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Comparison of the Acceptability of Various Oil Shale Processes

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Alternate Title
Oil Shale: Has Its Time Come or Gone?

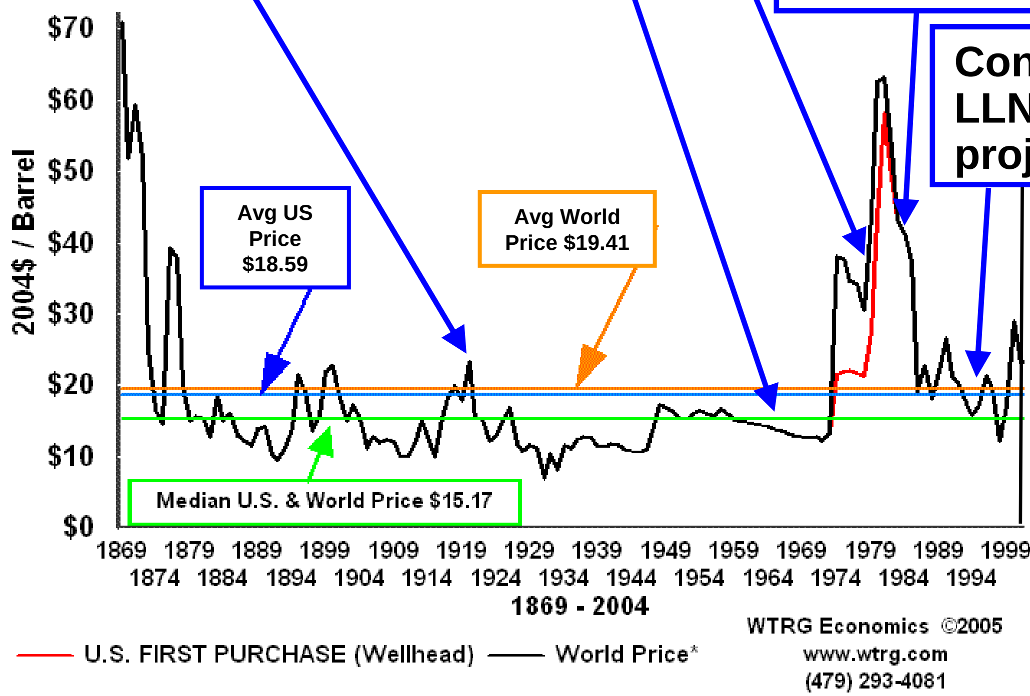
- **World War I**
  - **1918 National Geographic says oil production has nearly peaked and shale oil will provide for the future**
  - **Director of USBM says in 1919 that US production will peak in 2-5 years**

LLNL explores in-situ retorting of chimneys from nuclear explosions—abandoned a few years later for RISE

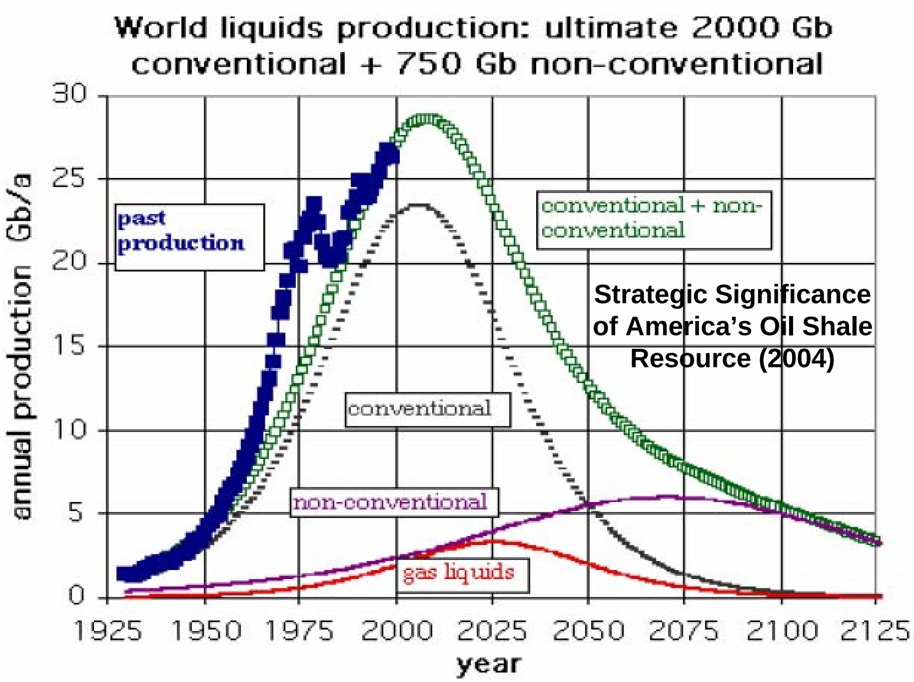
Crude oil predicted to be >$90 before the end of the century

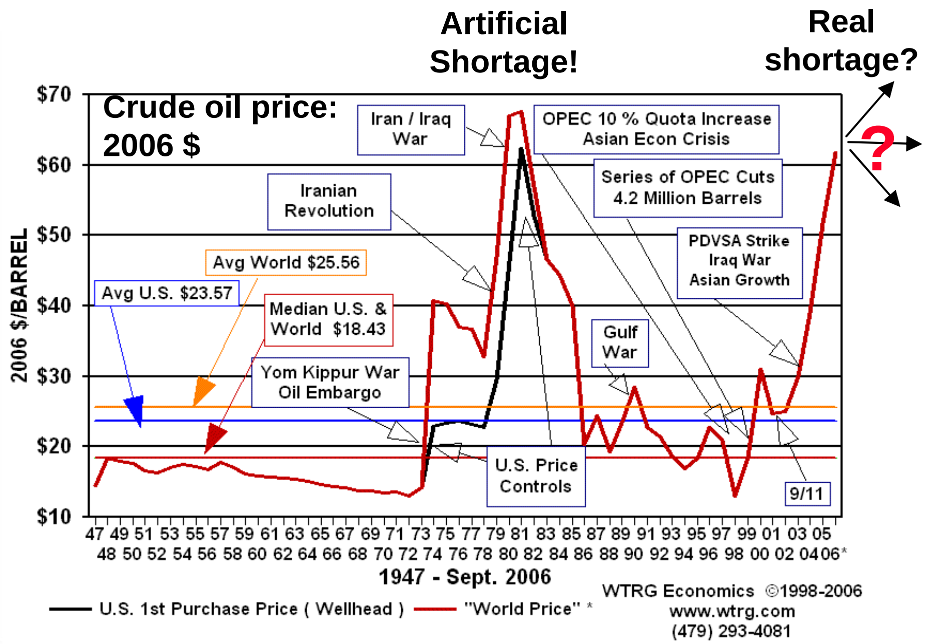
Exxon abandons Colony

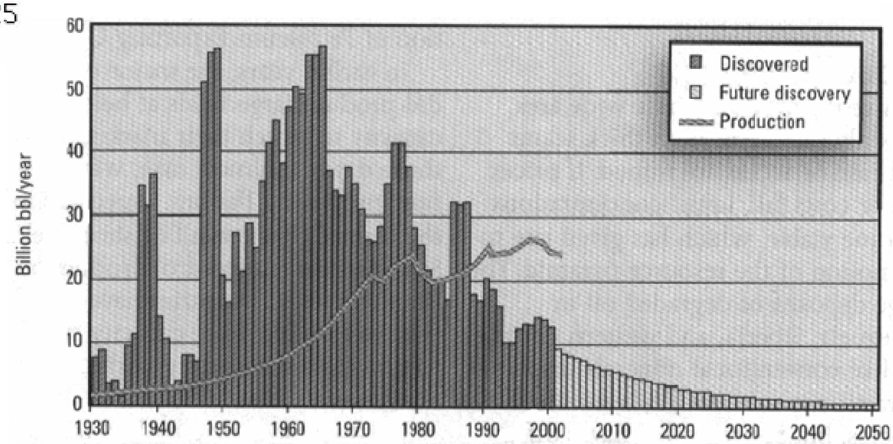
Congress kills LLNL oil shale project/CRADA



Are things different this time?







- There is growing evidence that demand for liquid fuels will soon outstrip petroleum supply
  - Backlog of discoveries is drying up
  - World excess production capacity is vanishing

The real issue this time is environment, not direct costs vs. demand-driven price

- **The time scale for implementing significant oil shale production is comparable to that predicted for shortfall of conventional petroleum, so there is less economic risk in the conventional sense**
  - **The exact time frame for "zero excess capacity" depends on world economic growth, but it is probably within the next 15 years**
  - **The time scale for ROI is increasing for new petroleum production**
- **Projected production costs for shale oil (mature industry) are equal to or less than projected prices for conventional petroleum ~$50/bbl)**
  - **Caveat: have we heard this before?**
- **However, growing concerns about global warming and support for "renewable" fuels might give shale oil a difficult future**
- **The challenge for the oil shale industry is to come up with processes that minimize environmental impacts, including CO_2 emissions**
  - **BP=Beyond Petroleum—solar panel fabrication plant in SF Bay Area**
  - **Bush State-of-Union Address mentioned hydrogen and ethanol, not oil shale**
  - **On the other hand, even the Danes are tiring of subsidies for renewable energy (WSJ, 2/09/06)**

Shale oil is principally for liquid transportation fuels, so what is the competition?

- Natural Gas
  - Compressed or cryogenic methane
  - Liquid petroleum gas
  - GTL technology
- Liquids from coal
  - Direct liquefaction
  - Indirect (gasification followed by Fischer-Tropsch)
- Electricity from coal or nuclear or solar or wind or waves or…
  - Battery powered cars
  - Advanced hybrid cars that can be plugged in to recharge batteries for short trips instead of using gasoline
  - Use electricity to reprocess metal-based fuel (Al-air or Zn-air)
  - Hydrogen fuel by electrolysis (nuclear only)
- Biomass fuels
  - Methanol
  - Cellulosic ethanol
  - Algal oils
  - Hydrogen from gasification

- **The 1990 NRC report has liquid fuels from oil shale at comparable cost to coal, while biomass liquids are significantly higher in cost**
  - **Can bioengineering reduce the cost of biomass liquids so they become a more attractive long-term option?**
  - **Will nuclear energy make a comeback based on an increasing concerns about global warming?**
  - **Can shale oil be produced with CO_2 emissions that are acceptable in the future?**
    - **How does shale oil compare quantitatively with other options?**
  - **What is the acceptable time frame for return on investment?**

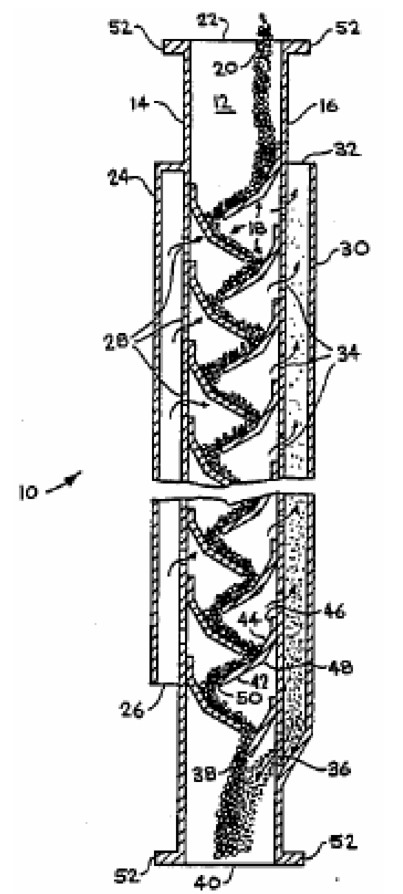
Oil shale processes can be categorized by various properties, including location and heating method

Heating Method	Above Ground	Below Ground
Conduction through a wall (various fuels)	Pumpherston, Fischer assay, Oil-Tech	Shell ICP (primary method), E.G.L.
Externally generated hot gas	Union B, Paraho Indirect, Superior Indirect, Petrosix	Chevron
Internal combustion	Union A, Paraho Direct, Superior Direct, Kiviter	Oxy MIS, LLNL RISE, Geokinetics Horizontal, Rio Blanco*
Hot recycled solids (inert or burned shale)	Galoter, Lurgi, Chevron STB, LLNL HRS, Shell Spher, ATP, TOSCO II	
Reactive fluids	IGT Hytort (high-pressure H_2), Donor solvent processes	Shell ICP (some embodiments)
Volumetric heating		ITTRI and LLNL radio-frequency

*This generic type has particularly challenging environmental issues related to combined poor oil yield, dilute offgas (HC and CO_2), and possibly aquifer contamination

Modeling of oil shale generic processes by LLNL in the 1980s concluded that hot recycled solid retorts were most promising for aboveground

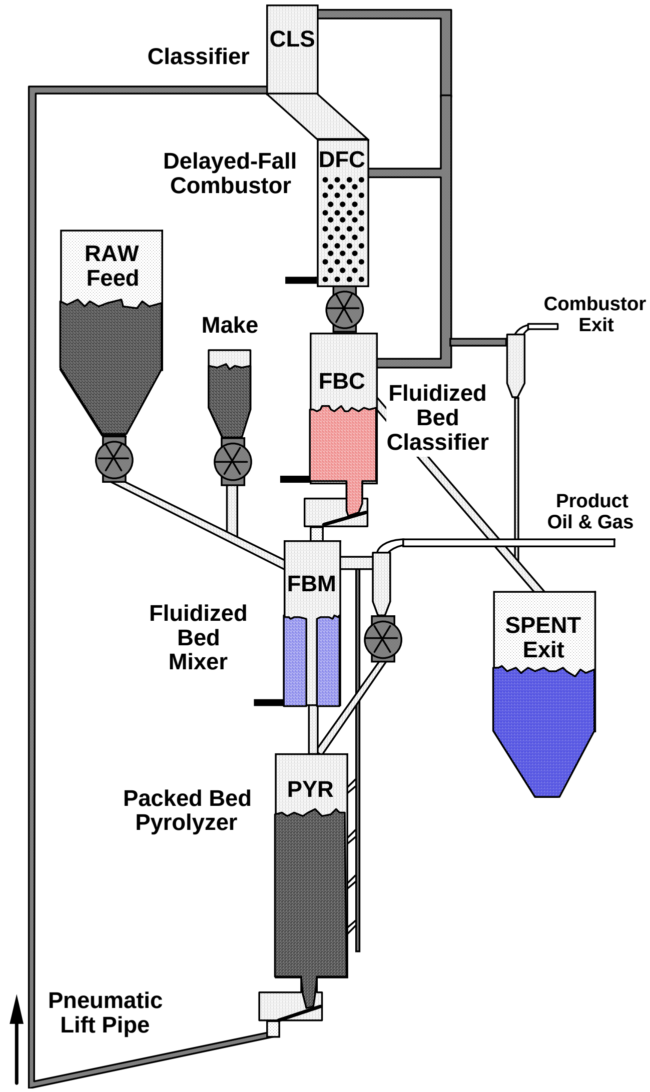
- **Separation of combustion and retorting chambers enables control needed for high oil yields and a concentrated pyrolysis gas stream**
- **Solids are a cheaper means of conveying heat, particularly when they already contain byproduct fuel by which they are heated**
- **Well designed spent-shale combustors using fine shale can achieve that heat with minimal carbonate decomposition and effective SO_2 capture**
- **Mixing of burned shale with pyrolysis products leads to effective capture of H_2S and COS, which are then converted to sulfates in the combustor**
- **Minimum reactor volumes and straightforward scaleup**



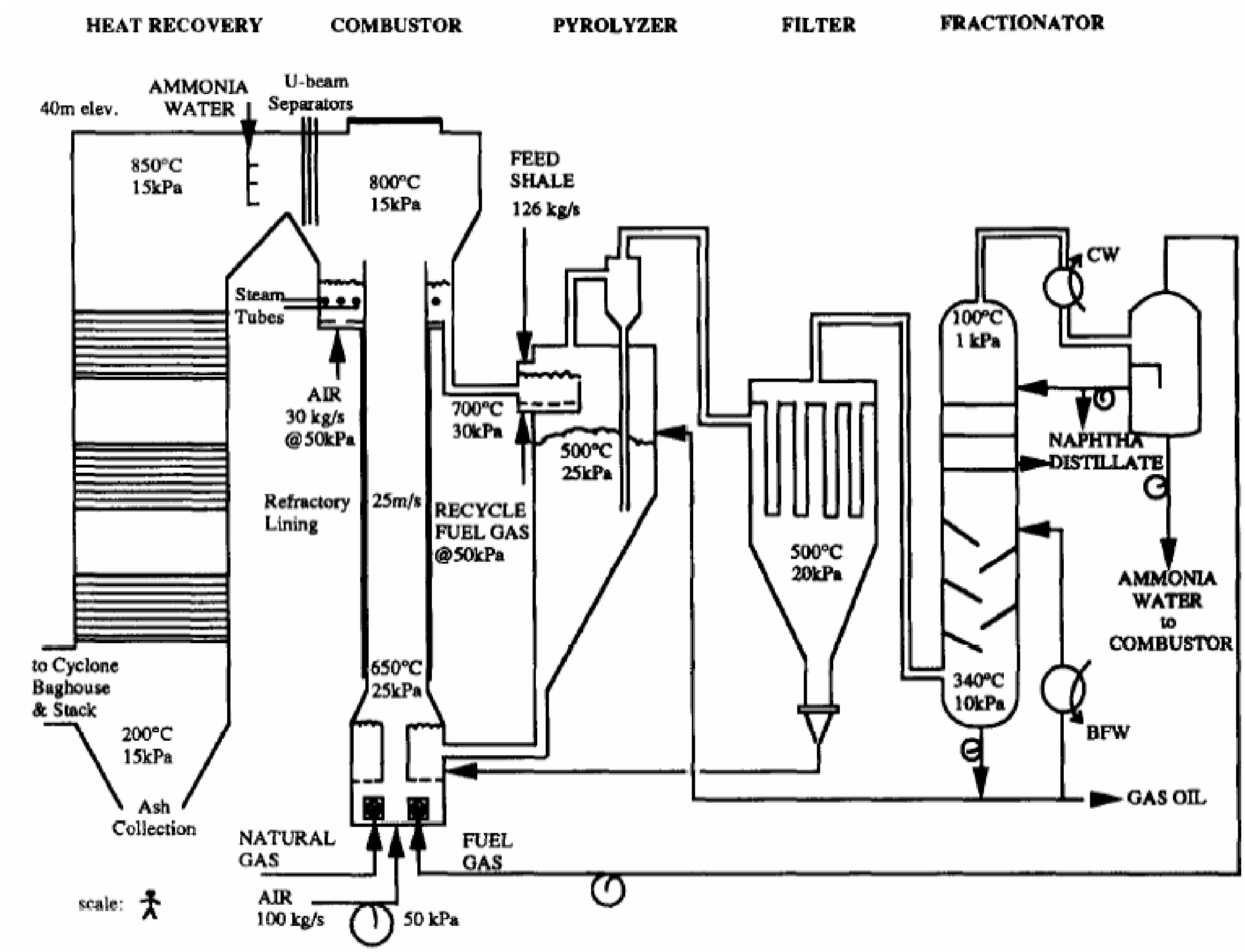
Mallon et al., US Patent 4539917
Lewis et al., US Patent 4619738

LLNL built and operated a 4 tonne/day hot solids retort to test the HRS process concept (1990-93) in a CRADA with Chevron-Conoco, Unocal, and Amoco

- A lift pipe, delayed fall combustor, fluid-bed mixer, and plug-flow pyrolyzer were used to:
  - Optimize residence times for both combustion and pyrolysis
  - Minimize reactor volume
- 27 runs between November 1990 and June 1993
  - 22 and 38 gpt; typically 96 and 102 % FA
- Separation of fines from shale oil was identified as the last remaining technical challenge
  - Tested hot gas filtering and heavy-oil recycling
- CO_2 mitigation must be added to the list in today's environment
  - Favors increasing the recycle ratio
  - Possibly makes O_2-enriched combustion gas more favorable



A process concept for 8,000 bbl/day of shale oil and 65 MW of electricity was developed that is prototypical of full commercial scale



P. H. Wallman, *Energy* **17**, 313-319 (1992)

There are still concerns about many processes if applied at massive scale

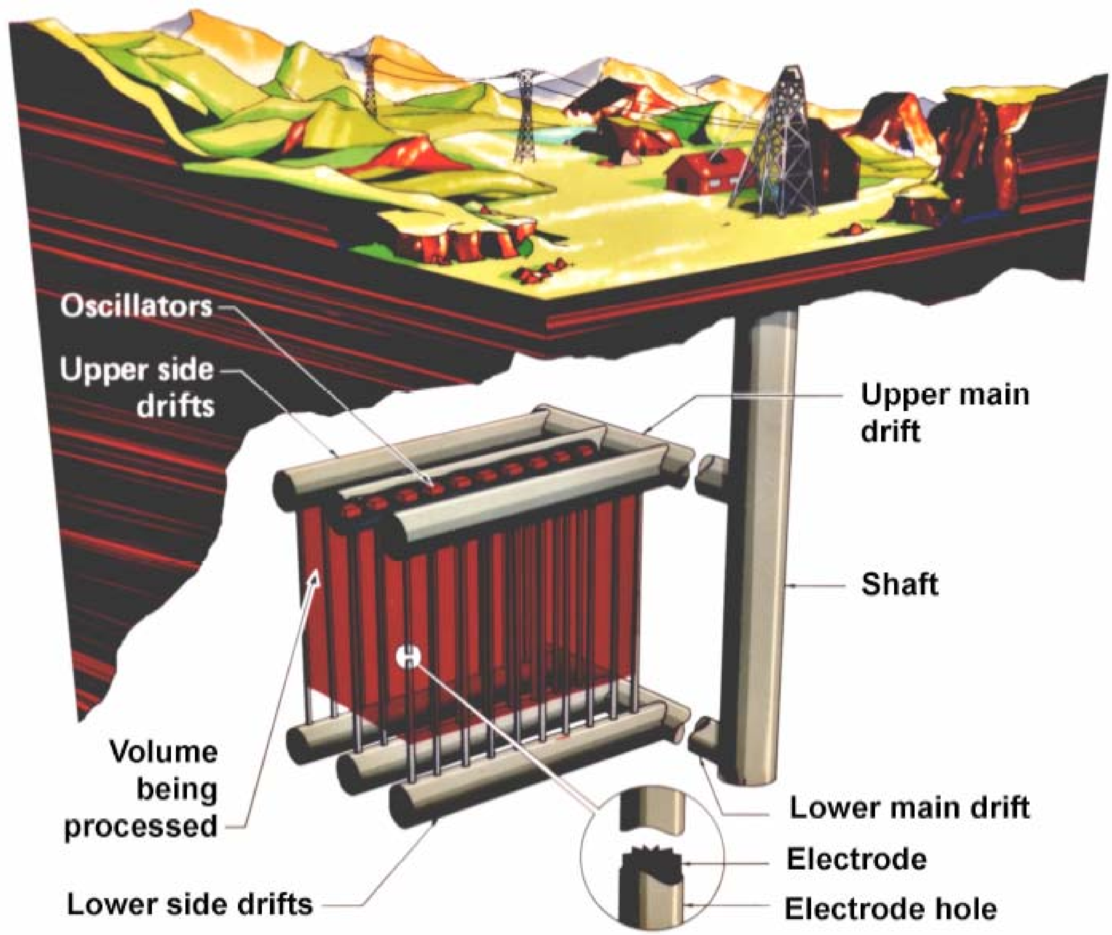
- **Modified In-Situ**
  - **Problems with yield due to flow problems**
  - **Concern for water quality degradation**
  - **Concerns for air emissions**
  - **What to do with mined shale needed for making in-situ retorts**
- **Aboveground**
  - **Requires strip mining of large areas for significant production**
  - **Concern for air emissions, shale disposal, and water quality/usage**
- **A mitigation cost of ~\$30/ton CO_2 will shift economics to lower carbonate decomposition and easier CO_2 sequestration***
  - **HRS: 0.13 tons/bbl = \$4/bbl, not counting CO_2 emissions from excess carbon combustion used to generate electricity**
  - **MIS: 0.46 tons/bbl = \$14/bbl**
  - **ICP: 0.06-0.16 tons/bbl = \$2-5/bbl, depending on direct or electrical heating and the efficiency of the electricity generation**

  burning shale oil makes 0.45 tons/bbl

Colorado residents will demand responsible development

In the early 1980s, LLNL explored the IITRI tri-plate rf waveguide concept for oil shale retorting

- **Surface disturbance is minimal if retorts are between drifts**
  - **Concept used modestly buried shale and relatively close borehole spacing**
- **Negligible carbonate decomposition and a high-BTU offgas**
- **Economics are favorable if inexpensive off-peak power is available**
  - **2¢/kW-h → $15/bbl total 1980 $s; 45% electricity**
  - **Could use solar, wind, or nuclear for electricity**



Laboratory experiments for understanding rf retorting led to a basic understanding of oil generation and degradation that was later applied to petroleum formation

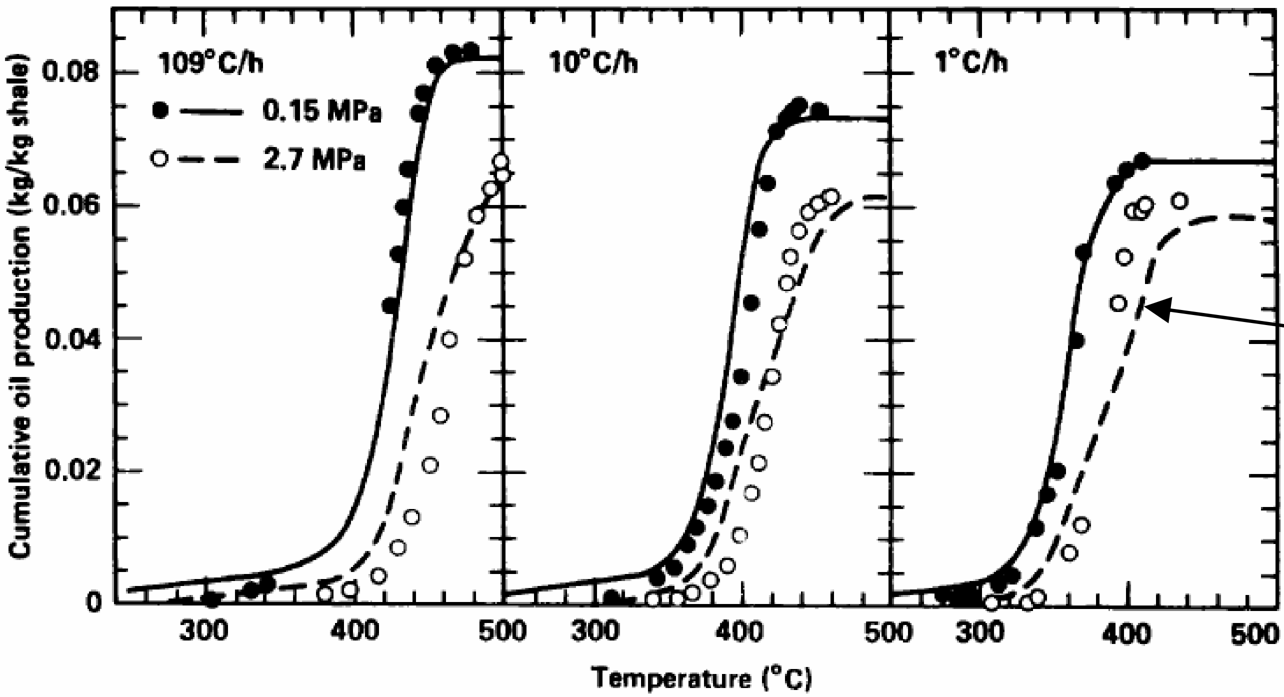
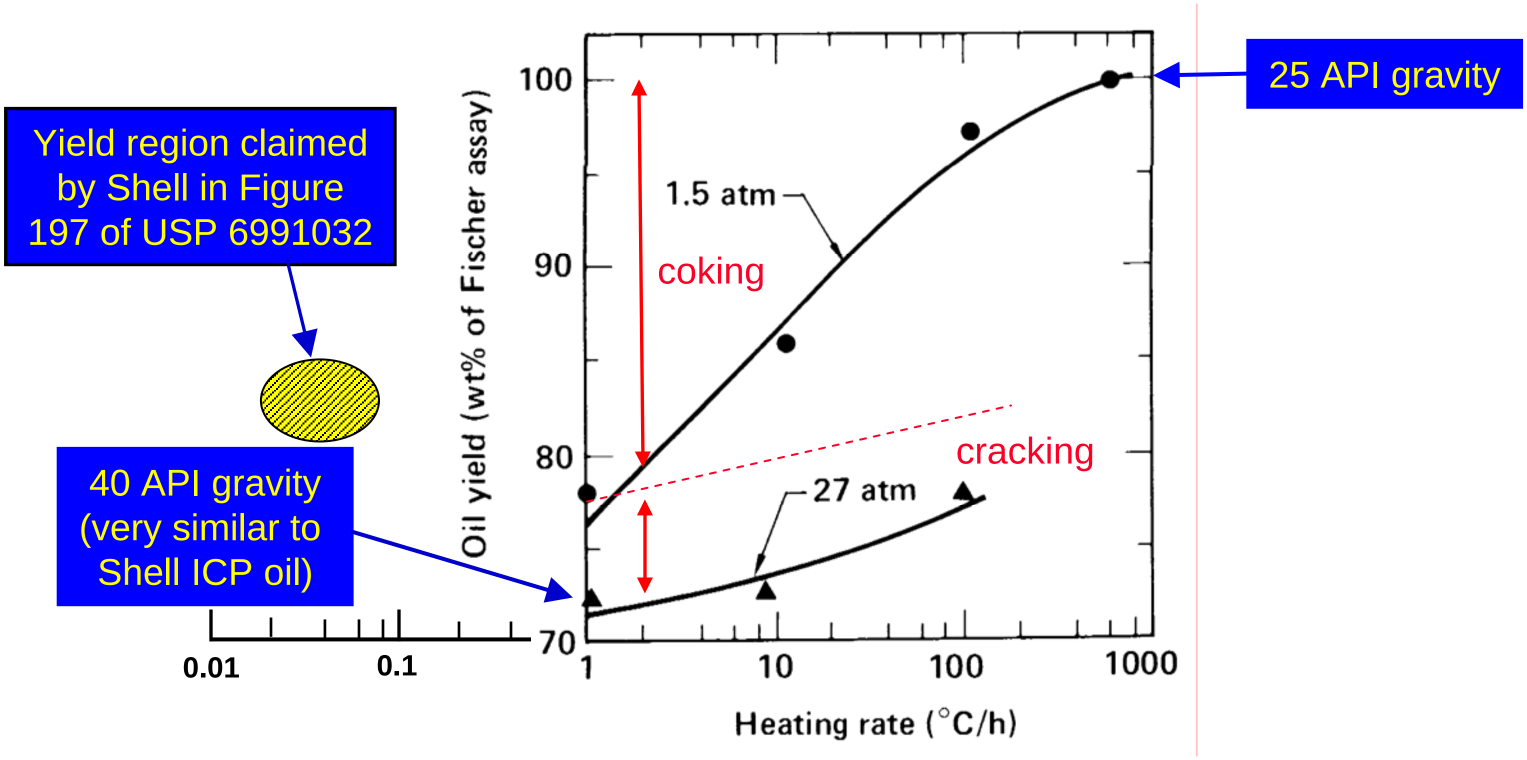


Figure 2. Comparison of calculated cumulative oil production with measurements of Burnham and Singleton (12).

Model calculations of Burnham and Braun, *In Situ* **9**, 1-23,1985

Vapor-phase expulsion mechanism for shallow depths
Pressure bounded by hydrostatic (long t) and lithostatic (short t) pressures

Although coking and cracking can decrease oil yields from slow, high-pressure retorting, oil quality will be improved



Shale Oil Properties From Burnham and Singleton (1983)

Conditions	Density, g/cm³	H/C ratio	Wt% N	Wt% S	90% distilled, °C
12 °C/min, 1 atm	0.906	1.61	2.7	0.66	504
1 °C/h, 27 atm	0.826	1.90	1.5	0.36	395

Slow high-pressure retorting produces more gas for either power production or FT synthesis

- Organic carbon distribution in products

	oil	gas	char
Fischer assay	70	6	24
Slow, deep retorting*	55	10	35

*estimated from limited LLNL experiments (Singleton & Burnham, 1983) and limited public information on Shell ICP yields

- Heating value of gas increases due to increased concentration of light hydrocarbons via in-situ coking and cracking
- Energy content in gas increases from ~425 MJ/Mg to ~800 MJ/Mg for average oil shale (25 gal/ton)
- Yields do have uncertainties
  - Poor carbon balance and possible gas loss at 27 atm by S&B, 1983
  - S&B got higher yields on unpublished experiments on cores
  - B&B (2005) estimated 5% higher possible with lower porosity
  - Uncertainties in yields retorted by Shell; 75-80% yield cited in text; could be due to a difference in yields calculated on volume and mass bases

Slow retorting has the advantage of requiring less energy per mass of shale

- Although the time to reach steady state is longer, the shale oil production rate is higher for a given energy input rate at slower heating rates

Heating rate	Final T (^oC)	MJ/Mg of 104 l/Mg shale[1]	MJ/Mg of 146 l/Mg shale
3 ^oC/mo	300	302	347
3 ^oC/day	350	364	400
3 ^oC/h	400	428	454

[1] 0.277 kW-h/MJ if using electrical power

- Slow heating rates have additional advantages
  - Thermal conduction can create more uniform heating over large volumes
  - Use of off-peak (diurnal and seasonal) or sporadic (solar, wind) electrical power for either conductive or volumetric heating

Basic question: what is the cheapest way to get energy into the formation over a timescale of a few years?

What are the relative advantages of conductive, advective, and volumetric heating?

- Conductive heating requires a lot of wells
  - Spacing depends on timescale for heating
  - Proposals exist for electrical heaters, downhole methane burners, and downhole tubes carrying steam or organic fluids
  - Can electrochemical conversion of coal to electricity at 80% conversion efficiency make electrical heating more interesting?
  - Could one sell direct heating by nuclear fuel/waste (e.g., synrock)?
- Advective heating with injected fluids has a lot of challenges
  - Can fracture permeability be created uniformly enough?
  - Will water injection lead to unacceptable corrosion and mineral dissolution?
  - Could an organic liquid be recovered with acceptable losses?
  - Do hot gases have enough heat capacity to justify pumping costs?
  - Can CO_2 sequestration be part of the process?
  - Is the heating value of the char worth pursuing for an in-situ process?
- What is the penetration depth of radio-frequency radiation?
  - Would have to be 10s of meters to have an advantage over conductive heating due to 3x cost of energy
  - Insufficient data exists to our knowledge to predict penetration depth as a function of retorting conditions

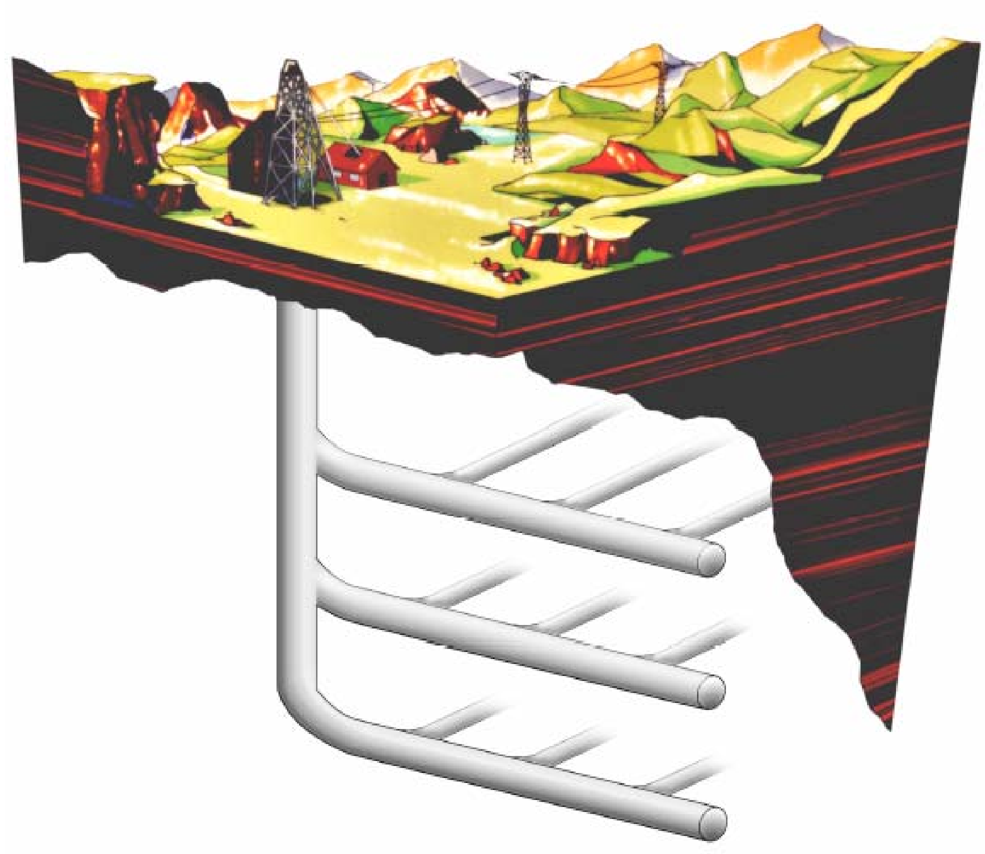
Is the heating value of the char worth pursuing for an in-situ process?

- Oil shale char has empirical formula of ~$CH_{0.4}$ and a heating value of 382 J per wt% C per g shale
  - For 25 gpt shale heated slowly (~35% org C as char),
    3.9 wt% org C in spent shale gives 1490 J/g exothermic
- Oil shale also has exothermic (sulfate) and endothermic (carbonate) combustion reactions
  - 0.5 wt% S gives 164 J/g exothermic
  - 20 wt% min CO_2 gives 413 J/g endothermic
- Net energy is 1240 MJ/Mg raw shale
  - 3-4 times the energy need for retorting
    - However, CO_2 emissions are 0.28 kg/MJ
    - Compare to methane at 0.07 kg/MJ or coal at ~0.1 kg/MJ

One should look at this energy resource with some skepticism

Horizontal (deviated) wells can provide parallel plates to adapt the IITRI concept to deep, slow retorting

- **Propose to slowly heat deep shale and produce shale oil over 5 to 7 years**
- **Expulsion by overburden-driven compaction much like in natural petroleum formation if deep enough**
- **Shale oil composition becomes even more like natural petroleum**
- **Aquifer contamination not as much of an issue if below fresh water depth**
- **Concept presented at Shell Bellaire Research Center on 1/27/1995**
  - **cited in Shell patents**



From A. K. Burnham, Slow Radio-Frequency Processing of Large Oil Shale Volumes to Produce Petroleum-like Shale Oil, LLNL Report UCRL-ID-15504 (Aug. 2003)

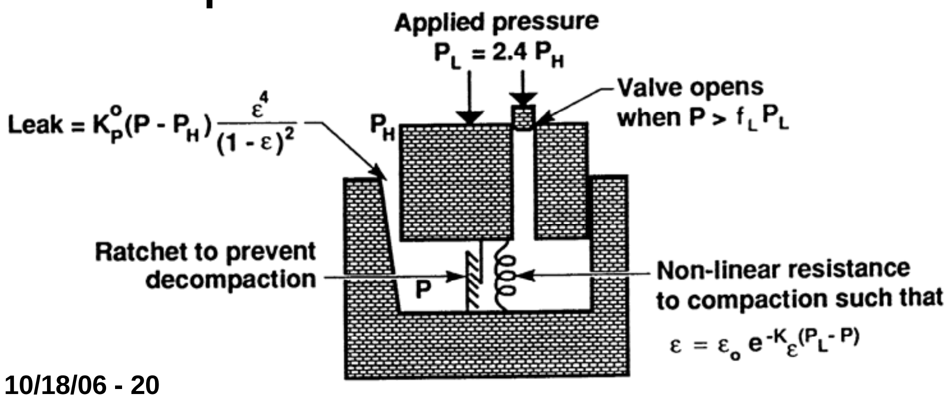
The primary challenge is to uniformly heat the formation with a minimum of wells

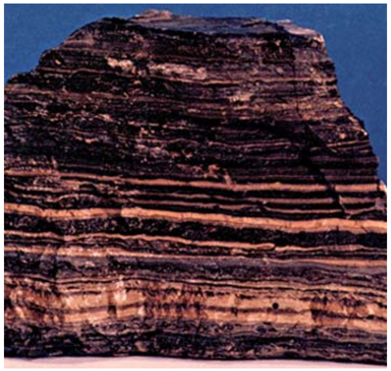
- **Drilling costs go as the square of the well spacing**
  - **Tenfold reduction if one replaces feet spacing with meters**
  - **Need well spacing ≤ 1/e distance for power**
  - **Cameron Engineering Handbook says a 1/e distance of 100 m can be obtained in the shortwave radio range**
  - **A 6.5 kW/m linear antenna can heat a radius of 50 m at 3 ^{o}C/mo**
- **The primary absorbing species changes with temperature**
  - **Water is the primary absorber at low temperature**
    - **Mineral dehydration depends on pressure (Braun & Burnham, 1985)**
  - **Char is the primary absorber upon retorting**
- **If the frequency is not well chosen, and possibly it needs to be variable, all the energy will be deposited near the well bore, thereby wasting the investment in expensive energy**

We've not seen a rigorous analysis that shows whether this concept will work or not

Any true in-situ process will have to deal with subsidence

- The expulsion mechanism depends on depth
  - Shallow deposits–oil and gas are expelled as vapors, and porosity replaces organic matter
  - Deep deposits–oil and gas are expelled as a single fluid phase by compaction of the rock by overburden pressure
- Supportable porosity is a function depth
  - Sweeney et al.: $\phi = 0.35\, e^{-0.7z}$, where ϕ is porosity and z is depth in km
  - 17% porosity at 1 km; 5% porosity at 2 km
  - 25 gal/ton oil shale is 30 vol% kerogen
- Organic matter is >50% by volume for grades greater than ~50 gal/ton
  - Rich layers, no matter how thin, will compact even at shallow depths
  - One needs the distribution of oil shale grades down to the mm level to predict compaction





Summary of tradeoffs for aboveground and in-situ processing

- **True in-situ (rf heating or dense wells as in Shell ICP) has the promise of producing oil from deeper deposits with less environmental disruption**
  - **Do lower environmental impacts of true in-situ counterbalance the lower production efficiency compared to aboveground processing?**
  - **Can downhole burners give more economical heating for conductive processes?**
  - **Does more effective deposition of heat using rf counterbalance its higher cost?**
  - **Can oil generated in situ be recovered with high efficiency?**
  - **Does increased oil quality counterbalance the lower yield?**
- **Aboveground retorting can produce oil at high efficiency**
  - **Increased process control comes at the expense of higher mining costs and shale disposal issues**
  - **CO_2 mitigation is a significant new cost that can shift process design**
  - **The remaining technical challenge is efficient hot-gas filtration if heavy oil recycle is not effective**