Investigation for Estimation Models of Liquid Density and Speed of Sound for Up & Midstream

Innovation Summit Software Conference

ENG-06 New Advances in Thermodynamic Modeling Methods

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Agenda

I. Motivation of This Study

Requirements to Liquid Density Models for Up & Midstream Applications

II. Summary of Liquid Density Models

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)

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Estimation of Liquid Density, Speed of Sound and Adiabatic Bulk Modulus

VI. Continuity of Density from Ordinary Liquid Phase to Dense Fluid Phase

Phase Envelop of Simplified Natural Gas and Density

VII. Conclusion Remarks

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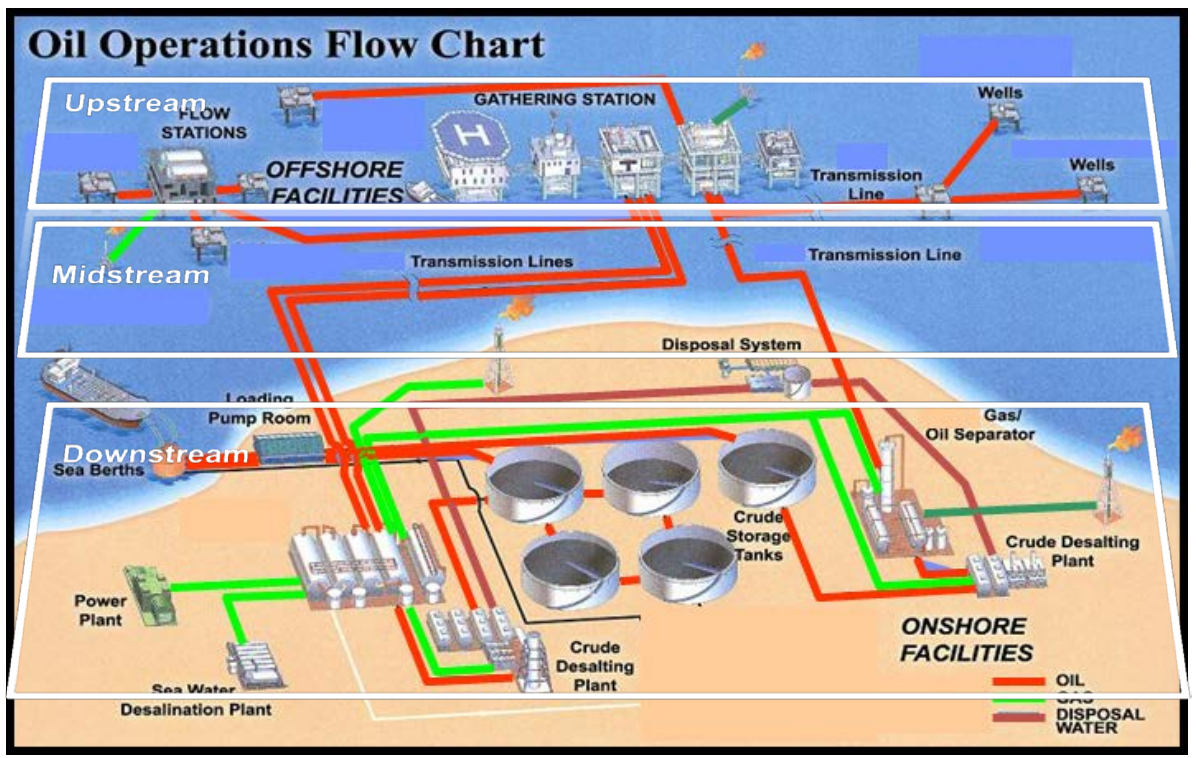
I. Motivation of This Study

Requirements to Liquid Density Models for Up & Midstream Applications

I. Reasonable handling of mixture of heavy compounds and dissolved supercritical compounds under high pressure conditions
II. Good handling for not only hydrocarbon phase but aqueous phase with gas hydrate equilibrium inhibitor
III. Continuity of density from ordinary liquid phase to dense fluid phase



I. Motivation of This Study

Typical Applications of Liquid Density and PvT Relationship

I. Equipment sizing for drum, tower etc.

II. Flow assurance for tubing, pipe, pipeline and valve etc.

III. Estimation of pump head and power

$$Power\ [kW] = \frac{W \cdot \Delta P}{3600 \cdot e \cdot \boldsymbol{\rho}}, \quad \mathrm{hav[m]} = \frac{1000 \cdot \Delta P}{g \cdot \boldsymbol{\rho}}, w : mass\ flow\ rate$$

IV. Studies for safety and trouble prevention

a) Water Hammer (Fluid Hammer) Study
Density and Speed of Sound (SOS) are required as physical properties.
SOS can be derived from PvT relationship.

b) Choking study
SOS is required to determine Mach number.

etc.

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II. Summary of Liquid Density Models

~ Introduction of Three Model Frameworks and Troubles of Each Framework

Model Frameworks for Estimation of Liquid Density and PvT Relationship

I. Pure Component Average

a) Overviews of this model

First of all, the density values of individual pure compounds are estimated. After that, the density value of the mixture is estimated using specific mixing rule of density. This estimation methodology is similar to estimation method for superficial density of two multi phase.

b) Models on PRO/II

Library method, Rackett (accessing from key word only)

c) Typical Predicted Troubles for this model

- ✓ Liquid density values of dissolved supercritical compounds are estimated from density value at NBP. Estimation results are questionable when the solubility is high.
- ✓ Basically, these models are corresponding to saturated. Therefore, PvT relationship cannot be estimated.

Pure Component Average (Library method) is not recommended for up & midstream applications.

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II. Summary of Liquid Density Models

~ Introduction of Three Model Frameworks and Troubles of Each Framework

Model Frameworks for Estimation of Liquid Density and PvT Relationship

II. Generalized Correlations

a) Overviews of this model

First of all, a pseudo one fluid is assumed for homogeneous liquid. Characteristic parameters are estimated using mixing rule of the parameter. Liquid density (saturated) can be estimated using these characteristic parameters.

b) Models on PRO/II

Rackett (one fluid), API and COSTALD (HBT)

c) Typical Predicted Troubles for this model

✓ Basically, these models are corresponding to saturated. Only COSTALD takes pressure effect (sub-cool region) into account in case of PRO/II. Therefore, Rackett on PRO/II and API cannot be applied for estimation of PvT relationship

Rackett on PRO/II and API are not recommended for estimation of SOS.

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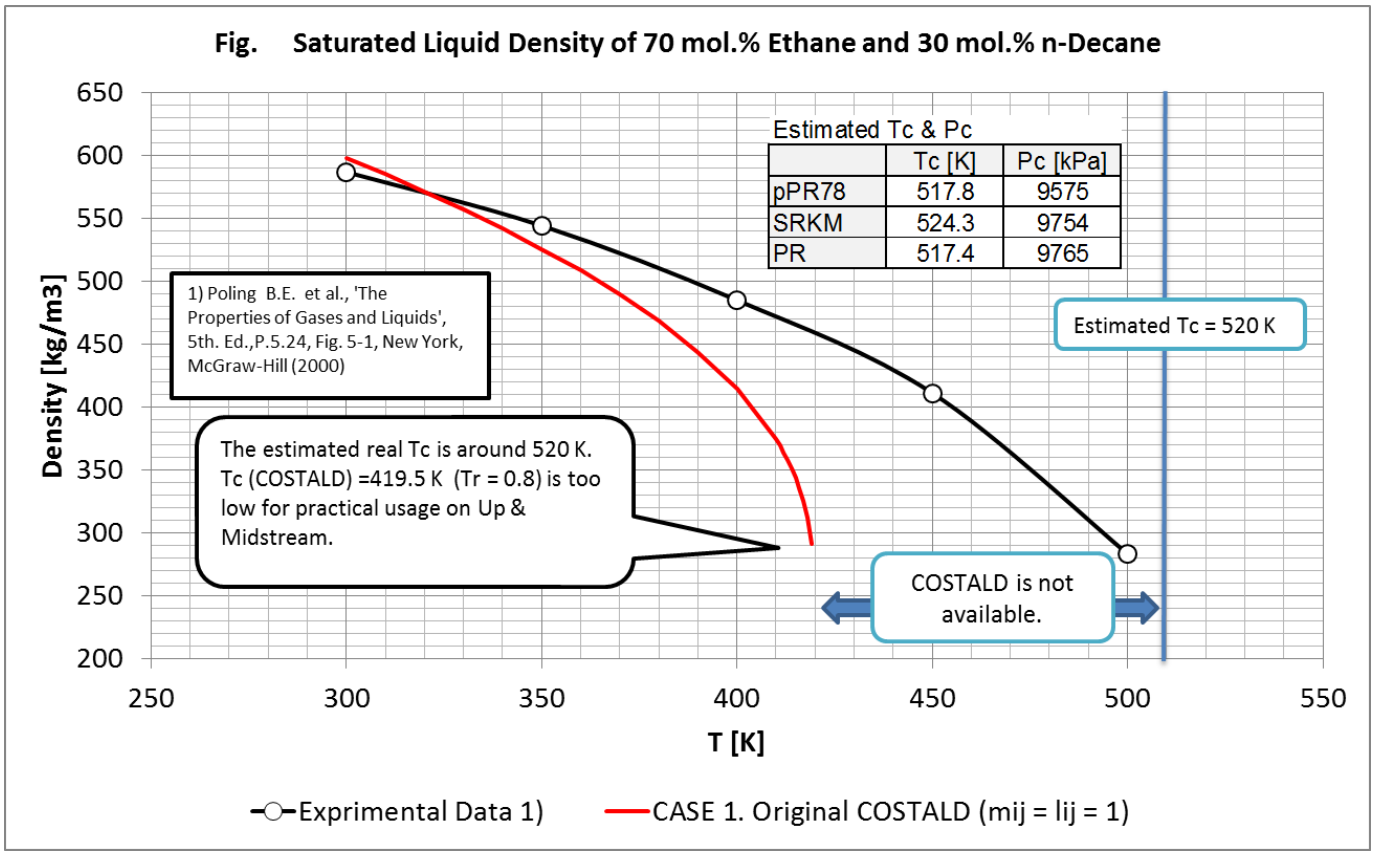
II. Summary of Liquid Density Models

~ Introduction of Three Model Frameworks and Troubles of Each Framework

Validation OF COSTALD

Poling et al. mentioned limitation of COSTALD (HBT). The big deviation in estimated Tc for mixture of light and heavy hydrocarbons between COSTALD and reliable estimated Tc value using suitable EOS is observed shown in the Figure.



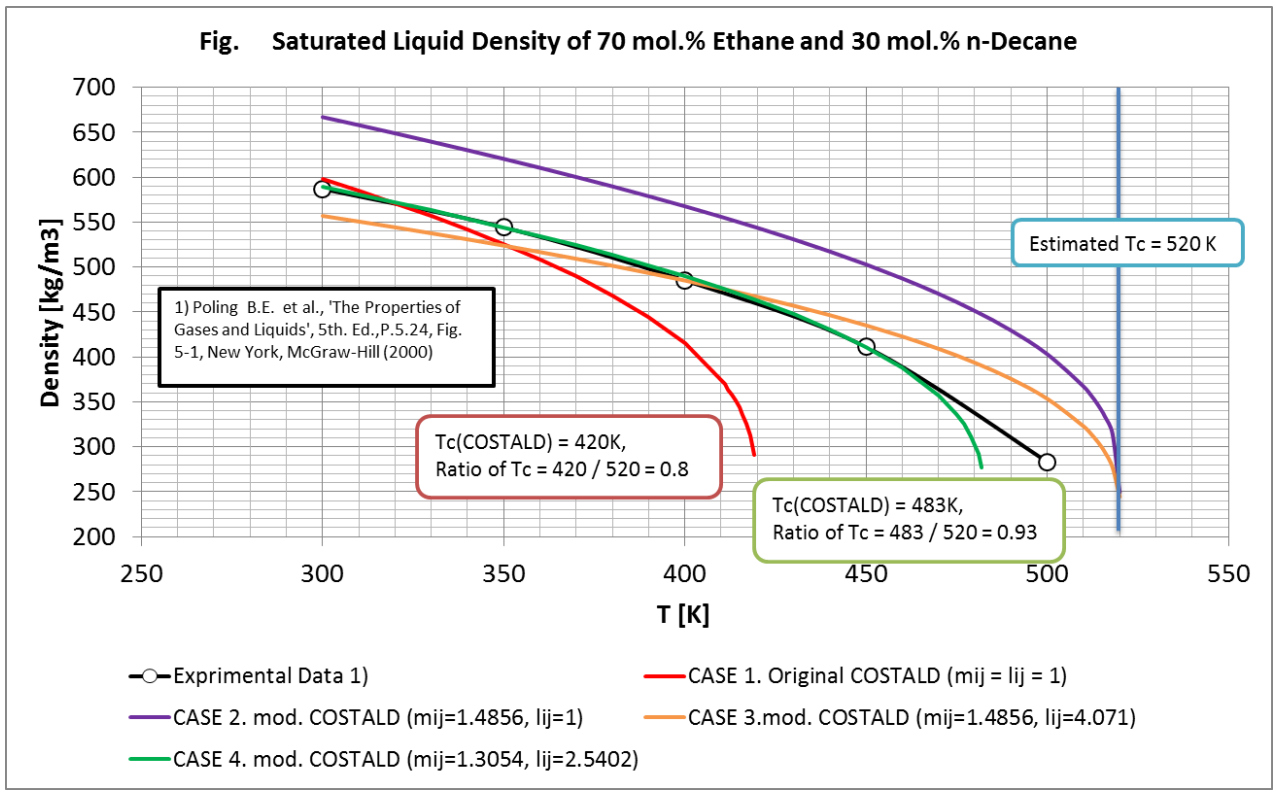
COSTALD is not recommended for up & midstream applications.

II. Summary of Liquid Density Models

~ Introduction of Three Model Frameworks and Troubles of Each Framework

Modification of COSTALD

New introduction of interaction parameters m_{ij} in T_{cm} and ℓ_{ij} in ω_m



It was able to extend available temperature range by this modification, but COSTALD is not recommended for up & midstream applications due to applicability of this modification.

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II. Summary of Liquid Density Models

~ Introduction of Three Model Frameworks and Troubles of Each Framework

Model Frameworks for Estimation of Liquid Density and PvT Relationship

III. Equation of State (EOS)

a) Overviews of this model

Cubic EOSs (SRK, PR etc.) : poor performance

Virial expansion EOS (BWRS, LK and LKP) : improved performance for Hydrocarbons, but not good for aqueous solutions

Reference EOSs (NIST REFPROP, IUPAC, IAPWS etc.) : very high performance, however, these reference EOSs are not generalized.

Volume Shift cEOS (PR-Peneloux, SRK-Peneloux) : simple and high flexibility, acceptable performance for Hydrocarbons and adjustable for aqueous solutions contains chemicals

b) Models on PRO/II

PR-Peneloux, SRK-Peneloux

Therefore, the testing results and required modifications of model framework for PR-Peneloux are discussed for TEG aqueous solution in this report. TEG is a typical gas hydrate equilibrium inhibitor.

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Data Source of Liquid Density of TEG aqueous solution

Dow Chemical Product Brochure 'Triethylene Glycol', Fig.6, Feb. 2007

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0952/0901b80380952386.pdf?filepath=ethyleneglycol/pdfs/noreg/612-00004.pdf&fromPage=GetDoc

Concentration : 0 – 100 wt.% of TEG
Temperature : -50 degF (-45.6 degC) ~ 300 degF (148.9 degC)
Freezing point curves : available, depending upon concentration and temperature

Triple point of pure TEG : 265.8 K (quoted from SimSci DB of PRO/II 10.0)

Applied PRO/II for this study : PRO/II 9.2.2 and 9.3.2

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Volume Shift Parameter and Tuning Parameters

1. Pure Component Parameter (PR-Peneloux)

for Hydrocarbons (no temperature dependency, but generalized)

Equation (2-125):

$$V_s = \sum_{i=1}^{N} \frac{RTc_i}{Pc_i} x_i [c_3 - c_4(c_1 - c_2 * \omega_i)]$$

Where,

$c_1 = 2.9056e-01$, $c_2 = 8.775e-02$

$c_3 = 1.1537e-01$, $c_4 = 4.4064e-01$

Quoted from PRO/II 10.0 Reference Manual

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Volume Shift Parameter and Tuning Parameters

1. Pure Component Parameter (PR-Peneloux)

for Water (with temperature dependency and not generalized)

Equation (2-126):

$$V_s = [A_1 + A_2(1 - T/373.15) + A_3(1 - T/373.15)^2]$$

$A_1 = 3.73625$

$A_2 = -2.70717$

$A_3 = 0.642567$

Quoted from PRO/II 10.0 Reference Manual

According to my study, it can be guessed that a temperature dependency volume shift parameter has been applied for TEG on PRO/II 9.2. On the contrary, unfortunately, the handling for DEG is similar to Hydrocarbons (no temperature dependency).

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Volume Shift Parameter and Tuning Parameters

2. Mixing Rule and Interaction Parameter (PR-Peneloux)

$$V_{actual} = V_{EOS} - V_s$$

1) V_{EOS} is estimated by PR EOS.
Temperature dependency k_{ij} for V_{EOS} is available to adjust excess volume.

$$k_{ij} = k_{ija} + {}^{k_{ijb}}/_{T} + {}^{k_{ijc}}/_{T^2}$$

2) Linear mixing for volume shift parameter of mixture

$$V_s = \sum_i x_i V_{si}$$

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Data Correlation of Isothermal Liquid Density for Water – TEG System

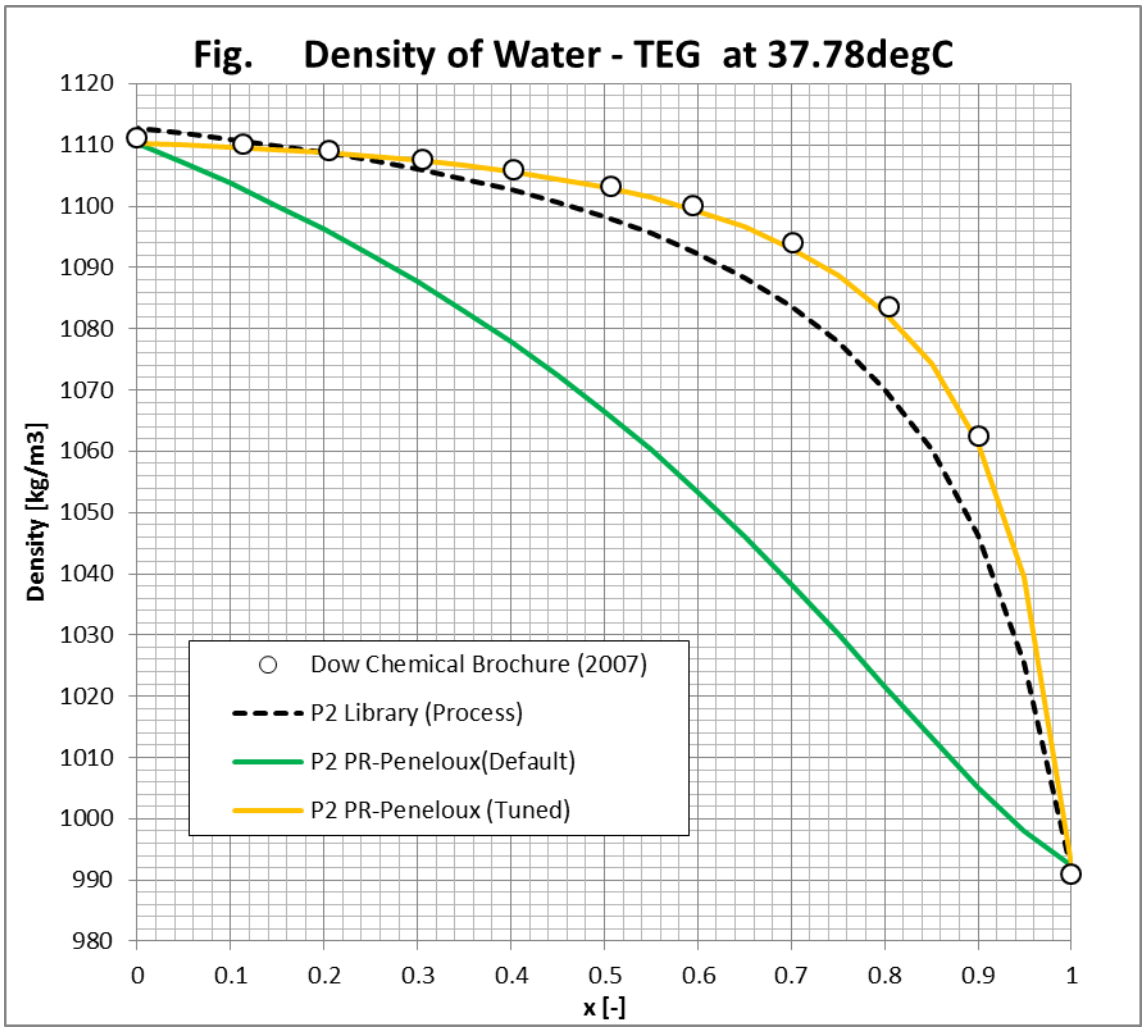

Table Correlated kij at Each Temepareture Level

T	T	1/T	above TEG triple point	below TEG triple point
			kij	
[degC]	[K]	[1/K]	[-]	
-45.56	227.59	0.00439		-4.5
-17.78	255.37	0.00392		-2
10	283.15	0.00353	-1.2	
37.78	310.93	0.00322	-1.1	
65.56	338.71	0.00295	-1	

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III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Determination of Temperature Dependency of kij

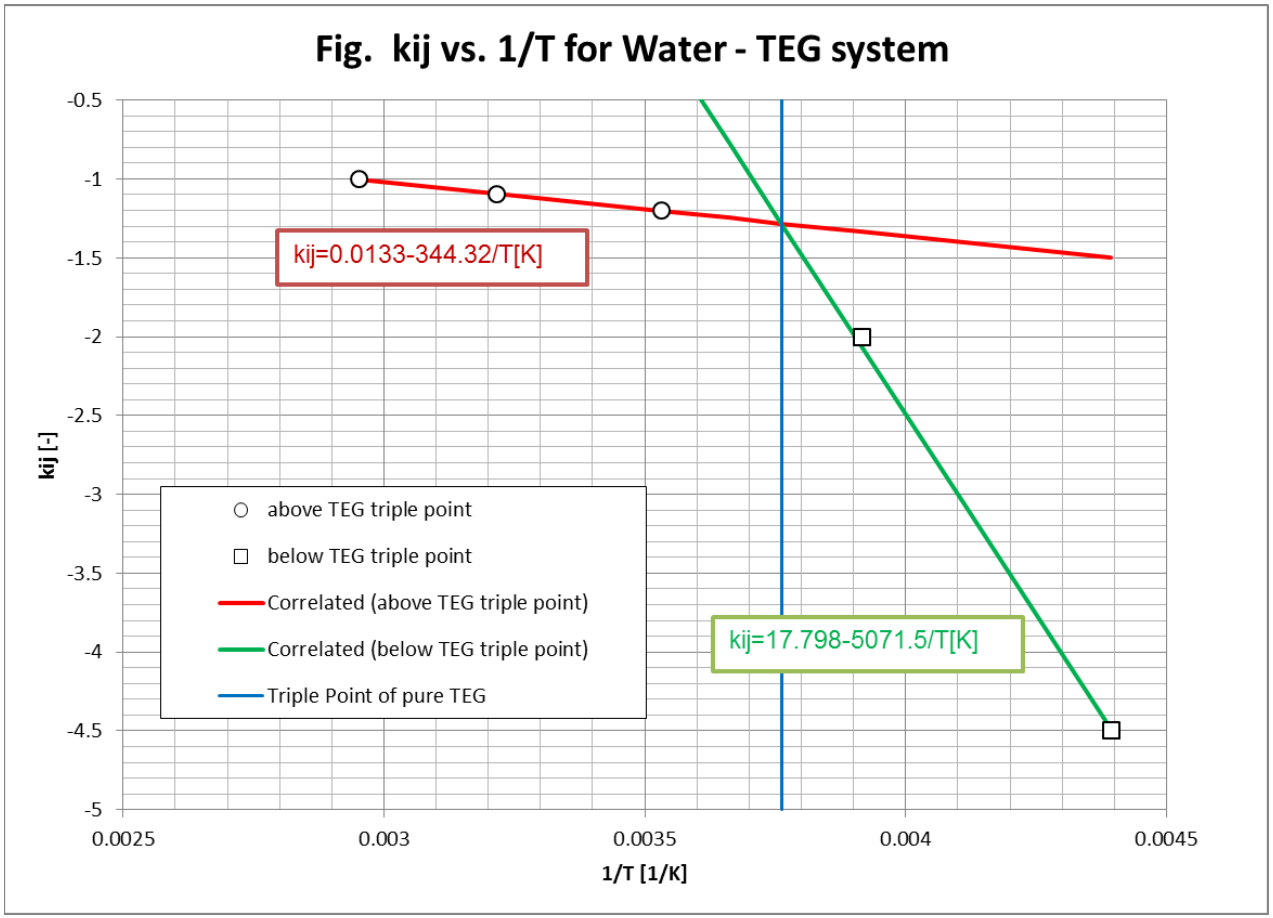

Table kij for Water - TEG system

	kija	kijb	kijc
above TEG triple point	0.0133	-344.32	0.0
below TEG triple point	17.798	-5071.5	0.0

Triple point of TEG is 265.8 K (-7.4degC).

$$k_{ij} = k_{ija} + {}^{k_{ijb}}/_{T} + {}^{k_{ijc}}/_{T^2}$$

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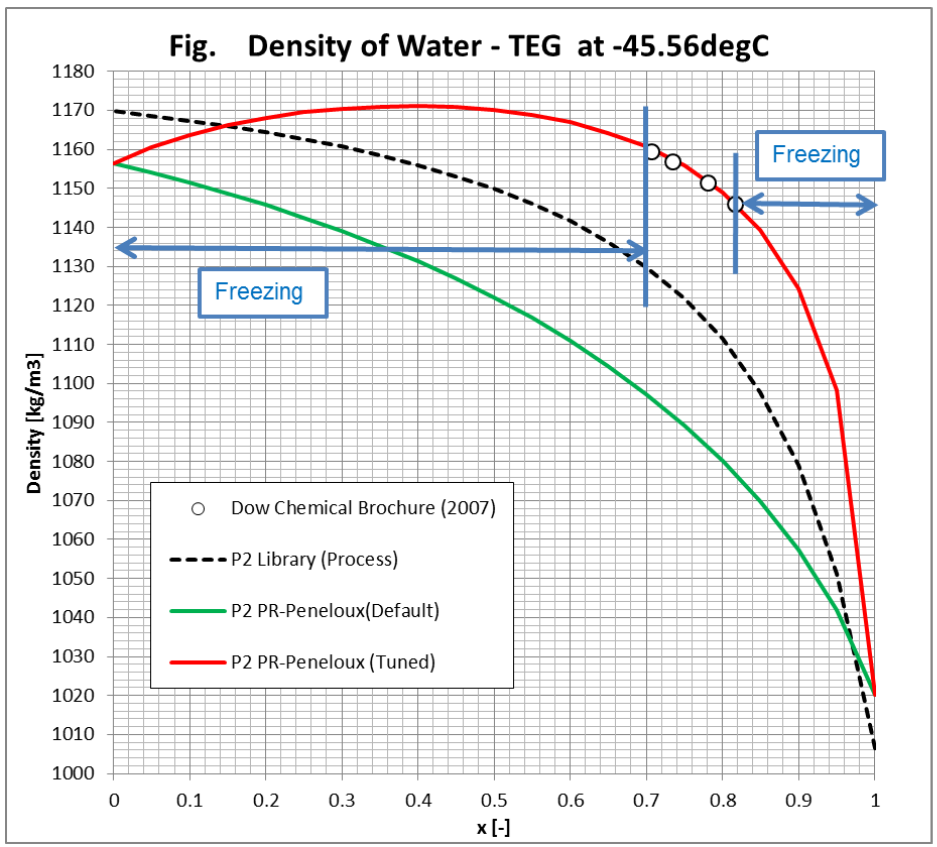
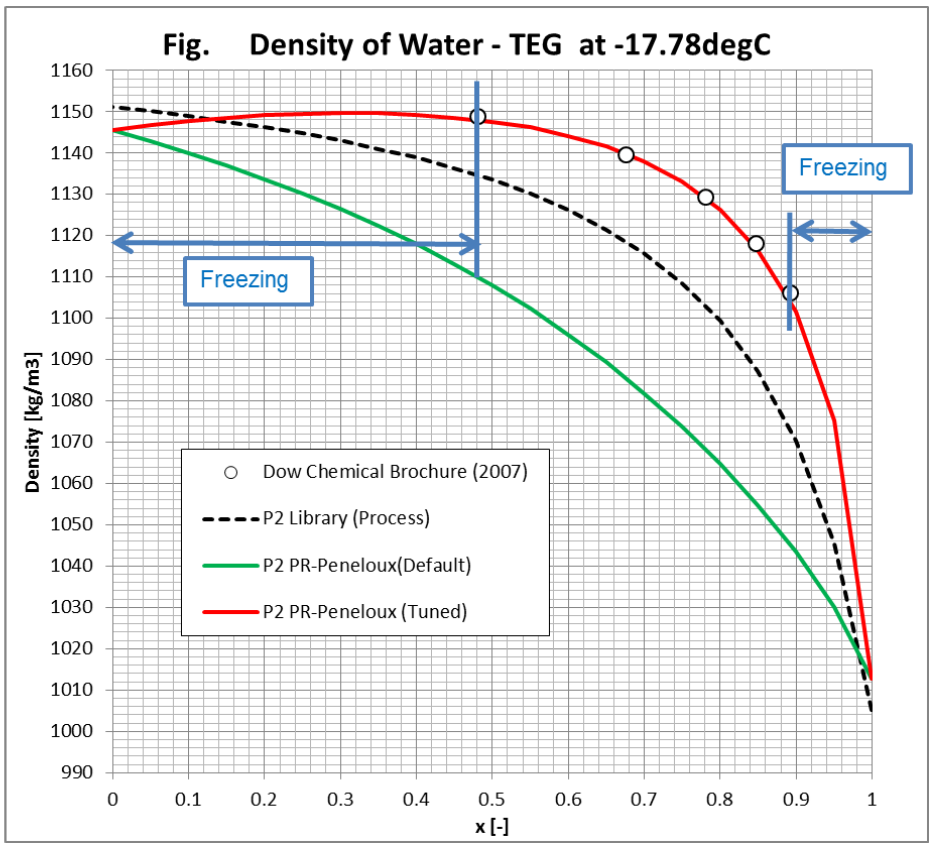
III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

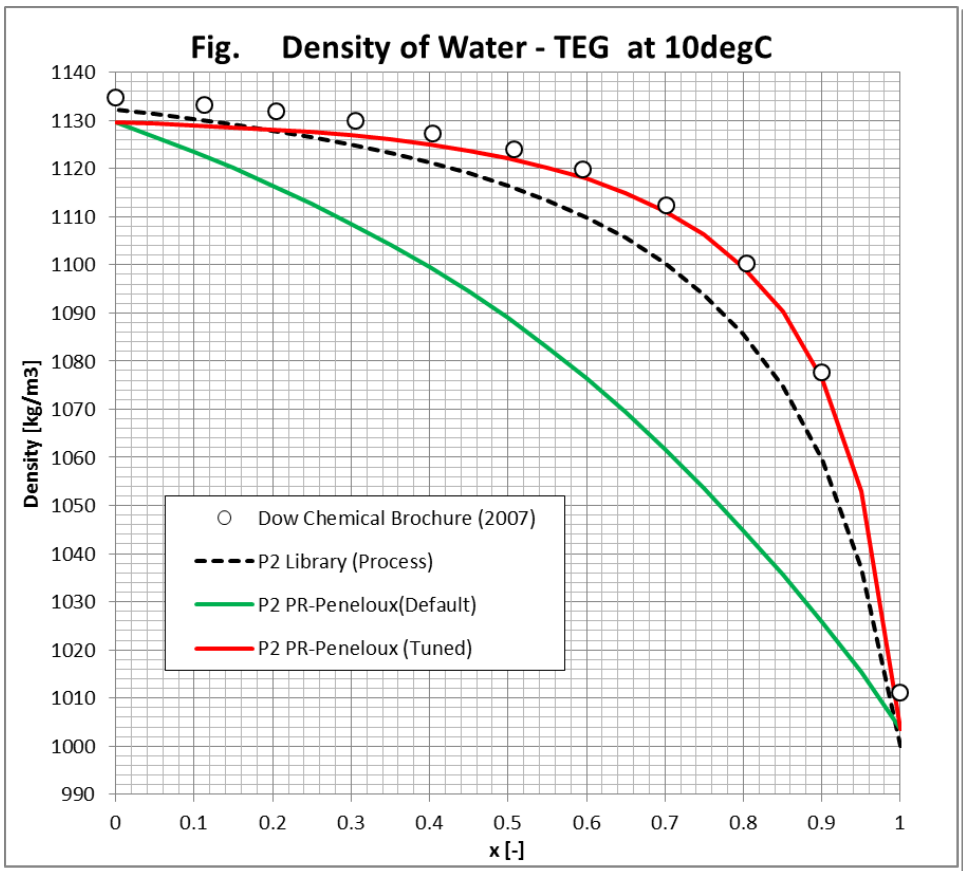
Correlation Results for Water – TEG System below Freezing Point

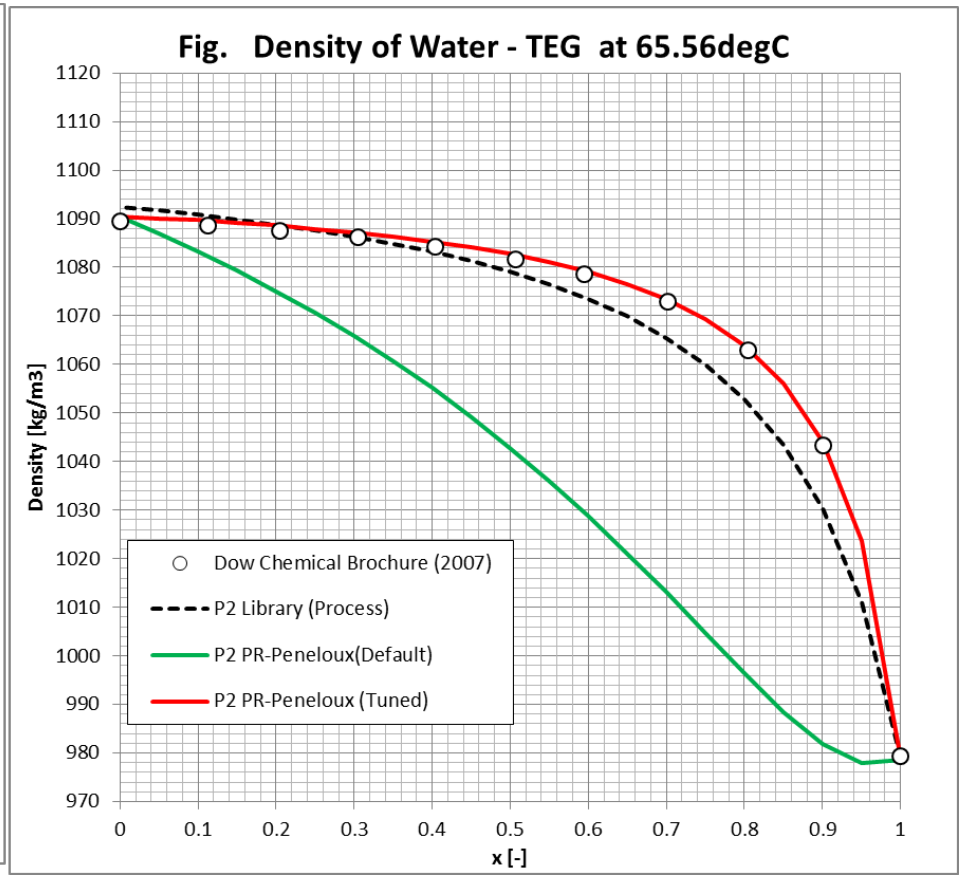




III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Correlation Results for Water – TEG System above Freezing Point

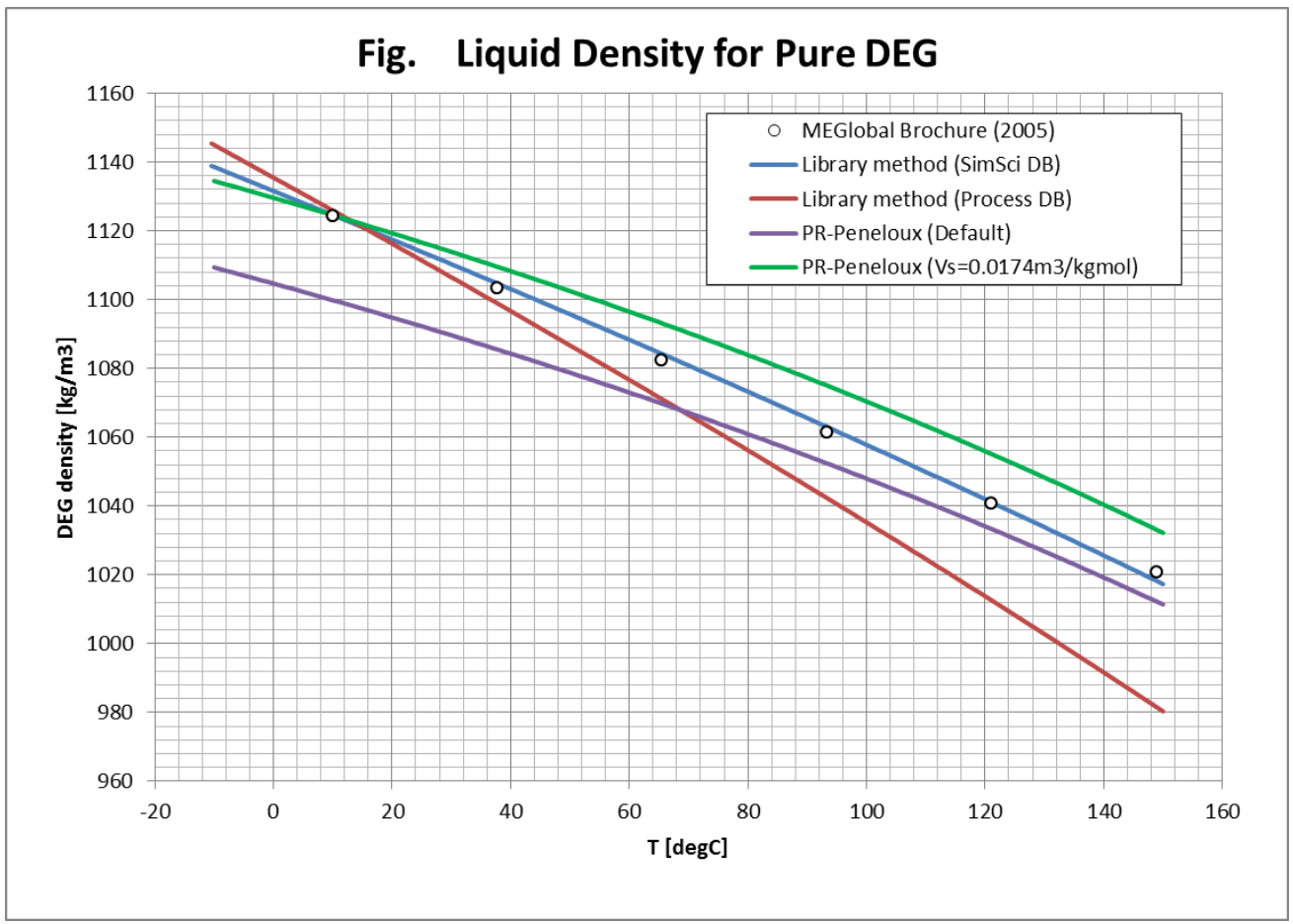




III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Additional Study for DEG Aqueous Solution

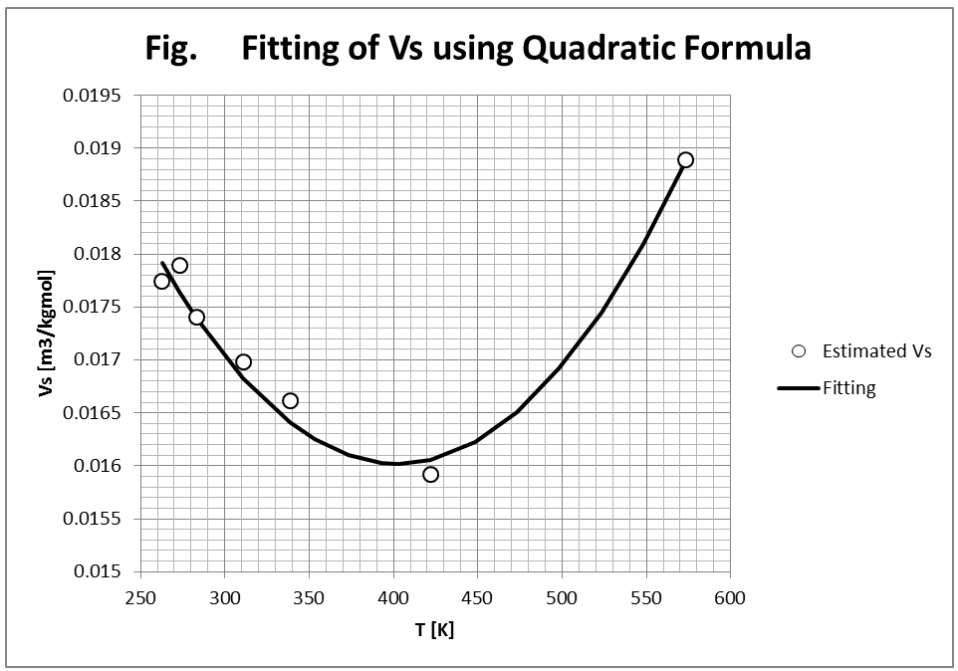
The default Vs is not tuned for DEG.



III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Additional Study for DEG Aqueous Solution

Temperature dependency of Vs can be considered. But, PRO/II cannot accept user supply for the parameters.



$$V_s\left[\frac{m^3}{kgmol}\right] = C_1 + C_2\left(1 - \frac{T[K]}{T_{base}[K]}\right) + C_3\left(1 - \frac{T[K]}{T_{base}[K]}\right)^2$$

C1=0.0174, C2=0.006572, C3=0.007815, T_{base}[K]=283.15

III. Trial Results for Model Flexibility of Volume Shift Model (Peneloux)
~ Correlation of Liquid Density of Water – TEG System

Feedback to SimSci regarding Peneloux

- It was possible to make fine tuning of PR- Peneloux for TEG aqueous solution at wide temperature conditions.
- A detailed tuning of Temperature dependency of Vs was possible. But, PRO/II cannot accept user input of temperature dependency Vs. It is necessary to improve PRO/II.
- There are no tuning utility for temperature dependency of Vs for pure compound and kij for mixture. This is not comfortable environment. We need a additional convenient utility tool for regression.
- Strictly speaking, relatively large estimation errors of pure water were observed below 10 degC to triple point.

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VI. Technical Background for Water Hammer ~ A Case of Requirement for Speed of Sound

Definition of 'Water Hammer (Fluid Hammer)'

'**Water hammer** (or, more generally, **fluid hammer**) is a pressure surge or wave caused when a fluid (usually a liquid but sometimes also a gas) in motion is forced to stop or change direction suddenly (momentum change). **A water hammer commonly occurs when a valve closes suddenly at an end of a pipeline system**, and **a pressure wave propagates in the pipe**. It is also called hydraulic shock.
This pressure wave can cause major problems, from noise and vibration to pipe collapse. It is possible to reduce the effects of the water hammer pulses with accumulators, expansion tanks, surge tanks, blow-off valves, and other features. '

Quoted from Wikipedia

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VI. Technical Background for Water Hammer ~ A Case of Requirement for Speed of Sound

Joukowsky Equation for Rough Estimation of Maximum Water Hammer Pulse

$$\Delta P = \rho \cdot SOS \cdot \Delta u$$

ΔP: $Pressure\ increazing\ by\ water\ hammer\ [Pa]$

$\boldsymbol{\rho}$: ***Density of the fluid*** $\left[\frac{kg}{m^3}\right]$

$\boldsymbol{SOS}$: ***Speed of sound of the fluid*** $\left[\frac{m}{s}\right] = \sqrt{\beta_s / \rho}$

$\boldsymbol{\beta_s}$: ***Adiabatic Bulk Modulus*** $[Pa] = \rho \left(\frac{\partial P}{\partial \rho}\right)_s$

Δu: $Change\ in\ the\ fluid\ velocity\ before\ and\ after\ shut-off\ of\ the\ valve\ \left[\frac{m}{s}\right]$

Finally, the maximum pressure which can be resulted by water hammer , P_{max} can be estimated from $P_{operation} + \Delta P$.

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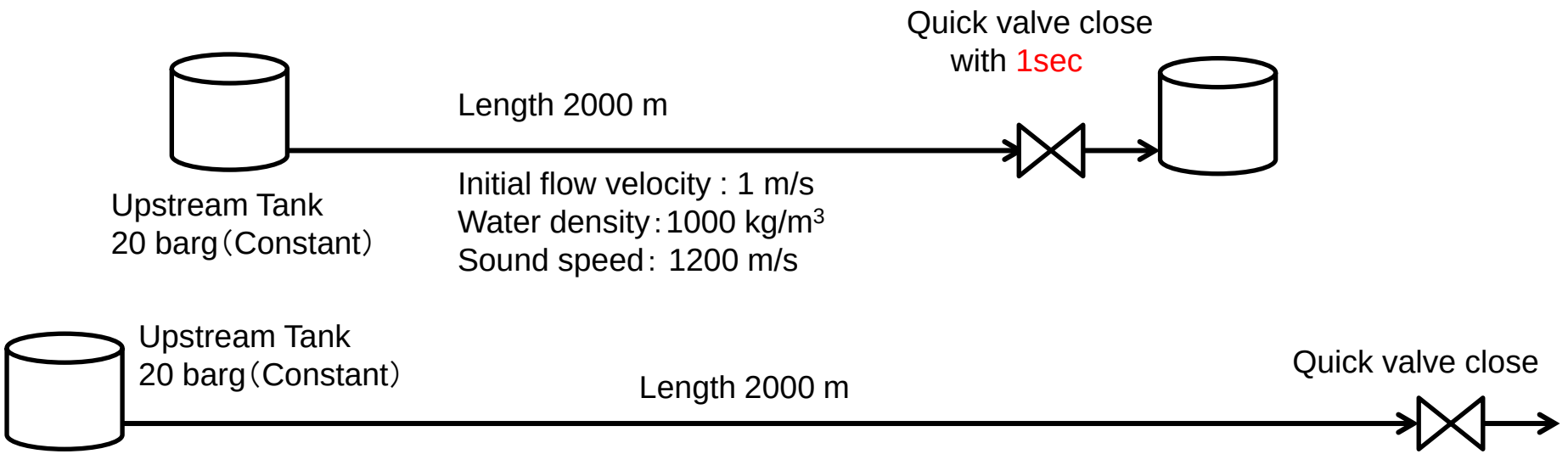
VI. Technical Background for Water Hammer
~ A Case of Requirement for Speed of Sound

Demonstration of Study for Water Hammer



Joukowsky Equation (estimation of maximum pressure increasing by water hammer)

$$\Delta P = \rho \cdot SOS \cdot \Delta u = 1000 \cdot 1200 \cdot 1 = 12 bar$$

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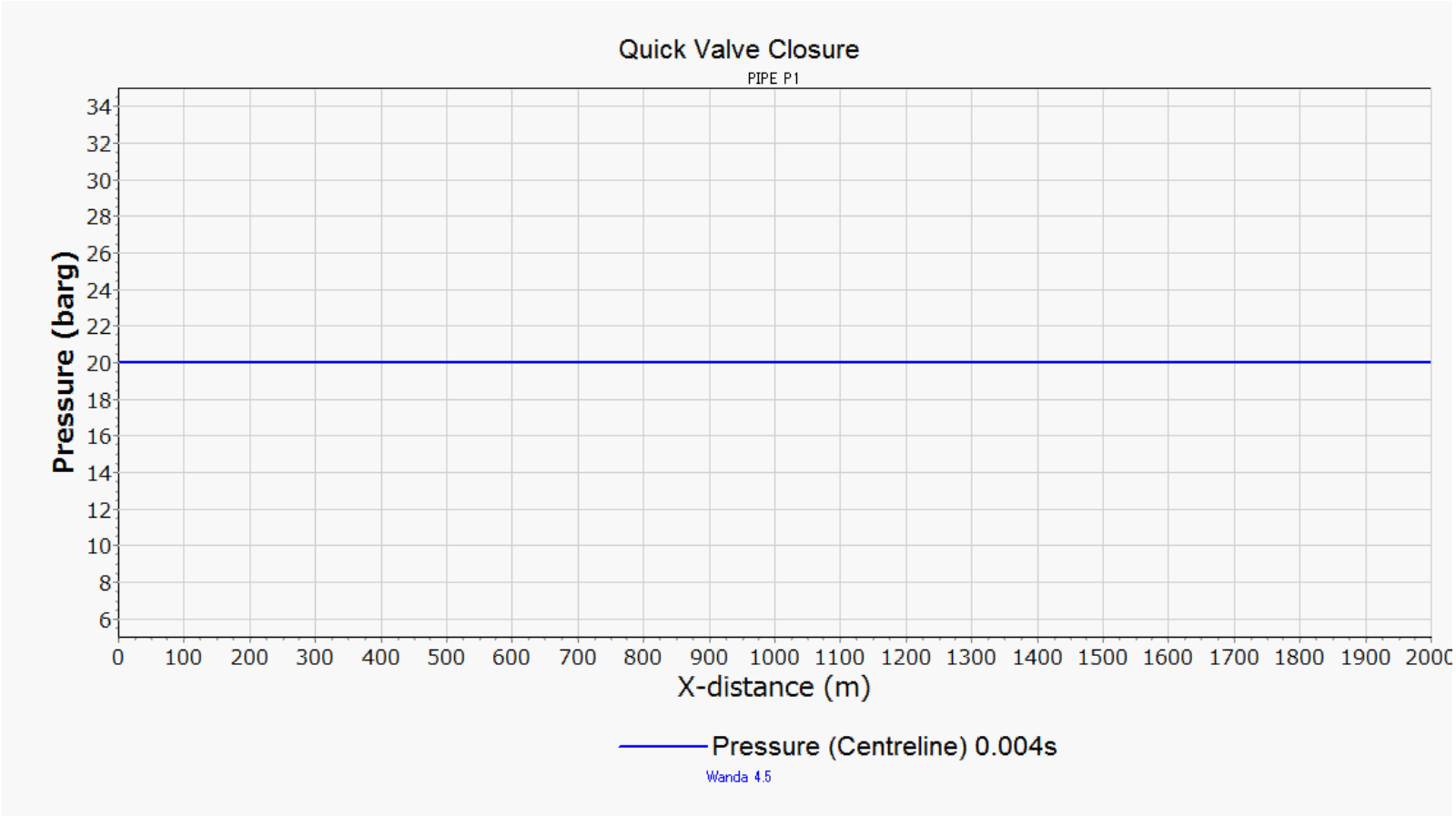
VI. Technical Background for Water Hammer ~ A Case of Requirement for Speed of Sound

Movie for Results of Dynamic Simulation for Water Hammer



$$\Delta P = \pm 12 bar \ \ and \ Pmax = 32 \ bar \ ; \ estimated \ from \ Joukowsky$$

V. Trial Results for EOS models for Physical Properties required for Water Hammer Analysis

Calculation Conditions for Trial in this Study

Pure Ethylene, P= 5barG and T=-104degC (Subcooled)

PRO/II 9.2.0 was applied for this study.

U1 (before shut-off of valve)	2	m/s
U2 (after shut-off of valve)	0	m/s
ΔU = U1 - U2	2	m/s

NIST REFPROP 9.1 is a benchmark. The following models were tested.

- ✓ PRO/II NIST23
- ✓ cEOS : SRK, SRKM (Pure DB=PROCESS and or SimSci), PR, PRM
- ✓ Volume Shift : SRK-Peneloux, PR- Peneloux
- ✓ Virial Expansion : BWRS, LK
- ✓ Empirical Correlation on PRO/II : API, COSTALD, Rackett

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V. Trial Results for EOS models for Physical Properties required for Water Hammer Analysis

Trial Results

	SOS [m/s]	Density [kg/m3]	Adi. Bulk Modulus [Pa]	Density*SOS [kg/m2/s]	Relative Deviation (Benchmark : NIST REFPROP9.1) SOS	Density	Density*SOS	Max Pressure Increasing estimated from Joukowsky Eq.[bar]	Max. Pressure [barA]
NIST REFPROP9.1	1313.3	568.5	9.805.E+08	746611	0.0%	0.0%	0.0%	14.9	20.9
P2 NIST23	1313.2	568.5	9.804.E+08	746555	0.0%	0.0%	0.0%	14.9	20.9
P2 SRK	1102.6	547.9	6.661.E+08	604085	-16.0%	-3.6%	-19.1%	12.1	18.1
P2 SRKM (Process DB)	1093.3	547.6	6.546.E+08	598692	-16.7%	-3.7%	-19.8%	12.0	18.0
P2 SRKM (SIMSCI DB)	1091.3	548.0	6.527.E+08	598097	-16.9%	-3.6%	-19.9%	12.0	18.0
P2 SRK-Peneloux	1196.1	505.1	7.225.E+08	604086	-8.9%	-11.2%	-19.1%	12.1	18.1
P2 PR	1135.9	618.6	7.982.E+08	702647	-13.5%	8.8%	-5.9%	14.1	20.1
P2 PRM (Process DB)	1117.7	619.0	7.733.E+08	691822	-14.9%	8.9%	-7.3%	13.8	19.8
P2 PR-Peneloux	1244.6	564.6	8.745.E+08	702646	-5.2%	-0.7%	-5.9%	14.1	20.1
P2 API	1959.9	673.6	2.587.E+09	1320090	49.2%	18.5%	76.8%	26.4	32.4
P2 LK	1685.9	562.0	1.597.E+09	947433	28.4%	-1.1%	26.9%	18.9	25.0
P2 COSTALD	1273.3	567.5	9.200.E+08	722543	-3.0%	-0.2%	-3.2%	14.5	20.5
P2 Rackett	NA	568.2	-1.165.E+09	NA	NA	-0.1%	NA	NA	NA
P2 BWRS	2028.3	579.9	2.385.E+09	1176095	54.4%	2.0%	57.5%	23.5	29.5

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V. Trial Results for EOS models for Physical Properties required for Water Hammer Analysis

Conclusion of Trial for SOS

- ✓ PR, PR-Peneloux and COSTALD show relatively good agreements with NIST REFPROP 9.1 for maximum pressure increasing (MPI).
- ✓ However, the errors in SOS and density cancelled each other for estimation of MPI in case of PR. Therefore, PR is not reliable.
- ✓ On the contrary, it can be guessed that PR-Peneloux and COSTALD are reliable.
- ✓ However, COSTALD is not recommended at high pressure range as discussed in the Chapter II. Therefore, only PR-Peneloux is acceptable.
- ✓ It is not clear why SRK-Peneloux cannot show good performance.
  (the parameter of SRK-Peneloux has been revised at new versions of PRO/II.)
- ✓ It was unexpected, but performance of virial expansion (LK & BWRS) was not good. Liquid density is acceptable, but big deviations were observed in adiabatic bulk modulus.
- ✓ PRO/II Racket showed $\rho_{\text{at P=5.1barG}} < \rho_{\text{at P=4.9 barG}}$. Therefore, the derivative became negative. Therefore, SOS was not be able to be estimated since Rackett model framework on PRO/II 9.2.0 (as well as PRO/II 10.0.0) cannot estimate sub-cool regions.

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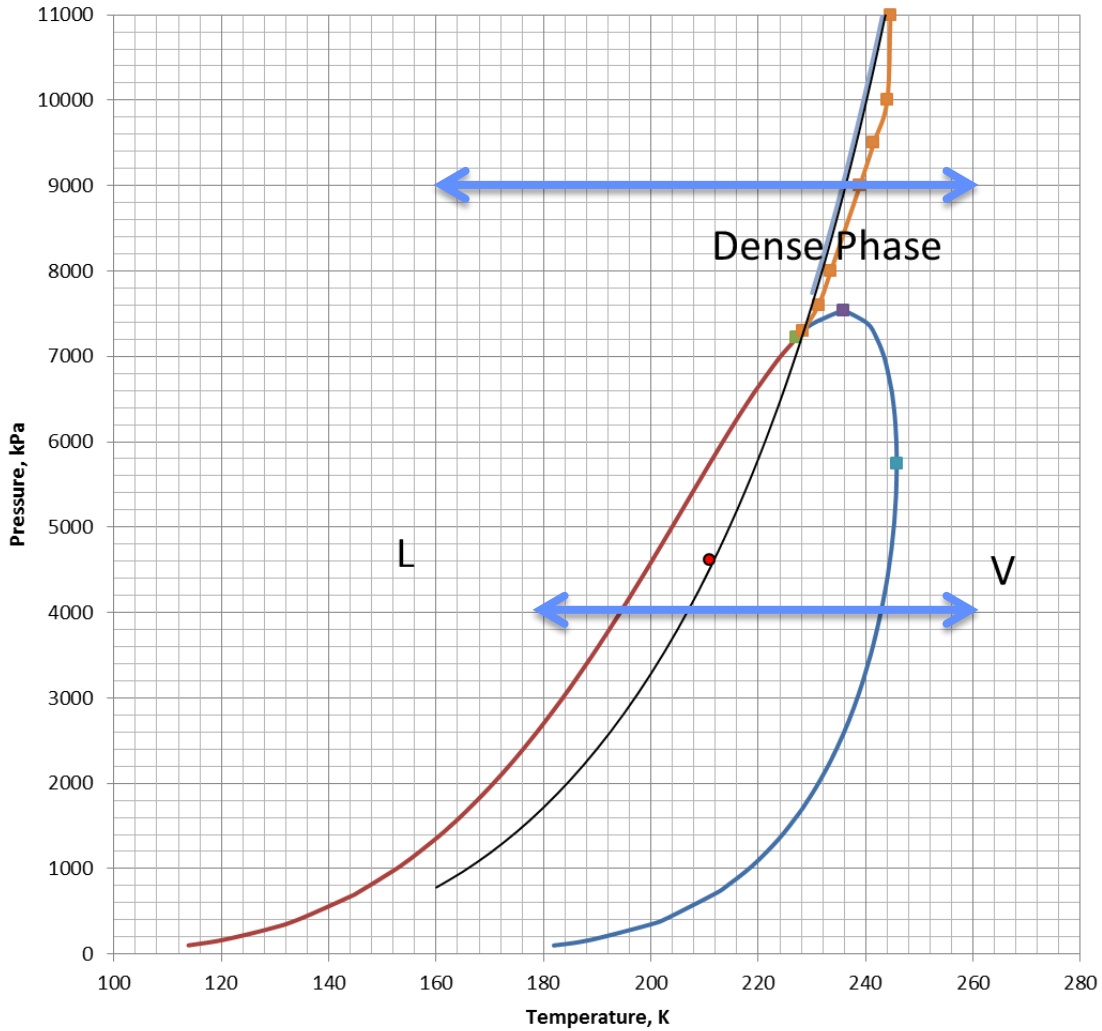
VI. Continuity of Density from Ordinary Liquid Phase to Dense Fluid Phase

Phase Envelop for Simplified Natural Gas



Molefraction	
METHANE	0.85
ETHANE	0.1
PROPANE	0.05

- Full Envelope (Dew Point Curve)
- Full Envelope (Bubble Point Curve)
- Critical Point
- Cricondenbar
- Cricondentherm
- Pseudo boundary between L and V by PRO/II
- Lee-Kesler Eq. with Kay's Rule
- Lee-Kesler Eq. with LK Mixing Rule
- Kay's Rule

Lee-Kesler Eq.

$$\ln P_r = f^{(0)} + \omega \cdot f^{(1)}$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \cdot \ln T_r + 0.169347 \cdot T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \cdot \ln T_r + 0.43577 \cdot T_r^6$$

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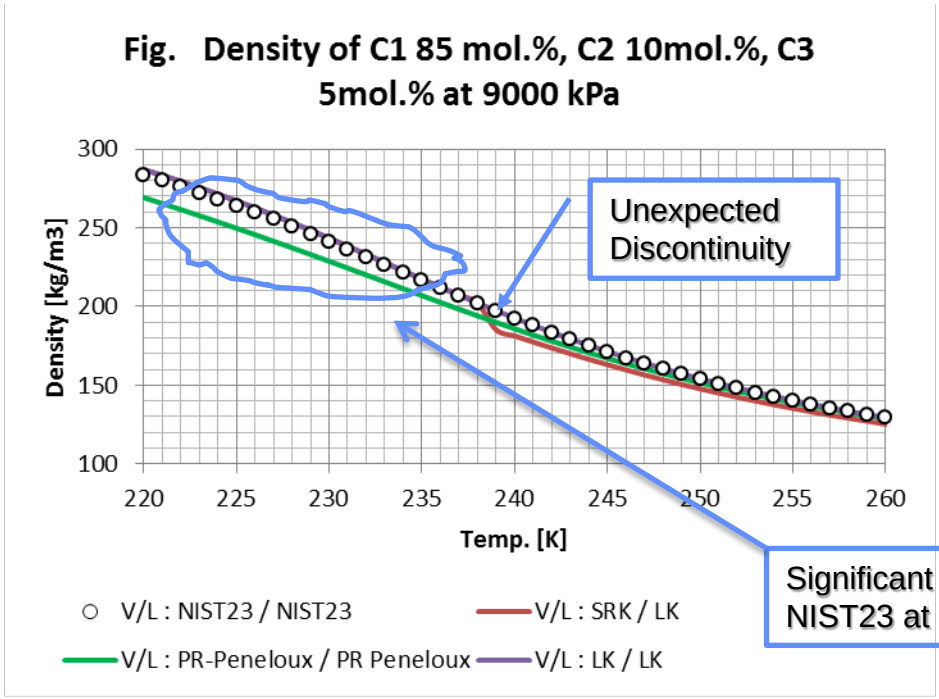
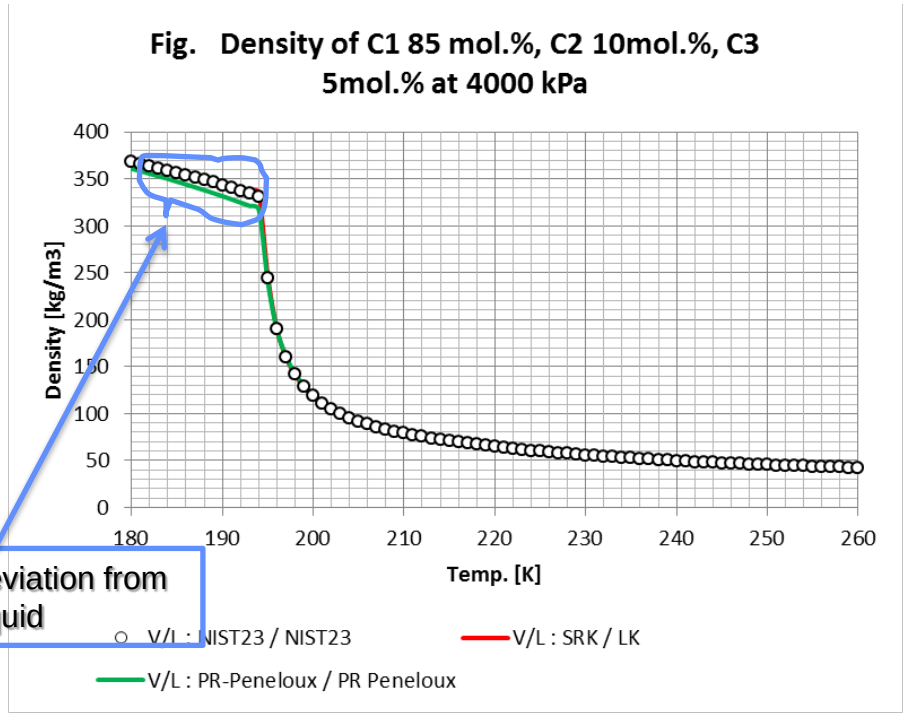
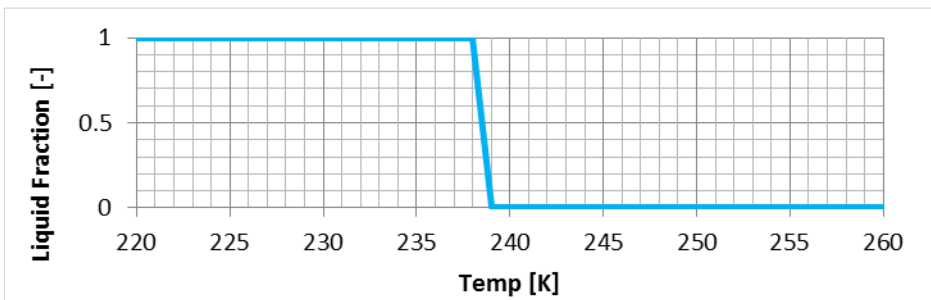
VI. Continuity of Density from Ordinary Liquid Phase to Dense Fluid Phase

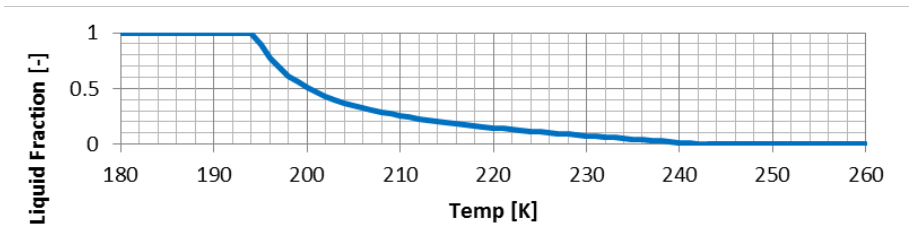
Liquid Density for Simplified Natural Gas (K Value : SRK EOS)





Significant Deviation from NIST23 at Liquid





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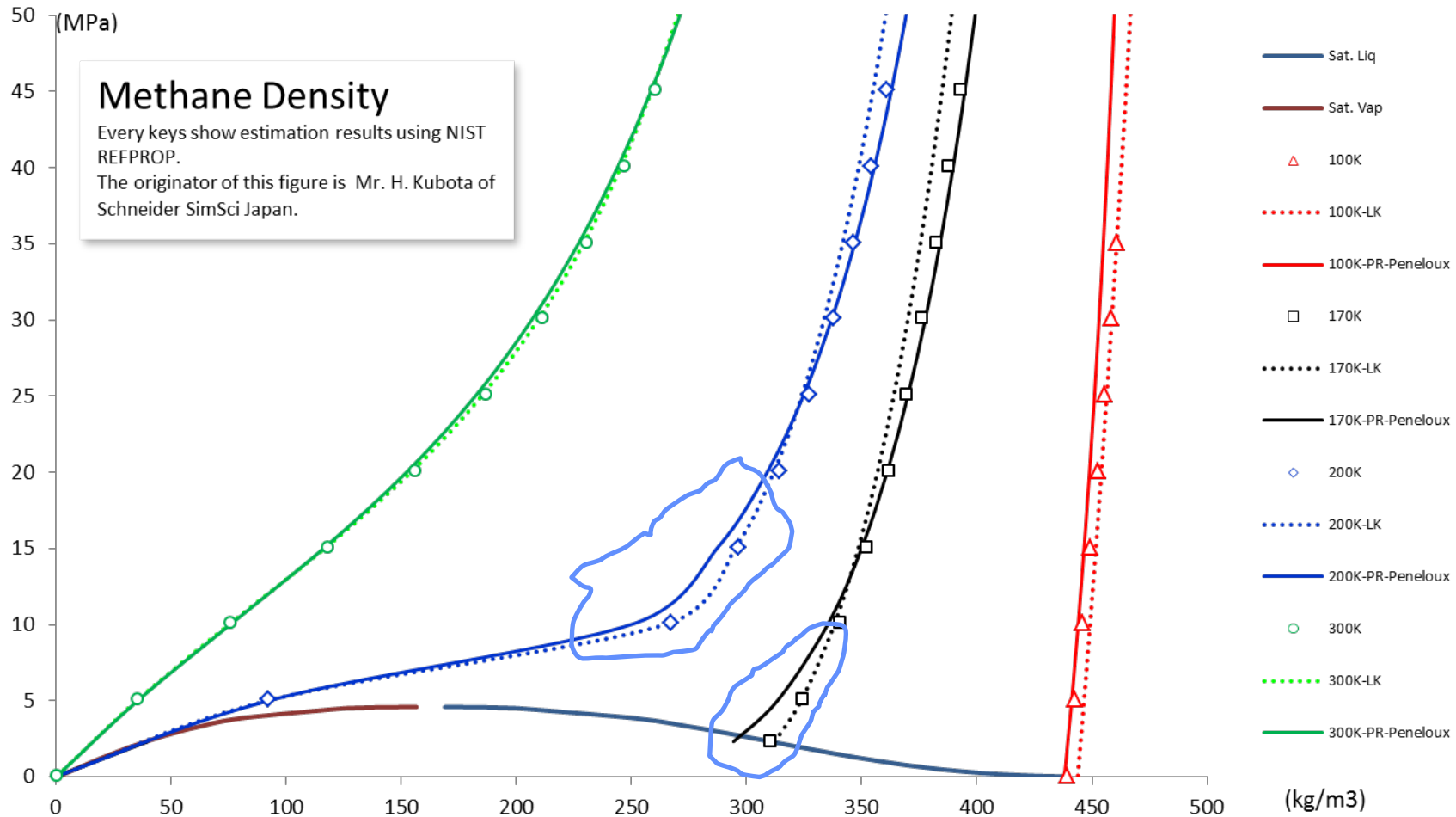
VI. Continuity of Density from Ordinary Liquid Phase to Dense Fluid Phase

Validation Results for PR-Peneloux and LK on PRO/II (done by Schneider SimSci Japan)



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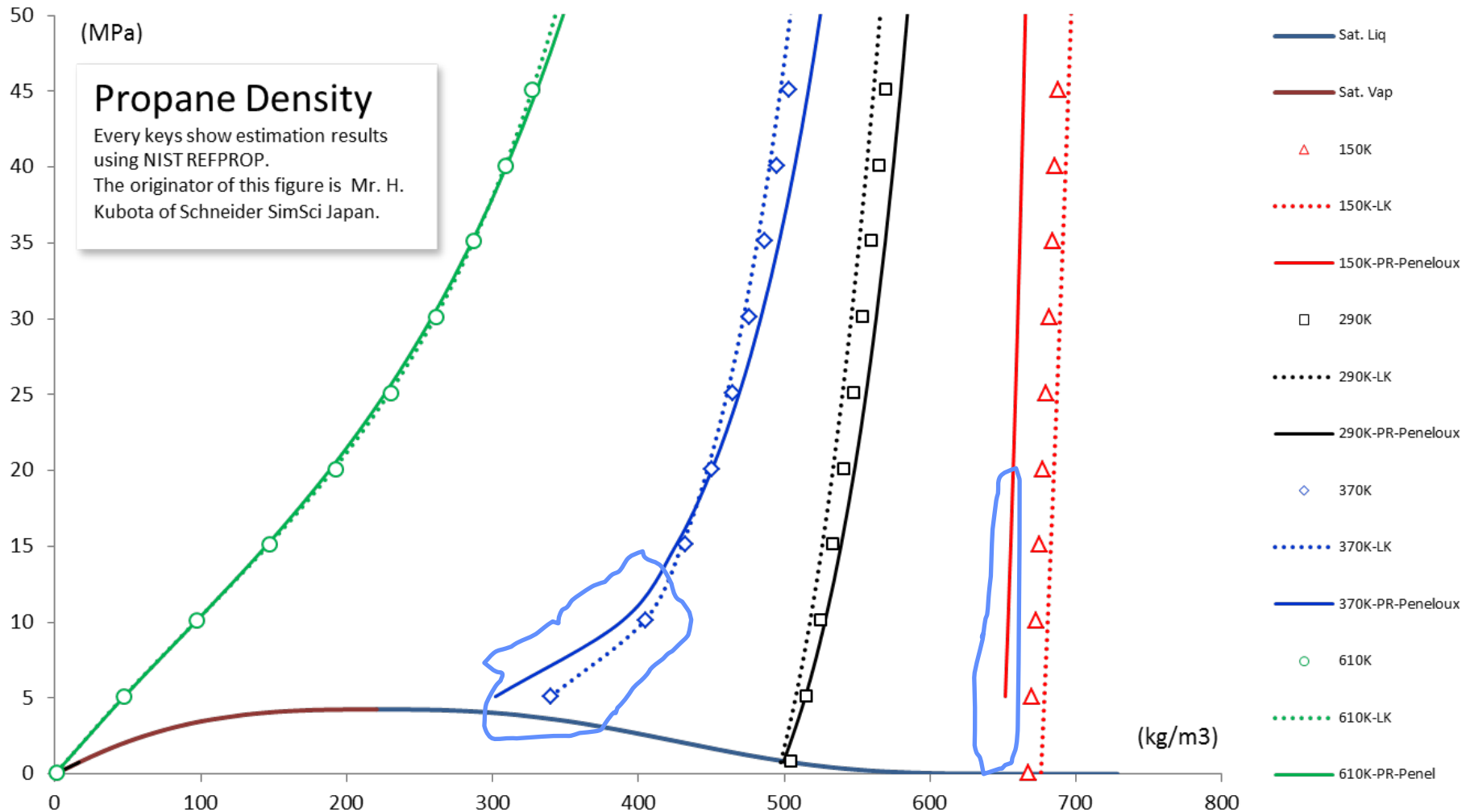

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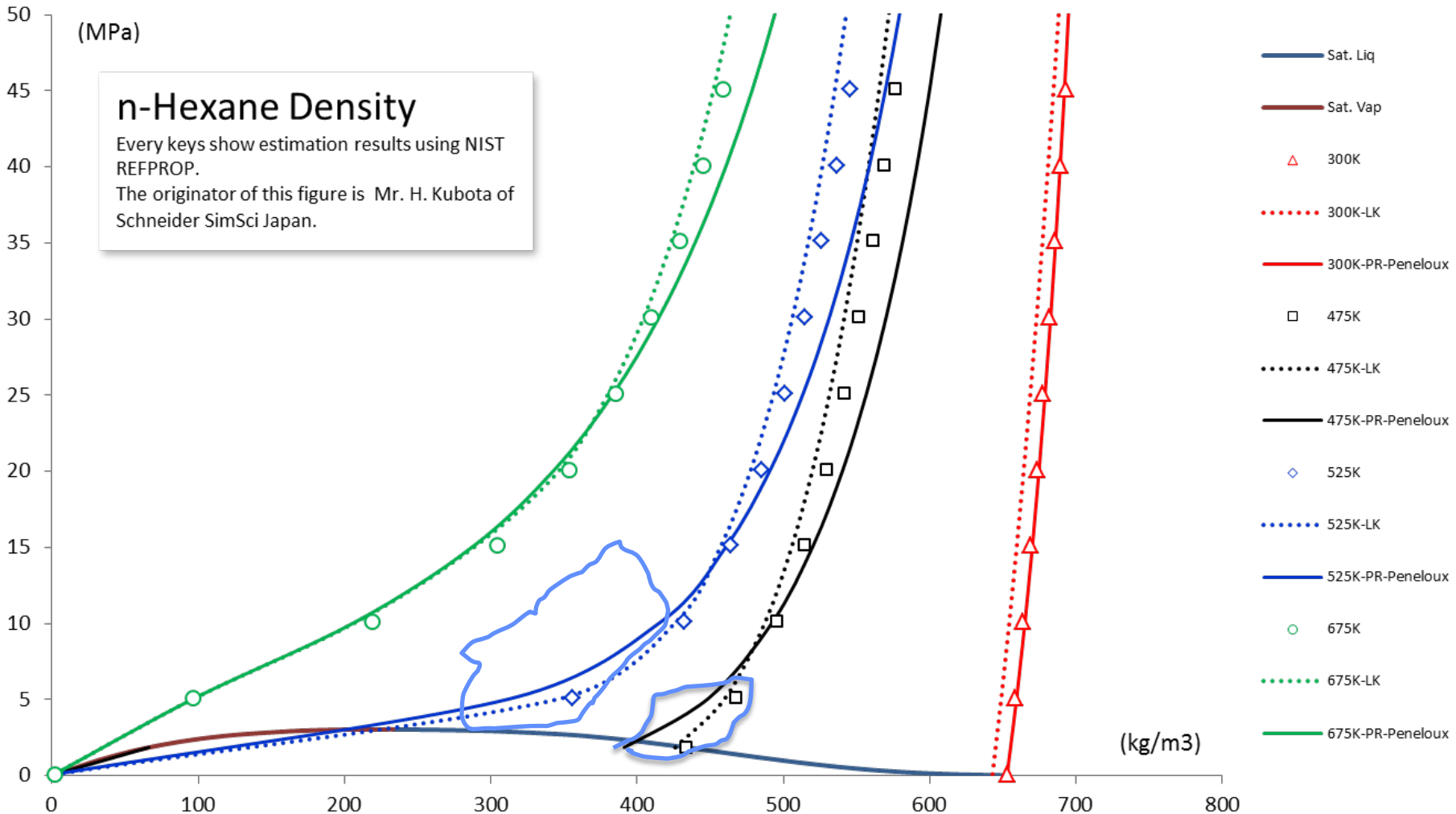

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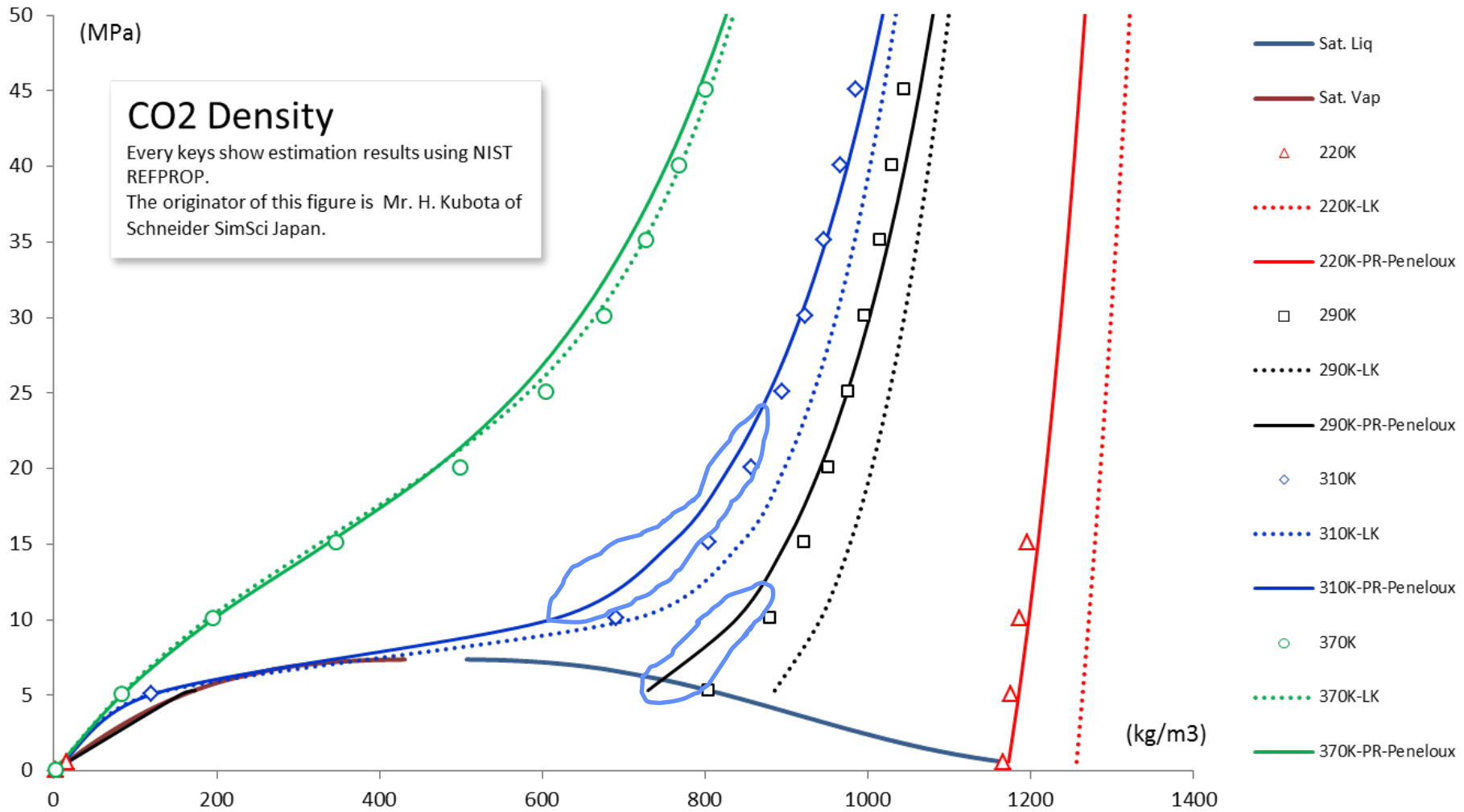

VI. Continuity of Density from Ordinary Liquid Phase to Dense Fluid Phase

Conclusions for Model Testing at Dense Fluid Phase

- ✓ Lee-Kesler showed better performance for simplified NG at dense fluid phase, but LK is not adjustable model and it is a tuned model for light hydrocarbons (C1 – C8).
- ✓ Peneloux presented generalized Vs for hydrocarbons, but it is not enough to correlate experimental density data at wide temperature range for liquid and vapor phase.
- ✓ User supplied temperature dependent Vs is necessary to tune at wide temperature range.
- ✓ Peneloux model seems to be a better model for up & midstream applications if temperature dependency Vs are supplied for major hydrocarbons. Therefore, user input of temperature dependency Vs and correlation utility tool are required.

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VII. Conclusion Remarks

Collaboration Work on Research Activities between Me, Schneider SimSci and Other Key Players at the Passed Several Years

- *VLE and VL-Aqueous Liquid Equilibria at Very High Pressure*

  (a mixture of continuous hydrocarbons, aromatics, sour gases, mercaptans, water-cut and a typical gas hydrate equilibrium inhibitor)

  PR(M) + pPR78 kij Filling, Revised Glycol DB, Petroleum Pseudo Handling

  [Reference paper] Francisco J. Braña-Mulero, Seiya Hirohama, PrasannaLakshmi Lingampally, Masakazu Sasaki, and Jean-Noël Jaubert, 'Application of PPR78 Thermodynamic Framework as Fill Method with Semi-Empirical Mixing Rule for Mixtures Involved in Gas Processing', J. Chem. Eng. Data, 61(12), pp.4164-4171 (2016)

  → Almost completed at PRO/II 10.1, but validation not yet.

- *Density and PvT at Atmospheric to Dense Phase Pressures*

  Further research works and enhancements are required.

There are several kinds of design factors for up & midstream applications. However, at least I hope to reduce design risk due to uncertainties on thermo model by further developments. In addition, we wish to contribute projects at up & midstream applications.

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Thank you for your attention.



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