Comparison of Green River Formation shale oils by Fourier transform ion cyclotron resonance mass spectrometry

Jang Mi Jin\textsuperscript{1}, Sunghwan Kim\textsuperscript{1,2} and Justin E. Birdwell\textsuperscript{3}

\textsuperscript{1} Kyungpook National University, Department of Chemistry – Daegu, South Korea
\textsuperscript{2} Green-Nano Materials Research Center – Daegu, South Korea
\textsuperscript{3} U.S. Geological Survey, Central Energy Resources Science Center – Denver, CO USA
This work is part of a laboratory study examining how different reaction conditions affect the composition of pyrolysis products for a variety of Green River oil shales.

Objectives include:

- Determine differences in oil & gas yields under different pyrolysis conditions
- Characterize shale oils generated by different pyrolysis methods
- Determine changes in shale residue mineralogy following pyrolysis
Two Mahogany zone samples (Piceance and Uinta Basins) and an illitic shale sample from the Garden Gulch Member (bottom R1)
Surface Retorting

How does it work?
• Mine and crush oil shale
• Rapidly heat to ~500°C to convert kerogen to oil & gas

Advantages
• High yields
• Proven technology

Concerns
• Disposal of spent shale
• Product requires significant upgrading

Alberta-Taciuk Process (horizontal rotary kiln)
(Fact Sheet: Oil Shale Conversion Technology, DOE Office of Petroleum Reserves – Strategic Unconventional Fuels)
**In Situ Retorting**

**How does it work?**
- Drill heater & production wells
- Gradually heat to ~360°C over 2-4 years (~0.5°C per day)
- Degrade kerogen to oil & gas
- Remediate spent retort

**Advantages**
- No mining
- Access deep oil shale
- Higher quality oil product

**Concerns**
- Impacts on groundwater
- Pyrolysis residues (organics)

Shell’s *In-situ* Conversion Process
(Vinegar, H. 26\textsuperscript{th} Oil Shale Symposium, 2006)
Pyrolysis Methods – *Fischer Assay*

ASTM standard method for determining oil yield potential of oil shale

100 g of shale is heated to 500°C at 12°C/min (20 min heat-up) and held for 40 min at atmospheric pressure

Oil, water and residual oil shale are collected

No gases are recovered (gas yield estimated)

Oil product yield and composition is comparable to surface retorting methods

Mimics surface oil shale retorting
Preparation

Pressure tested and purged with He (1000 psia) then evacuated $P_0 < 0.6$ psia

~20°C

Electric heater
$\Delta T/\Delta t = 3^\circ$C/min

100-g oil shale

250-mL Parr reactor

Valves closed

Forums closed

500-mL Parr reactor

<5°C

Coolant bath

He helium purged and evacuated $P_0 < 0.6$ psia

Mimics in situ oil shale retorting

Pyrolysis Methods – *In Situ Simulator*
Pyrolysis Methods – *In Situ Simulator*

Sample is heated to the desired temperature and held for between 6 and 288 hours.

- **500 < \( P_0 \) < 800 psia**
- **\( P_0 \) < 0.6 psia**

**Pyrolysis**

- **360°C**
- **<5°C**

Valves closed

**Oil vapor and Gas**

Sample is heated to the desired temperature and held for between 6 and 288 hours.
After the desired pyrolysis time has passed, the reactor is vented to the collector (complete in <1 min).
Both the reactor and collector are brought to room temperature (~24 hours) prior to recovery of spent shale and products.
Pyrolysis Methods – *Hydrous Pyrolysis*

**Preparation**
- 20°C

**Heat-up**
- 360°C

**Pyrolysis**
- He (25 psia)
- Water 400 g
- Source Rock 200 g

**Cool-down & Collection**
- 72 h
- 20°C

Generated Gases

Expelled Oil

Spent Rock

Mimics petroleum generation in nature

**Preparation**
- Rock 200 g

**Heat-up**
- 360°C

**Pyrolysis**
- He (25 psia)
- Water 400 g
- Source Rock 200 g

**Cool-down & Collection**
- 72 h
- 20°C

Generated Gases

Expelled Oil

Spent Rock

Mimics petroleum generation in nature
Effects of pyrolysis conditions on shale oil

**Fischer Assay, 500°C, 1 h; API = 23.0°**

- Volatiles (<C15) 60.7
- Saturates 25.4
- Aromatics 6.6
- Resins 5.9
- Asphaltenes 1.4

Elemental Ratios
- H/C = 1.85, N/C = 0.013, O/C = 0.006

**In-situ Simulator, 360°C, 120 h; API = 50.0°**

- Volatiles (<C15) 9.5
- Saturates 35.3
- Aromatics 22.2
- Resins 29.1
- Asphaltenes 3.9

Elemental Ratios
- H/C = 1.61, N/C = 0.023, O/C = 0.014

Yield = 65 wt.% of Fischer Assay
Introduction to Fourier Transform Ion Cyclotron Mass Spectrometry

Korea Basic Sciences Institute (15 T Instrument)

- **Electrospray ionization** – **ESI** (+/- modes)
  - Used to obtain molecular ions of acidic and basic components (polars)
- **Atmospheric Pressure Photoionization** – **APPI**
  - Used to obtain molecular ions of polar and aromatic components
Advantages of FT Ion Cyclotron Resonance MS

- Ultrahigh resolution ($\frac{m}{\Delta m_{50%}} > 400,000$)
- High mass accuracy ($< 10$ mDa): Assign chemical formulas to each peak
- Multiple soft ionization methods allow for analysis of different moieties

Intro to FT-ICR MS
Intro to FT-ICR MS

Data Presentation issues

- Complex mass spectra generated
- Data points (peaks) ~10,000
- This complicates data handling and presentation

Sorting of compounds based on their elemental compositions.

Compound class and Carbon number
Formula assigned to each peak using the molecular weight and a typical formula \((C_cH_hN_nO_oS_s)\) with constraints

Double Bond equivalents
Using the molecular formula, an estimate of the double bonds and rings in each compound can be calculated

\[ DBE = c - h/2 + n/2 + 1 \]

where \(c\), \(h\) and \(n\) are the number of carbon, hydrogen and nitrogen atoms in the molecular formula assigned to a particular peak

Intro to FT-ICR MS

Molecular distribution for O₂ compound class from Athabasca Bitumen, distillate cut (375-400 °C)

Results – *Oil yields & specific gravities*

**Fischer Assay** has the highest oil yield. **Hydrous Pyrolysis** and **ISS** yields were ~70% and ~30% of **Fischer Assay**, respectively.

**In Situ Simulator** generated the lightest oil, and **Fischer Assay** produced the heaviest. Differences between shales were minimal.

**TOC** = 19.3 wt%, 10.0 wt%, 29.7 wt%
Results – Whole oil GC-FID

Hydrous Pyrolysis

In Situ Simulator

Fischer Assay

Piceance Mahogany

Uinta Mahogany

Garden Gulch

Naphtha $<C_{9}$

Kerosene $C_{9} - C_{14}$

Diesel $C_{15} - C_{20}$

Resid $>C_{20}$

$C_{20}$ $T_b = 340°C$

$C_{35}$ $T_b = 488°C$
## General results FT-ICR MS

<table>
<thead>
<tr>
<th>Compound classes</th>
<th>Piceance Mahogany</th>
<th>Uinta Mahogany</th>
<th>Garden Gulch</th>
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<tbody>
<tr>
<td><strong>Hydrous Pyrolysis</strong></td>
<td>N&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;1&lt;/sub&gt;, HC</td>
</tr>
<tr>
<td><strong>In Situ Simulator</strong></td>
<td>N&lt;sub&gt;1&lt;/sub&gt;, N&lt;sub&gt;1&lt;/sub&gt;O&lt;sub&gt;1&lt;/sub&gt;, HC</td>
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<td><strong>Fischer Assay</strong></td>
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</table>

Average DBE for all classes highest in GGM shale oils, lowest in Uinta Mahogany
Average MW for all classes highest in Uinta Mahogany shale oils, lowest in GGM
Dominant classes – N<sub>1</sub>, N<sub>1</sub>O<sub>1</sub>
Results – *Ultrahigh resolution MS*

Piceance Mahogany N$_1$ compound class

Hydrous Pyrolysis

In Situ Simulator

Fischer Assay

Piceance Mahogany N$_1$O$_1$ compound class

Carbon Number
Results – *Ultrahigh resolution MS*

Uinta Mahogany $N_1$ compound class

**Hydrous Pyrolysis**

**In Situ Simulator**

**Fischer Assay**

Uinta Mahogany $N_1O_1$ compound class

Double Bond Equivalents

Carbon Number

[Graphs showing data for different processes and compound classes]
Results – *Ultrahigh resolution MS*

**Garden Gulch N$_1$ compound class**

- **Hydrous Pyrolysis**
- **In Situ Simulator**
- **Fischer Assay**

**Garden Gulch N$_1$O$_1$ compound class**

- **Hydrous Pyrolysis**
- **In Situ Simulator**
- **Fischer Assay**

<table>
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<tr>
<th>Double Bond Equivalents</th>
<th>Carbon Number</th>
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<tbody>
<tr>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
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<tr>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

**USGS**
Results – *Suggested compound structures*

**Uinta Mahogany zone oil shale – Fischer Assay**

Structures proposed based primarily on class and DBE. Carbon number determines lengths of aliphatic side chains (R).
Summary

General characteristics of pyrolysates

- Results show abundant nitrogen in all GRF shale oils regardless of pyrolysis method
- Samples dominated by $N_1$ and $N_1O_1$ classes
- Average Double Bond Equivalents 5 - 13
- Average Molecular Weights 365 - 540 Da
Conclusions

Effects of pyrolysis conditions on products

- Surface vs. In-situ Retorting Products
  - Fischer Assay yields a heavier oil – no surprise there
  - Hydrous pyrolysis generates a pyrolysate that is intermediate between the very light In Situ Simulator and Fischer Assay oils
  - In terms of DBE and carbon number distributions for the dominant compound classes, Fischer Assay and Hydrous Pyrolysis generate many similar FT-ICR MS amenable shale oil components
  - In Situ Simulator produces a very different shale oil at the molecular level, with much lower abundances of N$_1$ and N$_1$O$_1$ compounds and narrower DBE vs. C# distributions
  - High nitrogen will be a major issue for GRF shale oil and FT-ICR MS can help us understand the chemistry.