Oil Shale Pyrolysis Laboratory & Technique

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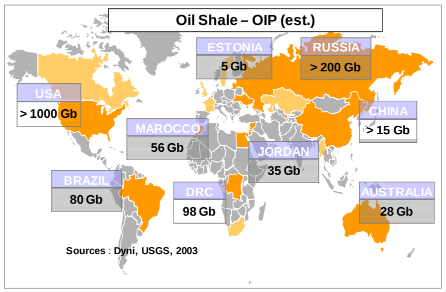
Oil Shale – Potential

Oil shale is a fine-grained sedimentary rock, containing significant amounts of immature kerogen (a solid mixture of fossil organic matter), from which shale oil and combustible gas can be extracted through heating.

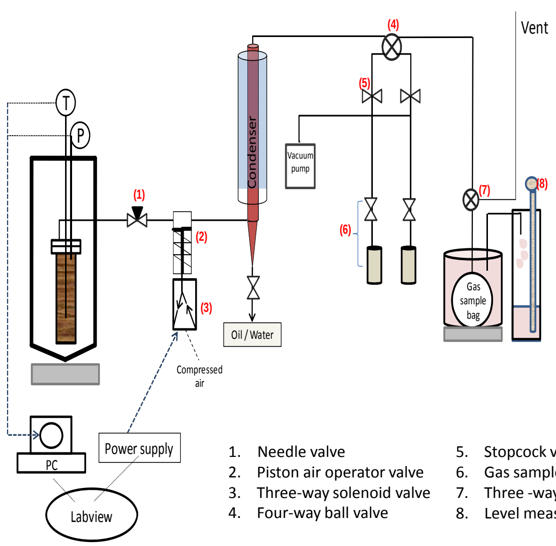


Why do we care about this resource? It is estimated that the Green River Formation contains from 1.2 to 1.8 trillion barrels of oil equivalent, 60% of world oil shale resources. Assuming half of this resource is recoverable, it is three times greater than the proven oil reserves of Saudi Arabia. Therefore several oil companies are looking for efficient ways to develop this resource.

Objectives

While standard laboratory tests such as Fischer Assay and Rock Eval provide information about the relative richness of oil shale intervals, they neither guide the design of production processes nor predict product quality and quantity that result from those processes. Our objective is to build a semi-open oil shale pyrolysis system to investigate the details of the transformation of kerogen to oil and gas. We believe this type of apparatus is the most relevant to describing in-situ oil shale pyrolysis conditions. An immediate goal is to determine the kinetic parameters for upcoming oil shale production tests in the R1 interval of the Green River formation.

Laboratory Pyrolysis Experimental Diagram

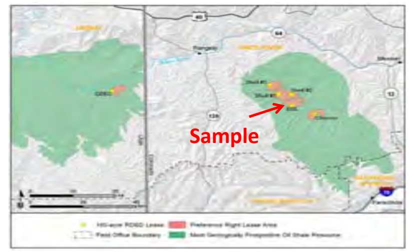


- Homogenized sample
- Semi-open system
- Programmable temperature profile (isothermal/non-isothermal)
- Automated back pressure regulator
- Monitor temperature, pressure & volume of pyrolysis gas
- Collect samples during the experiment

1. Needle valve
2. Piston air operator valve
3. Three-way solenoid valve
4. Four-way ball valve
5. Stopcock valve
6. Gas sample tube 4ml
7. Three -way stopcock valve
8. Level measurement probe

Samples

- <u>Source</u> : Illite-rich oil shale from the Green River R-1 zone (2012-2088 ft)



- <u>Sample preparation</u> : Homogenize, split & crush the bucket of cuttings into n x 100 g samples (100-200 µm particles)
- Rock–Eval data for split samples

Rock Eval 6 Parameters: Six Split Samples

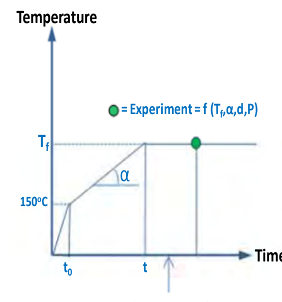
	TOC (%)	S1 (mg/g)	S2 (mg/g)	PI	Tmax (°C)	HI (mg/gC)	OI (mg/gC)
min	12.11	4.82	104.07	0.0399	441	855	4
max	12.72	5.42	110.02	0.0500	444	865	4

- Fischer Assay yield : 11.2 wt%

Design of Experiments (DoE) – Response Surface Method (RSM)

- A set of experiments is designed by using spherical design (RSM) where several factors (e.g. heating rate, final temperature, plateau duration, pressure) and 3 to 4 levels for each design factor are considered.

Factors	Spherical domain (3-4 levels)
Heating rate α (°C/h)	2 - 63
Final temperature T_f (°C)	331 - 394
Plateau duration d (h)	7.5 – 12.5
Pressure P (atm)	20- 40



N°Exp	Heating rate (°C/h)	Temperature (°C)	Plateau duration (h)	Pressure (atm)
1	6	331.25	7.5	20
2	63	331.25	7.5	20
3	6	393.75	7.5	20
4	63	393.75	7.5	20
5	6	331.25	12.5	20
6	63	331.25	12.5	20
7	6	393.75	12.5	20
8	63	393.75	12.5	20
9	6	331.25	7.5	40
10	63	331.25	7.5	40
11	6	393.75	7.5	40
12	63	393.75	7.5	40
13	6	331.25	12.5	40
14	63	331.25	12.5	40
15	6	393.75	12.5	40
16	63	393.75	12.5	40
17	20	362.5	10	30

Partial list of experiments

- The RSM method allows:
  - ✓ Assessment of the influence of each parameter with a far higher precision than “one-factor-at-a-time” approach.
  - ✓ Each experiment to contribute to the estimation of all the factors.
  - ✓ Optimization of the number of experiments.

Refs: www.weibull.com/doewebcontents.htm

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Analysis

Native state oil shale and pyrolysis products are characterized by an extensive analytical program.

Measurements	Native state (solids)				Post-pyrolysis fluids			Post-pyrolysis solids			
	Native State Shale	Post Extraction Shale	Extracted Bitumen	Kerogen Isolate	Pyrolysis Gas	Pyrolysis Oil	Pyrolysis Water	Spent Shale	Post Extraction Spent Shale	Extracted Bitumen	Kerogen Isolate
Yield					X	X	X	X	X	X	X
Demineralization	X							X			
Matrix density	X	X	X	X				X	X	X	X
Density - liquid						X	X				
Viscosity						X	X				
Fischer Assay	X	X									
Rock Eval	X	X	X	X				X	X	X	X
NMR Low Field	X	X	X	X				X	X	X	X
NMR High Field Time Domain	X	X	X	X		X		X	X	X	X
NMR Spectroscopy	X		X	X		X		X		X	X
TOC	X	X						X	X		X
Major oxides	X	X						X	X		
Water chemistry							X				
CHNSO	X	X	X	X		X		X	X	X	X
pH							X				
Trans. FTIR	X	X	X	X		X		X	X	X	X
Refl. FTIR	X	X	X	X		X		X	X	X	X
Dielectric	X	X		X				X	X		X
SARA			X			X				X	
GC/GC-MS			X		X	X					
ICR MS			X			X				X	
UV-Vis			X			X				X	
XRS			X	X						X	X
XANES			X	X		X				X	X
Surface area	X							X			
SEM	X							X			

Conclusion & ongoing works

➢ A semi-open pyrolysis laboratory system has been upgraded for kinetic studies of oil and gas generation

- Flexible, programmable temperature profiles (isothermal/non-isothermal), with maximum temperature of 425°C.
- Programmable gas pressure from 0 to 200 atm.
- Sample mass up to 100 g, small enough that the effects of heat and mass transport are negligible, but large enough to generate product volumes adequate for complete analysis.
- Measurement of volumes, compositions of oil produced via vaporization, bitumen retained in the shale, organic and inorganic gases, water, coke and ash.

➢ A set of experiments has been devised to maximize the efficiency of kinetic parameter determination.

➢ An extensive analytical program is designed to characterize the pyrolysis products.

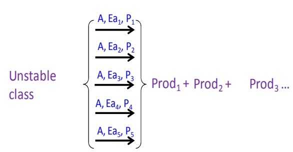
➢ Initial results are promising enough to encourage us to continue the experiments.

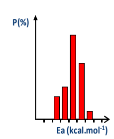
➢ The observed experimental data will be described by a compositional kinetic model

- Lumping species having similar chemical structure and similar thermal stability into same chemical class.
- Using first order reactions with Arrhénius formalism to describe the evolution of the unstable classes.

$$\frac{dC}{dt} = -A \cdot \exp\left(-\frac{E_A}{RT}\right) \cdot C$$

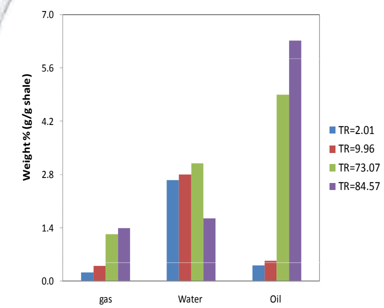
- Using a parallel reaction network with a discrete distribution of activation energies.





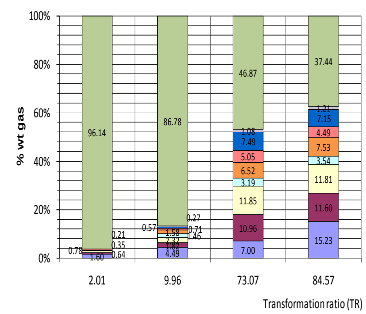
Preliminary Results

Evolution of pyrolysis products with thermal stress level

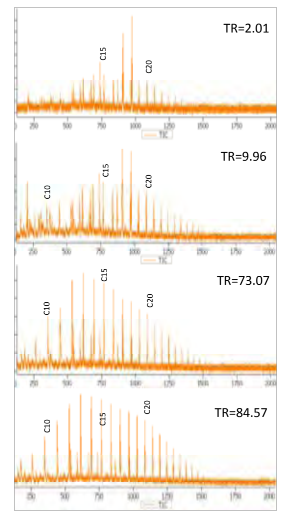


Pyrolysis product composition as a function of transformation ratio measured by Rock-Eval

Operating conditions				
Heating rate α (°C/h)	63	63	63	63
Final temperature T_f (°C)	332	332	393	393
Plateau duration (h)	7.5	12.5	7.5	12.5
Pressure (atm)	20	20	20	20
Transformation ratio %	2.01	9.96	73.07	84.57
TR= [S_2(initial)-S_2(final)]/S_2(initial)				



Gas composition as a function of transformation ratio measured by Rock-Eval

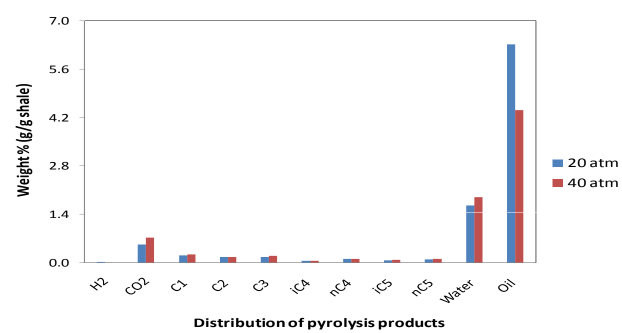


Evolution of pyrolysis oil chromatogram as a function of transformation ratio measured by Rock-Eval

- Gas & oil yield increase at higher thermal maturation (higher thermal stress). Water released includes "free" water and pyrolysis water.
- CO_2 is the first released gas, increasing quickly and then decreasing with thermal stress. For hydrocarbon gases, as the thermal maturity increases, the amounts of these hydrocarbon gases increase; methane is the dominant gas.
- The concentration of light ends in the oil fraction increases at high thermal maturity.

Higher pressure decreases oil yield

- For semi-open system, higher pressure decreases oil yield. We believe an increasing pressure inhibits oil volatilizing, thereby increasing oil residence time. This in turn causes further cracking and coking.



Operating conditions (α=63, T=393,d=12.5)