UNIVERSITY OF TECHNOLOGY
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CHEMNITZ

Thermophysical Property Model of Lubricant Oils and Their Mixtures with Refrigerants && OilMixProp 1.0

TUC tt
technische thermodynamik

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HERRICK CONFERENCES 2024
COMPRESSORS | REFRIGERATION | BUILDINGS
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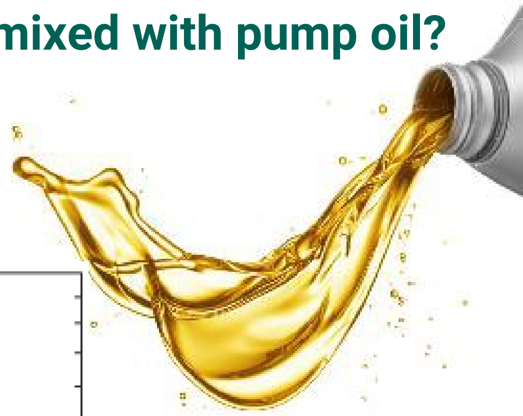
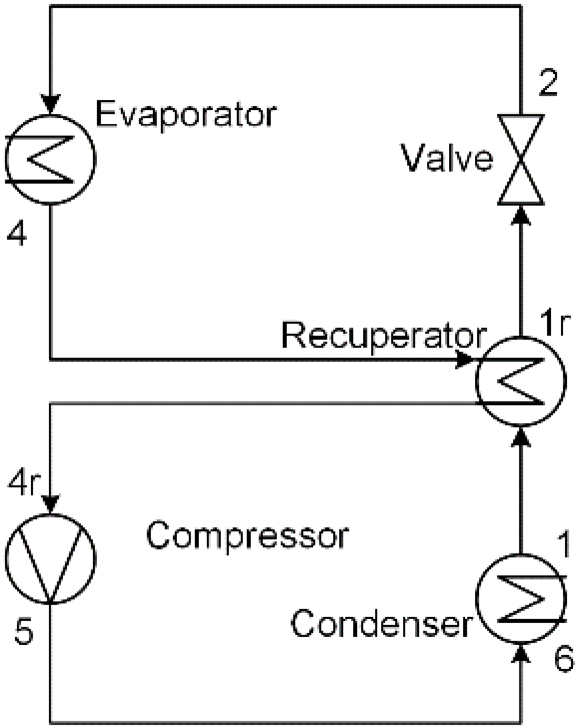
- **Fundamentals & Previous work**
- Recent improvements
- OilMixProp 1.0

Why? An old and hard question

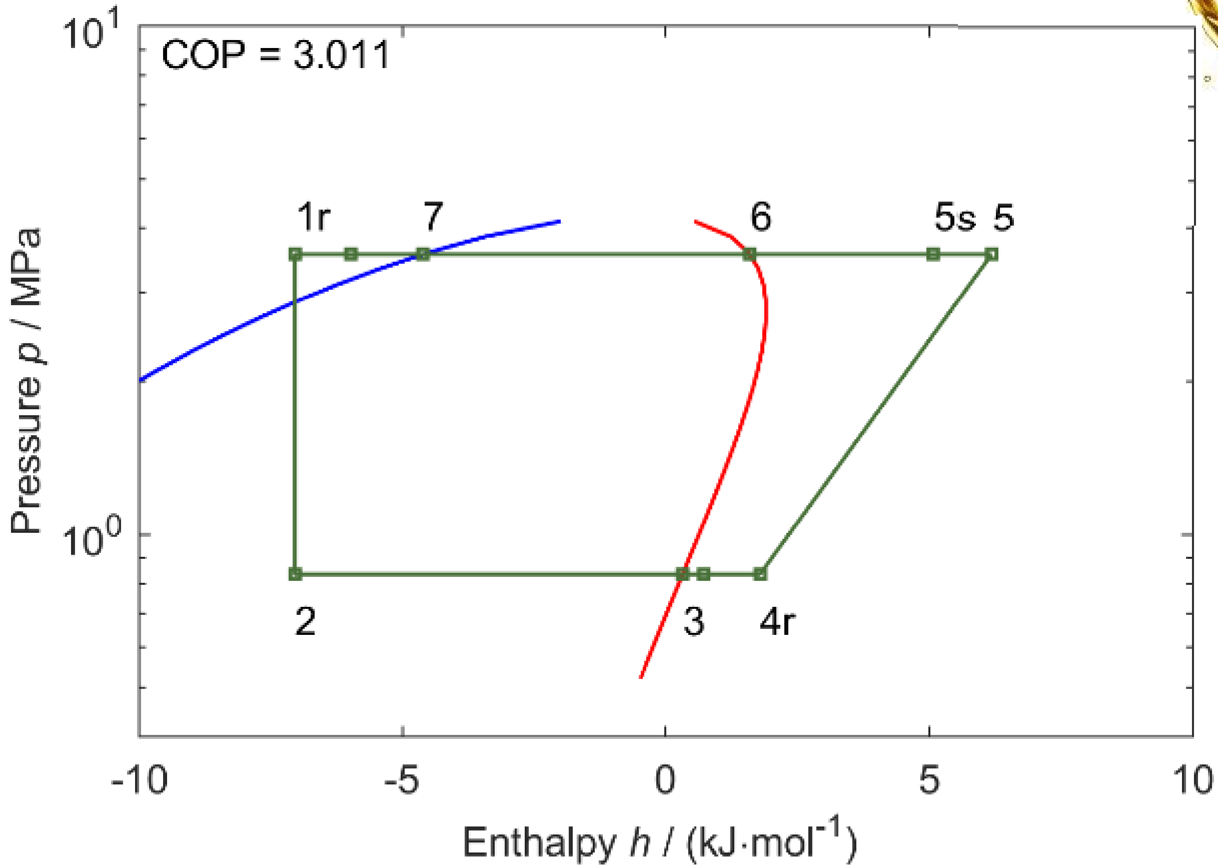
What happens if propane is mixed with pump oil?



Schematic of a heat pump cycle



p-h diagram of propane in a heat pump



Models for oil properties

Key thermophysical properties and calculation models

Properties	Calculation model
Density Liquid-Vaper-Equilibria Residual properties	Cubic equation of state (EoS) + van der Waals (vdW) mixing rule
Heat capacity Entropy Enthalpy Speed of sound	Cubic EoS + c_p^o as a linear function of temperature c_p^o: ideal gas isobaric heat capacity
Viscosity Thermal conductivity	Cubic EoS + Residual entropy scaling (RES) of Yang et al

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.
- Yang, X., Kim, D., May, E. F., & Bell, I. H. (2021). Entropy Scaling of Thermal Conductivity: Application to Refrigerants and Their Mixtures. *Industrial & Engineering Chemistry Research*, *60*(35), 13052–13070. https://doi.org/10.1021/acs.iecr.1c02154
- Yang, X., & Richter, M. (2024b). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Industrial & Engineering Chemistry Research*, (to be submitted).
- Yang, X., Xiao, X., May, E. F., & Bell, I. H. (2021). Entropy Scaling of Viscosity—III: Application to Refrigerants and Their Mixtures. *Journal of Chemical & Engineering Data*, *66*(3), 1385–1398. https://doi.org/10.1021/acs.jced.0c01009
- Yang, X., Xiao, X., Thol, M., Richter, M., & Bell, I. H. (2022). Linking viscosity to equations of state using residual entropy scaling theory. *International Journal of Thermophysics*, *43*(12), 183.

Constants of an oil

Models: cubic EoS + linear-$c_p^o(T)$ + RES

Molar mass ***M***

Lennard–Jones parameters ε/k_B and σ

for viscosity and thermal conductivity at dilute gas limit

Estimated from critical point information:

$$\varepsilon/k_B = T_c/1.2593 \qquad \sigma^3 = 0.3189/\rho_c$$

Critical point information:

- compressibility factor Z_c
- temperature T_c
- density ρ_c
- pressure p_c

RES-viscosity $n_{\mu k}$ (k = 1,2,3,4)

RES-thermal conductivity $n_{\lambda k}$ (k = 1,2,3,4)

for residual viscosity and thermal conductivity

RES: residual entropy scaling

Acentric factor ω

k_0 and k_1 in the linear-$c_p^o(T)$

c_p^o: ideal gas isobaric heat capacity

Critical enhancement parameters φ_0, Γ, q_D

for the critical enhancement of thermal conductivity

Question becomes: How to determine these constants using least amount of experiments?

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.

Summary of measurements needed

Less than 20 (at least 12) experimental points are needed → **parameters of an oil**

4 (0) → two masses and two boiling point temperatures → $\boldsymbol{M}$

0 (0) → Z_c fixed at a reasonable value (e.g., 0.2563) → $\boldsymbol{Z_c}$

4 (2) → four, could be down to two, points of (p = 1 atm, T, ρ) → $\boldsymbol{T_c}$, $\boldsymbol{p_c}$, **and** $\boldsymbol{\omega}$

4 (2) → four, could be down to two, points of (p = 1 atm, T, c_p) → $\boldsymbol{k_0}$ **and** $\boldsymbol{k_1}$

4 (4) → four points of (p = 1 atm, T, μ) → $\boldsymbol{n_{\mu k}}$ **(k = 1,2,3,4)**

4 (4) → four points of (p = 1 atm, T, λ) → $\boldsymbol{n_{\lambda k}}$ **(k = 1,2,3,4)**

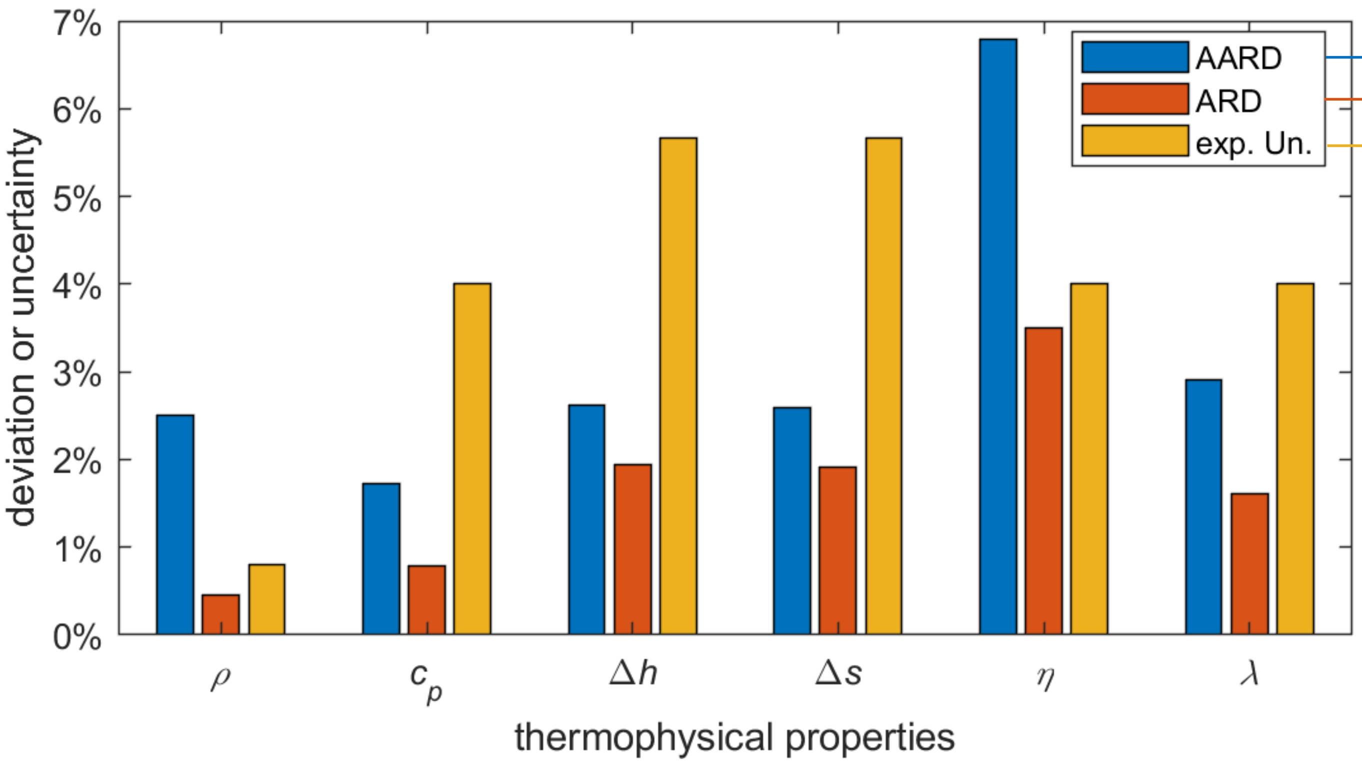
Note: Temperature could be (278.15 to 368.15) K or slightly smaller

Pressure can be another value rather than 1 atm and does not have to be constant.

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.

Pure fluid predictions

The modelling approach compared to REFPROP 10.0



Scattering: Average of the absolute value of relative deviation (AARD)

Offset: average relative deviation (ARD)

Typical experimental expanded uncertainty (exp. Un).

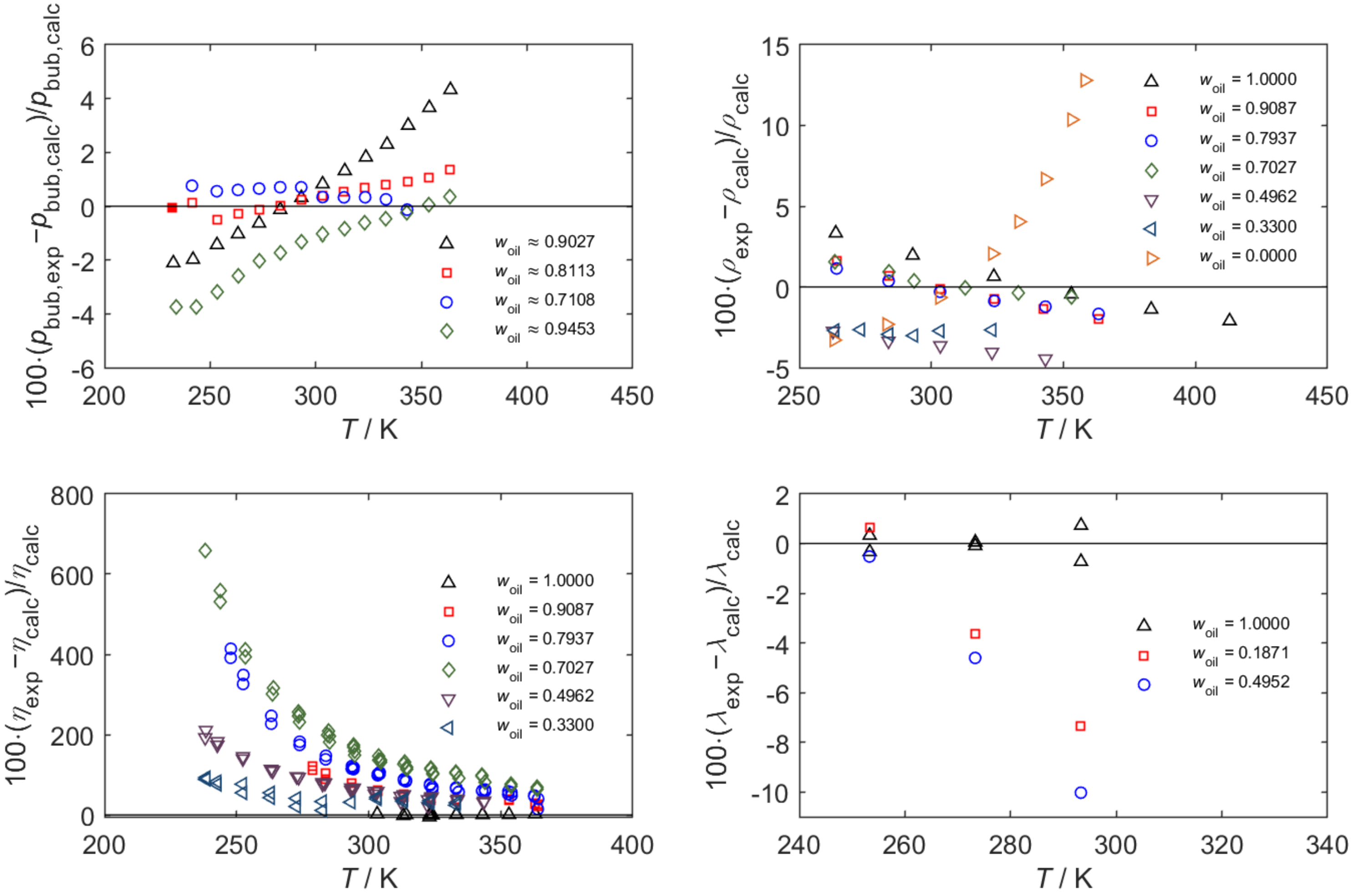
- For all pure fluids in the feasibility study
- In enlarged T-p ranges

  278.15 to 368.15 → 223.15 to 473.15 K
  0.1 MPa → 0.1 to 5.0 MPa.

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.
- Lemmon EW, Bell IH, Huber ML, McLinden MO. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology. 2018.

Real oil case: PAG68 + propane

Experimental data (exp) compared to model prediction (calc)



PAG68 + propane: measured in ILK Dresden

- An asymmetric binary system
- k_{ij} = 0.0381 (fitted with one vapor pressure)
- If M_{PAG68} changes
  → k_{ij} changes
  → but prediction almost unchanged

Relative deviation :

- vapor pressure: 5%
- density: 5%
- **viscosity: 700%**
- thermal conductivity: 10%

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.

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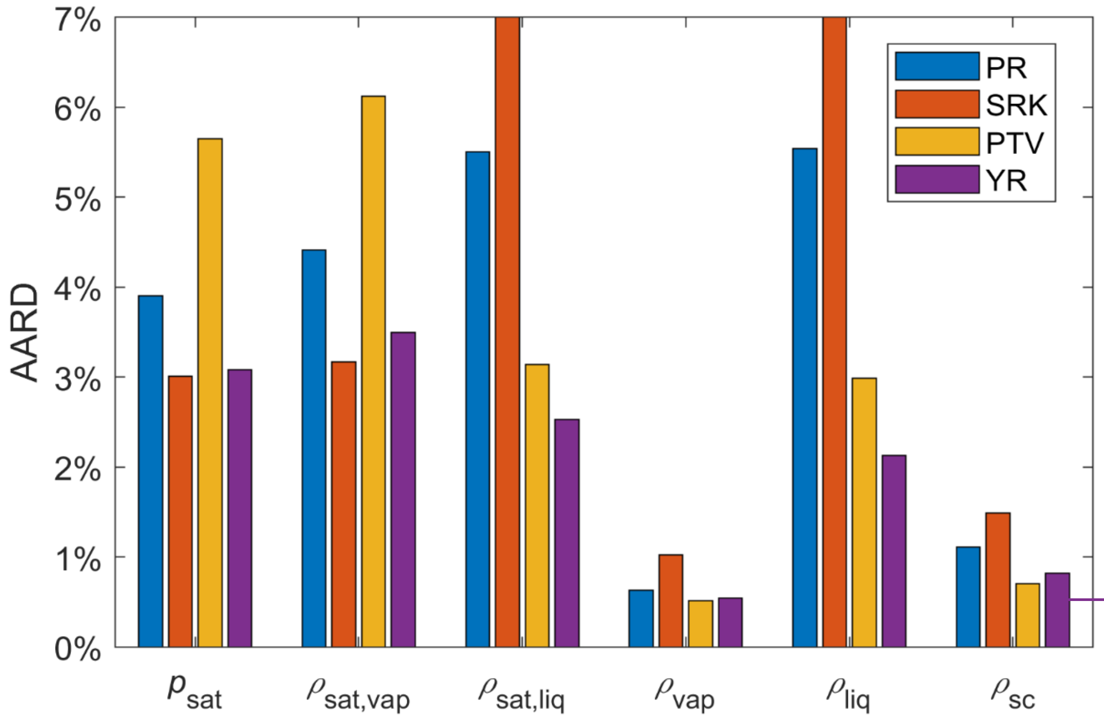
- Fundamentals & Previous work
- **Recent improvements**
- OilMixProp 1.0

Improvement 1: a new cubic EoS



The new one

Patel-Teja-Valderrama (PTV) EoS:

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + (b+c)v - bc}$$

$$a = \alpha(T_r, \omega) \cdot \Omega_a \frac{R^2 T_c^2}{p_c}$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad c = \Omega_c \frac{RT_c}{p_c}$$

$\Omega_a = 0.66121 - 0.761057 \cdot Z_C$
$\Omega_b = 0.02207 + 0.20868 \cdot Z_C$
$\Omega_c = 0.57765 - 1.87080 \cdot Z_C$

$$X = n_{X,1} \cdot \exp(-T_r^4) + n_{X,2} \cdot \exp(-T_r^3) + n_{X,3} \cdot Z_c + n_{X,4}$$
$$(X = \Omega_a, \Omega_b \text{ and } \Omega_c)$$

Symbolic Regression

$\alpha = (1+m \cdot (1-T_r^{1/2}))^2$
$m = 0.46283 + 3.58230\omega Z_C + 8.19417(\omega Z_C)^2$

$$m = n_{m,1} \cdot Z_c + n_{m,2} \cdot \omega Z_c + n_{m,3}$$

- Yang, X., Frotscher, O., & Richter, M. (2024). A new cubic equation of state developed with symbolic regression to improve liquid density calculation accuracy. *Industrial & Engineering Chemistry Research*, (to be submitted).

Improvement 2: state-of-the-art RES

Viscosity with residual entropy scaling

$$\mu = \mu_{\rho\to 0} + \mu^{\mathrm{r}}$$

$$\mu_{\rho\to 0} = f(\varepsilon/k_{\mathrm{B}}, \sigma, T)$$

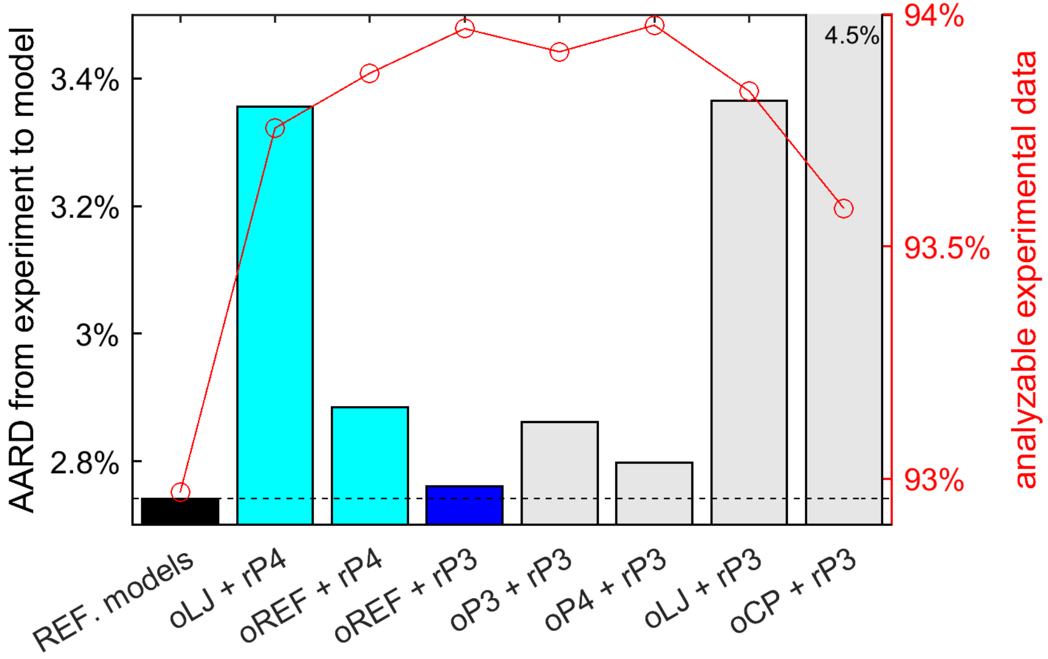
σ and $\varepsilon/k_{\mathrm{B}}$ are L-J parameters *estimated with critical point info.*

$$\mu^{\mathrm{r}} = \frac{\mu^{\mathrm{r}+}\rho_{\mathrm{N}}^{2/3}\sqrt{mk_{\mathrm{B}}T}}{(s^+)^{2/3}}$$

$$s^+ = -s^{\mathrm{r}}/R$$

$$\ln(\mu^{\mathrm{r}+}+1) = n_{\mu 1}\cdot(s^+) + n_{\mu 2}\cdot(s^+)^{1.5} + n_{\mu 3}\cdot(s^+)^2 + n_{\mu 4}\cdot(s^+)^{2.5} \longrightarrow \ln(\mu^{\mathrm{r}+}+1) = n_{\mu 1}\cdot(s^+)^{1.8} + n_{\mu 2}\cdot(s^+)^{2.4} + n_{\mu 3}\cdot(s^+)^{2.8}$$

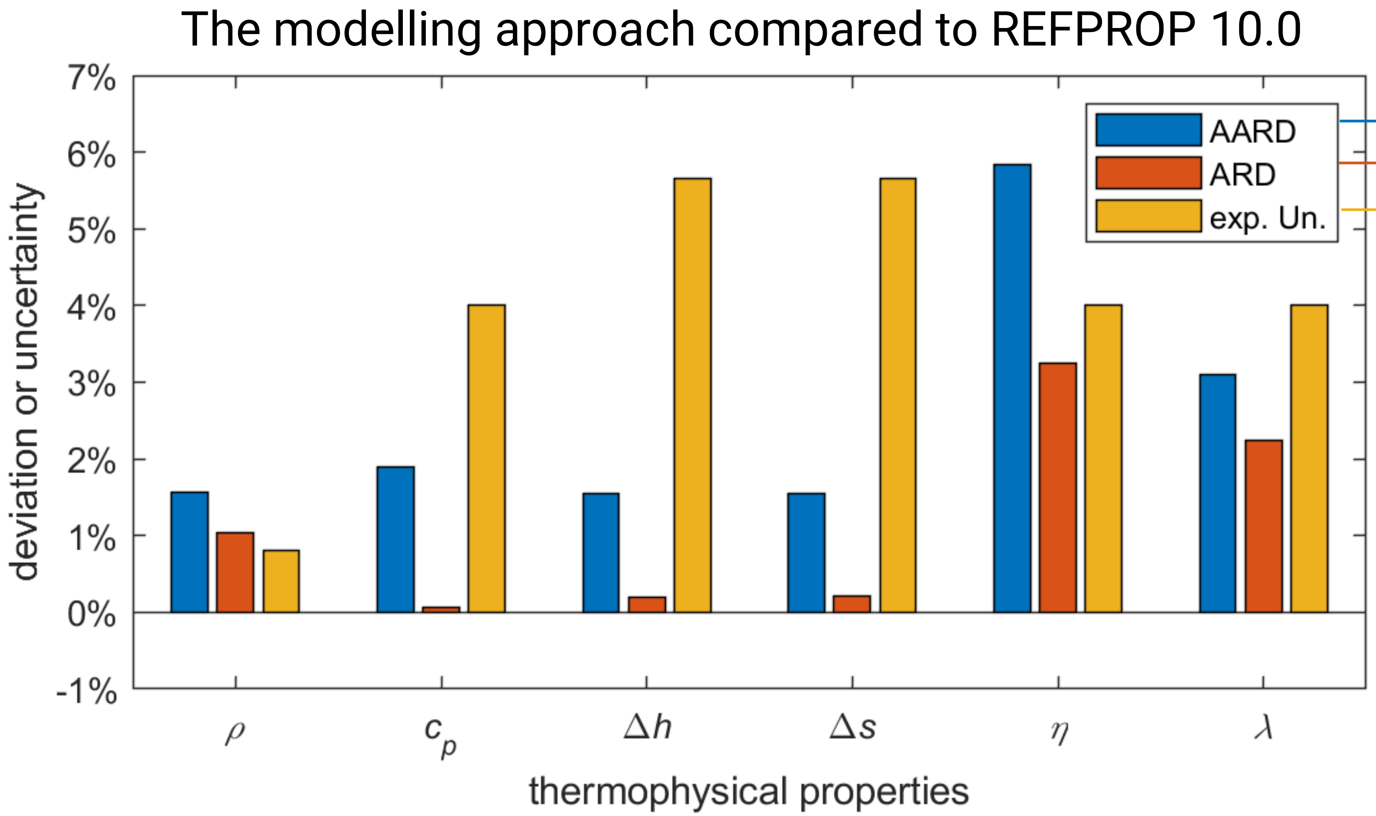
m is mass of one molecule, k_{B} is Boltzmann constant
ρ_{N} is number density and s^{r} is residual entropy, both calculated with Cubic EoS



a comprehensive fitting strategy

- Martinek, V., **Yang, X.,** Bell, I. H., Herzog, R., & Richter, M. (2024). Entropy scaling of viscosity IV - application to 124 industrially important fluids. *Journal of Chemical & Engineering Data*, (to be submitted).

Improvement in pure fluids



Scattering: Average of the absolute value of relative deviation (AARD)

Offset: average relative deviation (ARD)

Typical experimental expanded uncertainty (exp. Un).

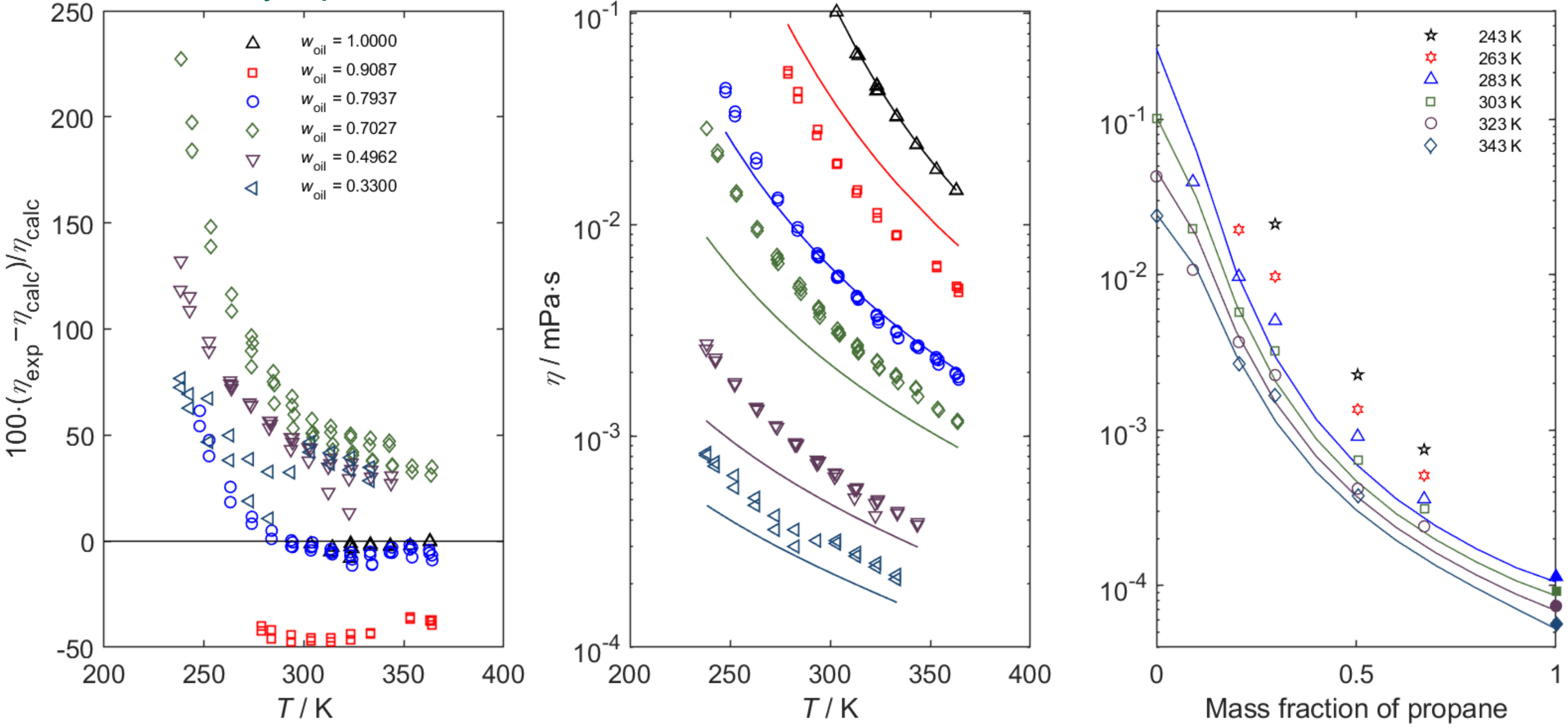
- Density: 2.5 % down to 1.6 %
- Viscosity: 6.8 % down to 5.8 %

- Yang, X.; Richter, M. Review and Evaluation of Experimental Thermophysical Properties of Oils and Their Mixtures with Refrigerants. *Industrial & Engineering Chemistry Research* (to be submitted).
- Lemmon EW, Bell IH, Huber ML, McLinden MO. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology. 2018.

Improvement 3: viscosity mixing rule

A vdW-type mixing rule with one adjustable parameter for each binary system.

Previously, up to 600 %



- Yang, X.; Richter, M. Review and Evaluation of Experimental Thermophysical Properties of Oils and Their Mixtures with Refrigerants. *Industrial & Engineering Chemistry Research* (to be submitted).

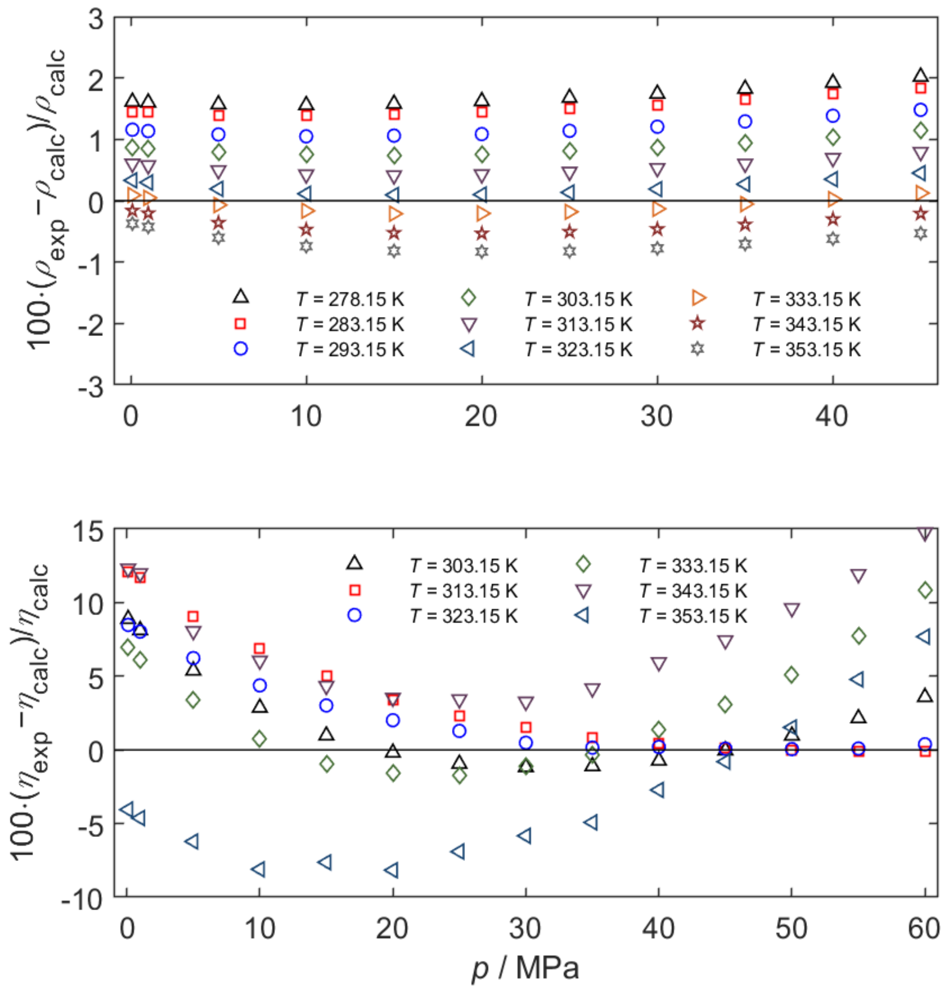
Experimental data review - density

Oil or refrigerant	Oil	*T* / K	*P* / MPa	Points	Author and year
	POE5	270.0 – 470.0	0.5 – 50.1	164	(Bruno et al., 2019)
	POE7	270.0 – 470.0	0.5 – 50.0	161	(Bruno et al., 2019)
	POE9	290.0 – 470.0	0.5 – 50.1	145	(Bruno et al., 2019)
	ISO VG 32	248.2 – 348.2	0.1 – 0.1	5	(Morais et al., 2022)
	PEB8	263.8 – 412.9	0.1 – 0.1	5	(Fandiño et al., 2005)
	DIDP	273.8 – 413.3	0.1 – 140	55	(Peleties et al., 2010)
R744	DIDP	288.0 – 413.3	0.1 – 80	66	(Weerakajornsak, 2019)
PEB8	PEC7	278.2 – 353.2	0.1 – 45.0	99	(Fandiño et al., 2007)
R600a	LAB ISO 5	296.0 – 353.2	0.0 – 1.3	53	(Neto & Barbosa, 2010)
R744	POE5	303.2 – 353.2	10.0 – 60.0	113	(Pensado et al., 2008b)
R744	POE7	303.2 – 353.2	10.0 – 60.0	110	(Pensado et al., 2008b)
R744	POE9	303.2 – 353.2	15.0 – 60.0	93	(Pensado et al., 2008b)
R744	PEB8	303.2 – 353.2	10.0 – 60.0	110	(Pensado et al., 2008a)
R1234yf	ISO VG 32	248.2 – 348.2	0.0 – 0.6	33	(Morais et al., 2020)
R1234ze(E)	ISO VG 32	248.2 – 348.2	0.0 – 0.4	21	(Morais et al., 2020)
R134a	ISO VG 32	248.2 – 348.2	0.0 – 0.5	28	(Morais et al., 2022)
R125	ISO VG 32	248.2 – 348.2	0.0 – 0.6	27	(Morais et al., 2022)
R32	ISO VG 32	248.2 – 348.2	0.0 – 1.0	31	(Morais et al., 2022)
…	…	…	…	…	…

Experimental data review - viscosity

Oil or refrigerant	Oil	T / K	P/ MPa	Points	Author and year
	POE5	275.1 – 430.1	0.1 – 137.4	269	(Bruno et al., 2019)
	POE7	280.0 – 450.1	0.1 – 137.5	286	(Bruno et al., 2019)
	POE9	289.9 – 450.1	0.0 – 137.7	161	(Bruno et al., 2019)
	ISO VG 32	248.2 – 348.2	0.1 – 0.1	5	(Morais et al., 2020)
	LAB ISO 5	281.0 – 353.0	0.0 – 0.0	9	(Neto & Barbosa, 2010)
	PEB8	303.2 – 363.0	0.1 – 0.1	14	(Pensado et al., 2006)
R744	DIDP	288.0 – 413.3	0.1 – 80	66	(Weerakajornsak, 2019)
PEB8	PEC7	303.2 – 353.2	0.1 – 60.0	84	(Lugo et al., 2007)
PEB8	PEC5	313.2 – 333.2	0.1 – 60.0	28	(Lugo et al., 2007)
R744	PEC5	303.2 – 353.2	10.0 – 60.0	113	(Pensado et al., 2008b)
R744	PEC7	303.2 – 353.2	10.0 – 60.0	110	(Pensado et al., 2008b)
R744	PEC9	303.2 – 353.2	15.0 – 60.0	93	(Pensado et al., 2008b)
R1234yf	ISO VG 32	248.2 – 348.2	0.0 – 0.6	33	(Morais et al., 2020)
R1234ze(E)	ISO VG 32	248.2 – 348.2	0.0 – 0.4	21	(Morais et al., 2020)
R134a	ISO VG 32	248.2 – 348.2	0.0 – 0.5	29	(Morais et al., 2020)
R125	ISO VG 32	248.2 – 348.2	0.0 – 0.6	27	(Morais et al., 2020)
R32	ISO VG 32	248.2 – 348.2	0.0 – 1.0	31	(Morais et al., 2020)
…	…	…	…	…	…

PEB8 + POE7



Relative deviations of experimental data from model.

- Density data: Fandiño et al., 2007
- Viscosity data: Lugo et al., 2007

Fluid full name:

- PEB8: pentaerythritol tetra(2−ethylhexanoate)
- POE7 (or PEC7): pentaerythritol tetraheptanoate

Only one adjustable parameter:

- $BIP_{\mu,12} = 0.1$.

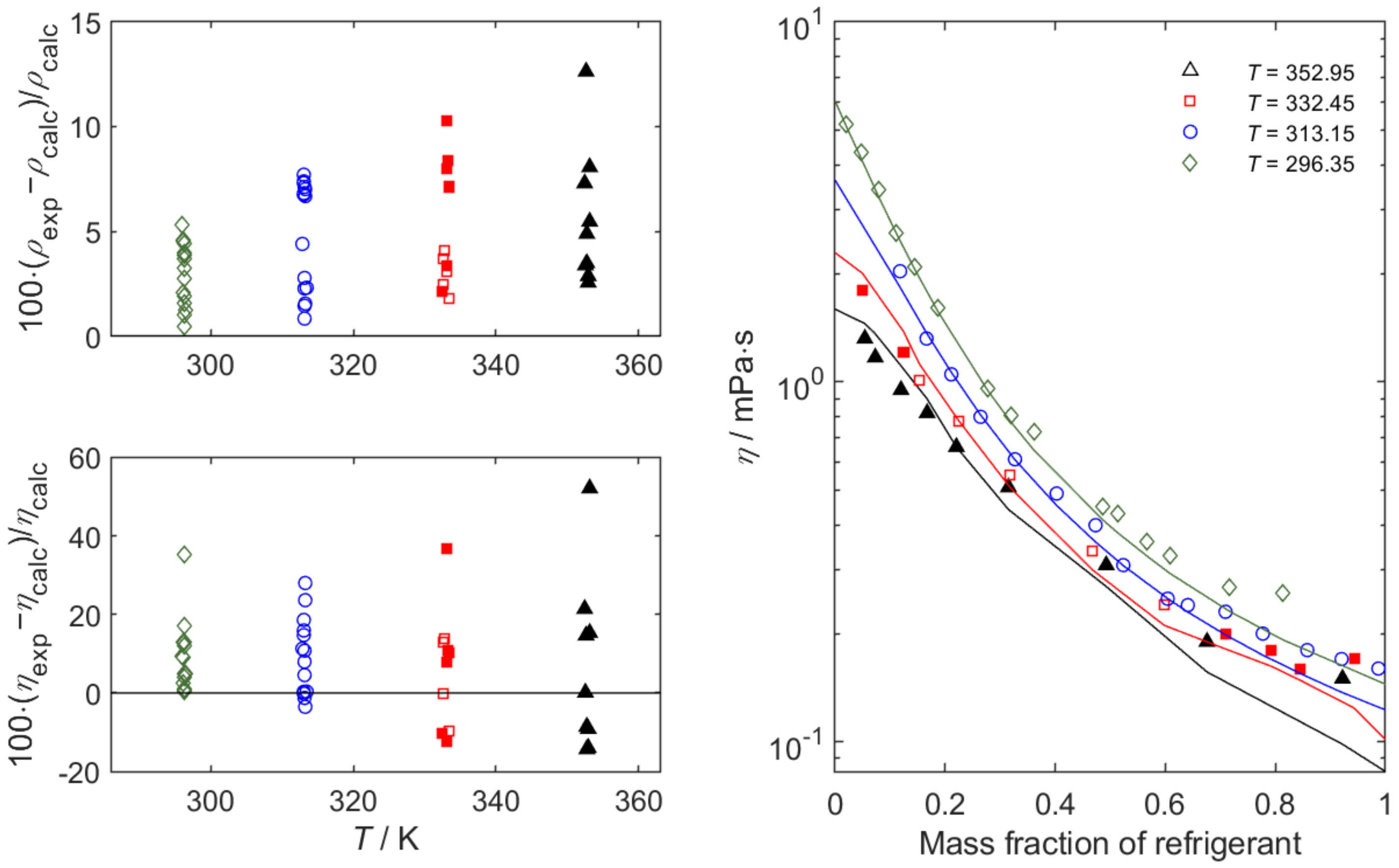
Relative deviations:

- Density: 2%, better than 3% of previous work
- Viscosity:15%, better than 30% of previous work

- Fandiño, O., Comuñas, M. J. P., Lugo, L., López, E. R., & Fernández, J. (2007). Density Measurements under Pressure for Mixtures of Pentaerythritol Ester Lubricants. Analysis of a Density−Viscosity Relationship. *Journal of Chemical & Engineering Data*, *52*(4), 1429–1436.
- Lugo, L., Canet, X., Comuñas, M. J. P., Pensado, A. S., & Fernández, J. (2007). Dynamic Viscosity under Pressure for Mixtures of Pentaerythritol Ester Lubricants with 32 Viscosity Grade: Measurements and Modeling. *Industrial & Engineering Chemistry Research*, *46*(6), 1826–1835.

LAB ISO 5 + isobutane

Relative deviations and viscosity data (Neto & Barbosa, 2010)



LAB ISO 5: a linear alkylbenzene lubricant oil

- $BIP_{\mu,12} = -0.15$.

Full symbols: two-phase region by OilMixProp 1.0.

- Density: up to 10%
- Viscosity: 60%

- Neto, M. A. M., & Barbosa, J. R. (2010). Solubility, density and viscosity of mixtures of isobutane (R-600a) and a linear alkylbenzene lubricant oil. *Fluid Phase Equilibria*, *292*(1), 7–12.

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- Fundamentals & Previous work
- Recent improvements
- **OilMixProp 1.0**

OilMixProp 1.0

Fluid Properties = *OilPropm*('all+', 'P', *p*, 'T', *T*, *Z*, FC, T_0, p_0)

Output indicators:
% 'All' all properties
% 'A' Speed of sound [m/s]
% 'D' Density [kg/m^3]
% 'H' Enthalpy [J/kg]
% 'K' Heat capacity ratio
% 'P' Pressure [kPa]
% 'Q' Vapor fraction [kg/kg]
% 'S' Entropy [J/(kg·K)]
% 'T' Temperature [K]
% 'U' Internal energy [J/kg]
% 'V' Viscosity [Pa·s]
% 'C' Isobaric heat capacity [J/(kg·K)]
% 'O' Isochoric heat capacity [J/(kg·K)]
% 'L' Thermal conductivity [W/(m·K)]
% 'X' Liquid & gas phase compositions in mass frac.
% 'Z' Compressibility factor
% '#' dP/dT (constant rho) [kPa/K]
% 'R' d(rho)/dP (constant T) [kg/m^3/kPa]
% 'W' d(rho)/dT (constant p) [kg/(m^3·K)]
% '+' optional, if the fluid is in a single phase

First input and value
% 'P' Pressure [kPa]
% 'T' Temperature [K]

Second input and value:
% 'P' Pressure [kPa]
% 'T' Temperature [K]
% 'D' Density [kg/m^3]
% 'Q' Vapor fraction [kg/kg]
% 'H' Enthalpy [J/kg]
% 'S' Entropy [J/kg/K]

Z: mass fraction
FC: Fluid constants

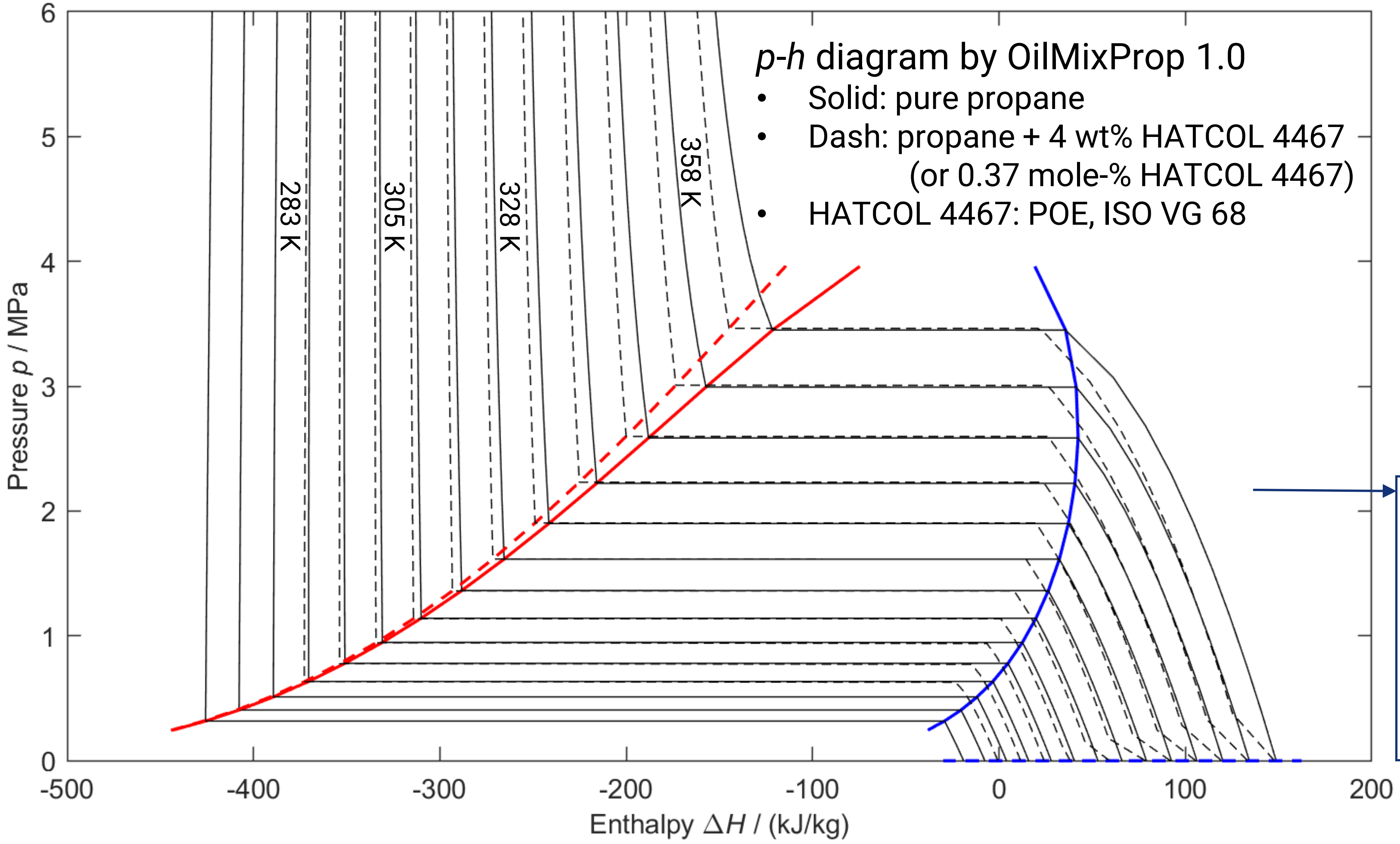
% Provide values only if *T* or *p* is to be solved and also good estimations are known. This speeds up the calculations.
% Otherwise set zeros

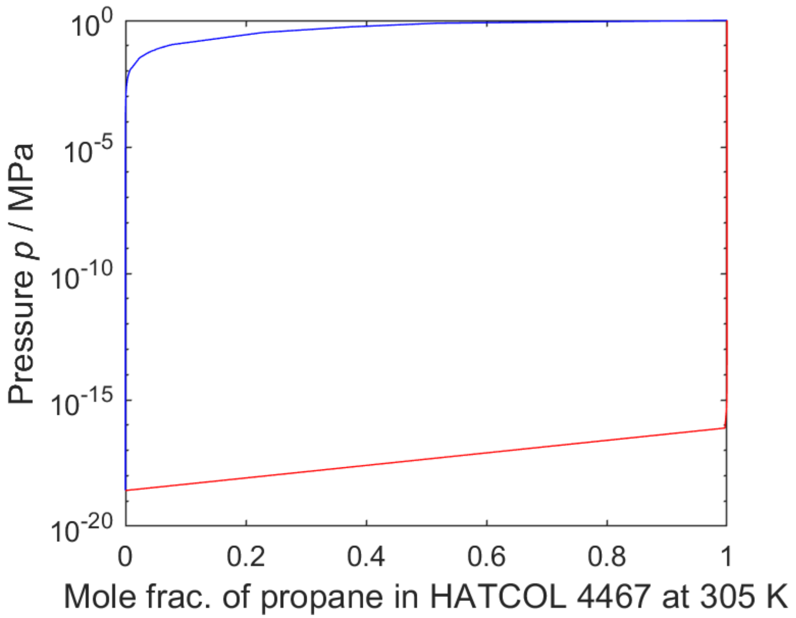
- A package developed in Matlab
- Package free to use for academia
  (contact: xiaoxian.yang@mb.tu-chemnitz.de)

- A software package for core thermophysical properties of oils, common fluids and their mixtures.
- Inputs and outputs are specially designed for thermodynamic cycle analysis (heat pump, etc.)
- First one capable of calculating all the core thermophysical properties of fluids involving user-defined oils

- Yang, X., & Richter, M. (2024). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Industrial & Engineering Chemistry Research*, (to be submitted).

Phase diagrams





Such curves can not be plotted without:

- density measurement of HATCOL 4467
- the model developed in TU Chemnitz

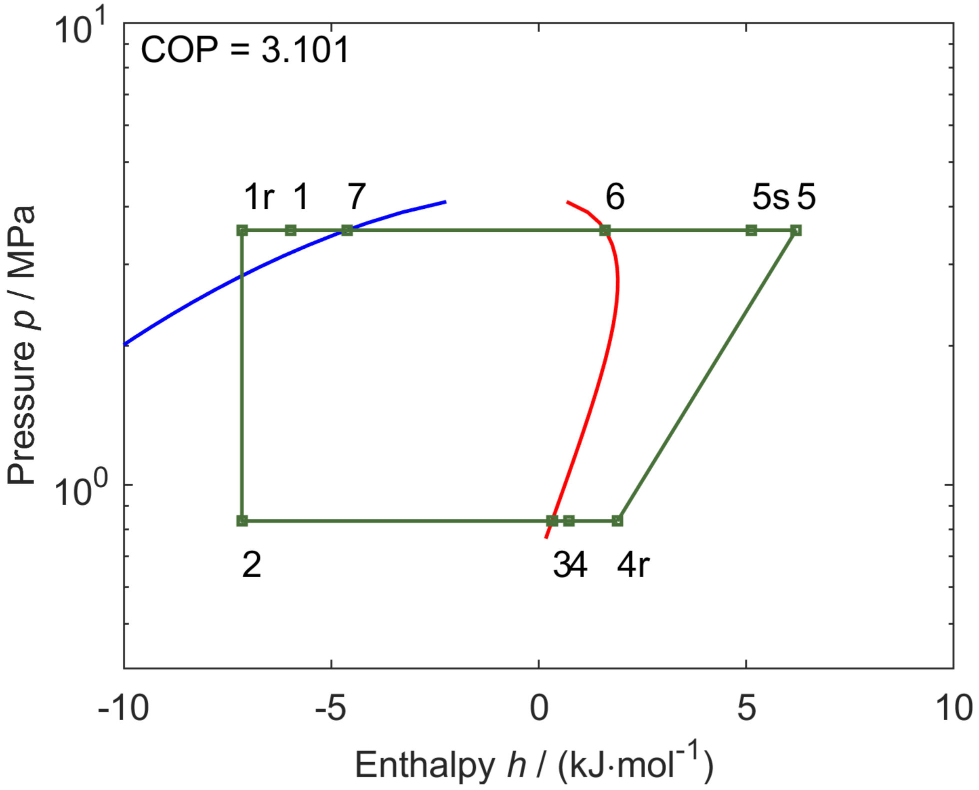
More accurate if there are data of:

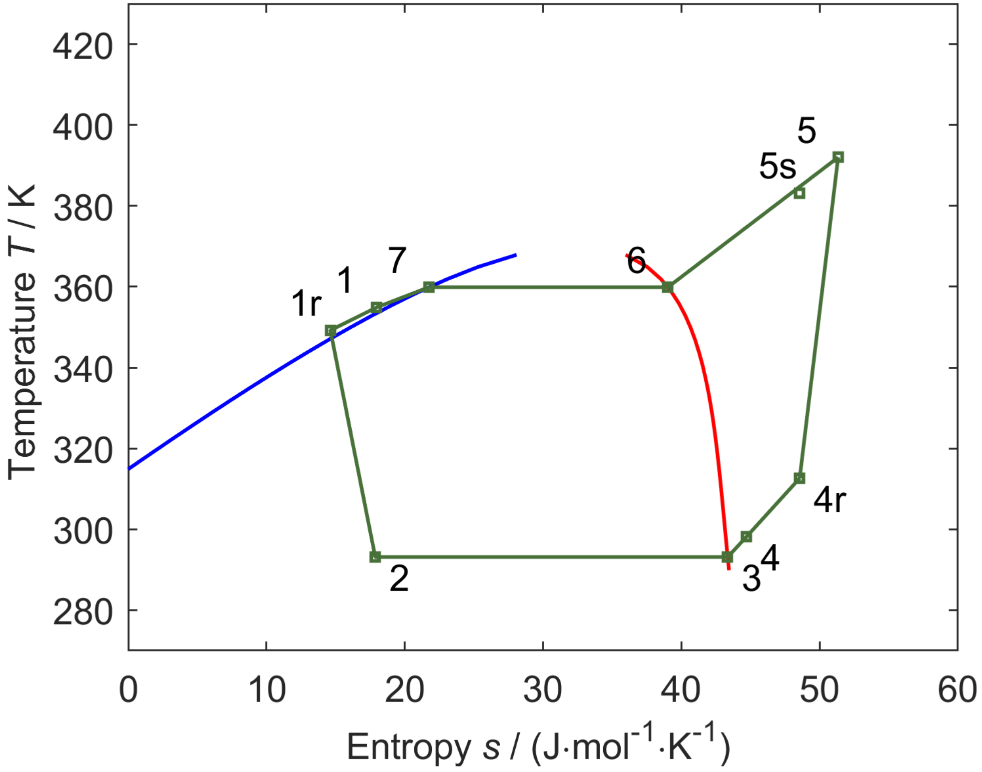
- vapor pressure of propane + HATCOL 4467

• Yang, X., & Richter, M. (2024). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Industrial & Engineering Chemistry Research*, (to be submitted).

Oil’s impact to COP (1)

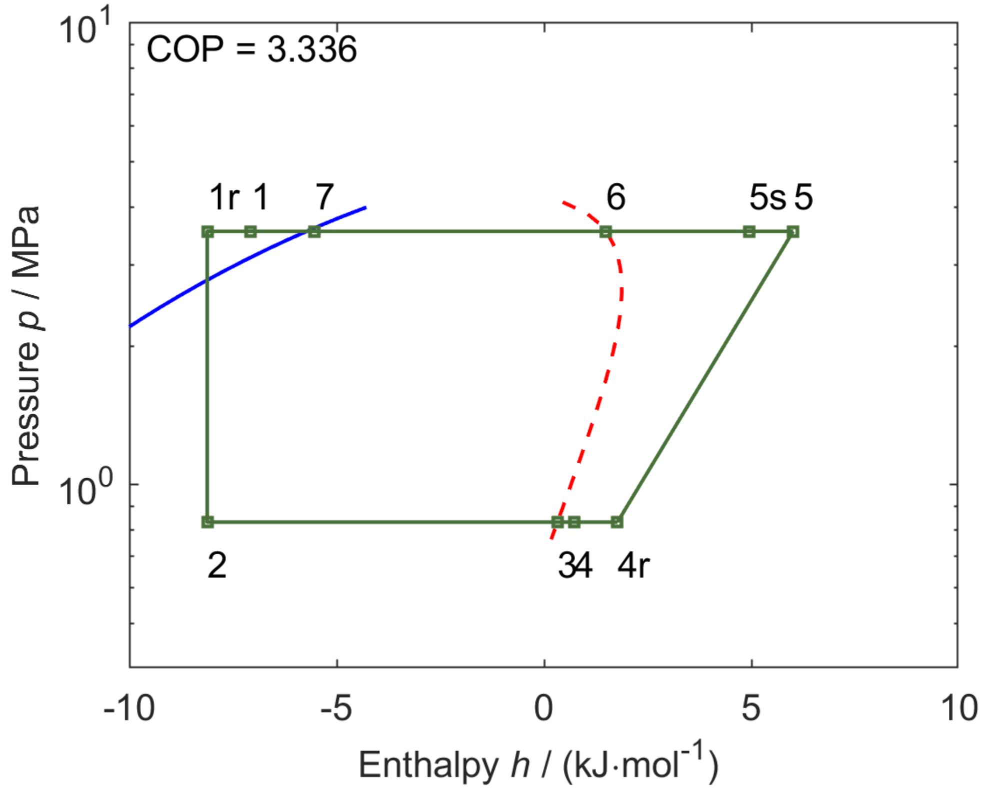
Pure propane

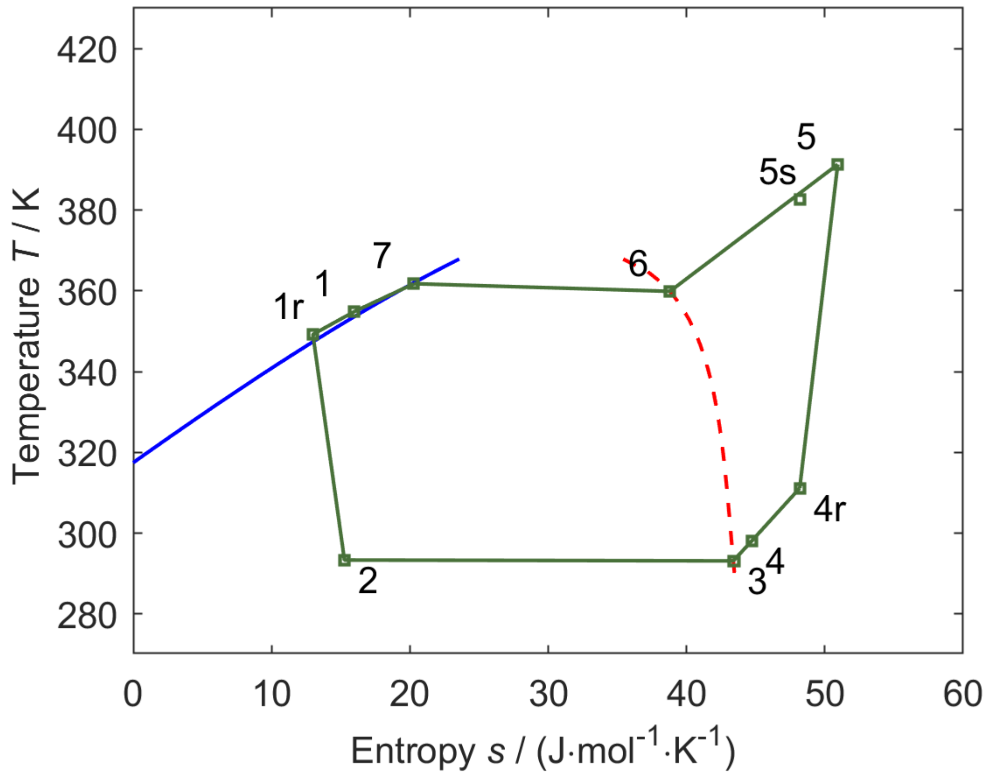




Oil's impact to COP (2)

Propane + 4 wt-% PAG68



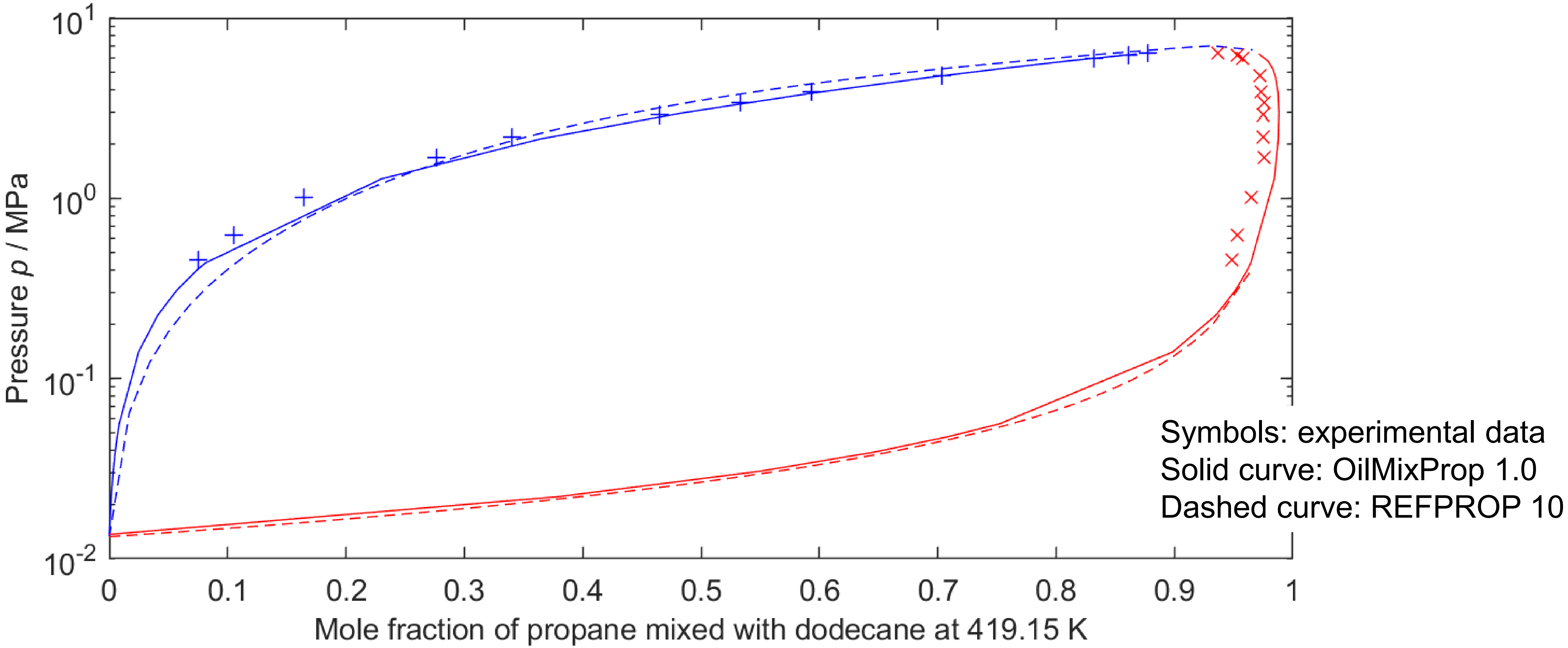


OilMixProp vs REFPROP (1)

	REFPROP 10.0 (*refpropm*)	OilMixProp 1.0 (*oilpropm*)
Aim	Reference package	Reliable solution when fluids are not in REFPROP
Fluids	151 pure fluids	632 pure fluids and unlimited user defined oils
Accuracy	0.02 % to 2.0 %	0.1 % to 6.0 %
Solid phase	No considered	Will be considered
Liquid vapor equilibrium	Not entirely reliable	Reliable, comprehensive
	Example: density of water + nitrogen in equal mass fraction at 303.15 K and 1.0 MPa	
	21.924 kg·m^{-3} liquid phase? vapor phase? overall phases?	Phase behavior in mass fraction. Vapor Frac: 0.501418 water nitrogen Liquid: 0.999999 0.000001 Vapor: 0.002829 0.997171 ---- Properties in each phase ---- Liquid Vapor rho: 979.698 11.113 kg/m3 … -- Properties with all phases combined – rho: 21.915 kg/m3

- Yang, X., & Richter, M. (2024). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Industrial & Engineering Chemistry Research*, (to be submitted).

OilMixProp vs REFPROP (2)



- Yang, X., & Richter, M. (2024). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Industrial & Engineering Chemistry Research*, (to be submitted).

OilMixProp 2.0

Future developments of OilMixProp includes:

- adding functions to calculate critical points of mixtures;
- updating constants of some fluids needed for transport property calculations based on the RES
- enable more phase diagram plots;
- adding solid constants to more fluids so that the LVE phase diagram could be updated to SLVE
- development of a graphical user interface (GUI)
- converting the package to other languages, e.g., python.

OilMixProp 2.0 is estimated to be released in the middle of 2025.

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KETEC Forschungsplattform Kälte- und Energietechnik

GEFÖRDERT VOM Bundesministerium für Bildung und Forschung

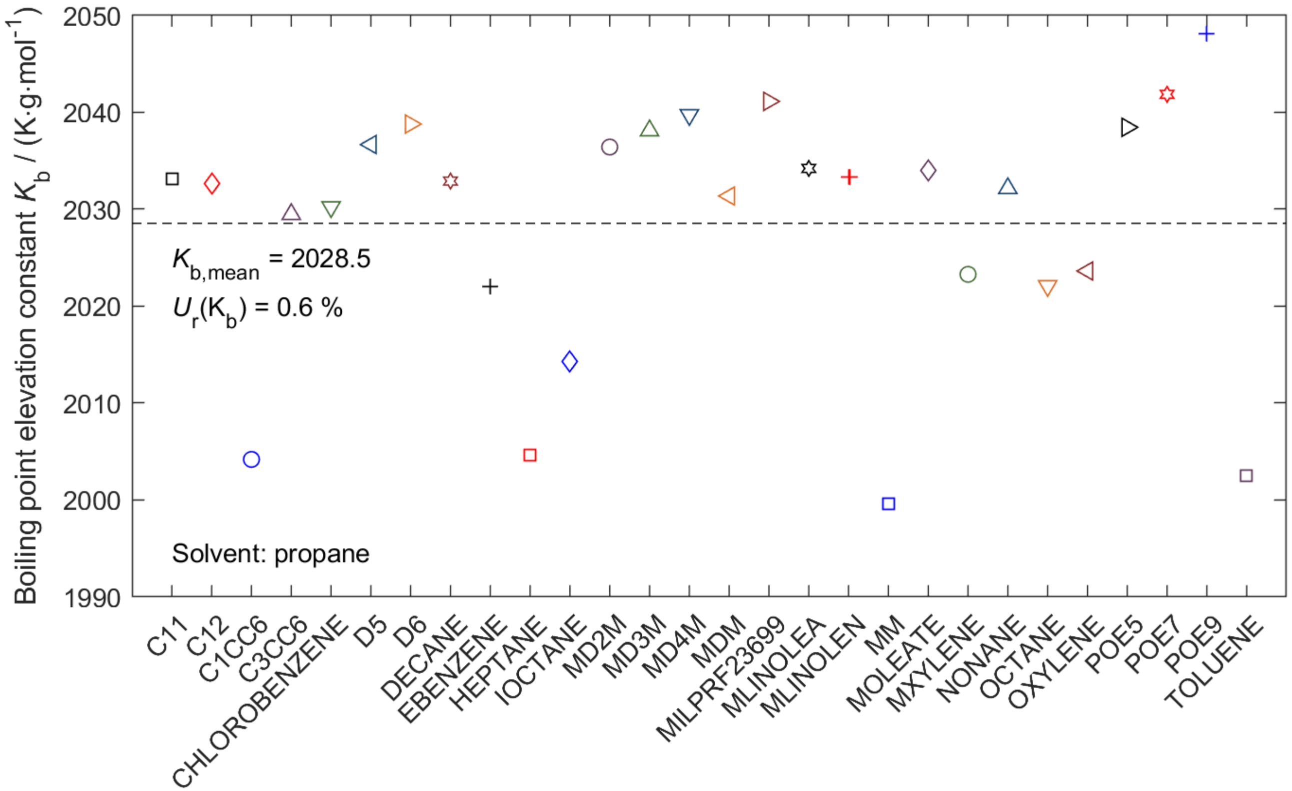
ptJ Projektträger Jülich Forschungszentrum Jülich

SACHSEN Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des von den Abgeordneten des Sächsischen Landtags beschlossenen Haushalts.

Auxiliary pages

Average molar mass of an oil

molar mass M critical points T_c, ρ_c, p_c acentric factor ω k_0 and k_1 in linear-$c_p^o(T)$ $n_{\mu k}$ and $n_{\lambda k}$ (k = 1,2,3,4)



Raoult's law of boiling point elevation:

Molality of solute $b_{\text{solute}} = (T_{\text{solution}} - T_{\text{solvent}})/K_b$

K_b is the boiling point elevation constant

- depends on solvent and pressure
- almost independent to the solute

Mole amount of solute: $n_{\text{solute}} = b_{\text{solute}} \cdot m_{\text{solvent}}$

Molar mass of solute: $M_{\text{solute}} = m_{\text{solute}}/n_{\text{solute}}$

Measurements needed: (1) two masses and two boiling point temperatures

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.

Critical point of an oil

molar mass M **critical points T_c, ρ_c, p_c** acentric factor ω k_0 and k_1 in linear-$c_p^o(T)$ $n_{\mu k}$ and $n_{\lambda k}$ (k = 1,2,3,4)

Rackett equation: $$\rho_{\mathrm{L,sat}} = \rho_c Z_c^{-(1-T/T_c)^{2/7}}$$ ← $\rho_{\mathrm{L,sat}}$ can hardly be measured as saturated pressure of an oil is very low (e.g., < 1 Pa)

$\rho_{\mathrm{L,sat}}$: saturated liquid density
ρ_c ,T_c and Z_c are density, temperature, and compressibility factor at the critical point

Modified Rackett equation: $$\rho_{\mathrm{atm}} = \rho_c Z_c^{-(1-T/T_c)^{2/7}}$$ ← Z_c has to be fixed, e.g., 0.2563 for esters (Vetere 1992)

ρ_{atm}: liquid density at 1 atm

Measurements needed:
(2) Z_c is fixed at a reasonable value (e.g., 0.2563 as recommended by Vetere 1992 for esters);
(3) four, could be down to two, points of (p = 1 atm, T, ρ) for T_c, p_c and ρ_c;

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.
- Vetere A. Again the Rackett equation. The Chemical Engineering Journal 1992;49:27–33.

Acentric factor of an oil

molar mass M critical points T_c, ρ_c, p_c **acentric factor ω** k_0 and k_1 in linear-$c_p^o(T)$ $n_{\mu k}$ and $n_{\lambda k}$ (k = 1,2,3,4)

More than six Cubic EoS were tested:

- Soave-Redlich-Kwong (SRK)
- Peng-Robinson (PR)
- Peng-Robinson-Stryjek-Vera (PRSV)
- Wilson-Redlich-Kwong (WRK)
- **Patel-Teja-Valderrama (PTV)**
- Redlich-Kwong (RK)
- Some volume-translated SRK and PR

Patel-Teja-Valderrama (PTV) EoS:

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + (b+c)v - bc}$$

$$a = \alpha(T_r, \omega) \cdot \Omega_a \frac{R^2 T_c^2}{p_c}$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad c = \Omega_c \frac{RT_c}{p_c}$$

$\Omega_a = 0.66121 - 0.761057 \cdot Z_C$

$\Omega_b = 0.02207 + 0.20868 \cdot Z_C$

$\Omega_c = 0.57765 - 1.87080 \cdot Z_C$

$\alpha = (1 + m \cdot (1 - T_r^{1/2}))^2$

$m = 0.46283 + 3.58230 \omega Z_C + 8.19417 (\omega Z_C)^2$

Measurements needed: (3) four, could be down to two, points of (p = 1 atm, T, ρ) for ω

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.
- Patel NC, Teja AS. A new cubic equation of state for fluids and fluid mixtures. Chem Eng Sci 1982;37:463–73.

Ideal gas properties of an oil

molar mass M critical points T_c, ρ_c, p_c acentric factor ω **k_0 and k_1 in linear-$c_p^o(T)$** $n_{\mu k}$ and $n_{\lambda k}$ (k = 1,2,3,4)

Ideal gas isobaric heat capacity: → Ideal gas enthalpy h^o and ideal gas entropy s^o

$$c_p^o = k_1 \frac{(T - T_0)}{T_c} + k_0$$

c_p^o is k_0 is the value of c_p^o at T_0 = 298.15 K
k_1/T_c is the gradient of c_p^o at T_0.

$$k_2 = k_0 - \frac{k_1 T_0}{T_c}$$

$$h^o = \int_{T_{ref}}^{T} c_p^o dT = \frac{k_1}{2T_c}\left(T^2 - T_{ref}^2\right) + k_2(T - T_{ref})$$

$$s^o = R\ln\frac{v}{v_{ref}} + \frac{k_1}{T_c}(T - T_{ref}) + (k_2 - R)\ln\frac{T}{T_{ref}}$$

T_{ref} and v_{ref} are the reference state, selected arbitrarily.

Residual terms calculated with Cubic EoS

Measurements needed: (4) four, could be down to two, points of (p = 1 atm, T, c_p) for k_0 and k_1

- Yang, X., Hanzelmann, C., Feja, S., Trusler, J. M., & Richter, M. (2023). Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data. *Industrial & Engineering Chemistry Research*, *62*(44), 18736–18749.

Viscosity of an oil

molar mass M critical points T_c, ρ_c, p_c acentric factor ω k_0 and k_1 in linear-$c_p^o(T)$ **$n_{\mu k}$ (k = 1,2,3,4)** and $n_{\lambda k}$

Viscosity with residual entropy scaling (Yang et al 2021, 2022):

$$\mu = \mu_{\rho\to0} + \mu^{\mathrm{r}}$$

$$\mu_{\rho\to0} = f(\varepsilon/k_{\mathrm{B}}, \sigma, T)$$

σ and ε/k_B are L-J parameters *estimated with critical point info.*

$$\mu^{\mathrm{r}} = \frac{\mu^{\mathrm{r}+}\rho_{\mathrm{N}}^{2/3}\sqrt{mk_{\mathrm{B}}T}}{(s^+)^{2/3}}$$

$$s^+ = -s^{\mathrm{r}}/R$$

$$\ln(\mu^{\mathrm{r}+} + 1) = n_{\mu1}\cdot(s^+) + n_{\mu2}\cdot(s^+)^{1.5} + n_{\mu3}\cdot(s^+)^2 + n_{\mu4}\cdot(s^+)^{2.5}$$

m is mass of one molecule, k_B is Boltzmann constant
ρ_N is number density and s^r is residual entropy, both calculated with Cubic EoS

Measurements needed: (5) four points of (p = 1 atm, T, μ) for $n_{\mu k}$ (k = 1,2,3,4)

- Yang X, Xiao X, May EF, Bell IH. Entropy Scaling of Viscosity—III: Application to Refrigerants and Their Mixtures. J Chem Eng Data 2021;66:1385–98
- Yang X, Xiao X, Thol M, Richter M, Bell IH. Linking Viscosity to Equations of State Using Residual Entropy Scaling Theory. Int J Thermophys 2022;43:183

Thermal conductivity of an oil

molar mass M critical points T_c, ρ_c, p_c acentric factor ω k_0 and k_1 in linear-$c_p^o(T)$ $n_{\mu k}$ and **$n_{\lambda k}$ (k = 1,2,3,4)**

Thermal conductivity with residual entropy scaling (Yang et al 2022):

$$\lambda = \lambda_{\rho\to 0} + \lambda^{\mathrm{r}} + \lambda_{\mathrm{C}}$$

$$\mu_{\rho\to 0} = f(\mu_{\rho\to 0}, c_{\mathrm{p}}^{\mathrm{o}})$$

$$\lambda^{\mathrm{r}} = \frac{\lambda^{\mathrm{r}+} k_B \rho_{\mathrm{N}}^{2/3} \sqrt{k_B T/m}}{(s^+)^{2/3}}$$

$$\lambda_{\mathrm{C}} = 0$$

$$s^+ = -s^{\mathrm{r}}/R$$

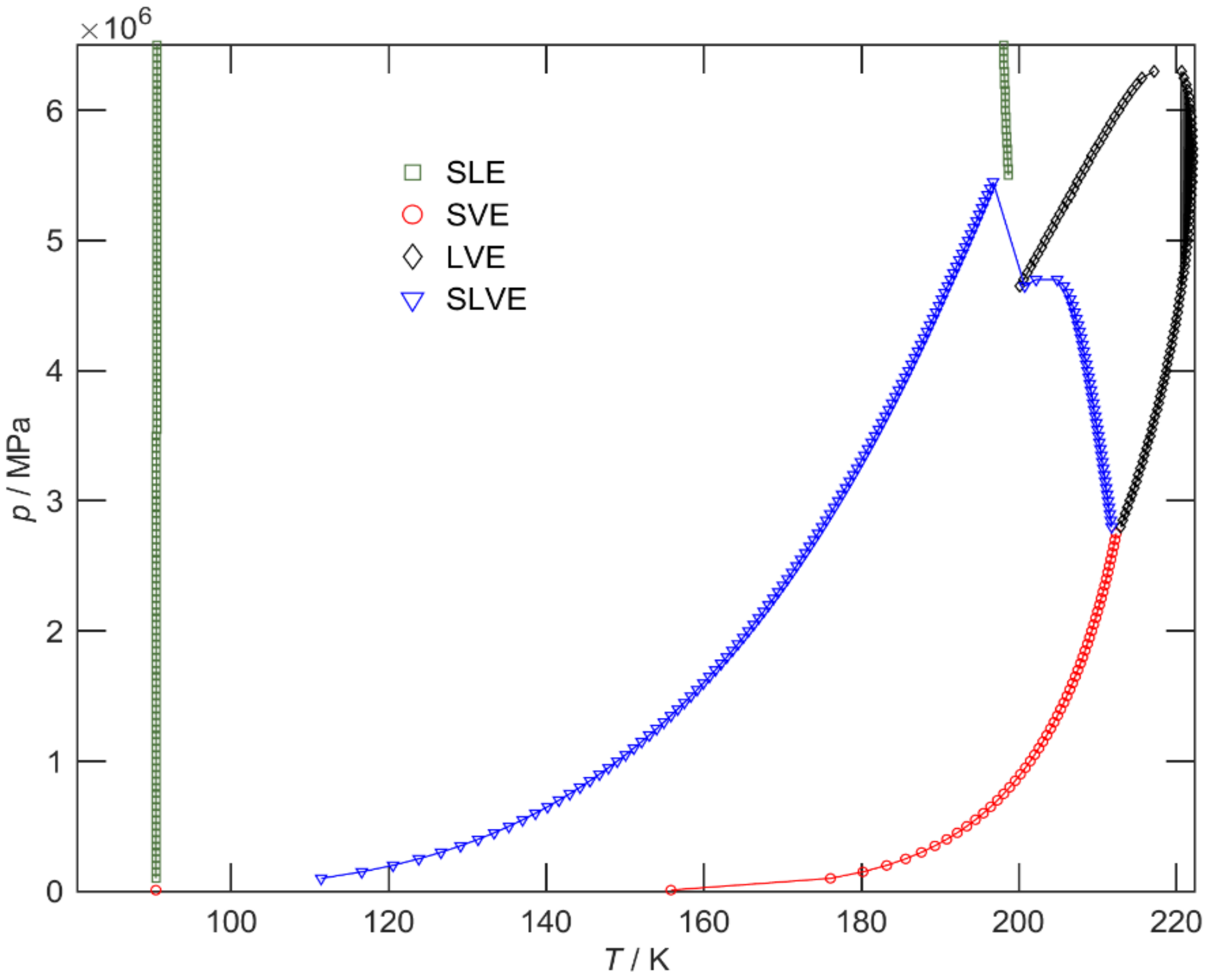
$$\lambda^{\mathrm{r}+} = n_{\lambda 1} \cdot (s^+) + n_{\lambda 2} \cdot (s^+)^{1.5} + n_{\lambda 3} \cdot (s^+)^2 + n_{\lambda 4} \cdot (s^+)^{2.5}$$

m is mass of one molecule, k_B is Boltzmann constant
ρ_N is number density and s^r is residual entropy, both calculated with Cubic EoS

Measurements needed: (6) four points of (p = 1 atm, T, λ) for $n_{\lambda k}$ (k = 1,2,3,4)

- Yang X, Kim D, May EF, Bell IH. Entropy Scaling of Thermal Conductivity: Application to Refrigerants and Their Mixtures. Ind Eng Chem Res 2021;60:13052–70.

Solid needs to be considered



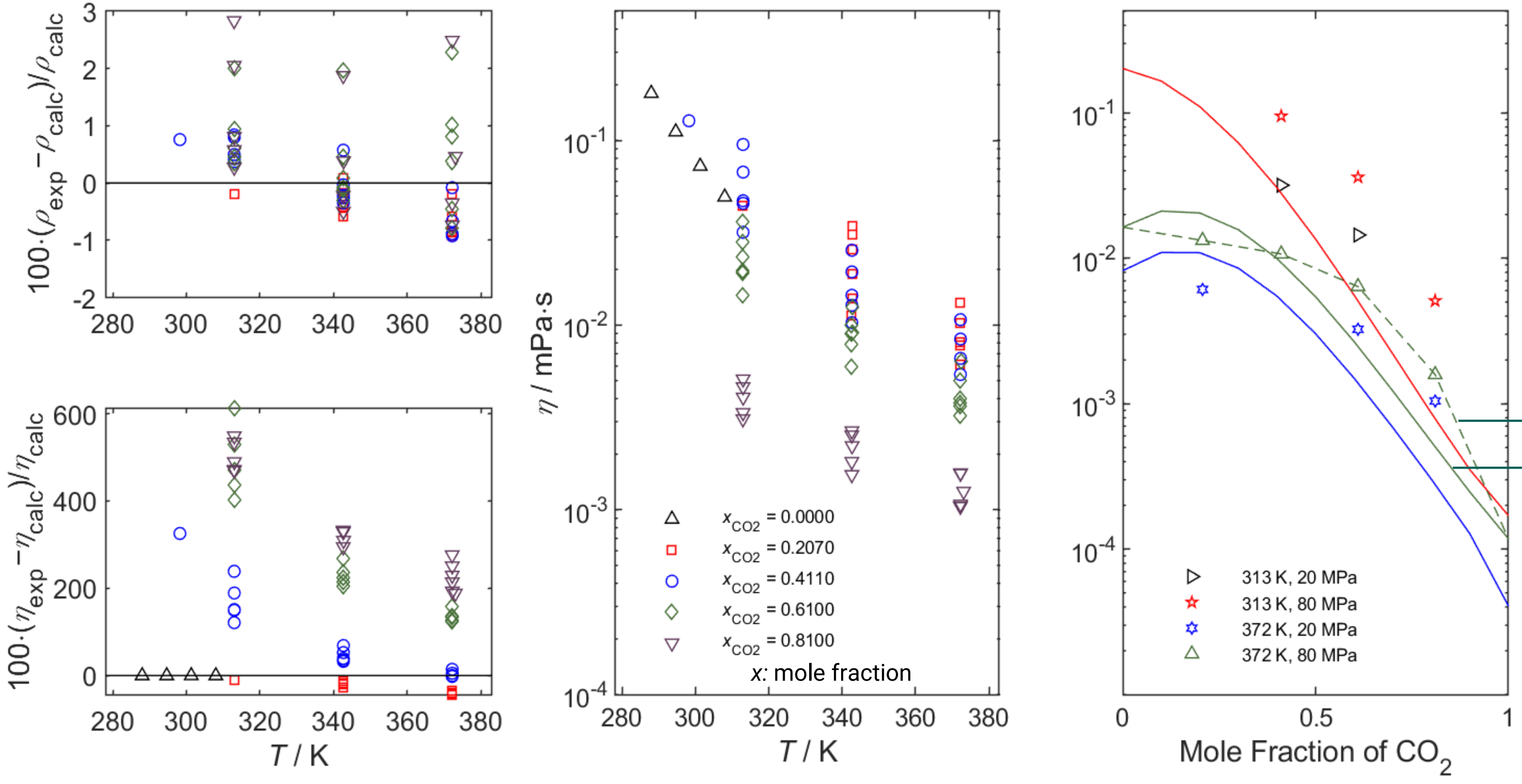
Solid-liquid-vapor equilibrium of a CO_2 + methane mixture.

available in the future OilMixProp 2.0.

- Yang, X., & Richter, M. (2024). OilMixProp 1.0: Package for thermophysical properties of oils, common fluids and their mixtures. *Computer Physics Communications*, (to be submitted).

di-isodecyl phthalate (DIDP) + R744 (CO_2)

Relative deviations and viscosity data (Weerakajornsak 2019)



$BIP_{\mu,12} = -0.15.$

Relative deviations:
- Density: 3.0%
- Viscosity: 600%

Exp. data: unsmooth

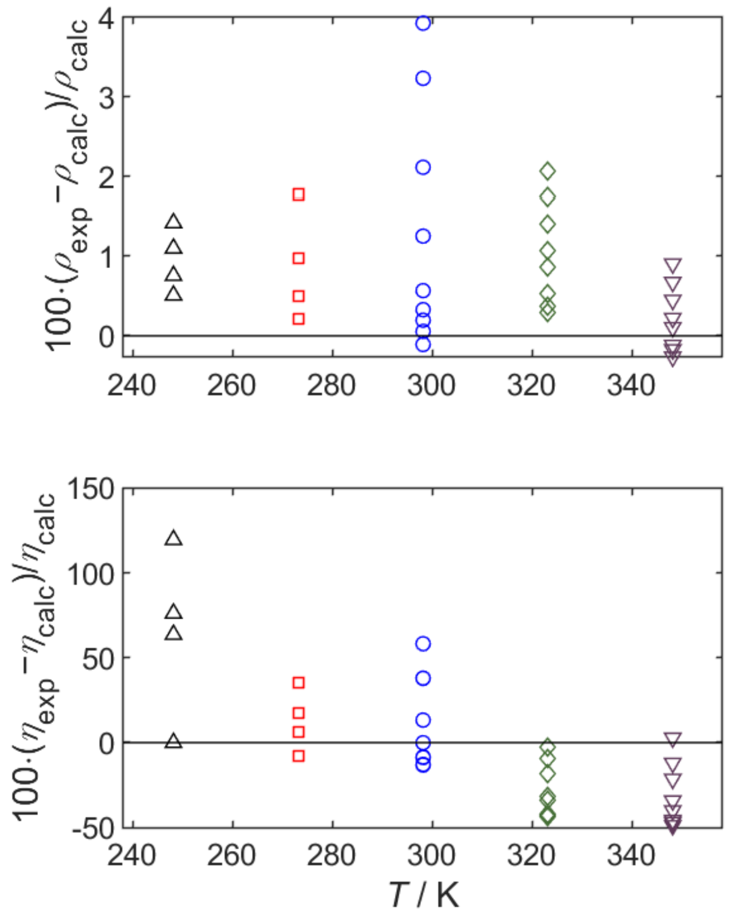
Model perdition: smooth

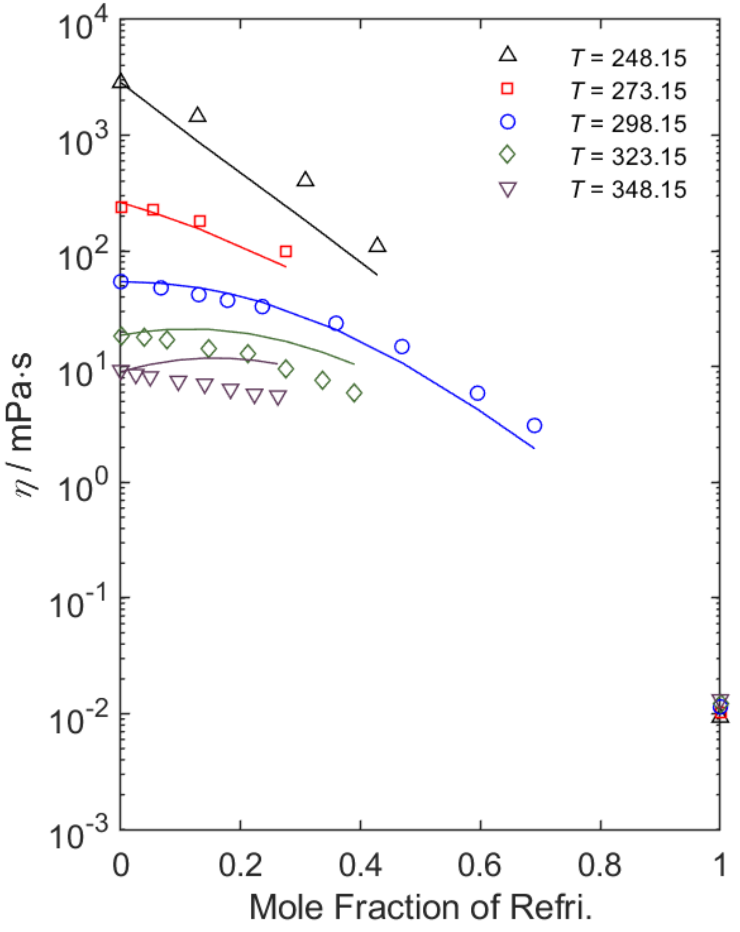
Accurate exp. data needed

- Weerakajornsak, W. (2019). *Thermal conductivity of Polyol ester synthetic oil-CO2 mixtures*. Imperial College London.

ISO VG 32 + R1234yf

Relative deviations and viscosity data (Morais et al., 2020)





ISO VG 32: Emkarate RL 32−3MAF of Lubrizol Corporation, USA

- $BIP_{\mu,12} = -0.6$.

Relative deviations:
- Density: 3.0%
- Viscosity: 120%

• Morais, A. R. C., Simoni, L. D., Shiflett, M. B., & Scurto, A. M. (2020). Viscosity and Density of a Polyol Ester Lubricating Oil Saturated with Compressed Hydrofluoroolefin Refrigerants. *Journal of Chemical & Engineering Data*, *65*(9), 4335–4346