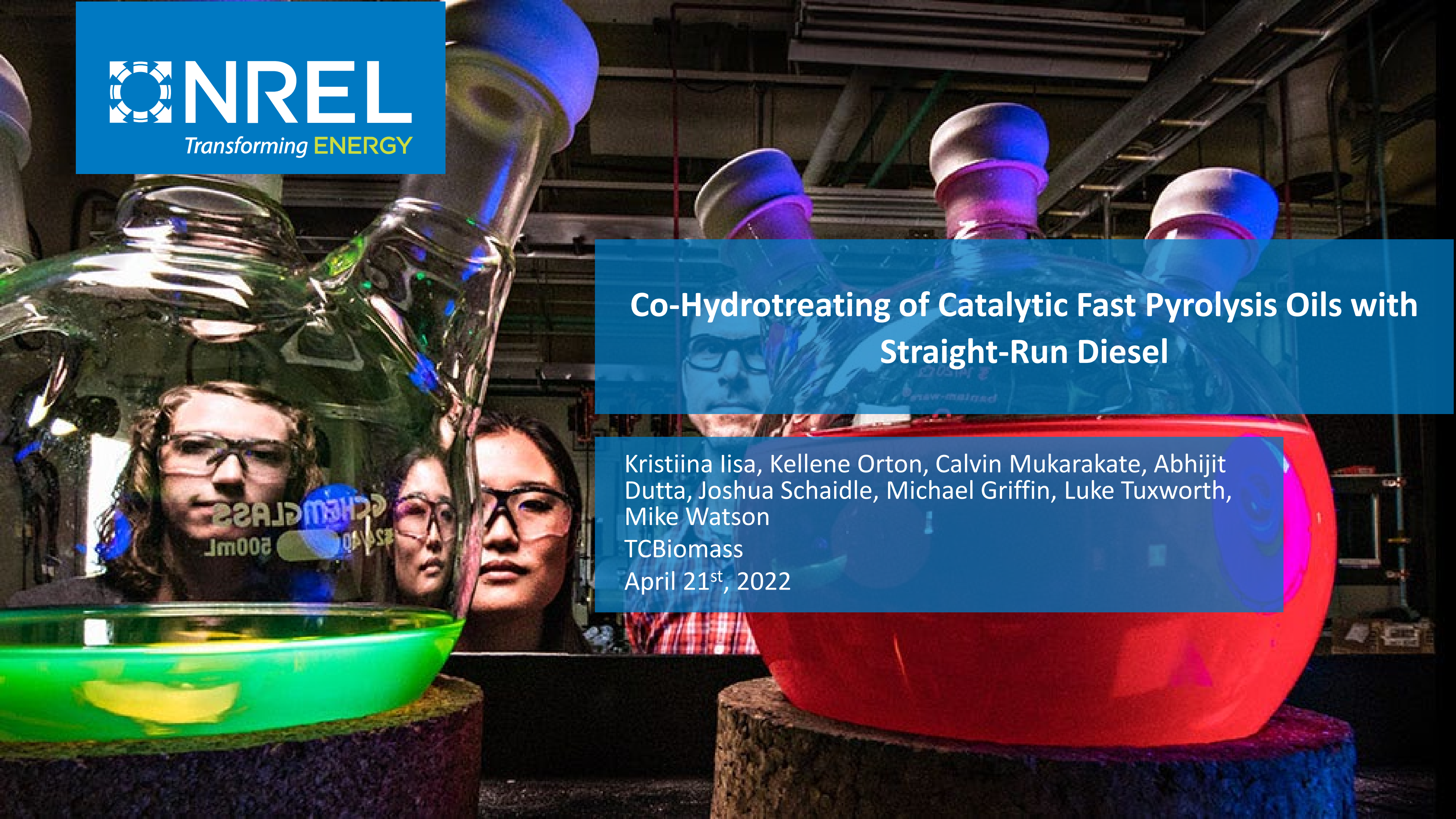

NREL Transforming ENERGY

# Co-Hydrotreating of Catalytic Fast Pyrolysis Oils with Straight-Run Diesel

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TCBiomass

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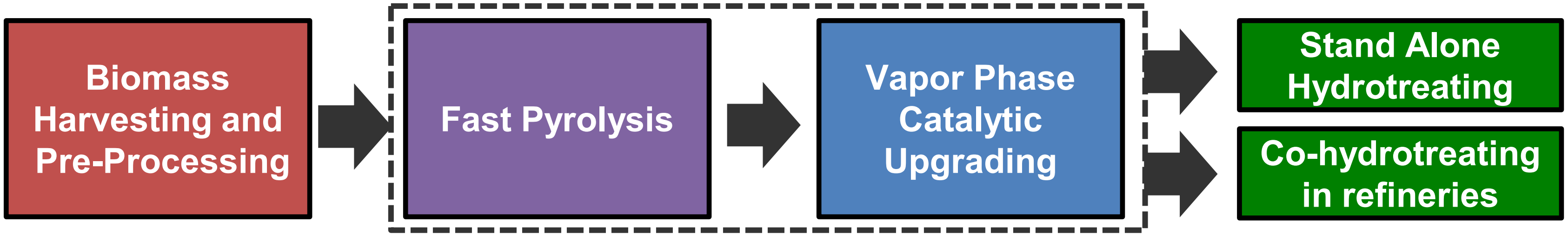
# Catalytic Fast Pyrolysis (CFP) Oil Hydrotreating




CFP = catalytic fast pyrolysis

HT = Hydrotreating

- Co-hydrotreating of CFP oil in a petroleum refinery offers several potential advantages
  - Reduces cost by enabling utilization of larger scale of petroleum refineries
  - Simplified process at biorefinery
  - Introduces biogenic carbon into refinery
- Introduces significant technical risk to refineries
  - Product quality
  - Plugging and fouling, corrosion

# Standalone vs. Co-Hydrotreating

## Standalone hydrotreating of CFP oil

- Process, catalyst and conditions can be developed to optimize CFP oil hydrotreating
- Need to generate product suitable as blendstock or further processing
- High temperature: 400°C
- High pressure: 125 bar
- Low liquid hourly space velocity (LHSV): 0.2 L/(L h)

## Co-hydrotreating

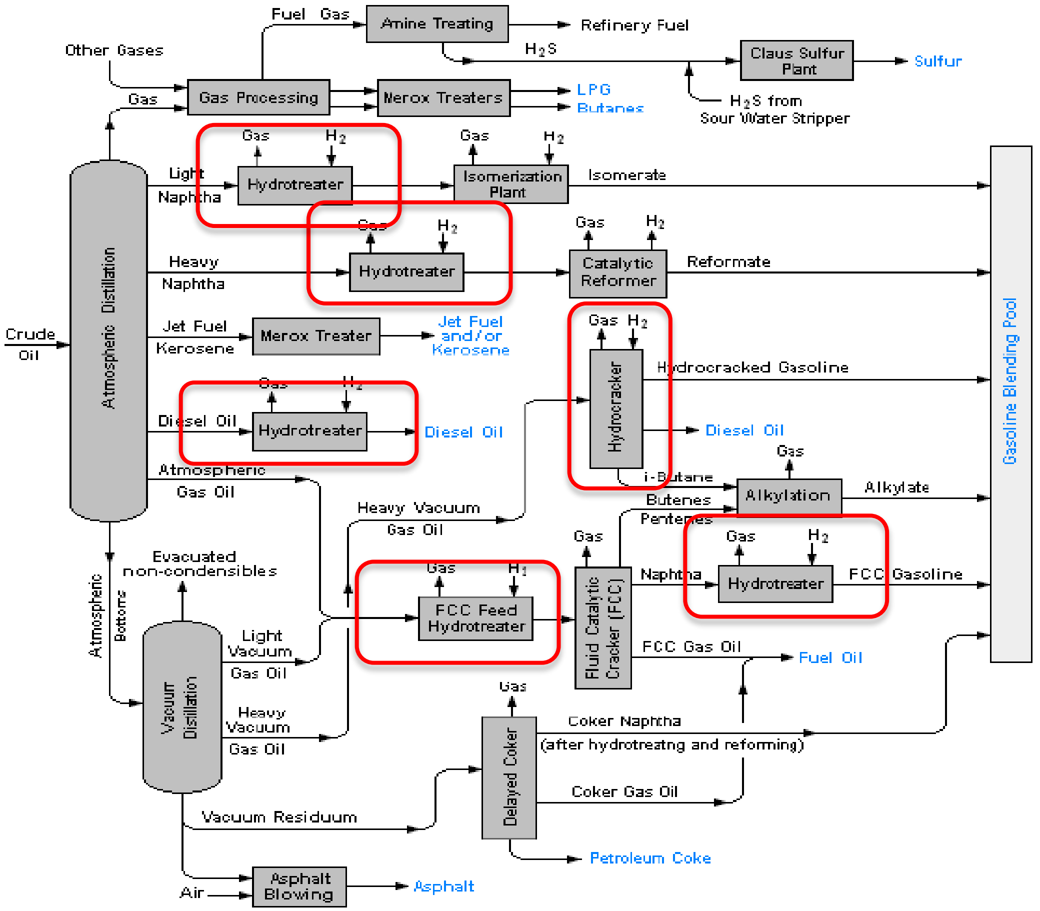
- Need to be performed at petroleum operating conditions and with petroleum catalyst
- Cannot interfere with efficiency of petroleum operation or product quality
- Lower temperatures: ~325°C
- Lower pressures: 60 bar
- Higher liquid hourly space velocity (LHSV): 1-2 L/(L h)

## Limited information on co-hydrotreating of CFP oil

- CFP oil deoxygenation efficiency at co-hydrotreating conditions?
- Impact of CFP oil addition on petroleum stream transformations?
- Carbon incorporation from CFP oil?

# Co-Hydrotreating in Refineries

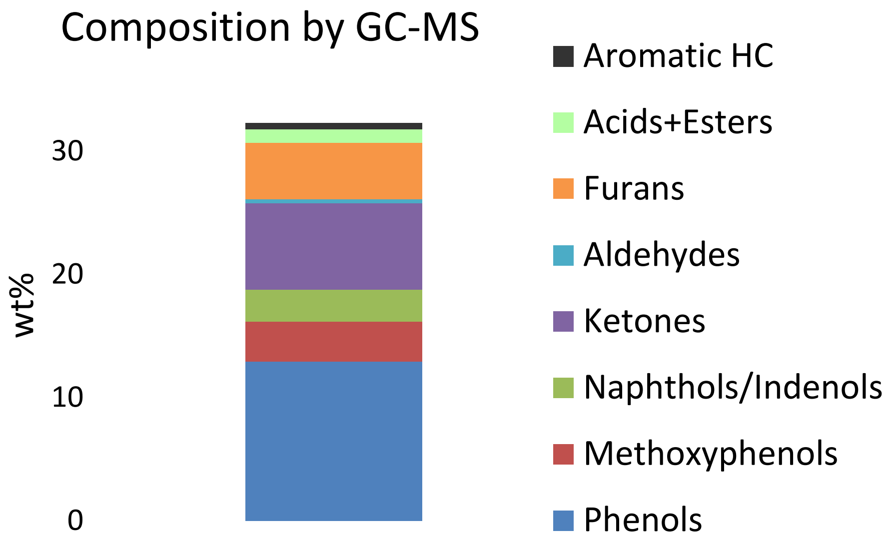
- Petroleum refineries contain several hydroprocessing units
  - Typically for denitrification and desulfurization
  - Same catalysts active for deoxygenation
- We chose diesel hydrotreating
  - Projected continued steady demand for diesel
  - Hydrotreated CFP oil volatility



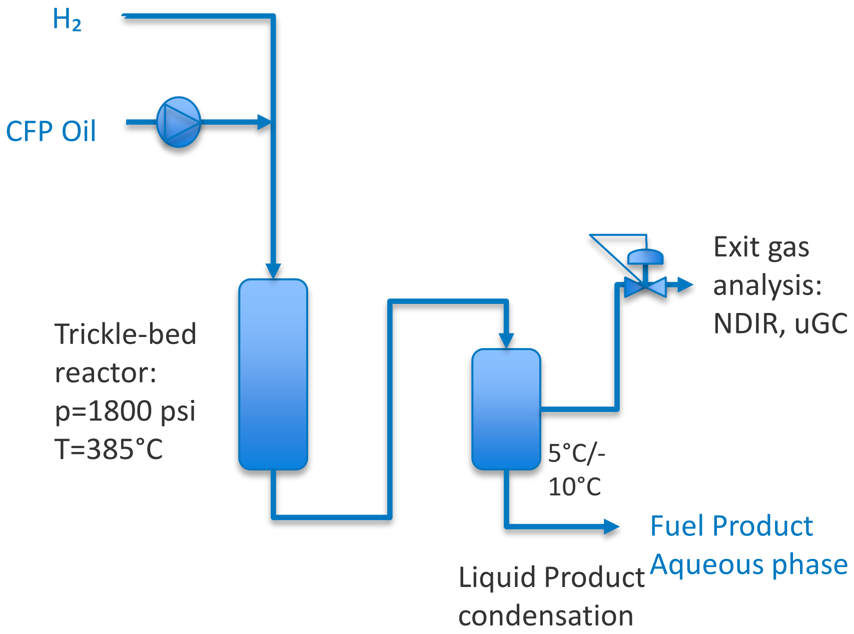
# CFP Oil for Experiments

- CFP oil produced from woody biomass (pine and forest residues) over a bifunctional metal-acid catalyst ($Pt/TiO_2$) in the presence of added hydrogen
  - Bifunctional CFP catalyst enables hydrogenation of coke precursors
    - → higher oil carbon yield for CFP step

| CFP Oil Composition | Value |
|---|---|
| C, wt% db | 76.4% |
| H, wt% db | 7.8% |
| O, wt% db | 15.6% |
| N, wt% db | 0.2% |
| $H_2O$, wt% | 2.8% |
| TAN, mg KOH/g | 217 |
| CAN, mg KOH/g | 39 |
| Carbonyls, mol/kg | 1.7 |



# Hydroprocessing in NREL's Continuous Hydrotreater



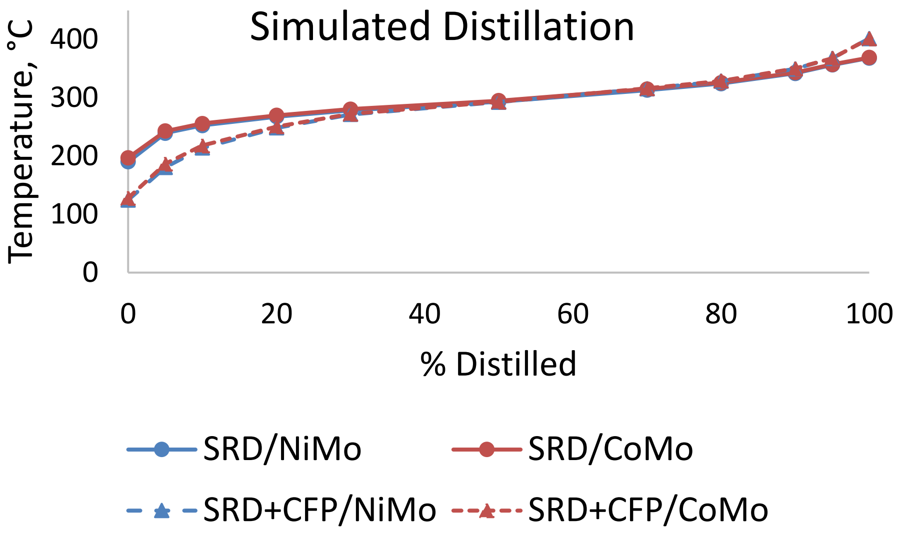

# Hydrotreating Catalyst: NiMo vs CoMo

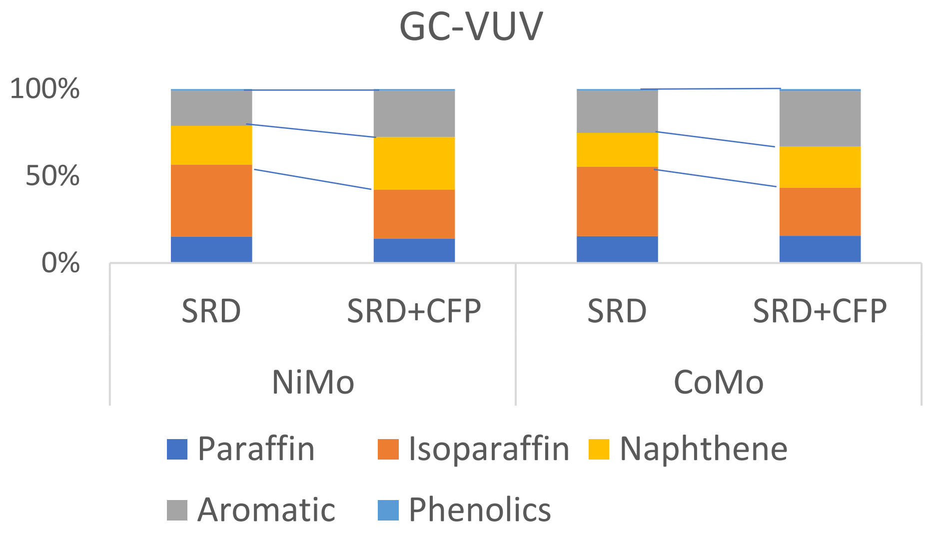
- 80 vol% Pt/$TiO_2$ CFP oil + 20 vol% straight-run diesel (SRD)
- Single-stage hydrotreating: 325°C, 55 bar, 1 g/(g cat h)
- Catalyst: sulfided NiMo/$Al_2O_3$ or CoMo/ $Al_2O_3$

| Feed | Cat. | Composition, wt% | | | $H_2$ | Mass Yields | | | C Yields | | | ICN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | O | N | S | % | Oil | Aq. | Gas | Oil | Aq. | Gas | |
| SRD | | 0.2 | 0.03 | 0.21 | | | | | | | | |
| CFP Oil | | 17.5 | 0.18 | 0.01 | | | | | | | | |
| SRD | NiMo | ≤0.3 | 0.03 | 0.01 | 0.1 | 100 | - | 0.3 | 100 | - | 0.3 | 50 |
| SRD+CFP | NiMo | ≤0.3 | 0.04 | 0.03 | 1.4 | 94 | 5.4 | 1.4 | 100 | 0.1 | 1.3 | 45 |
| SRD | CoMo | ≤0.3 | 0.02 | 0.02 | 0.0 | 101 | - | 0.0 | 101 | - | 0.0 | 48 |
| SRD+CFP | CoMo | ≤0.3 | 0.04 | 0.04 | 1.1 | 91 | 6.0 | 1.4 | 95 | 0.1 | 1.4 | 42 |

ICN = Indicated Cetane Number

# Hydrotreating Catalyst: NiMo vs CoMo




- SRD + CFP gave more of low-boiling products than SRD
- No difference between NiMo and CoMo

- SRD + CFP enhanced aromatics and naphthenes
- NiMo gave lower aromatics

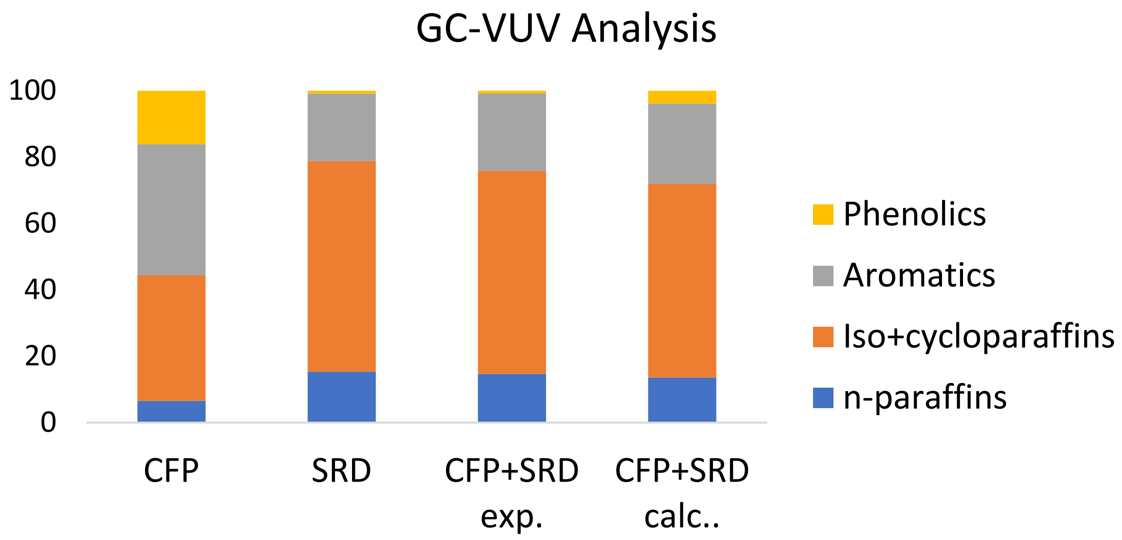
# Standalone vs Co-hydrotreating over NiMo

- Co-hydrotreating 80 vol% CFP oil + 20 vol% straight-run diesel (SRD) vs
- Standalone hydrotreating of CFP oil and SRD
- Operating conditions: 325°C, 55 bar, WHSV 1 $h^{-1}$, sulfided NiMo

| Feed | CFP | SRD | SRD+CFP experimental | SRD+CFP calculated |
|---|---|---|---|---|
| **Mass Yields, g/g CFP oil** | | | | |
| Oil | 85% | 100% | 96% | 97% |
| Aqueous | 16% | 0.0% | 5.5% | 3.6% |
| Gas | 5.8% | 0.3% | 1.4% | 1.5% |
| $H_2$ consumption | 3.6% | 0.1% | 1.4% | 0.9% |
| Oil C Yield | 94% | 99% | 99% | 98% |
| Product O content | 8.2% | <0.1% | 0.1% | 1.9% |

- Co-hydrotreating suggests better deoxygenation than by standalone hydrotreating at the same condition

# Standalone vs Co-hydrotreating over NiMo




- GC-VUV analysis also suggests lower oxygenates than predicted from standalone hydrotreating

# Fuel Properties and Biogenic Carbon

- Co-hydrotreating 90 vol% CFP oil + 10 vol% straight-run diesel (SRD)
- Operating conditions: 340°C, 83 bar, 1 g oil/(g cat h), sulfided NiMo
- Fractionated product and measured fuel properties

| Fraction | Atmospheric equivalent temp., °C | Mass fraction | Indicated cetane number (ICN) | Cloud point, °C |
|---|---|---|---|---|
| **Gasoline** | <182 | 6% | | |
| **Diesel** | 182-330 | 85% | 50 | -19 |
| **Residue** | >330 | 9% | | |

- C 14 analysis of whole hydrotreated product: 9.5% biogenic carbon
  - 95% of carbon in CFP oil incorporated in product

# Fuel Cut Properties and Biogenic Carbon

- Co-hydrotreating 90 vol% CFP oil + 10 vol% straight-run diesel (SRD)
- Operating conditions: 340°C, 83 bar, 1 g oil/(g cat h), sulfided NiMo
- Fractionated product and measured fuel properties

| Fraction | Atmospheric equivalent temp., °C | Mass fraction | Indicated cetane number (ICN) | Cloud point, °C | Fraction biogenic carbon |
|---|---|---|---|---|---|
| Gasoline | <182 | 6% | | | 40% |
| Diesel | 182-330 | 85% | 50 | -19 | 4.7% |
| Residue | >330 | 9% | | | 7.0% |

- C 14 analysis of whole hydrotreated product: 9.5% biogenic carbon
  - 95% of carbon in CFP oil incorporated in product

# Conclusions

- Co-hydrotreating of catalytic fast pyrolysis oil together with straight-run diesel:
  - $NiMoS_x$ more desirable HT catalyst than $CoMoS_x$
  - Good deoxygenation
    - Oxygen content in hydrotreated product below detection limit
    - Enhanced deoxygenation compared to standalone hydrotreating under similar conditions
- High carbon incorporation in fuel product
  - Overall, 95% C incorporation from CFP oil into hydrotreated product
  - Gasoline-range product enriched in CFP oil
- Opportunities to improve performance
  - C-C coupling to increase fraction in diesel range
  - Co-product formation from lighter compounds
  - Recycle to decrease residue fraction

# Acknowledgements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  - Mike Griffin, Josh Schaidle
- Johnson Matthey Technology Center
  - Luke Tuxworth
  - Mike Watson

# Acknowledgements


I hope you were able to visit our related presentations on CFP and hydrotreating

- **Sustainable Aviation Fuel via Hydroprocessing of Catalytic Fast Pyrolysis Oil**
  - Wednesday 11:15
- **Griffin et al., Improving Process Durability by Addressing Catalyst Deactivation During Upgrading of Biomass Pyrolysis Vapors**
  - Wednesday 1:30
- **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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