

Meandering Through the Oil Industry: Part 6

This technical article is in a series characterizing the process that the oil industry follows to bring us one of our favorite commodities, the gasoline that powers our Classics. This time, we continue to ponder the use of alcohol in fuels.

Water Makes its Splash

By Brian Rohrbach



Alcohol and water are inseparable in more ways than one. Ethanol is hygroscopic, which means it will absorb moisture from the air; it really wants to be wet. As we manipulate corn (mostly) to generate fuel ethanol, we need to have water at hand to grow that corn. We certainly have had to make special arrangements to the infrastructure of petroleum distribution in order to manage the water contamination problem posed by alcohol, but the availability of water for crops is the more significant problem.



Although mixing gasoline and ethanol minimizes the amount of water entrained in the fuel, the probability that some water gets into the fuel tank is higher with ethanol in the supply chain. For our 10% ethanoic gasoline, only about 0.5% water is possible to remain fully mixed with the alcohol and gasoline in the fuel; any more than that and the concentration will force water to form a separate phase (or layer) which will settle in the bottom of the pipe or fuel tank. So, there is the opportunity to collect water where we really don't want it. Water in a metal vessel can cause both chemical and galvanic corrosion. All this has caused us to make adjustments, inserting a production step into the fuel transport infrastructure simply to add 10% ethanol.

Not in My House! Water is enough of a problem to make it interesting that the refineries do not want to blend alcohol into gasoline on premises. As a result alcohol, along with other additives, is typically inserted at transfer facilities outside the refinery gates. Now that I have made this statement, it is (like everything else in my discussions) not completely true. There are instances where ethanol is made in conjunction with the

refining process; you can make ethanol from ethylene, a byproduct of the oil refining process – it involves mixing the hydrocarbon, ethylene, with sulfuric acid (another chemical we do not really like to deal with) and applying heat in a process called catalytic hydration. The refinery-sourced ethanol is a miniscule portion of the fuel ethanol that is produced.

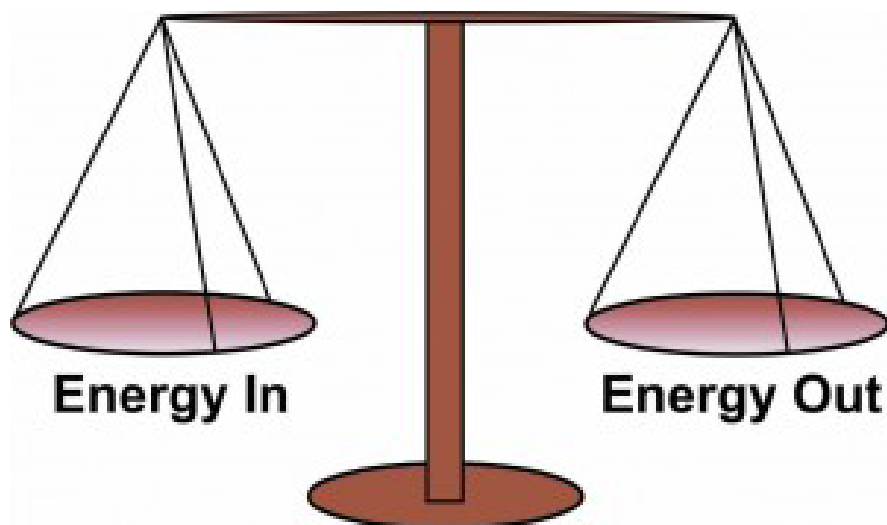
Not only do the refineries not want ethanol around, the water-absorbing nature of the commodity makes it tougher to ship through pipelines. Again, corrosion can raise its ugly head. Key to consider here is that there are costs beyond the growing, harvesting, and production of ethanol. Most of these hidden costs are on-going.



The engines in our Classics can probably easily withstand the 10% level in current fuels although we still must be vigilant in maintenance of parts in constant contact with fuel. I would anticipate a lot of problems if industry is forced to move to more alcohol-laden fuels. There has been a lot of effort evaluating the pros and cons of ethanol in gasoline. One factor stands out - it takes a lot of water to grow corn. Is water availability ultimately rate-limiting in the amount of alcohol we add to the gasoline? It probably is if we stick with corn.

About 400 gallons of ethanol is the expected yield for a one-acre cornfield. In turn, it takes about 560,000 gallons of water just to grow the corn occupying that single acre of land. More is used in the corn processing. That is a lot of water.

In addition, one unit of fossil fuels is required to produce 1.3 units of ethanol from corn. Given all the other costs associated with ethanol, that is not a



very positive margin. Sugarcane is better, yielding 8 units of ethanol for one unit of fossil fuels, but it does not grow as widely in US climes. The ultimate is to generate alcohol from cellulose (i.e., the woody bits), where we can expect at least 10 times the net energy yield as corn. Cellulose after all is a polysaccharide - just long chains of sugar (longer than the sugar chains comprising the structure of starch in corn). Unfortunately, we have not mastered an economic breakdown of cellulose to simple sugars (the stuff that yeast will eat and generate ethanol) quite yet (but we will!). In the food versus fuel tradeoff, it becomes possible to grow a source of food and still get fuel ethanol out of the waste. By increasing the yield, the water problem is largely mitigated.

This scientific effort means that alcohol is here to stay. So for us Classics owners, hold on to your pure-gas.org ap!



Oxygenates

Alcohol is one of several chemicals that have been added to gasoline that function as octane-boosting agents, loosely as a substitute for tetraethyl lead. Collectively, these additions to a refinery-generated fuel are called oxygenates because, unlike the crude-oil-generated liquid, these compounds all have oxygen in their structure. Ethanol is the only oxygenate in large-scale use in the US, but you do find other alcohols and ethers (methyl tertiary butyl ether-MTBE and the ethyl ether version-ETBE) in some locations and overseas. The four possible alcohols to find in fuel are methanol, ethanol, propanol, and butanol; these range in order from having one, two, three and four carbon atoms and each has characteristics that are conducive for use in an internal combustion engine. All four can be synthesized either chemically or biologically, but methanol and ethanol are by far the most economically efficient to produce.

We add the oxygenates both to increase the octane rating and to reduce the amount of unburned hydrocarbons and carbon monoxide in the exhaust. Alcohol is a more expensive option for motor fuels than is MTBE; alcohol primarily comes from an agricultural source whereas MTBE is made from fossil fuels. The reason we use the alcohols is two-fold:

1. MTBE is considered a cancer threat; and
2. Preferring alcohol provides an economic stimulus to the corn industry and its lobbyists.

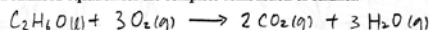
Chemistry Quiz



Note: Having read and studied all six articles on the production of ethanol, it is time to begin preparing for the mid-term exam. Good luck. In the next issue of the BG we will continue our in-depth coverage of automotive fuel.

- 5) Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (or $\text{C}_2\text{H}_6\text{O}$) is being developed as an alternative fuel since it can be produced from renewable resources like corn or sugar cane.

- a) Write a balanced equation for the complete combustion of ethanol.



- b) Suppose you have a 70.0 L (typical fuel tank size) of ethanol (density 0.7893 g/cc) and unlimited oxygen. Calculate the number of moles (theoretical yield) of carbon dioxide produced.

$$70000\text{ mL} \times \frac{0.7893\text{ g}}{\text{mL}} = 55250\text{ g} \quad \frac{55250\text{ g}}{46.07\text{ g/mol}} = 1199\text{ mol}$$

$$1199\text{ mol of C}_2\text{H}_6\text{O} \times \frac{2\text{ mol CO}_2}{1\text{ mol C}_2\text{H}_6\text{O}} = 2398\text{ mol of CO}_2$$

- c) What volume will be occupied by the CO_2 at STP?

$$PV = nRT$$

$$V = \frac{nRT}{P} = 53800\text{ L}$$

- d) Calculate the percent composition by mass of the elements in ethanol.

$$\frac{2 \times 12.01}{46.07} \times 100\% = 52.14\% \text{ C} \quad \frac{1 \times 16.00}{46.07} \times 100\% = 34.73\%$$

$$\frac{6 \times 1.008}{46.07} \times 100\% = 13.13\% \text{ H}$$

- 6) A solution is prepared by dissolving 2.50 g NaCl in 550.0 g H_2O . The density of the resulting solution is 0.997 g/mL.

- a) What is the molarity of NaCl in the solution?

$$2.500$$

$$0.0428\text{ mol}$$