HYDROTREATMENT OF WOOD DERIVED BIOCRUDES

TOPSOE

Investigation of Possibilities and Challenges Related to Refinery Integration

September 12, 2024

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PRESENTATION AGENDA

1	LEARNINGS FROM ANALYZING FAST PYROLYSIS OILS
2	A PATHWAY FOR REFINERY INTEGRATING OF HTL OIL
3	TAKE HOME MESSAGE

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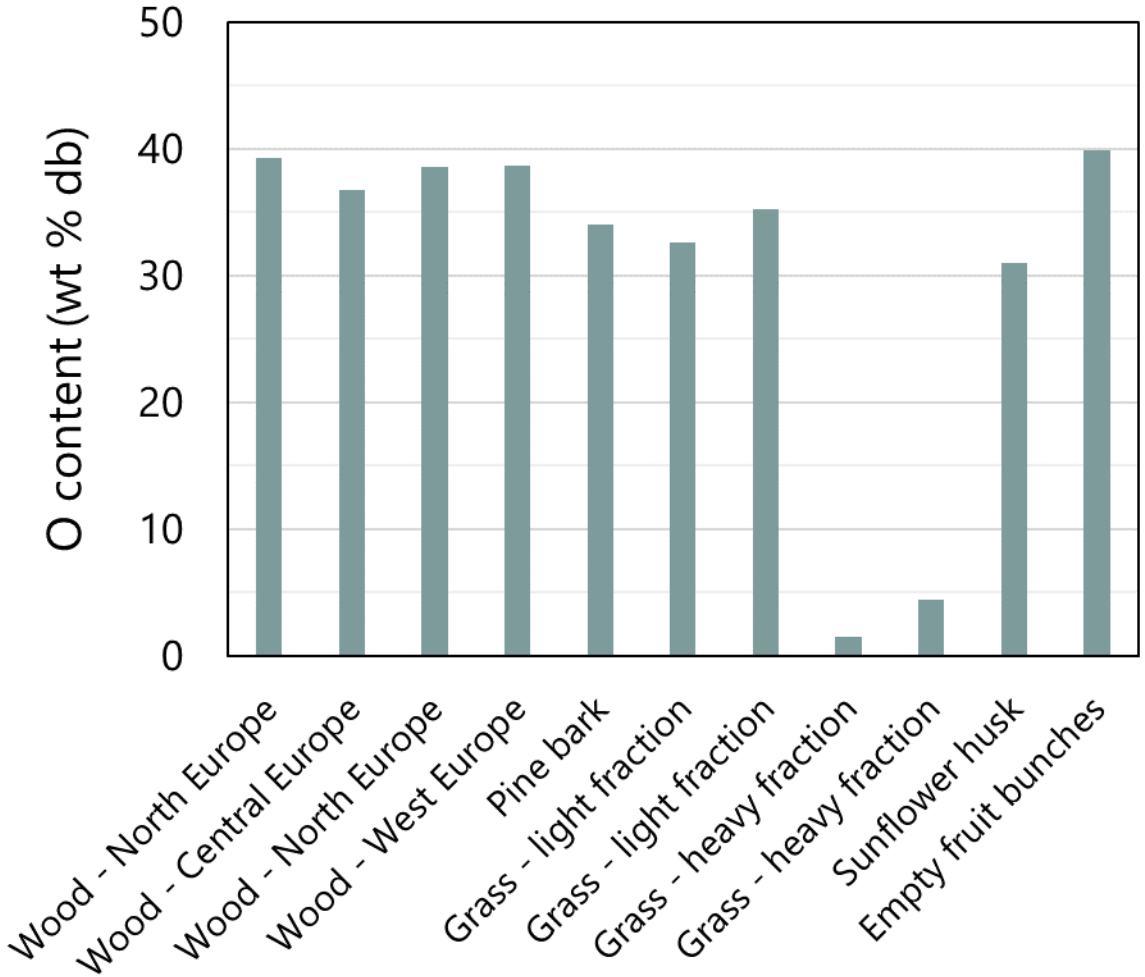
THE IMPACT OF THE BIOMASS COMPOSITION ON HYDROTREATMENT
5 DIFFERENT TYPES OF BIOCRUDES WERE ANALYZED

11 biocrudes produced by fast pyrolysis were analyzed:

- 4 biocrudes were produced from wood
- 1 biocrude was produced from pine bark
- 4 biocrudes were produced from grass
- 1 biocrude was produced from sunflower husk
- 1 biocrude was produced from empty fruit bunches

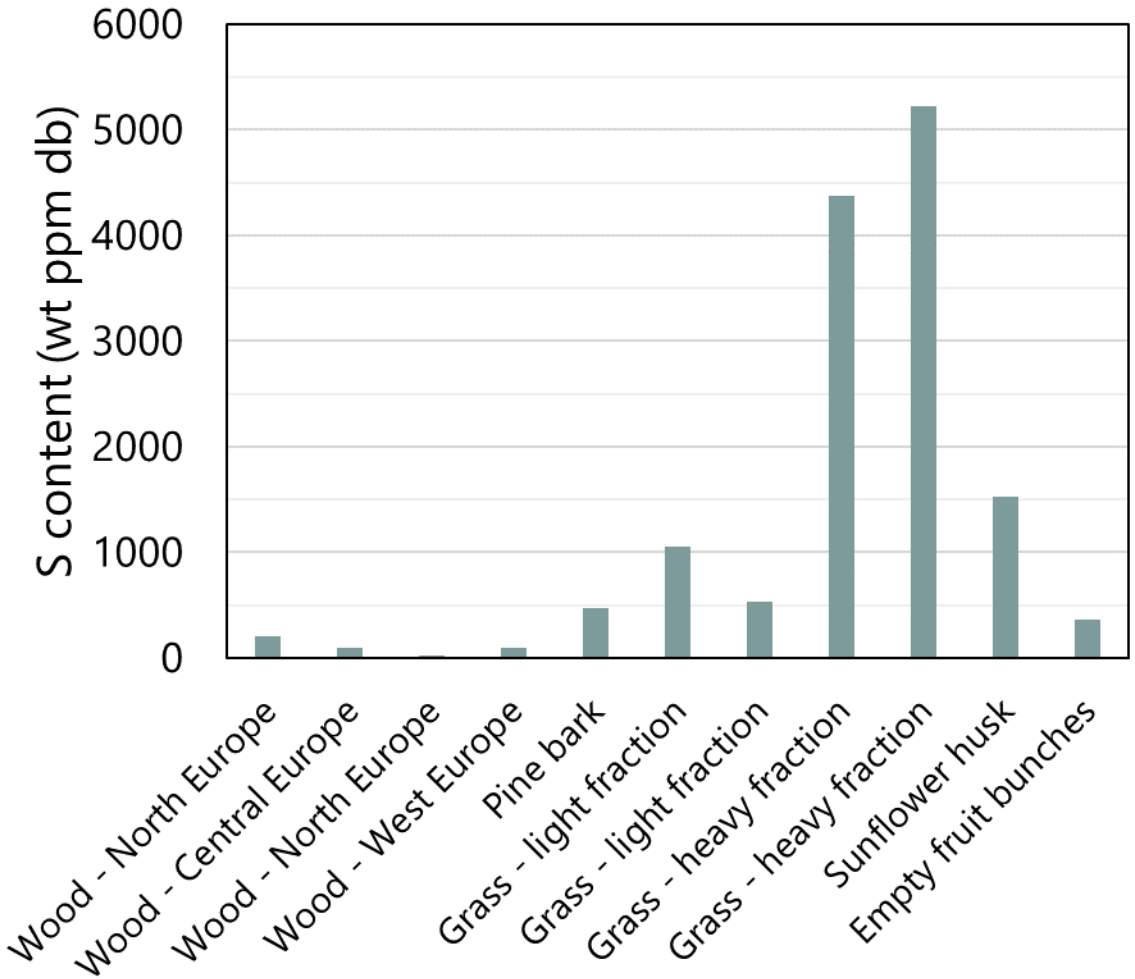
OXYGEN CONTENT IN BIOCRUDES
OXYGEN REMOVAL IS A MAJOR CHALLENGE

- A high hydrogen consumption is needed to selectively remove the oxygen from for these biocrudes.
- The hydrogen consumption for wood derived biocrudes are 2-3 times higher than vegetable oil
- The biocrudes are immiscible with fossil crudes because of the high oxygen content, thus making co-processing of these biocrudes in a hydrotreater challenging.



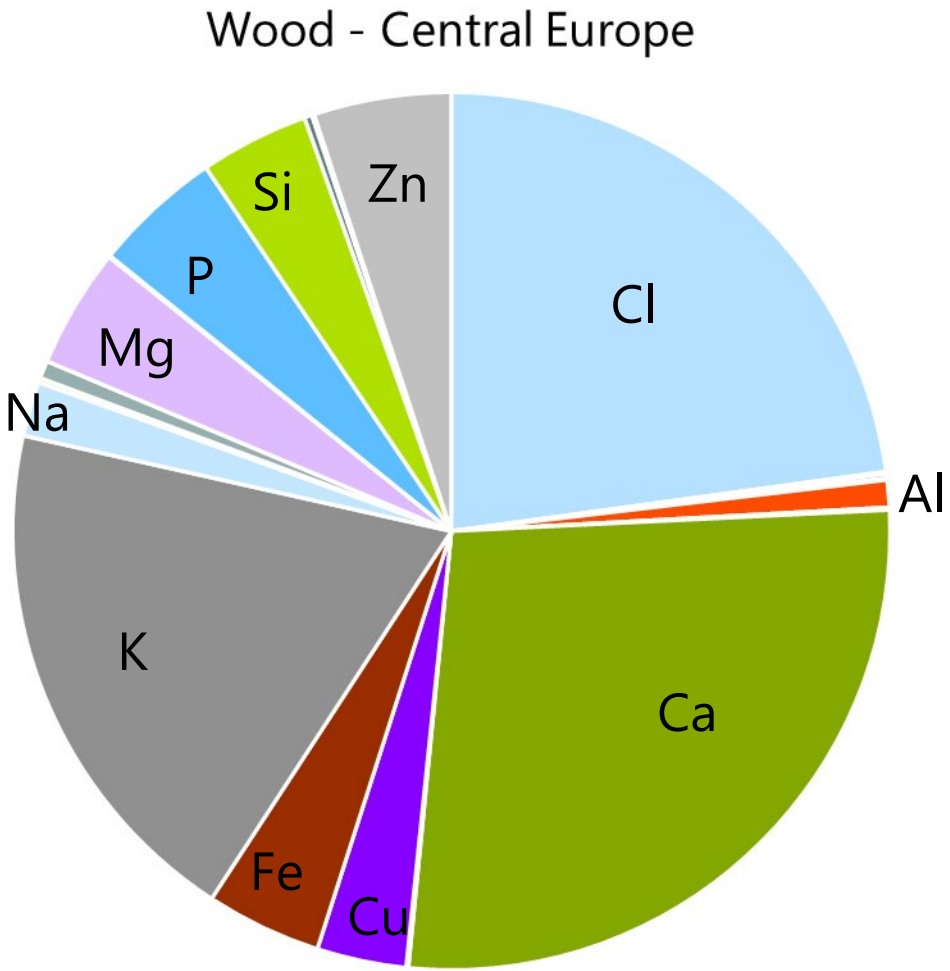
SULFUR CONTENT IN BIOCRUDES
NO BIOCRUDE IS SULFUR FREE

- Wood derived biocrudes have a low sulfur content (~200 wt ppm db)
- The heavy fraction from pyrolysis of grass has the highest sulfur content, but still low compared to many fossil crudes
- All biocrudes contains sulfur, thus the hydrotreating catalyst must be sulfur resistant



IMPURITIES IN BIOCRUDES
PRETREATMENT OF BIOCRUDES ARE NECESSARY

- Wood derived biocrudes have the lowest amount of impurities
- Pretreatment is critical to minimize the use of guard catalyst.
- The guard catalyst must be designed to capture a wide range of contaminates



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HTL OIL PROPERTIES

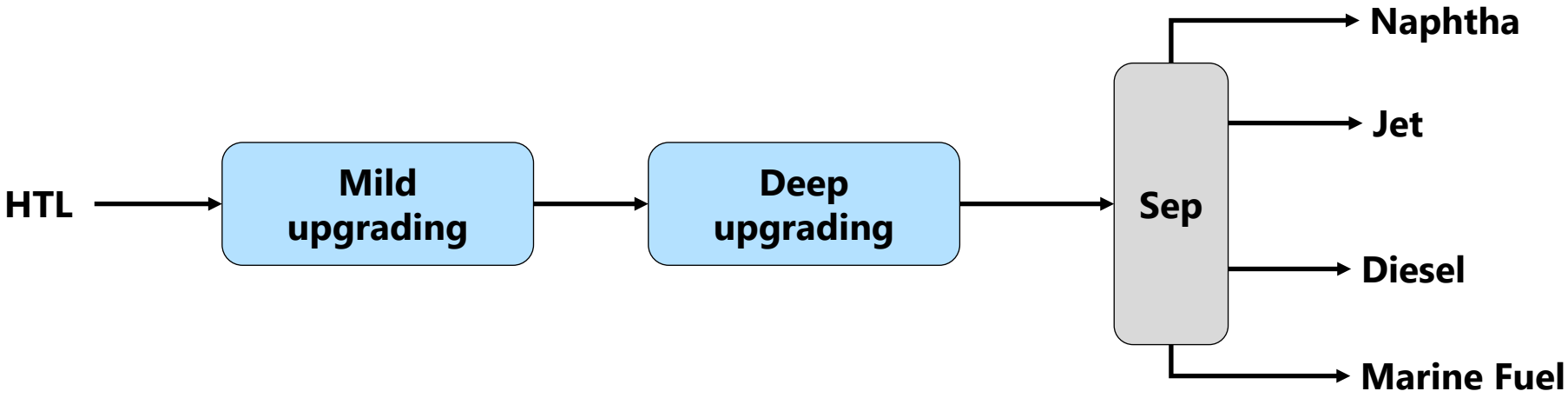
THE HTL OIL HAS A LOW OXYGEN CONTENT, BUT HIGH IMPURITIES CONTENT

	Received HTL Oil
SG	1.076
S, wt ppm	149
N, wt ppm	1479
H, wt%	8.6
O, wt% db	6.3
Cl, wt ppm	1.1
Br, wt ppm	0.3
F, wt ppm	2.1

	Received HTL Oil
Cr, wt ppm	48
Fe, wt ppm	76
K, wt ppm	41
Na, wt ppm	60
Si, wt ppm	8
Sn, wt ppm	11
Ti, wt ppm	12
MCR, wt%	24.1

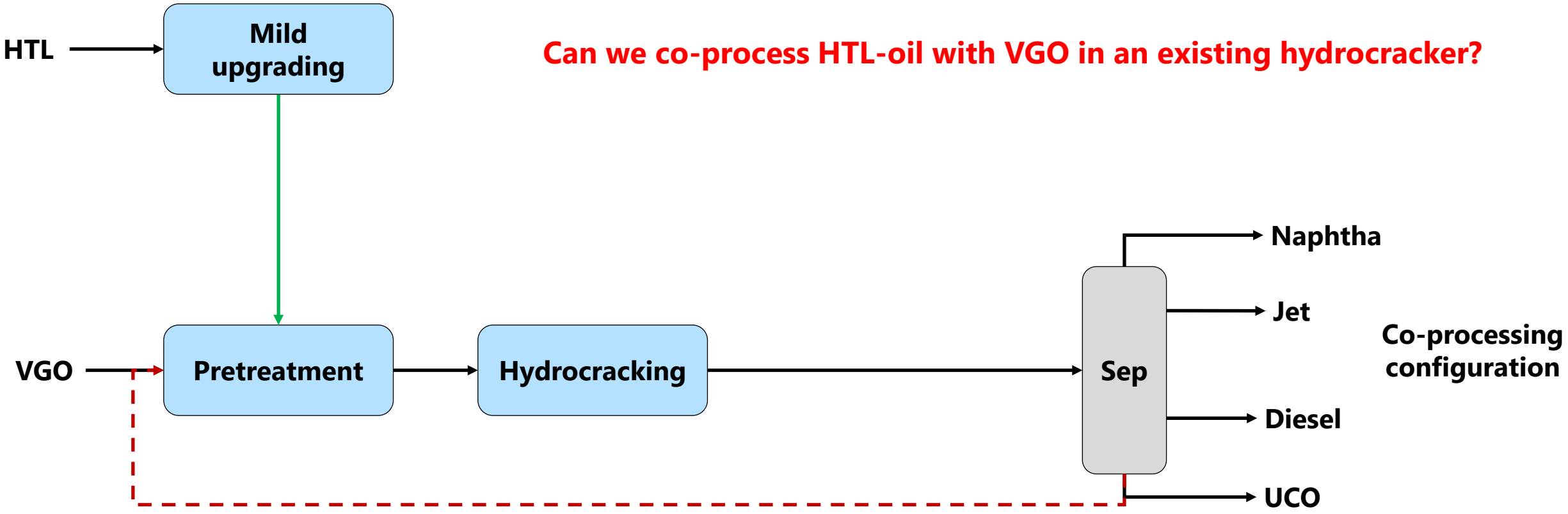
The HTL oil was produced by Aalborg university using their HTL pilot plant

UPGRADING OPTIONS
STANDALONE HYDROPROCESSING

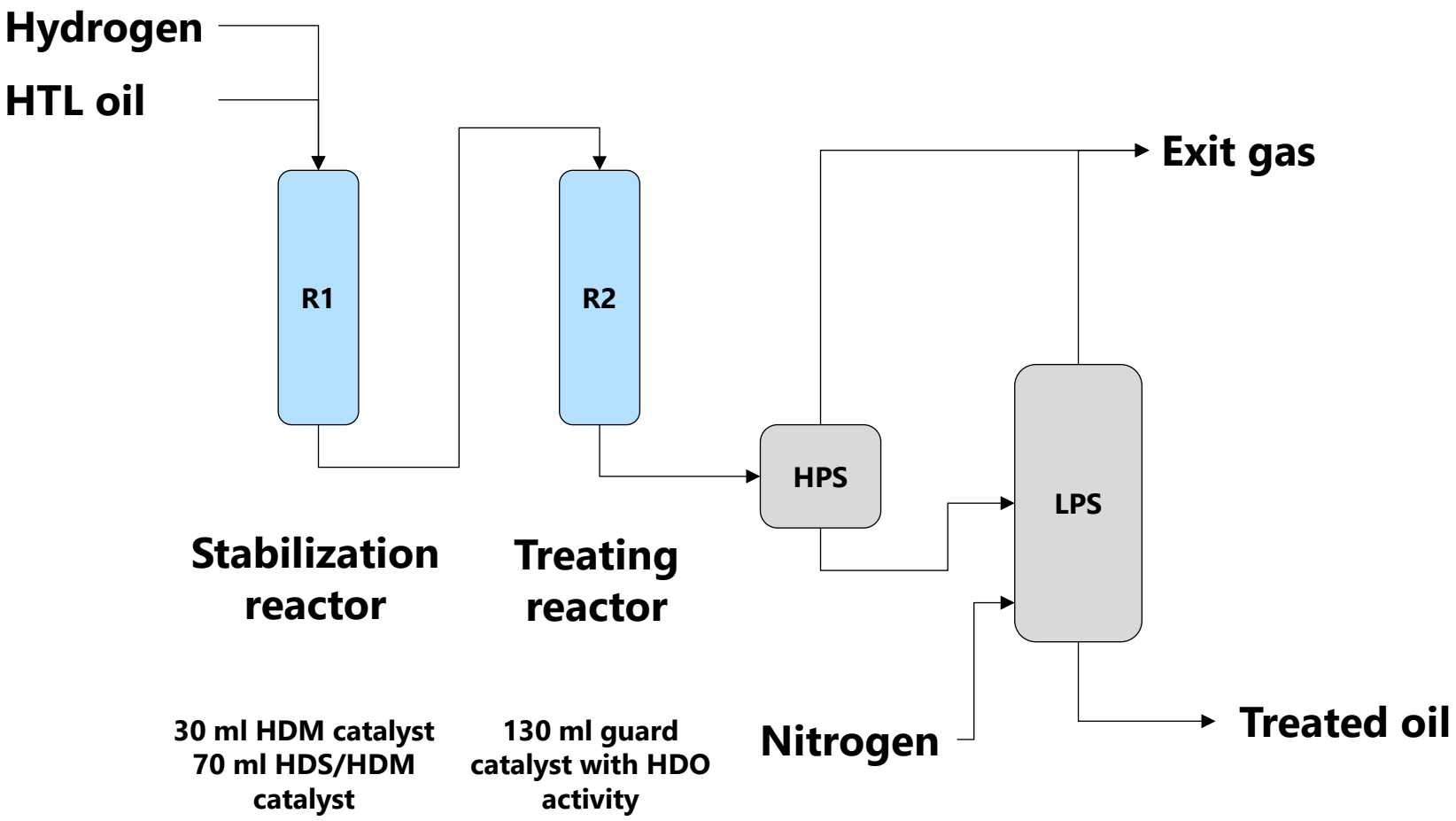


Stand-alone configuration

UPGRADING OPTIONS
CO-PROCESSING ROUTE



STABILIZATION AND MILD UPGRADING OF HTL OIL
TEST UNIT AND CONDITIONS



Process conditions

P: 121 barg

H2/oil ratio: 4,000 Nl/l

R1 T: gradient 140 to 200°C

R2 T: 340/350/360°C

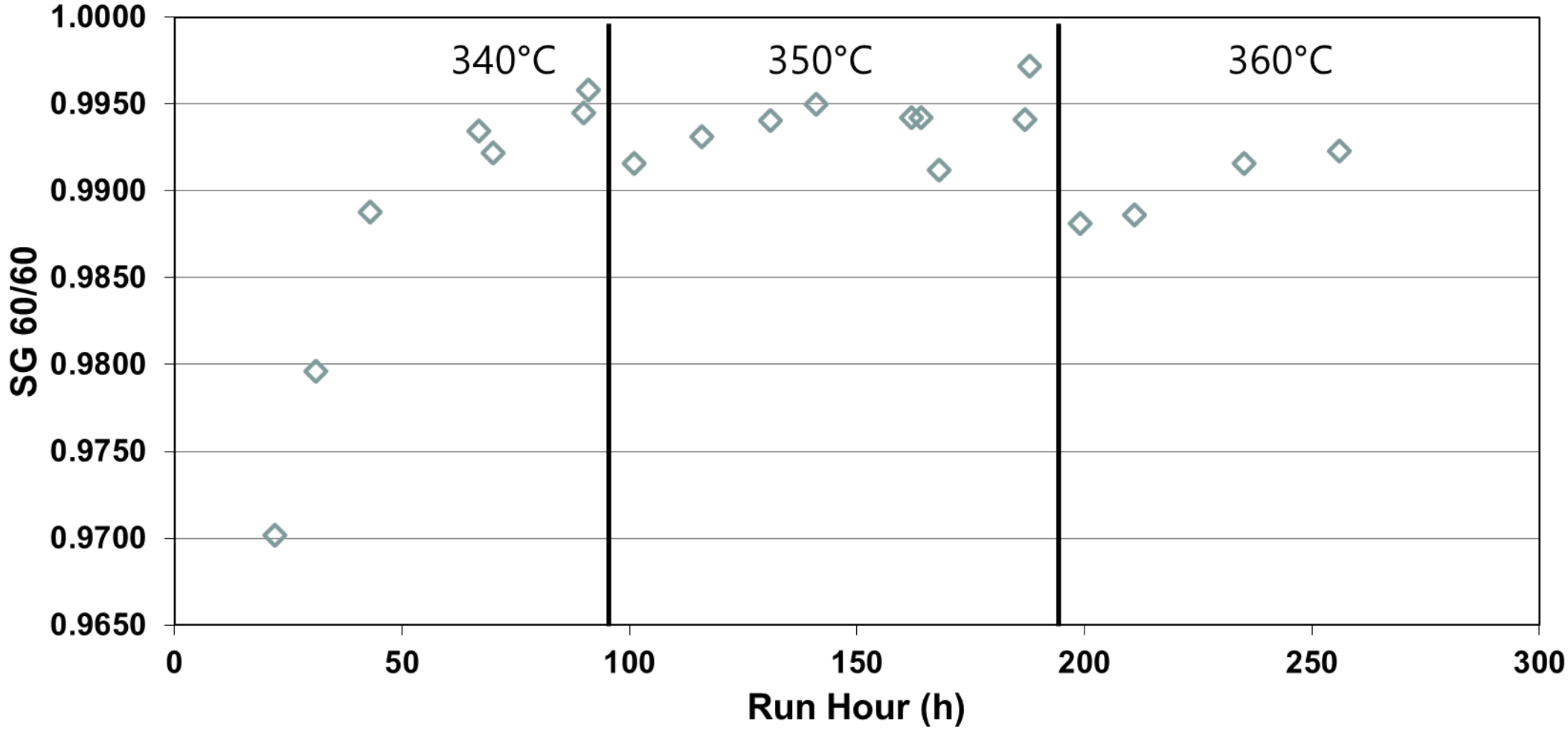
LHSV R1: 0.57 h^{-1}

LHSV R2: 0.44 h^{-1}

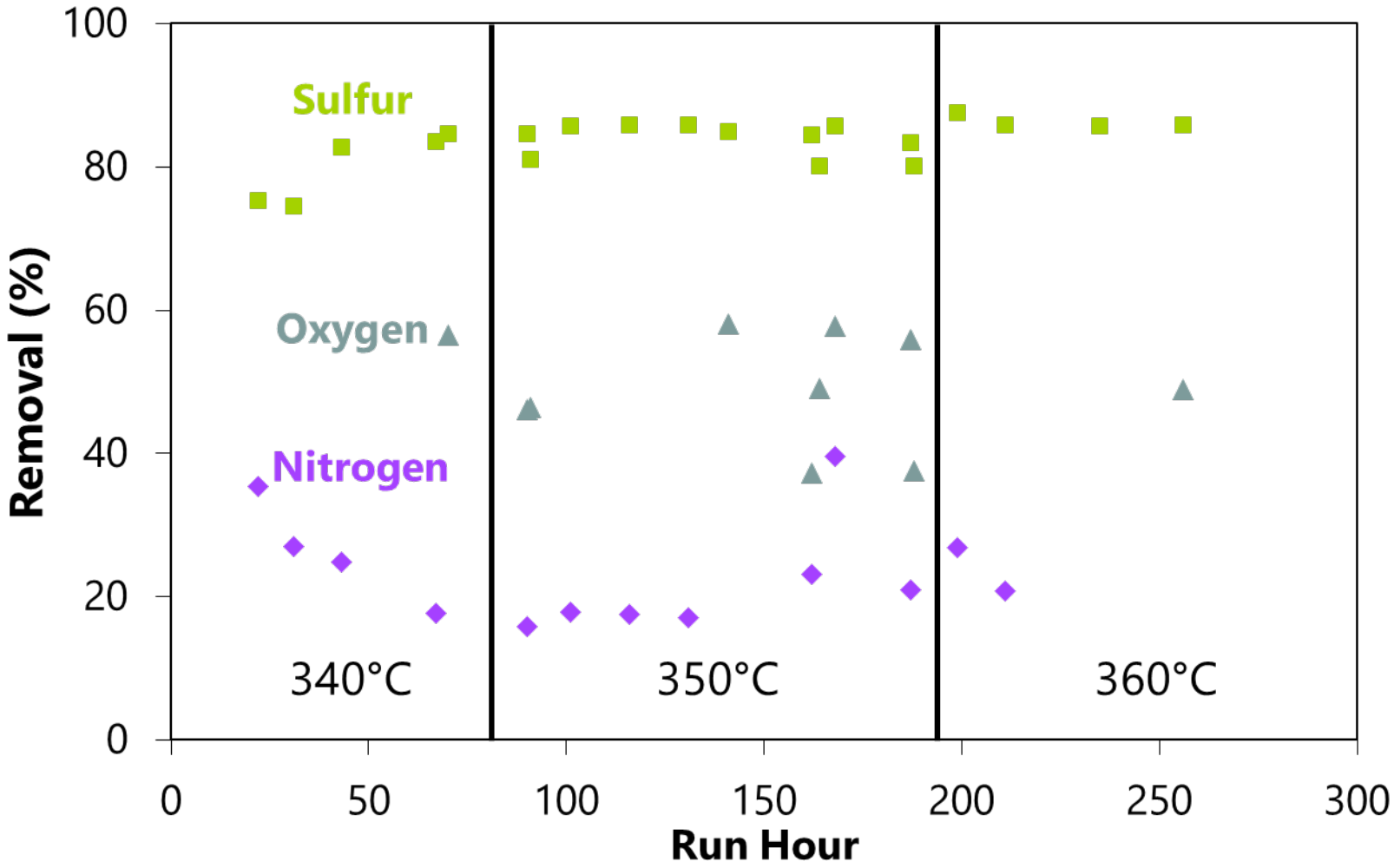
Treated oil was collected for co-processing with VGO

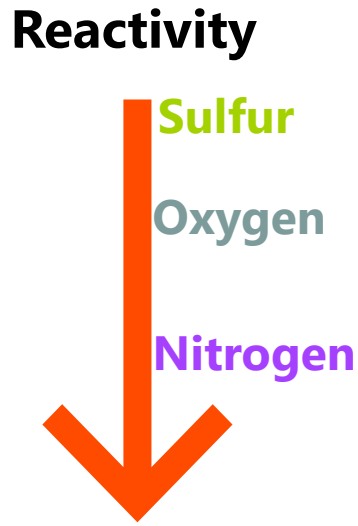
HYDROTREATMENT OF HYDROTHERMAL LIQUEFACTION OIL

THE CATALYST DEACTIVATES OVER TIME



MILD CATALYTIC UPGRADING OF HTL OIL
NITROGEN IN HTL IS VERY DIFFICULT TO REMOVE





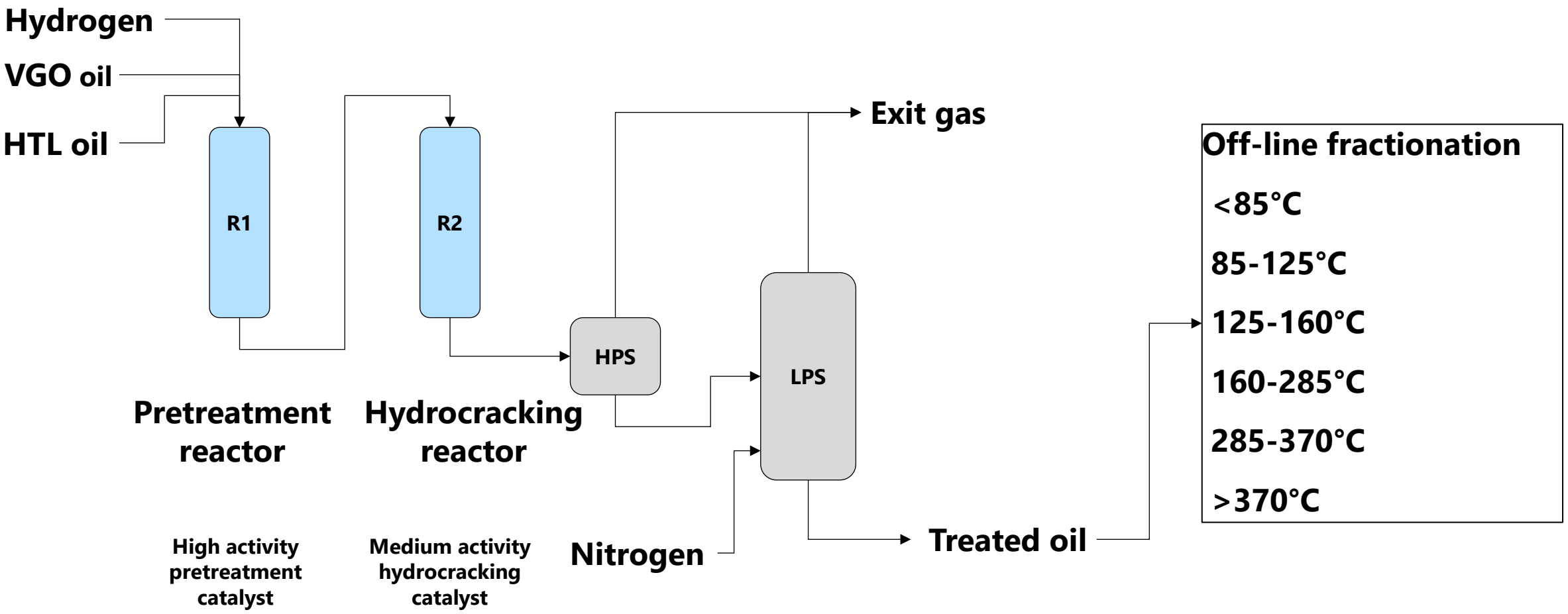
HTL OIL PROPERTIES

A SIGNIFICANT DECREASE IN OXYGEN AND MCR AFTER HYDROTREATING

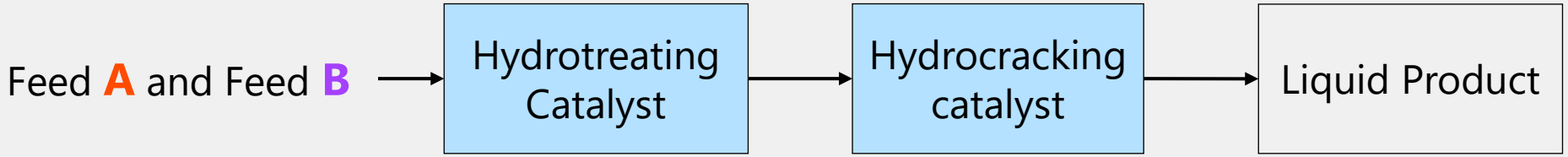
	Received HTL oil	Pretreated HTL oil
SG	1.076	0.9916
S, wt ppm	149	23
N, wt ppm	1479	1047
H, wt%	8.6	10.2
O, wt% db	6.3	2.4
Cl, wt ppm	1.1	0.8
Br, wt ppm	0.3	<0.2
F, wt ppm	2.1	0.4

	Received HTL oil	Pretreated HTL oil
Cr, wt ppm	48	30
Fe, wt ppm	76	25
K, wt ppm	41	10
Na, wt ppm	60	20
Si, wt ppm	8	<1
Sn, wt ppm	11	<1
Ti, wt ppm	12	8
MCR, wt%	24.1	13.1

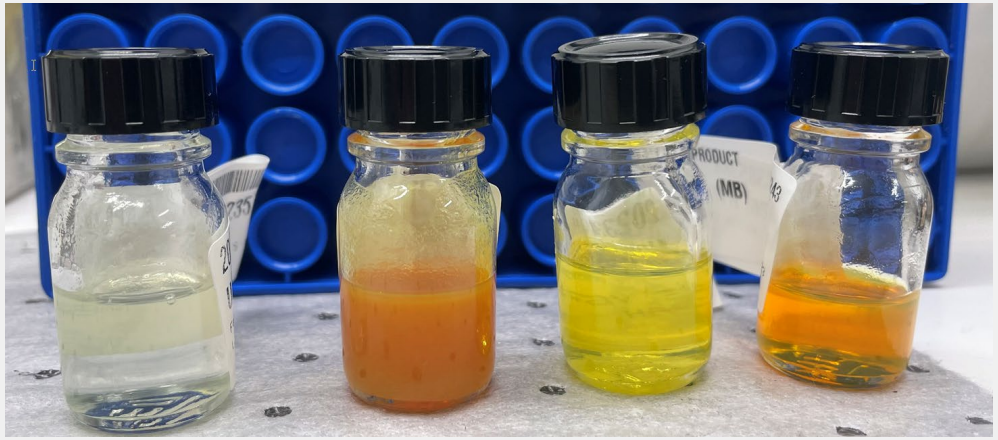
STABILIZATION AND MILD UPGRADING OF HTL OIL
TEST UNIT AND CONDITIONS



CO-PROCESSING
VGO AND PRETREATED HTL OIL



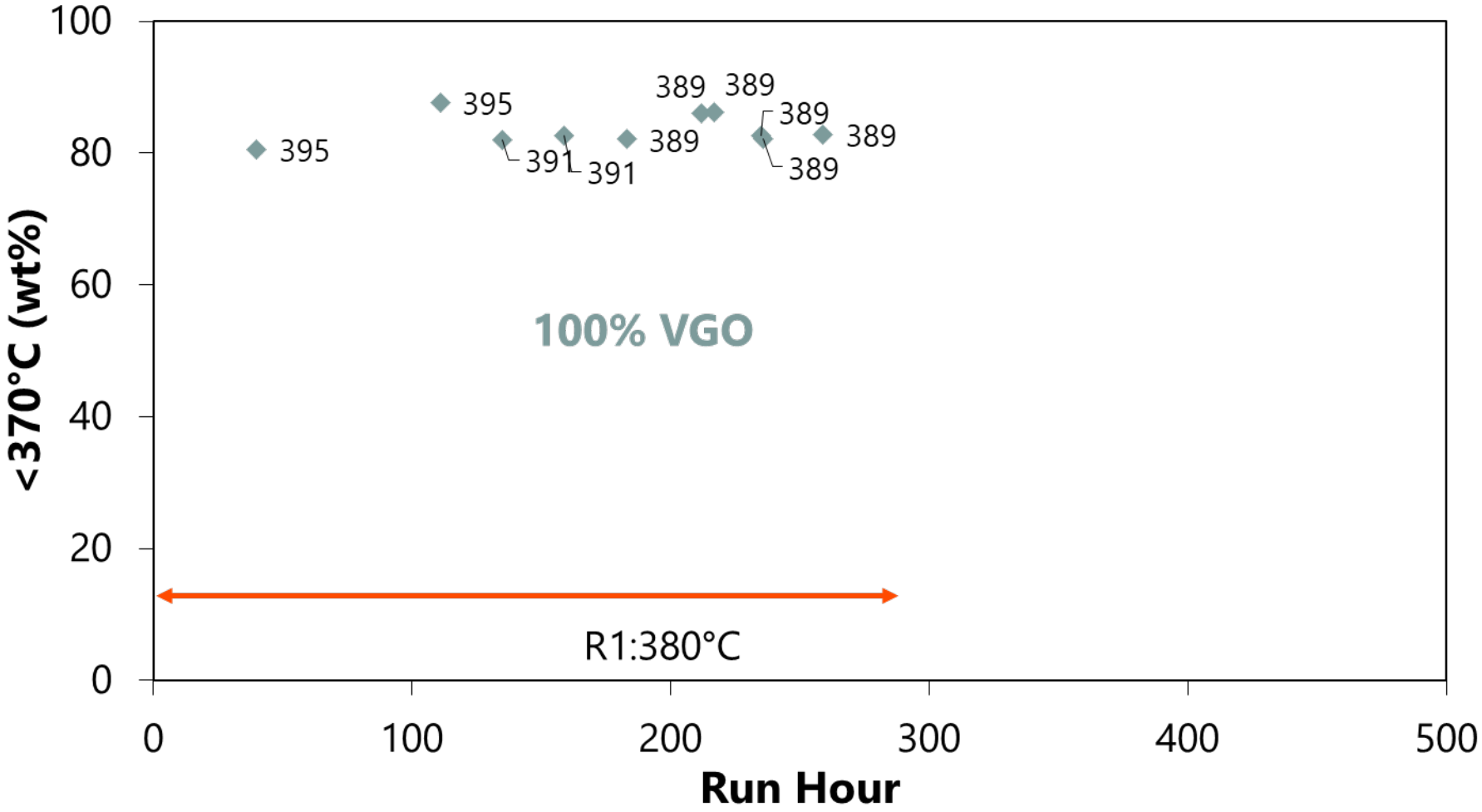
Feed	A	B	C
Vol, %	VGO	90%A+10%C	PT HTL product
SG	0.9258	0.9328	0.9919
H, wt%	12.20	11.91	10.12
S, wt ppm	14,435	11,900	23
N, wt ppm	1409	1370	1047
O, wt%	0	0.72	2.4
>370°C, %	84.7	80.3	40.7



100% VGO

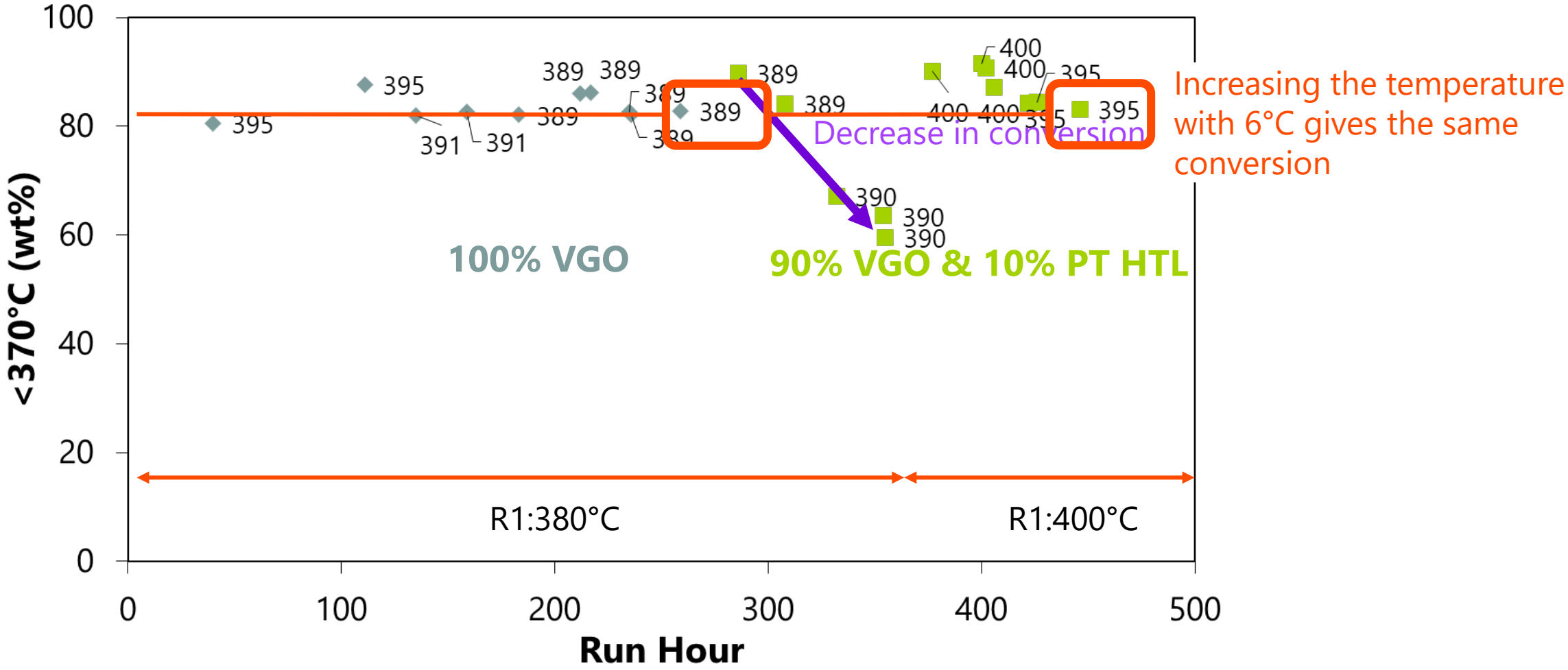
90% VGO and 10% HTL oil

CO-PROCESSING: HYDROCRACKING
HYDROPROCESSING OF 100% VGO



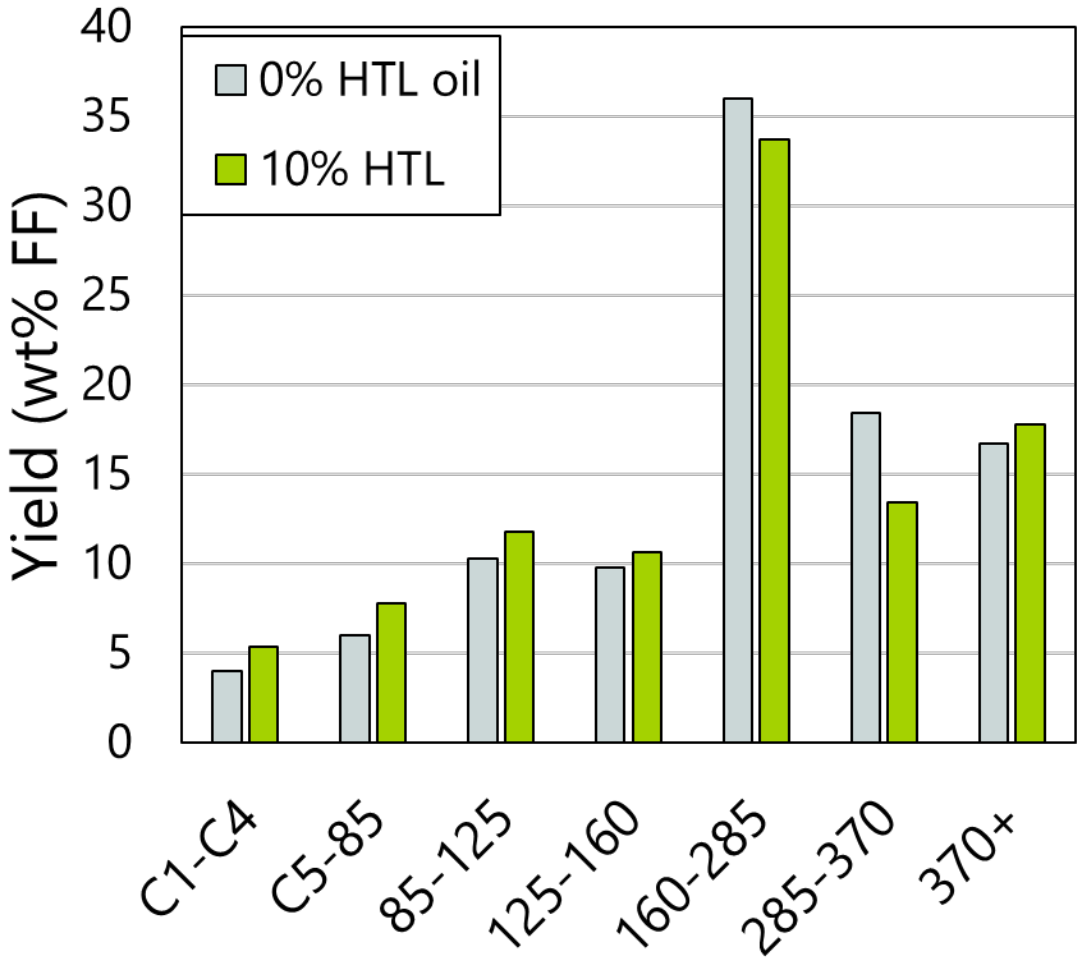
CO-PROCESSING: HYDROCRACKING

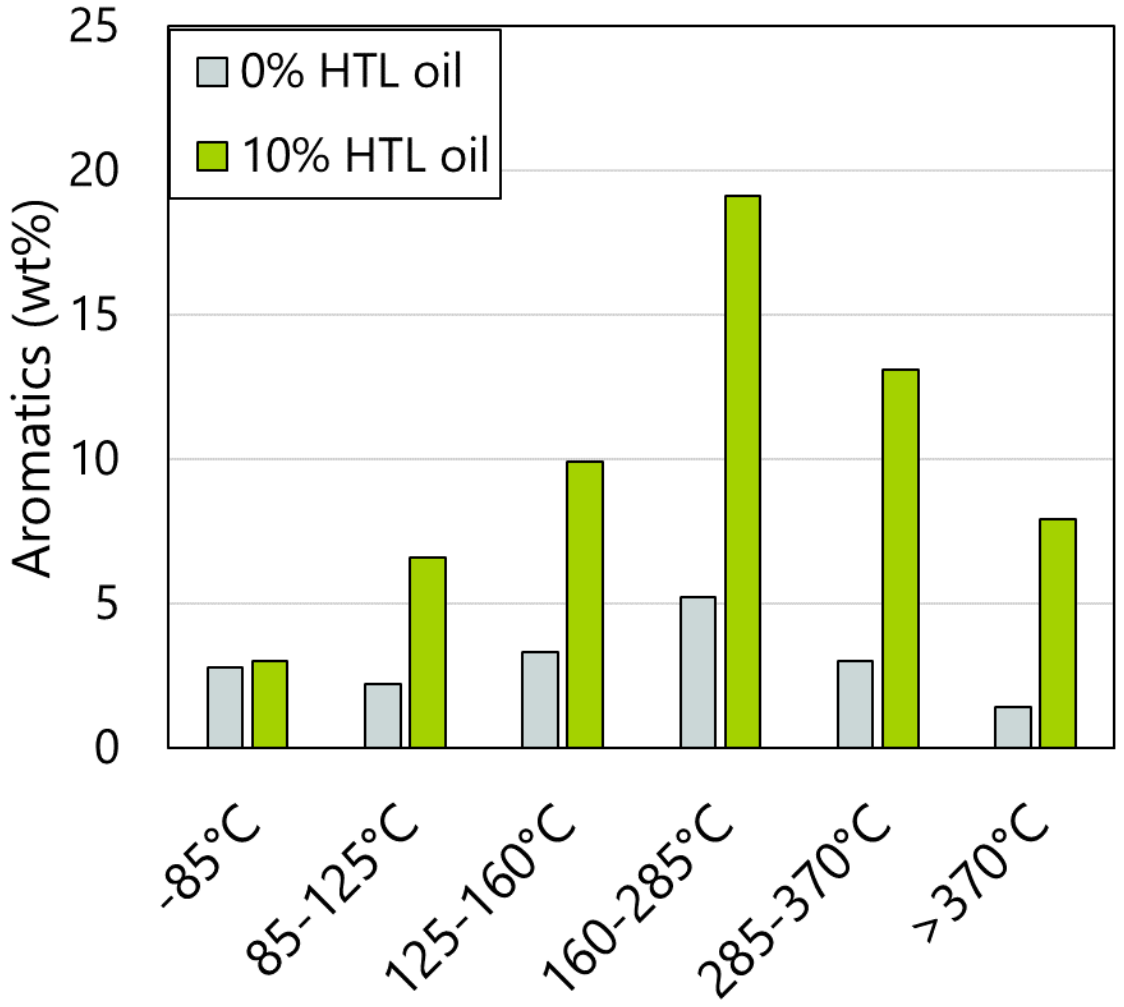
CO-PROCESSING OF PT HTL SIGNIFICANTLY DECREASES THE CATALYST ACTIVITY



IMPACT OF CO-PROCESSING OF HYDROTREATED HTL OIL ON YIELDS AND DENSITY

CO-PROCESSING HTL OIL INCREASE THE GAS AND NAPHTHA YIELD AND THE AROMATIC CONTENT





COMPOSITION OF JET FRACTION (160-285°C)

IT IS POSSIBLE TO PRODUCE JET FUEL BY CO-PROCESSING OF WOOD DERIVED BIOCRUDE

	0% HTL	10% HTL	Jet Fuel*
Aromatics	5.2 wt%	19.1 wt%	≤25 vol%
Freezing point	<-80°C	-57°C	≤-40 °C
SG 60/60	0.8138	0.8243	0.775-0.84
Smoke point	Est. 27-28	21.3 mm	≥18 mm

*Based on D7566

Pathway certification is needed

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TAKE HOME MESSAGE

- It is critical to remove impurities in biocrudes prior to hydrotreating

- HTL oil can be co-processed with VGO, but it requires a preliminary step of mild hydrotreatment.

- A significant increase in temperature is required to maintain the same conversion in the hydrocracker when co-processing mild hydrotreated HTL with VGO.

THANK YOU

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