SLIDES: Impacts of Oil Shale on Carbon Emissions

Jeremy Boak
Impacts of Oil Shale on Carbon Emissions

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Presentation for The Promise and Peril of Oil Shale
Denver, Colorado, February 5, 2010
Outline

- What is oil shale
- CO$_2$ emissions from oil shale
- Related issues
- COSTAR and the Oil Shale Symposium
- Backup information
What is oil shale?

- Organic rich mudstone formed in lake or marine environments
  - Commonly carbonate rich; many not classical clay-rich mudstones
  - Kerogen-rich, primarily algal and bacterial remains
  - Immature precursor to oil & gas
- Produces oil on short term heating to temperatures above ~300°C
The name *oil shale* represents a double *misnomer*, as geologists would not necessarily classify the rock as a shale, and its kerogen differs from crude oil.


The term "oil shale" is a *misnomer*. The rock is a *marlstone*, and the hydrocarbon is a waxy molecule called kerogen. Kerogen is a proto-petroleum — oil and gas are generated when kerogen is exposed to heat deep in the Earth's oven.


Hyping oil shale is nothing new. As geologist Walter Youngquist once wrote, "Bankers won't invest a dime in 'organic marlstone,' the shale's proper name, but 'oil shale' is another matter."

Oil shale terminology

- ...we propose that mudstone be the generic term for all fine-grained argillaceous rocks and that shale be restricted to laminated fine-grained argillaceous rocks, following its original definition by Hooson (1747)...although we grew up with and like shale (only one syllable is needed for pronunciation) as the general term for argillaceous rocks, here we restrict it to its original sense of a laminated, argillaceous rock.

- Marl, n. An old term loosely applied to a variety of materials, most of which occur in loose, earthy, or friable deposits and contain a relatively high proportion of calcium carbonate or dolomite....Certain varieties are excellent as cement materials....As the term covers a wide range of materials and designates no particular well-defined composition, it should not be used without specific definition.
  - Stokes and Varnes, Glossary of Selected Geological Terms, CSM, 1955, p. 89
Oil shale mineralogy

- Carbonate
- Clay/Silt
- Clastic

Ternary Boundary:
- Carbonate/Clastic
- Clay/Silt

Samples:
- Seam MS10 (diamond)
- Seam MS11 (teal diamond)
- Seam MS12 (yellow)
- Seam MS13 (red)
- Seam MS14 (blue)
- Seam MS15 (cyan)
- Seam MS16 (green)
- Seam MS17 (olive)

Mineral types:
- calcreous/dolomitic mudstone
- marlstone
- silty argillaceous mudstone
- calcareous/dolomitic siltstone
- siltstone
- argillaceous mudstone

Components:
- Qtz (Quartz)
- Fsp (Feldspar)
Determinants of CO$_2$ emissions from oil shale: the case of liquid fuel production

Adam Brandt, Jeremy Boak, Alan Burnham
29$^{th}$ Oil Shale Symposium
What causes CO₂ emissions from shale oil?

- **Direct emissions:**
  - Retorting of raw shale to produce liquid hydrocarbons
  - Upgrading and refining crude shale oil
  - Combustion of refined shale oil products

- **Indirect emissions:**
  - Energy consumption from capital inputs

- **Units used in this presentation**
  - MJ per tonne of raw shale (MJ/t = J/g)
  - gCO₂ per MJ of refined fuel delivered (reformulated gasoline)
Emissions from retorting raw shale

- Retorting raw shale to produce liquid hydrocarbons results in three kinds of emissions:
  1. Thermal energy requirements of retorting
  2. Other energy consumption during retorting (auxiliary energy consumption)
  3. Emissions of CO$_2$ from shale mineral and organic matter
Thermal energy requirements of retorting

- Thermal demand of retorting governed by:
  a) Heat content of shale minerals at final temperature
  b) Heat of reaction of kerogen decomposition
  c) Heat of reaction of mineral reactions
  d) Heat to vaporize bound and free water
  e) Heat content of produced hydrocarbons at final temperature

- Range: 450 – 750 MJ/t
  - Varies with specifics of process and target shale

- Heat recovery will reduce external heat inputs
How to reduce the heat of retorting

› Reduce shale quality
  – 150 l/t → 110 l/t ≈ −50 MJ/t

› Reduce moisture level
  – 1 wt% water ≈ −20 to −30 MJ/t

› Slow the rate of retorting
  – 12 °C/min → 0.5 °C/day ≈ −140 MJ/t

› Reduce carbonate decomposition
  – 1 wt% decomposed carbonate ≈ −0.9 to −1.8 MJ/t
**CO₂ emissions from retorting heat**

- Emissions depend on heat of retorting and carbon intensity of heat source

### Table 3: Carbon intensity of thermal energy sources

<table>
<thead>
<tr>
<th>Thermal energy source</th>
<th>Carbon density (gC/g fuel)</th>
<th>CO₂ intensity (gCO₂eq./MJ)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>&gt; 0.75</td>
<td>49-51</td>
<td>(22)</td>
</tr>
<tr>
<td>Coal</td>
<td>&lt; 0.75 to &gt; 0.92</td>
<td>88-97</td>
<td>(22)</td>
</tr>
<tr>
<td>Shale char&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.87 to 0.92</td>
<td>88-100</td>
<td>(23)</td>
</tr>
<tr>
<td>Electricity - Nat. gas&lt;sup&gt;b&lt;/sup&gt;</td>
<td>NA</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>Electricity - Coal&lt;sup&gt;c&lt;/sup&gt;</td>
<td>NA</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>Electricity - Colorado&lt;sup&gt;d&lt;/sup&gt;</td>
<td>NA</td>
<td>206</td>
<td>(24)</td>
</tr>
</tbody>
</table>
Auxiliary retorting energy requirements

- Varies with process, tend to be small
- In situ:
  - Sub-surface containment (Shell’s freeze wall)
  - Sub-surface cleanup (flushing)
  - Surface processing of produced fluids
- Ex situ
  - Crushing and pre-treating
  - Utilities for retort operation
  - Surface processing of produced fluids
## Inorganic CO₂ from shale mineral matter

- **CO₂ evolved from shale mineral matter**
  - Low T: saline minerals (e.g., nahcolite – NaHCO₃ – natural baking soda)
  - High T: dolomite then calcite

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (°C)</th>
<th>Emissions (per wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 )</td>
<td>600–900</td>
<td>4.4 kg CO₂/wt %</td>
</tr>
<tr>
<td>( \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2 )</td>
<td>700–900</td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CaMg(\text{CO}_3)_2} \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 )</td>
<td>600–750</td>
<td>2.3 kg CO₂/wt.%</td>
</tr>
<tr>
<td>( \text{CaMg(\text{CO}_3)_2} + 2\text{SiO}_2 \rightarrow \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2 )</td>
<td>700–900</td>
<td></td>
</tr>
<tr>
<td>Saline minerals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>100–150</td>
<td>2.6 kg CO₂/wt.%</td>
</tr>
</tbody>
</table>
Uncertainties in inorganic CO$_2$

- Difference between kinetic models of carbonate decomposition (Campbell 1978 vs. Thorsness 1994)
- 700 °C, 2/5 min:
  - Campbell: 24% / 50% of CaMg(CO$_3$)$_2$
  - Thorsness: 79% / 98% of CaMg(CO$_3$)$_2$
- Regularities:
  - Decomposition increases with increasing $T_{\text{max}}$ and increasing time at $T$
  - Saline minerals decompose at low $T$
  - Low $T$ decomposition of dolomite: quicker than calcite
  - Gas-phase CO$_2$ inhibits decomposition of calcite
    - Pushes $T$ up, favors silicate reactions
    - Other reactions possible
Other possible reactions

- Dolomite + Analcime + Montmorillonite ± Water = Calcite + Clay Minerals + CO₂  \[0.7 \text{ kg CO}_2/\text{wt %}\]
  
  \[3\text{CaMg(CO}_3\text{)}_2 + 2\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O} + 2\text{Al}_2\text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + x\text{H}_2\text{O} = 3\text{CaCO}_3 + \text{Mg}_3\text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + 2\text{NaAl}_3\text{Si}_3\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + 3\text{CO}_2\]

- Dolomite + K-feldspar + Montmorillonite ± Water = Calcite + Clay Minerals + CO₂  \[1.1 \text{ kg CO}_2/\text{wt %}\]
  
  \[3\text{CaMg(CO}_3\text{)}_2 + \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + x\text{H}_2\text{O} = 3\text{CaCO}_3 + \text{Mg}_3\text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + \text{KAl}_3\text{Si}_3\text{O}_{10} (\text{OH})_2 \cdot \text{nH}_2\text{O} + 3\text{CO}_2\]
Emissions from kerogen in shale

- CO₂ is evolved from kerogen during retorting
  - Kerogen contains 5–6 wt% O
  - Oxygen ends up in CO₂ and H₂O
  - Reaction: Decarboxylation of organic acids and esters
- **Yield**: ≈ 4–5% mass of kerogen as CO₂
Shale oil upgrading and refining

- Shale oil generally must be upgraded prior to transport
  - Stabilization of reactive hydrocarbons
  - Remove excess nitrogen and metals
  - Range: 1 – 8 gCO₂/MJ RFD

- After upgrading, refining to finished products
  - U.S. refinery: ≈ 12 gCO₂/MJ RFD (Wang 2008)
  - Shale oil refining will vary with quality and upgrading
Combustion of refined fuels

- Typically largest component of emissions
  - Exception: high-temperature surface retorting of low-grade shale

- Emissions identical to those from conventionally-produced fuels
  - Fuels refined to same standard → same tailpipe emissions

- Emissions $\approx 70 \text{ gCO}_2/\text{MJ}$
Example – ATP retort  (Brandt, 2009)

Carbonate decomposition

Char combustion
CO₂ emissions from oil shale

![Diagram showing CO₂ emissions from different oil shale processes](image-url)

- **Comb. of fuel**
- **Upgrading & Ref.**
- **Other extraction**
- **Thermal retorting**

**CO₂ Emissions from reform. gasoline (gCO₂eq./MJ)**

- HRS - Burnham
- ATP - SPP
- ATP - OSEC
- ICP - Brandt - Low
- ICP - Brandt - High
- MIS - Burnham
- Boak - 10%-90%

**COLORADO SCHOOL OF MINES**
Modeling CO$_2$ emissions transparently

Multivariate Distributions

Mineral

Mean Mineral Weight Percent

Mineral Composition

Shale Gas Production Efficiency

Mineral CO$_2$ Production

Kerogen

Element Percent

Kerogen Composition

Kerogen Weight Percent

Pyrolysis Oxygen Fraction

Fischer Assay

Pyrolysis CO$_2$ Production

Oil Shale Conversion Energy

Shale Oil Production Efficiency

Oil Shale Moisture Content

Power Plant Output

Oil Shale Moisture Content

Annual shale tonnage

Industry Production

Power plant CO$_2$ rate

Power plant energy efficiency

Results Module
Primary factors in oil shale CO$_2$ emissions

- Shale Oil Production Efficiency
- Power Plant Energy Efficiency
- Kerogen Weight Percent
- Power plant CO2 Rate
- Oil Shale Conversion Energy
- Mineral Composition
- Kerogen Composition
Recovery controls CO$_2$ release from shale
Mitigating CO$_2$ emissions

- **Use low CO$_2$ heat source**
  - Off-peak wind (Bridges 2007)
  - Nuclear (Forsberg 2008)

- **Reduce losses in heat transfer to shale**
  - Use heat directly rather than electricity
  - Increase scale to reduce heat loss

- **Reduce temperature**
  - Slow rate of heating to reduce final temperature
  - Eliminate carbonate decomposition

- **Capture CO$_2$ and store**
  - Easiest with concentrated CO$_2$ (e.g., upgrading H$_2$ unit)
**CO₂ emission – conclusions**

- **Main sources of additional emissions**
  - Heat of retorting
  - Carbonate decomposition

- **Minor sources of additional emissions**
  - Mining and pre-processing / auxiliary inputs (freeze wall)
  - Refining and upgrading (some cases)

- **Mitigating these additional emissions**
  - Reduce temperature
  - Reduce CO₂ intensity of primary fuel
  - Increase fraction of primary heat that gets into the formation
Other issues for alternative energy

- Environmental issues for oil shale
- Water use issues
- Growth rate of production
- Global energy picture
Environmental issues for oil shale development

- Issues
  - Water quantity and quality
  - Air quality
  - Surface and ecosystem impact
  - Social and economic impacts
- Data needs
  - Definition process
  - Baseline collection
  - Management
  - Dissemination
- Model development
- Impact assessment & policy
- Technology development for mitigation
Water consumption for energy extraction

Barrels Water/Barrels Oil


Gallons Water/MMBTU
Modeling water use for oil shale production

Block Description

- Surface Elevation
- Dawsonite Content
- Nahcolite Content
- Heater hole number
- Dewatering/Producing Holes
- Injection hole number
- Total Boreholes
- Power Plant Module
- Oil Production
- Constants & Conversions
- Water Content
- Water Use
- Results
Historic & projected production

- Brazil
- China
- Estonia
- US (EIA)
- Jordan

Barrels per Day

- 1,000,000
- 1,000,000

Years:
- 1990
- 2000
- 2010
- 2020
- 2030
Historic comparisons

Production (BOPD)

10,000,000
1,000,000
100,000
10,000
1,000

1980 2000 2020 2040

$y = 9 \times 10^{-121} \times e^{0.1427x}$

$y = 5 \times 10^{-81} \times e^{0.0981x}$

$y = 3 \times 10^{-72} \times e^{0.0873x}$

- Oil Shale
- US Oil 1862-1919
- Tar Sand 1968-2007
- Oil Shale 1999-2030
- Tar Sand Growth
- US Oil Growth
- Oil Shale Trend
Scramble – supply focus and late responses

Total primary energy demand

- Oil
- Coal
- Biomass
- Wind
- Gas
- Nuclear
- Solar
- Other Renewables

Direct CO₂ emissions from energy

- Middle East & Africa
- Latin America
- Asia & Oceania - Developing
- Asia & Oceania - Developed
- North America
- Europe

Sources: Shell International BV and Energy Balances of OECD and Non-OECD Countries ©OECD/IEA 2006
Shell energy projections – 2

Blueprints – multi-focus and early actions

Total primary energy demand

Direct CO₂ emissions from energy

Sources: Shell International BV and Energy Balances of OECD and Non-OECD Countries©OECD/IEA 2006
Conclusions

- Globally significant production still decades away
  - Even at 15% annual growth 1 MMBOPD takes ~25 years
  - Barring significant technological advances
  - Technology may not be rate limiting step
- Same is true for most alternative fuels
- Stable growth can provide time to enable carbon management
COSTAR and the Oil Shale Symposium

› Center for Oil Shale Technology and Research
  – Membership – Total, Shell, ExxonMobil
  – Research Team – Colorado School of Mines, University of Wisconsin, Binghamton University (SUNY), [National Center for Atmospheric Research]
  – Initial tasks – rock mechanics, geology and stratigraphy, geochemistry, GIS database development

› 30th Oil Shale Symposium and Field Trip
  – Symposium October 18–20, Mines Campus, Golden CO
  – Field Trip October 21–22, Western CO
Backup Information

- Global resources
- Critical issues
- Importance of updating resource estimates
- U. S. historic energy production
Global Oil Shale Resources

1. Green River Formation
   1,499 billion barrels

2. Other United States
   619 billion barrels

3. Russia
   271 billion barrels

4. Brazil
   52 billion barrels

5. Morocco
   37.8 billion barrels

6. Jordan
   34 billion barrels

7. Australia
   31.0 billion barrels

8. Estonia
   16.3 billion barrels

9. China
   15.6 billion barrels

10. Canada
    15.2 billion barrels
Changing Resource Estimates

1. Green River Formation: 1,499 billion barrels
2. Other United States: 619 billion barrels
3. China: 328 billion barrels
4. Russia: 271 billion barrels
5. Brazil: 52 billion barrels
6. Morocco: 37.8 billion barrels
7. Jordan: 34 billion barrels
8. Australia: 31.0 billion barrels
9. Estonia: 16.3 billion barrels
10. Canada: 15.2 billion barrels
Four issues for progress

Four main issues condition future progress of shale oil production:

- Access to the resource
- Technology development
- Environmental impact
- Economic viability

Importance of each different in every country

Issues not necessarily independent

Interplay affects how companies and countries progress:

- Natural influences (richness, depth, composition) with
- Human influences (innovation, economics, security, cultural values)
Economic viability

- Affected by all other listed issues
  - Access – time is money
  - Technology – energy, water, CO₂ efficiency
  - Environment – emissions, consumption, disruption
- Oil price, supply, demand, infrastructure
- Competing energy alternatives
  - Heavy oil
  - Global gas market
  - Renewable resources
Importance of resource estimates

- Resource estimates based on Fischer Assay,
  - Surface retort surrogate
  - New designs for retorts
  - In-situ methods
- Need for common basis of resource description
  - National interest in open databases for estimation
  - Technologic and economic factors will be more closely held