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December 11, 2006

26th Oil Shale Symposium
Golden, CO, United States
October 16, 2006 through October 18, 2006

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Comparison of the Acceptability of Various Oil Shale Processes

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Abstract

While oil shale has the potential to provide a substantial fraction of our nation's liquid fuels for many decades, cost and environmental acceptability are significant issues to be addressed. Lawrence Livermore National Laboratory (LLNL) examined a variety of oil shale processes between the mid 1960s and the mid 1990s, starting with retorting of rubble chimneys created from nuclear explosions (Lombard et al., 1967) and ending with in-situ retorting of deep, large volumes of oil shale (Burnham, 2003). In between, it examined modified-in-situ combustion retorting of rubble blocks created by conventional mining and blasting (Lewis and Rothman, 1975; Campbell, 1981), in-situ retorting by radio-frequency energy (Mallon, 1980), aboveground combustion retorting (Braun et al., 1984), and aboveground processing by hot-solids recycle (HRS) (Lewis et al., 1986). This paper reviews various types of processes in both generic and specific forms and outlines some of the tradeoffs for large-scale development activities. Particular attention is given to hot-recycled-solids processes that maximize yield and minimize oil shale residence time during processing and true in-situ processes that generate oil over several years that is more similar to natural petroleum.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under Contract No. W-7405-Eng-48. We thank James L. Williams of WGRT Economics for updating and giving us permission to use his figures on historical oil prices.

Introduction

The recovery of oil from oil shale dates back centuries. Although reserves of oil shale are comparable to remaining reserves of conventional petroleum and probably greater than the amount of petroleum still to be discovered (Johnson et al., 2004), it was never a significant energy source in the United States, and world-wide production has actually decreased over the past two decades due to its greater cost and environmental problems. A 1918 National Geographic article (Mitchell, 1918) proclaimed that shale oil was just about to replace crude oil due to dwindling crude supply, but new discoveries soon eliminated the need for oil shale. The real price of crude oil was nearly constant for almost 100 years until OPEC, primarily Saudi Arabia, became the supply controller in the mid 1970s, at which time the real price increased four-fold over a few years. Predictions of permanently high prices and proclamations of the national security importance of domestic energy supplies were rampant. Effort in synthetic fuels greatly increased in the United States, with oil shale being a principal player. However, OPEC could not retain control of supply and prices for long, and the sharp decline in oil prices after 1980 completely destroyed the national oil shale effort. LLNL was one of the final players, leading a CRADA to explore the HRS process with partners Amoco, Chevron-Conoco, Unocal.

The obvious question is whether the current spike will be different from the 1980 spike. Although a decrease in prices from the current high is likely, the drop probably won't be as much or as long lived. Although world-wide petroleum production has been primarily demand-limited for 125

years, it will probably reach its maximum rate within the next 15 years, while demand will continue to increase (Johnson et al., 2004). This imbalance will cause its price to rise to the level of alternatives, including conservation. In addition, the rate of production has exceeded discoveries for more than 10 years, and the gap is expected to persist. Finally, the time scale for significant shale oil production is certainly longer than the timescale for conventional petroleum meeting demand, and shale oil will probably be able only to slow the rate of production decline for conventional and non-conventional liquid fossil fuels 15 years hence.

A major difference between today and 1980 is the growing acceptance of global warming driven by fossil fuel use. The 1970-1980 boom was challenged for reasons of air emissions, water consumption, aquifer contamination, and surface disturbance. These environmental factors were all used in conjunction with the then unfavorable economics to kill the national oil shale program in 1993. They all remain, but concern about CO₂ has become substantially elevated with respect to the previous boom. These issues must be considered seriously in any process development, and the incremental cost of avoidance may be less than the economic risk of political backlash. Realistic comparisons should be made against the competition, which include biofuels and an effective electrical vehicle powered by non-fossil-derived electricity.

Oil Shale Process Classification

There are many conceivable classification schemes, but the one in Figure 2 is fairly typical in terms of its distinguishing characteristics of heating method and whether retorting is done above or below ground. Belowground retorting occurs in larger “vessels” with larger particles, hence longer thermal diffusion times and slower retorting by necessity. Aboveground retorting offers the possibility of more process control (not always achieved in poorly designed processes), but with the associated higher costs of shale handling and solids processing equipment. Heating methods are often broken down into *direct* and *indirect*, where *direct* is the same as *internal combustion* in Figure 2. However, different indirect processes have substantially different characteristics depending on how the heat is delivered to the shale.

One important difference is whether the heat is delivered by a solid or gas. Roughly equal masses of each are required, and it is, in principle, cheaper to deliver that heat via a solid, especially if that solid contains its own heating fuel, as is the case for retorted shale. On this basis, LLNL concluded that a recycled-hot-solids process (Lewis et al, 1986) had the greatest ultimate potential. Separation of combustion and retorting enables control needed for high oil yields and a concentrated pyrolysis gas stream. Well-designed retorted-shale combustors using fine shale can achieve that heat with minimal carbonate decomposition and effective SO₂ capture. Mixing of burned shale with pyrolysis products leads to effective capture of H₂S and COS by Fe₂O₃, and the resulting sulfides are then converted to sulfates in the combustor. Total residence times of a few minutes for retorting and combustion combined give minimum reactor volumes and easier scaleup.

Another generic process that is currently receiving much attention is true-in-situ retorting using externally generated heat. In-situ retorting has some basic constraints. Oil shale has little native permeability, so combustion retorting can only be achieved by adding porosity by mining (MIS) (Lewis and Rothman, 1975; Campbell, 1981) or explosive uplift (Geokinetics) (Zerga, 1980). Injecting hot fluids is not particularly effective, particularly on the time scale normally considered for enhanced oil recovery, because the highest permeability regions have the poorest oil yield and because the temperatures to be achieved require very hot fluids. If one is patient, one can achieve thermal diffusion of a few meters over a time scale of a year or more. Patience is the concept behind the primary Shell ICP method (Mut, 2005; Berchenko et al., 2006), which uses electric heaters in wells as the heat source.

Their patents also mention downhole burners, which would be twice as efficient. However, one must place wells very close together in such a process, and the time scale increases roughly as the square of the well spacing. Of course, the drilling costs also scale roughly as the inverse square of the well spacing, so the optimum spacing depends on the thermal and recovery efficiencies as a function spacing and the time value of money.

One possible way to improve in-situ processing is to use volumetric heating by radio waves (Bridges et al., 1979). The literature is inadequate concerning the penetration distances possible as a function of shale parameters, but it could be many meters under some circumstances. To be perfectly clear, the objective here is to choose the frequency with a sufficiently small absorption coefficient to maximize the penetration distance the extent allowed by maximum antenna power. One pays a two-fold energy cost by using electricity in any form, but that cost is potentially recoverable from either lower drilling costs for wider well spacing or faster retorting at a given well spacing than in the basic Shell ICP conductive process. We are unaware of any analysis that has done that tradeoff carefully, and available data on rf penetration makes the tradeoff difficult to do reliably at this time.

Details of the LLNL HRS Process

LLNL investigated hot-recycled-shale processing because it appeared to have the greatest promise for speed and intrinsic control of gaseous pollutants, which would minimize processing costs. A 4-tonne/day process pilot plant, shown schematically in Figure 3, was built and operated from 1990 to 1993 to test this concept (Baldwin and Cena, 1993). A delayed-fall combustor is used to achieve good mixing with air, plug flow, and a particle velocity roughly independent of particle size and slow enough that the combustion vessel is small compared to a lift pipe combustor. The lift pipe is still used to elevate the shale, and significant combustion occurs therein, but the use of a separate delayed-fall combustor gives greater control over the combustion process. A fluidized bed classifier then rejects the finest material to set the recycle ratio. A fluidized-bed mixer replaces the screw mixer in the Lurgi process, and the majority of the pyrolysis occurs in a settling-bed (plug flow) unit.

Oil yields were typically 96% and 102% of Fischer Assay for 22 and 38 gal/ton oil shale, respectively. Clogging due to melting of rich shale was never a problem, despite folk lore to the contrary. Separation of fines from shale oil was identified as the last remaining technical challenge. Hot-gas filtering and heavy-oil recycling were tested, but the results have not been publicly released. In today's environment, CO₂ mitigation must be added to the list of challenges. Carbonate decomposition ranged from 14 to 49% and correlated with combustion temperature. This implies that increased recycle ratios, which can tolerate a lower temperature in the recycled shale, may have an advantage with respect to CO₂ mitigation costs that counterbalance the larger vessels needed for a larger recycle ratio. Also, modeling suggested that one could get improved combustor performance with an O₂-enriched combustion gas. Perhaps that would be more favorable in a situation where the flue gas was scrubbed for CO₂. These examples indicate how process optimization would be different in today's environment.

Spent shale disposal was also a major concern for environmental groups. An early study of spent shale disposal had shown that reactions between carbonate and silicate minerals under the right conditions formed significant quantities of the active components of Portland cement (Mallon, 1979). Although that particular study focused on injecting a grout made from spent shale into the voids of MIS retorts, later unpublished studies showed that the burned shale from the HRS process, with much less added water, could be pressed into low-permeability bricks that return the shale to much closer to its original volume. More work is needed to optimize this process, but it is easily conceivable that large blocks could be formed and moved back into the mine or cast and compacted in place, thereby drastically reducing the need for surface disposal.

True In-Situ Retorting

LLNL (Mallon, 1980) examined the radio-frequency (rf) approach being developed by IITRI (Bridges, 1979). Although a significant amount of mining was required in Mallon's version, it was still substantially lower than MIS, since only access drifts were required. The concept was to retort the oil shale over four nights using inexpensive off-peak power. The economics depend on the assumed oil yield, and no data existed for the envisioned heating rates and pressures (7.5 °C/h and 10 atm). Nevertheless, an oil yield of 83% of FA was estimated from a variety of literature sources. Assuming an electricity cost of \$0.02/kW-h, Mallon derived an electricity cost of \$6.7/bbl and a total cost of \$15/bbl in 1980s dollars. Doubling that value for today's costs puts it in the ballpark of what is being discussed for Shell ICP.

To refine the economic predictions, a set of experiments were done to determine oil and gas yields and composition for autogenous sweep conditions at various heating rates and pressures relevant to in-situ rf processing (Burnham and Singleton, 1983). Initial experiments were conducted on compressed pellets having 24% porosity. It was found that the externally applied pressure delayed the vaporization of the oil and caused the oil yield to decrease due to coking and cracking into gas and lighter oil. Oil properties at the extremes of the processing conditions are shown in Table 2. This process was later modeled (Figure 3) using the most detailed chemical kinetic model of oil shale pyrolysis at the time (Burnham and Braun, 1985). It included a more explicit treatment of the coking reactions in earlier atmospheric retorting models (which reduce nitrogen content) along with a pressure-dependent oil cracking model that split the oil into 11 boiling-point fractions.

These results become particularly important today within the context of the Shell ICP. A plot of the oil yield versus heating rate from Burnham and Singleton is compared to oil yield results in the Shell patent (Berchenko et al., 2006). Superficially, their yields appear to be a lot higher than expected, but further discussion is warranted. First, Burnham and Braun calculated that yields would be 5% higher for full-density shale because of reduced oil-vapor residence time at high pressure. Second, Burnham and Singleton conducted additional unpublished experiments on cores which suggested that this yield improvement might be even greater, so a yield of 80% is plausible at 1 °C/h and 27 atm. Third, there is an accounting issue of whether one considers C₄ and C₅ species in the gas as oil or gas. Fourth, LLNL yields are reported on a mass basis while Shell yields are reported on a volume basis, which increases the apparent yield under ICP conditions by up to 10% relative to the mass basis. Finally, the oil yield relationship is almost certainly sigmoidal with heating rate, which would mitigate further decreases in oil yield as heating rate decreases. The sigmoidal behavior is consistent with both distributed reactivity kinetic models that have become prominent since 1983 and hydrous pyrolysis results from the geochemical community. Finally, there is also an uncertainty in the Shell result. The body of the patent says yields are 75-80% of Fischer assay. More information is needed to assess whether there actually is a discrepancy between the LLNL and Shell results. Independent of the precise yield estimations, the oil properties from the Shell ICP are consistent with predictions from the LLNL experiments to the extent the comparison is possible with publicly available information.

With the successful application in mid 1980s of the chemical model shown in Figure 3 to petroleum formation in the Uinta Basin (Sweeney et al., 1987), it was both evident and commonly discussed in the organic geochemistry community that oil shale is merely a petroleum source rock that didn't get buried deep enough. When one of us (Burnham, 1993) proposed the possibility of slowly heating large blocks of oil shale over a period of several years to convert it to and produce it as a more conventional crude oil, the common response from oil company personnel was that the time for return on investment was too long compared to new opportunities in deep water and the former Soviet Union.

The lone exception was a very guarded interest by Shell employees during a January 27, 1995, presentation at their Bellaire Research Center (referenced in their recent patents), for reasons which are now obvious. Perhaps their different view was due to their long-time association with the Belridge field in California, which has very close wells over a very thick pay zone.

The LLNL deep-rf concept, eventually documented (Burnham, 2003), was to use wells spaced at tens of meters, either vertically or in some type of triplate design following bedding planes using deviated drilling, to heat cubic kilometers of deep oil shale very slowly (e.g., Figure 5). The presumption based on the Cameron Engineers Synthetic Fuels Handbook (Baughman, 1978) was that it would be possible to find a radio frequency at which the skin depth would be many tens of meters, thereby overcoming the very long thermal diffusion times needed for conductive heating. Targeting deeper shale than the Shell ICP has disclosed to present, the expulsion mechanism would change from vapor-driven expulsion at a pressure limited by modest lithostatic load to compaction-driven expulsion at the greater lithostatic loads. Possible contamination of aquifers becomes less important. Of course, the deep and shallow characterizations of the LLNL and Shell processes are merely two end members of a continuum of situations.

One less-obvious advantage of slow retorting is that less energy is required. This is because the additional time at temperature enables the oil to be generated and expelled at a lower temperature. As the heating rate decreases from 3 °C/h to 3 °C/month, the completion of oil generation decreases from 400 to 300 °C (Burnham, 1993, 2003). The energy required (including losses) decreases from 124 to 87 kW-h/Mg shale. At steady state, the production rate has a correspondingly higher value for constant heat input. Neither of these values takes credit for possible recovery of residual heat, which would cut the need for newly generated heat.

There are obviously many questions about the viability of the LLNL deep-rf concept. Foremost is whether the energy deposition actually can occur over a scale of several tens of meters, because the higher costs of radio-frequency energy must be more than compensated by some combination of lower drilling costs, a shorter time between energy insertion and oil recovery, or both. Antenna technology appears to be available. Heating shale at 3 °C/month using 100 m well spacing would require a power of 6.5 kW/m, which is a few times greater than typical broadcasting antennae. More complicated is dealing with the shifting primary absorption mechanism (Roberts et al., 2006). Water appears to be the initial primary absorber, and pressure-dependent mineral dehydration will provide a continuous stream of free water up through pyrolysis (Burnham and Braun, 1985). A summary of these recent rf results is shown in Figure 6. In addition, char appears to be the primary final absorber (Baughman, 1978), so one must be careful not to retort and then absorb the rf energy nearby the well bore, or rf has no advantage over the electrical heaters currently used by Shell. It is less obvious whether rf can have an advantage over downhole burners (Shell) or hot fluids pumped through wells (E.G.L.), since they would be twice as efficient thermally. At a minimum, it appears that rf processing will require lower frequencies at the beginning and end of heating to be viable. No significant resources have been used at LLNL to rigorously evaluate deep, large-volume heating by radiofrequency energy. There may have been propriety evaluations by other organizations, but whether the proper frequencies were used for evaluation is open to question. If Shell is successful, perhaps rf heating will be more thoroughly evaluated in terms of incremental process improvement.

More generally, one might also consider heating by injection of hot fluids directly into the formation as was done by Equity Oil in the 60s and 70s and currently proposed by Chevron in their BLM lease application (Corilleran, 2006). Here, of course, one must consider not only the uniformity and efficiency of the heat deposition, which appears challenging to say the least, but also the recovery efficiency of any valuable injected fluid. Because of oil shale's low intrinsic permeability, it is doubtful

that any injected fluid could have adequate contact with the retorting shale to significantly affect oil and gas yields over autogenous expulsion.

One of the potential gains in carbon efficiency is to use non-fossil energy to generate the electricity or thermal heat used to retort the oil shale (Burnham, 1989). In fact, if electricity is generated from nuclear fission and then deposited by conduction, it would be even more efficient to design a nuclear fuel, perhaps even derived from reactor waste, that could be lowered directly in the well and double the energy efficiency. Independent of the technical challenge of creating an unleachable nuclear heat source, public acceptance is an important issue, and this approach would face a tough road. Another possibility is direct conversion of coal to electricity, which can be done at an efficiency of approximately 80% (Cooper et al., 2002). The coal is first pyrolyzed to produce hydrogen-rich volatiles and a conductive char, and the char is oxidized at a ceramic electrode saturated with molten salt. Direct electrical conversion of carbon has no entropy change and therefore no loss of thermodynamic efficiency as in a Carnot cycle. The main source of inefficiency is due to internal resistance losses. In addition, the effluent gas is a nominally pure CO₂—an easily recoverable stream with small amounts of NO_x and SO_x. If successfully developed, this would make electrical heating by either conduction or radio frequency more attractive environmentally.

The in-situ process proposed by Chevron (Corilleran, 2006) aims to use the energy remaining in the spent shale to provide the heat for pyrolysis. This process uses the hot gases generated during combustion of the fractured spent shale to heat raw shale in another region of the formation. Besides the obvious challenge of being able to create sufficiently uniform fracture permeability to adequately control the combustion and pyrolysis processes, combustion of the spent shale, because of decomposition of carbonate minerals, will generate 0.28 kg CO₂/MJ thermal energy, compared to 0.07 kg CO₂/MJ thermal energy from methane and ~0.1 kg CO₂/MJ thermal energy from coal. If one assigns a mitigation cost of \$30/ton CO₂, the Chevron and other combustion processes would pay several dollars more per barrel of oil. MIS retorting is the worst. These calculations are summarized in Table 3. Values depend on grade and oil-yield assumptions and are good to no better than 10%. Values for the Shell ICP are two ideal end members, since a variety of energy sources are under consideration, and they do not take credit for syngas BOE. Values for the Chevron process also do not take credit for syngas BOE and assume only enough shale combustion to generate the required process heat. For comparison, eventual combustion of the shale oil generates 450 kg CO₂/bbl.

A final issue for true in-situ retorting is subsidence. The supportable porosity in any formation decays exponentially with depth. At one km depth, which is relatively deep for the Piceance basin, one might be able to support ~17% porosity. Retorting 25 gal/ton shale creates ~30% porosity, which would predict at least 10% compaction. In addition, rich layers (<50 gal/ton) are >50% by volume organic matter and will compact upon pyrolysis even at shallow depths. In the absence of empirical data, one needs to know the distribution of oil shale grades down to the mm level to reliably predict compaction. At two km depth, which is easily possible in the Uinta basin, the supportable porosity is ~6%, so substantially more compaction and subsidence would occur.

Conclusions

Despite the mammoth size of the US oil shale resource, oil shale has not yet been a significant energy supply because of its higher cost than conventional crude oil. The OPEC-inspired price spike starting in the early 1970s spurred a large effort in oil shale, which collapsed utterly in the early 1980s due to a retreat of crude oil prices to their historical level. The obvious question is whether oil shale is a surer investment today than then? Although energy security arguments are increasing to the levels of the 1970s, it is doubtful that energy security alone will overcome economics in the global economy.

However, it is very likely that the peak in world oil production and corresponding permanent increase in price due to demand exceeding production capacity will occur sooner than significant oil shale production can be put in place, so the investment risk is lower from that perspective. On the other hand, environmental concerns are at least as important today, particularly with respect to CO₂ emissions, and it is more conceivable now than then that technology advances might actually make renewable biofuels economically competitive with fossil fuels.

In this arena of increased environmental constraints (existing and potential), it is more important to design and implement processes with lower environmental impact, including the amount of CO₂ generated per barrel of oil. This situation makes modified in-situ and any direct combustion process less attractive than in the 1970s. The HRS process, for example, produces three times less CO₂ per barrel of oil than an MIS process. In fact, the HRS process produces less CO₂ per barrel of oil than the Shell ICP process if fossil fuels are used to generate the electricity for ICP conductive heating. Even though it is much farther developed than is generally appreciated, significant effort is still required to update and demonstrate the HRS process to current standards.

When properly compared within the constraint of publicly available material, product yields and compositions from the Shell ICP process are consistent with experiments and models from LLNL in the early 1980s. In fact, those early results caused one of us (Burnham, 1993) to independently develop a process concept similar to Shell's in the early 1990s. One difference is to use radio-frequency waves to overcome the long thermal diffusion time for conductive heating, thereby decreasing the number of wells needed by an order of magnitude. Another difference is to target deeper deposits, where the expulsion mechanism changes from vaporization to compaction and where concerns of aquifer contamination are largely eliminated. The LLNL process has greater technical uncertainty, but the uncertainties could be reduced substantially with only a modest research investment.

A significant question is whether the 15-25% lower oil yields from an in-situ process, be it Shell ICP, LLNL radio-frequency, or some other variation, is counterbalanced by the improved oil quality and increased gas yield? The chemistry of yield loss by its very nature reduces refining cost by rejecting heteroatoms and carbon and increasing hydrogen and saturate content. A less obvious advantage is that the resulting shale oil has a 4% greater combustion energy content per mass of carbon dioxide eventually produced. Finally, a variety of methods might improve the energy efficiency of the in-situ processes compared to using electricity generated from fossil fuels.

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Figure 1. Oil prices since World War II showing the OPEC-inspired spike about 1980 and the current war-and-weather-related spike. Will the current spike be different from the 1980 spike?

Figure 2. Schematic of the 4 tonne/day pilot plant for the HRS process operated at LLNL between 1990 and 1993.

Figure 3. Ability of an LLNL kinetic model that includes liquid-vapor equilibrium calculations to match oil evolution data for conditions of shallow true-in-situ retorting.

Figure 4. Comparison of yield results from Shell ICP with experiments of Burnham and Singleton [16].

Figure 5. Artist conception of a deviated well pattern for insertion of radiofrequency antennas and withdrawal of produced oil with minimum surface disturbance.

Figure 6. Summary of penetration depths of rf fields as a function of frequency and saturation conditions. Retorted shale is comparable to brine-saturated shale.

Figure 1

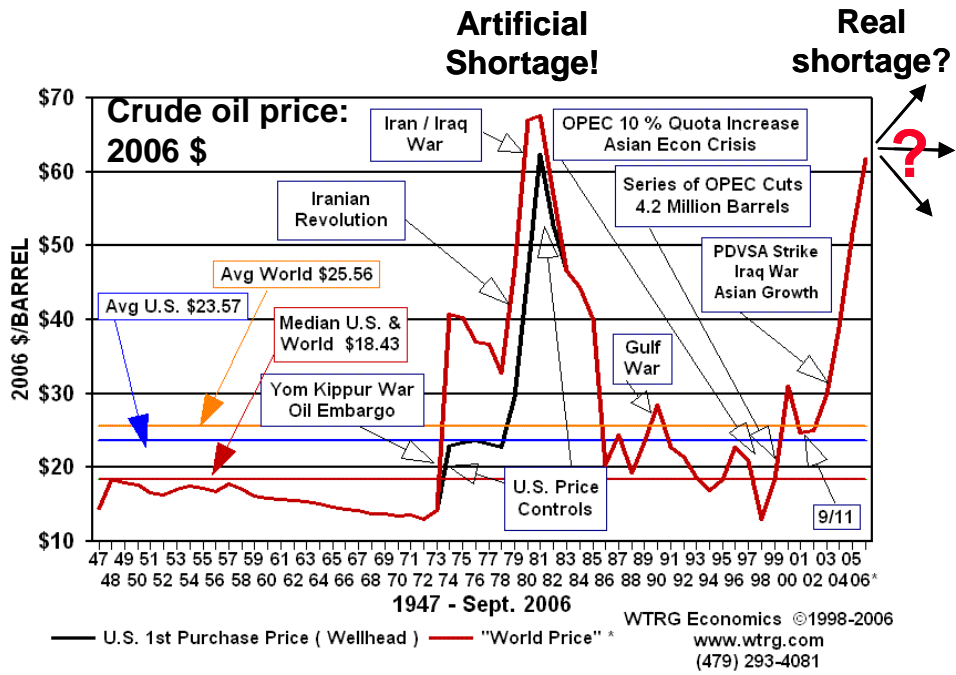


Figure 2

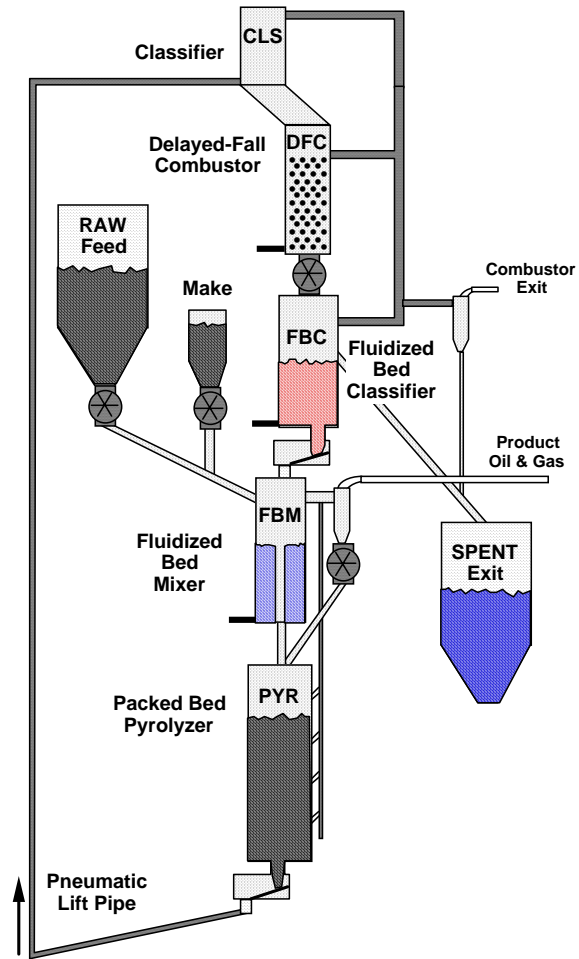


Figure 3

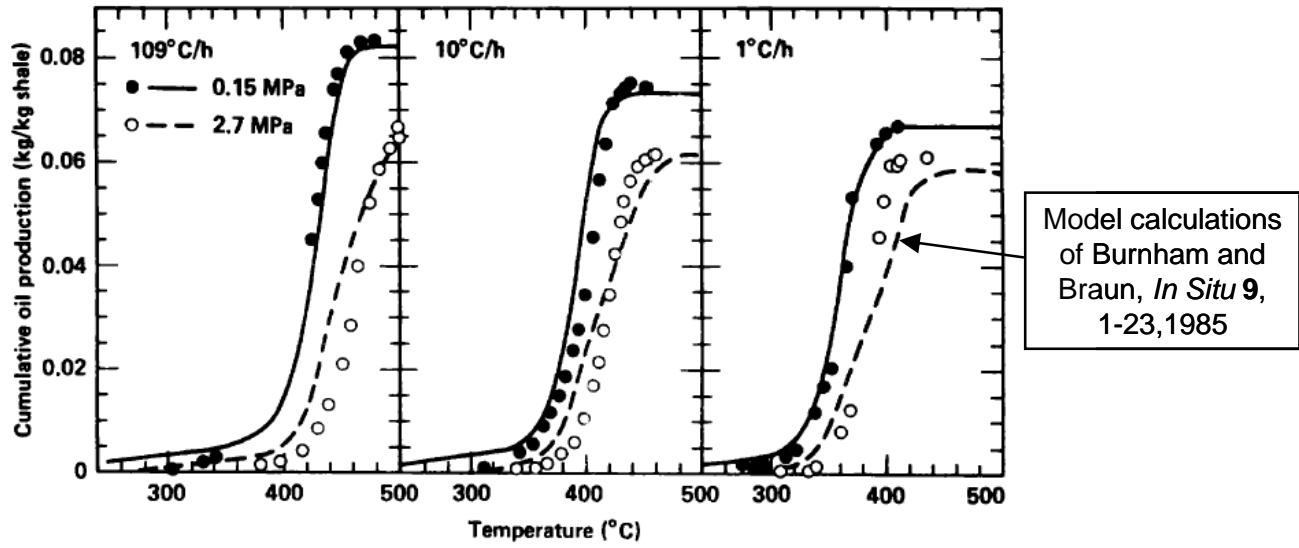


Figure 4

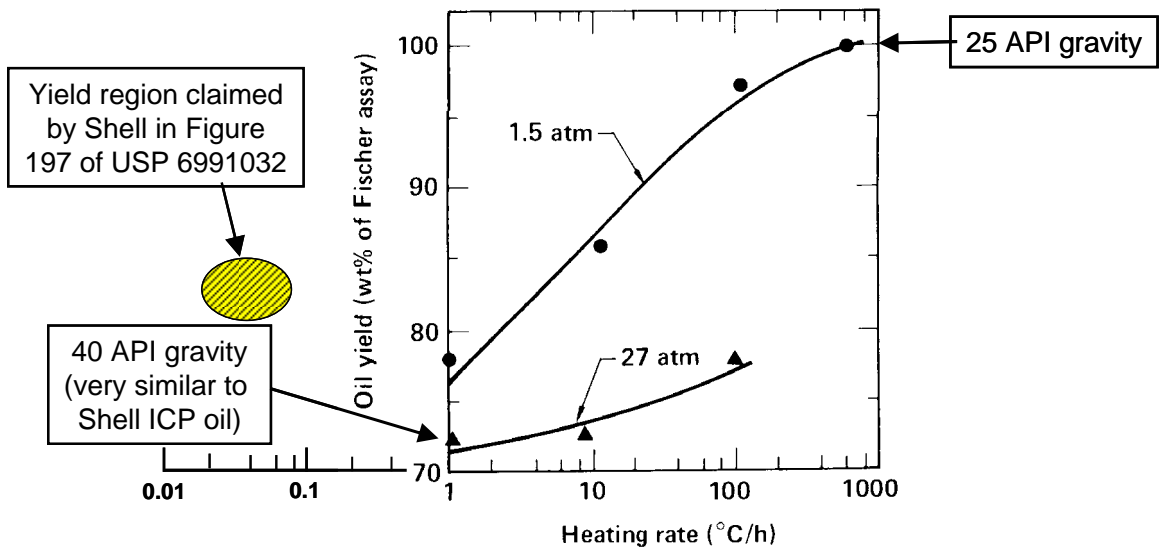


Figure 5

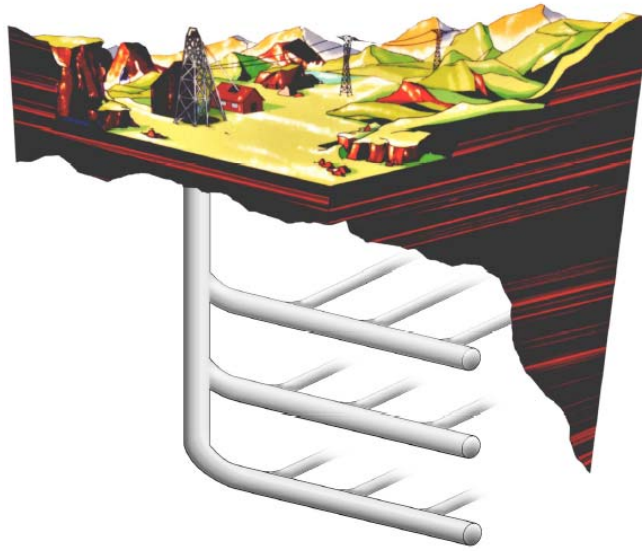


Figure 6

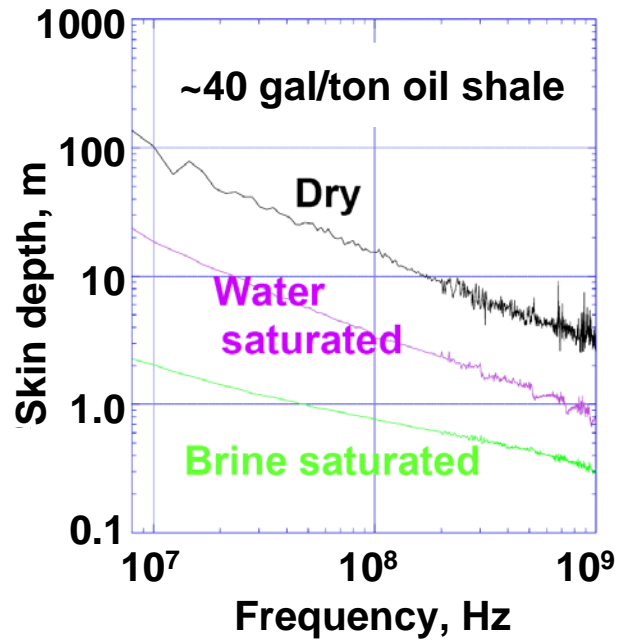


Table 1. Classification of oil shale processing according to heating method and location.

Heating Method	Above Ground	Below Ground
Conduction through a wall (various fuels)	Pumperston, 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 (hydrocarbons and CO₂), and possibly aquifer contamination

Table 2. Summary of shale oil properties at the extremes of the conditions examined by Burnham and Singleton [15].

Conditions	Density, g/cm ³	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

Table 3. Comparison of CO₂ emissions and hypothetical mitigation costs for various oil shale processes using an average grade of 25 gal/ton.

Process	Oil Yield, %FA	Pyrolysis CO ₂ , kg/bbl	Combustion CO ₂ , kg/bbl	Carbonate CO ₂ , kg/bbl	Total CO ₂ , kg/bbl	Mitigation cost, \$/bbl
HRS	100	11	77	40	128	3.8
Internal Comb.	90	12	85	150	247	7.4
MIS	80	14	96	352	462	13.9
Shell ICP ¹	80	14	146	0	160	4.8
Shell ICP ²	80	14	42	0	56	1.7
Chevron	80	14	96	120	230	6.9

¹using coal to generate electricity

²using downhole methane burners