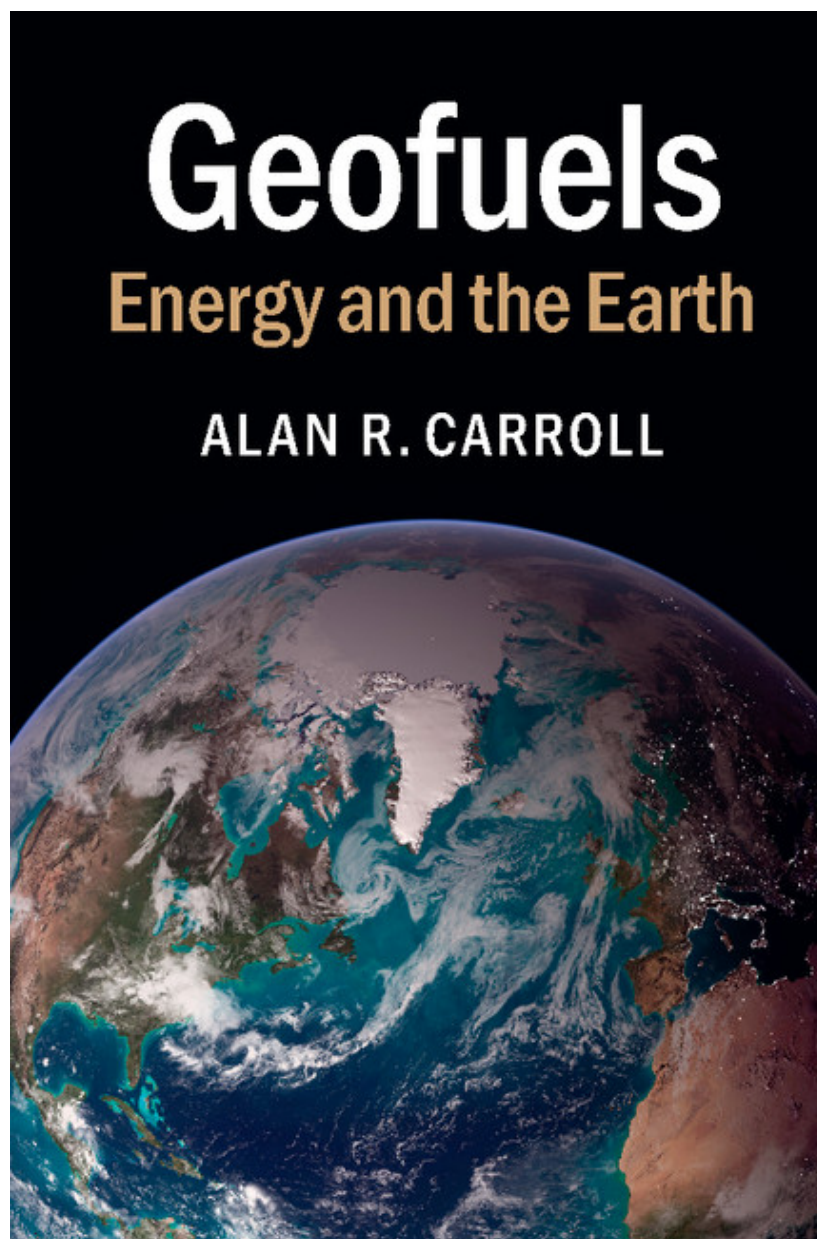


Fossil Fuel Origins

Excerpts from “Geofuels: Energy and the Earth” by Alan Carroll



Used with permission from



CAMBRIDGE
UNIVERSITY PRESS

Fossil Fuel Origins

Where do fossil fuels really come from? Put simply, coal, oil, and natural gas represent solar energy that was originally trapped by plants and stored in the Earth's crust. Fossil fuels can be roughly subdivided according to whether they originated from land plants, such as trees, herbs, and grasses, or aquatic plants, primarily one-celled algae. Coal deposits originate principally as land plants, and aquatic plants that lived in oceans and lakes are chiefly responsible for crude oil. Natural gas is a jack-of-all-trades that can be derived from any type of buried organic matter.

The Recipe for Coal

There is nothing especially mysterious about the geologic processes involved in making fossil fuels; in fact they can be thought of in terms similar to baking a cake. You start with the right mix of ingredients, stir them together, and bake at a certain temperature for a certain amount of time. The mixing bowl for making coal is a low-lying area of standing water called a mire. Swamps and marshes are both examples of mires; trees and other woody plants distinguish swamps, whereas grasses dominate marshes. Well-known modern examples of coal-forming environments in the United States include the Atchafalaya swamp in Louisiana, the Okefenokee swamp in Georgia, and the Everglades marsh in Florida. Areas of open water within mires also favor the growth of algae, the remains of which can make up a significant proportion of some coals.

The dead plant matter in mires is partially decayed by oxygen-breathing (aerobic) bacteria, in a process that is similar to what happens when making compost for your garden. If allowed to continue unabated, aerobic decay would completely consume all of the plant material and return its carbon to the atmosphere. However, submersion of dead plant material beneath water and burial by additional plant matter limit the available oxygen supply, and thereby slow bacterial decay. Mud and sand deposited above the layer of decaying plant material seal the deal, by effectively removing the dead organics from direct contact with atmospheric oxygen.

Baking occurs by progressive addition of layers of sediment, which push the natural compost formed in mires to deeper levels of the Earth's crust where temperatures are higher. The deepest burial occurs in sedimentary basins, which serve

Excerpts from *Geofuels: Energy and the Earth* (Cambridge University Press).

Copyright Alan R. Carroll 2015.

as the oven for coal and other fossil fuels. Sedimentary basins are areas where layers of sand, mud, and other sediment have accumulated to great thickness. Sedimentary basins commonly occur at the edges of continents, where rivers enter the sea and discharge sediment, for example, in the Gulf of Mexico. They are also found within continental interiors, where the Earth's crust has subsided. For example, nearly the entire state of Michigan is underlain by a bowl-shaped area of sedimentary rock that reaches up to 5 km thick at its center. The deepest sedimentary basins can reach downward more than 16 km below sea level and therefore are nearly twice as deep as Mt. Everest is tall.

As a rule of thumb, temperature increases at an average rate of about 25°C to 30°C per kilometer of burial depth. In the world's deepest mine, the Rand gold mine in South Africa, natural temperatures reach a sauna-like 70°C at a depth of 3,585 m. In general, temperatures at depths of 4 km or more exceed the boiling point of water at the Earth's surface. The water there does not actually boil, however, because of the immense pressure of overlying water and rock. The burial pressure at 4 km is about five hundred times the air pressure used to inflate automobile tires, and five times the bursting point of typical compressed gas cylinders. The Earth might therefore be thought of as the ultimate pressure cooker. These high pressures also compress the deep plant material in coal seams to one-tenth or less of its original thickness.

The temperatures required for making coal lie well within the range of the average household oven, but if you want to cook your own coal you'll need a timer scaled in millions of years rather than hours and minutes. Coal deposits span a wide range of geologic ages, from millions to hundreds of millions of years. As it cooks, coal undergoes a series of chemical transformations, converting the original plant material into a complex natural polymer called kerogen. The chemical structure of kerogen resembles that of plastics, consisting of thousands of atoms linked together in chains and three-dimensional networks. As it heats up, the coal is transformed through a series of increasing coal ranks that have progressively greater heating values. The lowest rank is lignite, followed by subbituminous and bituminous, and culminating with anthracite. As rank increases the coal also tends to become shinier, suggesting that diamonds might form with deeper burial. However, although diamonds are in fact made of carbon, they originate at much deeper levels in the Earth and are unrelated to coal.

Oceans, Algae, and Oil

The recipe for oil is similar to that of coal, but with different starting ingredients. Rather than land plants growing in mires, oil starts out as one-celled algae that float near the surface of lakes and oceans. These floating algae, also called phytoplankton, absorb sunlight and store it as chemical energy. Phytoplankton therefore need to live in well-lit parts of the water column, which practically speaking means no more than about 30 m below the surface. Phytoplankton are relatively simple organisms in comparison to land plants, and because they float freely they do not need to build woody support structures. They do use hydrocarbon compounds to build cell wall membranes, which regulate the flow of water, gas, and other substances between seawater (or lake water) and the interior of their cells. Phytoplankton therefore contain a relatively high proportion of hydrogen-rich organic compounds, called lipids (from the Greek word *lipos*, which means fat). These plant fats are very similar in structure to some of the molecules found in oil.

In addition to sunlight, phytoplankton need nutrients such as nitrogen, phosphorus, potassium, and others. Most of these derive from weathering of rocks on the continents and are carried by rivers (or wind) into the sea, where they can be used by phytoplankton. When phytoplankton die, they sink toward deeper waters of the ocean, taking the nutrients with them. The highest primary productivity of phytoplankton occurs where nutrient-rich waters return (or upwell) back toward the surface, commonly near the edges of the continents. Much of the open ocean is relatively dead by comparison to the continental margins. Local upwelling of nutrients from deeper parts of the ocean can cause exceptions to this pattern, for example, where the Labrador and Gulf Stream currents mix at the Grand Banks offshore of Newfoundland. If the flux of nutrients to the surface of the ocean (or a lake) is large enough, it can lead to eutrophication, similar to that which occurs in the Gulf of Mexico in response to river-borne nitrogen fertilizer.

Once buried in mud, phytoplankton and other organic remains are cooked in a manner similar to coal. Unlike coal, however, aquatic organic matter initially generates liquid oil rather than natural gas. You might expect crude oil to look something like the used motor oil from the crankcase of a car, and sometimes it does. However, crude oils span a surprisingly wide range of compositions, to the extent that it is difficult to

formulate a single precise definition of this common substance. Crude oil can in general be defined as a naturally occurring solution, in which the solute consists of relatively large molecules composed of hydrogen and carbon, as well as nitrogen, sulfur, oxygen, and other trace elements. The solvent consists of relatively small hydrocarbon molecules. This solution is staggeringly complex, containing tens of thousands of distinct chemical compounds.

Naturally occurring oils range in color from pitch-black to completely transparent, with various shades of brown, yellow, and even red being common. Oil can occur as a waxy solid at surface conditions or as a watery liquid. Some oils are so dense they sink in water, whereas others may be as light as gasoline. Some oils have little or no smell, but others are so sulfurous that the slightest whiff will quickly clear a room. Some crude oil actually starts out as a gas at reservoir conditions, but then condenses to a clear liquid at the surface. Called condensate, this liquid has a chemical composition not unlike that of refined gasoline. Oil field workers have been known to pilfer such oil, colloquially known to as “drip gas,” for direct use in their trucks.

There is no one standard crude oil, although certain oils such as West Texas Intermediate or North Sea Brent have been designated as benchmarks for price comparison. The actual price per barrel of any particular crude oil may differ from these benchmarks, depending on its characteristics. The highest prices are paid for relatively light, sweet (low sulfur) crudes, whereas heavy or sour (sulfur-rich) crudes bring lower prices.

The Many Faces of Natural Gas

Natural gas is a marketing department’s dream: it is all natural, organic, clean burning (except CO₂ emissions), and clear. In its natural state it is also odor free; the familiar gas smell results from an artificial additive. Without the additive natural gas would be imperceptible to humans, and gas leaks could easily result in asphyxiation or explosions. Methane, which consists of one carbon and four hydrogen atoms, is the most common component of natural gas. Gas molecules that contain two, three, or four carbon atoms (called ethane, propane, and butane, respectively) constitute most of the remainder.

Excerpts from *Geofuels: Energy and the Earth* (Cambridge University Press).

Copyright Alan R. Carroll 2015.

Natural gas might be thought of as the small change of the fossil fuels world, which is returned from a variety of transactions that occur during burial of organic matter. The first of these is the transformation of dead plant material into coal. As coal is heated it becomes more and more carbon-rich, through the loss of its other main constituents oxygen and hydrogen. These changes are accomplished by release of water, carbon dioxide, and methane. The cumulative release of methane during coalification can be quite large, equivalent to up to 10–20 percent of the total energy content of a bituminous coal. At greater depths and pressures, phytoplankton-rich source rocks can also generate substantial amounts of methane, typically after they've already generated most of their oil. Finally, even oil itself can generate gas, if it experiences elevated reservoir temperatures for long periods, by thermal cracking of large molecules into smaller ones.

Efficiency of the Geologic Solar Collector

The efficiency of any energy source can be simply defined as the percentage of the total available energy that can be used to generate electricity, propel an automobile, or satisfy other practical needs. For example, the efficiency of a photovoltaic solar collector can be defined as the electrical energy produced in a given time, as a percentage of the total solar energy striking its surface. The rated efficiency of photovoltaic cells is typically rather low – in the range of 10–20 percent conversion of sunlight into electricity – and their practical efficiency may be lower still. Most of the incident sunlight becomes wasted heat.

Following this same logic we can calculate the efficiency of the Earth itself as a giant solar collector. Although it doesn't directly produce electricity, the Earth actively stores energy in its crust in the form of fossil fuels. Most of this storage occurred during the Phanerozoic eon, which represents the most recent 541 million years of Earth history. The efficiency of the Earth as a solar energy collector can be calculated by comparing the total energy stored in fossil fuels to the amount of sunlight that reaches Earth in 541 million years. The result of this calculation is rather startling: The efficiency of the Earth as a solar collector is on the order of only 4 billionths of 1 percent! Put differently, the energy in fossil fuels that accumulated over the past 541 million years is roughly the equivalent of *1 week* of sunlight striking the Earth.

Excerpts from *Geofuels: Energy and the Earth* (Cambridge University Press).

Copyright Alan R. Carroll 2015.

Why is the Earth such a laughably poor solar collector? The explanation starts with the fact that plants are not particularly good at collecting sunlight, giving both biofuels and fossil fuels a built-in disadvantage. Matters go downhill quickly from there. The vast majority of dead plant matter never gets a decent burial and instead is left to rot on the surface. Of the plant matter that is buried and becomes incorporated into rocks, most of it is too scattered and dilute to generate concentrated oil accumulations. In many cases where organic matter *has* been buried in sufficient concentration to generate petroleum, it is buried either too deeply or not deeply enough. It might also be prematurely exhumed during the uplift of mountains and exposed to erosion.

Furthermore, much of the oil and gas that is actually generated does not remain trapped in rocks. Instead, it leaks all the way to the surface as natural seeps. Oil seeps are a common feature of the coastal waters of southern California, for example, and seeps led to the original historical discovery of petroleum as a fuel. Once at the surface, coal, oil, and natural gas cannot survive long in the presence of free oxygen. They are quickly destroyed, returning their carbon to the atmosphere as CO₂.

Given all these obstacles one might wonder how oil, gas, and coal have become so abundant. A clue exists in the famous multiple monkey theorem, which postulates that one thousand monkeys typing on one thousand typewriters for a long enough time will eventually reproduce the complete works of William Shakespeare. The details and attribution of this theorem vary, but at its heart lies the idea that even the most improbable events can occur if given enough time. The Earth may be an exceptionally poor solar collector, but it has been operating for an exceptionally long time.

An alternative way to calculate the efficiency of the geologic solar collector is to take into account all of the energy stored by organic matter in the Earth's crust, regardless of whether or not it can eventually be extracted. This calculation establishes the upper theoretical limit for how high the geologic solar efficiency can be.

The total energy in dead plant matter buried in the Earth's crust is the equivalent of about 100 years of sunlight striking the Earth (see Table 7.1), which is *5,200 times* greater than the energy contained in known fossil fuels! This difference is hugely important to our understanding of the ultimate potential of fossil fuel resources. Unlike the various estimates that have been made of economic fossil fuel abundance, the total amount of buried organic carbon represents a real physical limit of the Earth. Very little

of the total amount of organic matter in the Earth's crust will ever be profitable to extract, but its enormous magnitude proves that we have barely begun to scratch the surface of naturally stored solar energy. The ultimate limits of economic fossil fuel production will therefore depend not only on how much has already been proven to exist, but also on how far we can afford to dig into the Earth's much larger warehouse of "fossil sunlight."

Table: The Earth as a solar collector.

Sunlight Reaching Earth		
Sunlight intensity at Earth's surface ¹	1×10^3	W/m ²
Cross-sectional area of Earth	1.3×10^{14}	m ²
Total solar power reaching Earth's surface	1.3×10^{17}	W
Solar energy reaching Earth per day	1.1×10^{22}	J
Solar Energy Storage in Fossil Fuels		
Energy content of known fossil fuels ²	9×10^{22}	J
Efficiency of solar energy storage	0.000000004	%
<i>Fossil fuel - sunlight equivalent</i>	<i>~1</i>	<i>week</i>
Total Solar Energy Storage in Earth's Crust		
Energy content of all buried organic carbon ³	6×10^{26}	J
Efficiency of solar energy storage	0.00002	%
<i>Total carbon storage - sunlight equivalent</i>	<i>~100</i>	<i>years</i>

Notes:

1. Average solar intensity with the Sun directly overhead on a cloudless day.
2. Based on known, recoverable fossil fuels estimated by Rogner and others (2013).
3. Based on Berner (2001, 2003) isotopic mass balance model of organic carbon burial rates over past 541 million years. Organic matter assumed to contain 75 percent carbon by weight, and to have an energy value of 17.5 MJ/kg.