Historical Gasoline Compositional Data 1976 - 2010

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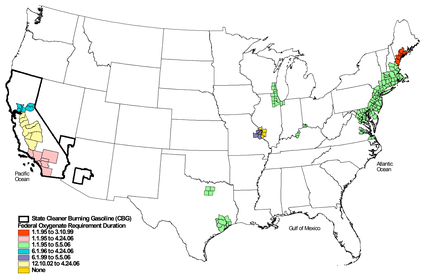
Abstract

Gasoline composition varies for technical, market and regulatory reasons. Knowledge of any one of these is insufficient for understanding the chemical composition of gasoline at any specific location in the U.S. Historical data collected by the National Institute of Petroleum and Energy Research and its successors was used to compare gasolines from 27 cities around the U.S. The Clean Air Act Amendments of 1990 provide a framework for gasoline which includes reformulated, conventional and oxygenated gasoline. Each of these has characteristics that were seen in data from some of the 27 cities. Reformulated gasoline has a benzene content that is less than 5% and from 1995 to 2006 contained 2% oxygen by weight. Several states began banning methyl *tert*-butyl ether (MTBE) in 2000, causing a shift to ethanol to meet the oxygen requirement. Conventional gasoline had benzene limits set by producer baselines and has had average contents higher than 3% in some cities. The Mobile Source Air Toxics Rule of 2007 limited benzene, nationwide to 0.62% in the beginning of 2011. MTBE and ethanol use varied among in conventional gasoline as both can be used as octane boosters. Oxygenated gasoline contains an oxygenated additive in winter months, which clearly established seasonal patterns in cities implementing this program.

Background

The National Institute of Petroleum and Energy Research (NIPER) and successors : the American Petroleum Institute, TRW Corp, and Northrop-Grumman collected and distributed data on gasoline composition from the 1930s through 2010 (Northrop Grumman, 2011). Samples were collected twice a year from cities around the U.S. The data sets typically included 1000 to 3000 samples. Over 175 cities were included at various times in the surveys, but a smaller number (approximately 60) have recent or mostly-complete data sets. The samples were analyzed by ASTM methods for physical properties and selected constituents of gasoline. The data were averaged by location and octane rating by EPA and the results presented below include benzene, methyl *tert*-butyl ether (MTBE), *tert*-amyl ether (TAME), *tert*-butyl alcohol (TBA) and ethanol.

Understanding some of the variability in gasoline composition requires a working understanding of federal clean air regulation that impacts gasoline. The clean air act amendments of 1990 established the framework for gasoline composition in the United States (Weaver *et al.*, 2010). Three basic types of gasoline were established: reformulated (RFG), conventional (CG) and winter-oxygenated (OG). Reformulated gasoline is used in the northeast corridor, some large interior cities, and California, which also has a state mandated reformulated gasoline program (**Figure 1**). Conventional gasoline is defined as all gasoline that is not reformulated and is used in all other parts of the country. Oxygenated gasoline is used to control carbon monoxide emissions in winter in specific cities around the U.S., most of these are now located in the southwest (US EPA, 2008).



Whole county boundaries shown for partial counties: Grundy & Kendall in Illinois, Bullitt & Oldham in Kentucky. Not represented: above 4500' on White Face Mountain in Essex County, New York. All areas not indicated on the map use conventional gasoline.

Figure 1. Map showing effective dates for oxygenated additives in reformulated gasoline (Weaver *et al.*, 2010). All areas not indicated for reformulated gasoline use conventional gasoline.

Until 2006, RFG was required to contain an oxygen-containing additive at 2% by weight. From the earliest days of the program (beginning in 1995), the most commonly used additive was methyl *tert*-butyl ether, although lesser amounts of other ethers were used, particularly *tert*-amyl methyl ether. In at least one location (Chicago) ethanol was used as the oxygenate of choice. Beginning in 2000, several states banned MTBE and, in some cases, other ethers and alcohols (**Figure 2**). See Weaver *et al.*, 2010 for details. Since the federal oxygenate mandate was in force until 2006, state MTBE bans led to increased ethanol usage. In 2006, the Energy Policy Act required increasing usage of alternative fuels causing increased ethanol use.

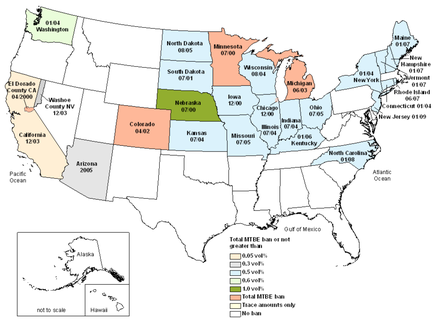


Figure 2. State and local MTBE, ether and/or alcohol bans showing the effective dates and maximum allowable levels for MTBE.

Benzene in reformulated gasoline was required to be below 1% by volume. Data from five RFG cities show average benzene concentrations below the limit after the initiation of the program in 1995 (**Figure 3**). The Mobile Source Air Toxics Act of 2007 limited benzene in all U.S. gasoline to 0.6%, which imposed a similar, but lower, limit on the entire country.

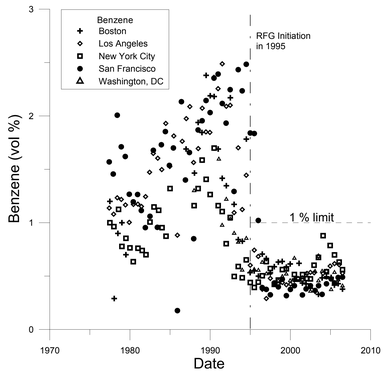


Figure 3. Benzene content in five reformulated-gasoline using cities. After the adoption of the RFG program in 1995 (dot-dash vertical line) in these five cities, the benzene content of gasoline dropped to below 1.0 vol % (horizontal dashed line), as required by the program (Weaver *et al.*, 2010).

Reformulated Gasoline Cities

RFG-using cities show consistently high levels of MTBE in gasoline for the period of the oxygenate mandate **(Figures 4 and 5).** In some of them (New York, San Francisco, Los Angeles and Louisville), MTBE usage ended before 2006, because of state MTBE bans **(Figure 2)**. Chicago showed little use of MTBE, rather meeting the oxygenate mandate with ethanol. Notably less ethanol is required to supply the required oxygen, so the ethanol concentrations are lower than the typical MTBE concentrations in other fuels. TBA was present in many of these gasolines at low concentrations (<0.1%). A few higher TBA concentrations may reflect TBA usage as an additive (e.g., Houston and Dallas/Ft Worth, **Figure 5**). TAME was used at higher concentrations in several of the cities. The levels of TAME usage in Boston, New York, Washington, San Francisco, Dallas/Ft Worth, and Houston made it a significant contributor to the total required oxygen. Ethanol usage in many of these cities was mutually exclusive with ether usage, although some show sporadic concurrent usage (e.g., Boston, New York, San Francisco), and Louisville showed nearly continuous use of both MTBE and ethanol.

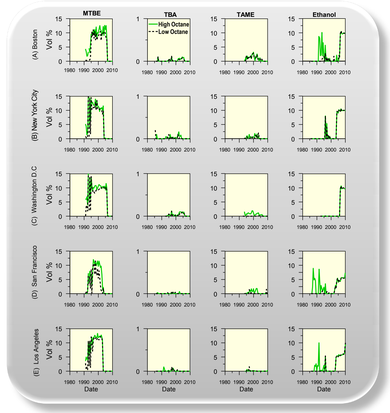


Figure 4. MTBE, TBA, TAME, and ethanol for RFG cities on the east and west coasts.

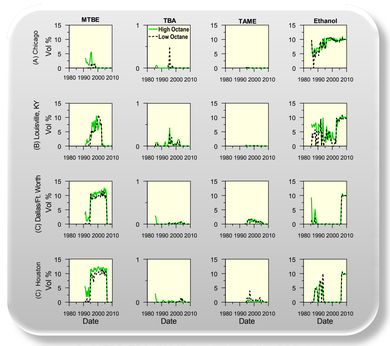


Figure 5. MTBE, TBA, TAME, and ethanol for RFG cities in the mid-continental United States.

Conventional Gasoline Cities

Benzene in conventional gasoline is limited by producer/blender baselines that were developed from 1990 outputs. For newer operations a default baseline of 1.54% benzene was imposed. Because the source of gasoline is not tied to a specific end-use location, historical data are the only means to assess benzene levels in conventional gasoline.

Average benzene levels have exceeded 3% at various times in certain locations: Memphis, Seattle and Portland **(Figures 6 and 7)**. Benzene levels have trended downward in several cities (Buffalo, Charlotte, Atlanta, Miami, Seattle, and Portland) and are expected to show further decline to meet the requirements of the Mobile Sources Air Toxics Rule of 2007. Because benzene boosts the octane rating of the gasoline, its usage can vary based on blending criteria and the amount of other octane-boosting components present. Because the latter are unknown, an explanation of varying benzene concentration or the observed higher benzene concentration in low octane ("regular") gasoline than in high octane ("premium") is not possible from these data (e.g., Cincinnati, Seattle, Portland, and Rapid City).

Likewise MTBE and ethanol boost octane ratings. In many of these cities—Buffalo, for example—more MTBE is found in premium than regular gasoline, indicating a likely use as an octane booster. With no mandate for use of oxygenated additives, conventional gasoline exhibits place-dependent variability in MTBE and ethanol contents. Some evidence of state MTBE bans can be seen in these figures—MTBE dropped out of use in Buffalo and Cincinnati by the time of their state's respective bans. For the most part MTBE use did not increase in states without MTBE bans, but Atlanta and Miami are exceptions **(Figure 6)**. Ethanol use was sporadic in many conventional gasoline cities. While MTBE was available, ethanol was not commonly used in Memphis, Atlanta, Miami and Amarillo. In other locations, Cincinnati, Seattle, Portland, Denver and Rapid City, ethanol use was common over the period of record. In several cities – Memphis, Atlanta, Miami, and Amarillo – ethanol usage spiked upward after 2006 due to the general increase in ethanol usage mandated by the Energy Policy Act.

Portland and Denver show a seasonal use of ethanol, because although using conventional gasoline, they also had mandates for wintertime oxygenate usage. Similarly, some RFG cities used the oxygenated gasoline program, prior to the beginning of RFG in 1995 (**Figure 4**, New York, Washington, San Francisco, and Los Angeles). After beginning to use RFG, there is still evidence of wintertime increase in oxygenates in these cities, but the levels remained high in summer also.

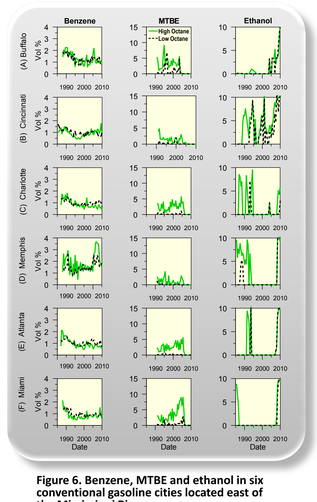


Figure 6. Benzene, MTBE and ethanol in six conventional gasoline cities located east of the Mississippi River.

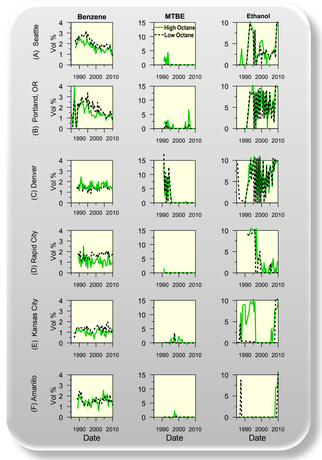


Figure 7. Benzene, MTBE and ethanol in six conventional gasoline cities located west of the Mississippi River.

Oxygenated Gasoline Cities

The oxygenated gasoline program was developed to control carbon monoxide in winter in selected cities. The choice to use this control measure lies with the states which may include oxygenated gasoline in their state clean air implementation plans. As attainment goals were met, many cities dropped out of this program. The remaining cities are in the western U.S.; primarily the southwest (U.S. EPA 2008).

Of the cities shown in **Figure 8**, all except Phoenix use conventional gasoline, thus the benzene content is variable and can average above 1% by volume. Both MTBE and ethanol show wintertime spiking throughout the period where winter oxygenates were required. Reno and Las Vegas had extensive use of MTBE from 1992 through 1995 and use of ethanol thereafter. Some of the cities (Spokane, Denver; see **Figure 7**) have dropped the program, ending the seasonal variation; others show year round elevated ethanol content – Reno, Albuquerque, Las Vegas. At least through 2010, gasoline in Phoenix and El Paso consistently showed ethanol usage in winter but not summer. A similar pattern is seen in Las Vegas until 2008 **(Figure 8)**.

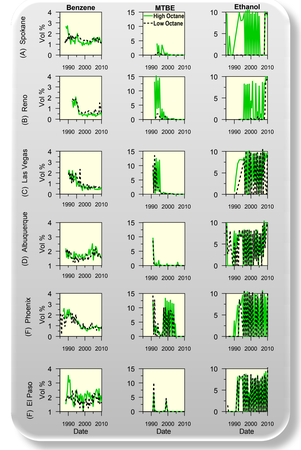


Figure 8. Data on benzene, MTBE, and ethanol for oxygenated gasoline cities.

Summary

Gasoline composition has been strongly influenced by provisions of the Clean Air Act Amendments of 1990, which established a framework for U.S. gasoline. Data from around the country illustrate the effects of these and other regulations—namely state MTBE bans. Because other factors determine which compounds are used to enhance gasoline octane ratings, some aspects of gasoline composition are only clear from evaluation of historical data.

References

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US EPA, 2008, State Winter Oxygenated Fuel Program Requirements for Attainment or Maintenance of CO NAAQS, United States Environmental Protection Agency, Transportation and Regional Programs Division, Office of Transportation and Air Quality, EPA420-B-08-006.

Weaver, J.W., L.R. Exum, and L.M. Prieto, 2010, Gasoline Composition Regulations Affecting LUST Sites, United States Environmental Protection Agency, Washington, DC, 20460, EPA 600/R-10/001.

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