

Octane Rating and Lead: Explaining The Chemistry of Gasoline



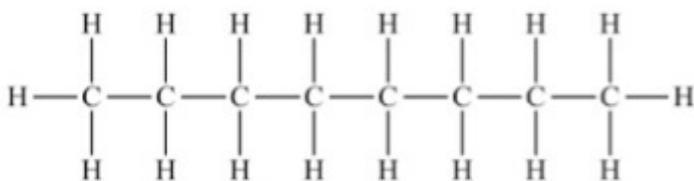
By Josh Bloom — February 22, 2017



No engine, no engine knock

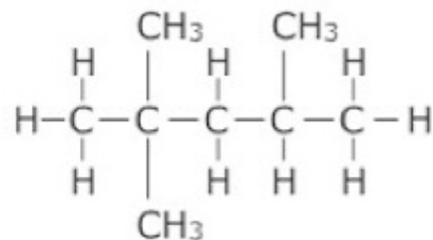
Useless trivia item for a Wednesday:

Whether you are choosing 87, 89, or 93-octane rated gasoline, you're not buying octane. Why? Because if you were actually putting octane into your car, it would screw it up big time.



Octane C_8H_{18}

Boiling point 258° F



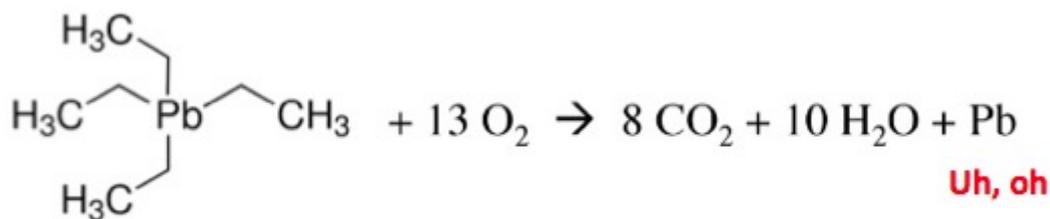
2,2-4-Trimethylpentane C_8H_{18} (Isooctane)

Boiling point 210° F

The "octane" rating of gasoline actually measures the amount of an additive called isooctane. The two are isomers- they have the same chemical formula but different structures and properties. Octane is a chain of eight contiguous carbon atoms. Isooctane has chain of five contiguous and three "branched" carbon atoms. Both are hydrocarbons. The branching is why cars need it. To burn fuel properly.

In an engine cylinder, fuel and air are compressed, and then the mixture is ignited by a spark plug. But, straight chain hydrocarbons have an annoying tendency to ignite too soon (before they reach the spark). This causes a pinging sound - engine knock. Engine knock causes very high pressure inside the cylinders, which can damage the engine. Branched chain hydrocarbons are "better behaved." They hang around long enough to get the timing right. So, the higher the percentage of isooctane, the less the engine will knock.

There are other examples of branched fuel additives, the most notorious being tetraethyllead. Note that the entire molecule is one big branch.



Tetraethyllead C₈H₂₀Pb

But tetraethyllead has a disturbing tendency to give off tiny particles of lead metal upon combustion, and plenty of them. In 1965, a total of [250 metric tons](#) [1] of tetraethyllead was used in gasoline, which means that burning it released 78 tons of lead into the atmosphere. Not good. Lead-based fuels were banned in the US in 1996.

So, without icky lead, how do you stop engine knock? The next idea wasn't all that bad—getting rid of the lead by substituting methyl t-butyl ether (**1,2**) (MTBE), but it didn't work out as expected. There were two problems with this substitute, which began to replace tetraethyllead in 1979, peaked in the 1990s and was gone by 2006.

doses to rats, but there are no epidemiological data regarding human health and the additive.

MTBE was banned in 19 states between 2000 and 2006, and nationwide by 2006. The real reason for the ban isn't entirely clear. Whether it was due to health fears, water taste and smell, the ethanol/corn lobby, or some combination of these, its presence on the scene was short-lived.

Ethanol is a pretty lousy additive too. It is expensive (comes from fermenting corn, so you are burning food), corrosive to certain metal components, is only partially miscible with gasoline (the two components can't be shipped together or the ethanol will come out of solution and sink to the bottom of the tank), and it has a particular affinity for water, so that (especially in cold weather) more water will find its way into your car's gas tank.

So, what's next? Hard to say. All additives have their own baggage **(4)**. Except maybe....



Notes:

(1) You will see the name methyl tertiary-butyl ether used as well. The shorthand— methyl t-butyl ether is perfectly acceptable.

(2) In addition to branching, MTBE also provided oxygen, which helps fuel burn more efficiently, and cuts down on carbon monoxide formation.

(3) We sometimes used it in lab. Pretty stinky.

(4) Other additives called aromatic hydrocarbons (toluene, xylene) can also increase the performance of gasoline, but they have their own toxicity and combustion issues.

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Links

[1] <http://www.baltimoreleadtesting.com/PAINTb.html>

[2] <https://www.ncbi.nlm.nih.gov/pubmed/8751991>

[3] <http://acsh.org/news/2016/02/25/stuff-you-didnt-know-about-formaldehyde>

[4] http://www.science20.com/pfired_but_still_kicking/will_aspartame_critics_now_be_less_bitter-156690?source=acsh.org