

Determinants of CO₂ emissions from oil shale: The case of liquid fuel production



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29th Oil Shale Symposium – Oct. 21st 2009
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What causes CO₂ emissions from oil shale?

- 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:

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 CO₂ 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 \rightarrow 110 l/t \approx - 50 MJ/t
- Reduce moisture level
 - 1 wt.% water \approx - 20 to - 30 MJ/t
- Slow the rate of retorting
12 °C/min \rightarrow 0.5 °C/day \approx - 140 MJ/t
- Reduce carbonate decomposition
 - 1 wt% decomposed carbonate \approx - 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

<i>Thermal energy source</i>	<i>Carbon intensity of thermal energy sources</i>		<i>Source</i>
	<i>Carbon density (gC/g fuel)</i>	<i>CO₂ intensity (gCO₂eq./MJ)</i>	
Natural gas	> 0.75	49-51	(22)
Coal	< 0.75 to > 0.92	88-97	(22)
Shale char ^a	0.87 to 0.92	88-100	(23)
Electricity - Nat. gas ^b	NA	111	
Electricity - Coal ^c	NA	280	
Electricity - Colorado ^d	NA	206	(24)

a – These values from formulas for char produced from secondary pyrolysis at ≈550°C and tertiary pyrolysis at ≈750°C (23, Table 3). HHV of the char is calculated using the Dulong formula. This does not include the associated carbonate decomposition.

b – Assumes combined-cycle turbine with 45% efficiency of generation and transmission. Assumes 50 gCO₂/MJ natural gas.

c – Assumes pulverized coal boiler with 30% efficiency of generation and transmission. Assumes 92.5 gCO₂/MJ of coal.

d – Data from EIA (24) for total electricity generation (MWh) and total emissions (Mt CO₂) in Colorado.

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 at varying temperatures from shale mineral matter
 - Low T: saline minerals (e.g., nahcolite)
 - High T: dolomite then calcite

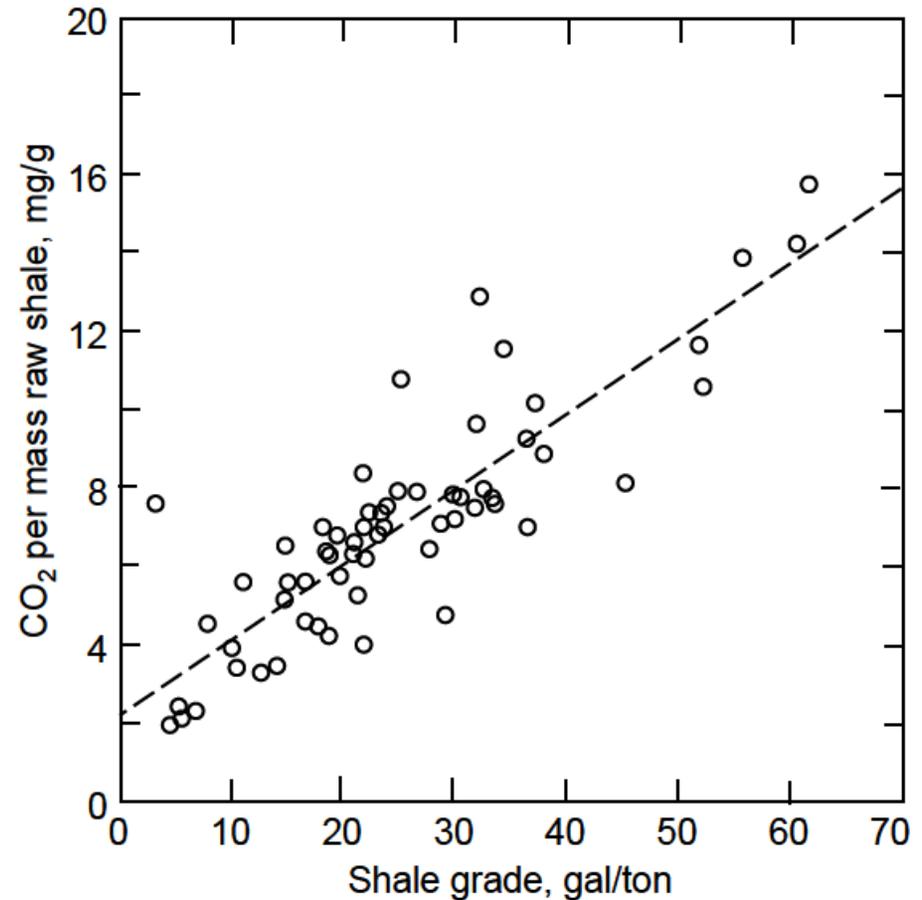
Reaction	Temperature (°C)	Emissions (per wt %)
Calcite: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$	600-900 700-900	4.4 kg CO ₂ /wt %
Dolomite $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2$ $\text{CaMg}(\text{CO}_3)_2 + 2\text{SiO}_2 \rightarrow \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2$	600-750 700-900	2.3 kg CO ₂ /wt. %
Saline minerals $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	100-150	2.6 kg CO ₂ /wt. %

Uncertainties in inorganic CO₂

- Significant deviation between kinetic models of carbonate decomposition (Campbell 1978 vs. Thorsness 1994)
 - 700 °C , 2/5 min:
 - Campbell: 24% / 50% of CaMg(CO₃)₂
 - Thorsness: 79% / 98% of CaMg(CO₃)₂
- Regularities:
 - Decomposition increases with max T and time at T
 - Saline minerals decompose at low T
 - Low T decomposition of dolomite: faster than calcite
 - Gas-phase CO₂ inhibits decomposition of calcite
 - Pushes T up, favors silica reaction

Emissions from shale - Organic

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



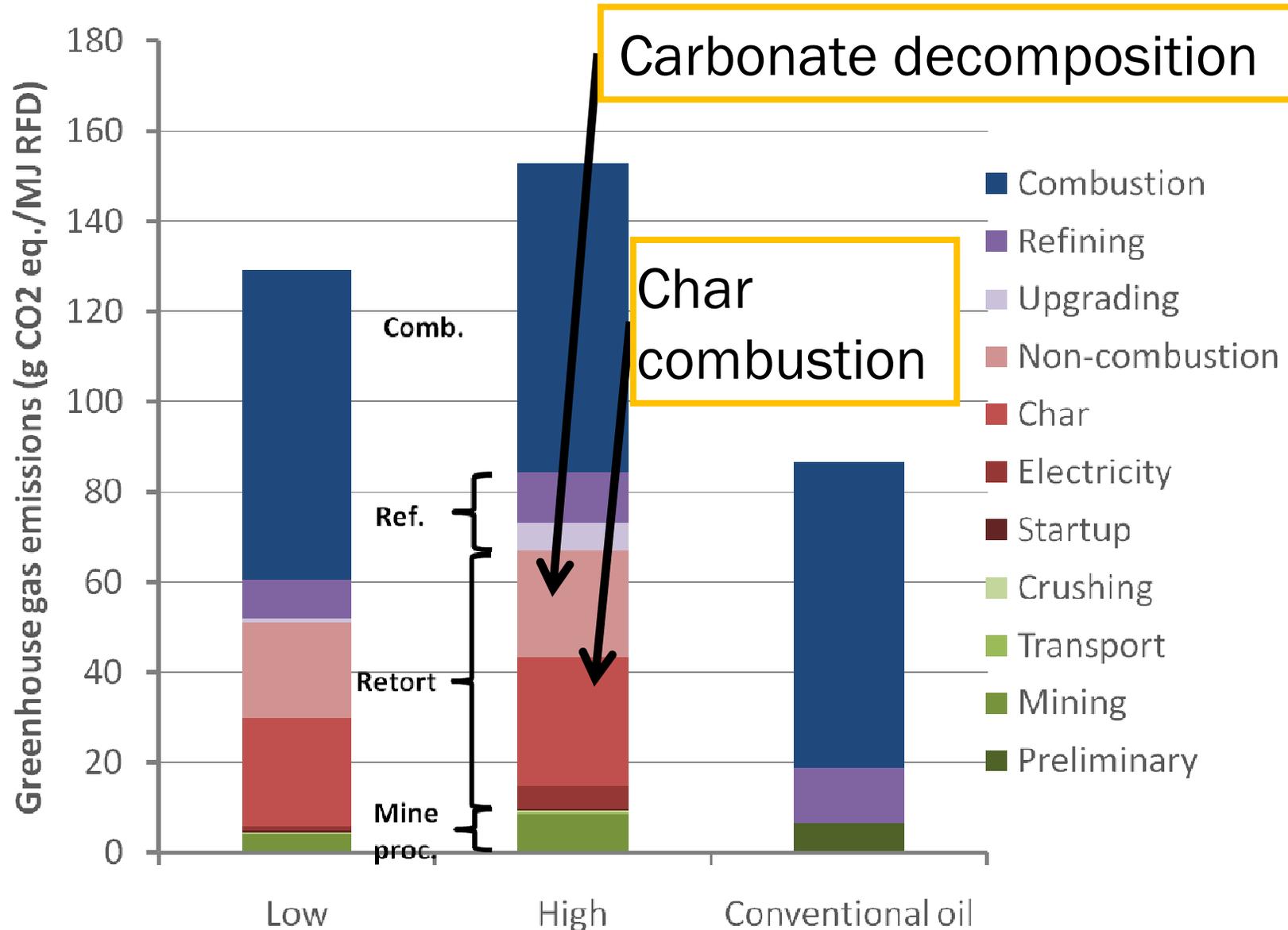
Shale oil upgrading and refining

- 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)



Mitigating CO₂ emissions

- Use low CO₂ 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 CO₂ and store
 - Easiest with concentrated CO₂ (e.g., upgrading H₂ unit)

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 fuel that gets into the formation

Thanks:

- Attendees of 29th Oil Shale Symposium
- Co-authors Jerry Boak and Alan Burnham
- Anonymous reviewer of ACS chapter on oil shale CO₂ emissions