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Converting Oil Shale to Liquid Fuels with the Alberta Taciuk Processor: Energy Inputs and Greenhouse Gas Emissions

Adam R. Brandt*

Department of Energy Resources Engineering, Stanford University, Green Earth Sciences 065, 367 Panama Street, Stanford, California 94305-2220

We calculate the greenhouse gas (GHG) emissions from producing liquid fuels from Green River oil shale with the Alberta Taciuk Processor (ATP). Kerogen contained in oil shale can be retorted to produce liquid and gaseous hydrocarbons. The ATP is an above-ground oil shale retort that combusts the coke or "char" deposited on the shale during retorting to fuel the retorting process. Using life cycle assessment (LCA), we calculate the energy inputs and outputs of each process stage. We then calculate the resulting full-fuel-cycle GHG emissions from producing reformulated gasoline using the ATP. Full-fuel-cycle GHG emissions are conservatively calculated at $\approx 130-150$ g CO_2 equiv/MJ of gasoline produced. These emissions are 1.5 to 1.75 times larger than emissions from conventionally produced gasoline. The results depend most sensitively on the grade of shale used and the rate of carbonate mineral decomposition, which causes inorganic carbon dioxide (CO_2) release.

Introduction

Oil shale is a sedimentary rock that contains fossil organic matter called kerogen. Kerogen is believed to be the source material from which naturally occurring oil and gas were formed.[1] The largest global oil shale deposits are found in the Green River formation of Colorado, Utah, and Wyoming. These deposits, which are equal to 1500 Gbbl oil equivalent, represent about half of all known oil shale deposits.[2]

Upon heating, kerogen decomposes into a mixture of hydrocarbon gases and liquids (HCs) and a carbon-rich "char" or shale coke that remains adhered to shale particles, as well as CO_2, water vapor, and other trace gases.[3] Kerogen decomposes at a temperature-dependent rate: decomposition of 90% of the kerogen takes 5000 min at 370 °C and only 2 min at 500 °C.[3] Shale quality is quantified by the volumetric oil yield per mass of shale retorted using the Fischer assay (FA), a standardized retorting method. Results are presented in liters per tonne (L/t) or gallons per ton (gal/ton). For a 110 L/t (26.7 gal/ton) shale, kerogen decomposes to 84% oil, 6% gas, and 10% char by higher heating value (HHV).[3]

There are two types of oil shale retorting processes: ex situ and in situ. Ex situ processes mine the shale and retort it in an above-ground retort. In situ processes apply heat to shale within the geologic formation. Current and historical commercial oil shale operations have been ex situ, while in situ processes remain in development.[1]

Because it is abundant and widely available, oil shale is seen as a resource to be used when conventional reserves of oil are depleted.[1,4] Unfortunately, oil shale production can cause significant environmental impacts, with traditional methods of production emitting high levels of criteria air pollutants, greenhouse gases (GHGs), and water pollutants.[5,6]

Recent oil shale efforts have been spurred by U.S. federal support for oil shale research and development, for example, the White River Mine research and development project, proposed by the Oil Shale Exploration Company (OSEC) in response to a Bureau of Land Management call for research proposals.[7] The largest stage of the project was proposed to produce 1.8 Mbbl of shale oil from 2.7 Mton of raw shale, using a 250 ton/h Alberta Taciuk Processor (ATP) retort.[7,8] More recently, OSEC has proposed using the Petrosix process, another oil shale retorting technology. Also of importance is a recent project in Queensland, operated by Southern Pacific Petroleum (SPP), which also used the ATP. This project was terminated in 2004 due to cost overruns and opposition on environmental grounds.[2,9,10] Current ATP development activities include the construction of an ATP retort for use in the Fushun shale of China.[11]

In this paper, we model two large-scale deployments of the ATP which have low and high energy and GHG intensities

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*Corresponding author. E-mail: abrandt@stanford.edu.

(1) Bartis, J. T.; LaTourrette, T.; Dixon, L.; Peterson, D.; Cecchine, G. *Oil shale in the United States: Prospects and policy issues*; RAND: Infrastructure, Safety and Environment; RAND: Santa Monica, CA, 2005.
(2) Dyni, J. R. *Geology and resources of some world oil-shale deposits*; Technical Report, U.S. Geological Survey, 2005-5294, 2006.
(3) Hendrickson, T. A. *Synthetic fuels data handbook*; Cameron Engineers, Inc.: Denver, Colorado, 1975.
(4) Johnson, H. R.; Crawford, P. M.; Bunger, J. W. *Strategic significance of America's oil shale resource: Volume II - oil shale resources, technology and economics*; Technical Report; Office of Naval Petroleum and Oil Shale Reserves: Washington, D.C.,2004.

(5) OTA *An assessment of oil shale technologies*; Congress of the United States, Office of Technology Assessment: Washington, D.C., 1980; Vol. 1.
(6) Sundquist, E. T.; Miller, G. *Science* **1980**, *208*, 740–741.
(7) OSEC *Oil shale research, development, and demonstration project: White River mine, Uintah County, Utah*; Technical Report Environmental Assesment UT-080-06-280, Oil Shale Exploration Company; Vernal, Utah, 2006.
(8) Some sources call this retort the AOSTRA Taciuk Process, after the Alberta Oil Sands Technology and Research Authority, the funding source for its original development as an oil sands processor.[47]
(9) *Call for investigation by Australian Stock Exchange: into the conduct of Southern Pacific Petroleum NL and Central Pacific Minerals NL in respect of their carbon liability arising from the Stuart Oil Shale Project*; Technical Report, Greenpeace: Amsterdam, 2000.
(10) Schmidt, S. *Oil Shale* **2003**, *20*, 333–346.
(11) Li, S.; Yue, C.; Qian, J. *Recent Chinese oil shale activities*, proceedings of The 28th Oil Shale Symposium, Golden, Colorado, October 13–17, 2008; Jeremy Boak, Ed.

(hereafter, the "low" and "high" cases). Both of these cases are of larger scale than existing operations. In each case, the ATP is applied to oil shales of the Green River formation. For each case, we estimate the energy inputs and outputs of the ATP retorting process, as well as the resulting GHG emissions.

Background

The ATP fuel life cycle consists of six stages: mining and preprocessing of shale, retorting, disposal of spent shale, on-site upgrading of raw shale oil, refining of upgraded shale oil, and combustion of refined liquid fuels.

Mining and Preprocessing of raw oil shale. United States oil shale developments of the 1970s and 1980s relied on under-ground mining of oil shale deposits.[12] Room-and-pillar mining is most likely to be used in underground mining[1] and has been proposed for use in the OSEC project.[7]

Many believe that a large-scale oil shale industry would rely on open-pit mining, because of higher recovery factors and lower costs. Recovery factors for underground mining can be as low as 10–20% for exceptionally thick seams, in which much Green River shale occurs.[1] Also, the thickness of Green River oil shale deposits creates a favorable strip-ping ratio.[13] A plausible size for a commercial operation is 100 000 bbl/d, which would require a mine of capacity ≈25 Mton/y (approximately 1/3 the capacity of the largest surface coal mines of Wyoming[1]).

After mining, the shale is hauled from the mine to the ATP for retorting. The retort will be placed near the mine so as to minimize hauling of inert rock. Before retorting, the oil shale is crushed to pieces less than 6−8 mm in diameter.[10,14]

Alberta Taciuk Processor. The ATP retort is an advanced ex situ retort. It has lower water requirements than previous surface retort designs,[4] and unlike some other retort designs like the vertical shaft kiln, it can utilize fine particles, thus reducing shale waste (other retort designs such as the Galoter process can also utilize fines).[7] In addition, most or all of the retorting energy is provided by the combustion of char and produced gas, making the process potentially energy self-sufficient from the point of view of the operator.[10]

The ATP retort is a rotating horizontal kiln with four main zones: preheat, retort, combustion, and cool-down.[7,14−16] It is classified as a hot recycled solids (HRS) retort: heat is transferred to fresh shale from hot, already-retorted shale that is recycled into the retorting zone.[17] The retort is operated slightly below atmospheric pressure to prevent escape of explo-sive gases (−30 to −50 Pa[15]). The chambers are operated at varying pressures to prevent undesired gas flow.[18]

The ATP mass and energy flows are illustrated in Figure 1. Mass flows are labeled with lower-case letters, and energy flows, with upper case letters. First, shale enters the retort and moves through the preheat zone (a), where it is heated to ≈250 °C by the outgoing spent shale (f, Y).[7,16] Water is driven off as steam in this stage (h, Q).

The shale then moves through a seal to the retort zone (b), where it is mixed with hot shale recycled from the combus-tion zone (e). The combination of hot-shale recycle and conduction from the outer combustion chamber raises the temperature of the incoming shale to above 500 °C (W, X).[10] The temperature of retorting is a design characteristic, with higher temperatures resulting in shorter retort residence times[3] and somewhat higher oil output (there is a limit to this effect: above 600 °C, there is a tendency to reduce oil yield, likely by cracking of oil[14]). Oil and noncondensable gases (HCs, H_2, CO_2, CO, and H_2S) are removed from the retort as vapors, carrying energy with them (c, U). The retorted shale is then moved to the combustion chamber (d).

After retorting, kerogen char remains adhered to the spent shale. Preheated air and recycled retort gas (c) are injected into the combustion chamber (k, T, and l). The char and any reinjected gas are combusted at approximately 750 °C (releasing heat V).[10] The rate of combustion is limited by air input rates.[14]

A portion of the combusted shale is recycled into the retort (e, W). Heat also conducts into the retort (X). The recycle rate is adjusted to maintain the correct temperature in the retorting zone.[15,19] Cited recycle rates range from 60 to 80% of the shale leaving the combustion zone at any time.[20]

From the combustion zone, flue gas travels (i) toward the inlet end of the retort and is removed (j, R). The waste shale, now combusted, also moves toward the inlet end (f), provid-ing heat to incoming shale in the preheat zone (Y). Spent shale is ejected (g) at above ambient temperature (Z). Heat loss also occurs through the outer shell of the retort (S).

The ATP process is designed to provide most of the process energy from the shale char and produced HC gas, minimizing purchased energy inputs. In one case of actual operation, the vast majority (86%) of the process heat required by the retort was provided by the oil shale itself, minimizing the need for external input energy from natural gas.[10] Note that this case was for an Australian Stuart shale, while the Green River shales studied here will be able to be retorted by combusting less than 100% of the shale char.

In the combustion chamber, high temperatures can cause carbonate minerals within the shale to decompose. The most important carbonates in Green River shale are calcite and dolomite, $CaCO_3$ and $CaMg(CO_3)_2$, respectively. These minerals release 1 and 2 CO_2 molecules upon decomposi-tion.[21] When contained in oil shale, carbonates begin decom-posing at ≈565 °C ($MgCa(CO_3)_2$) or 620−675 °C ($CaCO_3$), depending on the partial pressure of CO_2 in the retorting atmosphere.[22−24] These decomposition temperatures are

(12) The largest of these was the Colony Oil Shale Project of the early 1980s which began development of a very large 25 Mton/y room-and-pillar mining operation.[1]

(13) The stripping ratio is the ratio of the depth of inert rock over-laying the shale to the depth of shale, which is important for open-pit mining economics.

(14) Taciuk, W.; Turner, L. R. *Fuel* **1988**, *67*, 1405–1407.

(15) Taciuk, W. *Process for recovery of hydrocarbons from inorganic host materials.* US patent number 4,306,961, 1981.

(16) Taciuk, W.; Caple, R.; Goodwin, S.; Taciuk, G. *Dry thermal processor.* US patent number 5,217,578, 1993.

(17) Burnham, A.; McConaghy, J. *Comparison of the acceptability of various oil shale processes*; Technical Report, UCRL-CONF-226717, Lawrence Livermore National Laboratory: Livermore, CA, 2006.

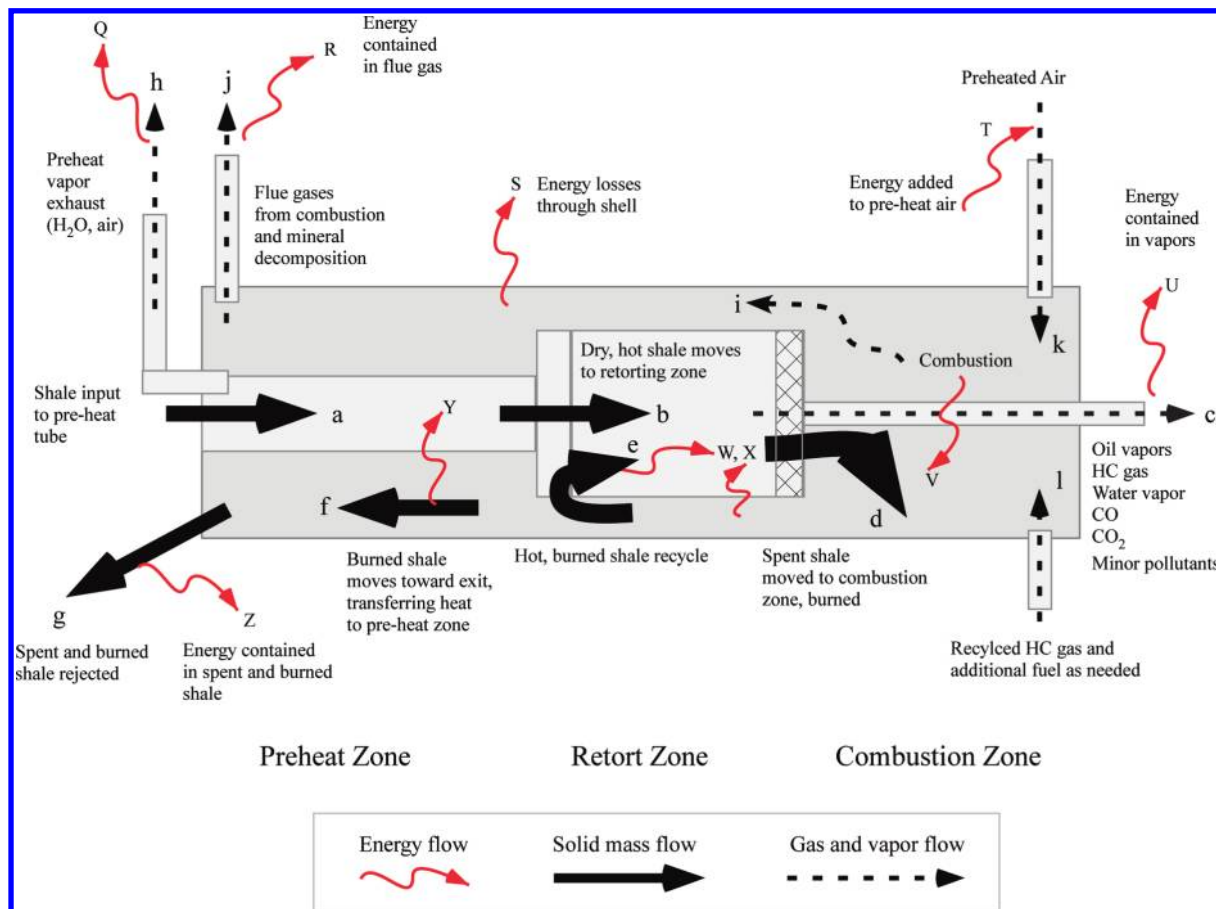(18) Reference 15, text column 11.

(19) Taciuk, W. *Aparatus and process for recovery of hydrocarbon from inorganic host materials.* US Patent number 4,285,773, 1981.

(20) Reference 19, text column 18.

(21) There are a number of other minerals, mainly saline minerals (e.g., nahcolite), that decompose at retorting temperatures.[23] These are assumed to be present in minimal quantities in this analysis. Shell describes an in situ project that retorts shales containing these minerals.[48]

(22) Burnham, A. K. *Chemical kinetics and oil shale process design*; Technical Report UCRL-JC-114129, Lawrence Livermore National Labora-tory: Livermore, CA, 1993.

(23) Campbell, J. *The kinetics of decomposition of Colorado oil shale II: carbonate minerals*; Technical Report UCRL-52089 Part 2, Lawrence Livermore National Laboratory: Livermore, CA, 1978.

(24) Thorsness, C. B. *Modeling study of carbonate decomposition in LLNL's 4TU pilot oil shale retort*; Technical Report UCRL-ID-118677, Lawrence Livermore National Laboratory: Livermore, CA, 1994.

Figure 1. Schematic of mass and energy flows in the ATP retort.[14,16,19]

significantly lower than those measured in pure mineral calcite and dolomite.[25] In addition to the release of inorganic CO_2, carbonate decomposition is endothermic, increasing the heat demand of retorting.[23]

Postretorting Operations: Disposal of Spent Shale, Oil Upgrading, and Refining. The spent and combusted shale is returned to a disposal location. Raw shale oil from the retort is upgraded to stabilize it and to improve its quality before refining.[7] Hydrotreating is the likely upgrading method.[4,7] The upgraded shale oil is sent to a refinery, potentially selling at a premium because of its high hydrogen content.[4]

Methods

A life cycle assessment (LCA) is performed for low and high cases. Energy inputs and outputs are tabulated, and energy output ratios are computed. Greenhouse gas (GHG) emissions are tabulated using fuel-specific emissions factors for each energy input. These emissions are compared to emissions from conventionally produced gasoline and other estimates of emissions from oil shale production.

Life-Cycle Assessment. A process-model LCA is performed to compute energy inputs per tonne of raw shale throughput for each process stage.[26] A detailed model of retorting is constructed, with mass and energy balances using flows in Figure 1. Full methodological details and additional documentation are provided in the Supporting Information.

Preliminary Stages. Preliminary operations such as grading, cement pouring, tank construction, etc. are uncertain but have a small impact. Estimates of energy consumption for steel and cement manufacturing are calculated.[7,27,28]

For mining energy use, estimates of energy consumption in large open-pit mines are used. In the low case, mining is modeled as equivalent to an open-pit coal mine, at 210 MJ/ tonne mined.[29] In the high case, mining is modeled as equivalent to tar sands mining operations, at 425 MJ/tonne mined.[4]

In the low and high cases, shale is transported 1 or 2 miles from the mine mouth to the retort, respectively. Crushing power requirements are assumed equal to crushing coal to 3 mm, at 1.1 kW/tonne·h.[30]

Retorting. Electricity inputs to retorting, both for rotating the kiln and other uses (e.g., compression) are estimated at 45 and 60 kWh/tonne[4,7] in low and high cases. Any HC gases not combusted in the retort are used to generate electricity onsite in a combined cycle natural gas turbine with an efficiency of 45%. Any electricity not supplied by on-site generation is modeled as the Colorado electricity mix (72% coal, 24% natural gas in 2005,[31] with minor contributions

(25) Sharp, Z.; Papike, J.; Durakiewicz, T. *Am. Mineral.* **2003**, *88*, 87–92.

(26) Ciambrone, D. F. *Environmental life cycle analysis*; Lewis Publishers: Boca Raton, FL, 1997.

(27) EIA, *Iron and steel manufacturing energy intensities*; Technical Report, Energy Information Administration: Washington, DC, 2006.

(28) Horvath, A. *Ann. Rev. Environ. Resources* **2004**, *29*, 181–204.

(29) Spath, P. L.; Mann, M. K.; Kerr, D. R. *Life cycle assessment of coal-fired power production*; Technical Report NREL/TP-570-25119, National Renewable Energy Laboratory: Golden, CO, 1999.

(30) *Handbook of crushing*; Pennsylvania Crusher, Inc.: Broomall, Pennsylvania, 2003.

(31) EIA, *Annual energy review 2006*; Technical Report DOE/EIA-0384(2006), Energy Information Administration: Washinton, DC, 2007.

from other sources).[32] Combined efficiency of generation and delivery of grid electricity is assumed to be 33%.

A mass and energy balance of the ATP retort is constructed per tonne of throughput, incorporating all flows represented in Figure 1. Baseline temperatures of 250, 500, and 750 °C are used for the preheat, retort, and combustion zones, respectively.[14,16] Temperatures are adjusted in increments of 5 °C to balance energy flows.

The heat requirements of retorting are modeled with the heat of retorting model of Camp.[33] This model accounts for the enthalpy changes of shale mineral matter, bound and free water, and kerogen pyrolysis. Shale char is the primary energy source, and the fraction of char combusted is adjusted in 1% increments to balance heat demands of retorting. In our model, the fraction of char combusted varies from 55−80% depending on the scenario. Air is injected into the combustion chamber at 10 −20% excess above stoichiometric requirements (low and high cases).

Energy losses through the wall of an early ATP retort were reported at 21% of total energy consumed.[34] Current retorts are stated to have losses closer to 10%.[35] In the low case, we assume 10% losses, while in the high case, we assume 15% loss. We assume that 50% of this heat is lost from the combustion chamber and 50% is lost from the cool-down zone. Waste heat is captured in our large-scale integrated system: combustion air is preheated using heat recovered from the condensation of retort product streams and flue gas vapor.

A key uncertainty is the amount of carbonate decomposition that will result from high combustion temperatures achieved in the retort. Published results disagree about the variation in carbonate decomposition with temperature and with partial pressure of CO_2.[22−24] This disagreement is significant: for retorting conditions modeled here and for a range of CO_2 partial pressures, the mass fraction of CaMg-$(CO_3)_2$ decomposed varies from 0.38 to 0.91, while that of $CaCO_3$ varies from 0 to 1. Both the low and high cases utilize a model with moderate values of carbonate decomposition (the OSP model of Thorsness[24]). We calculate that 44% to 50% of carbonates are decomposed, depending on the case.

Upgrading and Refining. It is difficult to generalize about oil shale upgrading due to variation in shale oils and upgrading technologies.[36] In the low case, energy consumed in upgrading is 76 MJ/tonne of shale processed,[4] while in the high case it is 425 MJ/tonne.[36] The heating value of upgraded shale oil is computed using the Dulong formula and is nearly equal to that of raw shale oil[37] because mass lost during upgrading is offset by the increased H content of the upgraded shale oil. In all cases, upgrading energy is supplied by natural gas. Transport of crude oil to the refinery is modeled as in the GREET full-fuel-cycle emissions model.[38]

We present results in terms of megajoules of refined fuel delivered to the end consumer (hereafter RFD), using U.S. federal standard reformulated gasoline as the refined fuel of comparison (as defined in the GREET model[38]). Refining energy and emissions are derived from the GREET model for consistency. In addition, noncombustion refinery emissions and transport of refined fuel from refinery to fueling station were added from the GREET model.[38]

Calculation of Energy Ratios and GHG Emissions. Using the results from the LCA, two energy ratios can be computed: the external energy ratio (EER) and the net energy ratio (NER):[39]

$$EER = \frac{E_{out}}{E_{ext}} \quad (1)$$

$$NER = \frac{E_{out}}{E_{ext} + E_{int}} \quad (2)$$

Here, E_{out} is the HHV of refinery outputs, E_{ext}, the primary energy input from outside the system boundaries (such as electricity purchased from the grid), and E_{int}, the primary energy input from the feedstock resource itself (e.g., coproduced HC gas consumed for electricity generation). The EER compares energy inputs from outside the system to net outputs from the process. It reflects the ability of a process to increase the energy supplied to society. The NER compares all energy inputs to net outputs, making it a better metric for understanding impacts from producing a fuel (e.g., GHGs).[39]

Energy inputs to each process step (expressed in terms of megajoules per megajoule RFD) are multiplied by the emissions factor for the fuel consumed in that step, giving the number of grams of carbon dioxide equivalent GHGs per megajoule of refined fuel delivered (g CO_2 equiv/MJ RFD).

Results

Energy Inputs and Energy Ratios. Table 1 shows energy inputs and outputs of each process stage per tonne of raw shale throughput. Energy inputs to all stages except mining, retorting, and refining are minor in comparison to the energy produced. In this table, total energy output is the yield of reformulated gasoline.

These results show that producing 1 MJ of reformulated gasoline for final consumption requires the consumption of 0.56 to 0.87 MJ upstream. For comparison, upstream consumption for reformulated gasoline produced from conventional oil is ≈0.2−0.25 MJ/MJ RFD.[40]

Comparing the NER and EER shows one characteristic of the ATP retort: much of the energy input comes from the fuel feedstock itself (i.e., EER is much higher than NER). In our cases, nearly all of the energy consumed by the retort is provided by the shale itself and much of the refinery energy input comes from the shale oil refinery feedstock.

Greenhouse Gas Emissions. Emissions from high and low cases are compared to emissions from the GREET model for conventionally produced reformulated gasoline in Figure 2. Full-fuel-cycle emissions are estimated to be 129 g CO_2 equiv/MJ in the low case and 153 g CO_2equiv/MJ in the

(32) This grid mix is chosen to allow congruence with another study of in situ oil shale production in Colorado.[43]

(33) Camp, D. W. Oil shale heat capacity relations and heats of pyrolysis and dehydration. *Twentieth Oil Shale Symposium*, Colorado School of Mines, 1987; pp 130−144.

(34) Reference 16, text column 19.

(35) Rojek, L. *Personal communication with L. Rojek regarding ATP reactor*, 2008.

(36) *Fuel science and technology handbook*; Speight, J. G., Ed.; Marcel Dekker: New York, 1990.

(37) Probstein, R. F.; Hicks, R. E. *Synthetic fuels*; Dover Publications: Mineola, NY, 2006.

(38) Wang, M. Q. *Estimation of energy efficiencies of U.S. petroleum refineries*; Technical Report, Argonne National Laboratory: Argonne, IL, 2008.

(39) Spitzley, D. V.; Keoleian, G. *Life cycle environmental and economic assessment of willow biomass electricity: A comparison with other renewable and non-renewable sources*; Technical Report CSS04-05R, Center for Sustainable Systems, University of Michigan: Ann Arbor, MI, 2004.

(40) Wang, M.; Lee, H.; Molburg, J. *Int. J. Life Cycle Assess.* **2004**, *9*, 34−44.

Table 1. Energy Inputs and Outputs Per Tonne Processed (MJ/t raw shale)

	low case		high case		
	input	output	input	output	input type[a]
preliminary op.	1		1		E
mining	211		426		E
transport	11		22		E
crushing	12		12		E
startup	22		22		
retort					
electricity[b]	361		543		I/E
oil		4040		3952	
gas[c]					I
char	861		976		I
upgrading	78	4038	425	3950	E
refining[d]		3637		3444	
crude shale oil	236		307		I
external energy	209		272		E
total[e]	2001	3637	3006	3444	

energy ratios	low case	high case
NER	1.8	1.1
EER	6.9	2.6

[a] Energy inputs are either internal (I), which come from within the system boundaries, or external (E), which are produced by external systems. [b] MJ thermal, converted from megajoules electric as described in text. For computation of the external energy ratio, electricity generated on site from produced HC gases is removed from the denominator (≈350 MJ primary thermal energy in both cases). [c] Coproduced HC gas consumed for electricity generation is counted (as thermal energy equivalent) in the electricity column. In these two cases, no produced gas is combusted directly in the retort, as shale char provides all energy requirements. [d] Energy consumed in refineries is derived from input crude shale oil (residual fuel oil and refinery still gas) and from external energy sources (natural gas, electricity, and coal). Refinery modeling in the high case is given by GREET model inputs for refining to reformulated gasoline,[38] while for the low case these inputs are multiplied by 0.75. See the Supporting Information for more detail. [e] Total output is the refined fuel delivered, modeled as U.S. federal standard reformulated gasoline.

high case. Emissions from carbonate decomposition are important in both cases.

Published estimates of emissions from oil shale retorting with the ATP include 141 g CO_2 equiv/MJ for treatment of the Stuart shale in Queensland[41] and 153 g CO_2 equiv/MJ for OSEC ATP treatment of Green River oil shale.[42] Note that the estimates from OSEC are approximately equal to our highest case for treatment of the same Green River shale. This is likely due the small scale of the project modeled in the OSEC EIS, which results in inefficiencies compared to our modeled large-scale operation. For the LLNL hot recycled solids (HRS) process, equivalent full-fuel-cycle emissions are likely ≈120 g CO_2 equiv/MJ.[17]

For comparison, typical full-fuel-cycle emissions for reformulated gasoline derived from conventional petroleum are 86.5 g C equiv/MJ RFD.[38] Therefore, emissions from the ATP are ≈1.5−1.75 times those of conventional crude oil on a full-fuel-cycle basis.

Sensitivity cases were also computed, exploring the effect of varying key parameters from their default values in the high case. We varied the following:
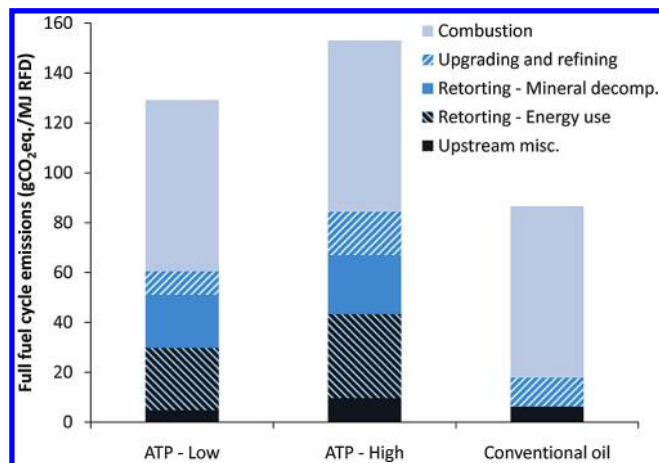
Figure 2. GHG emissions from low and high cases, grams of carbon dioxide equivalent per megajoules of final fuel delivered (g CO_2 equiv/MJ RFD).

- the fraction of heat lost through the retort shell from the default value of 15%;
- the volume fraction CO_2 in the atmosphere directly surrounding retorting particles from the default value of 0.75;
- the temperature that shale particles reach during combustion from the default value of 750 °C;
- the mass fraction of kerogen in raw shale from the default value of 0.16.

Figure 3 shows the resulting emissions (right numbers) from a given change in the varied parameter (left numbers), with the middle value for each bar being the high case default value. The results are most sensitive to the richness of the shale: the lower the shale quality, the more inert mineral matter must be heated per megajoule of oil produced. Results are also sensitive to the level of carbonate decomposition, illustrated by the variation with temperature and partial pressure of CO_2. Decomposition of $CaCO_3$ is quite sensitive to the fraction of CO_2 in the immediate atmosphere surrounding retorting particles.[23] The local fraction could be as low as ≈15%, which is the bulk CO_2 present in the retort atmosphere after combustion of the char, or it could be much higher. The actual value depends on how quickly the large amount of CO_2 generated during combustion and decomposition becomes mixed with the general retorting atmosphere.

Discussion

Without mitigation, fuels produced from Green River oil shale using the ATP process have emissions significantly higher than those from conventionally produced petroleum. Emissions from low and high cases are ≈1.5−1.75 times those from conventional oil production on a full-fuel-cycle basis. Other estimates of emissions from ex situ shale oil conversion support this conclusion.[43,44]

The two cases analyzed are conservative and could underestimate the actual operating impacts of oil shale production using the ATP. For example, it is unclear whether a mature shale industry using surface mining is comparable to the

(41) SPP, *Stuart oil shale project - Stage 2 consolidated report*; Technical Report; Southern Pacific Petroleum: Brisbane, Queensland, 2003.
(42) Reference 7, p 104.

(43) Brandt, A. R. *Environ. Sci. Technol.* **2008**, *42*, 7489–7495.
(44) Burnham, A. K. *Slow radio-frequency processing of large oil shale volumes to produce petroleum-like shale oil*; Technical Report UCRL-ID-155045, Lawrence Livermore National Laboratory: Livermore, CA, 2003.

existing coal and tar sands industries, especially given the depth at which much Green River shale exists. Thus, these estimates should be seen as conservative with regard to the energy requirements of surface mining. Also, these cases utilize moderate assumptions about carbonate decomposition rates: actual carbonate emissions could potentially be higher, as shown by the sensitivity analysis in Figure 3. Lastly, due to a lack of data, we do not include fugitive methane emissions, which could occur during processing and handling of shale and raw shale oil.

On the other hand, the GHG emissions from the ATP could be mitigated through a number of means: lowering the temperature of combustion, substituting external combustion of purchased natural gas for shale char as the retorting heat source, or postcombustion capture of CO_2, possibly with oxy-fuel combustion to result in higher CO_2 concentrations in the flue gas (and thus easier CO_2 capture). All of these measures increase cost and are therefore less likely to be applied without policies that assign cost to CO_2 emissions.

It is instructive to consider the implications of a very large oil shale industry that does not practice CO_2 mitigation. If we produce, refine, and combust fuel equal to 10% of 2005 US gasoline consumption (3.3×10^8 bbl/y, or 1.8×10^{18} J[45]) from oil shale using the ATP instead of conventional oil, full-fuel-cycle emissions could increase from about 42.5 million t of carbon (C as CO_2) to 65−74 million t of carbon. This is a rough increase of 20 to 30 million t. To put these figures in perspective, emissions from all sectors in the state of Colorado equaled 24 million t of carbon in 2001.[46] Thus, replacing 10% of U.S. gasoline with shale-derived fuels produced using large-scale ATP projects would result in additional emissions commensurate with the total emissions from the state of Colorado.

(45) EIA *Annual Energy Review 2006, Table 8.4a, consumption for electricity generation by energy source*; Technical Report DOE/EIA-0384(2006), Energy Information Administration: Washington, DC, 2007.

(46) EIA, *State carbon dioxide emissions*; Technical Report, Energy Information Administration: Washington, DC, 2006.

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(48) Shell. *2nd generation ICP project, oil shale research and development project*, 2006; http://www.co.blm.gov/wrra/WRFO_oil_shale.htm (accessed June 2008).
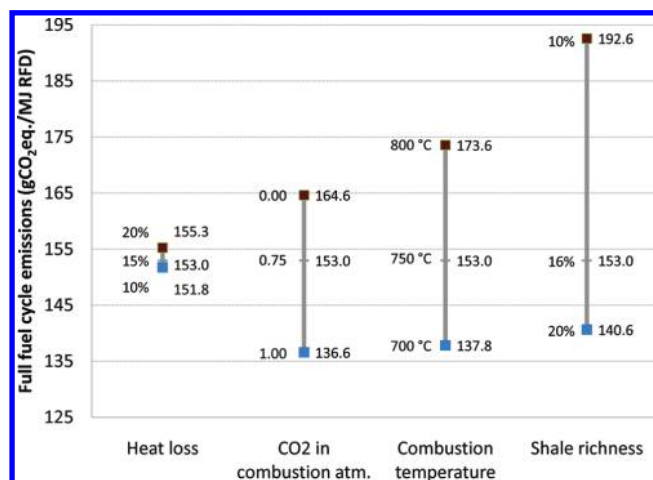
Figure 3. Variation in emissions with changing values of key model parameters: (left figures) values of varied parameters; (right figures) resulting GHG emissions in grams CO_2equivalent per megajoule RFD.

Given the uncertainties involved and the potential for large GHG impacts from oil shale production with the ATP, more research attention should be focused on understanding this technology and mitigating its impacts. It is especially crucial that this occur before the development of an oil shale industry in the United States.

Supporting Information Available: Additional methodological details, outlined by production stage, as well as additional results in tables. This material is available free of charge via the Internet at http://pubs.acs.org/.