

Reaction Kinetics and Transformation of Macromolecules during Wet Air Oxidation of Aqueous Products from Swage Sludge Hydrothermal Liquefaction

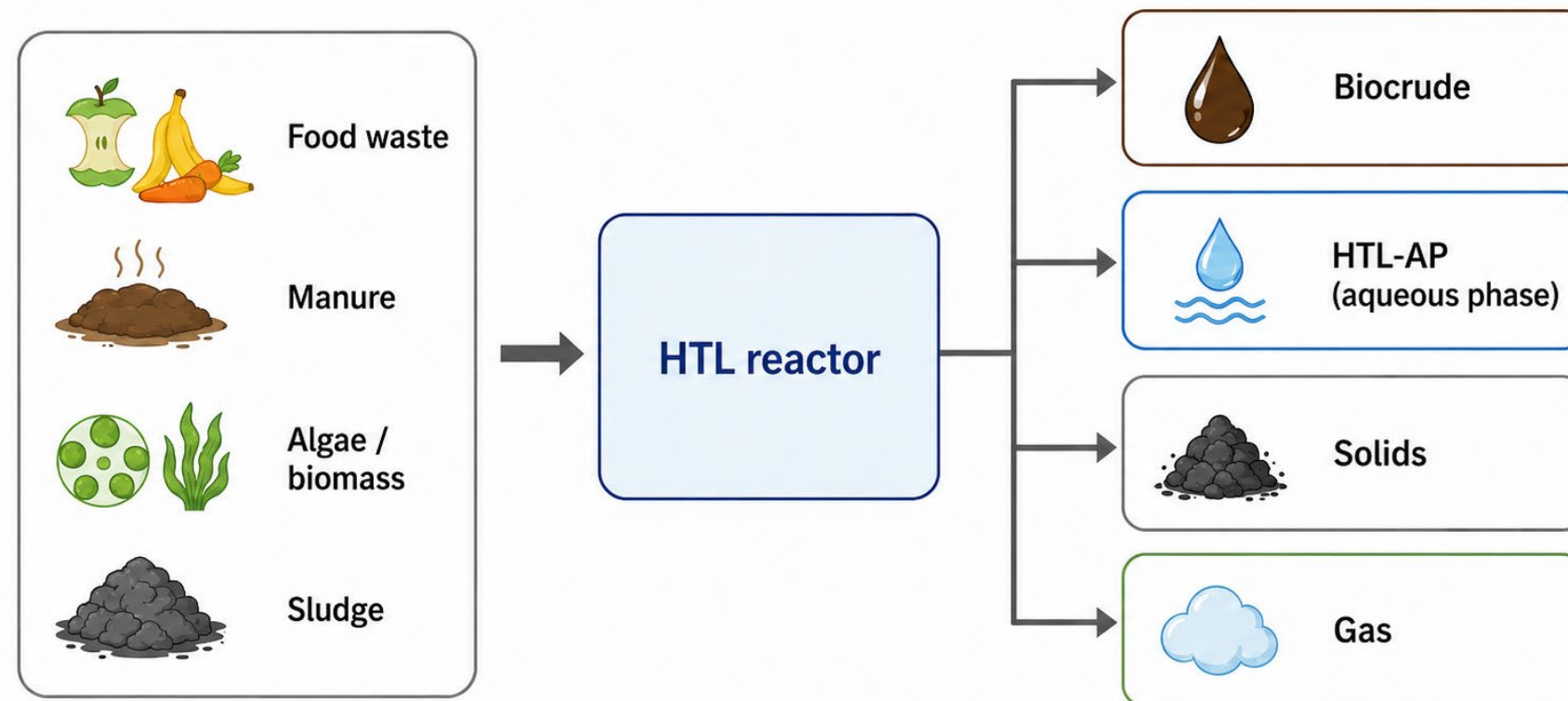
Min Soo Kim

PNNL

08.25.2026

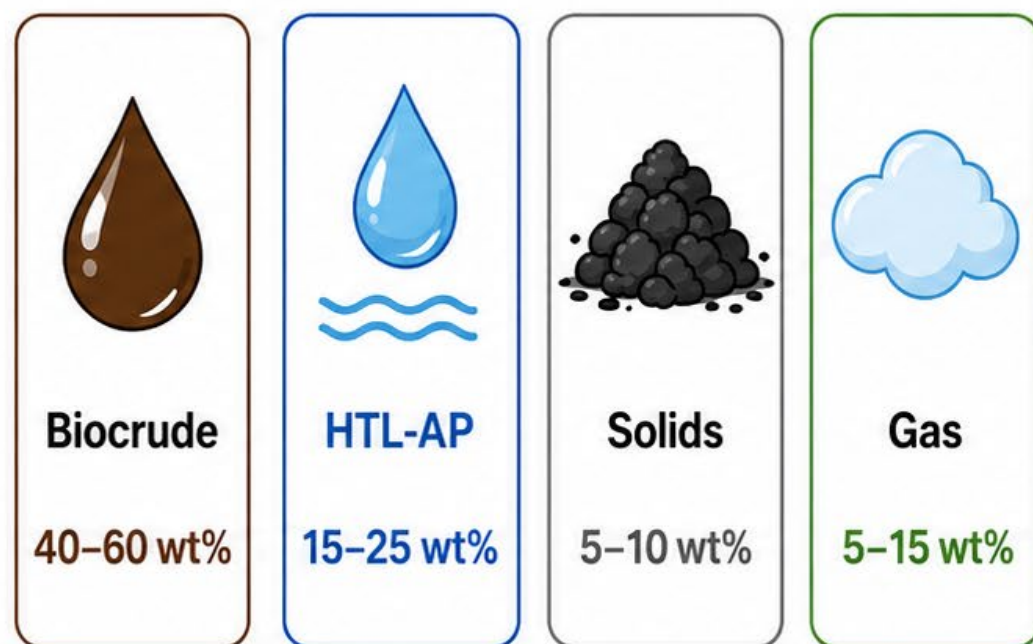
Converting wet feedstocks into renewable fuels

HTL (hydrothermal liquefaction) converts wet feedstocks into a fuel intermediate, **biocrude**, without energy-intensive drying

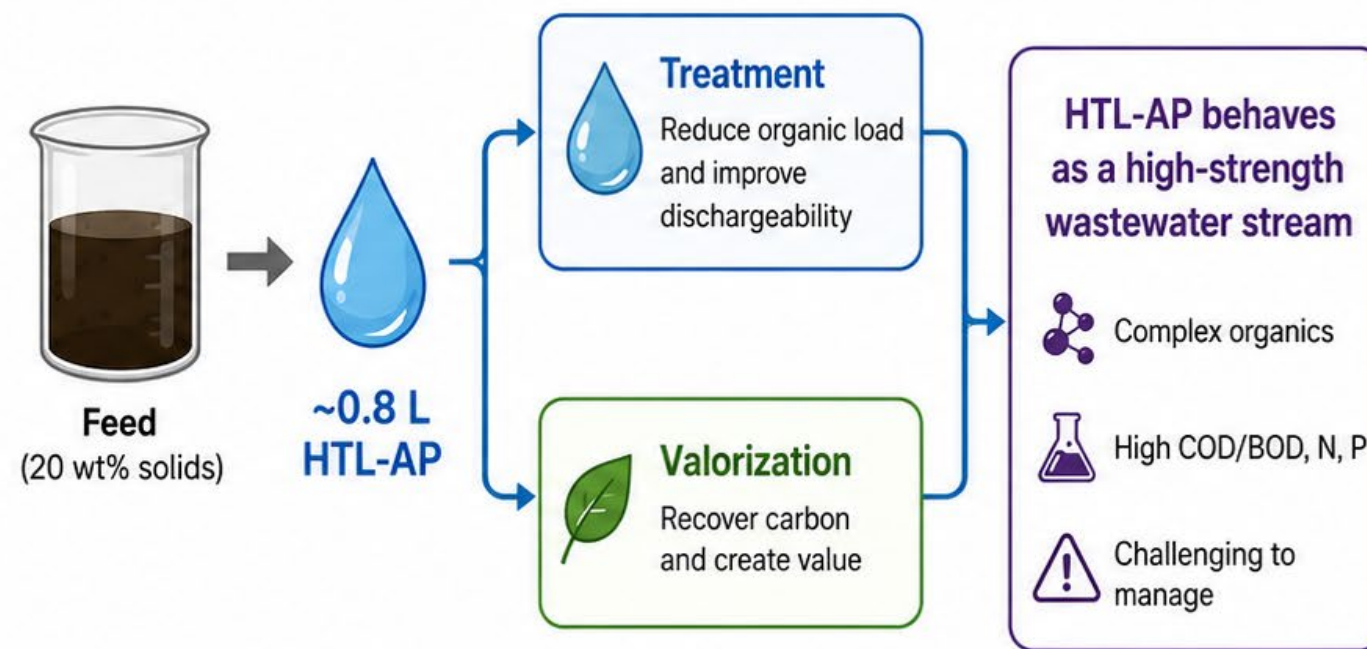


Why HTL-AP management matters

HTL product carbon yield (wt%)

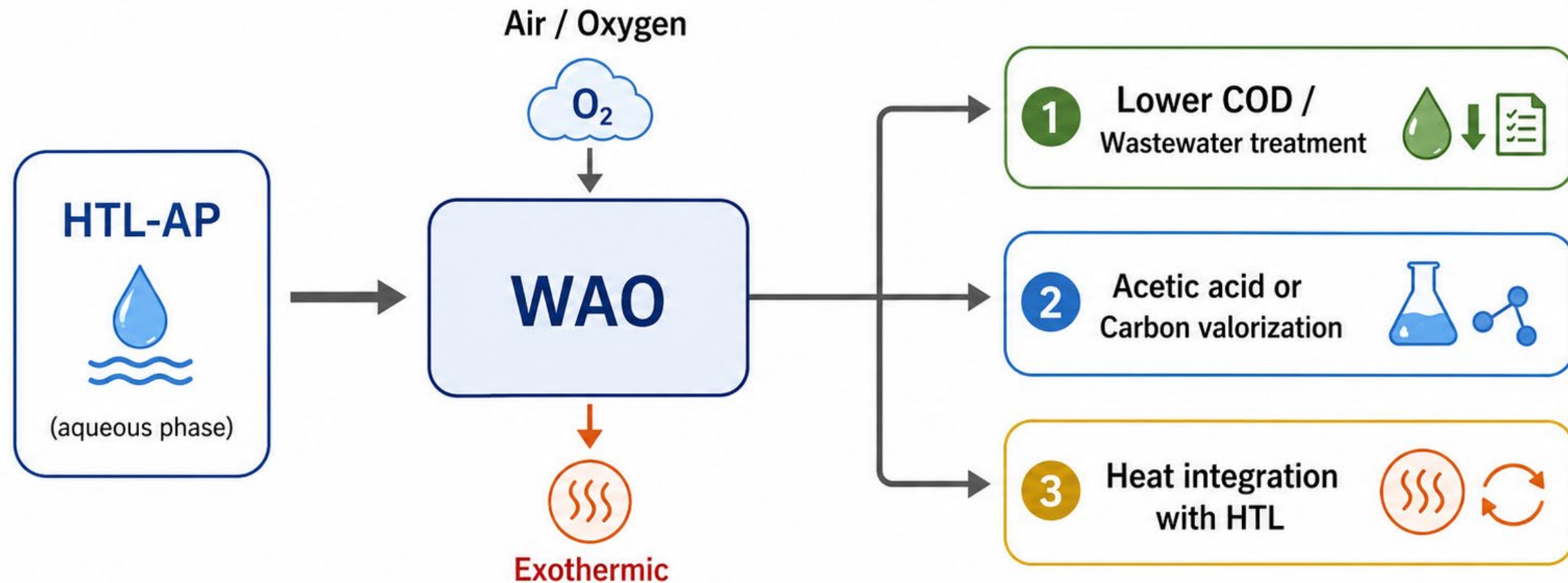


HTL-AP as a key process bottleneck



Large volume, complex composition, and toxicity make **HTL-AP treatment and valorization essential**

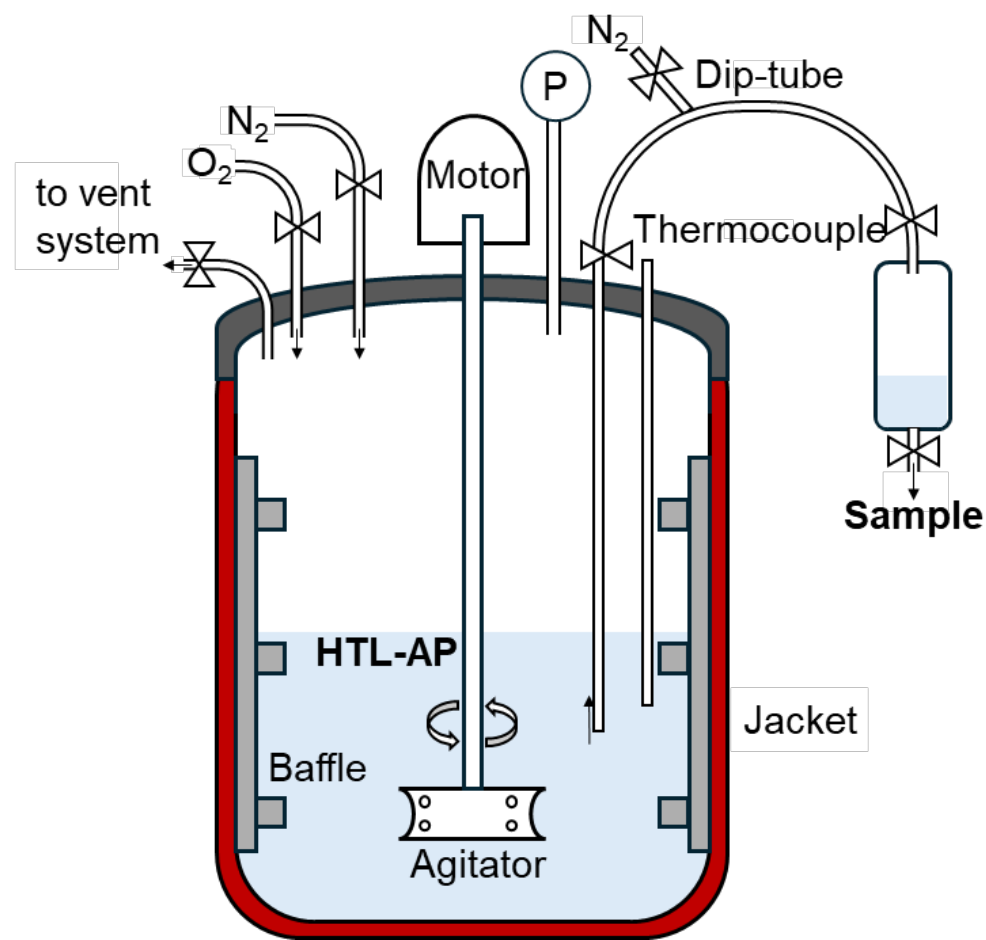
Why wet air oxidation (WAO) is attractive for HTL-AP



Challenge: Complex mixture containing thousands of compounds

Goal: Develop a kinetic model to describe transformation pathways and predict WAO performance

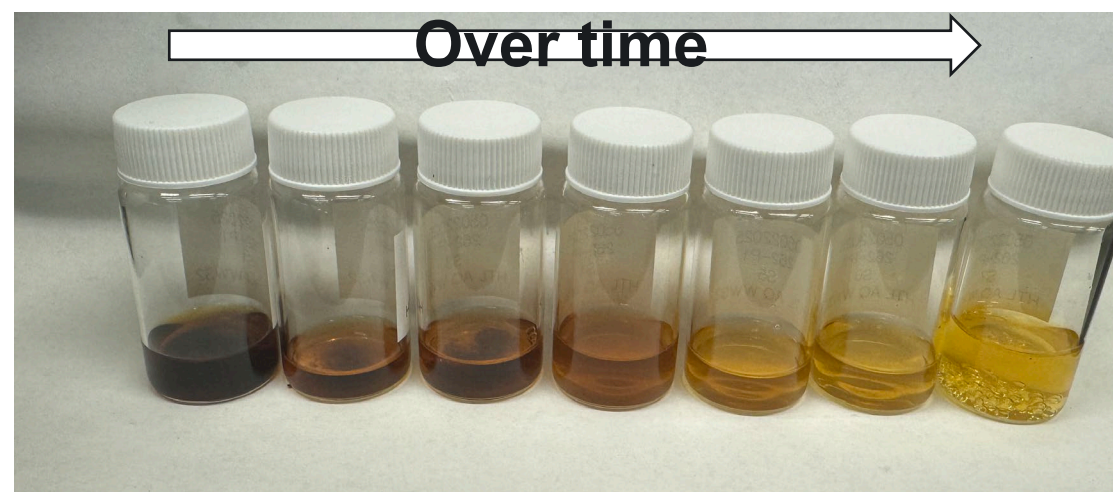
large excess O_2 and the stirring speed (1500 rpm) permit overcoming the mass transfer limitations



300 mL Parr reactor

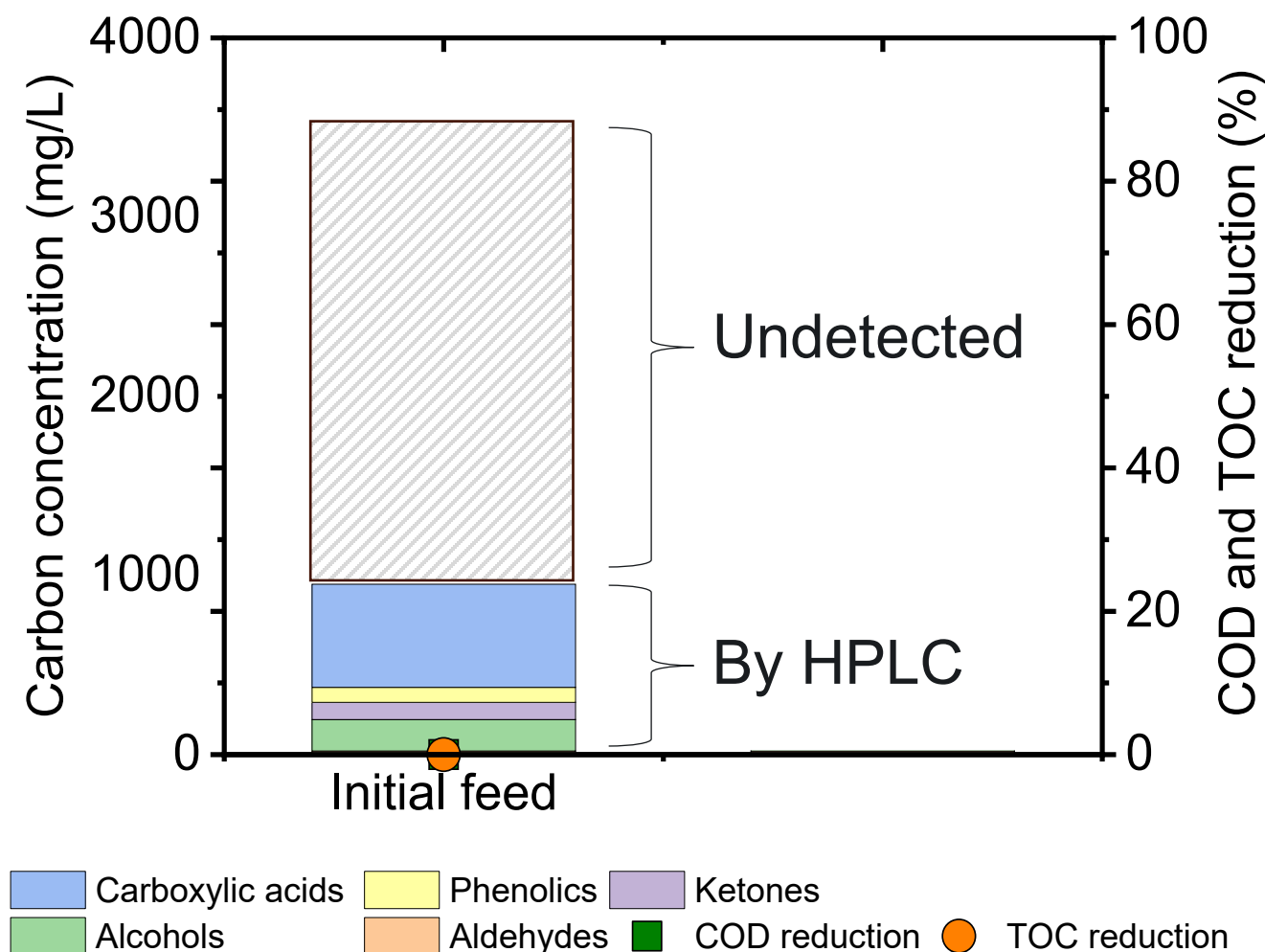
90 ml with HTL-AP with a COD of 10,000 mg/L
requires **0.028 mol of O_2**

O_2 in the headspace under 2100 psi (~900 O_2 partial pressure) is ~ **0.23 mol**, **8 times** the stoichiometric O_2 required for complete oxidation



- ✓ TOC
- ✓ COD
- ✓ HPLC
- ✓ FT-ICR-MS

~27% of HTL-AP carbon is detected by HPLC



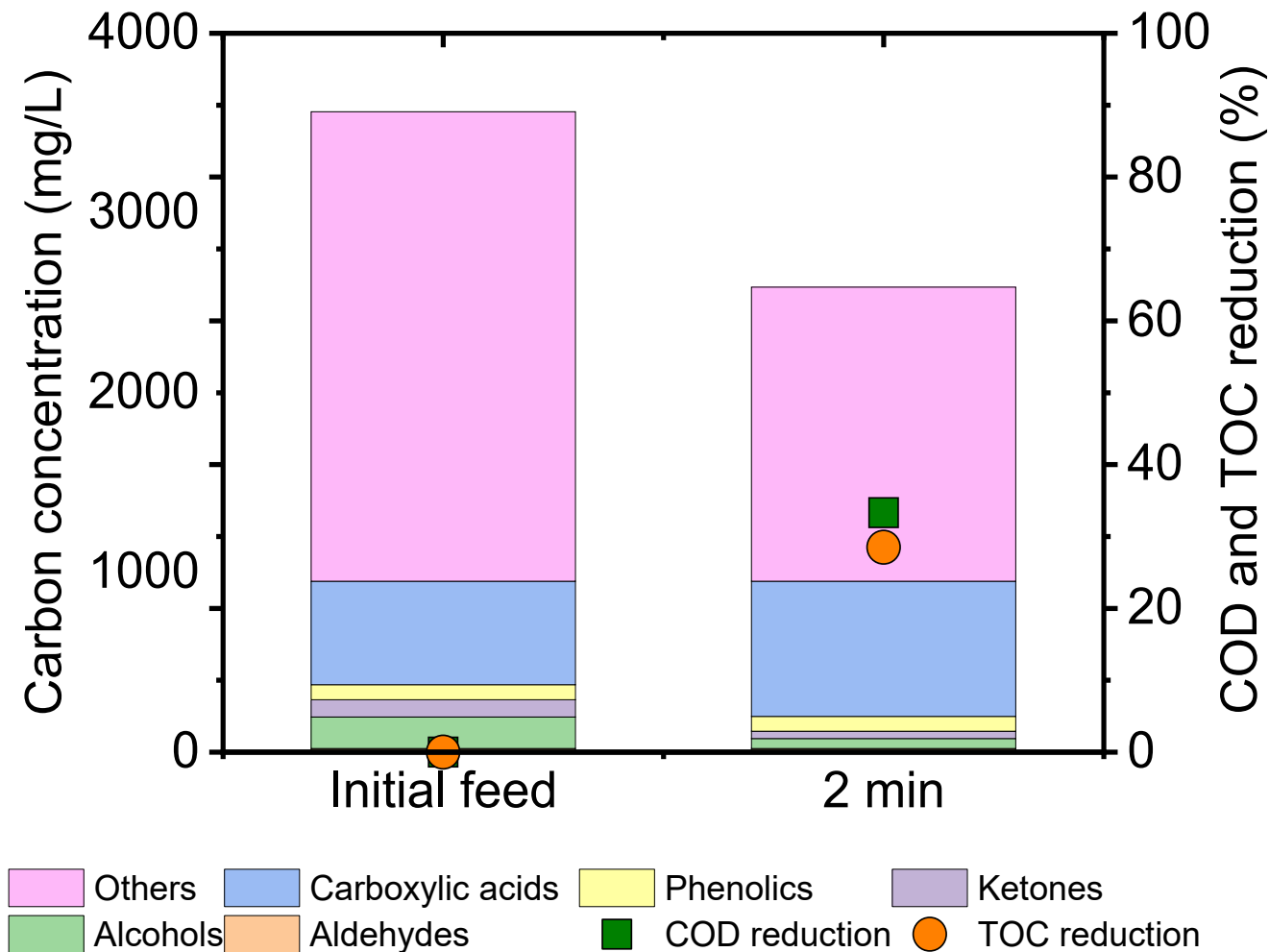
Initial carbon concentration (by TOC):
3,500 mg/L

Detected carbon concentration: 950 mg/L
undetected carbon concentration: 2,550 mg/L

Others (Undetected)
= TOC – HPLC-detectible carbon

Temperature: 325 °C; Pressure: 2100 psi (480 O₂ partial pressure,
4.7 times the stoichiometric O₂ demand based on the initial COD);
1500 rpm. Initial carbon concentration: 3564 mg/L. Initial COD: 9153 mg/L.

HPLC-undetected carbon participates in mineralization to CO₂.



Carbon concentration (by HPLC) remains similar despite rapid COD and TOC reductions

COD ↓ 33%

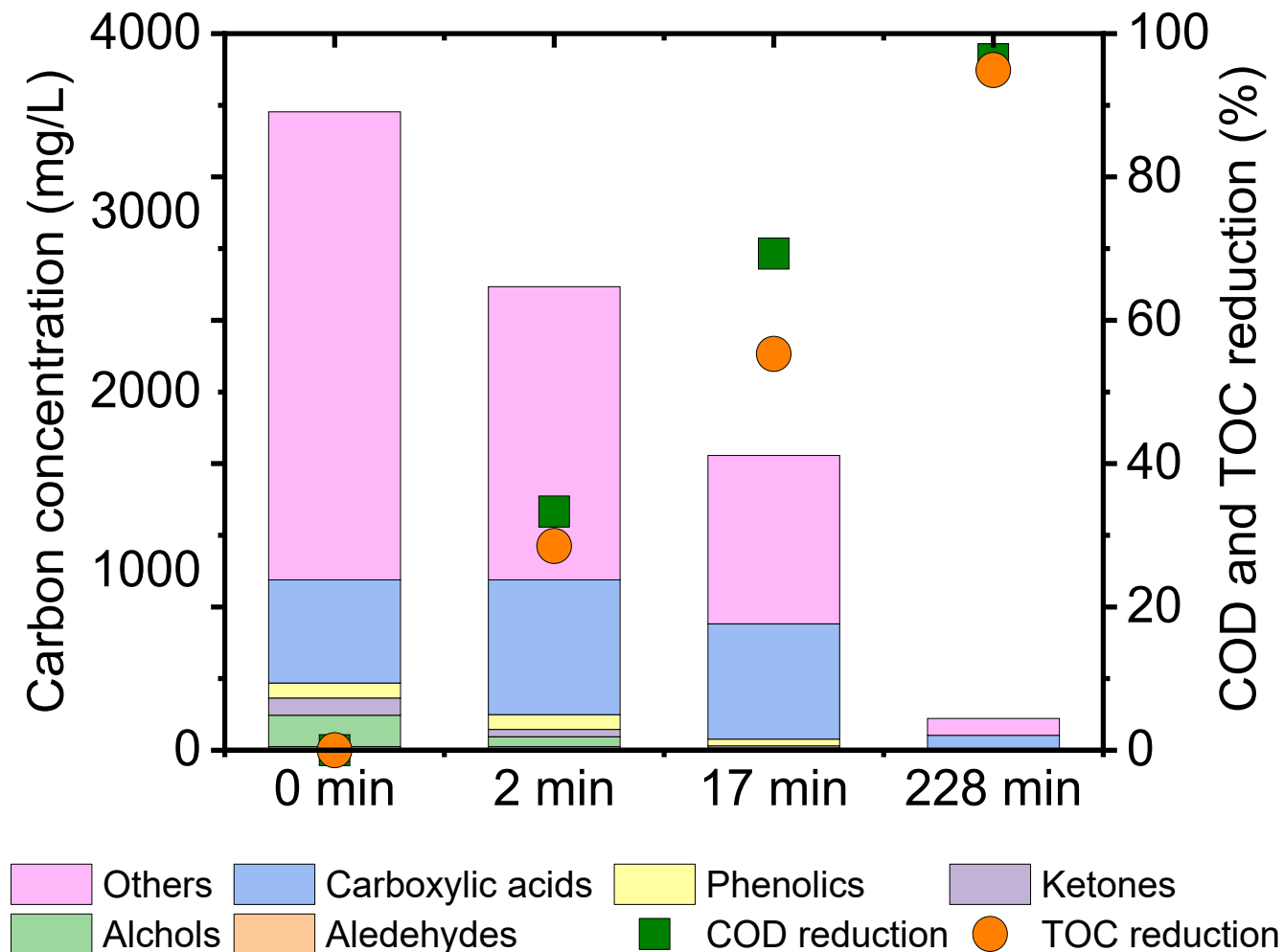
TOC ↓ 29%

in only 2 min

“Others” fraction undergoes a fast initial conversion to intermediates while participating in the mineralization to CO₂.

Temperature: 325 °C; Pressure: 2100 psi (480 O₂ partial pressure, **4.7 times the stoichiometric O₂ demand based on the initial COD**); **1500 rpm**. Initial carbon concentration: 3564 mg/L. Initial COD: 9153 mg/L.

What is “Others”?



Understanding the properties of “Others” and their oxidation behavior is essential for the WAO process.

- ✓ High MW compounds?
- ✓ Easily oxidized compounds?

Temperature: 325 °C; Pressure: 2100 psi (480 O₂ partial pressure, **4.7 times the stoichiometric O₂ demand based on the initial COD**); **1500 rpm**. Initial carbon concentration: 3564 mg/L. Initial COD: 9153 mg/L.

FT-ICR-MS reveals molecular-level complexity

Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (**FT-ICR-MS**)

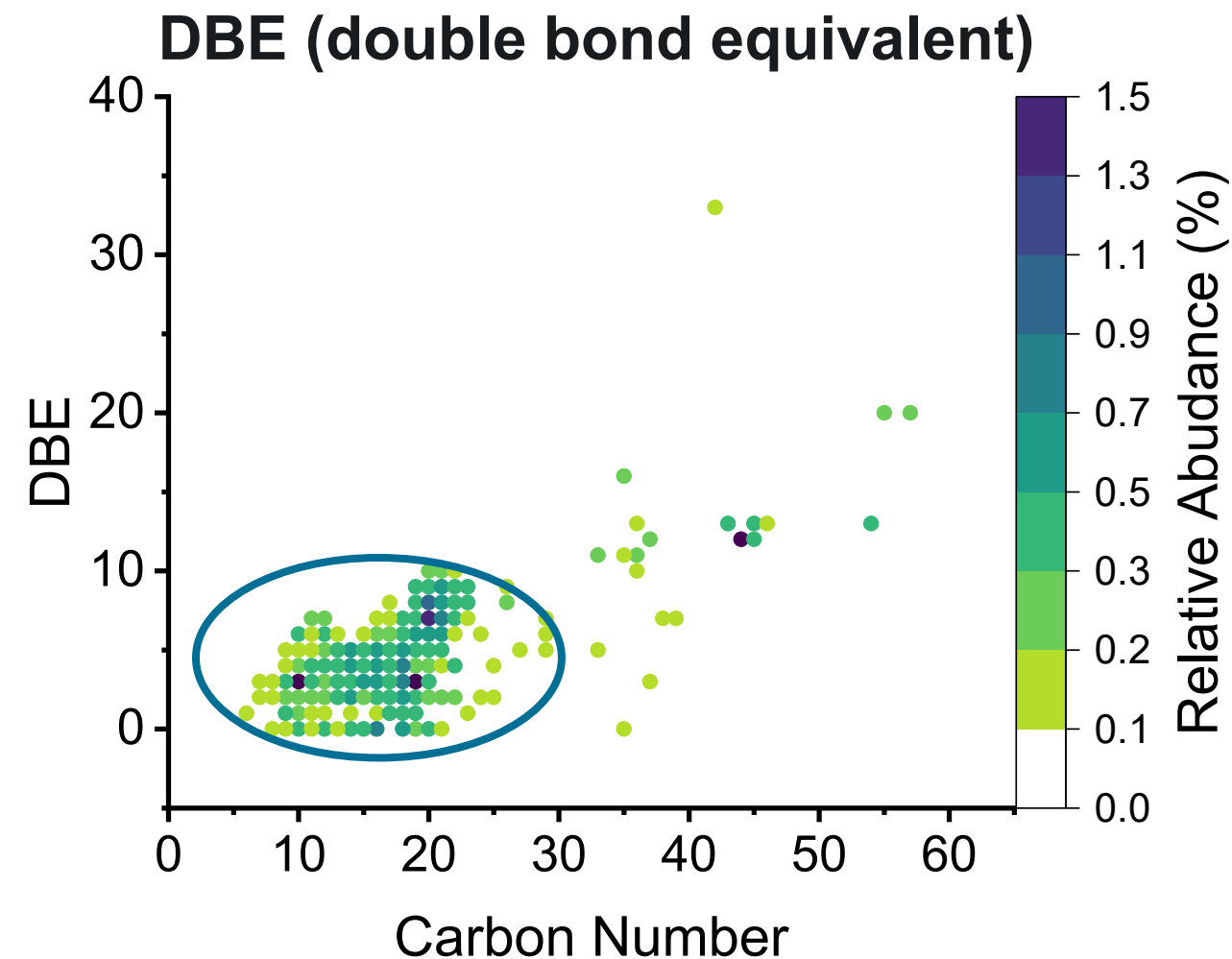
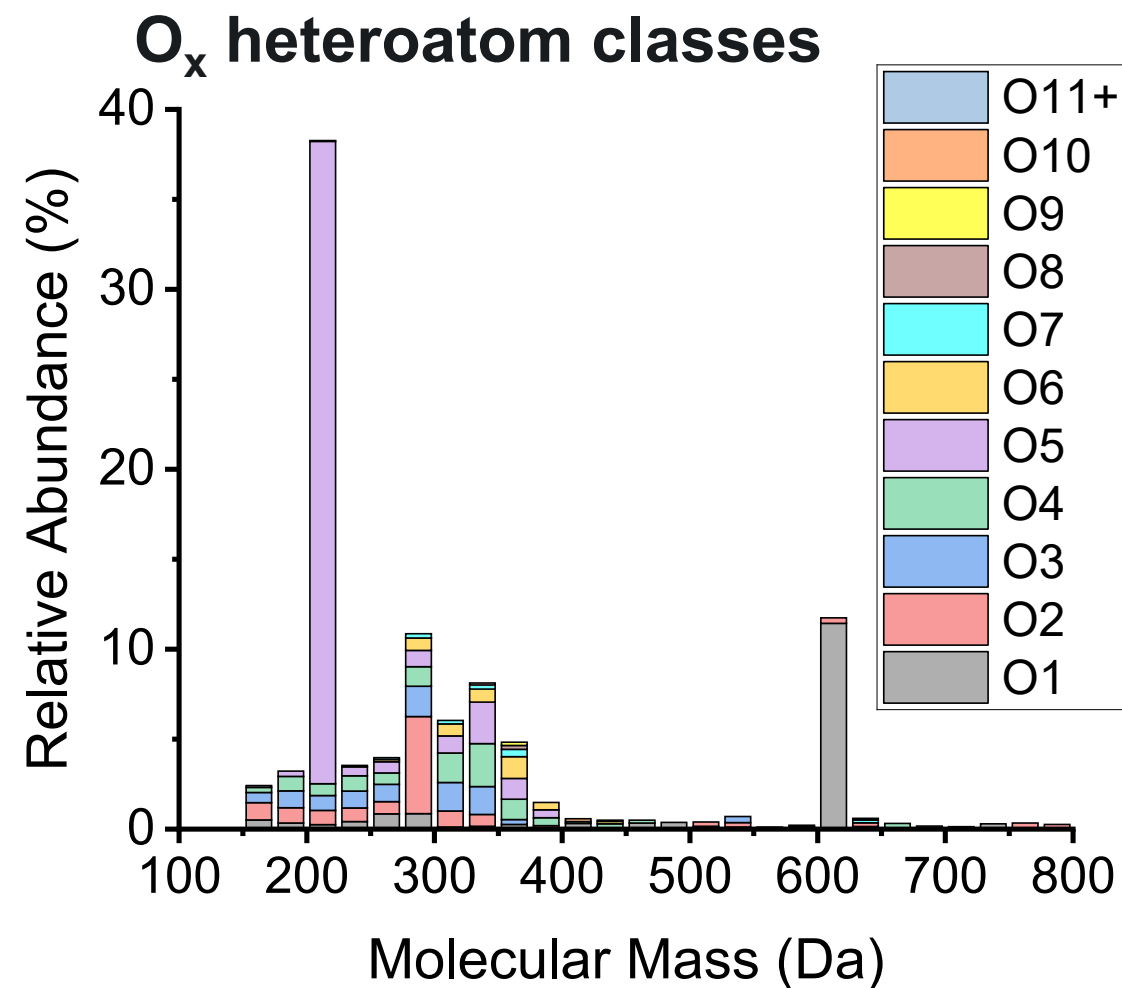


Bruker 7 Tesla FT-ICR-MS at PNNL



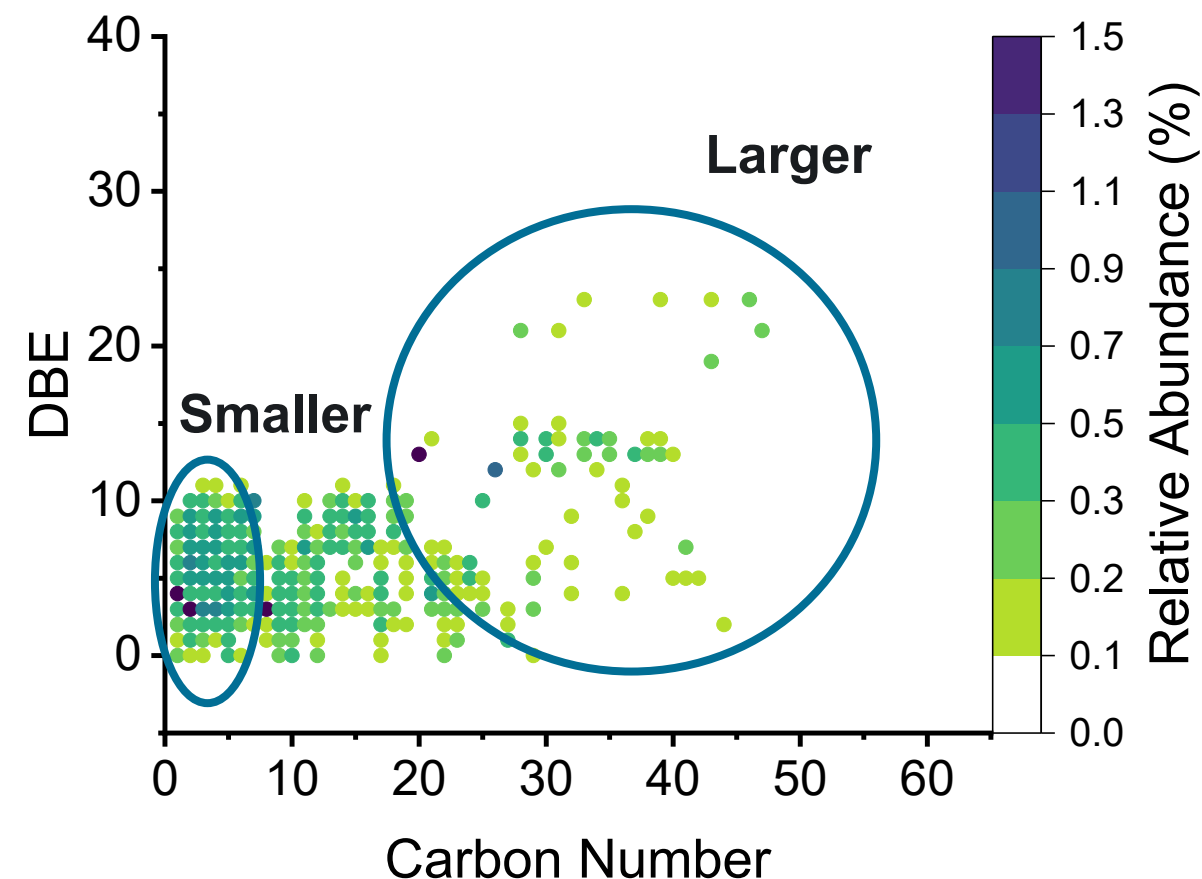
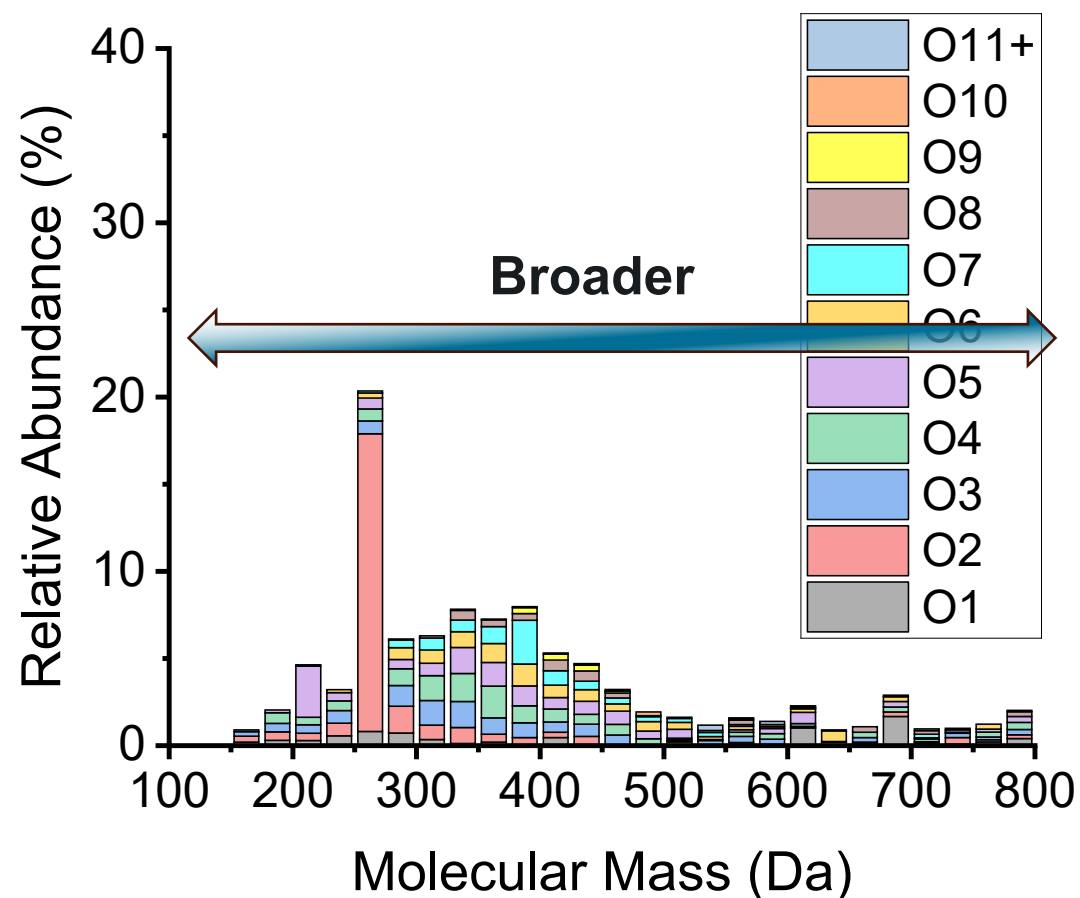
- ✓ Molecular formulas
- ✓ Elemental compositions (C,H,O,N)
- ✓ Heteroatom classes
- ✓ Carbon number and DBE

HTL-AP is dominated by O/N-containing macromolecules



C10-C20 range and a range of DBE value up to ~10, **representing partially aromatic and structurally complex molecules**

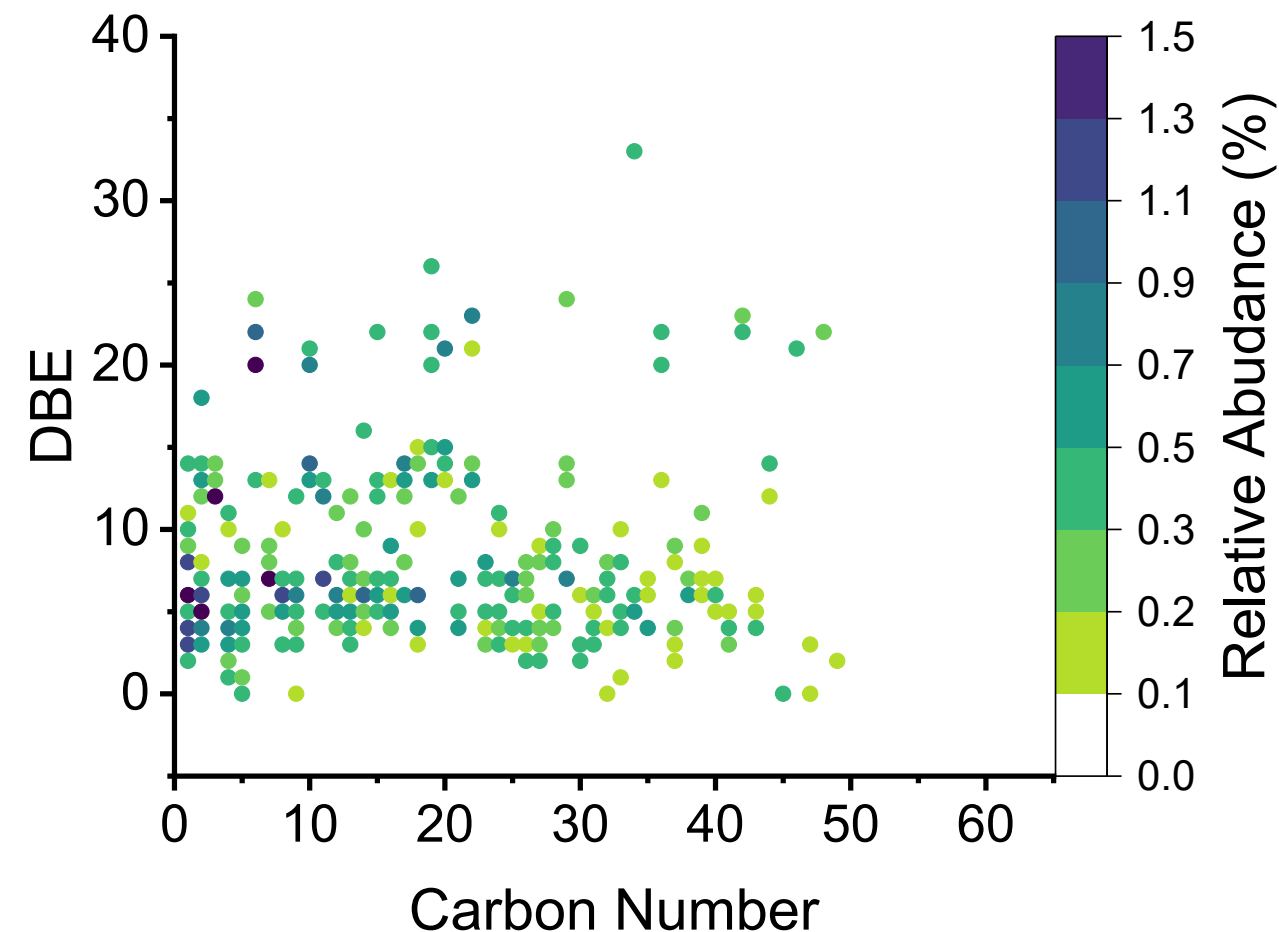
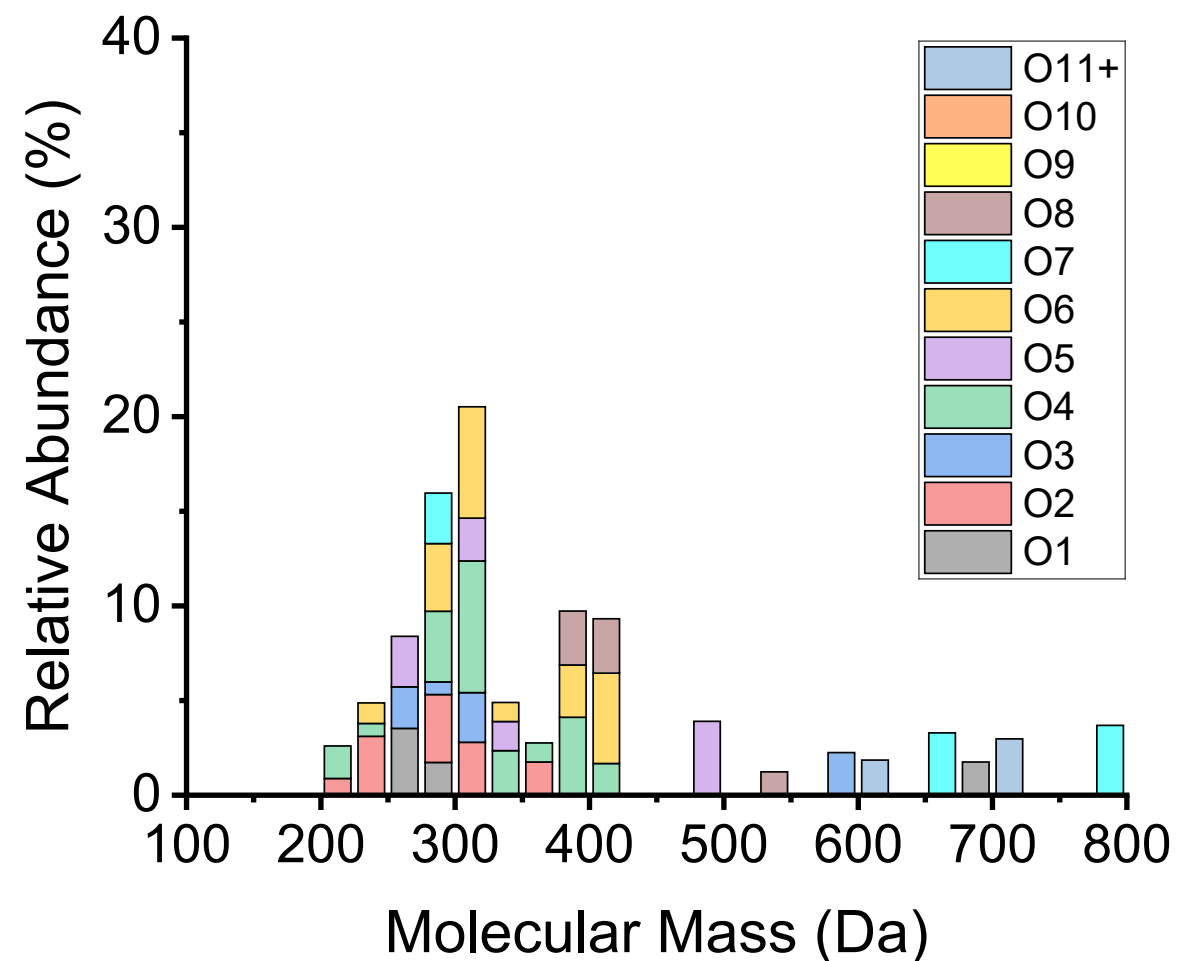
After 2 min, the molecular composition undergoes a profound transformation



New and highly oxygenated species

Fragmentation
Partial oxidation and rearrangement

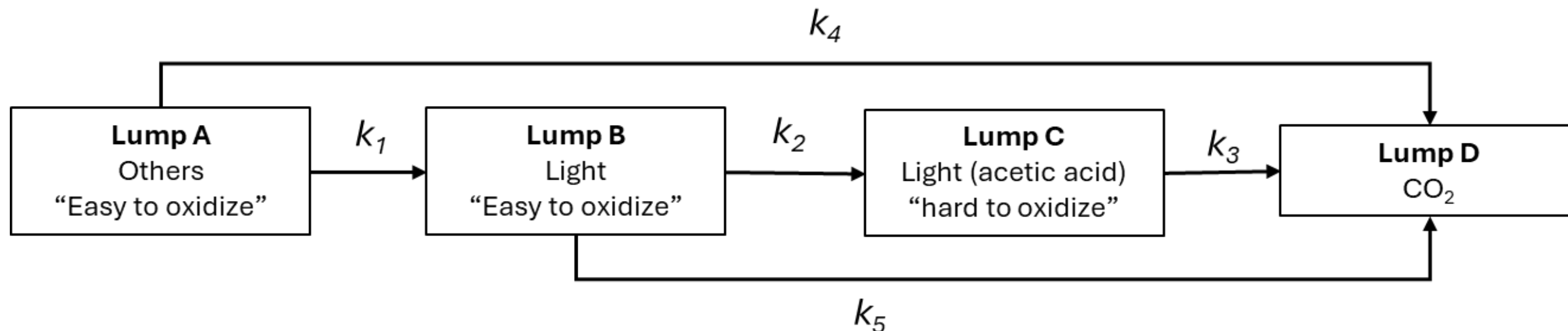
At 228 min, WAO product shows a simplified molecular composition



High-MW/high-DBE species were almost completely consumed

96% COD and 95% TOC reduction were achieved

To address the complexity of HTL-AP, chemically similar compounds are grouped into lumps



$$\frac{d[A]}{dt} = -k_1[A] - k_4[A]$$

Lump A: Carbon estimated by difference between TOC and HPLC

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_5[B]$$

Lump B: HPLC-detectable light oxygenates excluding acetic acid

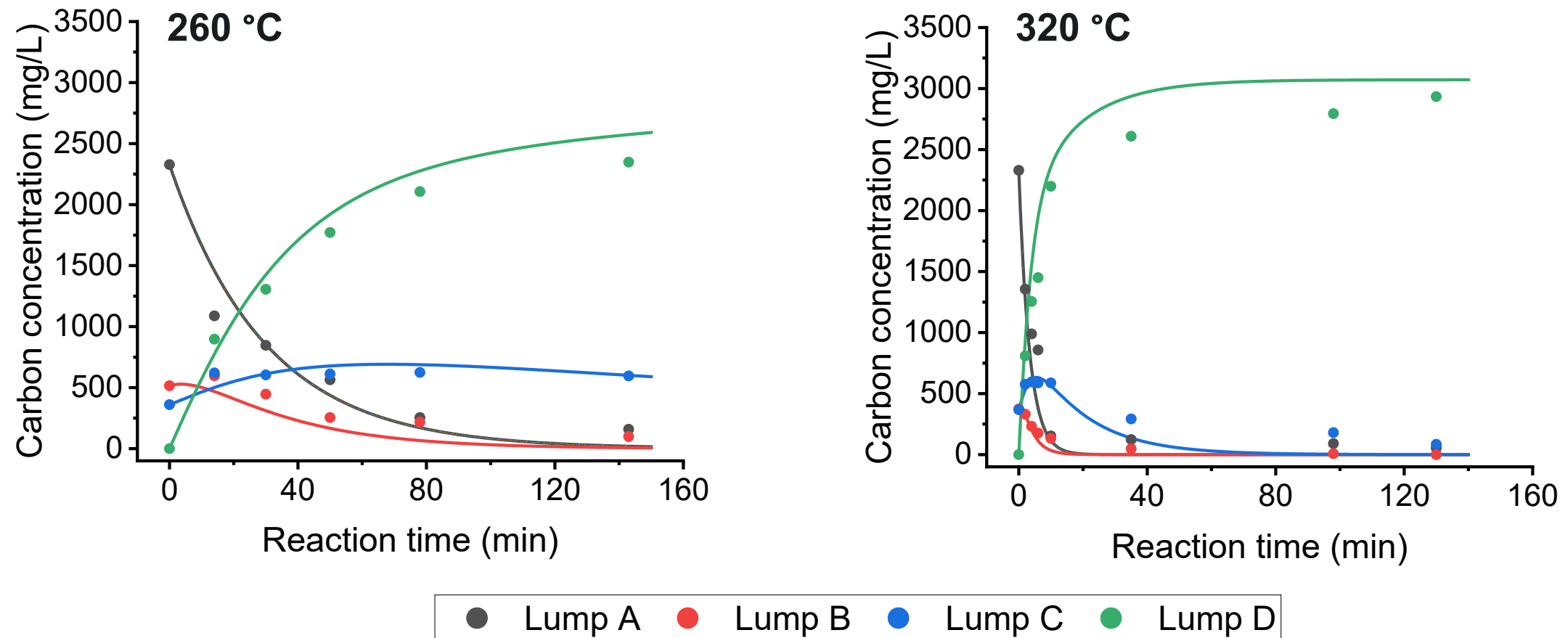
$$\frac{d[C]}{dt} = k_2[B] - k_3[C]$$

Lump C: Acetic acid

$$\frac{d[D]}{dt} = k_3[C] + k_4[A] + k_5[B]$$

Lump D: Carbon estimated by difference between the initial carbon and other measured lumps

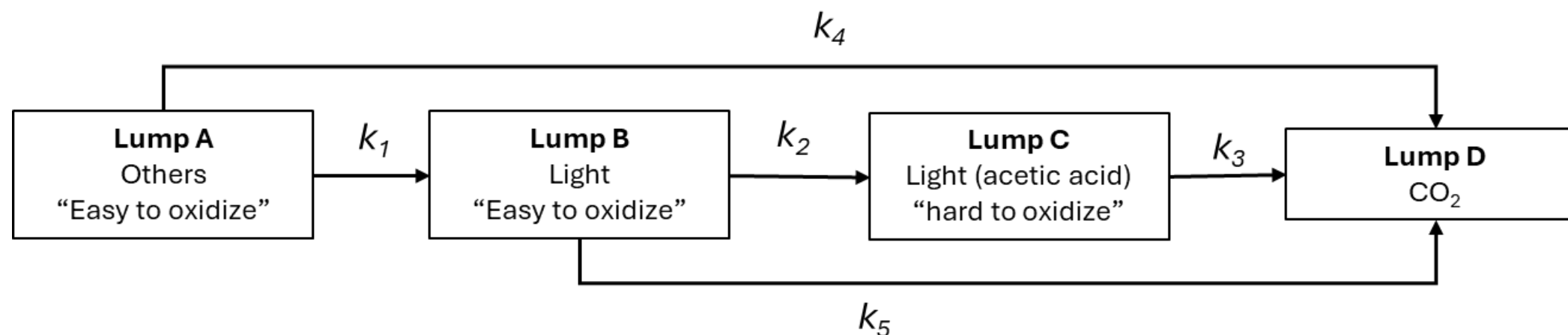
WAO of HTL-AP is conducted at six different temperatures



Lump B exhibited a classic intermediate profile

Lump C (acetic acid) accumulated as a major intermediate

The temperature dependence of the reaction rates is modeled using the Arrhenius equation

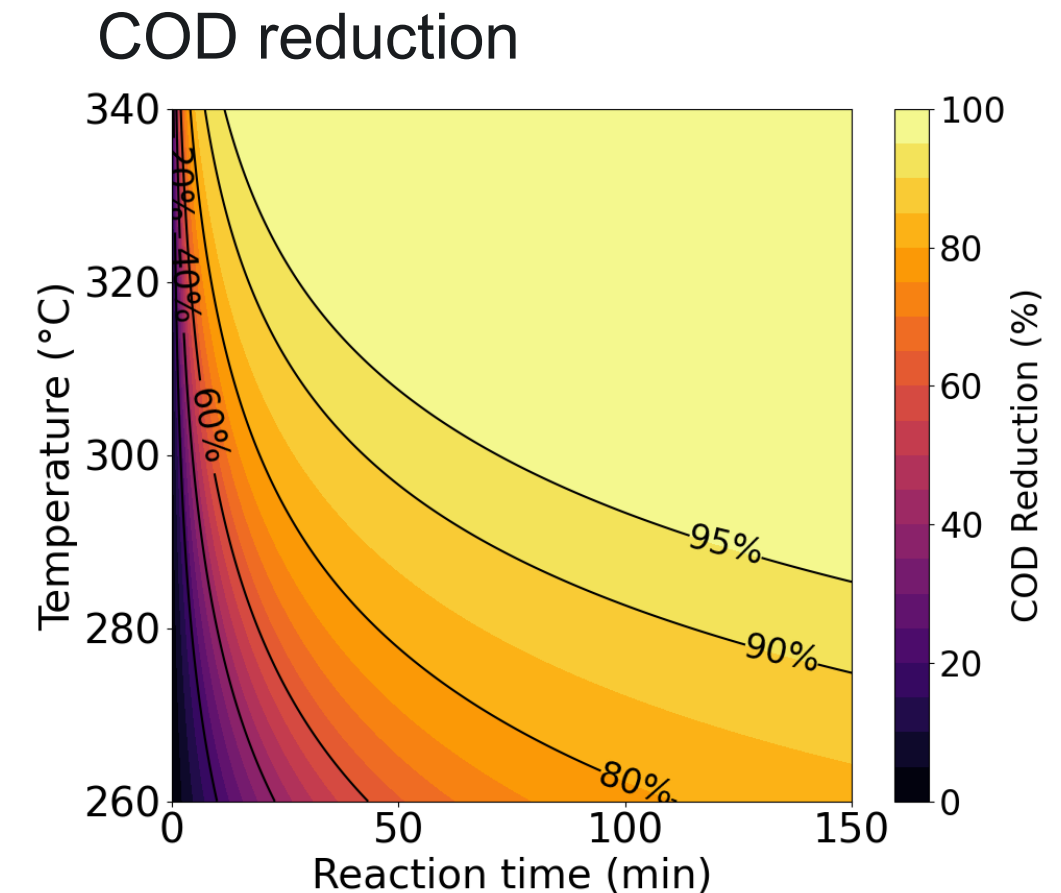
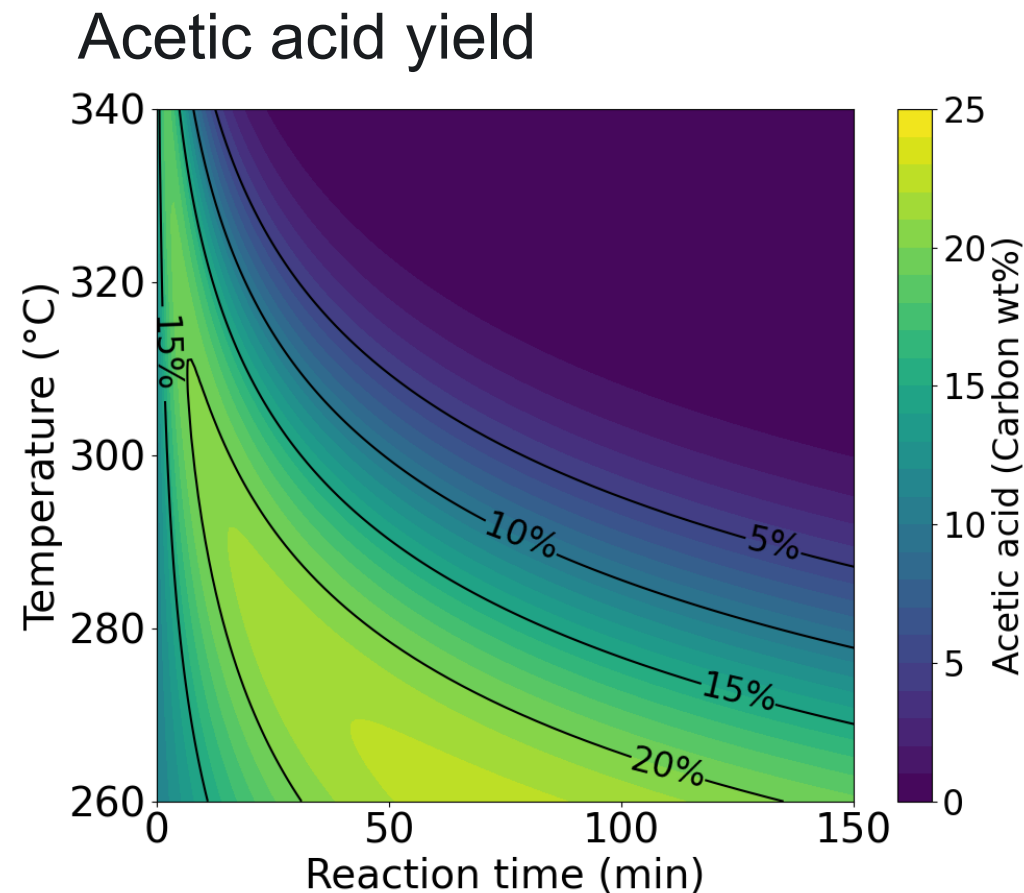


Reaction	E_a (kJ/mol)	$\ln(A/(\text{min}^{-1}))$
A→B (k_1)	90.4±8.8	16.8±1.9
B→C (k_2)	105.7±9.6	20.2±2.1
C→D (k_3)	136.1±7.2	24.8±1.6
A→D (k_4)	119.7±7.7	22.2±1.7
B→D (k_5)	94.8±6.4	18.9±1.4

➡ Highly sensitive to temperature

➡ The largest energy barrier and persistence at lower temperatures

Operating conditions can be tuned to favor either acetic acid formation or complete mineralization



This simulation offers the guidance for WAO process optimization

Conclusions

- ✓ The FT-ICR-MS characterization elucidated the molecular-level support
- ✓ The HTL-AP underwent rapid depolymerization, fragmentation, and partial oxidation
- ✓ The kinetic model captured the main reaction behavior
- ✓ This work provided an informed basis for understanding and optimizing WAO of HTL-AP

Acknowledgement

This work was financially supported by the U.S. Department of Energy (DOE), Office of Critical Minerals and Energy Innovation (CMEI), Alternative Fuels and Feedstocks Office (AFFO).

Thank you

