Learn About ...

METHANE

Methane, CH_4, is a colorless, odorless gas with a wide distribution in nature. It is the principal component of natural gas, a mixture containing about 75% CH_4, 15% ethane (C_2H_6), and 5% other hydrocarbons, such as propane (C_3H_8) and butane (C_4H_{10}). The "firedamp" of coal mines is chiefly methane. Anaerobic bacterial decomposition of plant and animal matter, such as occurs under water, produces marsh gas, which is another name for methane.

Properties and uses

At room temperature, methane is a gas less dense than air. It melts at –183 °C and boils at –164 °C. It is not very soluble in water. Methane is combustible, and mixtures of about 5% to 15% in air are explosive. Methane is nontoxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. A tiny amount of smelly organic sulfur compounds (tertiary butyl mercaptan, $(CH_3)_3CSH$, and dimethyl sulfide, CH_3SCH_3) is added to give commercial natural gas a detectable odor. This is done to make gas leaks readily detectible. An undetected gas leak is dangerous and can result in an explosion; many are reported every year, causing lost lives and occasional spectacular property destruction.

Methane can be produced in the laboratory by heating sodium acetate with sodium hydroxide and by the reaction of aluminum carbide (Al_4C_3) with water. It is synthesized commercially by heating a mixture of carbon and hydrogen and by the distillation of bituminous coal. Coal is a combustible rock formed from the remains of decayed vegetation that thrived on Earth about 300 million years ago. It is the only rock containing significant amounts of carbon. The elemental composition of coal varies between 60% and 95% carbon. Coal also contains hydrogen and oxygen, with small concentrations of nitrogen, chlorine, sulfur, and several metals. Coals are classified by the amount of volatile material they contain; that is, by how much of the mass is vaporized when the coal is heated to about 900 °C in the absence of air. Coal that contains more that 15% volatile material is called bituminous coal. Substances released from bituminous coal when it is distilled, in addition to methane, include water, carbon dioxide, ammonia, benzene, toluene, naphthalene, and anthracene. In addition, the distillation also yields oils, tars, and sulfur-containing products. The non-volatile component of coal, which remains after distillation, is coke. Coke is almost pure carbon and is an excellent fuel as well as a reducing agent in the smelting of metal ores, especially iron ore. However, it may contain metals, such as arsenic and lead, that can be serious pollutants if the combustible products are released into the atmosphere.

In the chemical industry, methane is a raw material for the manufacture of methanol (CH_3OH), formaldehyde (CH_2O), nitromethane (CH_3NO_2), chloroform (CH_3Cl), carbon tetrachloride (CCl_4), and some freons (compounds containing carbon and fluorine, and perhaps chlorine and hydrogen, many of which have been banned because of their harm to the stratospheric ozone layer {LINK to Ozone}). The reactions of methane with chlorine and fluorine are triggered by light. When exposed to bright visible light, mixtures of methane with chlorine or fluorine react explosively.

The principal use of methane is as a fuel. The combustion of methane is highly exothermic.

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \quad \Delta H = -891\ \text{kJ}$$

The energy released by the combustion of methane, from natural gas, is used directly to heat homes and commercial buildings. It is also used in the generation of electric power. During the past decade natural gas accounted for a little over 1/5 of the total energy used for power generation worldwide, and to about 1/3 in the United States. The use of natural gas for power generation is increasing and, in the United States, has overtaken coal (each at about 1/3 in 2016). What is driving the increasing use of natural gas (methane)?

Natural gas

Natural gas occurs in reservoirs trapped beneath the surface of the earth by overlying layers of rock. It is often found together with petroleum deposits. These reservoirs are tapped by drilling through the rock. Before it is distributed, natural gas usually undergoes some sort of processing. Usually, heavier hydrocarbons (propane and butane) are removed and marketed separately. Non-hydrocarbon gases, such as hydrogen sulfide and water vapor, must also be removed. The cleaned gas is then distributed throughout the country through more than 300,000 miles of pipeline, Figure 1. Local utility companies add an odorant before delivering the gas to their customers.

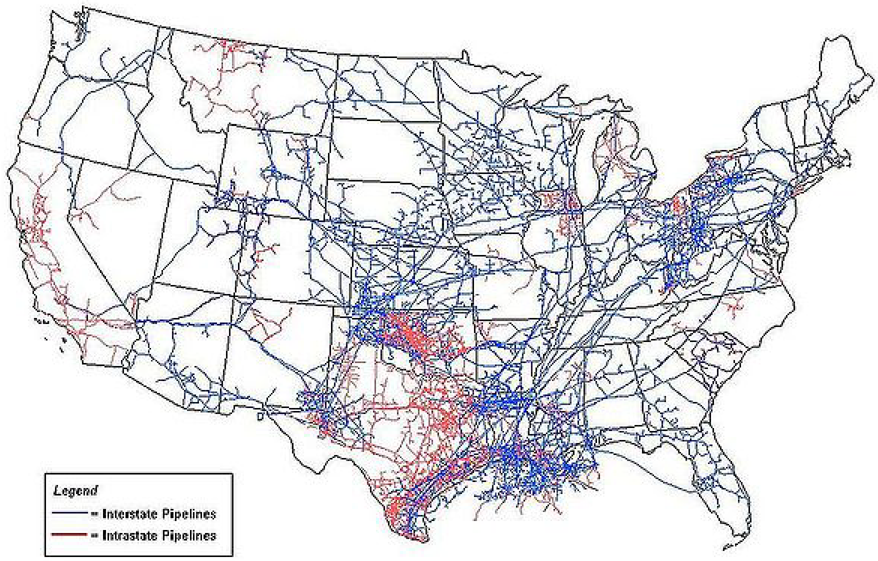

Figure 1. The network of pipelines that distribute natural gas through the United States.

Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

There are both environmental and economic factors (often in combination) driving the use of natural gas in competition with coal for world and U.S. power generation. Because of the impurities in coal, especially bituminous coal (the majority of what is burned), the emissions from smokestacks can contain substances such as sulfur dioxide (leading to acid rain) and mercury (toxic to most organisms, including humans). In addition, unburned particulates that are harmful, particularly to those who suffer respiratory problems, are released. To clean up the effluent gases, power plants are required to install expensive scrubber technologies that add to the cost of the power produced, even if the coal itself is relatively inexpensive. Processed (clean) natural gas has none of these problems, so the expensive power plant scrubbers are unnecessary. In the United States, many coal-fired power plants have been or are being converted to natural gas, or have been shut down entirely, and new ones are gas-fired.

A pollutant that is common to burning both coal and natural gas is, of course, carbon dioxide, a greenhouse gas driving human-caused global warming, ocean acidification, and consequent climate disruption. In this regard, natural gas is promoted as a "clean" energy source. What does this mean? The comparison is based on the amount of carbon dioxide produced for the same amount of energy output from burning natural gas versus coal. Natural gas produces about 50% less carbon dioxide for an equivalent energy output. Thus, natural gas is "cleaner" than coal—the conversion to more gas-fired power stations is probably the major factor in the reduction of about 12% in U. S. carbon dioxide emissions from power generation since 2005. Cleaner than coal, but still a "dirty" fossil fuel contributing to increasing levels of atmospheric carbon dioxide and global warming.

Hydraulic fracturing (fracking)

The largest economic factor driving the recent use of natural gas as an energy source is the large increase in its availability due to *hydraulic fracturing* (*fracking*) technology. A great deal of natural gas is trapped in shale (and other rock) formations that the gas cannot pass through, unless the rock has fractures the gas can seep through. Naturally occurring fractures are too rare to make natural extraction of shale gas economically viable. The technology that makes shale gas readily available is the ability to drill gas wells horizontally, so fracturing can be done over a large area of a horizontal shale layer.

To fracture the rock, a fluid is pumped into it at high pressure (the hydraulic part). The usual fluid is mostly water containing several percent of sand or some other particulate matter as a *proppant* (particles to keep the fractures in the rock *propped* open when the pressure is released). Small amounts of other chemicals, especially gelling agents that help to carry the proppants in the water and keep them in place in the fractures, are also part of the fracking fluid.

Fracking began in vertical wells, but is inefficient, because the fracturing effect extends only a few tens of feet from the bore hole. Many wells would be required to extract a large shale bed. With horizontal drilling, the vertical bore hole is drilled into the shale layer and then horizontal runs are extended into the layer for several thousand feet in many cases. Fracturing is done at intervals along the horizontal pipe and gas from the surrounding shale flows into the pipe when the fracking fluid pressure is released. Exploitation of horizontal fracking took off at the beginning of the 21st century, especially in the United States which, in a decade and a half, has become the world’s largest producer of natural gas.

Environmental impacts

The most apparent environmental impacts of methane use are in the extraction of natural gas by hydraulic fracturing. The well-head sites require several acres to house the supplies and equipment necessary for the process and disrupt the land. A prodigious amount of water is required for the fracking fluid and usually has to be hauled into the drill site in convoys of tanker trucks. In locations where water is scarce, fracking can use a substantial fraction of water available for agriculture and other human use. The waste fluid from the well is contaminated and unusable for these purposes and often pumped back into the rock formation. There is some concern that underground fresh water aquifers might be accidentally contaminated. Disruption of large areas of the foundation on which the Earth’s surface rests can lead to motion of the surface, resulting in tremors (small earthquakes). Oklahoma was a seismically quiet state where disruptions most often came from above the surface in the form of tornadoes and droughts, but now, with a large concentration of fracking, tremors have become a common occurrence.

A less apparent effect of methane is its role in global warming and climate change. As pointed out above, burning the gas produces carbon dioxide that adds to that produced by burning other fossil fuels. Further, methane is a greenhouse gas in its own right—even more powerful, and perhaps more important, than carbon dioxide. For the same mass of each gas, methane is at least 100 times more effective as a greenhouse gas than carbon dioxide. Unlike carbon dioxide that persists for centuries in the atmosphere, methane is oxidized in the atmosphere with a half-life of about a decade. After 20 years an initial mass of methane will have been equivalent in greenhouse effect to about 70 times that mass of carbon dioxide (and the carbon will still be present as carbon dioxide, the methane oxidation product).

Natural sources of methane, mostly wetlands, are abundant on Earth's surface. For almost all the past 10,000 years, the mostly natural atmospheric methane concentration was about 700 ppb (parts per billion). But, since the Industrial Revolution, methane has risen to about 1,870 ppb (in 2016) as human activities added to natural sources. At present, this atmospheric methane has about one-fifth the greenhouse warming effect as the atmospheric carbon dioxide.

About 33% of the methane emissions from the United States come from wetlands, about one-third of which is from rice fields that are flooded by humans, with the rest from natural marshes and bogs. Another 20% comes from fossil fuel extraction (coal mines and what is not captured from oil and gas wells) as well as leaks in the enormous natural gas distribution system. A further 20% is a result of raising large herds of cattle (for beef and dairy products). Cellulose makes up a great deal of the food, grass and grains, that cattle (and other ruminant animals like sheep, goats, and camels) eat. Animals cannot digest cellulose, but ruminants (and termites that also eat cellulose—wood) have digestive systems containing microbes that break down the cellulose for them. Unfortunately, one of the by-products of this process is a good deal of methane that the animals have to get rid of and mostly they do this by burping, Figure 2. The solid and liquid waste all these cattle (and other agricultural animals) produce is often stored to decay in waste ponds, where the decay microbes produce more methane. Similarly, landfills produce methane as the refuse decays. Some municipalities capture some of this methane and use it for heating and power.

Figure 2. Methane produced from their food is a waste of the carbon that could be used by cattle to make milk and meat. Research is going on all over the world to find ways to reduce the amount of this methane, both to keep it out of the

atmosphere and to save its carbon for the animals. These cows in Ireland are fitted with devices that measure the methane they burp out to monitor changes as their diets are changed.

Photo is from the Moorepark Research Centre of Teagasc - The Agriculture and Food Development Authority [of Ireland].

Methane hydrates (clathrates)

When water and methane are mixed at low temperature and elevated pressure, a soft solid is formed in which methane molecules are trapped in cages of water molecules. Methane hydrate is often called *clathrate* (a term from Latin meaning bars or a lattice and used to describe any inclusion solid like this). This mushy ice-like material can be ignited and the methane burned, so-called "burning ice," Figure 3.

Figure 3. This image of the flame from ignited methane hydrate (white solid) is from a YouTube video, "Burning Ice - Fire Ice - Methane Hydrate - (Dark room settings)".

Conditions for natural methane hydrate formation are found on sea floors and some bogs in the cold polar regions of the northern hemisphere. Methane formed by the action of anaerobic microbes on organic matter (or seeping from below the sea floor) is under pressure from the overlying water and/or soil and the environment is cold, favoring hydrate formation. These deposits of methane hydrate are widely distributed and there is no agreed upon estimate of the amount that actually exists. (A Japanese engineering study estimated that there is a deposit containing more than a trillion cubic meters of methane off the coast of Japan's main island and plans are afoot to extract this fuel.)

Natural gas is usually driven through the pipeline network under high pressure. A major reason for drying the gas during processing is to prevent the formation of methane hydrate, which will block the flow, if the gas passes through a cold pipeline. In 2009, the deepest oil well ever bored (almost seven miles deep) was drilled in the floor of the Gulf of Mexico. On 20 April 2010, the casing at the top of the well (on the sea floor at a depth of 4100 feet) failed and enormous amounts of crude oil and gas began to escape from the well head (continuing until finally capped on 15 July). One early attempt to capture the escaping material was to drop a “cage” over the well head with a tube leading to the surface where the effluent would be collected. Within a very short time of its deployment, the apparatus was completely clogged by methane hydrate and became useless.

An environmental concern about the methane hydrates scattered about the world is that they will become unstable in a warming world and break down, releasing methane into the atmosphere. Because the methane would increase greenhouse warming, this is an example of a positive feedback in the climate system—a change that increases the effect that brought it about in the first place. The permafrost, underground deeply frozen damp soil in north polar regions, is beginning to melt (structures are collapsing and new bogs are forming). Methane is being emitted as hydrates melt and anaerobic microbes awake to also produce methane by decaying buried organic matter. The extent of this feedback is still unknown, because measurements of the methane releases are recent and do not provide enough history to tell how rapid or slow the process is and will continue to be. Whether this is a minor or major effect, it adds to the burden of methane in the atmosphere and thus is a concern for global warming and climate disruption.