SAND2018-1944PE

Crude Oil Characterization Research Study

Task 2: Sampling and Analysis Methods Evaluation

Presentation to

CCQTA Crude Oil Flammability Project Meeting

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SAND 2018C-NNNN

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- Sponsoring Agencies
  - US Department of Energy
  - US Department of Transportation
  - Transport Canada
- Technical Team
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  - Ray Allen, Allen Energy Services
  - David Rudeen, GRAM, Inc.
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- Technical Support
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Presentation Outline

- Problem Statement
- Executive Summary
- Background
- Sampling Methods
- Analysis Methods
- Discussion

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

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

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

ASTM D6377-16 Sampling Guidance

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- Section 8.1.1
  - *The extreme sensitivity of vapor pressure measurements to losses through evaporation and the resulting changes in composition require the utmost precaution and the most meticulous care in the drawing and handling of samples.*
  - *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.*
- Section 12.1.4
  - *For measurements with V/L ratios < 1, the sample may not be exposed to the atmosphere and shall be contained in a floating piston cylinder. The sample introduction temperature of the measuring chamber shall be equal to the measuring temperature to avoid any influence due to sample expansion.*

CCQTA Light Ends Memo

- For live crude: Reported values of composition of light ends and vapor pressure would be considered suspect unless the samples were
  - Sampled in pressurized cylinders (ASTM D3700) or equivalent
  - Introduced into an analyzer under single-phase conditions
  - Not exposed to atmospheric air during sampling, transport, or handling operations
  - Analyzed by a standard test method capable of introducing, detecting, and adequately quantifying light end components as a percent of total sample

CCQTA (2014). CCQTA Information Regarding the Measurement and Reporting of Light Ends and Vapor Pressure of Live Crude. Edmonton, Alberta, Canada TR6 2V4.

Sampling & Analytical

TASK 2: METHODS

Task 2: 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
  - Treat the sampling method as an independent variable
- Measure those samples with an assortment of industry standard analysis methods
  - Treat the analysis method as an independent variable
- 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

Nomenclature

ND	– North Dakota Bakken
TX	– Texas Eagle Ford
FPC	– Line filled floating piston cylinder
MPC	– Manual piston cylinder
WD	– Water displacement cylinder
BR	– Boston Round
BRMPC/BRFPC	– Boston Round transferred into MPC
BPP	– Lab 1 TVP-95 bubble point pressure test
GOR	– Lab 1 TVP-95 GOR test

Task 2 Test Matrix

			Property Measurement									
Sample Technique	**Standard**	**Sample Transfer**	TVP	Compositional Analysis 1	Compositional Analysis 2	Compositional Analysis 3	Avg MW	Relative Density	Viscosity	Flashpoint	IBP
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+	frz pt dep	ASTM D5002	N/A	N/A	EOS with flash gas
Floating Piston Cylinder	ASTM D3700-14	N/A	ASTM D6377-M	GPA2103-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	frz pt dep	ASTM D5002	ASTM D7042	ASTM D56	D86 & GPA 2103
Water Displacement	GPA 2174-14	N/A	ASTM D6377-M	GPA2103-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	frz pt dep	ASTM D5002	ASTM D7042	ASTM D56	D86 & GPA 2103
Manual Syringe	ASTM D8009-15	N/A	ASTM D6377-M	GPA2103-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	frz pt dep	ASTM D5002	ASTM D7042	ASTM D56	D86 & GPA 2103
Boston Round	ASTM D4057-12	BR to MPC	ASTM D6377-M	GPA2103-M	GPA2177 + ASTM D7900 + ASTM D7169	ASTM D8003 + ASTM D7169 + GOR flash gas	N/A	N/A	N/A	N/A	D86 & GPA 2103
	ASTM D4057-12	BR	ASTM D6377-M	N/A	N/A	N/A	frz pt dep	ASTM D5002	ASTM D7042	ASTM D56	D86 & GPA 2103
Manual Syringe	ASTM D7975-14	N/A	ASTM D7975-14	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

TM1
TM2
TM3
TM4

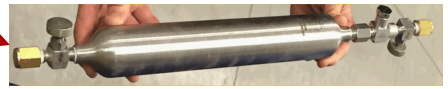
DBB6

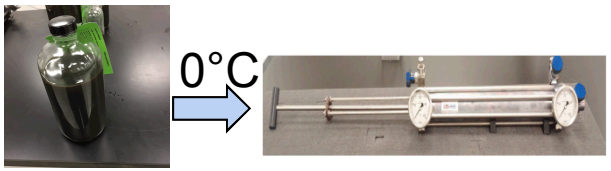
Slide 15

DBB6 It would be useful to specify how many labs conducted which tests.
Di Bacco, Barbara, 2/16/2018

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.

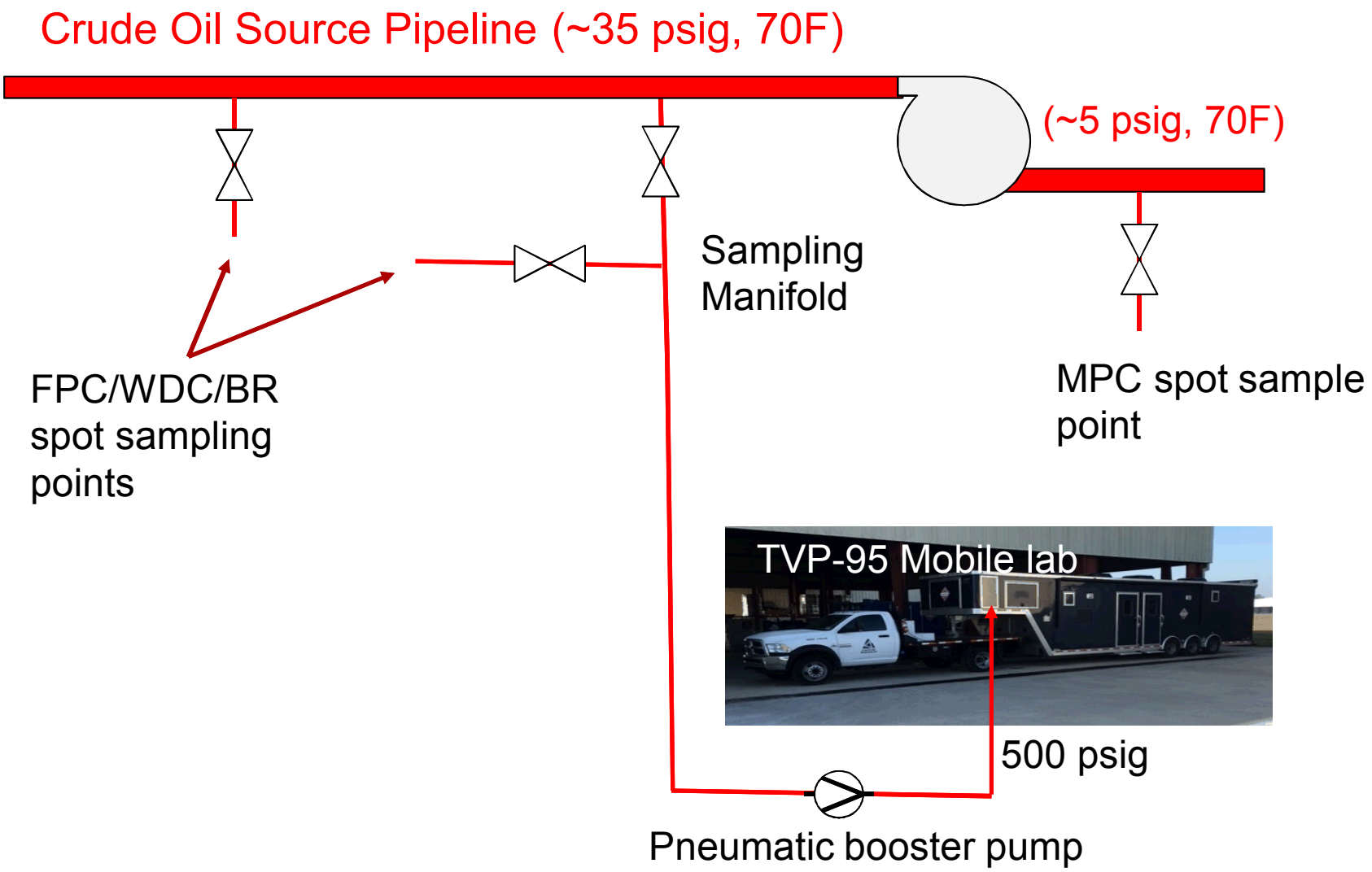




Sampling Overview

- ND Bakken Samples were collected in late August, 2016 from a truck terminal
  - Truck terminal was located upstream of a rail loading terminal
  - Pipeline oil temperature was reported at 70F (21C) during sample collection
- TX Eagle Ford Samples were collected in mid-October, 2016 from a truck/pipeline terminal
  - Terminal is upstream of a refinery
  - Pipeline oil temperature was reported from 94-98 F (34-37 C) during sample collection

Sampling Schematic (ND)



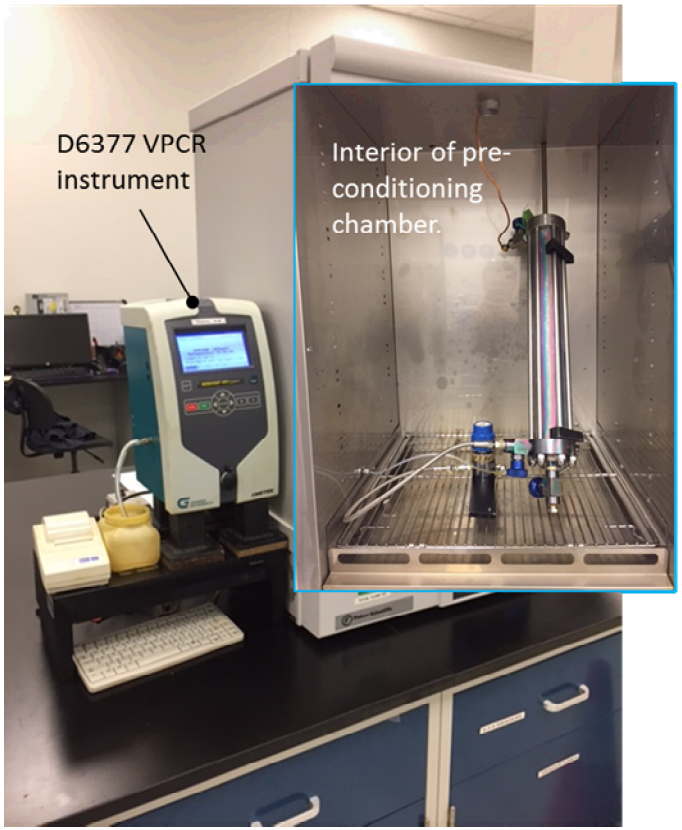
Analysis Methods Listing

- 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

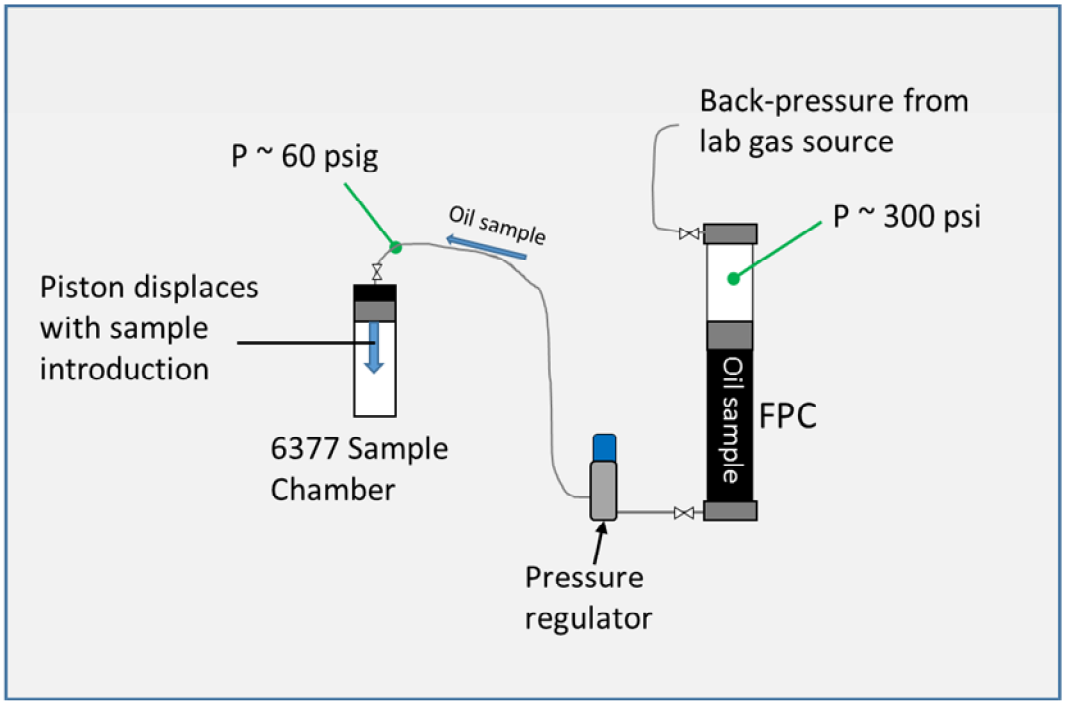
VPCR Sample Pre-Conditioning

- Sandia assumes pre-conditioning the sample to analysis temperature while retaining single-phase liquid during injection into 6377 test cell is critical to accurate VPCRx(T) measurements, especially at low V/L
- Each lab was required to pre-condition the sample

6377 Pre-Conditioning Example



Schematic of sample push from FPC into D6377 sample chamber



This example is from one lab. The other labs' pre-conditioning setups were conceptually similar, containing a heated, thermostat-controlled space immediately next to the 6377 instrument.

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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ND Bakken
Line T ~ 70F

Equivalent V/L calculated from measured GOR

GOR Separator Pressure

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

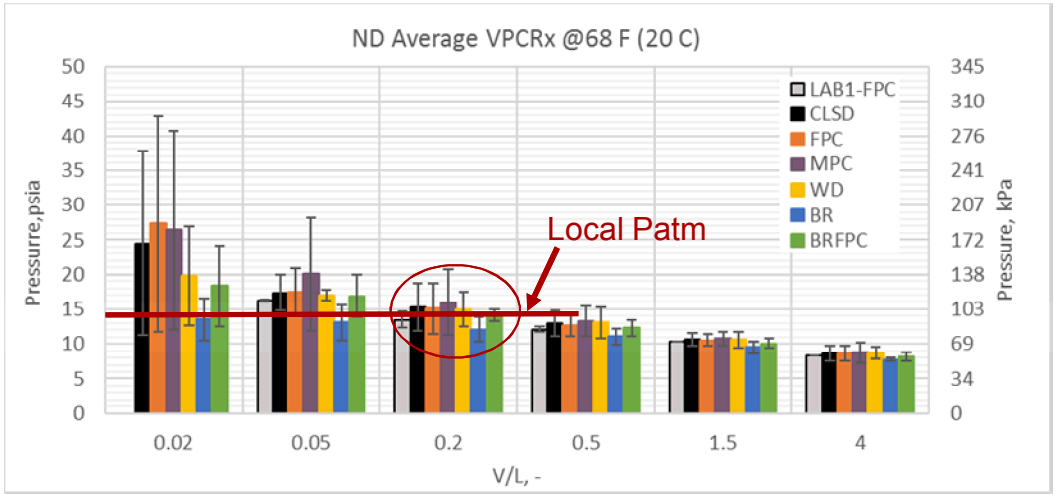
100°F

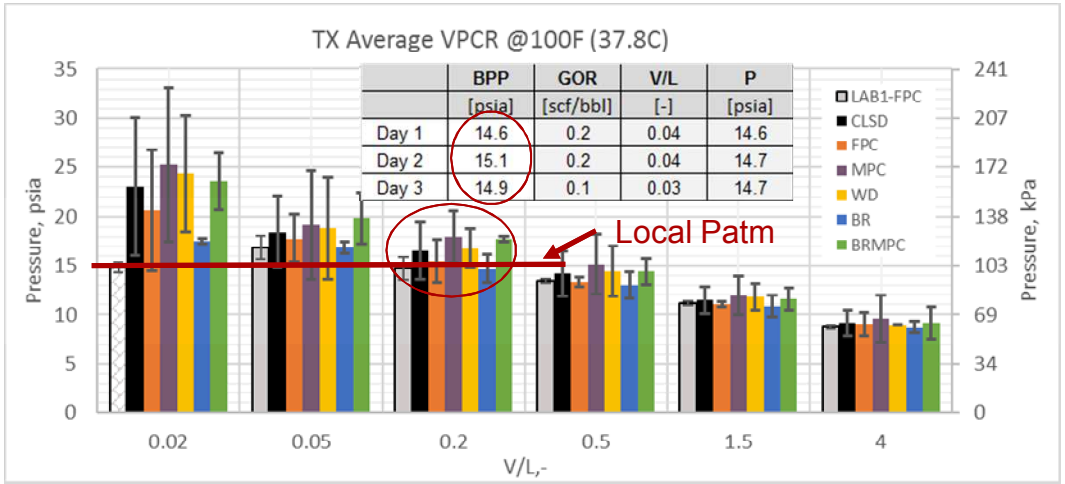
	BPP	GOR	V/L	P
	[psia]	[scf/bbl]	[-]	[psia]
Day 1	14.6	0.2	0.04	14.6
Day 2	15.1	0.2	0.04	14.7
Day 3	14.9	0.1	0.03	14.7

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.

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.

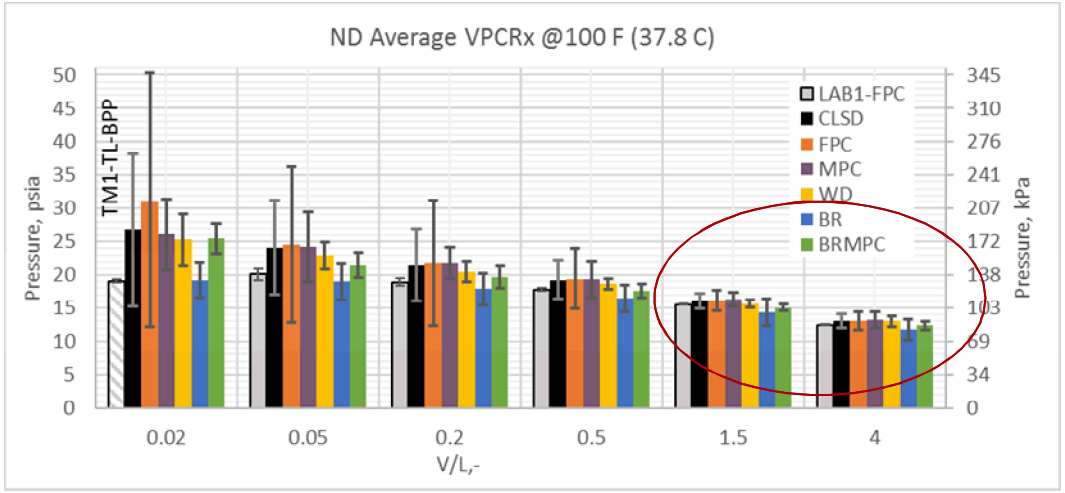


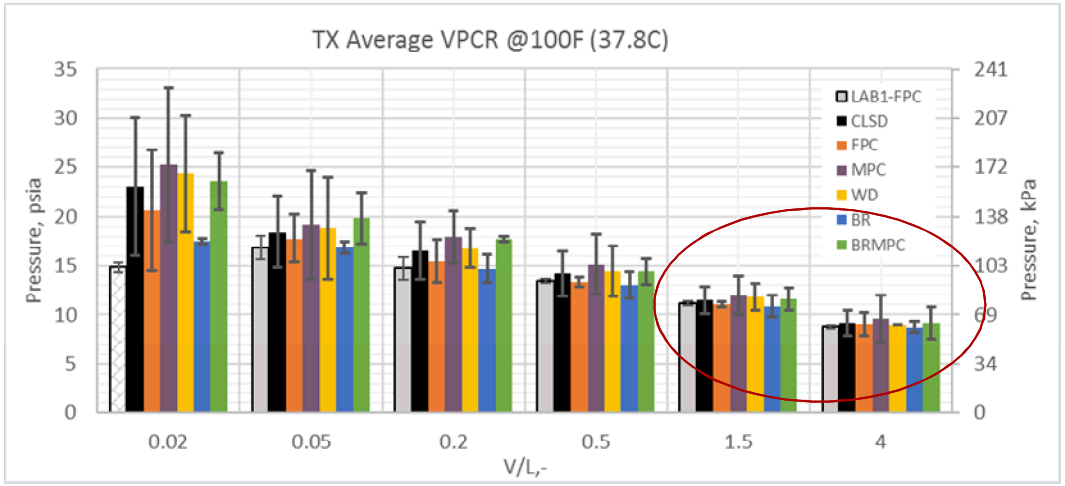


$VPCR_{0.2}$ compares well to BPP at same temperature

Sampling Methods for VPCR at High V/L

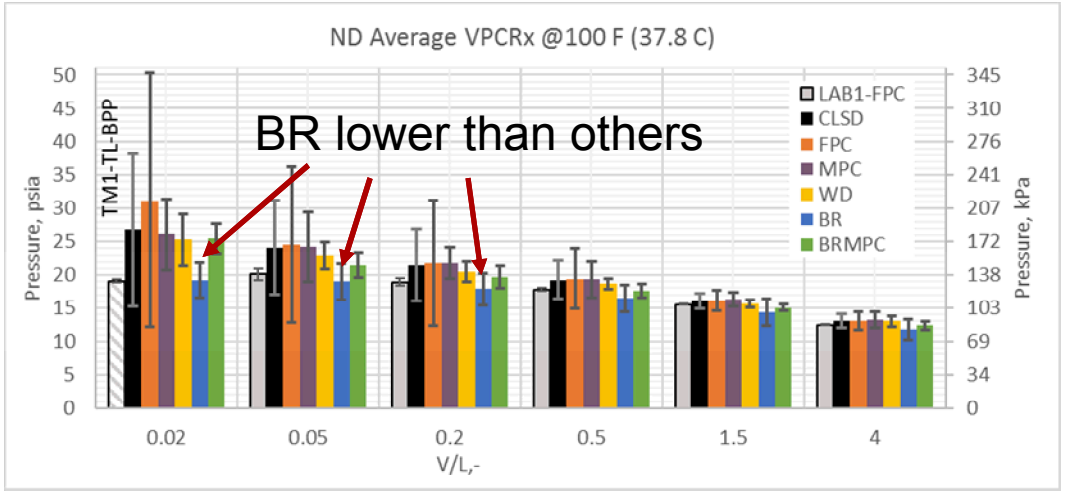
- All open and closed methods for sourcing VPCR give comparable results for high V/L (1.5, 4.0)

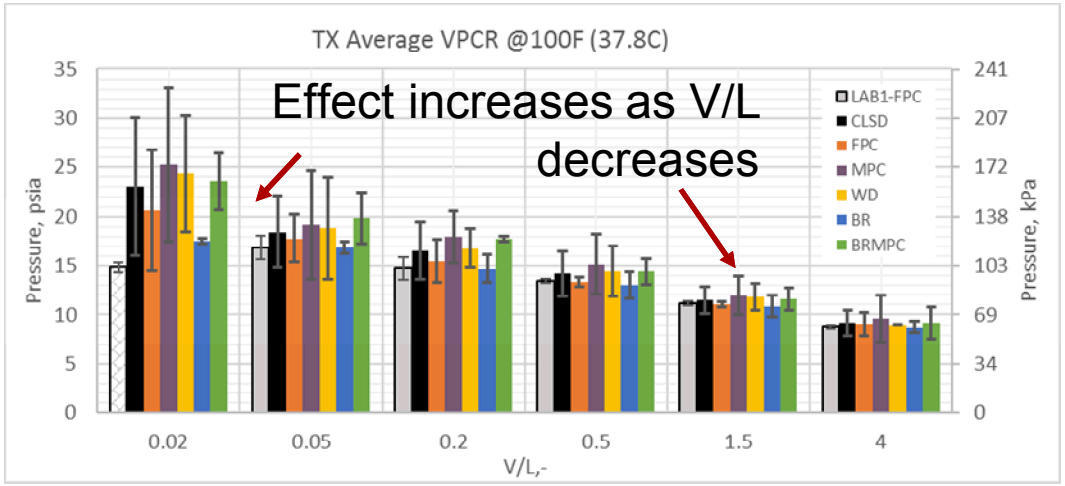




Methods not Equivalent for VPCR at Low V/L

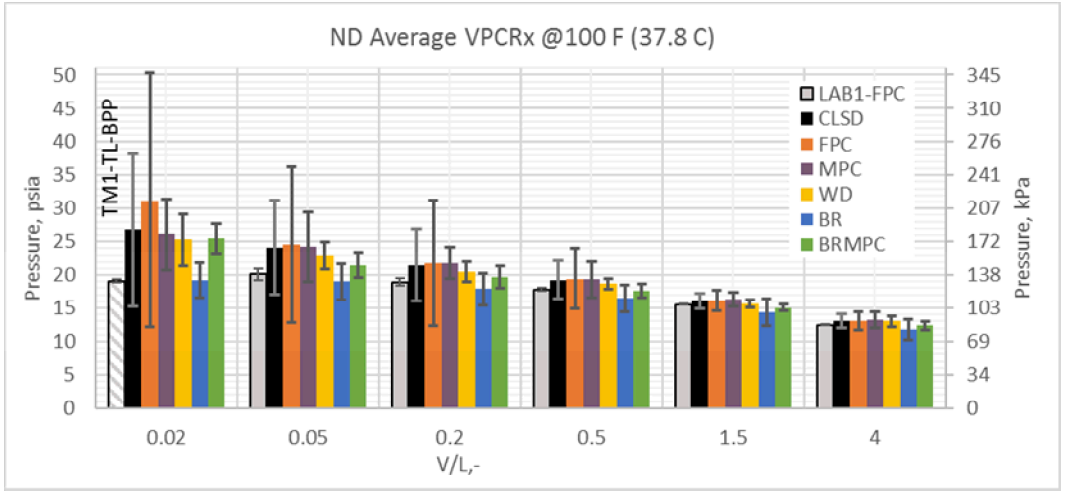
- Open and closed methods were not equivalent in their ability to deliver appropriate samples to the ASTM D6377 vapor pressure instrument for vapor-liquid ratio (V/L) < 1.
- Samples must be introduced into the VPCR instrument from pressurized containers (BRMPC) for testing at V/L < 1.

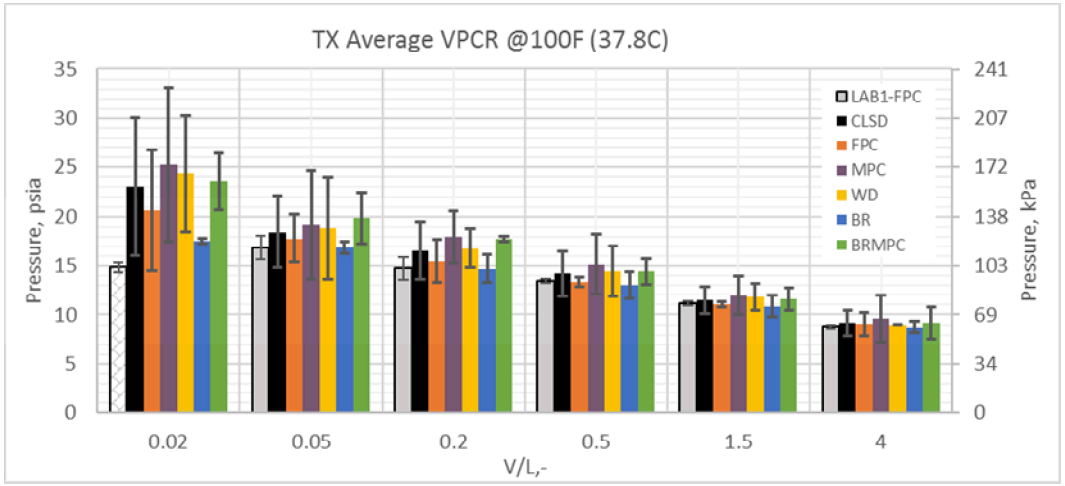




Uncertainty at Low V/L

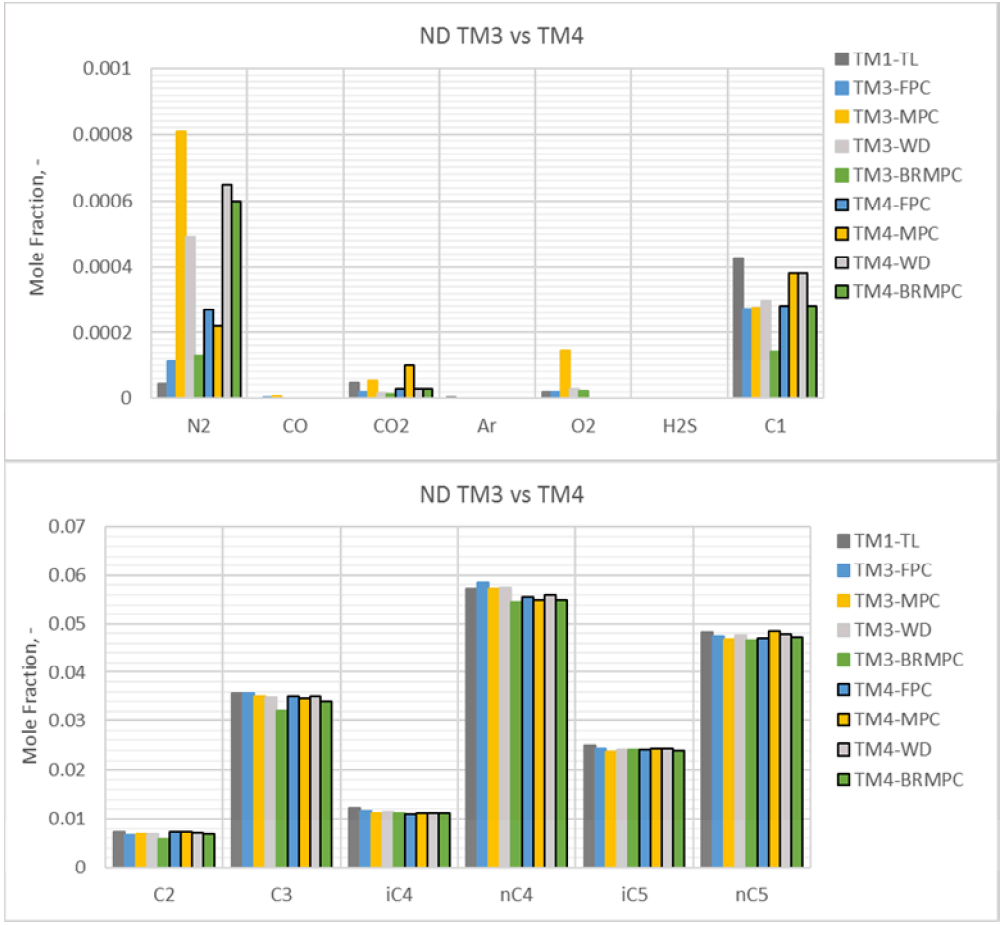
- All sampling methods generally showed high standard deviations and poor reproducibility at low V/L, especially 0.02 and 0.05





Compositional Analysis

- All spot sampling and pressurized analysis methods for hydrocarbon composition compare well to baseline tight-line system
- Exception is noted for inert gases, which may enter spot samples from handling procedures
- TM2 data unavailable at this time



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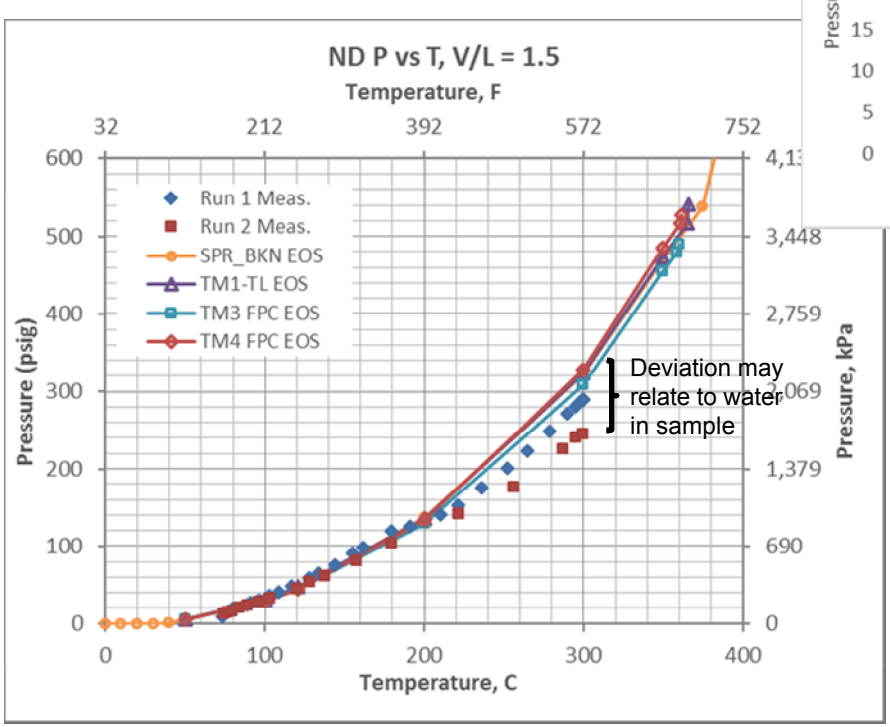
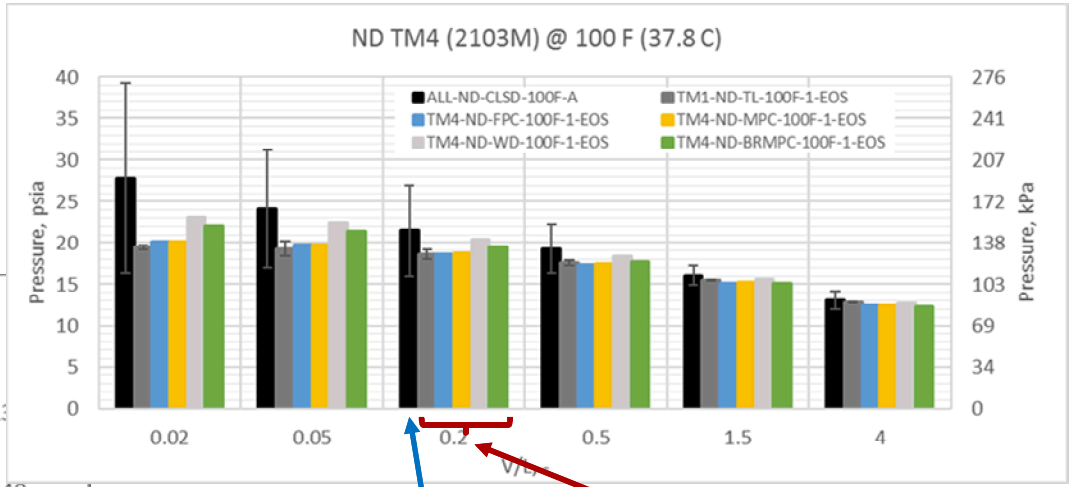
EOS Model Performance

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





EOS-Modeled VPCR

Measured VPCR

Slide 30

DBB16 Did Sandia measure water content for these samples to be able to confirm if deviation was in fact from water content?
Di Bacco, Barbara, 2/16/2018

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Slide 31

DBB17 See my comments on slides 7&8.
Di Bacco, Barbara, 2/16/2018

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- 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

Ongoing Work

- Winter Sampling
  - Oils obtained from the supply chain during cold seasonal conditions may retain more dissolved gas and show higher sensitivity to open vs. closed sampling than under warm conditions
  - Both ND and TX locations were sampled with open and closed methods during the winter
  - Results will be published as a revision to SAND 2017-12482
- 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
    - BR has many opportunities for light ends losses and uncontrolled temperature effects
    - Water displacement (WD) has potential contaminate oil sample with dissolved gas, especially if lab water was exposed to high pressure inert gas.
    - MPC/FPC – medium to back-pressure cylinder could contaminate sample
  - Testing standards
    - Atmospheric draw into 6377 is vulnerable to 2-phase formation as starting condition in test cell
    - ASTM may stipulate that all samples be pushed into 6377 under pressure (above BPP), bring cell to test temperature, then close cell to provide better assurance that sample is single-phase liquid when reading is V/L = 0

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 or true vapor pressure
- Determine where in the supply chain open versus closed sampling really does and does not matter for collecting VPCR and compositional samples

Project Publications

- 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.

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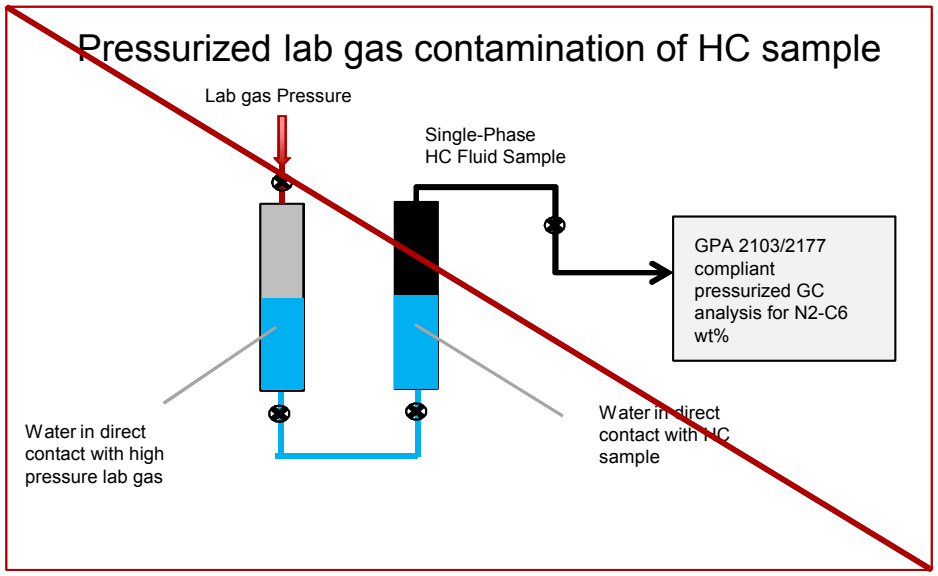
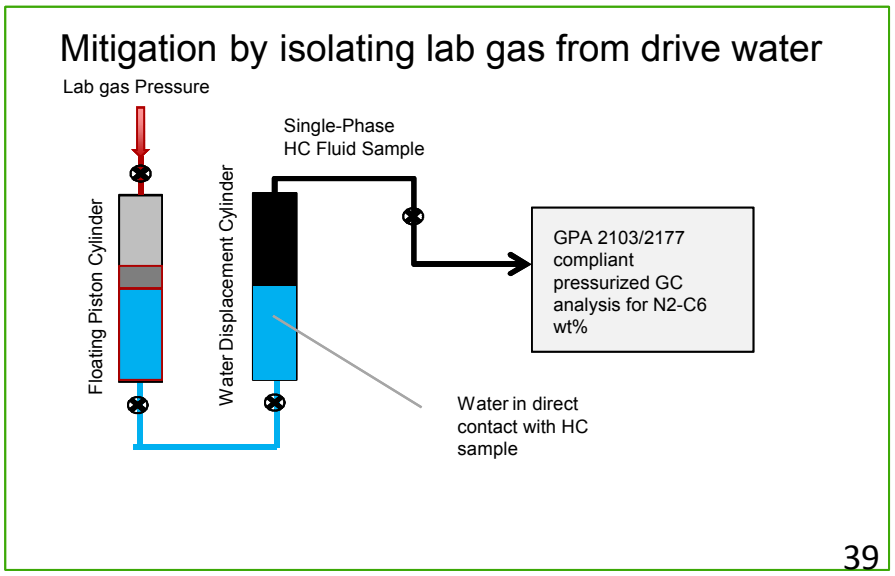
END OF PREPARED SLIDES

EXTRA SLIDES

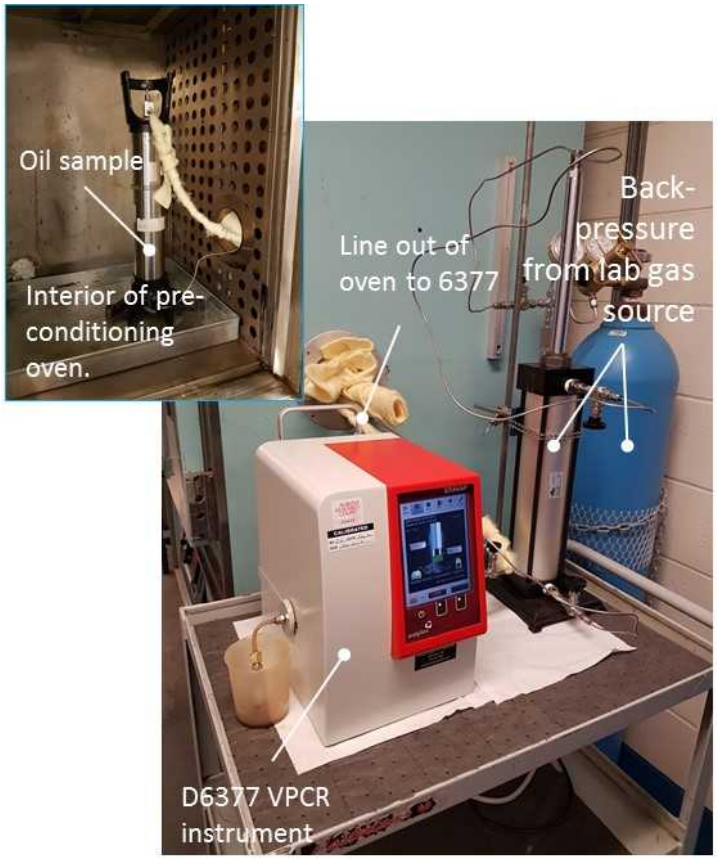
Water Displacement Issues

- Problem
  - Oil sample $VPCR_{0.05}$(68F) remaining in WDC increased 10 psi as a result of injecting sample into pressurized GC
  - Drive water in lab was previously stored under 1100 psi helium pressure. Hypothesis is that gas dissolved in drive water was transferred to oil sample.
- Mitigations:
  - When using water as a drive fluid, it must not have a history of storage under high pressure gas
  - Lab can utilize a FPC with clean water on the side hooked to hydrocarbon sample and house gas on the other and still meet pressurized injection requirement without contaminating HC sample

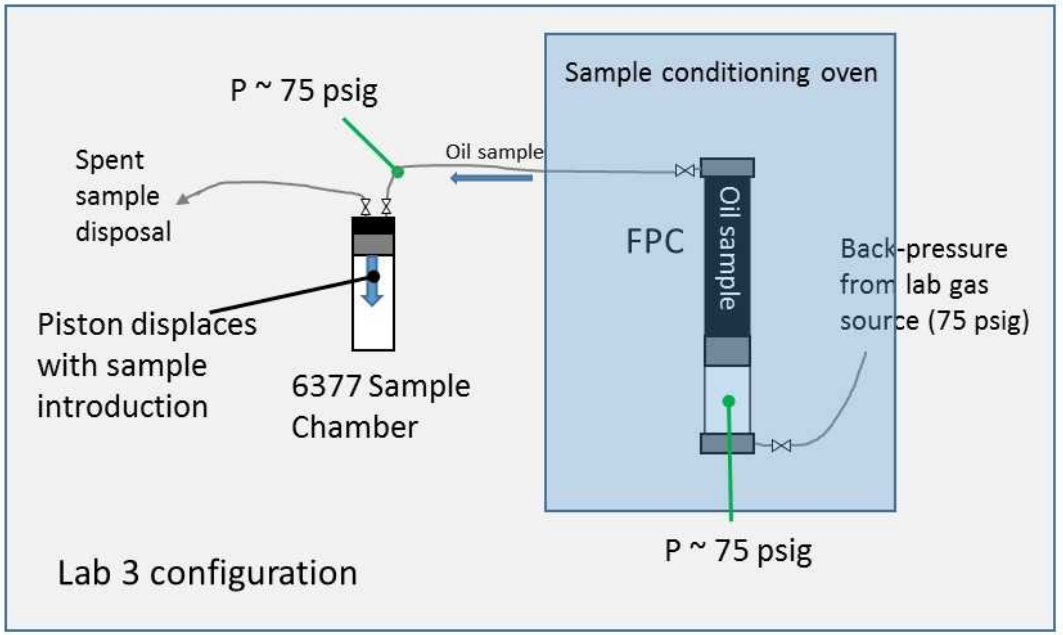




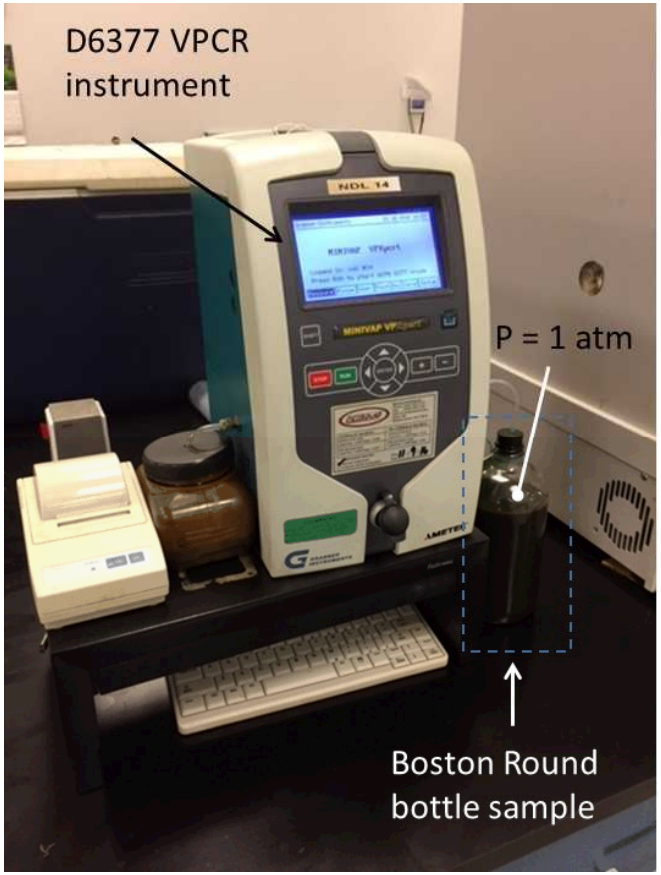
6377 Pre-Conditioning Example



Schematic of sample push from FPC into D6377 sample chamber



BR Ambient Fill Configuration



Schematic of vacuum draw from BR into D6377 sample chamber