Experimental Study of Green River Oil Shale Pyrolysis

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TOTAL

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Schlumberger

Purposes of the Study

Use modern analytical methods to characterize oil shale pyrolysis products

- N. Bostrom et al., "Realistic Oil Shale Pyrolysis Programs: Kinetics and Quantitative Analysis", 2009 Oil Shale Symposium

Explore relationship between formation evaluation and production performance

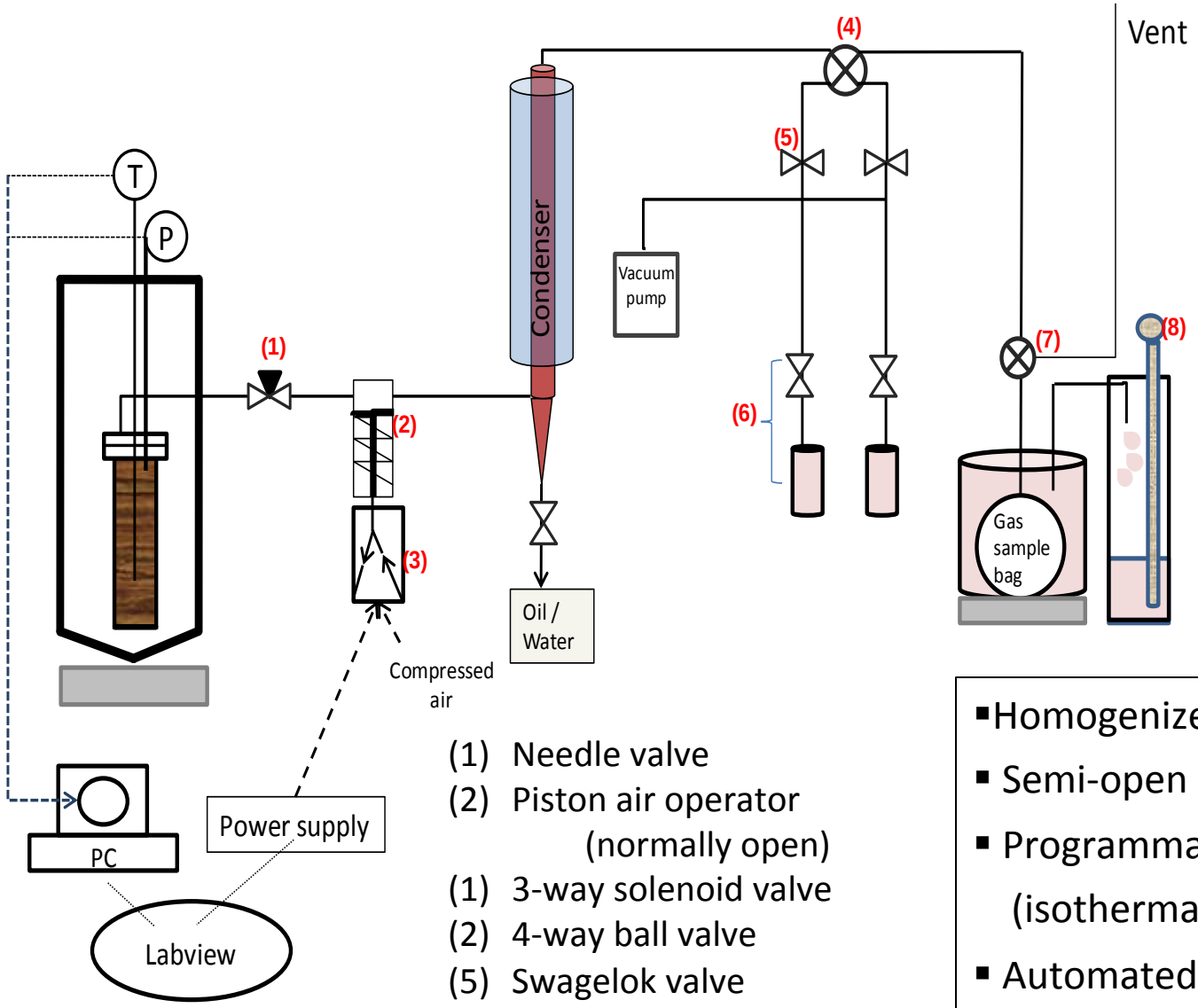
- R. Kleinberg et al., "Oil Shale Formation Evaluation by Well Logs and Core Measurements", 2010 Oil Shale Symposium
- S. Reeder et al., "A Multi-Measurement Core-Log Integration for Advanced Formation Evaluation of Oil Shale Formations", 2011 Oil Shale Symposium

Provide theoretical framework for AMSO/TOTAL Piceance Basin production test

- T.V. Le Doan et al., "Oil Shale Pyrolysis Laboratory & Technique", 2011 Oil Shale Symposium

See also Pomerantz et al., "Oil Shale Pyrolysis Products: Physical & Chemical Characterization", this meeting

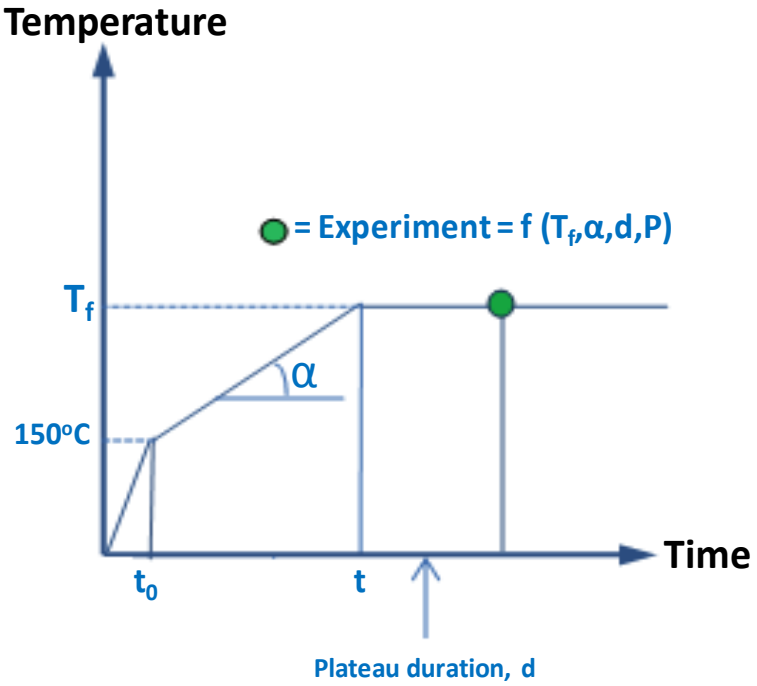
Laboratory Simulation of AMSO *in situ* Process



(1) Needle valve
(2) Piston air operator (normally open)
(1) 3-way solenoid valve
(2) 4-way ball valve
(5) Swagelok valve
(6) Gas sample tube
(7) 3-way stopcock
(8) Level measurement probe

- Homogenized sample
- Semi-open system
- Programmable temperature profile (isothermal/non-isothermal)
- Automated back pressure regulator
- Monitor temperature & pressure
- Measure volume of all products

Experimental Plan



28 Experiments

Heating Rate α (°C/h)	2-120
Plateau Temperature T_f (°C)	303-425
Plateau Duration d (h)	7.5-12.5
Pressure P (psi)	149-745

TOTAL

Heating rate (°C/h)	Temperature (°C)	Plateau duration (h)	Pressure (psi)
2	362.5	10	440
6	331.3	7.5	294
6	393.8	7.5	294
6	331.3	12.5	294
6	393.8	12.5	294
6	331.3	7.5	588
6	393.8	7.5	588
6	331.3	12.5	588
6	393.8	12.5	588
20	300	10	440
20	425	10	440
20	362.5	5	440
20	362.5	15	440
20	362.5	10	149
20	362.5	10	745
20	362.5	10	440
20	362.5	10	440
20	362.5	10	440
63	331.3	7.5	294
63	393.8	7.5	294
63	331.3	12.5	294
63	393.8	12.5	294
63	331.3	7.5	588
63	393.8	7.5	588
63	331.3	12.5	588
63	393.8	12.5	588
63	362.5	12.5	294
120	362.5	10	440

Samples

Illite-rich oil shale from the Green River R-1 zone (BH-1 2012-2088 ft)

Sample Preparation:

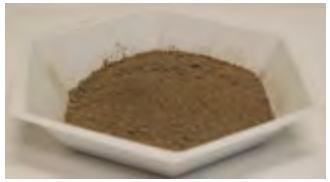
Homogenize, split & crush bucket of cuttings into 100 g samples

(particle size 100-200 µm)

Rock-Eval 6 Parameters : 13 Replicate Samples									
	TOC (%)	S1 (mg/g)	S2 (mg/g)	Tmax (°C)	PI (g/g)	HI (mg/ gC)	OI (mg/ gC)	RC (%)	Min C (%)
Mean Value	13.02	5.5	112.23	438.08	0.05	862.31	5.38	3.2	2.11
Std Dev	0.41	0.5	2.79	0.86	0.01	14.06	0.65	0.27	0.12

TOTAL

Analytic Flow Chart



Oil Shale (Native State)

Rock-Eval
Fisher Assay

Pyrolysis

Gas

GC-FID
GC-TCD
H_2S Drager

Water

Oil

CHNSO
GCXGC
LC
GPC
NMR
XANES

Spent Shale

Rock-Eval

DCM/MeOH

Extracted Bitumen

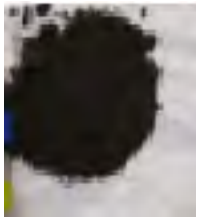
Rock-Eval
LC, GPC
XANES
CHNSO

Spent Shale after Bitumen Extraction

Rock-Eval

HCl/HF

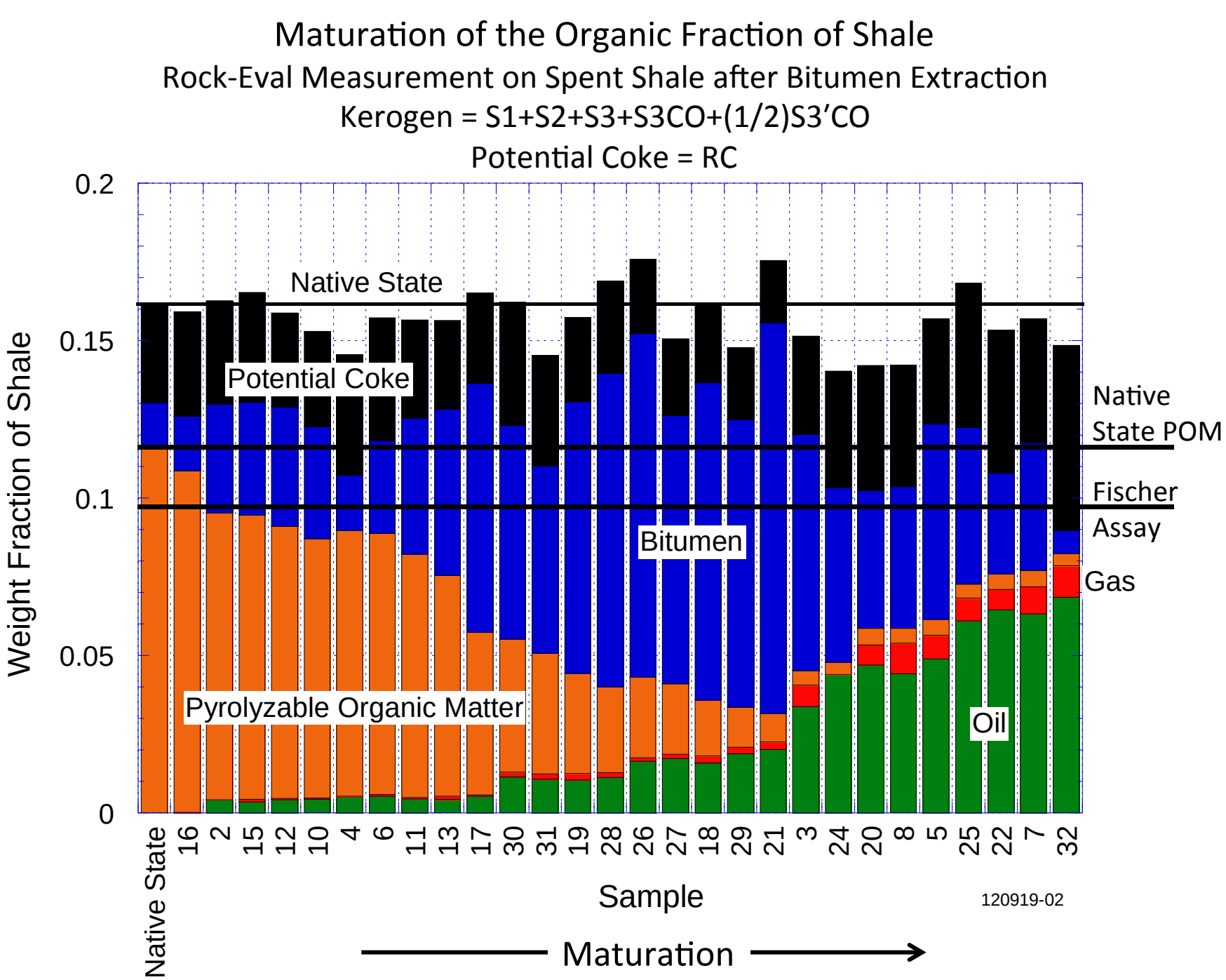
Isolated Kerogen + Coke + Impurities



Other measurements include matrix density, NMR low & high field, major oxides, FTIR, UV-Vis, organic elemental analysis, surface area and pore volume

⇒ *1983 analytic procedures*

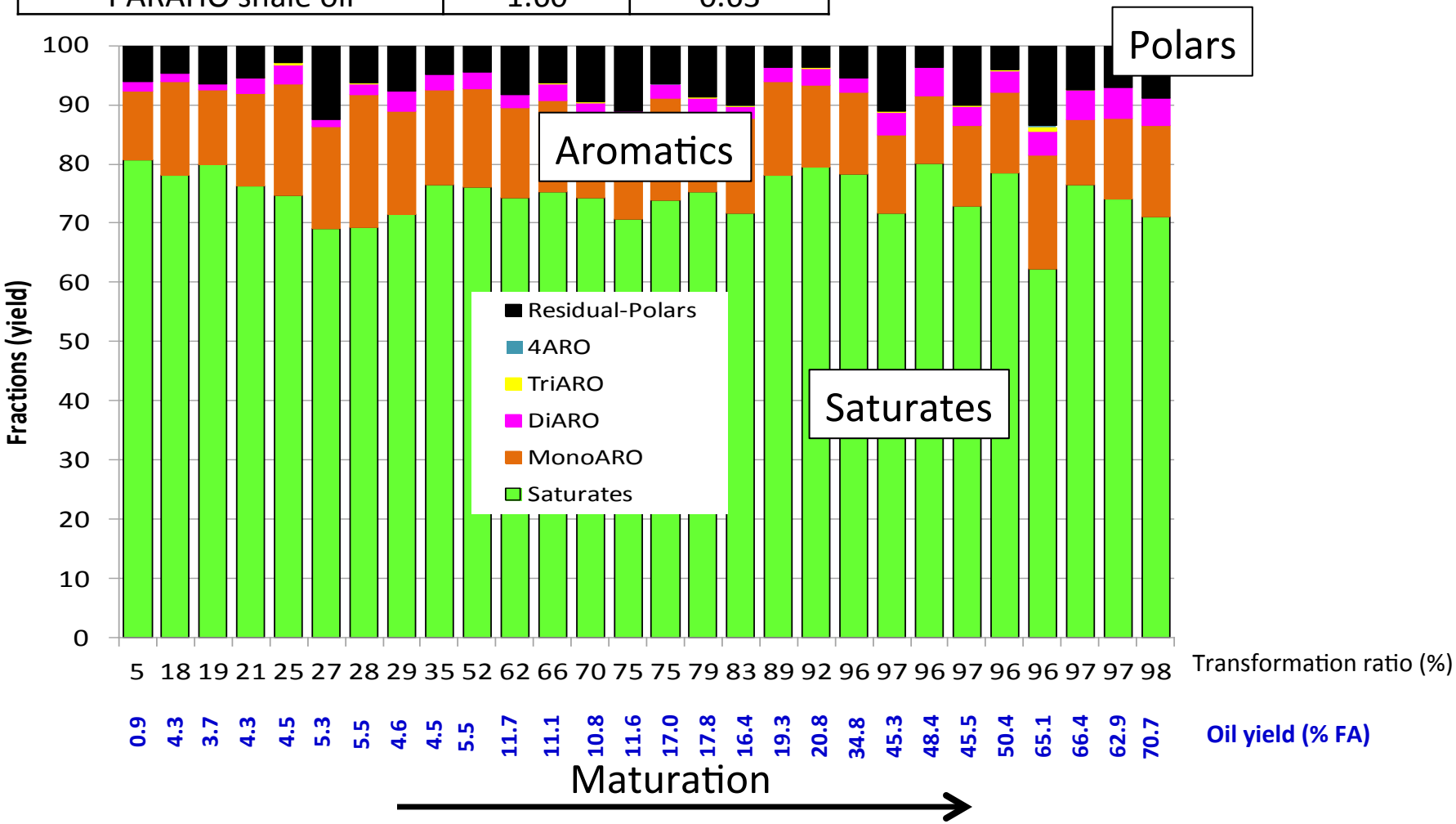
most performed by Schlumberger & TOTAL in-house labs


Maturation of the Organic Fraction of Shale
Rock-Eval Measurement on Spent Shale after Bitumen Extraction
Kerogen = S1+S2+S3+S3CO+(1/2)S3'CO
Potential Coke = RC
Weight Fraction of Shale
0.2
0.15
0.1
0.05
0
Native State
Potential Coke
Native State POM
Fischer Assay
Bitumen
Gas
Pyrolyzable Organic Matter
Oil
Native State
16
2
15
12
10
4
6
11
13
17
30
31
19
28
26
27
18
29
21
3
24
20
8
5
25
22
7
32
Sample
120919-02
Maturation

Oil Composition by 2D Gas Chromatography

Type of oils	H/C (atom)	S (wt%)
SDR shale oil	1.88	0.2-0.8
Arabian Light crude	1.94	1.7
TOSCO shale oil	1.58	0.76
PARAHO shale oil	1.60	0.63

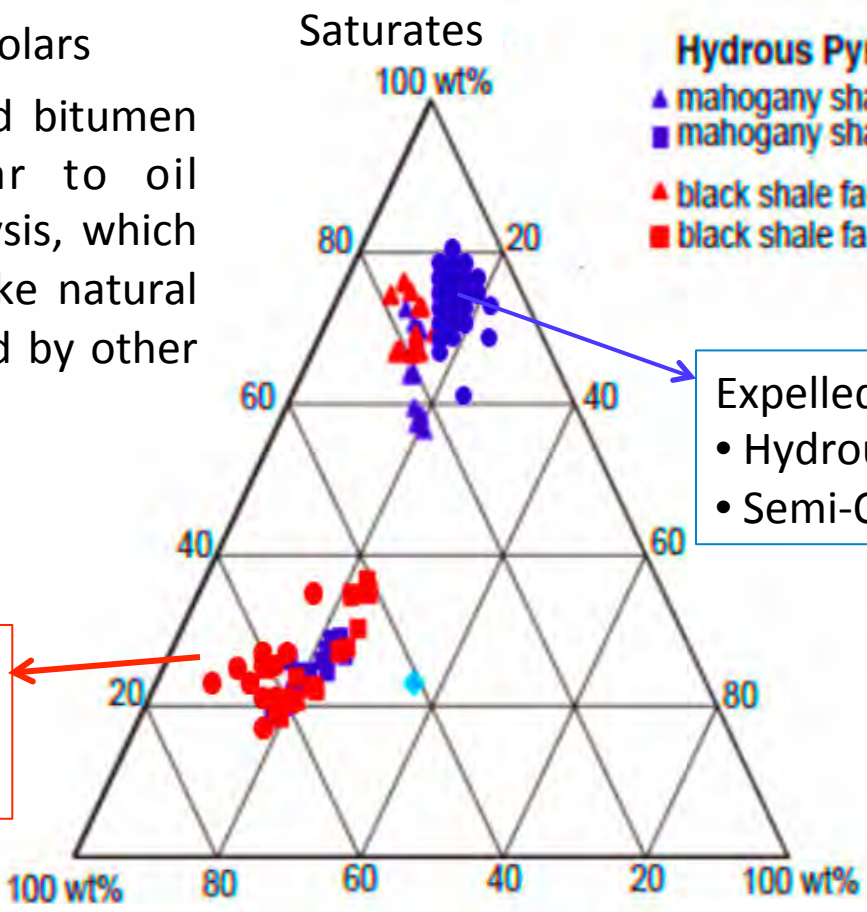
- Dominated by saturates
- Few polyaromatics - favorable for refinery processes



Compare to Hydrous Pyrolysis

Semi-open system

- Expelled oil rich in saturates
- Extracted bitumen rich in polars
- Expelled oil and extracted bitumen have composition similar to oil produced by hydrous pyrolysis, which is considered much more like natural petroleum than oil produced by other methods of pyrolysis



Expelled Oil
- Hydrous Pyrolysis (Ruble)
- Semi-Open (this work)

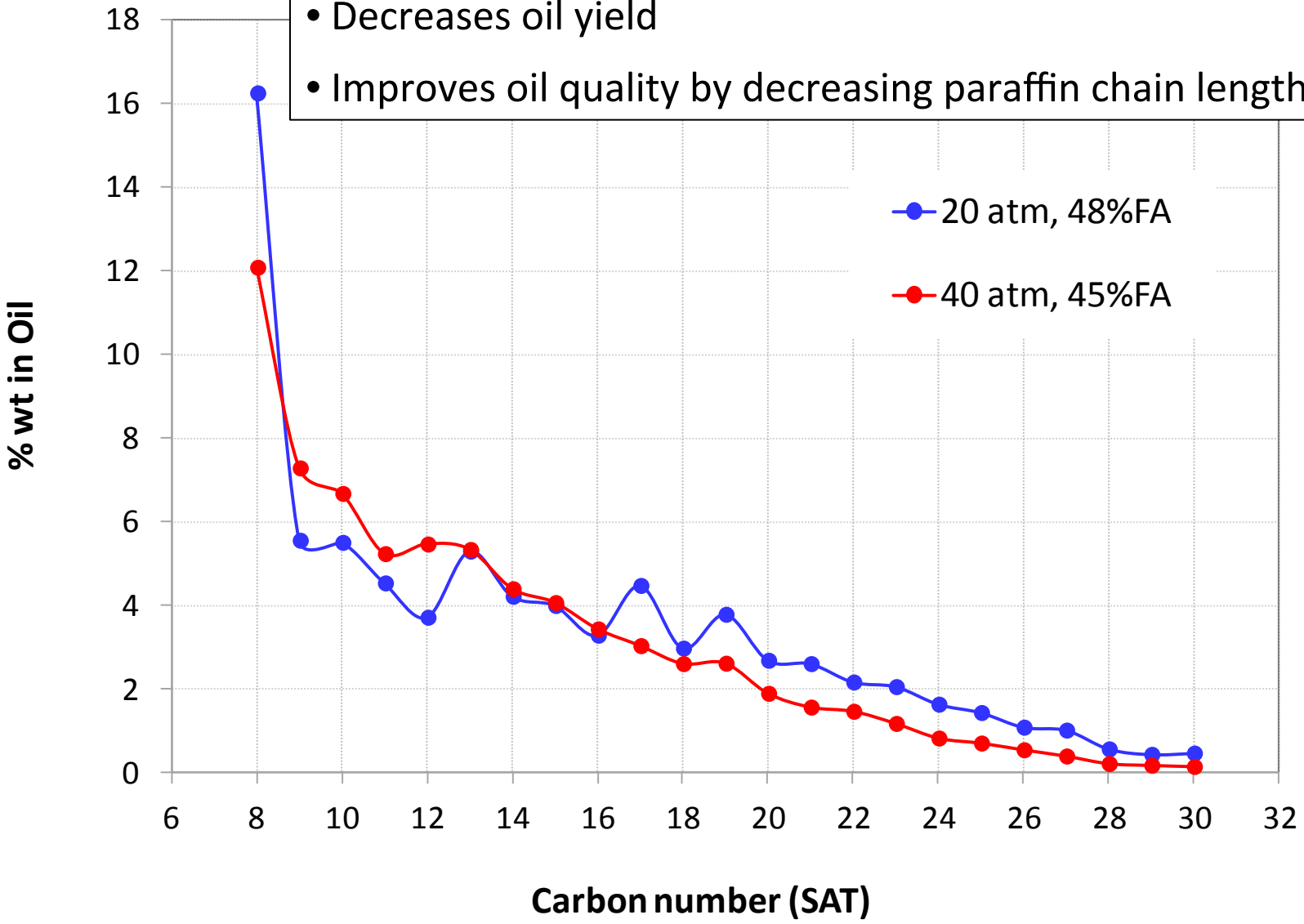
Extracted Bitumen
- Hydrous Pyrolysis (Ruble)
- Semi-Open (this work)

Adapted from Ruble et al., AAPG Bulletin 85, p.1333-1371, 2001

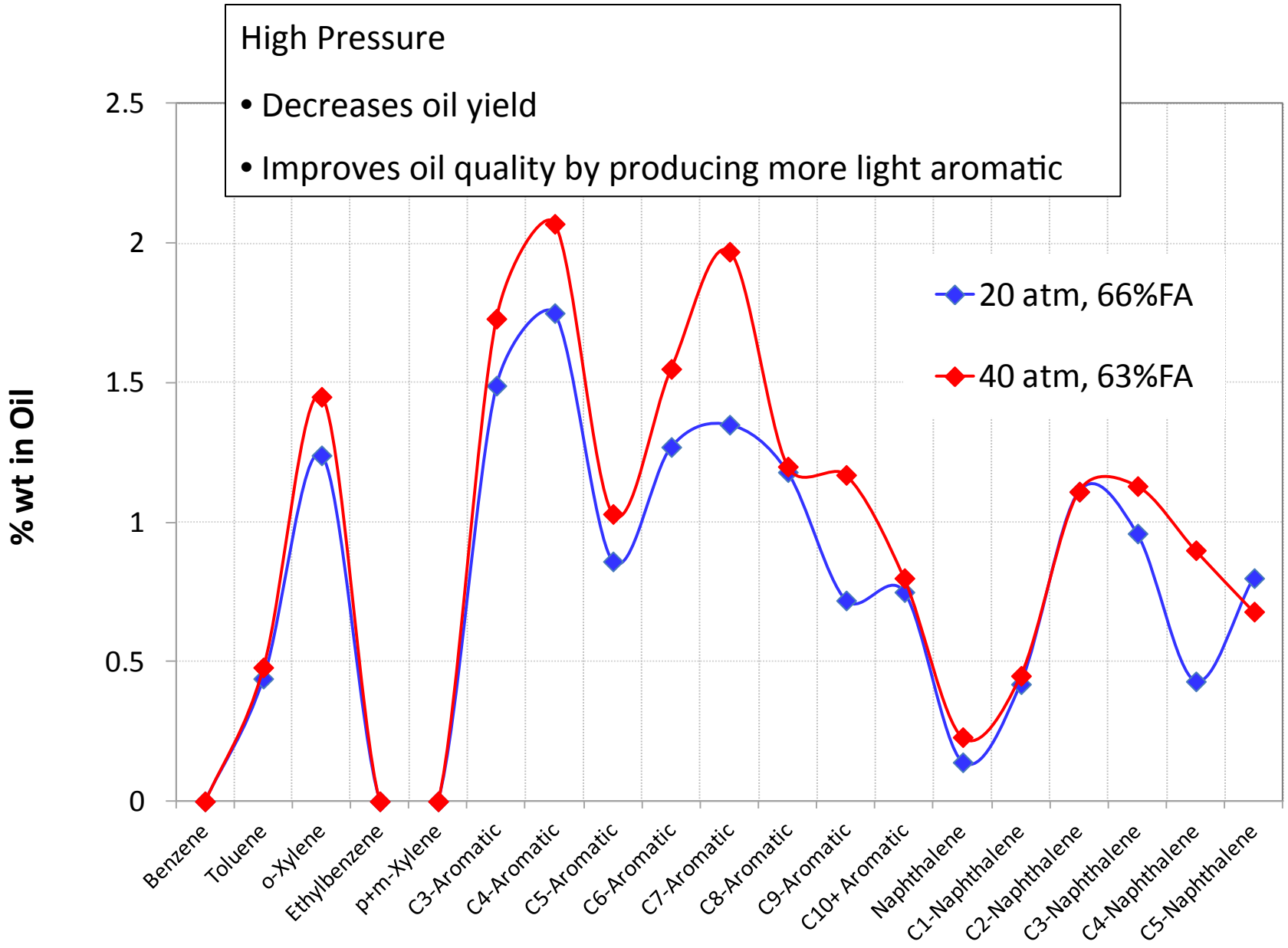
Effect of Pressure on Oil Yield & Composition (1)

High Pressure

- Decreases oil yield
- Improves oil quality by decreasing paraffin chain length



Effect of Pressure on Oil Yield & Composition (2)



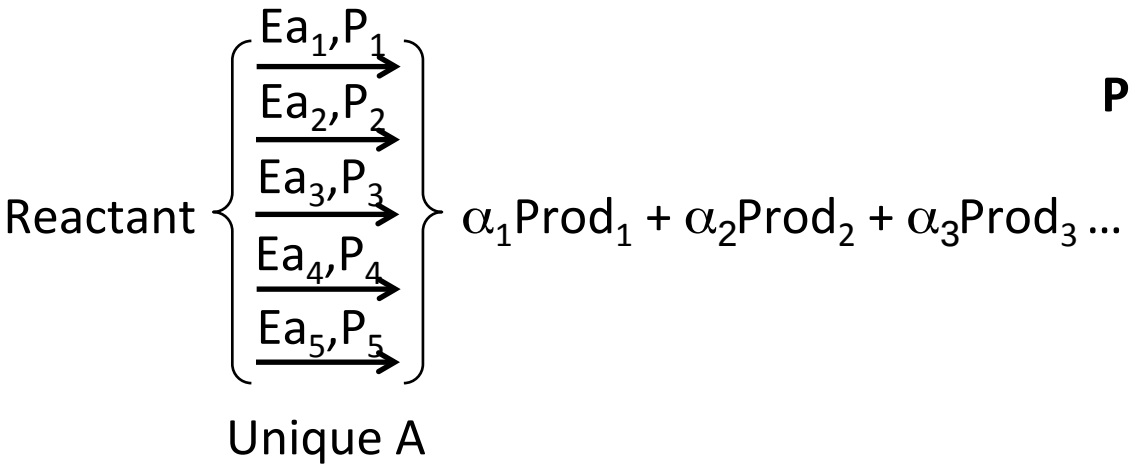
Compositional Kinetic Model (1)

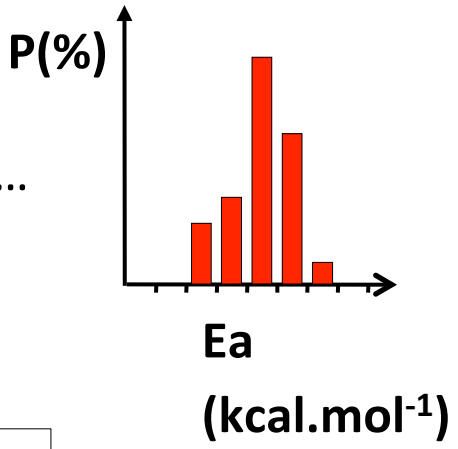
Arrhenius equation

$$k = A.\exp(-Ea/R.T)$$

- *A = frequency factor (pre-exponential factor)*
- *E_a = activation energy*
- *T = temperature*
- *$R = 1.98715\ cal \cdot mol^{-1} \cdot K^{-1}$*

Polyenergetic reactions





$Oil_{(L)} \leftrightarrow Oil_{(V)} \rightarrow$ Expelled Oil

$\downarrow$

Oil coking

Compositional Kinetic Model (2)

Adapted from Behar et al., Organic Geochemistry 41, 1235–1247 (2010)

$$\text{Kerogen} \rightarrow \text{nonHC-Gas} + C_1\text{-}C_{14} + C_{14}^{+}\text{SAT} + \text{DCM-NSO}$$

$$\text{DCM-NSO} \rightarrow \text{nonHC-Gas} + C_1\text{-}C_{14} + C_{14}^{+}\text{SAT} + C_{14}^{+}\text{ARO1} + nC_5\text{NSO} + \text{Prechar}$$

$$nC_5\text{NSO} \rightarrow \text{nonHC-Gas} + C_1\text{-}C_{14} + C_{14}^{+}\text{SAT} + C_{14}^{+}\text{ARO1} + \text{Prechar}$$

$$C_{14}^{+}\text{ARO1} \rightarrow \text{nonHC-Gas} + C_1\text{-}C_{14} + C_{14}^{+}\text{SAT} + C_{14}^{+}\text{ARO2} + \text{Prechar}$$

$$C_{14}^{+}\text{SAT} \rightarrow \text{nonHC-Gas} + C_1\text{-}C_{14} + C_{14}^{+}\text{ARO2}$$

Needs to be updated

- ✓ Secondary cracking of some product-fractions (such as C_6-C_{14})
- ✓ Gas generation from coke

} which can occur at high temperature

- ✓ Incorporate vapor-liquid equilibrium
- ✓ Possible catalytic effects of minerals in shale

Summary

- ❑ At our maximum maturity level, oil yield achieves about 70% FA
- ❑ Under semi-open conditions, SARA composition differs between expelled oil and extracted bitumen. Expelled oil is rich in saturates while extracted bitumen is rich in polars.
- ❑ Expelled oils under semi-open system
  - are dominated by saturates, explained by the highly aliphatic nature of type I kerogen
  - have very few polyaromatics (good for catalytic activity in refinery processes)
  - have H/C ratio and wt% sulfur similar to the Arabian light crude, and better than shale oil produced *ex-situ*
  - have SARA composition similar to oil produced by hydrous pyrolysis, which is considered much more like natural petroleum than oil produced by other methods of pyrolysis
  - have SARA composition similar to natural crude oils
- ❑ High pressure reduces oil yield, but improves oil quality.