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Equation of state methods for the development of accurate physical models in support of Co -Optima

PRESENTED BY

Alexander Landera, Ryan W. Davis, Anthe George

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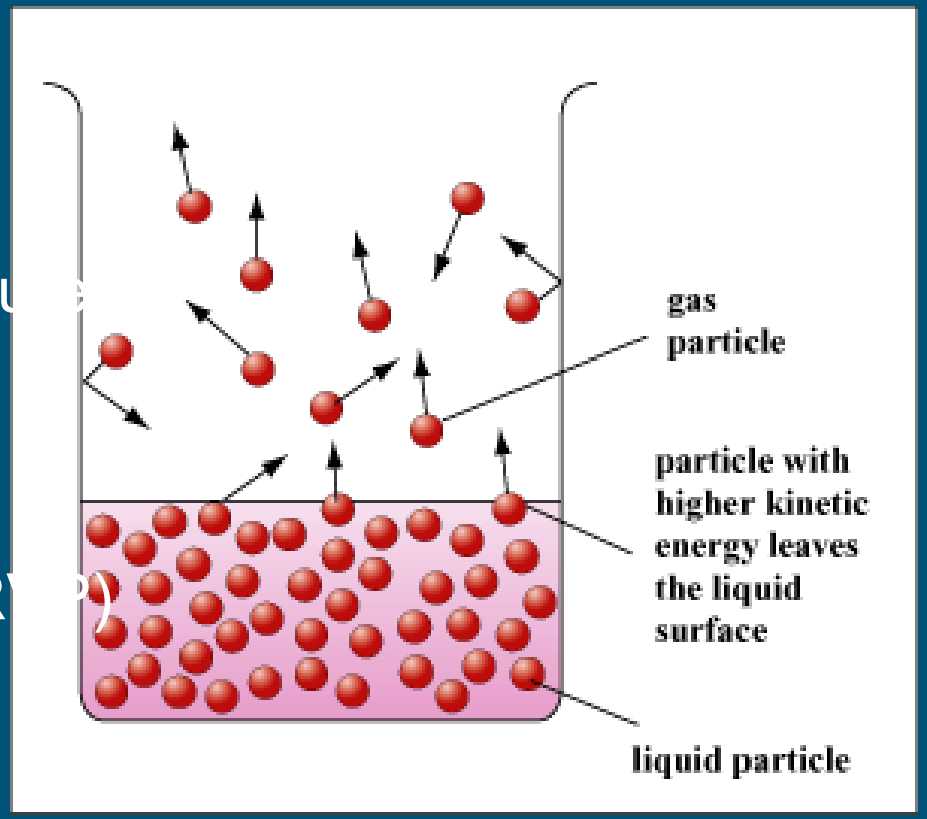
Reid Vapor Pressure (RVP)

Vapor pressure: Force pushing against the atmosphere, between the boundary of liquid and gas

- Caused by molecular collisions
- Causes liquid molecules to ‘escape’ into the atmosphere
- In the petroleum industry, a special vapor pressure metric exists
- Vapor pressure is measured at 37.8°C (100°F)
- 1:4 liquid vapor fraction
- This metric is called the Reid Vapor Pressure (RVP)



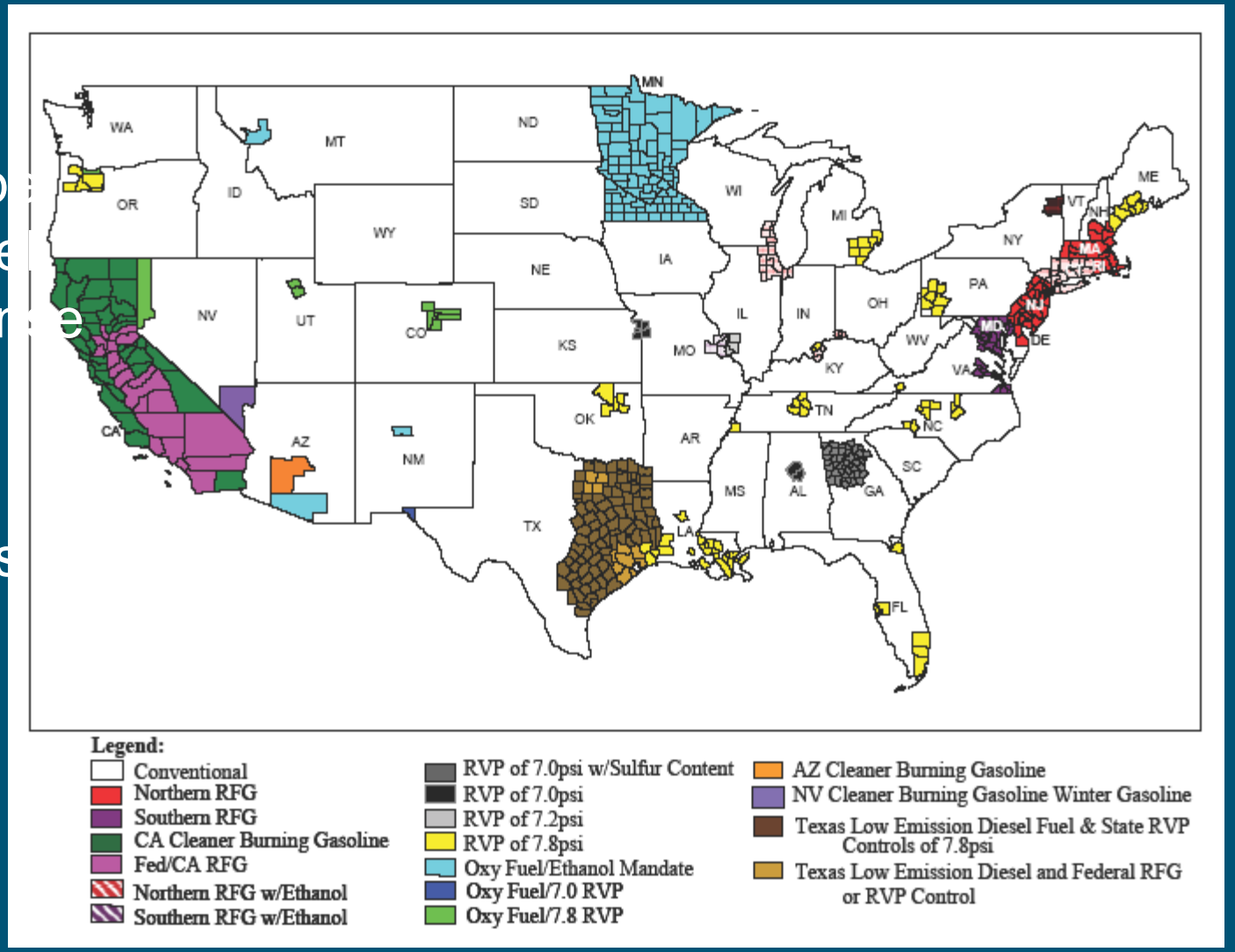
Instead of regulating vapor pressure

- RVP is regulated
- Convenient, fixed T, conditions
- Managed by ASTM-D5482-07

RVP regulation

- By region, state, principality
  - Geography, altitude
- Places natural limitations on the typ
and quantity of each component in fue
- Fuel composition changes in respon e
to location, and season
- Those interactions lead to RVP

Higher RVP fuels => larger emissions
- Human health impacts
- ↑ GHG emissions



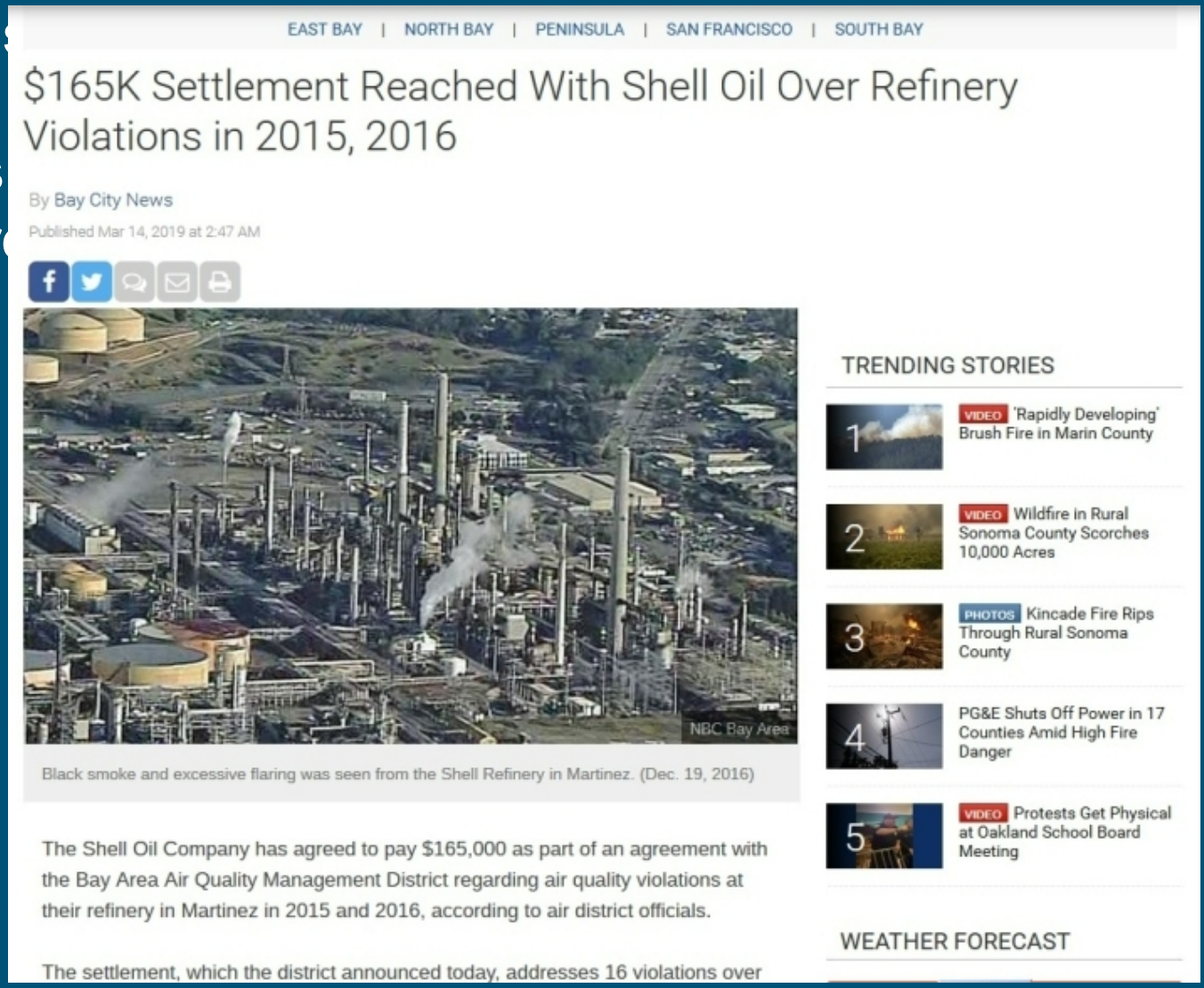
Refinery applications

- Losses from seals, valves etc.
- Overtime, contribute to GHG emissions

and can cost companies money

- ~ 0.17% of refinery hydrocarbon mass
- ~ $3.1 million/year (based on $40 barr

Image credit: U.S. Energy Information Administration
https://www.eia.gov/state/maps.php



EAST BAY | NORTH BAY | PENINSULA | SAN FRANCISCO | SOUTH BAY

$165K Settlement Reached With Shell Oil Over Refinery Violations in 2015, 2016

By Bay City News

Published Mar 14, 2019 at 2:47 AM

Black smoke and excessive flaring was seen from the Shell Refinery in Martinez. (Dec. 19, 2016)

The Shell Oil Company has agreed to pay $165,000 as part of an agreement with the Bay Area Air Quality Management District regarding air quality violations at their refinery in Martinez in 2015 and 2016, according to air district officials.

The settlement, which the district announced today, addresses 16 violations over

TRENDING STORIES

1 VIDEO 'Rapidly Developing' Brush Fire in Marin County

2 VIDEO Wildfire in Rural Sonoma County Scorches 10,000 Acres

3 PHOTOS Kincade Fire Rips Through Rural Sonoma County

4 PG&E Shuts Off Power in 17 Counties Amid High Fire Danger

5 VIDEO Protests Get Physical at Oakland School Board Meeting

WEATHER FORECAST

https://www.nbcbayarea.com/news/local/165K-Settlement-Reached-With-Shell-Oil-Over-Refinery-Violations-in-2015-2016-507132361.html

Approach: theory

SAFT-γ-Mie Equation of State (EoS)

- Goal is to find A (Helmholtz free energy)

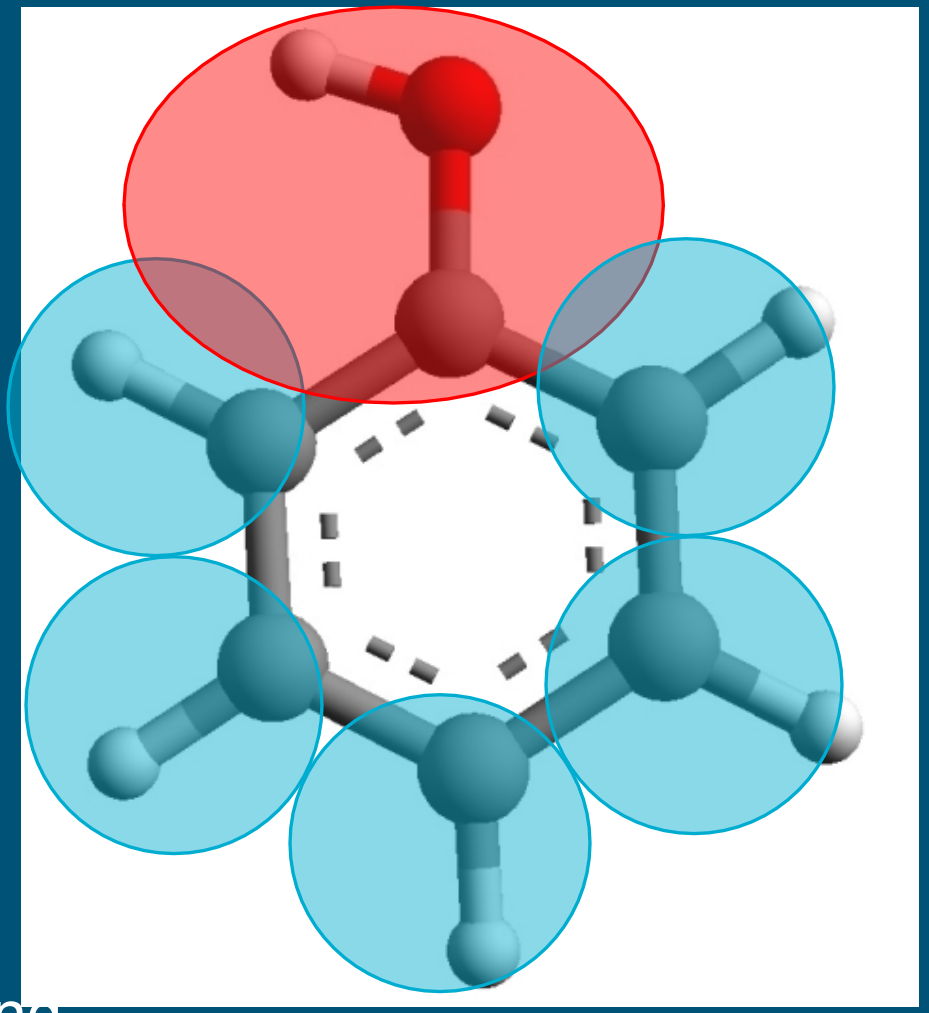
$$A = A^{ideal} + A^{mono} + A^{chain} + A^{assoc}$$

- A^{ideal} => statistical mechanics
- All other terms are perturbations meant to improve qualitative nature of A^{ideal}

Mie function

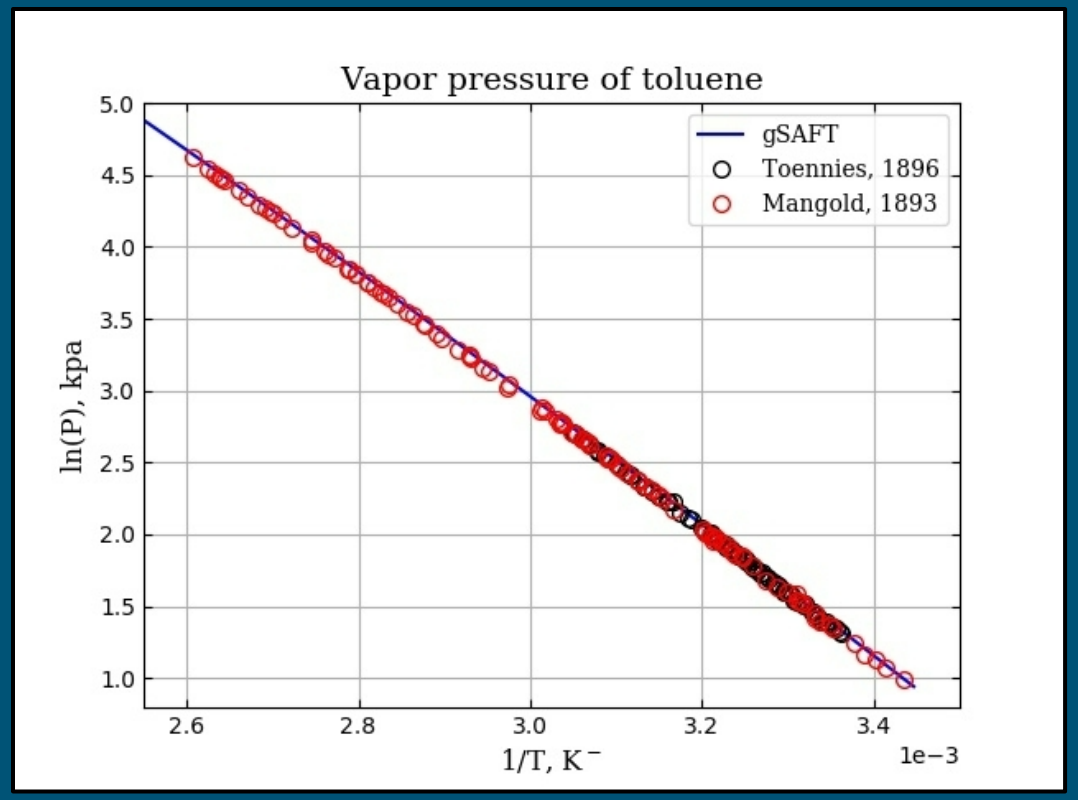
$$\Phi_{kk}^{Mie}(r_{kk}) = \mathcal{C}_{kk}\varepsilon_{kk}\left[\left(\frac{\sigma_{kk}}{r_{kk}}\right)^{\lambda_{kk}^{r}} - \left(\frac{\sigma_{kk}}{r_{kk}}\right)^{\lambda_{kk}^{a}}\right]$$

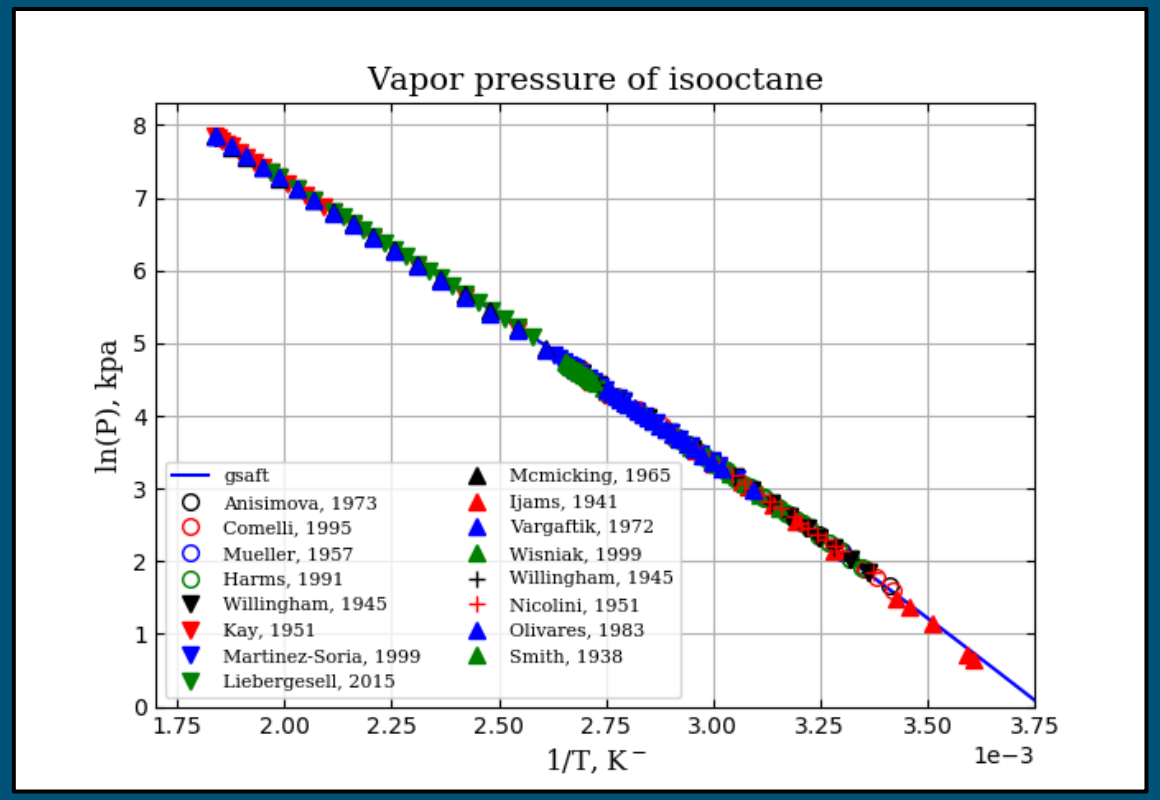
Each group is described by a Mie function, and Mie functions interact with each other to model fluids accurately. Physical properites are obtained through partial differentiation of A.



An example of groups used to describe phenol

Pure component vapor pressure



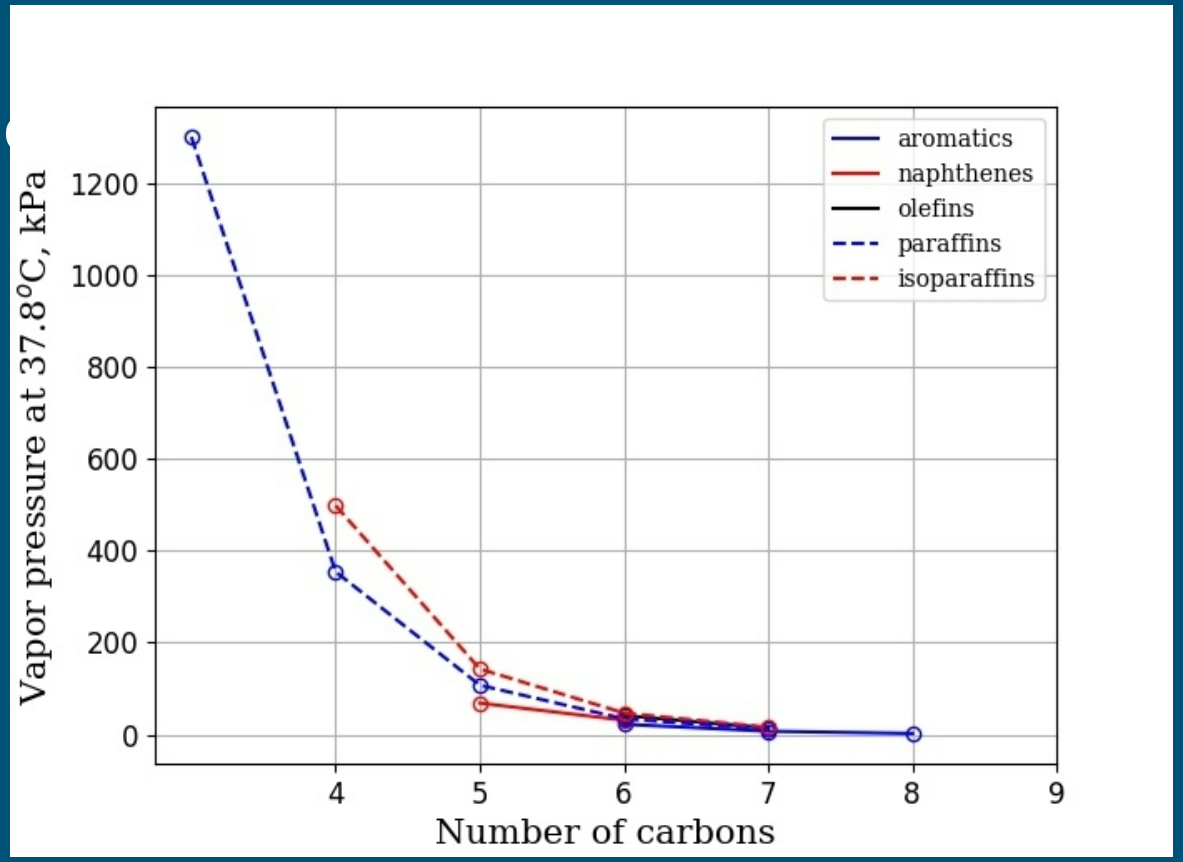


SAFT-γ-Mie is capable of providing very accurate vapor pressure predictions with little computational effort

Approach: models

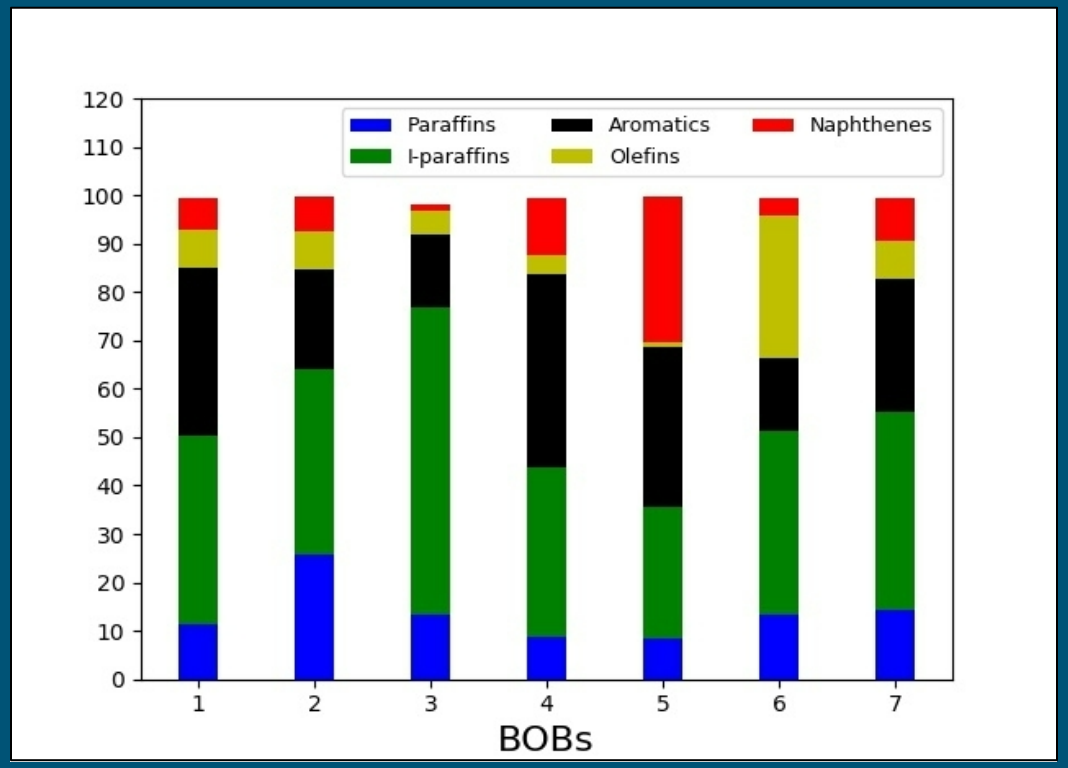
If we include the most important molecules, our RVP predictions should be accurate

- 3 models (small, moderate, large)
- Small: includes all components >= 1 mol%
- Medium: includes all components >= 0.5 m
- Large: n-paraffins => 0.1 mol%
  - Iso-paraffins => 0.1 mol%
  - Aromatics => 1 mol%
  - Naphthenes => 1 mol%
  - Olefins => only one or two of the most important



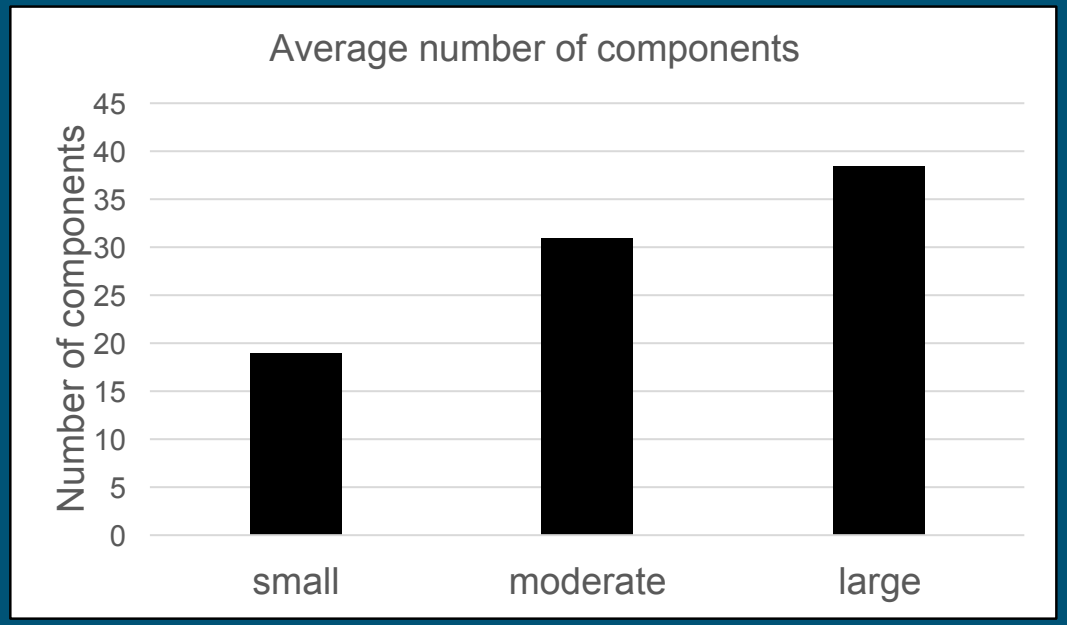
Approach: validation

- 7 BOBs were used for validation.
- Each BOB has
  - Experimentally measured RVP
  - Detailed Hydroc. Analysis (DHA)

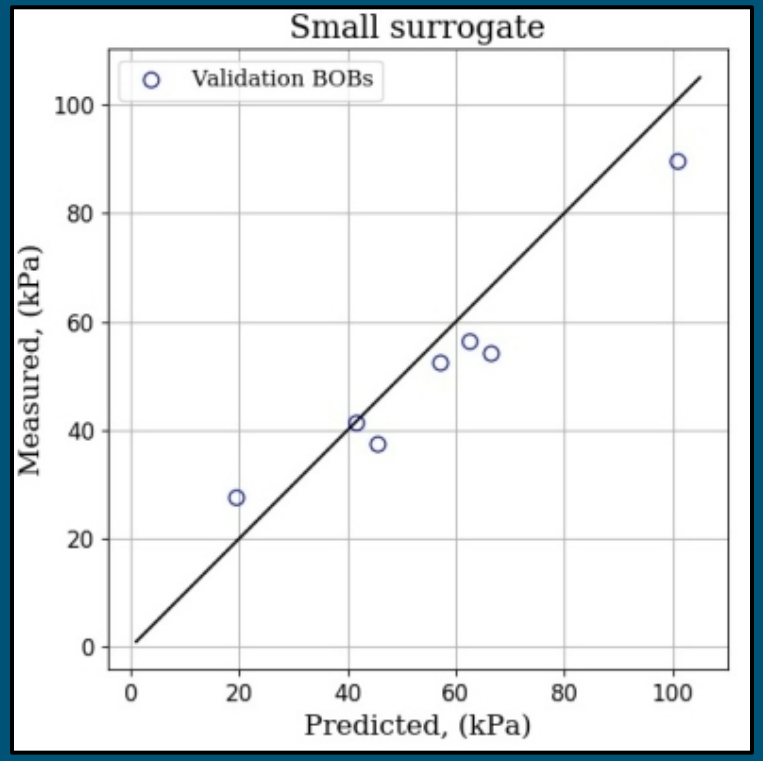


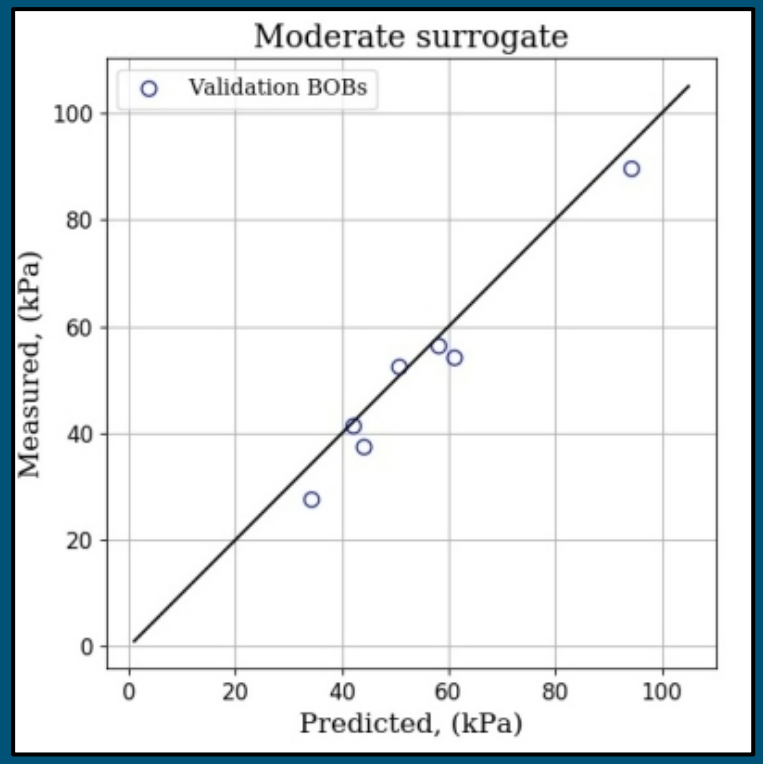
Defining characteristics of the 7 BOBs

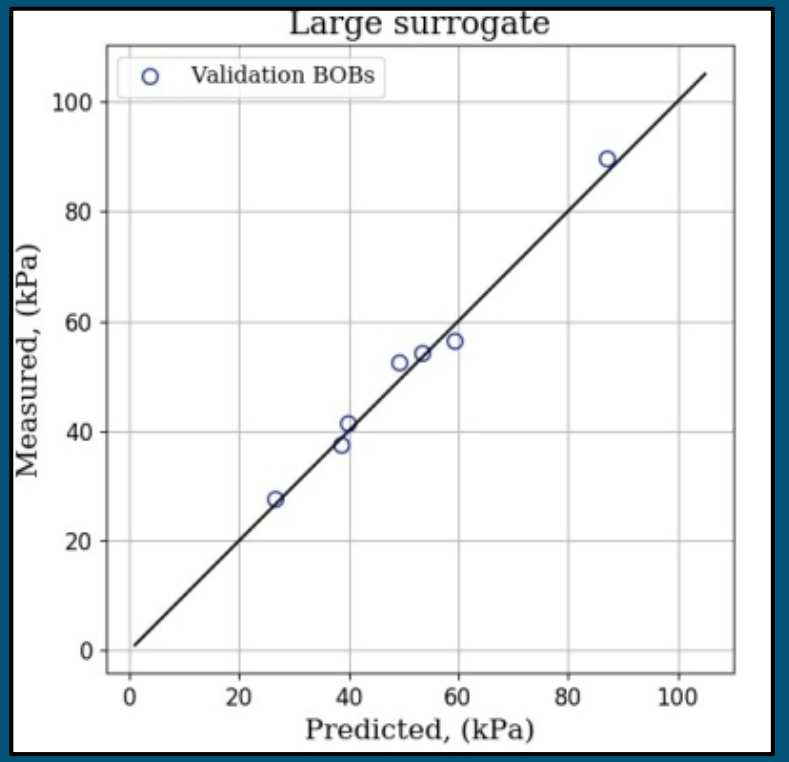
- Strong compositional changes
- n-paraffins range 8.4 to 25.8 mol%
- i-paraffins range 27.2 to 63.4 mol%
- Aromatics range 14.9 to 39.8 mol%
- Olefins range 0.9 to 29.7 mol%
- Naphthenes range 1.5 to 30 mol%
- RVP range 27.6 – 89.7 kPa



Results: Non-oxygenates



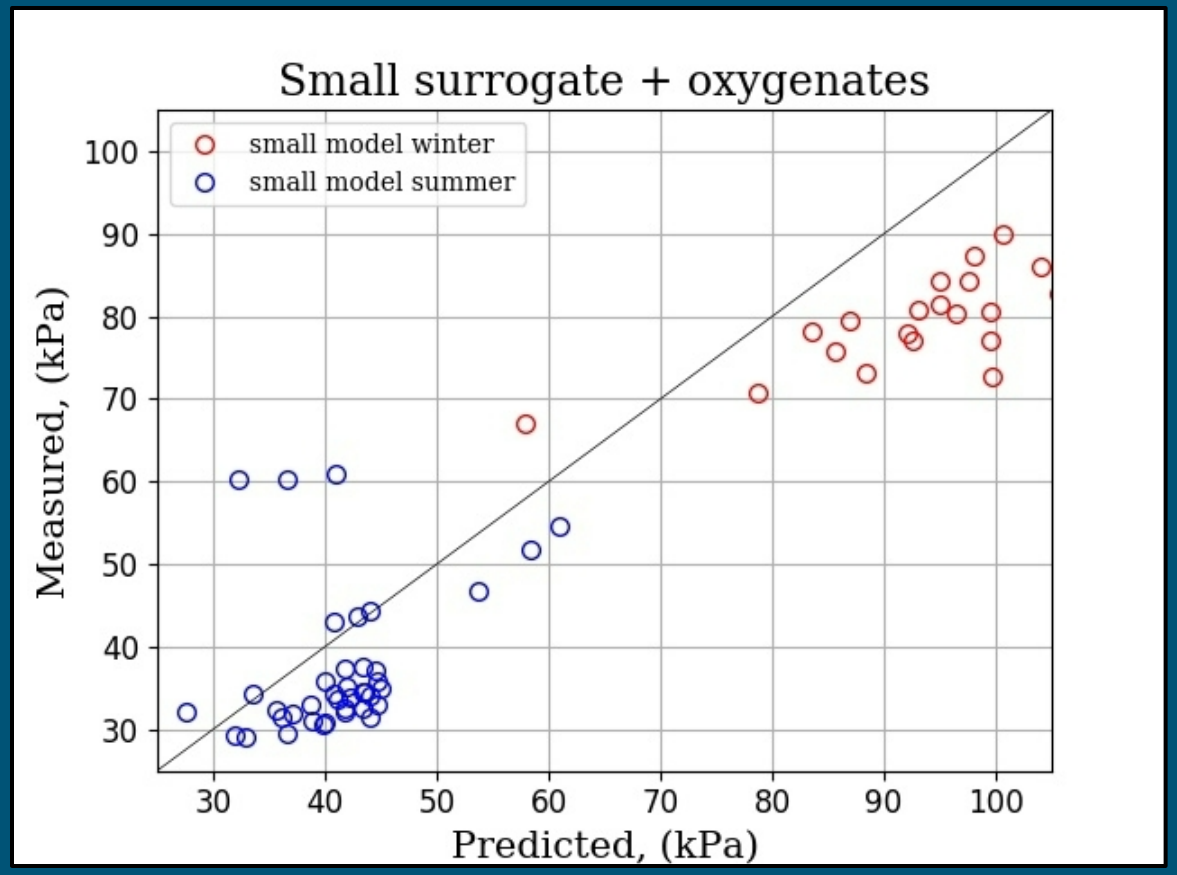




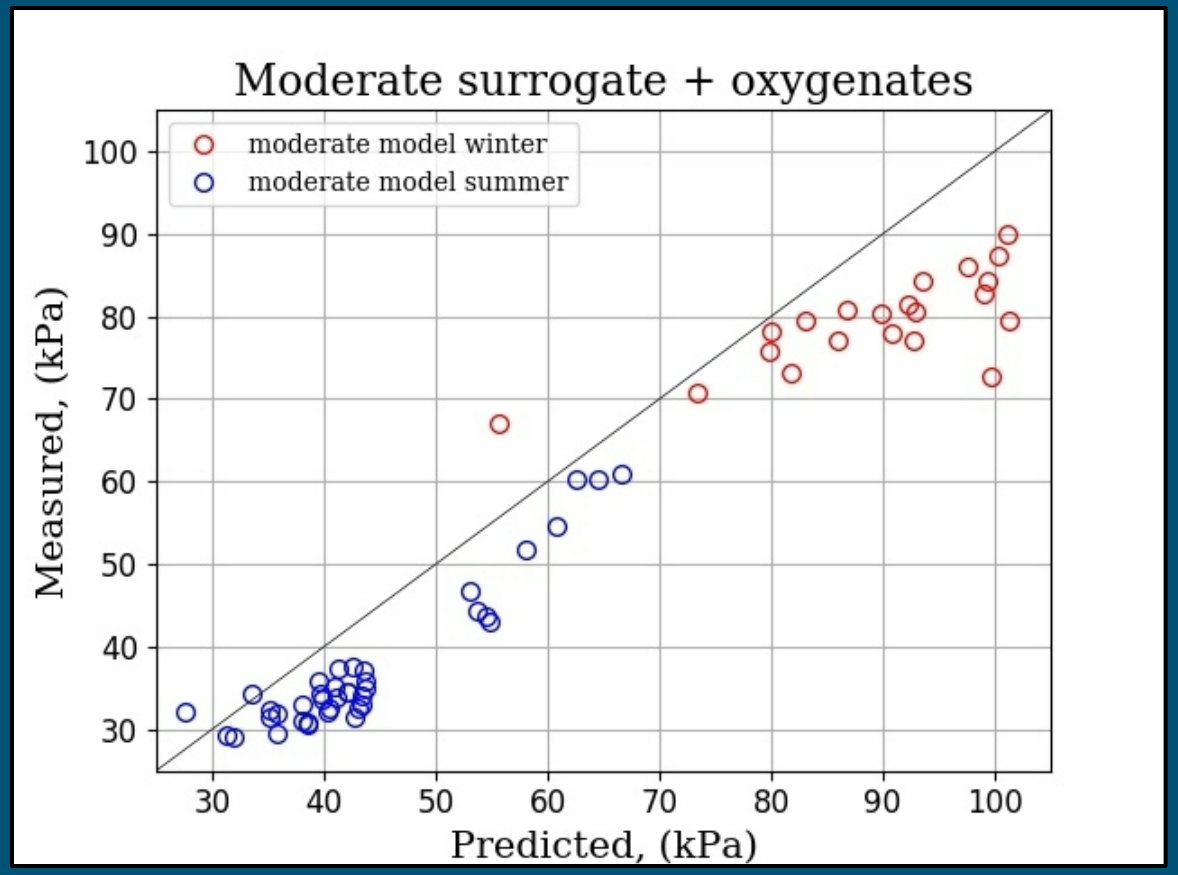
	Small	Moderate	Large	Measured
BOB 1	45.41	44.06	37.54	37.43
BOB 2	100.91	94.13	87.19	89.71
BOB 3	19.46	34.08	26.66	27.64
BOB 4	57.05	50.57	49.16	52.46
BOB 5	66.32	60.95	53.49	54.16
BOB 6	41.61	42.05	39.86	41.45
BOB 7	62.48	58.09	59.23	56.44
%AAD	15.09	9.49	3.28	

AD = 1.71 kPa
ASTM D5482-07 (14-100 kPa)
Repeatability = 2.69-4.14 kPa

Results: Oxygenates



Summer %AAD = 19.72
Winter %AAD = 15.50

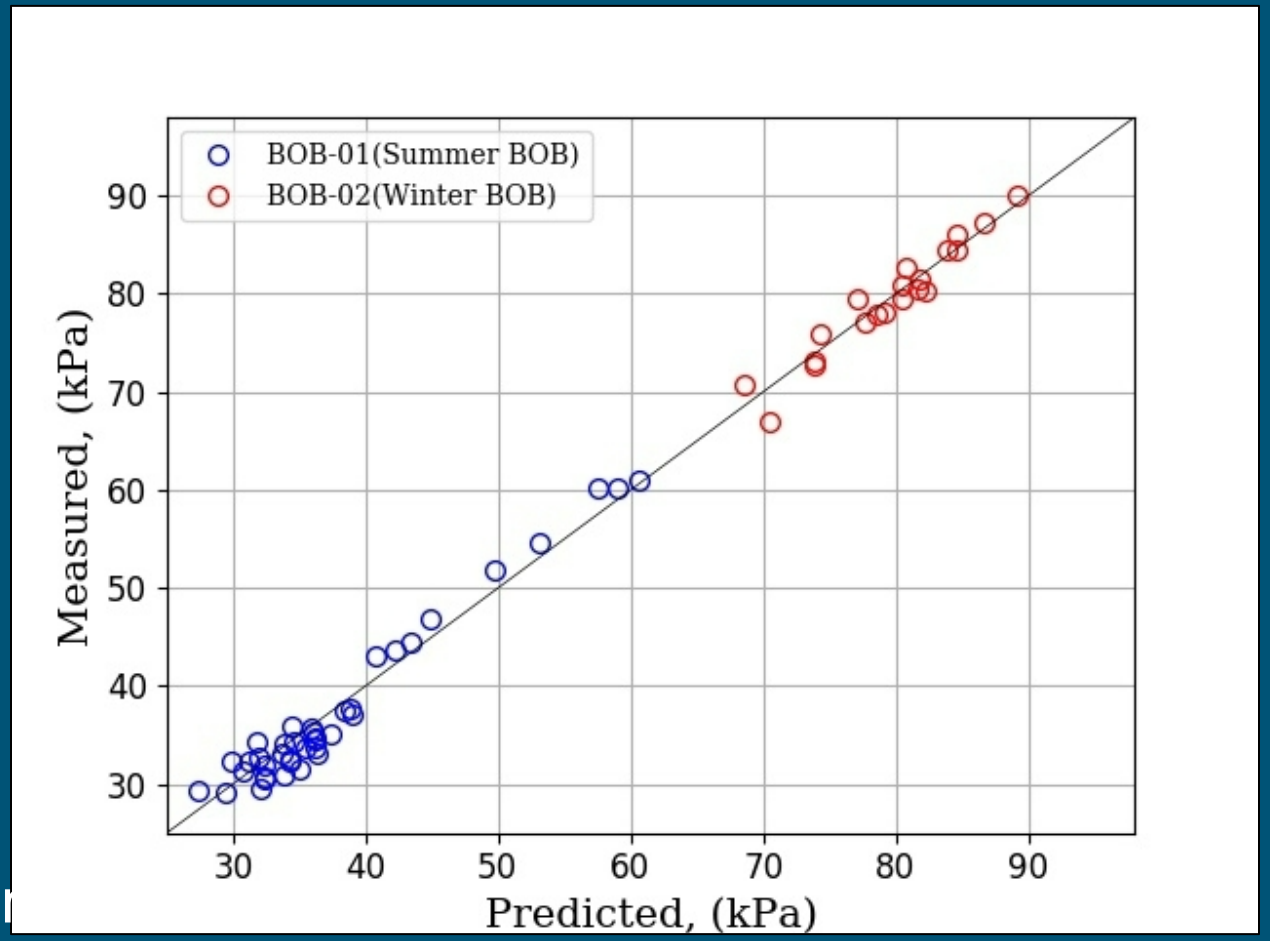


Summer %AAD = 14.90
Winter %AAD = 12.16

Results: Oxygenates: Cont.

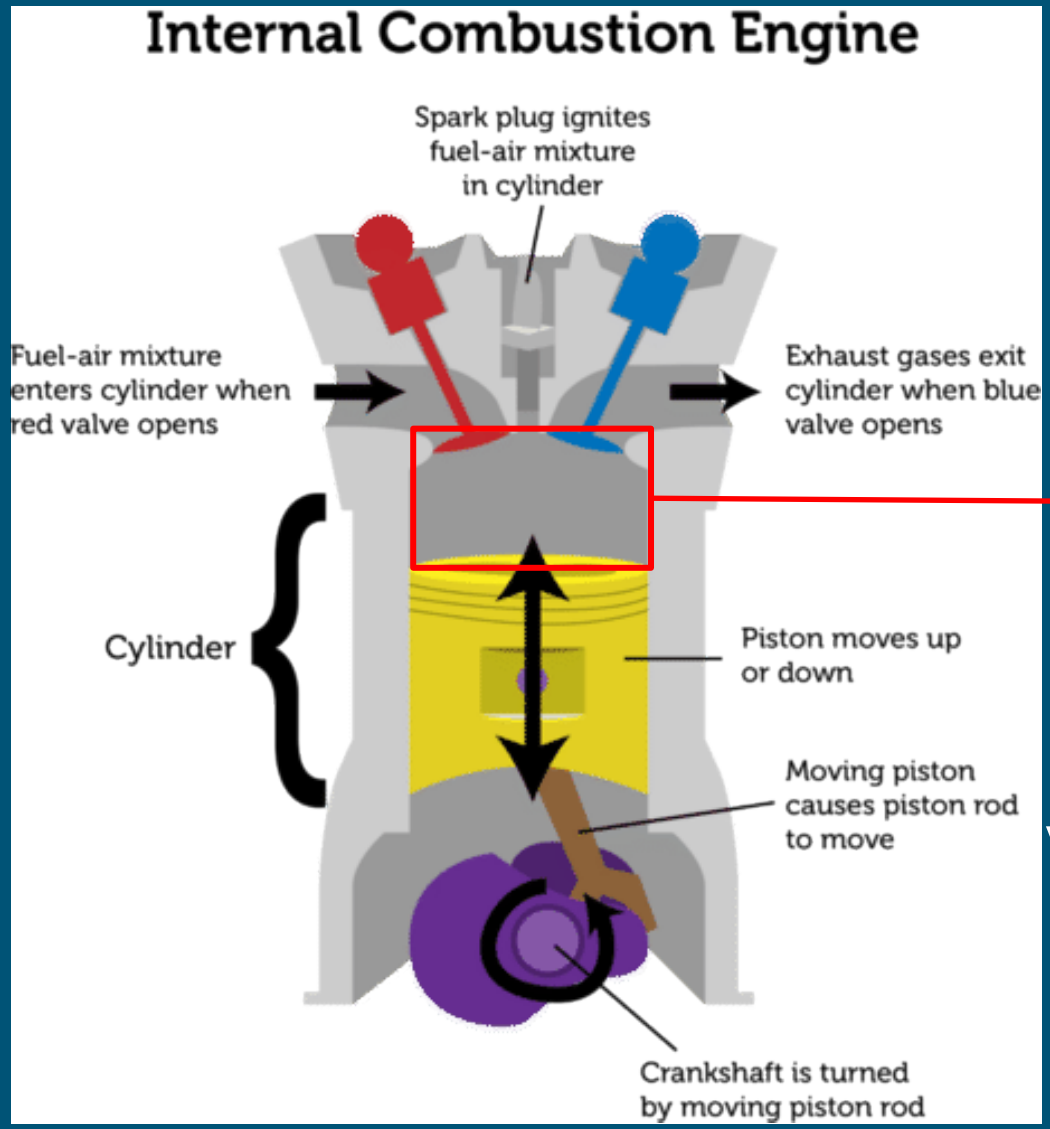
Data includes (10, 20, 30% by vol)

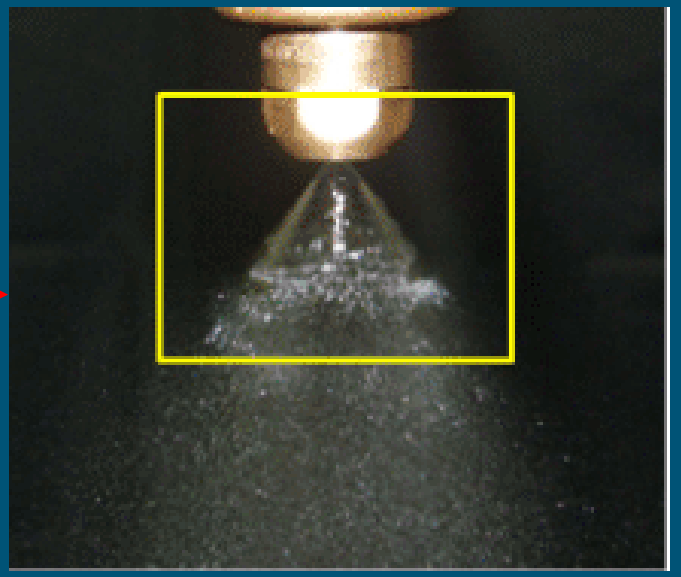
- Alcohols
  - Methanol, ethanol, 1-butanol, 2-butanol, n-propanol, isobutanol, 2-methyl-1-butanol, 2-pentanol, 3-methyl-1-butanol
- Esters
  - Butyl acetate, methyl acetate, ethyl acetate, isopropyl acetate
- Ketones
  - Cyclopentanone, 2-pentanone, 2,4-dimethyl-3-pentanon
- Aromatics
  - Anisole



Summer %AAD = 4.40
Winter %AAD = 1.55
Overall AD = 1.45 kPa

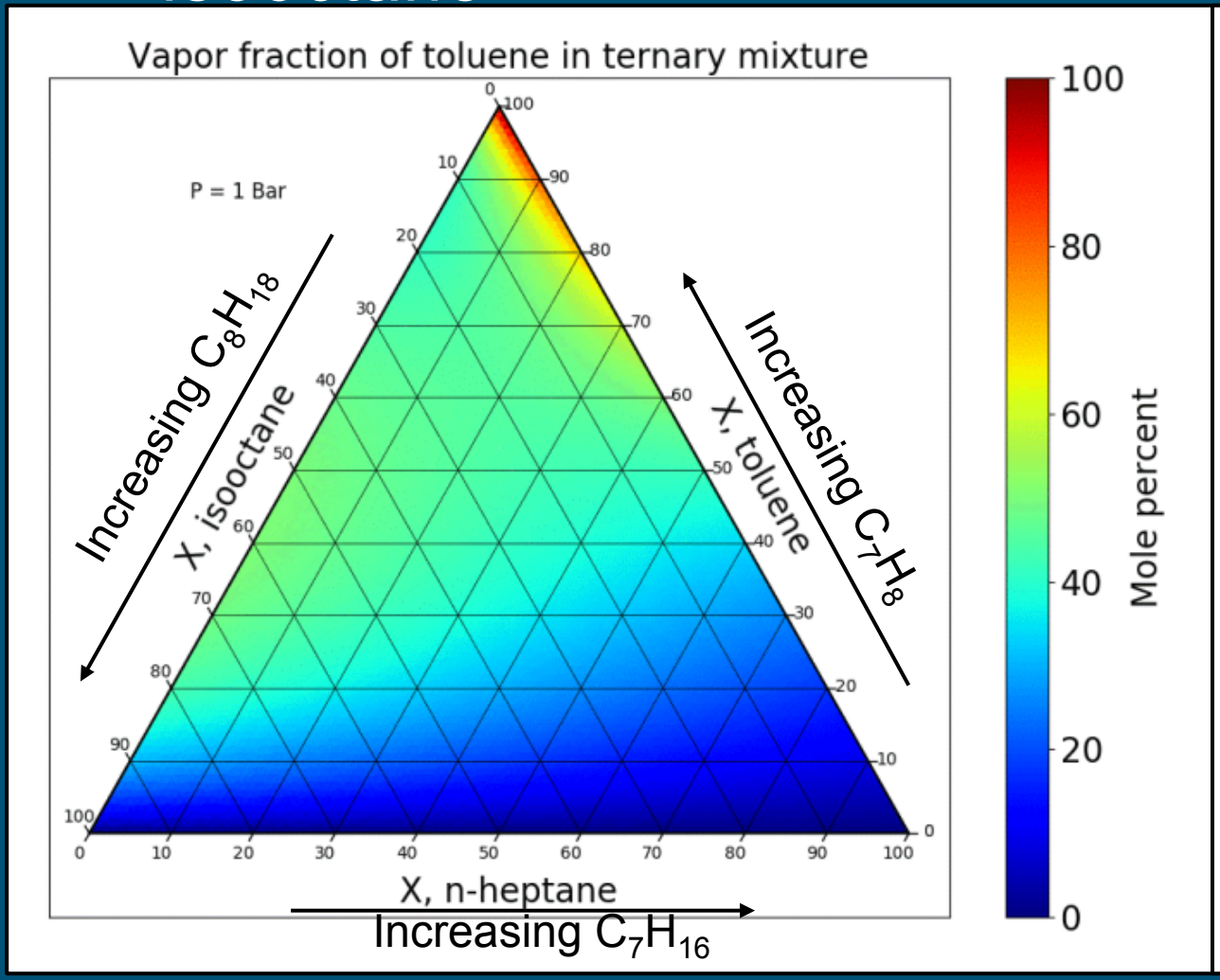
Differential evaporation (multimode engine)

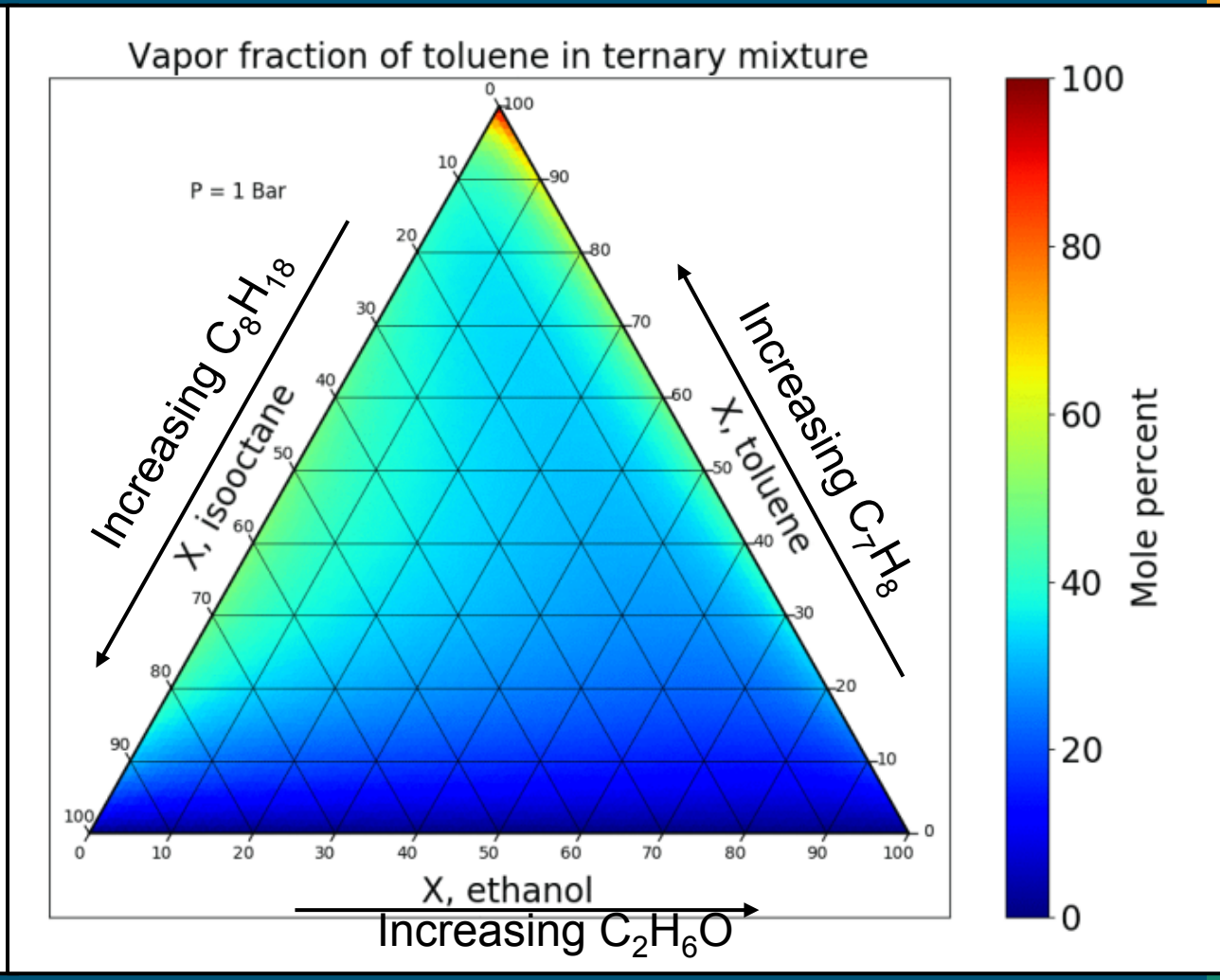




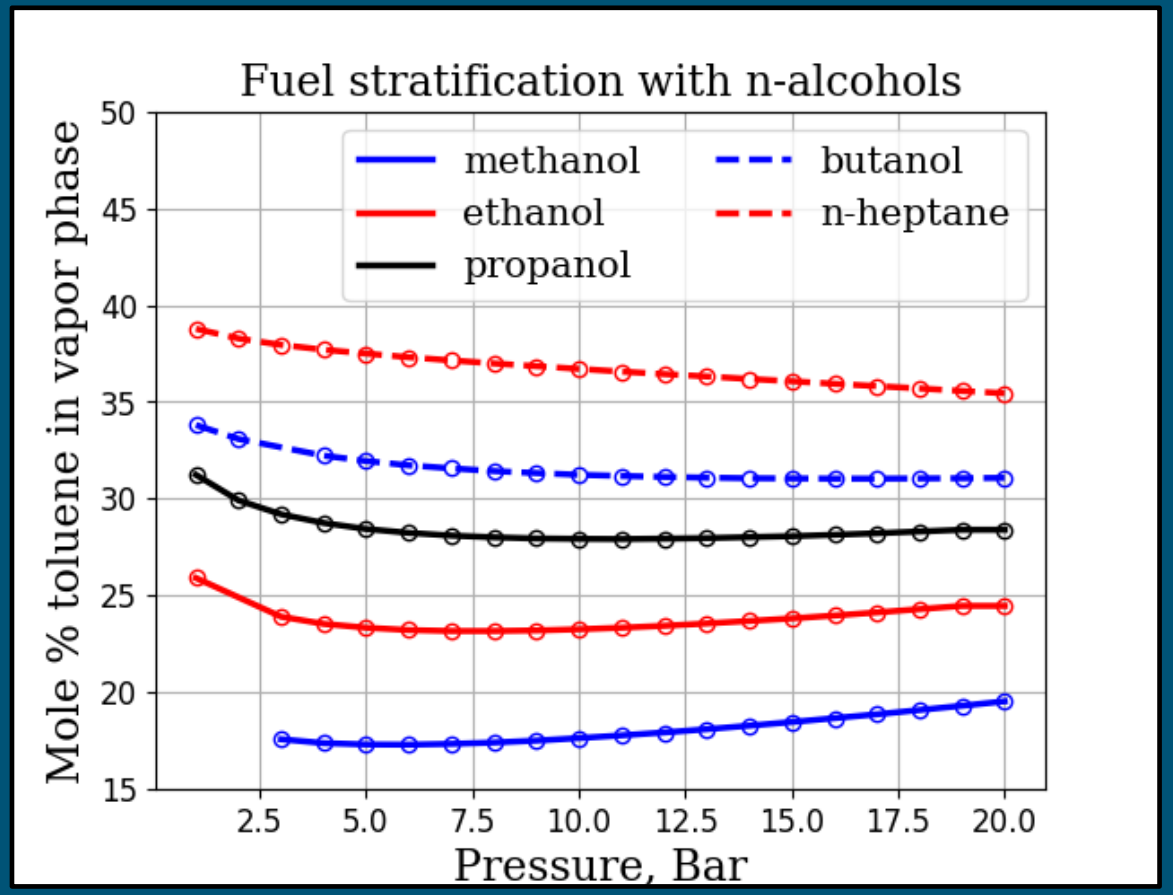
Vaporization characteristics greatly affect soot production !!!

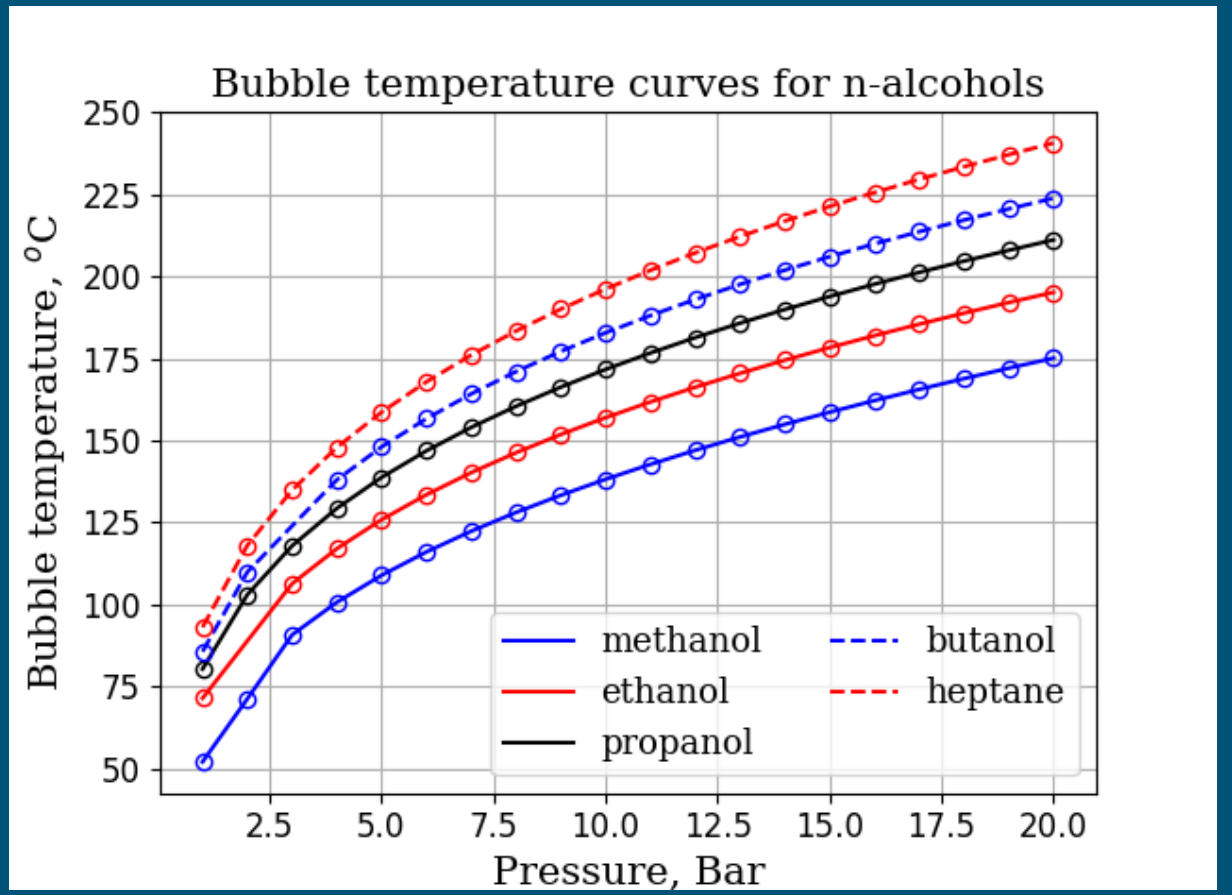
N-heptane, toluene, isooctane vs. ethanol, toluene, isooctane





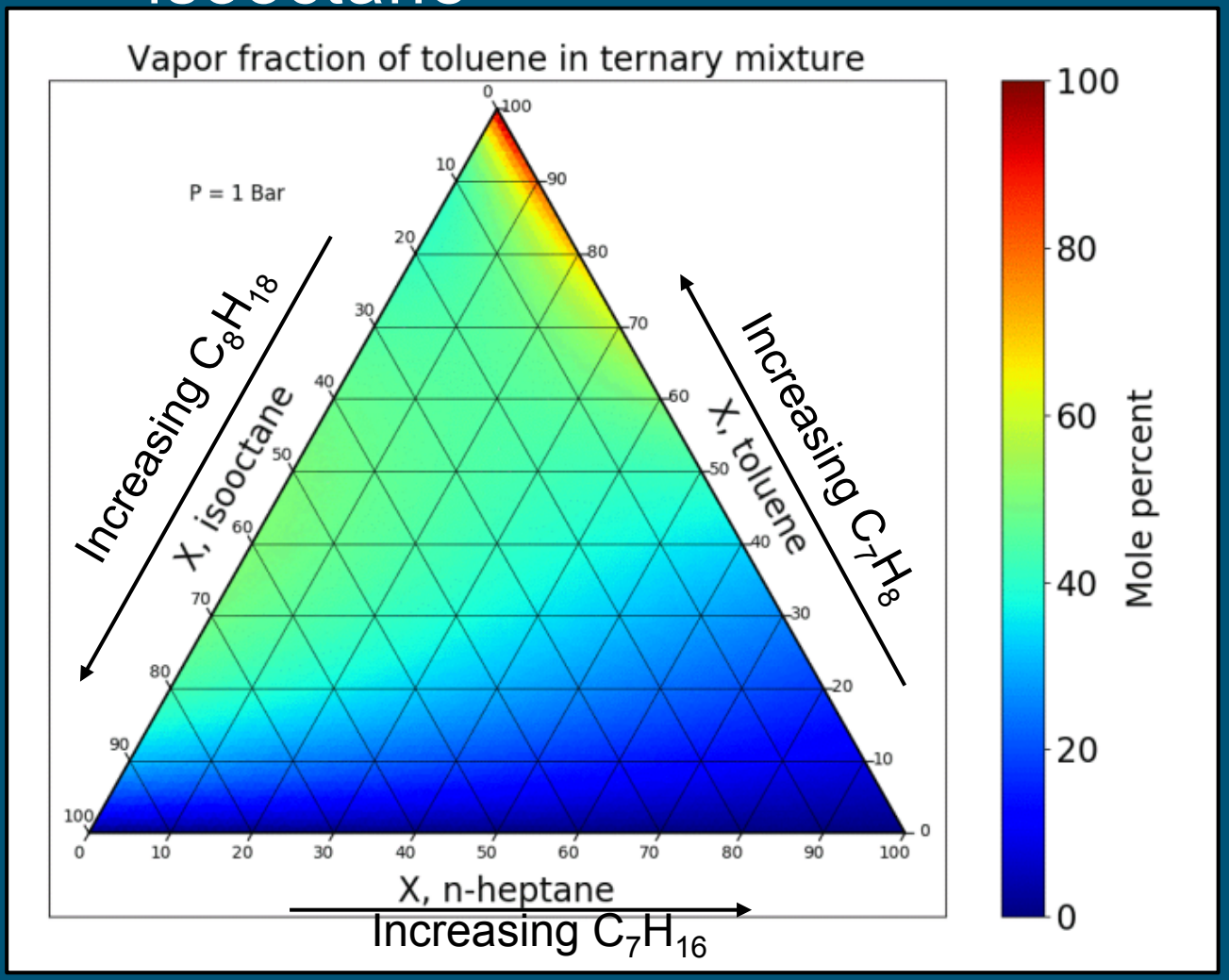
VLE results 1:1:1- isooctane : toluene : n-alcohol

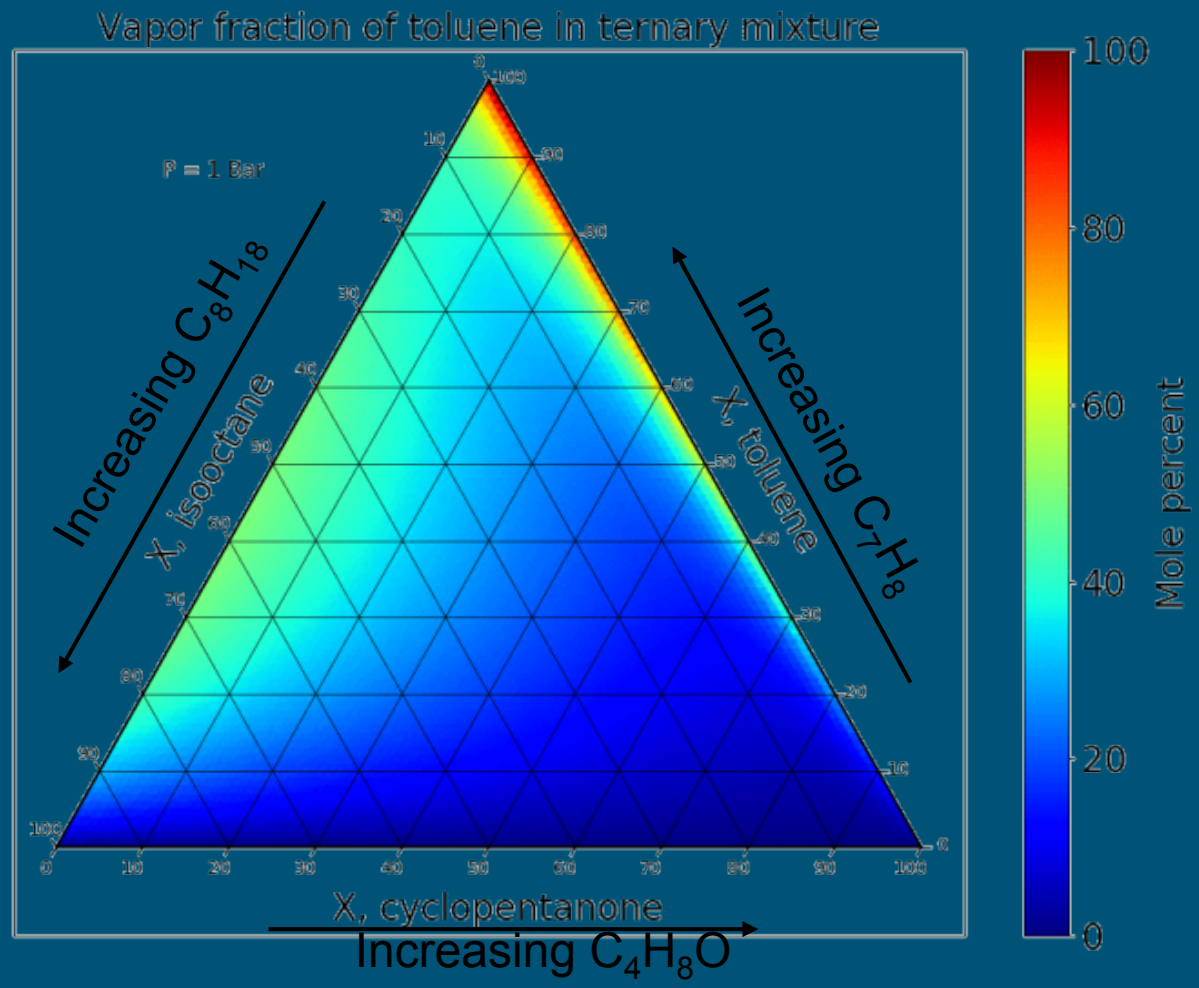




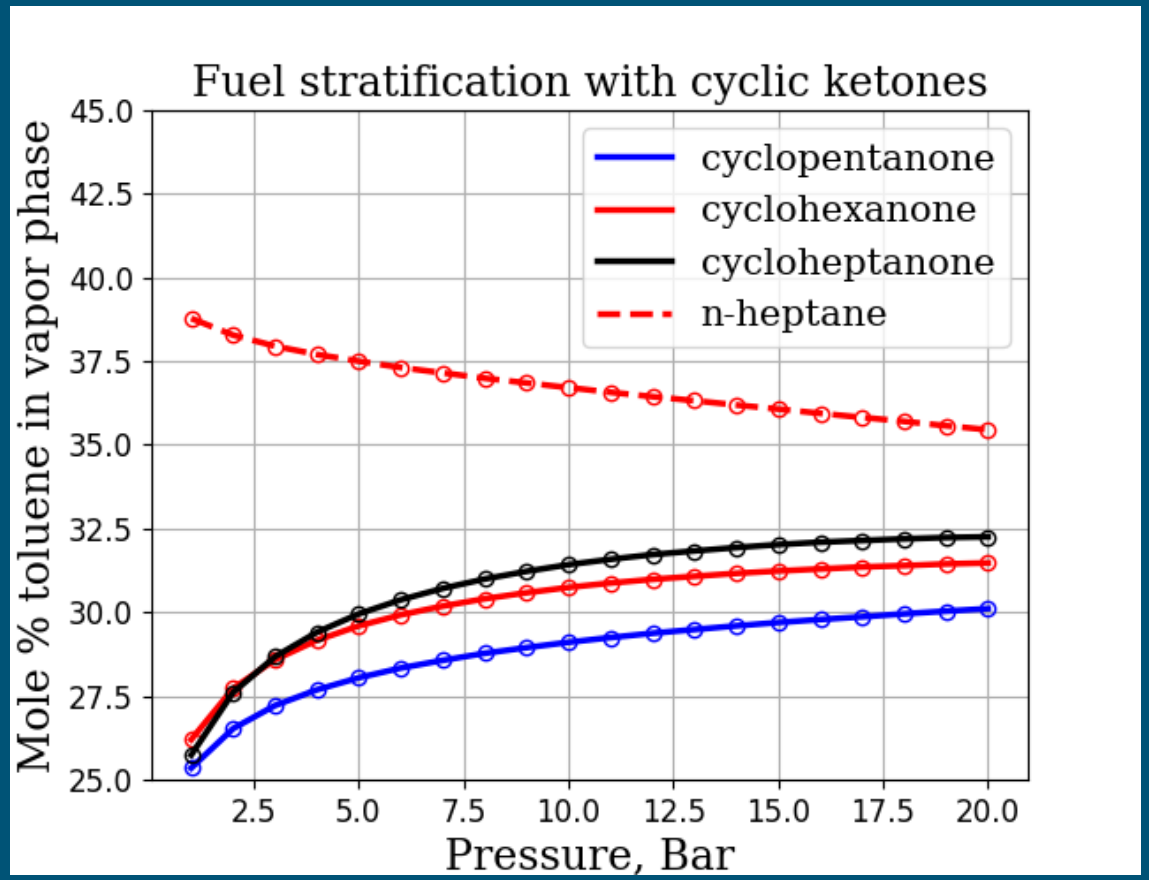
Differences in Bubble temperature curve are sufficient to explain fuel stratification

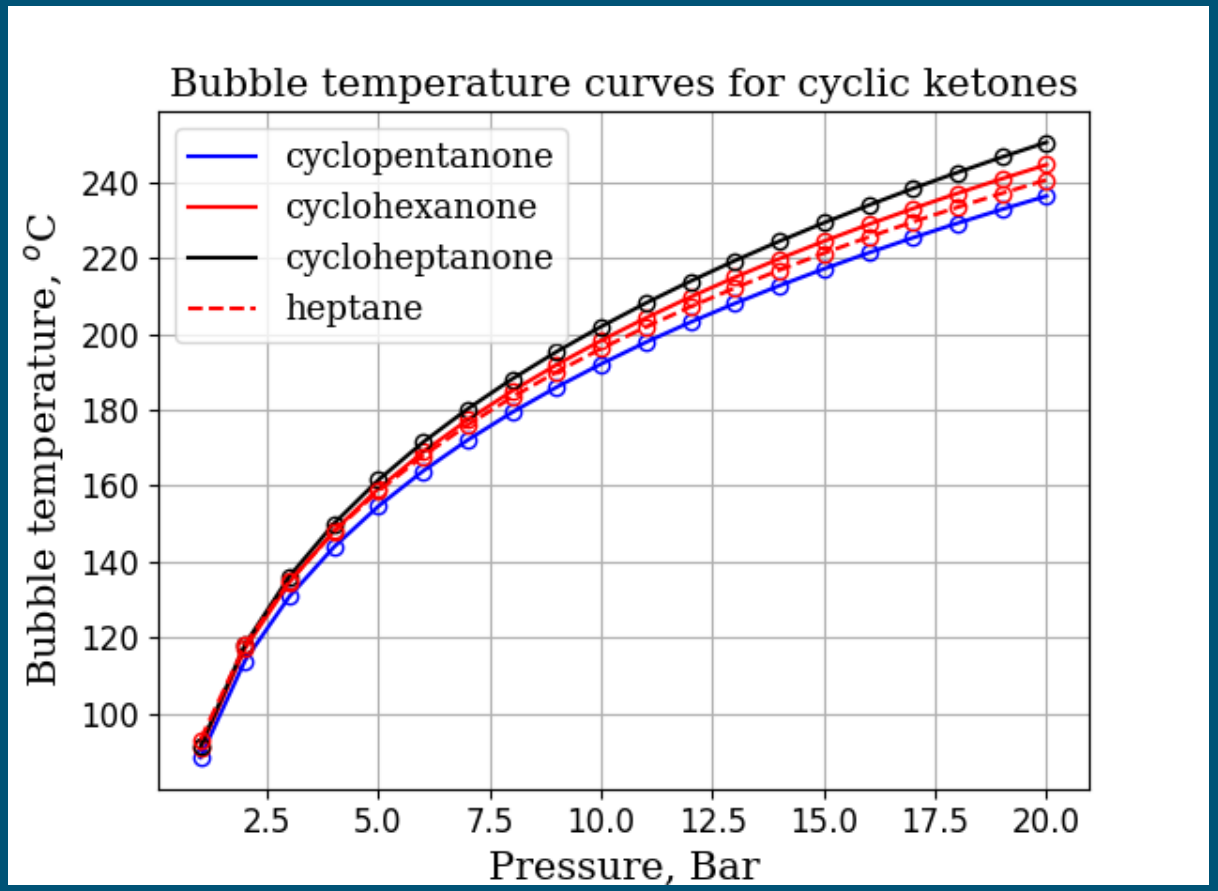
N-heptane, toluene, isooctane vs. cyclopentanone, toluene, isooctane





VLE results 1:1:1- isooctane : toluene : cyclic ketones





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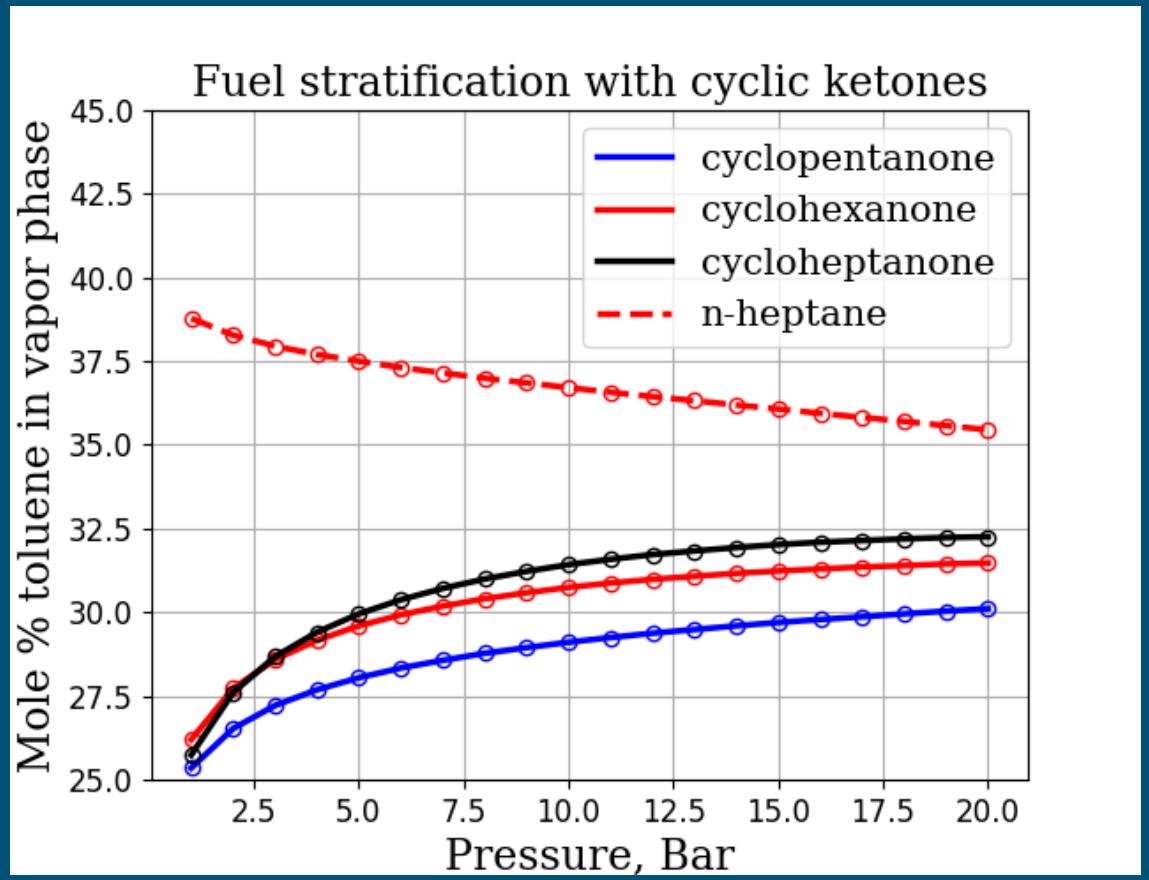
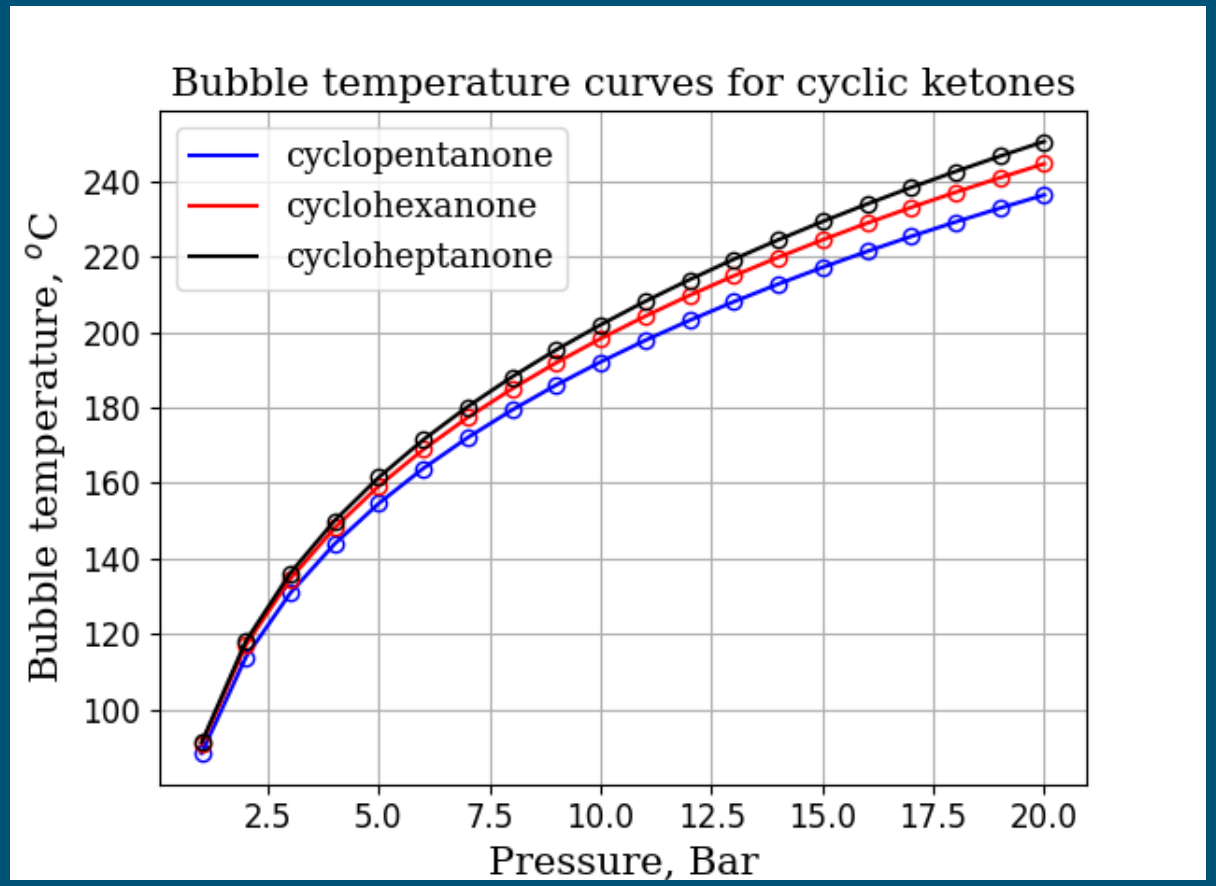
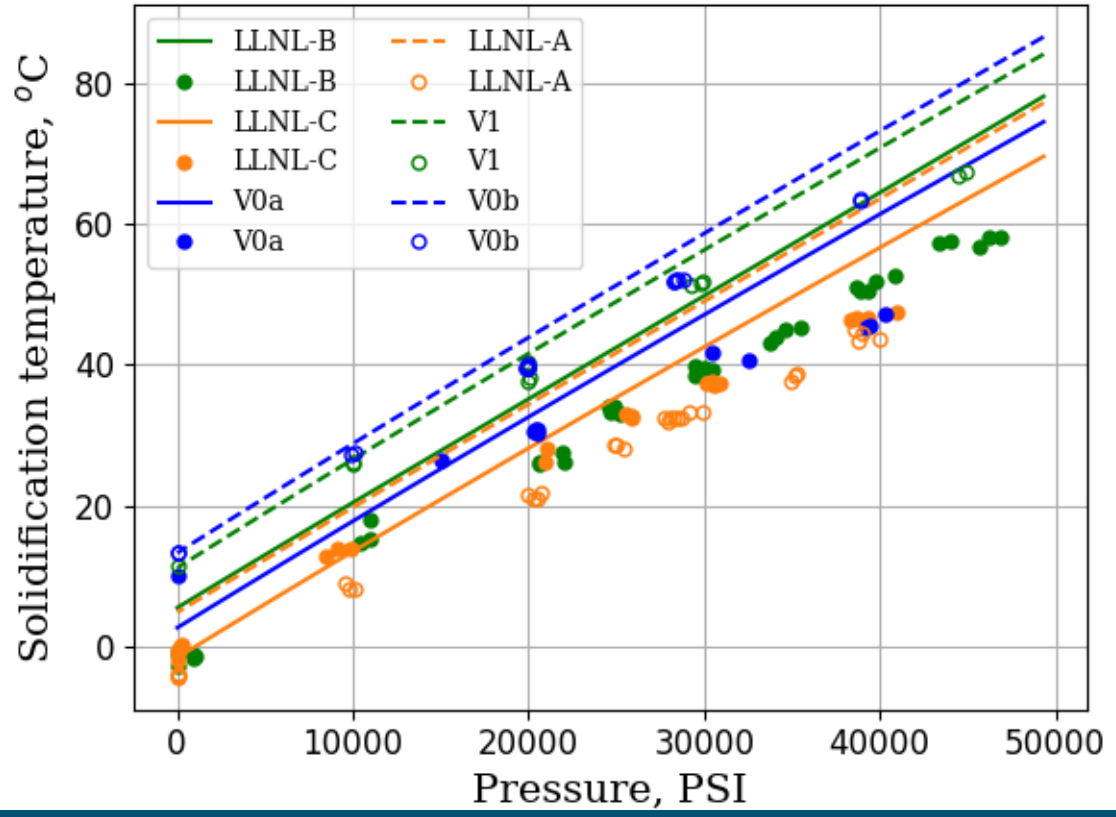


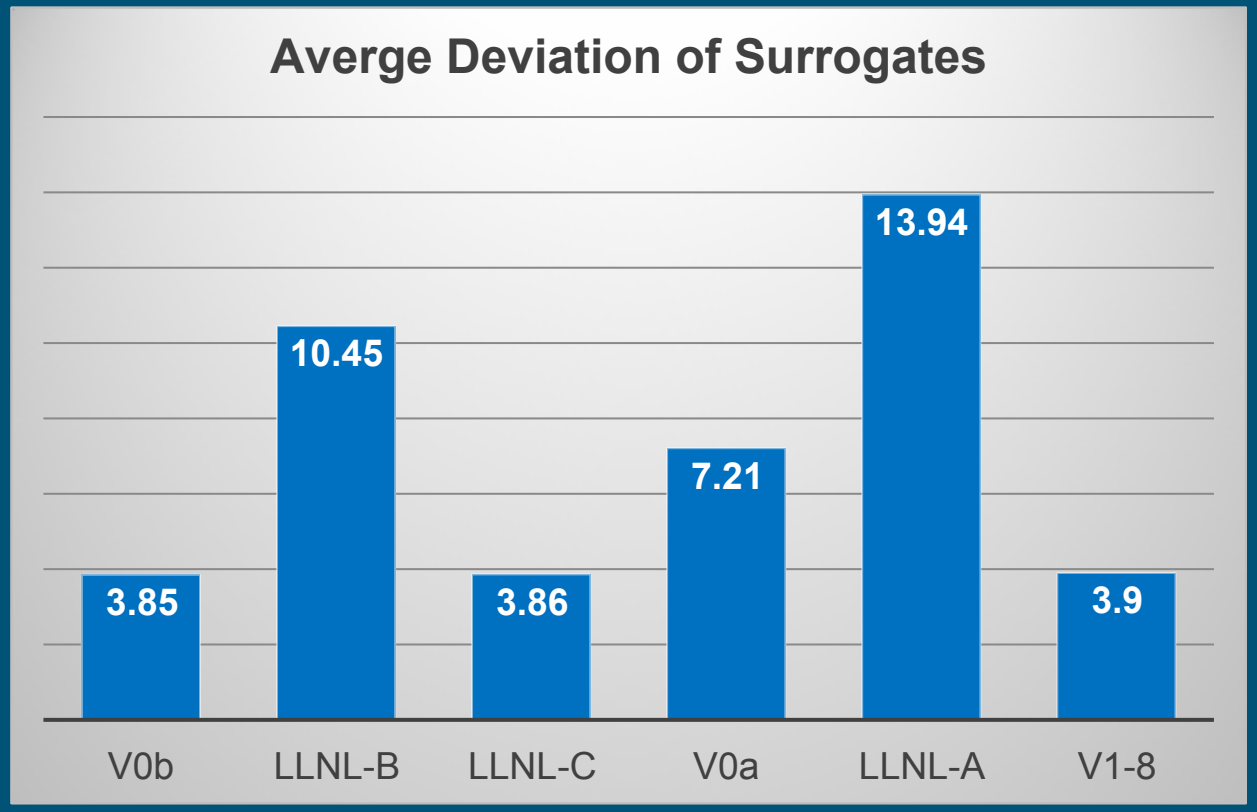


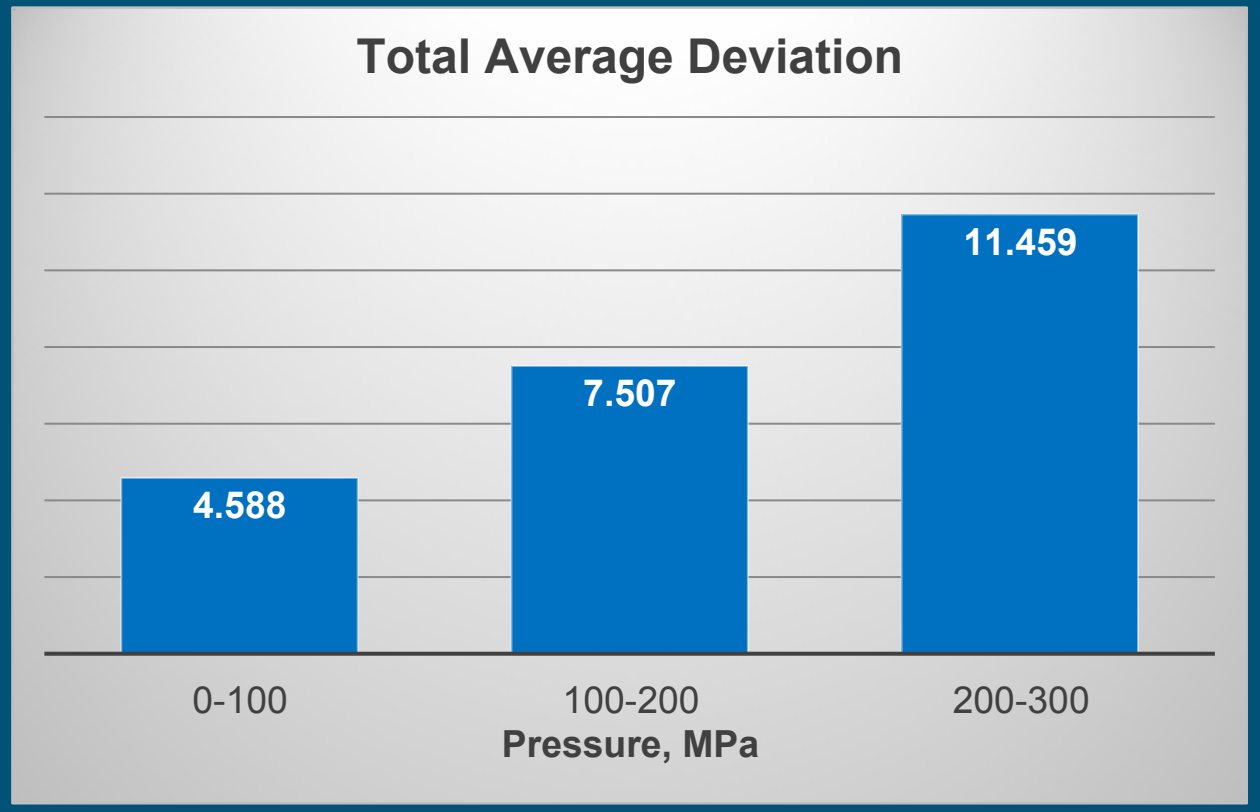
Solidification of MCCI fuels



Compound Name	V0a	V0b	V1	V2	LLNL-A	LLNL-B	LLNL-C
n-hexadecane	27.80		2.70		13.90	13.70	16.61
n-octadecane		23.50	20.20	10.80	3.26	3.51	
n-eicosane				0.80	3.02	3.51	
heptamethylnonane	36.30	27.00	29.20		19.10	20.31	19.00
2-methylheptadecane				7.30			
n-butylcyclohexane			5.10	19.10		7.22	10.50
1,3,5-triisopropylcyclohexane				11.00			
trans-decalin	14.80		5.50			20.07	20.08
cis/trans decalin mixture					29.70		
perhydrophenanthrene				6.00			
1,2,4-trimethylbenzene		12.50	7.50				
1,3,5-triisopropylbenzene				14.70			
n-dodecylbenzene							7.64
tetralin		20.90	15.40	16.40	16.00	13.95	13.78
1-methylnaphthalene	21.10	16.10	14.40	13.90	15.10	17.72	12.39

Average deviations





Summary

- EoS methods have been used to successfully model the RVP of fuels
  - Dependent on the availability of a DHA
  - Accuracy of model is better than currently available ASTM
- EoS methods have been used to determine the gas phase composition of a ternar
  - Low molecular weight oxygenates evaporate off before aromatics can
  - As pressure increases, aromatic volatility is inhibitied => engine cylinder impinc
- EoS methods have been used to accurately model the solidification temperature of MCCI fuels as a function of pressure

This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) Project sponsored by the Bioenergy Technologies and Vehicle Technologies Offices, Office of Energy Efficiency and Renewable Energy (EERE), U.S. Department of Energy (DOE). Co-optima is a collaborative project of multiple national laboratories initiated to simultaneously accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell a Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525