



Fuel Blending Guide for Ethanol

*Identifying Sound Practices for Acquiring or Blending Fuels
for Studies of Emissions Changes*

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The work on this project and the conclusions reached do not necessarily represent the views of the reviewers and any errors are solely those of the project team.

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Executive Summary

This Blending Guide Study identifies sound practice for acquiring or blending fuels for studies of emissions changes in response to fuel composition or specification changes in the marketplace, with emphasis on studies examining ethanol effects. Prior studies sought to identify effects of several fuel parameters and did not employ test fuel compositions expected in the marketplace. Recommendations are based on a review of the literature and prior fuel effects studies, consultation with experts in the field, and consideration of the fundamental differences between market fuels studies and multivariate fuel property studies. The objective is focused on determining the effects of blending ethanol at different levels with gasoline on light-duty vehicle exhaust and evaporative emissions, but the proposed approach may have value in a far broader array of fuel effects studies.

Differences in fuel blending approaches, vehicle technology, driving schedules, and study structure contribute to substantial differences between results of prior studies. Emissions levels for modern vehicles are low, causing run to run measurement variability, and differences are typically a fraction of those low numbers. In multivariate studies ethanol level, aromatic content, 50% and 90% distillation temperatures (T50 and T90) and the particle matter index (PMI) have all been used as emissions effect study variables. Additional fuel properties also impact emissions, but their effects on emissions are either assigned to the chosen study variables or to uncertainty. Multivariate studies require a substantial count of fuels and test runs to have statistical significance and address nonlinear blending behavior and are naturally resource limited. These studies do not examine market fuel compositions directly but infer their performance from interpolative or extrapolative models using assumed or measured market fuel properties.

Some prior studies have compared emissions of gasoline against a splash blend of ethanol with the same gasoline. These studies do not represent a typical present day market fuels comparison. An exception exists where 15% ethanol blend (E15) is produced using the same blendstock for oxygenate blending (BOB) that is used for E10: this splash blend represents a current market case.

A detailed literature review highlights the difficulties associated with characterizing the emissions effects of ethanol blending with a BOB. Gasoline properties are mixed with composition values as parameters for describing fuels, and properties are not necessarily aligned with combustion, permeation and emissions formation mechanisms. Distillation properties are used to describe the fuel but are altered in a highly nonlinear fashion by ethanol in the fuel. Vehicle to vehicle responses differ substantially, challenging generalized conclusions. Effects of vehicle operating history, engine deposits, and pre-test conditioning merit additional study, and differences in engine speed and load may change conclusions on fuel composition effects. Lastly, refinery variability is high, and economic forces dictate the blending at refineries. Typically, aromatic content of gasoline is reduced in response to an increase in ethanol content to meet equivalent octane rating. Formulation of the BOB may vary substantially due to refinery practices, and the ethanol effect on the BOB is influenced strongly by the precise BOB composition. It is therefore difficult to predict real world emissions effects from existing data.

Four recommendations for future market fuel study practice represent a departure from prior practice.

- **Fuels expected in the market should be used.** For most efficient use of resources, effects resulting from a change of ethanol level should be evaluated by employing only fuels with the ethanol levels of interest, and with hydrocarbon (BOB) compositions that are expected in the market at those ethanol levels. Each ethanol level should be represented by one fuel, with average expected market hydrocarbon composition, or by a suite of fuels, with a distribution of hydrocarbon compositions that reflect expected market variability in composition. In this way measurement effort is not devoted to fuel formulations that may never enter commercial use, and nonlinear blending effects are addressed directly by the study fuels. This approach is dedicated to a singular objective, rather than the development of a broad model for fuel formulation impact. It also provides results that are a strong test for broad models.
- **Fuel composition should be used to define fuels.** For precise fuel description, measures of fuel composition are preferable to properties that are determined using standardized protocols. Composition varies widely, and properties alone are insufficient to define a fuel's behavior. The fuel composition is unambiguous, whereas several fuels blended with diverse compositions may satisfy the same set of properties. Detailed hydrocarbon analysis (DHA) of fuels has become more reliable and rapid, permitting the grouping of molecular species by type, weight or expected influence. Use of composition to govern blending and fuel characterization avoids interference of non-linear blending effects on values of study parameters. Also, standardized protocols are not necessarily governed by the same chemistry, physics or time constants as the processes occurring in real-world injection, combustion, catalysis, adsorption and permeation. However, certain fuel properties, such as octane numbers, will continue to govern formulation of market fuels sold at the pump.
- **Influence of vehicle technology merits higher recognition.** Vehicles used in a study should be well characterized with regard to their powertrain technology and control strategy, and not treated as "black boxes." Although each automobile is a discrete species, the vehicle cohort may also be characterized by numerical descriptors, such as power to weight ratio, or engine power density, to appreciate the vehicle interaction with fuels at different loads and speeds. Prior studies have recognized major classifications, such as whether port fuel injection (PFI) or gasoline direct injection (GDI) is used, or if the engine is turbocharged. More thorough classification supports statistical analysis of vehicle-to-vehicle differences and defines the applicability of results from each vehicle for application to the on-road fleet. It is important that the practice of monitoring vehicle sensors and broadcast data during testing is adopted consistently and used in post-test evaluation of emissions effects. Understanding the role of engine control strategies in governing both emissions and fuel efficiency is of paramount importance. Involvement of automobile manufacturers or powertrain experts is beneficial in study planning and data interpretation.
- **Driving schedules should mimic on-road use.** During emissions testing, vehicles should be operated to mimic their real-world on-road use and environment as closely as possible if the intent is to predict

emissions inventory. Unfortunately, the diversity of speeds, accelerations, climate and grades is excessive. Practically, it is recommended that data are gathered from vehicles includes operation at idle, light to medium load, and near full load, because modern engine controls will manage combustion differently in these circumstances. It is best to measure all emissions of interest continuously over a test schedule. Otherwise one should employ a low power cycle such as the FTP, a high power cycle such as the US06, and, if possible, a segment of wide open throttle (WOT) acceleration. Each of these loads may elicit performance, efficiency and emissions in different ways when challenged with different fuels.

An additional recommendation is to increase the number of hot repeat runs as a cost effective way to improve confidence in determining the low values for hot running emissions.

Three report appendices provide data on gasoline composition variability and present two hypothetical examples of studies, one addressing emissions from E10 and E15 using the same BOB, and the other addressing a comparison of E10 and E20 PM emissions.

Summary of Recommended Protocol

- *Step 1: Identify the mission and study purpose.* Present the types or species of emissions, efficiency or performance to be characterized, the applicable fuel source or geographic region, restrictions or rules related to fuel composition, climatic and fleet limitations, and contemplated fleet activity.
- *Step 2: Identify resources and consider allocation.* Quantify and resolve tradeoffs between assigning resources to acquisition of fuels, acquisition of vehicles, data collection (typically on a dynamometer), and data analysis and reporting to address the purpose identified in Step 1.
- *Step 3: Determine representative fuel properties.* Identify a pathway for precise definition of the target fuel or suite of fuels. This will require estimation of the range of parameters (properties and composition) for the one or more BOBs to be used in the study.
- *Step 4: Define the fuels.* Sample baseline fuels to determine how the composition varies. Determine best estimate compositions for target fuels from expert consultation, modeling or existing refinery data. Determine whether a single fuel or a suite of fuels will represent each ethanol level. Set the composition of the baseline and target fuel(s) to represent two composition distributions.
- *Step 5: Procure the fuels.* It is possible to use market fuels, but generally the fuels must be blended to a specification. It is preferred that blending targets many parameters, typically expressed as composition, and employs streams that match refinery DHA.
- *Step 6: Determine representative vehicles.* Vehicle count should be balanced with tests per vehicle. Consider present fleet composition and technology versus current sales composition and technology in selecting the fleet for the Step 1 study purpose. Recognize and document differences between vehicles and develop a plan for in-test vehicle data logging.

- *Step 7: Procure and prepare the vehicles.* Vehicles may be procured in a variety of ways, should be inspected for malfunction. An emissions baseline test is recommended to verify normalcy of emissions. An engine lubricant change usually precedes the start of the testing.
- *Step 8: Determine representative vehicle activity.* Either existing driving schedules may be used, or a cycle may be customized to satisfy the objective. Recording of continuous emissions data and vehicle broadcast data should be considered.
- *Step 9: Choose test protocols and schedules.* Vehicle operation or activity should reflect the study objectives. A low power schedule such as the LA92 and a high power schedule such as the US06 may be chosen. Other schedules are available, and idle or wide open throttle (WOT) operation may be of interest.
- *Step 10: Address quality control and statistical confidence.* Before measuring emissions develop a statistical plan that includes rejection of outliers and anticipates most eventualities. Develop a data management plan. Define statistical analysis to be employed: simple analysis is possible for addressing basket blends or averages of suites.

Introduction

Emissions from gasoline spark ignited engines and the vehicles that they power vary with the composition of the fuel. A complex relationship exists between gasoline formulation and engine design to satisfy desires for power density, energy efficiency, climate change reduction, human health and environmental stewardship. There are economic constraints associated on the one hand with manufacturing and materials, and on the other hand with petroleum feedstocks, refining and blending and with biofuel production. Combustion processes in engines have become progressively more intensive, necessitating the blending of gasoline with acceptable knock resistance. At the same time the longevity of the light duty vehicle fleet necessitates the formulation of gasoline that can serve a range of different engine technologies.

Gasoline composition has evolved in response to changes in crude oil supplies, increases in sophistication of refining technology, adoption of renewable blendstocks and recognition of health impacts. Oudijk (2010) presented a substantial history of the use of organometallic additives in gasoline to raise knock resistance, until its phase-out in the 1980s and 1990s. Engine compression ratios rose substantially during Tetra-ethyl lead (TEL) use. TEL was followed by the use of methyl tert-butyl ether (MTBE), which provided oxygen content in the fuel, and which subsequently was identified as toxic (Lee et al., 2001). By 2000 five states had moved to curtail MTBE use as an entrée to a phase-out.

The renewable fuel standard (RFS) in 2005 enabled blending of ethanol with a petroleum BOB, for sale at the pump. Between 2006 and the present-day, a 10% (by volume) ethanol blend has been adopted widely. Production of knock resistant gasoline without oxygenates can be facilitated by the addition of high octane (typically aromatic) refinery streams. Refinery reformers provide aromatics for increased knock resistance and have current excess capacity in the US.

Gasoline composition also has influenced, and been influenced by, spark-ignited engine design. Splitter et al. (2016) have provided an informative account of the synergistic evolution of engines and fuels, with data starting from 1925. They observe that “historically fuel octane number has been an enabler for increases in fuel economy or performance through engine compression ratio; however, since the mid-1970s fuel octane number has remained stagnant.” Kalghati and Stone (2018) have reviewed gasoline requirements in the light of pressure-time histories in the cylinder and are critical of the application of some traditional parameters used to describe fuel.

Evaporative emissions from gasoline vehicles include escape of both vapor and liquid, and the permeation of fuel components through elastomers, such as seals or hoses. Materials for seals, tanks, pipes and canister walls are selected based on gasoline properties. Activated carbon properties and quantity for vapor control anticipate fuel composition. Permeability varies in a complex fashion with specific hydrocarbons or alcohols, or their mixtures. Onboard refueling vapor recovery (ORVR) systems have been implemented for two decades to reduce refueling emissions (Fung and Maxwell, 2011; Shearston and Hilpert, 2020), but some vapor is still released during the refueling process. Certification protocols for evaporative emissions have evolved and have become more extensive, reflecting the tightening of standards and the technology needed to meet them.

Even though the octane number has not varied, gasoline composition has changed substantially over the last five decades. The EPA offer fuel trends reports for the periods 1995-2005 (EPA, 2018) and 2006-2016 (EPA, 2017). The Reformulated Gasoline (RFG) program contributed to reductions of sulfur, benzene, and aromatic content, less volatility, and lower T50 and T90 to promote air quality in selected regions. Tier 2 and then Tier 3 gasoline requirements further reduced the sulfur level for conventional gasoline. The Mobile Source Air Toxics Program reduced benzene levels.

Gasoline has generally become lighter, as demand for distillates draws away some heavier streams. Further, ethanol now represents about 10% of US gasoline, E15 is being more widely adopted, and E85 is available for use in flex-fuel vehicles. Ethanol provides substantial knock resistance, allowing refiners to prepare BOBs with reduced aromatic levels and alter the refinery product balance. Separately, climate change mitigation is driving the use of renewable fuels and increasing the adoption of gasoline direct injection (GDI) engines. There is also interest in fuel effects for GDI engine emissions as they grow in fleet representation.

Changes in gasoline composition call for studies to determine the influence of fuel composition on tailpipe and evaporative emissions from automobiles and light trucks. Changes in engine design and control also affect emissions and appear to affect relative emissions between different gasoline blends. This necessitates frequent emissions effects studies, for which resources are limited. Developing sound, economical approaches to address real-world emissions changes quantitatively and accurately is an important contributor to air quality improvement and appropriate use of renewable fuels. When specific decisions need to be made with regard to fuel properties or emissions standards, dedicated studies should be used to address those changes, except in the cases where it is necessary to explore a composition landscape with several dimensions. This blending guide specifically addresses studies of the effect of changes in market fuel composition.

Objectives

This Blending Guide Study primary objective is to identify a sound practice for acquiring or blending fuels that will result in accurate real-world predictions of changes in response to fuel composition or specification changes in the marketplace. Tailpipe and evaporative emissions are the most important impacts, but the philosophy presented below applies to performance, driveability, durability and engine management studies as well. Although the objective is focused on determining the effects of blending ethanol at different levels with gasoline BOB, the proposed approach is applicable to a far wider array of fuel composition studies. The Blending Guide objective is not directed at fuel effects studies that seek to address the effect of several parameters on emissions. Those broader studies seek to employ orthogonal fuel parameters in a statistical matrix, rather than parameters that are expected to vary in sympathy with a change in fuel specification. The recommendations should extend readily to fuel effects evaluation for stationary and medium-duty on-road spark ignited engines burning gasoline.

Fuel Composition Effects

Human health concerns drive substantial regulation of both fuels and vehicle design. Internal combustion engine pollutants, such as particulate matter (PM) and oxides of nitrogen (NOx) from the tailpipe, are affected by the composition of the fuel due to its evaporation and combustion characteristics and the interaction of combustion products with exhaust aftertreatment. Further, there are some species in the exhaust and in gasoline vapors that are regarded as direct air toxics, and that vary with composition of the gasoline (Bolden et al., 2015; Karavalakis et al., 2014; Karavalakis et al., 2015).

The fuel composition is also implicated in fuel consumption, the durability of catalysts and deterioration of engine performance due to deposit formation, which is an elevated issue with direct injection gasoline engines. The burden of emissions certification is placed on the manufacturers, using a defined fuel and standardized vehicle operation (40 CFR Parts 86 and 1065), but this does not take into account varying fuel composition, differing duty cycles, and climatic impact, (both seasonal and regional). Additional studies are required to quantify the impact of market fuel changes and to provide a reliable emissions inventory to predict atmospheric chemistry and predict air quality. The approaches and methodologies used for these studies are the subjects of the recommendations in this blending guide.

Background, Review and Observations

Refining and Gasoline Composition

Refineries convert raw crude oil and other hydrocarbon input streams into a variety of petroleum products, each with a different market value. Both physical separation processes and chemical changes are employed.

Gasoline production involves blending several blendstocks originating from crude distillation and other downstream facilities. Blendstock quality is dependent on the type of processing and the severity of process operations. In addition to these refinery blendstocks, refineries may also procure gasoline blend components from non-refinery sources: natural gasoline from crude oil/natural gas production, low octane naphtha from petrochemical aromatics operations, aromatics (primarily toluene), heavy aromatic by-products of petrochemical aromatics operations, MTBE (for gasoline exports), miscellaneous imported gasoline components and transmix gasoline from pipeline operations.

The streams that provide blendstocks for gasoline include the following:

- Light Straight Run Naphtha (LSR) is a high volatility, low octane component produced directly from crude oil distillation.
- Isomate is a high volatility moderate octane component. The isomerization process increases octane by converting straight chain paraffinic (low octane) species to branched or iso species (higher octane).
- Reformate is a low volatility, high octane component produced via catalytic reforming of heavy naphtha from crude distillation. The reforming process takes very low octane naphtha and increases its octane level by converting straight paraffin compounds to branched and cyclic naphthene compounds and converting these and other feed naphthenes into high octane aromatics.
- Catalytically cracked gasoline (FCC gasoline) is a moderate volatility component with octane in the general range of average finished gasoline. The FCC cracks large compounds in heavy gas oil and, in some cases, crude oil bottoms, yielding products in the gasoline and distillate range. Olefins from the FCC feed alkylation units.
- Alkylate is a moderate volatility component with octane rating typically falling somewhere between regular and premium grade market octane. Alkylate is produced by combining light olefins from the FCC (butylene and propylene) with isobutane to produce largely C7 to C9 branched paraffins.
- Butane and pentane are used (or limited) in achieving target RVP.
- These streams may be blended in different proportions and have different molecular signatures at different facilities, since the gasoline is defined by relatively few parameters that can be met with different blends. The Energy Information Agency presents 138 US refineries, ranging in capacity from 2,000 barrels per day to 607,000 barrels per day. The refiner seeks to maximize profit by producing the highest value offering of products and using the lowest value blendstocks to achieve the required specifications.
- More refining detail is provided in a prior report (Clark et al., 2019b), and examples of gasoline composition are presented in Appendix I of this report.

For ethanol blends, the refiner produces a BOB that will meet specifications after blending with ethanol. The ethanol is not transported in pipelines and is blended subsequently at terminals. Increasing octane rating raises gasoline cost, and octane rating is kept to a minimum within the limit of confidence that the final blend will meet specifications. Ethanol addition enables reduction of the octane of the BOB produced at the refinery.

There are several processing options refiners can employ to increase octane but increasing catalytic reforming severity is the predominant octane management tool. Increasing the severity of the reforming process raises the reformate product octane, shifts yield from reformate to by-product LPG and hydrogen, and incurs additional fuel and miscellaneous operating costs. The incremental opportunity cost (revenue loss due to reformate to LPG/hydrogen yield shift) plus incremental operating cost per unit of increased octane establishes the marginal refinery gasoline octane cost.

From a molecular structure standpoint, the reformer increases octane by converting feed paraffins and naphthenes to high octane aromatics. Increasing refinery BOB octane will therefore result in a higher finished gasoline aromatic content.

Increasing or decreasing the level of ethanol use impacts final gasoline aromatic content and distillation characteristics. Increasing current market ethanol by 5% (moving to E15) will result in a reduction in gasoline aromatics and a shift in the ASTM distillation curve (see below) to the right. Initially, as E15 is introduced, E15 will be produced by blending 15% ethanol with the existing E10 BOB. In this case the impact of the additional 5% ethanol on aromatics will reflect only dilution effects, and the finished product will have slightly elevated octane rating. The distillation curve will shift further to the right (versus E10), resulting in significant T50 and T60 reductions.

Ultimately, in response to increasing E15 market share, refiners may shift to an E15 BOB to minimize refinery octane costs. For a 5% increase in ethanol content, the reduction aromatic content will be on the order of 3 to 4% while the change in distillation will be like blends with the E10 BOB. Aromatics will be replaced by paraffin/naphthene. There will also likely be a small reduction in olefin due to ethanol dilution effects. Reducing ethanol use by 5% (to 5% of US market share) would have the reverse impact on gasoline quality. Aromatics would increase (by 3 to 4 %) and the distillation curve would shift to the left. There may also be a small shift from normal to iso light paraffins as incremental isomerization processing is used.

EPA fuel quality trends reports demonstrate the historical impact of ethanol blending on gasoline aromatic and distillation parameters. Ethanol offers a high blending octane number. Between 2006 and 2016 gasoline ethanol content increased from 2.91% to 9.57%. The corresponding change in aromatics and other gasoline parameters to the historical addition of 6.7% more ethanol was accompanied by a reduction of 5.2% in aromatics, as shown below.

Parameter	Units	2006	2016
Ethanol	Vol%	2.91	9.57
Sulfur	PPM	49.2	23.1
Benzene	Vol%	1.04	0.58
Aromatics	Vol%	24.5	19.3
Olefins	Vol%	11.1	8.6
E200	Vol%	49.1	54.4
E300	Vol%	83.7	85.9
T40*	°F	177	155
T50*	°F	202	181

*Estimated, not reported by EPA

Table 1: Changes in US gasoline composition over a decade (EPA Fuel Trends Report)

EPA reported changes in 2006-2016 gasoline properties with increasing ethanol are not entirely attributed to ethanol addition. Other market/refinery changes occurred which resulted in increasing and decreasing influences on gasoline aromatics. Over this period, refinery gasoline production increased by roughly 7%, refinery processing capacities changed, gasoline exports increased (exports are of higher octane than BOB) and both gasoline sulfur and benzene were reduced (both requiring refinery octane enhancements). Nevertheless, the aromatic and distillation trends reported by EPA do attest to the general magnitude of anticipated change in aromatics and distillation with changes in ethanol use.

While history is not necessarily a predictor of future behavior, in the case of refinery processing and blending response to octane addition from ethanol, the structure of refinery gasoline blending and processing is such that adjustments in refinery octane will be dominated by reforming and the resulting impact on aromatics. The only other octane adjustment options are light naphtha blending, isomerization and alkylation. Due to blendstock supply, capacity limits and the impact on gasoline volatility, the first two options will have very little potential to influence overall octane adjustment.

Alkylation is more significant in terms of volume and octane contribution potential. But for economic reasons, alkylation will likewise not be a strong contributor to octane adjustment. Alkylation is one of the highest margin processes in the refinery and will be utilized at close to maximum regardless of changes in refinery octane requirements. The large difference in LPG and gasoline prices, due largely to growth in shale light oil/gas expansion, results in significant operating margin for the existing alkylation infrastructure. For 2018/19 market prices, alkylation net margins (product revenues, minus feed cost and minus operating cost) were \$30 to \$35 per barrel. If BOB octane targets are reduced, alkylation will continue at maximum capacity and the reduction in octane will be made elsewhere (reduced or less severe reforming). If BOB octane targets are increased (lower ethanol use) capacity and feedstock limits will preclude any substantial increase in alkylation. With alkylation already utilized at near capacity there is minimal opportunity for increased output from existing facilities. New capacity involves high capital costs, long construction lead time, and high confidence in market demand for investment. Although there has been a number of new projects recently, refiners have generally been conservative with regard to high cost alkylation investment projects, particularly with the prospect of longer-term reductions in gasoline demand.

Changes in ethanol use will continue to be reflected in gasoline aromatic content and in distillation. These properties need to be understood and incorporated into future test program planning and design. Also important are the species of aromatics included. Unfortunately, data in this area are not widely available and impacts of octane demand on aromatic species are not well documented. While it is believed that the proportion of light and heavy aromatics will not change dramatically with adjustments in reformer severity, additional research and understanding is needed in this area.

Although the EPA fuel trends reports provide details of the distribution of major gasoline properties, they do not document the various hydrocarbon groups or individual species. Limited DHA data are available in the public

domain to describe the individual hydrocarbon species in the fuel, although they may be used for fuel blending (EPA, 2014b). Data are available from the 2017 Texas survey, and include full DHA, and a more condensed grouping by hydrocarbon type and carbon number. Conclusions derived from this database are presented in Appendix I. Although all the data are for fuels at the E10 level, they provide valuable insight into composition and covariance of hydrocarbon groups for the study planner.

Prior Studies

Prior exhaust emissions studies including variation in ethanol content have been reviewed recently by Yang et al. (2019a, 2019b). Clark et al. (2019a) presented a review that identified causes of differences in conclusions between studies.

Zhao et al. (2019) observed that “[p]revious studies showed that burning of different levels of ethanol fuel in PFI engines and GDI engines would result in both an increase and decrease in PM and PN emissions.” Previous studies have not yielded unified conclusions with respect to regulated emissions and air toxics at the tailpipe and with respect to liquid, vapor and permeation losses contributing to evaporative emissions.

Clark et al. (2019a) documented causes for differences in conclusions between studies. Major contributors were the rapid changes in automotive technology in the last two decades, difficulty in measuring very low emissions levels, and quantifying even smaller differences due to fuel composition. Figure 1, a parity plot of NO_x emissions from repeat test runs on fuel-vehicle pairs, shows that even when fuel and controllable vehicle parameters are kept the same there may be large run-to-run variations. While some variation is expected due to measurement error, real engine and catalyst performance changes contribute as well. Other causes were the use of study variables such as aromatic content, where the molecular weight of the aromatics was not held constant, affecting PM formation.

Clark et al. (2019a) also observed that some fuels used in multivariate studies were atypical of market fuels found at the pump and commented on nonlinear properties of blending. Effects differ between altering ethanol concentration alone, and altering both ethanol concentration and aromatic content, reflecting market fuel composition. For example, a major study (EPA, 2013) yielded a model with a positive coefficient for ethanol alone regarding PM formation, but when the additional model terms for aromatics and distillation temperature were added, typical ethanol blends showed a PM reduction. The aromatic effect was derived using fuels with 15% and 35% aromatic content which is atypical of real-world fuels. Data from prior studies should be used with caution. When study models are used to compare emissions from two different fuels, it is important that the whole fuel composition is considered and that the model has the capacity to consider the composition in detail. This is discussed further in a recent paper (Clark et al., 2020).

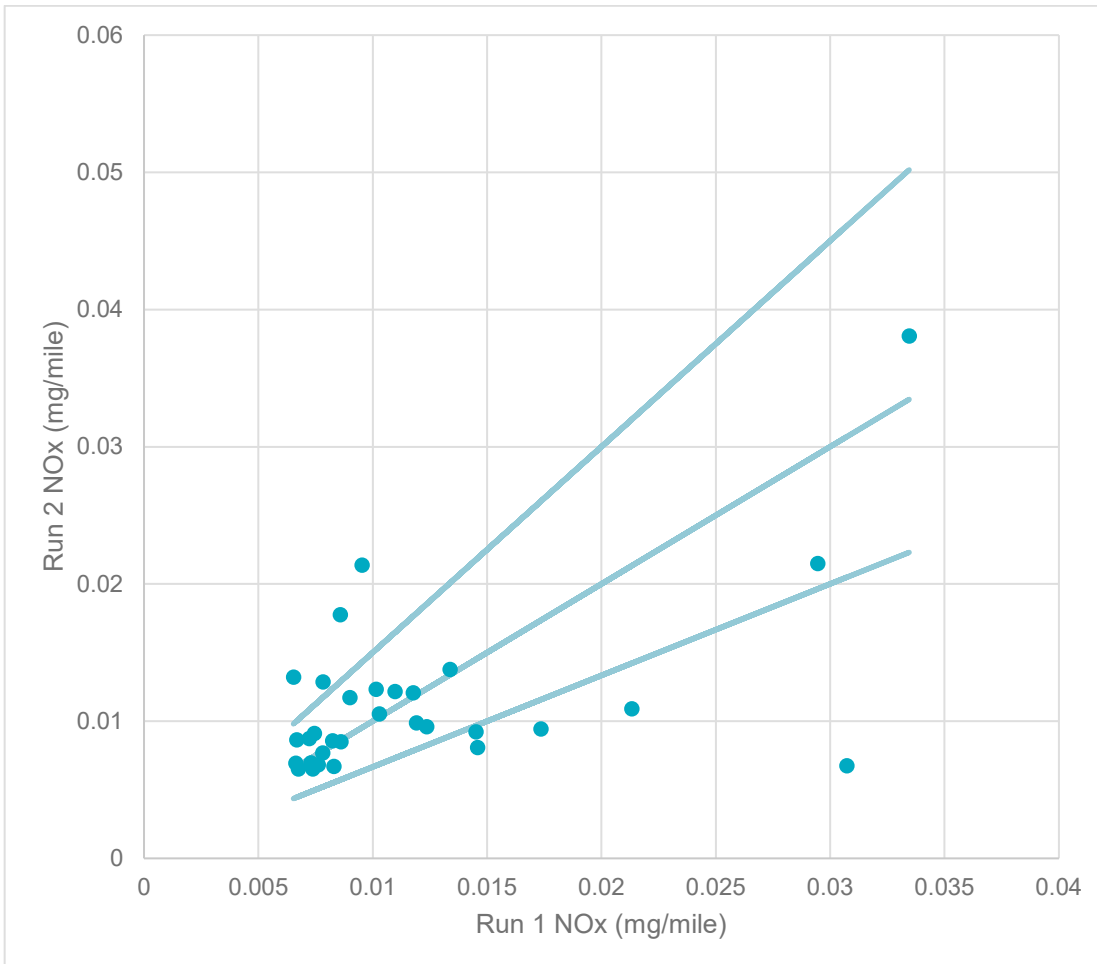


Figure 1: A parity plot showing the difference between first run and second run NOx emissions for Phase 1 of the E94-3 LA92 driving schedule. The diverging lines represent 50% above and 33% below the parity line.

Influence of Vehicle Technology

The US light duty fleet has an average age of 11 years. Vehicles from the beginning of the millennium, still in the active fleet, used PFI. To meet more stringent emissions standards, while satisfying fuel economy standards, manufacturers improved engine control strategies and use of exhaust gas recirculation and implemented variable valve timing and actuation. Improved catalyst technology, supported by lowered sulfur levels, has reduced emissions of CO, HC and NOx to near-zero levels during hot engine operation. PM emissions from PFI engines have been low due to the homogenous air-fuel mixture. PFI vehicles still account for more than half of the US light duty fleet.

GDI engines offer improved fuel efficiency (Chincholkar and Suryawanshi, 2016; Conway et al., 2018). Saliba et al. (2017) reported a 14.5% carbon dioxide reduction of GDI versus PFI for their test fleet. When turbocharged, GDI engines have high power density, and are downsized in displacement relative to PFI engines. GDI is also

successful because the quantity of fuel delivered to the cylinder is well controlled relative to PFI. Multiple in-cylinder injections can be employed. Engines with both PFI and GDI are also produced (Han et al., 2018; Fanick et al., 2019). Controls for these late model engines are more complex than for the PFI engines.

GDI tailpipe emissions of PM are reported as higher than for PFI engines (Zhang et al., 2012; Zhu et al., 2016; Xing et al., 2020). PN also is high (Raza et al., 2018). Saliba et al. (2017) observe that “GDIs had, on average, a factor of 2 higher particulate matter (PM) mass emissions than PFIs due to higher elemental carbon (EC) emissions.” However, they further observe that SULEV certified GDI vehicles showed decrease in PM. The PM arises from the short time period available for droplet evaporation with late injection. GDI may employ either wall guided or spray guided injection. Spray guided injection is less common but appears to offer advantages for PM reduction. Yang et al. (2019b) summarize that “[g]asoline composition can also play a critical role in the combustion process of GDI engines because of its influence on fuel spray development, which will ultimately affect pollutant formation.”

Figure 2 shows the emissions measured by four different major fuel effects studies, as reported by Clark et al. (2019a). The studies present substantially different distance-specific NO_x and CO emissions, representing changing emissions standards and advancing technology.

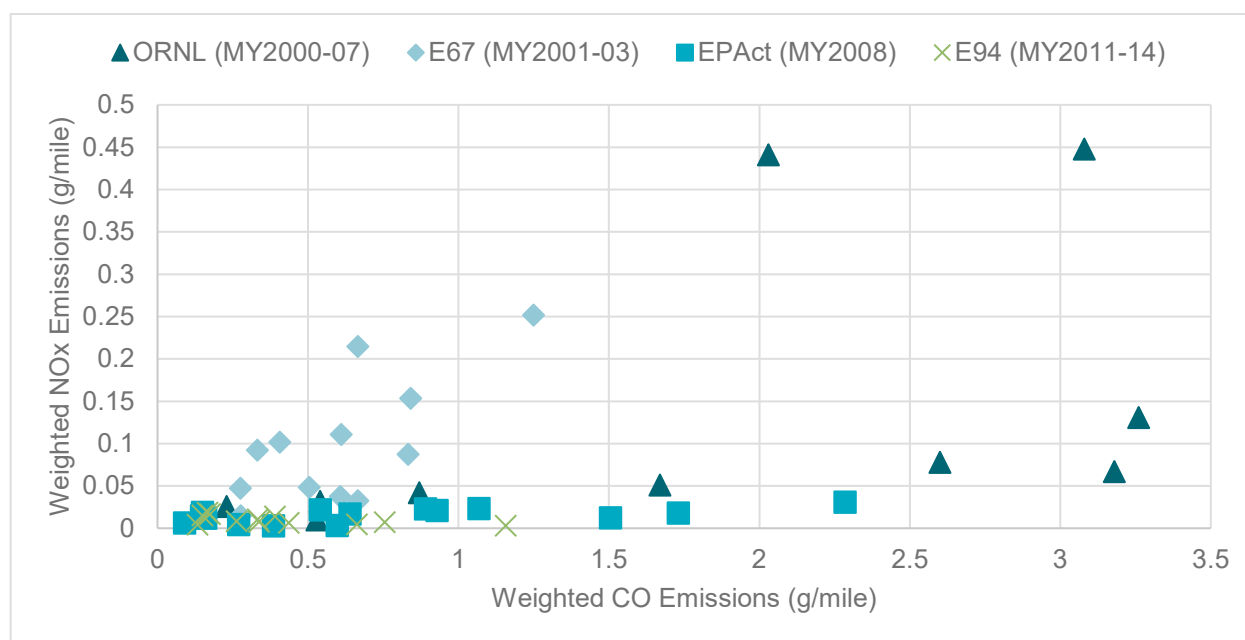


Figure 2: NO_x-CO emissions envelopes for four studies of different model year vehicles.

Influence of Study Vehicles

The CRC E94-2 study compared PM emissions from an E10 fuel and an E0 fuel, both with similar low AKI and low PMI. The data from all 12 PFI vehicles in E94-2 showed a 19% increase in PM for the E10 in comparison to

the E0 fuel. The data from a subset of four vehicles showed 53% increase with E10. When one of the four vehicles was excluded for cause, the difference was 44%.

CRC program E94-3 compared E0 and E10 in a splash blend using four vehicles. The PM increase for E10 was 29%. When one vehicle was excluded for cause, the increase was 23%. The E-129 study reblended the E-94-3 fuels and found a decrease of PM of 10% for E10 with a different four car fleet.

A recent study by Yang et al. (2019a, 2019b) employed five vehicles. For a comparison of E10 emissions to E0 emissions on Phase 1 of the LA92 cycle, three vehicles showed PM increases, and two showed decreases. For E15 versus E0 PM emissions, two showed increases, and three showed decreases. These results, and other data for PM and gaseous pollutants, suggest that the fuel response varies strongly between vehicles in studies. Figures 3 and 4 present gaseous NO_x emissions and percentage differences between NO_x emissions two fuels for vehicles in the study of Yang et al. (2019a), demonstrating different responses between vehicles. Similarly, Figure 5 presents the percent difference in NO_x emissions for four vehicles on four different fuel pairs: each pair consisted of an E0 fuel and E10 splash blended from that fuel. Both vehicles and E0 fuels show influence on the emissions difference.

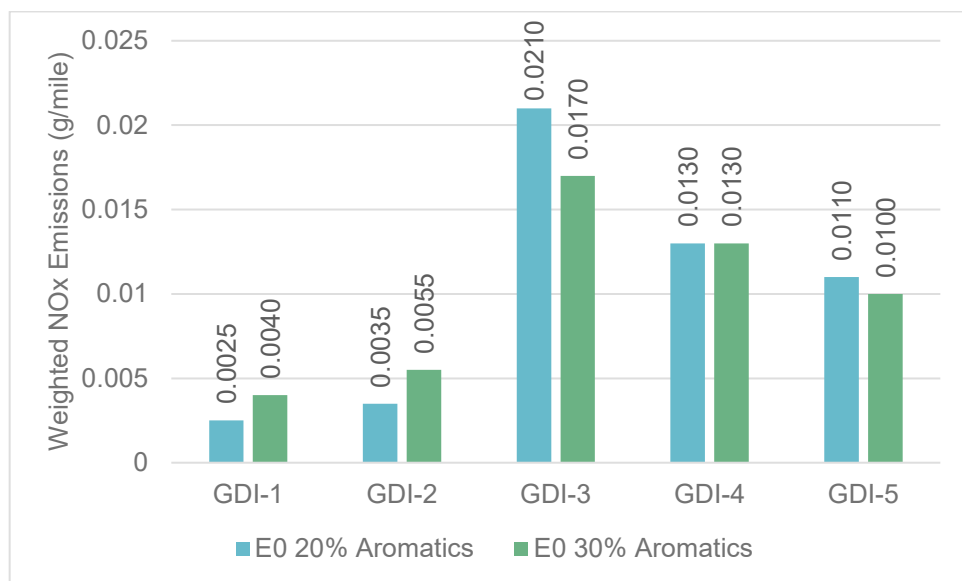


Figure 3: Data from Yang et al. (2019a) for five GDI vehicles on two fuels using the weighted LA-92 cycle. Distance-specific emissions vary between vehicles operated on two zero ethanol fuels with different aromatic levels.

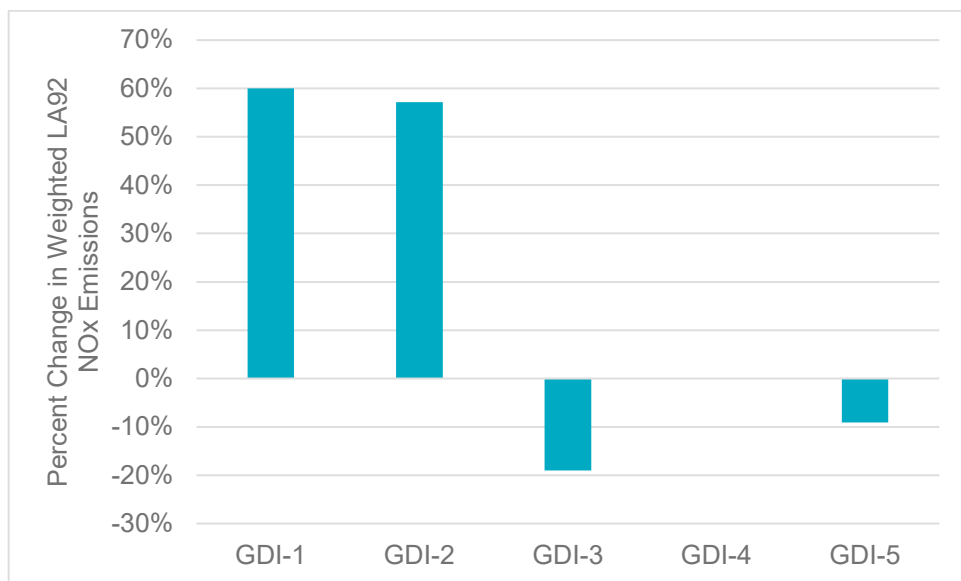


Figure 4: The data from Figure 3 presented as percentage change in NOx emissions caused by moving from 20% aromatic to 30% aromatic fuel, for the five GDI vehicles used in the study (Yang et al., 2019a). Vehicle GDI-4 showed no appreciable change.

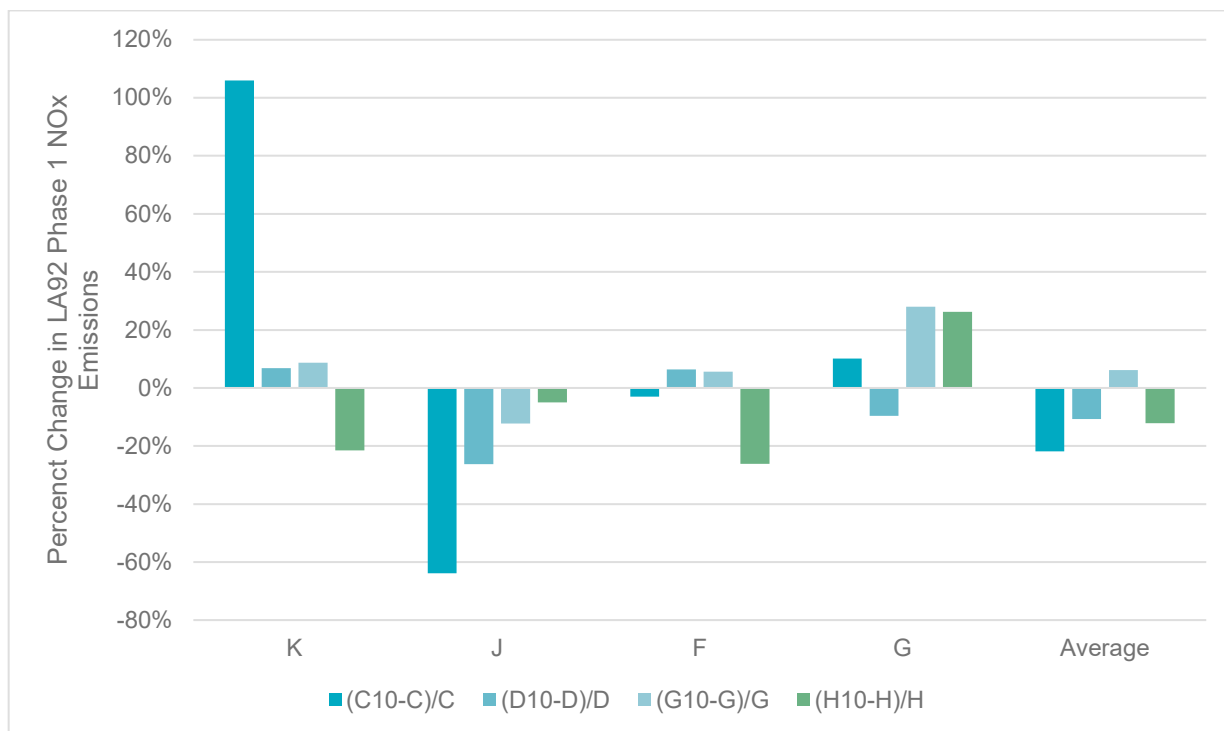


Figure 5: NOx differences as percentage change between E0 fuels and a splash blended E10 fuels from four vehicles and four E0 fuels used in the CRC E94-3 study. Each fuel set shows for percentage values, representing four different vehicles.

A reviewer of the EPACT study also commented on use of models to predict fleet emissions: “Because vehicles will naturally age and may respond differently to fuel properties, these relationships may not continue to hold true.”(EPACT Peer Review, 2012) In this way, vehicles of different age or mileage may differ in response, echoing the technology influence.

Conclusions are that each vehicle in future studies should have additional, repeat emissions tests to blunt the effects of run-to run variability. Re-testing selected vehicles twice on the same fuel would assist in separating test-to-test and vehicle-to-vehicle error. Also, future studies should employ a sufficient number of vehicles to account for vehicle-to-vehicle variability or recognize vehicle technology and controls groupings. Study conclusions should be explicit that their results should not be extrapolated to different vehicle technologies. Users of models should be cautious that they consider all likely changes in fuel composition when computing emissions differences from two fuels with different ethanol levels for real-world predictions.

Properties Not Aligned with Technology

Gasoline is characterized by several diverse parameters, some of which report on composition, but most of which are properties determined using a standard test. Content of sulfur and oxygen are often reported, along with benzene and total aromatic content. Measured properties include Reid Vapor Pressure (RVP), Distillation (often only T10, T50 and T90 are reported), Anti-knock indices, such as the Motor Octane Number (MON) and Research Octane Number (RON), and a Driveability Index. ASTM D4814 provides specifications expected of gasoline. Various federal, state and regional rules govern gasoline composition and properties, typically with the objective of improving air quality

Bundled gasoline parameters, such as the Particulate Matter Index (PMI) and Particulate Evaluation Index (PEI) (Aikawa et al., 2010; Chapman et al., 2016; Zhao et al., 2019) weight species from detailed hydrocarbon analysis (DHA) (e.g. ASTM D6729) to predict a fuel’s propensity to form PM at the tailpipe. These have been used as study variables, and to blend fuels to PMI targets for emissions measurement (e.g. for CRC E-94 studies). However, such indices may not anticipate the complexity and variety of fuel composition and engine technology effects (Sakai and Rothamer, 2019; Kalghati and Stone, 2016). Fatouraie et al. (2018), in explaining low correlation of particle number with PMI observed that “oxygenates.....are not explicitly accounted for in the calculation of PMI. There may also be other factors that are not captured by PMI such as density, viscosity, and surface tension and their effect on fuels spray penetration, spray angle and breakup, as well as ΔH_{vap} .” Normally, for market gasoline, one might expect PMI to be higher when fuel aromatic content is higher, but prior fuel effects studies have differed in the way fuels were blended, leading to disparate PMI-aromatic relationships, and assignments of PM in models variously to aromatics and to PMI.

Leone et al. (2015) questioned using the CFR engine (used to measure RON and MON) to describe knock resistance in modern engine designs. In fact, an ASTM manual observes that “[f]reedom from knock in service depends on many factors and cannot be predicted accurately from a single engine test of the fuel. The reasons for this are obvious as knock, as such, is strictly an engine-fuel relationship.” (ASTM, 1948). Knock is generally acknowledged to occur following an incubation period of an air and fuel mixture at elevated temperatures and

pressures. While RON and MON values reflect an incubation period of this kind, and may correlate with other time histories of temperature and pressure, it is unlikely that operation of an engine, designed in 1929, and operated at 600 rpm and 900 rpm can quantify knock propensity reliably in modern engines employing high boost and GDI. Hoth et al. (2019) have offered further criticism of CFR RON measurement due to air/fuel stoichiometry.

Fuel properties should be used with caution as study variables and to define blends. These properties depend on fuel composition, which is to be preferred as a source of parameters. However, it is appreciated that some properties, such as octane rating and RVP, are specified as product controls, and that those parameters may define the fuels that are used regardless of their ethanol content.

Complexity of Blending Gasoline

While there are only 18 isomers for C8 paraffin, there are 4,347 for C15 (Read, 1977), so that distillate characterization is more difficult than gasoline characterization. Some gasoline single components are present in substantial quantity at low boiling points, but the heavy ends of gasoline are more complex. Wu (2010) describes the difficulty of determining and characterizing the myriad of compounds.

Gasoline behavior is characterized by the nonlinear properties of mixing of different hydrocarbon groups and of hydrocarbons and ethanol. Several examples of nonlinearity are presented below.

Toluene, n-heptane and iso-octane do not blend linearly with respect to octane rating (Morgan et al., 2010). Wu (2010) stated that “different mixing rules should be built up to calculate the properties of the mixture based on the properties of pure compounds.” Ghosh et al. (2006) explored positive and negative nonlinearities and required 57 gasoline molecular “lumps” to develop a prediction for RON and MON of commercial gasoline. Waquas et al. (2018) have examined blending effects of ethanol and toluene as octane sources.

Pure ethanol has an anti-knock index (AKI, the average of Research Octane Number, RON, and Motor Octane Number, MON) of about 99 (Foong et al., 2013), but a blending anti-knock index that is far higher. Further, blending octane rating varies with the quantity of ethanol that is blended: for 10% ethanol gasoline ethanol exhibits a RON of approximately 128. When an additional 10% ethanol is added to yield E20, the incremental ethanol octane blend value drops to 122 RON.

Planners should be cognizant of laboratory to laboratory differences in measurement of fuel parameters, whether they are concentrations of components or fuel properties. The CRC study E94-2 presents analyses of the same fuels by several laboratories and exhibits these differences. For Fuel C, RON differed by 1.4 between two laboratories, aromatic content differed by 4%, RVP differed by 0.7 psi and T10 differed by 9.1 degrees. Relative measures, from the same laboratory, are likely more reliable than absolute measures. Ethanol blending distorts the distillation curve, as discussed in more detail in the next section.

Pure ethanol has RVP of 2 psi (13.8 kPa) whereas gasoline typically is blended to have an RVP of 7 to 12 psi. However, addition of 10% ethanol typically increases the base gasoline RVP by 1 psi to 1.2 psi. When an additional 10% ethanol is added to the blend, the RVP of the 20% blend is lower than that of the 10% blend and the resulting E20 is about 1 psi above the base blend.

The vaporization enthalpy for gasoline-ethanol mixtures varies in an unexpected fashion as the ethanol percentage rises (Kar et al., 2008). Other properties of mixing are discussed in detail in an American Petroleum Institute report (API, 2010).

The blending guide must address the complex composition of gasoline, but it is necessary to use composition grouping by weight and type to avoid an excessive count of parameters. Use of too few composition groups in comparing blends introduces inaccuracy due to nonlinear blending behavior.

Distillation and T50

The purpose of distillation of gasoline is to reveal the spectrum of boiling points of the constituent species. The ASTM D86 distillation standard method yields a smoothed distillation curve that does not provide a high degree of fractionation (Owen & Coley, 1995). Typically, T10, T50 and T90 are reported, providing a loose representation of the lightest, mid-range and heaviest components. Boiling points vary by hydrocarbon type as well as molecular weight: benzene boils at 176.2 degrees, while hexane boils at 154.4, though both have similar molecular weights and six carbon atoms. Further, there is nonlinear behavior in the fractionation due to molecular interactions. Excess energy is associated with the mixing of alcohols, aromatics and saturates. Other reference data that are determined from distillation express the fraction of the gasoline that has been distilled at a specific temperature. Using degrees Fahrenheit, E200 and E300 are commonly reported, as percentages.

Ethanol boils at 173 degrees F. Ethanol, even at very low blending levels, raises gasoline volatility and suppresses distillation temperatures T20 and T30. E10 also affects T40, but its effects on T50 are dependent on the composition of the gasoline and are difficult to estimate. In particular, a BOB with a lower mid-range volatility sees more suppression of the T50 value for E10 and E20, as shown by Anderson et al. (2014). This change in the distillation curve is not simply due to the physical distillation of a single component in the mixture, but rather exhibits a near-azeotropic behavior. E30 affects T50 and T60 and can affect even T70.

An API report presented details of the distillation curves from ethanol mixtures with a wide range of gasoline classes, and paid specific attention to T50 (API, 2010). Some of the blends, at the E10 level, showed a T50 that was not markedly different than for the baseline gasoline. Others showed T50 reduced by about 50 degrees, with many E10 T50 values around 150 degrees. Some heavier gasolines, particularly premium gasolines, showed the effects of ethanol on T50 to vary widely between blends. The report observes that “[f]or the low T50 base gasoline, the largest depression in the distillation curve occurs roughly between the 62% and 85% evaporated points, depending upon the amount of ethanol in the blend. For the high T50 fuel, the largest

temperature depression occurs between the 45% and 70% evaporated points, again depending upon the amount of ethanol in the blend.”

Figure 6 shows an exemplary distillation curve, where T40 and T50 differ substantially for an E10 blend. The E10 ethanol suppresses the curve over 40% of the distillation volume even though it is only 10% by volume. Higher blend levels lower the curve over progressively wider ranges.

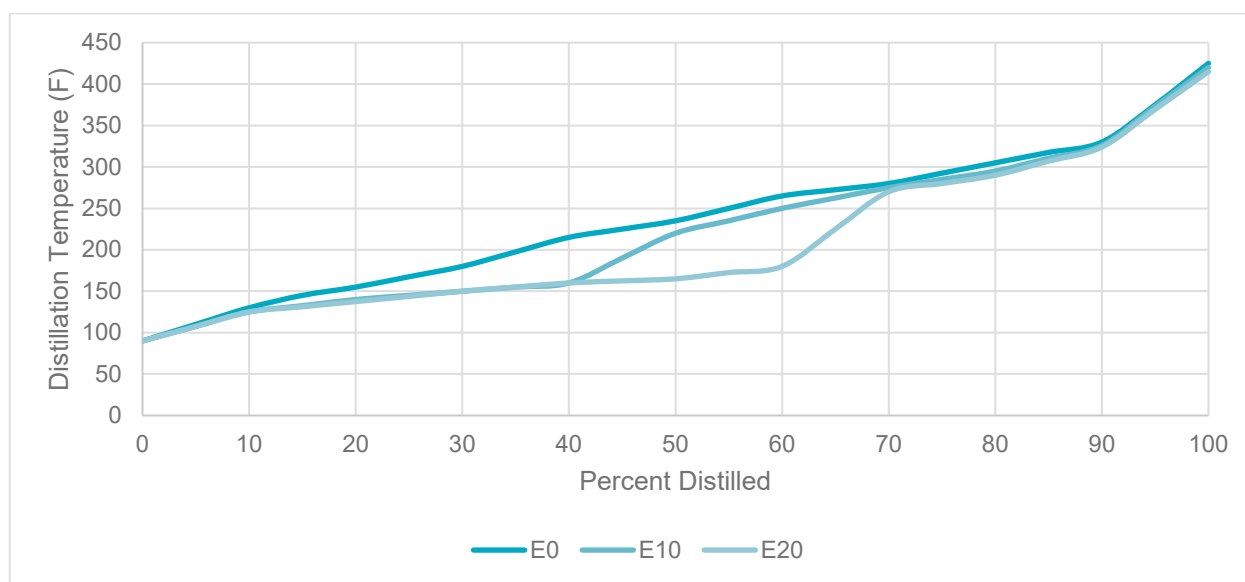


Figure 6: Example of the effects of ethanol data on the distillation curve. Data plotted from API (2008).

There is, therefore, a difficulty in using T50 as a study variable for a blend. First, due to nonlinear blending behavior, the T50 presents different information for an E15 blend than for a purely petroleum gasoline. It is similar for an E10 blend, except for fuels with very low mid-range volatility. Although the distillation curve changes for the ASTM D86 protocol when ethanol is added, there is no assurance that the T50 change specifically is relevant to the rapid processes and high heat fluxes in the combustion chamber of an engine. The distillation curve for an ethanol blend is very steep at the higher end of the temperature suppression region. E30 distillation curves show changes of 70 degrees for just 2 or 3 percent of distillation. For E10, this high rate of change can occur at or near the T50 point, with slopes of 5 degrees per percent of distillation. One might argue that T55 or T45 could be used equally well as T50 as a mid-level descriptor, but in many cases T45 or T55 may differ substantially from the T50 point and from T50 differences between blends and ethanol free gasoline. These arguments do not apply to the use of T50 to describe a petroleum BOB.

There is a further concern over the relationship between T50 and E200 for cases where T50 is not available. For ethanol free gasoline, the distillation temperature varies in a fairly linear fashion with the percentage that is distilled, with a slope of around 2 degrees per percent of change. Therefore, for E0 it is usually reasonable to predict T50 from E200, using a linear model, and this method, with a presented correlation, is used in preparing inputs for the MOVES model (EPA, 2017).

This dependency of T50 on E200 is questionable for ethanol blends. First, for E15 and E20 blends, the API study plots show, with rare exception, that the T50 value lies between 150 and 165 degrees F, dictated by the interaction of the ethanol. There is low dependence of an E15 or E20 blend T50 on the original T50 of the petroleum blendstock. E10 presents a far more difficult case, because in some instances its T50 resembles the T50 of the petroleum blendstock, while in others, it is influenced strongly by the ethanol, and approaches 150 degrees. In some cases, the distillation curve is at the higher end of the ethanol effect, where temperature varies substantially with percentage distilled. For these cases it is clear that T50 cannot be predicted reliably for E10 blends using E200 data, because the relationship is not linear, and reliable correlations do not exist. The EPA presents ethanol adjustment factors for T50 for E15 and E10 summer and winter fuel. These will not be sufficiently accurate to enable the use of a translated T50 as a study variable.

The D86 distillation rate is prescribed as 4ml to 5ml per minute for a 100ml fuel sample. It is also a standardized and precise process, but not accurate as to temperature. The method cautions “Due to the configuration of the boiling flask and the conditions of the test, the vapor and liquid around the temperature sensor are not in thermodynamic equilibrium. The distillation rate will consequently influence the measured vapor temperature. The distillation rate shall, therefore, be kept as constant as possible throughout the test.” In contrast, an injected droplet in a GDI engine is subjected to high temperatures and shear and must evaporate in as little as 2 or 3 milliseconds, with rapidly changing and spatially varying composition. This droplet evaporation is not uniquely dependent on volatility, but also on the heat of vaporization of the fuel, which is not traditionally considered as a study variable. In GDI engines, flash boiling arises when the pressure in the cylinder is lower than the saturation vapor pressure of the liquid. This complex “internal boiling” phenomenon serves to break up fuel jets from the injector or destroy the orderly evaporation of droplets (Mojtabi et al., 2008; Wood et al., 2014; Baldwin et al., 2016), and is far removed from the processes of the D86 distillation.

Engine Operating History and Conditioning

There is general acknowledgement of the need to condition vehicles to avoid bias introduced by the vehicle’s historical use. For example, most studies have ensured that the fuel used in the test is not contaminated by previously used fuel. The vehicle should also be operated on a new fuel for sufficient time to achieve stable, repeatable emissions before gathering data for the study record. The CRC E94-1 report addresses these issues, while the EPACT Program Design report (2013) documented a conditioning plan that was augmented. Spark-ignited engine controls adapt to changing fuel properties. There are adjustments to fuel trim in response to the stoichiometry reported as a transient voltage signal by the oxygen sensors. This facilitates future stoichiometric air/fuel management when the engine employs an open loop strategy. The engine adapts when it is refueled with gasoline having a different composition, as with E0 vs. E10, or due to other variations in carbon-hydrogen ratio and oxygenate content. Long-term fuel trim accounts for fuel stoichiometry changes, ageing of an engine and minor engine malfunctions. It is a matrix of values in engine speed and load (typically manifold air pressure) and is updated based on short term trim when the engine operates at each speed and load. Most engines will update long term trim fairly rapidly, but if an engine is conditioned over repeated runs of a first

cycle, and then operated on a second, different cycle, it is possible that the engine may still operate with long term trim from the prior fuel because the first cycle has not readjusted the whole matrix.

In a test of catalyst deterioration, West et al. [4], in a major study of ethanol blend effects, described that some vehicles employ long term fuel trim at wide open throttle, while others do not, leading to differences in stoichiometry (changes in enrichment) and exhaust temperature.

The CRC E-129 program found that one study vehicle exhibited a wide range of trim for four of the oxygenated fuels that were examined. These are valuable data to aid in interpretation of emissions changes. This same vehicle also exhibited emissions drift.

A vehicle's engine adopts an ignition timing strategy based on knock incidents reported by the knock sensor. Engine controls seek to run at best torque while avoiding knock. As with stoichiometry, conditioning must ensure that spark timing has adapted to a new fuel. Further, engines with the same octane rating may differ in knock resistance at different engine operating conditions, as evidenced by fuel sensitivity to difference in RON and MON CFR engine conditions.

Turbocharged GDI engine controls are complex, and seek to provide good fuel economy and satisfy power demand in various parts of the engine map (see, e.g. Stein et al., 2013, di Gaeta et al., 2011, Shuai et al., 2018, Singh, 2018, and Wei et al., 2012). Strategies will differ between steady state and transient power demands. A great deal of hardware may be governed, including boost, EGR flow, an intake throttle, variable valve timing, variable valve duration, spark timing, and stoichiometry. The controls may include multiple injections and the use of both port and direct injectors (Han et al., 2018; Fanick et al., 2019). Further, transmissions with a high number of ratios work hand in hand with the engine to provide performance and emissions compliance. It is unclear for any specific vehicle which strategies are or are not altered, directly or indirectly, for varying fuel composition and speed, which strategies are adaptive, how long it takes for strategies to change, and if they are changed at all loads and speeds. Lastly, the fuel influence may be interactive with both ambient temperature, and critical engine temperatures, such as those of the coolant, head and oil.

In another sense, even if fully stabilized, the engine may assume a different control posture with two different fuels. For example, a fuel with higher in-use knock resistance (as opposed to octane rating) is likely to elicit more advanced timing under high torque operation, which would increase engine efficiency. This may also raise engine-out NO_x, but tailpipe NO_x will be governed by the catalyst. Advanced timing may also decrease exhaust temperature, which may be beneficial for catalyst protection at high loads. The vehicle in many major fuel effect studies has been treated as a "black box." Since there is no attempt to manage the engine externally, emissions changes attributable to engine controls will be attributed to the fuel or a "fuel*vehicle" higher order parameter. Vehicle engines are likely to see fuels in studies that deviate from the fuels on which non-adaptive controls were calibrated, which may lead to control responses that are not fully optimized for an unseen fuel. Lower volumetric energy content of the fuel will also alter injection duration, which may affect physical fuel evaporation in GDI engines. Engines may show different emissions performance if designed and calibrated by the OEM with those fuels in mind.

Although these issues related to stoichiometry and knock may seem trivial, they should be considered in the light of the small changes in emissions associated with many of the fuel property changes. In addition, if the study results are to be used to model regional or national fleet performance, it is important to consider the general technology and control strategy of each vehicle, for proportioning the results to the fleet. Differences in vehicle effects may be attributed to differences in hardware and controls.

Deposits in Engines

Sakai and Rothamer (2019) have discussed the ability of ethanol to dissolve engine deposits and note that it “is worth keeping in mind when considering data from studies comparing ethanol-gasoline blends at varying blend levels.” (Sakai and Rothamer, 2019). Engine and injector deposits are of concern in many GDI engines and use of ethanol is presented to reduce injector fouling (Wang, 2014). Vilaro et al. (2007) compared numerous BMW intake valve deposit measurements between E0 and E10, concluding that E10 deposits were higher in mass. However, higher ethanol levels reduced the deposit formation (Vilaro et al., 2007). Schwahn and Lutz (2010) reviewed ethanol blend deposit studies and discussed the use of additives and additive concentration. They found that higher ethanol levels produced lower deposits than E10, both with and without additives. The literature on engine deposits often is anecdotal or specific, but certainly acknowledges fuel and additive effects. With direct regard to PM, and regarding emissions affected by valve or injector deposits, it is important to determine whether the deposits are formed or removed by changing fuels. There is widespread documentation that gum and deposit formation is attributed to olefins (Worldwide Fuel Charter, 2013).

When two blends have different deposit formation characteristics, it will be important to assess whether there is an influence on emissions due to depositing, cleaning, or engine performance effects.

Assignment of Effects to Parameters

Variables to be used for statistical analysis or modeling typically are identified during the planning stages of a study. For multivariate studies, these variables are usually employed as fuel blending targets as well.

Subsequent analysis will ascribe emissions variation only to the variables chosen and to selected combinations of variables. Residual variability will be assigned to unknown sources (that include measurement variability). If other fuel properties vary but are not employed as statistical variables, their effects will be assigned to variables that correlate or anti-correlate with those other fuel properties. The statistical analysis cannot identify cause, only correlation.

As an example, if heavy aromatics cause PM, but only total aromatic content is used as a study variable, then replacing light aromatics with heavy aromatics in the fuel will not be identified as a cause. Co-variance is of critical importance in this discussion. If two variables always change in lock-step, either may be used as the study variable, and the cause need not be divided between them.

It is not obligatory to use time-honored ASTM properties as study variables, particularly when ethanol may cause substantial non-linear changes in those properties, with uncertain linkage to real-world emissions behavior. However, ASTM parameters such as octane rating and RVP are likely to be used as a requirement in comparing two fuels. Detailed spectral hydrocarbon analysis has become more accurate, more rapid and less expensive over the last decade, and supports rapid blending. It is preferable to consider real measures of molecular weight and type as study variables rather than parameters that are affected by ethanol blending in a way that may not be relevant to combustion in the engine.

PMI is calculated from spectral analysis, yielding one variable, but many different formulations exist with the same value of PMI. However, fuels can be described by a number of composition descriptors to constrain fuel variability. It is not necessary to present every species in a DHA. For example, a fuel is reasonably constrained in its properties if it must match the following parameters that balance importance of structure, molecular weight, and typical content in gasoline.

- Butane
- Light straight chain paraffins (C5 to C8)
- Heavy straight chain paraffins (C8+)
- Four to six descriptors for iso-paraffin groups
- Light aromatics (C6 to C8)
- Mid aromatics (C9 and C10)
- Heavy aromatic (C10+)
- Olefins
- Napthenes

At a granular level, it would also be assumed that each of these groups would represent an expected spectrum of a refinery stream. As examples, the distributions of the iso-paraffins should reflect real-world isomerate and alkylate species, and the C9 and C10 aromatic group would not consist entirely of o-ethyltoluene. These parameters, or molecular groupings, could be changed or reduced in number for studies with a specific, limited objective.

In most studies, octane rating would be defined for the candidate fuels, and would be a study parameter only if low- and high-octane fuels were being compared. Some properties of the fuel, such as octane rating, may be difficult to predict for a composition that is not very tightly defined (i.e. defined by too few variables). For iso-paraffins anti-knock properties vary substantially with structure, as shown in the following list of C8 paraffins (Demirbas et al., 2016):

Hydrocarbons	RON	MON
n-Octane	0	0
2-Methyl heptane	21.7	23.8
3,4-Dimethyl hexane	76.3	81.7
3,3-Dimethyl hexane	75.5	83.4

Hydrocarbons	RON	MON
2,2-Dimethyl hexane	72.5	77.4
2,2,4-Trimethyl pentane	100	100
2,3,3-Trimethyl pentane	109.6	99.9
2,3,4-Trimethyl pentane	102.7	95.9
3-Ethyl Hexane	33.5	52.4

Table 2: Anti-knock properties for C8 paraffins

Also, as an aromatic example, o-Xylene offers a substantially lower octane number than m-Xylene and p-Xylene.

Detailed information has been presented in the literature addressing octane ratings (Kubic, 2016). RON and MON also differ between references. Furthermore, species may imply different RON and MON when blended with different mixtures of other hydrocarbons. These values are known as blending octane numbers. Ethanol has a substantially higher blending value than it exhibits as a neat alcohol, as discussed above.

Actual Vehicle Operation

Real-world impact of a change in fuel composition requires an assessment using relevant vehicle technology, as described above. The test fleet may represent the in-use distribution or may be forward looking, using only the most recent mix, or even a mix of the most advanced current technology. Results are not readily translated between technology eras or between nations with differing emissions rules.

It is equally important to measure the emissions from the vehicles at engine speeds and loads that reflect the way they are operated in real on-road use if the objective is to predict real impact on emissions inventory. Alternately, one may employ separate test schedules for low power and high power operation, and weight the results to reflect the real-world use.

Low power and high power operation will elicit different behavior from the powertrain. With turbocharged GDI vehicles, high power operation implies higher boost and engine speeds. The engine may encounter knock limits that cause ignition timing retard. Emissions formation is non-linear with respect to in-cylinder temperature and pressure, and with respect to engine speed. It is therefore inaccurate to attempt an adjustment of low-power emissions differences for application to high power operation.

If the objective is to determine the emissions differences for a specific certification cycle, then the objective differs from assessing real-world impact on air quality.

Evaporative Emissions Studies

There have been fewer studies of light-duty gasoline evaporative emissions than tailpipe emissions, but the fuel and vehicle interaction is equally complex. Evaporative emissions encompass liquid leaks, vapor leaks and venting, fugitive vapors and spitback (liquid) from refueling, and permeation (EPA, 2014a). The liquid and vapor have different compositions and different ozone forming potential (Passavant, 2015). Until 1998 for gasoline fueled light-duty vehicles and trucks, the EPA regulated the mass of hydrocarbon loss during a 1 hour soak test. Starting with a 1996 phase-in, enhanced evaporative emissions were determined using two day and three day diurnal tests and running losses. On-board refueling vapor recovery requirements began with a phase-in in 1998. Permissible levels of fuel loss steadily decreased over the Tier 2 emissions period. Tier 3 requirements have been added, along with evaporative emissions OBD requirements and a transition to the use of EPA Tier 3 fuel for testing (EPA, 2014 and see 40 CFR § 86.1813-17). A document by Haskew (2001a) reviews early studies.

The Coordinating Research Council contracted the E-65 and E-77 evaporative emissions programs. E-65 employed vehicles with model years between 1978 and 2001, representing the in-use fleet in 2002. E-77 used vehicles with model years 2000 to 2004. The E-65 study (Haskew et al., 2004) employed three fuels, with 5.86% ethanol, 10.5% MTBE with 1.12% TAME, and oxygenate free gasoline. These fuels were obtained commercially, then adjusted to match RVP, T10, T50 and T90. The E-65 report included conclusions that ethanol in the fuel increased permeation rates and that permeation of hydrocarbons increased as a result of the ethanol addition. However, it is not clear that distillation parameters are appropriate properties to match for assessing permeation effects. Rather, permeability, solubility and diffusion of species varies by molecular type as well as weight, with complex interferences between species. Temperature, pressure, concentration, molecular weight and molecular type (polarity) all affect the process: a recent study unrelated to evaporative emissions provides insights (Ewender and Welle, 2019).

The E-77 Pilot Study (Haskew & Liberty, 2008) presented that “[d]iurnal vapors and permeation were thought to be functions of ambient and vehicle temperature and fuel composition. Emissions from leaks are not thought to be a property of the fuel.” The E-77-2 study (Haskew & Liberty, 2010a) examined three fuels from an earlier program, (E0, RVP 7psi), (E10, RVP 7psi) and (E20, RVP 9psi). Butane was added to produce 9 psi E0 and 10 psi E20 as additional fuels. AKI was similar for all three base fuels. Aromatics were higher for the E10 fuel than the E0 fuel, which does not generally reflect market trends, and lower for the E20 fuel than the E0. T50 was similar for the E0 and E10. Higher permeation rates were found with ethanol and E10 had the highest hot soak emissions value. An add-on study E-77-2b (Haskew & Liberty, 2010b) used the same (E0, RVP 7psi) and (E10, RVP 7psi) fuels, and used butane to produce (E0, RVP 9psi) and (E10, RVP 10psi). Permeation was reported to increase with increasing ethanol, but vehicles meeting stricter standards were insensitive or less sensitive to the ethanol presence. Haskew and Liberty (2010c) presented the E-77c report that addressed RVP effects for E20.

Haskew and Liberty (2011) also conducted the CRC E-80 program, which examined E6, E32, E59, and E85, prepared by blending commercial E6 and E85 fuels. Vehicles were of 2006 and 2007 model years. Four vehicles were examined for evaporative emissions running losses on two LA92 cycles, a one hour hot soak followed by an FTP schedule, and a two day diurnal test. The vehicles differed in behavior. There was no trend

for running loss tests or hot soak tests regarding ethanol content. Diurnal results showed an increase on the first day, but not the second. Responses varied between vehicles.

Permeation studies have not compared gasoline blends that may be expected in the marketplace. Reddy (2007) declared that several prior permeation studies did not address hydrocarbon type, and used "Fuel C," which was a 50:50 blend of toluene and isooctane. Haskew (2001b) used Fuel C to conclude that 10% ethanol blending reduced permeation rate for one plastic but raised it by varying amounts for 12 others. Reddy (2007) examined the permeation of pure hydrocarbons through high density polyethylene (HDPE), finding effects of molecular size and solubility in HDPE. Mixtures of paraffins showed a linear permeation response, but blends of toluene and pentane permeated at rates higher than either constituent. Reddy continued by studying permeation of 32 test fuels through HDPE. Both RVP and aromatic content were varied, and a model was developed. Conclusions were that a 10% increase in aromatics led to 35% higher permeation and that doubling the RVP raised permeation by 46%. Reddy additionally reported that addition of ethanol to 30% aromatic fuel reduced permeation through HPDE substantially.

A conclusion is that data are still needed to provide reliable effects of market fuel composition on permeation rates, and that the fuel composition and type of plastic have profound effects on that rate.

Splash Blending

Commercial fuel production of ethanol blends is accomplished by splash blending at the terminal because ethanol is unsuited to pipeline transportation. Ethanol can be added to finished gasoline or blended with a petroleum-based BOB, where the BOB is designed to meet gasoline specifications after addition of a specified amount of ethanol. For example, a BOB also has a reduced octane rating, anticipating an octane increase on the ethanol addition. Splash blending alters the quality (e.g. heating value, distillation curve, vapor pressure) of finished gasoline but apart from elevated RVP, the final blends of finished gasoline with 10% to 15% ethanol will meet refinery target quality or ASTM specifications. In the case of RVP, regional gasoline specifications have granted E10 a "one-pound waiver" (i.e. waiver for a 1 psi increase) that allows for the RVP increase typically seen with 10% ethanol blending. Therefore, splash blended 10% ethanol was in compliance with specification requirements. Splash blending provides limited option to take advantage of the high-octane characteristics. Splash blending into finished gasoline does not provide the refiner with the option to take advantage of ethanol's high-octane characteristics. Refiners produce a BOB with reduced octane that matches the target octane when ethanol is added.

Several prior studies of emissions effects of gasoline composition elected to employ splash blending, where an ethanol blend was produced using finished gasoline, and where the emissions associated with the finished gasoline and the resulting blend were compared. The studies are not necessarily one-dimensional. For example, the CRC E-94-3 study blended ethanol with four different fuels, representing low and high AKI, and low and high PMI. This supported statistical analysis of AKI and PMI as variables, as well as ethanol content. Splash blending of E-85 and low ethanol blends has been used to study mid-blends of ethanol. In these cases, the properties of the resulting fuels are not independently controlled.

Splash blended studies offer the advantage of well-defined fuels for comparison but may represent compositions that differ from commercial fuels. A distinct exception may be the study of E-10 versus E-15, where a common BOB may be employed for both fuels during the introduction of E-15. In the longer term, where E15 captures a significant market share, a specific E15 BOB will likely be offered.

Match Blending

Studies that use match blending seek to determine the effect of several variables, using a multivariate analysis approach. For example, ethanol, aromatics, T50 and T90 and a Particulate Matter Index (PMI) have all been examined for individual and interactive effects. In these studies, the fuels have been blended to satisfy target values for the study variables.

For match blending, properties that are not considered as study variables may impact the statistical analysis that is employed. If the study seeks to address commercial fuels, then it is important that the blends used in the study have the undefined properties and constituents representative of those expected in commercial fuels. It is possible to meet the study variable targets with many different blends. For example, olefins, isoparaffins and straight chain paraffins may be blended in many different ways to satisfy study variable targets for AKI, aromatic content, T50 and T90, but some of those blends are contrived and atypical of species and proportions expected from alkyates, catalytic cracking and straight run naphtha. Not only will these species have different effects on combustion and permeation, but their interactions with other blend components are uncertain.

Proposed Approach for Market Fuel Study

Fuels used in future studies should reflect appropriately the components and compositions of fuels that will be sold at the pump, because the emissions effects cannot be described reliably by only a few variables. Results gained using this recommendation should be directly applicable to the prediction of changes in the real-world atmospheric burden.

The proposed approach offers efficient use of resources by concentrating data acquisition on fuels limited to the study comparison and avoiding exploration outside of this envelope. It is recommended that resources freed by this approach are dedicated to increasing vehicle count and to increasing repeat runs, thereby increasing statistical confidence in the study conclusions.

The proposed approach also favors the use of component composition as parameters (variables) rather than properties of the fuel. Component composition is a definitive and unique description approach. Properties such as octane rating may be retained to match two fuels or govern commercial production but are not preferred as parameters. Fuels may be blended in many ways to achieve the same octane rating.

Consider the pairwise comparison of emissions from two anticipated market fuels at different ethanol levels. For the recommended approach there is only one independent variable employed, namely the ethanol level. All

other fuel parameters are ascribed to the ethanol content because the change in ethanol content implies other, dependent changes in composition and properties of the two fuels. The two BOBs are diluted by different quantities of ethanol. However, the BOBs themselves are formulated differently by the refiner in anticipation of the level of ethanol to be blended at the terminal.

As an example, two fuels with different ethanol levels are formulated have the same antiknock properties. A refiner may elect to remove or add aromatics (as reformat) to match the octane rating with the different ethanol levels. The two fuels may contain roughly the same sum of ethanol and aromatics to achieve this goal. The aromatic content is therefore viewed as a variable dependent on the ethanol content, which is viewed as the primary independent variable. Only two fuels, one with high ethanol and low aromatics, and one with low ethanol and high aromatics need to be considered. This contrasts with a full matrix study, where four fuels might be used. Of the four full matrix study fuels, where (ethanol, aromatics) might be (low, low), (high, high), (high, low) and (low, high), only the last two would be of interest in a market fuel study. Also, there is concern that behavior of the (low, low) and (high, high) fuels may deviate from market fuel behavior, and cause conclusions to differ in the full matrix study.

In reality, the compensation in the BOB composition for a change in ethanol level is far more complex and includes refinery economic considerations. Further, even compensation by using aromatics to maintain octane rating necessitates other changes in composition, because octane surely is not the sole blending criterion. Multiple component concentrations may change, or component substitutions may occur in the BOB as part of the blending response to the ethanol difference. Even changes in nonlinear blending effects are attributable to ethanol as the independent variable.

An embellishment of the proposed approach exists to address the variability of properties from BOBs produced by, or marketed by, multiple sources. Instead of a pairwise comparison of two ethanol levels, two suites of fuels at two levels are compared. These suites acknowledge additional, minor independent variables that describe variations in the BOBs that suit each ethanol level. BOB parameters then vary for a given ethanol level within the suite.

As an example, an ethanol level may be suited to several BOB compositions with different levels of aromatics. Octane levels for all of these fuels would be substantially the same. The levels of aromatics could vary due to different precise aromatic species. Alternately the aromatic level may be lower, augmented by the presence of iso-paraffins (alkylate) as additional octane boosters. At each ethanol level, several BOBs could be chosen for the study. Each BOB would then have an overall composition that was determined by both the ethanol blend level and the aromatic fraction in the BOB. This overall composition would be described by parameters that were dependent on both the ethanol and aromatic levels as independent parameters. This may be seen as a multivariate study, but the variation still is anchored to one of the two ethanol levels. The variability of the aromatics is limited by the variation of projected in-use fuels at that ethanol level. There is no need to have the same count of fuels in each suite.

Illustrative detail is provided below in the recommended steps for a study and in two study examples.

Core Blending Protocol

The recommended approach for a comparative fuel study consists of ten steps. These are presented with an account of each step below. Although the approach is valid for any comparative fuel studies, it is couched in terms of a study evaluating effects of ethanol blending.

The protocol is most clearly explained as a comparison of effects of two different ethanol levels. This may be translated readily to a protocol for three or more levels, or a protocol for two different BOB formulations but the same ethanol level.

For clarity below, one of the two ethanol levels are termed a *baseline level*, associated with a baseline fuel composition or a baseline suite of fuels. The other is termed a *target level*, with a target fuel composition or a target suite of fuels.

The protocol addresses cases for splash blending, where only one BOB is used, for basket blends, where there would typically be one baseline fuel and one target fuel, and for a distribution of properties at each ethanol level, where one would employ a *suite of baseline fuels* (all with a substantially similar baseline ethanol level) and a *suite of target fuels* (all with a substantially similar target ethanol level).

In the text below, *composition* is used exclusively to refer to the molecular makeup of fuels. The term *properties* is used to describe a behavioral measure of a fuel, such as octane rating, distillation results or density. The term *parameters* is used as a collective for properties and composition measures. The steps needed to perform a study are presented below.

STEP 1: IDENTIFY THE MISSION AND STUDY PURPOSE

Precisely identify the objective of the proposed study. All planning decisions should be guided by and tested against this objective.

The objective should present the types or species of emissions, efficiency or performance to be characterized, the applicable fuel source or geographic region, restrictions or rules related to fuel composition, climatic and fleet limitations, and contemplated fleet activity.

The broader the objectives, the greater will be the resources required for satisfactory accuracy of results and conclusions.

STEP 2: IDENTIFY RESOURCES AND CONSIDER ALLOCATION

Confidence in the applicability and accuracy of study results is limited by resources, which must be identified. Major costs for a study include program and technical management, acquisition of fuels, acquisition of vehicles, data collection (typically on a dynamometer), data analysis and reporting. Compromises and tradeoffs between these costs cause reflection on the precise program objective.

Reducing the number of vehicles reduces acquisition costs and vehicle changes on the dynamometer, while permitting more emissions tests runs per vehicle. However, malfunction or outlier behavior needs to be anticipated. Although the statistical likelihood remains the same, the possibility may be more damaging to a study with a small vehicle count. Typically, vehicles are selected using shallow criteria, such as whether they are common in the fleet, or whether they use PFI or naturally aspirated GDI or turbocharged GDI, or by size and weight. However, a deeper investigation into vehicle technology and control strategies may permit the fleet to be represented well with fewer study vehicles. For evaporative emissions studies, technology generally is defined by the relevant EPA standard and testing procedure, but there still are variations in the materials used and in the designs for ORVR.

Fuel changes are costly. Multiple changes on the same vehicle may be avoided by testing each fuel fully and repeating the first fuel in final testing. The order of fuels may still be randomized for each vehicle. However, there is risk that drift in vehicle performance, test conditions and measurement equipment may mar the results, necessitate a questionable linear correction, or lower statistical confidence in conclusions.

Cold start testing is more costly than hot start testing, encouraging more hot start repeat runs than cold start repeat runs. However, emissions are highest during cold start and represent a substantial contribution to the inventory. Use of more than one test schedule adds another dimension to the study, increasing the complexity of data analysis and most likely reducing the number of runs per cycle per vehicle. However, a single test schedule may not capture all of the fuel effects, and it is valuable to know the difference between knock-limited, WOT, part load and idle performance for modeling inventory changes. Use of continuous emissions data during cycles is valuable.

A decision on the number of fuels is critical. If a single, average fuel is used at each ethanol level, resources will allow characterization of the ethanol effect to be robust. However, if the anticipated BOB compositions are likely to vary widely for the same ethanol concentration, use of two or more representative compositions is responsible. This is particularly true if the study is conducted to inform a large geographic area, but BOB vary by location within that area. In deciding on fuel count, it should be noted that refinery differences do not determine the extent of BOB variability. The EPA Fuel Trends Report presents observations relevant to the real-world blend approach that suggest that pooling is justified.

- “Batch data properties are measured at the refinery/importer, not at the retail station. Of greatest interest to the public, however, is understanding the quality of fuel going into vehicles at retail stations in particular areas.”
- “[T]he majority of gasoline batches are aggregated in pipelines and terminals, as well as mixed in retail stations, so the fuel dispensed at retail will be combinations of multiple refinery batches.”

- “[G]asoline distribution is fungible, meaning that gasoline of the same grade or type is combined together in large batches and is shipped across the country, so the gasoline produced in a given part of the country is not necessarily the fuel dispensed in that part of the country, and vice versa.”

Although the study objective may not include a mechanistic understanding of the causes of emissions changes, it is always valuable to monitor engine and vehicle operating parameters during testing. In some cases, these assist in determining whether the emissions data are representative of real use or are outliers as a result of a malfunction of the vehicle or test environment.

STEP 3: DETERMINE REPRESENTATIVE FUEL PROPERTIES

Study objectives are unlikely to address emissions from a single ethanol level in isolation. Most studies are comparative in nature. A target fuel or suite of fuels is compared to a baseline fuel or suite of fuels. In some cases, one of the anticipated ethanol levels may already be in use, and therefore parameters for a baseline fuel or suite of fuels may be determined by the current market. A basket blend approach implies a single baseline fuel for the study, representative of the average of market fuels.

A baseline suite of fuels is used to represent variation in the parameters of market fuels. The baseline fuel BOB compositions vary within this suite.

For rare cases where suitable fuel is available in the marketplace at the two different ethanol levels of interest, the target study fuel or fuel suite is defined in a similar way to the baseline fuel or fuel suite. Otherwise, target fuel formulation requires projection or estimation of the most likely distribution of future market parameters. For a market splash blended comparison (most likely limited to E10 and E15 in the short term), only one BOB would be needed.

The difference in fuel parameters between baseline and target is ascribed to the ethanol content as the major independent variable. However, the change in ethanol content will automatically imply other, dependent changes in market fuel composition and properties. Clearly the baseline BOBs and target BOBs will be diluted by different quantities of ethanol, but the baseline and target BOBs themselves will differ in a way that is dictated by market forces, fuel property regulation, and technology limitations.

It is important to distinguish fuel properties, such as octane rating or API density or T90, from fuel composition. Properties cannot be changed except by changing fuel composition. However, a property may be the same for two or more different compositions. In fact, one could blend two fuels that match several properties directly but contain very different molecular compositions. Varied compositions may cause substantially different behavior in an engine combustion environment or in permeating through an elastomer. This represents a danger in defining a fuel weakly, and not monitoring the underlying composition. Properties, typically determined using standardized test methods, do not necessarily determine the fuel behavior or performance during real-world use. Composition does so.

Of importance in this step is anticipating target fuel properties that will change, or that must be held constant, due to the ethanol addition, and then projecting intentional changes to the fuel composition associated with the property values. This is in strong contrast to a parametric study, where an effort may be made to hold selected parameters (often a mix of composition metrics and properties) at a constant level while changing ethanol concentration.

Changing fuel properties due to dilution may be estimated from prior study results, and include vapor pressure, volatility, anti-knock properties, density, and packaged variables such as PMI. The BOB composition is likely to change- in response to changes in ethanol content, and this will change some properties of the fuel, such as distillation values. However, if octane rating (as a property example) must remain the same, or where vapor pressure is regulated, property demands may dictate BOB composition. The relationship between BOB properties and BOB composition is complex, with composition determining properties to the extent that it is defined, and yet with required properties dictating composition in some cases.

To summarize, the planner should be cognizant of the need to match certain properties, such as octane rating, sulfur level or RVP (perhaps including a waiver) between the fuels to be compared. The planner should also be aware that the fuels should not fall outside of specifications, and should control composition to ensure compliance. However, there should be no attempt to match other properties, such as distillation values, between the fuels to be compared, unless that matching represents market practice. For example, it should be expected by the planner that T40 and T50 are substantially reduced in market E10 in comparison to market E0. To attempt to match these variables while blending the fuels would defeat the market fuels study approach.

The planner should identify a pathway for precise definition of the target fuel or suite of fuels. This will require estimation of the range of parameters (properties and composition) for the one or more BOBs to be used in the study. The planner's estimation may be enabled by:

- Knowledge of BOB compositions used in other regions or by early adopters.
- Analysis of market survey data, in particular at the (mid) meso- or detailed (micro-compositional level
- Knowledge of real-world volumes, proportions and qualities of potentially available BOB blend components.
- Use of a refinery model to determine the most likely target BOB compositions.
- Extrapolation or interpolation from prior work with knowledge of ethanol blending properties.
- Communication with refiners or experts on likely target BOB compositions or stream blends with consideration of refinery economics.
- Experimental work with specially blended bobs that are formulated to avoid incorporating high value refinery streams.

For national or major regional studies, the planner should also consider variability of refinery configurations, leading to increased range of the composition of both baseline and target BOBs that meet required specifications after blending with ethanol.

This definition of a target BOB may be viewed as an impossibility, but it presents no greater demand than is encountered in using a predictive emissions model developed from a parametric study. In both cases, weak definition of the fuel and neglect of reasonably detailed fuel composition will lead to potentially inaccurate conclusions on the ethanol effects.

Ideally, the composition of candidate fuels should be addressed at the DHA level, but this is impractical for unseen BOB compositions, and consumptive of resources in addressing the statistics of the study fuels. However, the fuels must be well defined, and the underlying detailed composition should be credible and representative of refinery streams. A reasonable approach would be to work between the simplicity of a PIANO (Paraffins, Isoparaffins, Napthenes, Aromatics and Olefins) analysis and the granularity of full DHA. As an example, aromatic content may not be regarded as a single parameter, but rather as two or more parameters that group the species by molecular weight or alkyl radicals. Likewise, iso-paraffins may be sub-divided by degree of branching.

It is critical in evaporative emissions studies to ensure that the target DHA is very closely matched, since the permeation rates through elastomers will be influenced by the species present, and since the fuel vapor and permeating fuel are likely to be characterized for composition. In air toxics studies, whether evaporative or tailpipe, the fuel composition is important to ensure that the toxics represent market fuel behavior.

Figure 7 shows a fuel composition set selected for a study. That composition can be met by blending streams from a refinery in specific proportion, and the more highly specified the composition, the more tightly is that blending defined. The blending must also meet gasoline property requirements if it is a market fuel. The refinery streams define the DHA, yielding precise species that will constitute the composition. The seven parameter composition in Figure 7 therefore implies more information about the fuel formulation than is apparent from just the seven parameters, if refinery stream limitations are considered. It implies a market fuel expectation or a normalcy on the part of the blender.

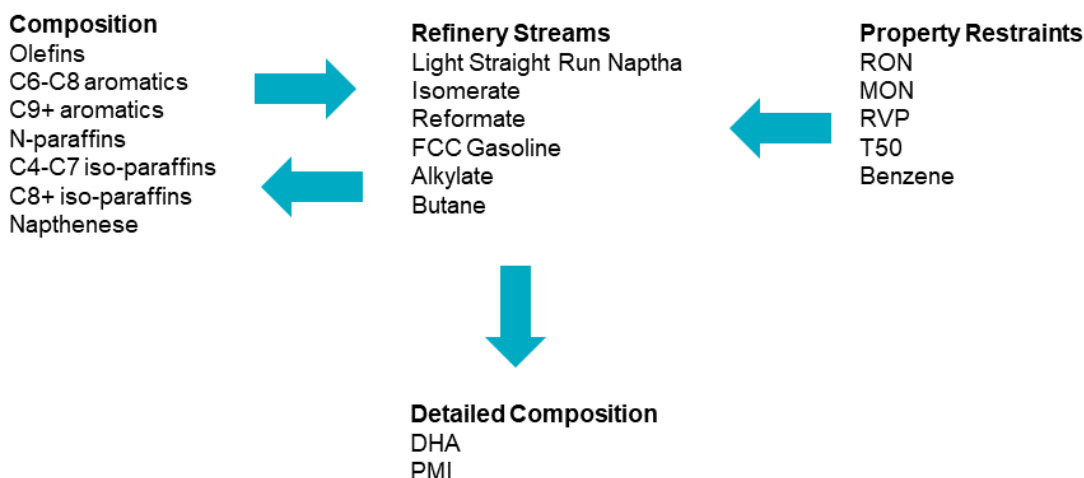


Figure 7: Illustration of a set of chosen fuel composition parameters and its relationship to blending of a test fuel.

The next action is to identify, through research of past programs or through application of scientific principles, those changing fuel parameters that will most likely affect the measurements of interest in the study. For example, in prior studies, both PMI (which is DHA-derived) and total aromatic content have been related to PM production. In a PM study, a planner should ensure that these specific, important parameters are employed in describing the baseline and target BOBs and comparing them statistically. Other parameters used would be those showing (or expected to show) high variation within the baseline or target fuel suite. They may have unknown influence but are selected based on their high variability.

Appendix I presents exploration of Texas DHA data for gasoline stations for 2017 and provides additional insight into gasoline variability. The fuels addressed in Appendix I are all E10, so that the Texas data alone cannot define compositions for different ethanol levels for study planning. However, they are valuable in supporting choice of composition parameters as study variables.

The planner should determine whether to employ and report BOB composition or finished fuel composition as parameters. The finished fuel properties are useful in that they include the nonlinear blending behavior of the ethanol and petroleum components. However, either approach fully defines the finished product, except for the small variability caused by the composition of the adulterant in the ethanol.

Based on the information on the anticipated range of BOB parameters, appropriate suites of fuels may be defined in the next step.

STEP 4: DEFINE THE FUELS

Based on the planning in Step 2, for cases where at least the baseline ethanol level is currently sold, market fuels are collected from blending facilities or at the pump and analyzed. The analysis should include parameters identified as important to the specific study objectives, and other parameters needed to define the fuels adequately. These parameters should then be considered statistically. The distribution of each parameter should be examined and co-variance between parameters should be determined. Composition is favored to define parameters.

If parameters that are believed to be important vary little, and no parameters show very high variability, it is appropriate to consider whether a basket blend of fuels (single fuel) could be used for the study, as opposed to a suite of separate fuels. Use of a single baseline fuel would permit the study to be conducted with reduced resources, or to acquire a more representative data set using more vehicles and test runs. A decision to use a basket blend would need to address whether the fuels would be expected to yield an average behavior when blended, and that emissions would not vary in a strongly non-linear fashion over one or more of the ranges of the measured parameters from the market fuels. In considering use of a basket blend, and in subsequent statistical analysis, expected variability in laboratory analysis should be considered.

When a basket blend is not employed, it will be necessary to determine a minimum number of fuels in the baseline suite that will represent the market spectrum, and to identify the parameters that will vary between

those fuels. These parameters must necessarily be small in number, or a full test matrix is not affordable. For example, ten to twenty fuels may have been procured for analysis to determine properties of the baseline suite. Consider a hypothetical case where the ten to twenty fuels would be represented by a suite of four baseline fuels for emissions testing. Based on statistical review of composition of the fuels collected in the field, it may be found that naphthenes and olefins varied substantially, but also enjoyed some co-variance, and that the range of heavy aromatics was of concern for emissions. The study may then proceed to use four gasoline blends to represent the baseline, with high and low heavy aromatics, and high and low olefins as minor independent parameters. Napthene concentration could be set in sympathy with the olefins. Other parameters would be set to the averages expected for each of those four baseline fuels, based on the statistics of the ten to twenty analyzed fuels. Using four fuels provides for a limited parametric study of two additional variables that are appropriate for the level of ethanol present in the market baseline fuel.

The primary variable in the study is the concentration of ethanol. For the market fuels, analysis of ethanol content should also be performed. It is most likely that the ethanol content for the test fuels can be locked at the anticipated baseline value, or otherwise set as the average for the ten to twenty market fuels that are sampled. However, if co-variance is found between ethanol concentration and another selected parameter, the ethanol content could be varied between the four fuels of the baseline suite as well.

For the target fuel or fuel suite with different ethanol concentration in the study, no finished fuel or BOB may exist, and the composition of the fuel is established using extrapolation, modeling or expert opinion methods described in the previous step. It is also recommended that the variability of the composition is considered, to allow the use of more than one target fuel composition. In many cases the target fuel compositions could be varied in the same way as the baseline fuel composition. However, if the baseline and target fuel suites both match their desired average properties, there is no compelling need to view the fuels as baseline and target selected pairs. Rather, the whole target suite performance is compared with the whole baseline suite performance, using all fuels in the study.

STEP 5: PROCURE THE FUELS

If a basket blend is used, there will be only one baseline fuel, and that could be blended from batches of commercially available fuel. Alternately, a single batch of baseline fuel could be blended from refinery streams to match the basket blend baseline fuel parameters. Since the target fuel would not be available commercially, a single batch of target fuel could be blended to match the target fuel parameters, with the provision that unspecified characteristics of the target fuel composition would be reasonably representative of a future expected market fuel.

In the event of a splash blended study (e.g. short term E10 and E15 comparison), both the baseline suite of fuels and the target suite of fuels use the same the same BOBs, but at different ethanol levels. In this case the E15 would exhibit an elevated octane rating relative to the E10.

Where multiple fuels are used for the target and baseline suites, it would be possible to use commercially available fuels for the baseline, but the composition would not be controlled precisely. Blending would enable matching to statistically determine fuel parameters. For an unseen, but predicted, target fuel or BOB, blending would be necessary. Fidelity of a study is improved when the blending seeks to match a large number of parameters, typically expressed as composition, and when the blending employs streams with refinery DHA.

STEP 6: DETERMINE REPRESENTATIVE VEHICLES

The vehicle model years or technologies to be considered should be addressed in the objectives. It is important to ensure that the vehicles selected for the study are truly representative of major portions of the fleet. Since studies have a long duration, bias to newer technology should be considered to ensure that results remain relevant. If study vehicle technology details and fleet vehicle technology details are determined, the fleet emissions footprint may be represented by a greater proportion of one vehicle type in the study than by another vehicle type. Therefore, there is no need to balance the study cohort to match the greater fleet precisely. As discussed regarding resource allocation, reducing the vehicle count in the study will yield resources for more runs per vehicle. Since both run-to-run and vehicle-to-vehicle variation have been high for certain emissions in previous studies, it is important to balance both counts. Run to run regulated pollutant variations of as much as 30% have been regarded as the norm in prior studies. In this case, additional runs per vehicle would add confidence in the results, clarify vehicle to vehicle variability, reduce the number of cases where differences were not statistically significant, and add confidence in determining outliers.

Although the study targets differences in fuel composition, and considers ethanol level as the primary independent variable, the vehicle engines, catalysts, evaporative emissions systems and controls all represent further independent variables. These variables are complex, nonlinear and interactive to the extent that they cannot be assigned a simple value or values and cannot be considered in a regression analysis. However, statistical variance can be assigned to the vehicle designs. Difference in response between vehicles is attributable to varying interactions with fuels and run to run variance, typically with a low count of runs per vehicle. Statistical analysis will differ for each emissions species that is considered. It is conceivable that a study could find no emissions effect between the fuels, on average, but find significant differences in emissions response for individual vehicles and between vehicles.

STEP 7: PROCURE AND PREPARE THE VEHICLES

Vehicle procurement requires little prescription. Unless the study objective states otherwise, vehicles should be within their useful emissions life, although odometer reading should be considered as a factor in interpreting data. Purchase, corporate rental, fleet loans, institutional and employee vehicles and incentivizing to obtain private vehicles have all been used for procurement. Generally, it is beneficial if the vehicle is available after the main body of testing is completed in case data quality assurance or statistical analyses raise issues that can be resolved only by retesting or examining the vehicle.

Vehicle inspection and maintenance protocols should be established in a test plan. Most studies seek to test vehicles that are in good working order. It would take a very large study to incorporate malfunctioning vehicles statistically, rather than by an adjustment factor. However, it would be beneficial to examine and report vehicle engine deposits, that represent a growing concern, since these may affect emissions responses. At a minimum, vehicle inspection should consist of insuring at least that the MIL is not illuminated, pending codes are not present (unless judged to be acceptable), and that no underhood tampering or failure is evident. Additional inspection may check details such as compression ratio and appropriate cooling fan operation.

Generally lubricating oil is changed prior to the start of a study, and it must be aged before testing commences. In some cases, the vehicle emissions are determined using certification fuel to assure that the engine and catalyst are in good working order before conducting study tests. This adds cost and may be avoided if the test fuels are reasonably representative of a certification fuel.: Absolute emissions are not expected to reflect original certification data exactly but should not exceed standards.

The vehicle conditioning procedure may be used to assess vehicle function. Conditioning is best performed on the same cycle that is to be run, to satisfy adaptive requirements. The CRC E94-1 study addresses conditioning of the vehicle to assure that adaptive tables, such as for fuel trim and spark timing, are suited to the fuel being employed for the forthcoming test.

STEP 8: DETERMINE REPRESENTATIVE VEHICLE ACTIVITY

The study objective should define the type of vehicle activity that will be addressed.

If the study is for compliance or used to determine relative emissions under constraint of a rule or regulation, or to address air quality exceedances, it is likely that the test schedule is prescribed. The measured differences would be used with an existing model to project inventory change. However, the study may be charged with gathering data under defined circumstances or producing results that are applicable to a specific region.

If a study is limited to a single region or a metropolitan area, it is likely that PEMS data are available to provide the basis for developing a driving schedule that is locally applicable. However, developing a schedule that is representative is fraught with difficulty. The distribution of speed, acceleration and braking differs due to congestion, which in turn depends on traffic demand and available roadways. There will be a substantial variation of behavior on different road classes and by time of day. If the planner elects to avoid creation of a dedicated test schedule or schedules, local data at least will provide insight into typical vehicle operation to assist in selecting an existing cycle. However, averaged data gathered in a boutique study are not readily compared to averaged data gained using standard cycles.

If a study is intended to be applied generically and nationally, there is little alternative than to select two or more cycles that attempt to cover the range from highly congested operation to high speed freeway operation, and to weight those data subsequently. Additionally, some existing cycles are divided into phases or bins, each in itself a separate cycle.

Advanced solutions exist for processing data from test schedules. One may measure emissions of many species continuously during the schedule and relate those emissions to the immediate vehicle speed and acceleration, or the engine speed and load. Algorithms to address measurement time delay and diffusion exist. Unfortunately, the human driver will not reproduce vehicle behavior exactly between runs, but aggregation of data over narrow time bins offers an attractive alternative to cycle-based average value comparisons. As an example, if one fuel offers low emissions at light loads or low temperatures, and the other at high loads and high temperatures, the granularity exists to detect the differences. Continuous data are also valuable for comparing data from different cycles for the same brief speeds, loads and transient behaviors. Continuous data are also advantageous in supporting advanced microscale emissions models and can feed models such as MOVES. Overall correction factors for fuel quality may be unrepresentative for certain types of vehicle activity, such as WOT operation.

Some emissions, such as filter-based PM or air toxics found using media, must be averaged over a period of time. In some cases, where the emissions are very low, media may be loaded using repeat runs.

Planners should recognize that run to run variation will occur, even when the same driver is used, and more so if drivers are changed during the study.

Vehicle activity is less relevant for evaporative emissions, although cycles are prescribed for conditioning and running. Most of the fleet is now equipped with on-board vapor recovery for refueling, which would be affected by fuel composition and the fuel system temperatures and pressures.

STEP 9: CHOOSE TEST PROTOCOLS AND SCHEDULES

The norm is to use a speed-time schedule that fails to consider road gradient. Road gradient can have a profound effect on the of power demand from a vehicle and may elicit sustained high load that represents altered control strategies that influence emissions. As examples, full throttle enrichment for catalyst protection may occur after sustained high power operation, and engine knock control strategies (using boost, EGR and ignition timing) are sensitive to the fuel's anti-knock properties at high loads. If these events occur during on-road use, but are not captured by the test schedule, study conclusions may be biased.

Typically, a speed-time schedule does not consider power to weight ratio of the tested vehicle. A vehicle with high power to weight ratio is likely to indulge in more high power events, but overall will operate at lower average overall fractional engine load. A vehicle with low power to weight ratio in real on-road operation may operate often at full throttle. The vehicle road load demand is based on weight, frontal area and drag coefficient, and may vary substantially as a ratio with maximum engine power.

In most studies, the planners will choose to use one or more standard cycles. The Urban Dynamometer Driving Schedule (UDDS) and the LA-92 cycles represent light to modest engine loads. The Federal Test Procedure (FTP-75) is usually operated with a cold start UDDS, followed by a repeat of the first 505 seconds of the UDDS as a hot start. The US06 schedule has sustained high speed operation and aggressive accelerations. However,

since schedule load is based on road load and not on engine load, vehicles with a high power to weight ratio will not be challenged by the US06 to mimic some of their on-road behavior. However, the US06 is more aggressive than the Highway Schedule, used for fuel economy evaluation.

Cycles are also available from European regulations and applications (See Dieselnets, 2020). The Artemis Rural Road cycle reaches 93 mph and the World Harmonized Cycle has four modes, the last of which reaches 82 mph.

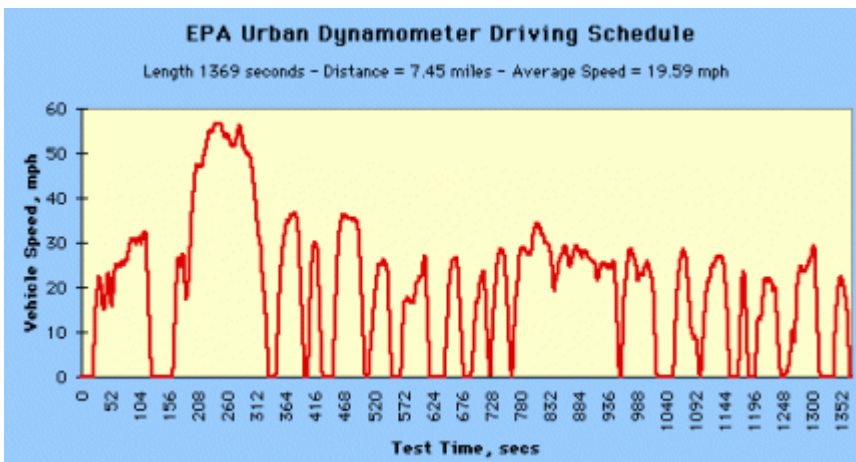


Figure 8: The UDDS and FTP are based on vehicle activity nearly 50 years old, and represent low power operation.

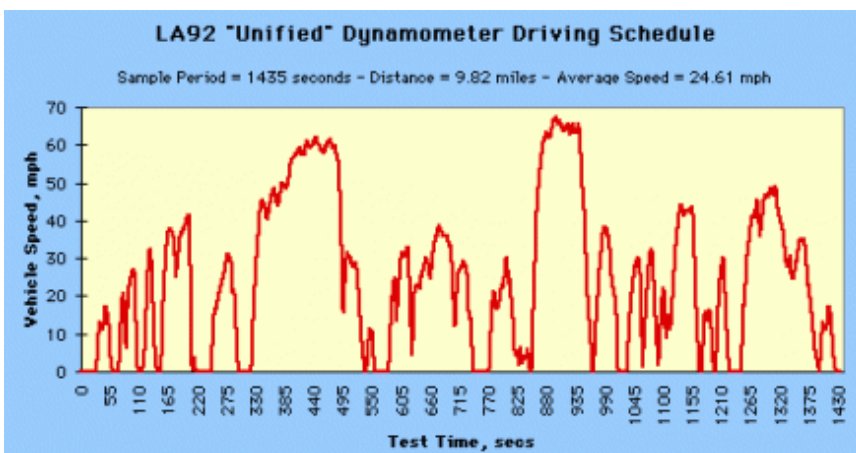


Figure 9: The LA92 schedule does not require high power operation

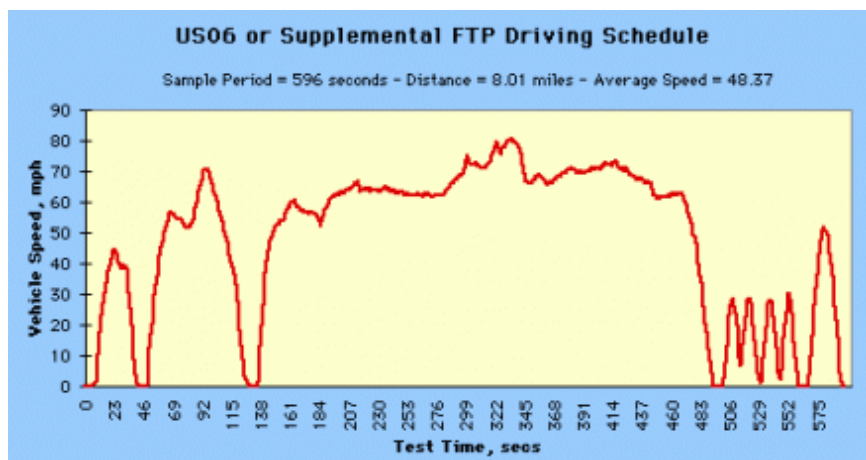


Figure 10: The US06 requires high acceleration and speed, but its challenge to a vehicle depends on the vehicle's power to weight and power to road load ratios.

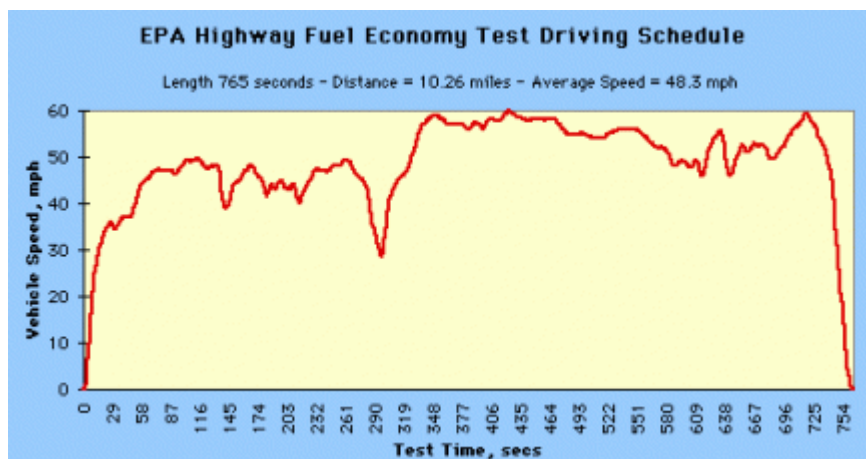


Figure 11: The Highway cycle is used in determining vehicle fuel efficiency

STEP 10: ADDRESS QUALITY CONTROL AND STATISTICAL ANALYSIS

A statistical plan should be developed to match the objective and evolve with the decisions made in the first eight steps. Statistics are rendered simpler if ethanol is the sole or primary independent variable among the fuels. A conclusion on the average ethanol effect (with other components all dependent on ethanol level) is readily reached.

If statistical planning is documented and declared before the measurement commences, appearance of bias is avoided. The order of testing fuels should be planned to avoid systematic bias from historical effects, and statistical testing for historical effects and for time-based trends is valuable. There is benefit to planning a scheduled number of cases where the first fuel used on a vehicle is re-employed for the last tests on the vehicle. However, it is not possible to prepare a detailed plan for all eventualities.

For a suite of B baseline fuels, T target fuels, V vehicles, and C cycles, there will be a possible product of $B \times T \times V \times C$ separate comparisons. Since the vehicles are regarded as individual species, and the ethanol levels are defined and substantially set at one value, analysis could be performed of the dependence of emissions on the composition of the BOBs. Such an analysis could consider either the minor independent fuel parameters (used to define the fuels) or a larger number of parameters (known from fuel analysis or DHA) for each ethanol level. Further, the analysis could be conducted separately at each ethanol level, avoiding some nonlinear blending issues, or could include ethanol as a variable and address the whole data set. In the latter case, nonlinear blending effects will beg for second order terms, because the range of, say, aromatic content would be substantially different at each ethanol level for most studies.

Regressions and models can be developed for each vehicle in the study, and for the average of all vehicles, presumably in log space to recognize the importance of emissions ratio. However, as with conventional multivariate studies, effects may be assigned to parameters that take on the mantle of co-varying factors that are not considered statistically. The more the fuel is representative of market fuel at the meso-level, the more appropriate these assignments of effects will be.

If there is a detailed understanding of the vehicle cohort technology versus the projected on-road fleet technology, results can be weighted by vehicle type.

A major duty of the statistical analysis is to determine the confidence in conclusions. Using a model or simulation, it is possible to test for sensitivity to accuracy of fuel analysis. Other sources of error, between emissions runs and between vehicles, are evident in the data set. If the study is configured to address one emissions species, the data may be used to examine other species statistically, but the fuel parameters may not be as well aligned with the emissions effects. In this case, if more parameters describing the fuel are available, the analysis may be conducted using parameters believed to contribute physically or chemically to those other emissions.

The tailpipe emissions statistical analysis for basket blends of baseline and target fuel, or for averages of suites of fuel, may be very simple, yielding an overall difference, a set of vehicle-specific differences, and a set of schedule-based differences. For evaporative emissions, differences would be available by vehicle and by evaporative emissions test component.

A robust skeleton for the statistical model, created early in the program, permits the simulation and testing of planning decisions, using expected run-to-run variability and vehicle-to-vehicle variability. Reducing vehicle-to-vehicle variability should not be a mission if true differences in vehicle-fuel interaction are recognized. Rather, it becomes more important that a representative (with or without weighting) vehicle cohort is used.

Examples of Studies

Two examples of objectives are presented in Appendices II and III, and these examples are carried through each step for illustration of the process.

- **E10 versus E15 with common BOB.** Identify the gaseous mass tailpipe emissions effects for the anticipated 2025 light-duty vehicle gasoline fleet associated with raising ethanol content in gasoline to 15% or 20% using existing BOB for E10 fuel in a defined metro area RFG.
- **E10 versus E20 market fuel.** Identify the impact on regulated particulate matter of the present day fleet between expected market E10 and E20 summer regular fuel, in contrast to present day E10.

Appendix I provides Texas gasoline station DHA data for E10 fuels for 2017. These data provide insight into variability of composition of gasoline meeting a common specification and would assist in identifying additional independent variables (beyond ethanol) required for well-posed studies, such as those addressed in Appendix II and Appendix III.

Discussion and Conclusions

Previous studies of fuel effects where ethanol concentration was varied do not provide unified conclusions on ethanol effects. Disagreement between studies and rapidly evolving technology drive the need for additional measurements. The blending guide study primary objective is to identify a sound practice for acquiring or blending fuels that will result in accurate real-world predictions of emissions changes in response to fuel composition or specification changes in the marketplace. This objective is not directly applicable to fuel effects studies that seek to address the effect of several parameters on emissions, but rather to compare two fuels as a pair or to compare fuels at two different levels of one parameter. It differs from multivariate studies and avoids the need to model nonlinear effects because they are measured directly.

For most efficient use of resources, tailpipe or evaporative emissions changes due to a change of ethanol level should be evaluated by employing only fuels with those relevant ethanol levels, and with BOB composition that is expected in the market at those ethanol levels. Each ethanol level should be represented by one fuel, with average expected hydrocarbon composition, or by a suite of fuels, with a distribution of hydrocarbon compositions. In this way measurement effort is not devoted to fuel formulations that may never enter commercial use.

For precise fuel description, measures of fuel composition are preferable to properties determined using standardized protocols. The fuel composition is unambiguous, whereas several fuels blended with diverse compositions may satisfy the same set of properties. Detailed hydrocarbon analysis (DHA) of fuels has become more accessible in the last decade. Moreover, it is being employed for in-line blending (EPA, 2014). The DHA data can be grouped by molecular type, weight and expected influence, in a manner that prescribes the overall composition reasonably and without an excessive count of parameters.

Vehicles used in a study should be recognized as having the same level of importance as the fuels in determining emissions. The vehicle cohort may also be characterized by technology and by numerical descriptors, such as power to weight ratio, or engine power density, to appreciate the effect of loads and

speeds and to facilitate better translation of study results to an inventory. During emissions testing, vehicles should be operated to cover their real-world on-road use, typically operating at idle, light to medium load, and near full load. An option is to use a low power cycle such as the FTP or LA92, a high power cycle such as the US06, and, if possible, a segment of wide open throttle (WOT) acceleration. Each of these loads may trade performance, efficiency and emissions in different ways when challenged with different fuels. Acquisition of continuous emissions and vehicle data is valuable for subsequent data analysis.

Two examples were presented for market blend studies. One, for examining E10 versus E15 emissions, with the same BOB used for both fuels, was proposed to use a basket blend for E10 fuel, with the E15 produced by splash blending. The second example compared E10 and E20 emissions, where fuel composition was based on six responses presenting likely E10 and E20 concentrations for seven hydrocarbon groups. Ethanol content, the primary independent variable, was the eighth concentration considered. Two minor independent variables, light aromatics and heavy aromatics, were used to narrow the six responses down to two E10 fuels and two E20 fuels.

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Appendix I: DHA and Fuel Property Trends

This Appendix presents detailed E10 composition data for Texas for 2017 and is included to illustrate the complexity of study planning. These data are not necessarily representative of national data, or data for other regions or nations. The appendix does not present the changes in the petroleum component due to changes in ethanol level. However, it may be used to support choice of variables for a study, and it may assist directly in planning a study where one of the ethanol levels is 10%, as in the examples in Appendix II and Appendix III. It may also assist as a jumping board to determine expected variability of composition at other ethanol levels, when coupled with expert opinion and with knowledge of refinery operations and blending.

The EPA fuel trends reports provide details of the distribution of major gasoline properties, but they do not provide breakdown of the various hydrocarbon groups. Limited DHA data are available in the public domain to describe the individual hydrocarbon species in market fuels, although DHA data have been provided for some study fuels. Data are available from the 2017 Texas survey, and include full DHA, and a more condensed grouping by hydrocarbon type and carbon number. The Texas data are gathered from retail fuel suppliers, and all fuels have a nominal 10% ethanol content. A total of 273 fuel samples are represented in the survey equally distributed between regular, mid-grade, and premium gasolines. The fuel samples were obtained over a short time window (< 2 weeks) in June of 2017 where a regular, mid-grade and premium sample were obtained during the same visit to a distinct fueling station.

These Texas data facilitate examining refinery blending relationships between hydrocarbon groups, molecular weights and even single species. They also differentiate regular, mid-level and premium blends. The fuel effects study planner should use data of this kind to examine correlations and covariance in the composition, and to determine how many independent variables are needed to describe the spectrum of fuels of interest. The Texas data are used here to provide examples of examining a data set in support of identifying study fuel composition. The regular grade data were examined at a high level to determine relationships between the PIANO groups. Regular grade gasoline should comply with an 87 octane requirement, except that the El Paso area uses an 86 octane standard. In most studies, where ethanol is the primary independent variable, it is likely that aromatic content would be a secondary independent variable. Relationships between aromatic content and content of other hydrocarbon groups are therefore important. Note that there is an implied trend for one hydrocarbon type to decrease with respect to another group, due to displacement of available volume: all species must add to 100%.

Figure I-1 shows that there is no relationship between naphthenic and aromatic content. Figure I-2 shows that there is a decreasing trend of olefins with respect to aromatics, but too high a scatter to propose a correlation. Figure I-3 shows an increasing trend of normal paraffins with respect to aromatics, but again the scatter is considerable.

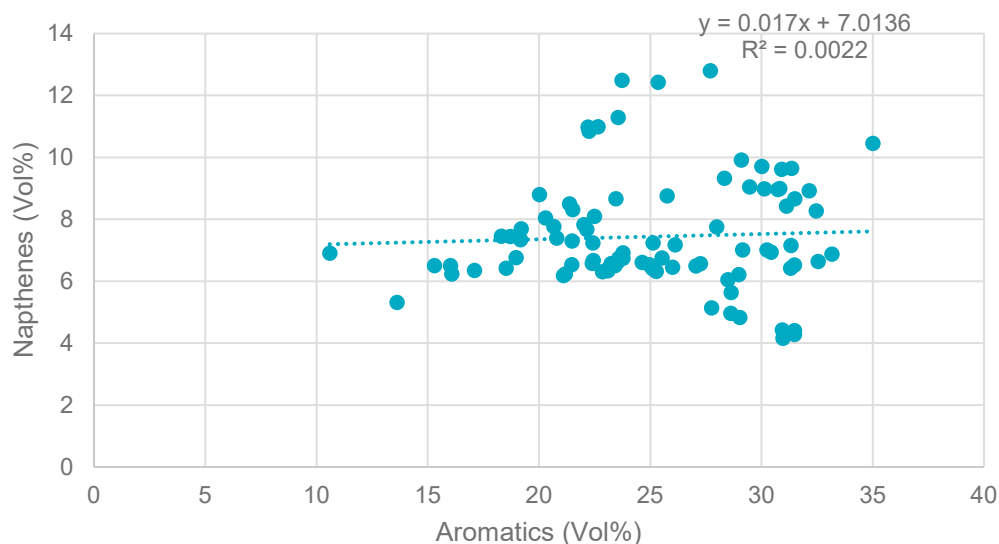


Figure I-1: There is no correlation between naphthene content and aromatic content for Texas study regular gasoline, and both species vary with a ratio of over three times.

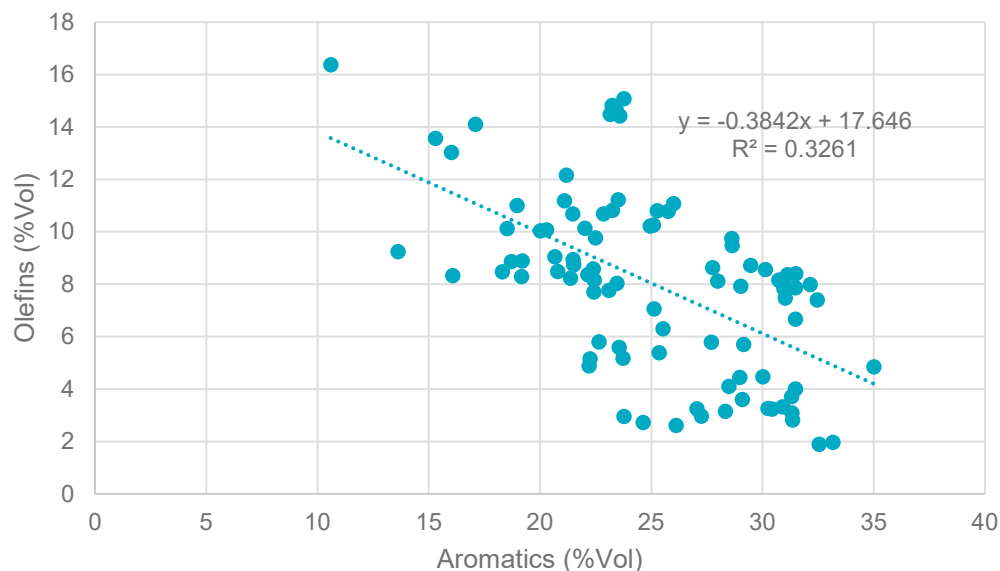


Figure I-2: Olefin content varies widely and shows a weak trend with aromatics for Texas study regular gasoline.

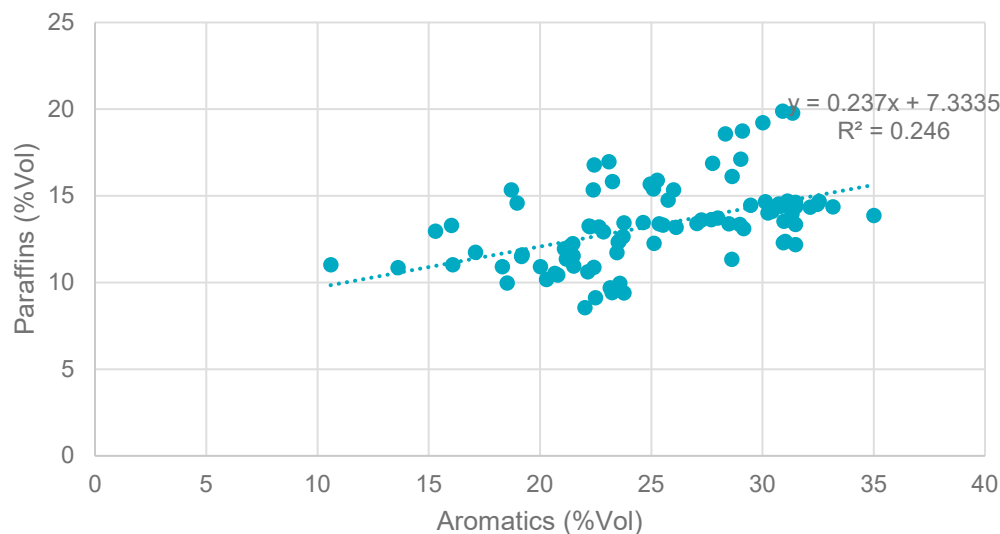


Figure I-3: The relationship between normal paraffins and aromatics for Texas study regular gasoline is weak.

In Figure I-4, there is a more definite counter-correlated trend between iso-paraffins and aromatics, both of which may be expected to raise octane rating to the required level. The correlation coefficient is below 0.6, but this relationship merits further examination. There is also a strong offset (y-intercept), suggesting that some isoparaffins do not play a role. Figure I-5 shows that there is a decreasing trend for iso-paraffins with respect to normal paraffins. This is to be expected, noting the high volume percent of iso-paraffins in the fuel.

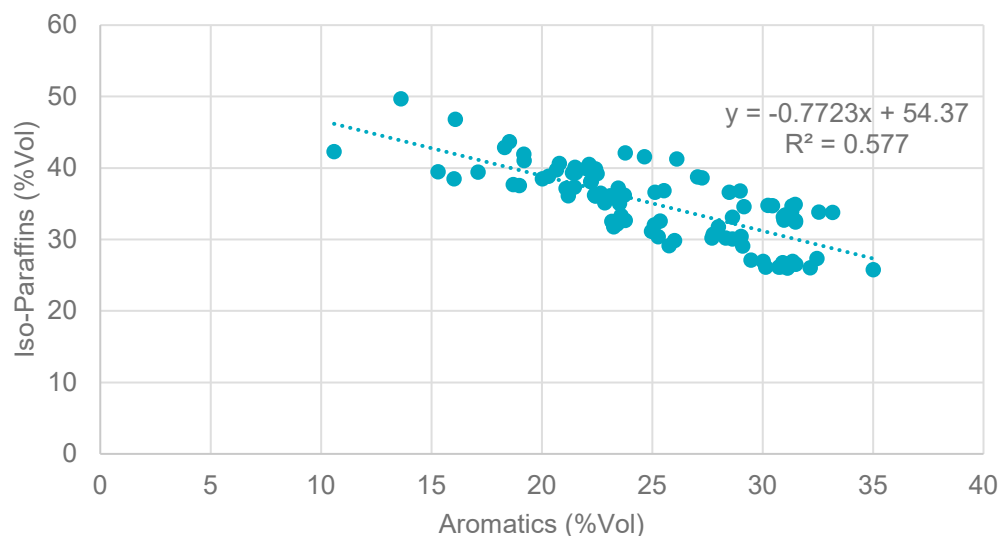


Figure I-4: Anti-correlation of iso-paraffins and aromatics for Texas study regular gasoline.

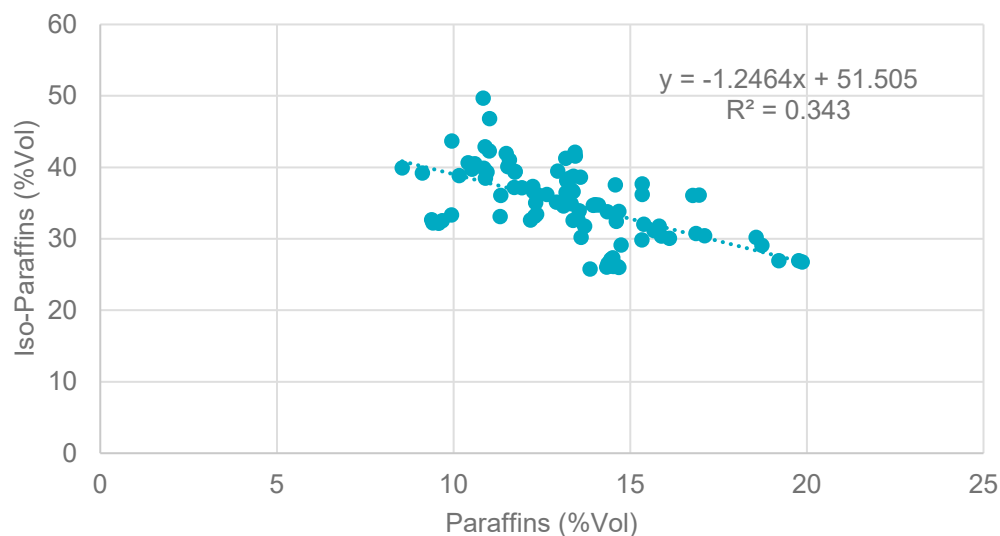


Figure I-5: Relationship between iso-paraffins and normal (straight chain) paraffins for Texas study regular gasoline.

Table I-1 presents additional data on relationships between hydrocarbon types. Green cells represent an acceptable positive correlation, and blue cells represent an acceptable negative correlation. Aromatics and mono-aromatics are highly correlated because there are few double ring compounds in gasoline. Some correlations relating to indexes and naphthalenes are not useful in defining fuels insofar as the quantities of those species are small, as shown in Table I-2. There is strong correlation between the olefin sub-groups, and they each have a high coefficient of variation, as shown in Table I-2. Further, in considering parameters that may be used as composition descriptors, it is important to note the distribution of molecular carbon counts, as shown in Table I-3.

	Paraffin	I-Paraffins	Aromatics	Mono-Aromatics	Naphthalenes	Naphtheno/Olefin o-Benzs	Indenes	Naphthenes	Mono- Naphthenes	Olefins	n-Olefins	Iso-Olefins	Naphtheno- Olefins	Di-Olefins	Oxygenates
REGULAR															
Paraffin	1.00	-0.59	0.50	0.55	-0.45	-0.68	-0.58	0.15	0.15	-0.46	-0.44	-0.48	-0.42	-0.52	-0.52
I-Paraffins	-0.59	1.00	-0.76	-0.75	-0.12	0.16	0.17	-0.22	-0.22	0.08	0.04	0.11	0.08	0.33	0.22
Aromatics	0.50	-0.76	1.00	0.99	-0.07	-0.28	-0.28	0.05	0.05	-0.57	-0.51	-0.60	-0.58	-0.61	-0.43
Mono-Aromatics	0.55	-0.75	0.99	1.00	-0.16	-0.37	-0.36	0.07	0.07	-0.62	-0.56	-0.64	-0.62	-0.65	-0.46
Naphthalenes	-0.45	-0.12	-0.07	-0.16	1.00	0.83	0.82	-0.04	-0.04	0.49	0.50	0.48	0.46	0.37	0.34
Naphtheno/Olefin o-Benzs	-0.68	0.16	-0.28	-0.37	0.83	1.00	0.85	-0.28	-0.28	0.65	0.66	0.62	0.65	0.59	0.45
Indenes	-0.58	0.17	-0.28	-0.36	0.82	0.85	1.00	-0.08	-0.08	0.50	0.52	0.48	0.47	0.53	0.25
Naphthenes	0.15	-0.22	0.05	0.07	-0.04	-0.28	-0.08	1.00	1.00	-0.28	-0.31	-0.27	-0.22	-0.40	-0.28
Mono-Naphthenes	0.15	-0.22	0.05	0.07	-0.04	-0.28	-0.08	1.00	1.00	-0.28	-0.31	-0.27	-0.22	-0.40	-0.28
Olefins	-0.46	0.08	-0.57	-0.62	0.49	0.65	0.50	-0.28	-0.28	1.00	0.99	0.99	0.96	0.80	0.57
n-Olefins	-0.44	0.04	-0.51	-0.56	0.50	0.66	0.52	-0.31	-0.31	0.99	1.00	0.96	0.94	0.80	0.55
Iso-Olefins	-0.48	0.11	-0.60	-0.64	0.48	0.62	0.48	-0.27	-0.27	0.99	0.96	1.00	0.94	0.79	0.57
Naphtheno-Olefins	-0.42	0.08	-0.58	-0.62	0.46	0.65	0.47	-0.22	-0.22	0.96	0.94	0.94	1.00	0.74	0.55
Di-Olefins	-0.52	0.33	-0.61	-0.65	0.37	0.59	0.53	-0.40	-0.40	0.80	0.80	0.79	0.74	1.00	0.53
Oxygenates	-0.52	0.22	-0.43	-0.46	0.34	0.45	0.25	-0.28	-0.28	0.57	0.55	0.57	0.55	0.53	1.00

Table I-1: Pearson correlation coefficients for component groups from the 2017 Texas regular AKI fuels using the Texas study composition groups.

	Average (% Vol)	StDev (% Vol)
Paraffin	13.30	2.41
I-Paraffins	34.93	5.13
Aromatics	25.17	5.04
Mono-Aromatics	23.58	5.18
Naphthalenes	0.49	0.20
Naphtheno/Olefino- Benzs	1.09	0.35
Indenes	0.01	0.01
Naphthenes	7.44	1.81
Mono-Naphthenes	7.44	1.81
Di/Bicyclo-Naphthenes	0.00	0.00
Olefins	7.98	3.39
n-Olefins	2.82	1.26
Iso-Olefins	4.43	1.83
Naphtheno-Olefins	0.73	0.35
Di-Olefins	0.00	0.00
Oxygenates	9.70	0.46
Unidentified	1.48	0.56

Table I-2: Content and standard deviation of content, by hydrocarbon group for the Texas survey regular gasoline.

Carbon Number	Average (% Vol)	StDev (% Vol)
2	9.73	0.42
3	0.10	0.05
4	1.40	1.03
5	13.06	2.06
6	16.44	2.08
7	16.93	2.50
8	19.61	2.49
9	11.88	1.69
10	6.00	0.92
11	2.15	0.66
12	1.06	0.50
13	0.07	0.05

Table I-2: Regular gasoline content by carbon count. The count of two carbons represents ethanol.

The total aromatic content of the Texas fuels varies substantially, in keeping with the data in the EPA Fuel Trends report, as shown in Tables I-2 and I-3. In considering tailpipe emissions and addressing the example E5 versus E15 comparison (presented in detail in Appendix III), the major independent variable would be the ethanol difference. One would expect the aromatic content of the fuel to change with ethanol content to maintain octane rating, but the Texas data show aromatic variation without ethanol variation.

Figure I-4 above presents that there is a tradeoff in the fuel between isoparaffins and aromatics, where both provide octane in the final blend. Isoparaffins and aromatics, though variable in content, do not vary independently of one another. Most octane that is delivered by the isoparaffins will be associated with alkylation products, such as trimethylpentane, along with other di- and tri-methyl alkanes.

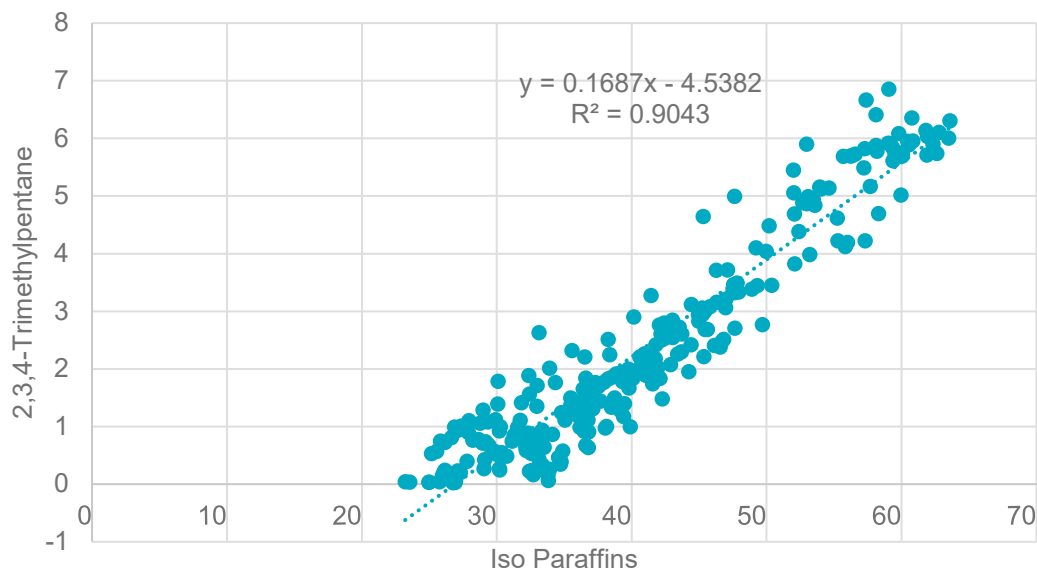


Figure I-6: Relationship between 2,3,4-trimethylpentane and total isoparaffins.

Figure I-6 shows the strong relationship between 2,3,4-trimethylpentane and isoparaffin content, and Figure I-7 shows the same for 2,4-dimethylhexane. Both show an offset (x-intercept) in isoparaffin content. Note that the strength of the correlation is indicated by the coefficient of determination (R^2) which, for regular linear regression, is the square of the Pearson correlation coefficient (R) used in the correlation matrix of Table I-1.

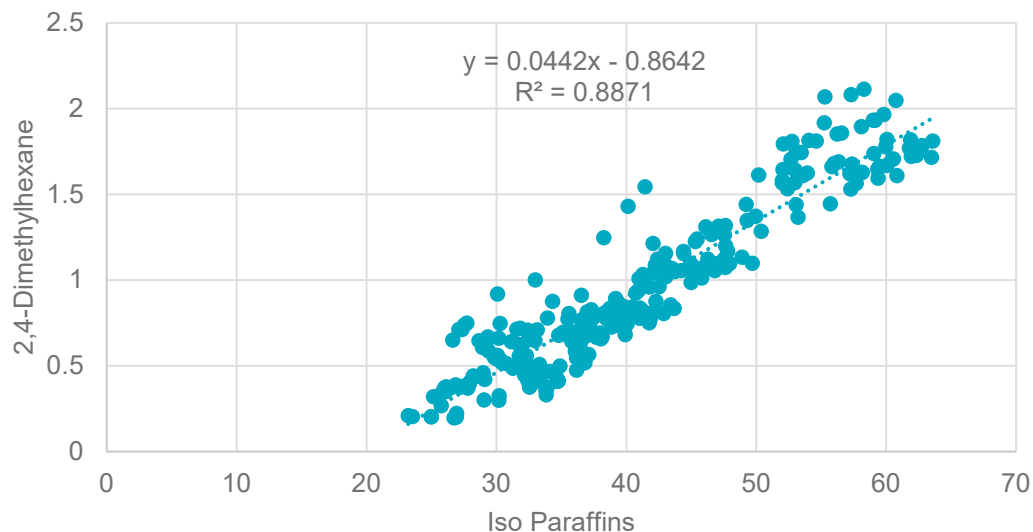


Figure I-7: Relationship between 2,4-dimethylhexane and total isoparaffins.

Figure I-8 shows a relationship, along with some outliers, for 2,4-dimethylpentane, suggesting that some dimethylpentane may be blended from a second source. The high correlation shown in Figure I-9 relates all C8 through C11 trimethyl alkanes to total isoparaffins. This high correlation coefficient is partly due to accounting for variation in product composition from different alkylation units and partly that this composite group

represents a substantial fraction of the total isoparaffins. Species such as isopentane, not fully associated with alkylation, are excluded in Figure I-9.

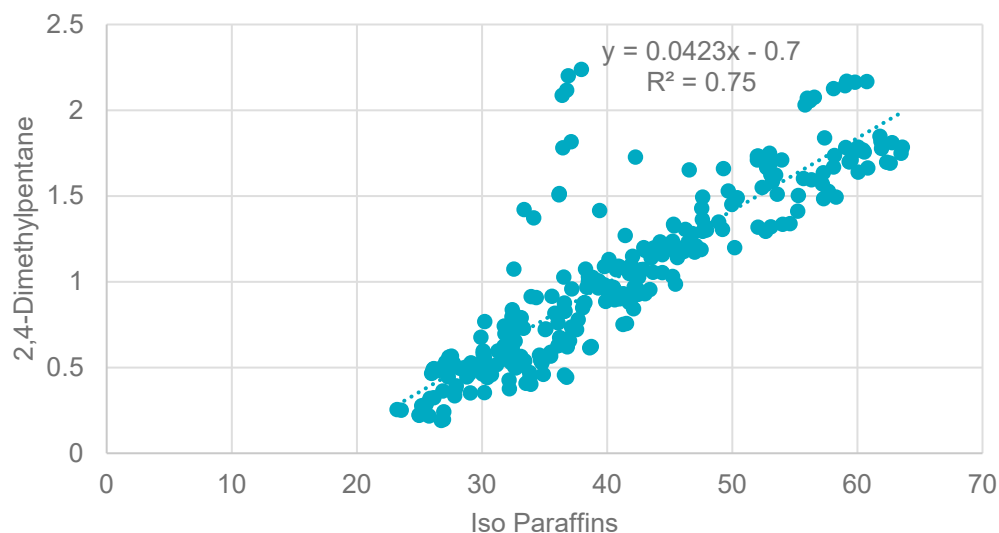


Figure I-8: Relationship between 2,4-dimethylpentane and total isoparaffins.

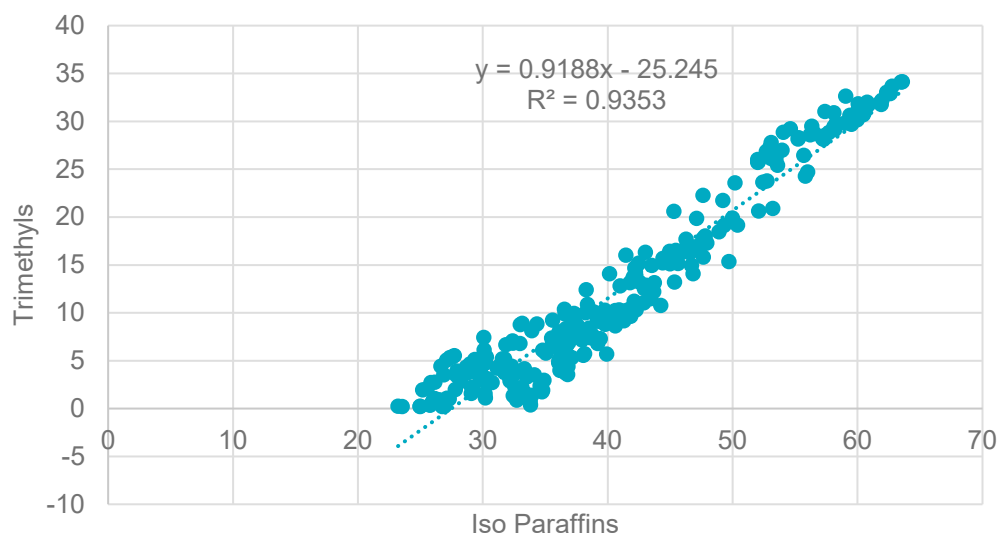


Figure I-9: The correlation is improved over the correlation of Figure I-6, I-7 and I-8 when all isomers of trimethyl alkanes (C8-C11) are considered.

Figure I-10 shows the lack of relationship between isopentane and the total isoparaffins, suggesting that the isopentane blurs the relationship between isoparaffins and aromatics. Isopentane represents almost half of the offset discussed above. Isopentane is known to come from many sources, including isomerizers, reformers and FCC, with a small amount from alkylation units. Its octane rating contribution is beneficial for regular fuel, but

not at the level of the aromatics and alkylates. Stronger anti-correlation is therefore anticipated between major alkylate species and aromatics.

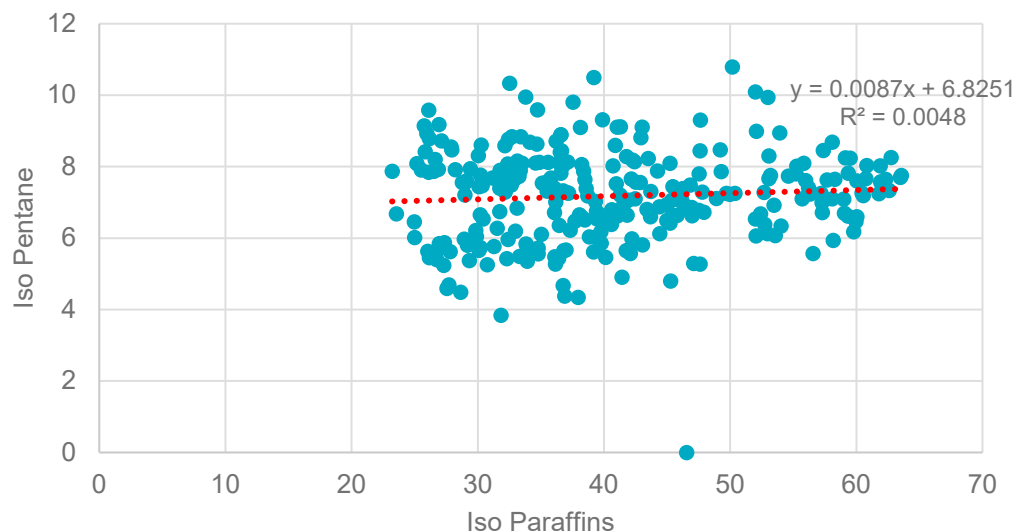


Figure I-10: Isopentane varies substantially but shows no clear trend with respect to total isoparaffins.

Figure I-11 shows strong relationships for both regular and premium fuels between the sum of all trimethylpentane isomers and the aromatic content. Further investigation of the Texas data can reveal an alkylate composition package that has the highest anti-correlation in response to aromatic level. Moreover, the Texas data also provide reasonable distributions of the various alkylate species within that package, so that study fuels can be formulated to match market fuels.

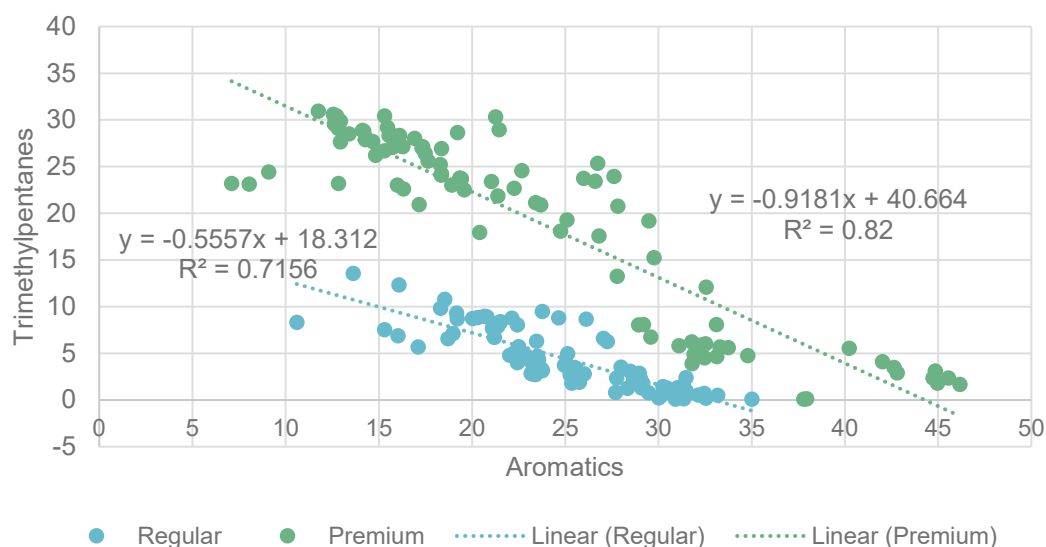


Figure I-11: The strong correlation between total trimethylpentane and aromatics for Texas regular and premium fuels, in units of volume percent.

Figure I-11 presents clearly that aromatic levels vary even without change in ethanol content. However, the figure also implies that it is not necessary to prescribe both aromatics and an alkylate content, because the two are sufficiently anti-correlated that one implies the other. With ethanol variation (as the major independent variable), either aromatic or alkylate content could be specified as a secondary independent variable, which would reasonably define the octane balance in terms of defining study fuels.

The volume of aromatics in the Texas survey was also examined. Neglecting benzene, the volume of C9+ aromatics was compared with C7 and C8 aromatics for regular gasoline, as shown in Figure I-12. Although both the heavier and lighter aromatic content varied substantially, there was little correlation between them. Since heavier aromatics will have a higher propensity to create PM than lighter aromatics, this suggests that two independent metrics for aromatics may be useful if resources for a study permit the additional runs. Use of a high and a low aromatic content would represent the upper right and lower left of Figure I-12, neglecting the other two quadrants. Choice of the $(C9+)/(C7+C8)$ ratio would be difficult for average levels of aromatics. Further study would be needed to examine the relationship of isoparaffins to each of the aromatic groups.

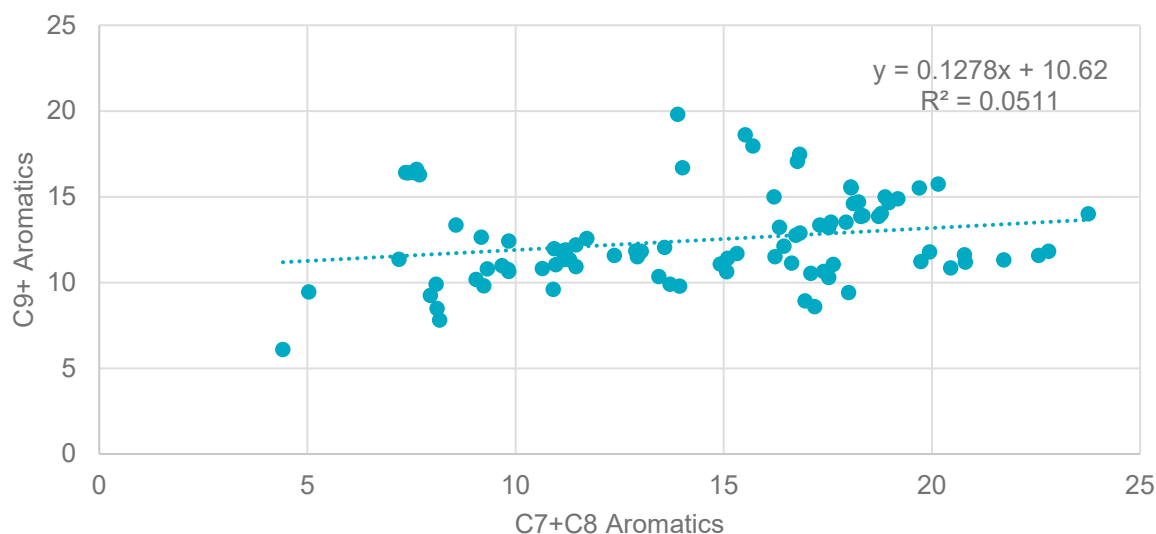


Figure I-12: There is no clear relationship between heavier and lighter aromatic content for the Texas regular gasolines.

The Texas data also provide insight into variables that may be used in studies of fuel effects other than tailpipe emissions. For air toxics studies, or studies of ozone forming potential, select species in the fuel may be known precursors to the toxics of interest and their concentrations in the fuel should be considered as study parameters. The Texas data show a lack of clear correlation between aromatic and olefin content, and high variability of concentration for both olefins and aromatics. For studies of engine deposits, often attributed to olefins, or to a combination of olefins and aromatics, both of those hydrocarbon groups should be considered as independent variables, because the one does not imply the other. If a clear relationship, characterized by a high correlation coefficient, existed between two species, only one need be used as an independent variable for a market fuel effects study. Of course, the resulting effects should not be attributed to only the species used as

the independent variable, but rather to the interplay of both species, since they are inseparable under market constraints.

Gasoline is limited in RVP, which limits the addition of species with high volatility. Normal butane has an RVP (vapor pressure at 100 degrees F) of 52, while iso-butane has an RVP of 72, iso-pentane has an RVP of 20, and normal pentane has an RVP of 15. Although properties of the pure substances may not reflect properties of blending, these values are all above permissible gasoline RVP and so would be expected to raise RVP and influence evaporative emissions. The first exploration revealed no tradeoff between butane and the sum of normal pentane and isopentane. Rather there was a weak positive correlation, as shown in Figure I-13. More research would be required to determine the distribution of sources of RVP for the Texas regular gasoline samples, although it will be blurred by non-linear blending effects and the presence of ethanol.

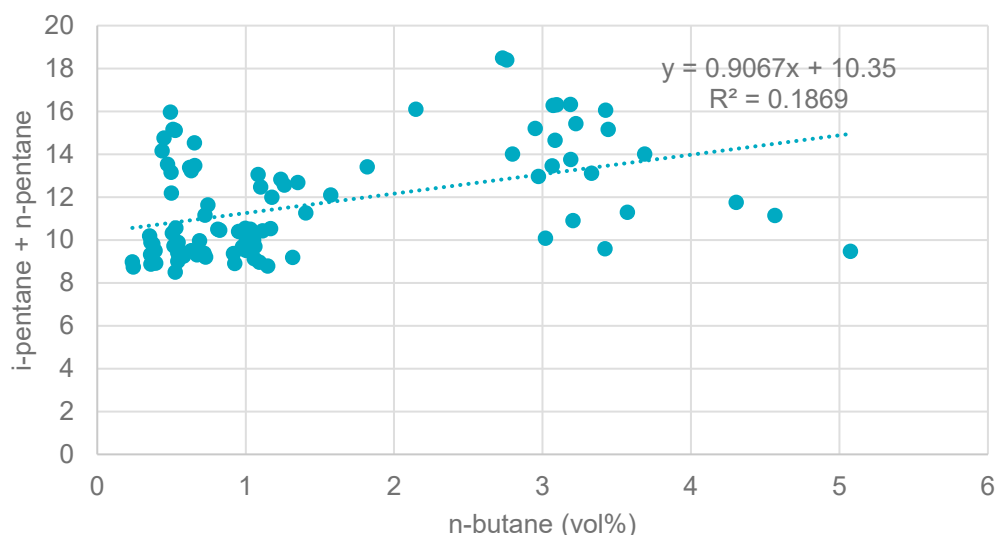


Figure I-13: A weak positive trend exists between the sum of pentane and isopentane, and butane, for Texas regular fuel.

In summary, the Texas data show no substantial correlation between total aromatics and olefins, naphthenes, and paraffins. Iso-paraffins are anti-correlated with total aromatics, dictated in part by meeting octane specification. Isopentane is poorly correlated with total iso-paraffins, but expected alkylates correlate well with total iso-paraffin content and are anti-correlated with total aromatic content. Light aromatic content does not correlate with heavy aromatic content.

The data presented above assist in identifying choice of study variables. In combination with expert and additional input, they also may assist in choosing values or ranges of values for these variables for a study. However, they cannot define study fuels precisely except in the case where both the target and baseline fuels use the same E10 BOB (as in Appendix II), and the gasoline supply is like that of Texas.

Appendix II: Fuel Composition Example – E10 Versus E15 with Common BOB

Generally, splash blending will not represent commercial fuel blending practice because a BOB would usually change to match the ethanol dilution that is anticipated. However, this study represents a real-world example of the splash blending of E15 from E10, and the comparison of emissions from E10 (baseline) and (E15 target). The Federal Register, presenting the EPA discussion of the E15 RVP waiver, states “With the 1-psi waiver, 15 percent ethanol could be blended using the same conventional gasoline BOBs (CBOBs) currently being distributed for use with 10 percent ethanol, year-round.” Infrastructure does not exist generally to distribute separate both E10 and E15 BOB. This implies that while E10 and E15 are both commonly available for sale, the only difference between E10 and E15 is the ethanol content. Further, the effect of E15 relative to E10 on fuel properties is small by most metrics compared to the E0 to E10 step. For example, in a recent study by University of California, Riverside, RVP changed little from E10 (8.97 psi) to E15 (8.77 psi). E15 is marketed to have an AKI one point higher than E10 with the same BOB (EIA, 2019).

A study of the difference in emissions effects between E10 and E15 would therefore involve either blending 5% additional ethanol with E10 or blending E10 and E15 using the same BOB. The study may proceed using just one E10/E15 pair, or two suites of fuels, in pairs that each use the same BOB. Conveniently, data points for the emissions differences (or ratios) associated with each pair can be gathered into a common database, even if they are acquired using different BOBs or in different studies. By using a ratio (E15 emissions)/(E10 emissions) for each fuel pair, the only effects of BOBs that are considered are driven by the ethanol blending effect itself, with ethanol as the only independent variable.

E10 BOB compositions already exist for the study in question. Such a study could address regular and premium, summer and winter fuels, and the planner would need to determine whether both RFG (using RBOB) and conventional gasoline (with CBOB) would be in question, or whether one was sufficiently dominant to satisfy the study need.

The BOBs vary from each refinery and over time, experience some mixing at the terminals, and blend in the tanks at fuel stations, but they still vary from gasoline station to gasoline station. A regional average BOB composition might be determined from refinery records. Alternatively, a sound plan for acquiring a representative range of parameters for the BOB would recommend sampling fuels from several gasoline stations or acquiring a representative number of BOBs from terminals. In the plan should be anticipation of variables that will not change between BOB compositions in the marketplace: if confirmed, those variables may be neglected in future analysis. As an example, it may be anticipated and confirmed that all regular finished E10 gasoline had an AKI at or near 87.

Presuming that the number of BOBs is too large for them all to be used as study fuels, a reduced number of selected compositions is used. The collected fuels or BOBs are analyzed to yield a set of parameters, defined

in the plan, and suited to the study. It is best if the full composition (DHA) of the BOBs is determined, so that any groupings of composition can be computed for statistical comparison on the fuels.

The planner would need to decide which properties of the fuel are important. Based on review of the EPACT study, NO_x emissions were modeled by aromatic and ethanol content and by T50. Total HC and CO emissions added RVP and T90 to the NO_x variables. If RVP values are found to be the same for all samples, their effect can be neglected. T50 is difficult to consider as a variable because it is influenced in a nonlinear fashion by the ethanol blending, but both T50 and T90 effects could be related to the distribution of molecular weights of compounds in the gasoline. Further, in EPACT, T50 and T90 were selected from distillation data, while other fractions were not. Additional research would be required to address conclusions for GDI studies, but it appears that total aromatic content, high molecular weight content, and mid molecular weight content would be important factors for gaseous emissions.

The collected BOB analyses should be compared statistically to determine how much the selected measures vary, and whether any other composition groupings vary by a large amount. If the variations of the identified variables are small, and no other groupings show excessive variation, the planner may elect to use a single BOB for the study. This could be a basket blend of the market fuels, or a blend to match the average composition closely. Otherwise vehicle count and test run needs should be balanced with the resources and number of fuels that can be accommodated. The study fuels, or BOBs, should reflect the distribution of variables of interest, or highly varying molecular groups, in the sampled fuels. The second example addresses a similar decision in more detail and serves to augment this information.

Appendix III: Fuel Composition Example – E10 Versus E20 Market Fuel

This example study seeks to determine the difference in emissions between E10 and E20 gasoline summer regular blends with separate BOB formulations dedicated to each ethanol level. The study targets PM emissions, so that fuel species known to affect PM should be emphasized, identified and considered. A BOB produced by refiners for E20 will have a different composition than an E10 BOB. Assuming that reformate is adjusted in the BOB to compensate for changes in ethanol levels, the E20 BOB would be shipped with lower aromatic content and a lower octane rating, because the ethanol will raise the anti-knock properties of the blend.

All fuel component concentrations presented in this appendix are hypothetical and prepared by the authors to illustrate the fuel selection process. The exemplary language below speaks of obtaining these concentrations based on Steps 1 to 4 of the blending guide, to illustrate the execution of a plan. The E10 values are proposed to be reasonably reflective of existing E10 market compositions and to provide a reasonable average concentration across the E10 fuels. There were no comprehensive market data to suggest E20 composition, but refinery economics provided guidance. It was assumed that E20 would be blended with reduced reformate or a less severe reformate product in response to the 10% ethanol increase: in this way about three quarters of the ethanol dilution effect is absorbed by aromatic reduction. For the E20, typical variability of other component groups is retained from the E10 market data. The composition data considered below do not emphasize molecular weight. A thorough study plan would need to address molecular weight at least to satisfy ASTM specifications and RVP limitations: the market would not demand matching of E10 and E20 distillation curves in detail.

The skill in planning this real-world study is to identify appropriate E10 and E20 projected fuel compositions that would be expected at the pump. In this case, one study fuel (E10) has an established BOB composition. However, E20 is not broadly available so that there is no current market fuel to define a BOB. This study therefore requires engagement with fuels experts, refiners and blenders to determine the expected fuel compositions. Alternately, the E10 may be defined by current market fuels, and the experts may be asked how the BOB will differ for E20 finished fuel. Conclusions are affected by issues as diverse as refinery flexibility and balance, ability to assess the interaction of the ethanol with new BOB formulations, regulatory constraints on composition and properties, and projections of how the scenario might evolve as the providers adapt to the change. There are also statistical decisions to be made on how many fuels should be used in the suite, their representativeness of the norm, their composition deviations, and any significant outlier sources that exist due to presence or absence of process units at refineries. The number of fuels is constrained by resources that are available. For this study example, detail of the hydrocarbon speciation has been reduced relative to that which would be expected for a real world study with high resource investment.

The planner contacts refiners and experts and seeks opinions on the most likely makeup of the E10 and E20 BOBs. The planner appreciates that full DHA may not be known, and requests estimates of the fraction of the following molecular groups in the BOBs. For simplicity, these compositions each add to 100%, neglecting heteroatoms and unclassified species in the mix.

- Olefins
- C6-C8 aromatics C9+ aromatics n-paraffins
- Iso-paraffins
- Napthenes
- Ethanol

Note that the fractions of hydrocarbon groups presented above necessarily are constrained. For example, as shown in the discussion of Texas data in Appendix I, there is an anti-correlation between aromatics and iso-paraffins because they both are used to establish octane rating. The olefin content is variable, but generally declines as aromatic content rises. Ethanol increase reduces the presence of other species through dilution, and group concentrations must sum to 100%.

The planner considers twelve hypothetical compositions; six for E10 and six for E20 finished fuel composition. These compositions are presented below in Table III-1 and Table III-2, along with the coefficient of variance for each group across each set of six fuels. In examining this high level composition summary, the planner appreciates that more detailed DHA must be considered when blending the fuels, so that the spectrum of molecular species in each composition group reasonably reflects refinery stream composition.

In a real study scenario, the planner would be expected to gather more than six fuel compositions at each level, to consider molecular weights in more detail, and to identify trends between composition groups to a greater extent than is presented in this simplified example. The planner would also need to ensure that the fuels met specifications and represented economically favored blends of refinery stream compositions.

Component	E10-1	E10-2	E10-3	E10-4	E10-5	E10-6	E10-Ave
Olefins	7.5	13.0	10.8	8.0	12.8	14.8	11.2
C6-C8 aromatics	10.1	11.3	15.3	17.7	10.5	9.5	12.4
C9+ aromatics	14.1	11.6	7.9	9.5	9.5	12.2	10.8
n-paraffins	15.5	7.6	16.7	15.3	12.9	10.6	13.1
iso-paraffins	34.8	39.8	31.0	33.8	38.7	34.6	35.5
Napthenes	8.1	6.9	8.3	5.7	5.5	8.4	7.2
Ethanol	9.9	9.8	10.0	10.0	10.1	9.9	10.0

Table III-1: Concentrations of major fuel groups for the E10 summer regular gasoline.

Component	E20-1	E20-2	E20-3	E20-4	E20-5	E20-6	E20-Ave
Olefins	6.9	11.5	10.0	8.0	10.8	12.6	10.0
C6-C8 aromatics	8.1	8.3	10.3	12.7	6.5	6.5	8.7
C9+ aromatics	10.2	6.6	4.9	6.8	5.5	8.8	7.1
n-paraffins	14.4	10.1	16.7	16.1	11.5	10.9	13.3
iso-paraffins	31.7	35.6	30.0	30.8	38.2	32.8	33.2
Napthenes	8.7	7.9	8.3	5.7	7.5	8.4	7.8
Ethanol	20.0	20.0	19.8	19.9	20.0	20.0	20.0

Table III-2: Concentrations of major fuel groups for the E20 summer regular gasoline.

Unless the planner has the resources to use all six E10 and six E20 fuels, the count of test fuels must be reduced. The E10 fuels have an average aromatic content of 23.2%, while the E20 fuels average 15.8, showing a reduction in aromatic content of 7.4% in response to the addition of 10% of ethanol. The planner examines the data and determines that there are high variations of the two most important parameters for PM, namely C6-C8 aromatics, and C9+ aromatics, and elects to consider those two groups as potential independent variables, along with ethanol, for selecting the suite of fuels to be used. There is also high variation in olefins, which may be considered as an additional independent variable.

Figure III-1 and Figure III-2 present the distribution of light aromatic and heavy aromatic concentrations. The relationship between the two weight groups is weak, although a slight anticorrelation exists for the E10 case. Therefore, defining a concentration of heavy aromatics would not provide strong guidance on the accompanying concentration of light aromatics (other than an expected average value) that should be used in that blend.

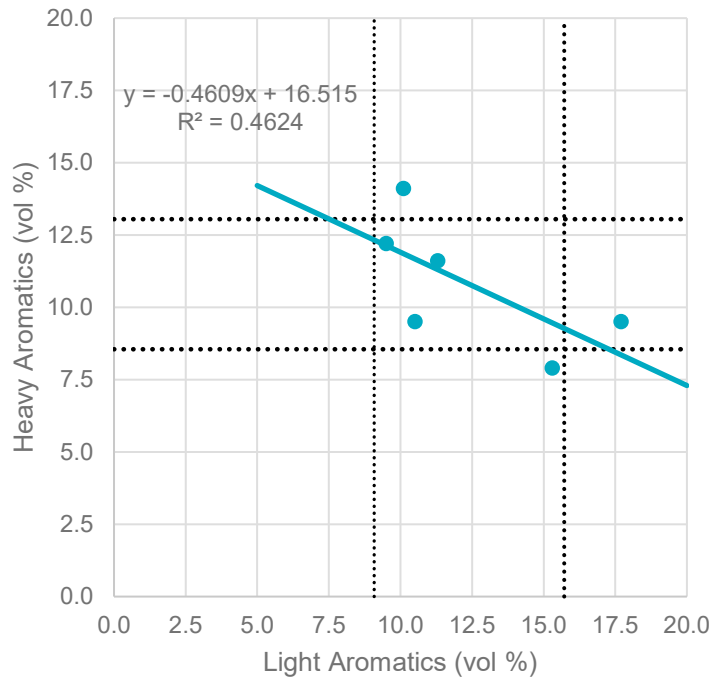


Figure III-1: Relationship between light and heavy aromatic concentrations for the six E10 fuels.

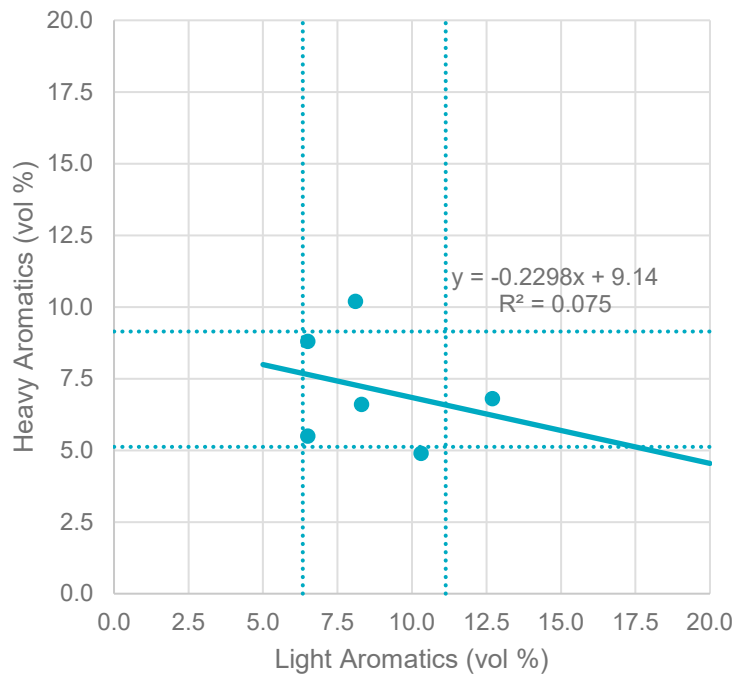


Figure III-2: Relationship between light and heavy aromatic concentrations for the six E20 fuels.

As shown in Figures III-3 and III-4, the iso-paraffins show low variation, but they are not subdivided as a group in the data sets that are being considered. The iso-paraffin group concentrations include both lighter species with moderate octane rating (e.g. isopentane) and heavier species with high octane rating (e.g. trimethyl pentanes from alkylate). The iso-paraffins vary inversely in concentration with the aromatic content, but weakly so. Noting that reformate and alkylate trade against one another to meet octane rating, isoparaffins could be used as an independent variable in place of total aromatic content. It is generally acknowledged that aromatics contribute to PM formation by known mechanisms. It is therefore more appropriate to use the aromatic content as an independent variable, and that decision embraces cause rather than correlation.

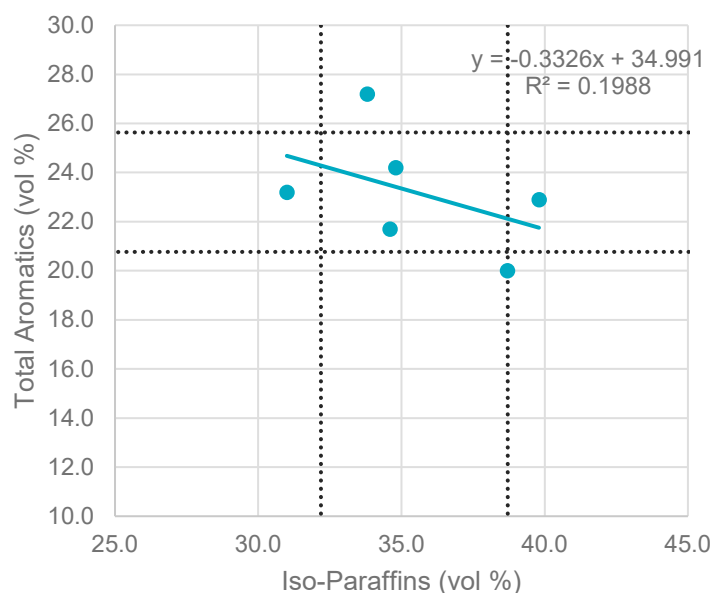


Figure III-3: Relationship between total (light plus heavy) aromatic concentrations and iso-paraffins for the six E10 fuels.

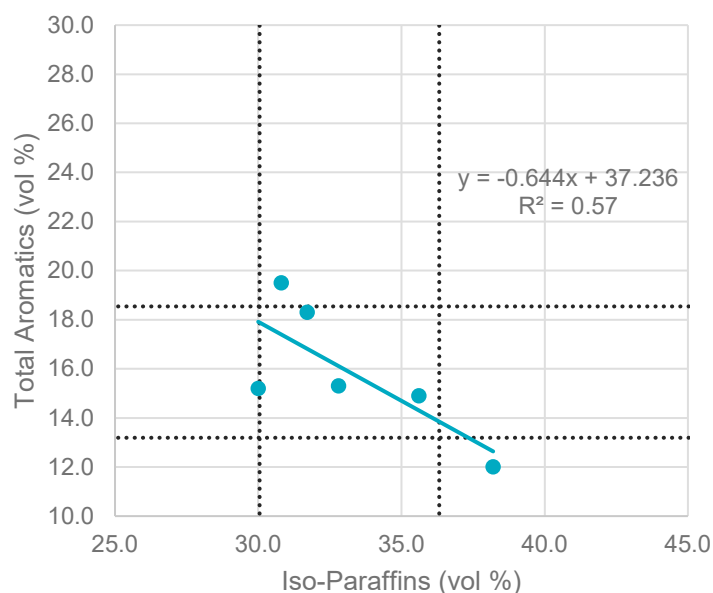


Figure III-4: Relationship between total (light plus heavy) aromatic concentrations and iso-paraffins for the six E30 fuels.

Spider plots for the six E10 fuels, with all concentration variables except ethanol concentration, are shown in Figure III-5, and those for E20 fuels are shown in Figure III-6. A variety of statistical analyses could be performed to determine how many fuels should be used for representation, and what compositions should be used for those fuels. However, these decisions will also be persuaded by the study mission (Step 1) and the available resources for the study (Step 2), because an increase in fuels must necessarily reduce the count of other study variables or the number of repeat runs that can be performed. The discussion below addresses the objective of examining PM. There may be other needs and drivers leading to the choice of a different count of test fuels if the study objective were to identify certain air toxics, or emphasized NO_x formation.

One fuel

For the case with the leanest resources, the planner may consider using one E10 and one E20 fuel, in which case the average composition for all species should be used for each fuel. The only independent variable would be the ethanol level.

Two fuels

If two E10 and two E20 fuels are considered, aromatics are clearly the target because they vary substantially for the six fuel sets and because they are known to be implicated in PM production. Desire is to understand the separate, independent influence of aromatics within the overall composition change from E10 to E20. There are three possibilities, and the final decision does not rely solely on statistical analysis.

- Two different values of heavy aromatic content could be chosen. The average for E10 heavy aromatics is 10.8% and the COV is 21%. Using one standard deviation to select the two points would yield heavy aromatic concentrations of 8.5% 13%. These values lie within the bounds of the six E10 fuels. To represent the average more closely, the 25th. and 75th. percentiles of the compositions could be used. For each of the two fuels, concentrations of other groups would be chosen as a best fit (using the six fuels data) to match the two levels of aromatics. A similar process would be used for the E20 choices.
- Total aromatic content could be used, by summing the light and heavy aromatic concentrations, and treating the total values in the same way that the heavy values were treated above.

For the E10 and E20 the values are:

- E10 Total Aromatics Average: 23.2%, Standard Deviation: 2.43%
- E20 Total Aromatics Average: 15.9%, Standard Deviation: 2.67%

If, say, 0.75 of the standard deviation were used to spread the aromatic content in the test fuels, the two E10 fuels would have total aromatic content of 21.4% and 25.0%, and the two E20 fuels would have aromatic content of 13.9% and 17.9%. This would be in contrast to multivariate study tradition, where the same high and low aromatic contents would be used for both the E10 and the E20. To match market fuel composition, the four points should not represent a rectangle in ethanol-aromatic planar space.

- A weighted aromatic factor could be used. One may expect that the heavier aromatics would have a greater propensity to form PM, based on the philosophy of the PMI calculation. From DHA of refinery streams, or estimation of the balance of specific aromatics in the C7-C8 and C9+ groups, one may conclude that an equivalent volume of C7-C8 aromatics would most likely produce PM at a certain fraction of the same volume for the C9+ group. An “effective aromatic contribution” (EAC) might therefore be $EAC = (C9+ \text{ volume fraction}) + k.(C7-C8 \text{ volume fraction})$, where k is less than unity. The EAC could then be treated statistically in the same way as for the two cases above.

Alternately, one could employ as the first fuel the average of composition for all species of the three fuels with the highest heavy aromatics (or the highest total aromatics, or the highest EAC). Similarly, the second fuel would be the average of composition for all species of the three fuels with the lowest heavy aromatics (or the lowest total aromatics, or the lowest EAC). One could also select the averages of the three fuels with the highest PMI and the three fuels with the lowest PMI, but blending should be performed to match the average compositions, and not merely to match the PMI values.

Three or four fuels

If resources are available to examine two independent variables, in addition to ethanol difference, it would be possible, but unusual, to fit a representative triangular set to the six fuels, using heavy aromatics and light aromatics as the two species. More traditionally, four points covering light aromatics and heavy aromatics would

be used. The choice of four variables would have better grounding if more than six proposed compositions were available. Any desire to increase the number of fuels further should result in the use of all six fuel compositions.

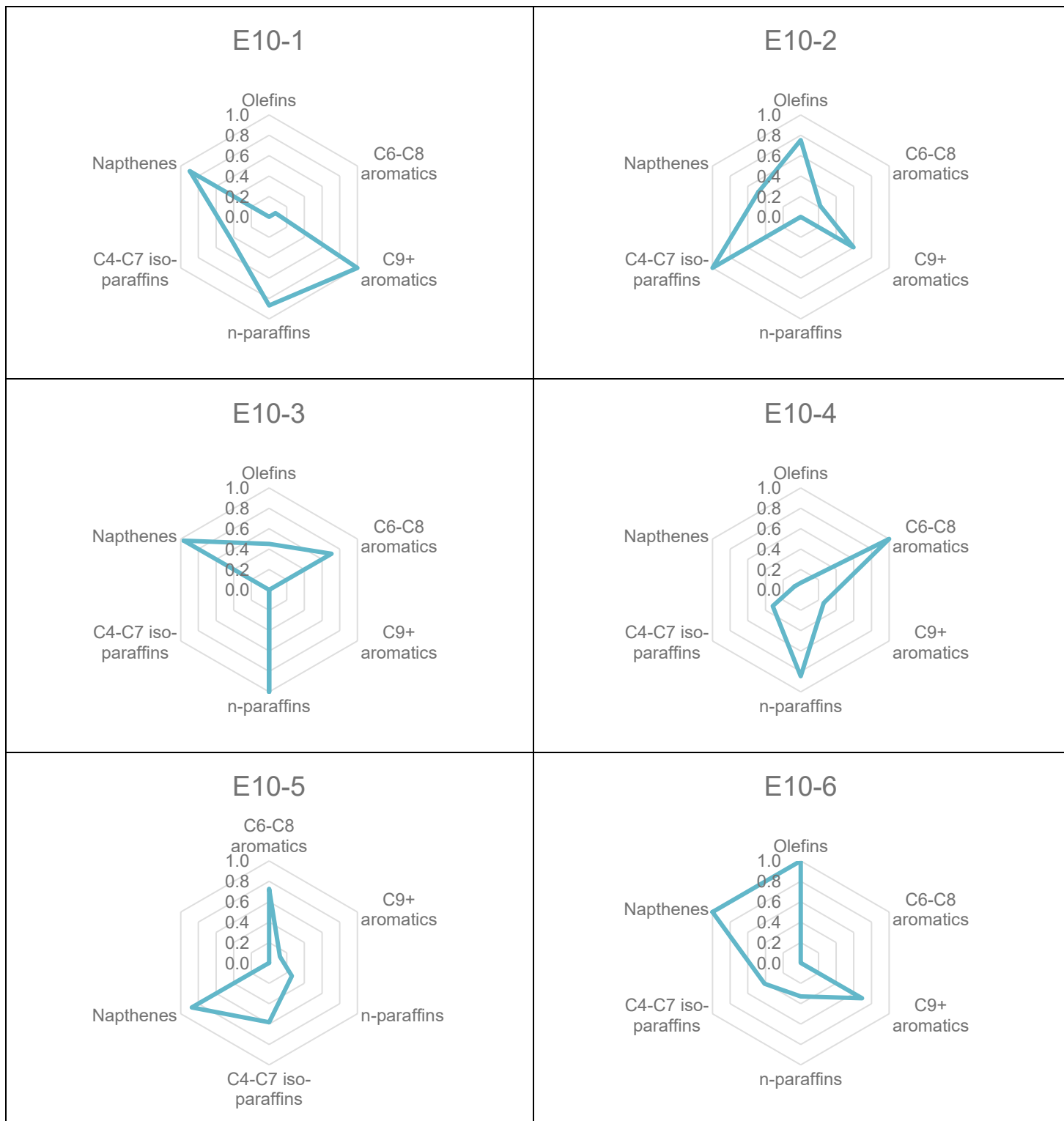
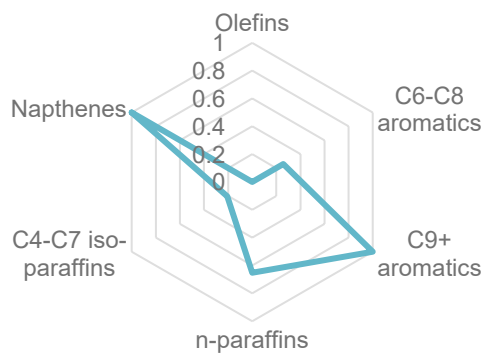
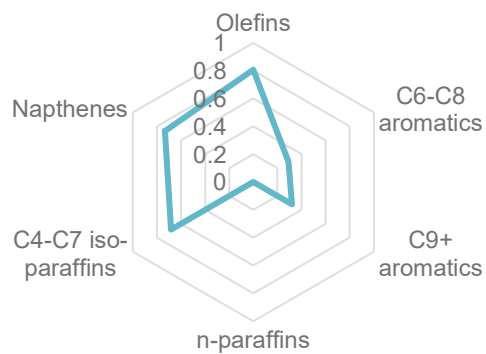


Figure III-5: Spider plots for the six E10 fuels showing the three independent variables. The concentrations are normalized to the range of data for the E10 fuels.

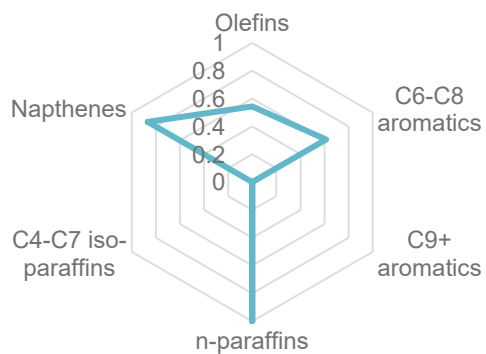
E20-1



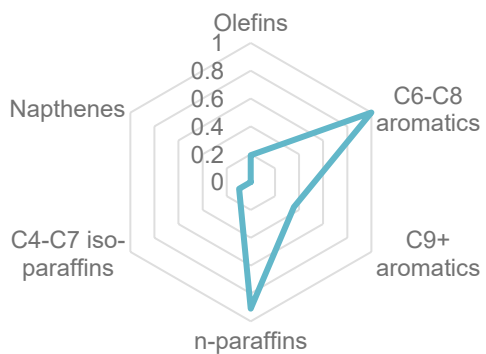
E20-2



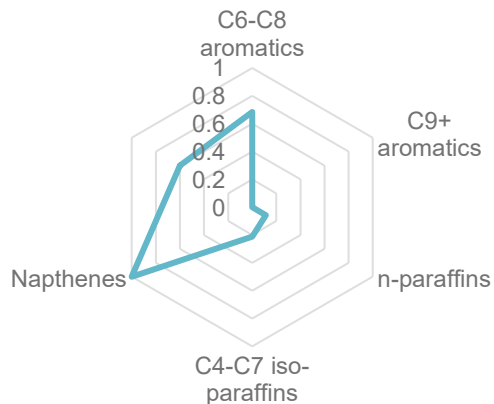
E20-3



E20-4



E20-5



E20-6

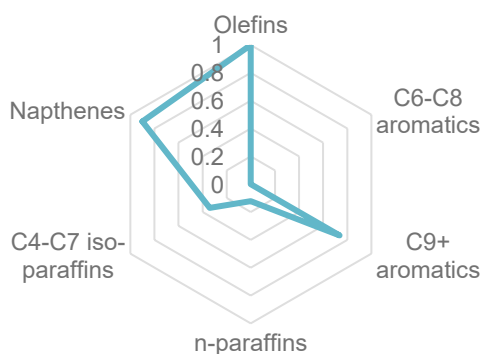


Figure III-6. Spider plots for the six E20 fuels showing the three independent variables. The concentrations are normalized to the range of data for the E20 fuels.