A future president's knowledge of chemistry should begin with gasoline — after all, three of America's five largest companies are petroleum companies. We wouldn't be able to drive our cars, fly our airplanes, heat our homes, or make electricity with such ease if it wasn't for the chemical reactions that these companies use to convert crude oil into usable products.

You can't just pump oil out of the ground and put it in your car — crude oil is, well, too crude. It has a huge variety of molecules of different shapes and sizes, some of which would not burn efficiently (or at all) in a vehicle engine. That's why oil gets refined before you use it. Let's evaluate the life cycle of gasoline from its origins as crude oil to your car's tailpipe.

**Oil formation**

Crude oil originally begins as living things, usually tiny plants and animals that lived in the ocean and took carbon from the air and combined it with water to grow. As these critters died and dropped to the bottom of the ocean, they were buried deeper and deeper. Over time, heat and pressure allowed chemical reactions where the relatively simple combinations of Carbon, Hydrogen, and Oxygen atoms bonded together into more and more complex molecules.

By the time they have baked, each molecule can be a chain of literally hundreds of atoms. The composition remains basically the same (C, H, and O, with small amounts of S and N), but the heat allows more and more chemical bonds to form between the atoms. The exact chemical composition and structure of crude oil depends on which critters originally went into it, how long it baked underground, and at what temperature.

**Oil refineries**

Once it comes out of the ground, the oil companies want to turn the complicated soup of molecules into the standard recipe for gasoline. Gasoline itself is still a relatively complex mixture, but most of the molecules in it contain less than ten carbons each (compared to chains of a hundred or more carbon atoms in some of the more complicated crude oil molecules). At oil refineries, crude oil gets heated up to very high temperatures so that it evaporates into a vapor. The vapor is then cooled, and the heaviest, most complicated molecules tend to condense back into a liquid first. The operators of the refinery quickly separate these out before cooling the vapor more. For example, tar and asphalt are the first to condense into a liquid and they are removed (easily accomplished because the liquid drops to the bottom). They repeat this process of cooling the vapor further until the next simplest type of molecule condenses so it can be separated. They are able to isolate diesel fuel, kerosene, and eventually the main ingredients of gasoline because each one condenses into a liquid at a different temperature. This process requires a great deal of understanding about how the number and type of bonds between atoms affects the physical properties of each fuel.
Chemistry of Oil

An oil refinery has lots of towers where oil is heated until it turns into a gas that rises. Different types of oil can be separated because they turn into liquid at different temperatures as they cool.


For one barrel of crude oil, the refining process only ends up with about half a barrel of usable gasoline. The remaining "waste" material that is separated out from the gasoline gets turned into, among other things, asphalt for roads, polyester fabric for clothes, fertilizers for crops, and plastics for just about everything we buy these days (almost all plastic today is petroleum based, though new eco-plastics based on vegetable oils are becoming more popular). Some of the big complicated molecules are refined further — usually heated up so that they vibrate so quickly that some of the covalent bonds break. If they do this correctly, the refiners can break what were once "unusable" large molecules into the correct smaller combinations of carbon, hydrogen, and oxygen that make up gasoline.

Without refineries, there would be no usable gasoline. However, as of 2009, there are only 150 operable oil refineries in the US1. When Hurricane Katrina hit, winds damaged nine refineries. Because they had to temporarily shut down for repairs, the nation's gasoline production got cut by nearly 10%2. There have been almost no new refineries built in the USA since 1976, and a large number have closed.3 One of the reasons that no new facilities have been built is because it is extremely expensive and time consuming to get the permits. Think about how a refinery works — it takes crude oil and heats it up so hot that even asphalt changes into a gas. Along with the oil, heavy metals that are toxic to humans (if ingested in large quantities) are also vaporized. To prevent these harmful gases from escaping, refineries have to invest huge amounts of money into technology to reduce their emissions. These measures are expensive, and even then refinery builders often face opposition from local community groups who do not believe that the measures are sufficient.

During a visit to a refinery, an oil company employee described to me the complexities of the refining process with great pride. He noted that they were able to accomplish all of that chemistry and sell their refined product for less than bottled water (gasoline was about $2 a gallon at the time; bottled water at $1 for a quart sized bottle ran $4 a gallon. Considering that many bottled water companies just filter regular tap water, oil seems pretty cheap!). When put in those terms, it does seem impressive.

Octane ratings

An oil refinery produces a range of gasolines for your car from "Regular" to "Super," adjectives which refer to the octane

1 http://tonto.eia.doe.gov/dnav/pet/pet_pnp_cap1_dcu_mus_a.htm
2 http://www.pbs.org/newshour/bb/weather/july-dec05/katrina/oil_background.html
3 Oil consumption hasn't gone up quite as much as you think during this time period — following the oil crisis in the late 1970’s, the country cut way back on its oil usage. Demand for oil grew slowly during the 80's and 90's, but it wasn't until around 1996 that we got back to using the same amount of oil as in 1976. Since 1996, oil use has grown another 20%, but still no new refineries. http://www.eia.doe.gov/emeu/aer/eh/petro.html
rating. Octane is a molecule that is one ingredient in gasoline. The "oct" stands for eight because there are eight carbon atoms. Its chemical formula, \( \text{C}_8\text{H}_{18} \), reflects the fact that each of the carbons is covalently bonded to one or two of the other carbon atoms and two to three hydrogen atoms. Octane burns really efficiently, so having more octane is good. An octane rating of 91 (typical super or premium gasoline) means that the fuel burns as well as 91% pure octane. Race car drivers that really want an extra boost use fuel with octane ratings as high as 110. That doesn't mean that there is 110% pure octane (you can't get more than 100% pure!); such a fuel is made up of other molecules that burn even more efficiently than the octane molecule (10% more efficiently, in this case). Octane ratings greater than 100 highlight the fact that modern fuel has many other ingredients besides octane (and may not contain any actual octane at all), that all combust efficiently.

An octane atom, \( \text{C}_8\text{H}_{18} \), with the eight dark balls representing the eight carbons and the lighter balls representing the hydrogens. 


Should you buy high octane gas? Most cars today have fuel injectors that are designed to work on 87 octane gasoline. Since these injectors are computer controlled to make the combustion act as efficiently as possible, you shouldn't buy higher octane gas unless the manufacturer recommends it. Some gasoline companies advertise other chemicals they add to gasoline to make it better — some of these are mandated by federal law to control emissions and will be present in any gas you buy anywhere. The cheap generic gas will perform the same as the name brands that spend a lot on marketing their additives. However, there are some brand-specific additives that a gas company may use that claim to reduce engine wear. You'll have to do your own web research to find out if these are worthwhile.

**Combustion: Releasing energy by changing covalent bonding partners**

A car's engine is designed to make chemical reactions happen and then harness the energy released during those reactions. Energy is stored in the bonds that keep the C's and H's of gasoline molecules together. They currently share electrons as part of a covalent bond that keeps them "happy" (meaning their outermost electron orbital is completely full; see previous article). The small input of energy from the spark plug can break these bonds. Returning to their original partners to reform a gasoline molecule is not the lowest energy state when there is extra oxygen around. The carbon from the gasoline combines with oxygen to form \( \text{CO}_2 \) while the hydrogen combines with different oxygen atoms to form \( \text{H}_2\text{O} \) (oxygen is clearly a desirable partner for covalent bonds!). Reactions where something combines with oxygen to form \( \text{CO}_2 \) and water are called combustion reactions. The chemical equation for octane combustion is written:

\[
2 \, \text{C}_8\text{H}_{18} + 25 \, \text{O}_2 + \text{energy (spark plug)} \rightarrow 16 \, \text{CO}_2 + 18 \, \text{H}_2\text{O} + \text{lots of energy}
\]

Even though it takes a small amount of energy to break the bonds on the left side of the equation, a whole lot more energy is released when the new bonds are formed. This reaction releases about 120 MJ of energy for each gallon of gasoline — that's about the same energy as 200 cans of soda! This extra energy is released primarily as heat, which causes the gases in the engine to expand and push against a crank that eventually turns the wheels of your car. The waste products (\( \text{CO}_2 \) and \( \text{H}_2\text{O} \)) are both gases at the high temperatures in the engine, so they both flow out the tailpipe.
**Emissions**

For an ideal engine, all of the fuel that you put into the combustion chamber will break apart and form new bonds with the oxygen. In reality, not all the fuel burns up. One reason might be that there is not enough oxygen for the amount of fuel injected into the combustion chamber.

Sometimes an oxygen deficiency (or other inefficiency in the combustion reaction) produces carbon monoxide (CO; a toxic gas) instead of carbon dioxide (CO₂). The fuel injectors in modern cars are designed to inject the perfect amount of fuel every time, so today's engines are more efficient than the days before fuel injectors but are still not perfect. Undesired products like CO along with the unburned fuel wind up being pushed out of the combustion chamber along with the combustion waste products. They head right out your tailpipe. Some compounds added to gasoline to make combustion more efficient are toxic, so you don't want these escaping out into the air. To prevent these problems, gasoline composition and additives must be carefully chosen by regulators.¹

**Carbon footprint**

A perfect combustion reaction produces nothing more than CO₂ and H₂O – the same byproducts you exhale with each breath as you read this article. Both are clean, odorless, and pose no direct human health risk. Unfortunately, even a perfect combustion reaction has a major problem. The CO₂ is a greenhouse gas that effectively traps heat in Earth's atmosphere, and combustion of gasoline in vehicles accounts for nearly a third of all CO₂ emitted in the USA.²

A typical car driven by a typical family releases about 8000 pounds of CO₂ into the air each year. Now that you understand combustion, you can understand an interesting "paradox" that I read recently on an environmental organization's website³: Every gallon of gas weighs about 6 pounds but produces 19 pounds of CO₂. That may sound impossible, but it's true (albeit a little misleading). In the CO₂ molecules of a car's exhaust, more than 2/3 the mass comes from oxygen that was already in the air (two oxygen molecules from air combine with every one carbon from the gasoline). So while that gallon may produce 19 pounds of CO₂, 13 of those pounds were already in the atmosphere as oxygen. Oxygen does not trap heat in the atmosphere when it's a gas by itself, but when it joins up with carbon to make CO₂ it has a dramatic impact on our planet's climate. In the end, it doesn't matter whether the mass comes from the gas tank or oxygen already in the air – the effect is most important.

**Biofuels: Harnessing the energy of plants**

The energy in the covalent bonds in gasoline molecules does not appear magically — it was harnessed from the Sun by the plants and animals that lived millions of years ago that form the raw materials for oil, and heat from deep inside the Earth added more energy while the oil was maturing underground. While it pays to be patient, we can combust many fuels besides gasoline and still harness some energy from the covalent bonds. The fancy name for a fuel source made from modern-day plant or animal materials is "biofuels." The simplest of all biofuels, dry wood cut from trees, contains about 10 MJ/kg — energy that was harvested from the Sun while the tree was growing. Gasoline still wins at 44 MJ/kg, but with wood you don't have to wait millions of years. Since wood won't run in

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¹ There are numerous examples of such regulation. In 1996, the EPA completely banned lead as an additive to gasoline and many states have recently banned the use of MTBE as an additive. A recent court ruling in 2007 reduces the amount of benzene, one cancer-causing molecule that occurs in gasoline, to no more than 0.6% of the total gasoline mixture. See http://www.nytimes.com/2007/02/10/washington/10benzene.html.


³ http://www.terrapass.com/blog/posts/how-to-turn-8-p
cars, chemists developed processes for extracting oils from crops and making either ethanol (often from corn) or bio-diesel (from a broader range of crops). These crops need to undergo a series of chemical reactions to prepare them to be used in a car, and those reactions do take some energy as input. The fuel that you get after these processes can have 30 MJ/kg (equal to 90 MJ/gallon), which is getting close to the energy content of gasoline.

When you burn wood or other biofuels, you still release CO$_2$ in the combustion reaction (just like with oil). The difference is that recently grown crops pulled that CO$_2$ from the atmosphere during the last few years while they were growing. When you burn them, you are just returning CO$_2$ that the crops "borrowed" from the atmosphere last year. If you borrow CO$_2$ and then give it back, you could argue that you are not increasing the amount of CO$_2$ in the atmosphere. When burning gasoline, you are taking CO$_2$ from the ground and adding it to the atmosphere. It's true that the CO$_2$ in gasoline originally came from the atmosphere millions of years ago, but a few years ago, it was underground where it was not a greenhouse gas. Using gasoline adds CO$_2$ into the air that was not already there a few years ago.

Using biofuels instead of gasoline may sound like a great way to reduce global warming, but there is one problem. A lot of the energy used to grow crops today comes not from the Sun but from chemical fertilizers. These fertilizers are often made from crude oil. It also takes additional energy to convert the plants to a usable biofuel. Some researchers think that more greenhouse gases get emitted in the process of making biofuels than they would end up saving.\(^7\) So even when you think you are using a biofuel, you might still be depending on fossil fuels and therefore releasing more carbon into the atmosphere. It's hard to avoid releasing greenhouse gases if we want to use fuels.

Summary

Gasoline stores energy in covalent bonds built up over millions of years, promoted by heat and pressure deep within the earth. The crude oil is brought to the surface where efficient burning gasoline is separated out (refined) from the bigger, even more complicated molecules. In a vehicle, the gasoline molecules combine with oxygen in a combustion reaction to harness the energy stored in the covalent bonds. When these bonds are temporarily broken and then reformed to produce CO$_2$ and H$_2$O, a huge amount of energy is released. Switching from gasoline molecules to the simpler molecules keeps all of the atoms happy (all their outermost electron orbitals are filled through sharing), but also results in a lower overall energy state. We want to make the combustion reaction as efficient as possible, so refineries add extra chemicals to the gasoline and cars have fuel injectors to create the correct mix of fuel and oxygen. Even if they do their jobs perfectly (which they don't), there is still the problem of huge amounts of greenhouse gas production.

Future presidents will have to deal with refinery capacity, fuel additives and composition, emissions regulations, and greenhouse gas emissions. They will face tough decisions about whether or not to invest in biofuels or other alternative energy programs. All of these require understanding where the energy in gasoline comes from and how it gets released in chemical reactions.

Further reading

(including some of the sources used for this article)


Crude oil maturation (slightly technical): [http://www.kingdomdrilling.co.uk/diggin/Oil%20and%20gas%20maturation%20688.pdf](http://www.kingdomdrilling.co.uk/diggin/Oil%20and%20gas%20maturation%20688.pdf)

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\(^7\) [http://coe.berkeley.edu/labnotes/0305/putzek.html](http://coe.berkeley.edu/labnotes/0305/putzek.html)
Questions to consider

1. Where does gasoline come from? What steps go into taking the raw material into usable gasoline?
2. What does an oil refinery do? Should we build more of them?
3. Where does gasoline get its energy? How does it store the energy? How can you get energy out of it to power a car?
4. If gasoline burned perfectly inside the engine, what would the emissions be out of your tailpipe? Are these emissions dangerous? Do they have any drawbacks? What if the combustion is not perfect?
5. What are bio-fuels? Are they good or bad for the environment?