SAND2018-9366PE

Crude Oil Characterization Research Study

Task 2: Sampling and Analysis Methods Evaluation

Presentation to

American Fuel & Petrochemical Manufacturers

Transportation & Infrastructure Committee Meeting

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SAND 2018-NNNN-PE

Participants

- Sponsoring Agencies
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  - US Department of Transportation
  - Transport Canada
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  - Chad Wocken, University of North Dakota EERC
  - Ted Aulich, University of North Dakota EERC

Project Publications

Today's presentation is a high-level summary of SAND 2018-5909 and SAND2017-12482

- Lord, D., R. Allen, D. Rudeen, C. Wocken and T. Aulich (2018). "DOE/DOT Crude Oil Characterization Research Study, Task 2 Test Report on Evaluating Crude Oil Sampling and Analysis methods, Revision 1 - Winter Sampling." *Unclassified Unlimited Release* ***SAND2018-5909***. Sandia National Laboratories, Albuquerque, NM 87185.
- 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

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

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

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. Single winter samples were tested from the same sources with no significant seasonal effect on oil properties or open vs closed sampling performance.
- 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)

- Four pressurized compositional methods based on spot sample analysis yielded results that compared well with the tight-line TVP-95 system for hydrocarbon compositions.
  - TM2: GPA 2177 + ASTM D7900 + ASTM D7169 data merge (all GC methods)
  - TM3: ASTM D8003 + GOR + ASTM D7169 data merge
  - TM4: GPA 2103M + physical shrink + ASTM 2887 data merge
  - TM4a: GPA 2103M + physical shrink + $C30^{+}$ GC data merge
  - 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.

Executive Summary (3)

- 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

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Sampling & Analytical

TASK 2: METHODS

Overall Approach

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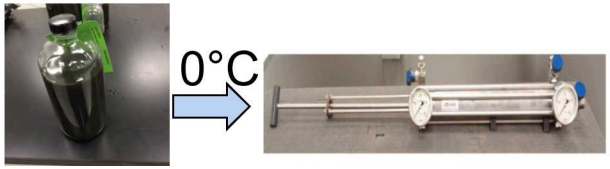
- Select two crude oil sampling sites within the US domestic supply chain to obtain a continuous, reasonably homogeneous sample for up to three consecutive sampling days
  - North Dakota Bakken terminal
  - Texas Eagle Ford terminal
- Capture samples by an assortment of open and closed industry standard 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

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 data merge (all GC methods)
  - TM3: GOR flash + ASTM D8003 + ASTM D7169 with numerical merge
  - TM4: GPA 2103-M + physical shrink + ASTM D2887 C7+ analysis with numerical merge
  - TM4a: GPA 2103-M + physical shrink + $C30^{+}$ GC data merge
- Selected physical properties
  - Total sulfur mass %, relative density, average molecular weight, kinematic viscosity, flashpoint, initial boiling point

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TASK 2: RESULTS

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

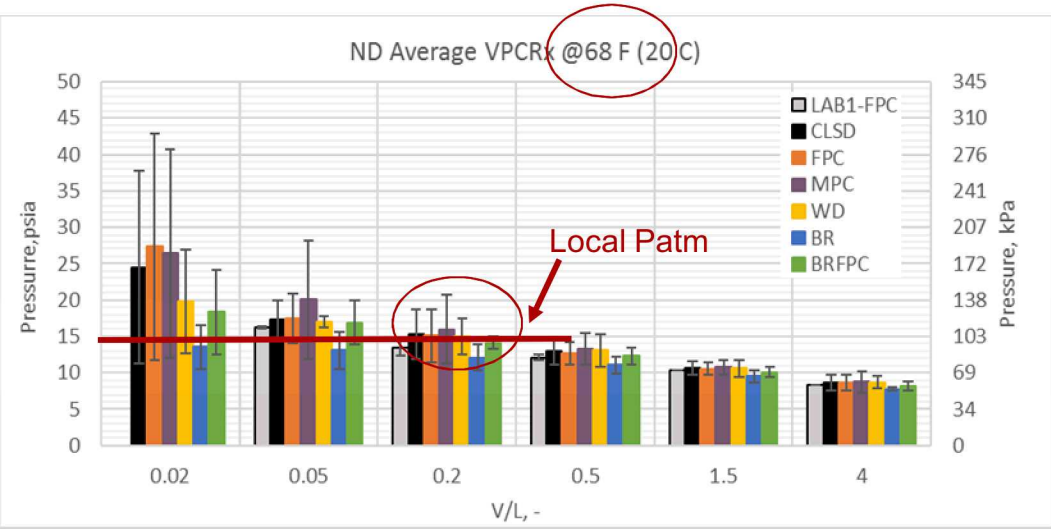
	BPP	GOR	V/L	P
	[psia]	[scf/bbl]	[-]	[psia]
Day 1	14.6	0.2	0.04	14.6
Day 2	15.1	0.2	0.04	14.7
Day 3	14.9	0.1	0.03	14.7

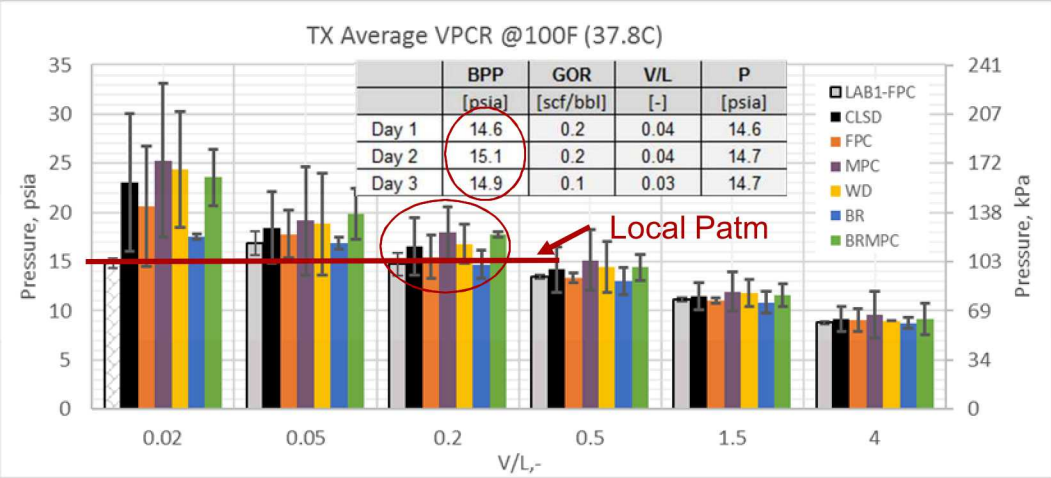
Both oil samples appeared to have been equilibrated with ambient conditions in atmospheric tanks elsewhere in the supply chain before they were sampled. As such, they were not visibly boiling at the conditions of sample capture.

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

Near line/sampling temperature

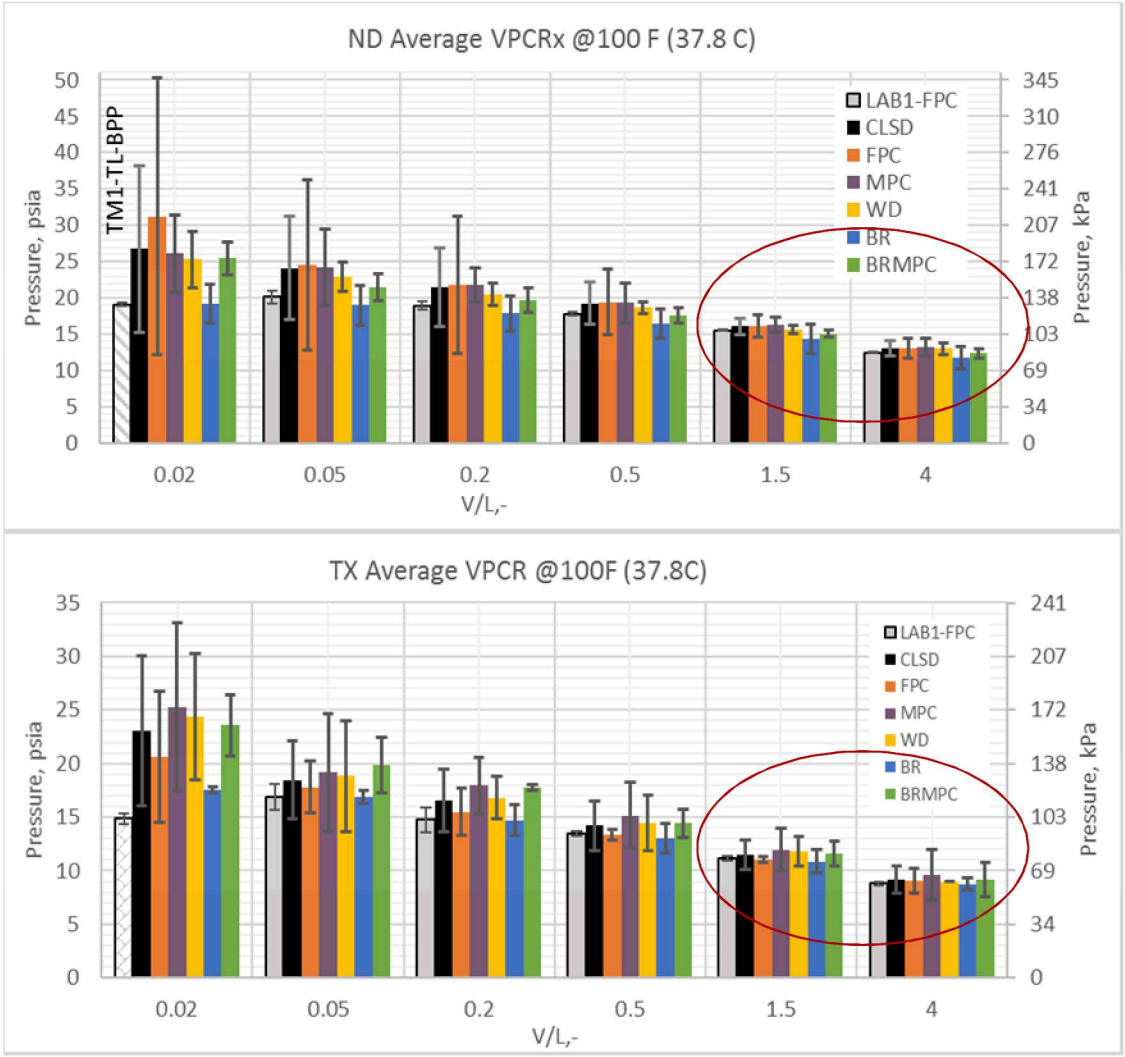




$VPCR_{0.2}$ appears to correlate well with BPP at a given temperature

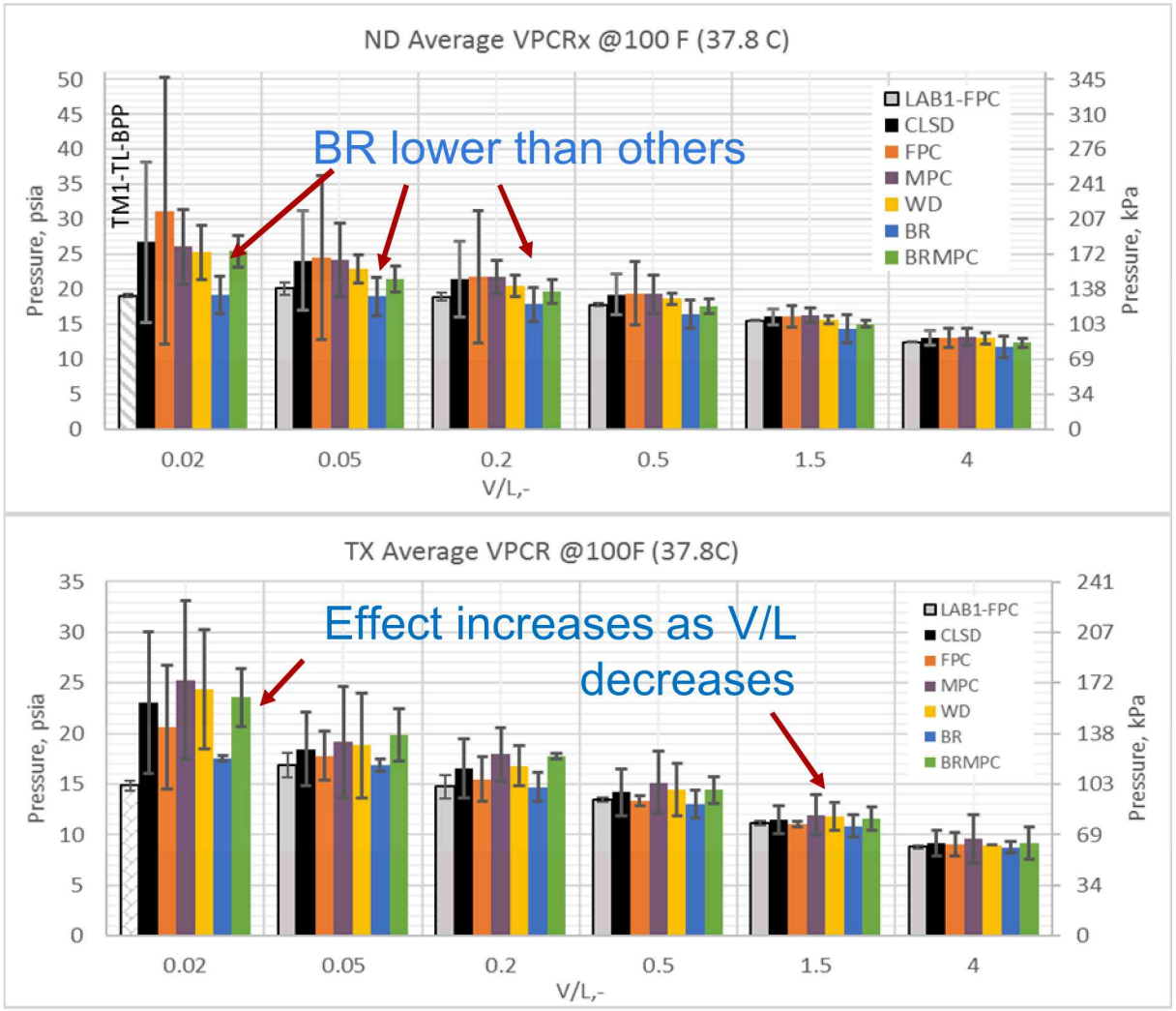
Sampling Methods Equivalent for VPCR at High V/L

- 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



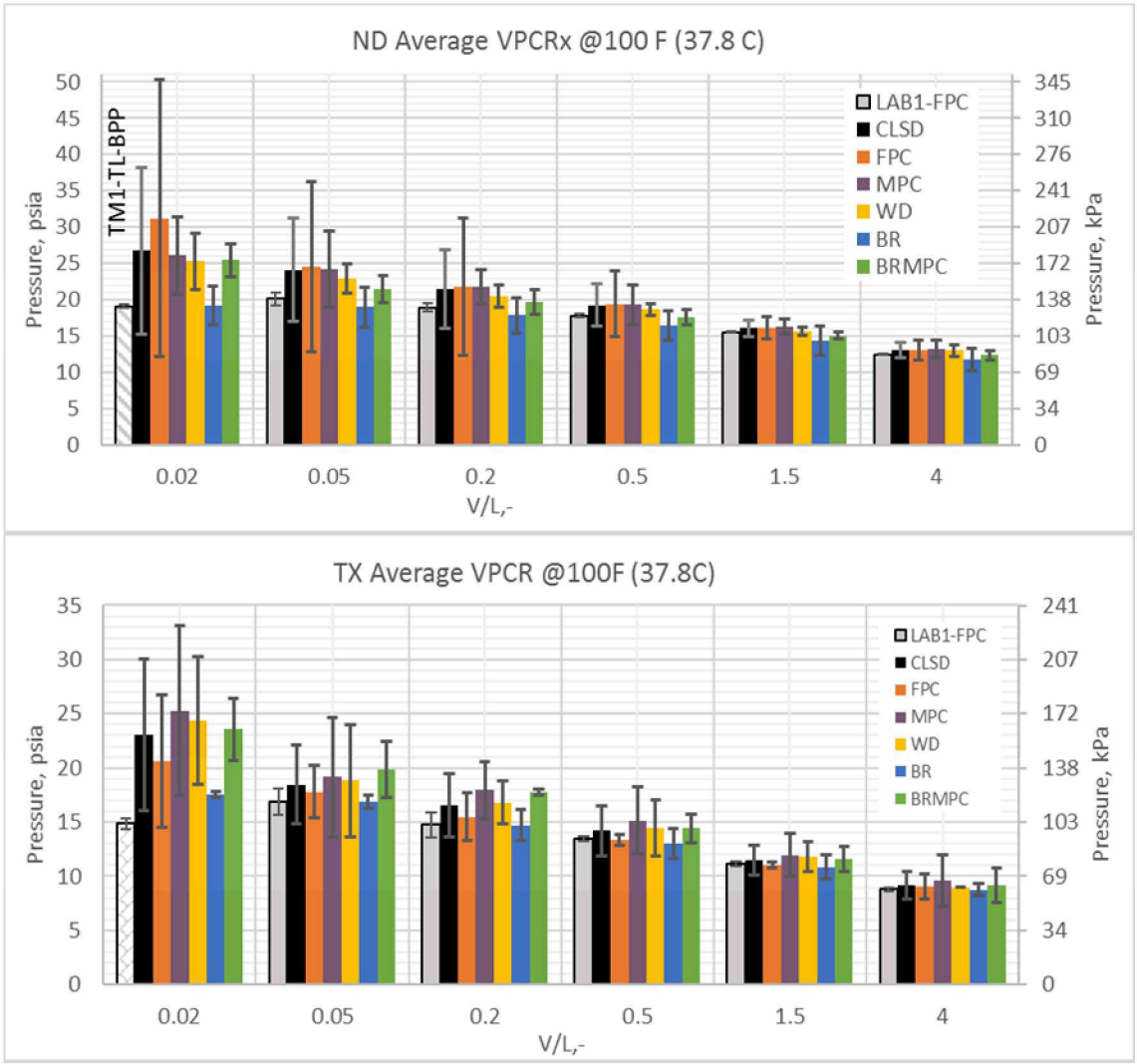
Methods not Equivalent for VPCR at Low V/L

- 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



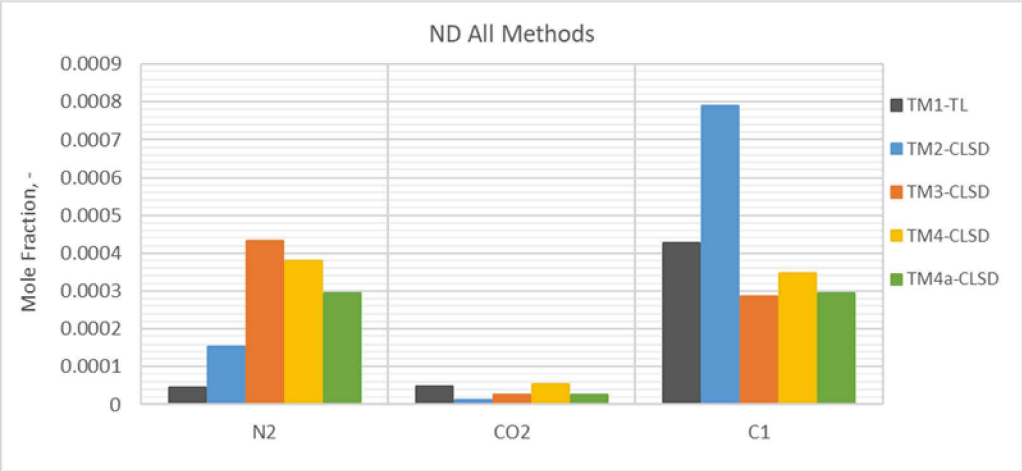
VPCR Uncertainty at Low V/L

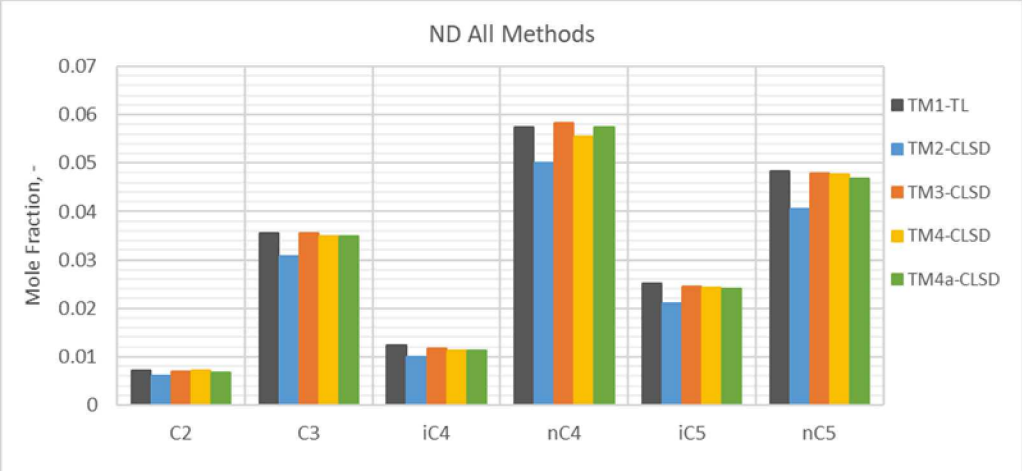
- All sampling methods generally showed high standard deviations and poor reproducibility at low V/L, especially 0.02 and 0.05
- Implication: Current capabilities demonstrated here for measuring VPCR of crude at low V/L (0.02, 0.05) are not sufficient to produce reliable property measurements



Compositional Analysis

- Most spot sampling and pressurized analysis methods for hydrocarbon composition compare well to baseline tight-line system
- TM2 performance is lower than others
- Inert gases vary across all methods, 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.





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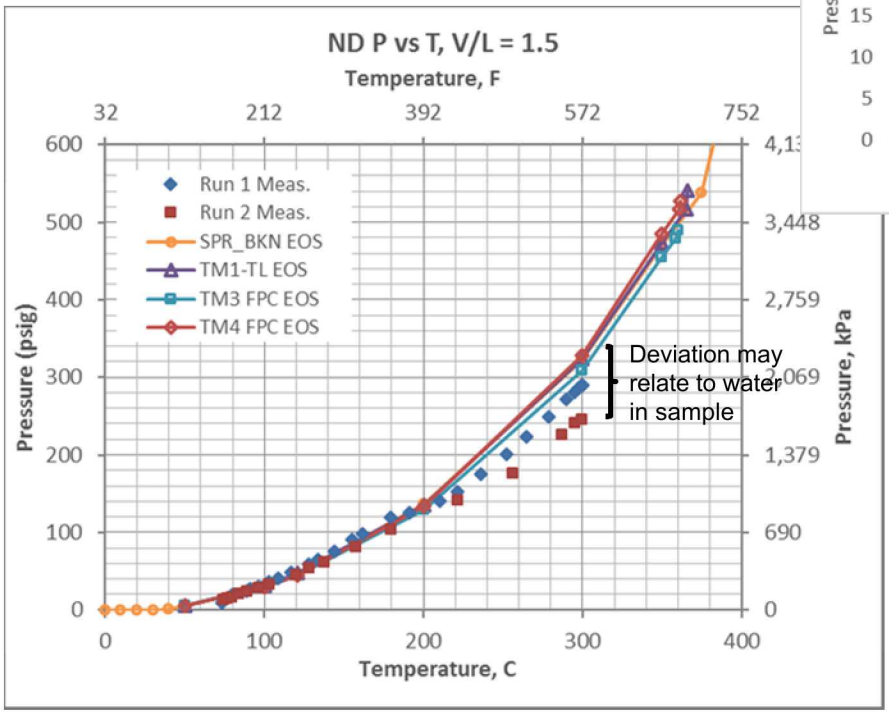
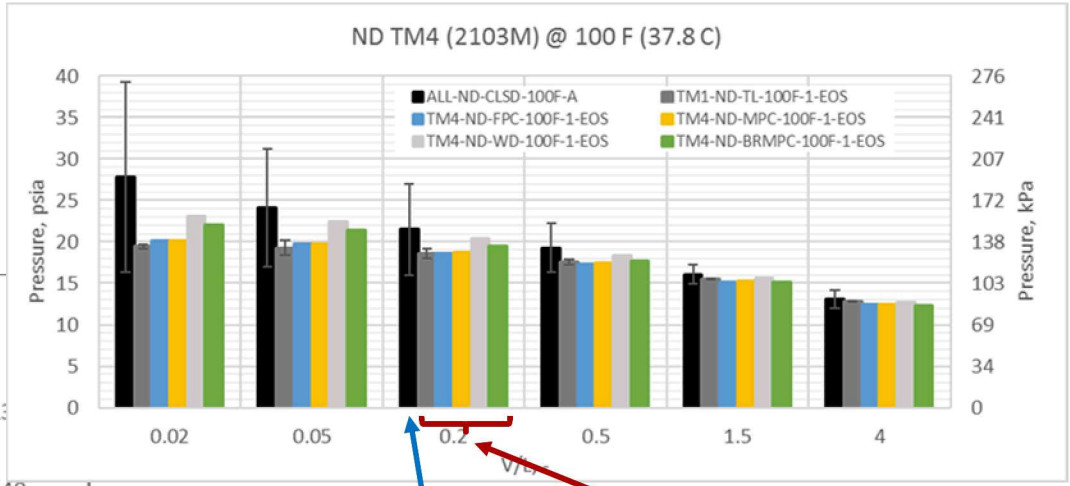
EOS Model Performance

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





EOS-Modeled VPCR

Measured VPCR

Ongoing Work

- Task 3: Combustion Testing at Sandia (in process)
  - Objective: Determine whether selected oils (i.e., Bakken, stabilized SPR, TX Shale oil) with differing physical and chemical properties (VPCR, pressurized composition) exhibit significant differences in combustion properties that control hazards from large-scale pool fires and fireballs
- Task 4: Crude Characterization: Tight vs. Conventional
  - Objective: Collect comparative data on physical and chemical properties of oils sourced from several producing regions in US and Canada, to include oils from "tight" and "conventional" reservoirs
  - Evaluate a selected set of properties (VPCR, pressurized composition, API gravity, flashpoint, possibly others…)
  - Provide context for the oils burned at Sandia
    - Demonstrate where the Sandia burn test samples sit in property space relative to oils within the US and Canada supply chains

Standards Work

- Peer review panel reached consensus 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

Possible Areas for Improvement

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- 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

Areas where AFPM could help

- Looking ahead to Task 4
  - Facilitate access to oil samples in the US and Canada
    - Permission to acquire and test samples from selected points in a supply chain according to a given test protocol
      - Sandia would contract 3rd party analytical lab to acquire and analyze samples
  - Facilitate access to relevant properties data in the US and Canada
    - Are there existing data we could access?
      - Example: Terminal or pipeline data with periodic VPCR, temperature, API gravity, …?
- Any use of industry partner samples/data would be controlled under site access and/or data sharing agreements
  - Provides terms and conditions for acquiring, analyzing, and publishing data

Links to Reports

- Record copies are maintained on the US DOE Office of Science and Technical Information website
  - www.osti.gov
  - Enter “crude oil” into search tool

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END OF PREPARED SLIDES