NREL
Transforming ENERGY

Sustainable Aviation Fuel via Hydroprocessing of Catalytic Fast Pyrolysis Oil

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TCBiomass

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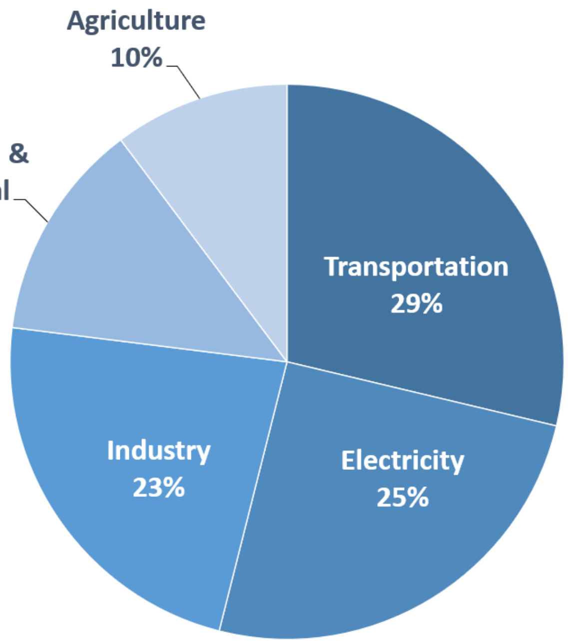
Aviation as Source of Greenhouse Gas Emissions

Total U.S. Greenhouse Gas Emissions by Economic Sector in 2019



U.S. Environmental Protection Agency (2021). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2019

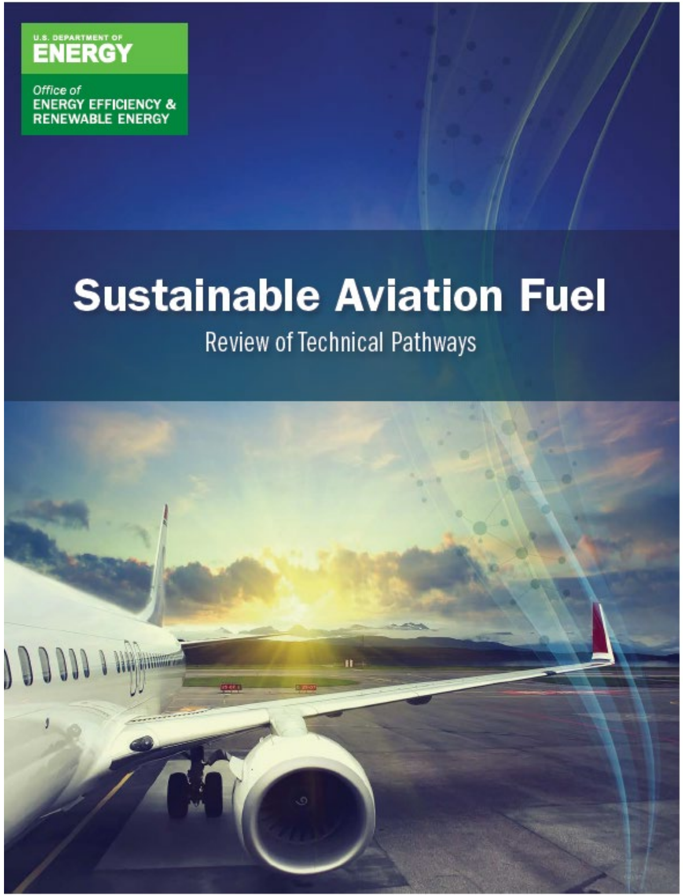
Aviation 11% of transportation sector

- Difficult to electrify

BETO Goals

- 3 billion gallons sustainable aviation fuel by 2030
- 35 billion gallons by 2050 (100% of projected need)
- >70% CO_2 emission reduction

Sustainable Aviation Fuel (SAF)



Jet Fuel

- Typically, C9-C18 carbon length
- Boiling point 125-290°C
- Composition varies

Group	wt%
n-Alkanes	13-26%
Isoalkanes	19-37%
Cycloalkanes	22-47%
Aromatics	14-21%

"Vision: Reduce aromatic content and increase isoalkanes and cycloalkanes"

Why Cycloalkanes?

Energy density key to jet fuel quality

- ASTM standard LHV >42.8 MJ/kg

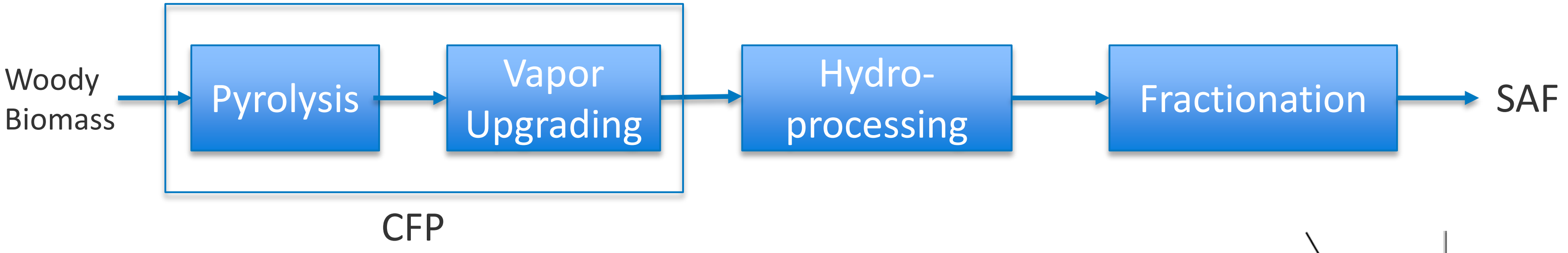
Aromatics limited to 25%

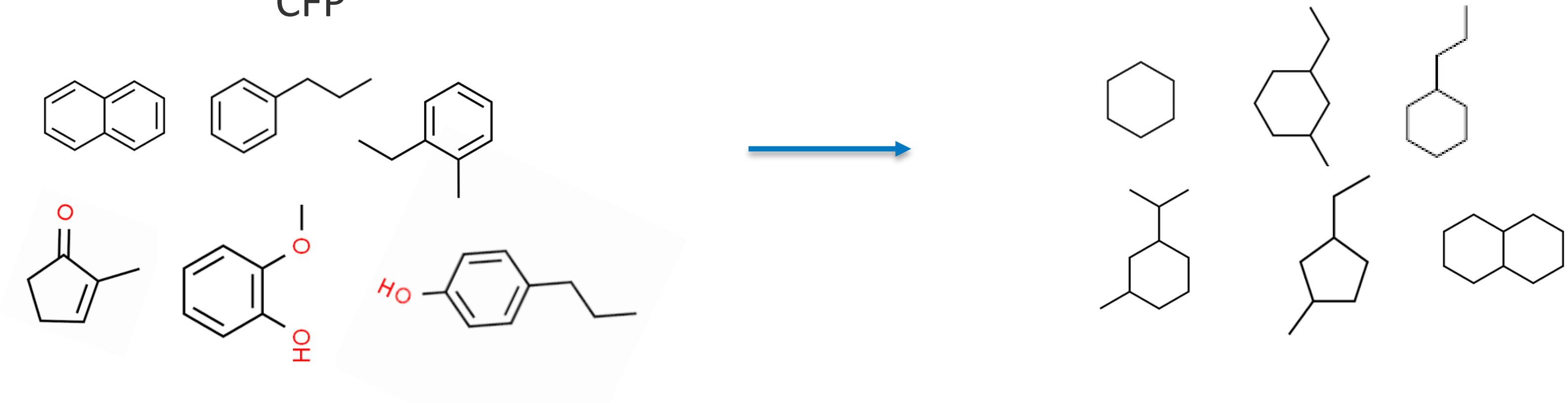
- Non-desirable combustion characteristics: low energy density, high sooting
- Needed to ensure seal swelling of nitrile O-rings
  - Cycloalkanes may be able to provide desired performance

Compound	LHV, kJ/mol	Density, kg/m^3
Propylbenzene	41.4	862
Propylcyclohexane	43.7	793
Butylbenzene	41.7	860
Butylcyclohexane	43.6	818
Naphthalene	39.0	1020
Tetrahydronaphthalene	40.7	970
Decahydronaphthalene	42.5	896

Pyrolysis and Catalytic Pyrolysis Oils as Source of Cycloalkanes

- Lignin a source of phenolics
- Carbohydrates can form cyclic compounds
- Catalytic fast pyrolysis (CFP) can convert carbohydrate fraction to aromatics
- All can be hydrotreated to cycloalkanes



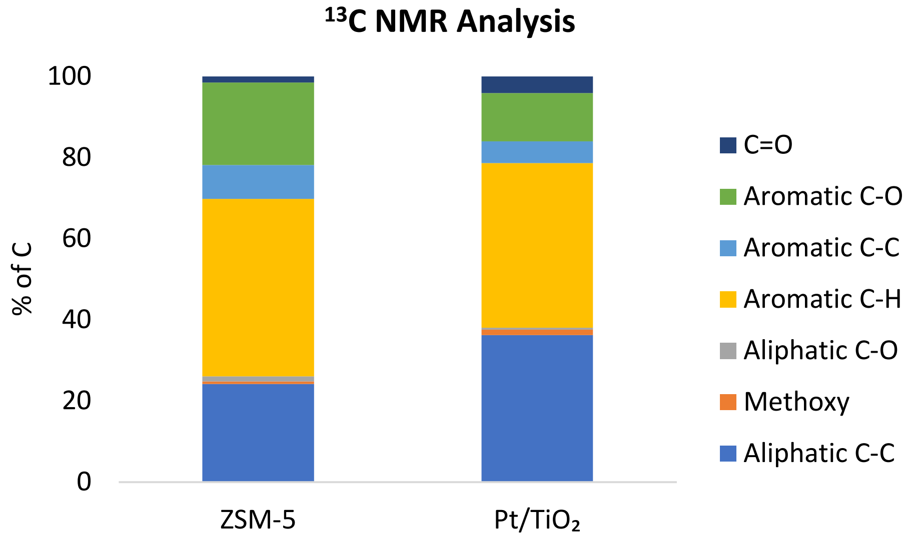


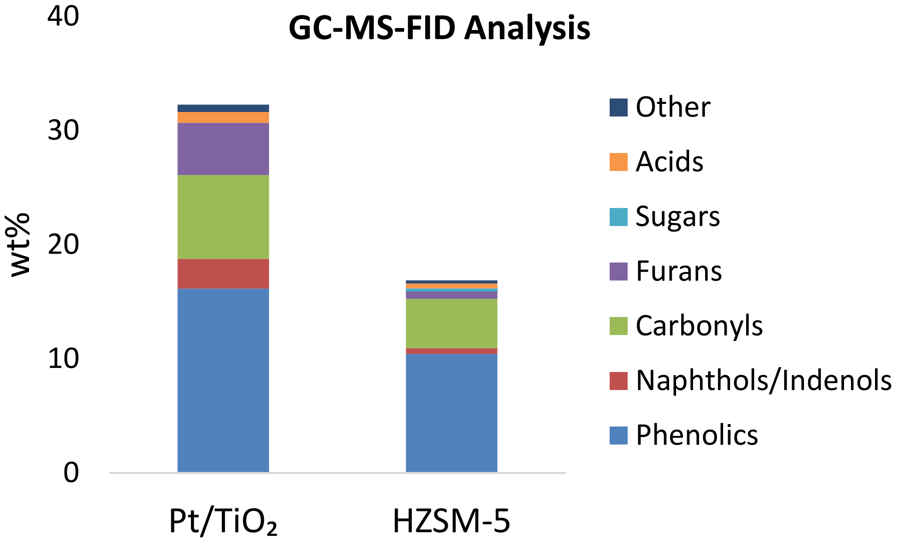
Experimental: Catalytic Fast Pyrolysis (CFP) Oils

- Two oils from different types of CFP processes
  - ZSM-5 oil prepared in NREL's pilot-scale reactor
  - Pt/TiO_2 oil prepared in NREL's bench-scale reactor

CFP Catalyst	Pt/TiO_2	HZSM-5
Catalyst type	Bifunctional (metal- acid)	Zeolite (solid acid)
Upgrading reactor	Fixed bed	Riser
Feed	50% Pine/50% FR	Pine
Gas	N_2	85% H_2
Pyrolysis temperature, °C	500	500
Upgrading temperature, °C	400	550
Biomass:Catalyst, g/g	12:1	1:16
O, wt% daf	16%	18%
H:C, mol/mol	1.22	1.11
$H:C_{eff}$, mol/mol	0.92	0.75

Catalytic Fast Pyrolysis (CFP) Oils

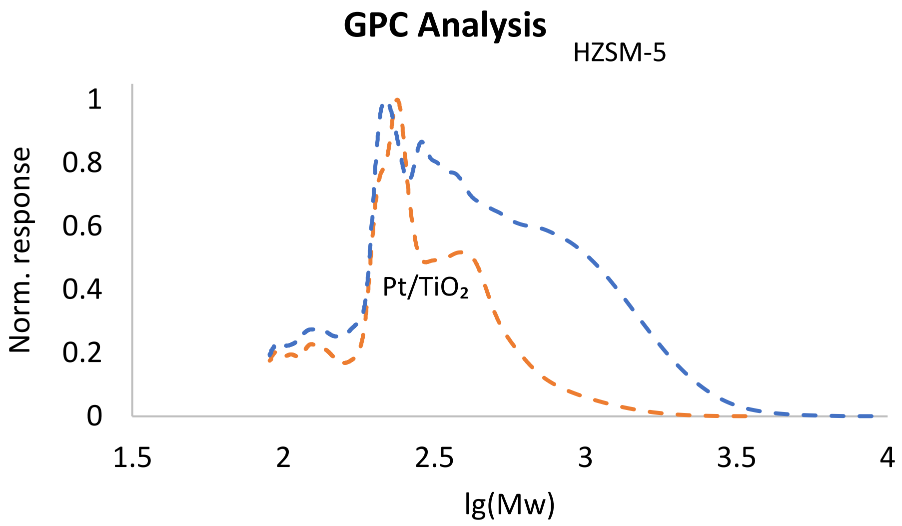


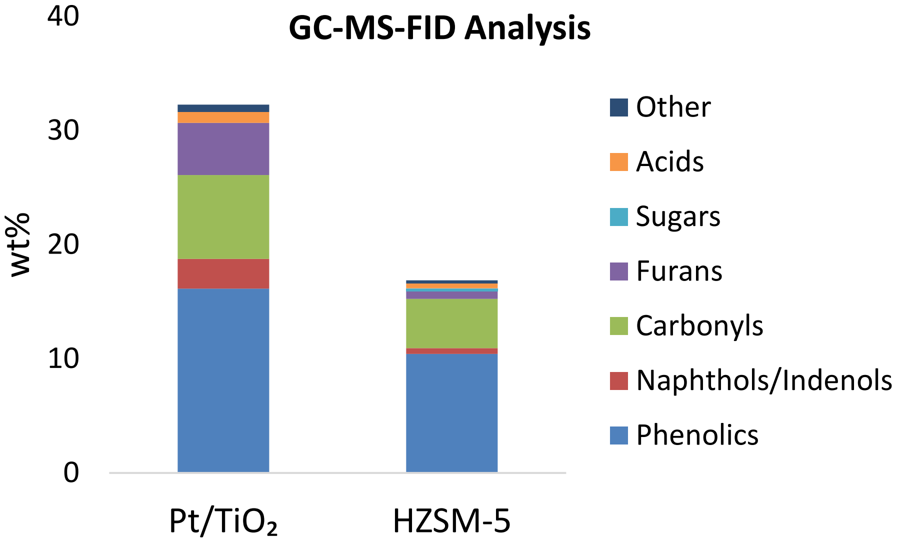


- ZSM-5 oil contained more aromatic C-O and C-C
- Pt/TiO_2 oil richer in aliphatic C-C (longer side chains) and carbonyls

- ZSM-5 oil contained more phenols, furans, and naphthols/indenols & more non-GC detectable (high-boiling) material

Catalytic Fast Pyrolysis (CFP) Oils

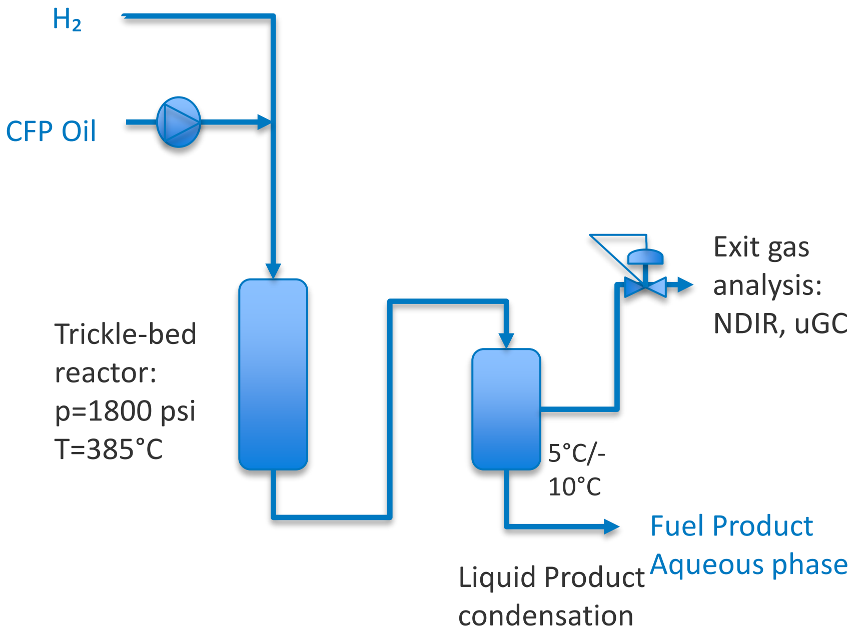




- ZSM-5 oil contained more high-MW material

- ZSM-5 oil contained more phenols, furans, and naphthols/indenols & more non-GC detectable (high-boiling) material

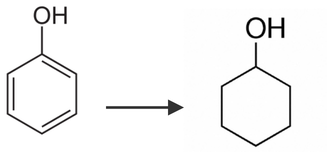
Hydroprocessing in NREL's Continuous Hydrotreater



Hydroprocessing

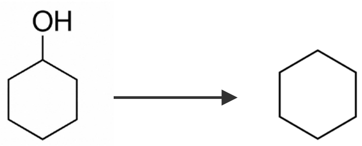
- One-stage hydrotreating of CFP oil produces a substantial fraction of aromatics
- Two-stage process:
- Low-temperature hydrogenation:

C=O → C-OH

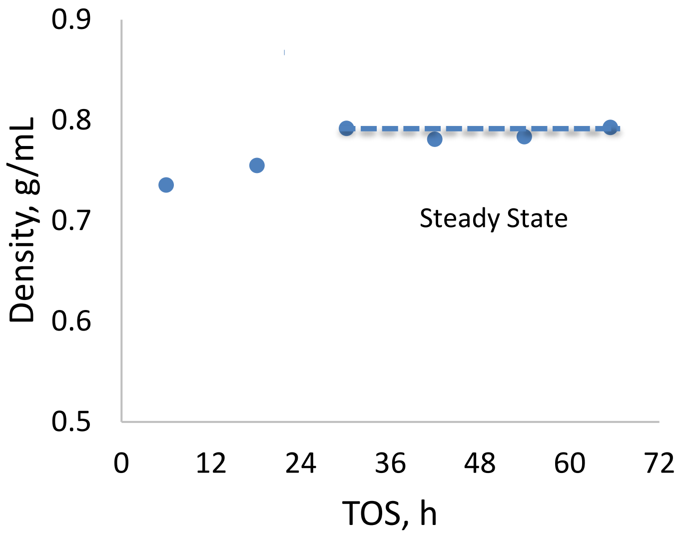


- High-temperature deoxygenation:

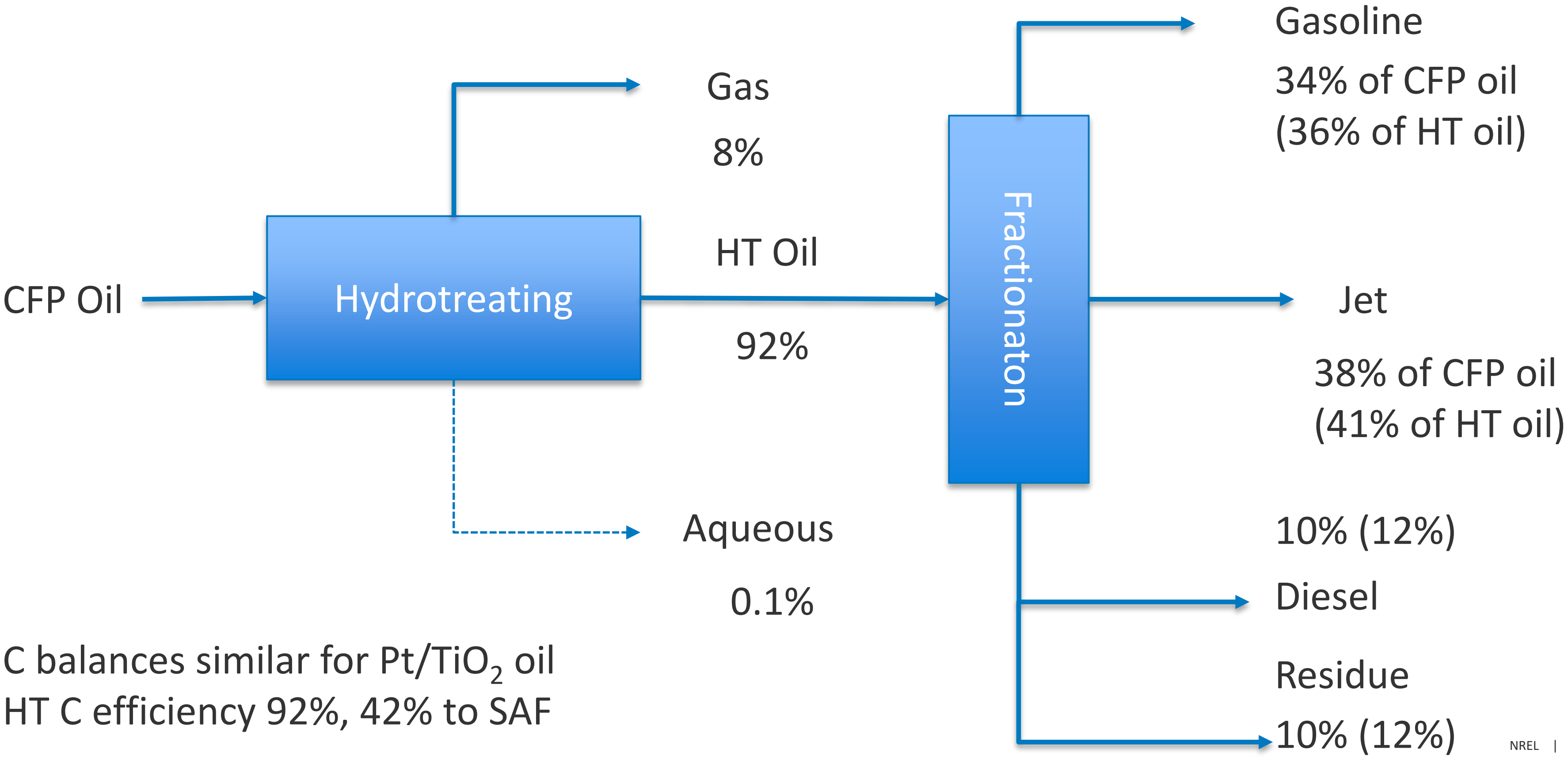
C-OH → C-H



Pressure	1800 psi/125 bar
Catalyst	$NiMoS_x/Al_2O_3$
Temperature, °C	~200 & 385
WHSV, h^{-1}	0.2 & 0.2 (0.1 total)

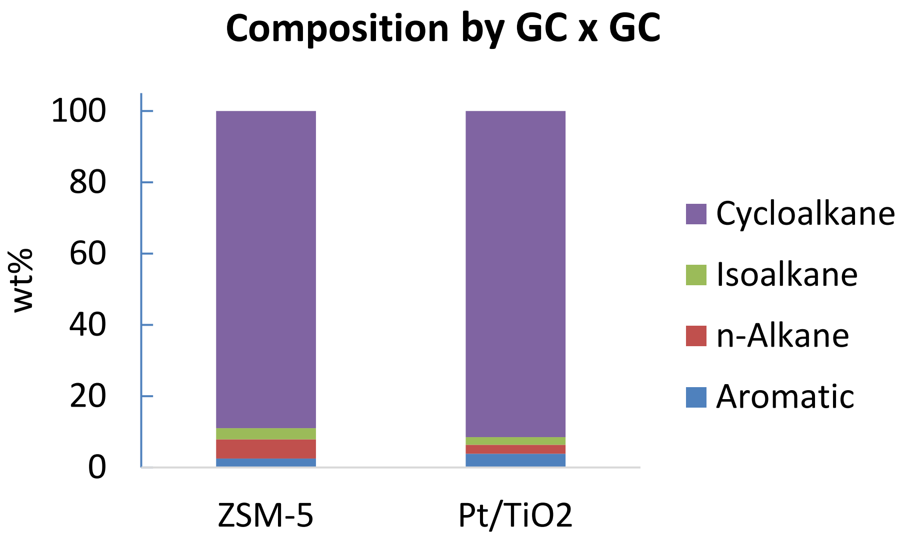


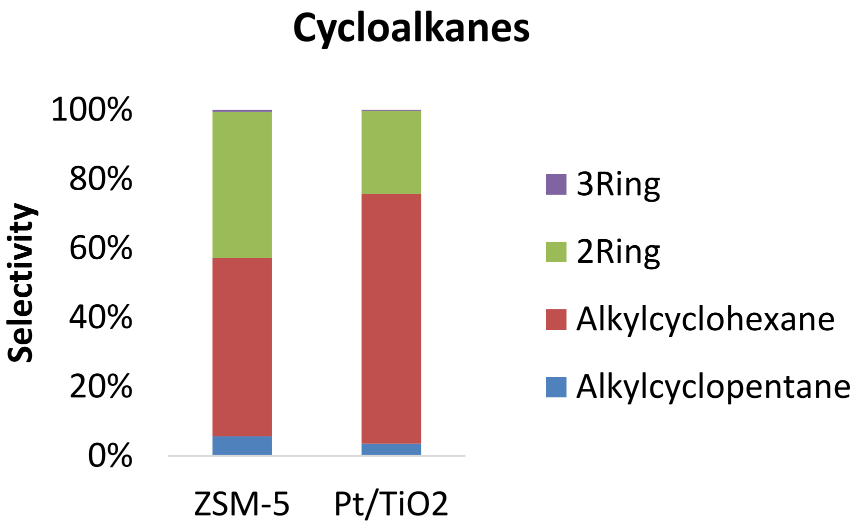
Carbon Distribution (ZSM-5)



C balances similar for Pt/TiO_2 oil
HT C efficiency 92%, 42% to SAF

Jet Fraction Properties





- 89-91% of products cycloalkanes (naphthenes)

- Majority of cycloalkanes 1-ring compounds
- ZSM-5 product contained more multirings due to its higher C-C coupling activity

Jet Fraction Properties

	Density, g/cm³	LHV, MJ/kg	SIMDIS, 10%, °C	SIMDIS, FBP, °C	Flash Point, °C	Freeze Point, °C	C, wt%	H, wt%	N, wt%	O, wt%
ASTM D7566/ D4054	775-840	>42.8	130-160	250-330	>38	max -40	NA	NA	NA	<0.5
ZSM-5	834	43.0	158	281	50	<-70	86.5	13.6	0.0	<0.5
Pt/TiO_2	833	43.0	158	286	47	<-70	86.5	13.8	0.0	<0.5

- Jet-range product met aviation fuel specifications with respect to density, heating value, volatility, freeze, and flash points

Challenges/Opportunities

- Overall conversion to SAF (ZSM-5)
  - CFP: C yield 28%
  - HT: C yield 92%
  - Distillation: C yield to SAF 41%
  - Overall C yield to SAF 11% (ZSM-5)
  - Overall C yield to SAF 13% (Pt/TiO_2)
- Co-products to reduce cost
- Increase yield in each step
  - Coupling, alkylation of products to reduce gasoline-range fraction
  - Increased cracking during HT (e.g., catalyst functionality, recycle of heavies)
- Process condition optimization
- Co-hydrotreating with petroleum streams

Acknowledgements

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- Johnson Matthey Technology Center
  - Luke Tuxworth
  - Mike Watson

Acknowledgements

Please visit our related presentations on CFP and hydrotreating

- **Griffin et al.: Improving Process Durability by Addressing Catalyst Deactivation During Upgrading of Biomass Pyrolysis Vapors**
  - Wednesday 1:30
- **Iisa et al.: Co-hydrotreating of Catalytic Fast Pyrolysis Oils with Straight-Run Diesel**
  - Thursday 2:00
- **Mukarakate et al.: Advancement of the Catalytic Fast Pyrolysis of Biomass Technology with Fixed-bed Reactor to Produce Renewable Fuels and Chemicals** (poster)
- **Dutta et al.: Techno-Economic Analysis of Fixed Bed Ex-Situ Catalytic Fast Pyrolysis Using a Pt/TiO2 Catalyst for the Production of Fuels and Oxygenated Co-Products** (poster)
- **Talmadge et al.: Comparative analysis of catalytic and non-catalytic pyrolysis oil co-processing by hydroprocessing and fluid catalytic cracking** (poster)

Thank you!

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