Comparison of Oil Generation Kinetics for Oil Shales as Determined by Rock-Eval and Hydrous Pyrolysis

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Objective

Determine whether oil-generation kinetics derived by different pyrolysis methods are critical to determining timing and extent of oil generation in surface and *in situ* retorting.
Natural Oil Generation

The laboratory pyrolysis method used to derive oil generation kinetics can have a significant effect on determining timing and extent of natural oil generation from source rocks in sedimentary basins.

Hydrous Pyrolysis (HP) kinetics for an 80-Ma source rock in a sedimentary basin with a heating rate of 2.5°C/m.y.
The laboratory pyrolysis method used to derive oil generation kinetics can have a significant effect on determining timing and extent of natural oil generation from source rocks in sedimentary basins.

**Rock Eval Pyrolysis (RE) kinetics for an 80-Ma source rock in a sedimentary basin with a heating rate of 2.5°C/m.y.**
Does the same hold true for oil shale retorting?

Does the laboratory pyrolysis method used to derive kinetics have a significant effect on determining timing and extent of oil generation in oil-shale retorting?
Pyrolysis Methods

**Rock-Eval (RE) Kinetics**
- Bulk (REb)
- Compositional (REc)

**Hydrous Pyrolysis (HP) Kinetics**

Graph showing pressure vs. temperature with markers for different stages of pyrolysis:
- Rock Eval (t = minutes)
- Hydrous Pyrolysis (t = days)
- Natural Oil Generation (t > 10^6 years)

Legend:
- CP: Critical Point
- n-C15 v/l curve
- H2O v/l curve
- v: vapor phase
- l: liquid phase

Graph showing temperature on the y-axis and pressure on the x-axis with various points indicating different stages of pyrolysis.
Samples

- **P** Phosphoria Retort Shale
  - 23.6 wt% TOC of **Type-II**

- **A** Alum Shale (Sweden)
  - 13.2 wt% TOC of **Type-II**

- **N** New Albany Sh. (EOS)
  - 14.3 wt% TOC of **Type-II**

- **G** Green River (Mahogany)
  - 15.2 wt% TOC of **Type-I**
Rock-Eval Pyrolysis Methods

Bulk RE

Compositional RE

Temperature = 250 to 650ºC
Pressure = ~1 atm
Heating Rates = 1, 5, 15, 30, and 50ºC/min
Hydrous Pyrolysis Methods

Isothermal Heating at
Temperatures = 250 to 365ºC
Times = 12 to 120 hours
Pressures = 600 to 3,000 psia

200 - 500g Crushed Source Rock (0.5 - 2.0 cm)
Hydrous Pyrolysis Products

Bitumen Oil

Kerogen

Hydrous Pyrolysis Products

Immiscible Oil
**Rock-Eval Products**

- Volatilized HCs
  - Carrier Gas
  - 20-50 mg Powdered Source Rock (< 25 μm)

- Electronic signal of volatilized hydrocarbons
  - To FID Detector

- S2 Rock Eval
  - (Behar et al., 1997)

- Time (min)

- FID Response

- HP Oil
- Bitumen
- SATURATES 100 wt%
Hydrous Pyrolysis Isothermal Kinetics

\[
\ln k = -27149 \left( \frac{1}{T} \right) + 39.74 \\
R^2 = 0.991 \\
E_a = 53.95 \text{ kcal/mol} \\
A_o = 1.814 \times 10^{17} \text{ h}^{-1}
\]
Rock-Eval Non-isothermal Kinetics

Heating Time (s)
- 50°C/min (70,300 mVs)
- 30°C/min (51,300 mVs)
- 15°C/min (32,500 mVs)
- 5°C/min (13,900 mVs)
- 1°C/min (6,300 mVs)

S2-Generation (mV)

% Overall Reaction

$A_0 = 9.41E+17/h$

Ea (kcal/mol)
# Comparison of Pyrolysis Methods For Deriving Oil Generation Kinetics

<table>
<thead>
<tr>
<th>Attribute</th>
<th>HP</th>
<th>RE</th>
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<td>Heating</td>
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<td>Temperatures (°C)</td>
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<td>Products</td>
<td>HC-rich oil</td>
<td>Polar-rich bitumen</td>
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Bulk RE versus Comp RE Timing at 95% Generation
Comparison of Timing at 95% Generation of Green River Shale (Type-I)
Comparison of Timing at 95% Generation of Green River Shale (Type-I)
Comparison of Timing at 95% Generation of New Albany Shale (Type-II)
Comparison of Timing at 95% Generation of Alum Shale (Type-II)

![Graph showing comparison of timing at 95% generation of Alum Shale (Type-II). The graph plots time (h) for 95% reaction against temperature (°C). Different symbols and lines represent in situ, REc, REb, and HP at various time scales (second, minute, hour, day, week, month, year).]
Comparison of Timing at 95% Generation of Phosphoria Retort Shale (Type-IIS)

Time (h) for 95% Reaction

Temperature (°C)
Conclusions

Pyrolysis Methods for determining oil generation can make a significant difference in determining timing and extent of natural petroleum generation.

do not make a significant difference in determining timing and extent of *in situ* oil-shale retorting.

may make a significant difference in determining timing and extent of *surface* oil-shale retorting (Type-IIS).