# Down the Cow Path with Gasoline Additives – Part 1

By Lisa Alexander

Every now and then, perusing our news clips for article ideas, something jumps out. For example, a "tabletop" Emergency Response (ER) exercise followed by a spill that occurs only three days later.

On May 14, 2013, MassDEP ER worked with a city in the Central Region to develop and conduct a tabletop exercise using the following parameters:

- A gasoline tanker carrying E85 (85% ethanol/15% gasoline) was struck and breached by a passenger vehicle;
- A sudden release of E85 occurred;
- The E85 impacted the crash scene, storm drains, and a commercial/residential section of the City.

The exercise involved planning the public safety response, including a change in tactics for new foam requirements to control spills with high alcohol content. Each of the participants was able to share what priorities they had and how they would carry out their responses. Conflicting priorities were identified and resolved. The scenario was chosen because a similar incident had occurred several months prior but (happily) *without* a release. Participants included: local Fire, Police, Emergency Management, Board of Health, DPW, Code Inspection, local hospitals, State agencies - MEMA and MassDEP/ER, and representatives from area businesses.

Then, on May 17, 2013 in the Northeast Region, MassDEP responded to the following incident:

- A tanker carrying 11,000 gallons of gasoline (90% gasoline/10% ethanol) was involved in an accident with a passenger vehicle;
- A sudden release occurred when two of the five compartments in the tanker were breached resulting in the release of approximately 4,000 gallons of gasoline;
- The gasoline impacted the roadway, storm drain system, a nearby brook and wetland;
- As a precaution, local water supply wells near the release were shut down.

Response actions were coordinated with a number of organizations including (but not limited to): local Fire (and likely police), Hazmat Team, Board of Health, MassDOT, EPA and local Water Department.

While the similarities of the accident particulars and response were interesting, it raised questions about ethanol as the latest gasoline additive in the quest to get the lead out. For anyone who lives in this part of the country who grew up being told that some of our roads were designed partly by meandering cows, well, the history of gasoline additives starts to seem a bit like a cow path.

A Primer on Octane and the Internal Combustion Engine:

For those who may not know, the "octane rating" refers to the percent of *octane* in gas, a hydrocarbon with eight carbons chained together. The percent of octane determines how much *pressure* the gas-air mix injected into the compression cylinder of a typical four stroke internal combustion engine can withstand before the fuel-air mix may spontaneously ignite. The "compression ratio" of an engine determines the required octane rating. (For those unfamiliar with the typical four stroke cycle in an internal combustion engine, there is an excellent, simple animation at: http://www.explainthatstuff.com/carengines.html.) The higher the octane rating, the higher the pressure that can be achieved prior to the *spark plug* igniting the

fuel-air mix. The advantage of a higher pressure tolerance is a higher engine horsepower for a given engine weight, with "high performance" engines requiring higher octane gasoline. If the octane of the gasoline is too low for the pressure in the compression cylinder, the fuel-air mix can spontaneously ignite due to the pressure before the spark plug triggers, causing a "knock" in the engine. Turns out, these knocks aren't just an annoying bit of noise, but a premature explosion of the fuel-air mix that can ultimately damage the cylinders and the engine. Higher octane gasoline costs more at the pump, but may be a small price to pay, relative to engine repairs.

Get the Lead In - TEL:

In the U.S., lead was first widely added to gasoline and other fuels as an octane enhancer in the form of Tetraethyl lead or "TEL" in the 1920s (note: this was right after Prohibition was enacted in 1919). Lead is an inexpensive octane booster at very low levels; it had a protective effect on the metals then in use in the exhaust valves in engines; and it gave gasoline good storage and transport qualities. During World War II (and during different times of year), it was easy to vary the ratios of TEL as a way to manipulate octane ratings for different aircraft engines (and weather conditions). After World War II, there was almost a worldwide switch to tetraethyl lead as the octane booster of choice, making lesser, cheaper grades of gasoline with initially lower percentages of octane more useable at very low cost.

TEL also had its critics. It was known to be toxic, and there were some who expressed opposition to the use of lead in gasoline from the earliest days of its use. While their concerns were not entirely dismissed, the official government and industry opinion was that better handling procedures and "more research" was needed. There were many decades of controversy and many studies conducted before research was widely published in the 1960s and 1970s. It was discovered that that vehicle exhaust had deposited lead on the ground along road ways and particularly in densely populated urban areas. Publication of studies linking leaded gasoline to higher lead levels in the bones and blood of children to lowered IQs, anti-social behavior, decreased school performance and health issues[i] finally turned the tide of public opinion against leaded gasoline. Some more recent research suggests that getting lead out of gasoline has also resulted in a decrease in violence and crime.[ii]

Early efforts by the U.S. EPA to phase out lead were met with industry lawsuits. Since lead could quickly clog a catalytic converter, emission controls were ineffective to address the problem. EPA eventually prevailed and a ten year phase out occurred from 1976 to 1986. By the end of 1995, leaded gasoline was officially banned in the U.S. for road vehicles. (There appear to be some exceptions allowed for some airplane and jet fuels and some older classic cars both in U.S. and Europe.)

Get the Lead Out - MTBE:

The price of gasoline began to rise in the 1970s. Although some blamed the oil embargo, it was also because it was no longer possible to cheaply boost the octane in lesser grades of fuels. The search began for a less toxic octane booster, some using different metals, others using derivatives of natural gas, methanol and ethanol. There were safety concerns about some of the other metals and methanol was found to be corrosive to certain engines and particularly to aluminum parts. Eventually, methanol (derived from natural gas) was combined with isobutylene (from crude oil or natural gas), to form methyl tertiary butyl ether, or "MTBE," and a solution seemed to be found.

Not only did MTBE increase octane levels, it also served as an oxygen source for a more complete combustion. This resulted in decreases in hydrocarbon emissions, carbon monoxide, nitrogen oxides, volatile organic compounds and particulates – all resulting in improved air quality without noticeable decrease in fuel efficiency or performance. By 1979, MTBE became the preferred gasoline additive in the U.S. and in much of Europe.

But, shortly after the widespread use of MTBE was adopted, it was discovered that air quality wasn't the only potential problem. Groundwater around the country began to show MTBE contamination. The sources were not only retail gasoline station spills or leaking tanks, but consumer disposal of gasoline, traffic accidents where fuel tanks ruptured and spills to ground during refueling operations. The effects were obvious when unpleasant tastes and odors were detected in private and public drinking water. Soon, there were new questions and another set of concerns.

MTBE from gasoline moved quickly through groundwater, ahead of other gasoline constituents. It was found in the leading edge of a gasoline plume. In an MTBE fact sheet discussing groundwater contamination issues, EPA points out that even though it moves quickly in groundwater, MTBE is resistant to natural biodegradation in groundwater (as opposed to surface water) compared to other gasoline components, with some monitoring wells showing little change in concentration over time.[iii] Health studies began to suggest that MTBE could be a possible carcinogen, raising additional issues about the safety of this octane booster. California was the first state to ban MTBE in 2003, followed by a few others before industry took the step of eliminating it by 2005. Soon, based on a number of factors, ethanol was in the public discussion as a fuel (E85) and as an octane booster.

Back to the Past – Ethanol:

Ethanol was not new. Historically, alcohol as ethanol had been used for lighting and heat as far back as the 1600s A.D. Savvy U.S. farmers had been making their own supplies for lighting since before the early 1800s. The first prototype internal combustion engine ran on alcohol. Alcohol as ethanol was widely used in Europe before World War II as an octane booster. It is interesting to note that in some of the earlier discussions of potential gasoline additives (particularly MTBE versus ethanol), there were articles opposing ethanol. Predictably, perhaps, it appears some, but not all, were from the MTBE industry.

The opponents of ethanol argued that it: was more expensive to produce, would cost more at the pump, would increase certain kinds of air pollution and had worse fuel economy than MTBE gasoline so would create more, not less, dependency on foreign sources of oil. Additionally, because of its affinity for water, ethanol could not be transported through existing pipelines and did not store well, resulting in a much shorter shelf-life (90 to 100 days versus several years)[iv].

Ethanol/alcohol has its own complicated, cow path history as a both a fuel and an octane enhancer – impacted at various times by artificial price hikes when taxes were imposed on it to pay for wars, social opinions on drinking, Prohibition, discoveries of domestic petroleum and people abandoning their farm stills during the dustbowl and Depression of the 1930s. Once hailed as something nearly anyone could make for themselves and be self-sufficient, it has suffered as a fuel from legal and economic barriers wholly unrelated to its technical efficiency or emissions as a fuel source. It seems ethanol warrants its own "Part 2." Stay tuned!

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[i] Several studies including: www.rachel.org/files/document/Bone_Lead_Levels_and_Delinquent_Behavior.pdf; and www.ncbi.nlm.nih.gov/pubmed/16002379

[ii] www.independent.co.uk/environment/green-living/ban-on-leaded-petrol-has-cut-crime-rates-around-the-world-398151.html

[iii] http://www.epa.gov/mtbe/faq.htm#cleanup

[iv] www.fuel-testers.com/ethanol_mtbe_vs_non_alcohol_gas.html