Latest Developments in Light Hydrocarbon Testing in Crude Oils

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Outline

- Terminology/Definitions
- “Light Ends”
- Sampling
- Analysis
- Modeling
- Future Work

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Vapour Pressure: TVP vs TVP

- True Vapour Pressure (TVP)
  - Pressure exerted by a liquid at a vapour/liquid (V/L) ratio of 0:1
  - Bubble point pressure (BPP)
- Total Vapour Pressure (TVP)
  - The pressure exerted by a liquid including the equilibrium contribution from all hydrocarbons and dissolved gases.

Test method vapor pressure terms

- Ptot - total pressure
- Absolute vapor pressure
- Vapor pressure (VP)
- TP – total pressure
- PPA - partial pressure of air
- DVPE dry vapor pressure equivalent
- RVPE Reid vapor pressure equivalent
- ASVP air saturated vapor pressure (IP481)
- VPCR vapor pressure of crude oil

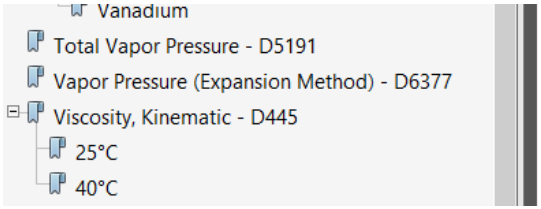
D4175-16 Terminology

- **true vapor pressure, TVP,** *n*—the pressure at which the fluid is in equilibrium between its liquid and gas state
- **vapor pressure of crude oil (VPCRx),** *n*—the pressure exerted in an evacuated chamber at a vapor-liquid ratio of X:1 by conditioned or unconditioned crude oil, which may contain gas, air, or water, or a combination thereof, where X may vary from 4 to 0.02

ASTM Definition of Live Crude Oil

- *Live crude oil,n* — crude oil with sufficiently high vapour pressure that it would boil if exposed to normal atmospheric pressure at room temperature.
- *Dead crude oil,n* — crude oil with sufficiently low vapour pressure that, when exposed to normal atmospheric pressure at room temperature, does not result in boiling of the sample.
- *Discussion* - Sampling and handling of live crude oils requires a pressurized sample system and pressurized sample containers to ensure sample integrity and prevent loss of volatile components.

ASTM Crude Oil PTP Vapor Pressure



Committee D-2
Proficiency Testing Program

Crude Oil
Sample ID: CO1511

ASTM Crude Oil
Sample ID: CO1511
November 2015
Vapor Pressure (Expansion Method) - D6377
(kPa)

Current Data					Historic Z Scores					
Lab	Test Results	Robust Deviation	Z Score	Notes	1507	1503	1411	1407	1406	1403
175	10.5	-2.58	-0.9		-1.1	-1.0	-0.5	-0.1	0.2	-0.1
179	** 29.6			R	NDS	R	0.0	R	NDS	1.7
181	18.5	5.42	1.9		0.1	-0.2	0.3	-2.7	0.9	-0.1
184	<25.0				-0.8	-0.4	NDS	NDS	NDS	NDS
186	12.9	-0.18	-0.1		NDS	NDS	NDS	NDS	NDS	NDS
188	7.2	-5.88	-2.0	2	NDS	-0.8	-0.6	0.3	-0.8	NDS
189	11.7	-1.38	-0.5		-0.7	NDS	-0.5	NDS	NDS	NDS
203	9.9	-3.18	-1.1		NDS	R	NDS	NDS	NDS	NDS
204	9.2	-3.88	-1.3		-0.4	-0.3	-0.3	-0.5	-0.7	-0.4
209	10.9	-2.18	-0.8		-0.5	0.2	0.7	0.1	-0.4	-0.2
216	13.7	0.62	0.2		-1.3	R	-2.3	R	-1.1	NDS
222	9.6	-3.48	-1.2		NDS	NDS	NDS	-0.2	NDS	3.4
223	11.0	-2.08	-0.7		NDS	-1.5	NDS	NDS	NDS	NDS
225	11.2	-1.88	-0.6		-0.7	-0.8	NDS	NDS	NDS	NDS
229	6.7	-6.38	-2.2	2, 3	R	-0.6	0.5	NDS	NDS	3.0
242	** 1.9			R	NDS	-1.0	NDS	NDS	-0.6	NDS

Pooled Standard Devia

No. Valid Results	56
Robust Mean	13.08
Robust Standard Deviation	2.90
Reproducibility ASTM Standard	5.26
Reproducibility These Test Data	8.03
Anderson Darling	0.63
TPI	0.66

Legend:
1 = Test re
2 = Test re
3 = Z-Scor
R = Rejecte
NDS = No Dat
$ = Data w
X = Lab pr
* = There i
** = Z-Scor
as "Rej
introdu
Unsatis
N/A = Not Ap
NSP = No Sta

$VPCR_4$, 37.8°C !!

Method	R (data set)	Mean	# labs
D323 RVP	8.5 kPa	11.1	48
D5191	7.4 kPa	11.6	27
D6377	8.0 kPa	13.1	56

Initial Boiling Point : IBP vs IBP

- Initial Boiling Point (IBP)

n—in D86 distillation, the corrected temperature reading at the instant the first drop of condensate falls from the lower end of the condenser tube.

Loss up to 5%, gasoline

- Initial Boiling Point (IBP)

n—in gas chromatography, the temperature (corresponding to the retention time) at which a cumulative corrected area count equal to 0.5 % of the total sample area under the chromatogram is obtained.

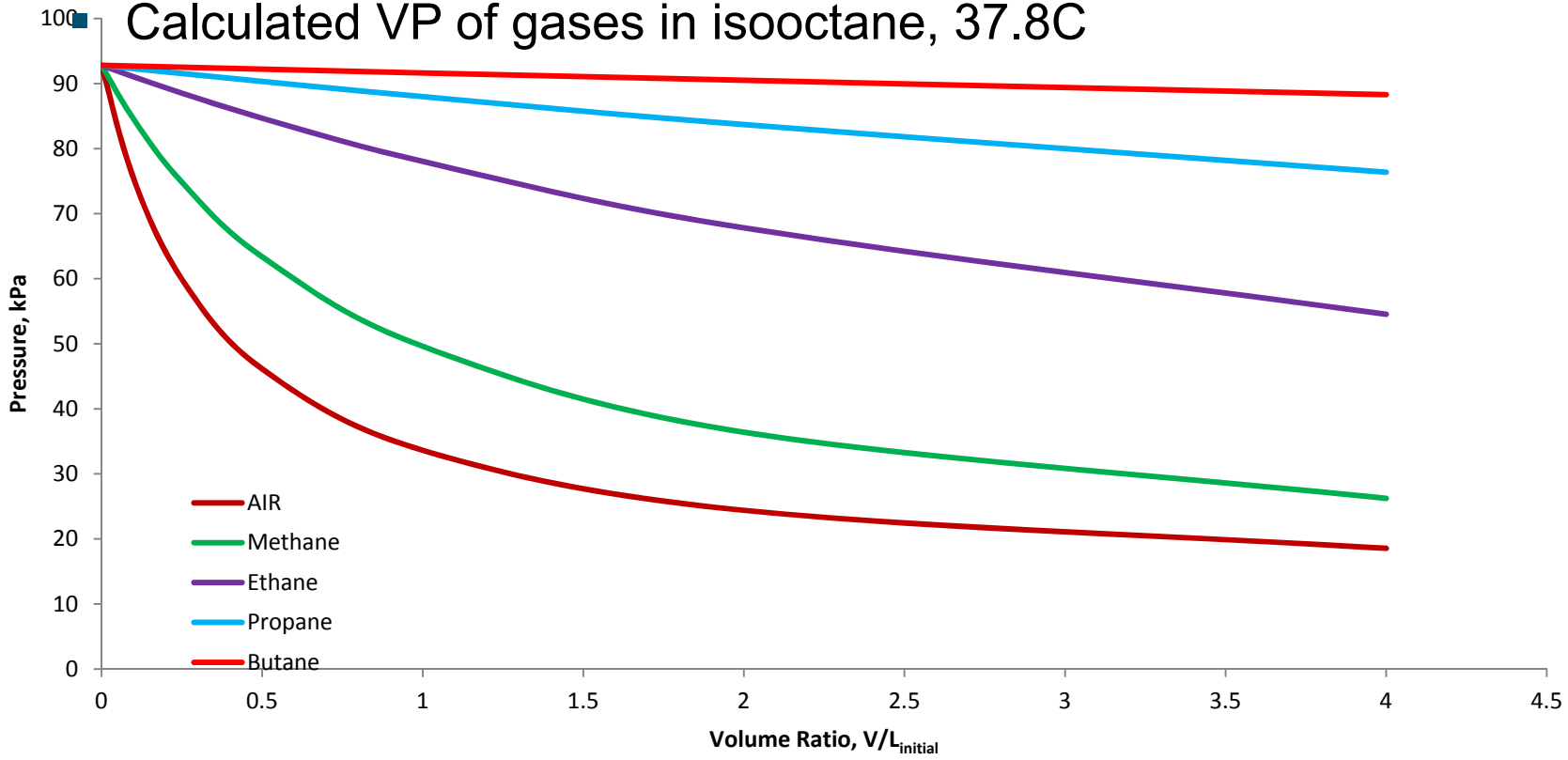
Minimal loss

“Light Ends” – Volatile Components

- Volatile Components include:
  - Hydrocarbon components that cannot be maintained as a liquid at atmospheric pressure at temperatures greater than 0°C
  - Fixed gases such as CO, CO_2, H_2, H_2S, N_2 and O_2
  - Water

Light Hydrocarbons AND fixed gases

- EOS SRK Modeling of Binary Mixtures
  - Calculated VP of gases in isooctane, 37.8C



Sampling

- Sealed sampling systems required to prevent loss of volatile components.
  - Floating Piston Cylinder (ASTM D3700)
  - Manual Piston Cylinder (ASTM D8009)
  - Liquid Displacement using a Fixed Volume Cylinder (GPA 2174, ASTM D4057, ASTM D1265)

Sampling

- pressurized samples - cylinders
  - ASTM D3700 Floating Piston Cylinder or ASTM D1265 LPG type with ullage

Sampling

- pressurized samples - cylinders
  - ASTM D8009 manual piston cylinder

Sampling

- Sealed sampling systems vs Open (Bottles)

- Recent work has shown that initial boiling point (IBP) determination and vapour pressure measurements are greatly affected by loss of volatile components.
  - Same sample point
  - Same time
  - Same product

Initial Boiling Point

Sample Type	IBP (°C), ASTM D86, Open Sampling	IBP (°C), ASTM D8003/ASTM D7169, Closed Sampling	Δ(°C)
Condensate	27.6	-42.2	**69.8**
Dilbit	29.7	-0.6	**30.3**
Diluted Heavy Oil	30.9	-0.6	**31.5**
Light Oil	35.8	-11.7	**47.5**
Medium Oil	92.8	62.4	**30.4**
Syn-Bit	52.8	-0.6	**53.4**
Synthetic Crude	35.2	-0.6	**35.8**

IBP-GC

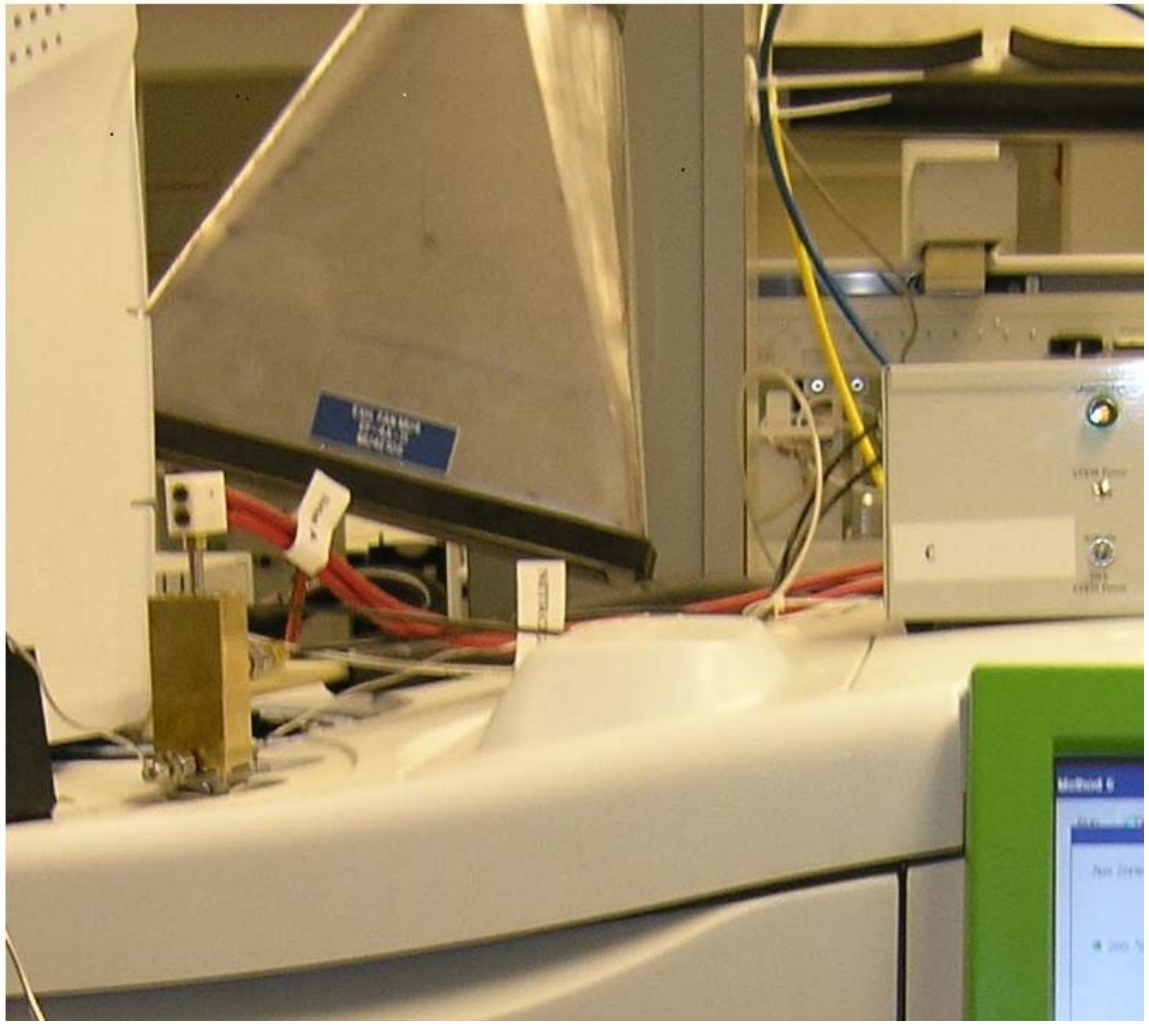
Vapour Pressure

Type	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D323M, Open Sampling	Vapour Pressure (4:1) @ 50°C (kPa), ASTM D6377, Closed Sampling	Δ kPa
Diluted Bitumen	88.0	107.9	**-20**
Diluted Heavy Oil	83.8	102.4	**-19**
Light Oil	115.5	128.3	**-13**
Condensate	130.5	144.9	**-14**

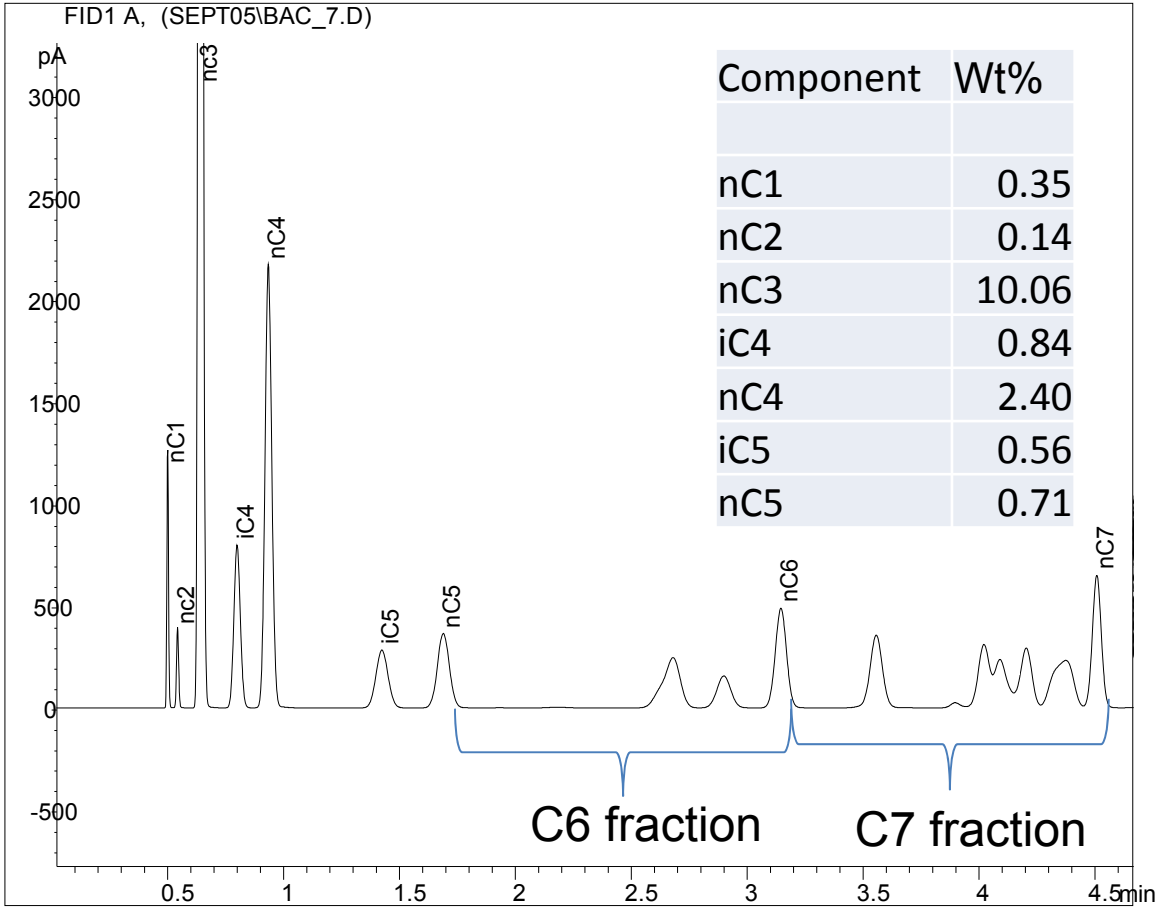
Analysis of Light Ends

- Requires direct transfer from sample cylinder to instrument.
- ASTM D8003
  - Methane (nC_1) to hexane (nC_6) including iC5, benzene, and benzene precursors are speciated and quantitated.
  - Cut point carbon fraction intervals from initial boiling point IBP) to nC24). nC24+ plus fraction reported.
  - Heated, pressurized liquid injection system (HPLIS)

HPLIS valve on GC



C1-C7 peaks resolution



Component	Wt%
nC1	0.35
nC2	0.14
nC3	10.06
iC4	0.84
nC4	2.40
iC5	0.56
nC5	0.71

ASTM D8003 Update

- Continued progress
  - Validated with gravimetric standards, theoretical EOS
  - Demonstrated excellent repeatability
  - Reproducibility studies have identified enhanced QC and maintenance requirements
  - AITF & CANMET > 1 year experience
  - Second calibration standard available
  - Two other labs setting up – Houston, Edmonton

Volatile Components - GOR

- GOR (gas/oil ratio): atmospheric flash
  - Flashed Gas: CO_2, CO, H_2S, H_2, O_2, N_2, C1 to C9
  - Flashed Oil: C30+ GC analysis
  - Recombined sample composition
  - Complex, time consuming procedure

Volatile Components - GPA

- GPA 2103/2177
  - Methods intended for natural gas condensate mixtures containing nitrogen/air and carbon dioxide.
    - GPA 2177: mixtures containing < 5 mole% C7+
    - GPA 2103: mixtures containing > 5 mole% C7+
  - N_2, CO_2, C1 to C6 speciated and quantified
  - C7+ fraction: volume, density and MW physically measured
  - Nitrogen and air are not differentiated
    - Source of nitrogen cannot be determined, i.e. air or pad gas

Volatile Components – New!

- Proposed helium equilibration method utilizing ASTM D8009 MPC
  - Sample volume within MPC reduced to 20%. A 4:1 V/L ratio is created in the MPC by extending the piston to 100%.
  - Inert gas injected into the vapour space at 200 kPa and sample is allowed to equilibrate.
  - Equilibrium vapour analyzed using a refinery gas analyzer (RGA) / ASTM D7833: CO_2, CO, H_2S, H_2, O_2, N_2, C1 to C4

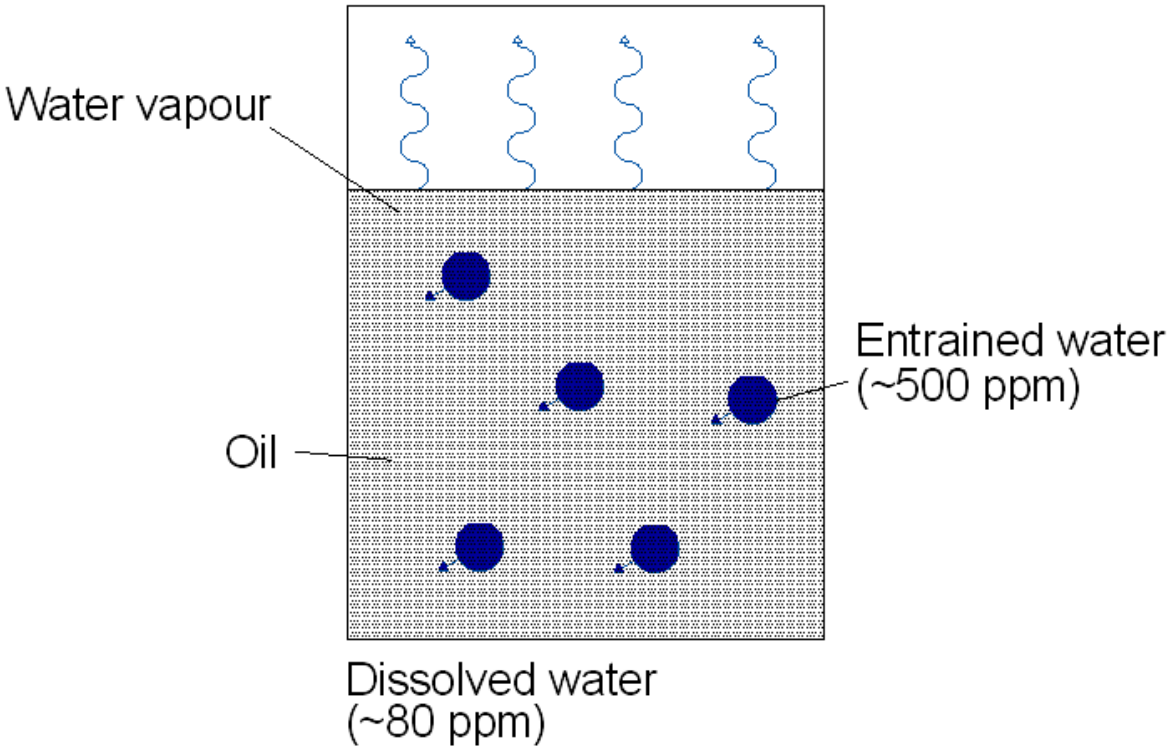
EOS modeling: Vapour Pressure Prediction

- ASTM D8003 data used as input for SRK equation of state to calculate vapour pressure
  - Compare modeled values to ASTM D6377 measured vapour pressure.
- No tuning of model
  - Default interaction parameters used
- Data sets
  - Seven samples from TransCanada Pipelines

Effect of Water on Modeled VP

- API COPP Ad-Hoc group suggested accounting for water in the sample to improve the model.
- Dissolved water vs. entrained
  - Effect of dissolved water (80ppm) very small
  - If it is assumed that oil is saturated with water, the effect on VP is significant

Dissolved Water vs. Entrained

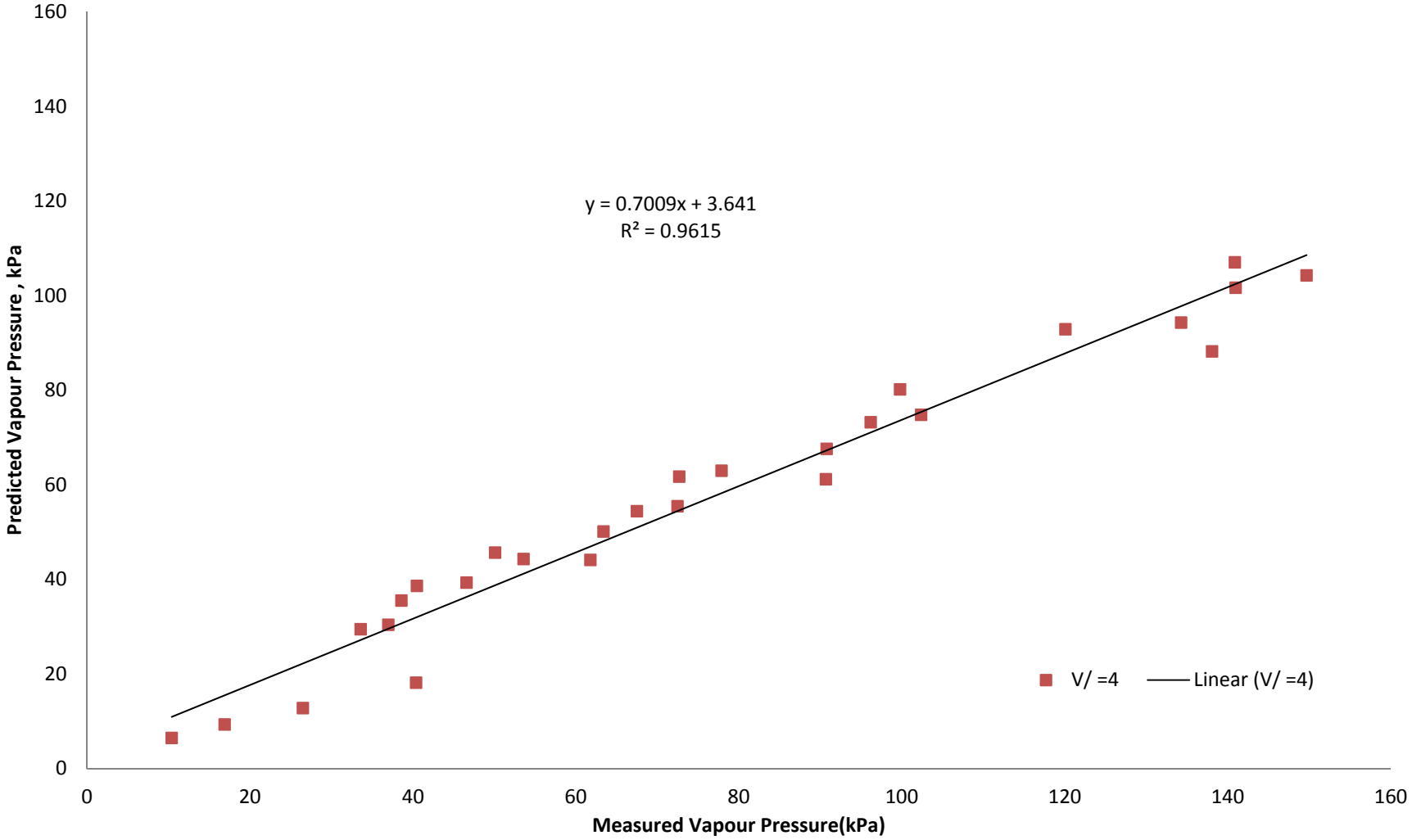


Three phase flash calculation

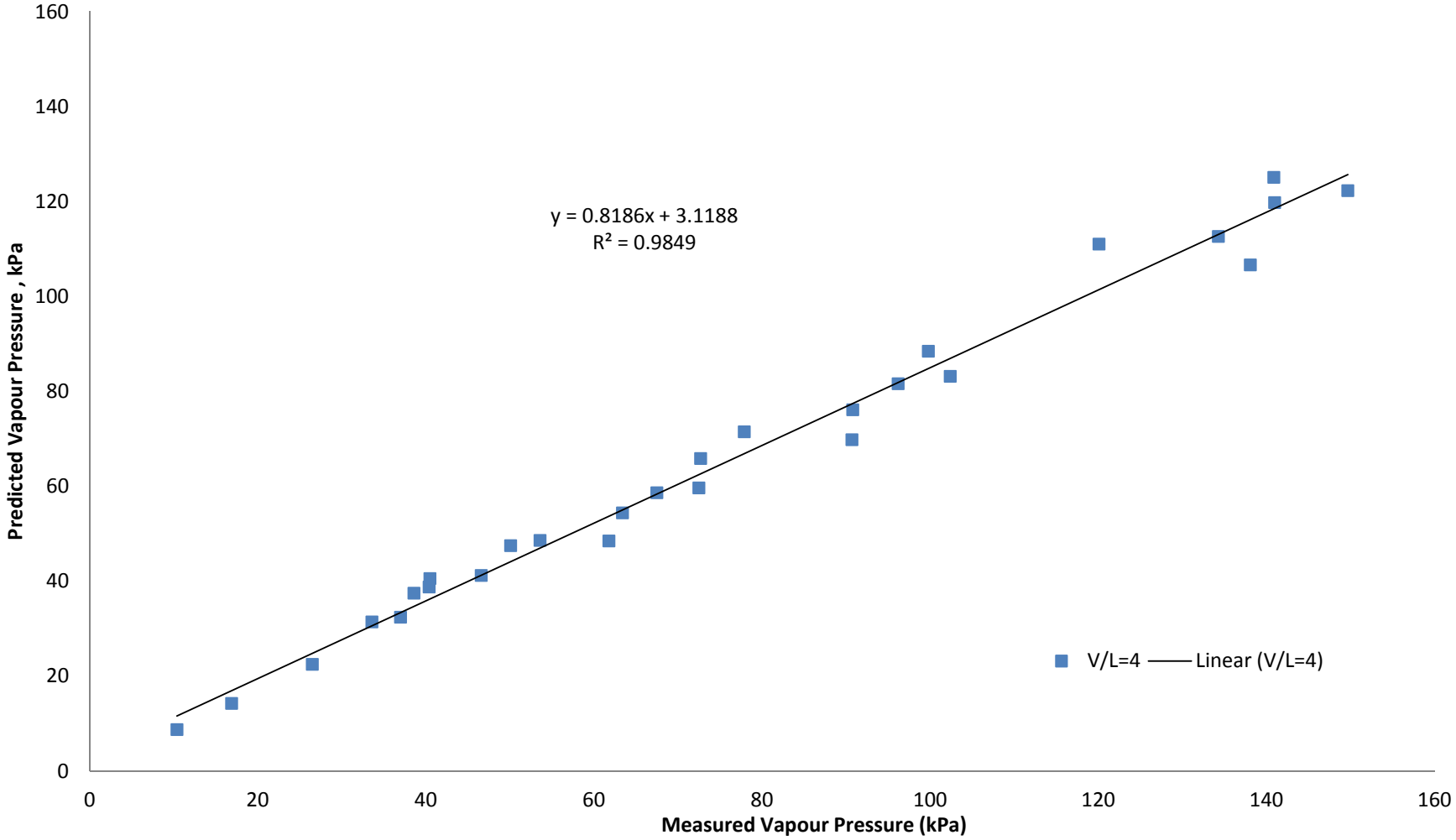
TCPL Samples

- Vapour pressure measured at V/L 4:1 and 25°C, 37.8°C, 50°C and 35°C
- Seven samples
  - Western Canadian Select (WCS) x 2
  - SWB – TCPL custom stream
  - Access Western Blend (AWB)
  - Bow River (BR)
  - Borealis Heavy Blend (BHB)
  - ACS – TCPL custom stream
- VP range of 10 to 150 kPa

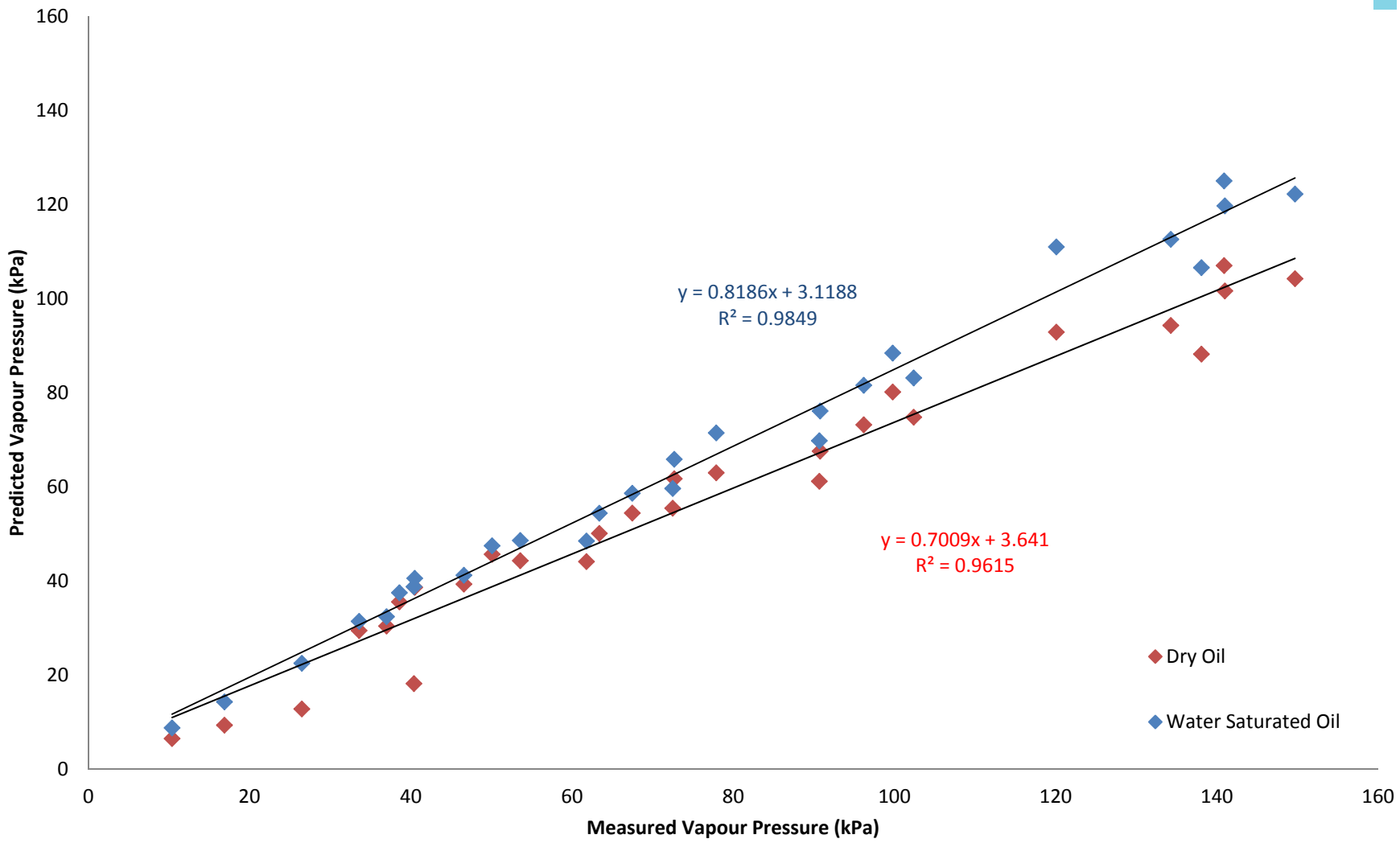
TCPL Samples: SRK EOS Predicted VP vs. ASTM D6377 VP, $VPCR_4$ @ 25,37.8,50,65°C



TCPL Samples: SRK EOS Predicted VP (H_2O Saturated) vs. ASTM D6377 VP, $VPCR_4$ @ 25,37.8,50,65°C



TCPL Samples: Effect of water on Correlation between SRK EOS Predicted VP and ASTM D6377 $VPCR_4$ @



EOS Accuracy

- Empirical – not exact
- Factors affecting correlation
  - Precision statement of D6377 VP
    - R = $VPCR_4$, 37.8°C = 4.26 kPa (FPC)
    - R = $VPCR_{0.02}$, 37.8°C = 20.3 kPa (FPC)
  - Precision D8003
    - R pending ILS
  - Precision of fixed gases, water
  - Molecular weight of residue

Future Work: Modeling Vapour Pressure using Merged Compositional Data

- Fifty Eight samples
  - Merged composition of fixed gases from GOR, D8003 and D7169
- Vapour pressure measured at:
  - V/L 0.2:1 and 50°C (fifty eight samples)
  - V/L 4:1 and 50°C (eight samples)
  - Vapour Pressure Range of 30 to 213 kPa

Future Work – Light Ends

- ASTM D8003
  - Method improvements – i.e. revision
  - QC protocols
  - Inter-laboratory study for r & R will be required
- Collaborative efforts for method comparisons
  - D8003 vs. GPA methods
  - Sampling technique comparisons

Future Work – Boiling Point distribution

- ASTM D7900
  - “merge” method that combines D7169 HTSD with detailed front end analysis to obtain a corrected boiling point curve
  - Active working group
  - Ensure compliant with D8003/D7169 merge
- IBP-GC, FBP-GC definitions?

Future Work Cont.

- ASTM D6377
  - Initial ILS study (2003 version) determined precision at 37.8°C and V/L 4:1 and 0.02:1 only. Range 25 to 180 kPa. Single instrument vendor, sample set?, method changes since initial study
  - Improve measurement at low V/L
  - Calculating/predicting VP at V/L 0 using V/L sweep measurements

  - Another ILS is warranted

Future Work Cont. – Fixed Gas

- Development and validation of gas equilibration method
  - Proposed item at ASTM
  - Utilize new D8009 manual piston sampler and readily available gas analyzers

Thank you

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Questions?

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