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Impacts of Oil Shale on Carbon Emissions

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Presentation for *The Promise and Peril of Oil Shale*
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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

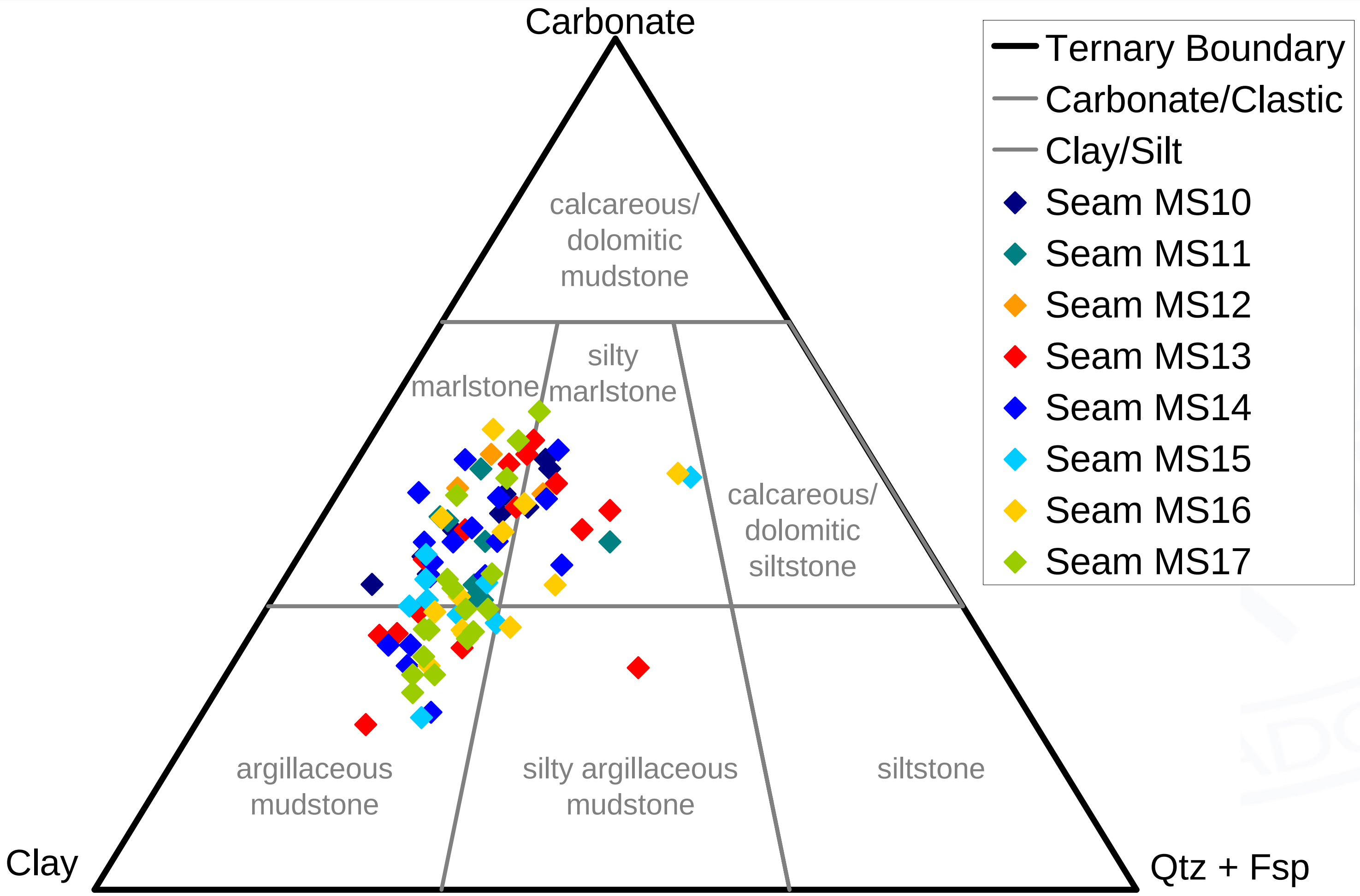
Is it oil? Is it shale?

- 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.
  - Wikipedia, http://en.wikipedia.org/wiki/Oil_shale
- 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.
  - Grinning Planet, http://www.grinningplanet.com/2005/12-13/oil-shale-article.htm
- 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."
  - Grinning Planet, http://www.grinningplanet.com/2005/12-13/oil-shale-article.htm

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.
  - Potter, Maynard, and Depetris, *Mud and Mudstones*, Springer, 2005, pp. 256-257
- 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



Determinants of CO_2 emissions from oil shale: the case of liquid fuel production

Adam Brandt, Jeremy Boak, Alan Burnham

29th Oil Shale Symposium

What causes CO_2 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)
  - gCO_2 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

CO_2 emissions from retorting heat

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

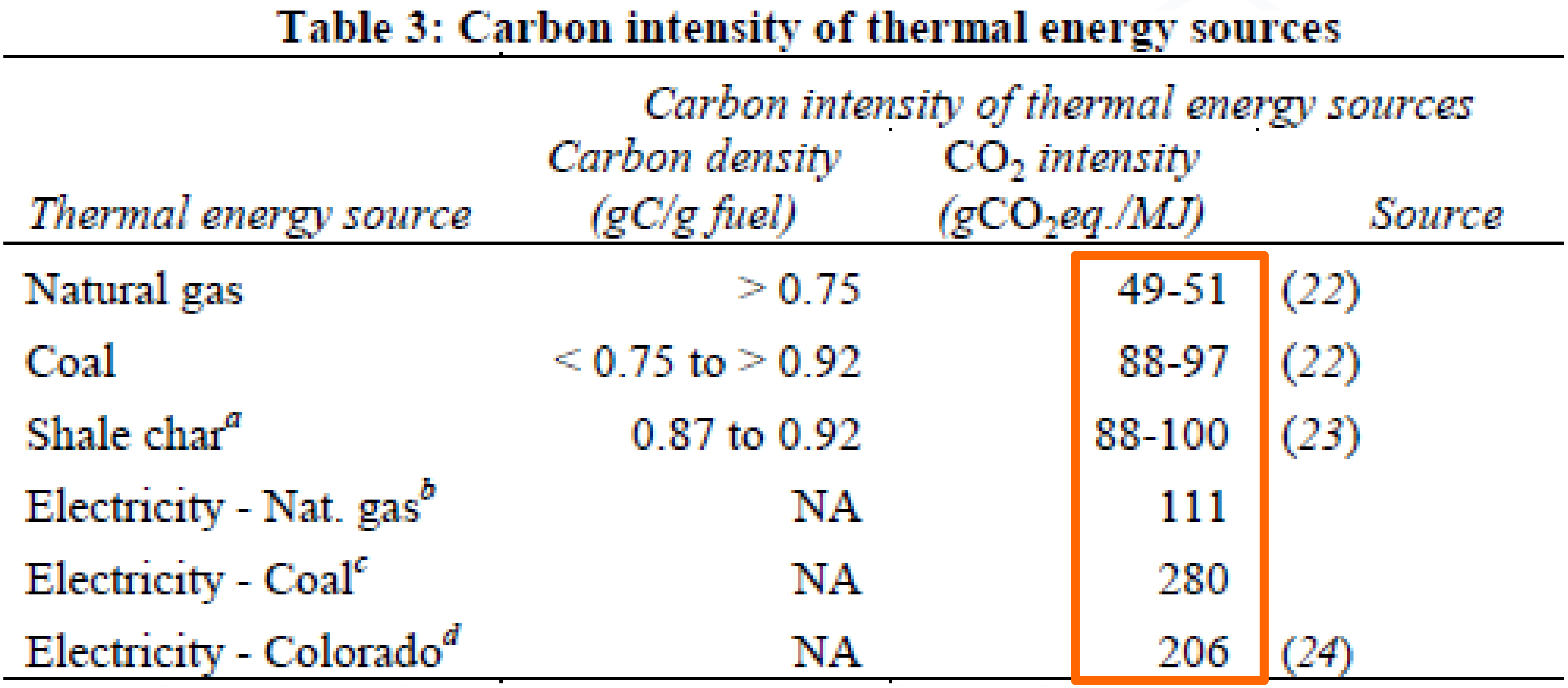


Table 3: Carbon intensity of thermal energy sources

	Carbon intensity of thermal energy sources		
Thermal energy source	*Carbon density (gC/g fuel)*	*CO_2 intensity ($gCO_2eq./MJ$)*	*Source*
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)

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 CO_2 from shale mineral matter

- CO_2 evolved from shale mineral matter
  - Low T: saline minerals (*e.g.*, nahcolite – $NaHCO_3$ – natural baking soda)
  - High T: dolomite then calcite

Reaction	Temperature (°C)	Emissions (per wt %)
Calcite: $CaCO_3 \rightarrow$ **CaO** $+ CO_2$ $CaCO_3 + SiO_2 \rightarrow$ **$CaSiO_3$** $+ CO_2$	600–900 700–900	4.4 kg CO_2/wt %
Dolomite $CaMg(CO_3)_2 \rightarrow$ **CaO** + **MgO** $+ 2CO_2$ $CaMg(CO_3)_2 + 2SiO_2 \rightarrow$ **$CaMgSi_2O_6$** $+ 2CO_2$	600–750 700–900	2.3 kg CO_2/wt.%
Saline minerals $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	100–150	2.6 kg CO_2/wt.%

Uncertainties in inorganic CO_2

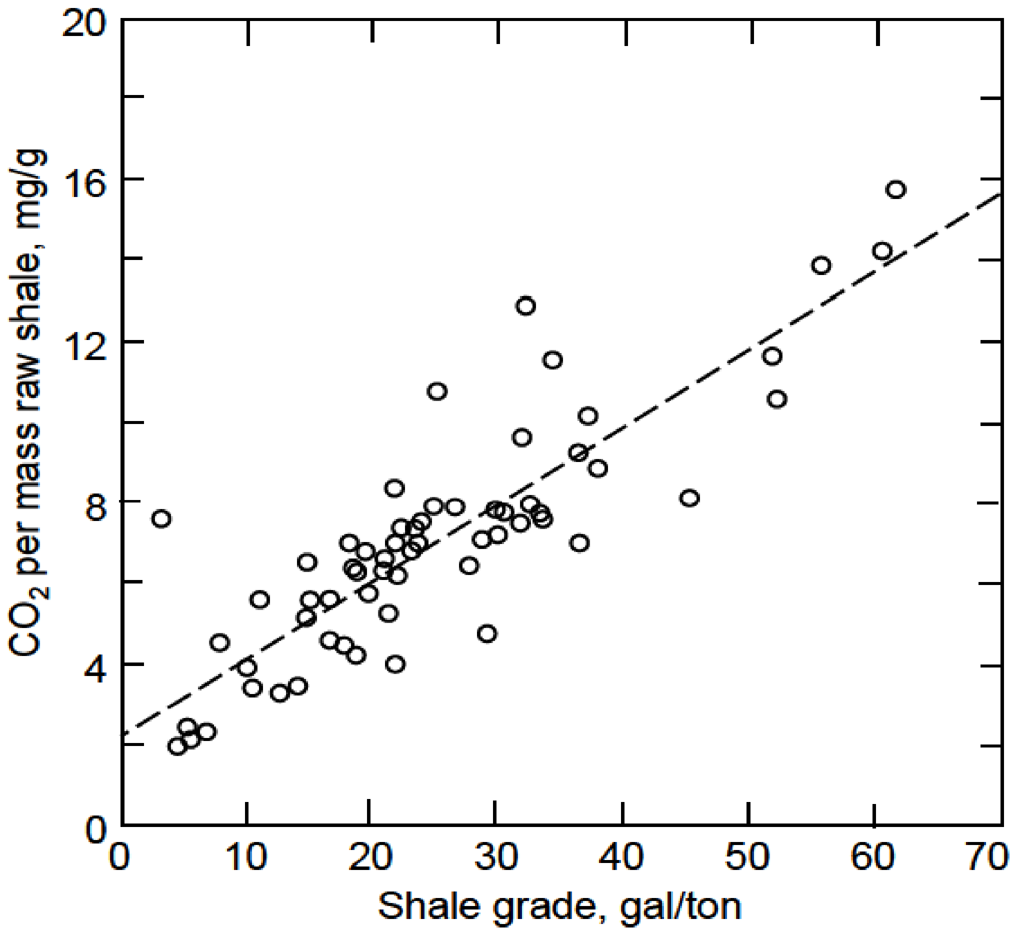
- Difference between kinetic models of carbonate decomposition (Campbell 1978 vs. Thorsness 1994)
- 700 °C , 2/5 min:
  - Campbell: 24% / 50% of $CaMg(CO_3)_2$
  - Thorsness: 79% / 98% of $CaMg(CO_3)_2$
- Regularities:
  - Decomposition increases with increasing T_{max} and increasing time at T
  - Saline 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 + CO_2 [0.7 kg CO_2/wt %]
  - $3CaMg(CO_3)_2 + 2NaAlSi_3O_8 \cdot H_2O + 2Al_2Si_4O_{10}(OH)_2 \cdot nH_2O + xH_2O = 3CaCO_3 + Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O + 2NaAl_3Si_3O_{10}(OH)_2 \cdot nH_2O + 3CO_2$
- Dolomite + K–feldspar + Montmorillonite ± Water = Calcite + Clay Minerals + CO_2 [1.1 kg CO_2/wt %]
  - $3CaMg(CO_3)_2 + KAlSi_3O_8 + Al_2Si_4O_{10}(OH)_2 \cdot nH_2O + xH_2O = 3CaCO_3 + Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O + KAl_3Si_3O_{10}(OH)_2 \cdot nH_2O + 3CO_2$

Emissions from kerogen in shale

- CO_2 is evolved from kerogen during retorting
  - Kerogen contains 5–6 wt% O
  - Oxygen ends up in CO_2 and H_2O
  - Reaction: Decarboxylation of organic acids and esters
- **Yield**: ≈ 4–5% mass of kerogen as CO_2



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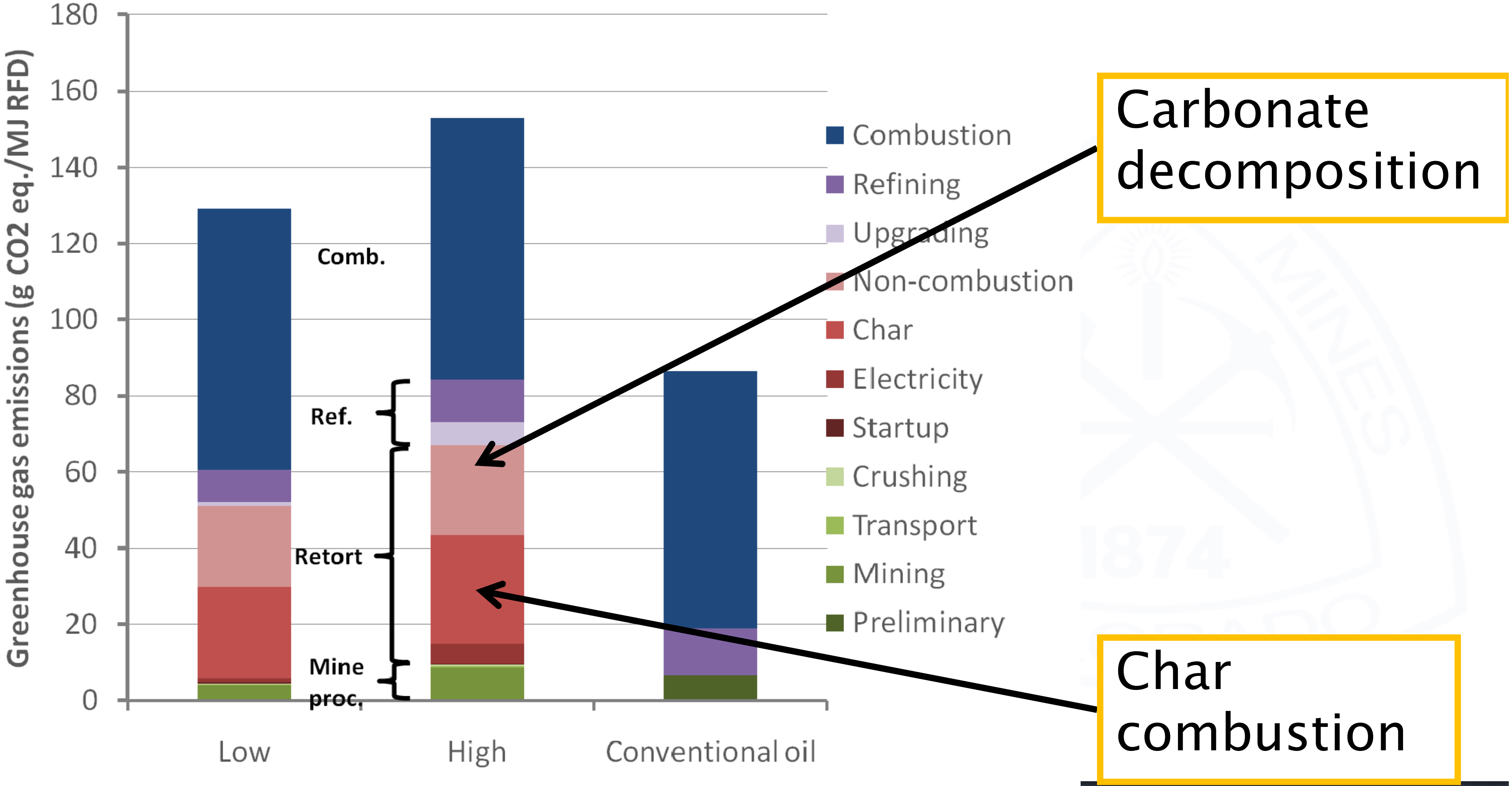
Shale oil upgrading and refining

- Shale oil generally must be upgraded prior to transport
  - Stabilization of reactive hydrocarbons
  - Remove excess nitrogen and metals
  - Range: 1 – 8 gCO_2/MJ RFD
- After upgrading, refining to finished products
  - U.S. refinery: ≈ 12 gCO_2 /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 ≈ 70 gCO_2/MJ

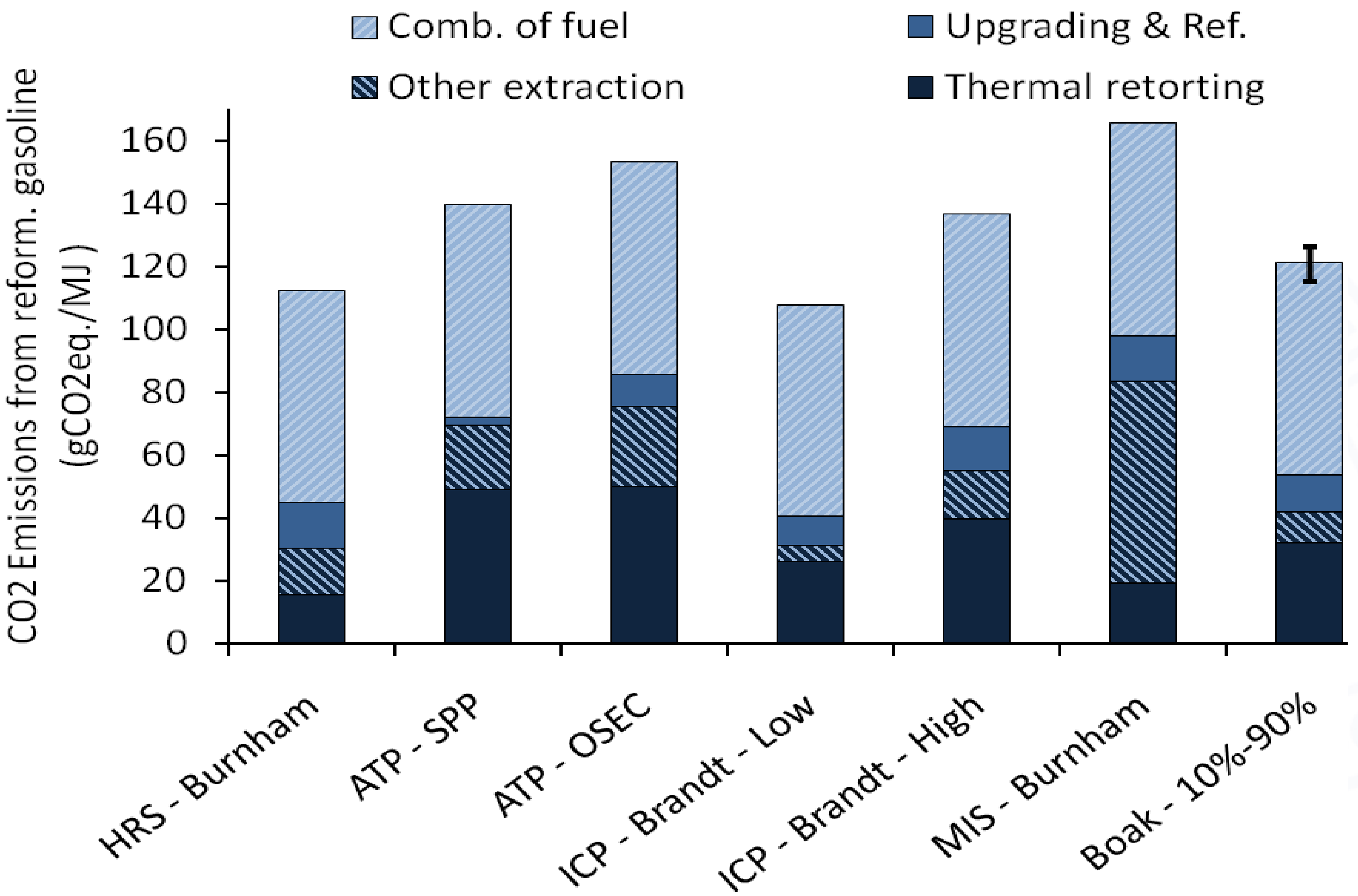
Example – ATP retort (Brandt, 2009)



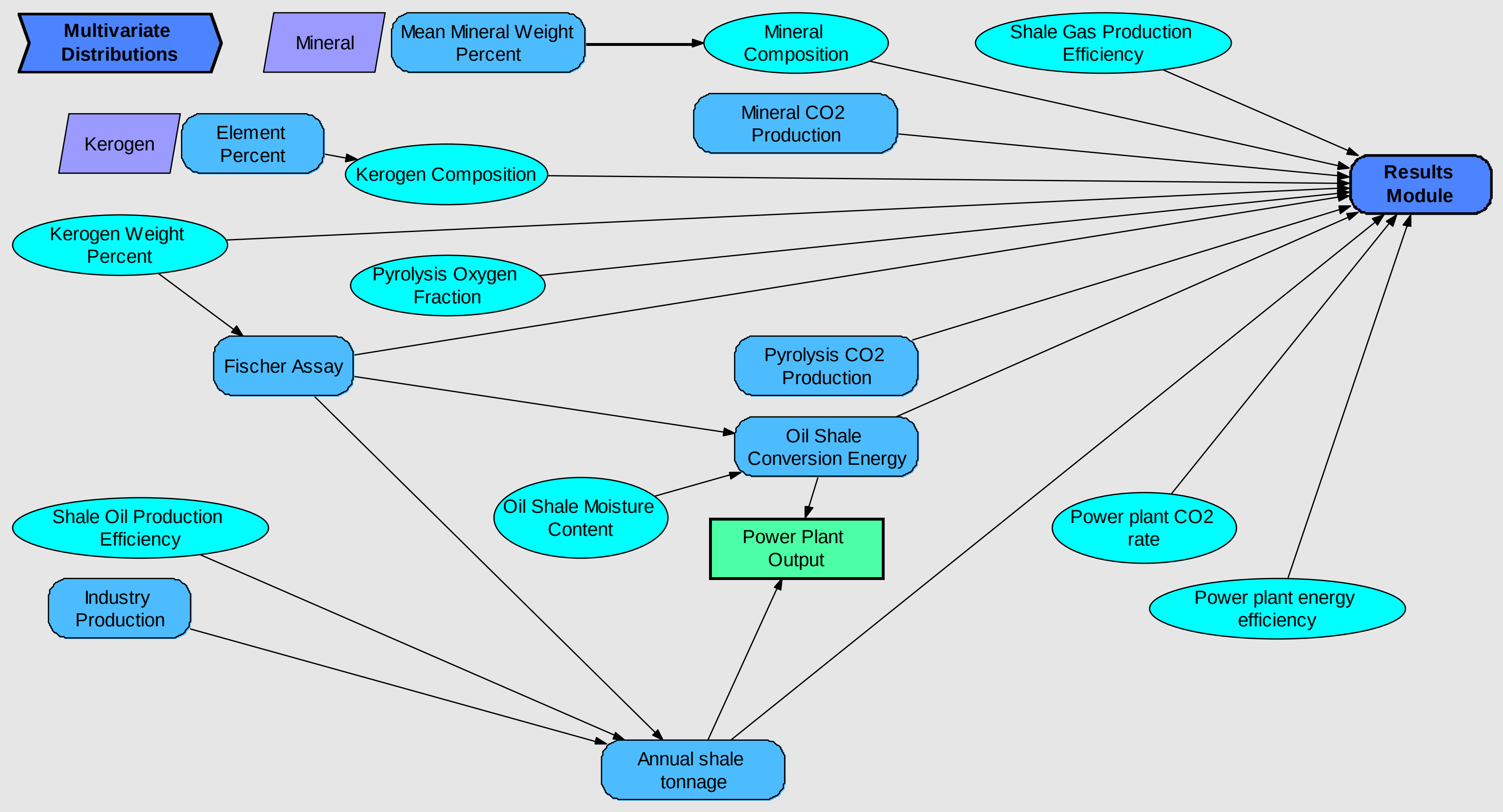
Carbonate decomposition

Char combustion

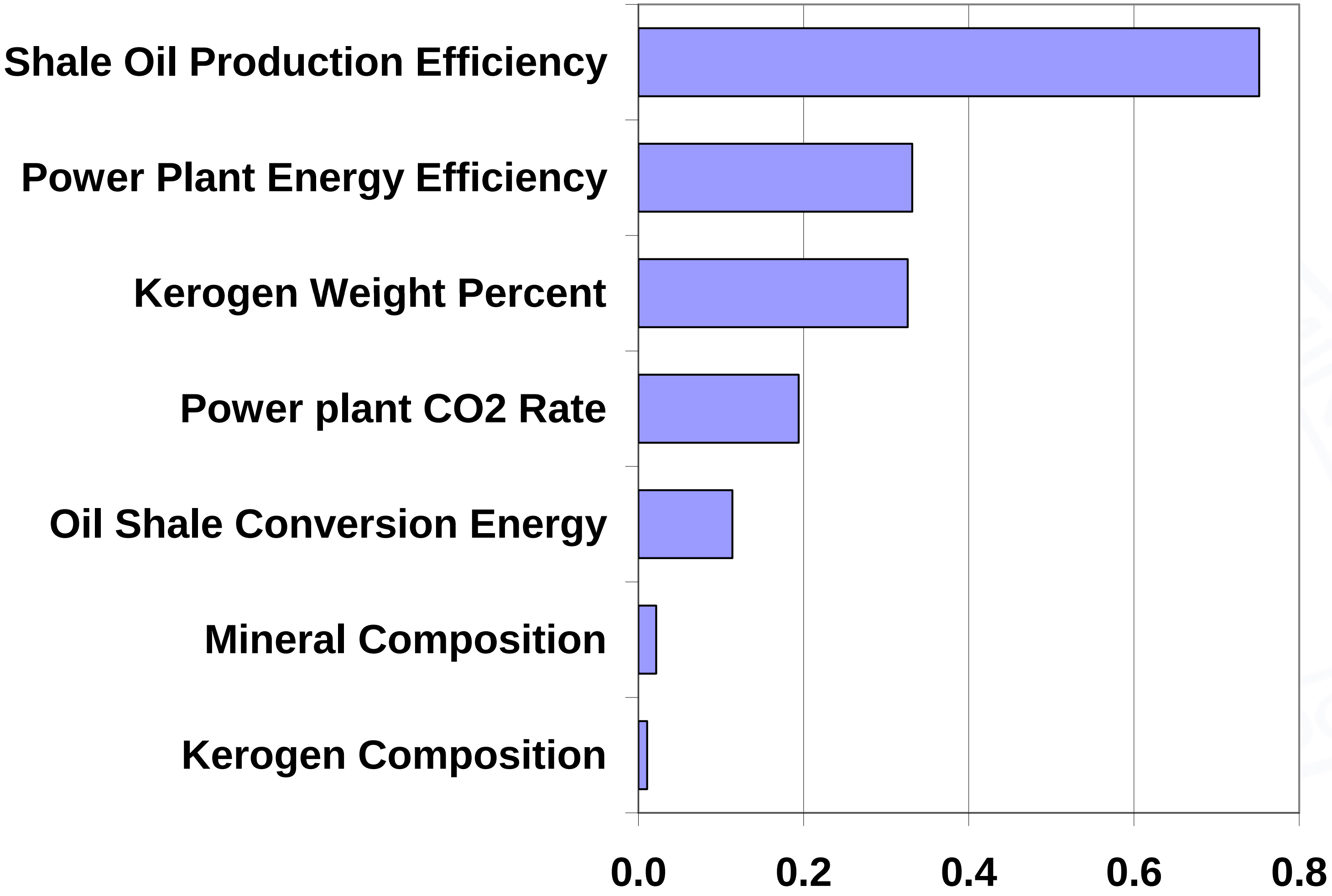
CO_2 emissions from oil shale



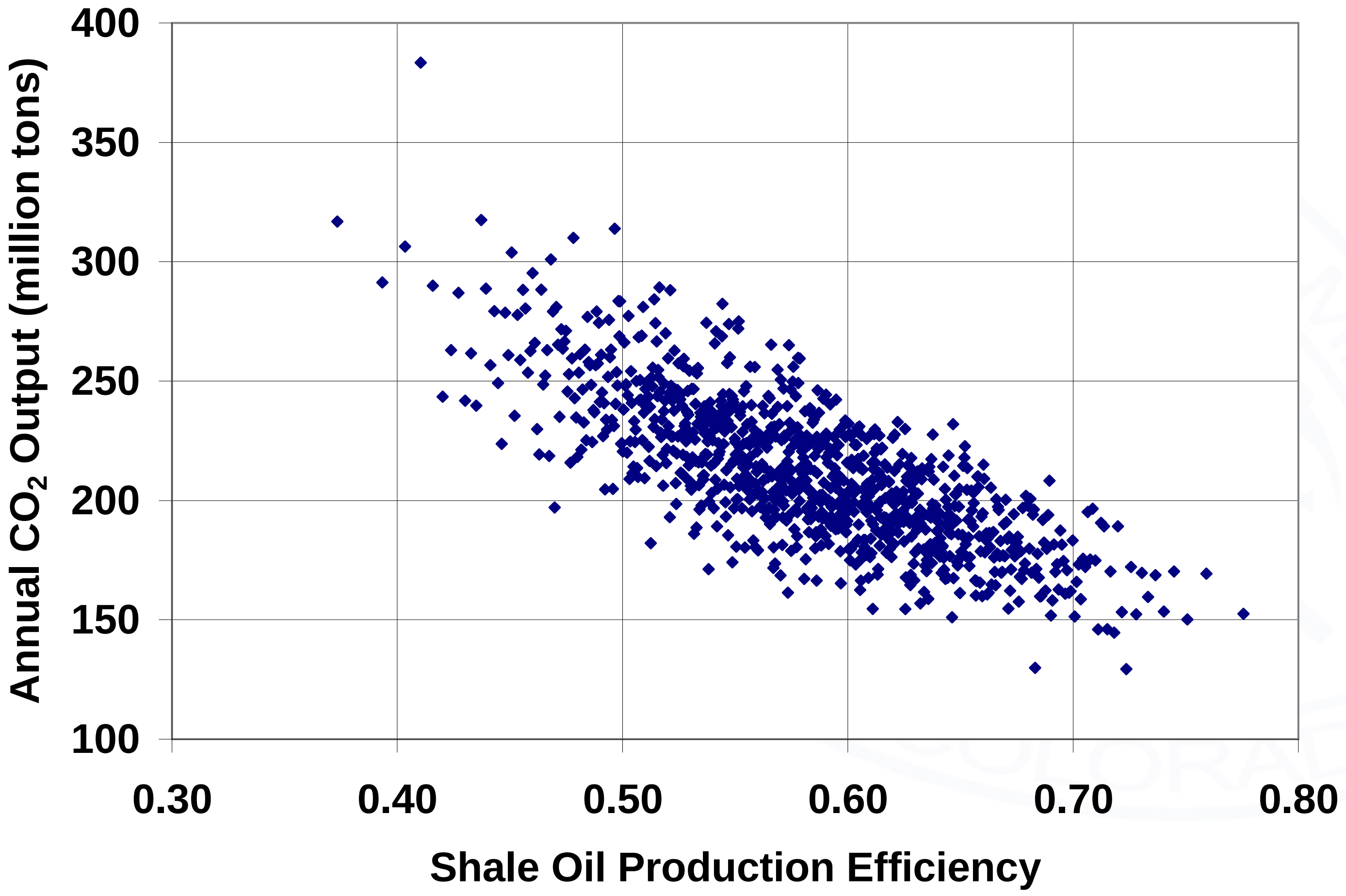
Modeling CO_2 emissions transparently



Primary factors in oil shale CO_2 emissions



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)

CO_2 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 CO_2 intensity of primary fuel
  - Increase fraction of primary heat that gets into the formation

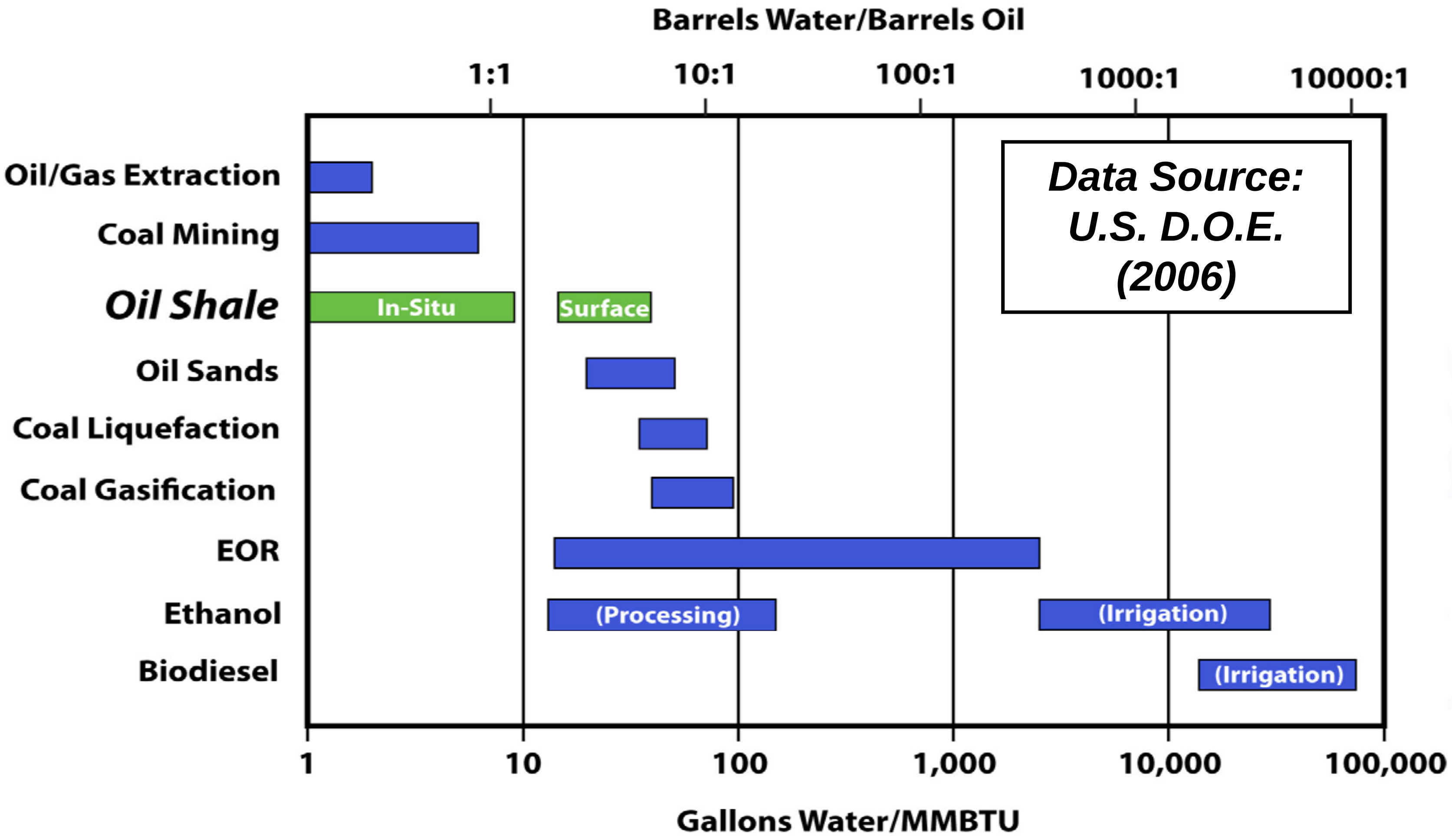
Other issues for alternative energy

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

Environmental issues for oil shale development

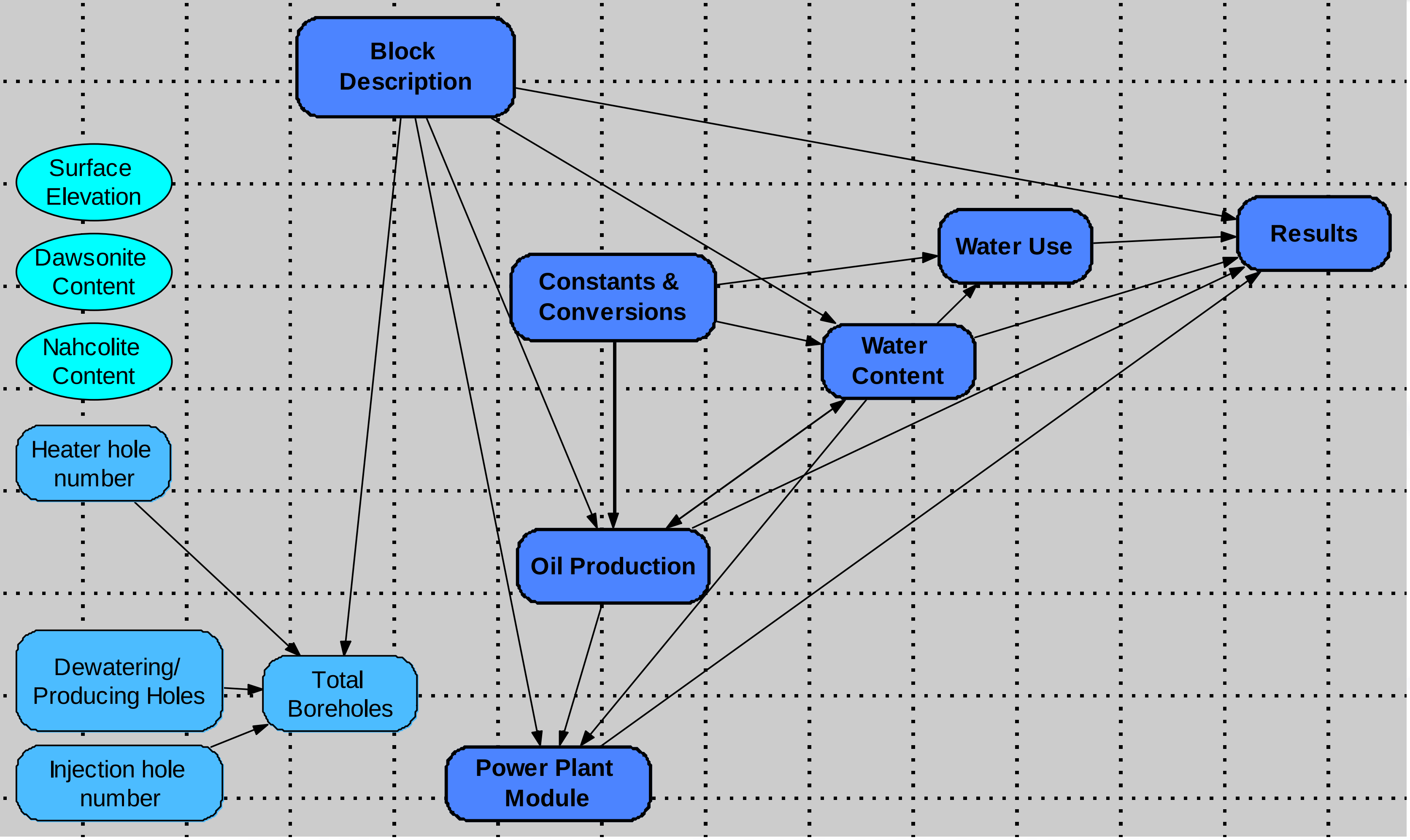
- Issues
  - Water quantity and quality
  - Air quality
  - Surface and ecosystem impact
  - Social and economic impacts
- Data needs
  - Definition process
  - Baseline collection
  - Management
  - Dissemination
- Model development
- Impact assessment & policy
- Technology development for mitigation

Water consumption for energy extraction

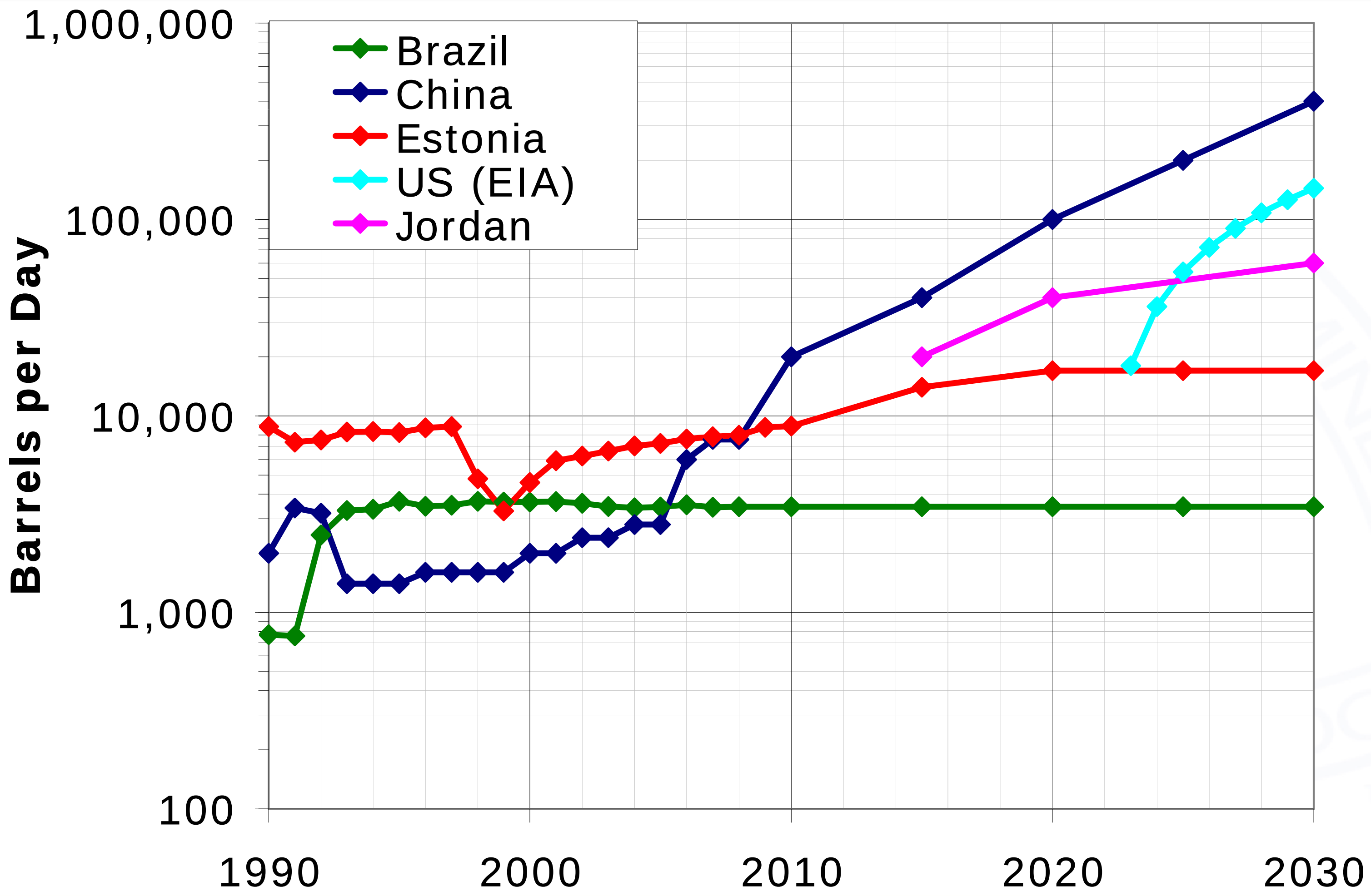


Data Source: U.S. D.O.E. (2006)

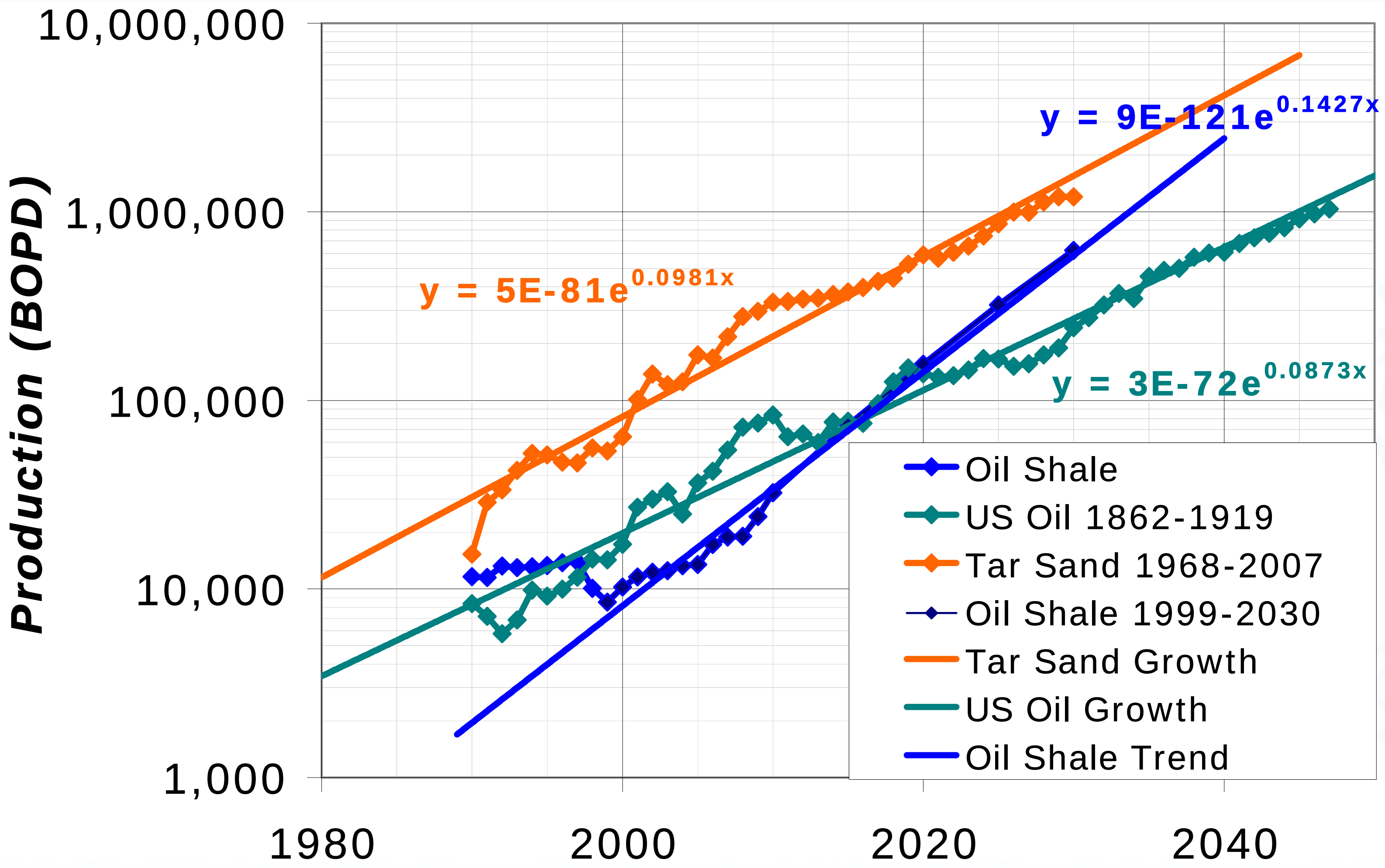
Modeling water use for oil shale production



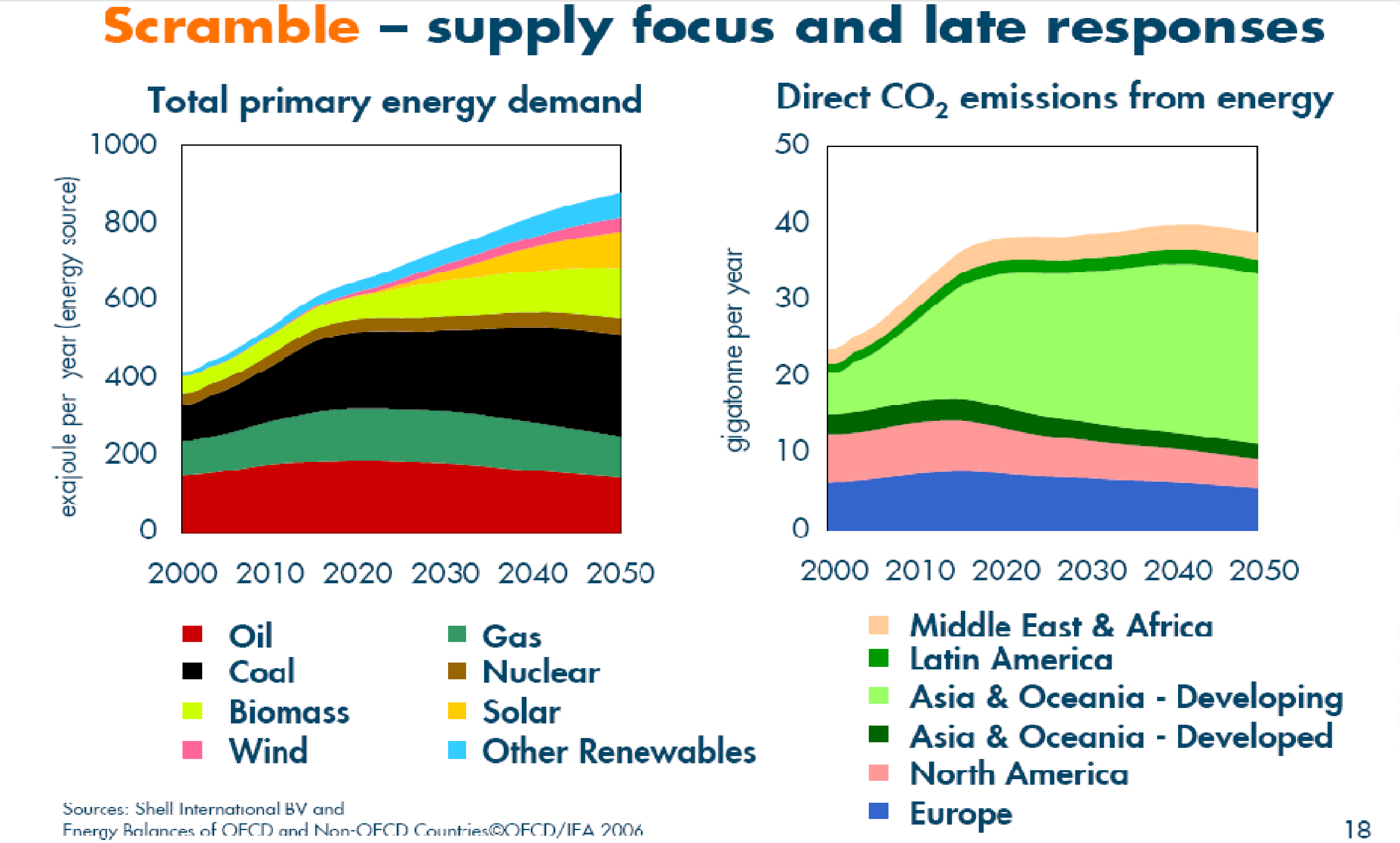
Historic & projected production



Historic comparisons



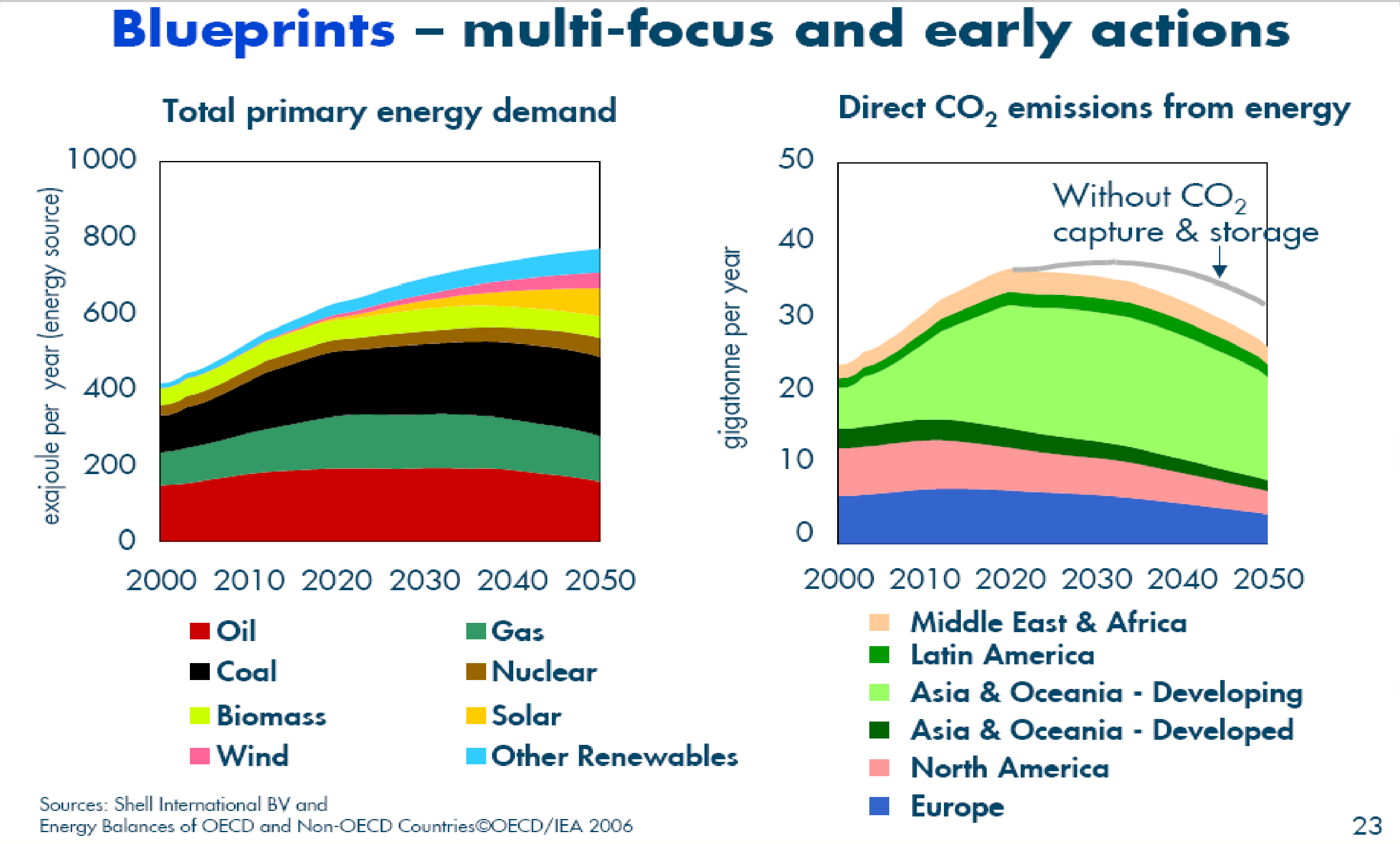
Shell energy projections – 1



Scramble – supply focus and late responses

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

- 🟥 Oil
- ⬛ Coal
- 🟩 Biomass
- 🟪 Wind
- 🟩 Gas
- 🟫 Nuclear
- 🟨 Solar
- 🟦 Other Renewables

Direct CO_2 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

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

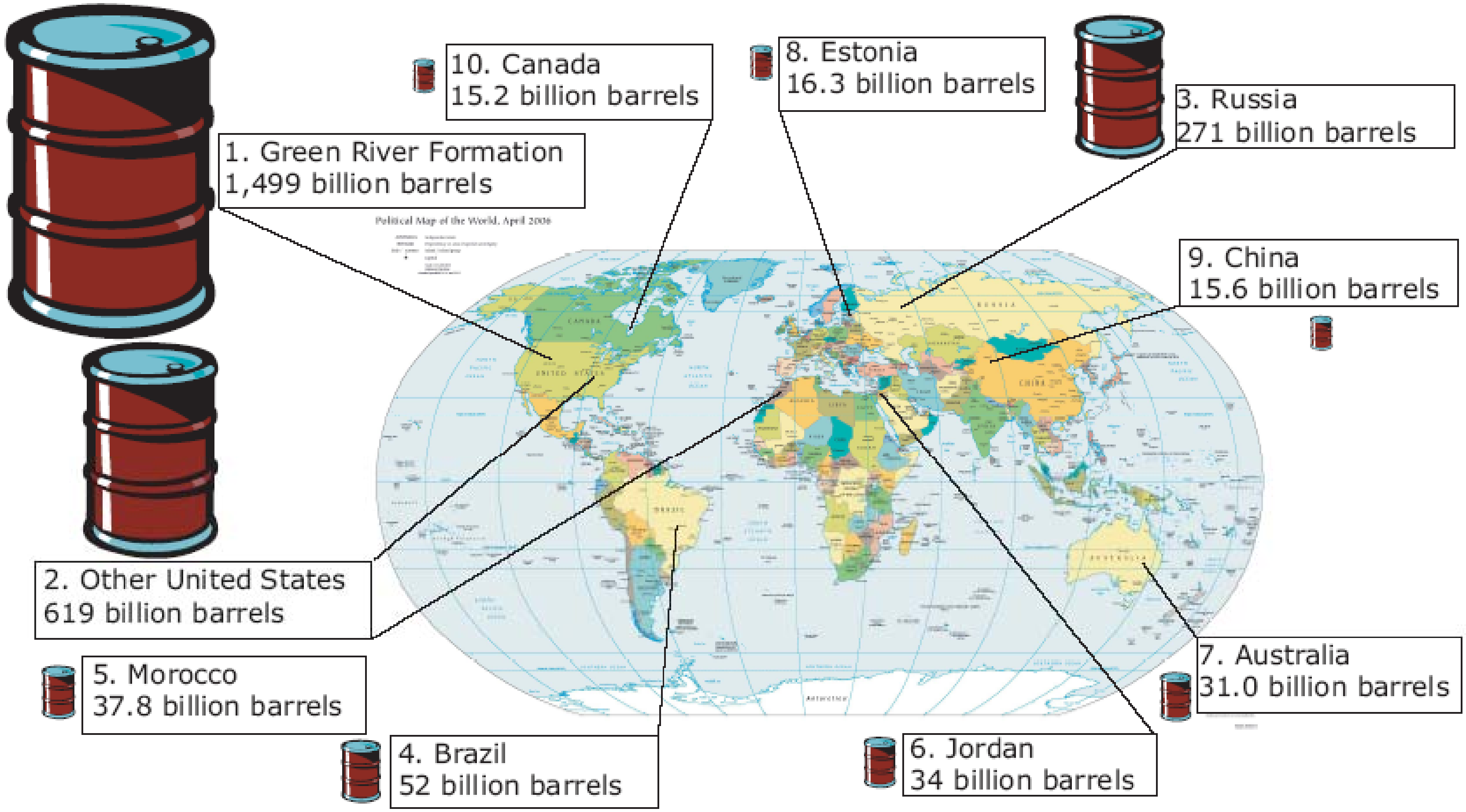
COSTAR and the Oil Shale Symposium

- 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

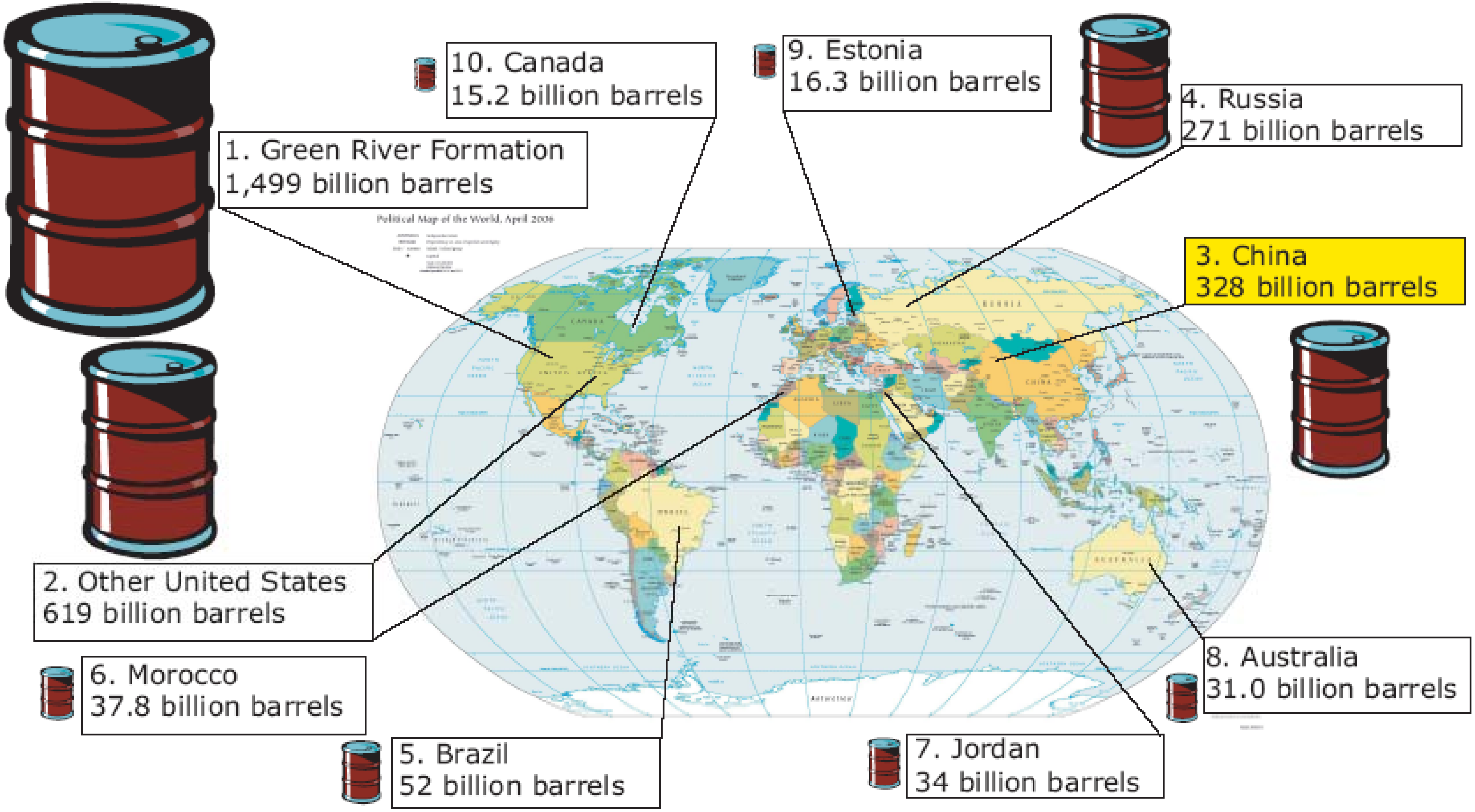
7. Australia
31.0 billion barrels

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
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15.2 billion barrels

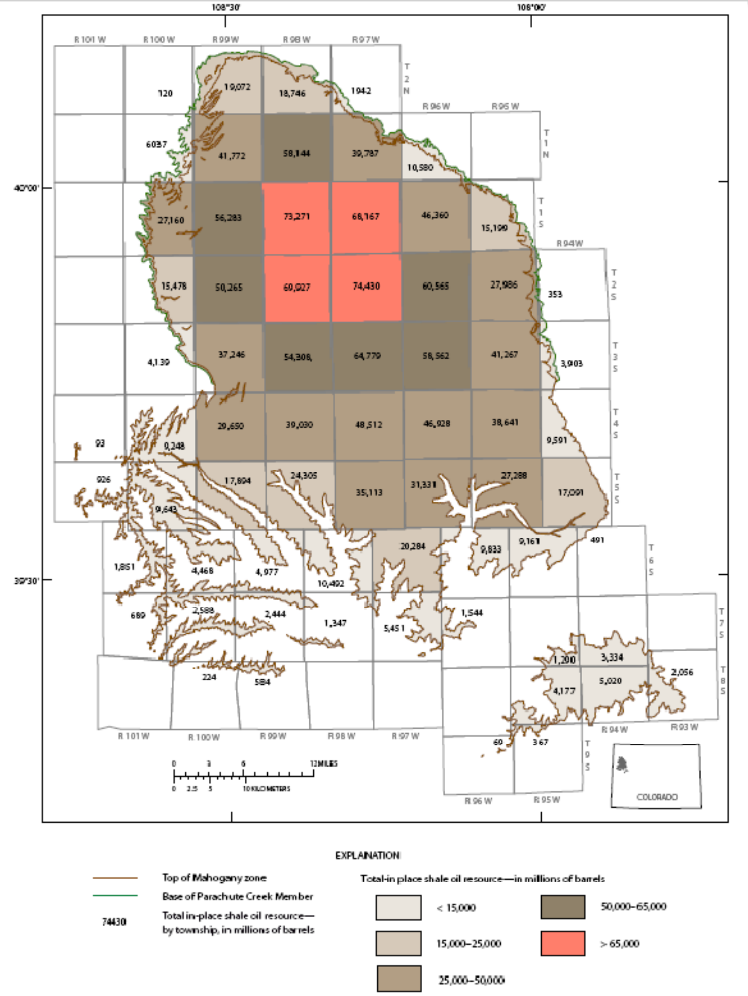
Four issues for progress

- 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

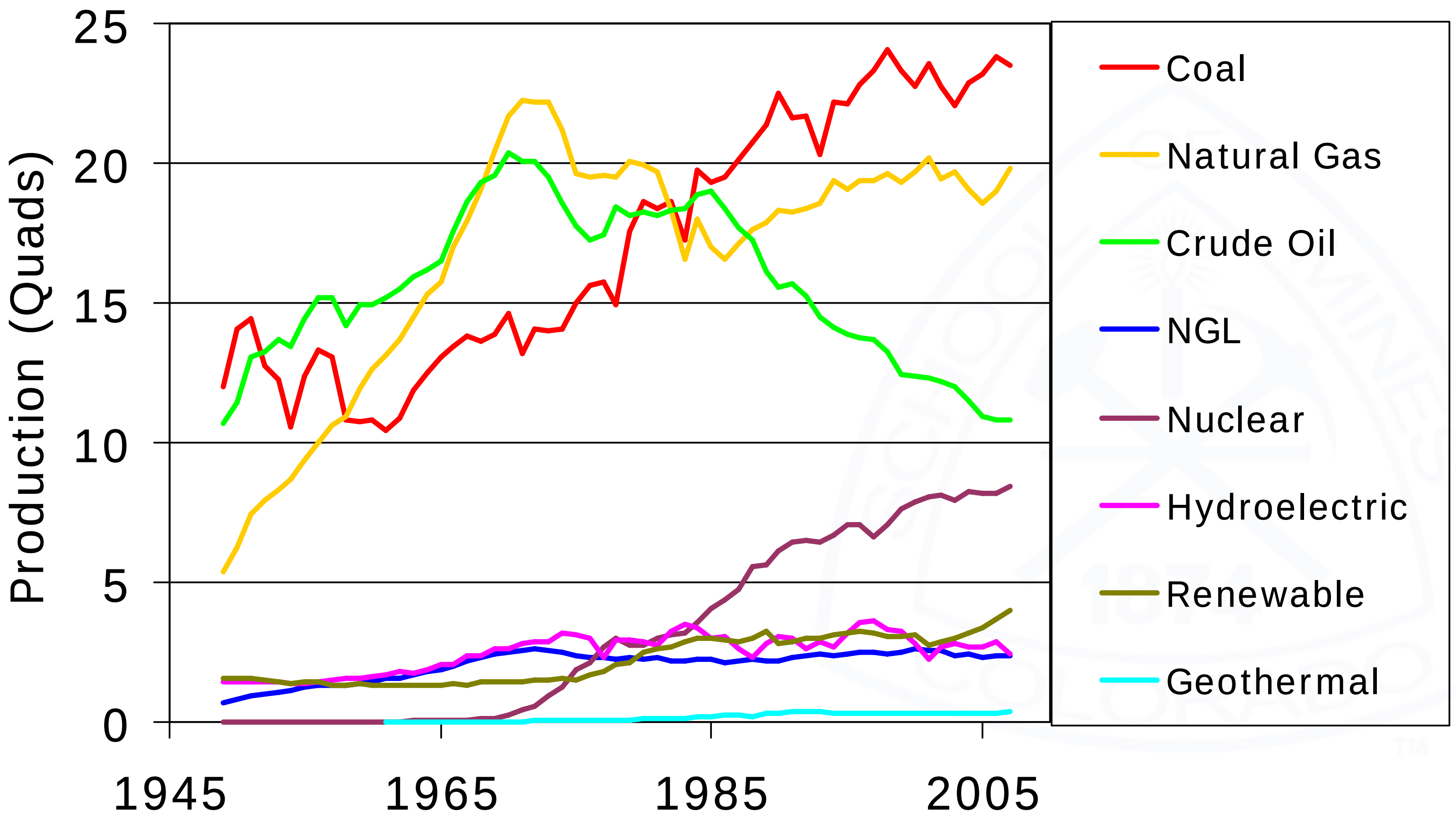
- Affected by all other listed issues
  - Access – time is money
  - Technology – energy, water, CO_2 efficiency
  - Environment – emissions, consumption, disruption
- Oil price, supply, demand, infrastructure
- Competing energy alternatives
  - Heavy oil
  - Global gas market
  - Renewable resources

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

U. S. Energy Production



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