CO_2 Release from In-Situ Production of Shale Oil from the Green River Formation in the Western United States

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Abstract

World resources of oil shale are likely to consist of trillions of barrels of hydrocarbon product, and are distributed worldwide. Estimates for the Green River Formation of Colorado, Utah, and Wyoming in the United States range from 700 to 2,000 billion barrels of shale oil. Recent oil prices have driven a resurgence of interest in oil shale development around the world. In-situ conversion of kerogen holds great promise, but economic production is still many years away. A recent issue for development of this resource is concern about the quantity of carbon dioxide (CO_2) co-produced as oil shale kerogen is pyrolyzed. CO_2 from oil shale processing includes that generated by the breakdown of carbonate minerals or oxidation of kerogen in the oil shale, and that generated by fossil fuel power plants that might be used to generate electricity to run the pyrolysis process. This paper considers the production of CO_2 for a nominal oil shale industry in the Western United States operating an in-situ process on oil shale of the Green River Formation. It discusses a simplified model for the quantity of CO_2 potentially requiring separation and segregation, and focuses on uncertainties in parameters of the model, and the sensitivity of the CO_2 output to those uncertainties, as a means of clarifying remaining questions to be resolved. The model confirms that CO_2 emission are large (in the range of 100->400 million tons of CO_2), that power plant emissions are likely the dominant source of CO_2, and that the average grade and the heat required to produce a barrel of shale oil are critical uncertainties.

Introduction

The world resource of oil shale is likely to consist of trillions of barrels of hydrocarbon product, and significant resources are distributed worldwide (Dyni, 2006). Investigation and production of these resources have been episodic, coinciding with peaks in the price of oil, reflecting the high cost of production. Recent prices have driven a resurgence of interest in oil shale development around the world.

Processes currently operating for production of oil shale involve mining and either retorting at the surface to convert immature kerogen to liquids and gas, or direct combustion for power generation. In situ conversion of kerogen holds great promise, but economic production is still many years away. Methods considered for heating include borehole electrical heaters, electrical heating through fractures propped with conductive material, fluid heat transport through boreholes, and borehole-installed fuel cell heaters (Boak, 2007).

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This paper considers the production of CO_2 for an in situ process operating on oil shale of the Green River Formation of Colorado, Utah and Wyoming, and provides a simplified model for, and an estimate of, the quantity of CO_2 requiring separation and segregation from a nominal oil shale industry in the Western United States. The model is sufficiently flexible that it could be replicated for any other oil shale deposit, and for various sources of energy for the in situ heating. Efforts are already underway in the western United States to identify targets for CO_2 sequestration and pathways to those targets.

Global Oil Shale Resources

Figure 1 shows the top ten oil shale resources of the world, including all of those containing more than 15 billion barrels of potential shale oil, along with the age of the primary oil shale formations, and their depositional environments (Dyni, 2006). The deposits are widely distributed around the world, although the largest share of the resource occurs in the United States.

The Paleocene Green River Formation of Colorado, Utah and Wyoming contains nearly half of the global resources estimated by Dyni (2006), as updated based on Boak (2007) and this proceedings volume (Boak and Whitehead, 2008). Estimates of potential resources in the Green River Formation range from 700 to 2,000 billion barrels. Additional very large resources exist in the Devonian shale deposits of the eastern United States and in a wide variety of marine shale formations in Russia. Seven other countries shown are estimated to have resources greater than fifteen billion barrels of shale oil. Reports from this Symposium of very large oil shale resources in China are shown in a substantial upward revision of the Chinese resource (Carroll, 2008; Liu, 2008)

Although more of the oil shale occurrences are found in marine shale, the massive size of the Green River shale ensures that lacustrine environments dominate the quantity of the resource. The total global resource of oil shale product is potentially greater than three trillion barrels.

Shale oil resources are strongly dependent upon the value used to define economically recoverable oil shale. The resources listed in Dyni (2006) vary widely in this value, so that perfect intercomparability may not be possible. In addition, most estimates have been predicated upon surface processing of mined oil shale, with high grade material probably being preferentially produced. The in situ heating and conversion of oil shale necessarily involves heating of an entire section of rock, both lean and rich in oil shale. Such a process might require a

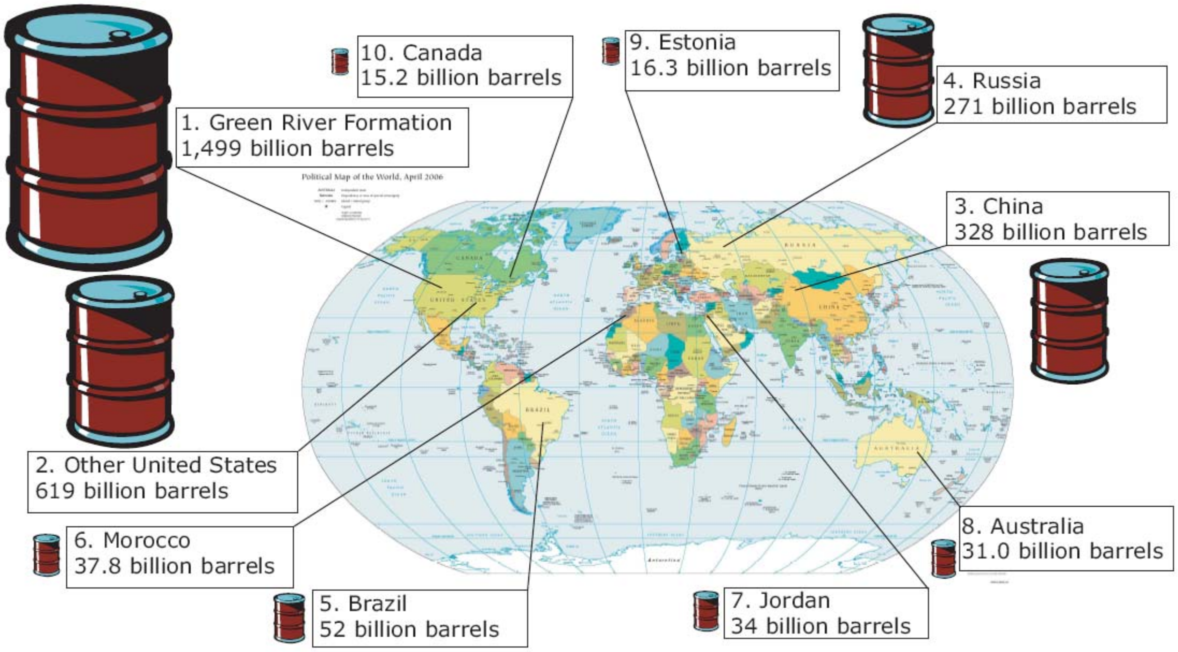

Figure 1: Ten largest resources of oil shale, with resource size, age, and environment of deposition. The barrels are approximately proportional in area to the resource size.

separate evaluation of the available resource, although U. S. estimates may already include both rich and lean zones in the resource.

Objectives

The objectives of this study were to:

- Develop an estimate of the CO_2 emitted by an oil shale industry producing three million barrels of shale oil per day from in situ processes and heating rock through natural gas fired electric power,
- Quantify uncertainties in the estimate,
- Develop a transparent model that captures both the estimated amount and its uncertainty with reasonable accuracy.

The scale of production was chosen to reflect a fully functional and globally significant oil shale industry. Estimates of U. S. production suggest that such a level might be achieved over the next few decades (US DOE, 2004). The uncertainties are important to quantify if research efforts are to be directed at resolving important issues regarding the impact of such an industry. The desire for transparency comes from the expectation that the issue of CO_2 emissions will need to be communicated to regulators, politicians, and the general public as well as to others involved in producing shale oil.

Shell In-Situ Conversion Process (ICP)

Many of the available data on *in situ* conversion of oil shale kerogen to shale oil come from Shell Exploration and Production, which is currently testing such a process in western Colorado (Vinegar, 2007). The process (shown schematically in figure 2) uses electric resistance heaters placed in boreholes drilled to the depth of the rich oil shale to gradually heat the rock over several years. This approach accelerates the natural maturation of the kerogen in the oil shale at a temperature in the vicinity of 350°C. This temperature is significantly lower than the temperature of traditional retorts for surface processing of oil shale, which operate at 500-1000°C. The products of the heat-induced chemical reactions within the kerogen are removed through traditional production wells as gas and liquid. The long slow heating of the oil shale results in high recovery percentages and light hydrocarbon products that can be readily used as high quality transportation fuels with little or no upgrading, according to Shell (Vinegar, 2007). They compare favorably to products of traditional retorts (Figure 3). Similar *in situ* processes are under evaluation by ExxonMobil and EGL Resources (Symington et al, 2007; Lerwick et al., 2007)

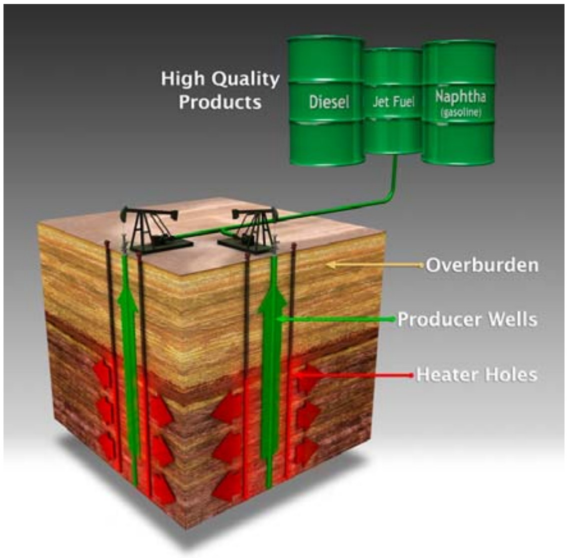

Figure 2: Shell In situ Conversion Process (ICP) for oil shale development

Heating such a large volume of rock and removing a significant portion of the rock volume as petroleum liquids might be expected to alter the ground water in the surrounding rock. To mitigate these negative environmental impacts, Shell plans to place a freeze wall around the heated volume, freezing the groundwater in place in a zone surrounding the heater wells. Much of the ground water will be removed prior to heating the rock. The freeze wall would only be released once cooling and testing of the remaining ground water demonstrated minimal risk of contamination of adjacent ground water.

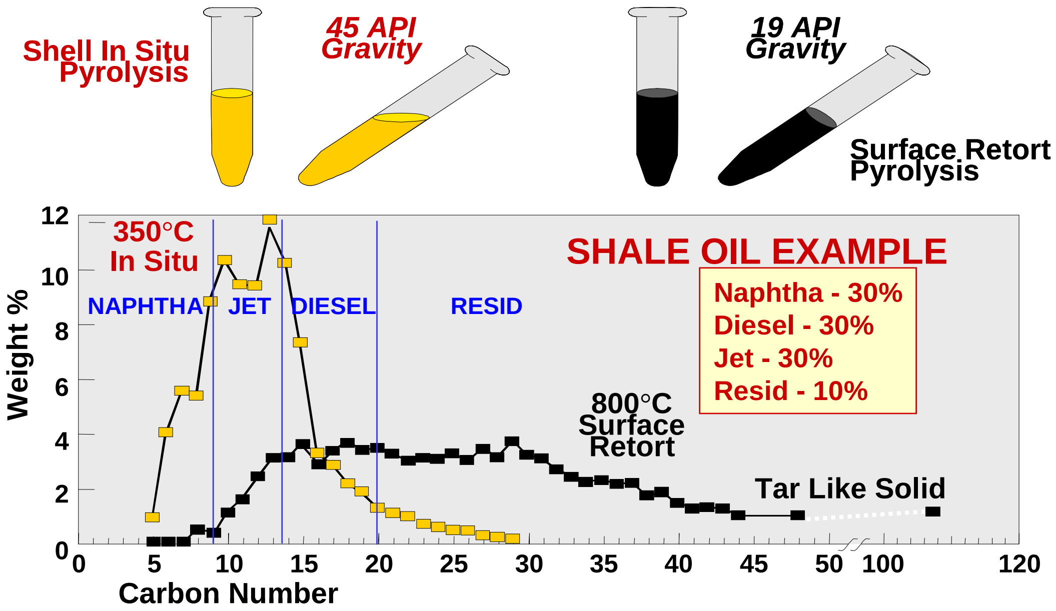

Figure 3: Shell ICP product properties compared to surface retort product

Production of CO_2, a greenhouse gas, may be expected to be substantial from any processing of oil shale. Heating of oil shale requires very large quantities of energy, most likely produced by the burning of hydrocarbons, either within the retort for surface processing, or in the power plant that produces the electric power for the downhole heating of the oil shale. Shell proposes to use gas fired electric generators ultimately running on the gaseous portion of the oil shale product (Vinegar, 2007, and personal communication at the time of presentation).

Retorting of oil shale may be expected to release significant quantities of CO_2 from oil shale, as the bulk of the rock consists of calcium and magnesium carbonates (calcite and dolomite). In addition, parts of the section contain sodium carbonate and bicarbonate minerals such as nahcolite, dawsonite, and trona. The lower temperature of the in-situ process is likely to reduce the fraction of calcite and dolomite that breaks down to nearly zero, but some concern exists that trace amounts of the sodium bicarbonates might release CO_2. Other reactions between silicate and carbonate minerals might also release CO_2. In addition, oxidation of the kerogen might lead to additional CO_2 generation. Thus, it may be of value to estimate the relative proportions of CO_2 derived simply from generating power above ground for heat and from chemical processes downhole.

Model for CO_2 Generation from Production of Shale Oil

The simplified model developed for the output of CO_2 from the three sources uses the sparse available data on the processes available in the public domain. The model runs in Lumina Decision Systems' *Analytica*TM, a visual tool for creating, analyzing, and communicating decision models. *Analytica*TM performs multiple calculations using a Monte Carlo algorithm to provide a statistically based distribution of results for calculations involving uncertain parameters. The system supports easy linking of variables in a graphical manner, and is especially useful for probabilistic modeling where many variables are uncertain. It is therefore relatively easy to evaluate the importance of uncertainties in the model result, and therefore determine what parts of the model most require refinement. In addition, the graphical interface makes the model relatively transparent, so that anyone can reasonably understand how the model calculates a result. In addition, it can be very easily modified to correct mistakes identified by others.

The model (shown graphically in Figure 4) incorporates submodels for each of the three sources of CO_2 described above – power plant, rock minerals, and kerogen. The collection of results derived from the model is illustrated in Figure 5.

At this point the model is simplified, with some potentially significant processes not incorporated. In addition, the ranges entered for fractions of carbon converted to CO_2 in the minerals and in the kerogen are considered conservatively large. Nevertheless, the model is expected to at least capture the range of possible values, and to provide insights into the problems that may need to be addressed to define better the likely emissions of an oil shale industry. A few specific details are highlighted here to indicate the current state of the model. Refinement and a more detailed description of the model are still underway.

Features of the model

Power plant emissions in the model use data from various sources. The estimated release of CO_2 from natural gas fired power plants is based upon a value of 117,000

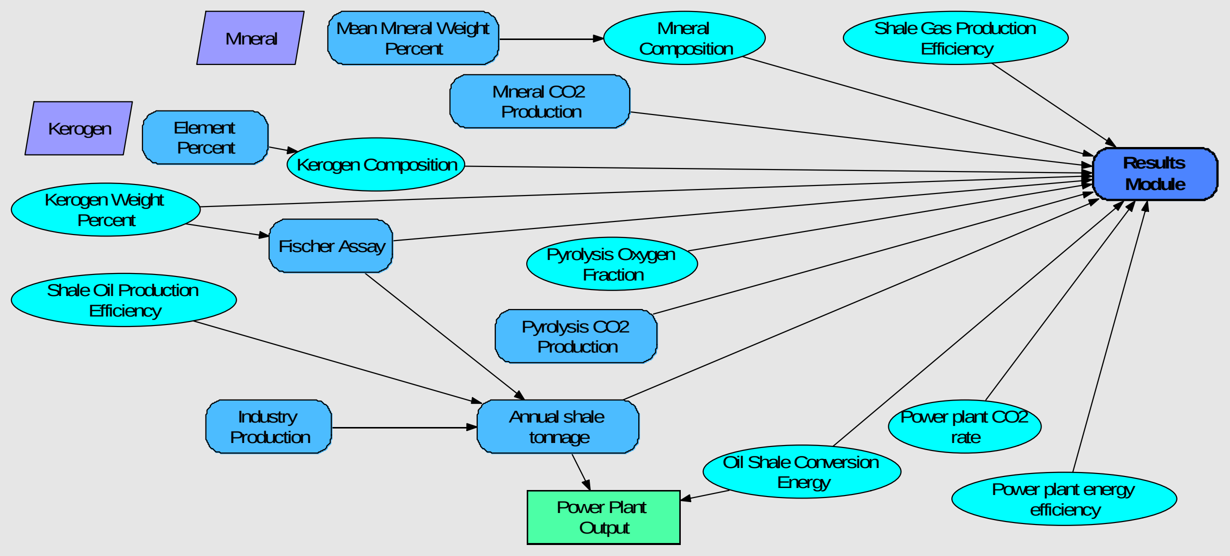

Figure 4: Structure of the model for CO2 emissions from oil shale production

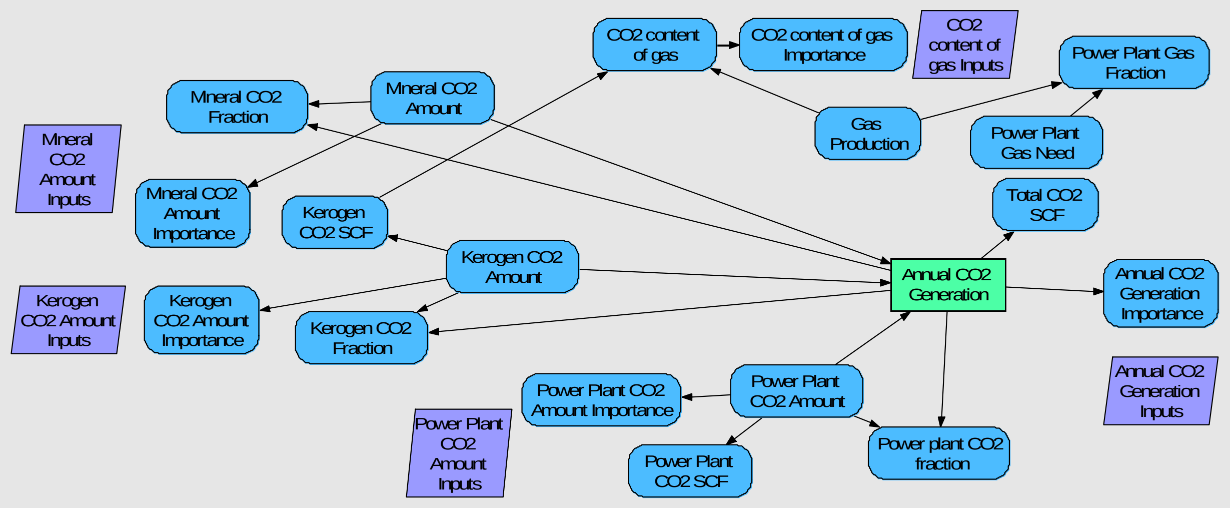

Figure 5: Results module of the model for CO2 emissions from oil shale production

pounds per billion British Thermal Units (BTUs) (DOE/EIA, 1999), with an estimated uncertainty applied based on the author's judgment.

The energy efficiency of generation was presumed to be 35-40%, which is low for gas-fired turbines. The quantity of electricity is very large, so the calculations assumed that electricity supply is diversified, and that some fraction comes from lower efficiency coal-fired power plants. No allocation was made of additional energy expended in maintaining the freeze wall to contain the local ground water. In this respect the model is non-conservative. However, the model also did not consider the potential to preheat a block of rock using heat recovered from a previously heated block.

Burnham and McConaghy (2007) provide an estimate of the amount of energy required to break down the kerogen in oil shale of (87-124 kwh per metric ton) in the range from 300-400°C.

Release of CO_2 from mineral reactions in the oil shale was estimated by presuming that any trace of nahcolite present in the rock would break down at temperatures below about 150 °C (Yamada and Koga, 2005) in accordance with the following reaction

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O \quad (1)$$

Results from Lawrence Livermore National Laboratory (Campbell, 1981; Singleton et al. 1986) provide data on the amount of nahcolite present in the Mahogany zone of the Green River Formation. The average value is 0.8 weight percent (wt %).

Additional CO_2 is expected to be released from the kerogen. Kerogen from the Mahogany zone of the Green River formation contains 5.75 wt % oxygen on average, whereas shale oil contains 1.2 to 1.8 wt % (Baughman, 1981). At the point at which the model was run, little or no information was available on the fraction of oxygen that might form CO_2 during in-situ pyrolysis. So a mean value of 50% with a standard deviation of 15% was assigned. This number is probably conservative.

Values for the amount of oil and gas produced were derived from the chart in Figure 3 for Shell's experiments. It was assumed that an average of 78% of Fischer Assay was removed from the rock as oil, and that gas was removed at an energy equivalent 30% of Fischer Assay. The average Fischer Assay value for the entire industrial production was derived from average Fischer Assay values over the entire Green River Formation from 200 wells assembled by Y. Bartov at the Colorado School of Mines. All Fischer Assay data are tabulated by the U. S. Geological Survey. The Fischer Assay data were related to kerogen content based upon the relationship shown in Baughman (1981), Figure 10.

The model calculates oil & gas production from organic matter content and expected process efficiency. It calculates CO_2 both as tons/year and as SCF/day, which allows comparison to global CO_2 figures, but also allows comparison of the size of gas operations for production and separation.

Results

Results of the model are shown in Figures 6 through 10. The quantity of CO_2 generated annually varies by a factor of about eight from about 100 million tons to greater than 600 million tons (Figure 6). The modal value is less than 200 million tons, but the median and mean are both above that amount.

The cumulative distribution of values is shown in Figure 7, which indicates that the probability of exceeding 350 million tons is less than 10%. Burning of the resultant oil and gas products would add further to this output.

Figure 8 shows the fraction of the CO_2 produced by the power plant, which is greater than 90% at the midpoint of the range. The values for CO_2 generated downhole from breakdown of carbonate minerals and oxidation of kerogen probably include val-

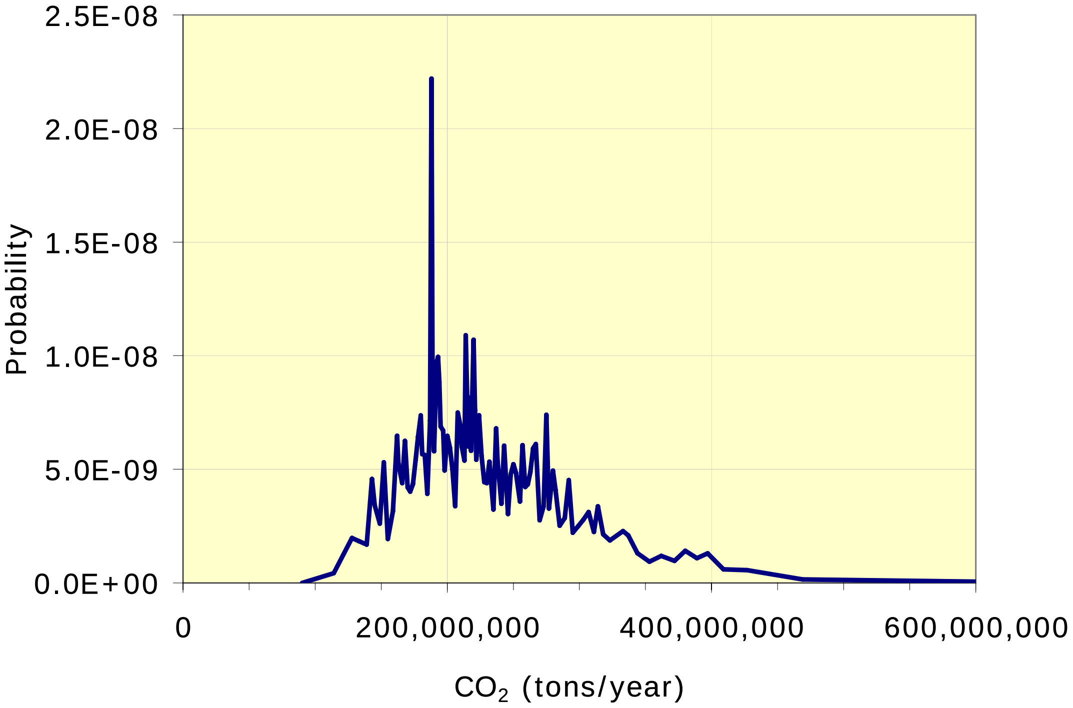

Figure 6: Annual CO_2 generation from oil shale production

ues that are higher than is likely for an entire operating industry.

As a consequence, revision of the model to more accurately reflect these fractions should shift the distribution toward much higher fractions coming from the power plant. This change should also reduce the total quantity of CO_2 produced by in-situ conversion.

Figure 9 shows the result of a sensitivity

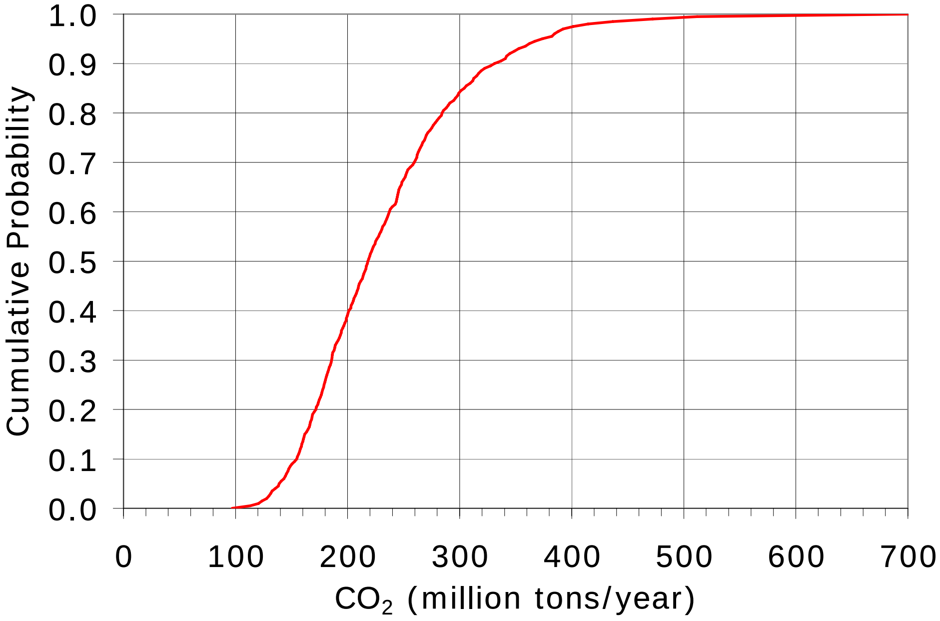

Figure 7: Cumulative probability plot for CO_2 release

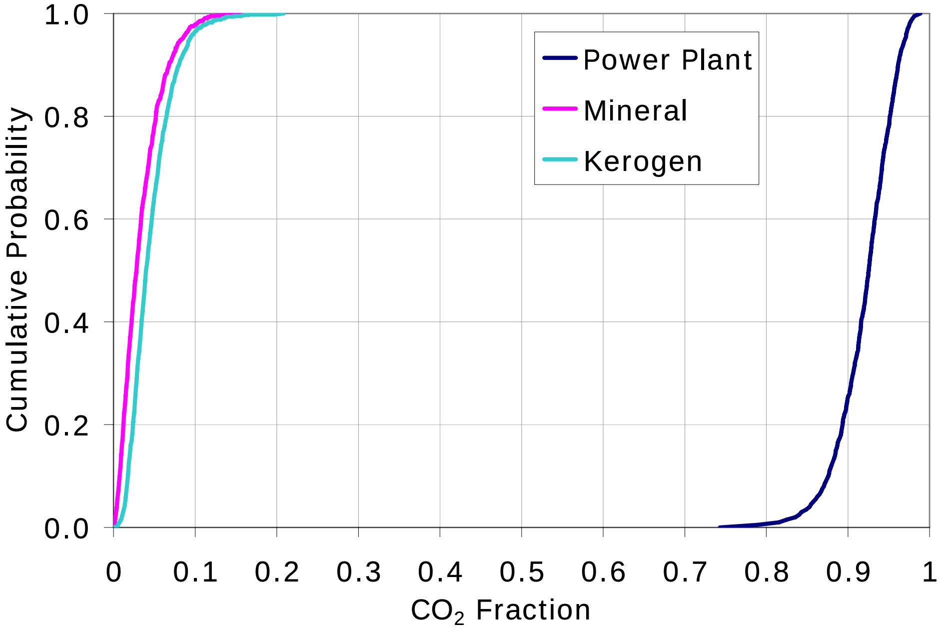

Figure 8: Fraction of CO_2 produced by power plant, mineral breakdown, and kerogen oxidation

analysis of the outcome for total CO_2 production. It illustrates the importance of the various input parameters to the uncertainty in the output. The most significant variable is the Kerogen Weight Percent, a rough estimate of the richness of the oil shale.

Figure 10 shows the relationship between Fischer Assay (which is linearly related to the kerogen content, but provides a more familiar measure of oil shale richness). It indicates that, although the emission rates are nearly 700 million tons for one or two simulations, the bulk of the values lie between 150 million and 400 million tons. The mean value of Fischer Assay in the sampling distribution is ~15 gallons/ton. It is highly unlikely that the industry will produce oil shale from the lower grade portions of the section in the Green River Formation for many years. Thus, the CO_2 emission projected from this model are highly unlikely to exceed 300 million tons per year, and relatively unlikely to exceed 250 million tons per year.

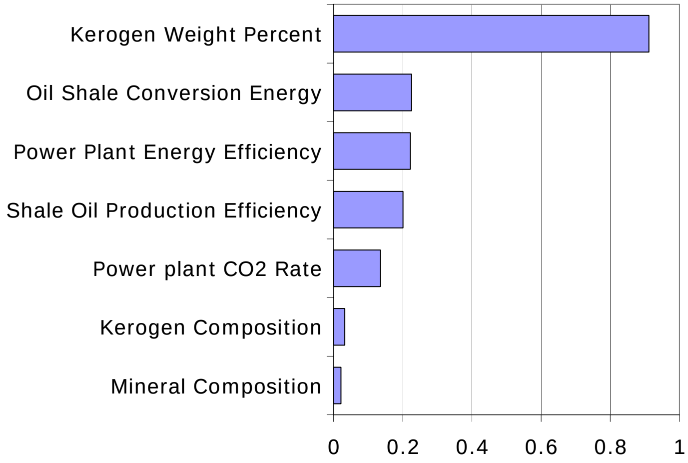

Figure 9: Importance of variables to CO_2 produced by oil shale

The CO_2 emissions are also sensitive to the quantity of energy required to pyrolyze the rock (Oil Shale Conversion Energy). A significant fraction of this energy simply goes into heating the rock to the pyrolysis temperature. The efficiency of the power plant generating the electricity for the downhole heaters is also important to the uncertainty of the emission estimate. In addition, the CO_2 emissions are significantly sensitive to the efficiency of extraction of the in situ process. The value used here may reflect laboratory experiments rather

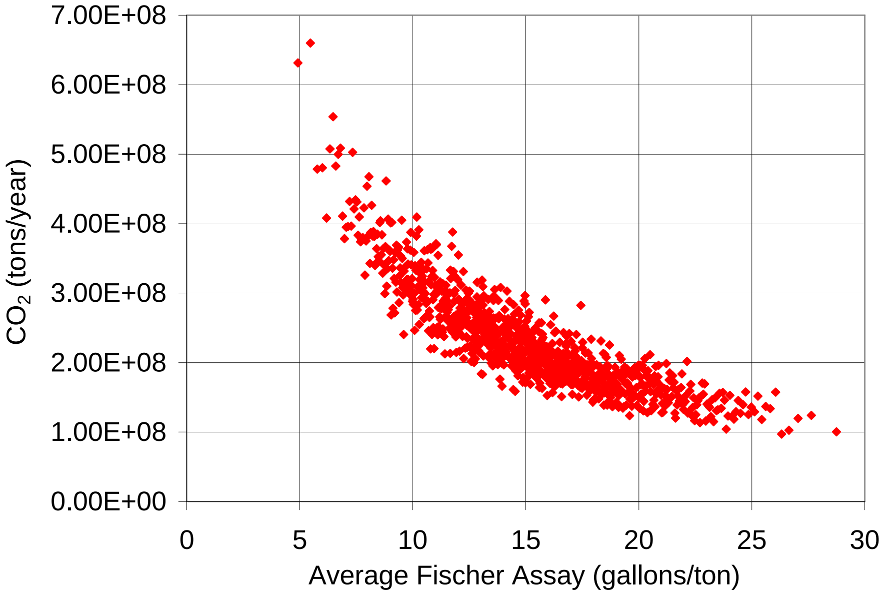

Figure 10: CO_2 produced as a function of average Fischer Assay of oil shale

than actual practice in the field. Comments from Shell personnel in the field suggest that the 78% of Fischer Assay number may have been higher than what is achieved in practice.

The breakdown of carbonate minerals and the oxidation of kerogen, although a minor fraction of the total CO_2 produced, can affect the quality of the gas produced. Figure 11 shows the relationship of CO_2 fraction in produced gas to the quantity of nahcolite and to the fraction of the kerogen oxygen that combines with carbon to make CO_2. The figure also shows the mean value assumed for each of the underlying parameters. Nearly all of the higher values of CO_2 content in gas come from samples for which the input parameter values were above the mean for one or both measures. One other parameter, the kerogen content, is important to this result. Higher kerogen content provides a larger oxygen content to be converted. Even for values below one weight percent nahcolite, the fraction of CO_2 can be remarkably high. Likewise, relatively small amounts of oxygen in kerogen converted to CO_2 can produce a lower quality gas.

Modeling Conclusions

The quantities of CO_2 expected to be emitted by an oil shale industry are very large. United Nations data on CO_2 emissions by country for 2004 (Wikipedia, 2007) show that 300 million tons is slightly less than the CO_2 emission of Saudi Arabia, and that 200 million tons is between that of Thailand and Turkey. Thus, an oil shale industry in western Colorado would be a major global emitter. On the other hand, carbon dioxide emissions from flaring of gas associated with oil production are reported to be approximately 400 million tons (Elvidge et al., 2007). It is clear that work to reduce carbon emissions through sequestration, already a major objective of climate change initiatives, will be needed to ensure that future use of hydrocarbons does not negatively impact earth's climate.

If all power were generated from gas turbines, it would reduce the emissions from the values presented here, perhaps by 30 percent. Capture of heat from previously heated blocks could also reduce the power requirements, and the CO_2 emissions. Finally, use of downhole heaters, which would presumably have very high efficiency, might substantially reduce CO_2

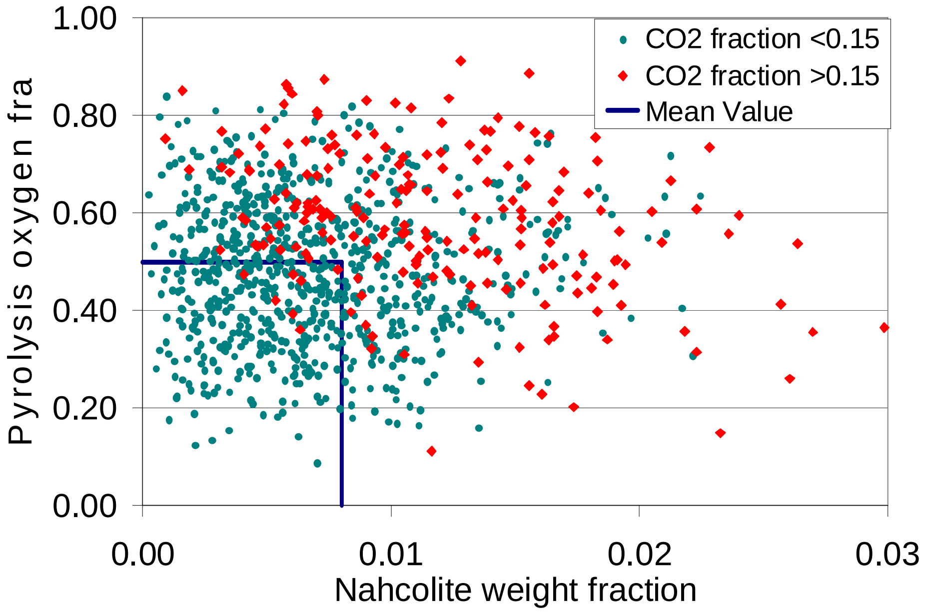

Figure 11: The fraction of oxygen removed from kerogen as CO_2 plotted against nahcolite weight fraction. Individual points reflect sampling of the range of uncertain parameters, and the symbols distinguish samples for which the resulting CO_2 fraction in the gas is less than or greater than 0.15.

emissions. On the other hand, power requirements for the freeze wall and for ground water remediation after production, and transmission losses from the power plant, not incorporated in this model, might increase the power requirements and emissions.

The natural gas component of the oil shale pyrolysis products is large in its own right. In addition to the three million barrels per day of shale oil produced, the output of the process averages about 6.5 billion cubic feet (BCF) per day. This product can meet much of the demand of the power plants used to heat the rock in-situ. However, the calculations for the fuel requirements of the natural gas power plants suggest a mean demand of nearly ten BCF per day, indicating that the oil shale industry will consume most of the gaseous products, and may require additional sources.

The mean value of the power requirement to produce the oil and gas from oil shale is 46,000 megawatts (MW). This amount suggests that it may be very difficult to derive the power for a full scale oil shale industry from local sources, as individual power plants are commonly less than 1,000 MW in capacity.

The CO_2 produced by breakdown of minerals and oxidation of kerogen may be significant if it reduces the quality of the natural gas product of the pyrolysis. The low temperature breakdown of nahcolite is likely to result in an early pulse of CO_2-rich gas unlikely to be a significant problem. Higher temperature reactions could be a problem at remarkably low levels of reaction. Less than one wt % of mineral reaction and similar quantities of kerogen reaction to CO_2 can add up to 10% or more of the gaseous product. On the other hand, questions of this sort are likely to be readily resolved by experiment, once research testing is conducted. Figure 11 shows the impact of these two contributions on the gas quality. Very few simulation results that have gas fractions of CO_2 greater than 0.15 result from below average fractions of one or the other (or both) of these two parameters.

The CO_2 emissions model developed for this paper is a simple illustrative one, intended to highlight the potential value of the transparent, probabilistic modeling tools to estimate the potential release and to define the most significant parameters, so that improvements can readily be made to those parts that are most likely to affect the outcome. Further refinement of this model is necessary to more accurately reflect the expected CO_2 release from an in-situ oil shale industry.

Nevertheless, the simplified model supports the conclusion that the dominant CO_2 source would most likely be the power plant emissions. Refinement of the model is likely to further strengthen this conclusion. Concern about the amount of CO_2 produced with the gaseous fraction is reasonable. Further refinement is likely to reduce this concern with relatively modest inputs. It will be important to better define both potential sources of CO_2 from underground, the kerogen and the rock. It is likely to be possible to demonstrate that much less than 1% of the rock mass is reacted, thereby reducing the fraction of CO_2 from underground sources.

Conclusions

Renewed global interest in the production of shale oil raises significant questions about the production of CO_2 from processing oil shale either at the surface or in-situ. Modeling indicates that the expected quantities generated (potentially 250 million tons per year or more for a robust oil shale industry in the U. S.) will be large. Planning for its capture and sequestration is wise, even if not yet required. Relatively long lead times for putting in place the infrastructure suggest the prudence of such a course. Efforts are underway to examine both pathways and targets for sequestration of CO_2 in the western U. S. If the large volumes of CO_2 from an oil shale industry are to be securely sequestered as the industry ramps up, significant research and testing will be necessary, and routing design and construction of major new transportation systems will be required. It will also be necessary to identify, secure and develop transportation pathways to large scale target formations for these volumes of CO_2.

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