Wax Deposition

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Introduction

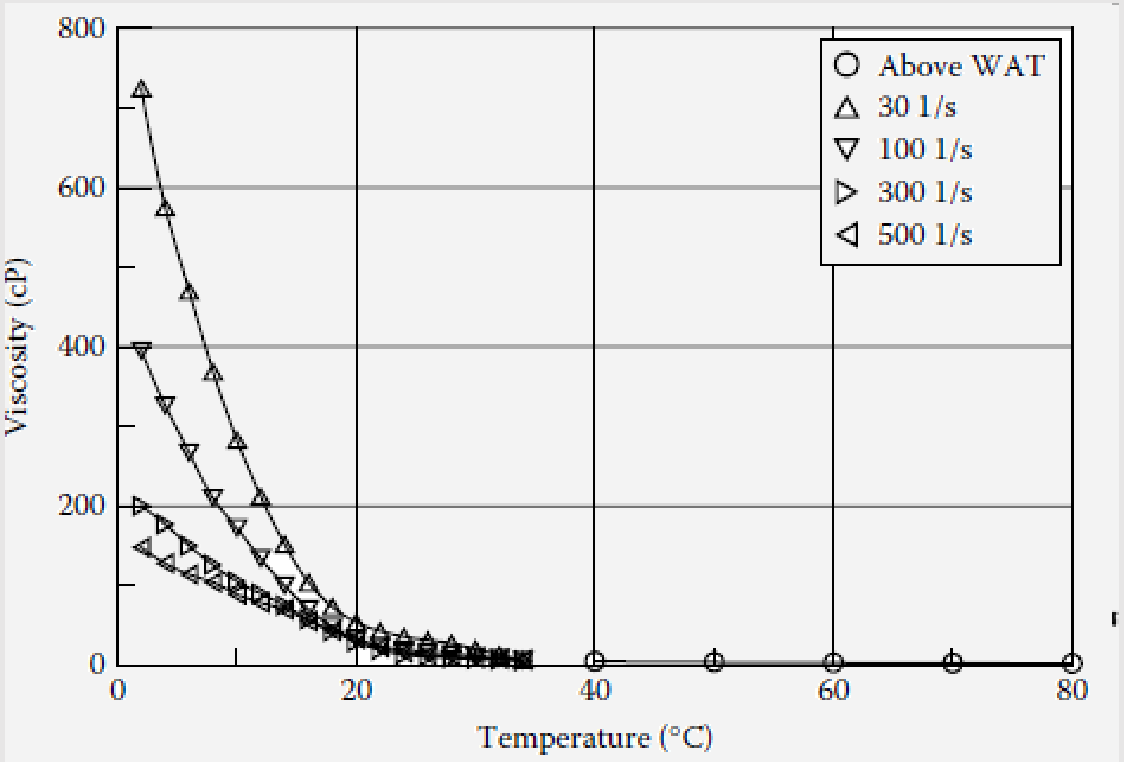
- Definition
- Wax appearance temperature (WAT)
- Subsea pipe line

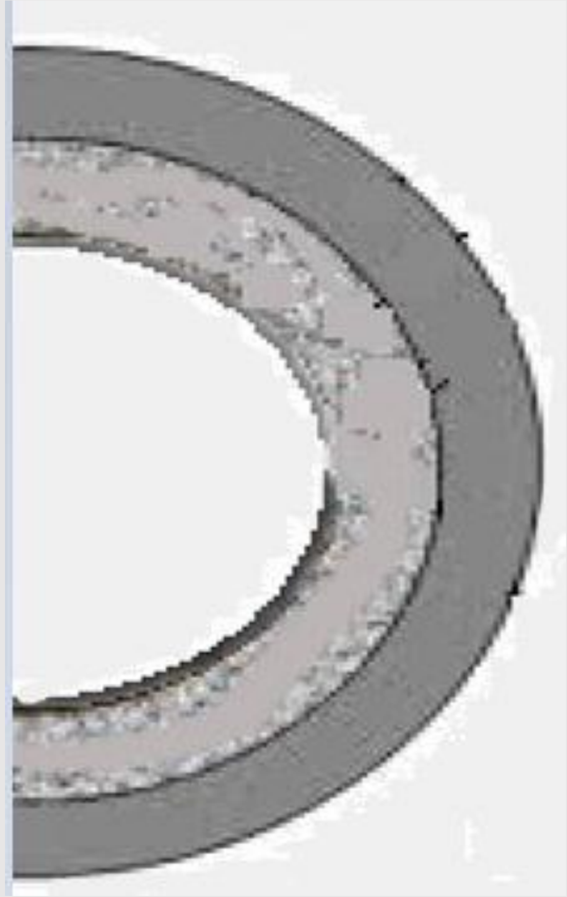
Wax deposition, Singh et al (2000)

Hydrocarbon	Average	Range
Alkanes (Paraffins)	30%	15 to 60%
Naphtenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltenes	6%	remainder

Problems Triggered by Wax

- High viscosity, which leads to pressure losses
  - Non-Newtonian behavior below WAT
- High-yield stress for restarting flow





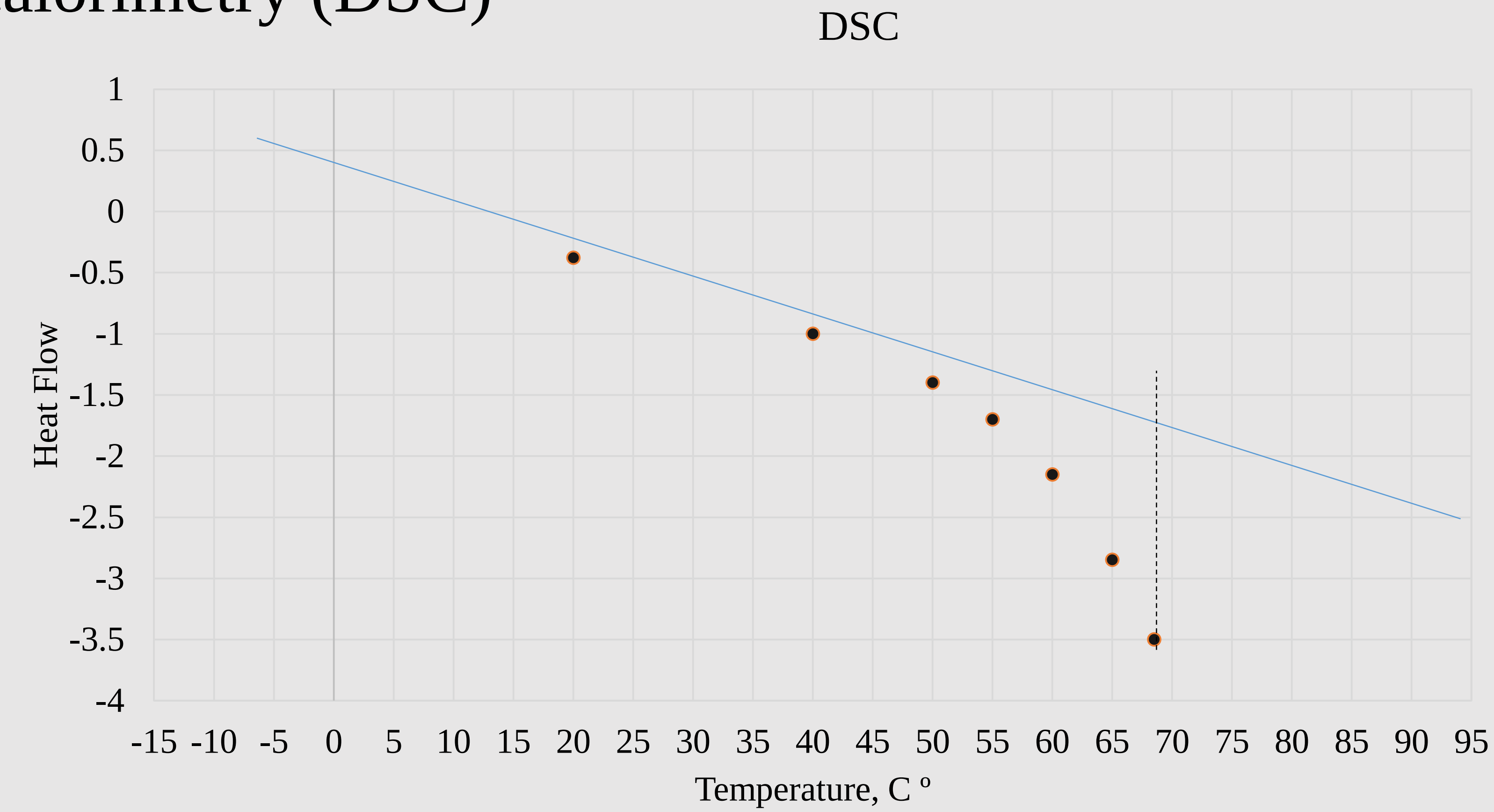
Problems Triggered by Wax

- Pigging frequency
  - Solid wax fraction
- Isolation layer design
  - Precipitation rate
- Platform abonnement
  - Production stoppage
  - Remedial actions (changing the pipe)
- Flow rate restriction

Cleaning pig

WAT and Measurement Techniques

- Microscopy
- Differential scanning calorimetry (DSC)
- Viscometry



Thermodynamic Description of Melting: Pure Components

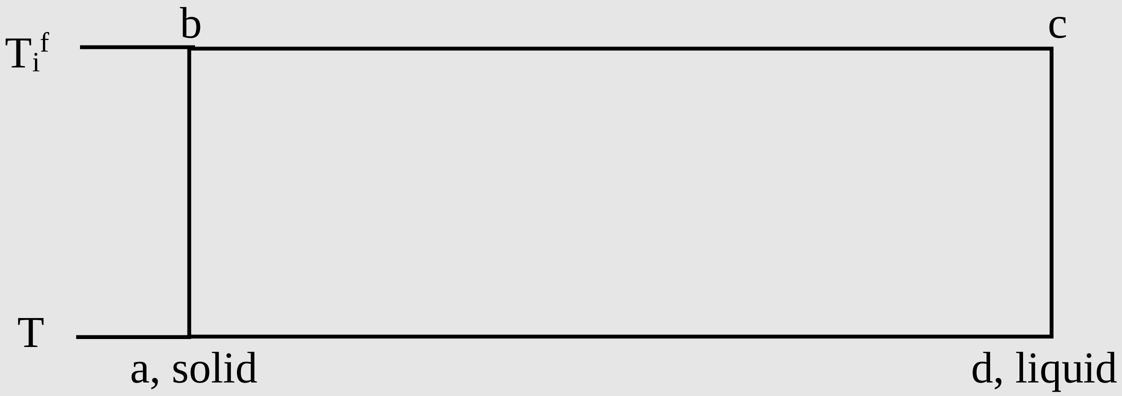
$$\Delta G_i^f = \Delta H_i^f - T\Delta S_i^f$$

$$\Delta H_{ad} = \Delta H_{ab} + \Delta H_{bc} + \Delta H_{cd} = \Delta H_i^f + \int_T^{T_i^f} \Delta C_{pi} dT$$

$$\Delta \mathrm{G}_{\mathrm{ad}} = \Delta \mathrm{H}_{\mathrm{i}}^{\mathrm{f}}\left(1 - \frac{\mathrm{T}}{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}}\right) + \int_{\mathrm{T}}^{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}} \Delta \mathrm{C}_{\mathrm{pi}} \mathrm{dT} - \int_{\mathrm{T}}^{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}} \frac{\Delta \mathrm{C}_{\mathrm{pi}}}{\mathrm{T}} \mathrm{dT}$$

$$\Delta \mathrm{G}_{\mathrm{ad}} = \mathrm{RT} \ln\left(\frac{\mathrm{f}_{\mathrm{i}}^{\circ \mathrm{L}}(\mathrm{p}_{\mathrm{ref}})}{\mathrm{f}_{\mathrm{i}}^{\circ \mathrm{S}}(\mathrm{p}_{\mathrm{ref}})}\right)$$

$$\mathrm{f}_{\mathrm{i}}^{\circ \mathrm{S}} = \mathrm{f}_{\mathrm{i}}^{\circ \mathrm{L}} \exp\left(-\frac{\Delta \mathrm{H}_{\mathrm{i}}^{\mathrm{f}}}{\mathrm{RT}}\left(1 - \frac{\mathrm{T}}{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}}\right) - \frac{1}{\mathrm{RT}} \int_{\mathrm{T}}^{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}} \Delta \mathrm{C}_{\mathrm{pi}} \mathrm{dT} + \frac{1}{\mathrm{RT}} \int_{\mathrm{T}}^{\mathrm{T}_{\mathrm{i}}^{\mathrm{f}}} \frac{\Delta \mathrm{C}_{\mathrm{pi}}}{\mathrm{T}} \mathrm{dT}\right)$$



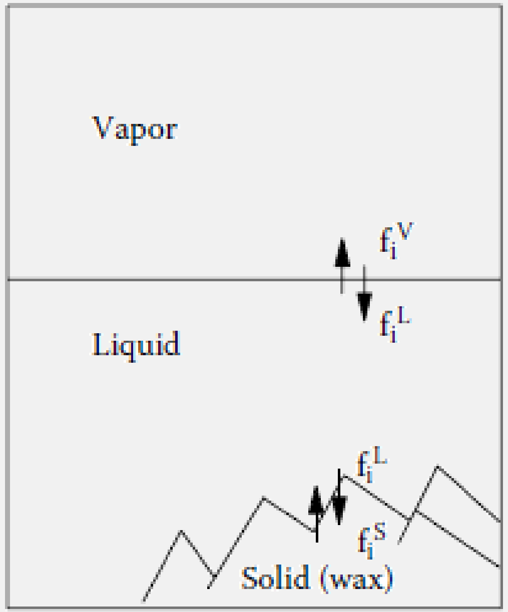
Liquid-Solid Equilibrium

- f_i^V: EOS
- f_i^L: EOS or activity coefficient
- f_i^S: Activity coefficient
  - $f_i^L = x_i^L\,\gamma_i^L f_i^{\circ L}$
  - $f_i^S = x_i^S \gamma_i^S f_i^{\circ S}$

$$\frac{x_i^L}{x_i^S} = \frac{\gamma_i^S}{\gamma_i^L}\exp\left(-\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)-\frac{1}{RT}\int_T^{T_i^f}\Delta C_{pi}dT+\frac{1}{RT}\int_T^{T_i^f}\frac{\Delta C_{pi}}{T}dT\right),$$

$$\gamma^L = f(\delta_i^L) = f(\Delta H_i^{vap}, T, V_i^L, x_i^L)$$

$$\gamma^S = f(\delta_i^L) = f(\Delta H_i^{vap}, T, V_i^S, x_i^S)$$



Phase equilibrium:

$f_i^V = f_i^L = f_i^S$

Problems with Won

$f_i^L = f_i^V$,EOS

$f_i^L = f_i^S$, Activity Coe

$\Longrightarrow$ $f_i^L \neq f_i^L$!

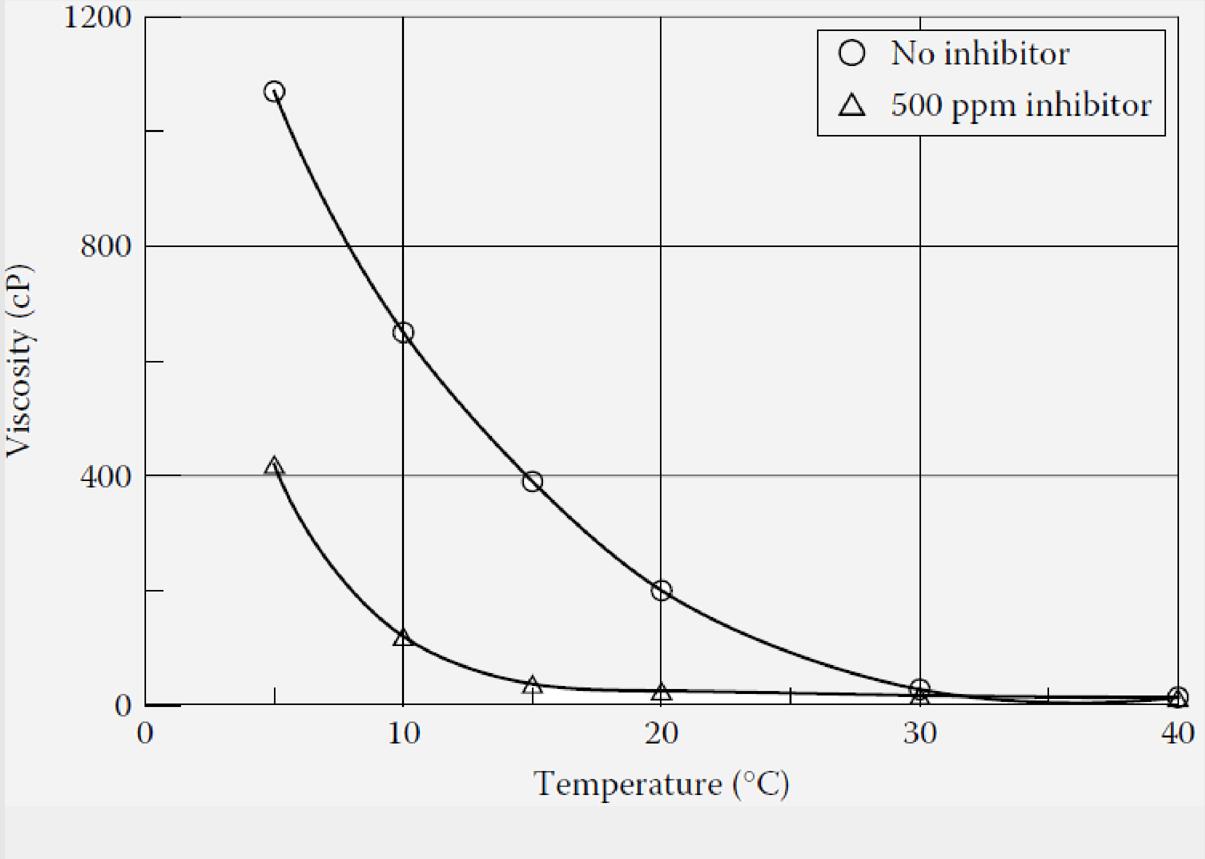
- Higher WAT
- Solid phase, less thermodynamically favorable
- $f_i^S\uparrow$, $f_i^L\downarrow$ from $\mathrm{f_i^L = x_i^L\ \gamma_i^L{\downarrow}f_i^{\circ L}}$
- Polymer Solution theory

Ideal Solution Wax Model

- Iso-paraffins contribution
- Depressing effect on WAT!
- Melting enthalpies and temperatures lower that n-paraffins
- Activity coefficient is zero (ideal solution)

Inhibitors

- Lower the apparent viscosity and pour point
  - Wax Crystal modifiers
  - Detergents
  - Dispersants



Method of Won

Thermodynamic model:

$$\frac{x_i^L}{x_i^S} = \frac{\gamma_i^S}{\gamma_i^L} \exp\left(-\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right) - \frac{1}{RT}\int_T^{T_i^f} \Delta C_{pi} dT + \frac{1}{RT}\int_T^{T_i^f} \frac{\Delta C_{pi}}{T} dT\right)$$

Won first simplified the model:

$$\frac{x_i^L}{x_i^S} = \frac{\gamma_i^S}{\gamma_i^L} \exp\left(-\frac{\Delta H_i^f}{RT}\left(1-\frac{T}{T_i^f}\right)\right)$$

Method of Won: Regular Solution Theory

$$\ln\gamma_i^L = \frac{V_i^L\left(\bar{\delta}^L - \delta_i^L\right)^2}{RT}, \ln\gamma_i^S = \frac{V_i^S\left(\bar{\delta}^S - \delta_i^S\right)^2}{RT}$$

$$\delta_i^L = \sqrt{\frac{\Delta H_i^{vap} - RT}{V_i^L}}, \delta_i^S = \sqrt{\frac{\Delta H_i^{vap} - \Delta H_i^f - RT}{V_i^S}}$$

$$\bar{\delta}^L = \sum_{i=1}^{N} \Phi_i^L \delta_i^L, \bar{\delta}^S = \sum_{i=1}^{N} \Phi_i^S \delta_i^S$$

$$\Phi_i^L = \frac{x_i^L V_i^L}{\sum_{j=1}^{N} x_j^L V_j^L}, \Phi_i^S = \frac{x_i^S V_i^S}{\sum_{j=1}^{N} x_j^S V_j^S}$$

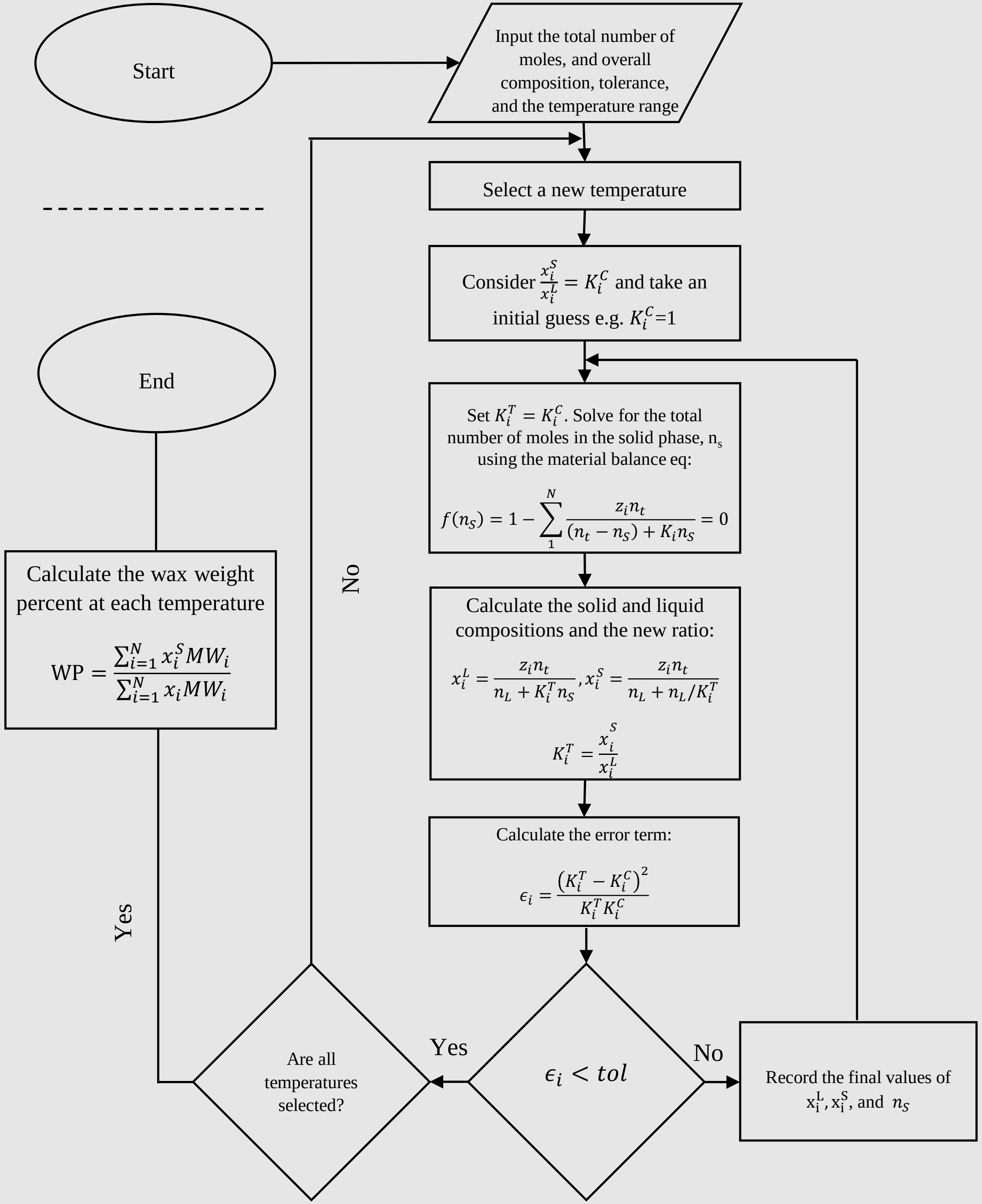
Method of Won: Correlations

- Won suggested correlations for calculating the enthalpy of melting, melting temperature, and molar volume for each component:

$$\Delta H_i^f = 0.1426 M_i T_i^f$$

$$T_i^f = 374.5 + 0.02617 M_i - \frac{20172}{M_i}$$

$$V_i^L = V_i^S = \frac{M_i}{d_{i,25}^L} \text{ where } d_{i,25}^L = 0.8155 + 0.6273 \times 10^{-4} M_i - \frac{13.06}{M_i}$$



3N+2 equations & 3N+2 unknowns:

$$K_i^T = \frac{x_i^S}{x_i^L} = \frac{\gamma_i^L}{\gamma_i^S}\exp\left(\frac{\Delta H_i^f}{RT}\left(1 - \frac{T}{T_i^f}\right)\right)$$

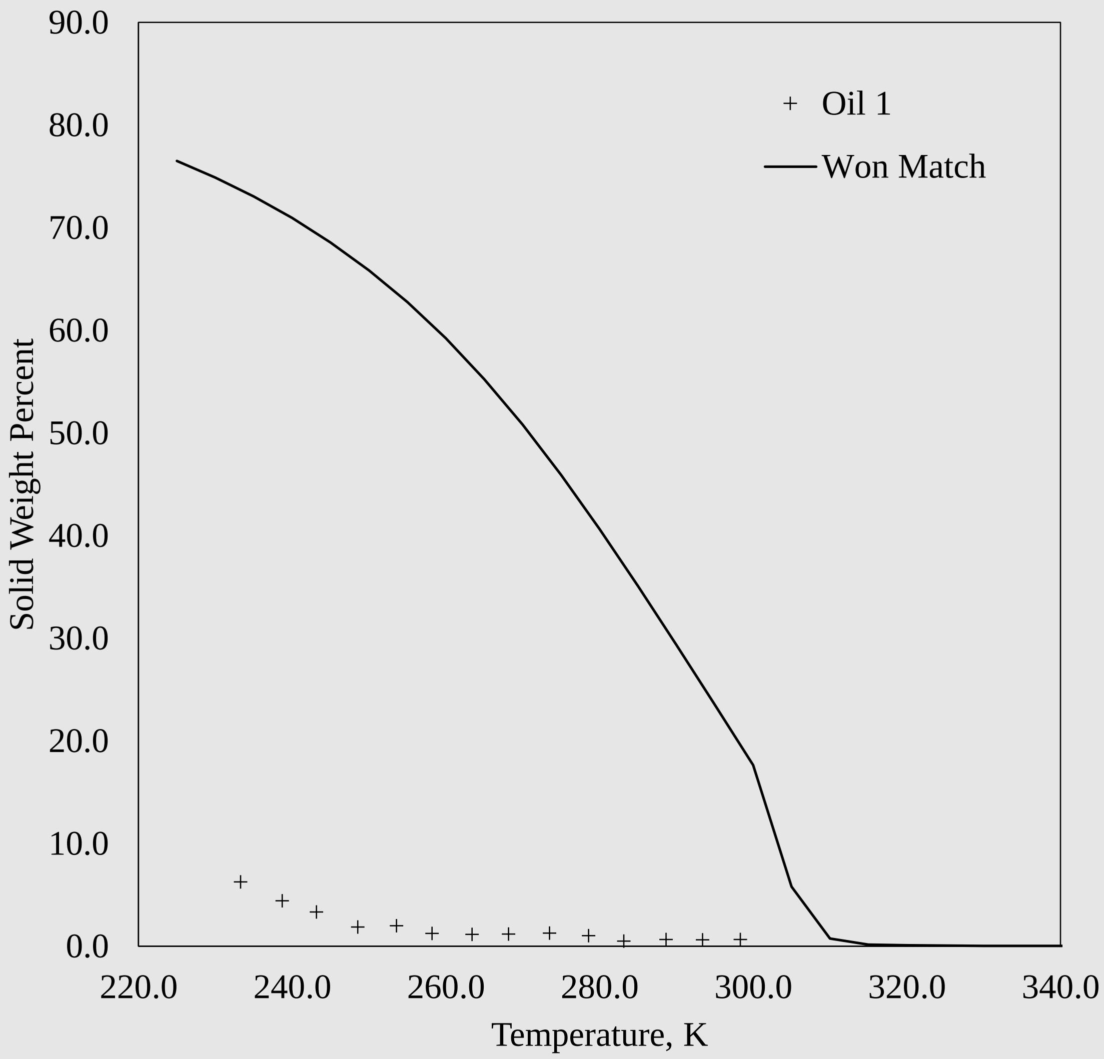
$$x_i^L = \frac{z_i n_t}{n_L + K_i^T n_S}$$

$$x_i^S = \frac{z_i n_t}{n_L + n_L/K_i^T}$$

$$f(n_S) = 1 - \sum_1^N \frac{z_i n_t}{(n_t - n_S) + K_i n_S} = 0$$

$$n_t = n_S + n_L$$

Method of Won: Results



Method of Pedersen: Correlations

- The solubility parameter, δ_i^L, δ_i^S

$$\mathrm{\delta_i^L = 7.41 + a_1(\ln C_N - \ln 7)}$$

$$\mathrm{\delta_i^S = 8.5 + a_2(\ln C_N - \ln 7)}$$

- The melting enthalpy of components, ΔH_i^f

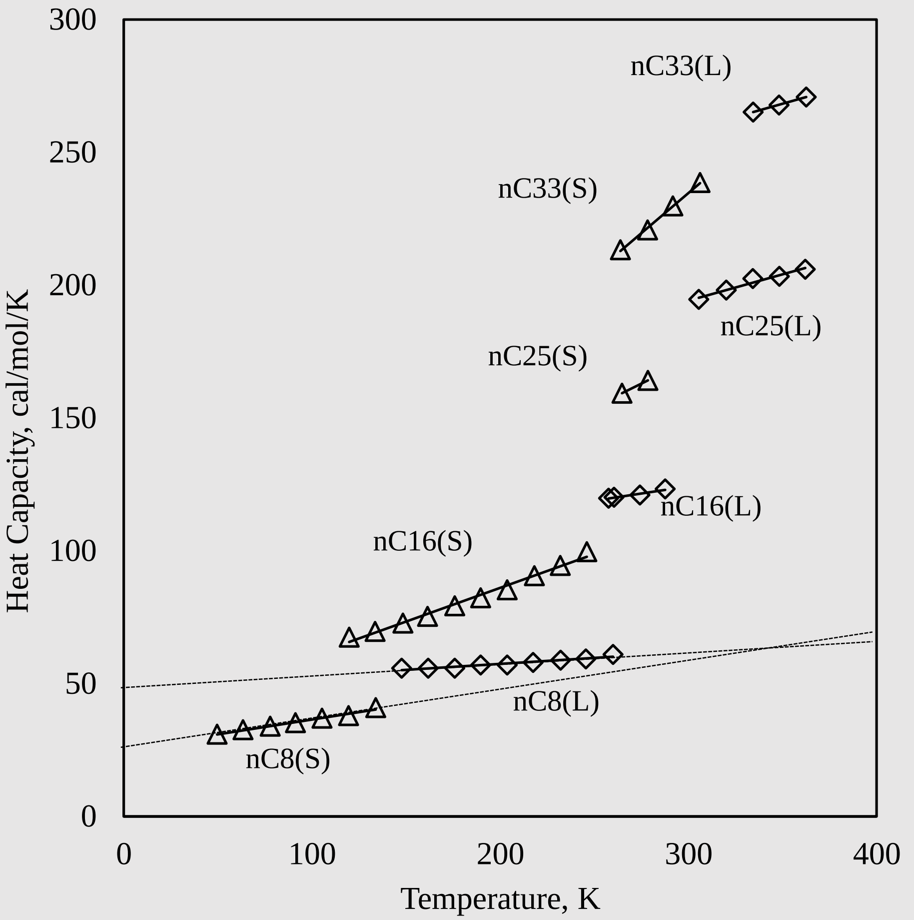
$$\mathrm{\Delta H_i^f = a_3 \Delta H_{o,i}^f}$$

Method of Pedersen: Correlations

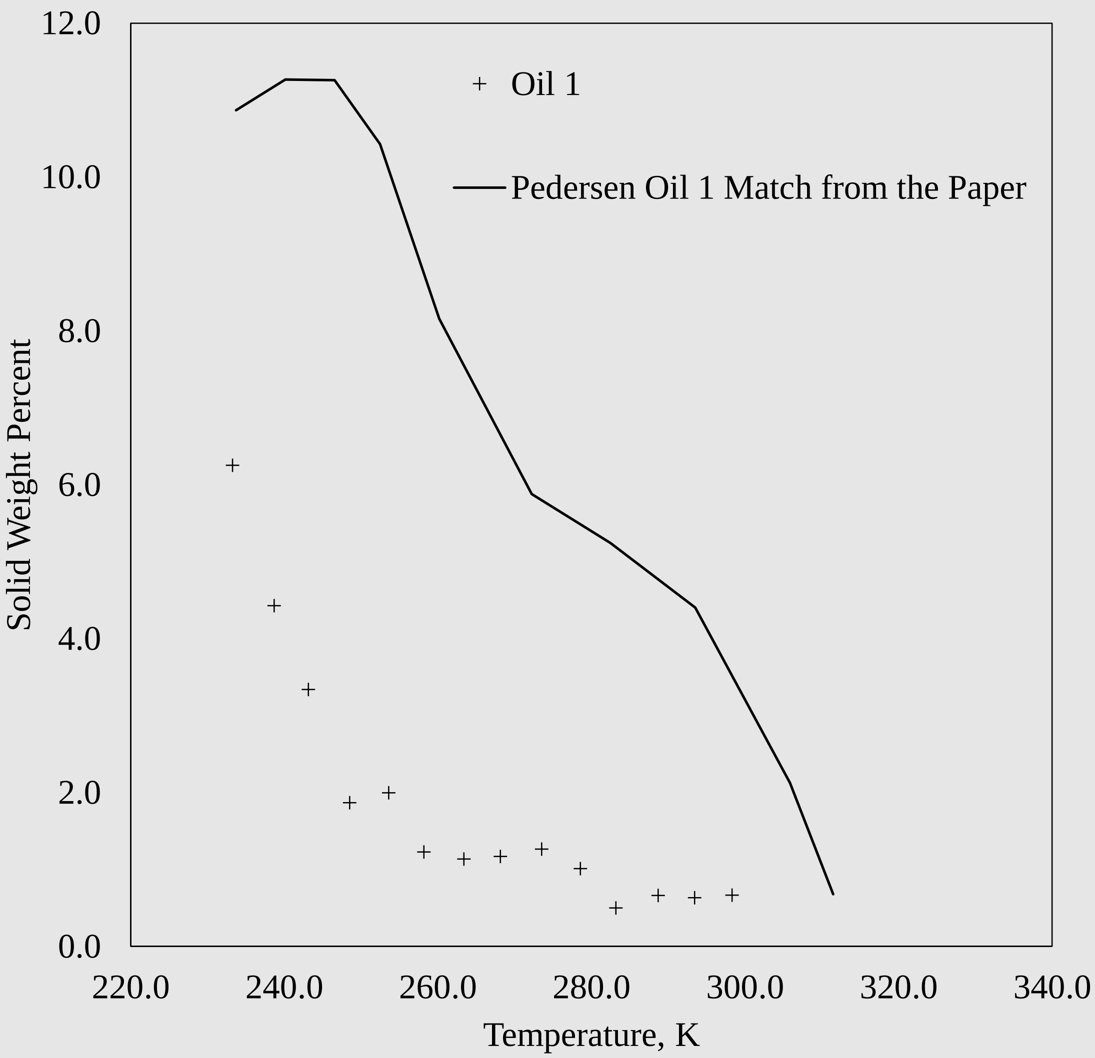
- The solid and liquid phase heat capacities

$$\Delta C_p^i = C_p^S - C_p^L$$

$$\Delta C_p^i = a_4 M_i + a_5 M_i T$$



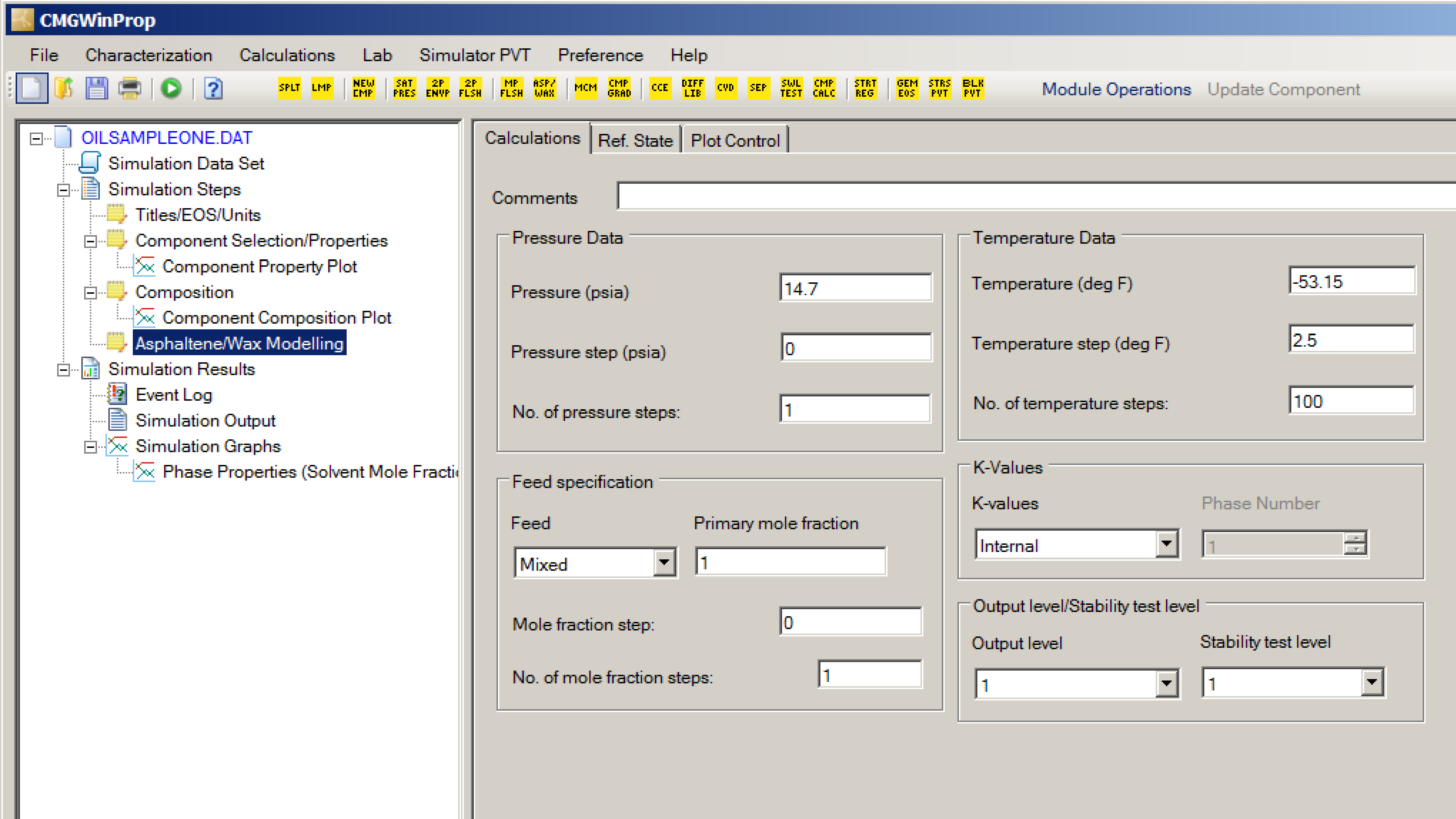
Method of Pederson: Results



WinProp: Model

- Naghiem et al. (1993, 1996) and Kohse et al. (2000)

$$\ln f_S = \ln f_S^* + \frac{V_S}{R}\left[\frac{p - p_{tp}}{T} - \frac{p^* - p_{tp}}{T^*}\right] - \frac{\Delta H_{tp}}{R}\left[\frac{1}{T} - \frac{1}{T^*}\right] - \frac{\Delta C_p}{R}\left[\ln\left(\frac{T^*}{T}\right) - T_{tp}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right]$$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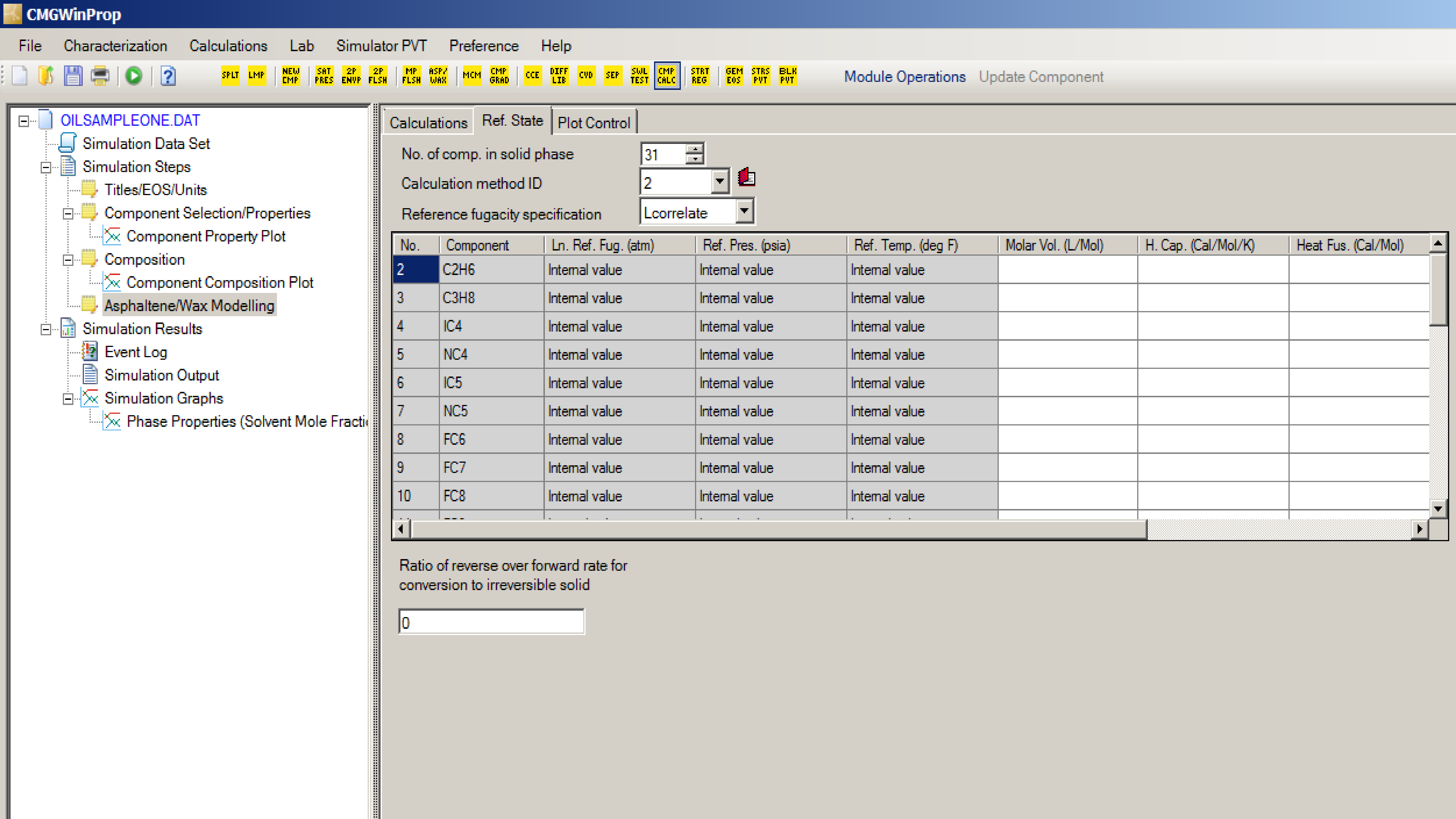
Characterization
Calculations
Lab
Simulator PVT
Preference
Help
SPLT
LMP
NEW CMP
SAT PRES
2P ENVP
2P FLSH
MP FLSH
ASP/ WAX
MCM
CMP GRAD
CCE
DIFF LIB
CVD
SEP
SWL TEST
CMP CALC
STRT REG
GEM EOS
STRS PVT
BLK PVT
Module Operations
Update Component
OILSAMPLEONE.DAT
Simulation Data Set
Simulation Steps
Titles/EOS/Units
Component Selection/Properties
Component Property Plot
Composition
Component Composition Plot
Asphaltene/Wax Modelling
Simulation Results
Event Log
Simulation Output
Simulation Graphs
Phase Properties (Solvent Mole Fracti
Calculations
Ref. State
Plot Control
Comments
Pressure Data
Pressure (psia)
14.7
Pressure step (psia)
0
No. of pressure steps:
1
Temperature Data
Temperature (deg F)
-53.15
Temperature step (deg F)
2.5
No. of temperature steps:
100
Feed specification
Feed
Mixed
Primary mole fraction
1
Mole fraction step:
0
No. of mole fraction steps:
1
K-Values
K-values
Internal
Phase Number
1
Output level/Stability test level
Output level
1
Stability test level
1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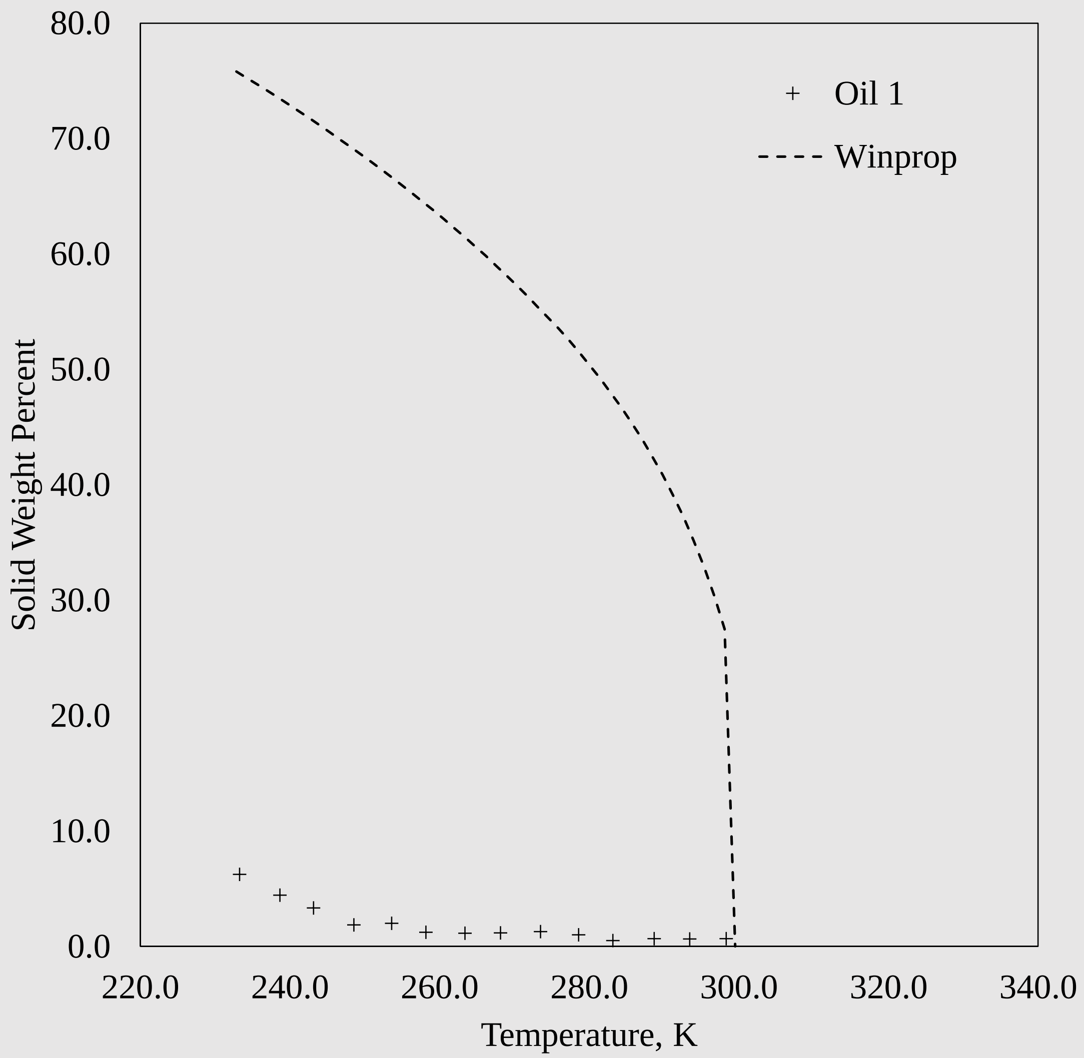
Simulation Output
Simulation Graphs
Phase Properties (Solvent Mole Fracti
Calculations
Ref. State
Plot Control
No. of comp. in solid phase
31
Calculation method ID
2
Reference fugacity specification
Lcorrelate
No.
Component
Ln. Ref. Fug. (atm)
Ref. Pres. (psia)
Ref. Temp. (deg F)
Molar Vol. (L/Mol)
H. Cap. (Cal/Mol/K)
Heat Fus. (Cal/Mol)
2 C2H6 Internal value Internal value Internal value
3 C3H8 Internal value Internal value Internal value
4 IC4 Internal value Internal value Internal value
5 NC4 Internal value Internal value Internal value
6 IC5 Internal value Internal value Internal value
7 NC5 Internal value Internal value Internal value
8 FC6 Internal value Internal value Internal value
9 FC7 Internal value Internal value Internal value
10 FC8 Internal value Internal value Internal value
Ratio of reverse over forward rate for
conversion to irreversible solid
0

WinProp: Results



References

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