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Development of robust models for the prediction of Reid Vapor Pressure (RVP) in fuel blends and their application to oxygenated fuels

PRESENTED BY

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Reid Vapor Pressure (RVP)

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

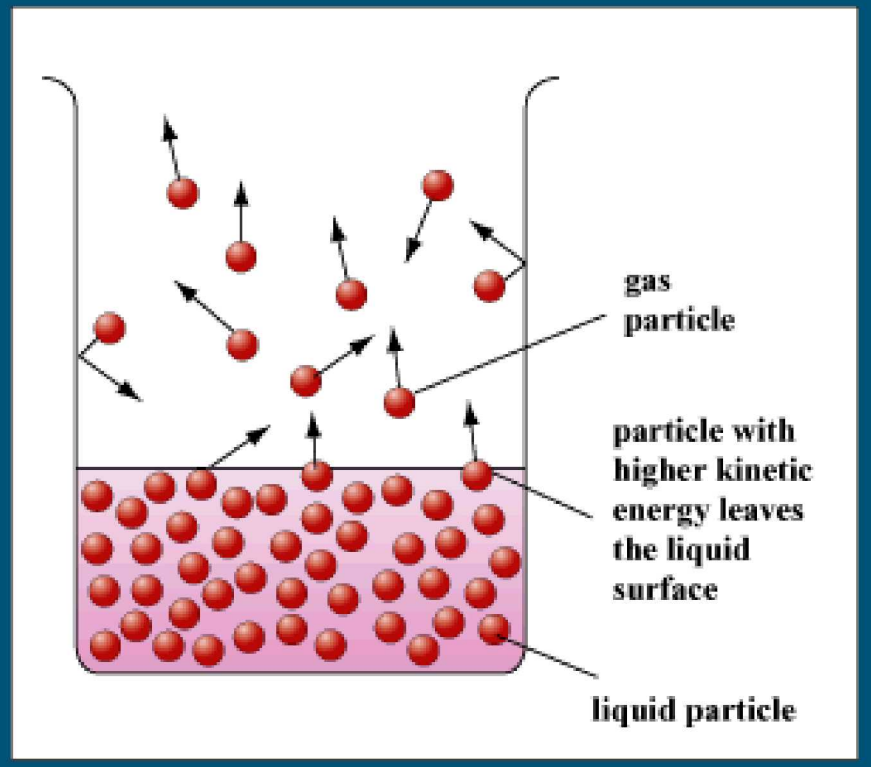
- Caused by molecular collisions
- Causes liquid molecules to ‘escape’ into the atmosphere

In the petroleum industry, a special vapor pressure metric exists

- Vapor pressure is measured at 37.8^{o}C (100^{o}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



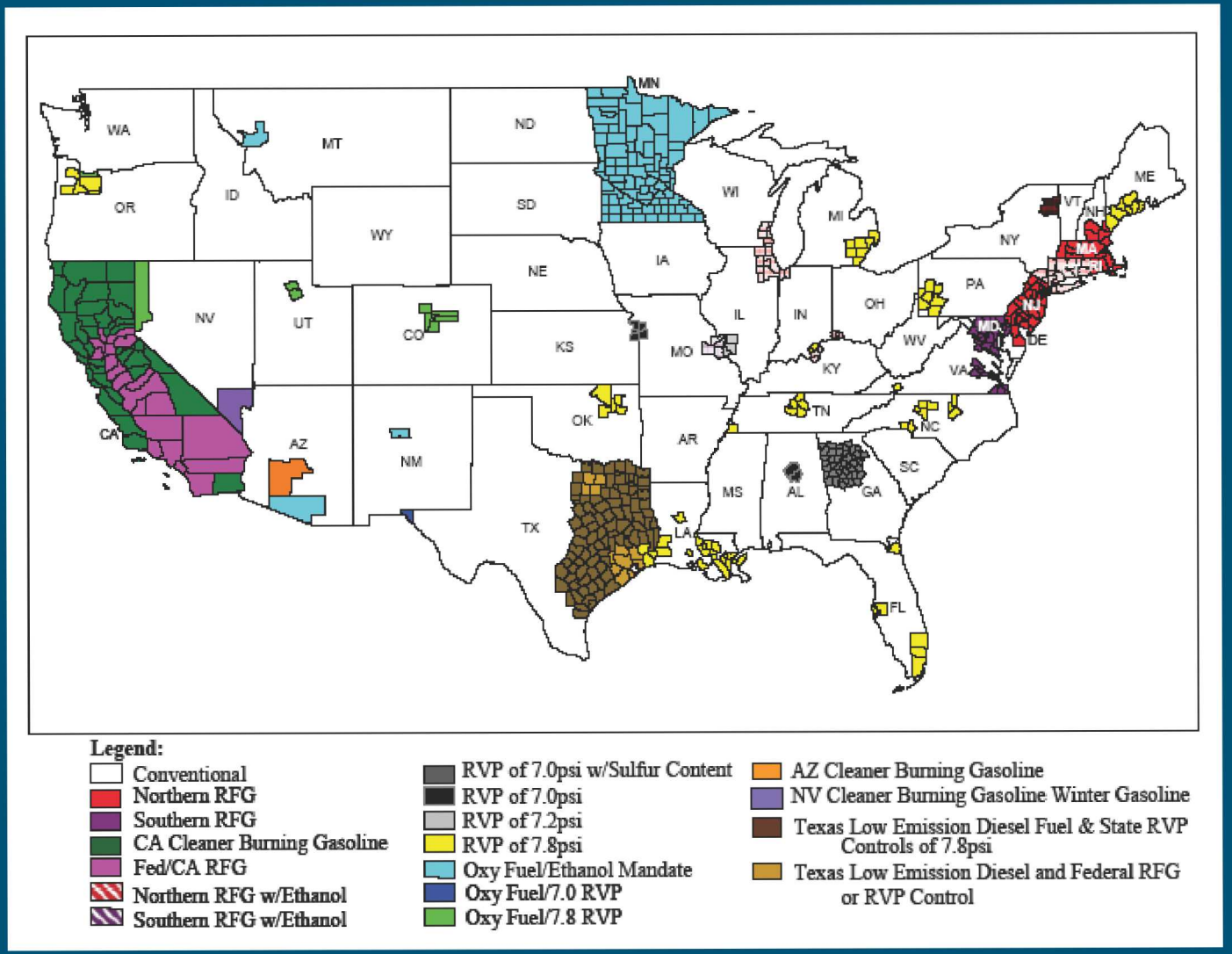
RVP regulation

Regulation

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

Higher RVP fuels lead to larger emissions

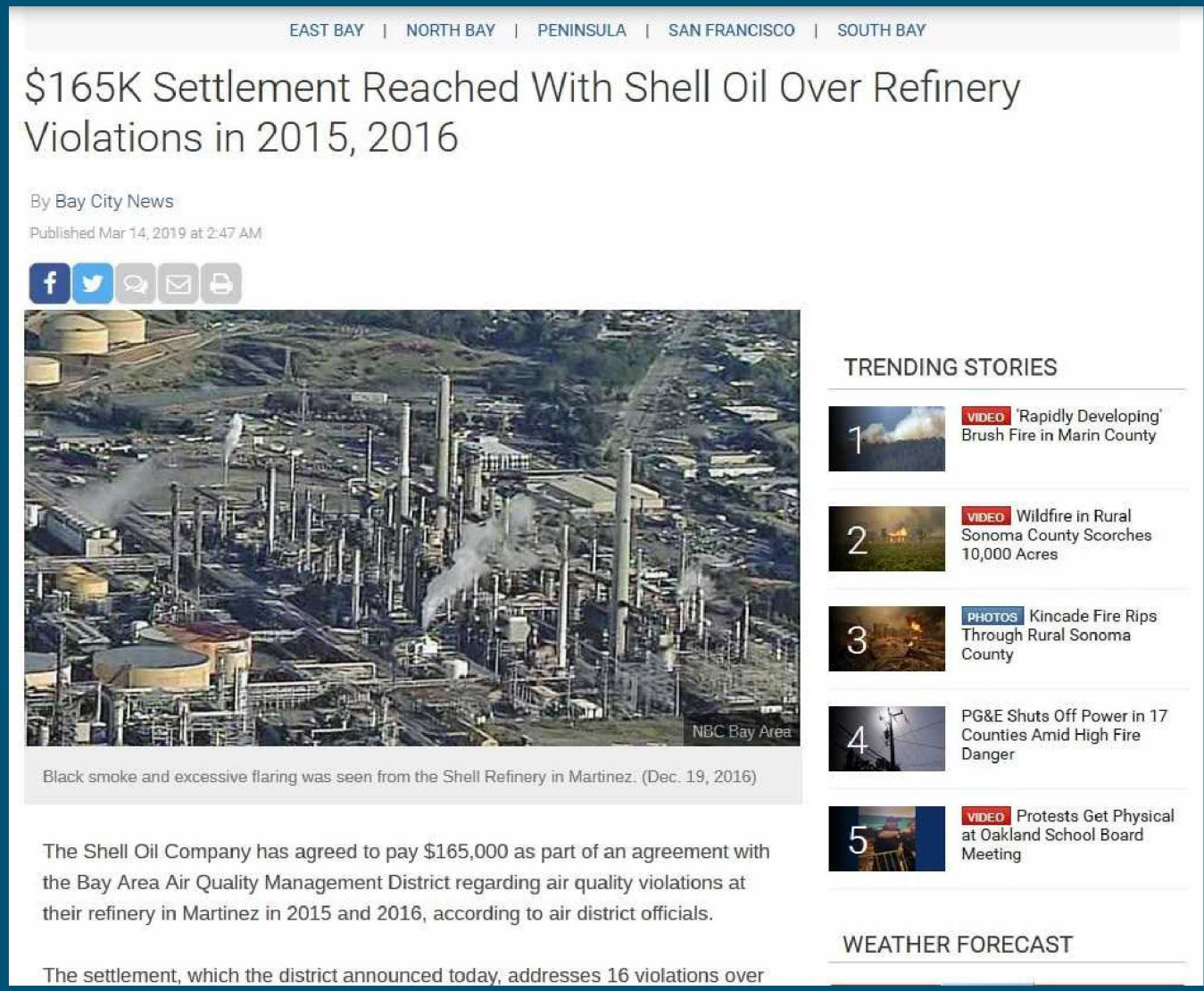
- Human health impacts
- ↑ GHG emissions



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 barrel)

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)

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

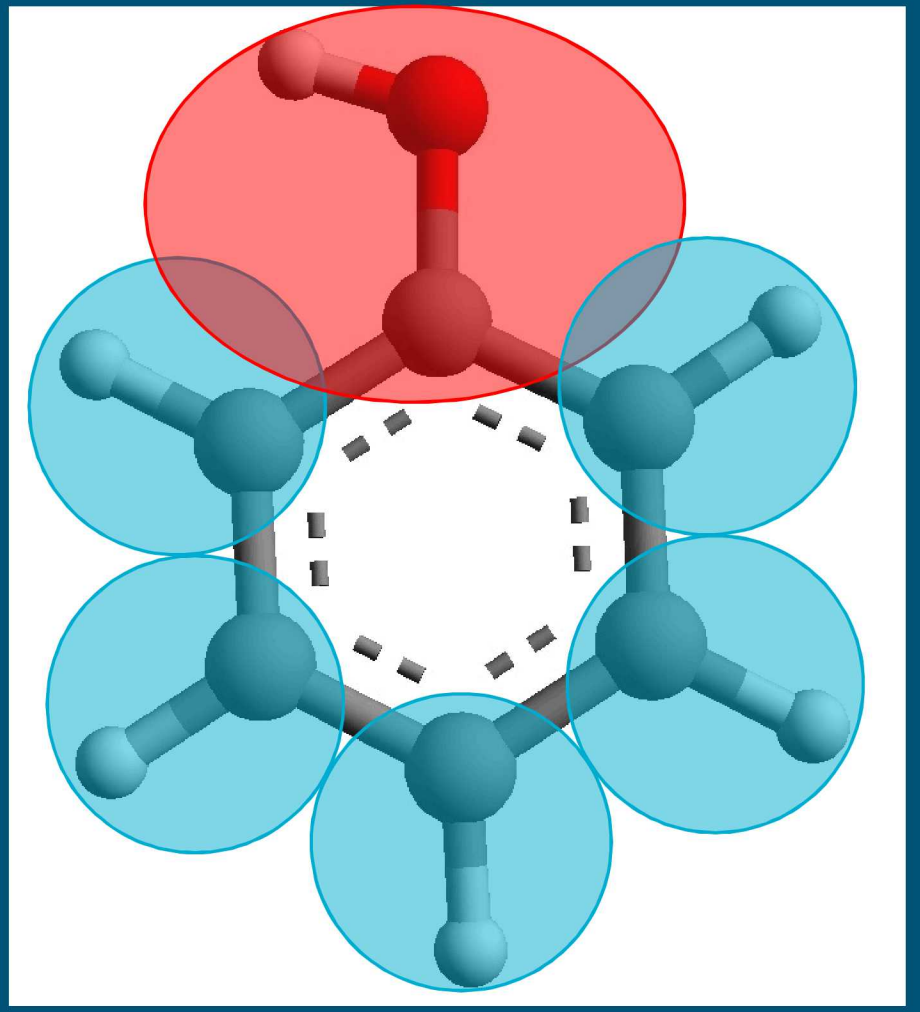
- A^{ideal} => statistical mechanics
- All other terms are perturbations meant to improve qualitative nature of A^{ideal}

Mie function

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

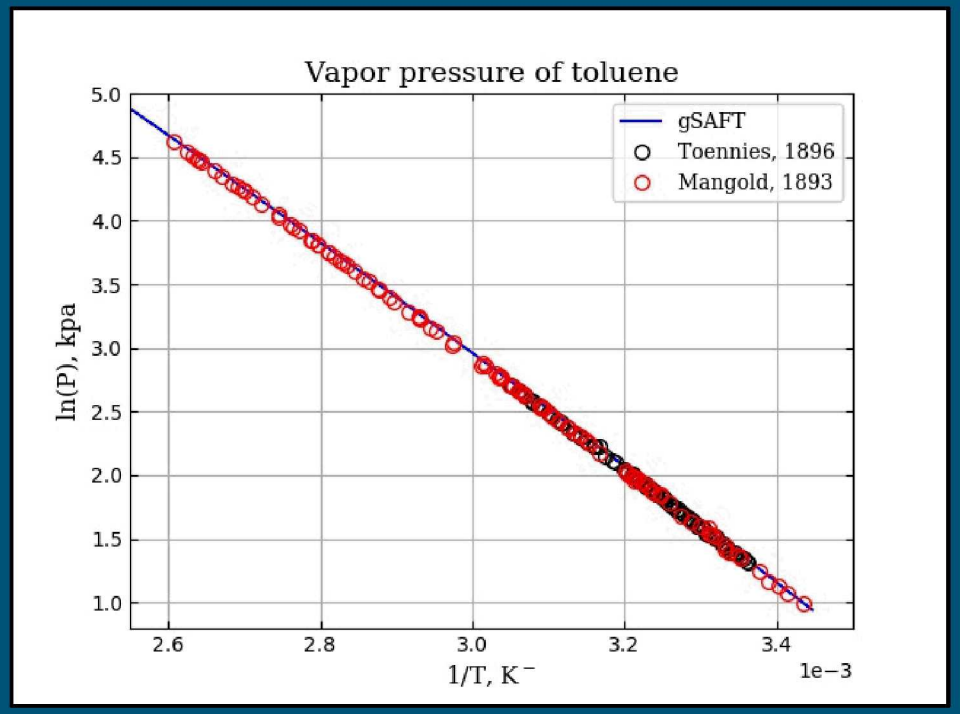
Each group is described by a Mie function, and those Mie functions interact with each other to approximate the Helmholtz free energy

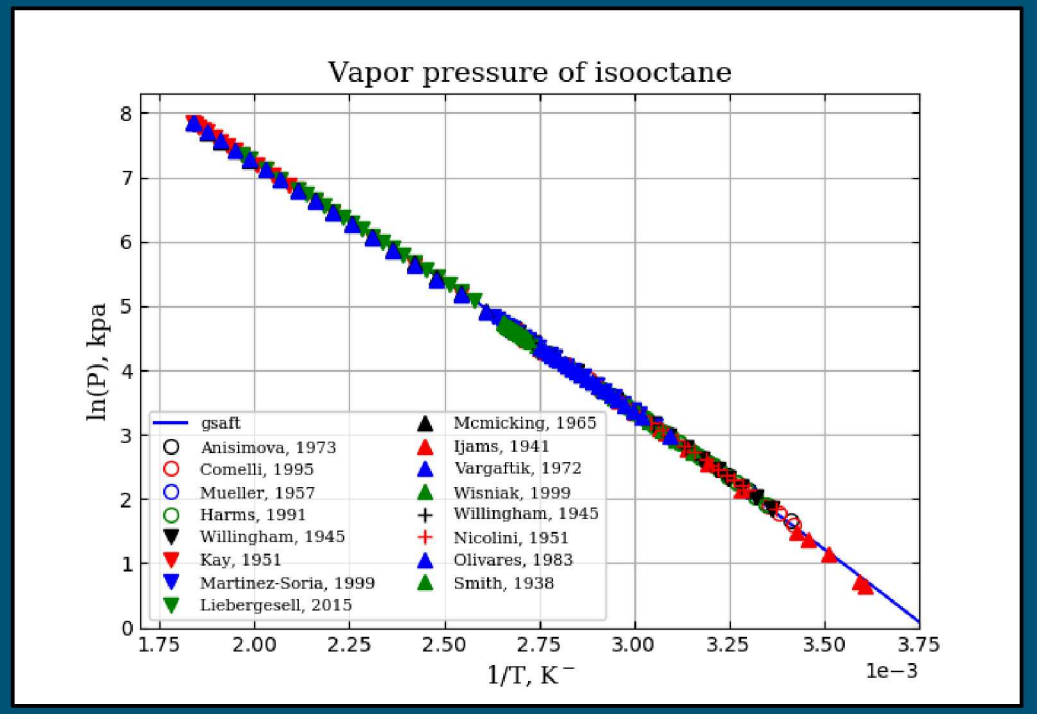
$$P = \frac{\partial A}{\partial V}$$



The secondary structure is not considered in gSAFT, only the type and number of each group

Pure component vapor pressure



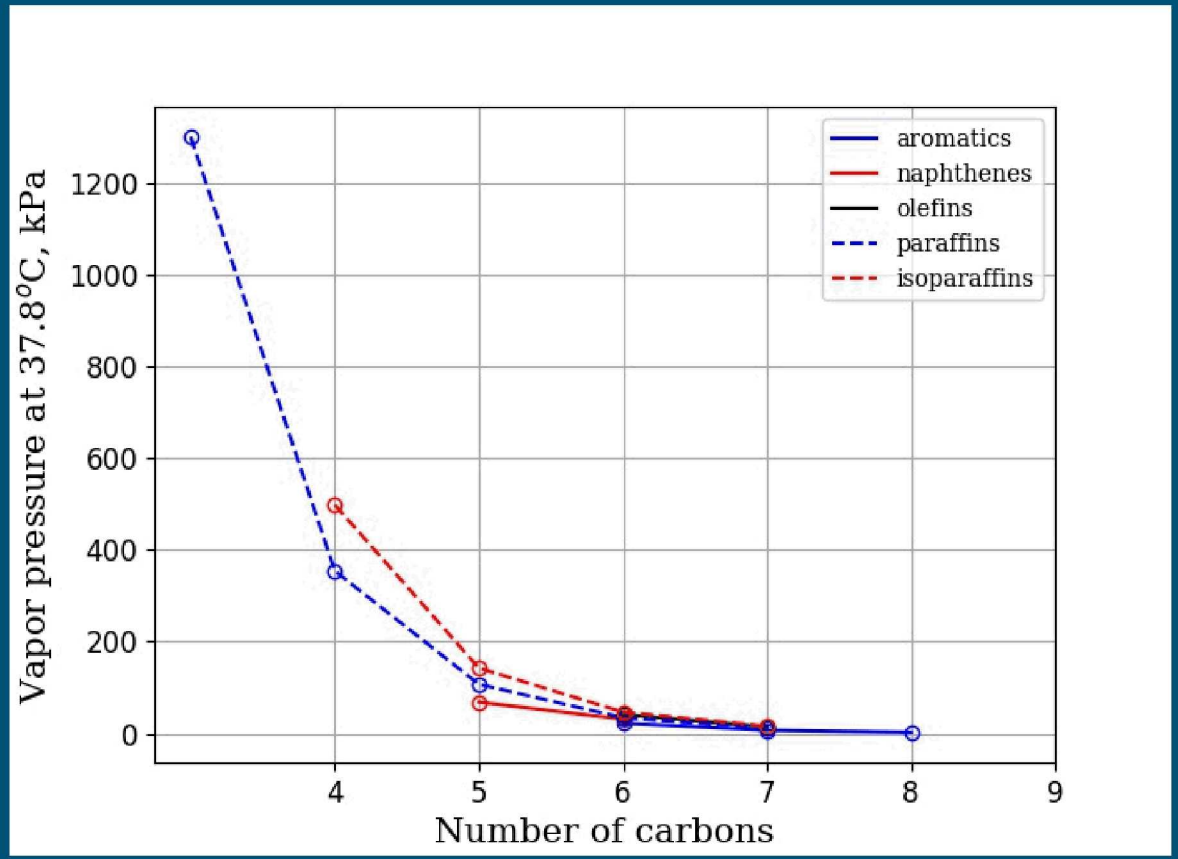


SAFT-γ-Mie is capable of providing very accurate vapor pressure predictions

Approach: models

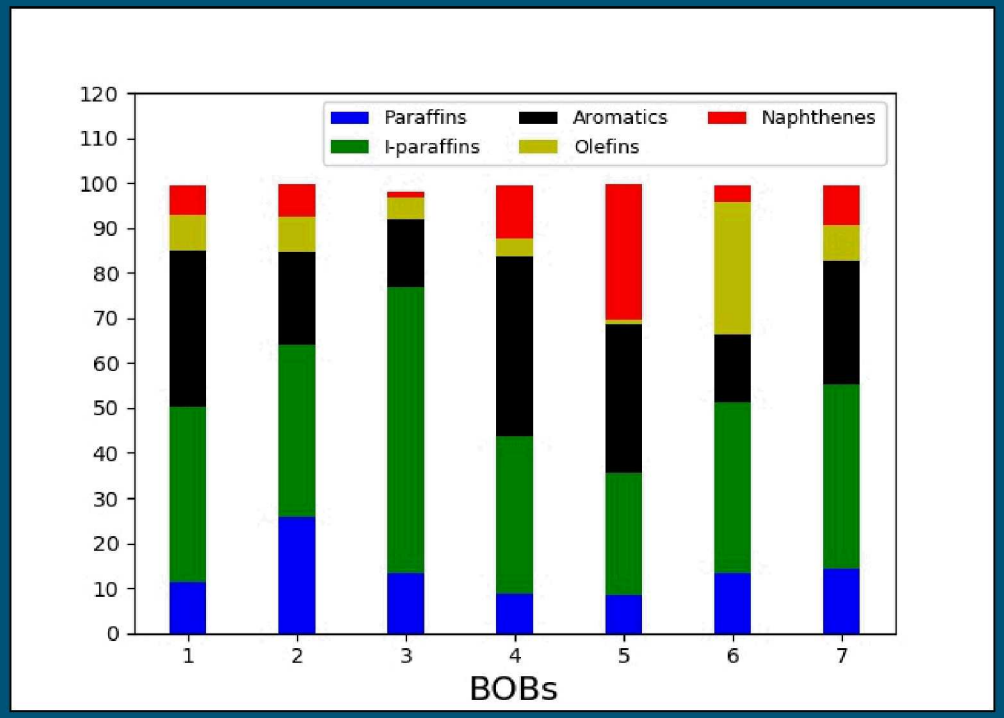
If we include the most important molecules, our RVP predictions should be accurate

- 2 models (small, moderate, large)
- Small: includes all components >= 1 mol%
- Medium: includes all components >= 0.5 mol%
- 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

The RVP of 7 BOBs were measured. Their composition was obtained using a Detailed Hydrocarbon Analysis (DHA)

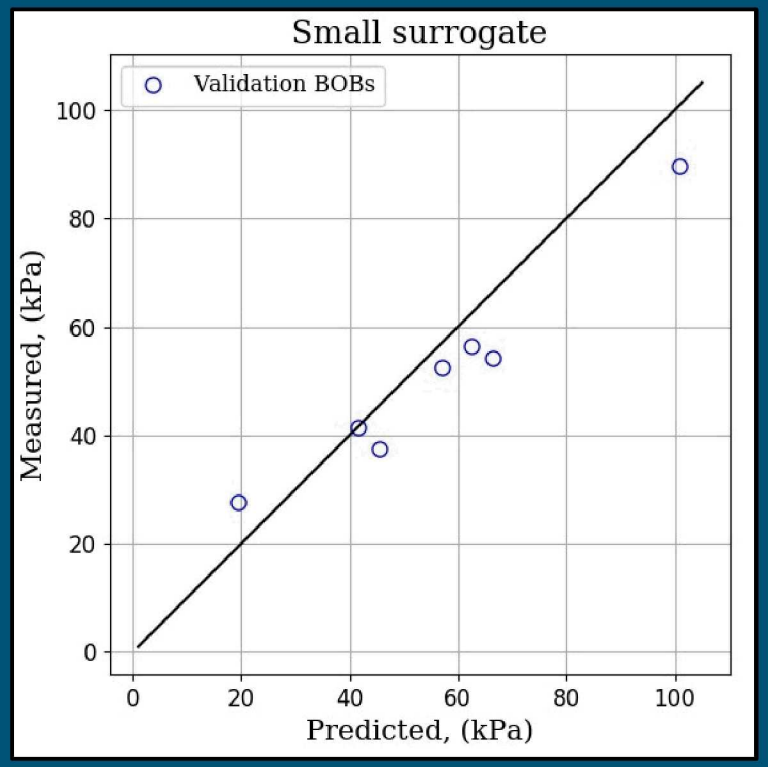


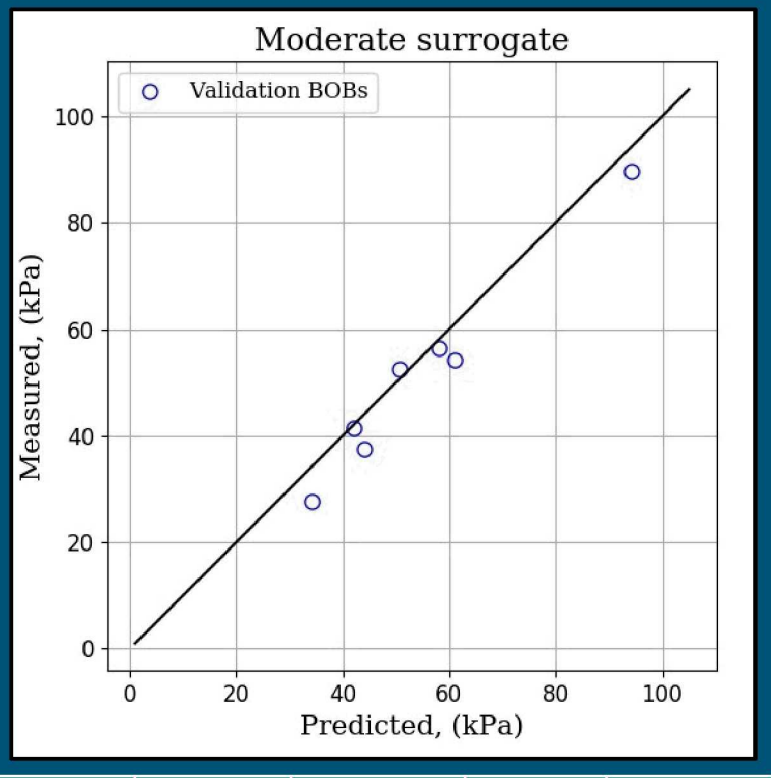
Varying composition of BOBs

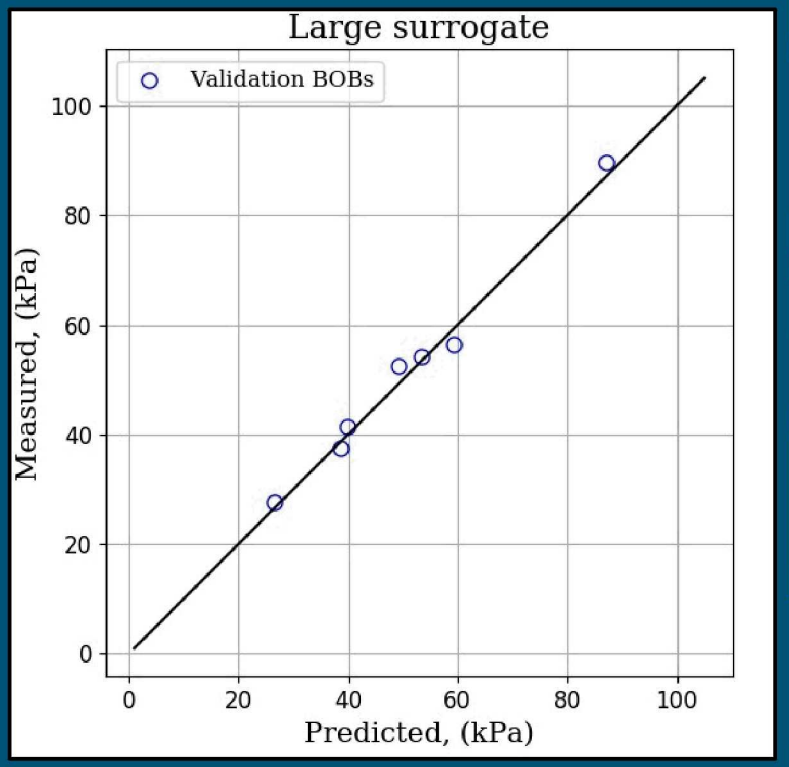
Defining characteristics of our 7 BOBs

- 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



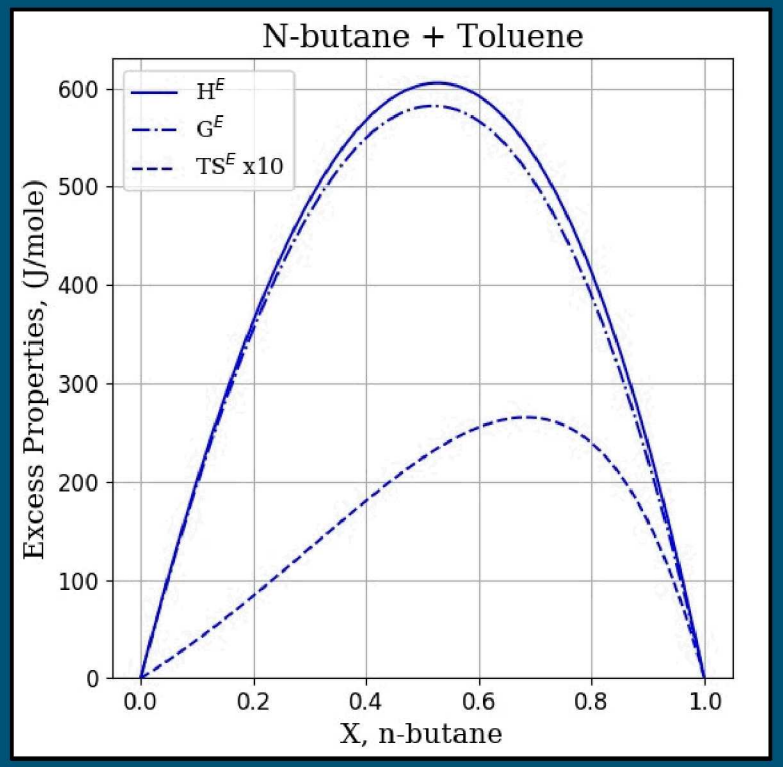


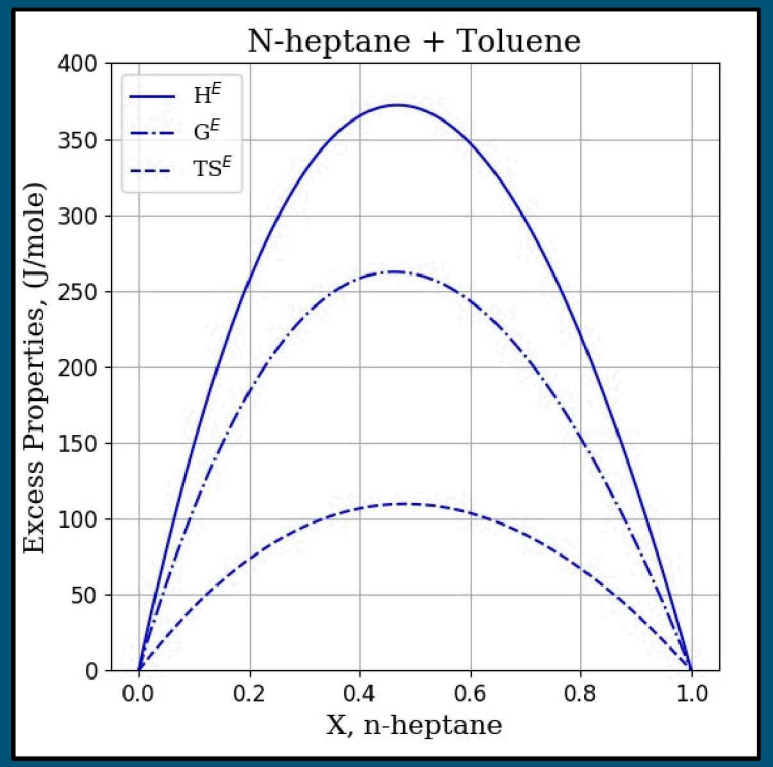


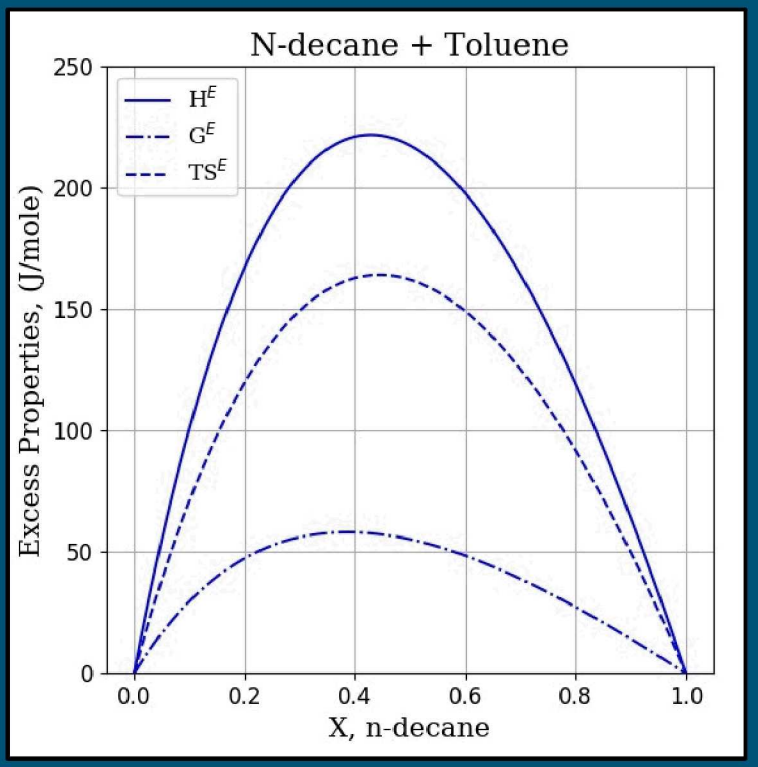
	Small	Moderate	Large	Measured
BOB 1	45.41	44.06	37.54	37.43
BOB 2	100.91	94.13	87.19	89.71
BOB 3	19.46	34.08	26.66	27.64
BOB 4	57.05	50.57	49.16	52.46
BOB 5	66.32	60.95	53.49	54.16
BOB 6	41.61	42.05	39.86	41.45
BOB 7	62.48	58.09	59.23	56.44
%AAD	15.09	9.49	3.28	

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

Excess thermodynamic properties: non-oxygenates

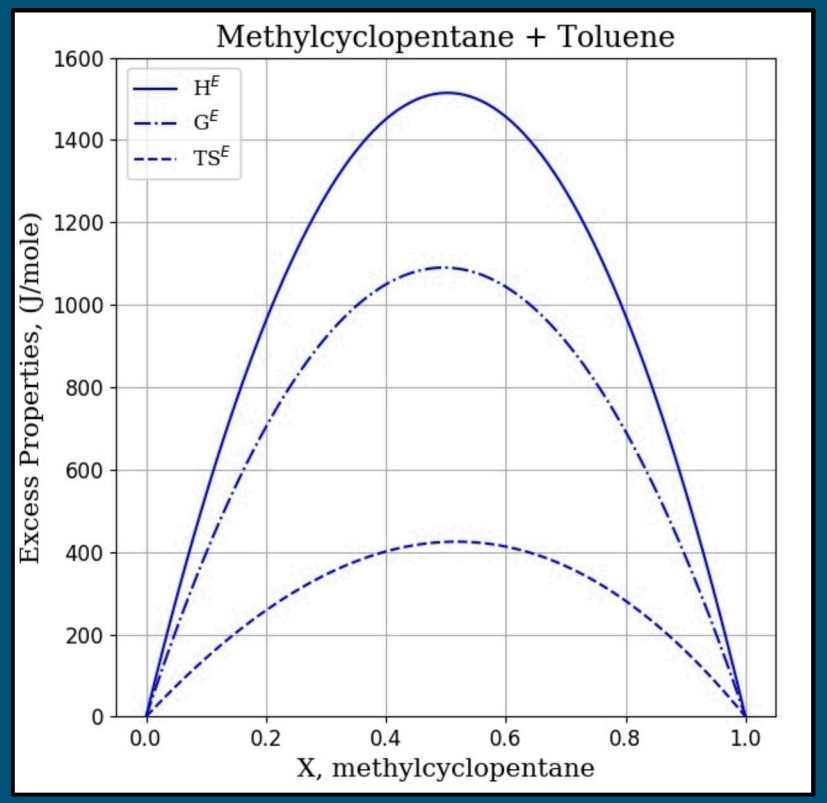


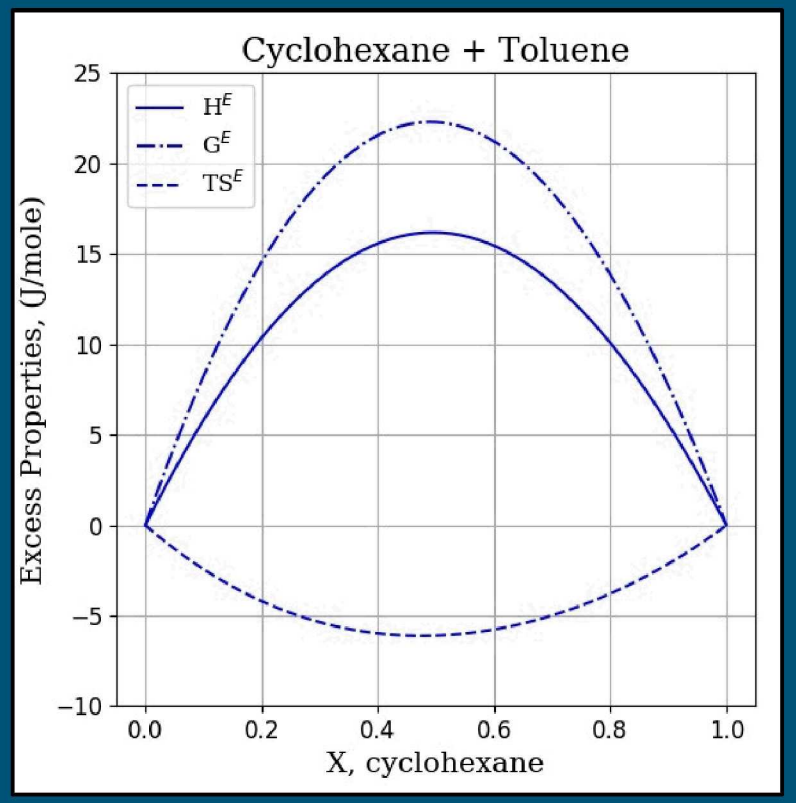


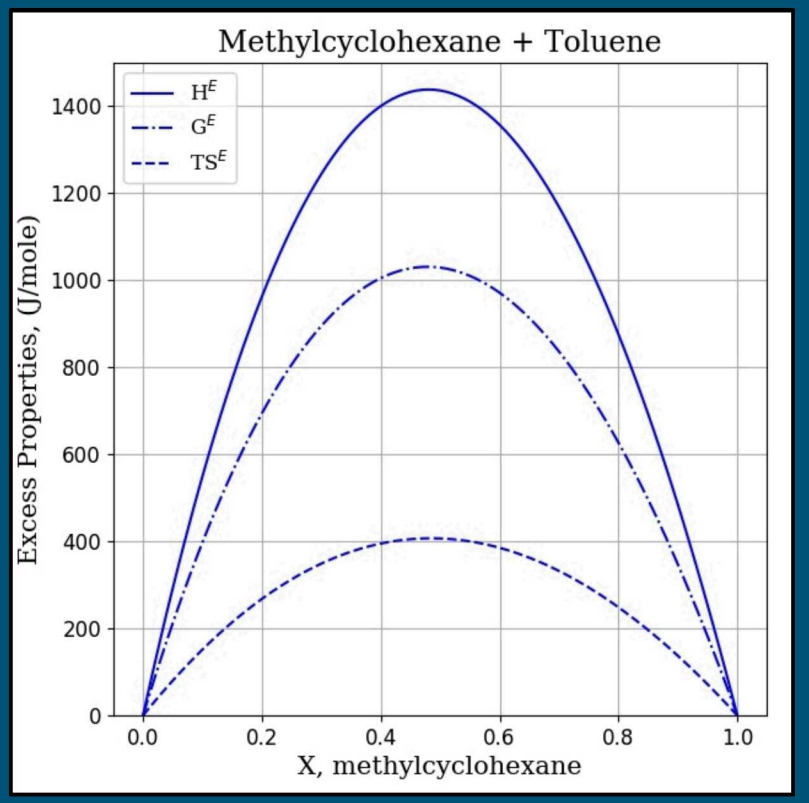


- S^E indicates that ratio moves from 2:1 to 1:2 alkane:toluene.
- Trend is from H^E and G^E to decrease indicating a lessening of the breaking of bonds.

Excess thermodynamic properties: non-oxygenates: cont.

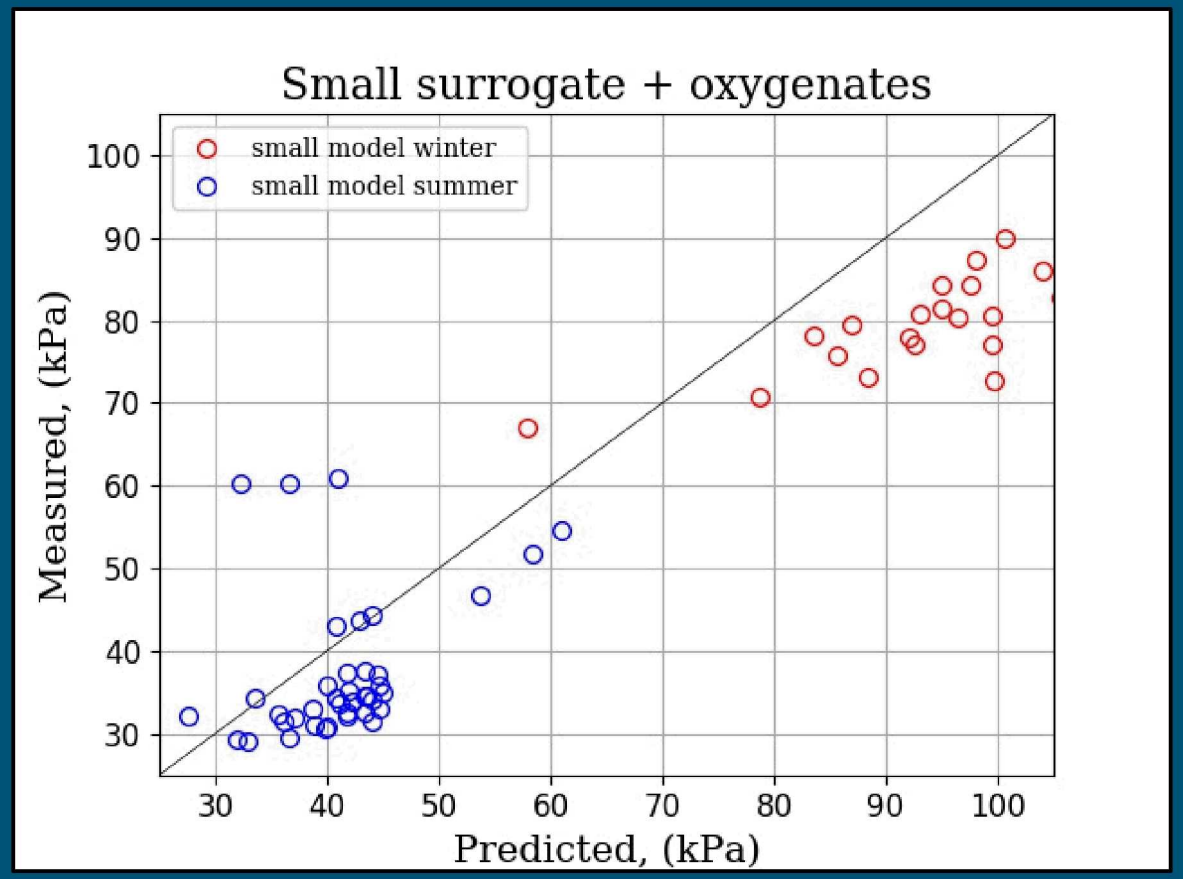




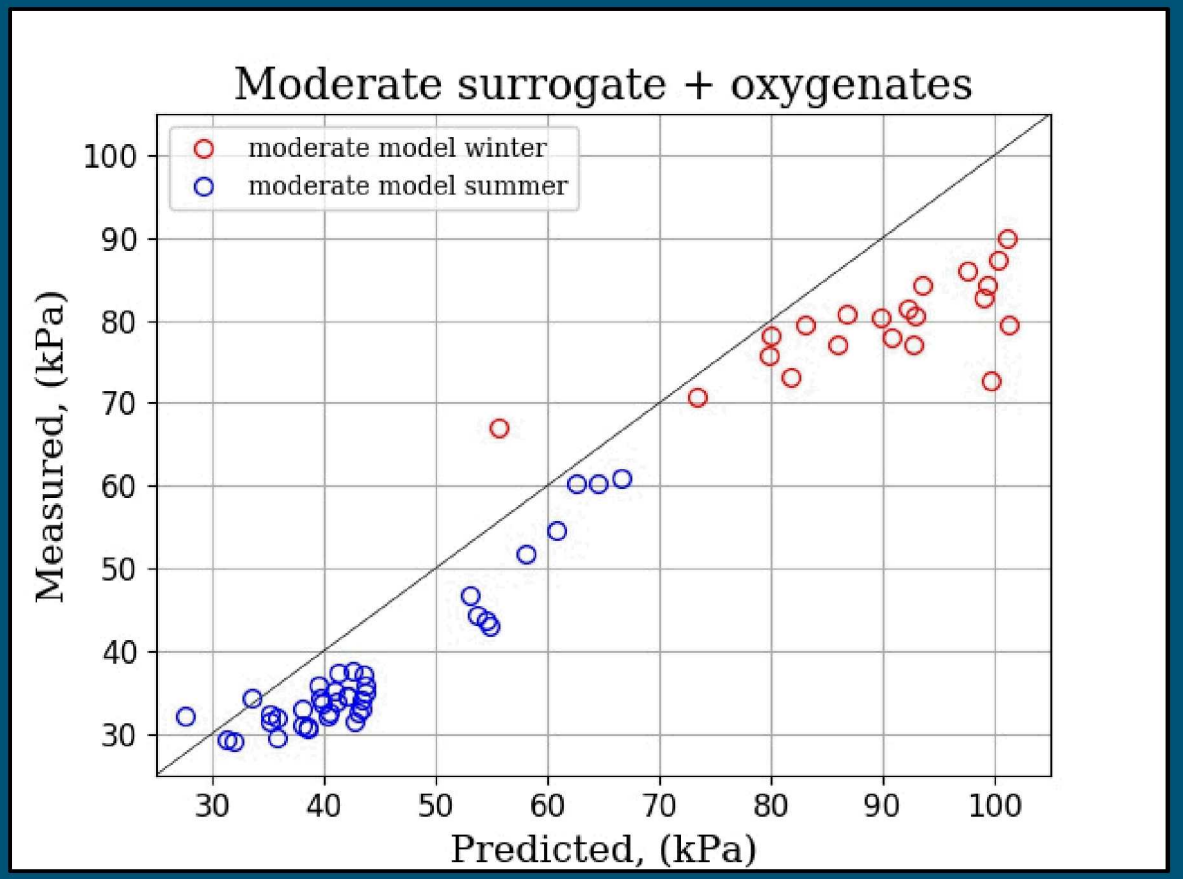


Alkyl chains have strong impacts on association

Results: Oxygenates



Summer %AAD = 19.72
Winter %AAD = 15.50

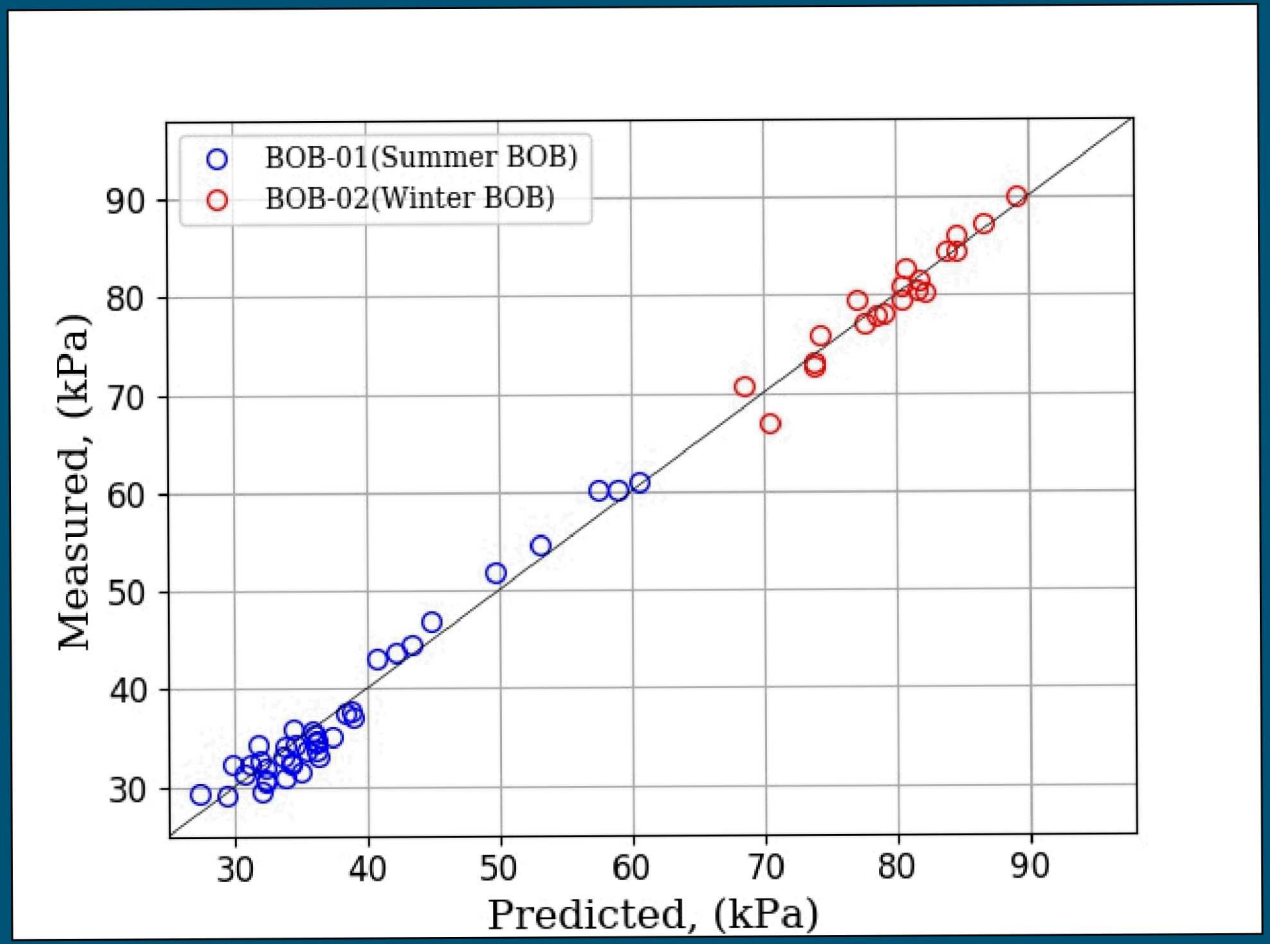


Summer %AAD = 14.90
Winter %AAD = 12.16

Results: Oxygenates: Cont.

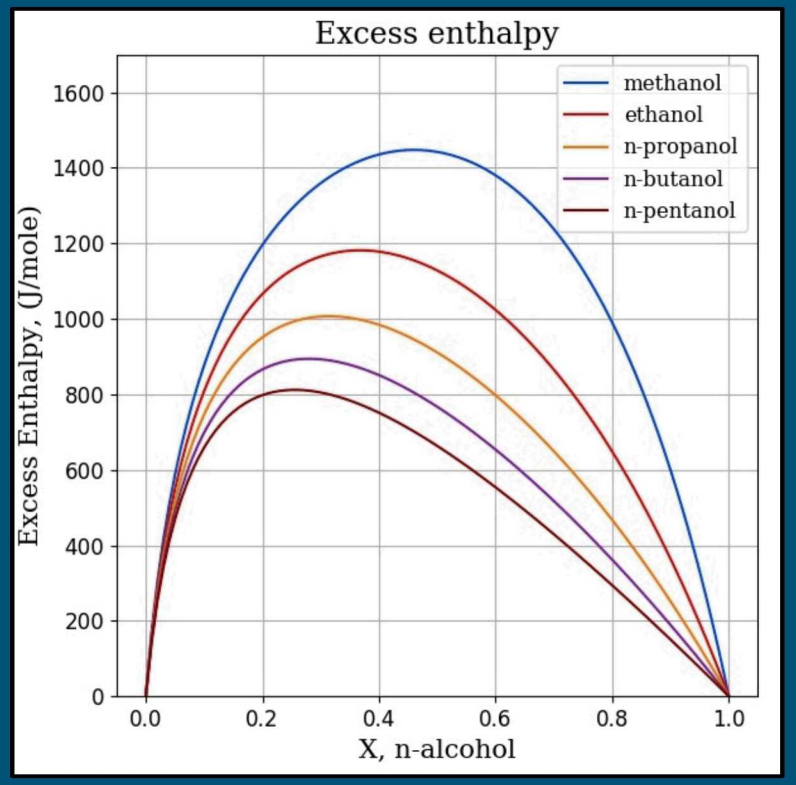
Data includes (10, 20, 30% by vol)

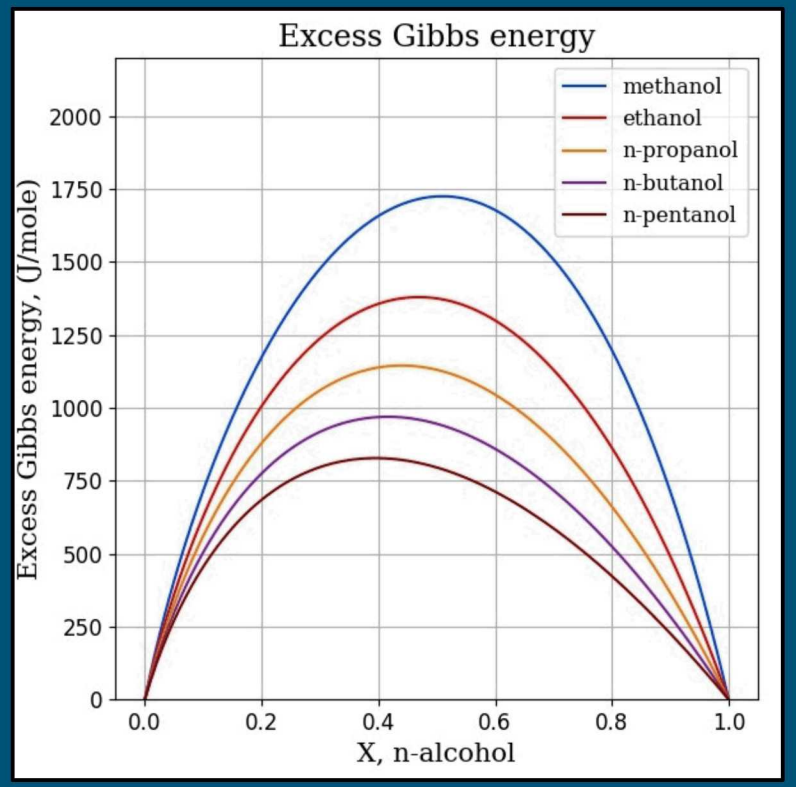
- Alcohols
  - Methanol, ethanol, 1-butanol, 2-butanol, n-propanol, isobutanol, 2-methyl-1-butanol, 2-pentanol, 3-methyl-1-butanol
- Esters
  - Butyl acetate, methyl acetate, ethyl acetate, isopropyl acetate
- Ketones
  - Cyclopentanone, 2-pentanone, 2,4-dimethyl-3-pentanone
- Aromatics
  - Anisole

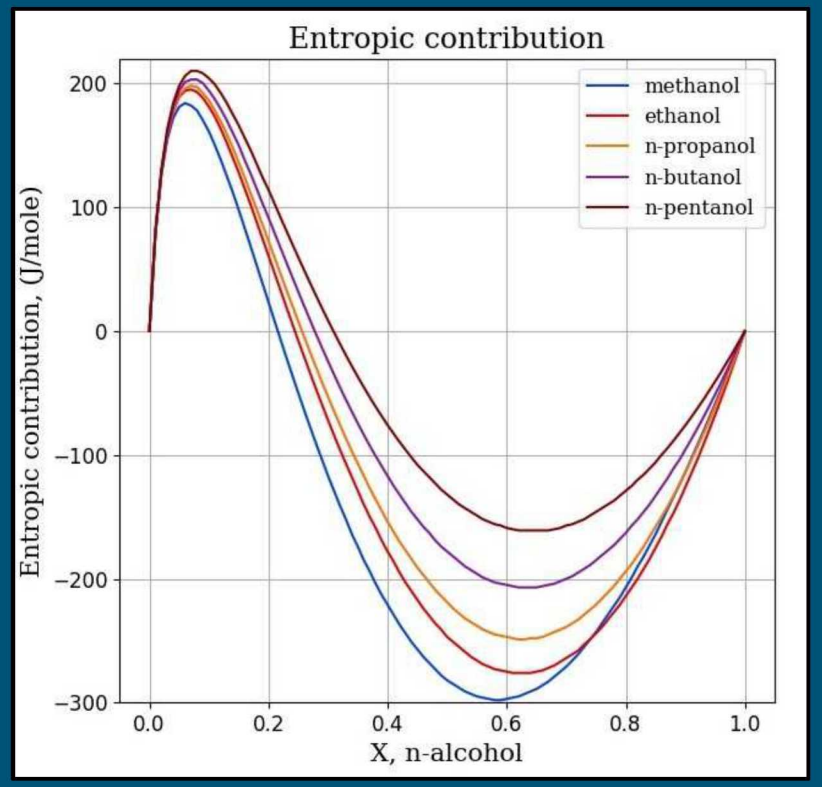


Summer %AAD = 4.40
Winter %AAD = 1.55
Overall AD = 1.45 kPa

Excess thermodynamic properties: oxygenates

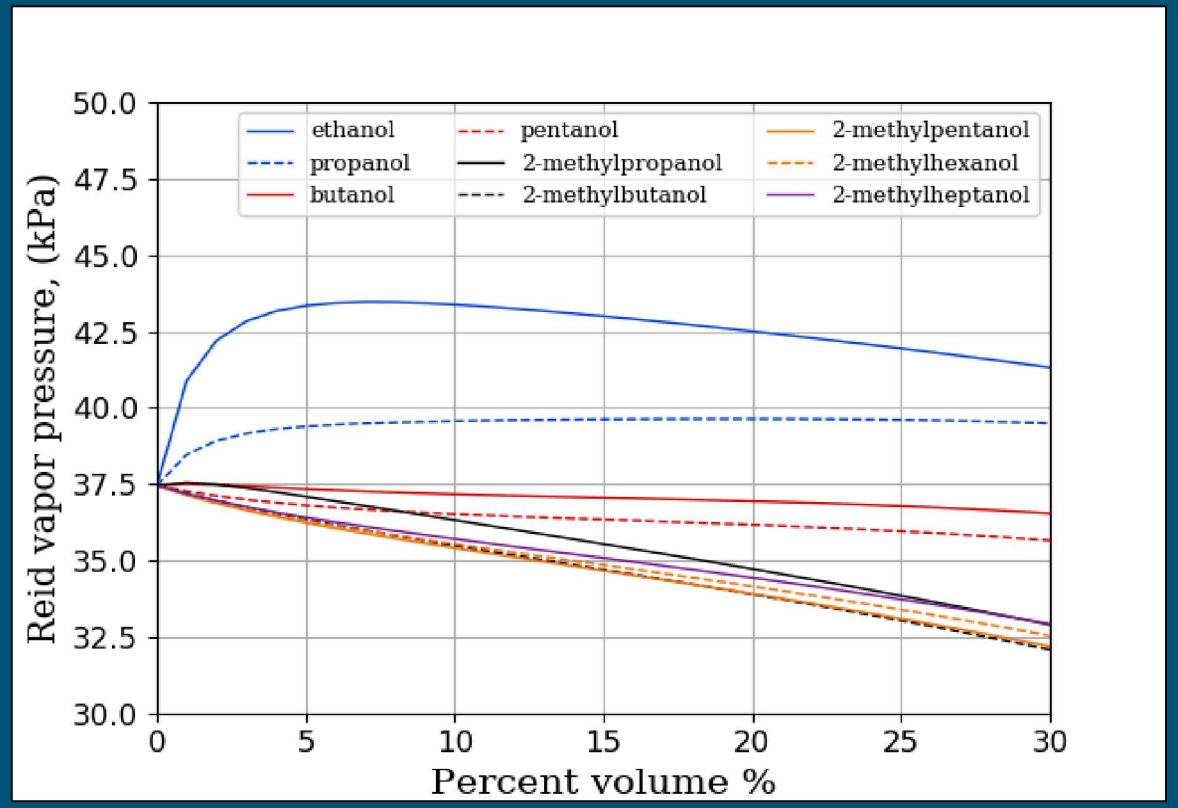




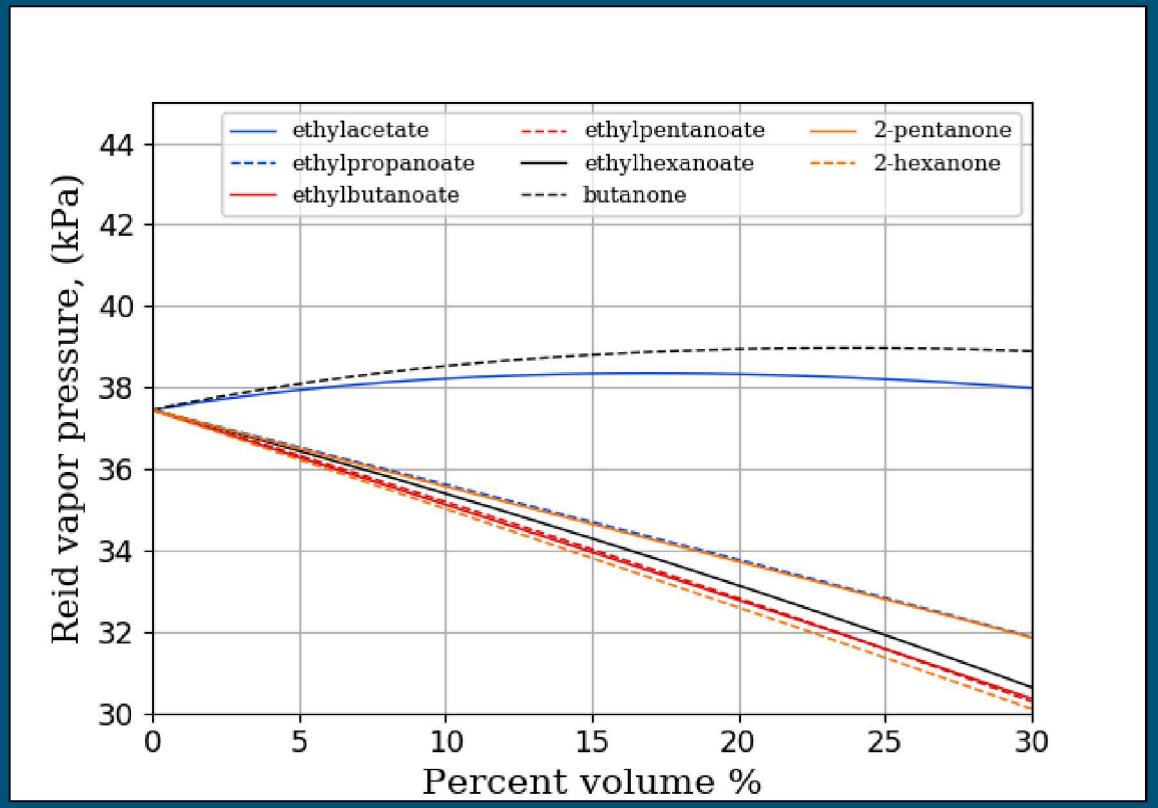


- Lower molecular weight alcohols disrupt arom-arom interactions more than higher weight alcohols
- S^E plot shows strong bond breaking/bond forming interactions

Results: application: alcohols, esters, ketones



Alcohols are not very good at lowering RVP



Small esters and ketones are better at lowering RVP

Questions: