### The Complications in Defining Oil-In-Place Estimates in Source Rock Reservoirs – Total vs. Producible Oil and Mass Balance Characterization\*

#### Chad Hartman<sup>1</sup>

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<sup>1</sup>Stratum Reservoir, Houston, Texas (<u>chad.hartman@stratumreservoir.com</u>)

#### **Abstract**

At the onset of hydrocarbon generation no prolific expulsion (even into the inorganic porosity of the source rock itself) will occur until the absorption potential of the kerogen is first accommodated. This is a direct result of the oleophilic nature of kerogen and the parent-child relationship between the precursor solid kerogen and soluble hydrocarbon byproducts. Once the kerogen is fully saturated a "pre-migration" can finally occur wherein oil is expelled from the kerogen and begins to fill the mineral matrix scaffolding of the source rock. Eventually the entire source rock will become saturated at which point oil pressure will continue to build until either primary migration into adjacent carrier beds occurs, or the oil pressure finally exceeds the mechanical strength of the adjacent beds and fractures them, causing a "burping" event. Even after a source rock has ceased any further hydrocarbon generation or expulsion it is important to recognize that the kerogen itself is still fully saturated to whatever extent the remaining kerogen structure can accommodate absorbed oil.

This kerogen associated oil is, for all practical purposes, trapped and not producible due to the extremely strong chemicophysical interactions between the two components. For this reason it might be more appropriate to consider this fraction of oil as nothing more than a soluble fraction of the kerogen's intrinsic biomass rather than oil that can be exploited and produced. Furthermore, carbonate source rocks are usually composed of mudstones or wackestones which contain pore throats small enough that they can behave like a molecular sieve, resulting in preferential production of the smaller, lower molecular weight hydrocarbon compounds, while the larger, higher molecular weight components are left behind in the rock. Collectively these attributes make it challenging to determine what exactly is being described by a given OIP estimate, which can differ dramatically depending upon what laboratory techniques are employed. These concepts and the various lab-based analytical methods that can be used to derive Oil-In-Place (OIP) estimates will be discussed followed by some proposed ideas on how to integrate and interpret the resulting data to facilitate a partitioning between total OIP and producible OIP which we believe is necessary to better characterize these unique reservoirs and make improved predictions of potential recovery.





# The Complications in Defining OIP Estimates in Source Rock Reservoirs - Total vs. Producible Oil and Mass Balance Characterization

**Chad Hartman** 

Chief Technical Advisor – Unconventional Reservoir Services
STRATUM RESERVOIR

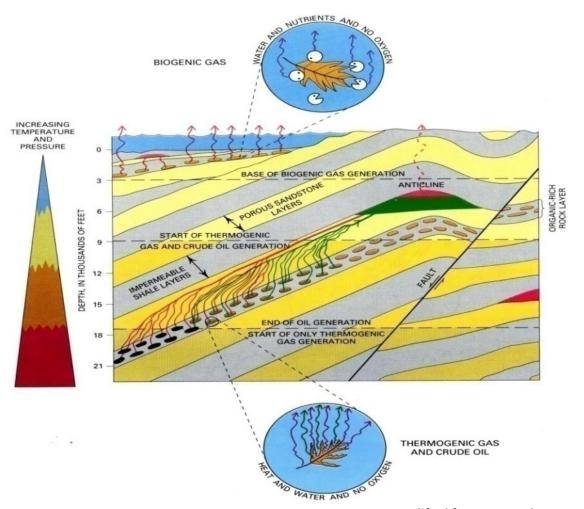


# **Essential Elements of Liquid Bearing Source Rock Reservoirs**



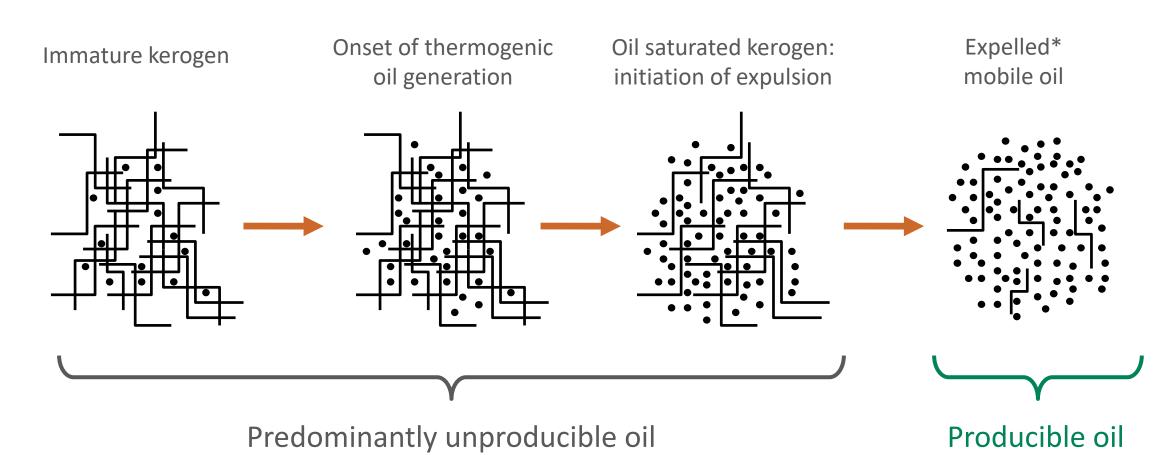
### Characteristics of Unconventional, Continuous Tight-oil Accumulations

- Mature source rocks containing Type II kerogen
- Frequently associated with adjacent, organically lean, carrier beds
- Pervasive petroleum saturation (NOC > 100)
- Oil composition at various maturity levels is an important factor in oil producibility and recovery
- Abnormally pressured
- Generally lack down-dip water
- Reservoir properties enhanced by fracturing and partings
- $\phi S_o > 1\%$  BV





# Hydrocarbon Generation Caveats and Source Rock "Pre-Migration"



\*Expulsion here refers to expulsion from kerogen and does not necessarily suggest primary expulsion and migration from the source rock.



Perhaps a few mm in thickness

# Hydrocarbon Generation Caveats and Source Rock "Pre-Migration"

Absorbed Immobile Oil **Accumulated mobile oil** Absorbed Immobile Oil **Accumulated mobile oil** Absorbed Immobile Oil Continuous Kerogen Lamina **Inorganic Source Rock Scaffolding** 

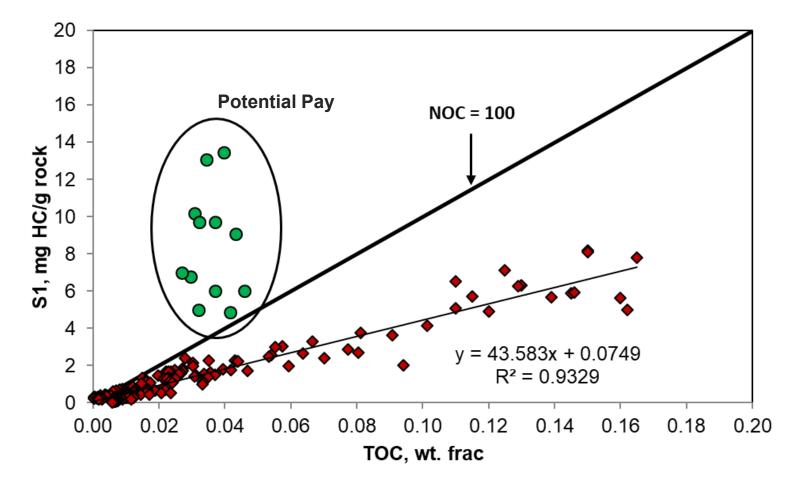


# Importance of Prolific Oil Saturation on OIP Producibility

- When NOC > 100, whenever tested, always flowed oil/gas\*.
- When NOC < 100, variable results but usually negative\*.
- Most economic unconventional oil plays have oil saturations greater than 100 mg of oil per gram of TOC and contain over 1 mg HC/g Rock\*.

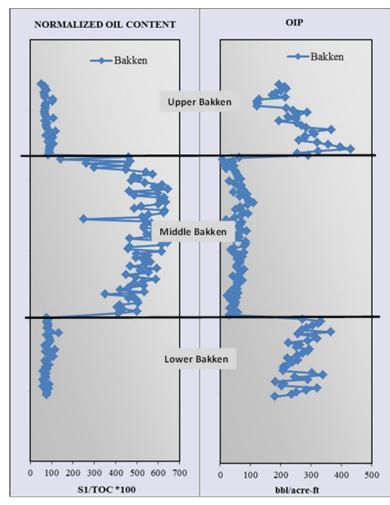
$$NOC = \frac{S1}{TOC} 100$$

NOC normalized oil content, mg HC/g TOCSI pyrolysis S1 peak, mg HC/g RockTOC total organic carbon, wt. %

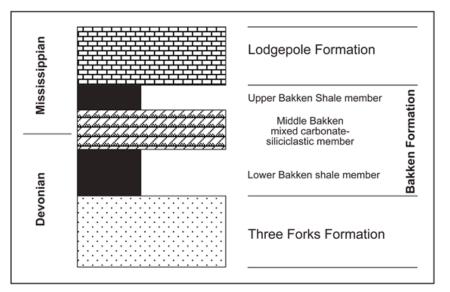




# Importance of Prolific Oil Saturation on OIP Producibility



 ${\it Pyrolysis\ data\ obtained\ from\ the\ ND\ Geological\ Survey}$ 

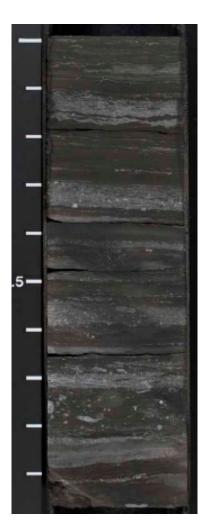


Egenhoff et al, 2010

### **Flagged Pay**

- NOC > 100
- Oil > 1 mg Oil/g Rock
- $\phi S_o$  (frac BV) > 0.01

- 1 ft core interval.
- Carbonate lithology.
- Contains the same laminated facies on a much smaller scale.





# Hydrocarbon Molecular Weight, Phase, and Viscosity Considerations

 $C_{70} - 984 \text{ g/mol}, 6 \text{ API}^{\circ}$ 

C<sub>45</sub> – 633 g/mol, 10 API°

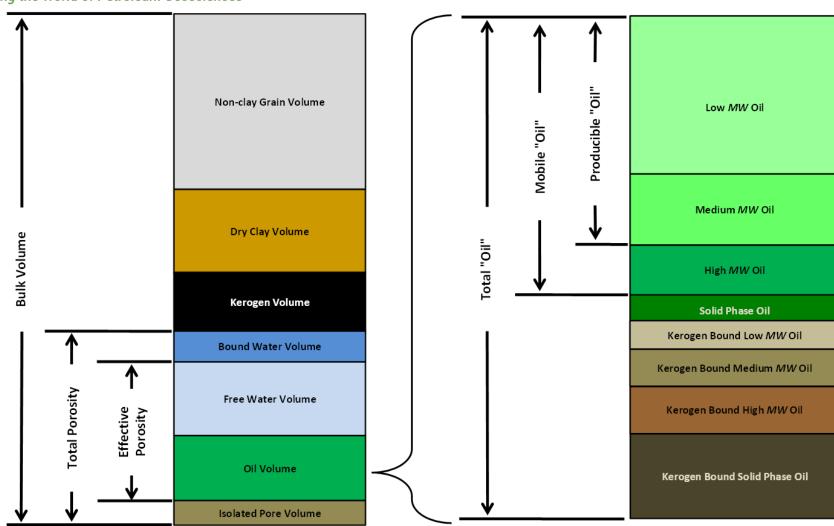
 $C_5 - 72 \text{ g/mol}, 92 \text{ API}^\circ$ 



Nomenclature	Formula	Molar mass (g)	Boiling point (°C)	Phase at 25°C
Methane	CH4	16.04	-162.00	gas
Propane	C3H8	44.10	-42.00	gas
Pentane	C5H12	72.15	36.00	liquid
Heptane	C7H16	100.20	98.00	liquid
Nonane	C9H20	128.26	150.80	liquid
Undecane	C11H24	156.31	195.90	liquid
Tridecane	C13H28	184.37	235.40	liquid
Pentadecane	C15H32	212.42	270.60	liquid
Heptadecane	C17H36	240.47	302.00	liquid
Nonadecane	C19H40	268.53	330.00	solid
Heneicosane	C21H44	296.58	356.50	solid
Tricosane	C23H48	324.63	380.00	solid
Pentacosane	C25H52	352.69	401.00	solid



# Petrophysical Components of a Liquid Bearing Source Rock Reservoir

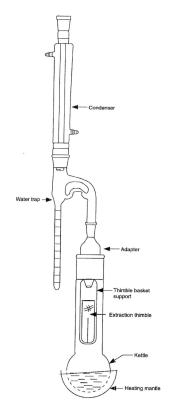




# **Laboratory Methods for OIP Determination**



- Dean-Stark toluene extraction removes free water, bound water, and oil (including bitumen).
- Water is measured. Oil is calculated by weight difference.



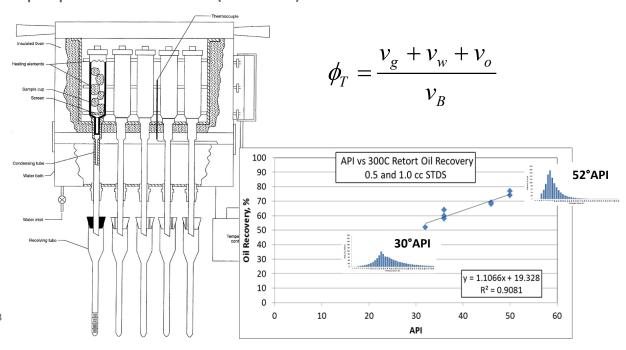
$$v_o = \frac{m_{pre} - (m_{post} + m_{water})}{\rho_o}$$

#### where:

$\phi_T$	total porosity, fctn
$V_g$	volume gas, cm <sup>3</sup>
$v_w$	volume water, cm <sup>3</sup>
$v_o$	volume oil, cm <sup>3</sup>
$v_B$	bulk volume rock, cm <sup>3</sup>
$v_o$	volume oil, cm <sup>3</sup>
$m_{pre}$	pre-test sample mass, g
$m_{post}$	post-test sample mass, g
$m_{water}$	extracted water mass, g
$\rho_{o}$	assumed oil density, g/cr

# OIP Estimates from "Routine" Analysis (CRA and Retort)

- 300°C thermal extraction. Volatilized compounds are condensed and captured (water and oil).
- Total porosity is not measured, instead it is determined via summation of fluids.
- Oil volume is directly measured.
- Fraction of oil recovery (relative to solvent based methods) is proportional to API° (i.e. MW).





#### TPH IR Analysis - Processor: C:\Program Files\Thermal Station\Data\JAN15B\526A.RAW \_ 🗆 × File Help CO: 28.64mV Tmax · IR CO 853.94mV IR CO2 853.94mV 15:00 20:00 10:00 25:00 30:00 35:00 VTPH (S1): 0.99 mg/g pTPH (S2): 12.14 mg/g cTemp(Tmax): 418.6 °C tTemp: 457.6 °C S3: 1.35 mg/g TOC: 3.65 % PI: 0.08 S1/TOC: 0.27

### OIP Estimates from Programmed Pyrolysis Analysis

 Reasonable assumptions are made for oil and rock densities. Or if known, real values can be applied.

$$\rho_{oil} = \frac{0.886g}{cc} \qquad \rho_{shale} = \frac{2.5g}{cc}$$

• S1 values are quantitative and reported as mg HC/g rock. Using the assumed oil and rock densities simple unit conversion can be used to estimate OIP volumes.

$$\frac{mg\ HC}{g\ Rock} = \frac{\frac{1 \times 10^{-3}\ g\ HC}{0.886\ g\ oil}}{\frac{g\ Rock}{2.5\ g\ shale}} = \frac{1.13 \times 10^{-3}\ cc\ oil}{0.4\ cc\ shale} = 2.82 \times 10^{-3}\ \frac{cc\ oil}{cc\ shale}$$

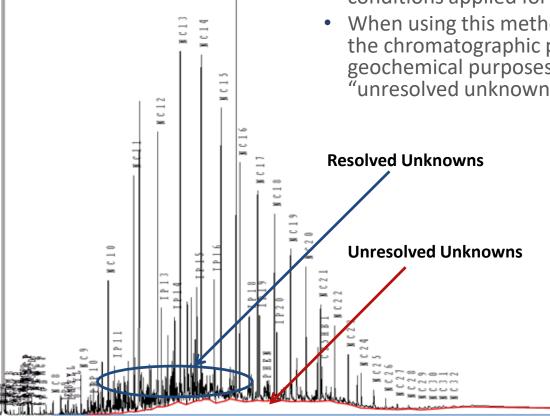
$$2.82 \times 10^{-3} \frac{cc \ oil}{cc \ shale} \left( \frac{6.29 \times 10^{-6} \frac{bbl}{cc}}{8.11 \times 10^{-10} \frac{acre - ft}{cc}} \right) = 21.89 \frac{bbl}{acre - ft}$$

$$S1 \times 21.89 = \frac{bbl}{acre - ft}$$



### OIP Estimates from Cold CS<sub>2</sub> Extraction and HRGC

- The sample material is taken through a series of unheated extractions using cold CS2 and the resulting extract is spiked with an internal standard (trans-2-heptene).
- The extract is then subject to high resolution gas chromatography using the same standard conditions applied for whole oil/extracts.
- When using this method determining OIP estimates requires an analysis of the total area under the chromatographic peaks, to include complex oil components typically not evaluated for geochemical purposes. These complex components included "resolved unknown" and "unresolved unknown" oil isomers



$$C = \frac{m_{ISTD}}{A_{ISTD}} \longrightarrow m_o = A_T C \longrightarrow V_o = \frac{m_o}{\rho_o}$$

C quantitative conversion constant, g ISTD/ISTD integrated peak area

 $m_{ISTD}$  mass of internal standard, g

 $A_{\it ISTD}$  integrated area of the internal standard peak, unitless

 $m_o$  mass of oil in the extract, g

 $A_T$  total integrated area of all peaks in the extract, unitless

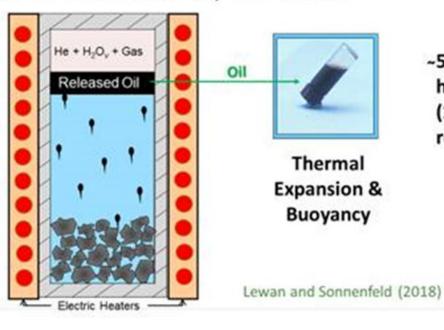
 $V_o$  total volume of oil in the total mass of the  $i^{th}$  component, g

 $\rho_o$  assumed oil density, g/cm<sup>3</sup>



# OIP Estimates from Low Temperature Hydrous Pyrolysis (LTHP)

Low-Temperature Hydrous Pyrolysis (LTHP) is performed under aqueous conditions in a closed-system reactor



### Conditions

~500 g of 12/20 mesh crushed rock is heated at 300°C (572°F) and 9 MPa (1300 psi) for 24 hours in a 1-liter reactor in the presence of liquid water

### **Products**

Producible Retained Oil
Water
Gas
Remaining Core Material

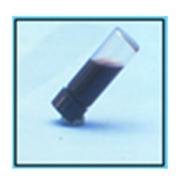




### LTHP Released Oil vs. Retort Released Oil

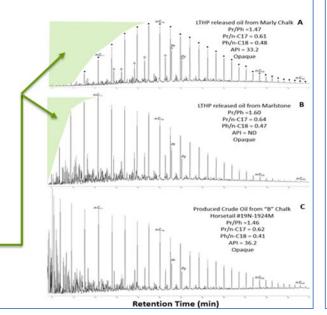
**LTHP** 

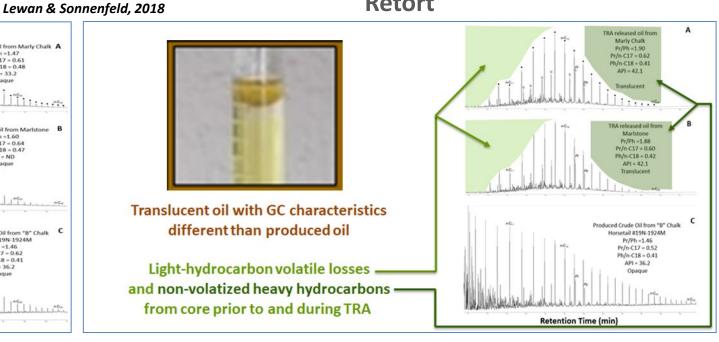
Retort



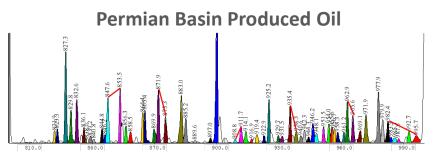
Opaque black oil with GC characteristics similar to produced oil

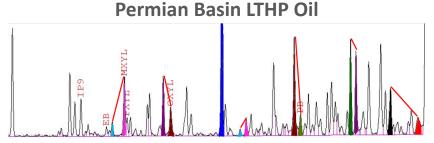
Light-hydrocarbon volatile losses from core prior to LTPH





LTHP results in oil yields that are characteristic of produced oils. So much so that there are indications LTHP oil yields might very well be suitable for endmember production allocation.







# Data Integration and Total Oil Mass Balance Characterization



## Comparison of OIP Estimates from All Methods

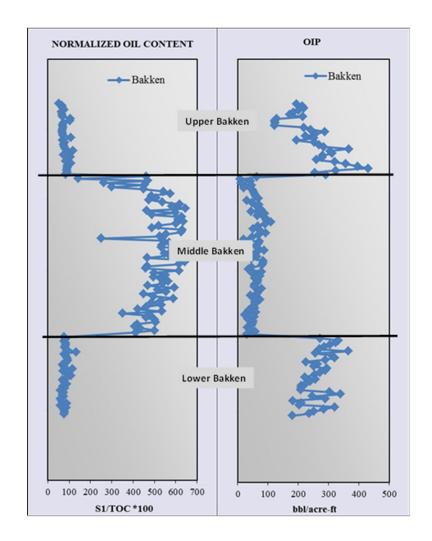
### This table contains no real data and serves only as an example based on observed trends.

Method	Attributes	OIP	NOC*
Method	Attributes	bbl/acre-ft	
Pyrolysis	300°C Thermal extraction, mass/mass basis converted to volume/volume basis	69.32	103.00
Retort	300°C thermal extraction, volume/volume basis (and mass/mass basis)	82.49	122.57
LTHP	300°C, 1300 psia, aqueous submerged extraction in a closed system reactor	131.16	194.89
Cold Solvent Extraction - HRGC	Cold CS <sub>2</sub> solvent extraction, mass/mass basis converted to volume/volume basis	223.90	332.69
CRA	Toluene reflux solvent extraction, mass difference converted to volume/volume basis	263.42	391.40



### **Conclusions**

- Solvent based methods result in an overestimation of producible OIP.
- Solvent based methods also result in oil compositions that are heavier than produced oils.
- Pressure core evaluation, wherein both gas and oil are quantified, result in:
  - Oil composition that is "heavier" than an oil sample obtained from a surface separator
  - GOR < Surface separator GOR</li>
  - CGR > Surface separator CGR
- Its probably safe to say that thermal based extraction methods provide more reasonable estimates of producible OIP compared to solvent based OIPs.
- Comprehensive work involving an integration of solvent, thermal, and other laboratory methods hold great promise to help partition producible oil volumes, composition, and fluid behavior from total estimates of the same.





## For additional information, please contact:

### Emirates Link Stratum Reservoir ICAD II Abu Dhabi

### **Chad Hartman**

Chief Technical Advisor <a href="mailto:chad.hartman@stratumreservoir.com">chad.hartman@stratumreservoir.com</a>

### AJ - Abul Jamaluddin, Ph.D.

Director, Technical Services & Business Development Eastern Hemisphere abul.jamaluddin@stratumreservoir.com

