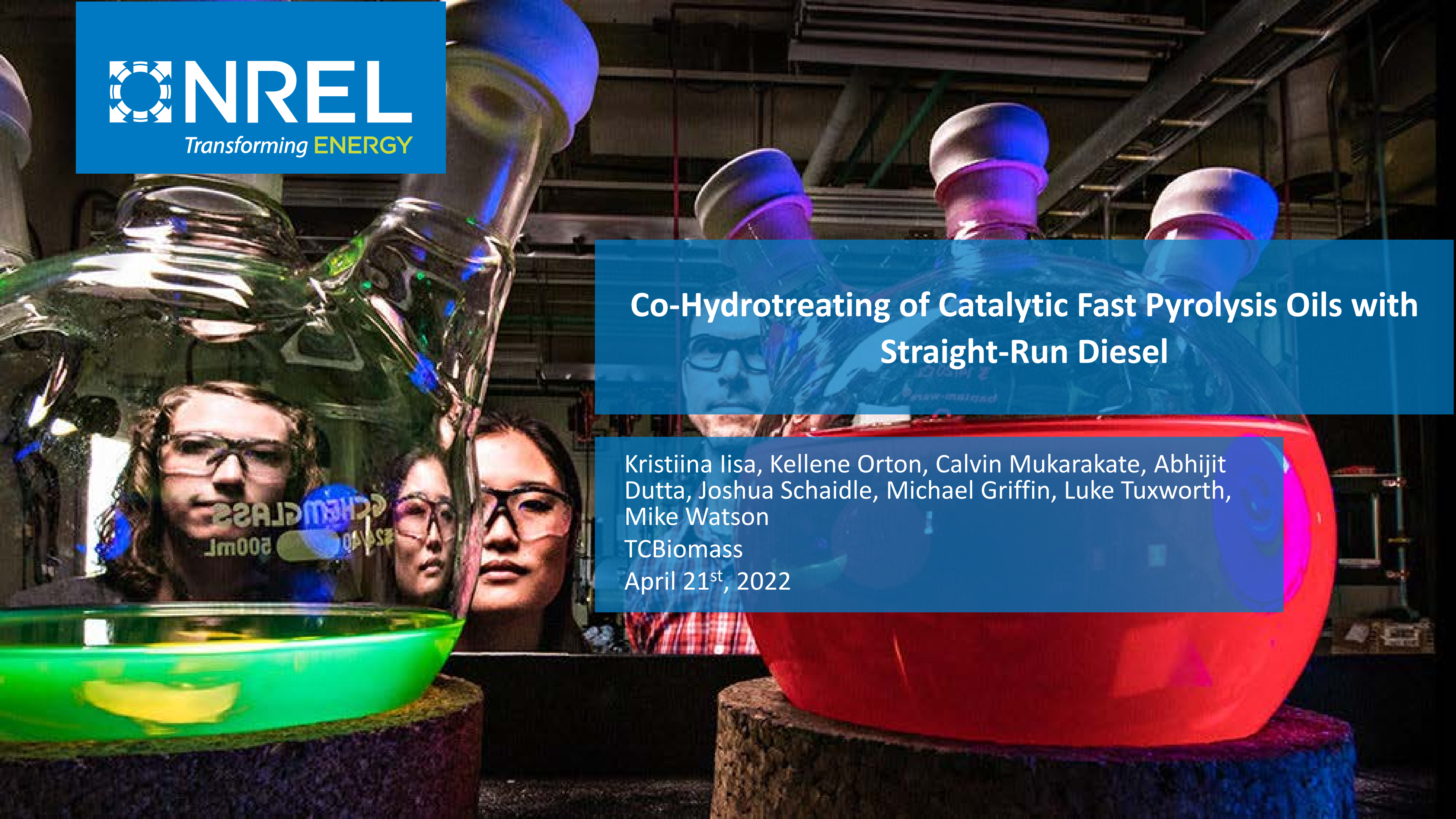

Co-Hydrotreating of Catalytic Fast Pyrolysis Oils with Straight-Run Diesel

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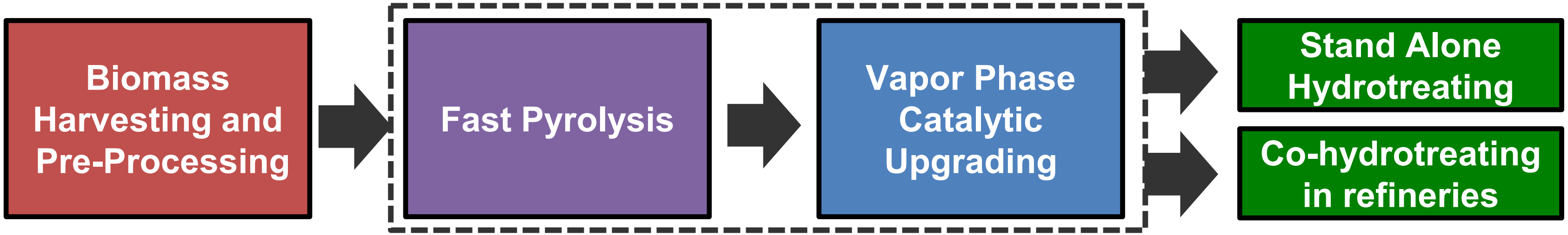
TCBiomass

April 21st, 2022

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

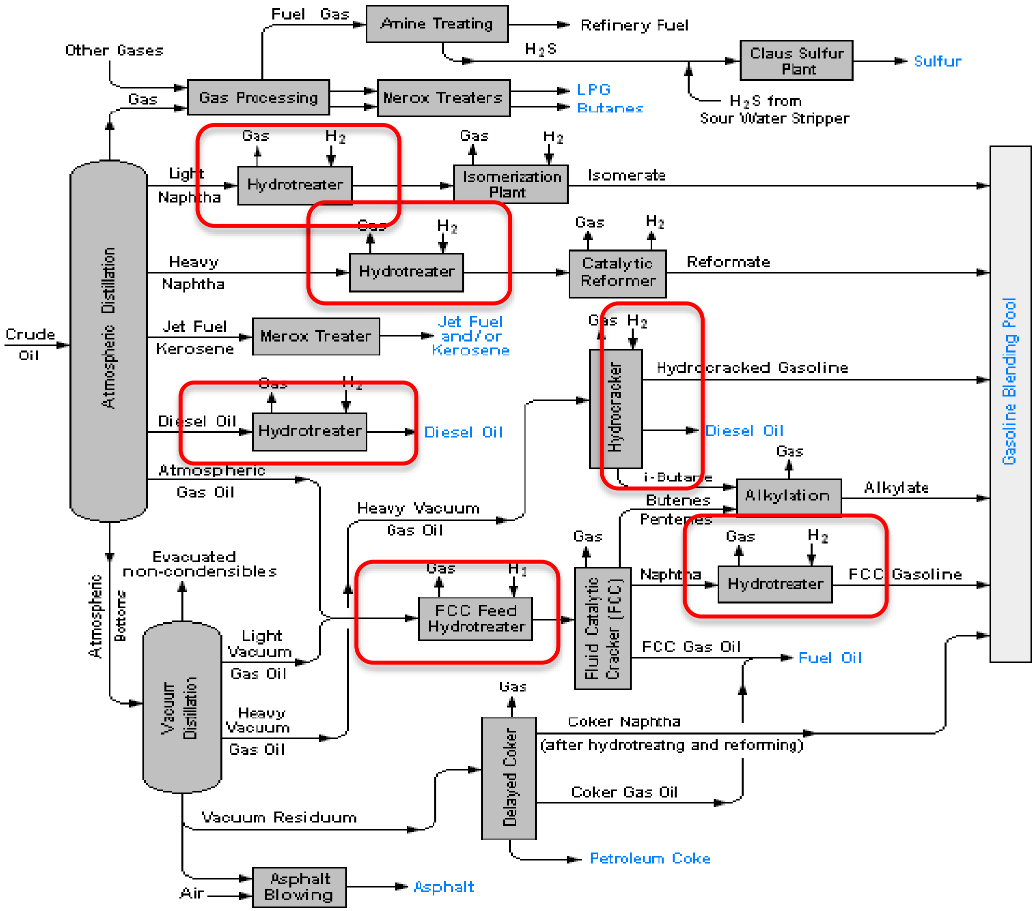
- Need to be performed at petroleum operating conditions and with petroleum catalyst
- Cannot interfere with efficiency of petroleum operation or product quality
- Lower temperatures: ~325°C
- Lower pressures: 60 bar
- Higher liquid hourly space velocity (LHSV): 1-2 L/(L h)

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

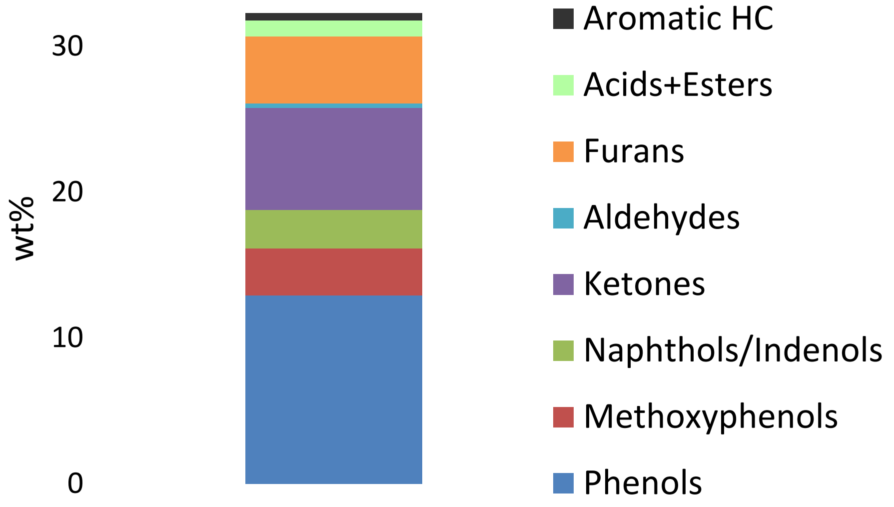
- Petroleum refineries contain several hydroprocessing units
  - Typically for denitrification and desulfurization
  - Same catalysts active for deoxygenation
- We chose diesel hydrotreating
  - Projected continued steady demand for diesel
  - Hydrotreated CFP oil volatility



Experimental

- 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

Property	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



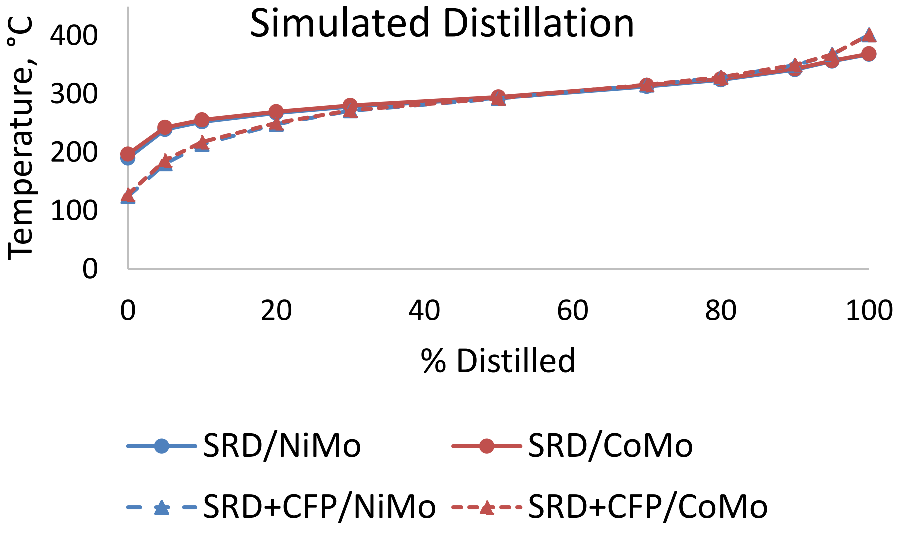
Hydrotreating Catalyst: NiMo vs CoMo

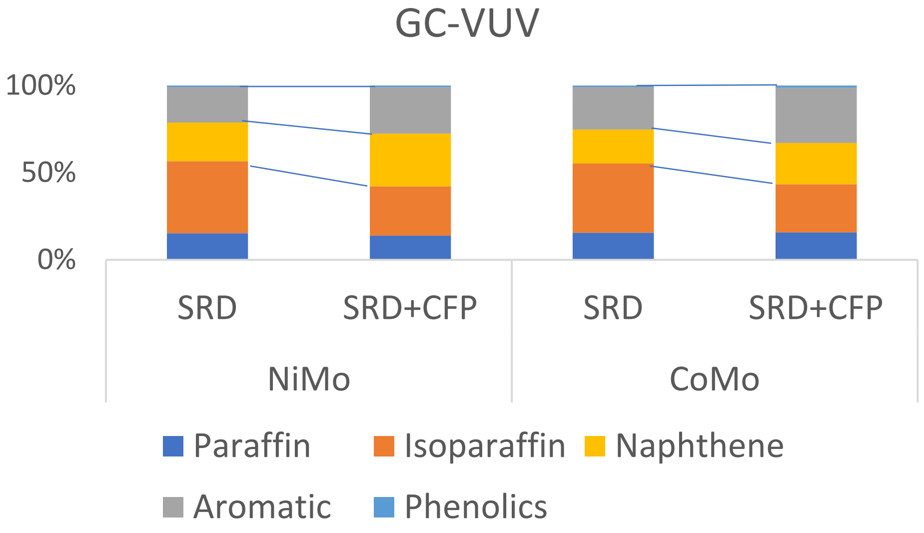
- 80 vol% Pt/TiO_2 CFP oil + 20 vol% straight-run diesel (SRD)
- Operating conditions: 325°C, 55 bar, 1 g/(g cat h)
- Catalyst: sulfided NiMo/Al_2O_3 or CoMo/ Al_2O_3

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
- No difference between NiMo and CoMo

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

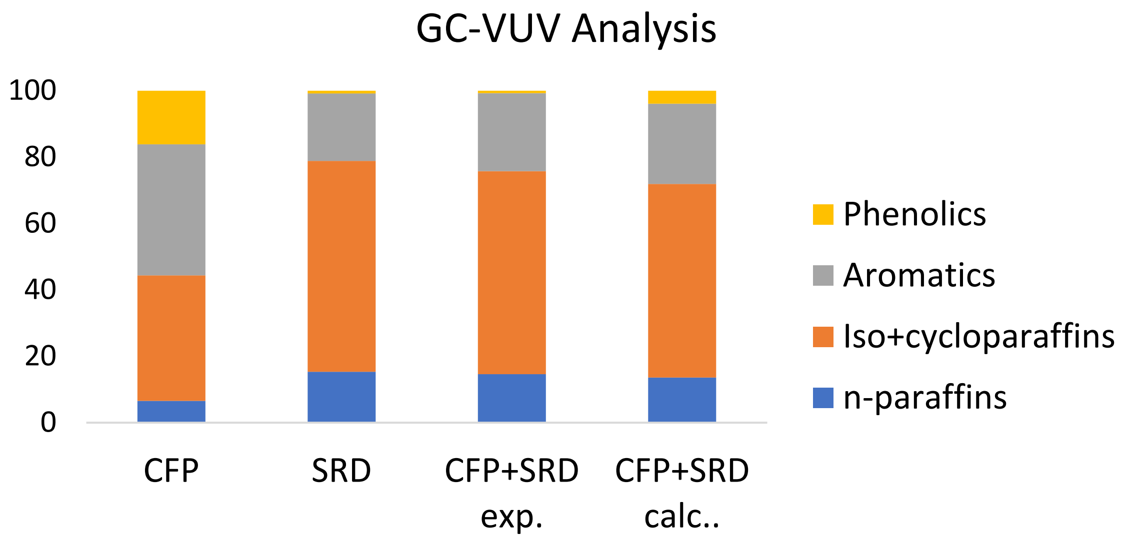
Standalone vs Co-hydrotreating over NiMo

- 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

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Acknowledgements

Please visit our related presentations on CFP and hydrotreating

- **Sustainable Aviation Fuel via Hydroprocessing of Catalytic Fast Pyrolysis Oil**
  - Wednesday 11:15
- **Improving Process Durability by Addressing Catalyst Deactivation During Upgrading of Biomass Pyrolysis Vapors**
  - Wednesday 1:30
- **Co-hydrotreating of Catalytic Fast Pyrolysis Oils with Straight-Run Diesel**
  - Thursday 2:00
- **Advancement of the Catalytic Fast Pyrolysis of Biomass Technology with Fixed-bed Reactor to Produce Renewable Fuels and Chemicals** (poster)
- **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)
- **Comparative analysis of catalytic and non-catalytic pyrolysis oil co-processing by hydroprocessing and fluid catalytic cracking (**Poster)

Thank you!

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