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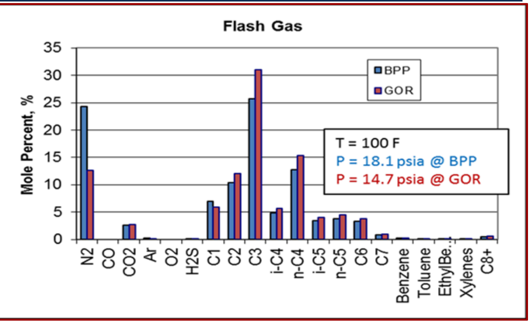

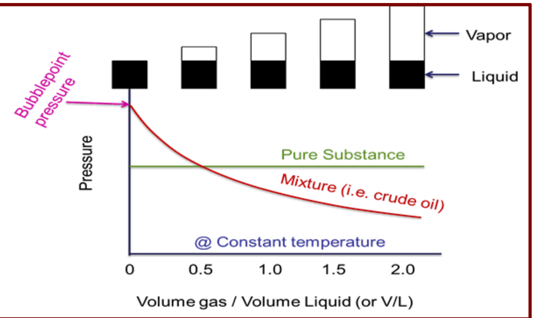

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Crude Oil Properties Overview

DOE/DOT Tight Oil
Flammability & Transportation Spill Safety
Project Review

Albuquerque, NM
Nov 19-20, 2014

by
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U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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Outline

- Executive Summary
- Problem Statement
- Describing Crude Oils
- Crude oil Phase Behavior
- SPR Vapor Pressure Program
- Data Comparisons

Executive Summary

- Objective is to describe physical properties of crude oil relevant to flammability and transport safety
- 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
- Bakken crude, a representative tight oil, exhibits higher vapor pressure and gas oil ratio that typical SPR oils due to slightly higher mole fractions of light hydrocarbons
- There is room for improving QA/QC and associated understanding of crude oil vapor pressure measurements for characterizing volumes and compositions of gases that are likely to evolve from crudes in transport spill scenarios
- If and how these properties will relate to fire and explosion hazard is the key research question we need to address

Problem Statement

- 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

BASIC DESCRIPTION OF CRUDE OIL

Basic Description of Crude Oil

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- Crude oil is a complex mixture of primarily liquid hydrocarbons with dissolved gases and trace amounts of suspended water, inorganic sediments
- Average crude contains (approximately)
  - 84% carbon
  - 14% hydrogen
  - 1-3% sulfur
  - 1% nitrogen
  - 1% oxygen
  - 0.1% minerals and salts

Source: API (2011). "Crude Oil Category Assessment Document." High Production Volume Testing Group. American Petroleum Institute, Washington, DC 14-Jan-2011.

Property Changes During Handling

- Sequential conditioning, stabilization, separation, and commingling steps moving away from the wellhead create material streams that may vary significantly from their initial wellhead condition
  - "Live oil" at the wellhead contains dissolved gases that will spontaneously evolve (flash) at ambient pressure conditions
  - "Dead oil" downstream of separation processes will not flash at ambient pressure conditions
- Variety of factors affect the degree to which an oil is conditioned and stabilized for transport (engineering, economics, safety, regulatory)
  - Chad Wocken (EERC) will elaborate on this topic in a subsequent presentation

API Gravity & Sulfur

- Designation of "light" or "heavy" is based on density
  - API gravity is common unit of measure
  - $\geq 33^\circ$ API for "light" oil
  - $\leq 28^\circ$ API for "heavy" oil
- Sulfur content is described as "sweet" or "sour"
  - General rule
    - "Sweet" < 1% total mass sulfur
    - "Sour" > 1% total mass sulfur
  - Strategic Petroleum Reserve crude oil quality specifications
    - "Sweet" < 0.5% total mass sulfur
    - "Sour" < 1.99% total mass sulfur

Source: API (2011). "Crude Oil Category Assessment Document." High Production Volume Testing Group. American Petroleum Institute, Washington, DC 14-Jan-2011.

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

Tight Oils

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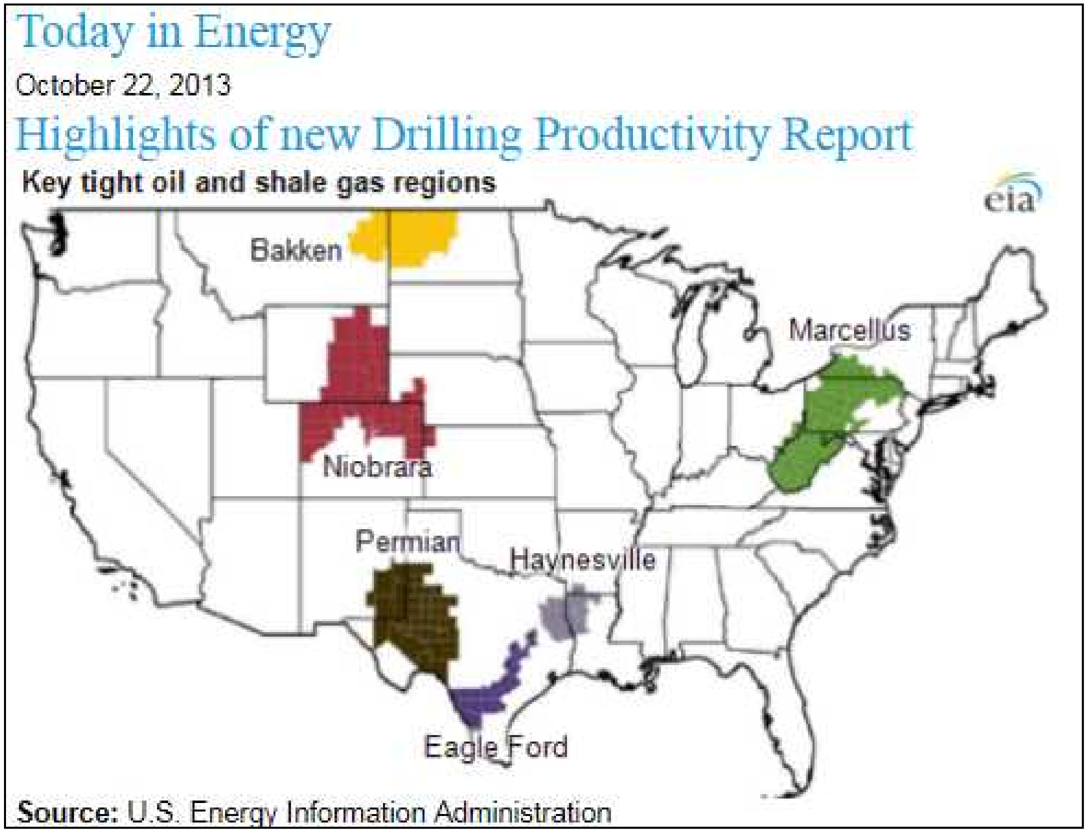
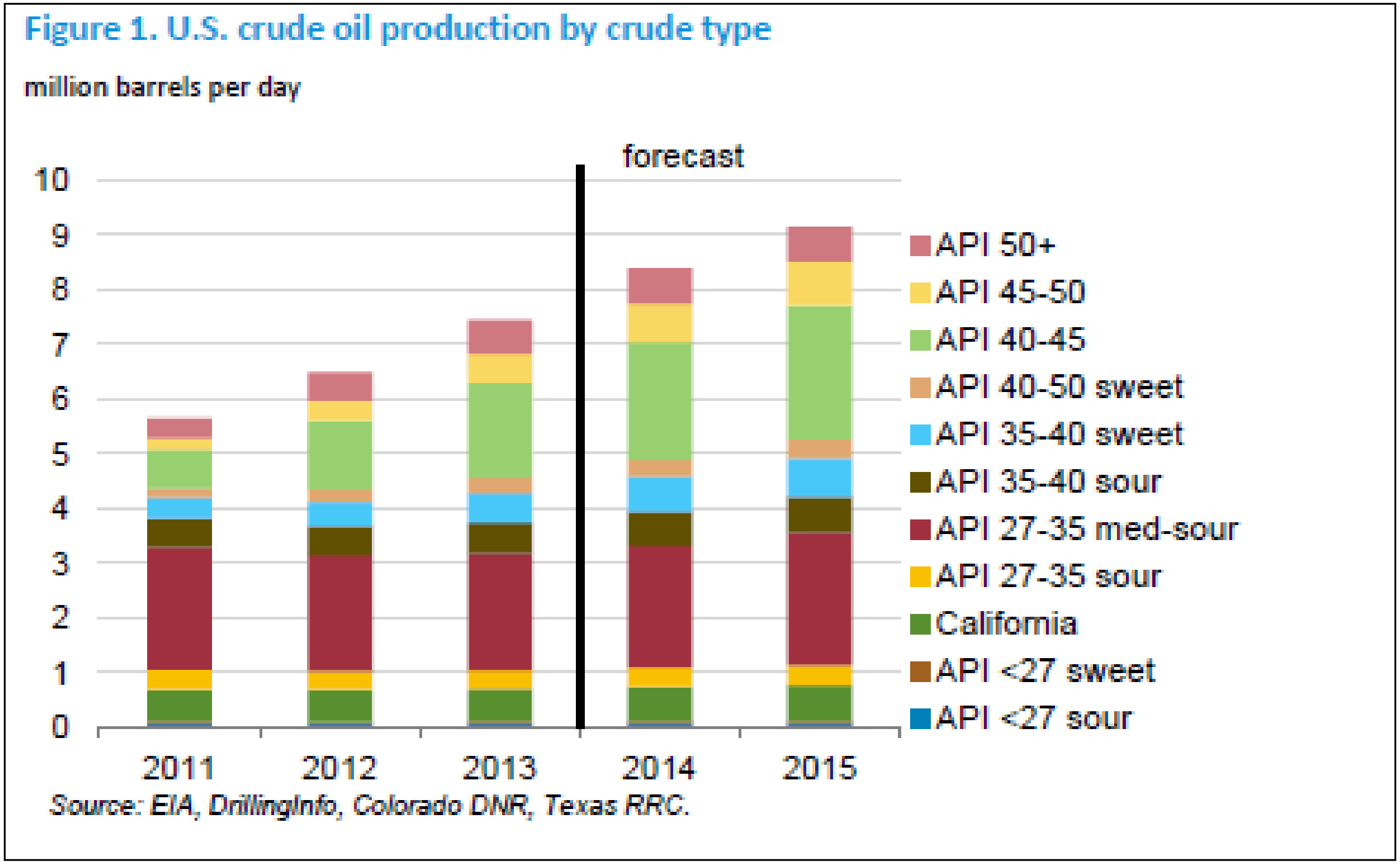
- Oil produced from low-permeability reservoir rock
- Typically stimulated with hydraulic fracturing to produce at economic rates



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.

EIA Forecasts for US Production



Source: EIA. (2014). "U.S. Crude Oil Production Forecast - Analysis of Crude Types." U.S. Energy Information Administration. U.S. Department of Energy. Washington, DC 20585.

Conditions that lead to gas emissions from low-vapor-pressure crude

CRUDE OIL PHASE BEHAVIOR

Why 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
  - 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, if any, 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

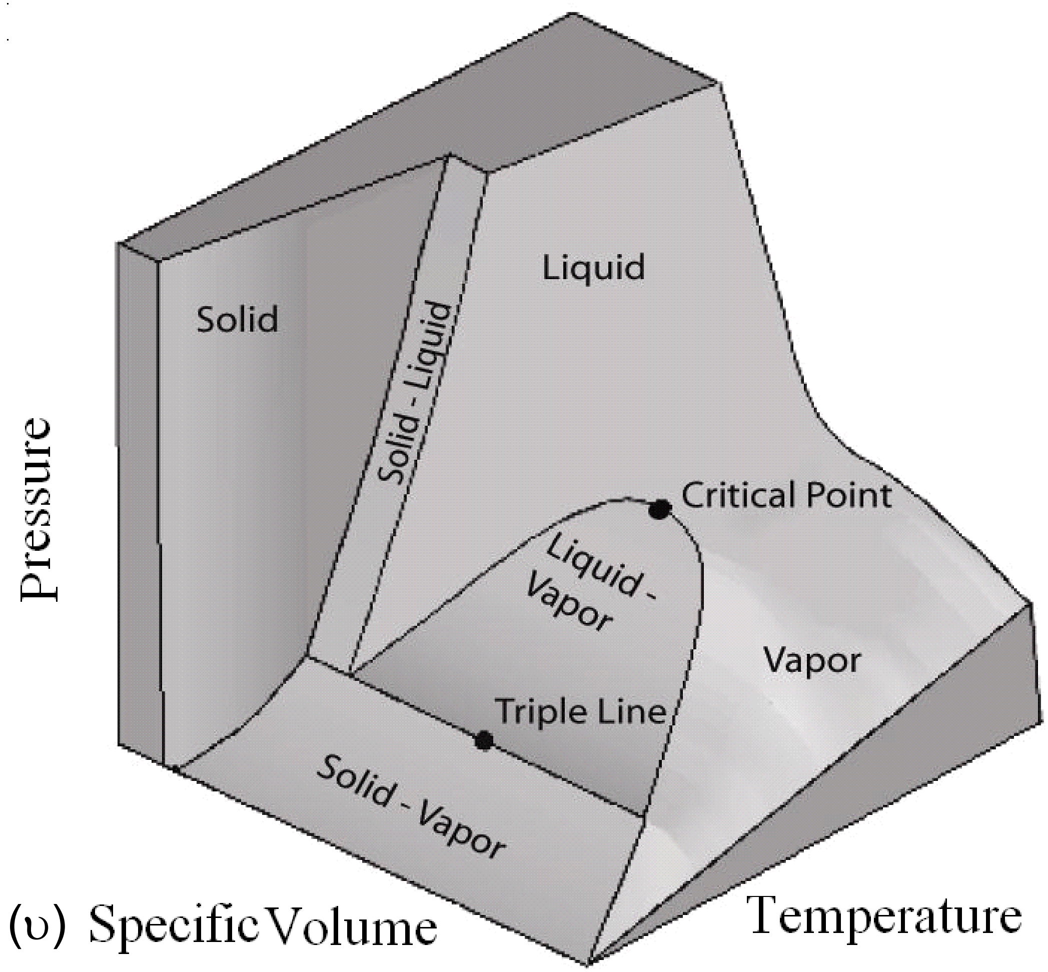
What is Phase Behavior?

- Phase behavior describes what phases (solid, liquid, gas) are present under certain thermodynamic ((P) pressure, (υ) specific volume, (T) temperature) conditions
  - Crude oil can also exhibit very complex phase behavior with multiple solid phases (asphaltenes, waxes) or supercritical fluids
- Crude oils relevant to this study at ambient pressure and temperature can produce co-existing gas and liquid phases
  - Waxes and asphaltenes may also be present but assumed irrelevant to fire risks, though they do create problems for flow assurance.
- Addition of fire and possible trapping of crude inside a pressurized vessel (i.e. railcar full of oil exposed to pool fire) will extend relevant parameter space from simple ambient conditions

Source: Mansoori, G. A. (2009). "A unified perspective on the phase behaviour of petroleum fluids." International Journal of Oil Gas and Coal Technology **2**(2): 141-167.

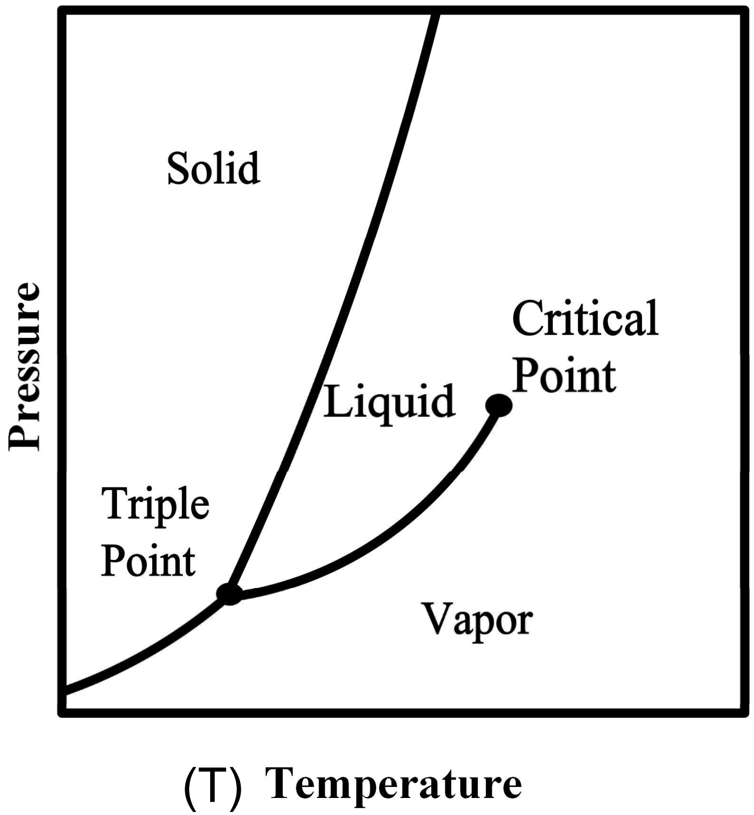
Pure Substance Phase Behavior

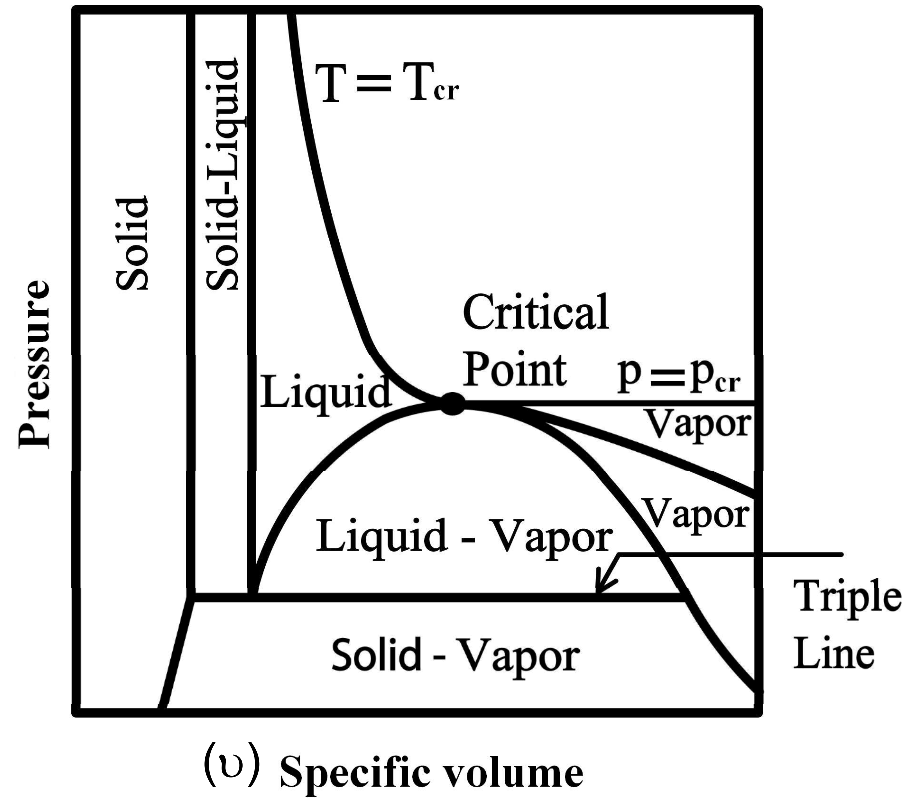
Representative pure light alkane



Source: https://www.thermalfluidscentral.org

Pure Substance Phase Behavior





Pure Substance vs. Mixture

Contrasting behavior in vapor-liquid region of phase diagram

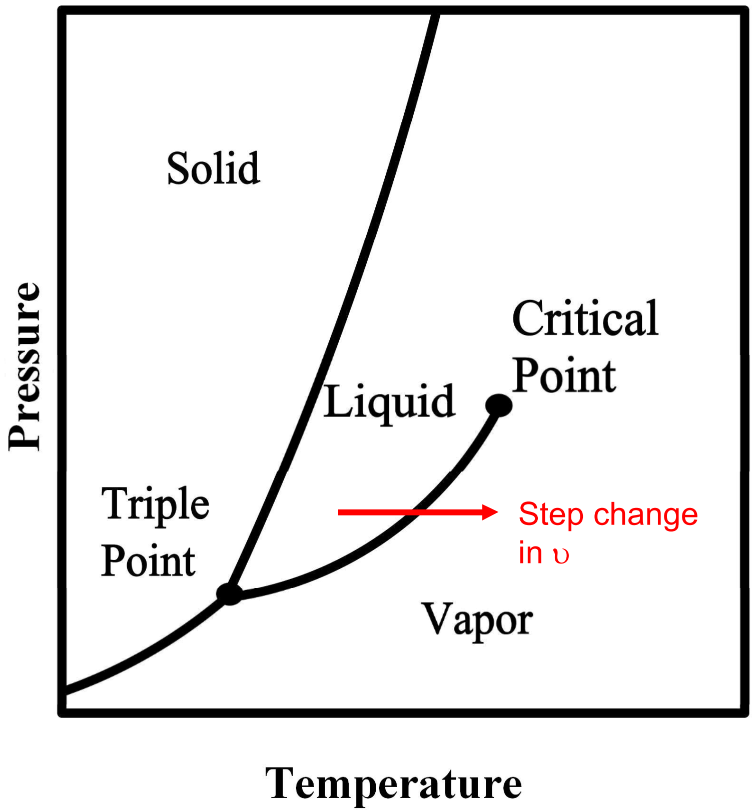
Pure Substance (typical light alkane)

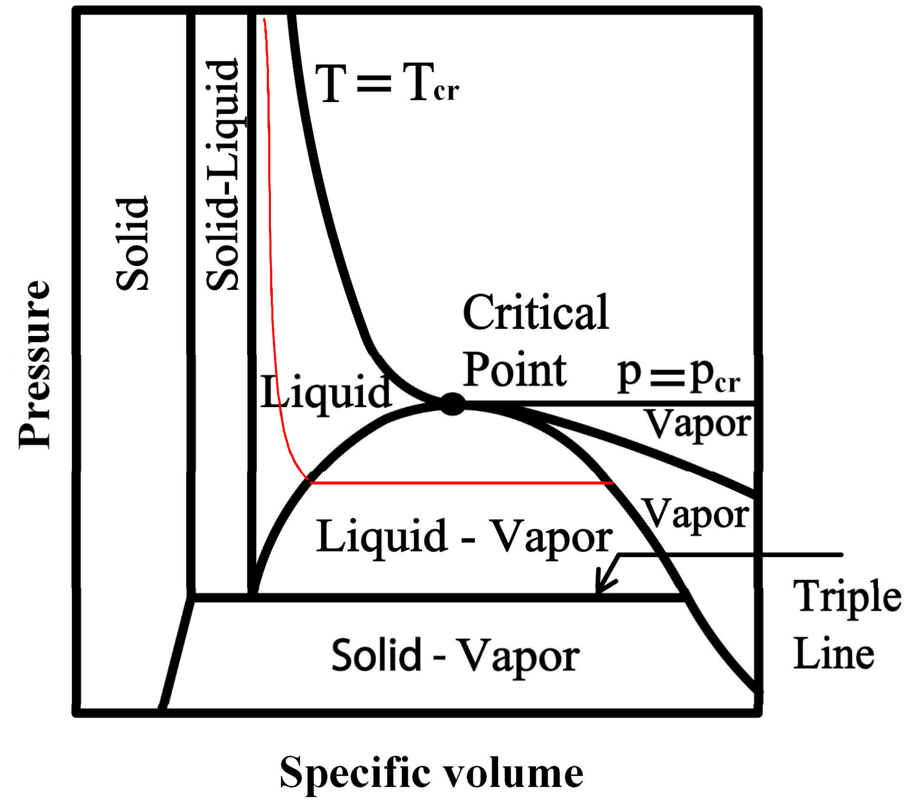
- Single boiling point temperature at a given pressure
- Vapor pressure is constant with V/L at a given temperature
- Step change in υ as temperature crosses boiling point at constant pressure

Mixture (crude oil)

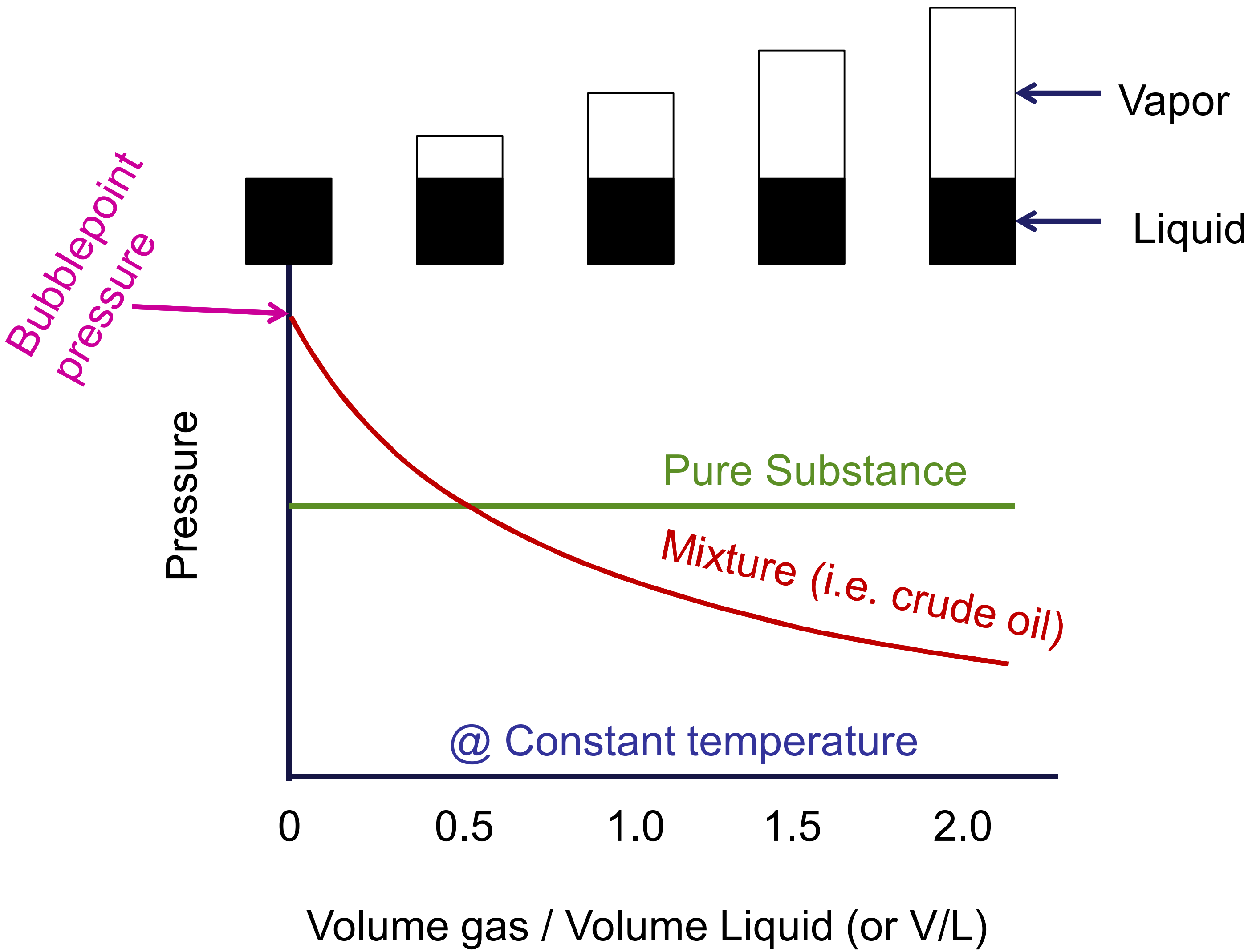
- Series of component boiling temperatures at a given pressure
- Vapor pressure is variable with V/L at a given temperature
- Gradual increase in υ as temperature increases through boiling range at constant pressure

Pure Substance Phase Behavior



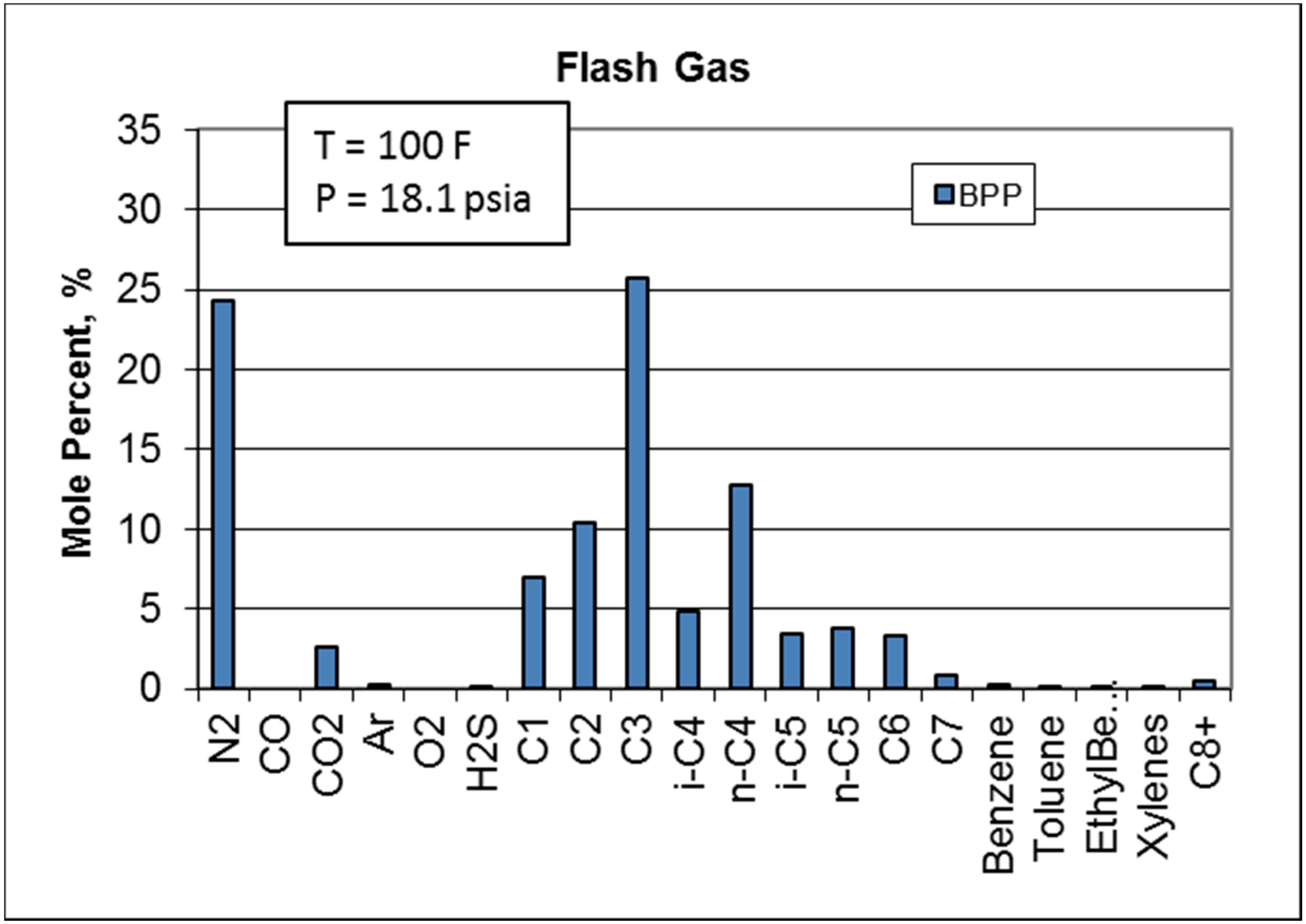


Pure Substance vs. Mixture



Flash gas composition

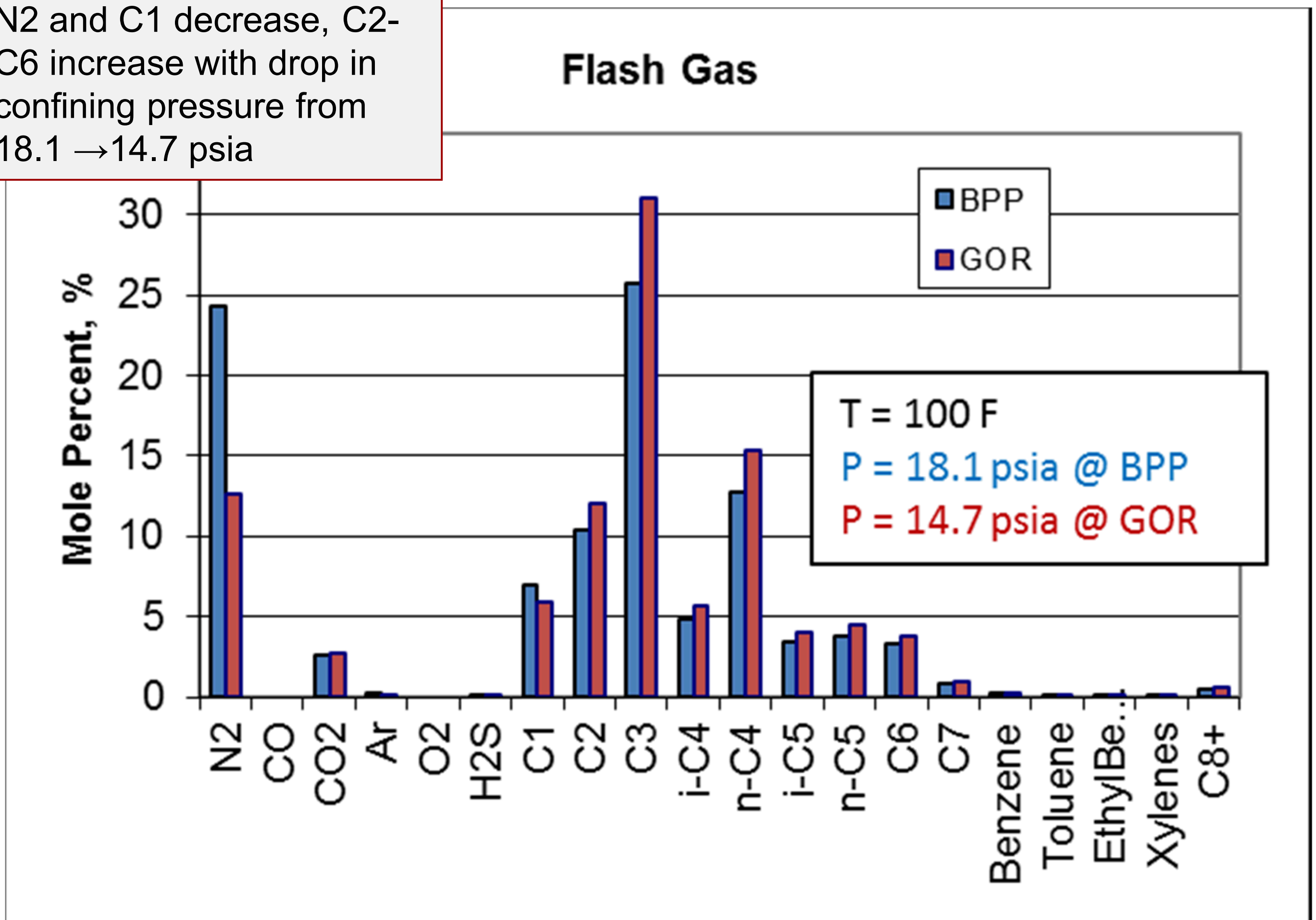
SPR crude oil WH108, April 2011, API = 37.2



Flash gas composition

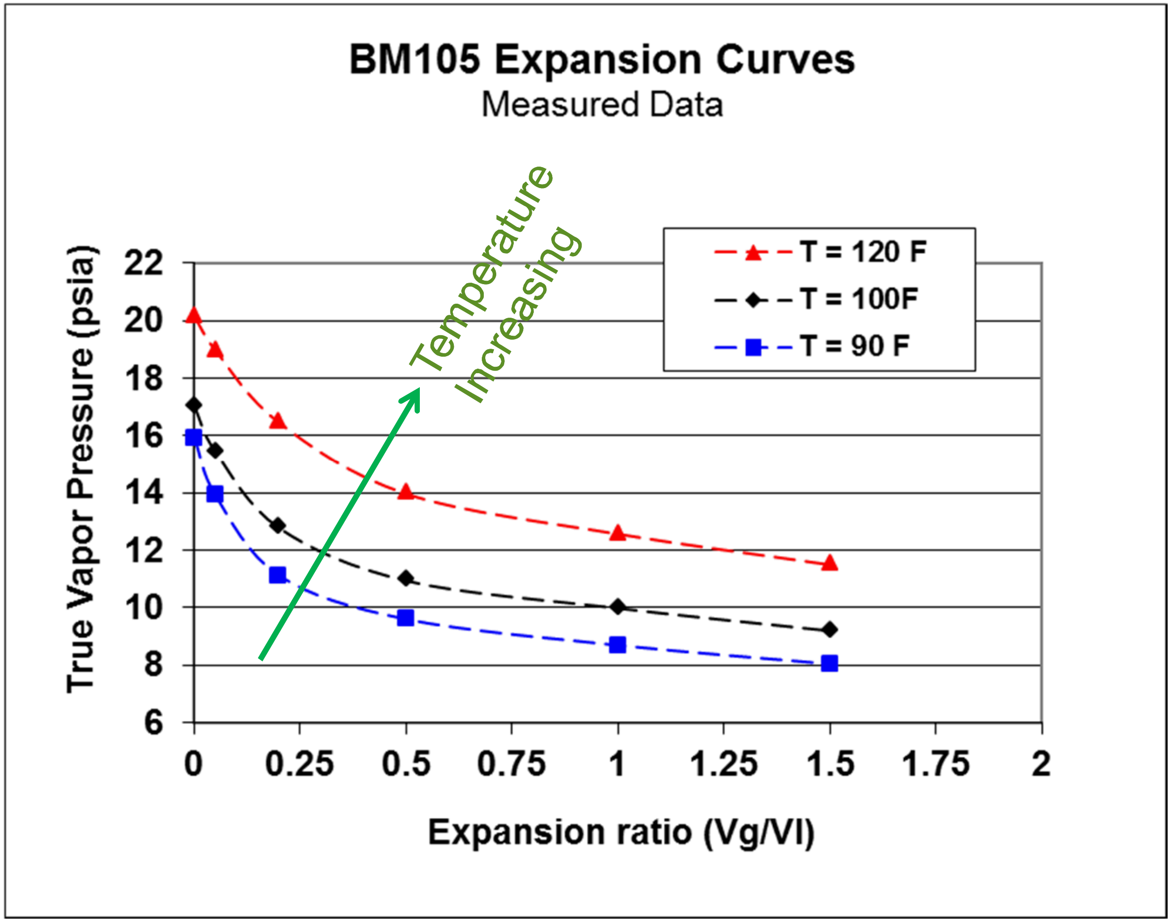
SPR crude oil WH108, April 2011, API = 37.2

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



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
- Functional definition for crude oil 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 such as floating piston-cylinder to minimize light ends loss during sample collection

Examples of process safety criteria based on crude oil vapor pressure

SPR VAPOR PRESSURE PROGRAM

Vapor Pressure and Process Safety

- The SPR vapor pressure program maintains vapor emissions from crude oils within acceptable safety limits during inventory drawdown
- SPR receives stabilized “dead” crudes at nominally 70-80˚F
- Oils are stored in underground salt caverns for years to decades
- Geothermal heating and methane intrusion in salt cavern storage lead to increases in oil volatility with time
- Oil drawn out of salt caverns after years of storage will “flash” a mixture of light hydrocarbons, poisonous gases, and inorganic gases if left untreated
- SPR found that crude oil vapor pressure is a useful parameter to measure and control for the purpose of mitigating hazards associated with crude oil volatility

Safety Drivers

- OSHA federal law sets exposure limits on some of the gaseous components that flash from crude oils (H_2S, benzene)
- Working backward from the regulatory exposure limits, SPR used a plume dispersion model to calculate the maximum allowable emissions rate (mscf/hr) from a floating roof tank receiving SPR oil at SPR design rates
- The mscf/hr allowable emissions was then used to calculate an upper limit gas-oil ratio for an SPR oil entering the floating roof tank
- Crude oil equation of state modeling was then used to determine the extent of vapor pressure mitigation (cooling, degasification) was required to meet the emissions limits

Role of Vapor Pressure

- Accurate, repeatable measurements of true vapor pressure were required in order to evaluate SPR oils and set crude oil conditioning (vapor pressure mitigation) goals
- Commercially available technologies were unable to characterize the “gassy” SPR crudes and distinguish from the more stable crudes
- Reid vapor pressure was explored and dismissed due to poor reproducibility and fundamental issues of flashing light ends during sample prep
- SPR developed custom instruments TVP-95 and TVP-2000 to capture necessary vapor pressure data
  - Ray Allen will give more detail in subsequent presentation

SPR Relevance to Tight Oils Project

- SPR invested about 15 years of R&D into sample acquisition, sample analysis, and equation of state modeling to finally arrive at a reproducible, self consistent means to measure, model, and control crude oil vapor pressure
- Methods are not standardized
  - Documented in internal project reports
  - Need to publish work in peer-reviewed scientific journals
- Many useful analogs from SPR to the current tight oils safe transport work

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.
- Wybenga, F. (2014). "A Survey of Bakken Crude Oil Characteristics Assembled for the U.S. Department of Transportation." Dangerous Goods Transport Consulting Inc., American Fuel & Petrochemical Manufacturers. 14-May-2014.
  - Referred to as “AFPM report”
- SPR vapor pressure program data

Challenges for Comparison

- Sampling methods are not consistent
  - NDPC study used sealed glass jar
  - PHMSA used floating piston cylinder
  - 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

Bases for comparisons

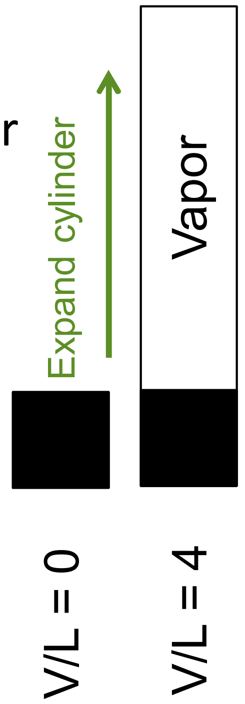
- API gravity
- True vapor pressure @ 100° F
  - VPCR(4)
  - Bubblepoint pressure (BPP), where V/L = 0
- Gas-oil ratio (GOR) @ 100° F
  - Standard cubic feet of gas per barrel of liquid at P = 1 atm
- Whole oil composition
  - Light ends vol%, wt%

Approach

- Compare SPR light crude vapor pressure with Bakken and other light crudes analyzed by NDPC, PHMSA
- Bases for comparison
  - API gravity
  - True vapor pressure
    - VPCR(4)
  - Gas-oil ratio (GOR)
- SPR received one Bakken pipeline shipment in December 2012
  - Run through test separator for bubblepoint pressure, GOR, and associated flash gas compositions
  - Denoted "SPR Bkn" in following graphics

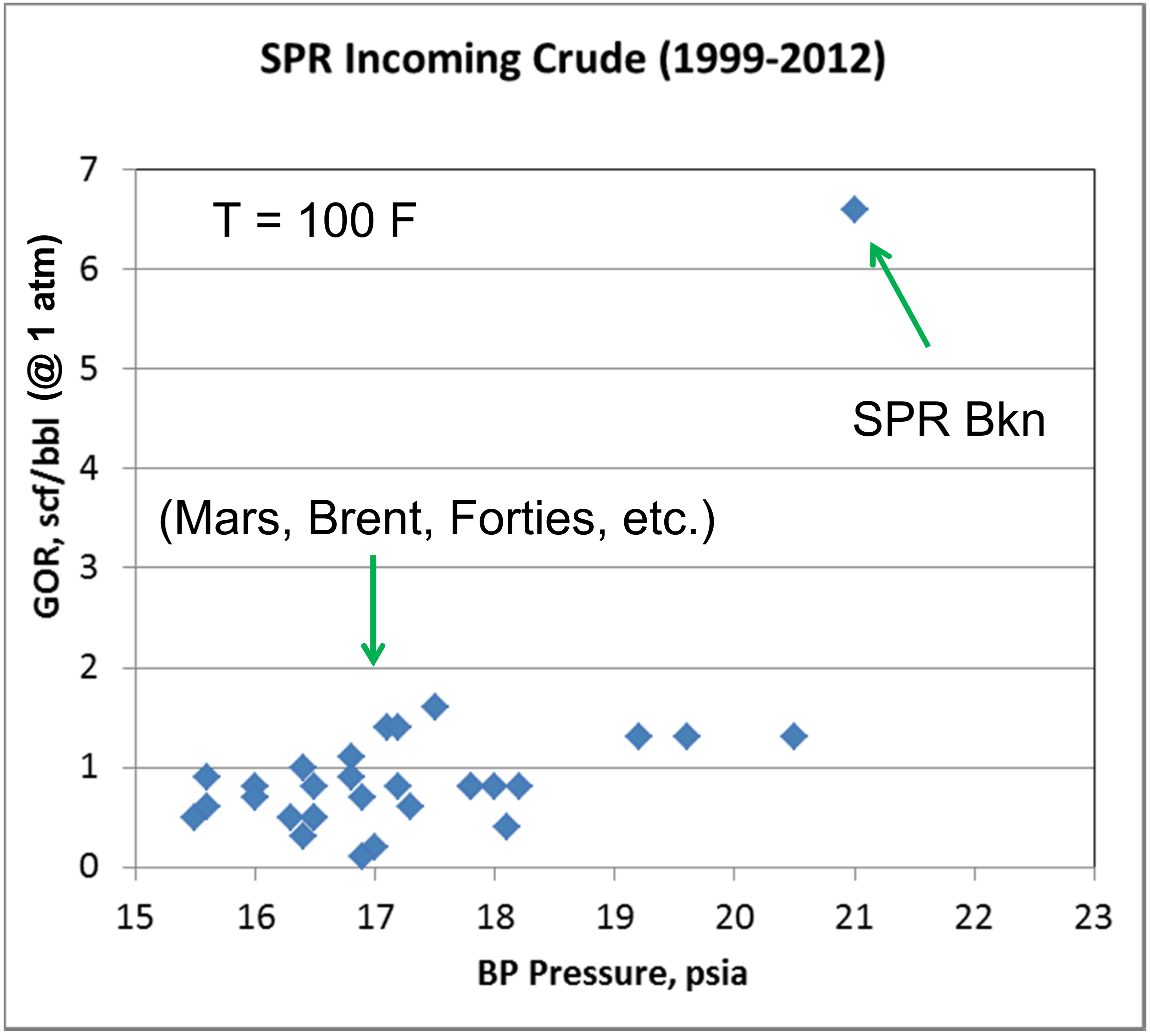
V/L expansion = 4

- 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



Survey of SPR Crude Receipts

The 2012 Bakken pipeline receipt at SPR was an outlier in both BPP and GOR relative to other light crudes received during period 1999-2012.



PVT Curves for SPR Crude Receipts

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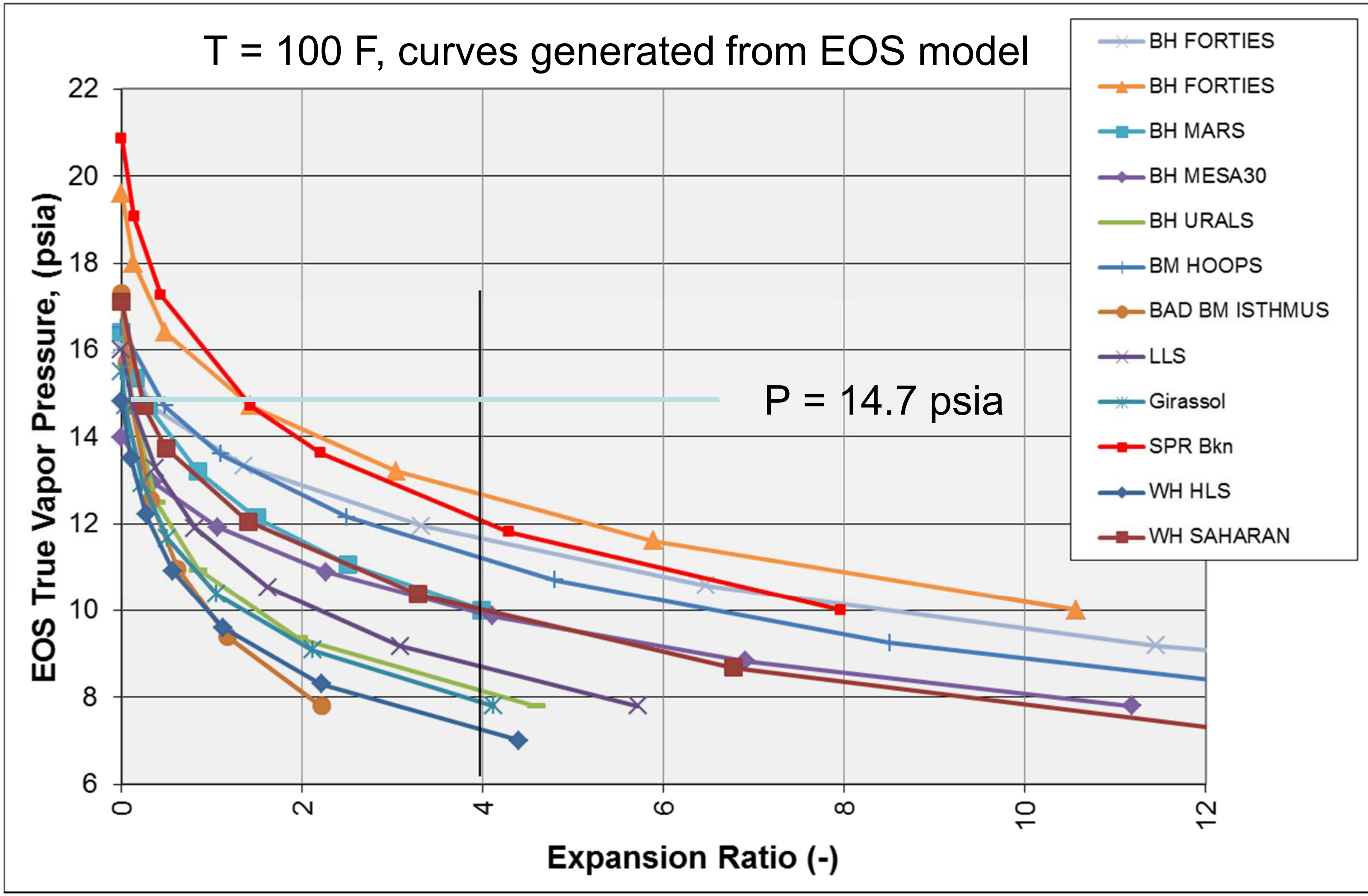
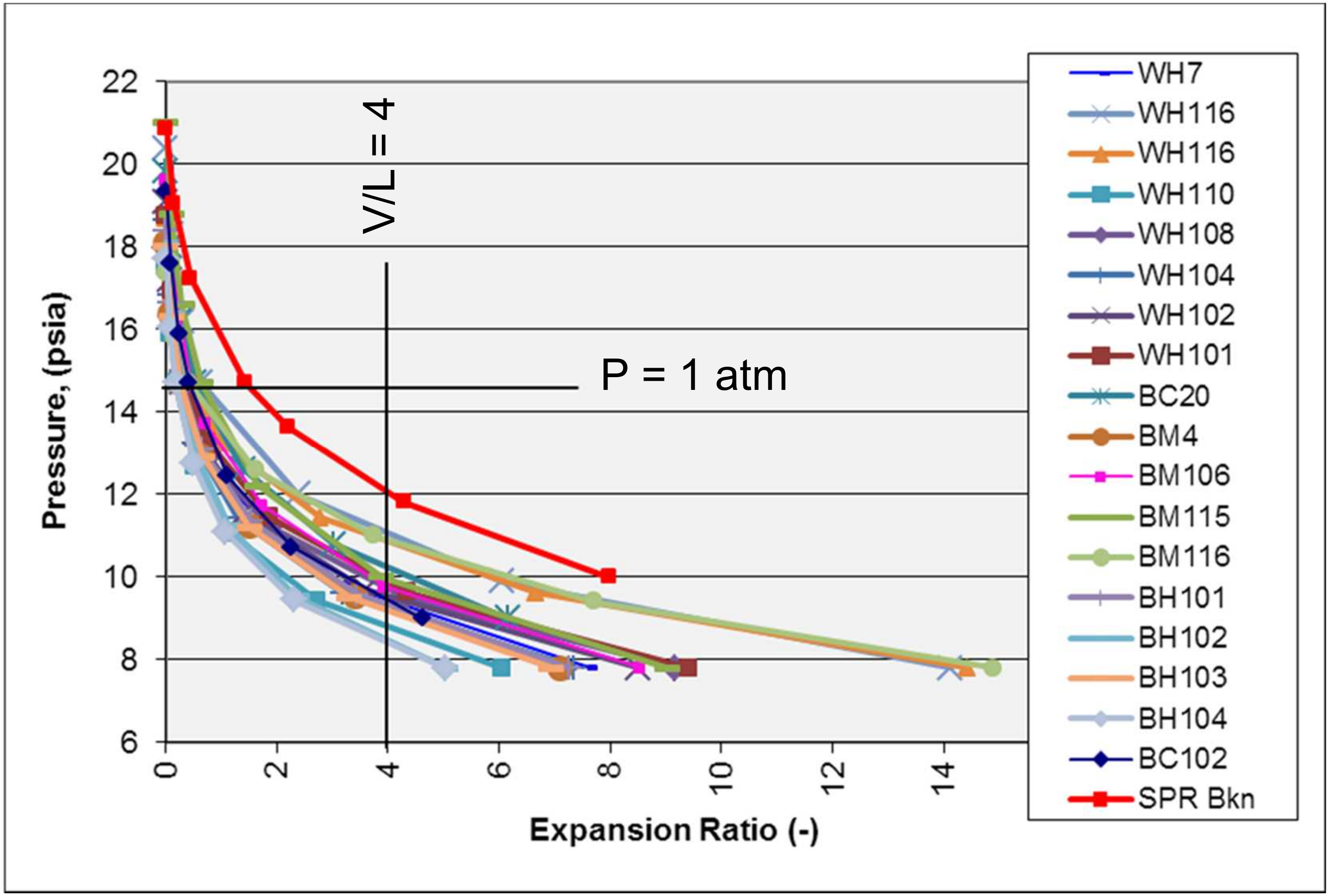
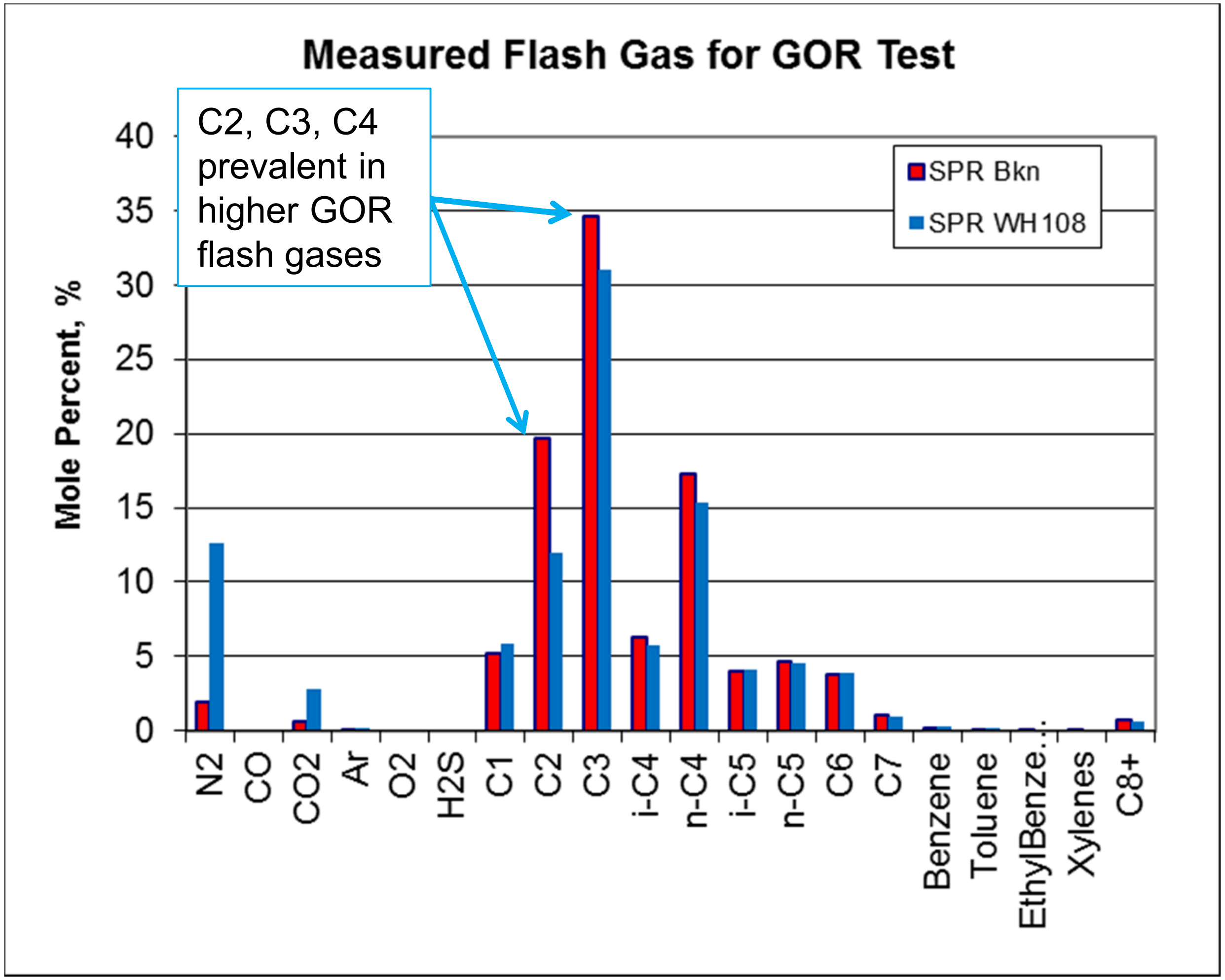


PVT Curves for SPR Sweet Crudes

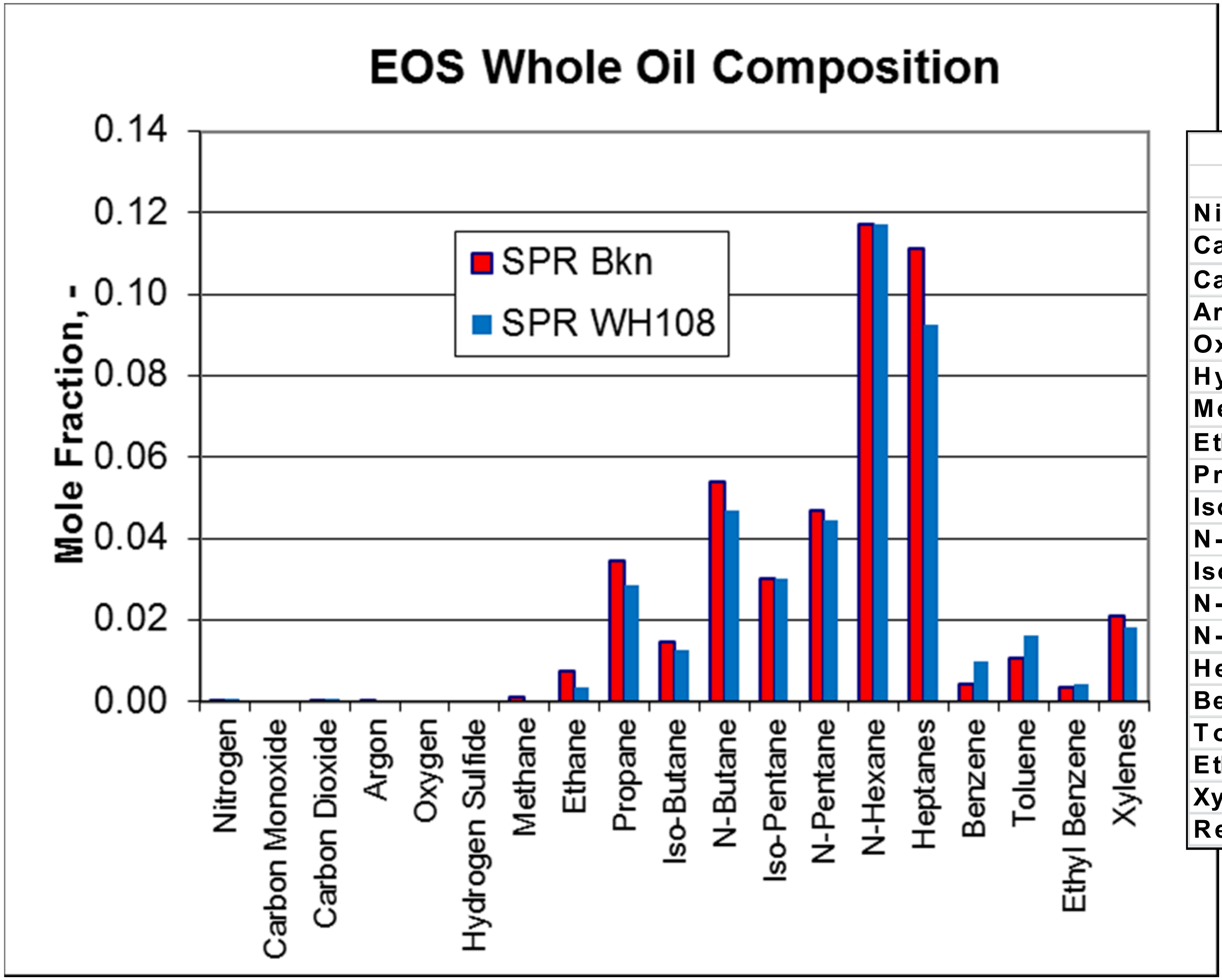
T = 100 F, curves generated from EOS model



Flash Comps, SPR Bkn vs. WH108



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

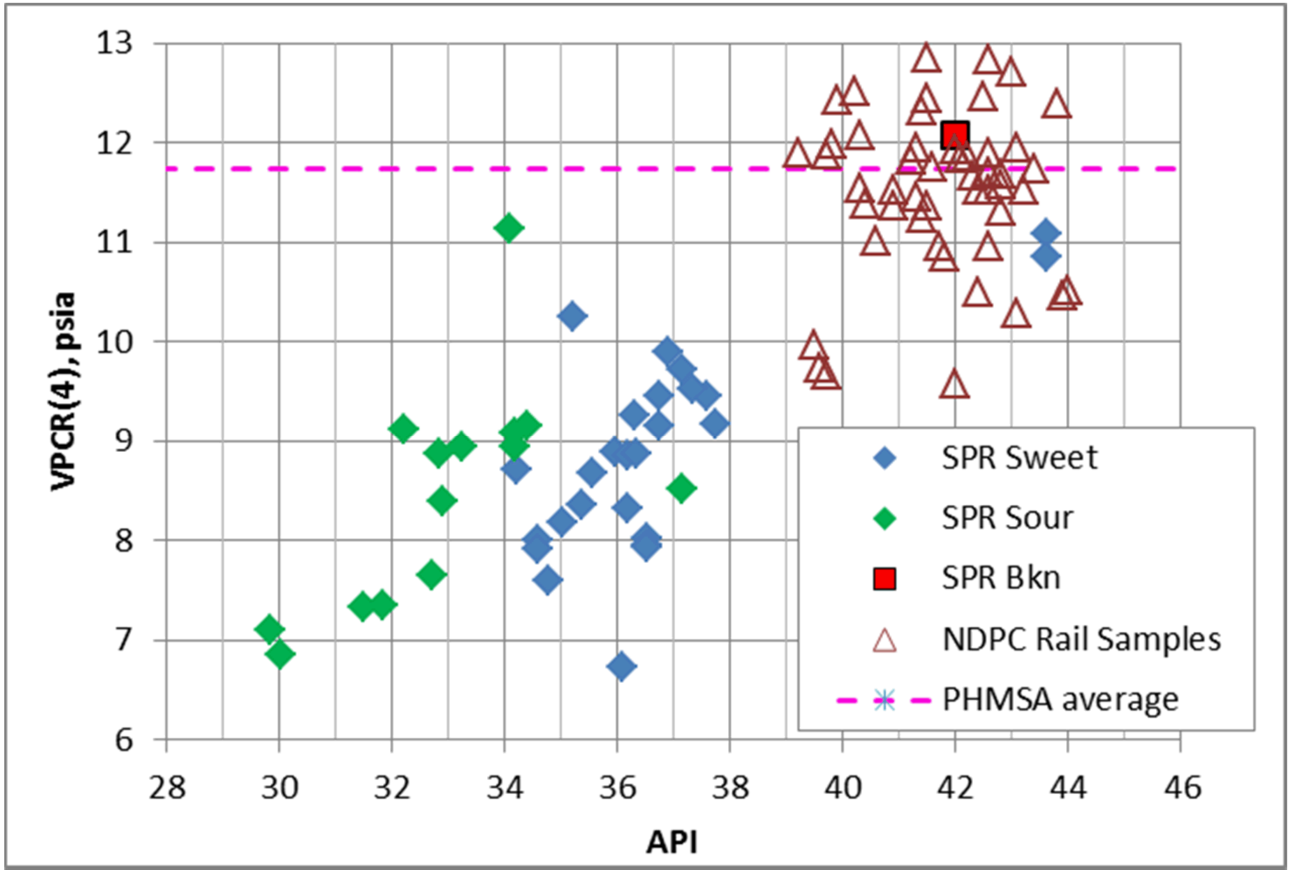
Observations so far...

- 2012 pipeline Bakken receipt at SPR exhibits slightly higher BPP and notably higher GOR that most other receipt crudes and current¥ sweet inventory
- Compositional comparison
  - FGOR fash gas analysis shows more C2-C4 in headspace above 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) vs. API Gravity

T = 100 F, SPR data from EOS, NDPC measured



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

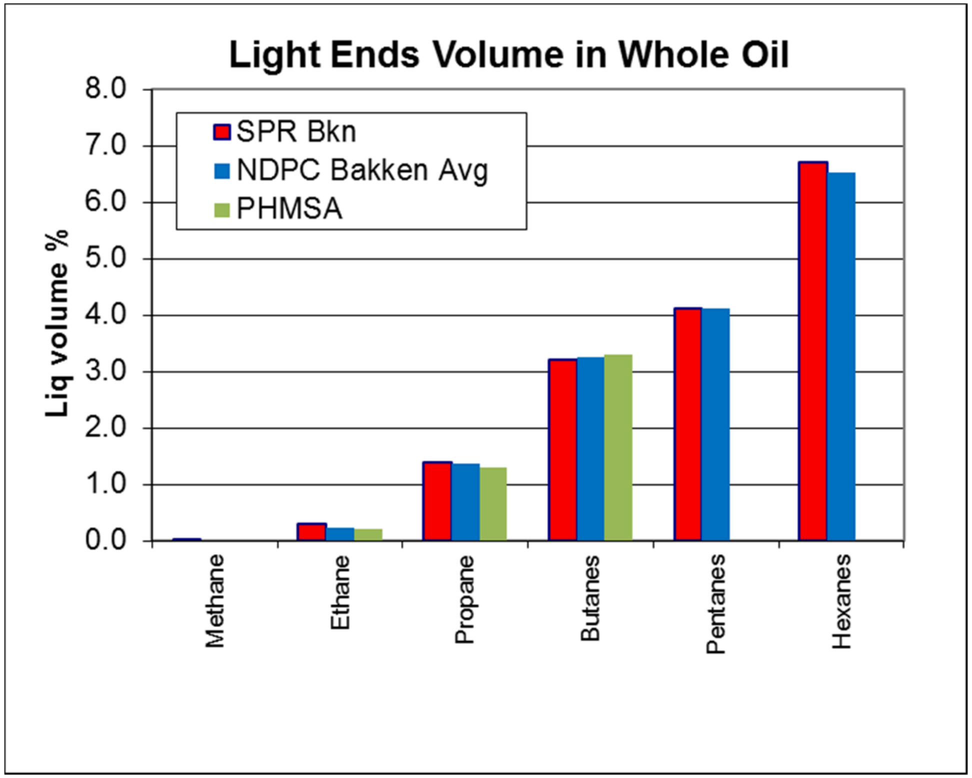
VPCR(4) preliminary comparisons

- Bakken data from three sources compare well for VPCR(4)
- Note SPR Bkn is one pipeline sample, run through flash separator, and simulated with EOS model

	VPCR(4) [psia]	Stdev [psia]
NDPC	11.5	0.8
PHMSA	11.7	1.0
SPR Bkn	12	

NDPC light ends vs. SPR Bkn

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



	NDPC	SPR Bkn	PHMSA
	liq vol %	liq vol %	liq vol %
Methane	0.00	0.02	0.00
Ethane	0.23	0.29	0.21
Propane	1.36	1.40	1.30
Butanes	3.25	3.20	3.29
Pentanes	4.11	4.11	0.00
Hexanes	6.52	6.71	0.00

Comparisons in Summary

- Sampling and analysis techniques differ among NDPC, PHMSA, and SPR, so direct comparison is difficult
- In spite of above, VPCR(4) @ 100 F 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
- VPCR(4) of Bakken independent of source (PHMSA, NDPC, SPR Bkn) is avg ~30% higher than typical light crude received and stored at SPR

Executive Summary

- Objective is to describe physical properties of crude oil relevant to flammability and transport safety
- 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
- Bakken crude, a representative tight oil, exhibits higher vapor pressure and gas oil ratio that typical SPR oils due to slightly higher mole fractions of light hydrocarbons
- There is room for improving QA/QC and associated understanding of crude oil vapor pressure measurements for characterizing volumes and compositions of gases that are likely to evolve from crudes in transport spill scenarios
- If and how these properties will relate to fire and explosion hazard is the key research question we need to address

END OF PREPARED SLIDES

TECHNICAL MEMBER BIOS

David Lord

- Principal Member of Technical Staff in the Geotechnology & Engineering Department, Sandia National Laboratories
- Currently Sandia technical lead on the U.S. Strategic Petroleum Reserve project
  - Scope includes storage system integrity, crude oil quality, and process safety related to long-term storage of crude oils in salt caverns
  - 10 years' experience as technical advisor to DOE on crude oil vapor pressure program
- Committee work
  - Co-author on pending American Petroleum Institute draft standard on crude oil phase behavior application to allocation (2009-present)
  - Member of API ad-hoc group on Crude oil Physical Properties (2014)
- Education
  - B.S. and M.S. Mechanical Engineering, U. of Michigan, Ann Arbor
  - Ph.D. Environmental Engineering, U. of Michigan, Ann Arbor

Anay Luketa

- Dr. Anay Luketa is currently a Principal Member of Technical Staff at Sandia National Laboratories in the Fire Science and Technology Department. She received a Doctor of Philosophy in Mechanical Engineering at the University of Washington. Her work pertaining to fires includes conducting blast, dispersion, and pool fire calculations using shock-physics and CFD models that include thermal-mechanical coupling. She has also been involved in model development and simulation of wildfires, fires involving composite materials, and solid propellant fires. Her work as pertained to applications involving Liquefied Natural Gas, NASA launch accidents, local wild land fires, and abnormal thermal environments involving nuclear weapons.

Steven Schlasner

Dr. Schlasner is a Research Engineer at the EERC and has over 30 years' experience in industry and government developing, designing, operating, and managing energy, chemicals, materials, and biological process technologies in R&D, engineering, and manufacturing environments. Steve led ConocoPhillips' R&D activities in the areas of CO_2 capture and hydrogen production, with related service as the company representative on the Executive Board of the European Commission's CACHET CO_2 capture project and as the industrial co-lead of DOE's FeedomCAR and Fuel Partnership's Hydrogen Production Technical Team. His experience also includes a decade as a process engineer in Phillips Petroleum's flagship refinery in Texas. His current R&D activities at the EERC focus on issues related to processing, utilization, and transportation of crude oil, natural gas, and CO_2. Dr. Schlasner holds Ph.D. and M.S. degrees in chemical engineering from The Ohio State University, an M.B.A. from the University of South Dakota, a B.S. in chemical engineering from the South Dakota School of Mines & Technology, and a B.A. in chemistry and mathematics from St. Olaf College. He is a registered Professional Engineer in Ohio and a licensed Professional Engineer in Oklahoma.

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Chad Wocken

Chad A. Wocken is a Senior Research Manager at the EERC where he leads projects related to oil and gas processing, alternative fuel development, and process optimization. His activities include research and development of technologies at the bench-, pilot-, and field demonstration scale. He holds a B.S. degree in Chemical Engineering from UND. Prior to his position at the EERC, he worked as a Project Engineer at URS/Radian International in Salt Lake City, Utah, and Milwaukee, Wisconsin, in the fields of emission control and environmental remediation.

Chad Wocken, Senior Research Manager
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David Rudeen

- Applied mathematician, programmer, data analyst on contract to Sandia for SPR, WIPP, DOE Tight Oils
  - Manages Sandia data and numerical codes related to SPR vapor pressure program
- 13+ years GRAM, Inc. (Contractor to SNL)
  - Drilling intrusion modeling in support of WIPP
  - 10 years VP and solution mining support of SPR
- 25+ years at New Mexico Engineering Research Institute (UNM-NMERI)
  - Ground-shock and air-blast modeling for the Air Force Weapons Lab
  - Ground-water-flow and contaminant-transport modeling in support of WIPP and YMP (nuclear waste repositories) as contractor to SNL.
- BS Mathematics UNM 1975

EXTRA SLIDES

EIA Definition of Domestic Crude Types

Measure of density

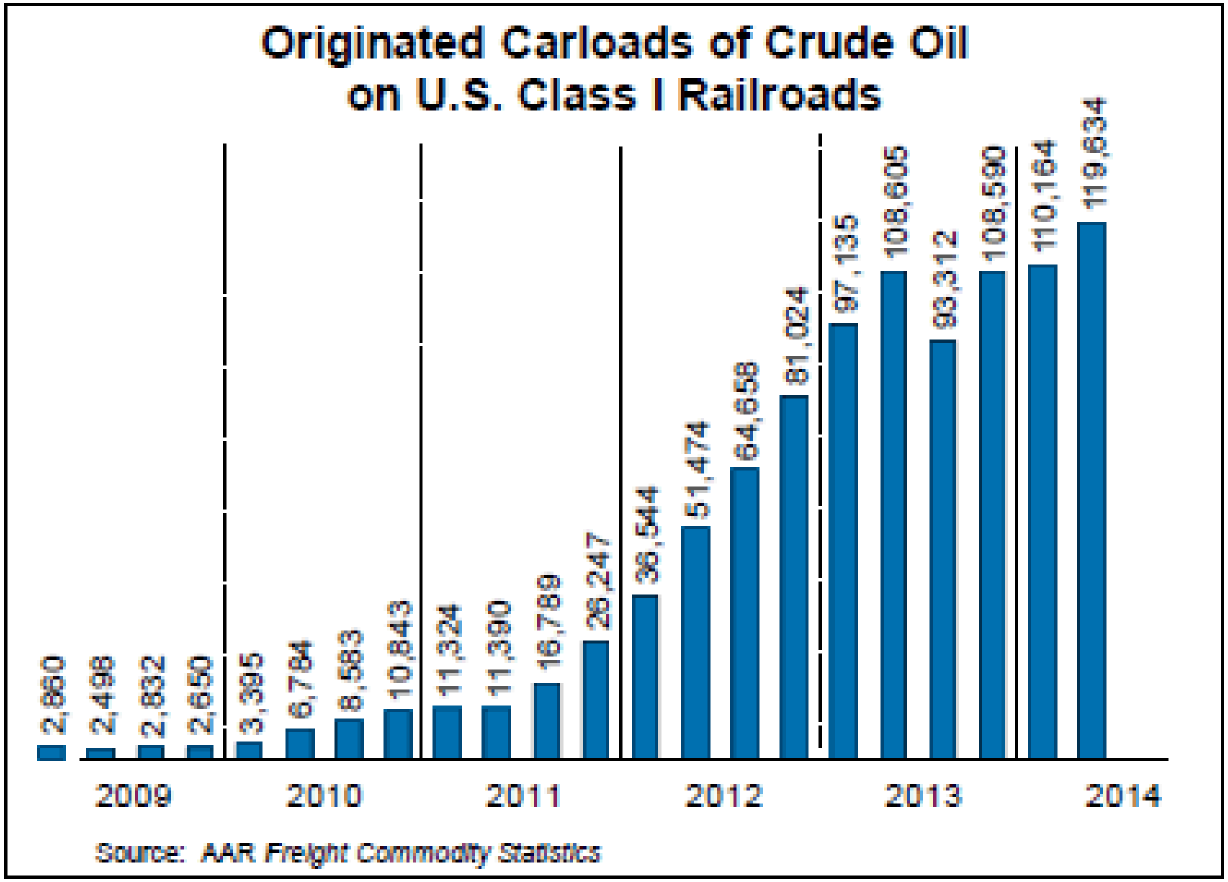
Sulfur

Table 1. Crude oil types considered in this analysis

Chart Color	Crude Oil Type	API Gravity (degrees)	Sulfur Content (%)	a.k.a.
	API 50+	API>=50	<0.3	
	*API 45-50	45<=API<50	<0.3	
	*API 40-45	40<=API<45	<0.3	Light Sweet
	API 40-50 sweet	40<=API<50	<0.3	
	API 35-40 sweet	35<=API<40	<0.3	
	API 35-40 sour	35<=API<40	<1.1	Light Sour
	API 27-35 med-sour	27<=API<35	<1.1	Medium Medium Sour
	API 27-35 sour	27<=API<35	>=1.1	Medium Sour
	California	API<27	1.1-2.6	
	API<27 sweet	API<27	<1.1	Heavy Sweet
	API<27 sour	API<27	>=1.1	Heavy Sour

*Specified only where additional well-level API gravity data are available.

Source: EIA. (2014). "U.S. Crude Oil Production Forecast - Analysis of Crude Types." U.S. Energy Information Administration. U.S. Department of Energy. Washington, DC 20585.



~900,000 bbl/day for first half 2014

Source: AAR. 2014. "Moving Crude Oil by Rail," American Association of Railroads, Washington, DC.

API gravity

API	RHO	RD
[deg]	[kg/m^3]	[-]
50	779	0.780
45	801	0.802
40	824	0.825
35	849	0.850
30	875	0.876
25	903	0.904
20	933	0.934
15	965	0.966
10	999	1.000

$$API = \left(\frac{141.5}{RD}\right) - 131.5$$

$$RD = \left(\frac{\rho_{oil}}{999.016 \, {}^{kg}\!/_{m^3}}\right)$$

Relative density (as compared to water at 60 F)