

# UPGRADING OF BIO-BASED OILS TO FUELS



TOPSOE

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Verdier, A. Hansen, J. Gabrielsen, C. Strebel, N. Ammitzboll, J. Kristensen

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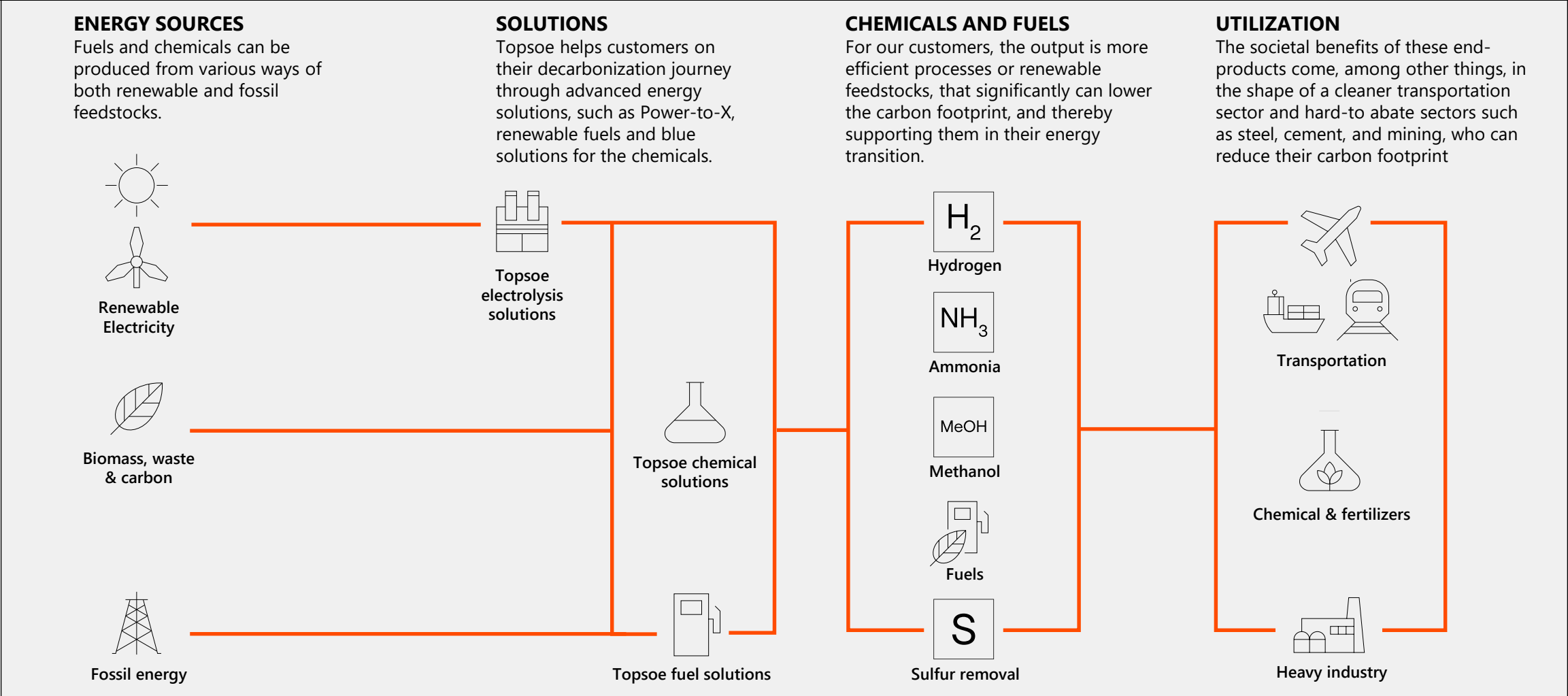
## AGENDA

- |          |                            |
|----------|----------------------------|
| <b>1</b> | <b>TOPSOE</b>              |
| <b>2</b> | <b>CATALYTIC PYROLYSIS</b> |
| <b>3</b> | <b>FRACTIONATION</b>       |
| <b>4</b> | <b>PYROLYSIS OIL</b>       |
| <b>5</b> | <b>OUTLOOK</b>             |

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# TOPSOE SOLUTIONS ACCELERATE THE ENERGY TRANSITION

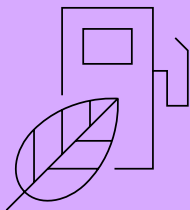


# TOPSOE AT A GLANCE

Topsoe is a leading developer and provider of solutions and technologies to produce fuels and chemicals essential to the energy transition. For more than 80 years, we have been perfecting chemistry to help industries produce more efficiently. Today, it is our ambition to lead the global transition of heavy industry and transport to a zero-carbon future.

#1

In renewable diesel



#1

In ammonia

9%

Of revenue  
invested in R&D



6,225

In revenue  
(DKK million)

903

EBIT before  
special items  
(DKK million)

2,133

employees

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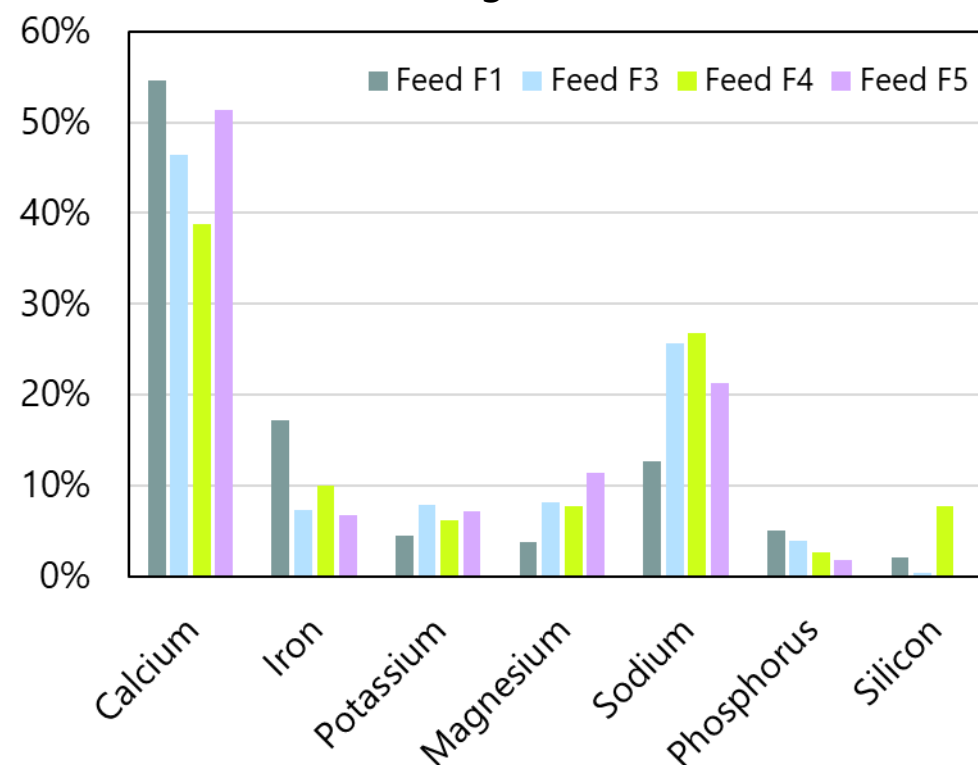
# CATALYTIC PYROLYSIS

## FEED PROPERTIES

### Physical properties

	F1	F3	F4	F5
S, wt ppm	27	108	102	58
N, wt ppm	708	987	767	-
H, wt%	8.30	7.28	7.02	6.49
O, wt%	17	26	28	29
Water, wt%	8.0	9.4	9.9	10.4
Inorganics, wt ppm	34	40	41	185

### Distribution of inorganics



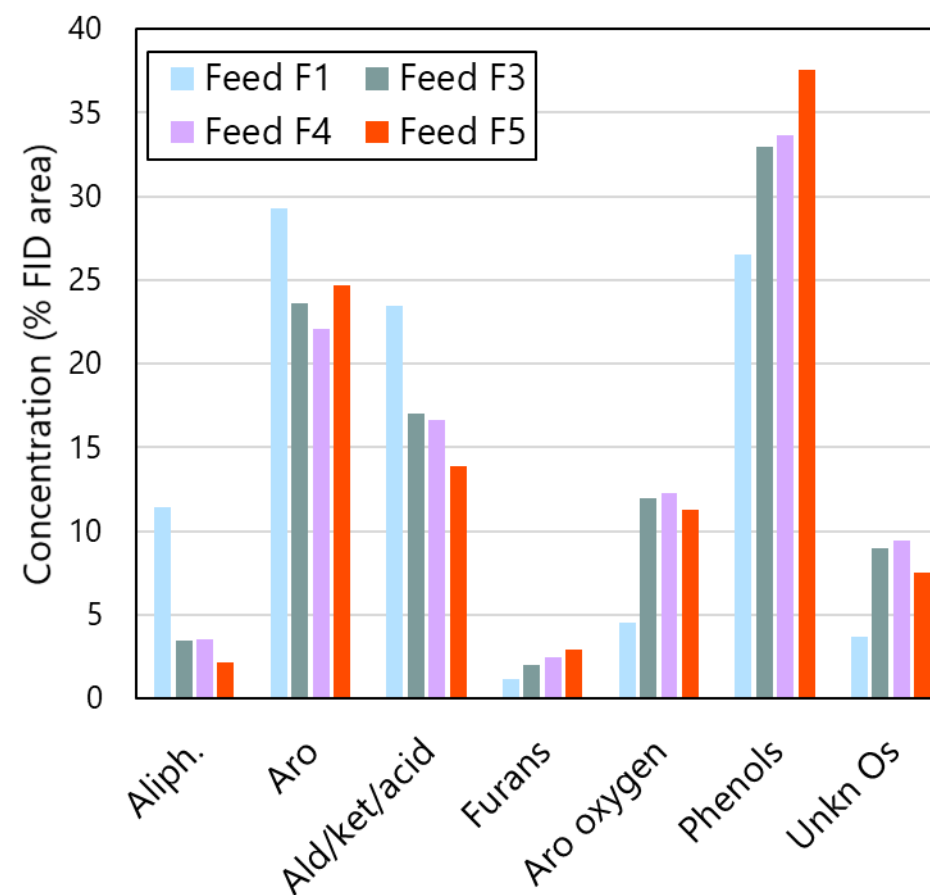
# CATALYTIC PYROLYSIS

## DETAILED CHARACTERIZATION

<sup>13</sup>C-NMR (relative % carbon total)

	F1	F3	F4	F5
Aliphatic	31.8	32.8	38.5	23.0
Methoxy in phenolics	3.3	4.1	4.3	2.0
Anhydrosugers, alcohols, ethers	0.5	4.1	4.3	18.4
Aromatic C-H bonds	27.0	27.1	22.1	24.0
Aromatic C-C bonds	25.6	19.8	16.0	17.4
Aromatic C-OH bonds	7.9	8.9	11.9	12.1
C=O (acids and derivatives)	2.0	2.0	1.9	2.2
C=O (carbonyls)	1.9	1.2	1.0	1.0

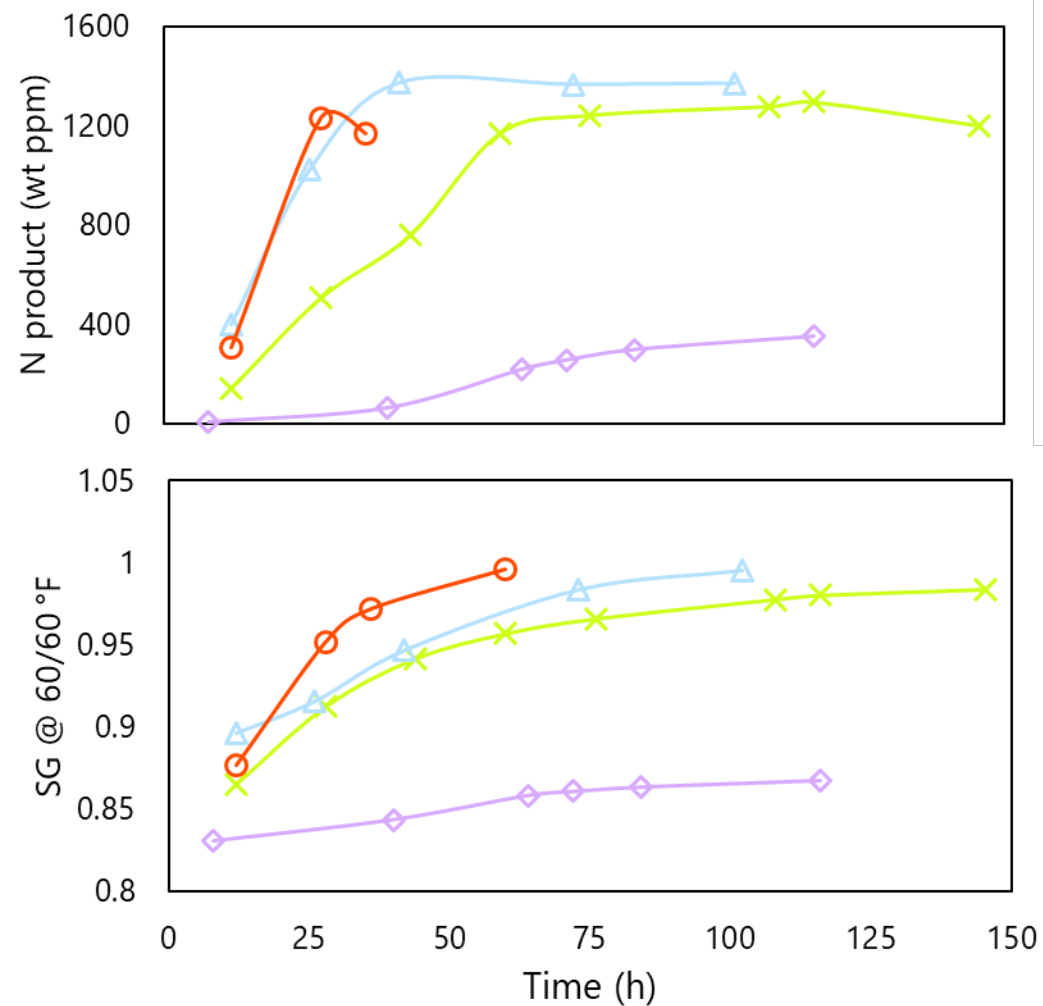
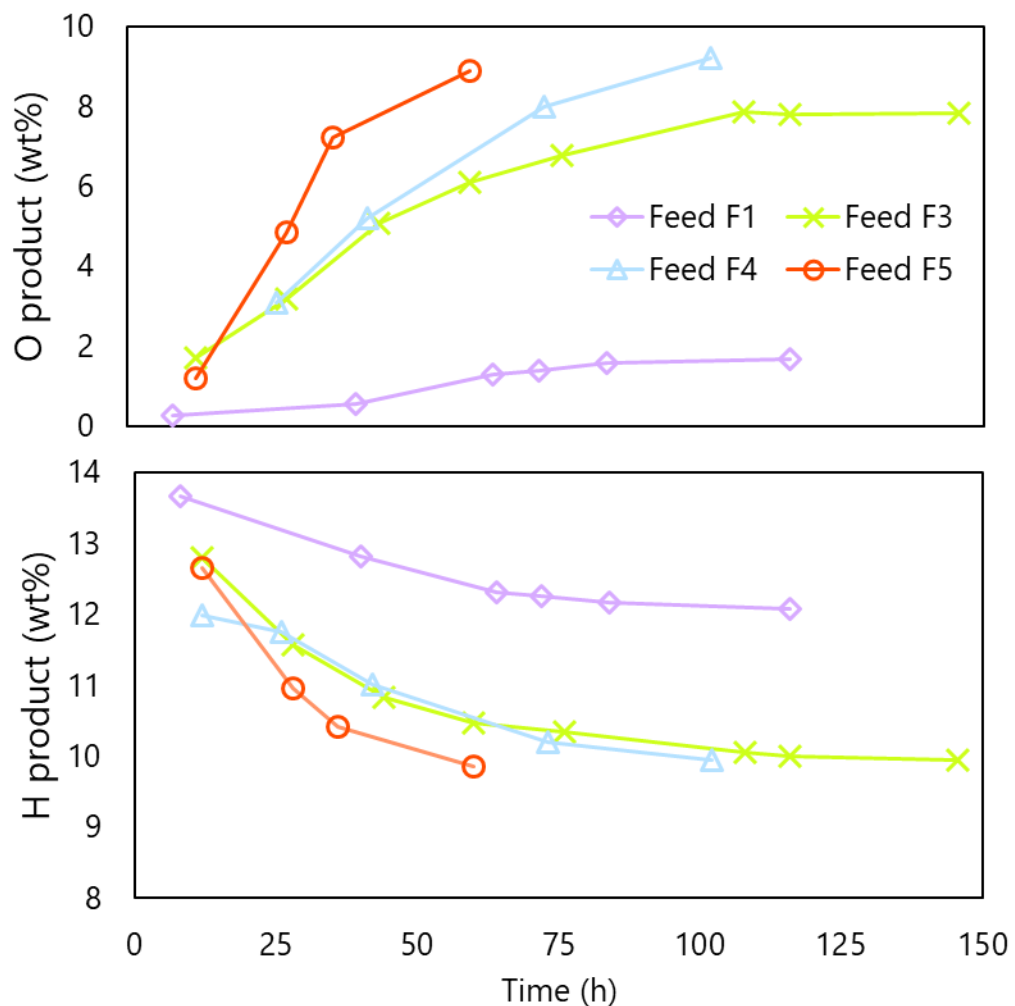
GC×GC-MS/FID





# CATALYTIC PYROLYSIS

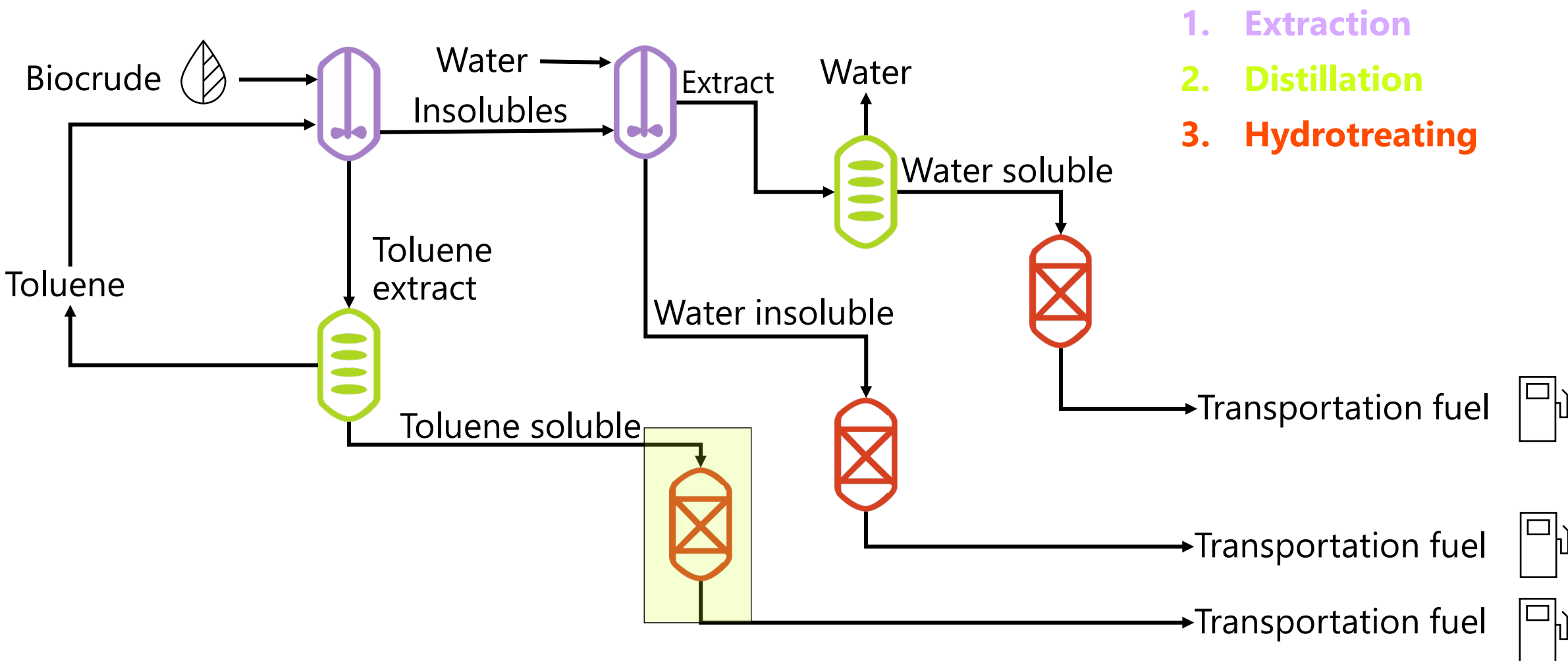
THE FEED PROPERTIES HAVE A LARGE IMPACT ON THE DEACTIVATION RATE



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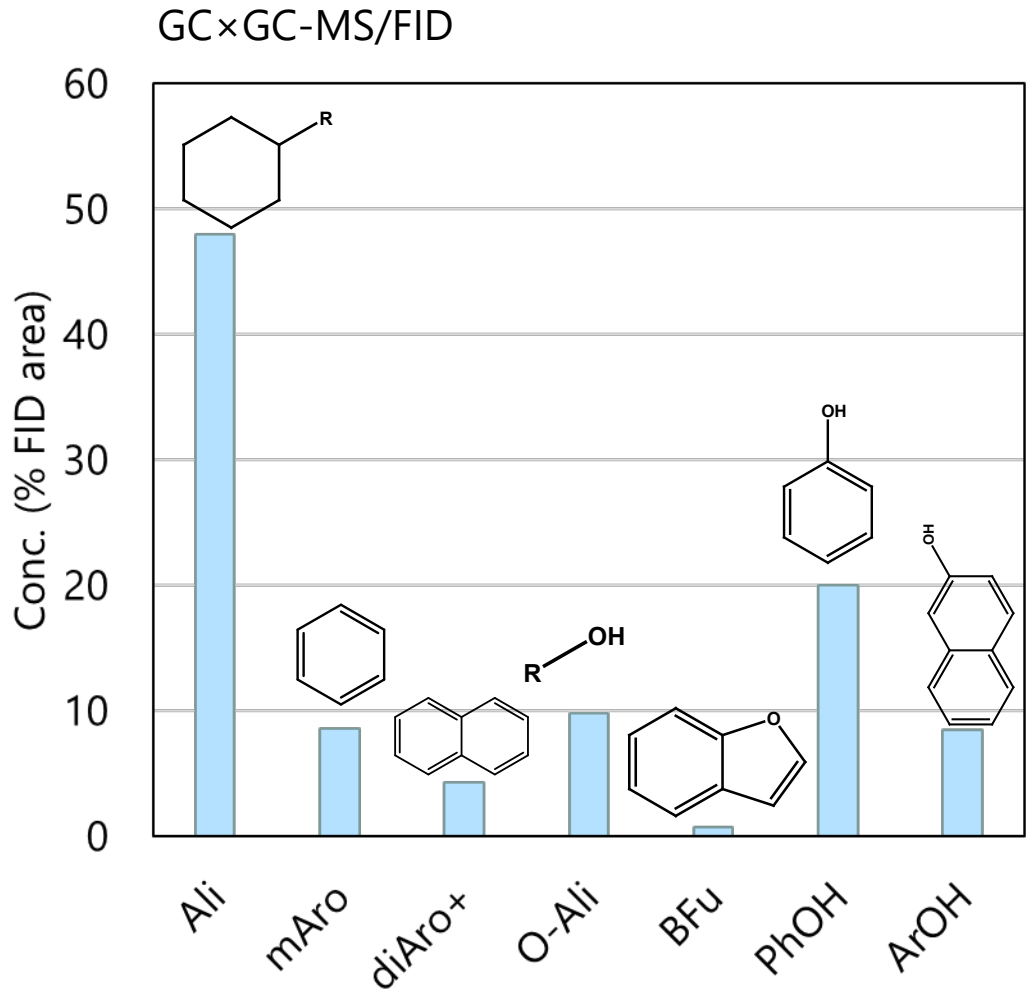
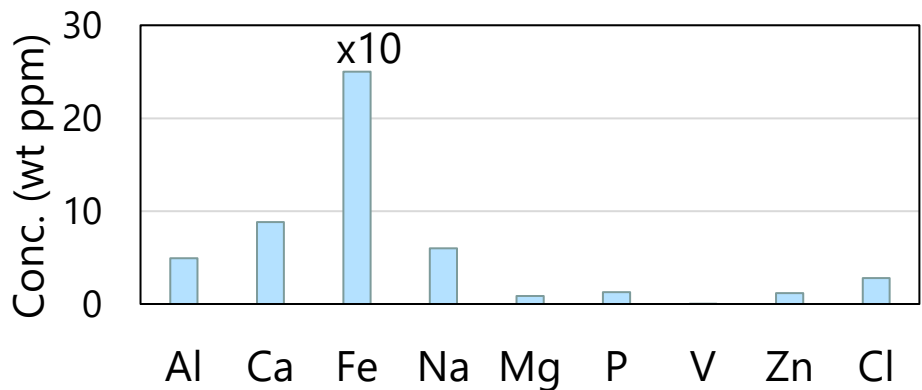
# FRACTIONATION



# FRACTIONATION - HYDROTREATMENT OF TOLUENE EXTRACTED BIOCRUDE

## FEED PROPERTIES

Analysis	Value	Unit
H	6.78	wt%
N	431	wt ppm
S	62	wt ppm
O	22.3	wt%
Water	1.47	wt%
TAN	26.5	mg KOH/g
SG 60/60°F	1.1688	



# FRACTIONATION - HYDROTREATMENT OF TOLUENE EXTRACTED BIOCRUDE

## TEST CONDITIONS AND MASS BALANCES

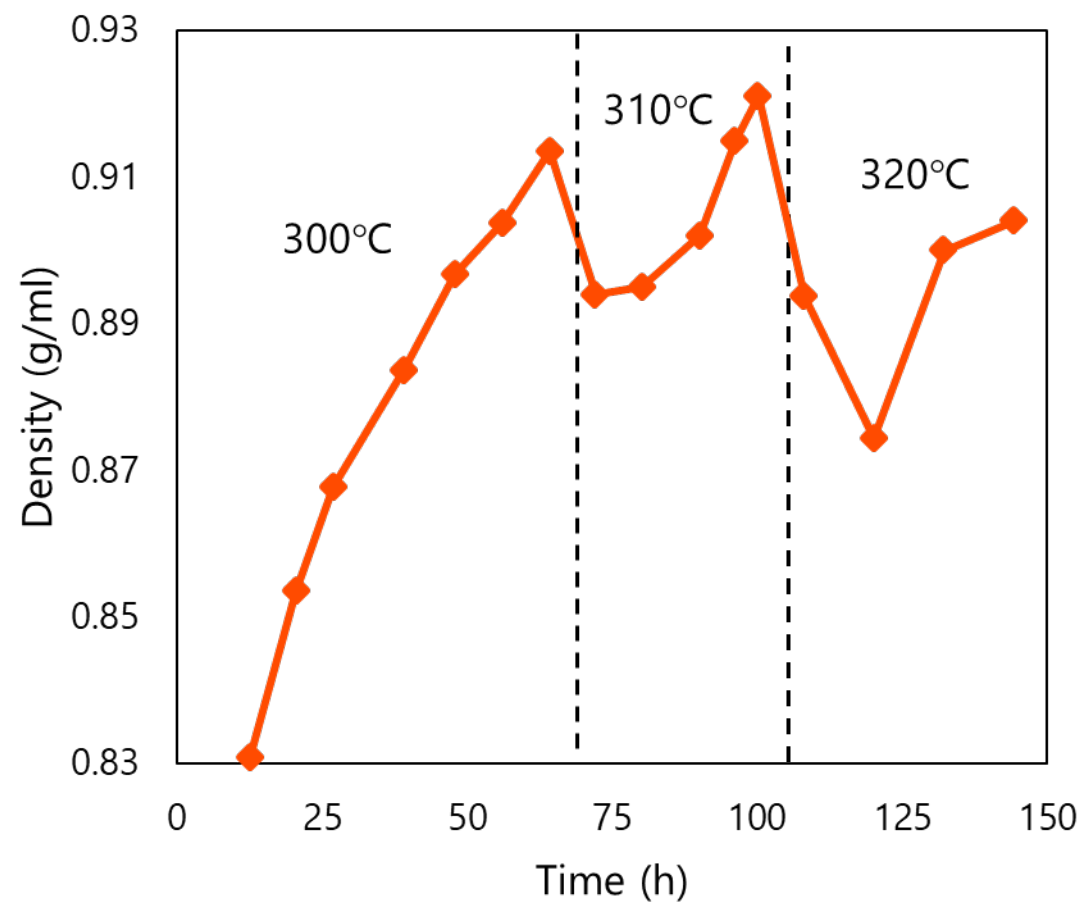
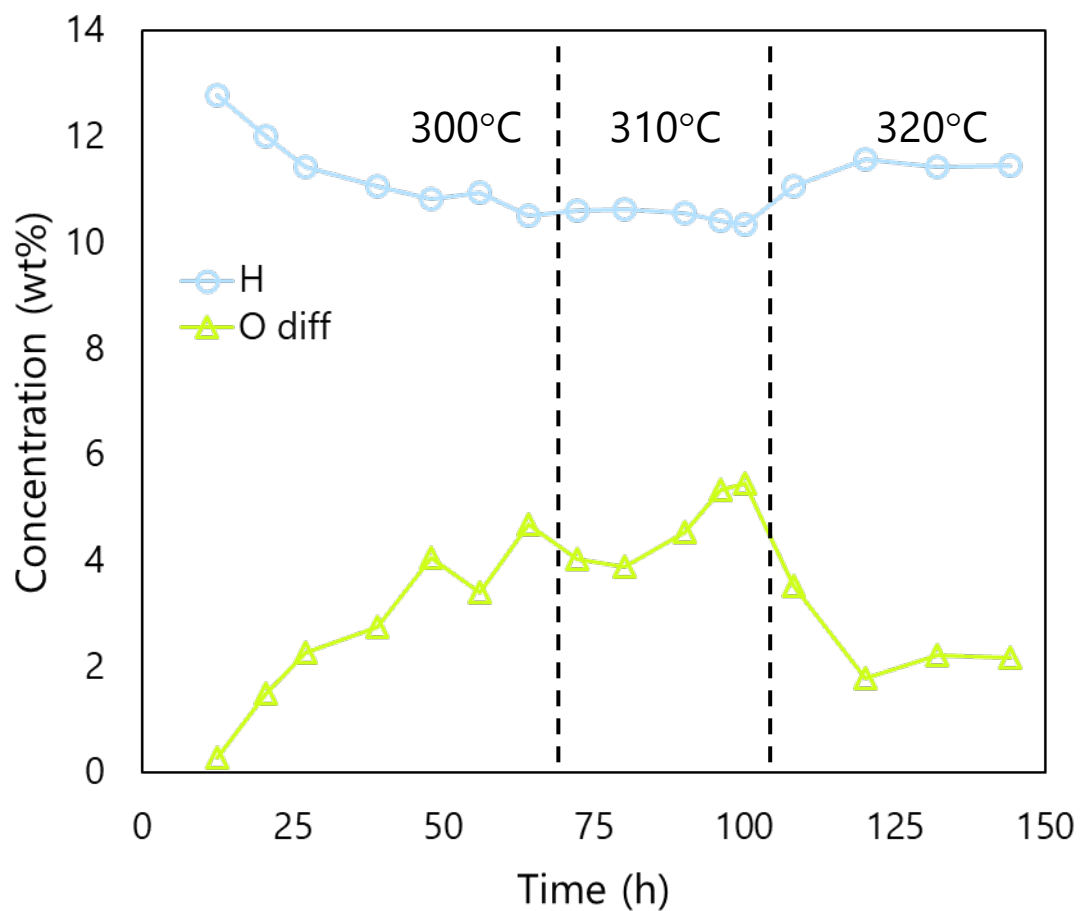
### Test conditions

Pressure	139 bar
Avg. Temperature	300 °C
LHSV	0.35 h <sup>-1</sup>
H <sub>2</sub> /oil ratio	3300 NI/I

### Mass balance

Parameters	MB1 (6.5 h)	MB2 (8 h)	MB2 (10 h)	Average
Mass yield of product oil, wt.%	76.6	77.4	77.3	77.10
Carbon yield of product oil, %	98.7	99.02	99.9	99.21
Mass yield of aqueous fraction, wt.%	19.1	17.39	17.8	18.10
Carbon yield of aqueous fraction, %	0.3	0.27	0.28	0.28
Product Gas yield, wt.%	2.0	1.97	1.66	1.88
Carbon yield of product gas, %	1.8	1.93	1.57	1.77
H <sub>2</sub> consumed, g of H <sub>2</sub> /g of dry bio-oil	0.071	0.088	0.087	0.082
Mass Balance, %	97.1	96.15	96.13	96.46
Carbon Balance, %	100.8	101.22	101.72	101.25

## FRACTIONATION - HYDROTREATMENT OF TOLUENE EXTRACTED BIOCRUDE



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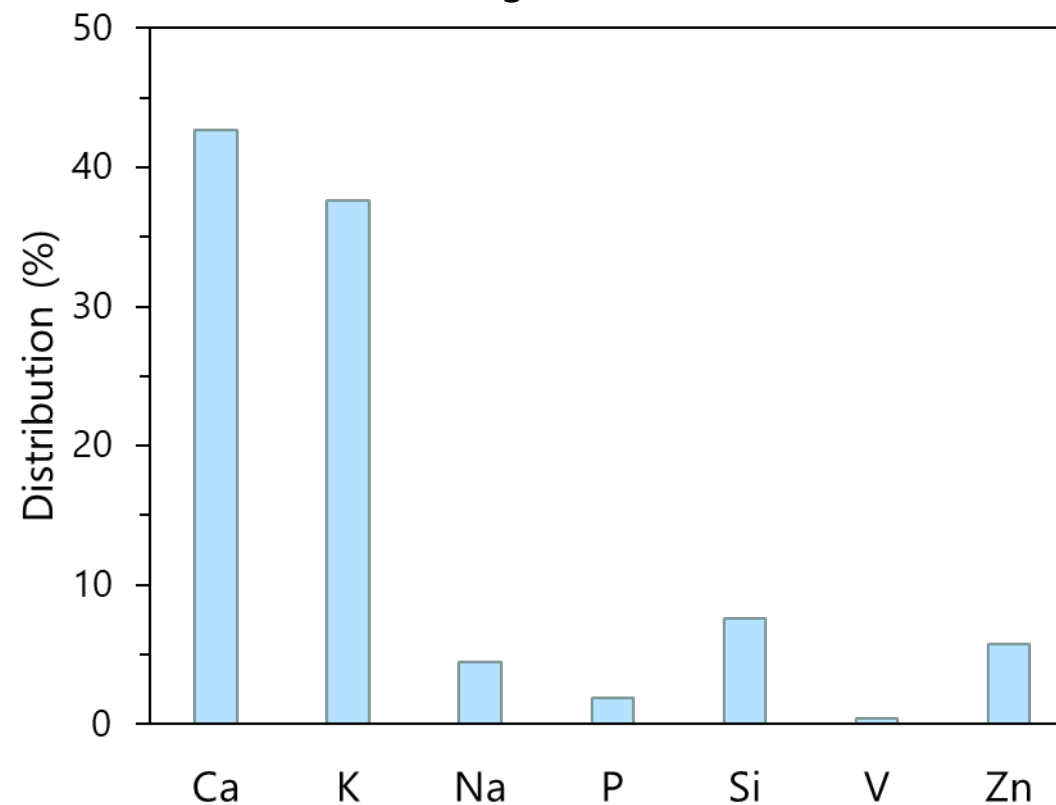
# PYROLYSIS OIL

## CHARACTERISATION – PHYSICAL PROPERTIES

### Feed properties

Analysis	Value	Unit
N	416	wt ppm
S	63	wt ppm
H	7.6	wt %
H	7.79	wt %
O	46	wt %
SG 60/60°F	1.1997	
Viscosity at 30°C	53.8	cSt
Total acid no.	79.7	mgKOH/g
Water	21.3	wt %
Carbon Residue	19.57	wt %
Carbonyls	5.0	mol/kg
Inorganics	69	wt ppm

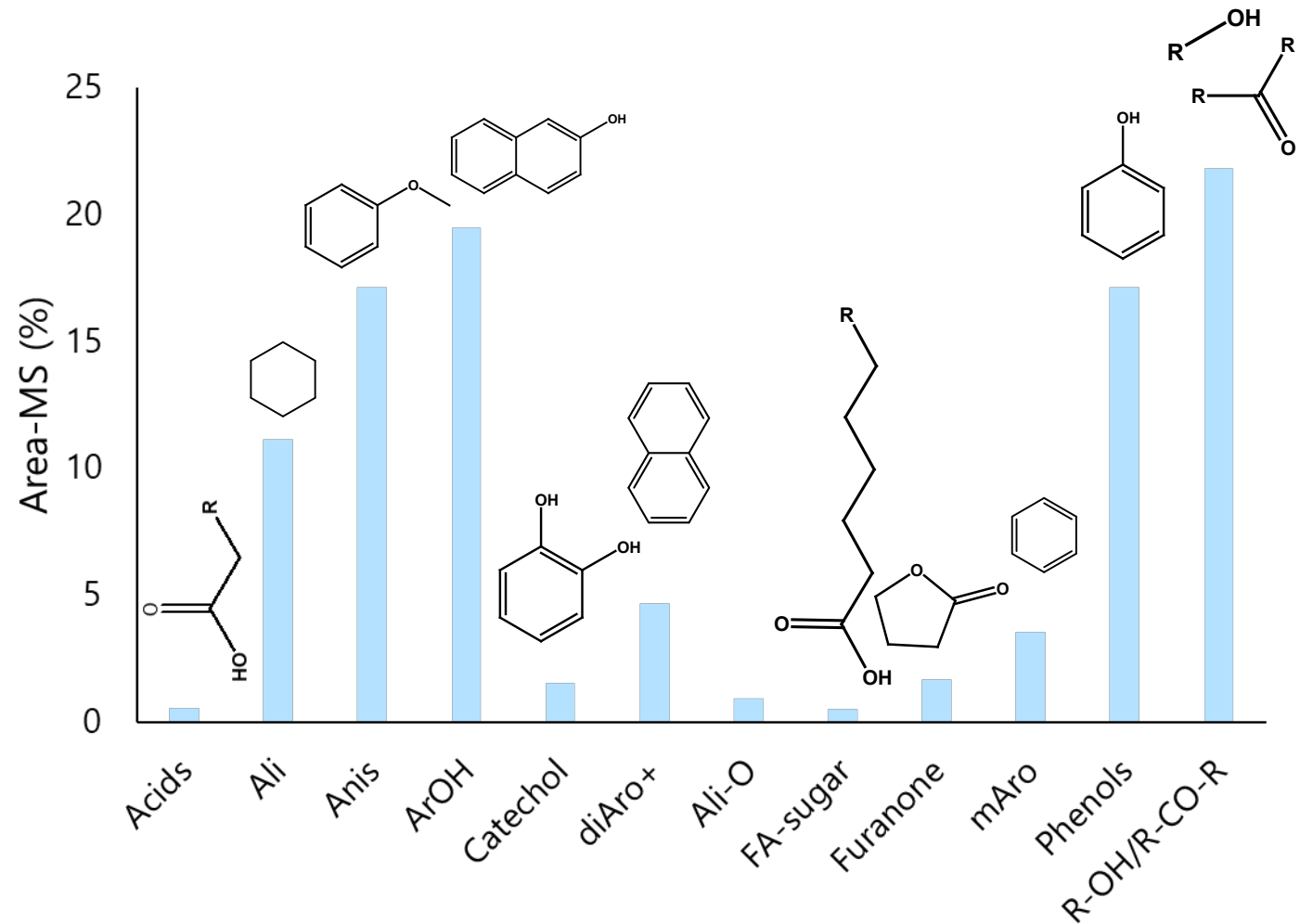
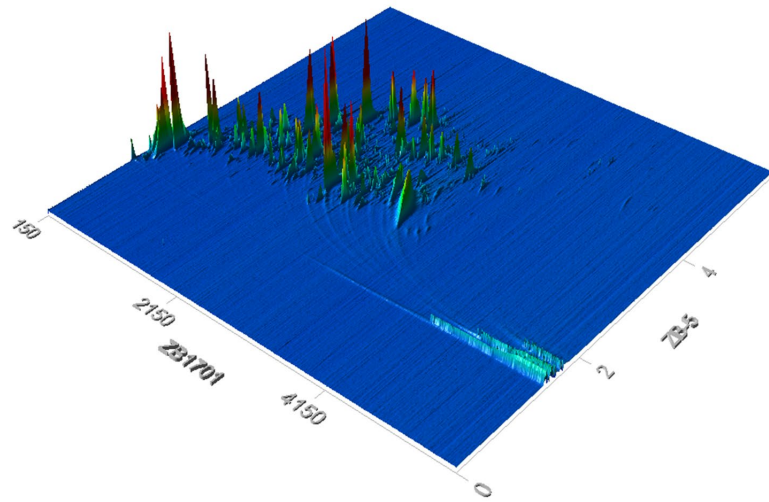
### Distribution of inorganics



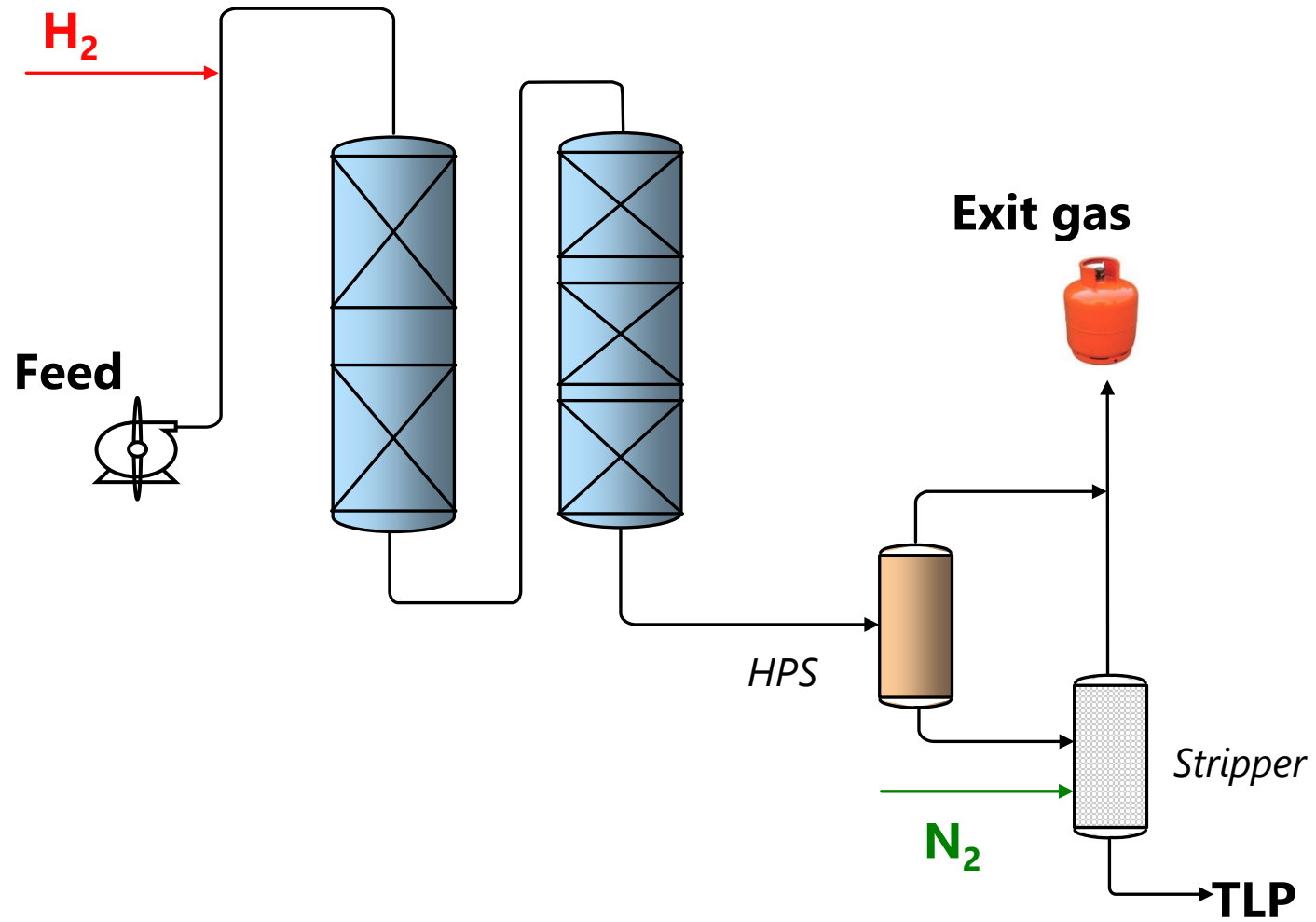


# PYROLYSIS OIL

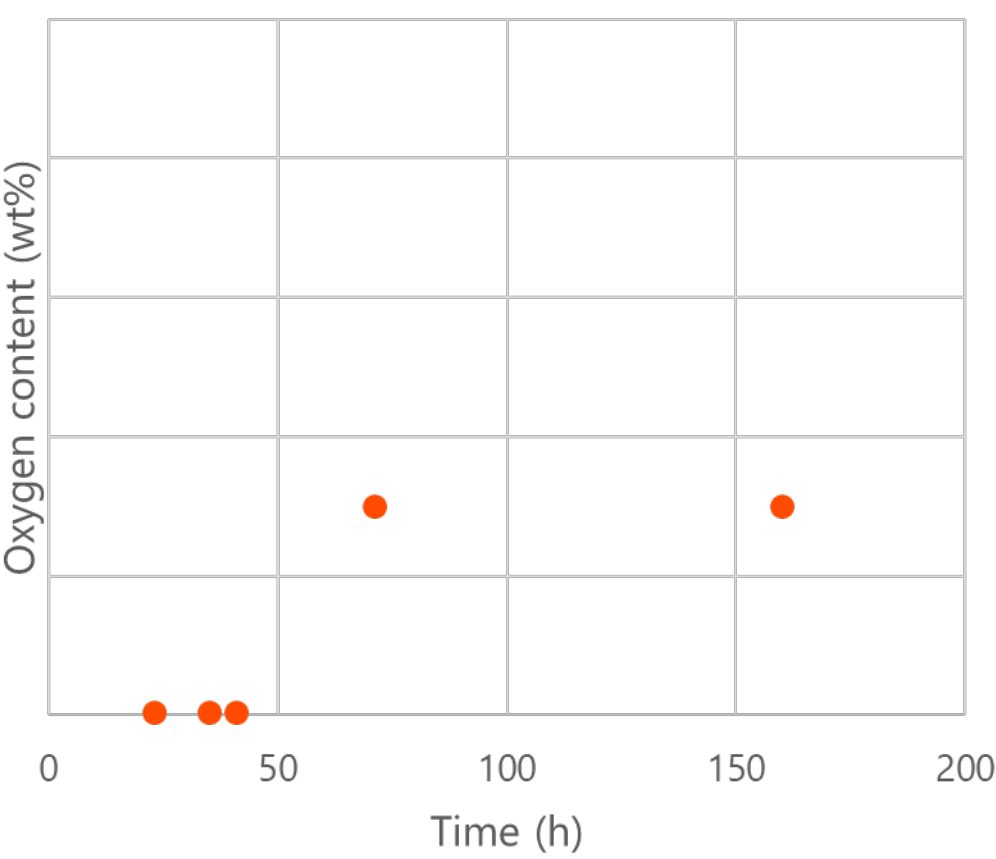
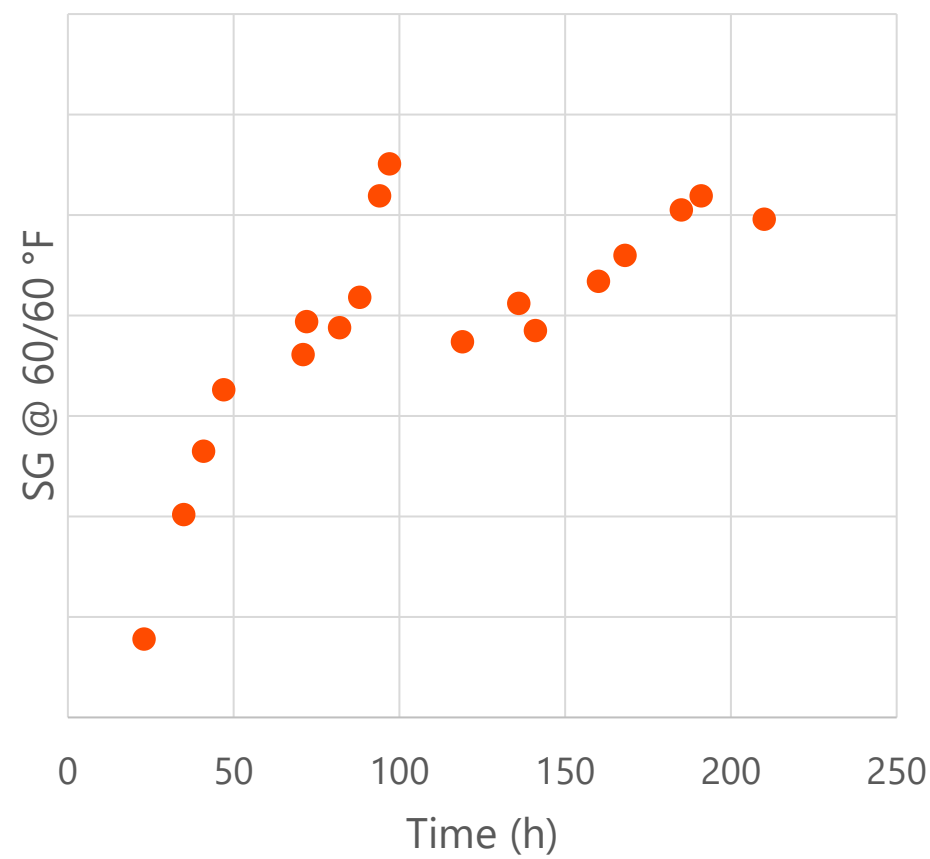
## CHARACTERISATION - GC×GC-MS



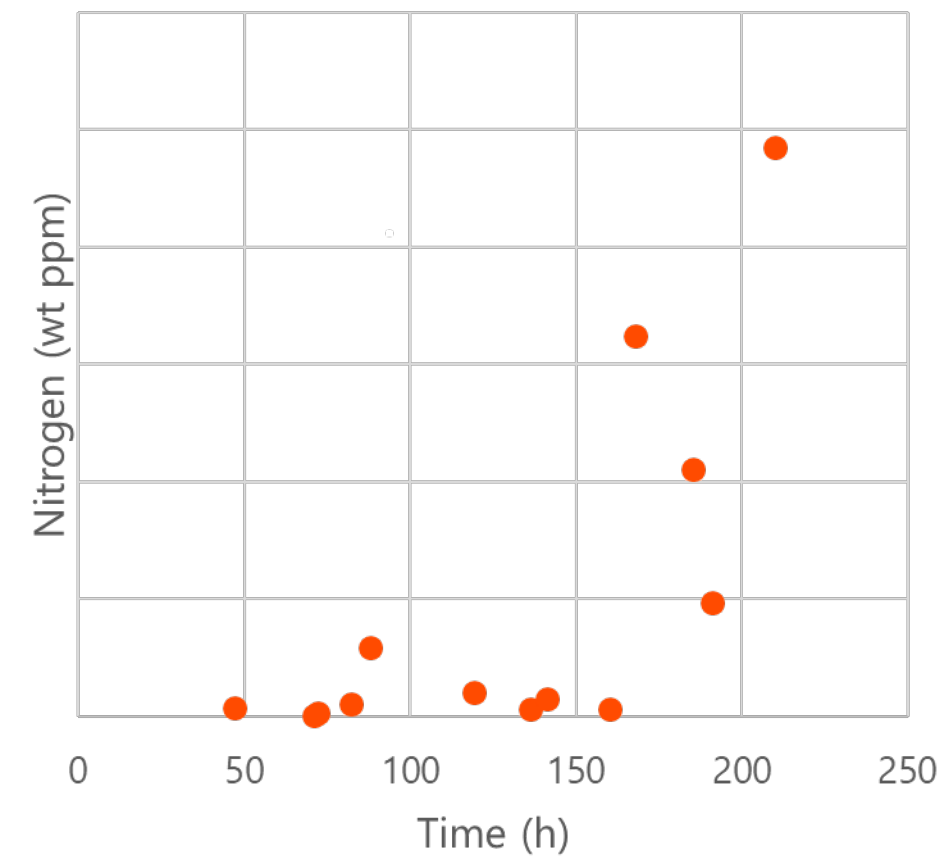
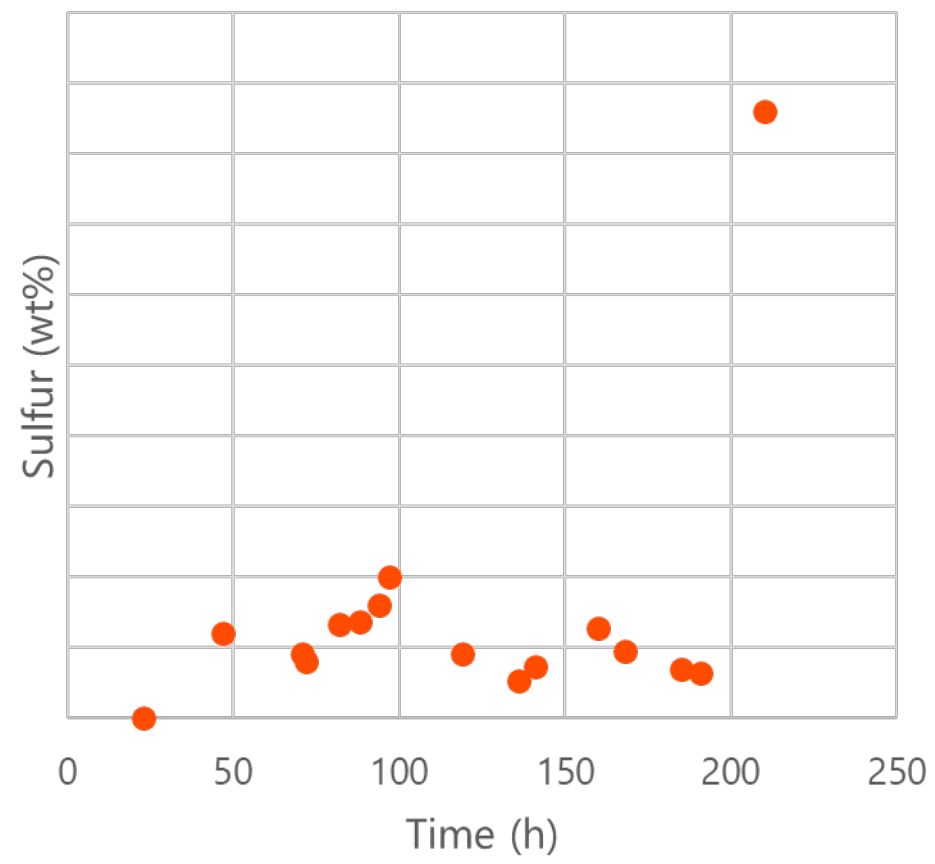
# PYROLYSIS OIL TOPSOE PILOT PLANT



# PYROLYSIS OIL HYDROTREATING RESULTS



**PYROLYSIS OIL**  
**HYDROTREATING RESULTS**



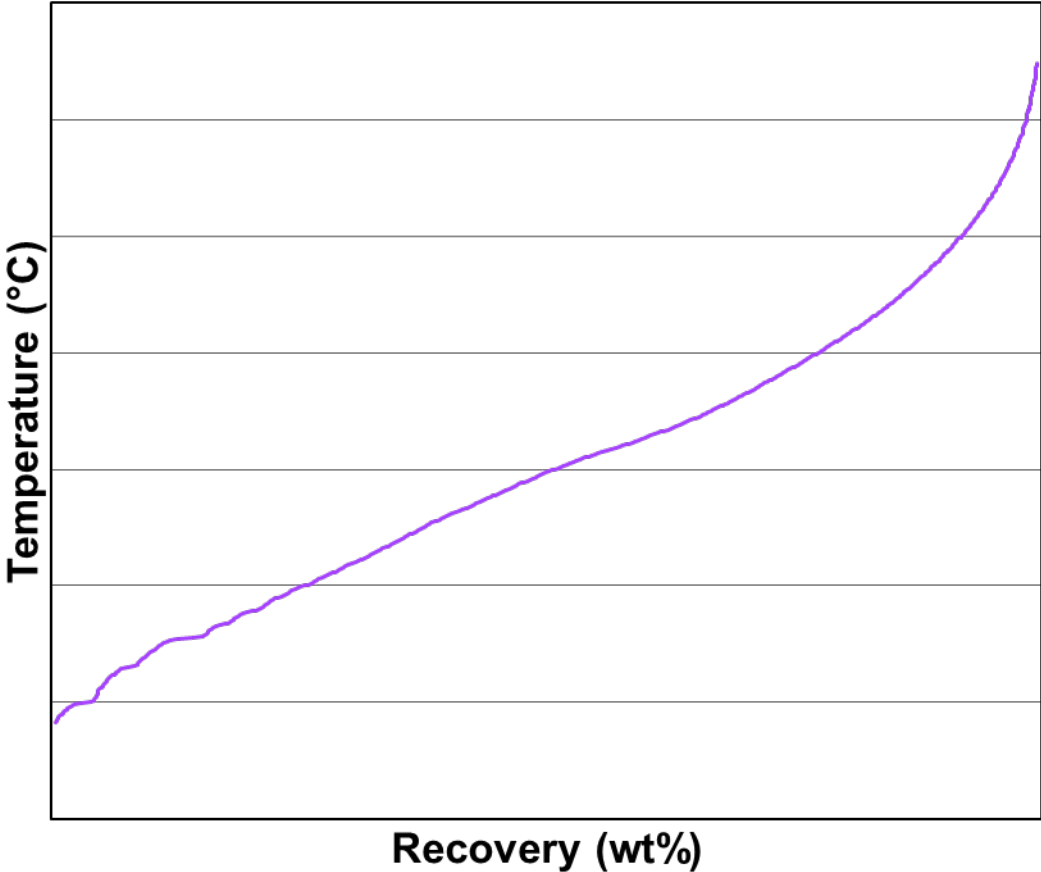
# PYROLYSIS OIL

## PRODUCT COMPOSITION

Product properties

Analysis	Value	Unit
Hydrogen	13.04	wt%
Sulfur	13	wt ppm
Nitrogen	1.2	wt ppm
Oxygen	6	wt%
Monoaromatics	7.17	wt%
Diaromatics	0.23	wt%
Tri+aromatics	0.09	wt%

Boiling point curve



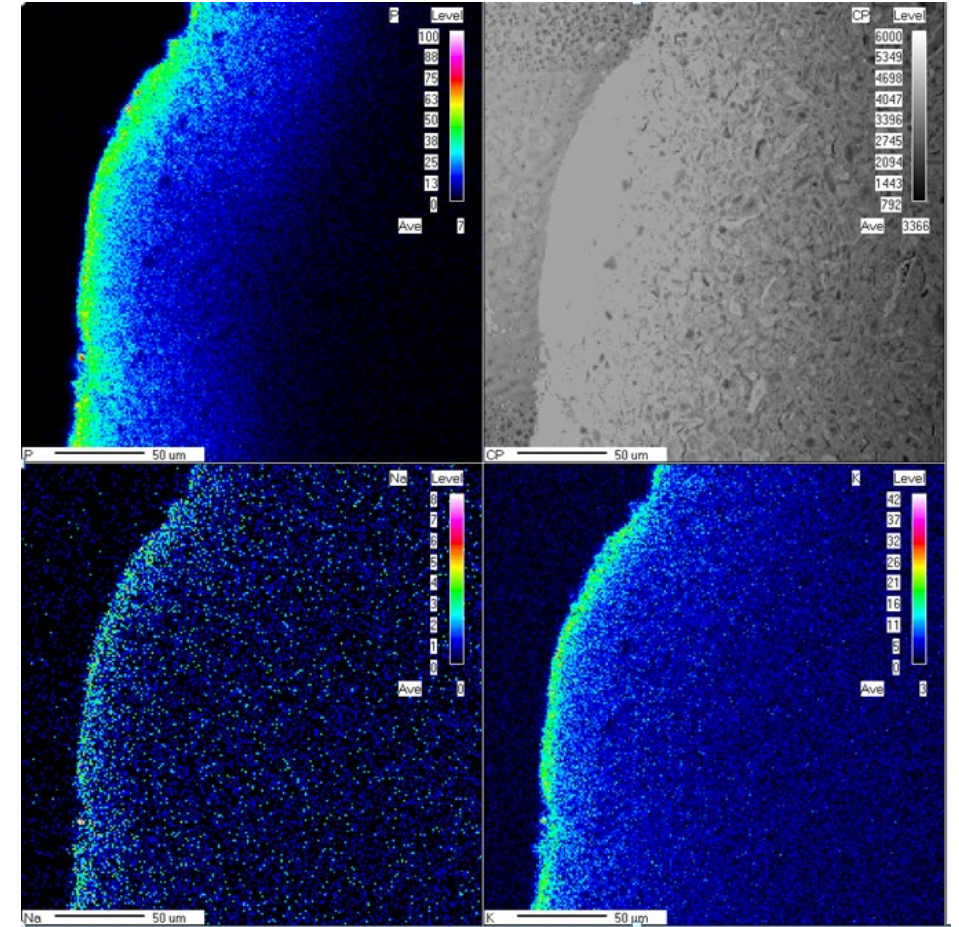
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# REFINERY INTEGRATION

## CHALLENGES WHEN INTRODUCING A BIO-CRUDE INTO A REFINERY

- High oxygen content – low hydrogen content
  - Not miscible with fossil feedstock
  - Thermally unstable
  - Extremely high hydrogen consumption
- High concentration of impurities/catalyst poisons
  - Short catalyst life time – > inhibiting amounts of guard bed catalyst
  - dP problems
- High acidity
  - Material selection





# REFINERY INTEGRATION POSSIBILITY

## PRE-TREAT BIO-CRUDE IN A STAND ALONE HYDROTREATER<sup>1</sup>

- May run at very low LHSV and high pressure
- All catalyst poisons removed
- Stabilizes bio-crude

## CO-PROCESS LIGHT GAS OIL WITH PARTLY DEOXYGENATED PYROLYSIS OIL<sup>2</sup>



<sup>1</sup>Mante, O.D. et al. Integration of catalytic fast pyrolysis and hydroprocessing: A pathway to refinery intermediates and "drop-in" fuels from biomass, Green Chemistry, Volume 18, Issue 22, 2016, Pages 6123-6135

<sup>2</sup> Gabrielsen J., Upgrading of Catalytic Fast Pyrolysis Oils From Pine Tree, Lignofuels 2017, Helsinki Finland



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- Nadia L. Ammitzboll
- Jeppe Kristensen



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# QUESTIONS?

## Contact

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# TOPSOE