Pacific Northwest
NATIONAL LABORATORY

Co-processing Bio-crudes with Petroleum Stream in Hydrotreating: Impact on Chemistry and Catalyst Stability

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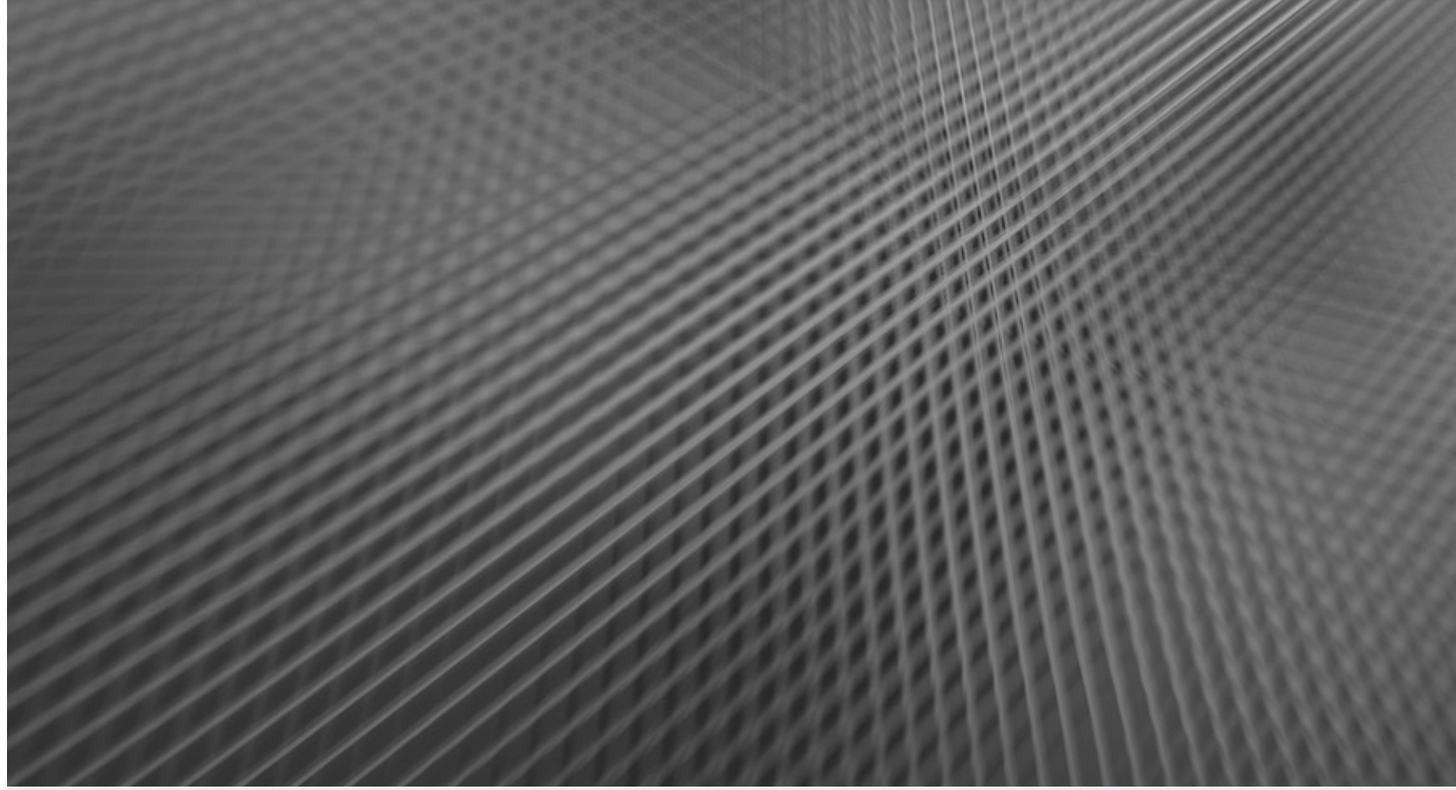

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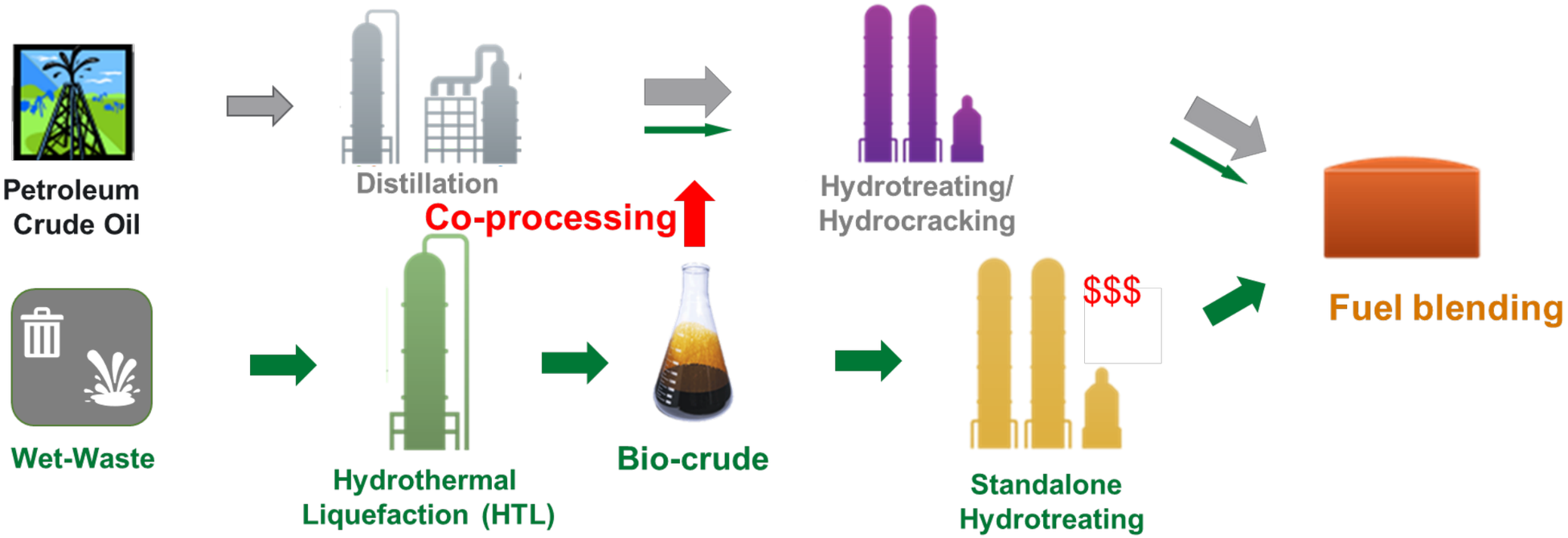
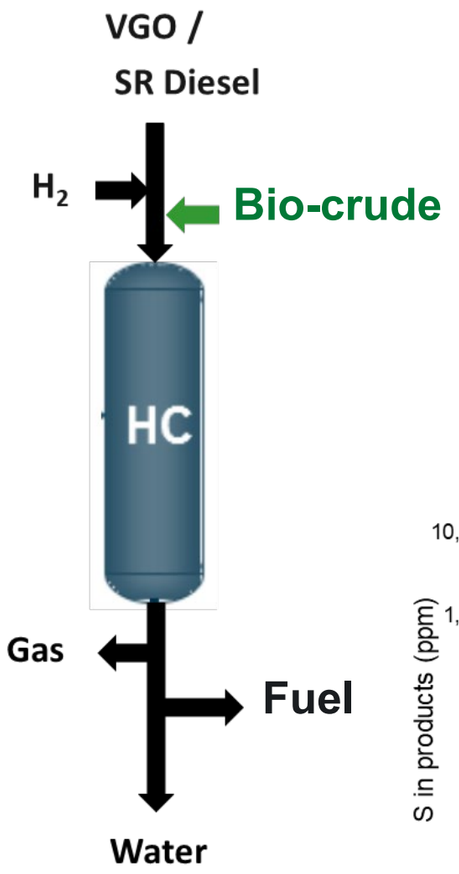
Co-processing of HTL bio-crude leverages existing refinery infrastructures and could reduce cost



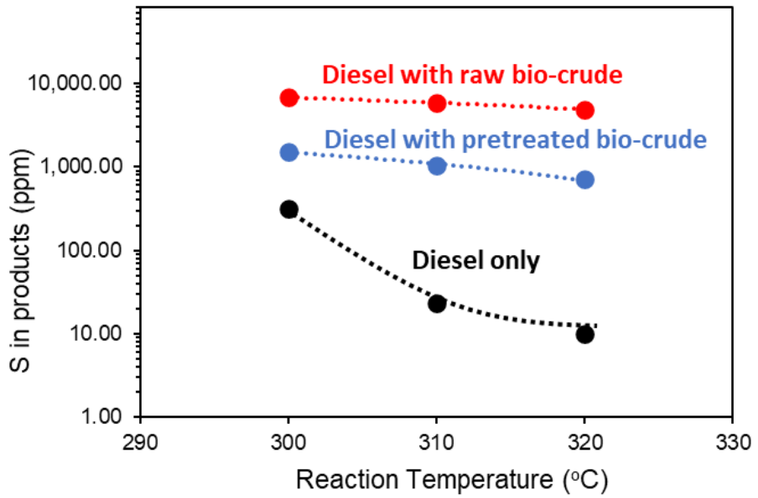
- Hydrothermal liquefaction (HTL) offers a fast and relatively simple process to convert wet wastes and biomass into liquid fuels with bio-crude upgrading required
- Hydrotreating is one of the most common and well-established upgrading technologies available in existing oil refineries
- Co-processing HTL bio-crude with petroleum stream can reduce the capital cost to construct independent units for upgrading and introduce biofuel to market faster

HTL bio-crude brings new challenges for hydrotreating: competing reactions and catalyst deactivation



	WWTP Sludge HTL Bio-crude	Petroleum
C (wt.%)	~77	83-87
O (wt.%)	~2-8	0.1-1.0
S (wt.%)	~0.5	0.1-6
N (wt.%)	~3-6	0.1-2
H_2O, wt.%	~2-12	0.02-0.1
Contaminants	Fe Si Ca P Al (100-1000 ppm)	Low

- HTL bio-crudes has high content of N, O, and S, are contaminated with inorganics, and contains some reactive oxygenates
- Co-processing bio-crudes with VGO or SR diesel in a typical hydrotreating leads to significant loss of catalyst performance



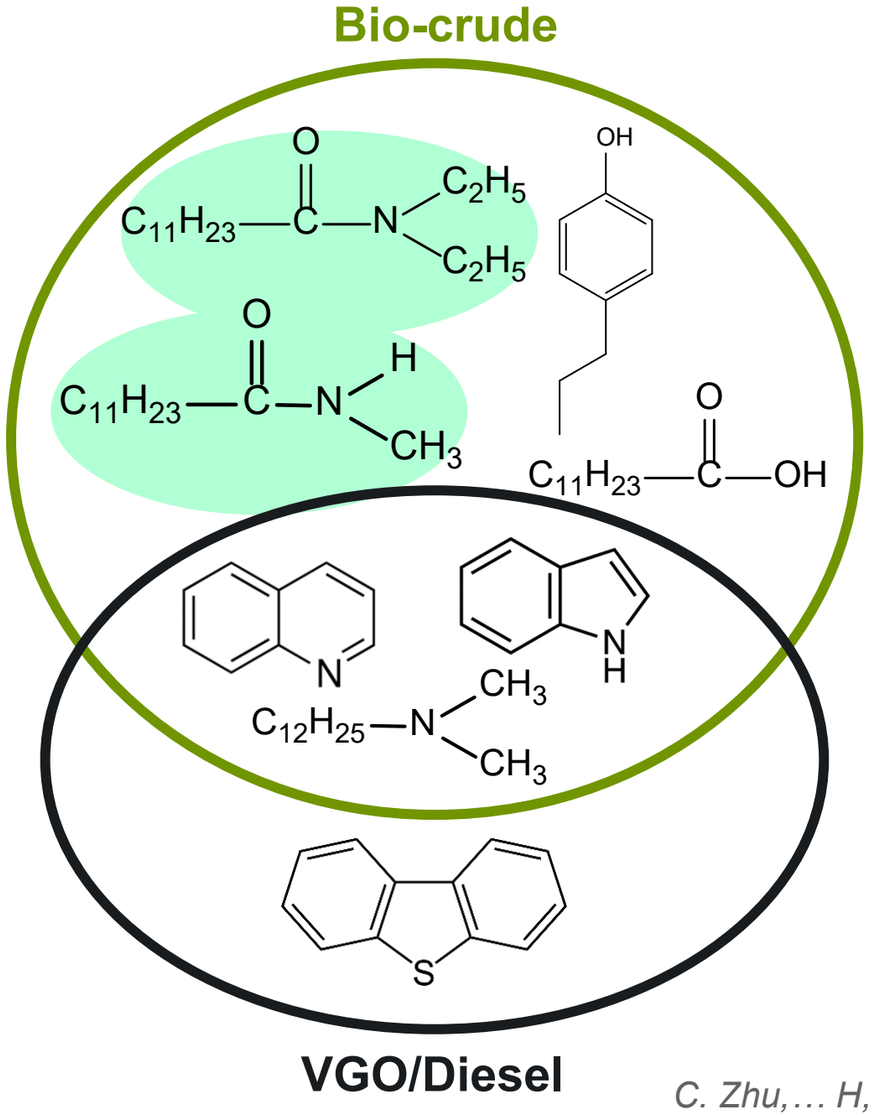
5% bio-crude blending

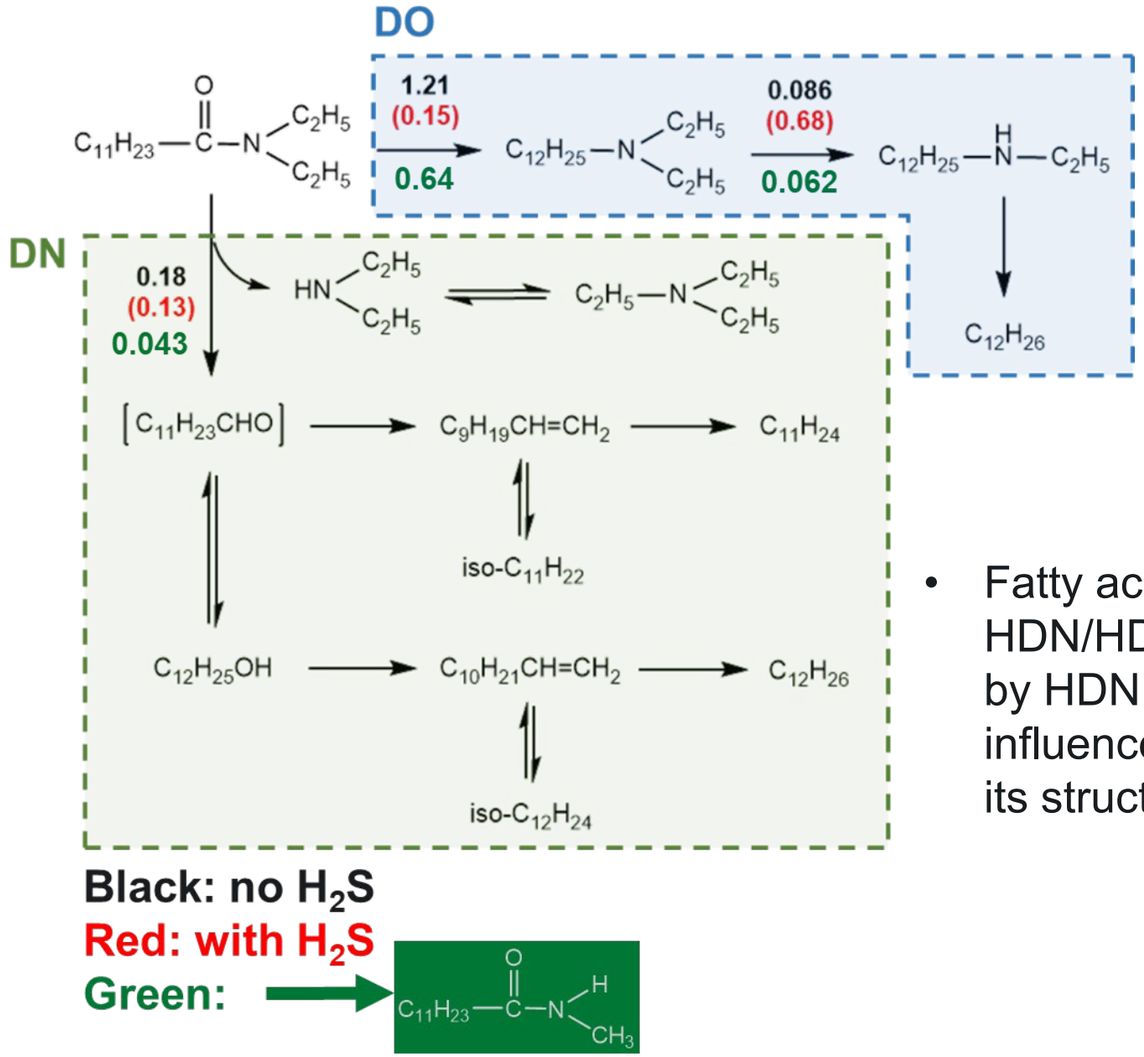
Objective:

Influence on Hydrotreating Chemistry
- Kinetics study of model compounds
- Mutual impact
- Co-processing reactor model

Influence on Catalyst Stability
- Detail catalyst characterization
- Catalyst deactivation mechanism
- Mitigation strategies

We use a bench-scale hydrotreater to determine reaction kinetics of the hetero-atom species HDS/HDN/HDO





- Fatty acid amide HDN/HDO is limited by HDN step and influenced by H_2S and its structure

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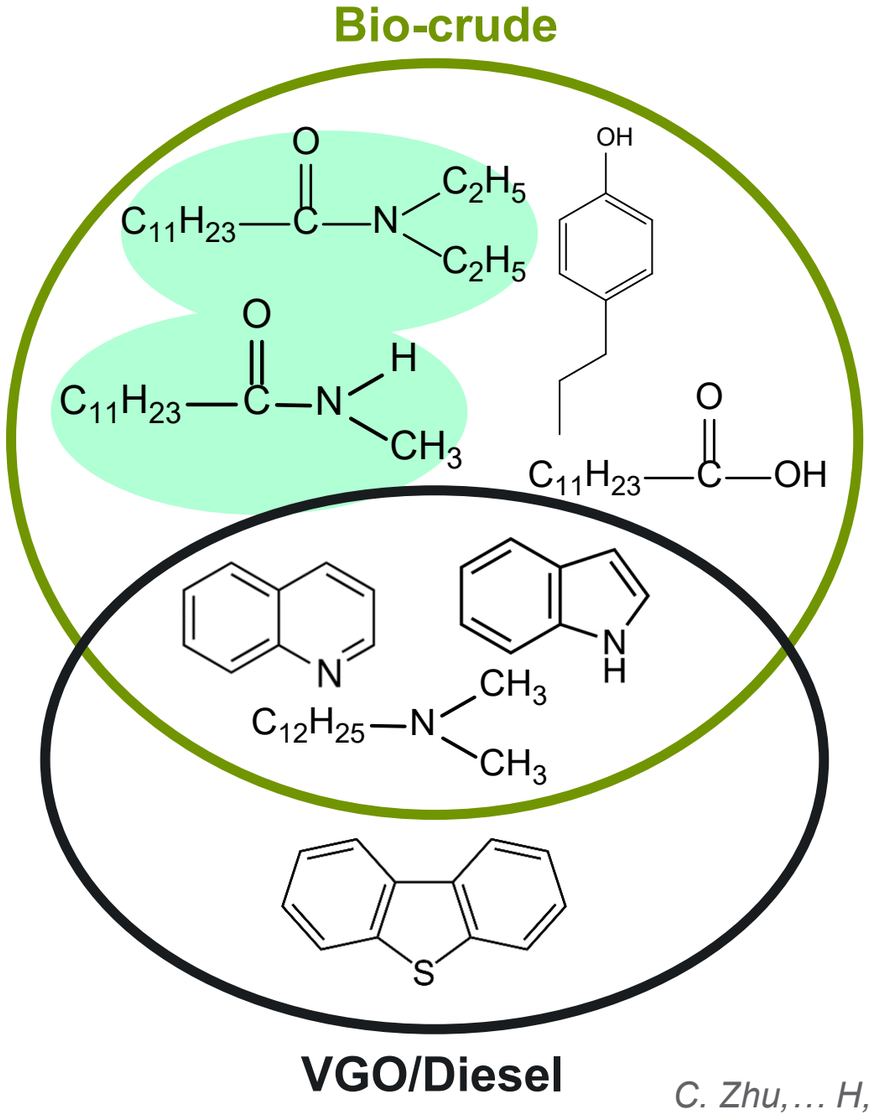

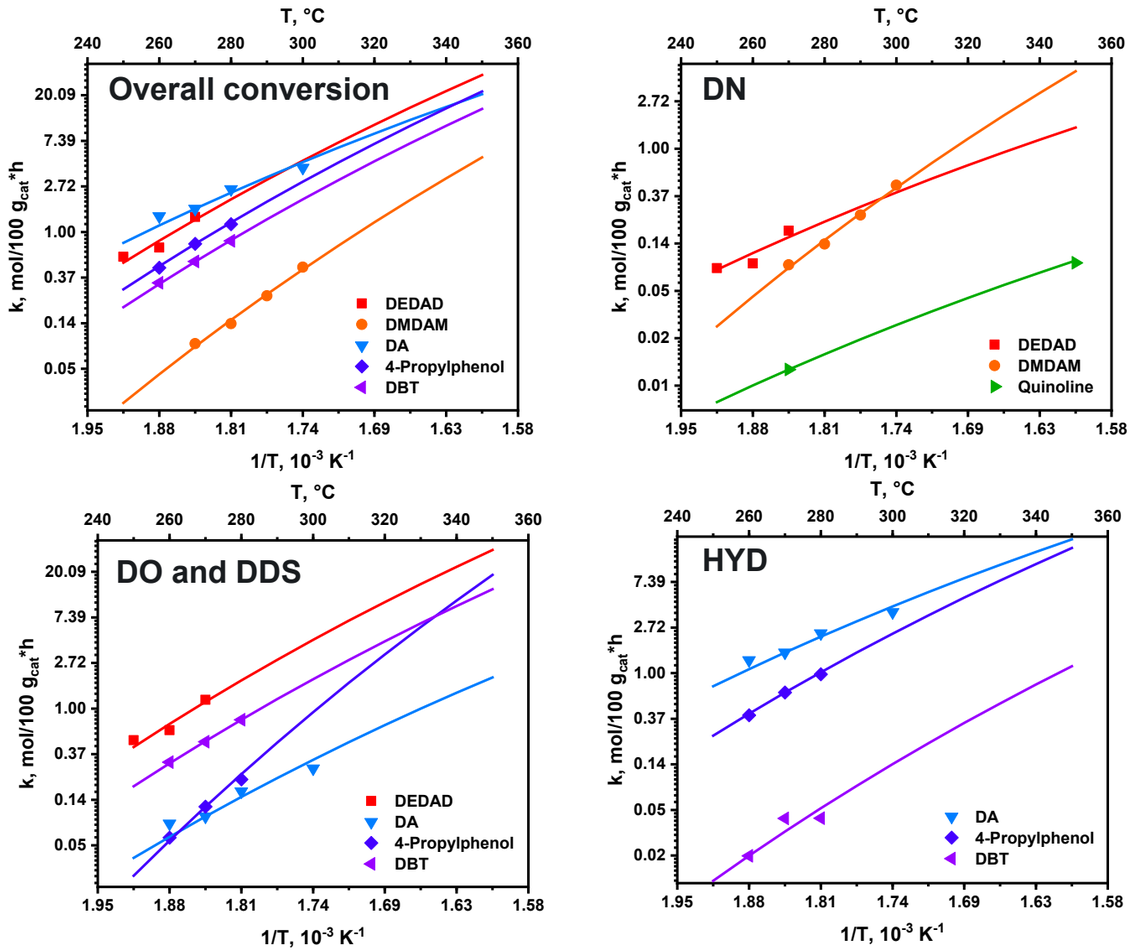

- HDN is critical for bio-crude co-hydrotreating, especially the aromatic heterocycles which inhibits HDS and cracking reactions

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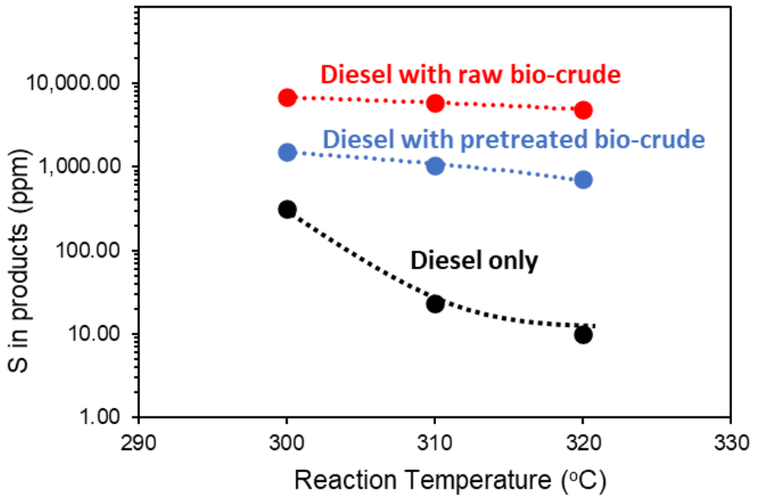
Bio-crudes influences hydrotreating by reversable inhibition and irreversible catalyst deactivation

Feedstock properties

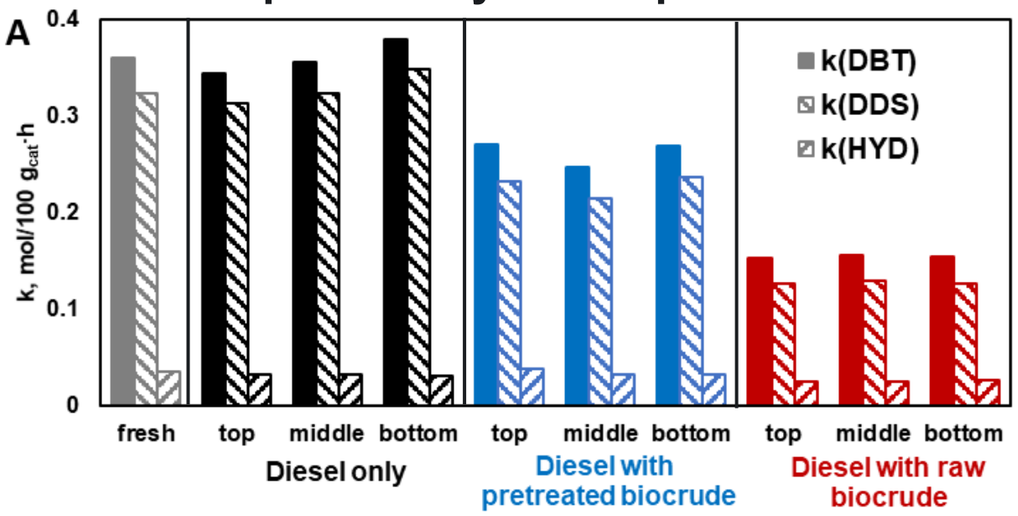
	Raw bio-crude	Pre-treated bio-crude	Diesel
O (wt.%)	6.5	1.24	<0.5
S (wt.%)	0.26	<0.1	1.2
N (wt.%)	4.3	2.5	<0.05
H_2O, wt.%	0.99	0.87	N.D.
Contaminants	Fe: 305 ppm Si: 298 ppm Ca: 188 ppm	<5 ppm	<5 ppm

Co-processing performance

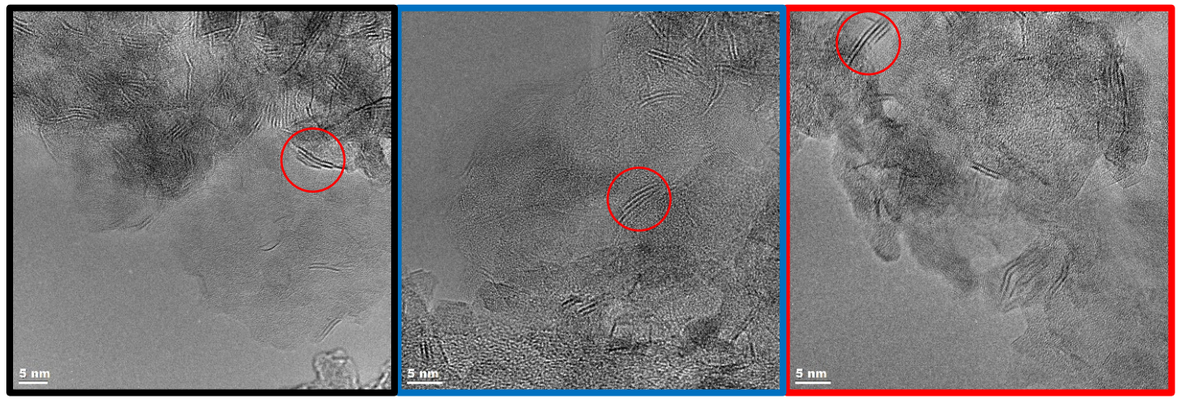


- Testing of spent catalyst (after >300 h co-processing test), after re-sulfidation, using clean model compounds showed the irreversible loss of activity by deactivation
- Pretreatment of bio-crude reduces the negative impact

Spent catalyst HDS performance



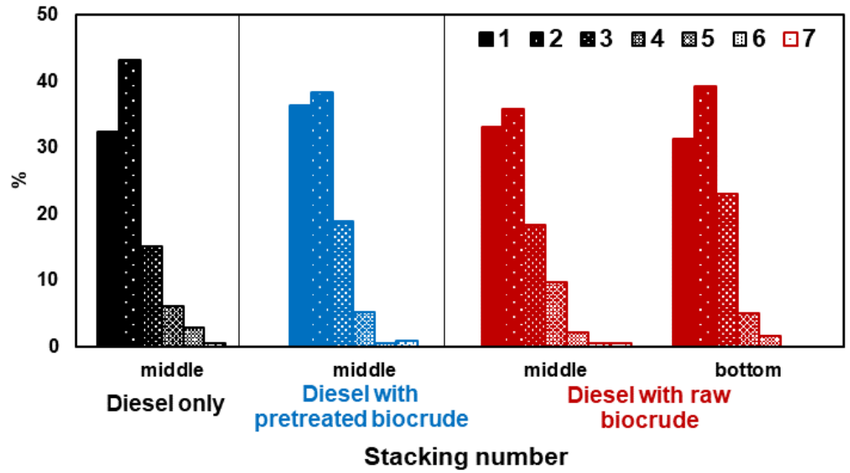
No structural change of the catalyst after co-processing

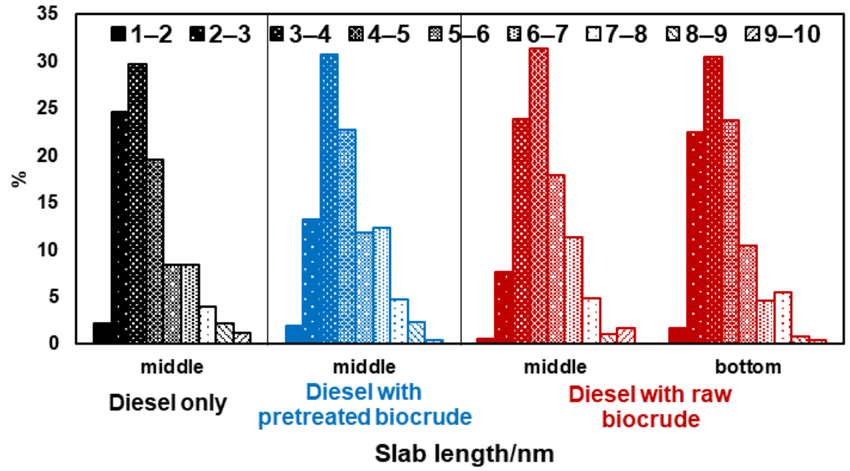


	Diesel only	Diesel + pretreated bio-crude	Diesel + raw bio-crude
Atom on edge (μmol/g)	512	452	473
NO titration (μmol/g)	88	67	44

- No structural change of catalyst on its support or active phase ($NiMoS_x$)
- Loss of active sites by fouling and poisoning

$NiMoS_x$

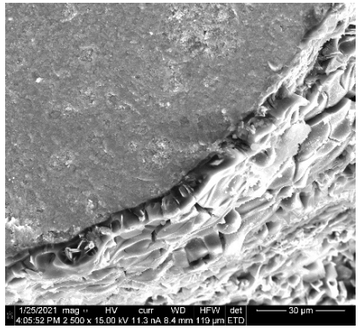


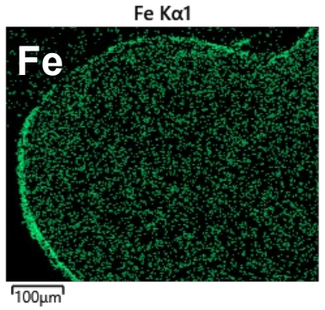


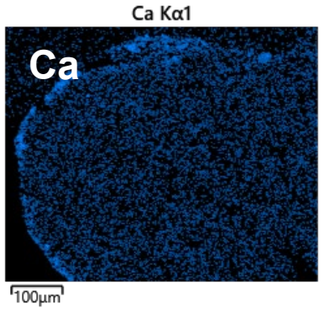
Fouling of the catalyst by co-processing raw bio-crude

Diesel + raw bio-crude

Top

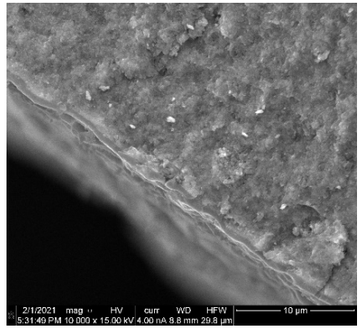






Fe: 4422 ppm
Ca: 480 ppm
K: 927 ppm

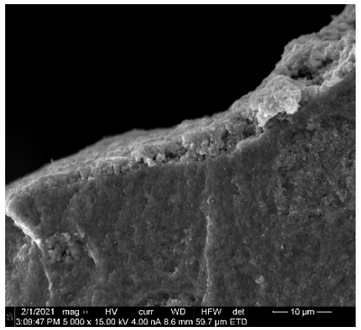
Bottom

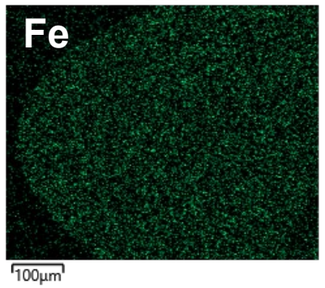


Fe: 982 ppm
Ca: 412 ppm
K: 564 ppm

Diesel + pretreated bio-crude

Top

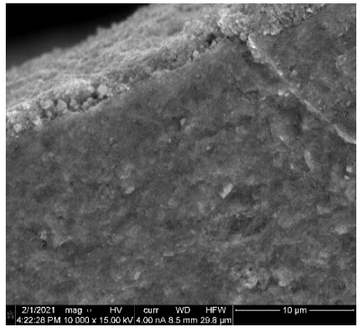


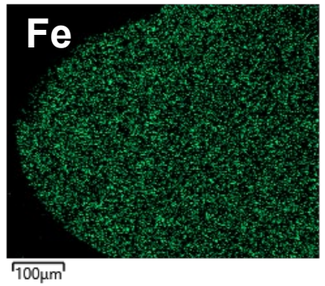


Fe: 281 ppm
Ca: 370 ppm
K: 412 ppm

Diesel only

Top

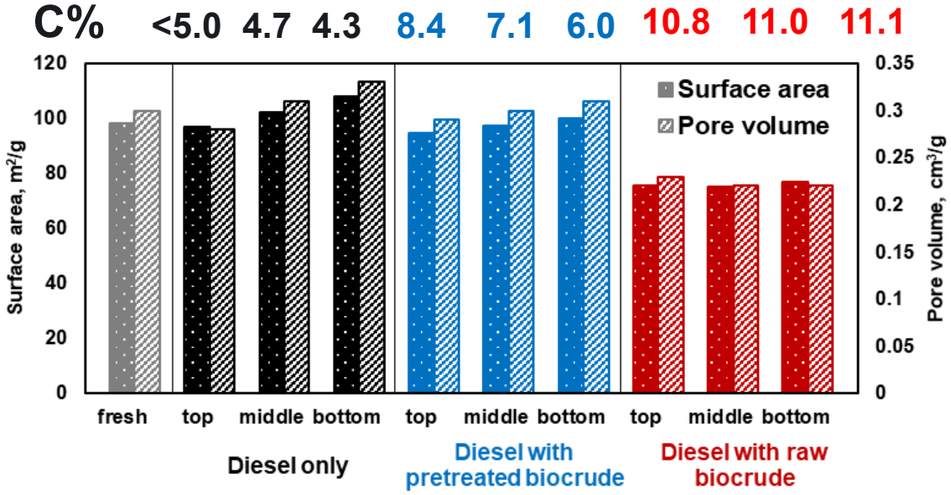




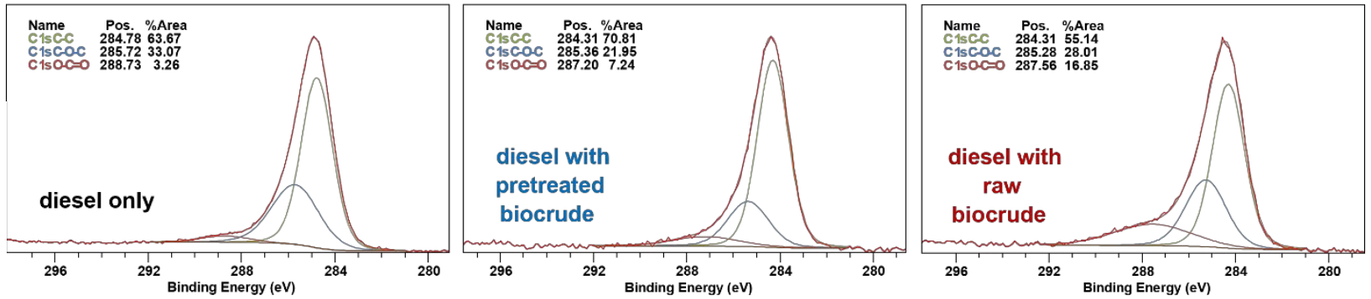
Fe: 612 ppm
Ca: 331 ppm
K: 487 ppm

- Fouling of the catalyst observed when co-processing raw bio-crude, especially occurring on top portion of the catalyst with an inorganic rich layer encapsulating the catalyst pellet
- Bio-crude pretreatment removes inorganics and mitigate fouling
- The fouling is not the major cause of activity loss

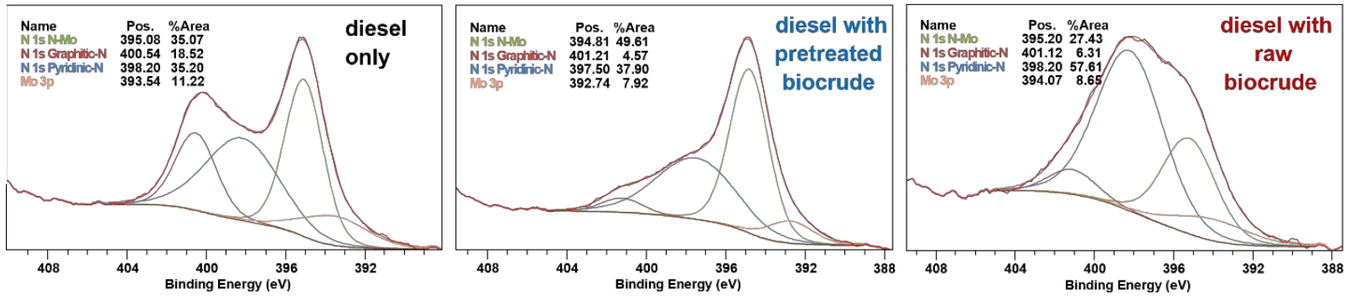
“Coke” formation from reactive oxygenates are likely the major deactivation mode



C by XPS



N by XPS

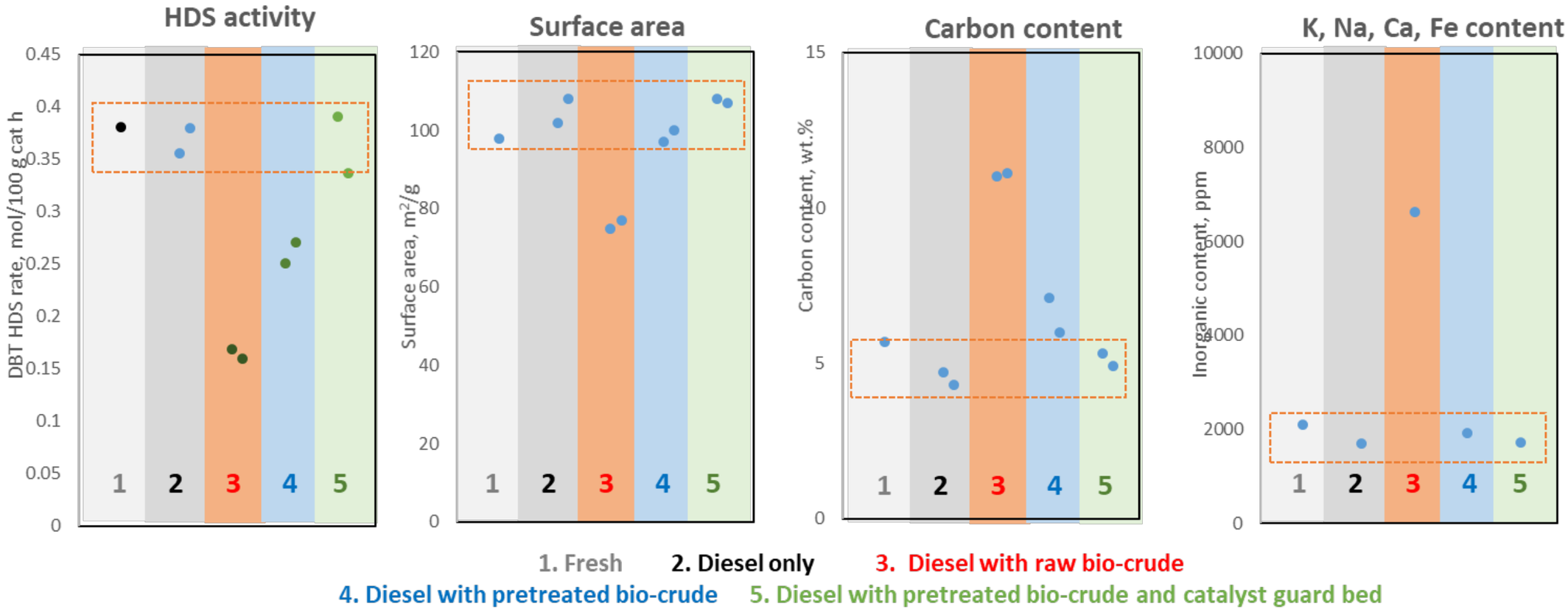


Pyro probe-GC-MS

Category	Product, %	Diesel only	Diesel with pretreated biocrude	Diesel with raw biocrude
Hydrocarbons	Aliphatic	71	65	67
	Aromatic	5	13	20
O-containing compounds		19	12	9
N-containing compounds		<2	<2	3.8

- Faster “coke” formation observed after co-processing bio-crudes, especially the raw bio-crude
- The coke are rich of oxygen, nitrogen, and aromatics
- Both pore blocking and active sites poisoning by the “coke” leads to activity loss

Mitigation of catalyst deactivation by co-processing suggested

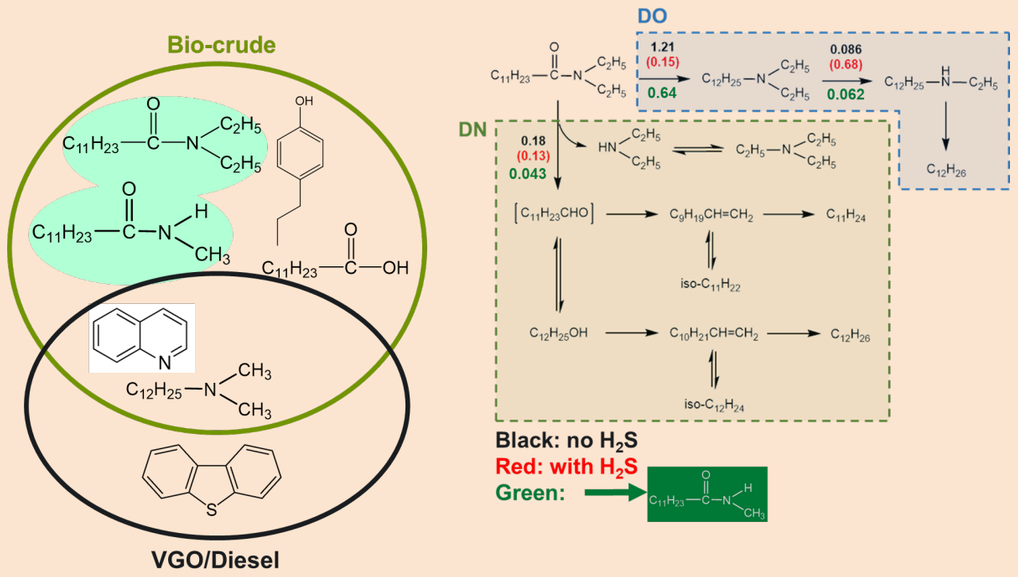


- Bio-crude pretreatment and guard bed use mitigate catalyst deactivation
- Future efforts include pretreatment methods and guard bed development/selection

Co-processing of HTL bio-crude leverages existing refinery infrastructures and could reduce cost

Influence on Hydrotreating Chemistry

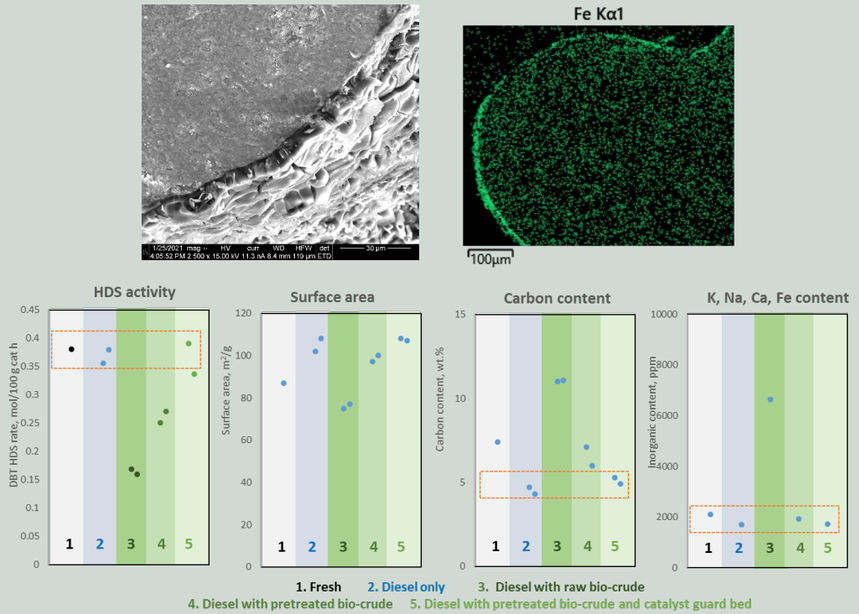
- Kinetics study of model compounds
- Mutual impact
- Co-processing reactor model



- HDN is critical for bio-crude co-hydrotreating
- Development of kinetic-based reactor model for co-processing is ongoing
  - Aspen HYSYS Refinery Models

Influence on Catalyst Stability

- Detail catalyst characterization
- Catalyst deactivation mechanism
- Mitigation strategies



- Catalyst deactivation by inorganic deposition and faster “coke” formation
- Mitigation includes bio-crude pretreatment and guard bed use

Acknowledgement

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