SAND2018-5398PE

Crude Oil Characterization Research Study

Task 2: Sampling and Analysis Methods Evaluation

Presentation to

COQA-CCQTA General Meeting

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David L. Lord, Ph.D.
Geotechnology & Engineering Department
Sandia National Laboratories
Albuquerque, NM 87185

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Participants

- Sponsoring Agencies
  - US Department of Energy
  - US Department of Transportation
  - Transport Canada
- Technical Team
  - David Lord, Sandia National Laboratories
  - Ray Allen, Allen Energy Services
  - David Rudeen, GRAM, Inc.
- Peer Reviewers
  - Robert Falkiner, MSc, P.E.
  - Dr. Kesavalu Bagawandoss, Ph.D., J.D.
  - Thomas Hurstell, P.E.
  - Robbie Lansangan, Ph.D.
- Technical Support
  - Kirsten Chojnicki, Sandia National Laboratories
  - Chad Wocken, University of North Dakota EERC
  - Ted Aulich, University of North Dakota EERC

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Project Publications

Today's presentation is a high-level summary of SAND2017-12482

- Lord, D. L., R. Allen and D. Rudeen (2017). "DOE/DOT Crude Oil Characterization Research Study, Task 2 Test Report on Evaluating Crude Oil Sampling and Analysis Methods." *Unlimited Release* ***SAND2017-12482***. Sandia National Laboratories, Albuquerque, NM 87185.
- Lord, D., A. Luketa, C. Wocken, S. Schlasner, R. Allen and D. Rudeen (2015). "Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport." *Unlimited Release* ***SAND2015-1823***. Sandia National Laboratories, Albuquerque, NM 87185.

Presentation Outline

- Problem Statement
- Executive Summary
- Background
- Sampling Methods
- Analysis Methods
- Results
- Ongoing Work
- Possible Areas for Improvement

Drivers for Conducting this Work

- Crude transport by rail poses risks recognized by US and Canadian regulators and stakeholders
- Hazards have been realized in a number of high-profile train derailments leading to oil spills, environmental contamination, fire, property damage, and fatalities
- Open debate on whether the types of crude (tight oil vs. conventional production) have significant bearing on severity of transportation accidents
- Additional uncertainty around which sample capture and analysis methods are appropriate for crude and also relevant to potential combustion hazard levels in an accident

TSBC (2014). "Runaway and Main-Track Derailment Montreal, Maine & Atlantic Railway Freight Train Lac-Megantic, Quebec 06 July 2013." ***R13D0054***. Transportation Safety Board of Canada, Gatineau QC K1A 1K8. Railway Investigation Report.

Problem Statement

- Crude Oil Characterization Research Study
  - Objective: Evaluate whether crude oils currently transported in North America, including those produced from "tight" formations, exhibit:
    - physical or chemical properties that are distinct from conventional crudes, and
    - how these properties associate with combustion hazards that may be realized during transportation and handling
- Project Structure
  - Task 1: Project Administration and Outreach
  - Task 2: Sampling & Analysis Methods Evaluation ← Today's focus
  - Task 3: Combustion Experiments and Modeling
  - Task 4: Crude Characterization, Tight vs. Conventional

Task 2: Methods Evaluation

- Problem
  - Unclear from current literature which sample capture and analysis methods are suitable for measuring vapor pressure and light ends content for oils to be compared in Tasks 3 and 4
- Task 2 Objectives
  - Investigate which commercially available methods can accurately and reproducibly:
    - capture, transport, and deliver hydrocarbon fluid samples from the field to the analysis laboratory, and furthermore
    - analyze for properties related to composition and volatility of the oil, including true vapor pressure, gas-oil ratio, and dissolved gases and light hydrocarbons
  - Performance will be directly compared to a well-established mobile laboratory system that currently serves as the baseline instrument system for the U.S. Strategic Petroleum Reserve Crude Oil Vapor Pressure Program
  - Methods that perform well in Task 2 will be utilized in Tasks 3 and 4

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Executive Summary (1)

- Both oil samples appeared to have been equilibrated with ambient conditions in atmospheric tanks elsewhere in the supply chain before they were sampled. This was evidenced by bubblepoint pressures at or near local atmospheric pressure at line sampling temperature.
- The study generally found that both open and closed industry standard spot sampling methods yielded comparable results for vapor pressure of crude oil, VPCR, and hydrocarbon content against the tight-line TVP-95 system for the two oils that were tested here
- However, open and closed methods were not equivalent in their ability to deliver appropriate samples to the ASTM D6377 vapor pressure instrument for vapor-liquid ratio (V/L) < 1. Samples must be introduced into the VPCR instrument from pressurized containers for testing at V/L < 1.
- Vapor-liquid ratio (V/L) has important implications for reproducibility of results and sensitivity to small amounts of gas for VPCR measurements. This study was unable to generate reproducible results for V/L = 0.02 and 0.05.

Executive Summary (2)

- Two pressurized compositional methods (GPA-2103-M and ASTM D8003-M) based on spot sample analysis yielded results that compared well with the tight-line TVP-95 system for hydrocarbon compositions.
  - Equation of state modeling with these same compositional data calculated vapor pressure that compared well to measured.
- The inadvertent addition of pressurized nitrogen, air, or inert gas associated with sample handling for spot samples likely contributed to poor reproducibility in VPCR at low V/L. Tight-line samples in the TVP-95 did not show this issue. Improvements in current standards for spot sample acquisition and handling are proposed.
- In summary, the study found that there are a number of viable options for sample capture and analysis to accurately determine VPCR and composition of crude oils that exhibit bubblepoint at or below local atmospheric pressure, though there are issues with reproducibility of VPCR at low V/L (0.02, 0.05) and inert gas content in spot sampling that appear to be related, which could potentially be mitigated with improved spot sample handling methods

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Background

- Sampling method matters when source material contains enough gas such that net losses during sample capture, transport, storage, and handling and analysis in the lab affect measured vapor pressure
- Simple distinction of “live” vs. “dead” oil is coarse
  - Methods and equipment designed to these end members may not be best suited to the oils and conditions we are looking at here
- Recent revisions (‘14, ‘15, ‘16) to VPCRx method ASTM D6377 and introduction of manual piston cylinder (ASTM D8009-15) and pressurized compositional method (ASTM D8003-15) indicate industry is adapting to these needs
- Unclear which commercially available sampling and analysis methods are appropriate for use in this study

Sampling Guidance

- ASTM D6377-16, VPCRx(T) for Crude Oils
  - *Sampling of live crude oil shall be performed in accordance with Practice D3700.*
  - *Sampling in accordance with D4057 shall only be used for dead crude oil and if Practice D3700 is impractical.*
- CCQTA Light Ends Memo (2014)
  - *"CCQTA Information Regarding the Measurement and Reporting of Light Ends and Vapor Pressure of Live Crude," Edmonton, Alberta, Canada TR6 2V4.*
  - *Provides specific guidance for sample handling for live crudes intended for vapor pressure and compositional analyses*

Sampling & Analytical

TASK 2: METHODS

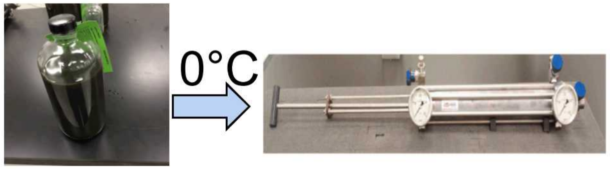
Overall Approach

- Select two crude oil sampling sites within the US domestic supply chain to obtain a continuous, reasonably homogeneous sample for up to three consecutive sampling days
  - North Dakota Bakken terminal
  - Texas Eagle Ford terminal
- Capture samples by an assortment of open and closed industry standard sampling methods
  - <u>Treat the sampling method as an independent variable</u>
- Measure those samples with an assortment of industry standard analysis methods
  - <u>Treat the analysis method as an independent variable</u>
- Compare analytical results across sampling methods, analysis methods, and laboratories
- Move forward in Tasks 3 & 4 with methods found to give acceptable performance for accuracy, reproducibility, and self-consistency between physical properties and composition

Sampling Methods

- Closed methods
  - "Tight Line" to on-site test separator
  - ASTM D3700 floating piston cylinder (FPC)
  - ASTM D8009 manual piston cylinder (MPC)
  - GPA 2174 water displacement cylinder (WD)

- Open methods
  - ASTM D4057 bottle sample, Boston Round (BR)
    - BR ambient fill: vacuum pull used to draw sample straight from ambient P/T bottle into 6377 VP tester
    - BRMPC: sample was chilled & transferred to MPC prior to pressurized injection into D6377 VP tester. Sample then pre-conditioned to 6377 test cell temperature prior to injection.



Analysis Methods

- Crude Oil Vapor Pressure VPCRx(T) by ASTM D6377-16M
  - “M” requires sample pre-conditioning and minimum equilibration criteria
  - V/L = 0.02 through 4.0; T = 68, 100, 122 F
- TVP-95 mobile separator unit for bubblepoint pressure (BPP) and gas-oil ratio (GOR) at T = 100 F
- Pressurized compositional analyses
  - TM1: BPP and GOR flash gas analysis with C30+ with numerical merge
  - TM2: GPA 2177 + ASTM D7900 + ASTM D7169 with numerical merge
  - TM3: GOR flash + ASTM D8003 + ASTM D7169 with numerical merge
  - TM4: GPA 2103-M + physical shrink + ASTM D2887 C7+ analysis with numerical merge
- Selected physical properties
  - Total sulfur mass %, relative density, average molecular weight, kinematic viscosity, flashpoint, initial boiling point

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Task 2 Test Matrix

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Abbreviated test matrix for today's presentation

			Property Measurement			
Sample Technique	**Standard**	**Sample Transfer**	TVP	Compositional Analysis 2	Compositional Analysis 3	Compositional Analysis 4
Tight Line to TVP-95 Mobile Laboratory		N/A	Separator shut-in	BPP flash gas GC analysis	GOR flash gas GC analysis	Separator liquid C30+
Floating Piston Cylinder	ASTM D3700-14	N/A	ASTM D6377-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	GPA2103 M + shrink + ASTM D2887
Water Displacement	GPA 2174-14	N/A	ASTM D6377-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	GPA2103 M + shrink + ASTM D2887
Manual Piston Cylinder	ASTM D8009-15	N/A	ASTM D6377-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	GPA2103 M + shrink + ASTM D2887
Boston Round	ASTM D4057-12	BR to MPC	ASTM D6377-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	GPA2103 M + shrink + ASTM D2887
	ASTM D4057-12	BR	ASTM D6377-M	N/A	N/A	N/A

Color coding	Comment
Test Method 1 (TM1)	
Test Method 2 (TM2)	Results currently unavailable; will be included in a subsequent report
Test Method 3 (TM3)	
Test Method 4 (TM4)	

See SAND2017-12482 for full Task 2 test matrix

TASK 2: RESULTS

Physical Properties

Property	Method	Acronym	Units	ND Bakken		TX Eagle Ford	
				average	stdev	average	stdev
Relative Density at 60°F (15.6°C)	ASTM D5002	RD	-	0.8142	0.0016	0.7955	0.0039
API gravity at 60°F (15.6°C)	ASTM D5002	°API	°API	42.3	N/A	46.4	N/A
Total Sulfur	ASTM D4294	S	mass%	0.0863	0.0064	0.1147	0.0250
Avg Molecular Weight	Frz. pt. dep.	MW	g/mole	168.9	3.7	178.4	1.8
Kinematic Viscosity at 68°F (20°C)	ASTM D7042	ν_{20}	mm^2/s	2.726	0.121	3.449	0.394
Kinematic Viscosity at 100°F (37.8°C)	ASTM D7042	$\nu_{37.8}$	mm^2/s	2.085	0.124	2.552	0.098
Flashpoint	ASTM D56	FP	°F	< 50	N/A	< 50	N/A
Initial Boiling Point	ASTM D86	IBP	°F	84.1	0.8	89.4	1.6

TVP-95 BPP and GOR Results (100F)

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Baseline Instrument Results

Equivalent V/L calculated from measured GOR

GOR Separator Pressure

ND Bakken

Line T ~ 70F

100°F

	BPP	GOR	V/L	P
	[psia]	[scf/bbl]	[-]	psia
Day 1	19.0	12.4	2.5	14.0
Day 2	19.2	12.8	2.5	14.1
Day 3	19.2	**9.7**	2.0	13.7

TX Eagle Ford

Line T ~ 96F

100°F

	BPP	GOR	V/L	P
	[psia]	[scf/bbl]	[-]	[psia]
Day 1	14.6	0.2	0.04	14.6
Day 2	15.1	0.2	0.04	14.7
Day 3	14.9	0.1	0.03	14.7

Both oil samples appeared to have been equilibrated with ambient conditions in atmospheric tanks elsewhere in the supply chain before they were sampled. As such, they were not visibly boiling at the conditions of sample capture.

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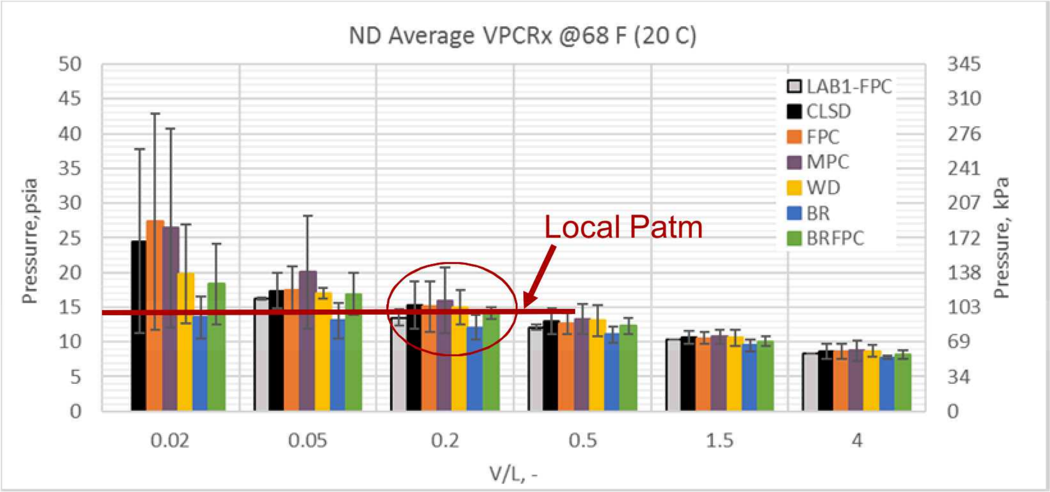
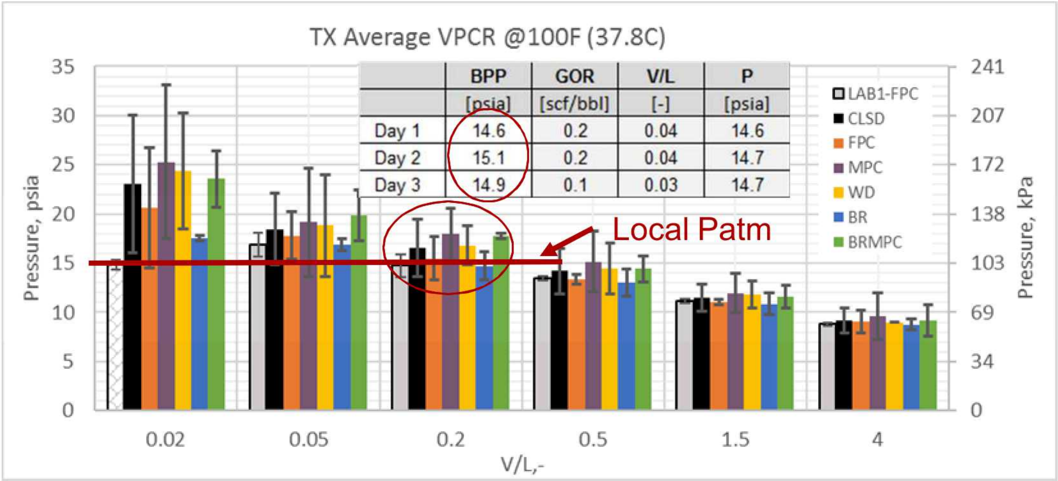
Oils Exhibit BPP = 1 atm at Line T

- Both oil samples appeared to have been equilibrated with ambient conditions in atmospheric tanks elsewhere in the supply chain before they were sampled.
- This was evidenced by bubblepoint pressures (BPP) at or near local atmospheric pressure at line sampling temperature.
- Implication: VPCR of a crude oil in unpressurized storage will likely reflect local ambient conditions

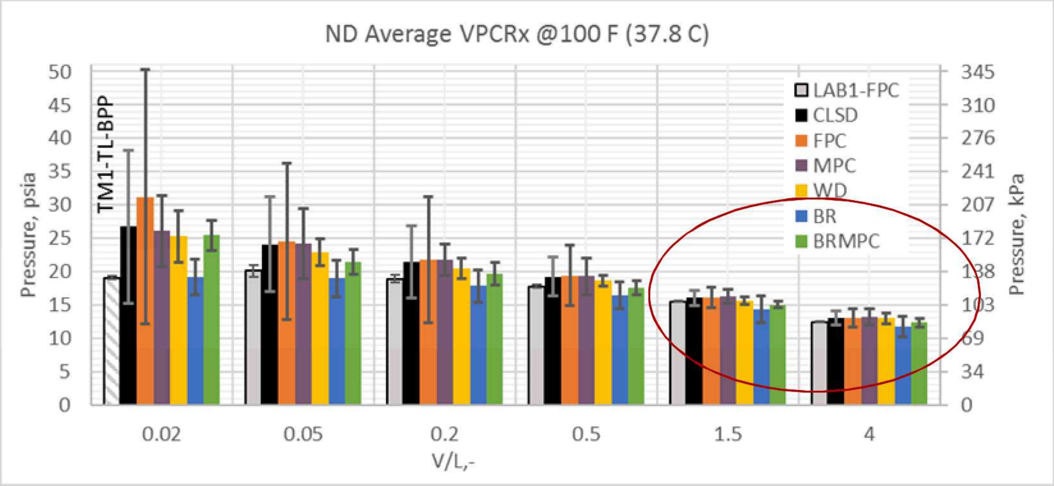


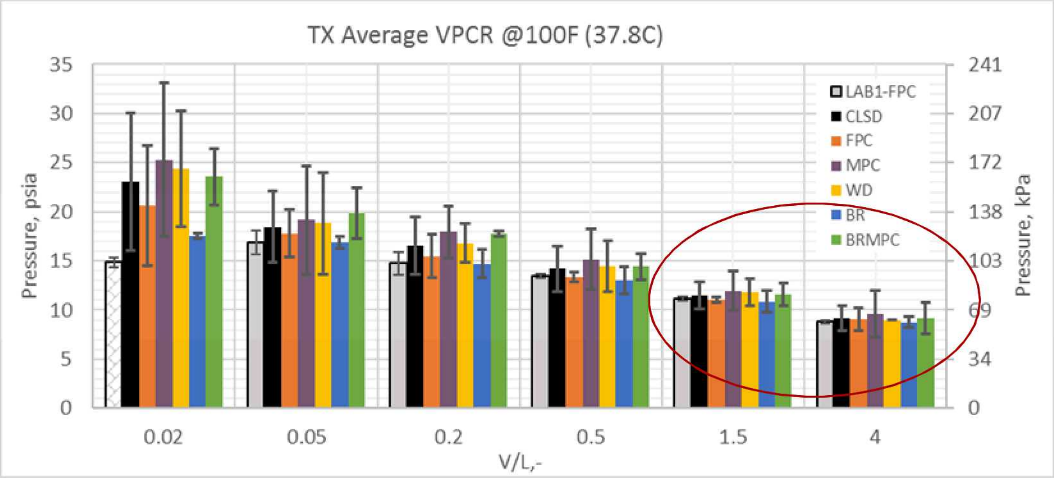


VPCR$_{0.2}$ appears to correlate well with BPP at a given temperature

Sampling Methods Same for VPCR at High V/L

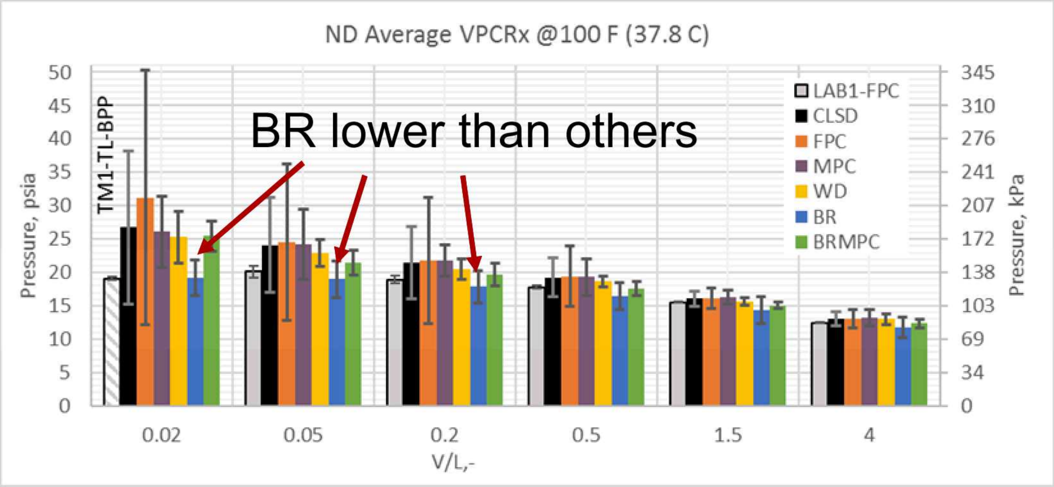
- All open and closed methods for sourcing VPCR give comparable results for high V/L (1.5, 4.0)
- Implication: Oils sampled from a supply chain point equilibrated with ambient conditions and tested for VPCR at high V/L (1.5, 4.0) will likely be relatively insensitive to sampling method

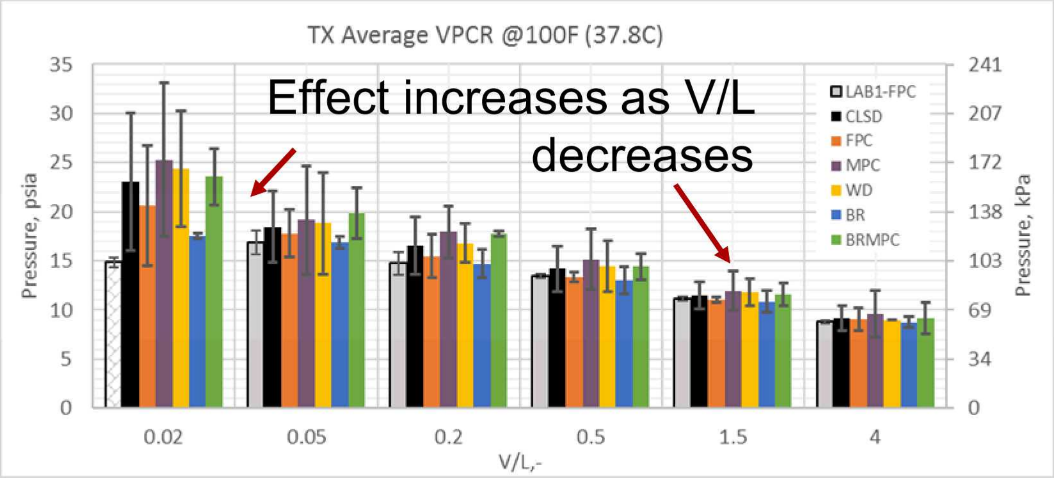




Methods not Equivalent for VPCR at Low V/L

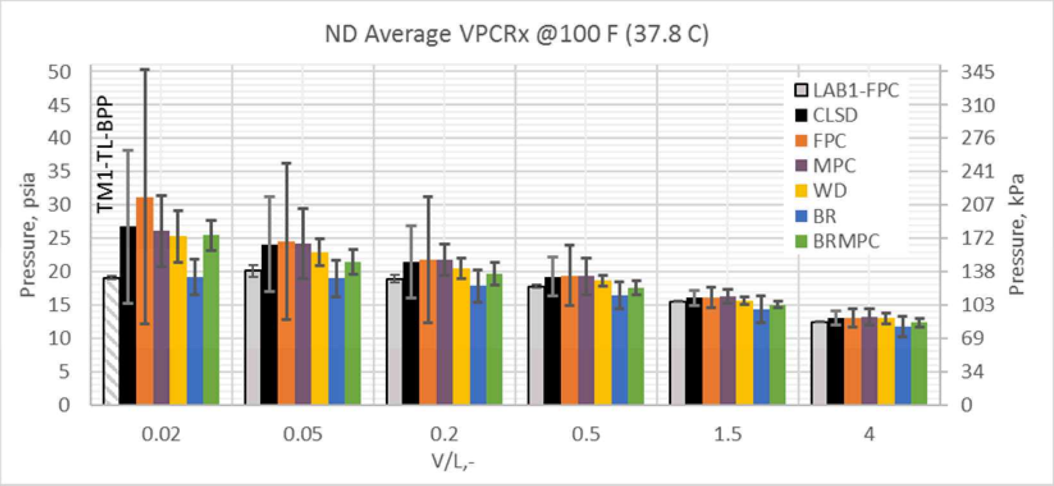
- Open and closed methods were not equivalent in their ability to deliver appropriate samples to the ASTM D6377 vapor pressure instrument for vapor-liquid ratio (V/L) < 1.
- Samples must be introduced into the VPCR instrument from pressurized containers (BRMPC) for testing at V/L < 1.
- Implication: VPCR sample acquisition and handling for V/L < 1 require higher level of rigor than V/L > 1

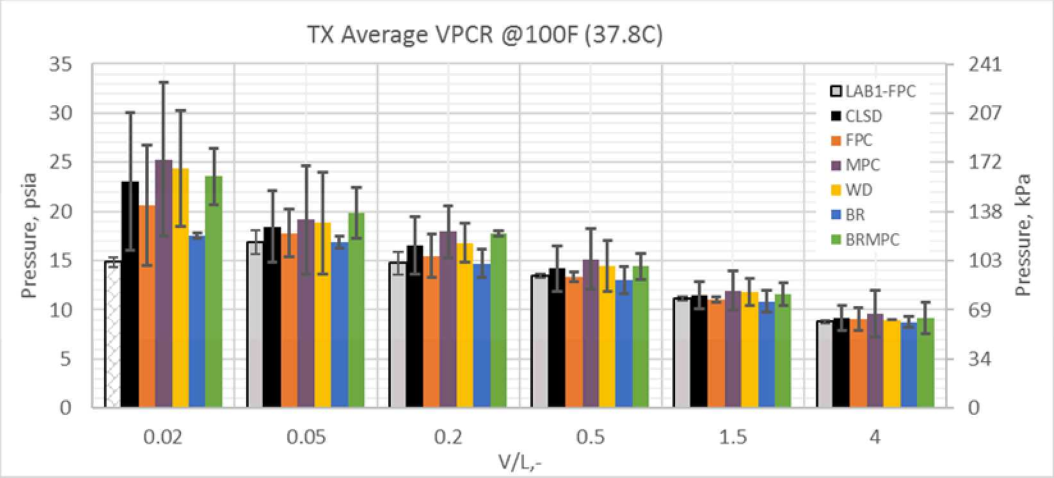




Uncertainty at Low V/L

- All sampling methods generally showed high standard deviations and poor reproducibility at low V/L, especially 0.02 and 0.05
- Implication: Current capabilities demonstrated here for measuring VPCR of crude at low V/L (0.02, 0.05) are not sufficient to produce reliable property measurements





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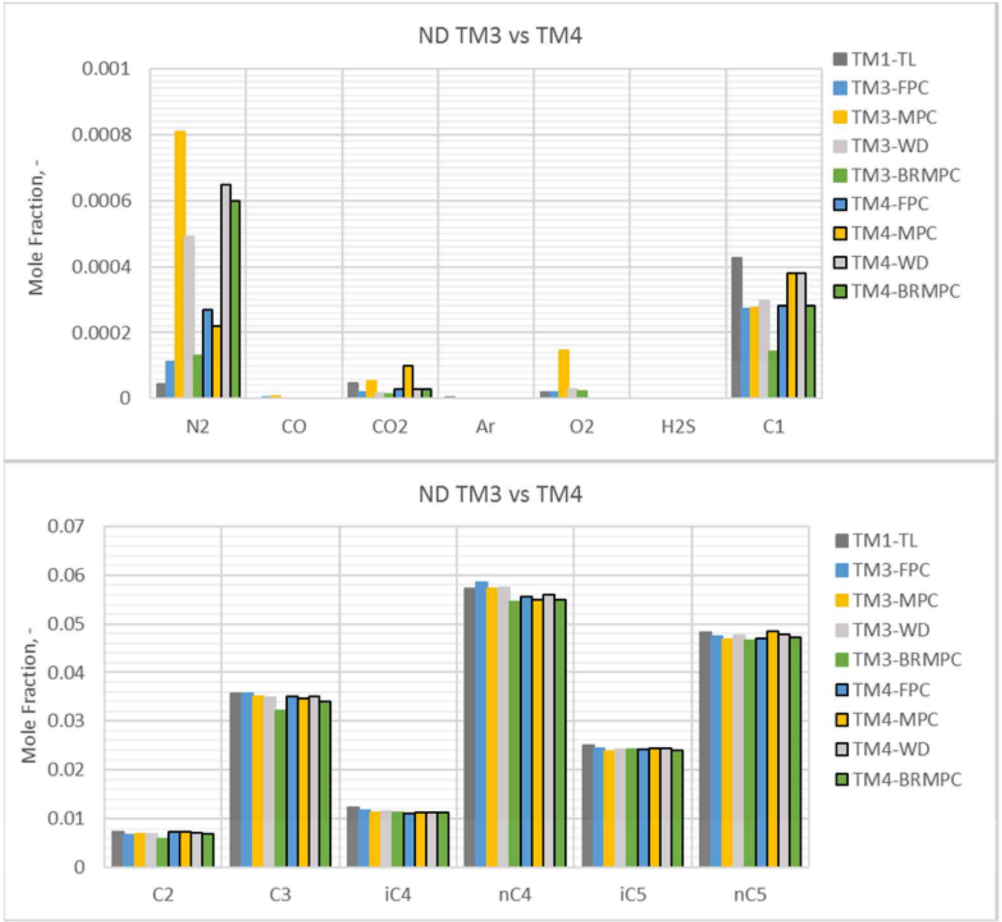
Compositional Analysis

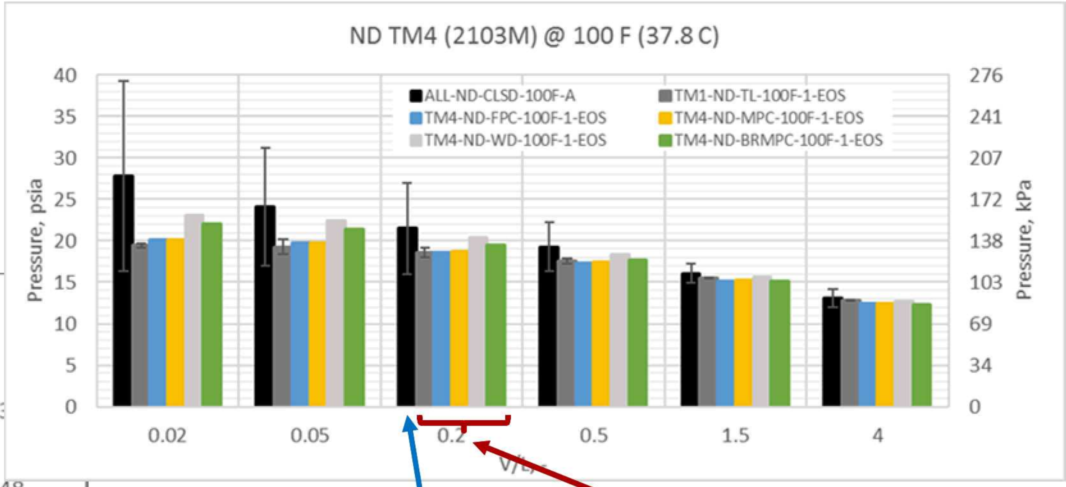
- All spot sampling and pressurized analysis methods for <u>hydrocarbon composition</u> compare well to baseline tight-line system
- Exception is noted for inert gases, which may enter spot samples from handling procedures
- Implication: There are several commercially available options for obtaining pressurized compositional analysis (N2, CO2, C1-C30+) for crude oil spot samples that compare well with a baseline flash separator approach.

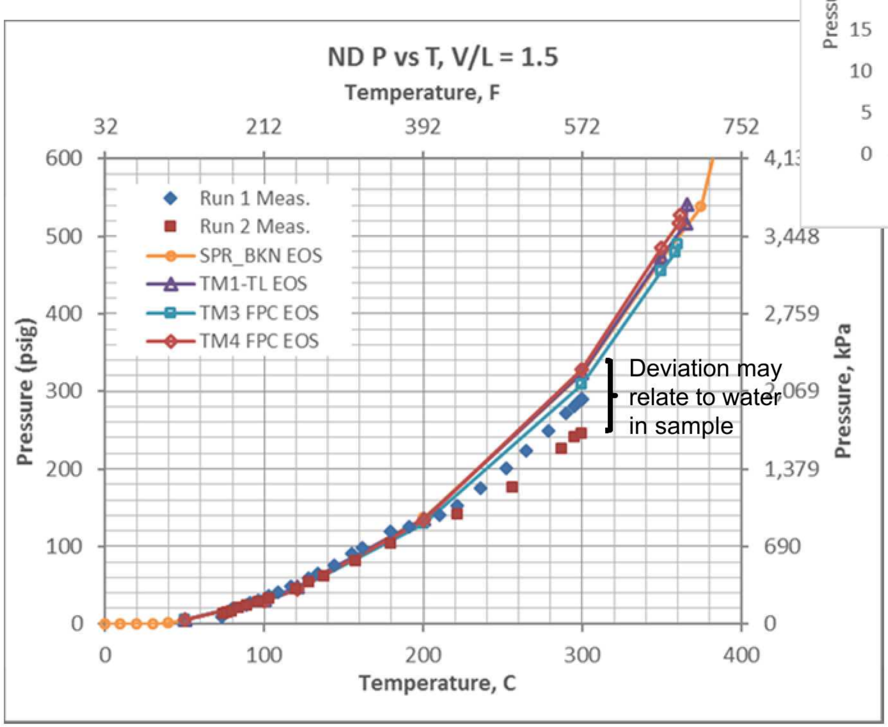


- TM1: BPP and GOR flash gas analysis with C30+ with numerical merge
- TM2: GPA 2177 + ASTM D7900 + ASTM D7169 with numerical merge
- TM3: GOR flash + ASTM D8003 + ASTM D7169 with numerical merge
- TM4: GPA 2103-M + physical shrink + ASTM D2887 C7+ analysis with numerical merge

EOS Model Performance

Equation of state (EOS) modeling with these same compositional data calculated vapor pressure that compared well to measured.





Ongoing Work

- Revision to SAND 2017-12482 is in review and should be published later in 2018 addressing:
  - Additional Compositional Analyses
    - Two more compositional analysis methods (TM2, TM4a) were applied to Bakken and Eagle Ford samples for comparison against the data shown in prior slides (TM1, TM3, TM4)
  - Winter Sampling
    - Both ND and TX locations were sampled with open and closed methods in March 2017 to explore possible seasonal effects on sampling performance
- Combustion Testing at Sandia
  - Crude oils representing a measurable range of vapor pressure and light ends content are being subjected to pool fire and fireball experiments to determine if these properties relate to measurable differences combustion properties that control hazards in large-scale combustion events

Standards Work

- Peer review panel reached consensus that that current shortcomings in sampling and analysis standards associated with crude oil vapor pressure determination has some role in the variations that were observed in the VPCR data presented in this report
- Outcomes from this work will be taken to industry standards drafting committees as revision points moving forward
  - Sampling methodology issues
    - Steps to minimize inert gas and light ends losses/gains relative to parent sample
  - Testing standards
    - Address issues caused by atmospheric (vacuum) sample draw into 6377 test cell

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Possible Areas for Improvement

- Improve reproducibility of D6377 VPCR at low V/L for spot sampling. Need to isolate sample handling effects from instrument limitations.
- Reduce frequency/magnitude of introducing inert gas into VPCR and compositional samples that create a lab sample different from the parent material
- Explore the viability of VPCR(V/L =0.2) or similar as an estimate for bubblepoint pressure
- Determine where in the supply chain open versus closed sampling really does and does not matter for collecting VPCR and compositional samples

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END OF PREPARED SLIDES