Reports

Oil Shales and Carbon Dioxide

Abstract. *During retorting of oil shales in the western United States, carbonate minerals are calcined, releasing significant amounts of carbon dioxide. Residual organic matter in the shales may also be burned, adding more carbon dioxide to the atmosphere. The amount of carbon dioxide produced depends on the retort process and the grade and mineralogy of the shale. Preliminary calculations suggest that retorting of oil shales from the Green River Formation and burning of the product oil could release one and one-half to five times more carbon dioxide than burning of conventional oil to obtain the same amount of usable energy. The largest carbon dioxide releases are associated with retorting processes that operate at temperatures greater than about 600°C.*

Recent national energy policy proposals have focused attention on the uncertain climatic consequences of CO_2 released by producing and burning synthetic fuels (*1*). Throughout these discussions, the potential for CO_2 release during the production and consumption of oil from shale has not been fully considered. Certain processes for developing some U.S. oil shales may generate more CO_2 per unit of usable energy produced than any other synfuel development. Specifically, methods utilizing high-temperature retorting (that is, retorting at temperatures above about 600°C) of our western oil shales may cause more CO_2 to be released through decomposition of carbonate minerals than the amount of CO_2 that will subsequently be generated by burning the oil produced. Thus the Green River oil shales should not be ignored as a potentially significant future source of CO_2.

Approximately 90 percent of the nation's (and 60 percent of the world's) identified oil shale resources occur in the dolomitic marlstones of the Green River Formation of Colorado, Utah, and Wyoming (*2*). Dolomite is found throughout the formation, and the marlstones also contain significant local occurrences of carbonate minerals such as calcite, nahcolite, and dawsonite (*3*). The oil (and accompanying gas) is extracted by heating the rock to temperatures from about 500° to 1100°C, depending on the retorting technique used. At high temperatures (greater than about 600°C), significant amounts of the carbonate minerals are calcined, liberating CO_2 (*4*).

Many oil shale retorting techniques have undergone small-scale testing. In general, the retorting temperatures depend on how the shale is heated. Low-temperature indirect retorting processes, in which heat is typically derived from an external source, operate at temperatures near 500°C. Indirect retorting does not appear significantly calcine the carbonate minerals. High-temperature retorting processes typically utilize heat generated directly by the combustion of some of the organic carbon in the shale inside the retort. Such processes commonly result in temperatures of 700° to 1100°C—high enough to calcine the carbonate minerals. Recent testing has demonstrated that some high-temperature methods may cause complete decomposition of the carbonate minerals in oil shales that reach these temperatures (*5*).

In addition to creating the potential for carbonate decomposition, oil shale retorting releases CO_2 from the combustion of organic carbon. Like the other synthetic fuels, shale oil typically requires more energy for its production than does its conventional counterpart, crude oil. Most of the extra energy required is the heat used to convert the solid kerogen into liquids and gases. This heat may be supplied by burning some of the retorted oil or gas; or, in some retorting processes, by burning organic matter left in the shale after the oil and gas are extracted. In preliminary field tests of one method of high-temperature direct retorting, less than half of the organic matter was recovered as oil (*5, 6*). Much, if not all, of the remaining organic matter may be burned inside the retort. Although this and many other methods of shale oil recovery are still in the early stages of development, expected improvements are not likely to substantially reduce the CO_2 produced at high retorting temperatures.

The amount of CO_2 produced by extracting and burning shale oil can vary widely depending on variations in mineralogy, organic content, and retorting technique. Estimates can be based on preliminary data from pilot retorts of oil shale from the Green River Formation in and around the Piceance Creek basin in Colorado (*7*). These data indicate that shale oil produced by low-temperature retorting yields about 30 kg of carbon as CO_2 (kgC) (*8*) for every million British thermal units (Btu's) of usable energy (MBtu). This figure represents CO_2 generated by retorting and burning the oil, and is significantly higher than the CO_2 produced by burning conventional fuels (about 15 kgC/MBtu for natural gas, 21 kgC/MBtu for crude oil, and 25 kgC/MBtu for bituminous coal). Extraction and consumption of several other synthetic fuels likewise generate about 30 kgC/MBtu (*9*). In contrast, retorting and burning shale oil produced by high-temperature direct retorting of the Green River Formation could generate as much as 70 kgC/MBtu for shale that assays at 25 gallons of oil per ton and 110 kgC/MBtu for shale that assays at 10 gallons of oil per ton (*10*).

Like all current efforts to anticipate future CO_2 production rates, our calculations are tentative. We have assumed that high-temperature direct retorting methods completely calcine the carbonate minerals and burn all of the unextracted organic matter, yet no complete material balance data are available (*6*). Inhomogeneous temperatures in the retort may leave regions of incomplete reaction, and some CO_2 may be consumed by recarbonation reactions during or following the retorting process. These effects might decrease our estimates for CO_2 production. On the other hand, temperature inhomogeneities might also decrease recovery efficiency and hence reduce the usable energy yield relative to the amount of CO_2 generated. Moreover, we have not taken into account the additional CO_2 generated by energy requirements for construction, mining, pollution control, preliminary refining, and marketing.

How much CO_2 will shale oil production and consumption add to the atmosphere? An industry in the Piceance Creek basin producing 1 million barrels of oil per day would require retorting

0036-8075/80/0516-0740$00.50

each year the equivalent of 0.8×10^9 to 1.3×10^9 tons of shale assayed at 20 gallons of oil per ton. The corresponding annual release of carbon as CO_2 from retorting and burning the shale oil could range from about 0.06×10^9 tons (for low-temperature retorting, 100 percent recovery as measured by modified Fischer assay) to 0.17×10^9 tons (for high-temperature direct retorting, 60 percent recovery as measured by modified Fischer assay). For comparison, burning 1 million barrels of conventional crude oil per day generates about 0.04×10^9 tons of carbon as CO_2 each year.

The present rate of production of carbon as CO_2 from conventional fuels is close to 5×10^9 tons per year; hence, if 1 million barrels of shale oil were consumed each day in addition to present consumption of conventional fuels, the annual global production of CO_2 from fossil fuels would increase by 1 to 3 percent. If 1 million barrels of shale oil were substituted each day for the same amount of conventional oil in the present worldwide fuel mix, the corresponding increase in CO_2 production would be 0.5 to 2.5 percent of the present annual global flux of CO_2 from utilization of fossil fuels.

Although extrapolation into the future is quite speculative, recent government reports suggest an upper limit for the cumulative production of CO_2 from western U.S. oil shales by the year 2000 (*11*). Loosely based on commercialization projections, our estimate for this limit is the equivalent of production by high-temperature retorting of 1 million barrels per day for 20 years. During this time, retorting and burning that much shale oil would produce 3×10^9 to 4×10^9 tons of carbon as CO_2, or 1 to 2 percent of the 150×10^9 to 300×10^9 tons anticipated from utilizing conventional fossil fuels between 1980 and 2000 (*12*). The total identified resources (*2*) in the Green River Formation amount to about 1.8×10^{12} barrels contained in 5×10^{12} tons of rock. If half of these resources is eventually recovered with high-temperature techniques and subsequently burned, the total release to the atmosphere of carbon as CO_2 could be about 300×10^9 tons. The rate of CO_2 release from oil shales will ultimately depend on the method and rate of exploitation which could last for more than a century.

ERIC T. SUNDQUIST
U.S. Geological Survey,
Reston, Virginia 22092

G. A. MILLER
Area Oil Shale Supervisor's Office,
U.S. Geological Survey,
Grand Junction, Colorado 81501

References and Notes

1. See, for example, L. H. Carter, *Science* **205**, 376 (1978); *ibid.*, p. 884.
2. W. C. Culbertson and J. K. Pitman, in *U.S. Geol. Surv. Prof. Pap. 820* (1973), p. 497. Estimates of total (as opposed to known or identified) oil shale resources ascribe much less relative importance to the Green River Formation. For details and a discussion of resource terminology, see D. C. Duncan and V. E. Swanson [*U.S. Geol. Surv. Circ. 523* (1965)].
3. W. A. Robb, J. W. Smith, L. G. Trudell, *Mineral and Organic Distribution and Relationships Across the Green River Formation Saline Deposition Center, Piceance Creek basin, Colorado* (LETC RI-78/6, National Technical Information Service, Springfield, Va., 1978).
4. E. E. Jukkola, *Ind. Eng. Chem.* **45**, 2711 (1953).
5. J. W. Smith, Laramie Energy Technology Center, Department of Energy, personal communication.
6. See, for example, R. A. Loucks, *Occidental Vertical Modified in situ Process for the Recovery of Oil from Oil Shale* (TID-28053, National Technical Information Service, Springfield, Va., 1977), parts 1 and 2.
7. For data and references, see *Synthetic Fuels Data Handbook* (Cameron Engineers, Inc., Denver, Colo., ed. 2, 1978), pp. 3–145.
8. Carbon as CO_2 refers to the mass of the carbon contained in CO_2 gas. This mass can be converted to the corresponding mass of CO_2 gas by multiplying by a factor of 44/12.
9. G. J. F. MacDonald, *An Overview of the Impact of Carbon Dioxide on Climate* (MITRE Corp., McLean, Va., 1978).
10. We assumed the organic fraction of the shale to be 7 and 15 percent in shale assayed at 10 and 25 gallons of oil per ton, respectively. We also assumed the organic fraction to be 80.5 percent carbon [J. W. Smith, *U.S. Bur. Mines Rep. Invest. 5725* (1961), p. 13] and the inorganic fraction to be 32 percent dolomite and 16 percent calcite [J. W. Smith, *U.S. Bur. Mines Rep. Invest. 7248* (1969), p. 5]. We used a heating value of 18,000 Btu's per pound for crude shale oil and assumed that 60 percent of the oil assayed can be recovered during high-temperature direct retorting by modified in situ methods. In addition to the energy available from recovered oil, we allowed for energy from recovered gas amounting to 7 percent of the total energy from recovered oil [K. E. Stanfield, *U.S. Bur. Mines Rep. Invest. 4825* (1951), p. 14].
11. H. D. Guthrie, E. H. Blum, R. J. Braitsch, *Commercialization Strategy Report for Oil Shale*, parts 1, 2, and 3 (TID-28845, Department of Energy, Washington, D.C., 1979).
12. This range of conventional fossil fuel consumption corresponds to an increase in the concentration of atmospheric CO_2 of 30 to 60 parts per million by the year 2000, assuming that half of the CO_2 produced will remain in the atmosphere.

13. We thank numerous reviewers, particularly J. W. Smith and P. B. Barton, Jr., for their constructive comments and criticisms.

6 November 1979; revised 20 February 1980

Soot in Urban Atmospheres: Determination by an Optical Absorption Technique

Abstract. *We have used the high optical absorptivity of urban and source particulates to trace their "graphitic" component. The optical absorptivity and the particulate carbon loading show a strong correlation. Analyses of the data indicate that primary soot emissions compose a major fraction of the carbonaceous aerosol and put a low limit on secondary organic material produced in correlation with the ozone concentration.*

Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenically generated particulate burden in urban areas. Considerable attention has been devoted to understanding the origin and speciation of the sulfur and nitrogen components, but until recently relatively little effort has been directed toward the carbonaceous aerosol, which is often the single most important contributor to the submicron aerosol mass and is expected to have a large impact on visibility and health.

The major cause of these carbon particles is fossil fuel combustion, which produces both primary particulate carbonaceous emissions (soot) and gaseous hydrocarbons, which can be transformed in the atmosphere by gas-to-particle conversion processes to secondary organic material. There has been considerable uncertainty and debate over the relative importance of primary and secondary carbonaceous particles in the urban air (*1*). It is important to resolve this issue since it is obvious that a control strategy and technology for particulate carbon pollution abatement will depend on which of these alternatives prevails.

We describe here the application of a new analytical method which uses the unique optical properties of "graphitic" (*2*) soot to trace the primary component of the carbonaceous particulates under widely different atmospheric conditions over a wide geographical area. Our results are consistent with the earlier work of Novakov *et al.* (*3*) and indicate that primary soot emissions compose a major fraction of the urban carbonaceous aerosol.

Soot consists of a graphitic component and an organic component. The graphitic component can be conveniently monitored because of its large and uniform optical absorptivity, which has recently been shown to be responsible for the gray or black appearance of ambient and source particulate samples collected on various filter media (*4, 5*). The graphitic content of the aerosol can be measured by an optical attenuation method developed in our laboratory (*4*). We have also determined the total particulate carbon, which enables us to study the correlation between the graphitic and the total carbon content of the aerosol (*6*). The correlation or lack of it should depend on the relative amounts of primary and secondary material.

0036-8075/80/0516-0741$00.75