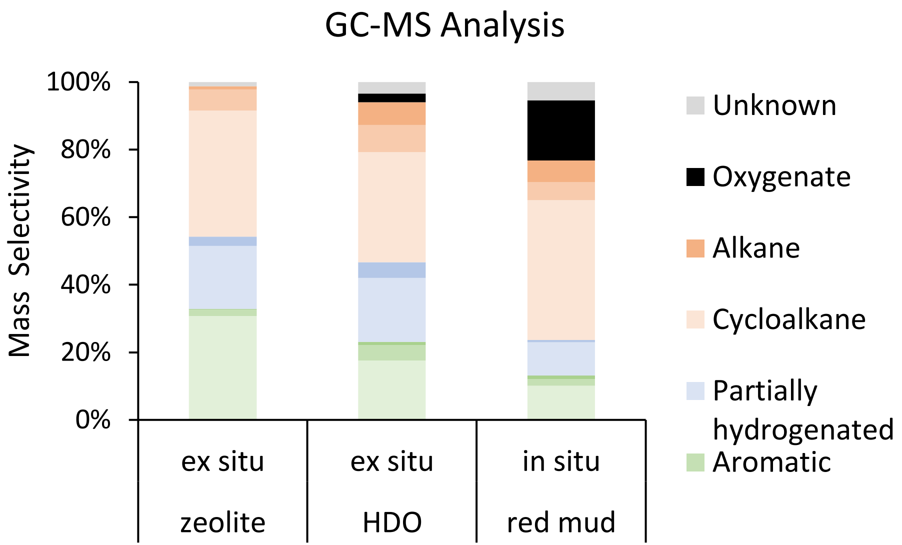


- *Ex situ* zeolite and *ex situ* HDO catalyst produced CFP oils with low oxygen contents: 17 wt% O on dry basis
- *Ex situ* HDO catalyst and *in situ* red mud catalyst gave high carbon yields of CFP oil: 37-38%

- CFP oil compositions varied
  - Zeolite: aromatic hydrocarbons and oxygenates
  - HDO: carbonyls and phenols
  - Red mud: methoxyphenols & other oxygenates

Hydrotreating Results

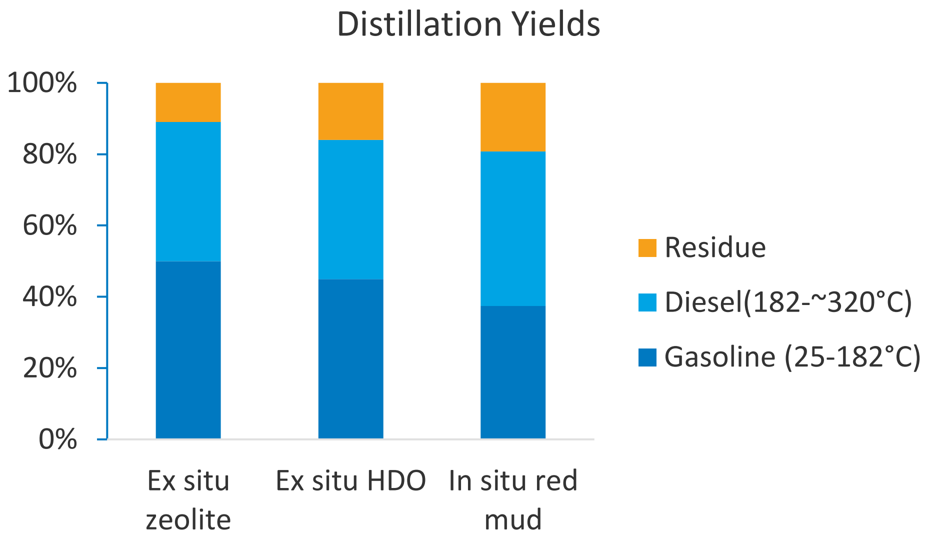




- Low oxygen content in products for ex situ
- High hydrotreating carbon efficiency for ex situ processes
- Overall carbon efficiency from biomass to fuels highest for HDO (Pt/TiO_2) catalyst

- Fully aromatic hydrocarbons (benzenes, naphthalenes)
- Partially hydrogenated aromatics (e.g. tetralins)
- Cycloalkanes (e.g., cyclohexanes, decanes)
- Oxygenates

Fractionation and Fuel Properties



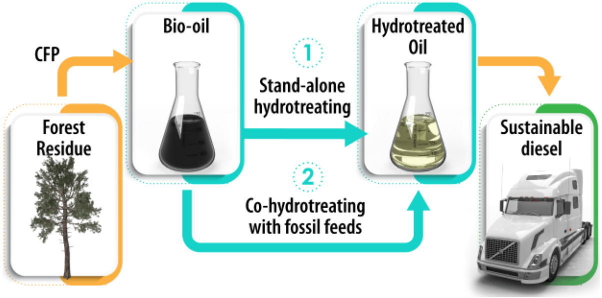
	Riser ex situ CFP	Fixed-bed ex situ CFP	In situ CFP
Gasoline: RON	74	67	59
MON	69	62	55
(RON+MON)/2	**71**	**65**	**57**
Vapor pressure, psi	1.8	2.6	2.8
Diesel: Cetane Number DCN	**22**	**24**	**26**

Diesel with Higher Cetane Number

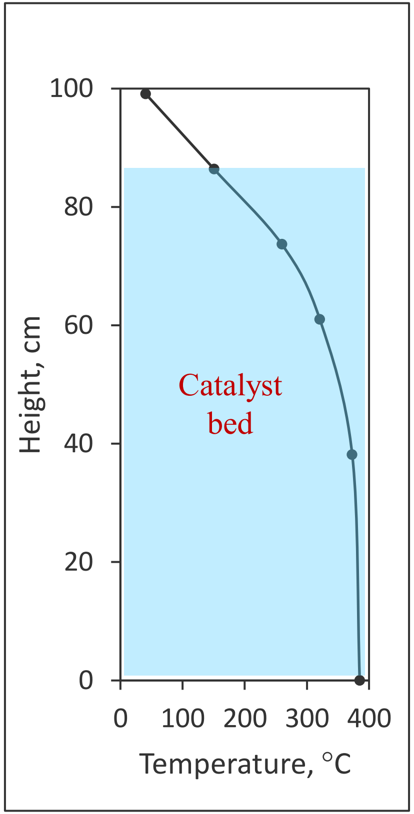
- Diesel of poor quality
- Hypothesis: add hydrogenation zone prior to hydrotreating

Standalone hydrotreating with

- $NiMo/Al_2O_3$, 385°C, 125 bar (1800 psi), 0.2 h^{-1}
- Long non-isothermal zone with $NiMo/Al_2O_3$



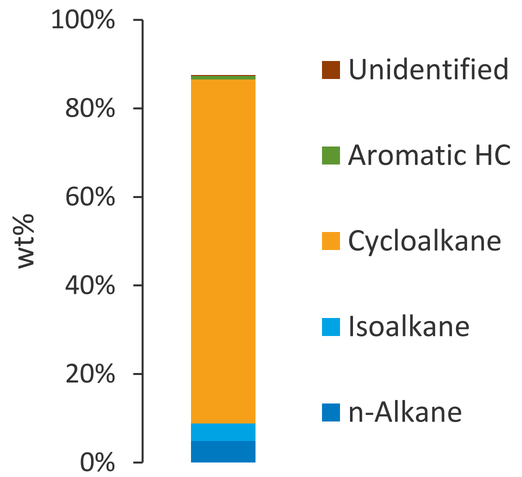
Chen et al., *Energy Adv., 2024, 3, 1121*
https://doi.org/10.1039/d4ya00098f



Standalone HT for Diesel

HT Operating Conditions	Previous 400°C 130 bar	Modified 385°C, 125 bar
CFP oil O content, wt% db	16%±1%	17%
Product Yield, g/g CFP oil	76%±2%	75%±1%
Product C Yield	89%±2%	89%±1%
O, wt%	0.4%	≤ 0.3%
H:C, mol: mol	1.71	2.01
Density, g/ml	0.851	0.740
Distillation Yields		
Gasoline range, wt%	45%	51%
Diesel range, wt%	39%	45%
Residue, wt%	16%	4%
Diesel cetane number	**24**	**45**

GC x GC Analysis of Diesel



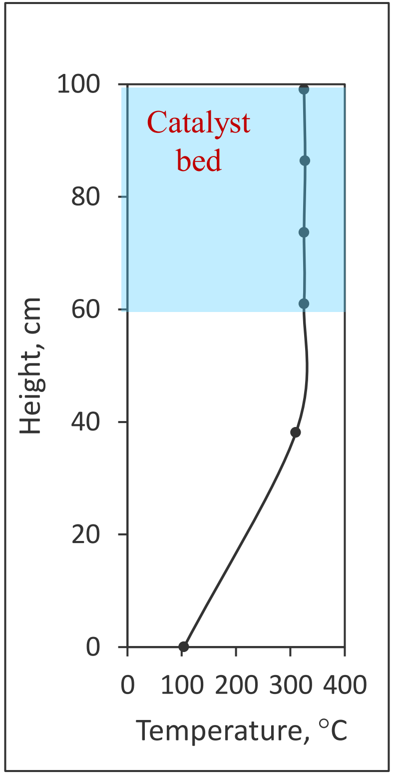
- Adding a long transition zone enhanced hydrogenation and cetane number without negatively impacting product yield
- **78 wt% of products cycloalkanes**

Co-Hydrotreating of CFP Oil to Diesel

- Co-hydrotreating with **straight-run diesel (SRD)** Hydrotreating conditions milder than typically used for standalone hydrotreating of CFP oil

	Typical SRD HT	Standalone CFP oil HT	Used here
Pressure, bar	40-60	>100	55
Temperature,	320-350	385-400	325
LHSV, h^{-1}	1-2.5	~0.2	1.0

	CFP oil	SRD
C, wt%	72.6	86.6
H, wt%	7.3	13.2
O, wt%	19.4	≤ 0.3
N, wt%	0.2	0.03
S, wt%	< 0.01	0.2
% Modern carbon	104.1±0.3	< 0.44



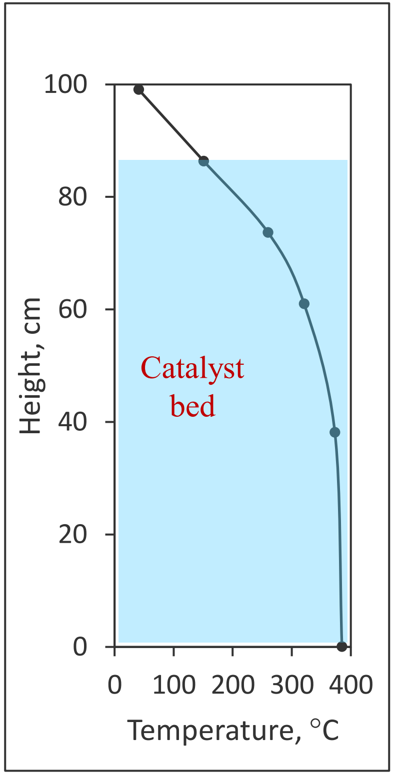
Co-Hydrotreating for Diesel

Catalyst	$NiMoS_x/Al_2O_3$		$CoMoS_x/Al_2O_3$	
Feed	**SRD**	**80%SRD/20%CFP**	**SRD**	**80%SRD/20%CFP**
Carbon Efficiency	100	100	101	95
C, wt%	86.34	86.98	87.01	86.77
H, wt%	13.39	13.22	13.48	12.95
O, wt%	≤0.3	≤0.3	≤0.3	≤0.3
N, wt%	0.03	0.04	0.02	0.04
S, wt%	0.01	0.03	0.02	0.04
H:C, mol: mol	1.86	1.82	1.86	1.79
Cetane (ICN)	**50**	**45**	**48**	**42**
Density, g/mL	0.83	0.83	0.83	0.83
Modern carbon, %	<0.44	19.6±0.1	<0.44	19.0±0.1

- Good deoxygenation was achieved during co-HT despite milder operating conditions
- NiMo gave a higher hydrogenation and cetane number than CoMo did
- C-14 analysis suggested ~95% C incorporation from CFP oil

Hydrotreating for Sustainable Aviation Fuel (SAF)

CFP Catalyst	Pt/TiO_2	HZSM-5
Catalyst type	Bifunctional HDO (metal- acid)	Zeolite (solid acid)
Upgrading reactor	Fixed bed	Riser
Feed	50% Pine/50% FR	Pine
Gas	85% H_2	N_2
Pyrolysis temperature, °C	500	500
Upgrading temperature, °C	400	550
O, wt% daf	16%	18%
H:C, mol/mol	1.22	1.11
$H:C_{eff}$, mol/mol	0.92	0.75



Hydrotreated in a process similar to that for diesel

- Final temperature 385°C, pressure 125 bar (1800 psi), 0.2 h^{-1},
- $NiMo/Al_2O_3$ catalyst

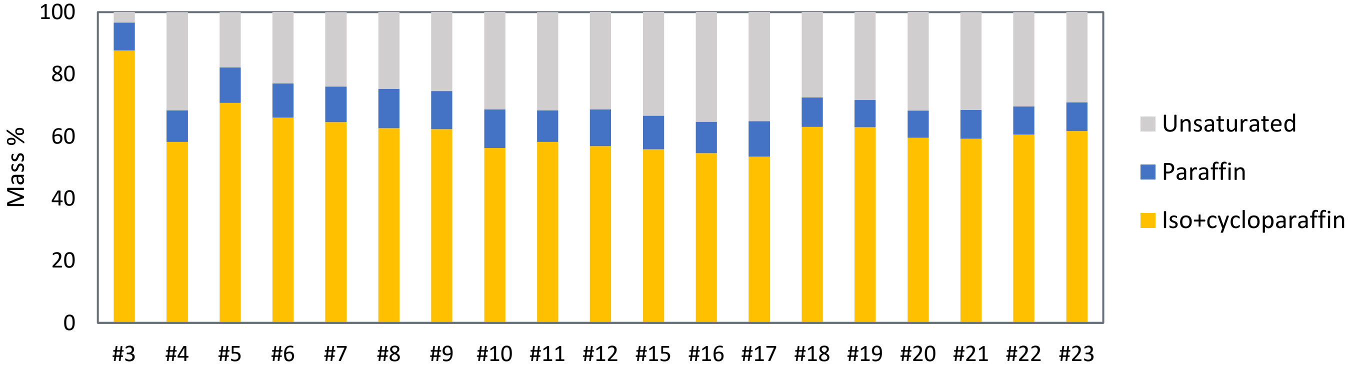
Distilled to fuel cuts

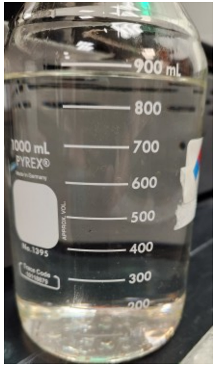
SAF Fraction Properties

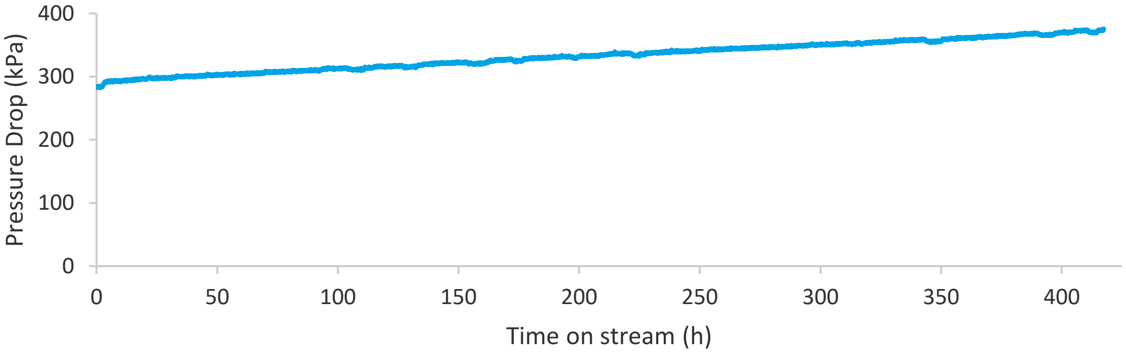
	SIMDIS, 10%, °C	SIMDIS, FBP, °C	Flash Point, °C	Freeze Point, °C	Density, g/cm^3	LHV, MJ/kg	C, wt%	H, wt%	N, wt%	O, wt%
ASTM D7566/ D4054	130-160	250-330	>38	max -40	775-840	>42.8	NA	NA	NA	<0.5
ZSM-5	**158**	**281**	**50**	**<-70**	**834**	**43.0**	**86.5**	**13.6**	**0.0**	**<0.1**
Pt/TiO_2	**158**	**286**	**47**	**<-70**	**833**	**43.0**	**86.5**	**13.8**	**0.0**	**<0.1**

- Product distilled to fuel cuts
- Jet-range product met aviation fuel specifications with respect to volatility, flash and freeze points, density, heating value, and oxygen content.

Hydrotreating of CFP Oil to SAF for 400 h





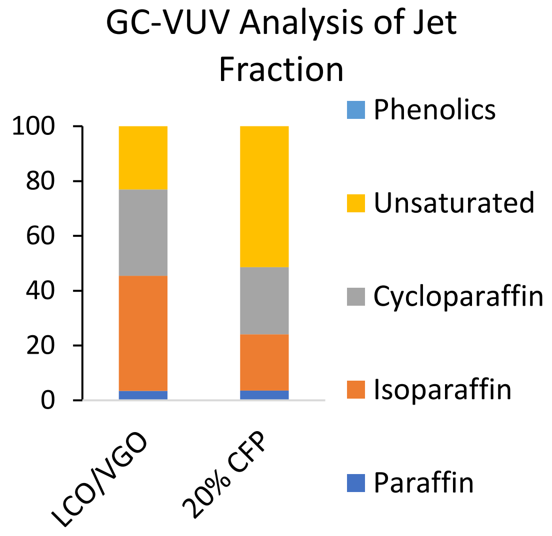


- Completed 400+ hours of hydrotreating for SAF
- O content remained below detection limit (<0.01 wt%)
- Unsaturated (aromatics) slightly increased
- No plugging (pressure drop increased linearly – instrument drift?)

Co-Hydrotreating/cracking CFP Oil to SAF

- Co-hydrotreating/hydrocracking with a mixture of light cycle oil and vacuum gas oil (LCO/VGO)
  - 385°C, $NiMoS_x/Al_2O_3$, 1 h^{-1}
  - 400°C, NiW/Zeolite, 1 h^{-1}

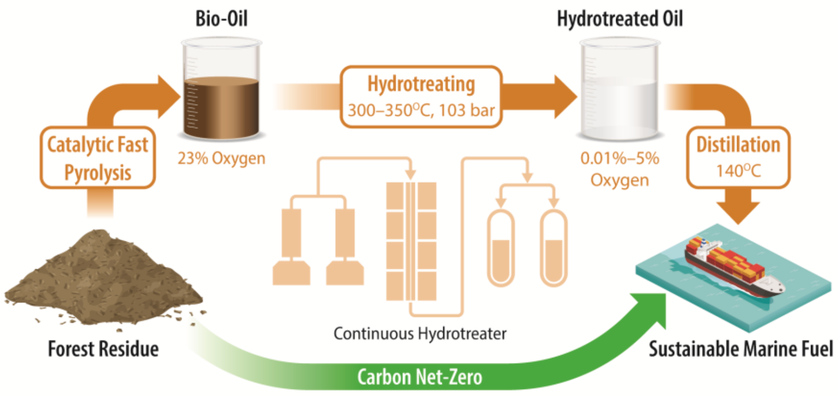
Jet Fraction Properties	**D4054/D7566**	**LGO/VGO**	**20%CFP/ 80%LCO/VGO**
Flash point, °C	38-66	43	45
Freeze point, °C	≤-40	<-75°C	<-75°C
LHV, MJ/kg	≥42.8	43.4	42.9
Density @ 15°C, kg/m3	755-884	811	831
Viscosity @–20 °C, mm2/sK	≤8	3.8	3.9
Surface Tension @ 20°C, mN/m	~26	26.2	27.2



- Co-hydrotreating/hydrocracking with CFP oil increased unsaturated (aromatics and olefins)
- No phenolics or O detected
- Measured jet properties within range

Hydrotreating for Marine Fuel

- Goal to produce marine fuel compatible with very low sulfur fuel oil (VLSFO) and residual marine fuel ISO8217 guidelines
- Complete deoxygenation may not be necessary



Hydrotreating condition	ISO 8217 RMK 700 grade	300°C, 0.2 g/(gh)
O, wt% daf		5
Density, g/L	≤ 1010	1013
Acid number, mg KOH/g	≤ 2.5	0
H_2O, wt%	≤ 0.5	0.07
Flash point, °C	≥ 60	66.7
Spot test with 50 vol% VLSFO	≤ 2	1
Thermal aging, wt%	<0.1	0.01
Chemical aging, wt%	<0.1	0.02

Opportunities and Challenges

- Catalytic fast pyrolysis oil can be upgraded to different fuel cuts
  - Diesel, SAF, marine
  - Via standalone hydrotreating or co-processing with petroleum streams
- Challenges remain
  - Quality of products
    - Additional processing (e.g., hydrogenation)
  - Severe conditions (temperature, pressure, space velocity) required
    - Good deoxygenation for co-processing at milder conditions
  - Catalyst deactivation
    - Hydrogenation activity
    - Deoxygenation activity stable
  - Oil polymerization and plugging problems possible
    - Quality criteria for feeds

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