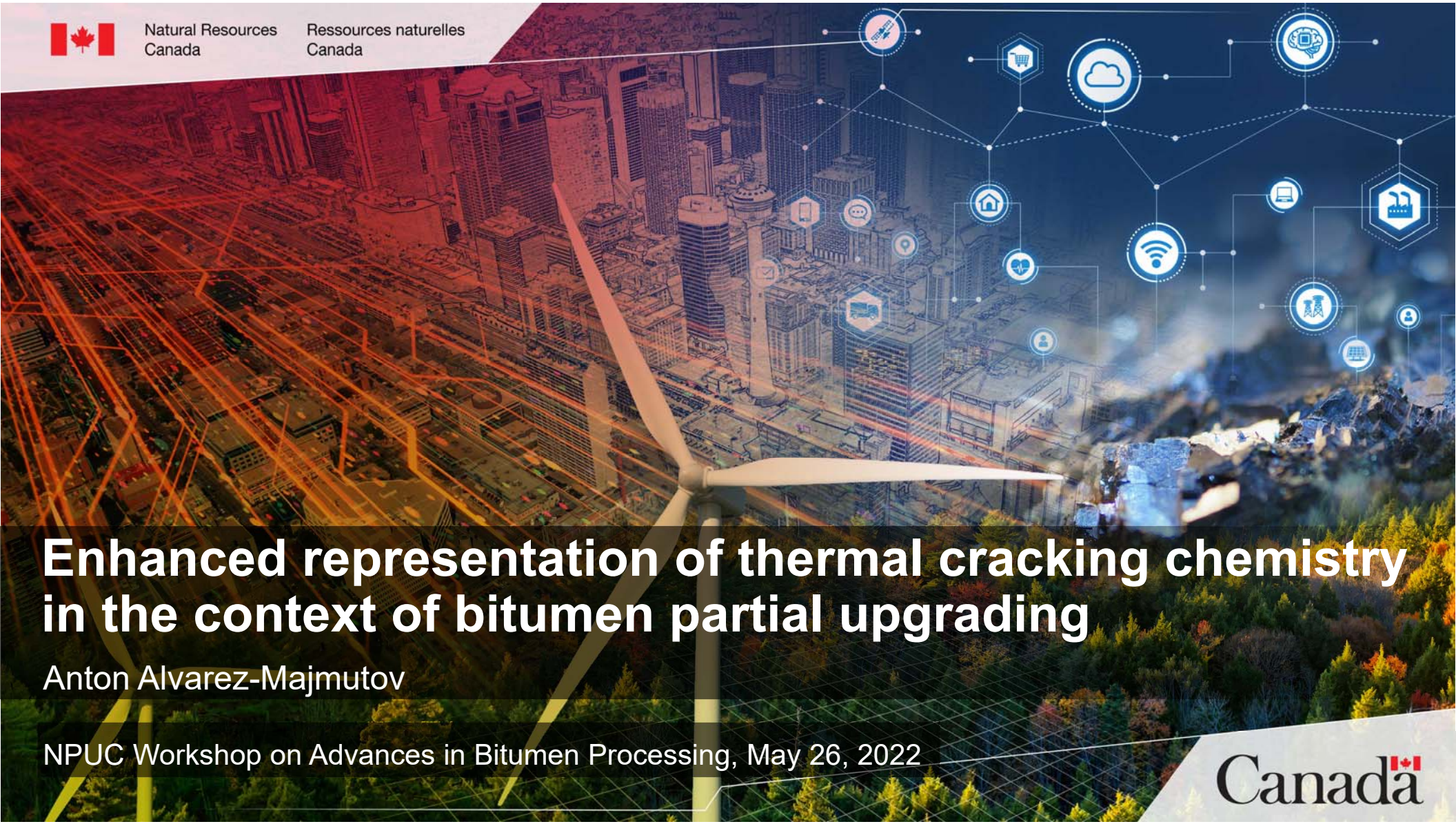
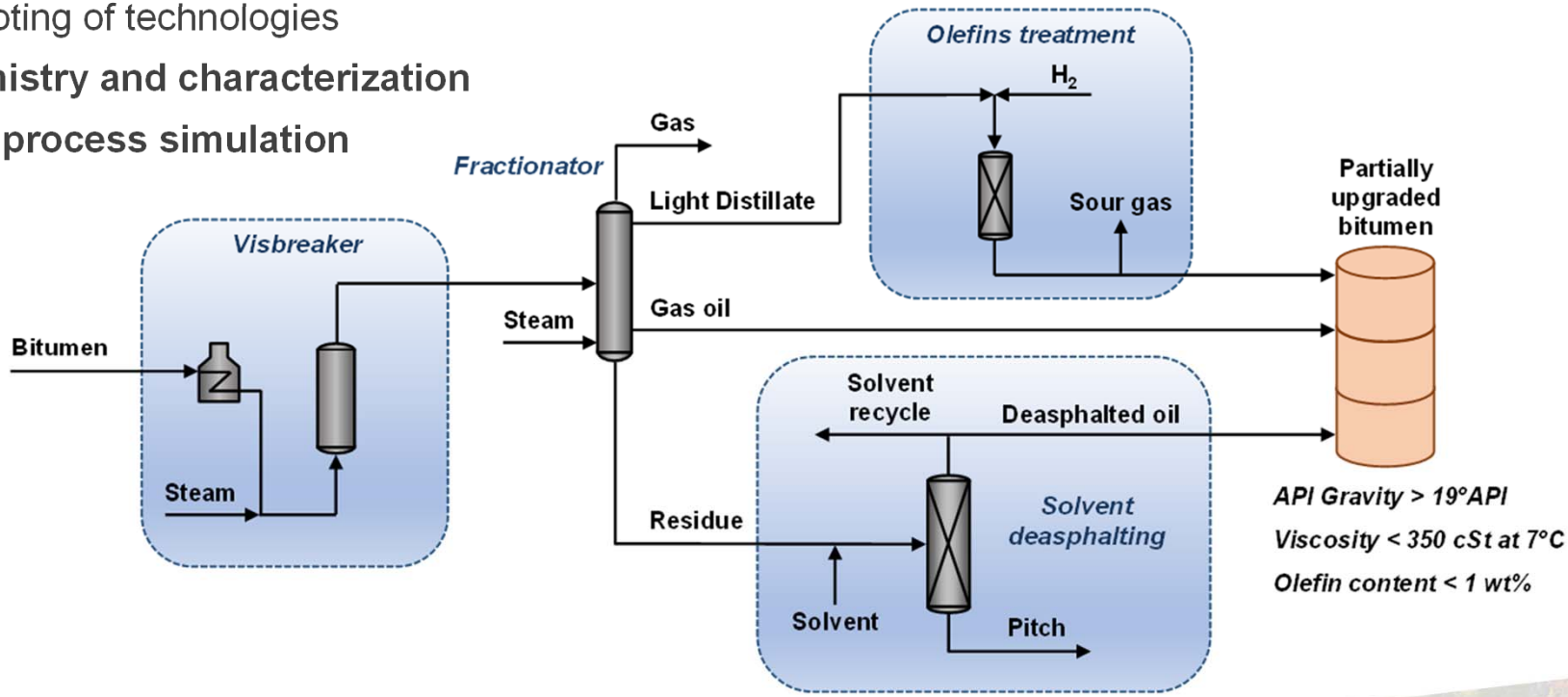

Natural Resources Canada
Ressources naturelles Canada
Enhanced representation of thermal cracking chemistry in the context of bitumen partial upgrading
Anton Alvarez-Majmutov
NPUC Workshop on Advances in Bitumen Processing, May 26, 2022
Canada

# Bitumen partial upgrading

CanmetENERGY Devon's R&D program since 2015:

- Testing and piloting of technologies
- **Bitumen chemistry and characterization**
- **Modeling and process simulation**

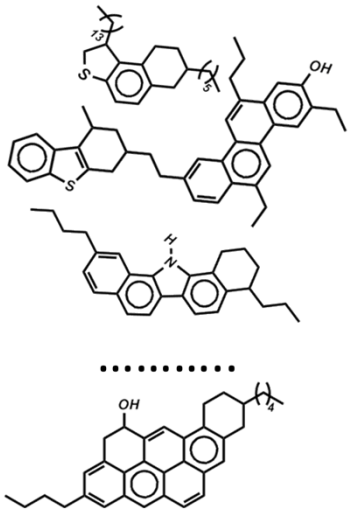


# Our modeling approach to bitumen partial upgrading

**Bulk oil properties**
**+**
**advanced characterization**

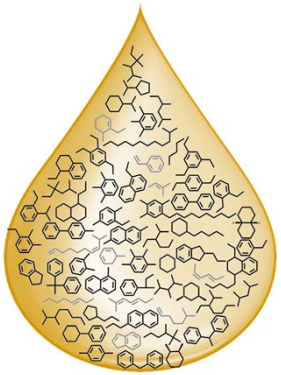
**Composition modeling**

**Molecular representation**



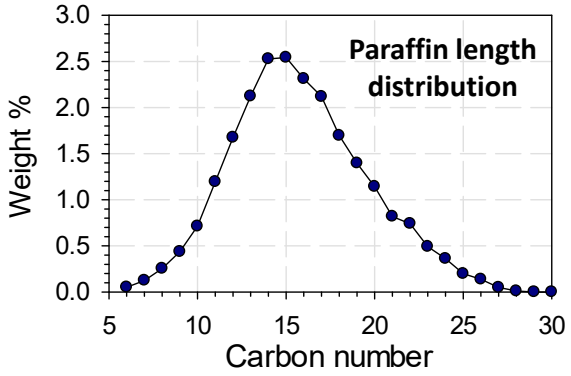

**Reaction modeling**

**Detailed product composition**

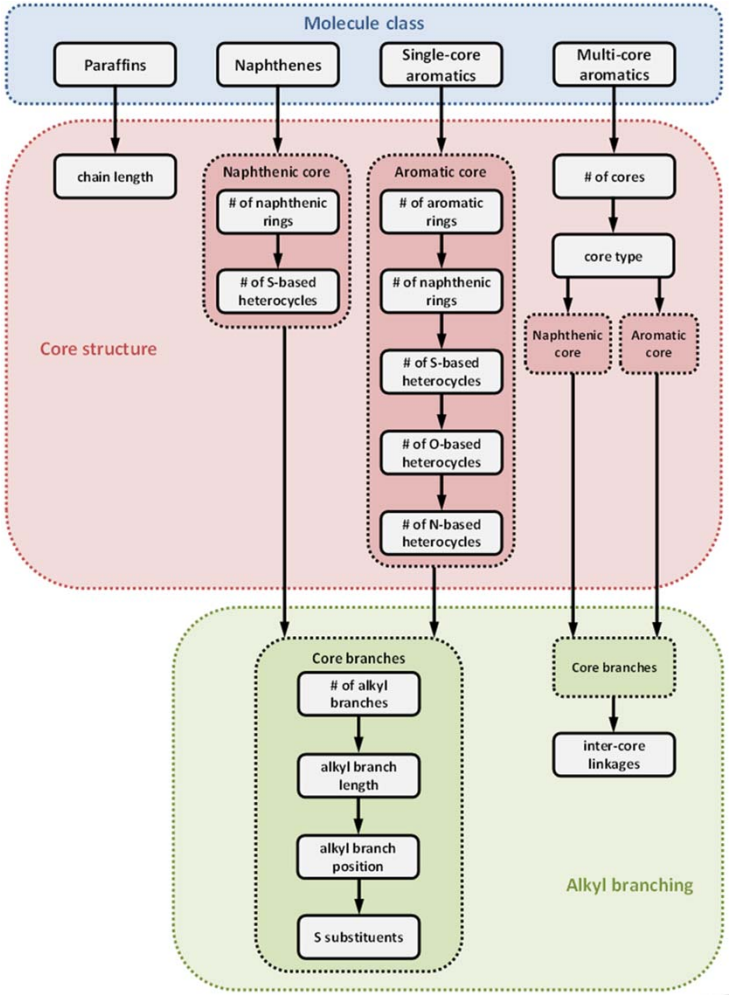


# Bitumen composition modeling

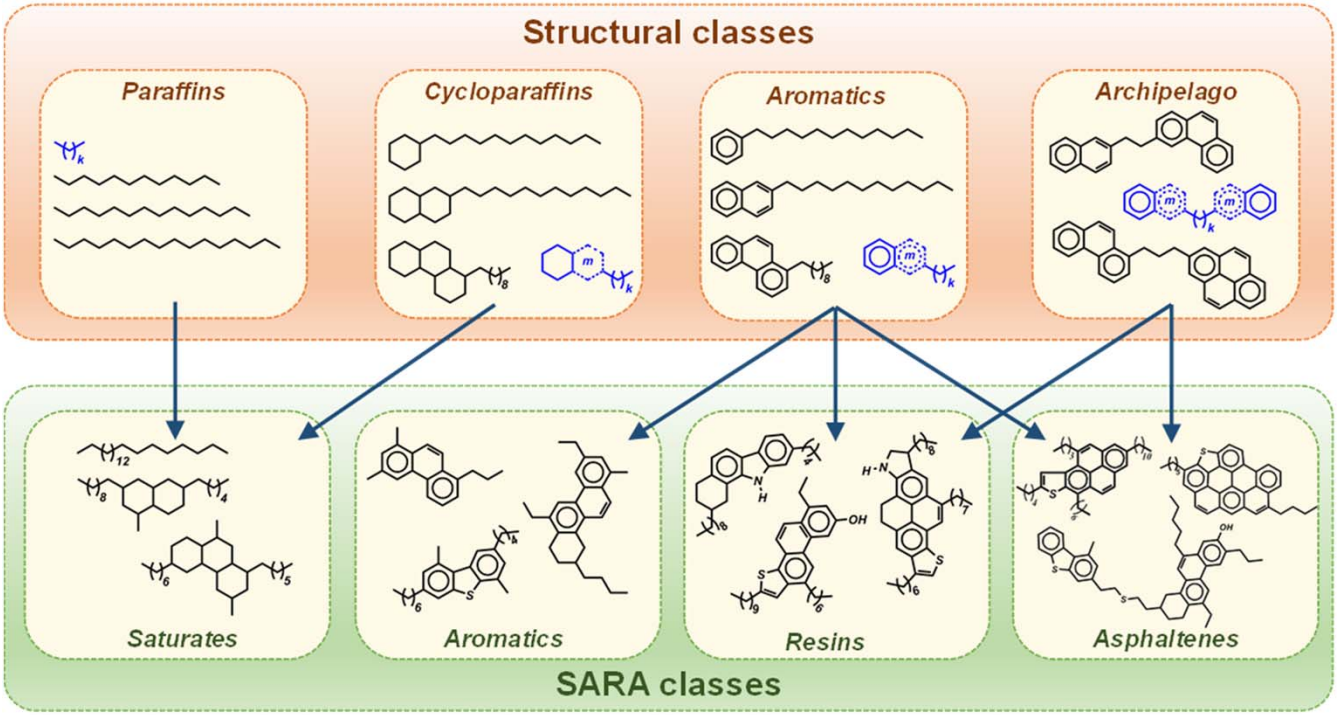
- Molecular structure features follow statistical distributions




- Each molecule class (paraffins, aromatics, etc.) characterized by its own structural descriptors
- Mixture of molecules ($10^3$-$10^5$) is created via Monte Carlo simulation to match analytical feed properties



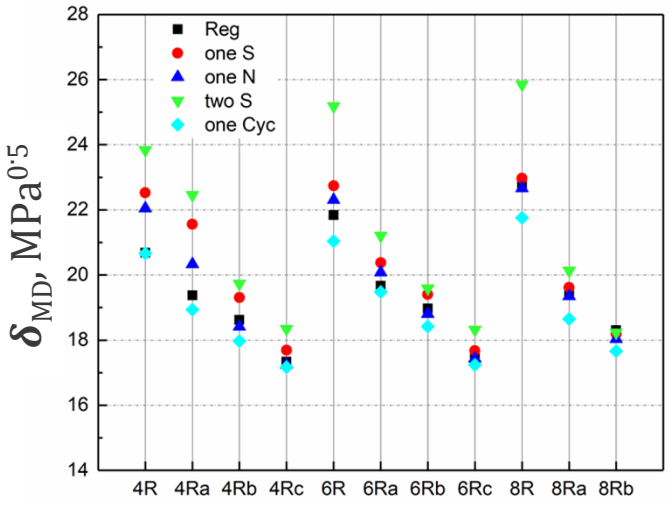
# Classification of bitumen molecules



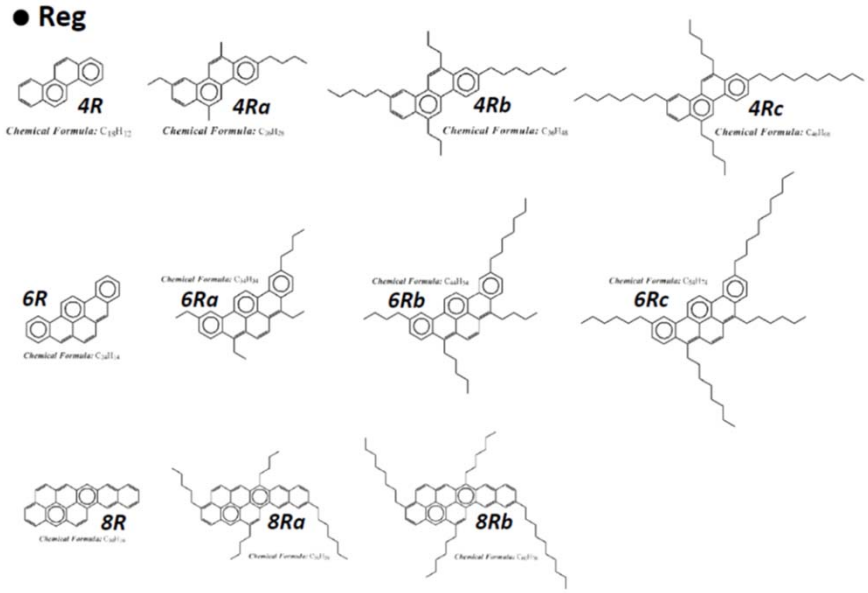

- SARA classes are formed by the grouping of molecules based on structural features and theoretical solubility

# Asphaltenes distinction based on solubility

- Asphaltene character assigned based on the solubility criterion of the SOL method (Jaffe *et al.*, Ind. Eng. Chem. Res., 2005, 44)
- Hildebrand solubility parameters ($\delta$) of model bitumen molecules in *n*-pentane obtained by molecular dynamics




**Model bitumen molecules**



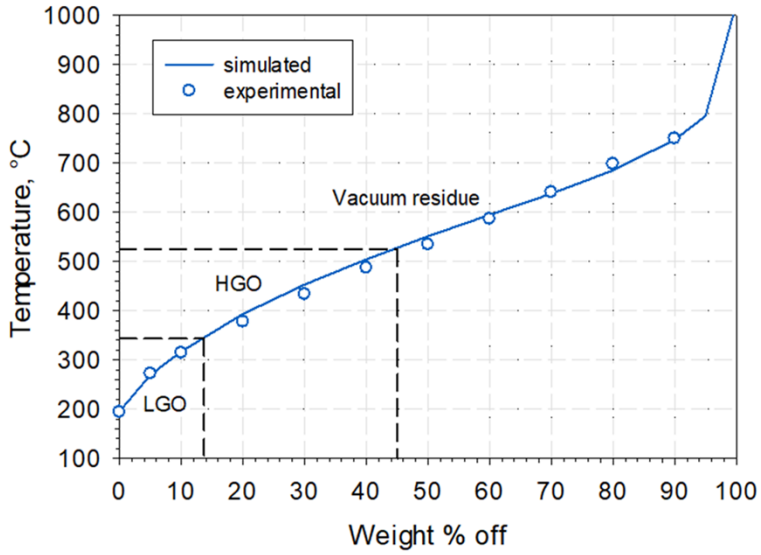
# Bitumen composition modeling – bulk properties

- Bitumen composition represented by an ensemble of 100k molecules
- Molecules were reconstructed from bulk property measurements and NMR spectroscopy data

**Bitumen feed properties**

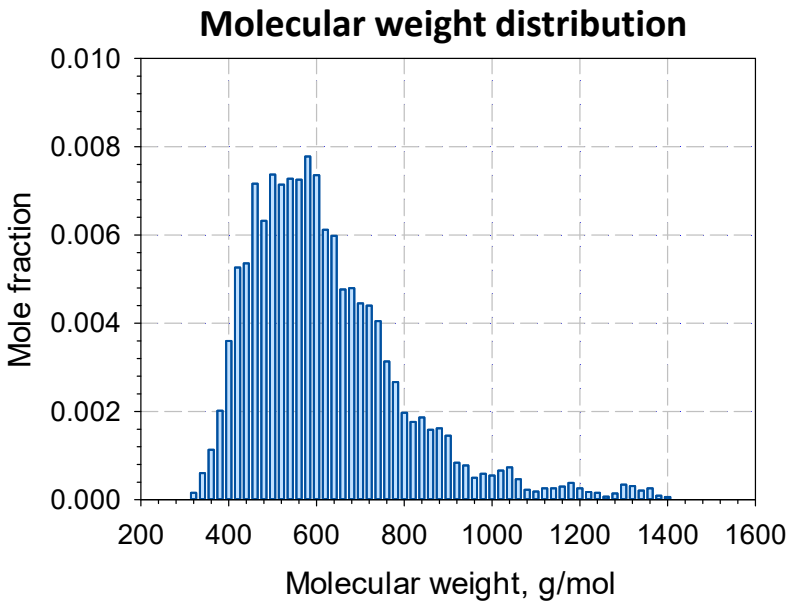
| Property | Experimental | Simulated |
|---|---|---|
| Density at 15.6°C, g/mL | 1.0146 | 1.0139 |
| API gravity, °API | 7.8 | 7.9 |
| Carbon, wt% | 83.38 | 83.94 |
| Hydrogen, wt% | 10.64 | 10.39 |
| Sulfur, wt% | 4.95 | 4.74 |
| Nitrogen, wt% | 0.49 | 0.41 |
| Oxygen, wt% | 0.54 | 0.52 |
| *SARA analysis* | | |
| Saturates, wt% | 20.7 | 19.2 |
| Aromatics, wt% | 39.0 | 39.6 |
| Resins, wt% | 25.1 | 22.0 |
| $C_5$ asphaltenes, wt% | 19.3 | 19.3 |

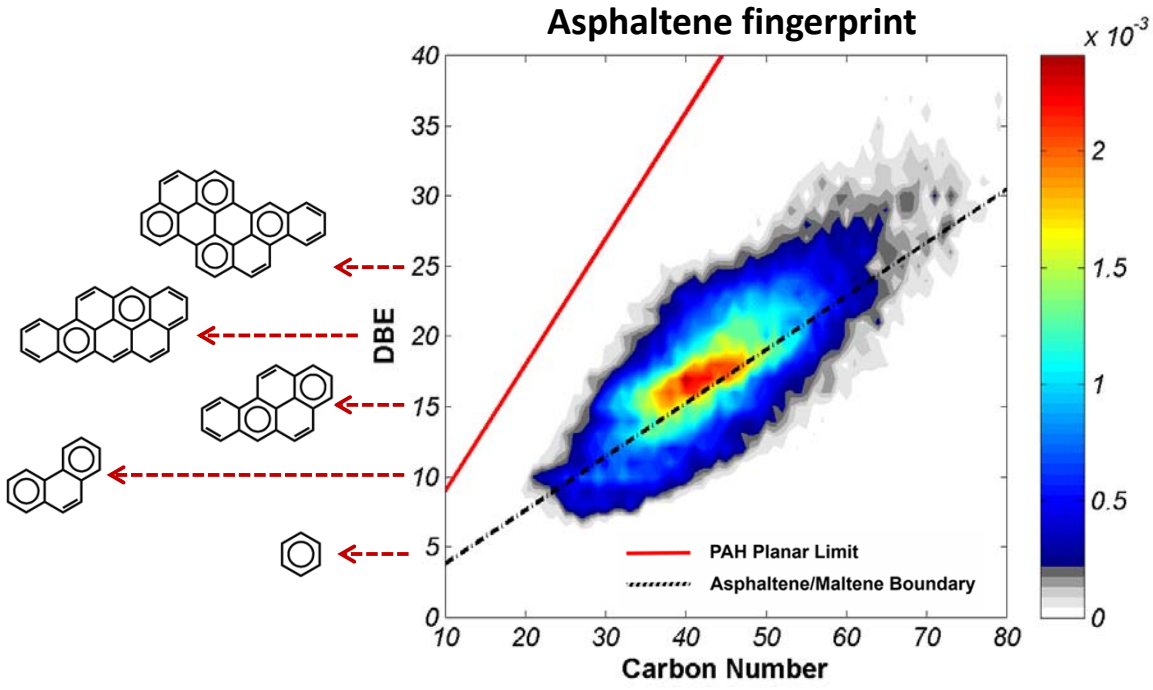
**Distillation curve**



# Bitumen composition modeling – asphaltenes

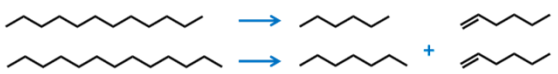
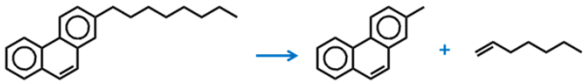
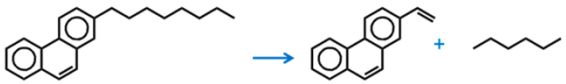
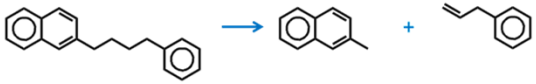
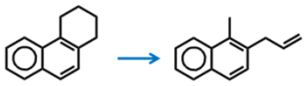
- Asphaltene fraction consists of monomeric island and archipelago structures

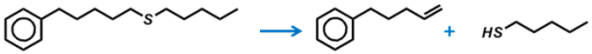
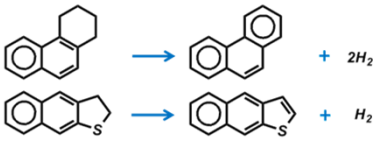
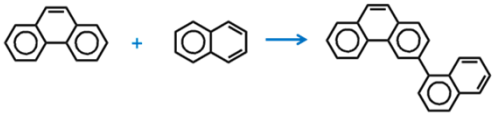


# Reaction modeling of thermal cracking

- Thermal cracking chemistry organized into reaction families

| Cracking reaction |
| --- |
| ***Carbon-carbon bond cracking*** |
| Paraffin cracking |
|  |
| Dealkylation pathway 1 |
|  |
| Dealkylation pathway 2 |
|  |
| Archipelago fragmentation |
|  |
| Naphthenic ring opening |
|  |

| Cracking reaction |
| --- |
| ***Sulfur-carbon bond cracking*** |
| Thioether chain cracking |
|  |
| Thiol chain cracking |
|  |
| Tetrahydrothiophenic ring opening |
|  |
| ***Dehydrogenation*** |
|  |
| ***Condensation*** |
|  |

# Reaction modeling of thermal cracking

- Rate parameters organized by similarity into a small set of quantitative structure-reactivity correlations (QSRC):

$$\ln k_{ij} = \ln A_j - \frac{\alpha_j}{RT} - \frac{\beta_j \Delta H_{ij}}{RT}$$

**Enthalpy of reaction: structure-reactivity index calculated using semi-empirical quantum chemistry calculations**

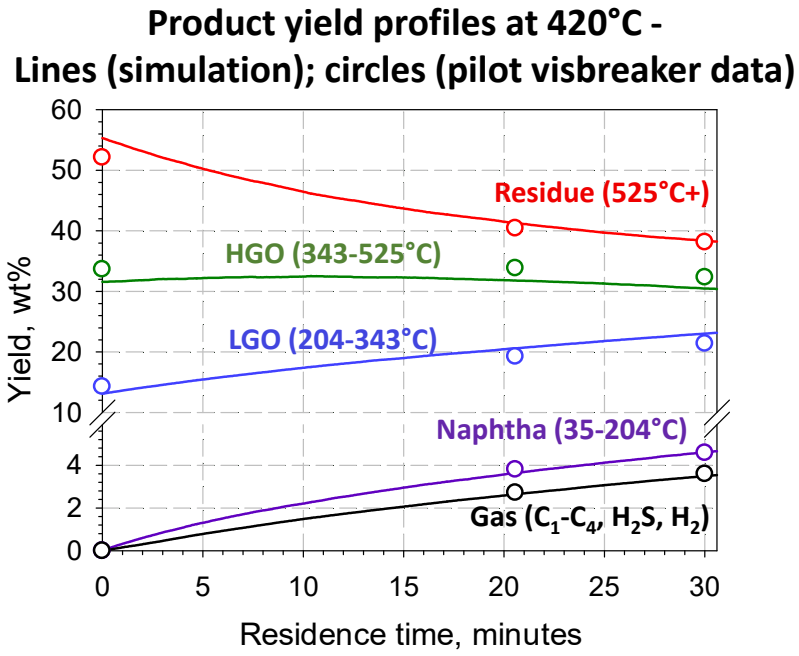
**Rate constant of reaction family "j"**

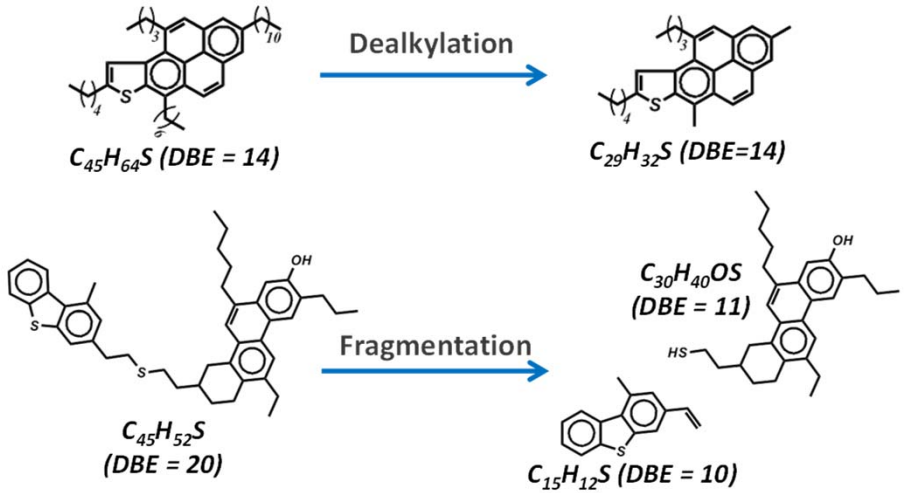
**Reaction family parameters**

- Massive reaction network generated on-the-fly with a kinetic Monte Carlo (kMC) algorithm, whereby molecule cracking reactions progress one by one over time

# Visbreaker simulations – product yields

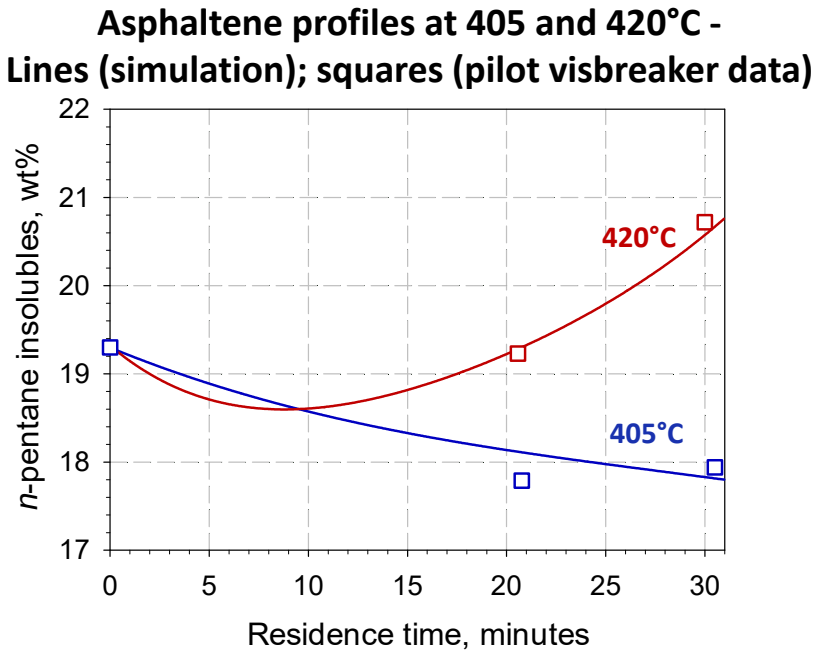
Product yield structure evolves as a result of C-C and S-C bond cracking reactions

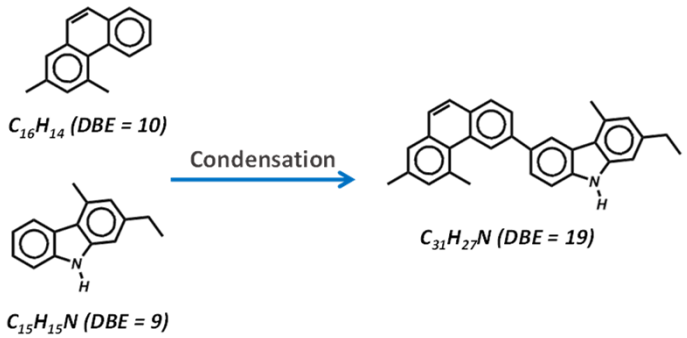


# Visbreaker simulations – asphaltenes

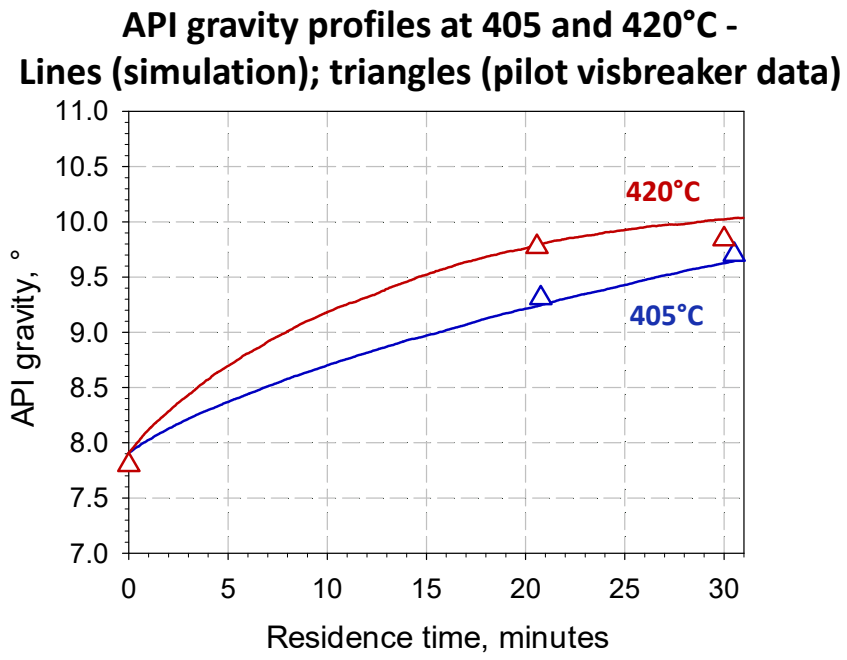
Condensation and dealkylation reactions drive formation of new asphaltenes



# Visbreaker simulations – API gravity

The model enables tracking product properties of interest

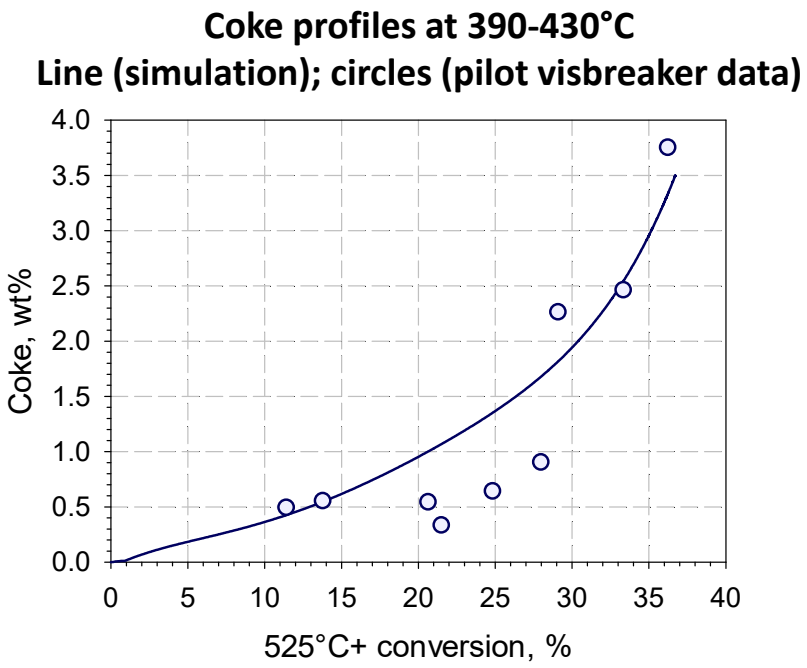



- API gravity estimated by applying a linear mixing rule on the individual densities of molecules
- The rise in condensation and dehydrogenation reactions at 420°C makes the simulated API gravity curve gradually bend

# Visbreaker simulations – coke modeling

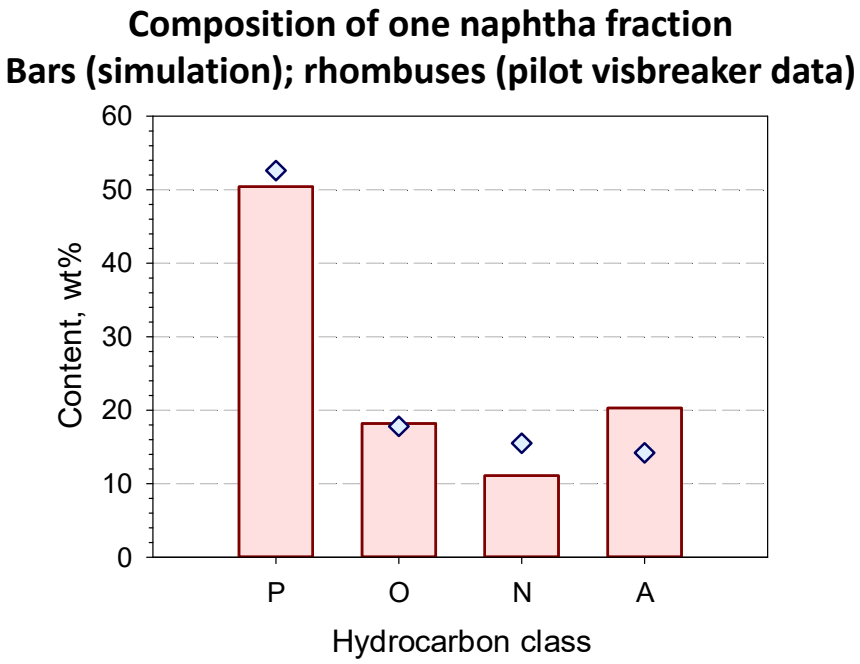
Coke (toluene insolubles) is represented as a sub-fraction of pentane insolubles:

- Pentane insolubles boiling above 555°C as per the SOL method (Jaffe *et al.*, Ind. Eng. Chem. Res., 2005, 44)
- Pentane insolubles with H content below 6 wt% as per Wiehe's Solvent-Resid Phase Diagram (Wiehe, Ind. Eng. Chem. Res., 1992, 31)



# Visbreaker simulations – cracked naphtha composition

The model can generate the hydrocarbon type composition of products of interest




- The explicit distinction between two possible dealkylation pathways allows approximating paraffins and olefins with good precision
- The model has a tendency to yield more aromatic products than naphthenic ones

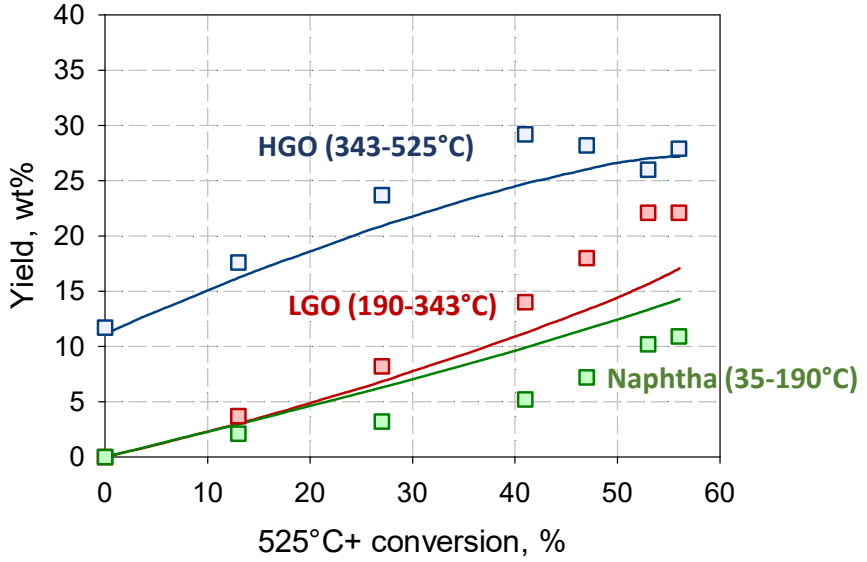
# Modeling different feedstocks – DAO cracking

Model was tested against the data set from Yan *et al.*, Energy Fuels, 2020, 34

**Bitumen VR DAO feed properties**

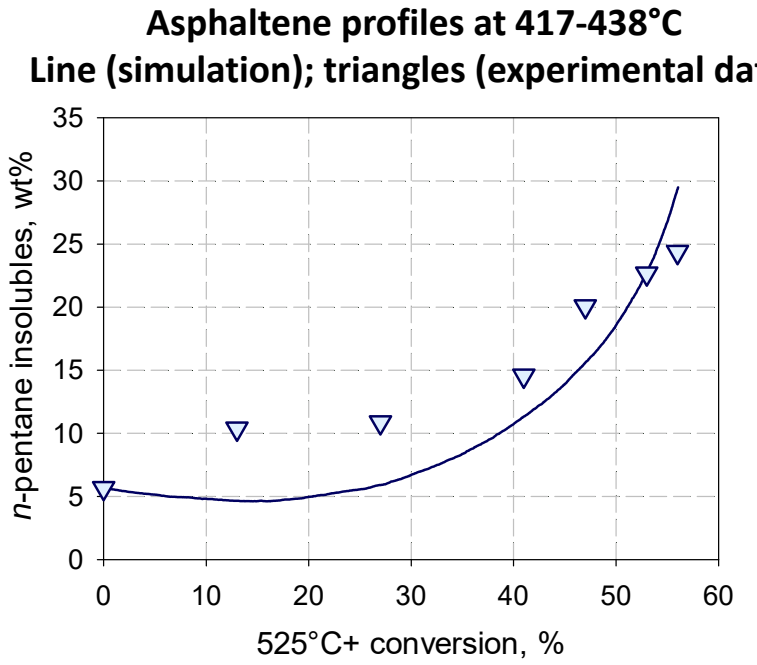
| Property | Experimental | Simulated |
|---|---|---|
| Density at 15.6°C, g/mL | 1.0772 | 1.0695 |
| API gravity, °API | -0.3 | 0.7 |
| Carbon, wt% | 83.20 | 83.68 |
| Hydrogen, wt% | 9.80 | 9.69 |
| Sulfur, wt% | 5.40 | 5.46 |
| Nitrogen, wt% | 0.60 | 0.55 |
| Oxygen, wt% | 1.00 | 0.61 |
| $C_5$ asphaltenes, wt% | 5.7 | 5.7 |
| *Distillation fractions* | | |
| HGO(343-525°C), wt% | 11.8 | 11.1 |
| Vacuum residue (525°C+) | 88.2 | 88.9 |

**Product yield profiles at 417-438°C**
**Lines (simulation); squares (experimental data)**



# Modeling different feedstocks – DAO cracking

Model predicts formation of new asphaltenes



# Summary

- Approaching refinery process modeling from a fundamental perspective offers a number of advantages in terms of capabilities
- Feed compositional modeling is the starting point for molecular reaction modeling
- Reaction modeling of complex chemistries must be done so that the system is manageable in size
- Quantum chemistry and molecular dynamics play a key role in modeling properties of molecules
- The framework is general in essence and can be extended to other process chemistries (*e.g.* hydrocracking)

**Anton Alvarez-Majmutov, Ph.D.**
Renewables, Hydroprocessing and Modeling R&D Lead
Email: anton.alvarez-majmutov@nrcan-rncan.gc.ca
Telephone: 780-987-8348

Canada