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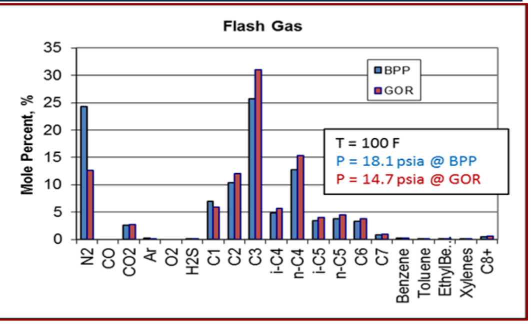

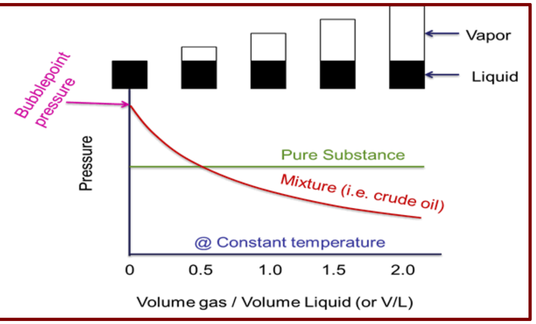

DOE Tight Oil Flammability & Transportation Spill Safety Project Update

Crude Oil Quality Association Technical Meeting

Marriott West Loop

Houston, TX

Feb 19, 2015

by

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PRELIMINARY DATA

Preliminary Data

- Information given in this presentation is based on preliminary analysis prepared for the DOE Tight Oils Study Committee project review, November 19-20, 2014, Albuquerque, NM
- Abridged versions were subsequently presented at the American Petroleum Institute Crude Oil Physical Properties ad-hoc Technical Group meeting, Houston, Nov 21, 2014 and Crude Oil Quality Association meeting, Houston, Feb 19, 2015
- A more thorough analysis of these data and modeling results is forthcoming, and will be documented in written reports to the DOE sponsor in CY2015

Outline

- Project Management and Technical Team
- Project Workflow and Problem Statement
- Executive Summary
- Tight oils Operating Environment
- Crude Oil Properties
- Combustion Events

Project management

- DOE funding agency point-of-contact
  - Richard Elliott, PE, CEM
    - U.S. Department of Energy, Office of Fossil Energy, Office of Oil & Natural Gas
    - *rick.elliott@hq.doe.gov*
    - *202-586-0859*
- Sandia project manager
  - David Borns, Ph.D.
    - Sandia National Laboratories, Geotechnology & Engineering Department
    - *djborns@sandia.gov*
    - *505-844-7333*

Technical team

- David Lord (Ph.D., Env E.), Principal member of technical staff
  - Geotechnology & Engineering Department, Sandia National Laboratories
- Anay Luketa (Ph.D., Mech E.), Principal member of technical staff
  - Fire Science & Technology Department, Sandia National Laboratories
- Chad Wocken (B.S., Chem E.), Senior research manager
  - University of North Dakota Energy & Environmental Research Center
- Steven Schlasner (Ph.D., Chem E., MBA), Research engineer, PE (OH, OK)
  - University of North Dakota Energy & Environmental Research Center
- Ray Allen (B.S. Chem E.), PE (TX)
  - President of Allen Energy Services engineering consulting firm
- David Rudeen (B.S. Applied Math), Code developer and data analyst
  - GRAM, Inc. technical services company

Project Workflow

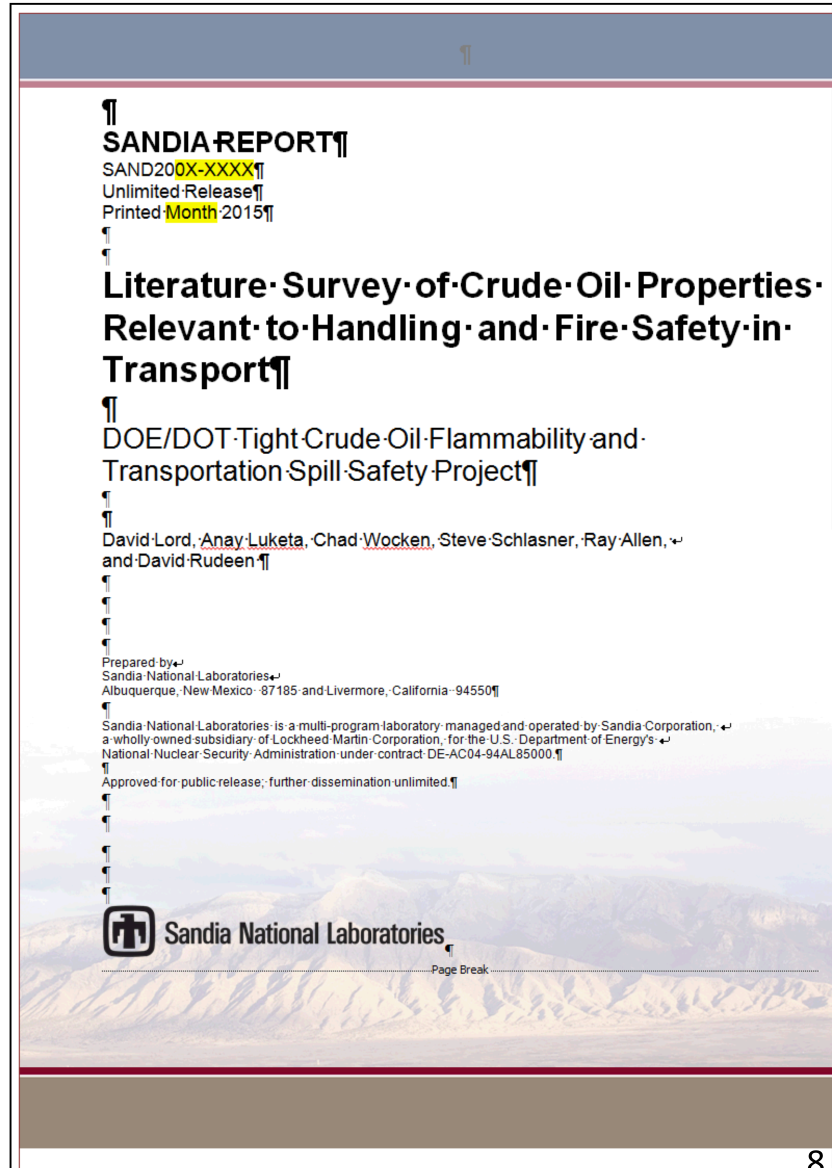
- Problem definition phase (current SNL/EERC work scope)
  - Define crude oil properties that have a bearing on handling and transport safety with attention to flammability risks in spill scenarios
- Experimental phase (possible SNL/EERC future work scope)
  - Measure parameter ranges for relevant crude properties in transport system, compare with literature and other parallel efforts (PHMSA, API)
  - Explore if/how these properties affect the degree of hazard realized in scenarios where fire may be involved
- Application phase (all stakeholders)
  - Utilize knowledge gained during above phases to inform decisions on industry best practices, standards, regulatory requirements to assure safe, economical transport of crude to market

Deliverables

- Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport
  - Draft version is in review at DOE sponsor
  - Intended to be available for public release ~March 2015
- Sampling and Analysis Plan
  - Written to identify and close important knowledge gaps
  - Initial version currently being drafted, preliminary stages
  - DOE will administer a formal peer review process to include external stakeholders
  - Timeline is uncertain right now due to iterative process of peer review, but expecting public release in CY 2015

Focus for today's presentation

- Highlights of literature survey
  - Tight oils operating environment
  - Crude oil properties, data comparisons
  - Potential combustion events relevant to rail transport



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Printed Month 2015

Literature Survey of Crude Oil Properties Relevant to Handling and Fire Safety in Transport

DOE/DOT Tight Crude Oil Flammability and Transportation Spill Safety Project

David Lord, Anay Luketa, Chad Wocken, Steve Schlasner, Ray Allen, and David Rudeen

Prepared by
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Albuquerque, New Mexico 87185 and Livermore, California 94550

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Page Break

Executive Summary

- Objective is to describe physical properties of crude oil relevant to flammability and transport safety
- If and how these properties will relate to fire and explosion hazard is the key research question we need to address
- The vapors (not liquid) from a flammable liquid actually burn, so understanding what leads to vapor formation during handling, transport and spill scenarios is key to understanding the flammability risks
- General lack of uniformity in methods and QA/QC across industry makes comparisons of crude oil vapor pressure difficult, leaving room for improvement
- Bakken crude, a representative tight oil, exhibits statistically higher vapor pressure and gas oil ratio that typical oils stored at SPR due to slightly higher mole fractions of light hydrocarbons
- Several combustion events (pool fire, BLEVE, fireball, explosion, flash fire, flare) can occur from an accidental release of a liquid hydrocarbon
- No single parameter defines the degree of flammability of a fuel; rather, several parameters are relevant

TIGHT OIL OPERATING ENVIRONMENT

Coverage in Written Report

Tight Oils

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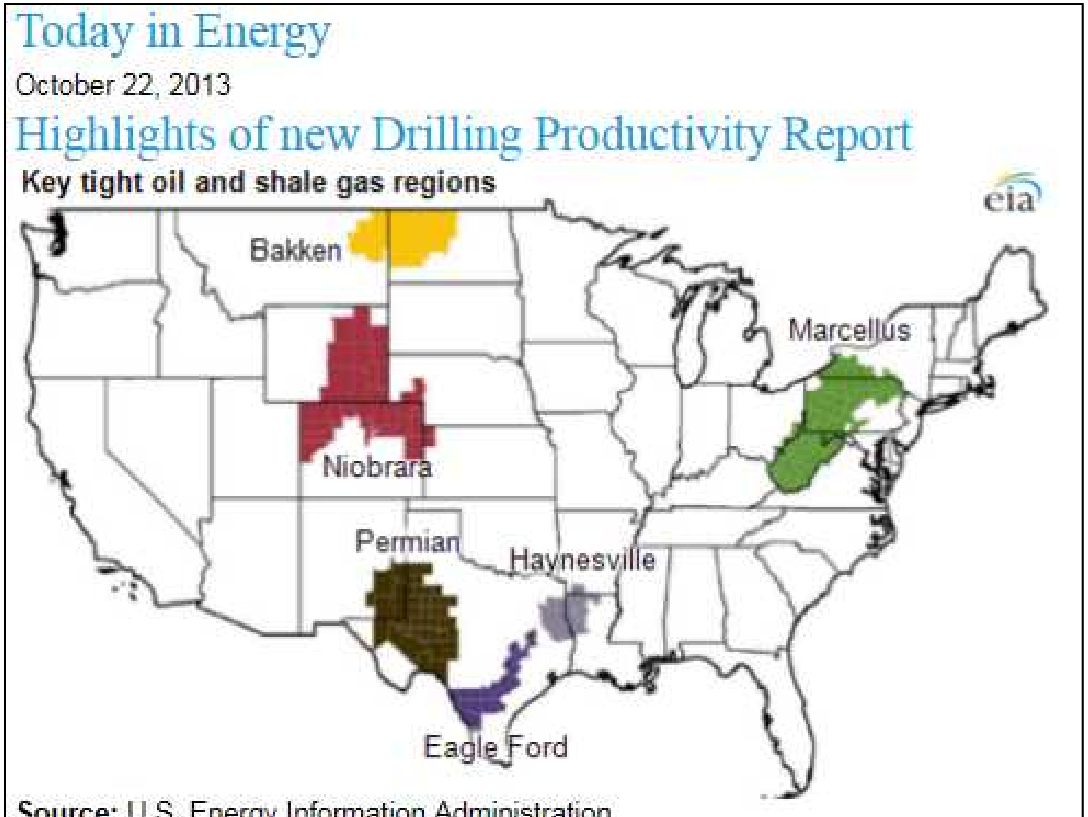
- Oil produced from low-permeability reservoir rock
- Typically stimulated with hydraulic fracturing to produce at economic rates



Crude	API gravity	Sulfur (wt%)
Bakken	40-43	0.1
WTI	37-42	0.42
LLS	36-40	0.39
Eagle Ford	47.7	0.1
Eagle Ford Light	58.8	0.04

Source: Auers, J. R., R. M. Couture and D. L. Sutton (2014). "The North Dakota Petroleum Council Study on Bakken Crude Properties." Bakken Crude Characterization Task Force. North Dakota Petroleum Council, Bismarck, ND 58501. 4-Aug-2014.

Relevance of API Gravity & Sulfur

- Higher API gravity "lighter" oils tend to exhibit
  - Lower viscosity, flow better for production and transport
  - Lower average molecular weight
  - More "light ends" hydrocarbons
  - Greater volatility
  - …than their medium and heavy counterparts
- Total sulfur content (mass%) determines "sweet" vs. "sour" designation
  - Sulfur is an impurity and must be separated from crude during the refining process

CRUDE OIL PROPERTIES

Properties of interest

- Useful to predicting combustion-related events, fire sciences perspective
  - Heat of combustion
  - Flammability limits
  - Fuel composition in liquid phase
  - Fuel composition in evaporating phase
  - Density
  - Molecular weight
  - Boiling point temperatures

Already have these for many oils in U.S. Strategic Petroleum Reserve (SPR)

- True vapor pressures
- Flash gas compositions
- Whole oil compositions
- Avg. MW
- Liquid density

Importance of Phase Behavior

- A primary motivation for this study is understanding the fire and explosion hazards associated with accidental release of crude oil in the transport environment
  - It is the vapor emissions from a “flammable liquid” that actually burn
  - Conditioned/stabilized crude is typically tested, transported, and sold in the liquid phase and associated vapor losses during handling and transport, if any, are not well-characterized
  - Vapor losses may not cause measurable financial impact from a sales perspective but could lead to elevated risk from a hazards perspective
- It is therefore prudent to examine the phase behavior of crude, specifically the potential for formation of vapor phase emissions, in order to understand the conditions that contribute to fire and explosion hazards around spills

Vapor Pressure of Crude Oil

- Terms vapor pressure, Reid, and true vapor pressure are often used in literature with reference to crude oils, sometimes interchangeably, leading to considerable confusion
- Crude oil true vapor pressure
  - Total pressure exerted by a gas phase in equilibrium with a liquid at a specified temperature and V/L
  - Bubblepoint pressure is a special case at V/L = 0
  - Maritime/tanker references to true vapor pressure as P @ V/L = 0
- Reid Vapor Pressure (ASTM D323)
  - Routinely measured oil quality parameter
  - Introduces air saturation and cooling/heating steps with 4:1 V/L, so not directly applicable as a material property of the crude
- ASTM 6377: VPCR(x)
  - Applied to crude oils where x (= V/L) can vary from 0.02 to 4
  - Best coupled with closed sampling to minimize light ends loss during sample collection

Pure Substance vs. Mixture

Contrasting behavior in vapor-liquid region of phase diagram

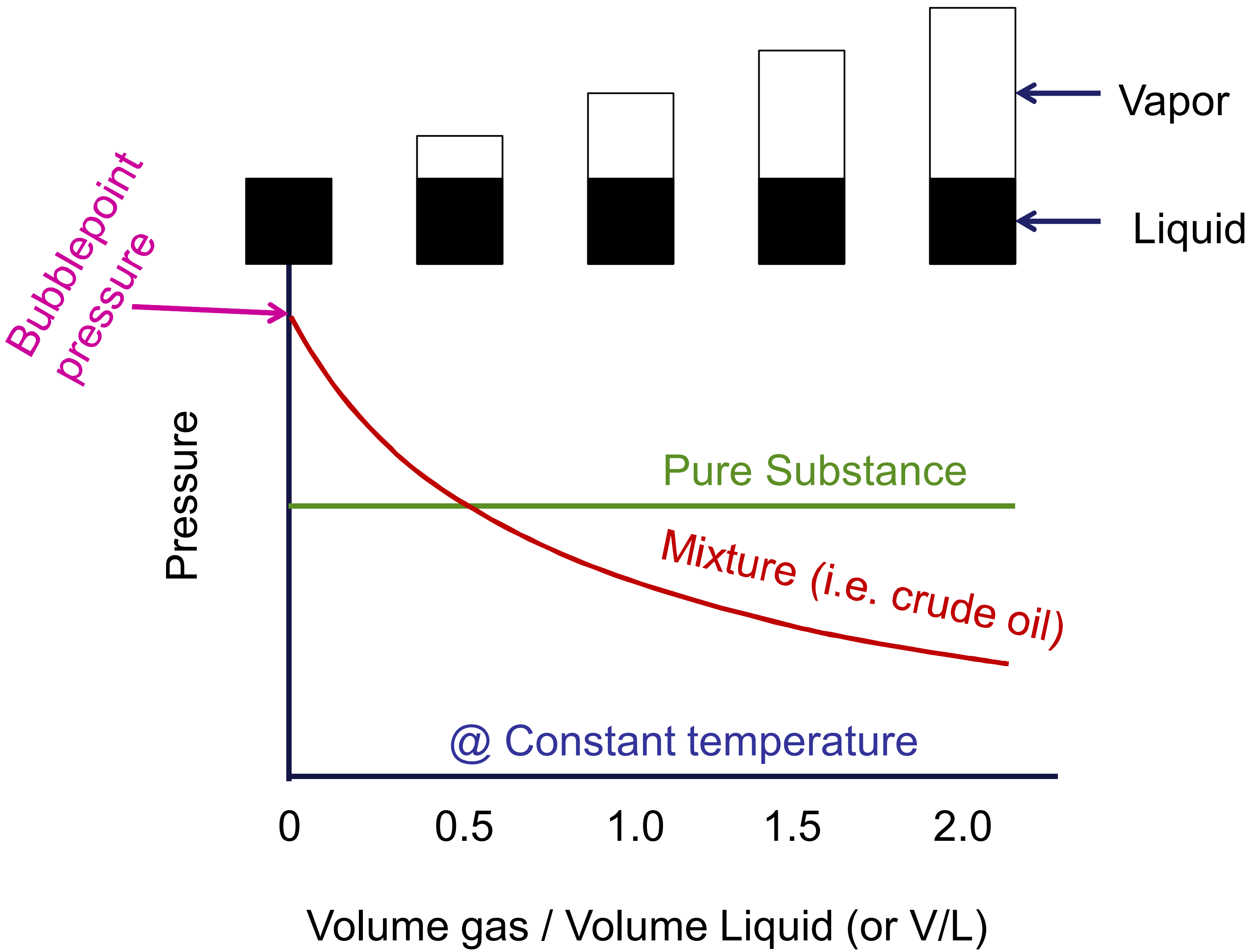
Pure Substance (typical light alkane)

- Single boiling point temperature at a given pressure
- Vapor pressure is constant with V/L at a given temperature
- Step change in density as temperature crosses boiling point at constant pressure

Mixture (crude oil)

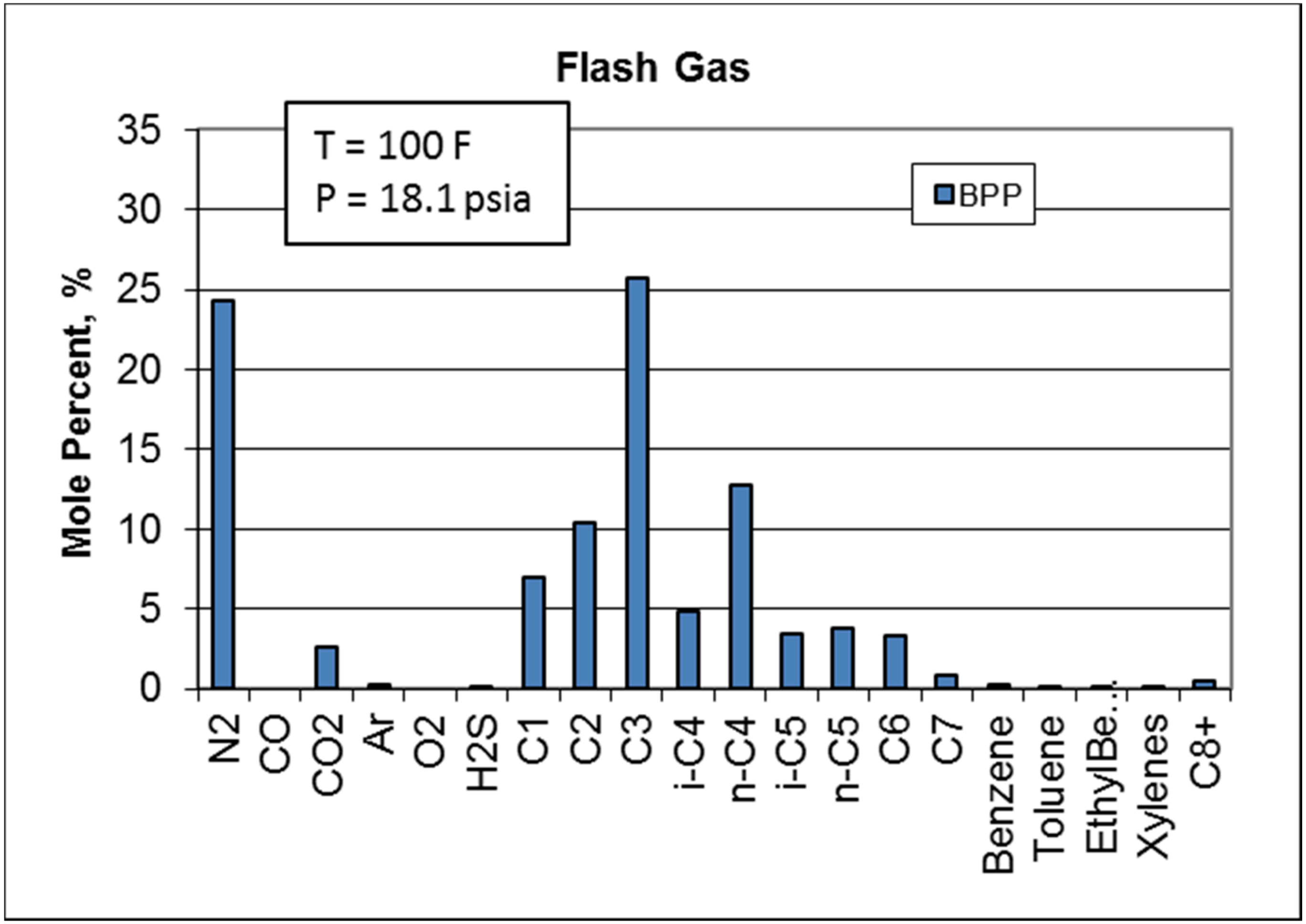
- Series of component boiling temperatures at a given pressure
- Vapor pressure is variable with V/L at a given temperature
- Gradual decrease in mixture density as temperature increases through boiling range at constant pressure

Pure Substance vs. Mixture



Flash gas composition

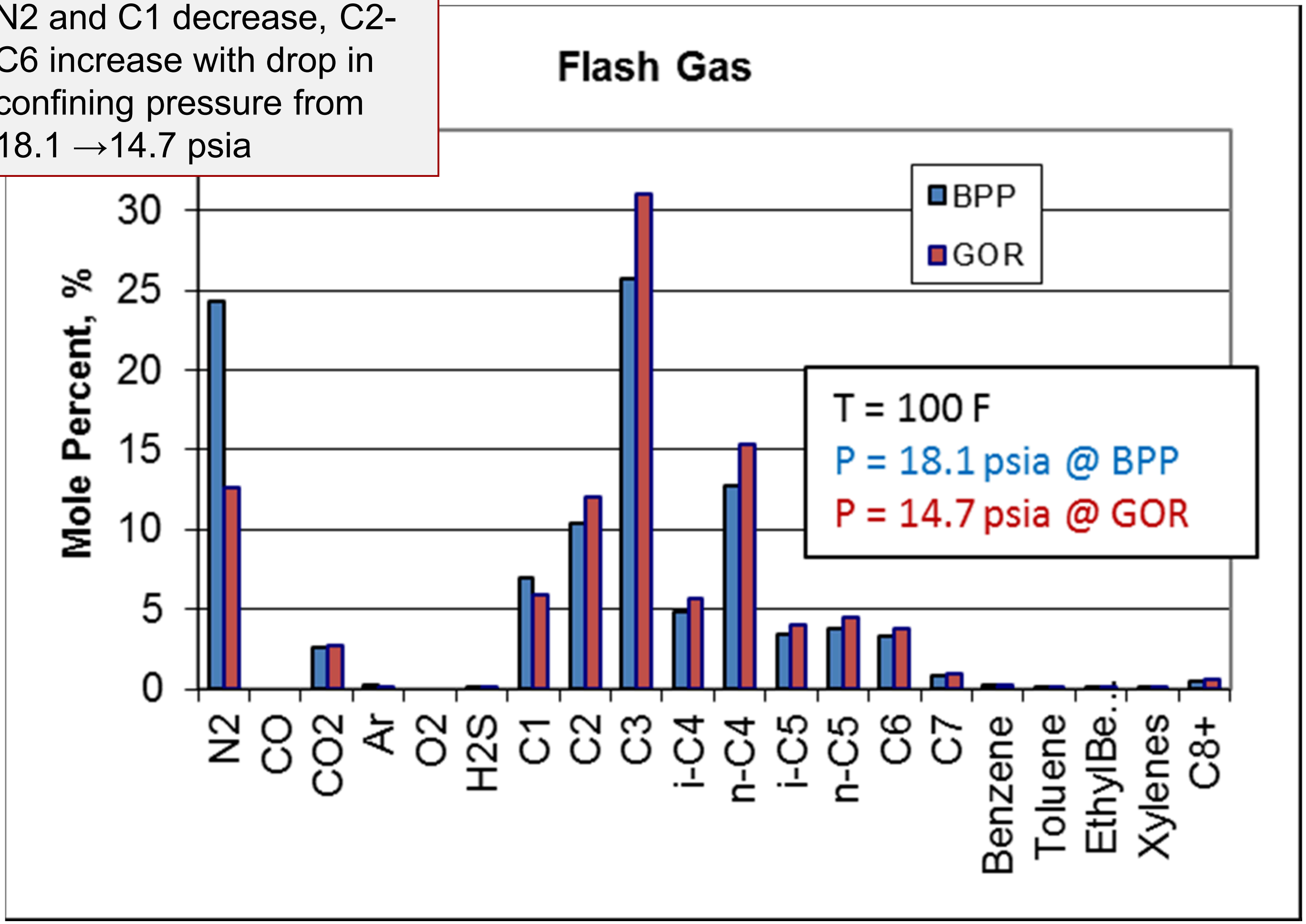
SPR crude oil WH108, April 2011, API = 37.2



Flash gas composition

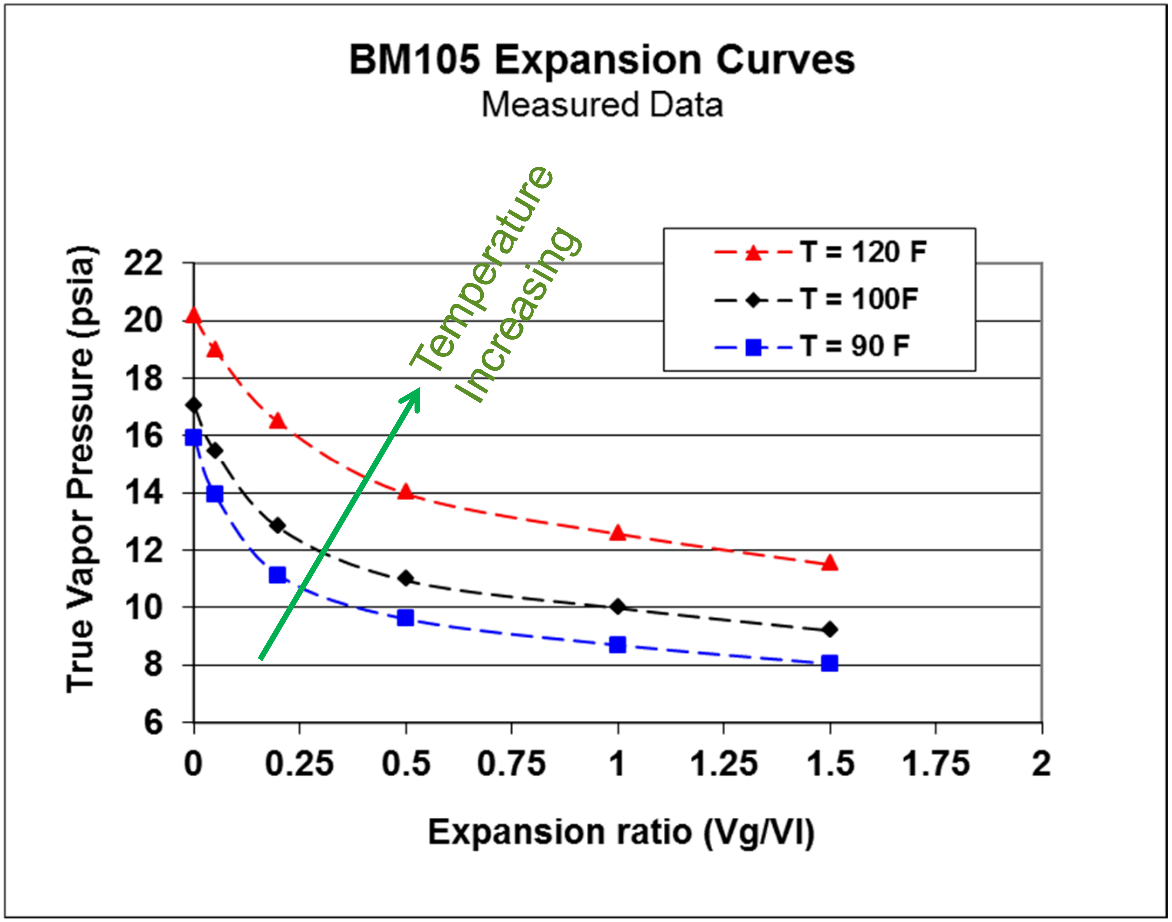
SPR crude oil WH108, April 2011, API = 37.2

N2 and C1 decrease, C2-C6 increase with drop in confining pressure from 18.1 →14.7 psia



Vapor space composition will change to favor incrementally heavier components with decrease in confining pressure and/or increase in V/L

Mixture PVT Behavior, SPR Example



Physical/chemical properties of Bakken and SPR oils

DATA COMPARISONS

Sources

- Auers, J. R., R. M. Couture and D. L. Sutton (2014). "The North Dakota Petroleum Council Study on Bakken Crude Properties." Bakken Crude Characterization Task Force. North Dakota Petroleum Council, Bismarck, ND 58501. 4-Aug-2014.
  - Referred to as “NDPC report”
- PHMSA (2014). "Operation Safe Delivery Update." U.S. Department of Transportation, Washington, D.C. Jul-2014.
  - Referred to as “PHMSA report”
- Strategic Petroleum Reserve (SPR) vapor pressure program data
  - Crude receipts 1999-2012
    - One Bakken pipeline sample from December 2012 (^{o}API = 42)
  - Oils in storage

Challenges for Comparison

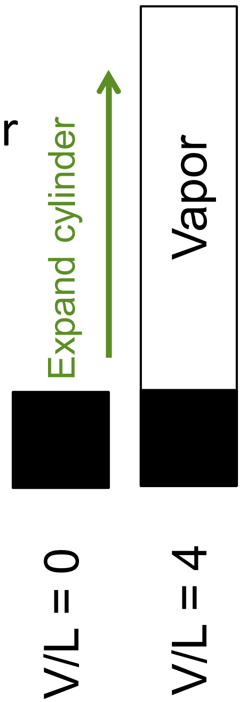
- Sampling methods are not consistent
  - NDPC study used open catch with sealed glass jar
    - Small number of floating piston cylinder
  - PHMSA used open catch sampling method
    - Small number of closed syringe-style
  - SPR used closed tight-line or floating piston-cylinder
- Test conditions not consistent
  - NDPC and PHMSA ran ASTM D6377 VPCR(4) @ 100 °F
  - SPR ran flash separator at 100° F and imported into EOS to simulate VPCR(4)
- Short Timeline
  - Many sources of Reid Vapor Pressure, but we did not have time to process and interpret for this project review
  - Did not have time to carefully analyze PHMSA and NDPC closed sample results

Bases for comparisons

- API gravity
- Vapor pressure @ 100° F
  - $VPCR_4$
  - Bubblepoint pressure (BPP), where V/L = 0
- Gas-oil ratio (GOR) @ 100° F and P = 1 atm
  - Standard cubic feet of gas per barrel of liquid
- Oil composition
  - Light ends vol%, wt%

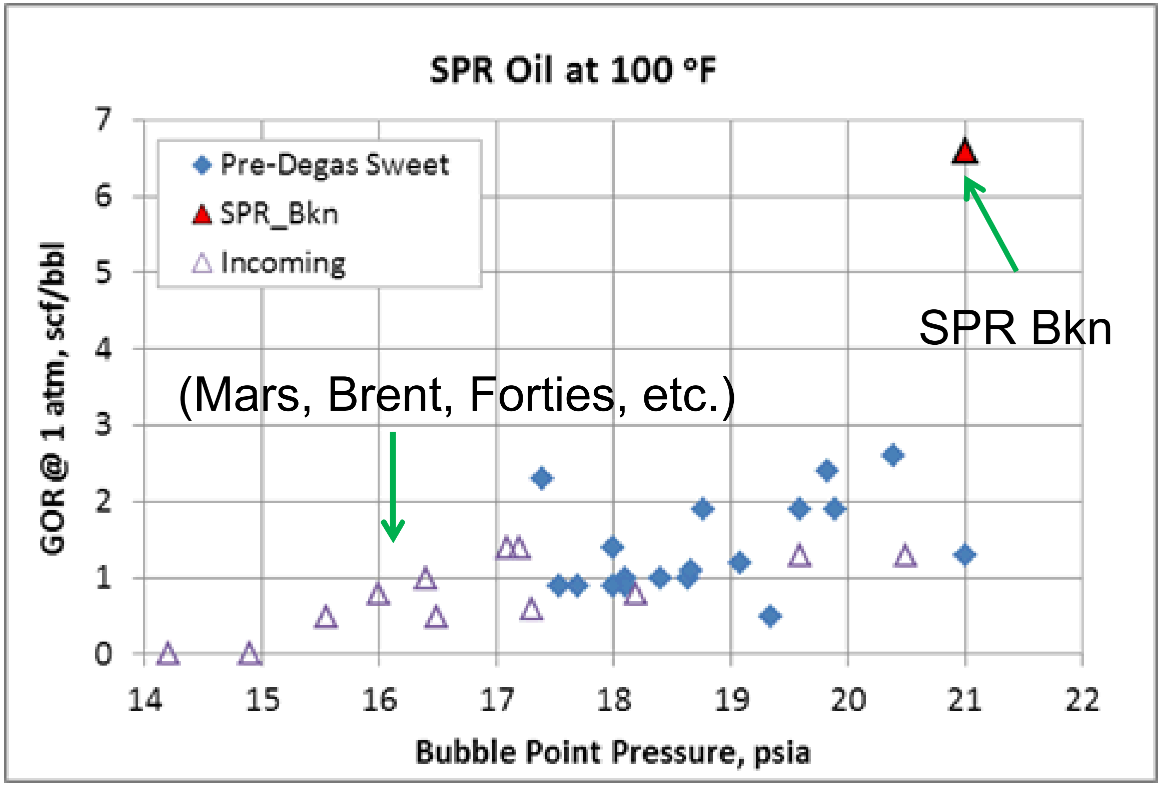
V/L expansion = 4

- Appears to have origins in Reid method, though relevance to current operating conditions is not clear
- Experimental method
  - ASTM D6377 Standard Test Method for Determination of Vapor Pressure of Crude Oil, $VPCR_4$ (Expansion Method)
  - Expand crude oil sample to selected V/L at fixed T, measure P
- Numerical modeling method
  - Utilize equation of state (EOS) model to estimate P
  - Requires knowledge of “whole” oil compositions
  - SPR does not collect expansion data at VPCR(4)
  - SPR VPCR(4) is simulated with an EOS model
    - SPR collects flash separator data for compositions at VLE
    - SPR collects some VPCR(0.05, 0.2, 0.5) data



Bubblepoint and GOR for SPR Oils

The 2012 Bakken pipeline receipt (°API = 42) at SPR was an outlier in both BPP and GOR relative to medium-light crudes received during period 1999-2012.



PVT Curves for SPR Sweet Crudes

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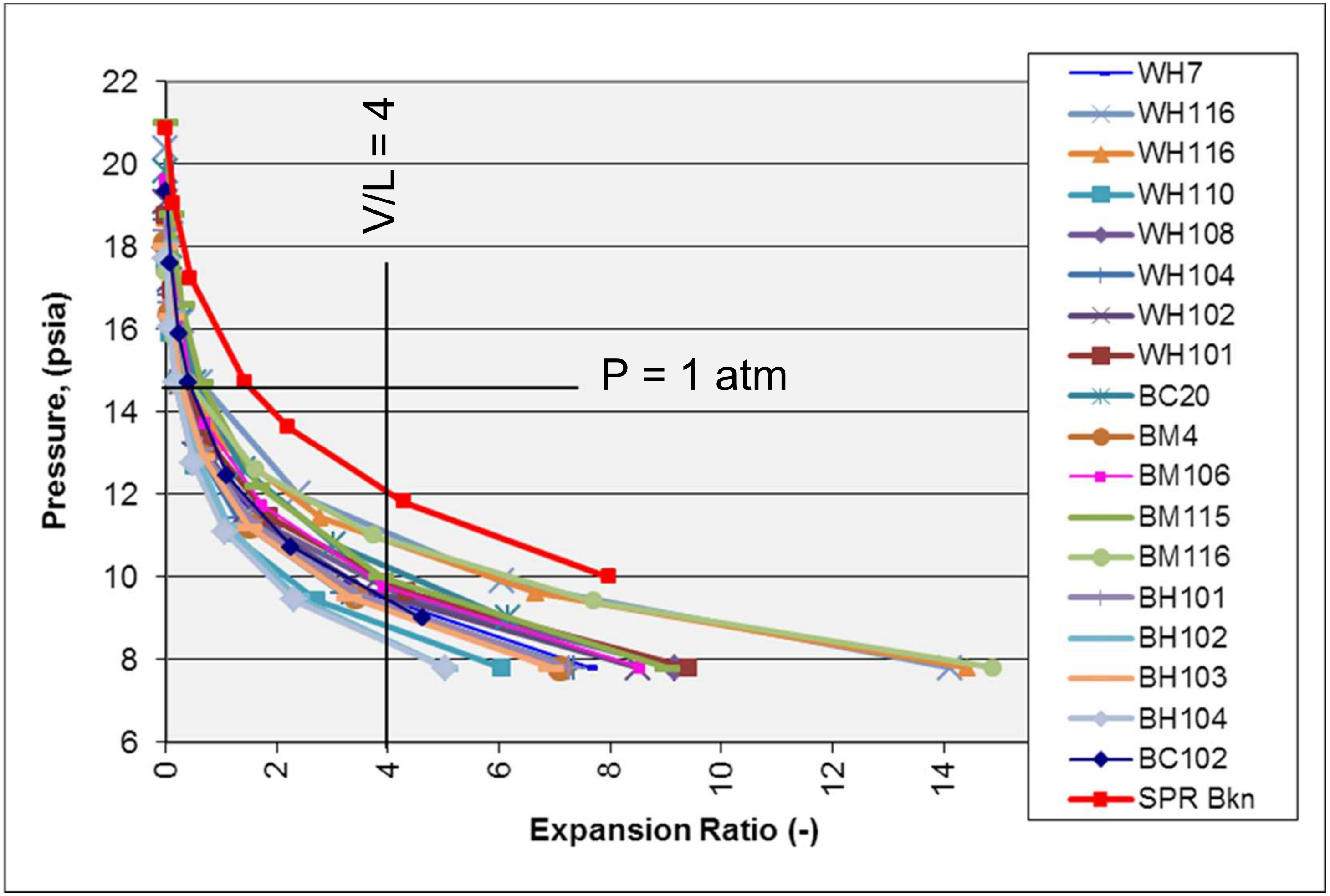
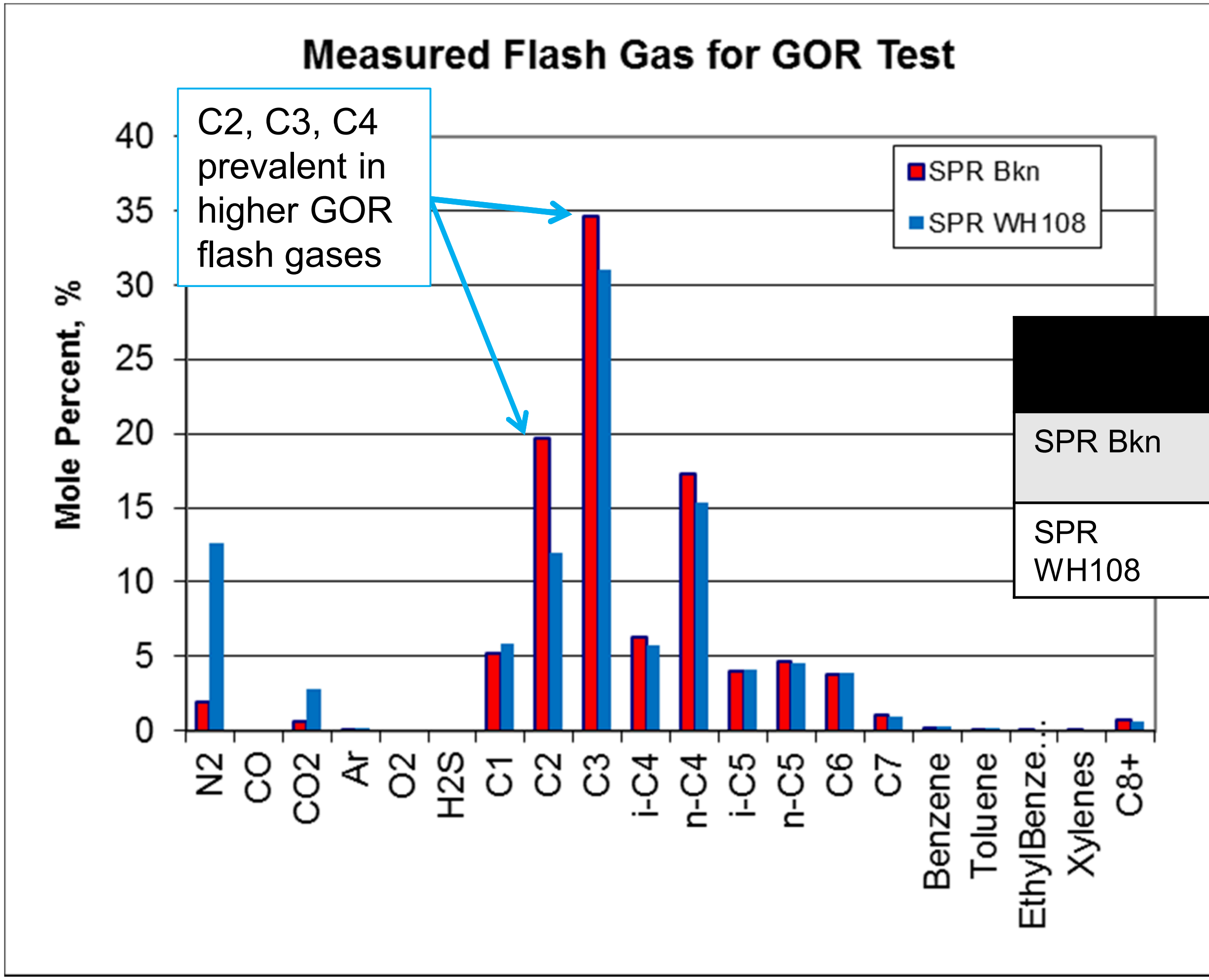
T = 100 F, curves generated from EOS model



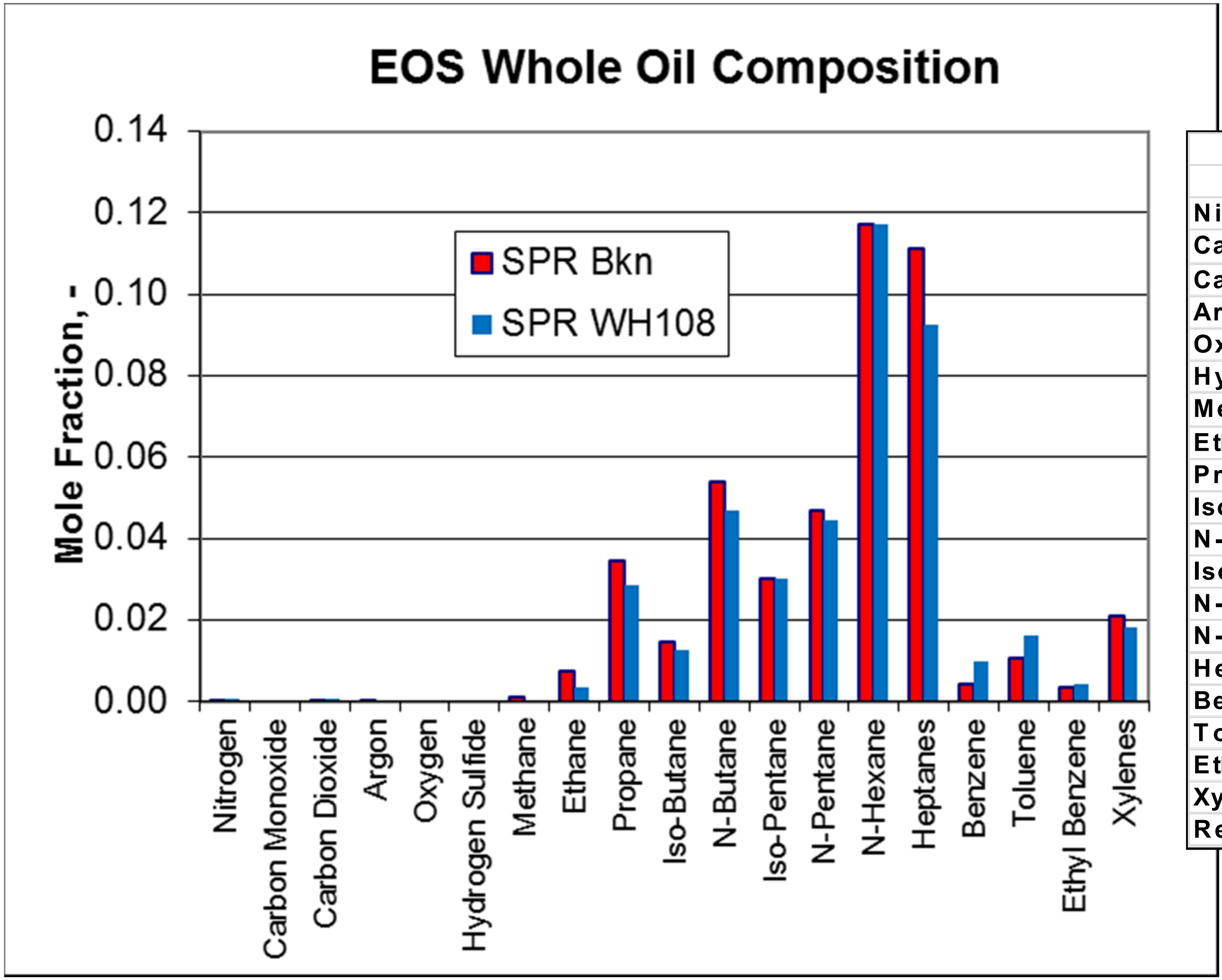
PRELIMINARY DATA

Flash Comps, SPR Bkn vs. WH108



	BPP [psia]	GOR [scf/bbl]
SPR Bkn	21.0	6.6
SPR WH108	18.1	1.4

Whole Oils, SPR Bkn vs. WH108



	SPR Bkn mole frac	WH108 mole frac
Nitrogen	0.0004	0.0006
Carbon Monoxid	0.0000	0.0000
Carbon Dioxide	0.0002	0.0007
Argon	0.0000	0.0000
Oxygen	0.0000	0.0000
Hydrogen Sulfid	0.0000	0.0000
Methane	0.0009	0.0004
Ethane	0.0073	0.0035
Propane	0.0345	0.0285
Iso-Butane	0.0145	0.0126
N-Butane	0.0541	0.0468
Iso-Pentane	0.0300	0.0301
N-Pentane	0.0468	0.0443
N-Hexane	0.1172	0.1173
Heptanes	0.1110	0.0927
Benzene	0.0044	0.0096
Toluene	0.0105	0.0162
Ethyl Benzene	0.0034	0.0042
Xylenes	0.0211	0.0183
Residual	0.5438	0.5745

Observations so far…

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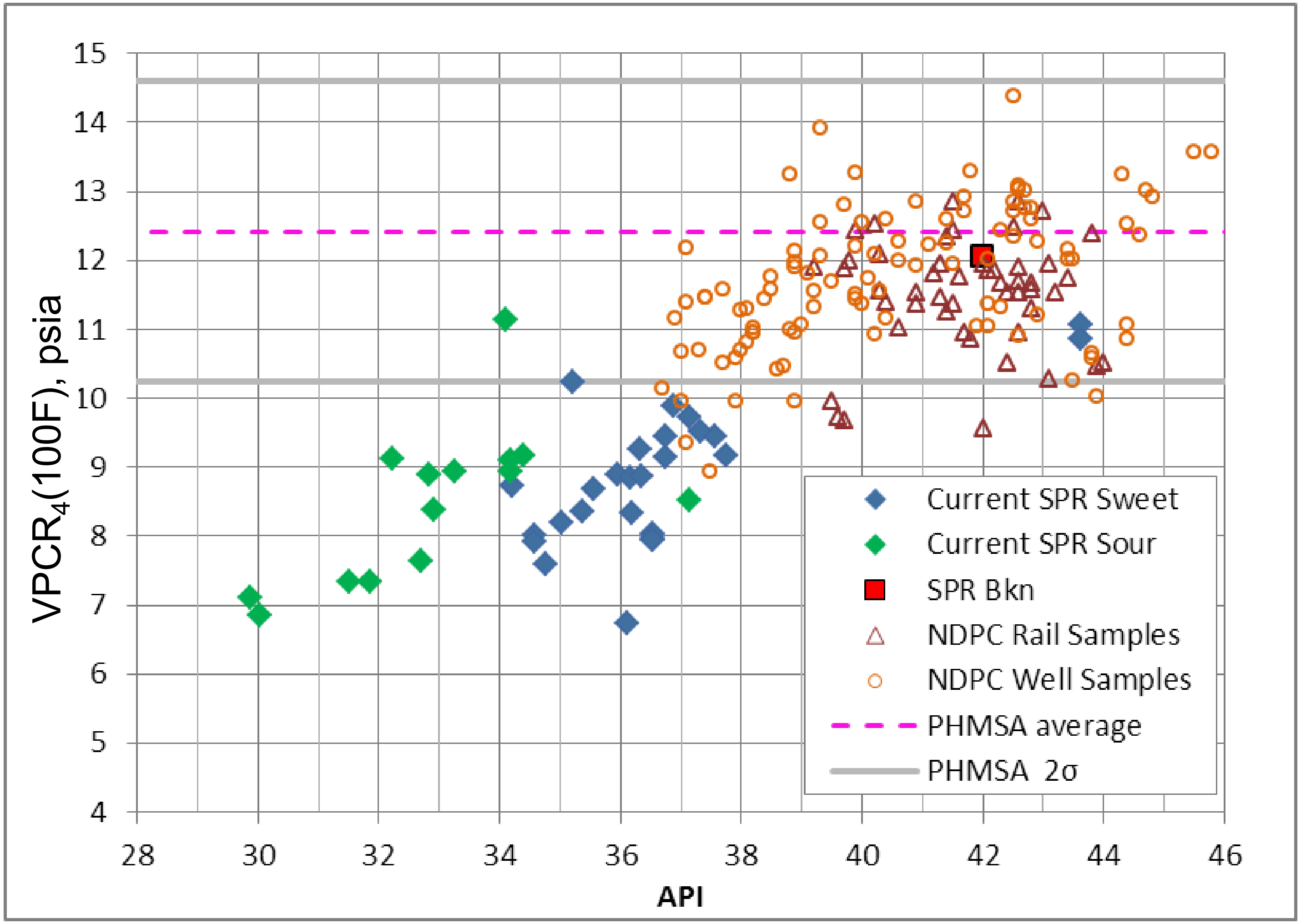
- 2012 pipeline Bakken receipt at SPR exhibits slightly higher BPP and notably higher GOR than current[¥] sweet inventory
- Compositional comparison
  - GOR flash gas analysis shows more C2-C4 flashed from SPR Bkn than a typical SPR sweet
  - Whole oils show more C1-C7 in SPR Bkn than a typical SPR sweet
- How do SPR oils and SPR Bkn compare to Bakken from recent field studies by NDPC and PHMSA?

[¥]Includes only SPR oils prior to degasification

$VPCR_4$(100F) vs. API Gravity



- NDPC rail data from "Appendix 6 - Lab Data – Rail"
- PHMSA data from "Table E"

$VPCR_4$(100F) preliminary comparisons

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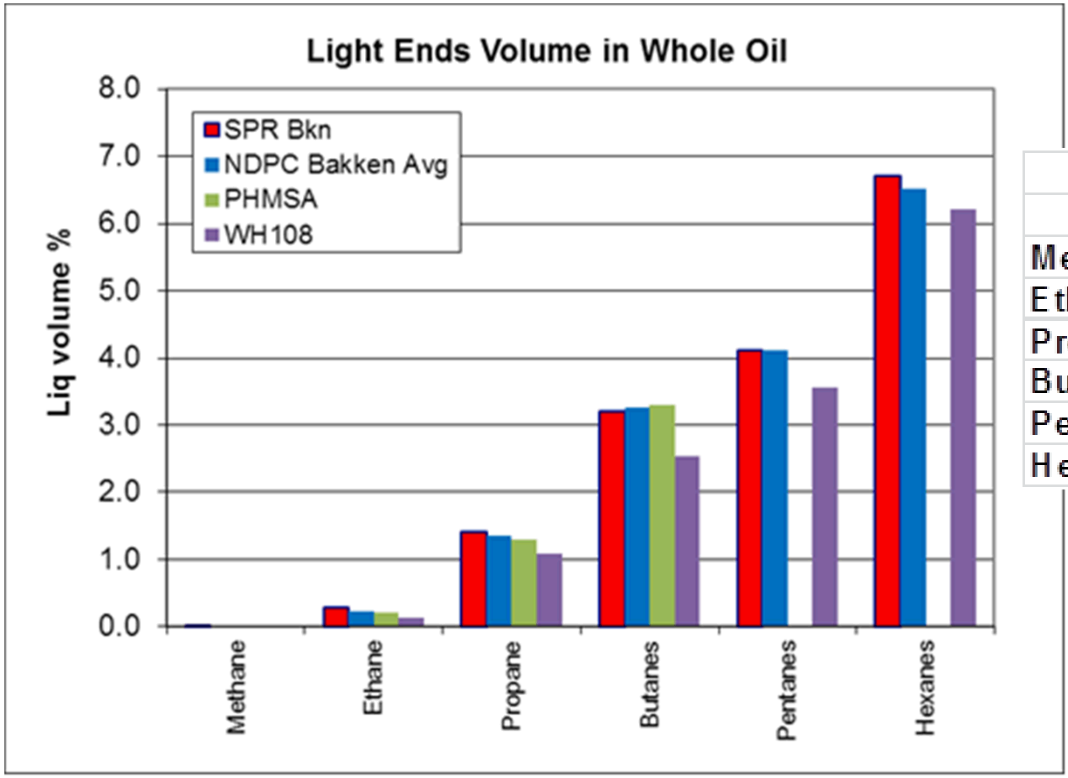
- Bakken data from three sources compare well for $VPCR_4$(100F)
- Bakken $VPCR_4$(100F) about 30-40% higher than typical crudes stored at SPR

Source	$VPCR_4$(100°F)	2*σ
	[psia]	[psia]
NDPC Bakken (rail)	11.5	1.6
PHMSA Bakken	12.4	2.2
SPR Bkn	12.0	-
SPR Sw	8.9	2.0

Light Ends Comparisons

- Averaged NDPC Appendix 8 – IP344 Light Ends Data – Rail, vol % for Bakken samples
- Averaged PHMSA table E Light Ends Liq vol %
- SPR Bkn and SPR WH108 samples



	NDPC liq vol %	SPR Bkn liq vol %	PHMSA liq vol %	WH108 liq vol %
Methane	0.00	0.02	0.00	0.01
Ethane	0.23	0.29	0.21	0.13
Propane	1.36	1.40	1.30	1.08
Butanes	3.25	3.20	3.29	2.53
Pentanes	4.11	4.11	N/A	3.56
Hexanes	6.52	6.71	N/A	6.21

Comparisons in Summary

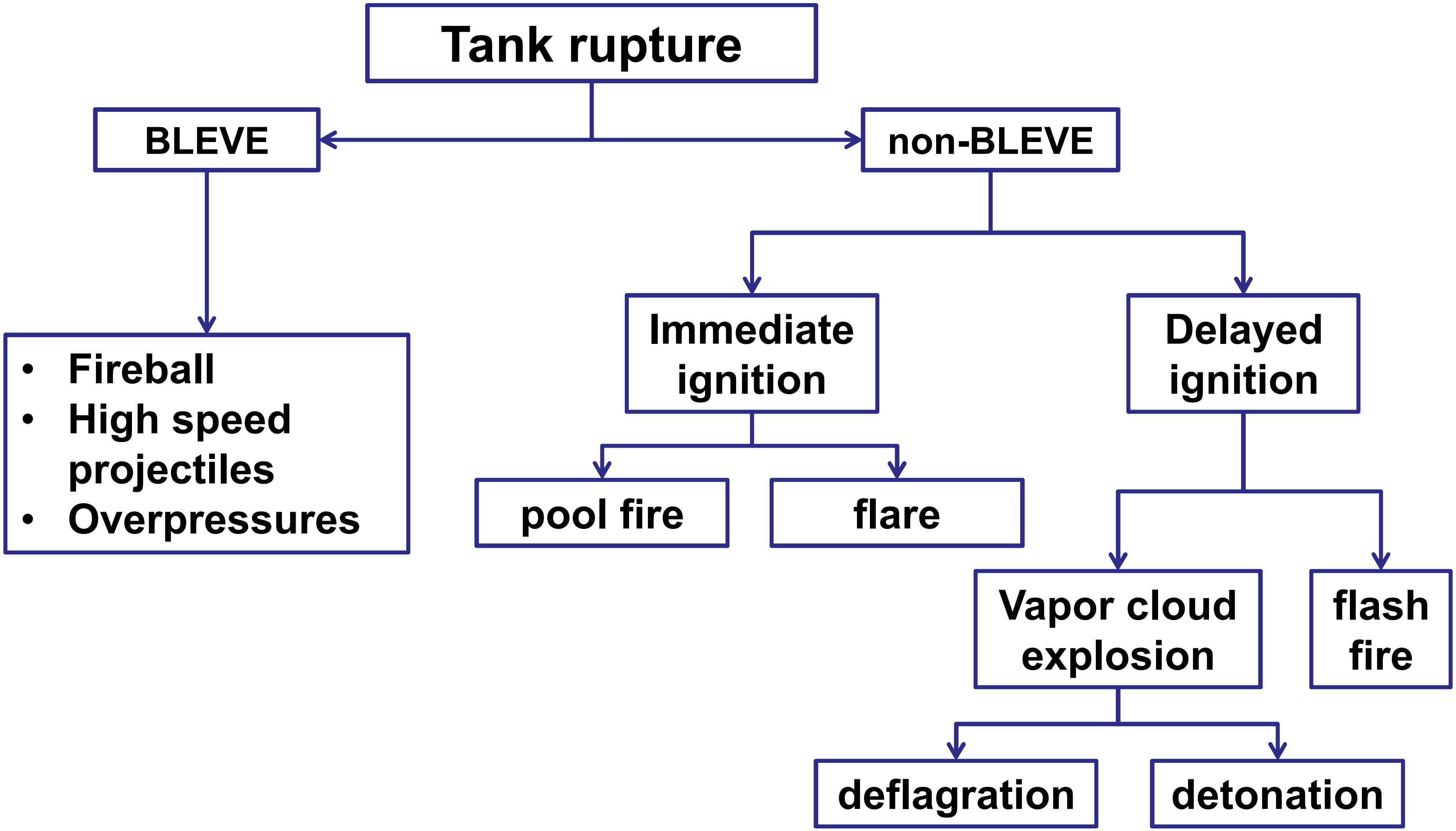
- Sampling and analysis techniques differ among NDPC, PHMSA, and SPR, so direct comparison is difficult
- In spite of above, $VPCR_4$(100F) appear to compare well for Bakken data from different sources
- Light ends (C2-C6) also compare well among Bakken samples from different sources
  - No-detect on methane and absence of nitrogen masks some important players
  - C2-C6 vol % of SPR WH108 sample all lower than avg. Bakken
- $VPCR_4$(100F) of Bakken independent of source (PHMSA, NDPC, SPR Bkn) is avg. ~30-40% higher than typical crude stored at SPR

Context for hazards in a crude oil rail car breach

POTENTIAL COMBUSTION EVENTS

Coverage in Written Report

Combustion Event Tree



Combustion events

- These events can occur with any liquid hydrocarbon
- Severity of an accident will depend upon the amount of fuel, surrounding infrastructure, and environment
- No single parameter defines the degree of flammability
  - Lower flashpoint, wider range of flammability limits, lower auto-ignition temperature, lower minimum ignition energy, and higher maximum burning velocity is considered more flammable

Properties for Hazard Calculations

Large-scale tests

Combustion Event	Properties	Scale
Pool fire measurements	• Burn rate • Surface emissive power • Flame height	• ~1 to 10 m, • bund and free spill
Fireball/BLEVE	• Geometry • Surface emissive power • Duration • Fragment characterization (velocities, geometry, range) • Overpressures	Rail car (could help design/test the modified rail car)
Vapor cloud (flash fire, explosion)	• Composition	Rail car ('Damaged' mock)

Executive Summary

- Objective is to describe physical properties of crude oil relevant to flammability and transport safety
- If and how these properties will relate to fire and explosion hazard is the key research question we need to address
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- General lack of uniformity in methods and QA/QC across industry makes comparisons of crude oil vapor pressure difficult, leaving room for improvement
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- Several combustion events (pool fire, BLEVE, fireball, explosion, flash fire, flare) can occur from an accidental release of a liquid hydrocarbon
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END OF PREPARED SLIDES