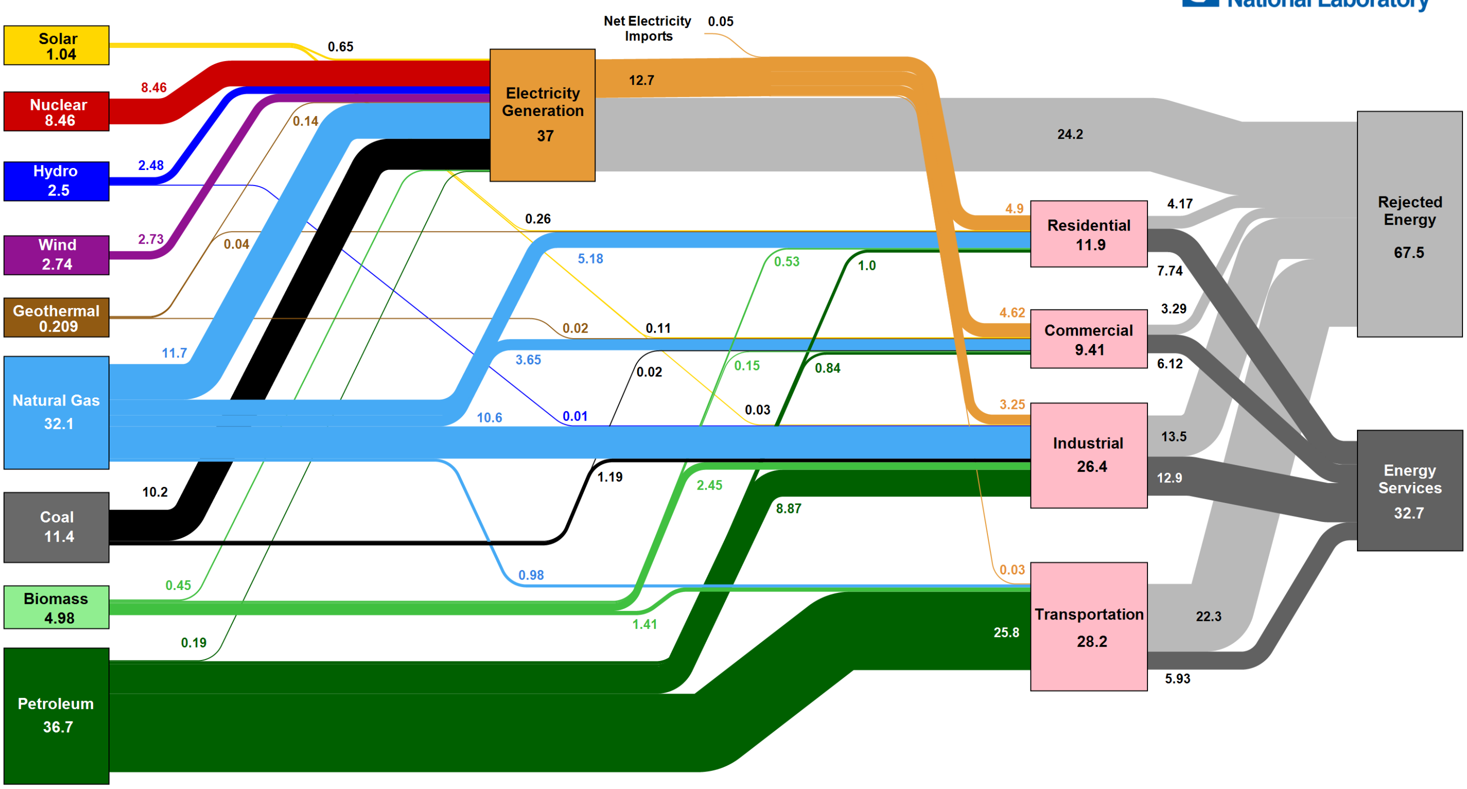
The diagram below shows the US energy use. The sources are on the left (Petroleum or Oil, Biofuels, Coal, Natural Gas, Geothermal, Wind, Hydroelectric, Nuclear, and Solar). End uses are on the right (Transportation, Industry, Business, and Residential) with Electricity shown in the middle.) The numbers give the energy produced or used in that category in units of British Thermal Units (BTU) for the year. You can see that in 2019 the United States used around 100 BTU. Globally, total energy use was around 600 BTU.

Estimated U.S. Energy Consumption in 2019: 100.2 Quads

Lawrence Livermore National Laboratory



Source: LLNL March, 2020. Data is based on DOE/EIA MER (2019). If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant heat rate. The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential sector, 65% for the commercial sector, 21% for the transportation sector and 49% for the industrial sector, which was updated in 2017 to reflect DOE's analysis of manufacturing. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Combustion of fossil fuels (petroleum or oil, coal, and natural gas) supplies over 82% of this energy. Combustion of biofuels (ethanol, biodiesel, butanol, wood products) supplies 5%. The rest is supplied by nuclear fission (8.5%) and renewable energy (6.5%). (Biofuels are sometimes categorized with renewables to give 11.5% for renewables.

Combustion reactions are a fuel + oxygen (O2) ----> carbon dioxide (CO2) + water (H2O). Sometimes there are nitrogen or sulfur atoms in the fuel. If these are present we will also have NO2 and SO2 as products. You should be able write and balance an equation for a combustion reaction given the chemical formula for any fuel.

Although the gasoline we put in our cars is a mixture of hydrocarbon liquids all having nearly the same boiling point, we will use octane (C8H18) as the formula for gasoline. So the balanced formula is2C8H18(l) + 25O2(g) ----> 16CO2(l) + 18H2O(g)Heat is also produced (as with all combustion products) and is usually the product we are interested in. Heat to warm our indoor environments and heat to convert water to steam to turn turbines to make electricity and heat (with explosions) to move pistons in internal combustion engines to move cars.

A formula you can use for coal is C135H96O9NS(s). Try writing and balancing the combustion of coal equation. Don't forget to use NO2(g) and SO2(g) as products.
Natural gas is CH4. Ethanol is CH3CH2OH. Like gasoline biodiesel is a mixture of compounds. We'll use C20H40O2 as a typical biodiesel. Butanol is C4H10O. Wood and paper are complicated materials but we will simplify them to a polymer of glucose which we will approximate as a dimer, so C12H22O11.

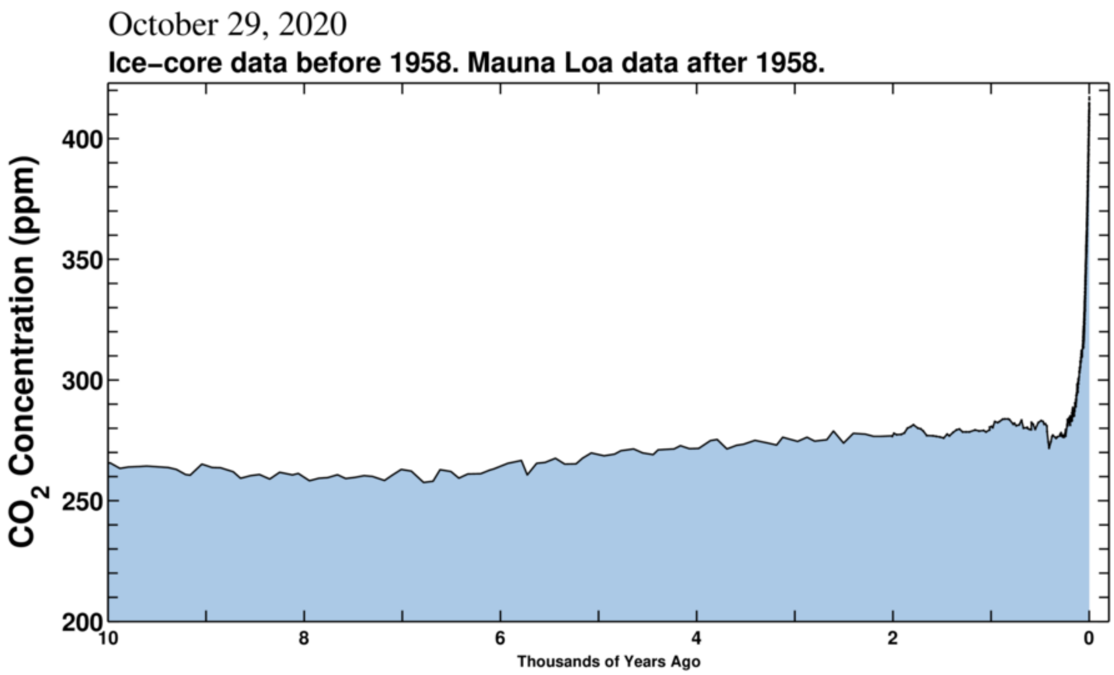
As you can see if you write balanced combustion reactions for each of these fuels, CO2 is a product for all of these reactions. In all cases the carbon in the fuel gets released as CO2.
A close look at the combustion of gasoline shows us how much CO2 is produced. Say your car has a 15 gallon gasoline tank. Through a series of dimensional analysis steps we can convert from gallons to pounds of CO2. There at 3.8 L in a gallon, and the density of gasoline is 0.75 g/mL

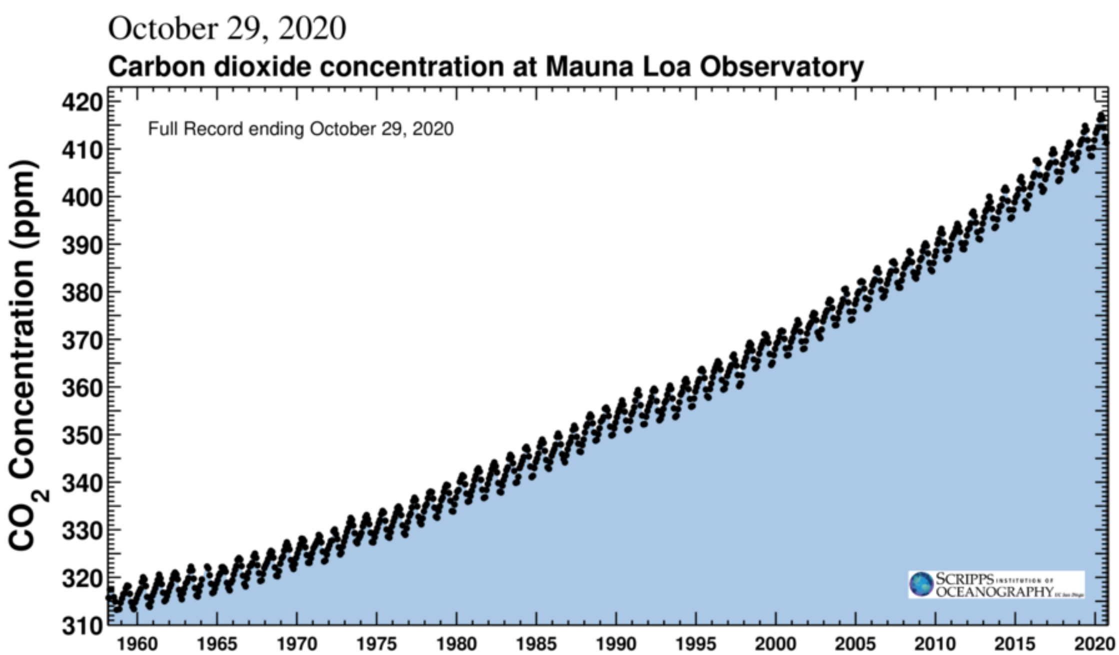
15 gal x 3.8 L/gal x 1000 mL/L x 0.75 g/mL x 1 mol octane/114 g octane x 16 mol CO2/2 mol octane x 44 g CO2/mol CO2 x 1 lb CO2/454 g CO2 = 291 lb CO2

Think about what that means. Fill your tank up with this brown liquid and you get out 3x as much colorless gas out the tailpipe that you barely think about because you can't see it. Image if it were a purple gas or a green gooey liquid. (See this clip from Cosmos https://www.youtube.com/watch?v=jVlS5-jB8aw or this video from the Ocean Preservation Society https://www.youtube.com/watch?v=iH-W3gYx8vY.)Let's get the numbers in kilograms (since we're scientists). We start with 15 gal x 3.8 L/gal x 1000 mL/L x 0.75 g/mL x 1 kg/1000 g = 42.75 kg octaneWe get out 291 lb CO2 x 1 kg/2.2 lb = 132.3 kg CO2. The CO2 to octane ratio is 3:1 to 1. You get similar numbers for other fuels. (You should figure out the ratio for all the combustible materials listed above.)

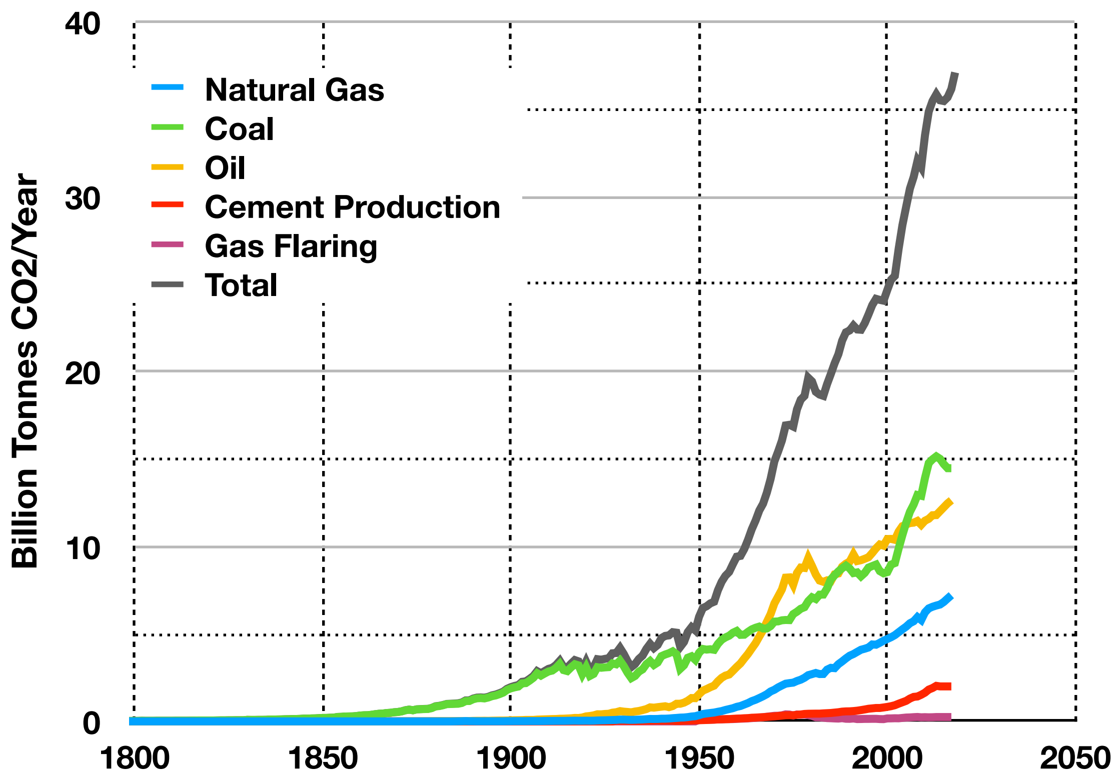
This CO2 is continuously being added to the earth's atmosphere. In the case of biofuels there is no net addition of CO2 because the fuel was created recently by photosynthesis from growing plants that pulled CO2 out the atmosphere--a cycle. However, for coal, oil, and natural gas (fossil fuels) the fuel was dug out of the ground where it had been for millions of years--the product geochemical processes acting on ancient plant and animal life, hence the name fossil fuels. The CO2 produced continuously increases the concentration of the atmosphere. Human beings have been burning biofuels for hundreds of thousands of years, ever since the mastery of fire. But significant fossil fuel use has only started with the beginning of the industrial revolution in the 18th century.

The first graph below show the increase in CO2 concentrations from the beginning of the iindustrial revolution at around 275 ppm until today at about 411 ppm a dramatic increase of 136 ppm, nearly 50%. The data before 1958 (62 years ago) is taken from pockets of air trapped in ice cores from Greenland or Antarctica. Since 1958 the data (the second graph) comes from more direct measurements from an observatory on Mt. Mauna Loa in Hawaii. This curve is known as the Keeling Curve, named after the researcher who began this long term project. The jagged line is due to variation where plant growth and photosynthesis in the spring and summer caused by seasonal drops in atmospheric concentrations.





As we have seen CO_2 is a greenhouse gas that absorbs IR light coming from the earth and the sun. The increase in CO_2 concentration in the atmosphere due to fossil fuel burning is a very reasonable explanation for global warming. There is a feedback loop at work as well. A warmer earth means a warmer ocean. Gases are less soluble in water as the temperature goes up. This is known as Henry’s Law. So a warming ocean gives up dissolved CO_2 much the way your warming soda loses its fizz.



The figure above shows the history of global CO_2 emissions since 1800. As you can see between 35 and 40 billion metric tonnes of CO_2 are being emitted into the atmosphere. CO_2 lasts several hundred years. More less once it is emitted it stays in the atmosphere. As noted in our previous discussion there are other human generated substances such as CH_4, N_2O, CFCs and HFCs, SF_6, and O_3 that are also greenhouse gases. CO_2 however is the most significant in total effect.

Not every fuel produces the same energy per mass of fuel because of the presence of non-carbon and non-hydrogen elements or because the are carbon-carbon multiple bonds. We will learn out to measure or to calculate energy density in the discussion of thermochemistry in a later chapter. Here is a table of some of the fuels discussed about showing fuel to CO_2 ratios and energy densities.

FUEL	CO_2:FUEL RATIO (g CO_2/g fuel)	ENERGY DENSITY (kJ/g fuel)	CO_2:ENERGY RATIO (g CO_2/kJ)
coal ($C_{135}H_{96}O_9NS$)			
sub-bituminous	3.12	24	0.130
anthracite; bituminous	3.10	31	0.100
octane (C_8H_{18})	3.10	46.5	0.0667
natural gas (CH_4)	2.73	55.8	0.049
diesel		45.8	
biodiesel		39.6	
ethanol		29.7	
butanol			
wood	1.28	14.9	0.086
hydrogen	–	141.9	

The table shows that not all fuels are equal. Some fuels emit less CO_2 to give the same amount of energy. Natural gas produces fewer CO_2 emissions than coal for each unit of energy produced. The transition from coal to natural gas in electricity production is in part why US CO_2 emissions have dropped.

WHAT TO DO

The most obvious solution is to reduce our dependence on fossil fuel generated energy by moving to alternative energy sources—nuclear, hydroelectric, wind, solar, and geothermal. Switching from coal to natural gas has been viewed as bridge solution. Biofuels can be added to the list as well, since in principle, the CO_2 emitted in the combustion of these fuel originally came from CO_2 in the atmosphere. But this has been and continues to be a slow in coming solution. We have been at 80% fossil fuel use for decades and it doesn't really seem to be changing despite our efforts. Not only do we need to transition to carbon neutral sources, but we need to meet an ever growing need for more energy.

Electrifying our transportation potential will enable a transition away from about half of our fossil fuel use. The one caveat is the question of how the electricity is made that charges the electric cars (and other electrified energy uses). If the electricity used to charge our car batteries comes from a coal or natural gas fired power plant, then we've just replaced emissions at the tailpipe with emissions from the smokestack. On the other hand an electrified transportation system can transition to zero carbon or zero net carbon system by moving from fossil fuel fired power plants to nuclear, solar, wind, and other alternative energy sources.

Another possibility is to remove CO_2 from the smokestack emissions (known as flue gases) similar to the way we currently remove SO_2 that causes acid rain. Flue gases contain N_2, unreacted O_2, H_2O, and CO_2 (15%) after having been treated to remove particulates, SO_x, and NO_x. The collection of technologies to do this is known as carbon capture, utilization, and sequestration (CCUS). Reacting CO_2 with alkaline sodium hydroxide and calcium hydroxide produces insoluble carbonates. Organic amines can also bind CO_2. In both cases the CO_2 can be liberated at high temperatures to produce pure CO_2 and regenerate the CO_2 capture material. The mineral serpentine ($Mg_3Si_2O_5(OH)_4$) absorbs CO_2. In gasification technologies relatively pure CO_2 can be removed from hydrogen gas before combustion. Performing the combustion reaction in pure oxygen (rather than air) results in a simple mixture of water and CO_2 where the water is easily removed by condensation thus producing a pure CO_2 stream. This is called the oxy-fuel method.

Post combustion CO_2 Capture
$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$
$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

$2R\text{-}NH_2 + CO_2 \longrightarrow R\text{-}NHCO_2^- + R\text{-}NH_3^+$

$Mg_3Si_2O_5(OH)_4 + CO_2 \longrightarrow 3MgCO_3(s) + 2SiO_2 + 4H_2O$

Pre combustion CO_2 Capture
$C + H_2O \longrightarrow CO + H_2$
$CO + H_2o \longrightarrow CO_2 + H_2$
$2 H_2 + O_2 \longrightarrow H_2O$

Oxyfuel

Physical separation of N_2 and O_2 and then combustion with pure oxygen
Fuel + O_2 ➛ $CO_2 + H_2O$ (normal combustion)
Flue gases are pure CO_2 and water

A pure CO_2 stream can be stored in deep underground caverns (sequestration or storage, the S of CCUS) or, better yet, can be used in synthetic fuel creation using chemistry such as the Fischer-Tropsch reaction where CO_2 is reduced from CO_2. Successful carbon capture plus synthetic fuel creation would result in a cycle. CO_2 released in combustion could be captured and turned back into fuel.

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$
$n\ CO(g) + (2n+1)\ H_2(g) \rightarrow C_nH_{2n+2}(g,l) + n\ H_2O(g)$

Currently most hydrogen is produced from the steam reforming of natural gas

$CH_4 + H_2O \rightarrow CO + 3H_2(g)$

To have a clean fuel the hydrogen would have to come from the electrolysis of water using solar power or some other non-carbon source of electricity.

$2\ H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

A significant challenge to carbon capture technologies is the scale of it (35-40 billion metric tonnes per year). If CO_2 were counted as an industrial chemical instead of a waste product, it would be the most produced chemical. For example, the amount of steel, one of the largest industrially produced materials, is 1.6 billion metric tonnes per year.

LEARNING GOAL

Relate the burning of fossil fuels to the increase of CO_2 concentrations over the past several decades as seen in the Keeling curve and other historical records.

STUDY QUESTIONS

1. What are the main fossil fuels and, roughly, what percentage of the world's energy source comes from them?
2. Write combustion reactions for fossil fuels and other carbon based fuels? What is the "product" that we find most useful (i.e. why do we burn things)? What is the product that is now understood to be a dangerous waste product?
3. What is the difference between fossil fuels and biofuels?
4. What is CCUS? (Don't worry about the detailed chemistry here, just the basic ideas—pre-combustion capture, post-combustion capture, the oxy-fuel method)
5. What is synthetic fuel and the Fischer-Tropsch reaction (again, don't memorize the formula but understand the basic idea)?