



Natural Resources  
Canada

Ressources naturelles  
Canada

# A Structural-Level Framework for Modeling Biocrude Upgrading: From Feed Composition to Reaction Pathways

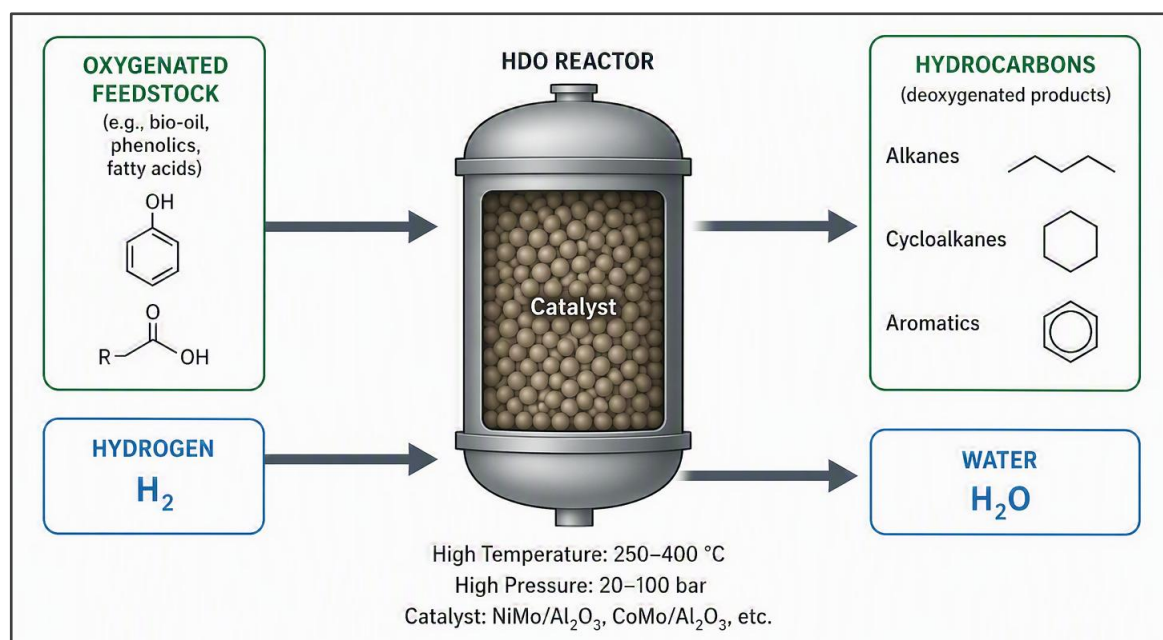
Anton Alvarez-Majmutov, Rafal Gieleciak, and Jinwen Chen  
CanmetENERGY Devon, Natural Resources Canada

tcbiomass+2026, Denver, CO, USA, August 25–27, 2026

Canada

# Biocrude Upgrading

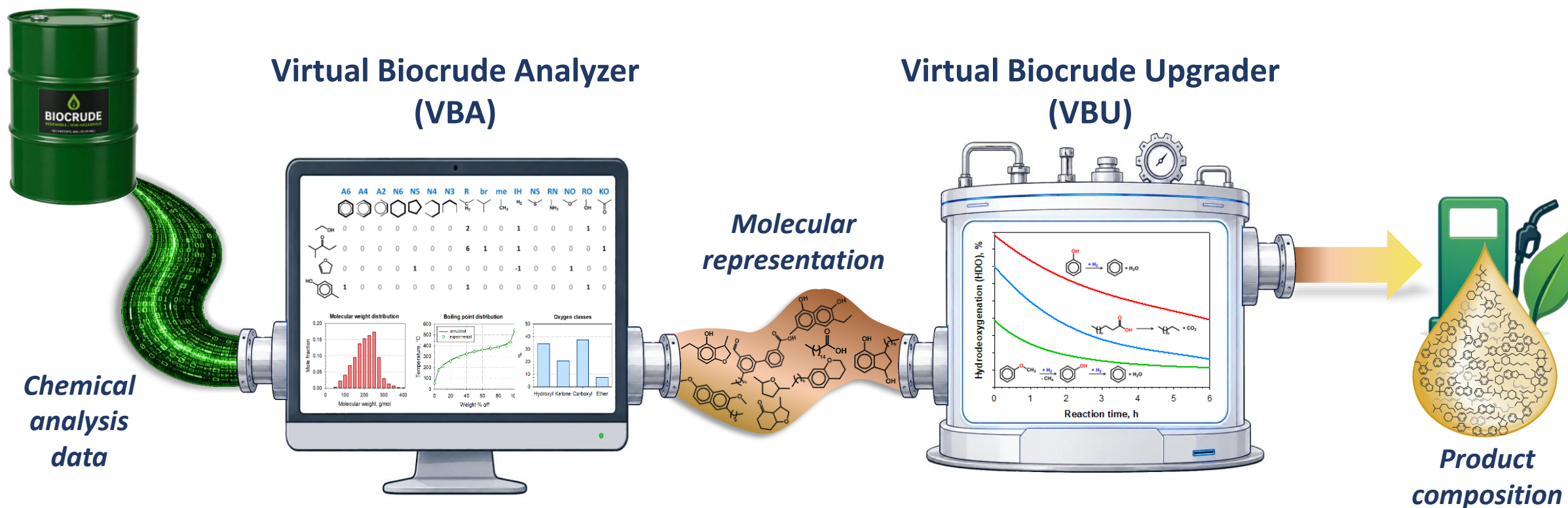
## Hydrodeoxygenation (HDO) – a key pathway for biocrude upgrading



- HDO for pyrolysis and hydrothermal liquefaction biocrudes remains under active development
- Challenges:
  - **Processability:** thermal instability, catalyst deactivation, equipment plugging
  - **Chemical complexity:** difficulty to analyze, presence of “mystery” compounds, high composition variability

# Addressing the Molecular Complexity of Biocrude Oils

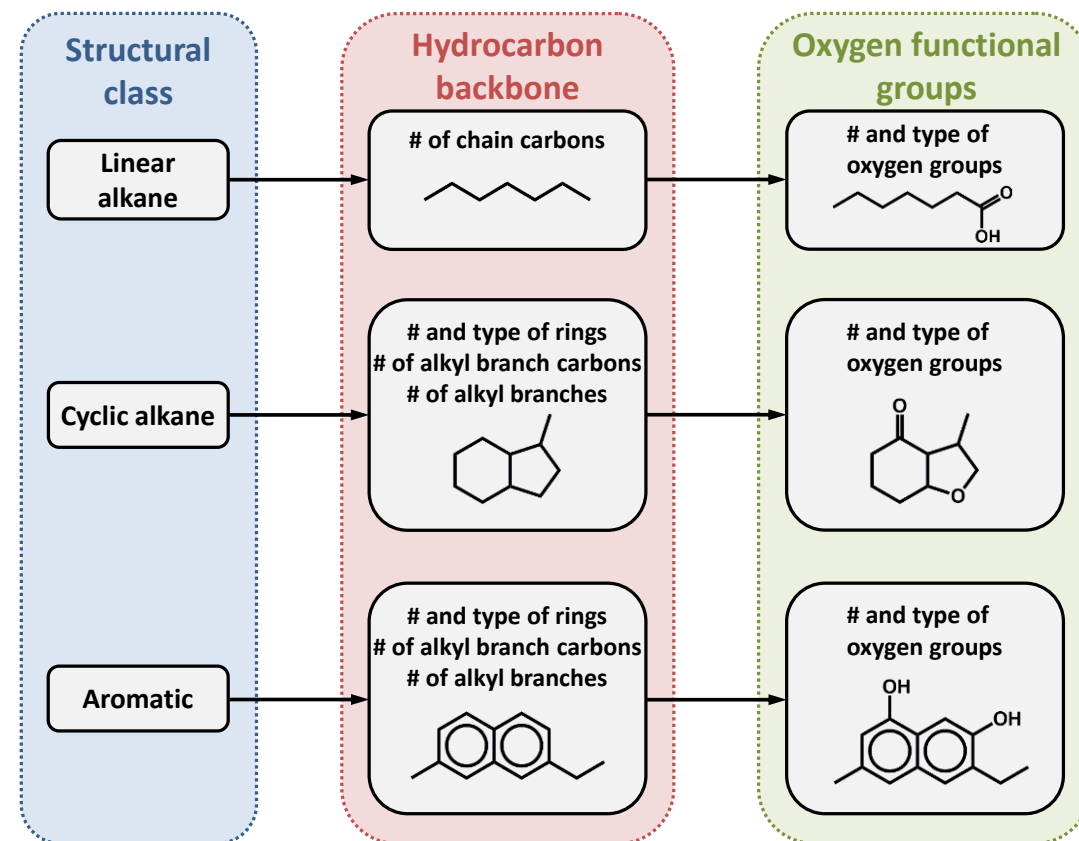
## Proposed modeling framework for biocrude HDO



# Biocrude Composition Modeling

VBA module derives a molecular representation from analytical chemistry data

- Based on the concept of “*molecular reconstruction*”
- Molecular spectrum decomposed into limited structural descriptors with statistically modeled occurrence
- Biocrude molecules sequentially built from a hydrocarbon backbone and oxygen functional groups
  - Large ensemble of *in silico* molecules ( $10^3$ – $10^4$ ) created via Monte Carlo simulation to match analytical properties
  - Molecular concentrations optimized via entropy maximization



# Biocrude Composition Modeling (continued...)

## Biocrude molecules coded as vectors using the SOL formalism

|  | A6 | A4 | A2 | N6 | N5 | N4 | N3 | N2 | N1 | R | br | me | IH | AA | NS | RS | AN | NN | RN | NO | RO | KO |
|--|----|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|
|  |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |
|  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 2 | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  |
|  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 6 | 1  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  |
|  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 6 | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  |
|  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0 | 0  | 0  | -1 | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  |
|  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 2 | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  |
|  | 1  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 0  |
|  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 3 | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 1  |
|  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1 | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  |

- SOL: structure-oriented lumping
- VBA output is a composition table:
  - SOL vectors
  - Molecule concentrations
  - Properties (molecular weight, density, boiling point, etc.)
- Composition table feeds into reaction module (VBU)



Natural Resources  
Canada

Ressources naturelles  
Canada

Canada

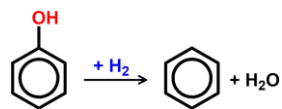
# Reaction Modeling of HDO

## VBU module simulates the transformation of *in silico* biocrude molecules

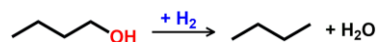
- HDO chemistry organized into reaction families

### Hydroxyl group removal

Phenolic OH hydrogenolysis

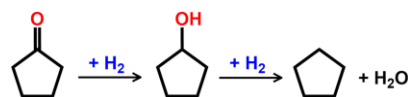


Aliphatic OH hydrogenolysis



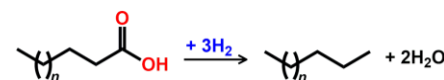
### Carbonyl group removal

Hydrogenation

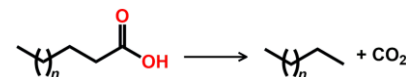


### Carboxyl group removal

Hydrodeoxygenation

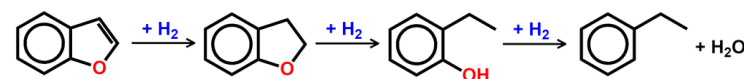


Decarboxylation



### Ether group removal

Ether ring opening



- Reactivity profile

- Family rate constant (*from experimental data*)
- Family reaction order (*from experimental data*)
- Component adsorption coefficients (*from quantitative structure-reactivity correlation*)

- Reaction network generated on-the-fly during the simulation via the kinetic Monte Carlo method
- Reactions executed using the SOL notation

# Proof-of-Concept Case Study

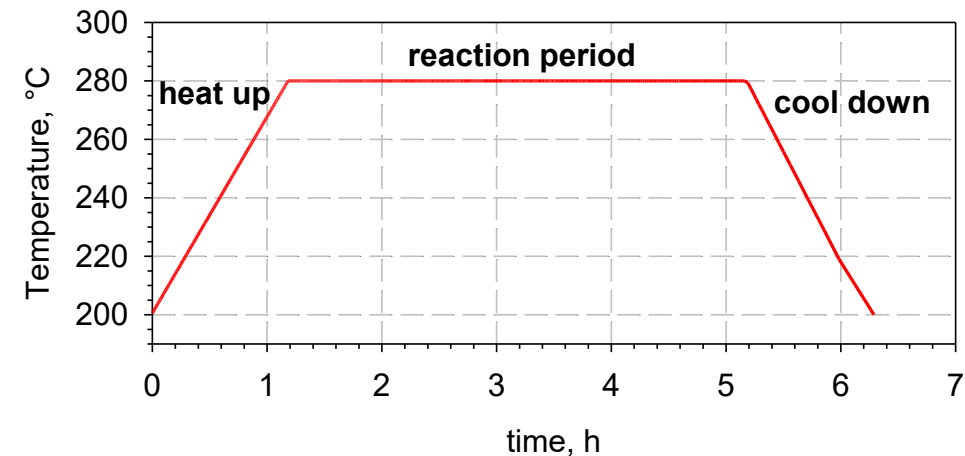
## Biocrude feed preparation

- Hydrothermal liquefaction of woody biomass
- Raw biocrude distilled to the highest possible cut-off temperature (460°C) to facilitate chemical analysis

| Property                          | Raw biocrude |
|-----------------------------------|--------------|
| density at 15.6°C, g/mL           | 1.0954       |
| oxygen, wt%                       | 10.9         |
| <i>Distillation yields</i>        |              |
| <b>distillate (52–460°C), wt%</b> | <b>45.7</b>  |
| residue (>460°C), wt%             | 54.3         |

## Batch reactor HDO experiments

- Commercial NiMo hydrotreating catalyst
- Experiments at varying temperatures (260–300°C) and reaction times (0.5–6 h)
- Reactor heating and cooling effect accounted for



Natural Resources  
Canada

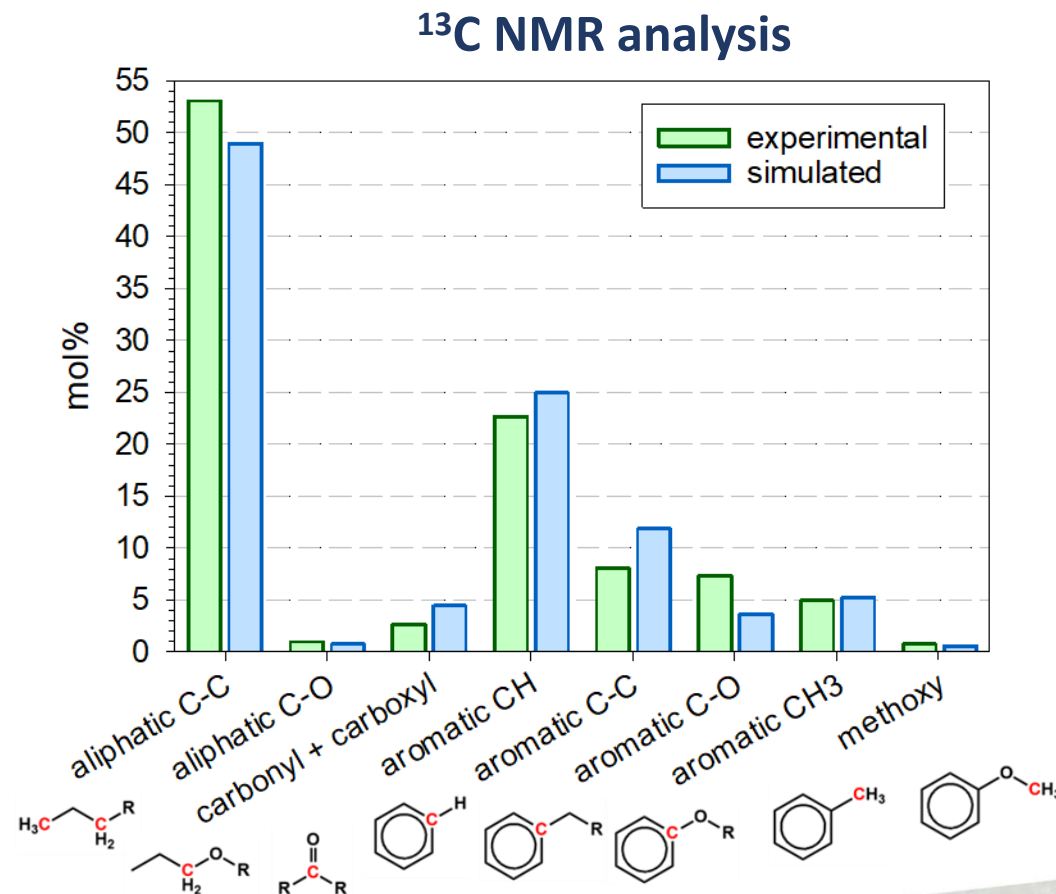
Ressources naturelles  
Canada

Canada

# Feed Composition Simulation

Biocrude distillate feed represented by an ensemble of 5,000 molecules

| Property                           | Experimental | Simulated |
|------------------------------------|--------------|-----------|
| density at 15.6°C, g/mL            | 0.9947       | 0.9872    |
| carbon, wt%                        | 79.9         | 80.0      |
| hydrogen, wt%                      | 10.0         | 9.8       |
| oxygen, wt%                        | 10.1         | 10.2      |
| total carbonyl, mmol/g             | 1.3          | 1.3       |
| <i><sup>31</sup>P NMR analysis</i> |              |           |
| carboxylic OH, mmol/g              | 1.2          | 1.2       |
| phenolic OH, mmol/g                | 1.9          | 1.9       |
| aliphatic OH, mmol/g               | 0.2          | 0.2       |



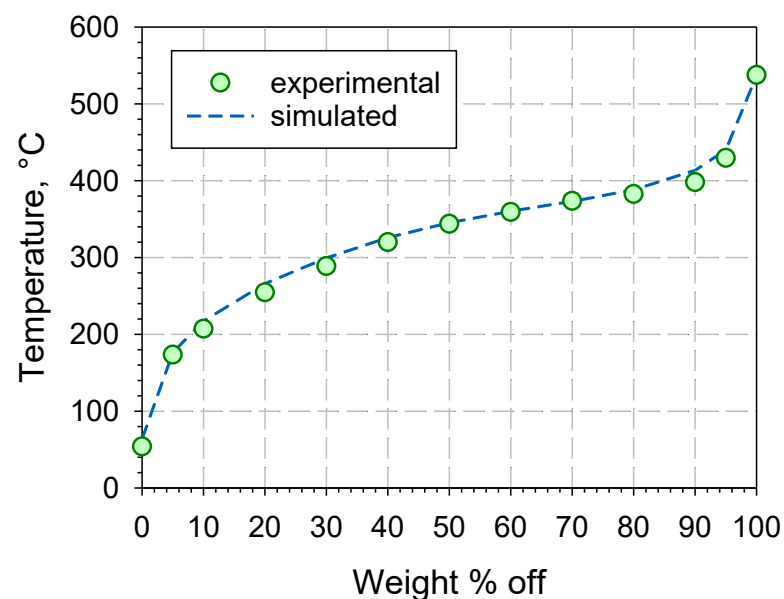
Natural Resources  
Canada

Ressources naturelles  
Canada

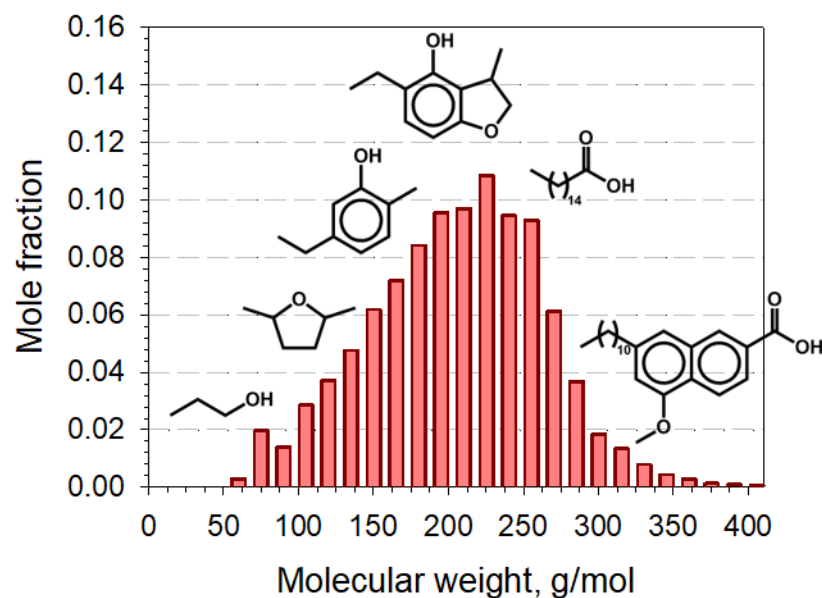
Canada

# Feed Composition Simulation (continued...)

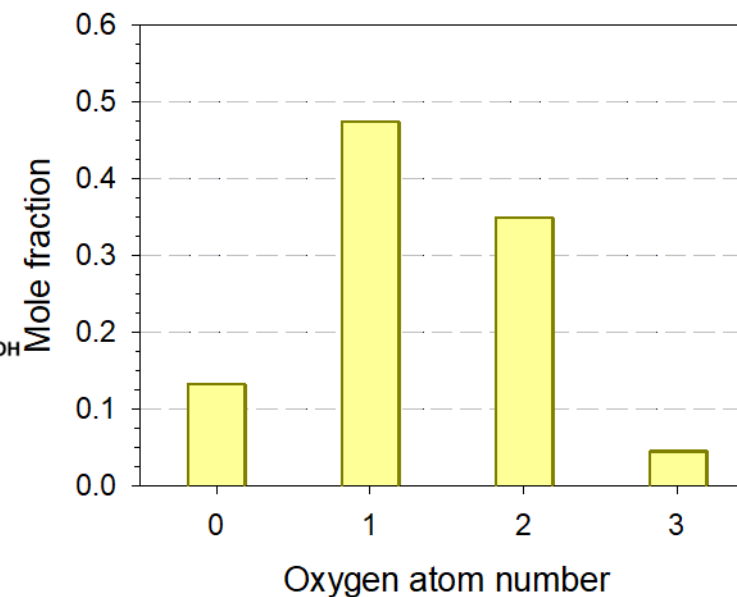
## Boiling point distribution



## Molecular weight distribution



## Oxygen atom distribution

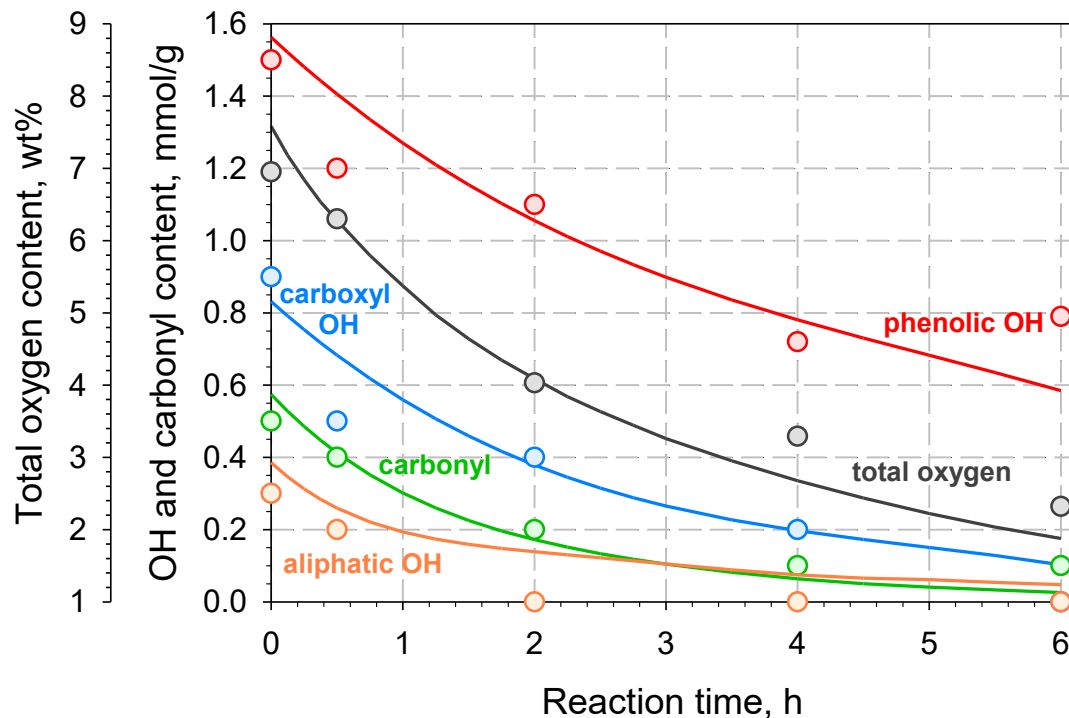


# HDO Simulation – Evolution of Oxygen

## Capturing HDO reactivity patterns in the biocrude distillate

### Effect of reaction time at 290°C

*lines (simulation); symbols (batch reactor data)*



- Reactor heat-up and cooling periods (0 h reaction time) contributed about 33% oxygen removal
- ~13,700 molecular reaction steps for 0 h reaction time, ~29,800 for 6 h
- Carbonyls most reactive group, phenolic OH most resistant group
- Removal of carbonyl and phenolic OH groups followed 2<sup>nd</sup> order kinetic behavior



Natural Resources  
Canada

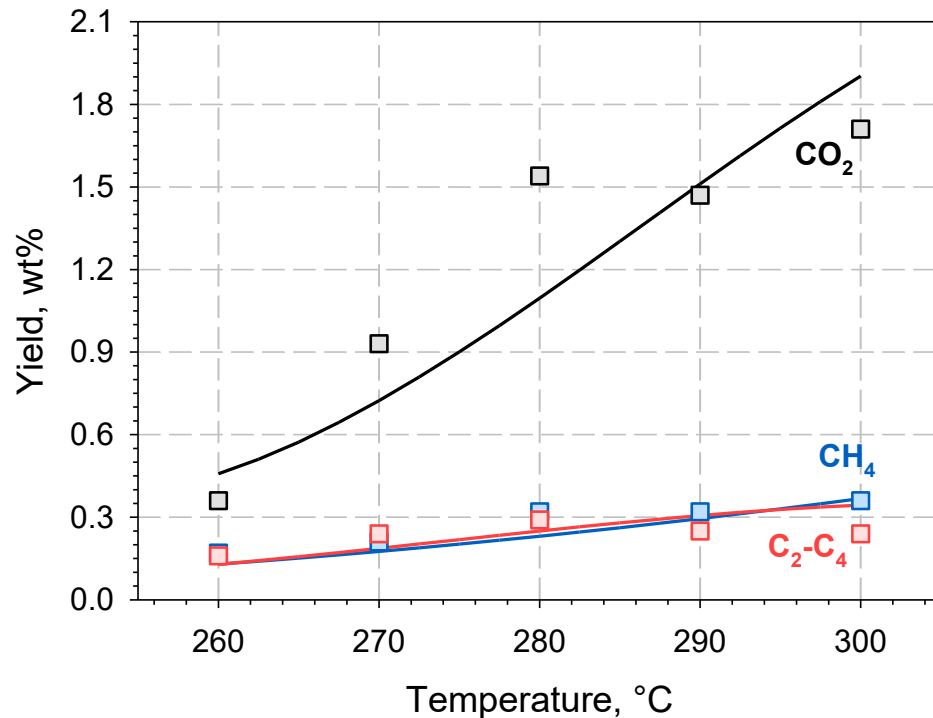
Ressources naturelles  
Canada

Canada

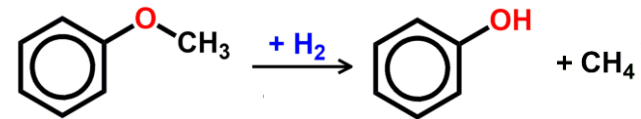
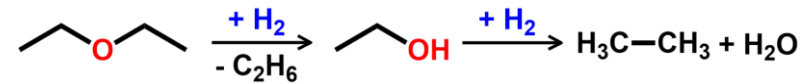
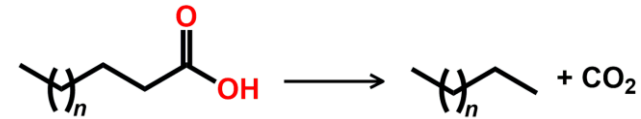
# HDO Simulation – Evolution of Gas Yields

VBU module estimates the different gas products formed during HDO

Gas yields vs. reaction temperature (4 h)  
lines (simulation); symbols (batch reactor data)



- Gas generation pathways:



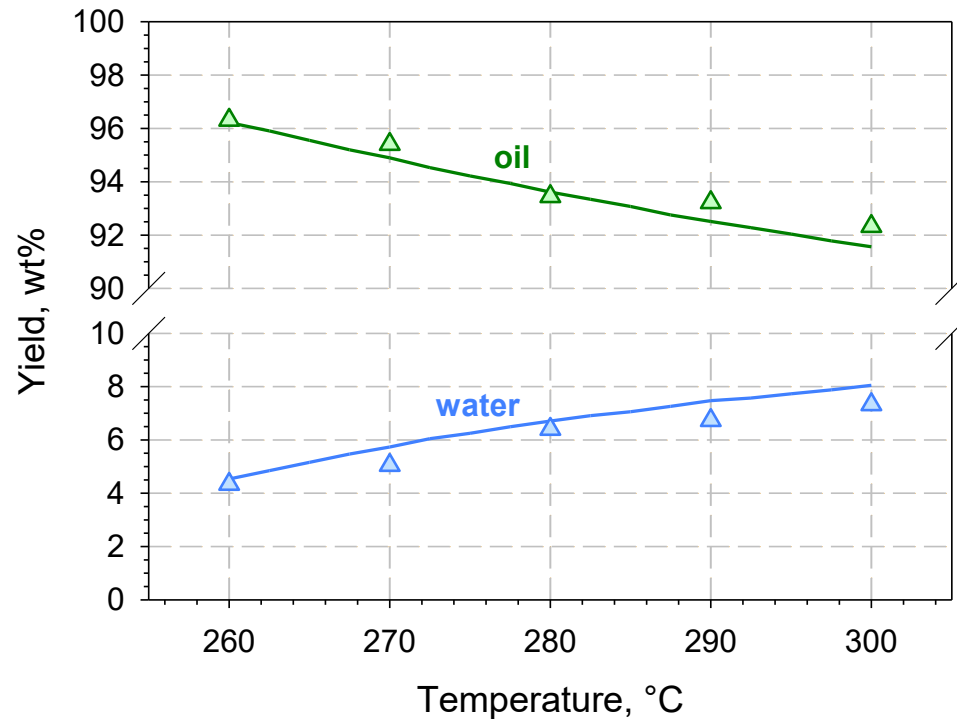
- CO<sub>2</sub> formation a strong function of temperature
- No CO was detected

# HDO Simulation – Evolution of Liquid Yields

Oil and water yields can also be tracked

## Liquid yields vs. reaction temperature (4 h)

*lines (simulation); symbols (batch reactor data)*



- Oxygen removal forms water while reducing oil yield
- Lowest oil yield was ~92 wt%, corresponding to 77% oxygen removal and a water yield of 7 wt%
- Oil and water yield changes calculated based on a stoichiometric description of HDO reactions



Natural Resources  
Canada

Ressources naturelles  
Canada

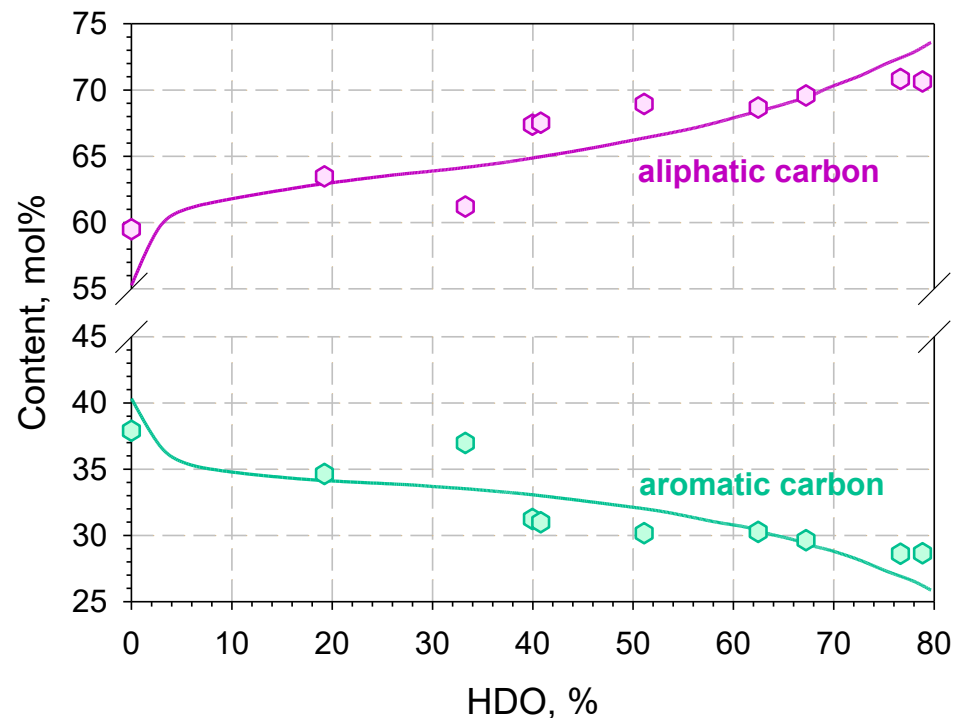
Canada

# HDO Simulation – Changes in Oil Quality

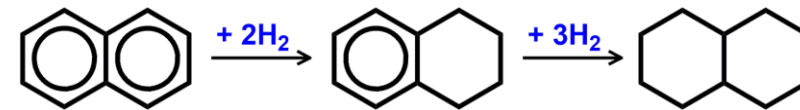
VBU module determines structural changes in the oil product

## Oil aromaticity as a function of HDO

*lines (simulation); symbols (batch reactor data)*



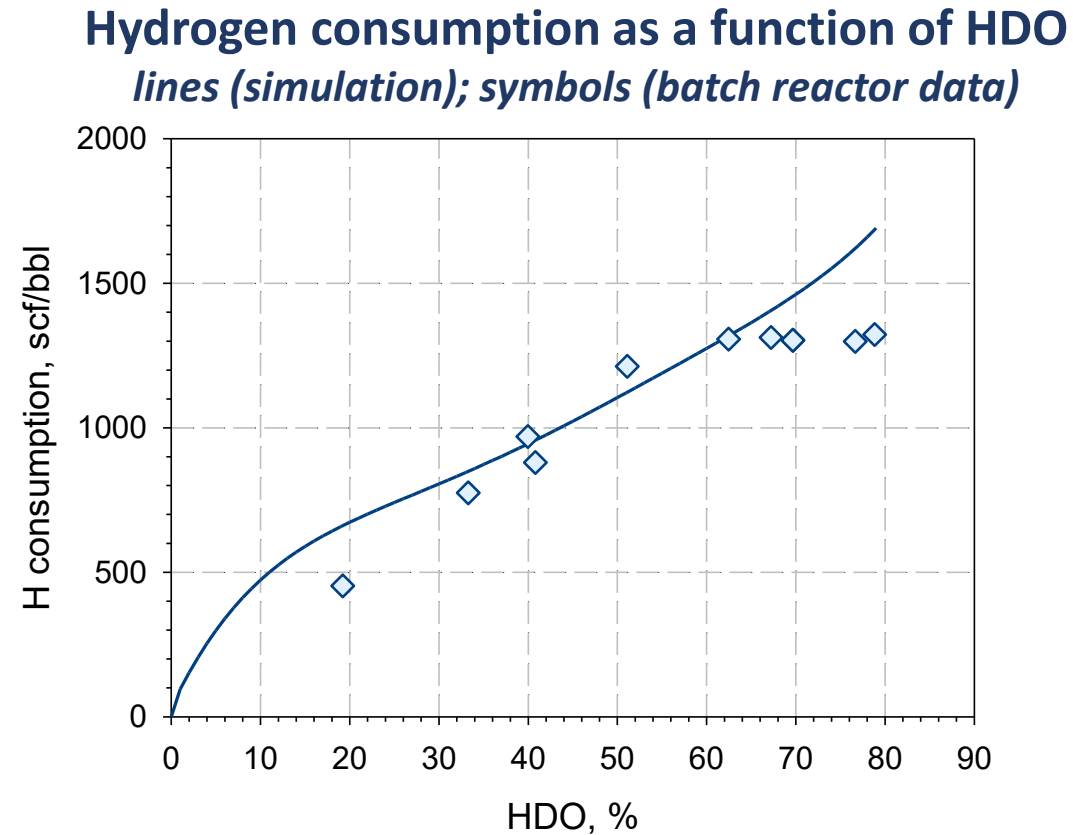
- As HDO grows, aromatic carbon is transformed into aliphatic one via the saturation of aromatic rings



- Aromatics hydrogenation rates modeled using quantitative structure-reactivity correlations

# HDO Simulation – Hydrogen Consumption

Hydrogen demand calculated from HDO reaction stoichiometry



Natural Resources  
Canada

Ressources naturelles  
Canada

Canada

# Summary

- Proposed modeling framework enables molecular-level representation of biocrude HDO
  - The VBA module generates molecular representations of biocrude feeds from available analytical data
  - The reaction module, VBU, simulates molecular transformations during HDO
- Key simulation capabilities
  - Tracks the evolution of oxygen functional groups and reactivity patterns of oxygen compound families
  - Estimates yields of gas products, oil, and water
  - Quantifies changes in oil product properties and hydrogen consumption
- Ongoing development
  - Extending model scope to cover high-boiling fractions and other biocrude types



Natural Resources  
Canada

Ressources naturelles  
Canada



Canada

# Acknowledgement

- CanmetENERGY Devon's Technical Services Team and Analytical Service Team
- Government of Canada's Office of Energy Research and Development (OERD) and the Canadian Forest Service (CFS)
- Industry partners



Natural Resources  
Canada

Ressources naturelles  
Canada

Canada

**Anton Alvarez-Majmutov, Ph.D.**

Team Lead, Biofuels and Process Modeling

Email: [anton.alvarez-majmutov@nrcan-rncan.gc.ca](mailto:anton.alvarez-majmutov@nrcan-rncan.gc.ca)

Telephone: +1 587-334-6268

# Canada

© His Majesty the King in Right of Canada, as represented by the Minister of Natural Resources, 2026



Natural Resources  
Canada

Ressources naturelles  
Canada

# Canada