

# A Brief History of Octane in Gasoline: From Lead to Ethanol March 2016

A cornerstone of U.S. environmental policy has been the reduction of harmful tailpipe emissions from cars and trucks. Thanks to EPA regulations of mobile sources, air pollutants have been reduced by millions of tons in the urban environment.<sup>1</sup> Several EPA fuel regulations have concerned octane. Octane is a gasoline additive that is needed for the proper functioning of modern engines. Octane sources have taken many forms throughout the years, both renewable and petroleum-based. They include lead, methyl tertiary butyl ether (MTBE), benzene, toluene, ethyl-benzene and xylene (BTEX), and ethanol (a biofuel). As adverse health and environmental consequences have been discovered for lead and petroleum-based octane providers, they have been removed from the fuel supply or decreased. Today, there are two primary sources of octane used in the U.S. gasoline supply, the BTEX complex (a petroleum refining product commonly referred to as gasoline aromatics), and ethanol.

#### Octane

The octane rating is a measure of a fuel's ability to avoid knock. Knock occurs when fuel is prematurely ignited in the engine's cylinder, which degrades efficiency and can be damaging to the engine. Knock is virtually unknown to modern drivers. This is primarily because fuels contain an oxygenate that prevents knock by adding oxygen to the fuel. This oxygenate is commonly referred to as octane.



Fig. 1: octane rating of gasoline, as displayed at a typical gas station.

At most retail gasoline stations, three octane grades are offered, 87 (regular), 89 (mid-grade), and 91-93 (premium). The higher the octane number, the more resistant the gasoline mixture is to knock. The use of higher octane fuels also enables higher compression ratios, turbocharging, and downsizing/downspeeding—all of which enable greater engine efficiencies and higher performance. Currently, high-octane fuel is marketed as 'premium,' but automotive manufacturers have expressed interest in raising the minimum octane pool in the United States to enable smaller, more efficient engines. Doing so would increase vehicle efficiency and lower greenhouse gases through decreased petroleum consumption.<sup>2</sup>

### Lead

In the early 20<sup>th</sup> century, automotive manufacturers were searching for a chemical that would reduce engine knock. In 1921, automotive engineers working for General Motors discovered that tetraethyl lead (better known as lead) provided octane to gasoline, preventing engine knock.<sup>3</sup> While aromatic hydrocarbons (such as benzene) and alcohols (such as ethanol) were also known octane providers at the time, lead was the preferred choice due to its lower production cost. Leaded gasoline was the predominant fuel type in the United States until the U.S. Environmental Protection Agency (EPA) began phasing it out in the mid-1970s because of proven serious health impacts.

#### Leaded Gasoline & Health Concerns

Early in its use as a fuel additive, health concerns were raised regarding the use of lead in gasoline. In 1924, 15 refinery workers in New Jersey and Ohio died of suspected lead poisoning. As a result, the Surgeon General temporarily suspended the production of leaded gasoline and convened a panel to investigate the potential dangers of lead use in gasoline. While the panel found insufficient evidence of lead poisoning over a short time period, the panel warned that longer exposure to lead could result in "chronic degenerative diseases of a less obvious character."<sup>3</sup>

Despite these warnings, the Surgeon General set a voluntary standard of lead content, which the refining industry successfully met for decades. It was not until the 1960s, following extensive health research, that the devastating health impacts of low-level lead exposure were established.<sup>3</sup> Children's developing bodies are particularly sensitive to low-level, ambient exposures to lead. The health impacts of lead exposure in children include anemia, behavioral disorders, low IQ, reading and learning disabilities, and nerve damage. In adults, lead exposure is associated with hypertension and cardiovascular disease.<sup>4</sup> Prior to the lead phase-out in gasoline, the total amount of lead used in gasoline was over 200,000 tons per year.<sup>5</sup>

#### Leaded Gasoline Phase-out in the United States

Congress passed the *Clean Air Act* in 1970, setting in motion the formation of the EPA and, ultimately, the removal of lead from gasoline. EPA estimates that between 1927 and 1987, 68 million children were exposed to toxic levels of lead from leaded gasoline alone. The phase-out of lead from gasoline subsequently reduced the number of children with toxic levels of lead in their blood by 2 million individuals a year between 1970 and 1987.<sup>3,5</sup>

#### **Timeline of Lead Phase-out**

**1970:** Congress passes the *Clean Air Act.* The EPA is formed and given the authority to regulate compounds that endanger human health.<sup>6</sup>

**1973:** EPA mandates a phased-in reduction of lead content in all grades of gasoline.

**1974:** EPA requires availability of at least one grade of unleaded gasoline, in order to be compatible with 1975 make and model year vehicles. Lead damages the catalytic converters used in these new vehicles to control tailpipe emissions. Catalytic converters are still used in vehicles today.

**1996:** EPA bans the use of leaded fuel for on-road vehicles (leaded gasoline was down to 0.6 percent of 1996 gasoline sales).<sup>7</sup> Lead is still used in some aviation fuels.

Thanks to coordinated efforts, lead is now absent from gasoline in most of the world. Following the lead phase-out in the United States, the oil refining industry chose to construct additional refining capacity to produce octane from other petroleum products, rather than from renewable sources such as ethanol.<sup>8</sup>

## Methyl Tertiary Butyl Ether (MTBE)

The *Clean Air Act* Amendments (CAAA) of 1990 were the next major regulation of fuels.<sup>9</sup> Among other things, CAAA requires areas that do not meet ground-level ozone standards to use reformulated gasoline (RFG). RFG has an increased oxygenate content, which helps it burn more completely.<sup>10</sup> As a result, RFG lowers the formation of ozone precursors and other air toxics during combustion.<sup>10</sup>

Petroleum refiners were not required to use any particular oxygenate in RFG, but by the late 1990s, a petroleum product, methyl tertiary butyl ether (MTBE), was used in 87 percent of RFG due to its ease of transport and blending. In the Midwest, ethanol was a more common component of RFG. Despite its success at reducing ozone precursors, MTBE was phased out of the gasoline pool due to concerns over its solubility in water, which resulted in the contamination of water resources in numerous states. As of 2005, EPA reported that MTBE was not being used in significant quantities in the United States. Currently, 30 percent of gasoline sold in the United States is reformulated gasoline. Ethanol is providing the additional octane required by RFG.<sup>11</sup>

#### **Timeline of MTBE Phase out**

1998: EPA convenes a Blue Ribbon Panel, which finds MTBE poses a threat to groundwater supplies. At the time, the U.S. Geological Survey (USGS) finds MTBE present in 20 percent of groundwater supplies in RFG areas.
2000: EPA announces the phase-out of MTBE to protect drinking water. At the same time, EPA and the U.S. Department of Agriculture (USDA) call for an increase in the use of ethanol to preserve air quality.
2000 – 2005: Seventeen states ban or significantly limit the use of MTBE in gasoline pools.<sup>12</sup>

## The BTEX Complex

The BTEX complex is a hydrocarbon mixture of benzene, toluene, xylene and ethyl-benzene. Commonly referred to as gasoline aromatics, these compounds are refined from low-octane petroleum products into a high-octane gasoline additive. While some volume of BTEX is native to gasoline, it is also added to finished gasoline to boost its octane rating. The total volume of BTEX (aromatics) in finished gasoline depends on the desired octane value and other desired fuel properties.<sup>13</sup>

#### The Rise of BTEX Use

A consequence of lead's phase-out was the increase of BTEX in gasoline. When faced with the removal of lead as the primary octane provider in gasoline, refiners had two available alternatives, BTEX and ethanol. The refining industry invested in additional refining capacity to replace lead with BTEX, a high-octane petroleum refining product.<sup>9</sup> As a result of its substitution for lead, BTEX volume rose from 22 percent to roughly a third of the gasoline pool by 1990. In premium gasoline grades, the BTEX volume content was as high as 50 percent.<sup>10</sup> In mandating cleaner fuels, through reformulated gasoline and other programs, **EPA has reduced the volume of aromatics to between 25 to 28 percent of the conventional gasoline pool, though some health professionals question the safety of even these levels.<sup>9</sup>** 

#### **BTEX & Health Concerns**

After the lead phase-out, there were early concerns regarding the BTEX complex. In 1987, Senator Tom Daschle expressed concern over gasoline aromatics, writing, "A revolutionary change is occurring in the gasoline industry which poses a serious threat to the environment and public health – namely the increased concentration of benzene and other aromatics."<sup>14</sup>

Today, health research indeed suggests that even very low-level exposure to the BTEX complex, from gasoline additives and other petroleum products, may contribute to negative developmental, reproductive and immunological responses, as well as cardio-pulmonary effects.<sup>15</sup> Upon incomplete combustion of the BTEX complex contained in gasoline, ultra-fine particulates (UFP) and polycyclic aromatic hydrocarbons (PAHs) are formed, which carry their own adverse health impacts even at low levels. UFP and PAHs are carcinogenic and mutagenic. Both UFP and PAHs have also been linked to developmental and neurodegenerative disorders, cancers, and cardio-pulmonary effects.<sup>16</sup> Considerable attention has been given to benzene in fuel, as it is highly toxic. At the same time, the partial replacement of benzene with other aromatic compounds (xylene, ethyl-benzene, toluene) may not be sufficient in reducing exposure to BTEX's toxic effects.

#### **Timeline of Benzene Regulation**

**1990:** Congress passes the *Clean Air Act* Amendments, which, among other things, require lowering the content of benzene in areas that do not meet ground-level ozone standards. Passed as part of the CAAA was S.1630, the **Clean Octane** amendment, which gives EPA the authority to use "benign additives to replace the toxic aromatics that are now used to boost octane in gasoline."

**2007:** EPA updates the **Control of Hazardous Air Pollutants from Mobile Sources** (MSAT2), which caps the total content of benzene in gasoline at 0.62 percent, down from an average of 1.3 percent. The other aromatics, such as toluene and xylene, are not capped.<sup>17</sup>

### Ethanol

Early automakers expressed interest in plant-based alcohol fuels, such as ethanol. Henry Ford designed the first Model T to run on ethanol.<sup>9</sup> But, at the time, gasoline was a much cheaper fuel. Additionally, Standard Oil was "reluctant ... to encourage the manufacture and sale of a competitive fuel produced by an industry in no way related to petroleum."<sup>9</sup> The petroleum industry has controlled the fuels market ever since.

During the 1973 oil embargo, regular unleaded gasoline prices jumped 57 percent and routine gasoline shortages also occurred.<sup>8</sup> These events, and the regulation of many air pollutants, sparked a renewed interest in fuel efficiency, electric vehicles, and renewable fuels such as ethanol, which were seen as ways to meet the new regulations and reduce petroleum consumption. Today, the majority of ethanol in the United States is blended with gasoline to produce E10 (10 percent ethanol, 90 percent gasoline). Over 95 percent of gasoline sold in the United States is E10.

#### **Ethanol as an Octane Booster**

In addition to having lower lifecycle greenhouse gas emissions than conventional gasoline, ethanol is an excellent octane provider, with neat (pure) ethanol having an octane rating of over 100. Currently, refiners create 'sub-octane gas,' which has a lower octane rating than required. Ethanol, which is generally the cheapest octane provider, is then used to bring the octane rating of the gasoline up to the labelled octane value on the gas pump. For example, 84 octane gasoline is typically blended with 10 percent ethanol to reach the minimum octane requirement of 87 for retail gasoline.<sup>18</sup>

#### **Ethanol & Health Concerns**

While ethanol has a higher volatility than gasoline, meaning it vaporizes more quickly, it is a cleaner-burning alternative to petroleum-based octane boosters. Additionally, the toxicity of ethanol is low compared to the health effects of BTEX and its combustion products, such as ultrafine particulates (UFPs) and polycyclic aromatic hydrocarbons (PAHs). A modest increase of ethanol content in fuel from 10 to 15 percent would result in an anticipated 6.6 percent reduction in cancer risk from tailpipe emissions.<sup>19</sup>

#### The Search for Additional Octane

Currently, there are two ways of increasing the octane content of gasoline: increasing the volume of gasoline aromatics or increasing the volume of ethanol.

There is contradictory evidence that increasing ethanol content in gasoline increases nitrous oxide (NOX) emissions, an ozone precursor. Several studies find either no relationship between ethanol blending and NOX emissions, or find decreased NOX emissions with increasing ethanol volumes.<sup>19,20</sup> Other studies suggest older cars emit more NOX when using ethanol blends. However, a study of 2012 make and model year vehicles found no increase in NOX emissions between E10, E15 and E20 blends, suggesting that both engine design and engine age play a role in NOX emissions. Overall, the effect of ethanol on NOX and carbon monoxide (CO) emissions is minor in newer engine emission control systems.<sup>19</sup>

#### Timeline of Ethanol Phase-In<sup>21</sup>

**1975:** Congress passes the *Energy Policy and Conservation Act* (EPAct), establishing Corporate Average Fuel Economy (CAFE) standards for cars and trucks.

1988: The Alternative Motor Fuels Act establishes incentives under CAFE for alternative fuel vehicles.

**1992:** The *Energy Policy Act of 1992* defines alternative fuels and establishes programs at the federal level to increase the use and research of alternative fuels.

**2005:** Congress passes the *Energy Policy Act of 2005*, establishing the Renewable Fuel Standard (RFS). RFS sets a minimum volume of renewable biofuels to be blended into the transportation fuel supply.

**2007:** Congress passes the *Energy Independence and Security Act* (EISA), significantly increasing the volume of renewable fuels mandated under the RFS, to 36 billion gallons by 2022.

**2013:** Citing a lack of renewable fuels infrastructure, **EPA proposes reducing the volume of renewable fuels** under the RFS.

**2015: The Administration sets renewable fuel volumes for 2014 – 2016**. Final renewable fuel volumes for 2016 are 18.11 billion gallons, set at approximately 1 billion gallons higher than the 2013 proposal, and at just over 10 percent of the fuel supply.<sup>22</sup> This includes the categories of renewable fuels, cellulosic biofuels, advanced biofuels and biomass-based diesel.

## Conclusions

Lead and various petroleum products have provided octane to gasoline for over 100 years, but evolving health and environmental concerns have led policymakers to reconsider the widespread use of many of these compounds. As the United States looks to reduce the greenhouse gas intensity of the transportation sector, increasing the octane value of gasoline is a promising avenue, as it would enable more fuel-efficient engines. But the health and environmental impacts of the octane sources that are used must be considered as well. By adding ethanol to finished gasoline, called "splash blending," octane ratings can be increased while simultaneously lowering toxic octane sources.

A national transition to an optimized mid-level ethanol blend, between E25 (25 percent ethanol, 75 percent gasoline) and E40 (40 percent ethanol), would lower consumer fuel costs and standardize the fuel supply. The Department of Energy recognizes that increasing the ethanol content of gasoline is a potential pathway to increasing the octane rating of the gasoline supply.<sup>23</sup> A mid-level ethanol blend would enable the design of highly fuel-efficient engines that would significantly reduce petroleum consumption, reduce lifecycle greenhouse gas emissions, and help meet higher fuel economy standards. As of now, the Department of Energy and the EPA have approved the use of E15 for make and model year 2001 and newer vehicles, which account for 80 percent of the vehicles on the road today.<sup>24</sup>

Automotive manufacturers are examining clean octane sources as a way to meet efficiency and greenhouse gas regulations.<sup>25</sup> It is here that the greatest benefit to health, the environment and vehicle efficiency can be realized in the near-term.

This fact sheet is available electronically (with hyperlinks and endnotes) at <u>www.eesi.org/papers</u>.

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- <sup>5</sup> <u>EPA Requires Phase-Out of Lead in All Grades of Gasoline</u>, U.S. EPA, Nov. 1973
- <sup>6</sup> Understanding the Clean Air Act, U.S. EPA, Sept. 2015
- <sup>7</sup> EPA Takes Final Step in Phaseout of Leaded Gasoline, U.S. EPA, Jan. 1996
- <sup>8</sup> Petroleum Chronology of Events 1970 2002, EIA, 2002

<sup>9</sup> Grey, C.B. and Varcoe, A.R., <u>Octane, Clean Air, and Renewable Fuels: A Modest Step toward Energy Independence</u>, Texas Review of Law & Politics, Jan. 2006

- <sup>10</sup> <u>Clinton-Gore Administration Acts to Eliminate MTBE, Boost Ethanol</u>, U.S. EPA, March 2000
- <sup>11</sup> <u>Assumptions to the Annual Energy Outlook: Petroleum Markets Module</u>, U.S. EIA, 2012
- <sup>12</sup> Overview of State MTBE Bans, U.S. EIA, 2003
- <sup>13</sup> Catalytic reforming boosts octane for gasoline blending, U.S. EIA, 2013
- <sup>14</sup> Daschle, T., Letter to Vice President Bush, Mar. 1987

<sup>15</sup> Bolden, A.L., Kwiatowski, C.F., Colburn, T., <u>New Look at BTEX: Are Ambient Levels a Problem?</u>, Environmental Science & Technology, May, 2015

<sup>16</sup> Perera, F.P., <u>Children are Likely to Suffer Most from Our Fossil Fuel Addiction</u>, Environmental Health Perspectives, Aug. 2008

- <sup>17</sup> Control of Hazardous Air Pollutants from Mobile Sources: Final Rule to Reduce Mobile Source Air Toxics, U.S. EPA, Feb. 2007
- <sup>18</sup> <u>Midwest Pipelines to discontinue 87 Octane Unleaded Gasoline</u>, CHS, Inc., 2013.

<sup>19</sup> Unnasch, S. and Henderson, A., <u>Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10</u>, Lifecycle Associates, LLC, July 2014

<sup>20</sup> The Impact of Ethanol Fuel Blends on PM Emissions from a Light-Duty GDI Vehicle, Aerosol Science and Technology, Jan. 2012

<sup>21</sup> Key Federal Legislation, Alternative Fuels Data Center, U.S. DOE

<sup>22</sup> Final Renewable Fuel Standards for 2014, 2015 and 2016, and the Biomass-Based Diesel Volume for 2017, U.S. EPA, Nov.
 2015

- <sup>23</sup> <u>Quadrennial Technology Review: An Assessment of Energy Technologies and Research Opportunities</u>, U.S. DOE, Sept. 2015
- <sup>24</sup> E15 Approved for Use in 2001 and Newer Vehicles, Alternative Fuels Data Center, U.S. DOE, Feb. 2011
- <sup>25</sup> The Effect of Compression Ratio, Fuel Octane Rating, and Ethanol Content on Spark-Ignition Engine Efficiency,

Environmental Science & Technology, Aug. 2015.

<sup>&</sup>lt;sup>1</sup> Second Integrated Urban Air Toxics Report to Congress, U.S. EPA, 2014

<sup>&</sup>lt;sup>2</sup> <u>Higher Octane Fuel Could Add MPG</u>, SAE Panel Says, Automotive News, Apr., 2015

<sup>&</sup>lt;sup>3</sup> Lewis, J., <u>Lead Poisoning: A Historical Perspective</u>, U.S. EPA, May 1985

<sup>&</sup>lt;sup>4</sup> <u>The Secret History of Lead</u>, The Nation, 2000