Quantifying Ethanol CI Benefits in Gasoline Composition

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Table of Contents

Executive Summary

The US consumes about 135 billion US gallons per day of gasoline, more gasoline than diesel, accounting for 53% of US total transportation energy use (EIA, 2021a). Light duty vehicles drive about 2,200 billion miles per year (NHTSA, 2021). The primary combustion species of this gasoline is carbon dioxide (CO_2), while remaining carbon in the fuel appears in the exhaust as regulated pollutants. Greenhouse gas (GHG) concerns have risen to the point that both fuel economy and CO_2 are now separately regulated. Traditionally reduction has been achieved through engine and vehicle design improvement and the use of biofuels, primarily ethanol. Currently most US gasoline is sold as a 10% blend of ethanol (by volume) with a 90% blendstock for oxygenate blending (BOB). The BOB is configured to yield a gasoline meeting specification after the ethanol is blended. Both petroleum components and ethanol blend in a way that changes properties in a nonlinear fashion, increasing difficulty in predicting gasoline composition effects.

Although much of the US fleet consists of vehicles with port fuel injection (PFI) and older vehicles still contribute substantially to the emissions inventory, gasoline direct injection (GDI) is now considered to represent the future. However, concern is expressed over the increase in PM associated with GDI. It is unclear whether wisdom gained from fuel effects research on PFI vehicles should be applied quantitatively to GDI vehicles.

When renewable fuels are considered, typically the reduction is assessed for their production and upstream CO_2 impact relative to conventional petroleum fuels. This results in a well to tank (WTT) analysis. However, the fuel change also affects the CO_2 produced by the vehicle, suggesting the tank to wheels (TTW) analysis presented in this report. TTW CO_2 reduction for ethanol blends may be examined from either a fuel-based perspective or a vehicle exhaust inventory perspective. Fuels are typically characterized using a carbon intensity (CI), calculated as a ratio of carbon in the fuel, or carbon dioxide production potential, per unit of mass-based heat of combustion in the fuel. Ethanol has both a reduced carbon content and a reduced lower (or net) heating value (LHV) relative to petroleum species. The CI of ethanol is slightly lower than that of typical petroleum gasoline. CI of Ethanol is around 4% higher than for paraffins in the fuel, but 12% to 18% less than the aromatics in the fuel. The high aromatic CI is associated with a high C:H molecular ratio. Aromatics (mainly from a refinery reformer), ethanol and branched paraffins (mainly from a refinery alkylation unit) serve to raise the octane rating of a gasoline blend.

Gas chromatography has now advanced to the point where gasoline may be characterized by concentrations of its individual constituent species, termed detailed hydrocarbon analysis (DHA). CI may be calculated by employing DHA. ASTM D6729 presents the analytic method. Species may also be gathered into hydrocarbon groups, such as paraffins, isoparaffins, olefins, napthenes and aromatics. DHA species or groups may each be characterized with respect to carbon content and LHV and summed in a weighted fashion to yield CI. Total fuel LHV and carbon content analyses can also yield CI. Generally, variability of fuel analysis has a small effect on conclusions when considering fuels that are intentionally blended or splash blended, but caution is needed in

comparing CI of two unrelated fuels, analyzed in different ways, due to measurement variability. C:H ratio was found to be a good correlational estimator of CI for market gasoline blends.

Refinery operations and blending practices are dictated by the best overall value of products sent to the market. These economic considerations, availability of feedstocks and examination of gasoline properties support the conclusion that as ethanol is blended into gasoline, so aromatics are reduced to maintain a constant octane rating. The primary refinery option for lower petroleum octane is through lower severity or throughput for the gasoline reformer, which in turn decreases gasoline aromatic content and carbon intensity. The reduction of aromatics in preparing a BOB for E10 and higher blends results in a net reduction in CI for market fuels. While the actual percentage reduction in CI of 10 percent and higher ethanol blends is not large, the TTW reductions are impressive when applied to national or global fuel consumption. This reduction opportunity applies to nearly all US gasoline consumption of about 140 billion gallons/year. Only 14 billion gallons of ethanol are required to produce the national E10 demand.

CI reductions for ethanol blending were demonstrated for a three component mixture of ethanol, toluene and iso-octane. The findings were confirmed through gasoline modeling covering a variety of scenarios and E10, E15 and E20 blends. Scenarios included maintaining current refinery production and increasing exports to compensate for incremental ethanol, adjusting refinery down to meet domestic demand and keep base E10 case exports constant, and splash blending E15 and E20 using an E10 BOB. CI reduction relative to E0 ranged from 1.41% for E10 to 3.04% for E20 with a dedicated BOB under the scenario of maintaining production with increasing exports, as shown in the figure below.
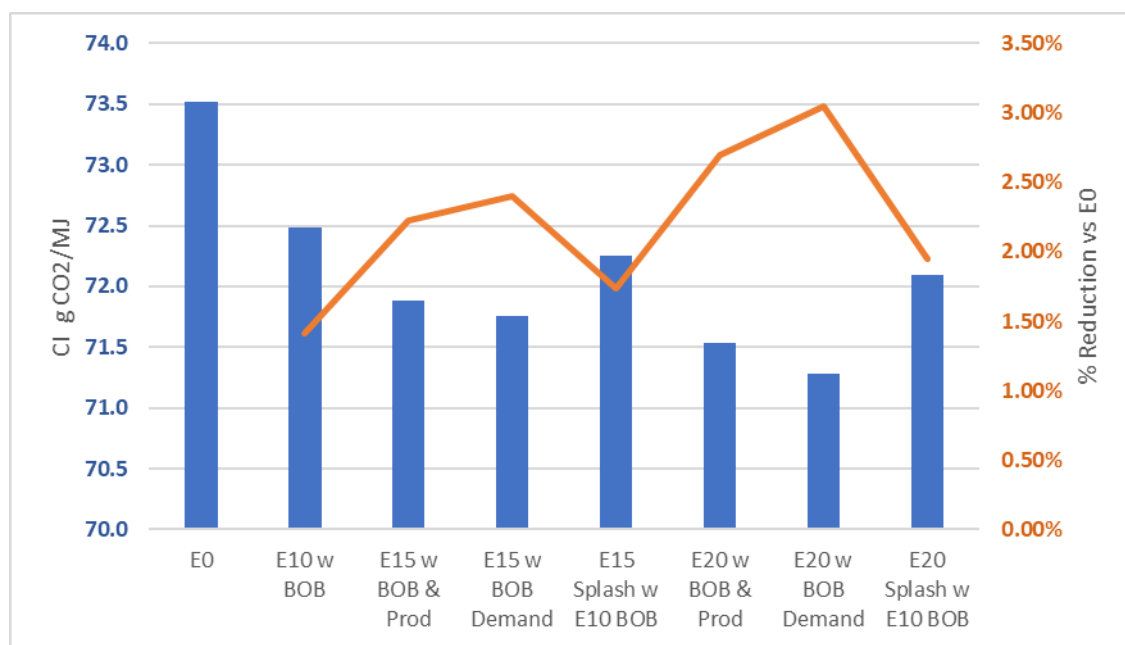

Figure ES-1: Carbon Intensity for "Set 1" Scenarios (mid-level aromatics) examined in the report

The US gasoline consumed represents about 700 billion pounds of carbon annually, which yields 1.3 billion short (US) tons of CO_2. From the fuel-based CI expected from an informed refinery model, a reversion from very high E10 penetration to a high aromatic E0 gasoline would raise the US CO_2 inventory by 18.3 million tons per year. Conversely, just from fuel CI effects on TTW emissions, a move to E20 would offer a beneficial reduction as high as 33 million tons per year relative to E0 use. Taking into account vehicle efficiency effects embodied in the EPA 1.66% value (NPRM, 2020) for moving from E0 to E10 suggests that E10 currently offers a national TTW reduction of 21.6 million tons of CO_2 annually.

The TTW advantages should be incorporated into WTW comparisons to assure overall accuracy. While the TTW reductions discussed above are more modest than the WTT GHG emissions effects discussed in the literature, the TTW effects are certain. In contrast, the cited WTT emissions component changes vary widely, with US government sources varying in WTW reduction predictions from 21 to 39%, and with far greater variation in the broader literature, due to disparate factors and assumptions such as those related to plant source, agricultural practices, production methods, energy sources and soil effects.

Although this report does not address WTT emissions broadly, the effect of BOB formulation and volume on refinery CO_2 emissions associated with the ethanol blending was explored. Increasing ethanol blend levels results in lower refinery energy and lower CO_2 emissions, but with a more than offsetting increase in CO_2 emissions from hydrogen production requirements. The net is a small increase in refinery CO_2 as more ethanol is used, comprising about 0.5 to 2.5 percent of overall refinery fuel and CO_2 emissions. The change in refinery CO_2 emissions does not have a significant impact on changes in gasoline carbon intensity as ethanol blending is increased.

The modeling demonstrating aromatic reduction resulting from ethanol addition is in strong contrast to the MOVES 3 Fuel Wizard scenario presented by the EPA for a high alkylate E0 (EPA, 2018b). Such a scenario would demand new refinery infrastructure and attractively priced feedstocks that are unlikely to become available.

Aromatic reduction, explained in this report, not only favors CI but also reduces PMI, with implied tailpipe PM 2.5 reduction. Gasoline exhaust PM is considered a major health care concern and has gained greater visibility as a result of GDI adoption and the relative improvement of diesel exhaust PM reduction. PMI is not directly correlated with CI, because the weight and structure of the aromatic components have a complex effect on PMI, but efforts to reduce CI have favorable PMI effects. The figure below demonstrates the disparate contributions of petroleum components to the PMI.
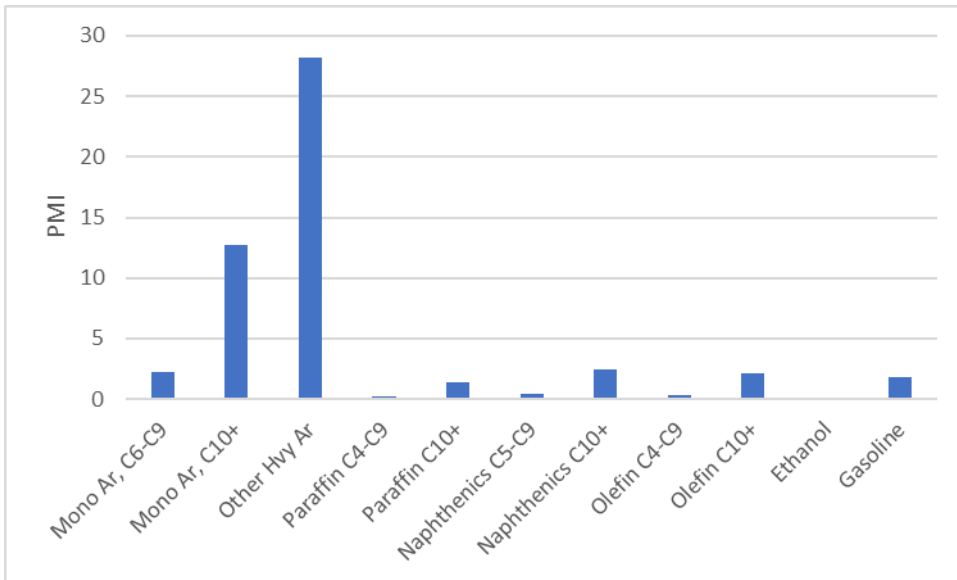
Figure ES-2: PMI of Gasoline, Ethanol and Gasoline Compounds

Measurements of CO_2 from vehicles operated on a dynamometer provide information both on the fuel CI and on the reaction of the engine to properties of the fuel other than LHV. In particular, recent model year GDI engines with high compression ratios will take advantage of a fuel with superior in-use knock resistance to improve efficiency. CO_2 is reduced by the small amount of unburned fuel, other hydrocarbons, particulate matter and non-methane organic gases that are present in the exhaust downstream of the catalyst. The more efficient use of fuel is related to the R-factor, which is employed to assure constancy of data over time as certification fuel specifications are changed. The change from the indolene (used for certification four decades ago) to the present Tier 3 E10 certification fuel is proposed by the EPA to have an R-factor of 0.81, implying that the engine does not show the full penalty of the reduced LHV of the E10. However, there is uncertainty in comparing fuel economy numbers from separate test runs. Data from other programs have shown variation in the reaction of engines to LHV changes, suggesting that the cause for fuel economy change is not one dimensional in LHV.

In summary, ethanol blending into gasoline offers an attractive route for reduction of light duty vehicle TTW GHG emissions while maintaining or raising gasoline octane rating, and while reducing PMI of the fuel.

Introduction

Fuel Consumption and Alternative Fuels

The world consumes approximately 100 million barrels per day of petroleum products, while the US daily gasoline demand is 8 to 9 million barrels per day (EIA, 2021a). The US consumes more gasoline than diesel, accounting for 53% of US total transportation energy use (EIA, 2021a). The primary combustion species of this gasoline is carbon dioxide (CO_2), three million metric tons per day of which is produced in engine exhaust alone in the USA. In this way, small fractional reductions of CO_2 from automobiles represent a substantial mass deduction from the greenhouse gas (GHG) inventory.

Traditionally, reduction of gasoline automotive CO_2 production was motivated by efficiency and energy security concerns, to which were added rising GHG concerns in the last two decades. Reduction was achieved through engine and vehicle design improvement, but biofuels have offered an equally attractive pathway. Fuel efficiency of light-duty vehicles is regulated using fleet-averaged Corporate Average Fuel Economy (CAFE) standards, leading to less gasoline burned per vehicle mile traveled. Average CO_2 emissions for 2020 are estimated at 344 g/mile (EPA, 2021b). Light duty vehicles drive about 2,200 billion miles per year (NHTSA, 2021).

Alternative fuels for automobile propulsion have a long history (Hoyer, 2008), and the subset of renewable fuels has received attention both to reduce climate change and embrace sustainable resources. Numerous studies exist to show that fuels derived from agricultural products offer a different carbon footprint than petroleum-based fuels, when the fixation of carbon by plant growth is taken into account. These studies vary in prediction largely due to the disparate factors and assumptions related to plant source, agricultural practices, methods of production and soil effects (Wang et al., 2012; Mekonnen et al., 2018; Holzman, 2008; EPA, 2010; Lewandrowski et al., 2018; Scully et al., 2021). Corn-based ethanol is the most visible renewable fuel in the USA. The US Department of Energy Alternative Fuels Data Center cites the 34% GHG reduction of Wang et al. (2012) for ethanol use. A report commissioned by the US Department of Agriculture presents that "the current GHG profile of U.S. corn ethanol is, on average, 39 percent lower than gasoline" (USDA, 2018). The US Environmental Protection Agency presents several values based on process used, including an oft-cited 21% value for ethanol produced using dry milling and natural gas (EPA, 2016).

Well to Wheels Studies

"Well to wheels" (WTW) studies seek to quantify and compare environmental effects arising from competing technical or economic pathways. In comparing use of petroleum fuels and biofuels, the studies include "upstream" impacts. As examples, for petroleum production, emissions signatures from prospecting, drilling, production, refining and transportation would all be considered, as would the footprint of materials employed in these activities. For biofuels, such as ethanol, analyses would include emissions arising from agricultural activity, fermentation, distillation and transportation, with negative and positive corrections made for

agricultural supplies (fertilizer and pesticides) and for by-products of value. Difficulty exists in determining the scope of analysis and the components that should be considered. WTW may be divided into "well to tank" (WTT) and "tank to wheels" (TTW) components. While the WTW predictions vary widely due to varying assumptions and circumstances, as described above, comparative TTW is more readily addressed with regard to CO_2 production through vehicle emissions testing or fuel consumption measurements under controlled vehicle road load. Although TTW CO_2 differences between similar fuels are subtle, the results are of strong interest for climate change reduction noting the volume of gasoline that is consumed in the US and worldwide for light duty transportation. The primary thrust of this report is to address fuel-associated differences in TTW GHG (CO_2) impacts. The fuels being considered consist of petroleum-based gasoline, ethanol, and blends of these two fuels. The engine controls may be influenced by the change in fuel, adding to the tailpipe emissions changes that are attributable to the fuel carbon content itself (Stein et al., 2013). A TTW assessment may be approached either by considering relative vehicle exhaust emissions or by considering the composition of the fuels themselves. The two approaches differ, but are nearly synonymous, due to the high combustion and conversion efficiency of spark-ignited engine fuels, as described below.

Relating Fuels and Exhaust

It is reasonable to assume that nearly all of carbon in the fuel is burned to form CO_2 and all of the hydrogen in the fuel is burned to produce water in a modern vehicle tailpipe stream, with minor exceptions. The combustion efficiency, or fraction of fuel that is burned in the cylinder, is typically high. Engine design and control seek to maximize that efficiency within constraints that are often associated with pollutant abatement.

In-cylinder combustion efficiency can be found from pre-catalyst exhaust gas analysis. With closed loop crankcase systems in modern vehicles, blowby gas passing by the piston rings is re-burned and therefore captured in the pre-catalyst emissions. Heywood (2018) points out that combustion efficiency is 95% to 98% for lean equivalence ratios, and presents data clustered around 95% for spark ignited stoichiometric combustion. Exhaust gas composition data presented by Heywood show exhaust gas mole fractions for carbon monoxide (CO) and oxygen to be less than 1% for gasoline and isooctane under stoichiometric conditions. CO emissions rise for rich operation and oxygen emissions rise for lean operation, so that a port fuel injected (PFI) engine during transient operation may see swings in stoichiometry that erode average combustion efficiency. Further, a small fraction of CO_2 dissociates into oxygen and CO, so that full conversion of fuel to CO_2 is not possible. Some hydrocarbons typically escape full combustion as a result of quench zones in the cylinder and cyclic storage of fuel in the cylinder oil film. Direct injection (DI) engines with advanced controls for air/fuel ratio are expected to have higher efficiency than legacy engines. Wang (2014) presented combustion efficiency data for ethanol, gasoline and furans, showing ethanol near 97% and gasoline near 95.3% for a direct injection engine, with stoichiometric air fuel ratio, at 1500rom and indicated mean effective pressures (IMEP) from 3.5 to 8.5 bar. Wang (2014) cites the oxygenated nature of ethanol as a contributing factor to its high combustion efficiency.

That fuel that is not oxidized by in-cylinder combustion is oxidized further by the vehicle catalyst. Light duty vehicles vary substantially in CO_2 emissions, largely due to road load (vehicle mass and frontal area) and driving schedule, but a range of 300g/mile to 600 g/mile is a reasonable representation. Durbin et al. (2006) measured emissions of PFI vehicles on gasoline and gasoline-ethanol blends. The vehicles were tested on the FTP and twelve different fuels. As an example, a 2002 Ford Taurus ("Vehicle 1") yielded average hydrocarbon (HC) emissions of 0.008 g/mile over "bag 2" of the FTP and 0.045 over "bag 3." For CO the corresponding values were 0.074 and 0.654 g/mile. These values are typical for other vehicles in the study and are a very small fraction of the CO_2 produced. Both bag 2 and bag 3 represent hot running conditions with an active catalyst. For the cold start "bag 1," the emissions include combustion effects due to a cold engine, and the period when the catalyst is not active, so that the tailpipe emissions are closer to engine-out emissions. For the Ford Taurus, the HC emissions were 0.220 g/mile and the CO emissions are 2.051 g/mile. In this case the CO/CO_2 ratio was 0.48%.

Recent GDI vehicles have lower tailpipe emissions. In a study by Yang et al. (2019a) that included five GDI vehicles, eight fuels, and weighted average emissions from all three phases (including cold start) of the LA92 cycle, HC emissions ranged from under 0.004 to slightly over 0.012 g/mile. CO emissions ranged from 0.05 to 0.4 g/mile. PM mass is typically low and was less than 0.045 g/mile even for cold start in the companion study by Yang et al. (2019b). Therefore, a carbon balance between fuel and exhaust using CO_2 alone may err at the 0.5% level only for older model year cars over a cold start.

Exceptions arise if an enrichment burst is used for engine cold start, or if enrichment is used for engine and catalyst protection under sustained full throttle operation. In these cases, the quantity of CO produced will represent a greater fraction of the fuel burned, because the catalyst lacks sufficient oxygen to eliminate CO under rich burn conditions.

If substantial CO is produced, CO_2 production at the tailpipe will be overestimated if fuel consumption is used as the basis for the CO_2 calculation. CO_2 at the tailpipe would be determined more accurately by emissions measurement. However, it is important to consider the ultimate fate of CO and whether it, too, may represent a greenhouse gas in the long term. Jaffe (1968) observed at that time that the CO levels in the atmosphere were not rising although the anthropogenic CO production was rising. Jaffe observed that CO is oxidized slowly to CO_2 in the lower atmosphere, with residence time estimated at between 0.3 and 5 years. IPCC (2018) cite the ability of CO to modulate concentrations of methane and tropospheric ozone, and discuss the argument for a CO global warming potential. King (1999) opines that 10 to 25 percent of CO may be consumed by soils. However, the major sink of CO is by reaction with the hydroxyl radial OH, leading to CO_2 formation and a CO global lifetime of two months. (Rozante et al., 2017) It appears reasonable that one might consider CO as a precursor to CO_2, with a faster conversion than the loss of CO_2 from the atmosphere. In this way fuel-based CO_2 determination may be a more faithful climate change assessment than the use of CO_2 alone in tailpipe discharge.

Carbon Intensity

Regardless of the source of fuels and their upstream environmental impact, one may assess the carbon dioxide production by fuels as they are burned or as they produce energy to accomplish some measurable task. A TTW value is often cited. Generally speaking, a higher carbon to hydrogen ratio in hydrocarbon fuels suggests a higher output of carbon dioxide for a given application. An atom of pure carbon, burned stoichiometrically with one molecule (two atoms) of oxygen, produces one molecule of CO_2. Carbon has a heating value of 14,100 BTU/lb. (32.8 kJ/kg). One molecule of methane, having the highest possible hydrogen to carbon ratio, also produces just one molecule of CO_2, but also produces two molecules of water, and gains the energy from the burning of the associated hydrogen. Methane has a lower heating value (LHV), where the water is taken to be vapor, of 21,433 BTU/lb. The higher heating value, where the water in the products is a liquid, is 23,811 BTU/lb. Unless otherwise stated in this report, lower heating values are employed.

The heating value 21,433 BTU/lb. of methane represents 28,577 BTU/lb. of carbon in the fuel. This is approximately twice the heat output of that for pure carbon, although the CO_2 production is the same. A ratio of CO_2 produced (leading to a GHG effect) to the heating value (suggesting work that can be done) represents one measure of carbon intensity. Other hydrocarbons, such as higher paraffins, aromatics and olefins lie between carbon and methane in their carbon to hydrogen ratios. Their heats of combustion are raised by the presence of hydrogen, but ultimately determined by the molecular structure of the hydrocarbon. The molecular structure effects are complex. For example, in the case of napthenes, the number of carbon atoms in the ring causes "ring strain" due to enforced bond angles, with attendant differences in heats of combustion. Straight chain paraffins are not constrained in this way and thereby exhibit higher heats of combustion.

Carbon intensity is a loosely defined term, even represented as the "measure of CO_2 produced per dollar of GDP." (USDOE, 2016). It may include upstream contributions when discussing CO_2 production per kW-hr of electric power. EIA (2020) employs the definition as a ratio of CO_2 mass to energy produced: "The amount of carbon by weight emitted per unit of energy consumed (CO_2/energy or CO_2/Btu)." It can also be cited in terms of carbon mass instead of CO_2 mass, using the molecular weights for a translation factor of 12/44. In terms of real environmental impact in the transportation world some fuels and fuel blends are used more efficiently by engines than others, so that a carbon intensity of CO_2 mass/mile can be employed. This impacts CO_2 emissions regulation, as discussed below. The primary value employed in this report is in units of grams CO_2/MegaJoule (g/MJ), although the CO_2/mile values are also of strong interest. The two values differ in practical terms because the efficiency of use of the fuel by an automobile can vary with respect to fuel composition.

Some differences exist between published values for LHV of a species, because the value may be determined experimentally or using different modeling approaches. If consistent values are employed, or if the dilution of a defined fuel with ethanol is considered, it is unlikely that these differences will cause changes in conclusions, as discussed in Appendix B. However, the carbon intensity determined by two separate agents would differ in reflecting that variation in LHV.

PARAFFIN SPECIES	FORMULA	Grams CO_2/gram	LHV (MJ/kg)	Grams CO_2/MJ
Butane	C4H10	3.028	45.3	66.9
Hexane	C6H14	3.064	44.7	68.6
Octane	C8H18	3.082	44.4	69.5
Decane	C10H22	3.093	44.2	70.0
ISO-PARAFFIN SPECIES				
Iso-butane	C4H10	3.029	45.2	67.1
2,2,4 Trimethylpentane	C8H18	3.082	44.0	70.1
2,3,4 Trimethylpentane	C8H18	30.82	44.3	69.6
3-Ethylhexane	C8H18	3.082	44.3	69.6
3-Methyloctane	C9H20	3.088	44.5	69.4
AROMATIC SPECIES				
Benzene	C6H6	30380	40.1	84.3
ortho-Xylene	C8H10	3.316	40.8	81.3
para-Xylene	C8H10	3.316	40.4	82.2
Indane	C9H10	3.352	40.3	87.4
Napthalene	C10H8	3.434	38.8	88.6
NAPTHENE SPECIES				
Cyclopentane	C5H10	3.138	43.8	71.7
Cyclohexane	C6H12	3.138	43.4	72.3
1,1-Dimethyl-cyclohexane	C8H16	3.138	43.2	72.6
n-Butyl-cyclohexane	C10H20	3.138	43.9	75.2
OLEFIN SPECIES				
Butene-2	C4H8	3.138	44.7	70.2
2-Methyl-pentene-1	C6H12	3.138	44.2	74.6
Octene	C8H16	3.138	44.2	73.3
1,3-Pentadiene	C5H8	3.230	44.5	76.3
ALCOHOL SPECIES				
Ethanol	C2H5OH	1.953	26.9	71.0

Table 1: LHV, carbon content and CI for selected hydrocarbons and ethanol, to demonstrate CI variation

Table 1 shows the variation of heating value, carbon content and CI for selected hydrocarbons and ethanol, and shows that LHV varies by molecular weight and structure. Normal paraffins and iso-paraffins have a low

carbon-to hydrogen ratio, particularly at low molecular weights, and enjoy low values of CO_2 (in units of g/MJ) Ethanol has a carbon intensity about 5% higher, only slightly above the intensity for diolefins (low hydrogen content) and napthenes (low heating value). However, aromatics have a low heating value and a high carbon content, and so exceed the carbon intensity of ethanol by about 12 to 18%. Historically the addition of ethanol to gasoline displaced aromatics and olefins, leading to an environmental gain with respect to carbon intensity.

Fuel may contain heteroatoms, in addition to hydrogen and carbon. Sulfur in a fuel will contribute to its energy production, but not to CO_2 production, actually reducing CI. This contribution is meaningful for some legacy marine bunker fuels, but insignificant for gasoline. However, one must consider oxygenates in evaluating the CI of fuel blends. Ethanol, as C_2H_5OH carries one oxygen with it as an alcohol. This oxygen displaces atmospheric oxygen demand during combustion, reduces the heating value of the fuel relative to an alkane, and reduces the stoichiometric air/fuel ratio to 9, rather than the values of 14 to 15 for petroleum gasolines. Although upstream renewable arguments may be offered with regard to bioethanol, in a tank to wheels CI analysis the CO_2 emissions from a mass of fuel burned in the engine are driven by definitive fuel chemistry. Each molecule of ethanol produces two molecules of CO_2. If a water molecule is subtracted from the ethanol molecule, the hydrogen to carbon ratio is 2. When blended with petroleum gasoline, the CO_2 and energy contributions of the ethanol are considered proportionally, as with each petroleum species in the mix.

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. Since 2006 in the USA, ethanol has replaced MTBE as the oxygenate of choice for blending with gasoline. Use of ethanol is also supported by the Renewable Fuel Standard (EIA, 2019). More recently these changes have been attributed to ethanol blending and its impact on high carbon intensity aromatic compounds. In 2016 The Health Effects Institute published an executive summary relating to ethanol and aromatics in gasoline (HEI, 2016).

The renewable fuel standard (RFS) in 2005 facilitated blending of ethanol with a petroleum blendstock for oxygenate blending (BOB), for sale at the pump. Ethanol offers both knock resistance and oxygen content. Between 2006 and the present day 10% (by volume) ethanol blend, E10, has been adopted widely. Production of knock resistant gasoline without oxygenates can be facilitated by the addition of aromatics such as toluene, ethylbenzene and xylene. In general, production of aromatics from a refinery reformer offers a pathway for increasing knock resistance without use of additives. Sulfur in gasoline has been reduced to enable more efficient three-way catalyst use for reduction of hydrocarbons, CO and NOx.

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 in 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."

Carbon Intensity and Surrogate Blends

Ethanol blending effect on CI may be examined through a surrogate mix of ethanol, toluene and iso-octane. The toluene represents aromatics, which have a high CI, attributable to their high carbon to hydrogen ratio. The iso-octane represents paraffins broadly and has a slightly lower CI than ethanol.

A base fuel, or fulcrum, for Figure 1 was a blend by weight of 10% ethanol, 25% toluene and 65% iso-octane. This was chosen because real world US fuels typically are E10, with less than a third of the remainder as aromatics. Four cases were considered to examine varying ethanol content and are reflective of real-world blending discussed in a section below in this report.

1. As ethanol content was adjusted upward or downward, toluene was adjusted in the opposite direction by the same mass as for the ethanol. This was a direct mass substitution.
2. As ethanol content was adjusted upward or downward, toluene was adjusted in the opposite direction by 0.75 of the mass of ethanol. The balance remained isooctane.
3. As ethanol content was adjusted upward or downward, toluene was adjusted in the opposite direction by 0.5 of the mass of ethanol. The balance remained isooctane.
4. Ethanol was increased in mass by "splash blending." The toluene and iso-octane were reduced or increased in mass fraction as displaced by the ethanol.

Figure 1 shows the relative mass fraction of ethanol and toluene in each case, with the balance being iso-octane.
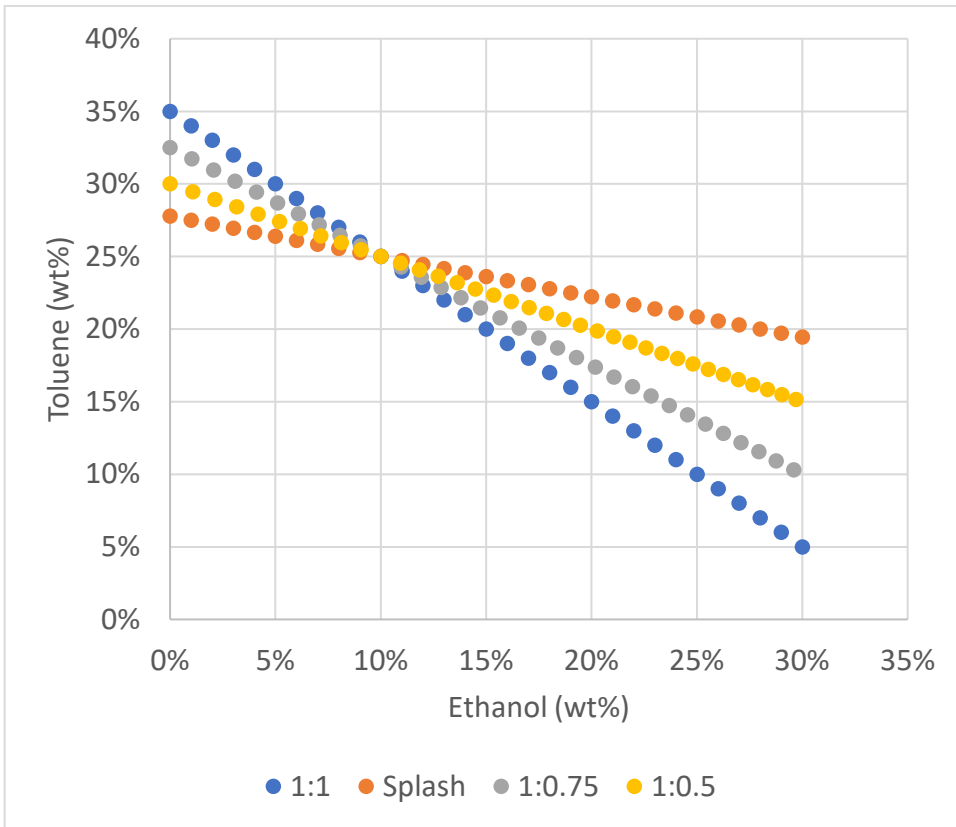
Figure 1: Variation in carbon intensity due to four different blending strategies of ethanol and toluene in a balance of iso-octane.

In all four cases ethanol blending served to reduce the carbon intensity of the fuel. It would actually require addition of both toluene and ethanol to yield a horizontal line of constant carbon intensity in Figure 2. The blending of ethanol also reduces the Particulate Matter Index (PMI), a variable that correlates with particulate emissions, as described later in this report. Figure 3 shows that the PMI varies in a similar pattern to that for CI, because both are increased by the fraction of aromatics (specifically toluene in this case) in the blend. The trends shown in Figures 1, 2 and 3 present an important introduction to the CI and PMI behaviors of real-world fuels with more complex compositions.
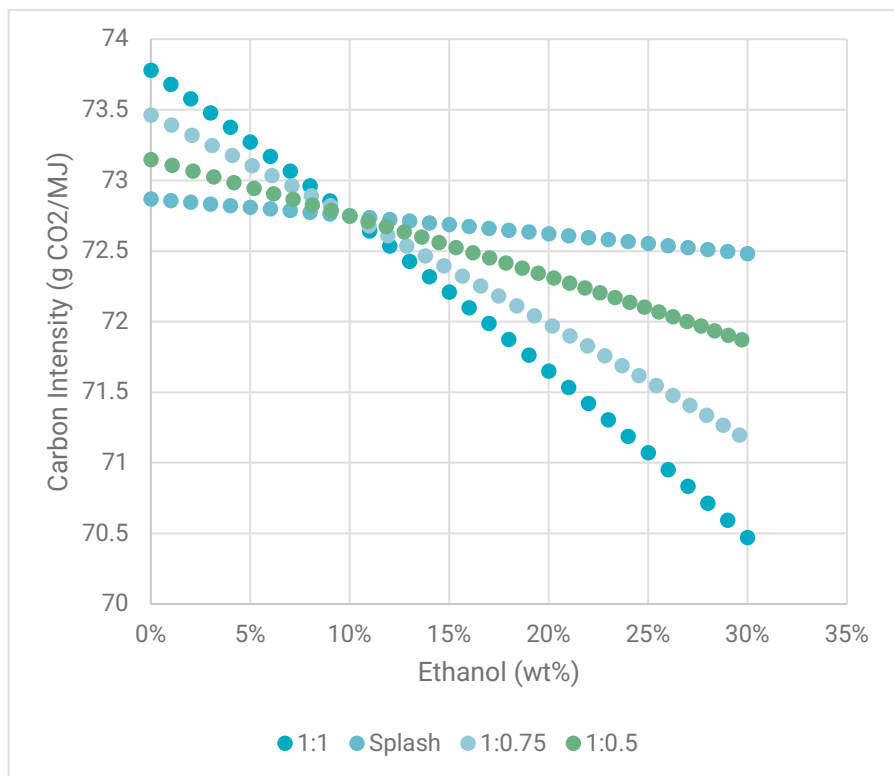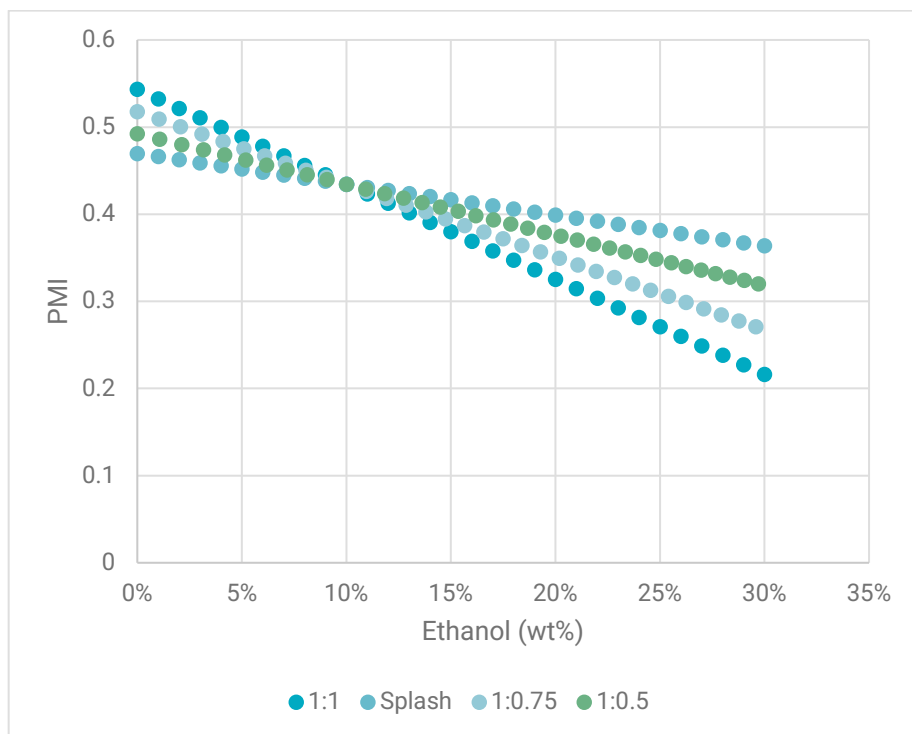
Figure 2: Variation in toluene fraction as ethanol content is increased in the three component mixture

Figure 3: Variation in PM due to four different blending strategies of ethanol and toluene in a balance of iso-octane.

Detailed Hydrocarbon Analysis

Understanding of the influence of gasoline variation on vehicle efficiency and emissions has evolved with the ability to determine composition accurately, rather than rely solely on fuel properties. ASTM D4814 presents the "Standard Specification for Automotive Spark-Ignition Engine Fuel." Gasoline analyses typically have measures of density (and specific gravity and API gravity), which provide an indication of the weight of the hydrocarbons in the fuel. Since the specific gravity of aromatics is about 0.87, and paraffins and olefins have specific gravity of about 0.7, a high density indicates high aromatic content, with a smaller influence from the carbon count of the molecules in the mix. Density adjustment is needed for ethanol, with specific gravity of 0.79.

Fuels are also fractionated to yield a distillation curve, as standardized by ASTM D86. This provides a further indication of weight of the species in the fuel. The lightest species typically have a lower carbon to hydrogen ratio. Generally, the highest boiling point fractions contain a large proportion of aromatic species.

ASTM D5580 presents a standard method using gas chromatography for an aromatic speciation, determining benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, and C9 and Heavier Aromatics in the fuel. D5769 determines benzene, toluene, and total aromatics by gas chromatography and mass spectrometry. D1319 determines aromatic, olefin and saturates content of the gasoline. D6839 speciates the gasoline into saturates, olefins, aromatics, and oxygenates by carbon number. Separate methods exist for determination of specific compounds or groups, such as ethanol or olefins.

Gas chromatography has now advanced to the point where gasoline may be characterized by concentrations of its individual constituent species, undergoing detailed hydrocarbon analysis (DHA). ASTM D6729 is dedicated to the speciation of spark ignition fuels, including those with oxygenate content, including common alcohols and ethers. A gas chromatograph with a fused silica capillary column is used, with a flame ionization detector. The method cautions that some species may elute together and that use of D6729 to determine a group presence (PONA – paraffins, olefins, napthenes and aromatics) through summation may have some error due to co-elution and due to lack of identification of some species. 888 species are listed in the standard.

Each species in the fuel has an identifiable carbon content DHA enables calculation of both CI and PMI of fuels. PMI is calculated using the summation of the weight fraction and the individual PMI values of each species (Aikawa et al., 2010; Chapman et al., 2021). The individual values are calculated as

(DBE + 1)/VP,

where DBE is the double bond index, (2C+2-H)/2, and where C and H are the molecular counts of carbon and hydrogen. VP is the vapor pressure of that hydrocarbon species at 443K (337.7 degrees F).

Each species in the fuel has an identifiable carbon content and LHV (See Appendix D). To compute CI, the total carbon weight fraction can be determined by summing the contribution of each species in the gasoline using DHA, and by summing the individual LHV components using published values or a correlation. The CI is then calculated from the total C (or CO_2) and the composite lower heating values.

Of concern for the current study on CI and PMI is the accuracy of measuring ethanol content and aromatic content. CI difference between two fuels may be small, and therefore their relative CI impact may be inverted by measurement error or difference. Concern is higher in cases where CI is computed for two market fuels analyzed using different methods or by different laboratories. ASTM D6729 presents data for D6729 total aromatic measurement against D5580. For all samples shown in the D6729 document, D5580 yielded a lower total aromatic level, with an average of 2.2% (mass) lower than D6729 in samples averaging 29.8% (mass), i.e., a 7.6% difference. Appendix C presents additional data and discussion on differences in fuel composition measurements between ASTM methods.

CI may also be computed directly from an overall mass fraction of carbon in the gasoline, and an experimentally determined value for the LHV. The gasoline blends used in the EPAct study (EPA, 2013) are described by DHA, LHV and carbon mass fraction. Figure 4 shows the good agreement between calculation of LHV using the overall fuel properties and the computation from the components in the DHA. The plot includes one fuel that is E85. Figure 5 excludes the E85 fuel to provide greater detail for the remaining fuels, which have ethanol content of 0% to 20%, and aromatic content of either approximately 15% or approximately 35%.
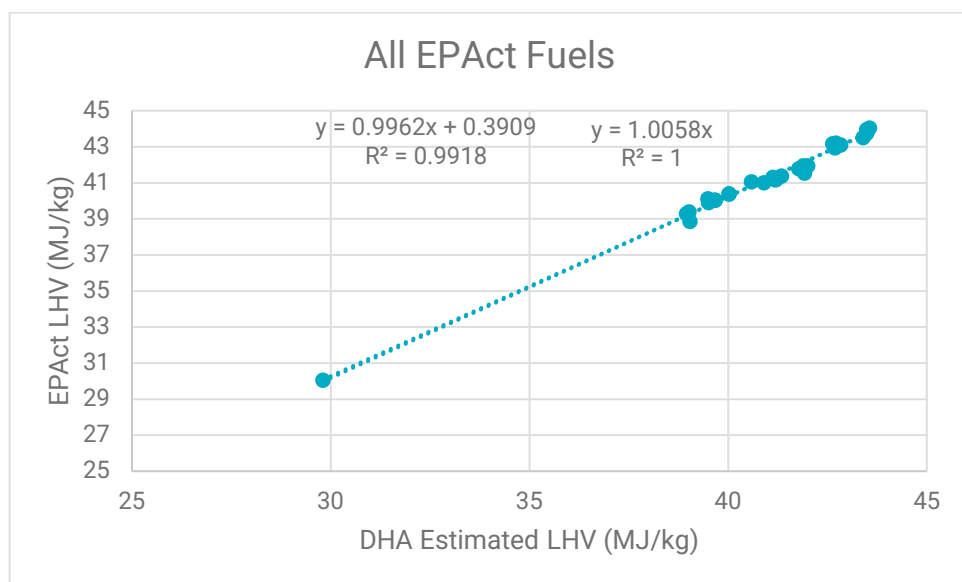
Figure 4: Comparison of reported gasoline LHV and LHV calculated from DHA for the EPAct fuels, including an E85 fuel with low LHV.
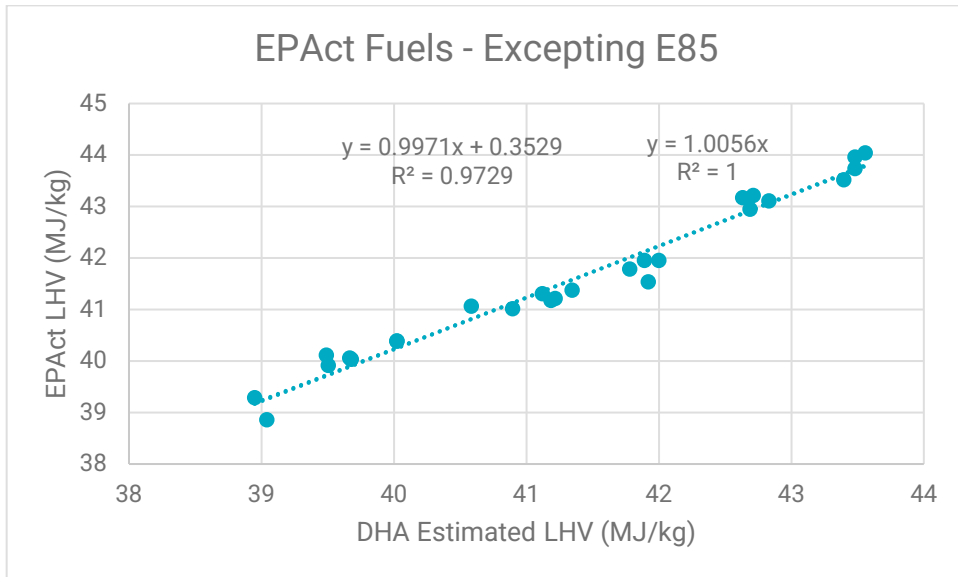
Figure 5: Comparison of reported gasoline LHV and LHV calculated from DHA for the EPAct fuels, with the single E85 fuel excluded.

LHV may also be estimated from grouped components in the fuel, such as paraffins, aromatics, olefins, napthenes and ethanol. Figure 5 shows that for the EPAct fuels, there is reasonable agreement between reported LHV of the gasoline and a predictive equation, found by regression, only aromatic and ethanol content:

LHV (MJ/kg) = 44.38 − (0.0364 * aromatic vol%) - (0.189 * ethanol vol%)

Fit of this equation is shown in Figure 6. Scatter may be attributed to varying content of olefins and napthenes of the fuel.
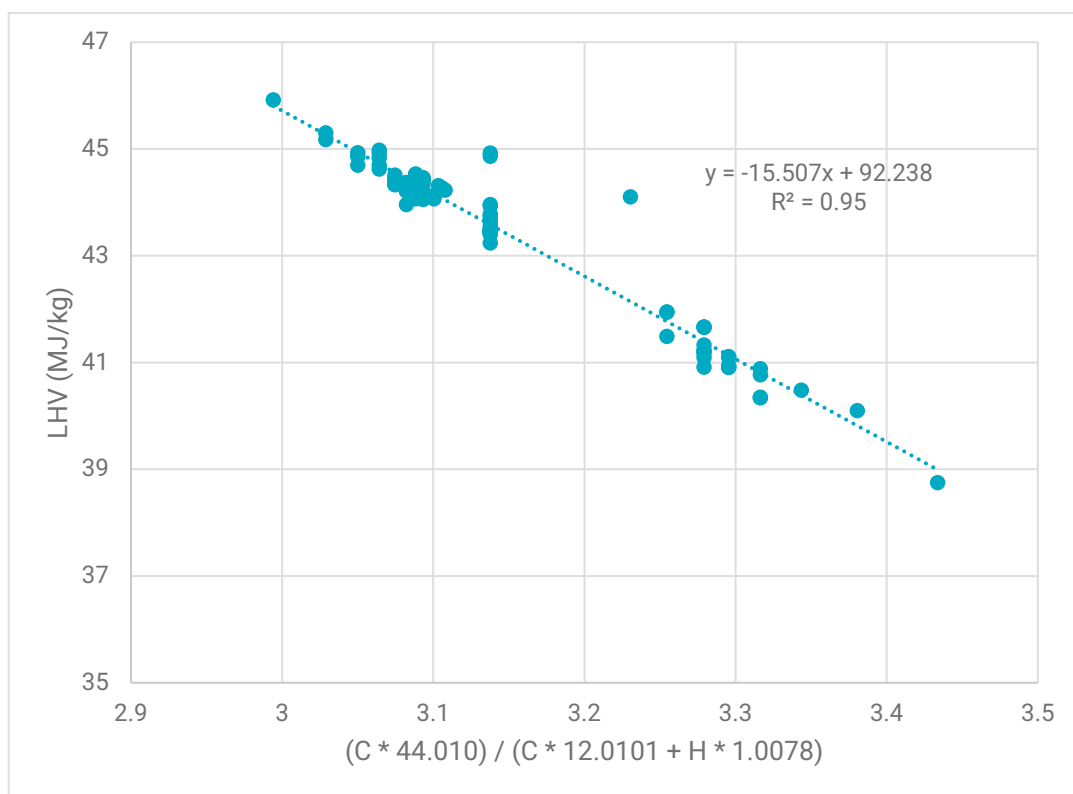
Figure 6: Success of a linear model using aromatic and ethanol content in predicting LHV of EPAct fuels.

Carbon Intensity and Market Fuels

As noted previously, the amount of carbon or CO_2 emitted per mile by vehicles is related to the fuel composition. Aromatic compounds, particularly the heavier more complex aromatics, have a higher carbon content and lower energy content per unit mass than paraffins, olefins or naphthenic species. As a result, potential CO_2 emissions per BTU of energy supplied by the aromatic compounds are more than 20 percent higher than that of gasoline paraffins. In its notice of proposed rulemaking (NPRM) covering test procedure adjustments for Tier 3 certification fuels, EPA noted that aromatic and ethanol content changes in fuel "affect the amount of carbon and energy per unit of volume of the fuel. These differences result in small, but not insignificant, changes in the tailpipe emissions of CO_2." EPA has estimated the impact of Tier 3 (E10) versus Tier 2 (E0) certification fuels (driven primarily by differences in aromatics and ethanol) at a 1.6% difference (EPA, 2018a).

From a chemical property perspective, ethanol does not have a significant effect on gasoline carbon intensity. The energy per mass of ethanol is less than two-thirds of that of the non-oxygenated fuel but this is offset by its relatively low carbon content. The net CO_2 of 384 g/MJ for ethanol is a little lower than comparable market non-

oxygenated gasoline (about 3.5 percent). However, ethanol has a large impact on gasoline blending and the final gasoline properties and chemical composition. The high-octane characteristics of ethanol allow refiners to lower refinery produced octane with the increasing volume of ethanol. The primary refinery option for lower octane is through lower severity (octane) or throughput on the gasoline reformer, which in turn decreases gasoline aromatic content and reduces CI.

Figures 7 and 8 illustrate the potential impact of ethanol blending on gasoline CI by examining carbon and energy characteristics of major gasoline chemical species: mono ring aromatics with 6 to 9 carbons, heavier mono ring aromatics, multiple ring heavier aromatics, light and heavy paraffins, light and heavy olefins and light, heavy naphthenic compounds, and ethanol. Figure 7 shows carbon content and energy content per mass. Aromatics have higher carbon content and lower energy per mass than other gasoline constituents. Ethanol, as an oxygenate, has a low energy content which, relative to carbon intensity, is offset by its low carbon content.
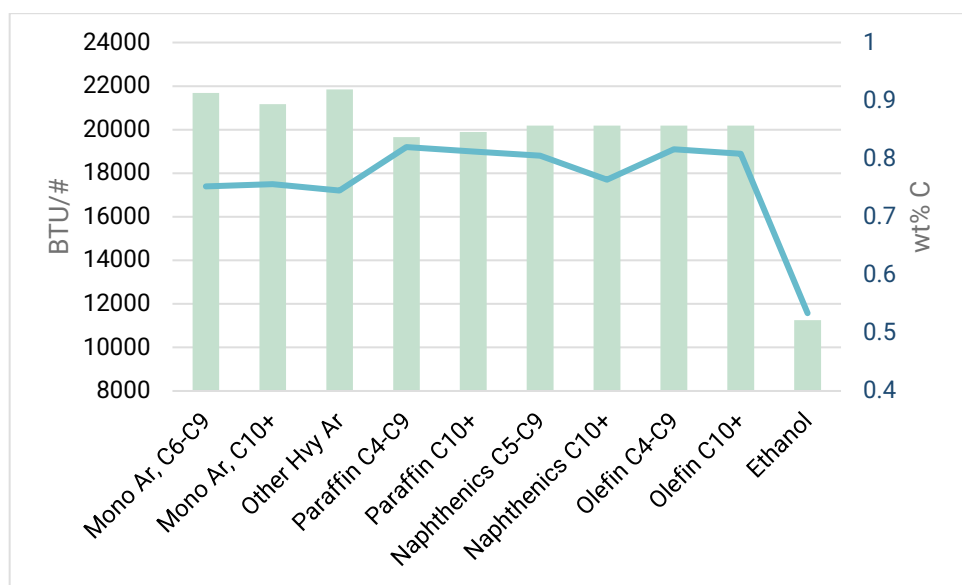
Figure 7: Carbon and Energy Content of Gasoline Compounds (Source: Compiled by Transport Energy Strategies from various technical sources)

Figure 8 shows the resulting compound carbon intensities as well as that for representative current E10 gasoline. Carbon intensities of the pool of aromatics are roughly 16 percent higher than other species and about 19 percent higher than the paraffins. When gasoline octane is lowered through ethanol addition, the chemical species shift from the higher carbon intensity aromatics to lower carbon intensity species, reducing the overall gasoline carbon intensity. Most of the shift is to the lowest carbon intensity paraffins.
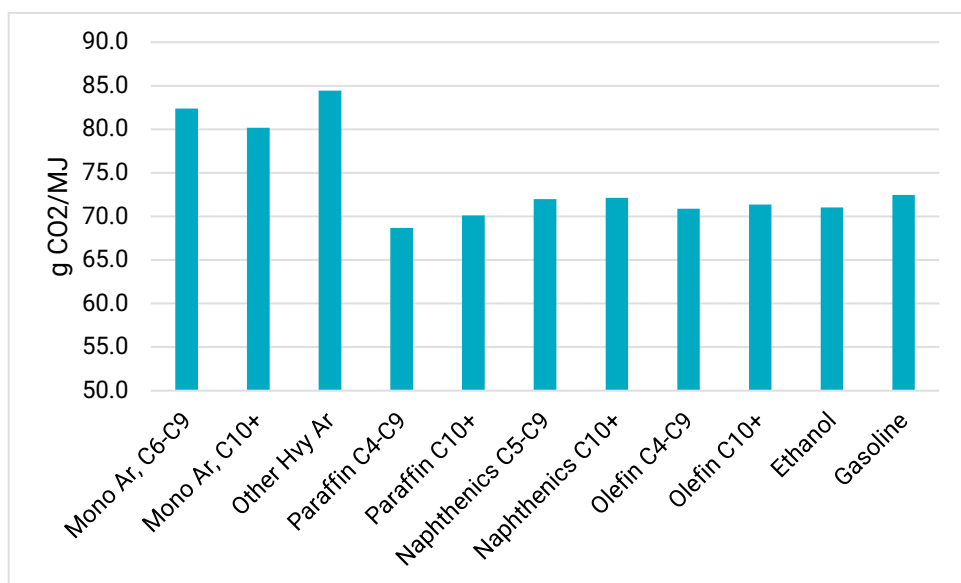
Figure 8: Carbon Intensity of Gasoline and Gasoline Compounds (Source: Compiled by Transport Energy Strategies from various technical sources)

The previous sections illustrate ethanol blending and gasoline composition relationships for three component surrogate gasoline blends. This can be extended to real world gasoline blending by quantifying the refinery relationship between ethanol blending, gasoline quality/composition and carbon intensity. This is accomplished through a review of historic gasoline quality, refinery operations and gasoline blending practices. This information can then be utilized to develop correlations to predict gasoline quality/composition as a function of refinery production and ethanol blend levels, and eventually the carbon intensity of resulting gasoline blends. Such a review is presented in Appendix A which discusses available data and information sources for understanding real-world ethanol blending and gasoline quality relationships and development of a gasoline model capable of characterizing ethanol-gasoline quality for historic, current, and future blend scenarios.

Historic data (for example, EPA, 2017 and EPA online fuel quality data) show a strong correlation between aromatics and ethanol blend levels. The model presented in Appendix A can reproduce the aromatic-ethanol blending relationship as shown in Figure 9. Ethanol blending increased from an average of 3 percent (2006) to 9.6 percent (2013) and resulted in an aromatics reduction of 4.8 to 5.6 percent (versus model calculated 5.1 percent reduction). Beyond 2013 aromatics increased despite a small further small increase in ethanol blending (0.3 % blend increase), but this also reflects other refinery changes such as lower sulfur requirements and increases in gasoline production. As discussed in Appendix A, available data and the model support a reduction in aromatics of approximately 9 percent when ethanol is increased from 0 to 10 volume percent.
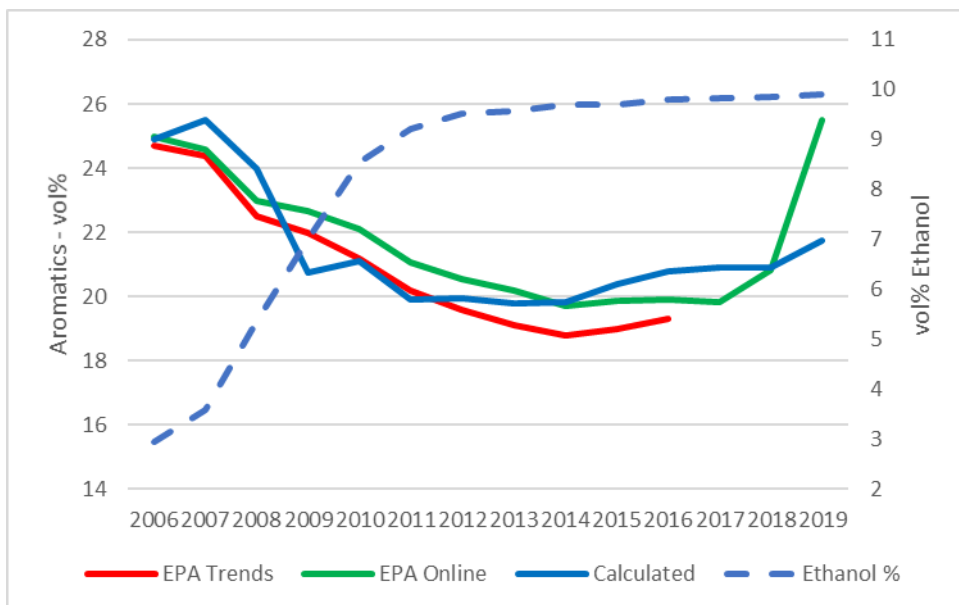
Figure 9: Gasoline Aromatics Data and Calculated 2006-2019 (Source: Transport Energy Strategies)

There is general support in the literature for these decreases in aromatic content as ethanol is added to the petroleum mix. Waquas et al. (2017) present the high blending RON and MON characteristics of ethanol in a range of test fuels. These increases relieve the need to raise the AKI using selected petroleum streams (Kirgina et al., 2012). Stratiev et al. (2017) include both ethanol and reformate as octane blending choices. Their data suggest that a 10% change in ethanol would correspond to a change in aromatic level of about 7.7%.

The MOVES 2014 model is employed by the EPA to compute emissions inventories, and states are obliged to employ MOVES for their State Implementation Plans (SIP). MOVES 2014 is now being replaced by MOVES 3. MOVES 2014 allows for an aromatic adjustment for changes in ethanol content via the Fuel Wizard. The adjustment is labeled as a 2.3 percent reduction for E0 to E10. This adjustment represents EPA's allowance and not necessarily a representation of change in aromatics content between E0 and E10. As discussed in the appendix to EPA's Fuels Supply Defaults report (2021) this adjustment factor was based on refinery modelling of a change in conventional gasoline ethanol content from 2 percent to 10 percent (equivalent to the conventional plus RFG gasoline pool increasing from 6 percent to 10 percent ethanol). For MOVES3 EPA has adjusted the Fuel Wizard aromatic reduction for E0 to E10 down to 2.0%. The adjustment is reported to be based on modeling of a conventional gasoline E10 to E0 scenario. However, the cited refinery modeling is inappropriate to support a real world E10 to E0 change and in no way should be considered as representing such a scenario, (as presented in Appendix A). In this report, market fuels are presented that have a reduction of aromatic content associated with an addition of ethanol to the blend.

The refinery/gasoline blend model discussed above was expanded to include detailed DHA analyses of refinery gasoline blending streams used to create the final refinery gasoline blends. A description of the data and model capabilities is presented in Appendix B. The extended data include speciation of individual aromatic, olefin,

paraffin and naphthene data by carbon number and (for aromatics) by aromatic ring structure. Each of the species is characterized as to quality parameters (such as gravity, carbon type and energy content), allowing for calculation of carbon intensity. As such the model can calculate carbon intensity for various gasoline blending strategies and for blends at various ethanol levels.

Several scenarios were established to examine carbon intensities as defined in Appendix B. The first set ("Set 1") of scenarios considered E0, E10, E15 and E20 blends consistent with a current E10 market quality. For the E15 and E20 cases three blend scenarios were considered:

- Blend 1, maintaining current refinery production and increasing exports to compensate for incremental ethanol,
- Blend 2, adjusting refinery production down to meet domestic demand and keep base E10 case exports constant, and
- Blend 3, splash blending incremental ethanol with E10 BOB. (note that for the E0 case, the E10 volume of gasoline could not be maintained with the removal of ethanol so refinery production volumes were reduced accordingly).

Note that the E0 versus E10 case thus does not represent a precise comparison, because current (E10) gasoline quality and volume cannot be met under current real-world refining constraints. The gasoline volume for E0 was reduced which does not provide for a true volume for volume comparison, but rather reflects real world blending constraints for this scenario.

A subsequent set of scenarios examined a range of aromatic content. A low aromatic case (Scenario Set 2) was represented by winter gasoline starting with a higher portion of non-aromatic high-octane components. A high aromatic case (Scenario Set 3) was represented by summer gasoline starting with a lower portion of non-aromatic high-octane components. The same blend scenarios were examined as in the first set but not for the splash blend scenarios. This second scenario set provides insight to the impact of higher or lower base aromatics on carbon intensity with changes in ethanol blend levels.

Figure ES-1 (in the Executive Summary) and Table 2 provide resulting carbon intensities and other quality characteristics from the first case set. Blending with 10 percent ethanol reduced gasoline aromatic content from 29.9 percent to 21.7 percent, a change of 8.2 percent aromatic content. Ethanol reduces both the carbon fraction and energy content, but the net result is a reduction in the carbon intensity of all the blends relative to E0. The carbon intensity reduction increases as ethanol blending expands. When blended with a BOB produced for 15 percent ethanol addition, the carbon intensity is reduced by about 2 percent. For 20 percent ethanol, the carbon intensity reduction increases to around 2.5 percent. As noted previously, the analysis was based on a representative current E10. A corresponding E0 could not be produced at the same volume of refinery production or exports with the level of octane removed. This likely has resulted in the E0 to E10 reduction in aromatics and carbon intensity being slightly understated.

These reductions echo the CI reductions demonstrated with the ethanol-toluene-octane blend scenarios shown in Figures 1 and 2 above. Specifically, for Figure 1, the case for reduction of toluene at 0.75 of the rate of ethanol addition showed more CI change than the splash blend.

	RON	Aromatics	Carbon	Energy	C Intensity	CO2 CI	CI Reduction
		vol%	wt%	MBTU/#	#C/MMBTU	g/mg Joule	% vs E0
E0	92.4	29.9	86.60	114.4	46.67	73.52	
E10 w BOB	93.0	21.7	82.34	109.9	46.01	72.48	-1.41%
E15 w BOB & Prod	93.3	17.9	80.14	107.4	45.63	71.89	-2.23%
E15 w BOB Demand	93.4	17.2	80.06	107.2	45.55	71.76	-2.40%
E15 Splash w E10 BOB	94.6	20.3	80.37	107.9	45.86	72.25	-1.74%
E20 w BOB & Prod	93.3	15.4	78.14	105.3	45.41	71.54	-2.70%
E20 w BOB Demand	93.4	14.0	77.98	105.0	45.25	71.29	-3.04%
E20 Splash w E10 BOB	96.0	19.2	78.49	106.0	45.76	72.09	-1.95%

	RON	Aromatics	Carbon	Energy	C Intensity	CO2 CI	CI Reduction
		vol%	wt%	MBTU/#	#C/MMBTU	g/mg Joule	% vs E0
E0	92.4	29.9	86.60	114.4	46.67	73.52	
E10 w BOB	93.0	21.7	82.34	109.9	46.01	72.48	-1.41%
E15 w BOB & Prod	93.3	17.9	80.14	107.4	45.63	71.89	-2.23%
E15 w BOB Demand	93.4	17.2	80.06	107.2	45.55	71.76	-2.40%
E15 Splash w E10 BOB	94.6	20.3	80.37	107.9	45.86	72.25	-1.74%
E20 w BOB & Prod	93.3	15.4	78.14	105.3	45.41	71.54	-2.70%
E20 w BOB Demand	93.4	14.0	77.98	105.0	45.25	71.29	-3.04%
E20 Splash w E10 BOB	96.0	19.2	78.49	106.0	45.76	72.09	-1.95%

Table 2: "Set 1" Scenario values for Aromatics, Carbon and Energy content, and Carbon Intensity

Figure 10 shows the carbon intensity for the scenario sets 2 and 3. The impact of ethanol blending on carbon intensity is similar to the initial scenario set and there is little difference in the magnitude of carbon intensity reduction between the low and high aromatic scenarios. The actual carbon intensity of blends using the high aromatic E0 remain higher than for the blends originating from the low aromatic E0. As shown in Figure 11, the actual magnitude and percentage of carbon intensity reduction is similar for all three cases examined. Under real world blending scenarios, the addition of ethanol tends to have the same positive overall impact on carbon intensity. The refiner responds to anticipated octane enhancement provided by ethanol with lower use of high aromatic, high octane refinery components. High carbon intensity refinery components will be replaced by lower carbon intensity ethanol and even lower carbon intensity alternate refinery streams.
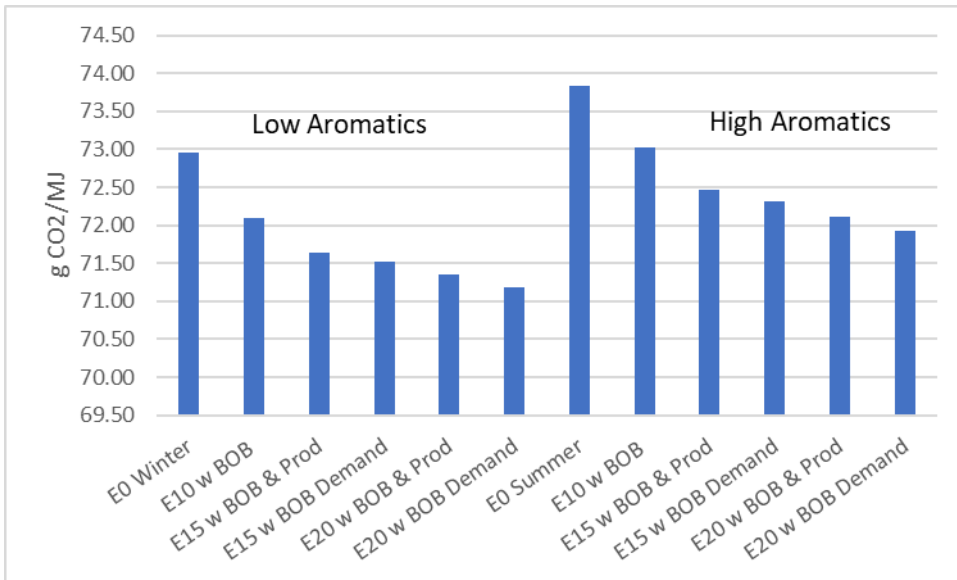
Figure 10: Carbon Intensity Low (Set 2) and High (Set 3) Aromatic Scenarios
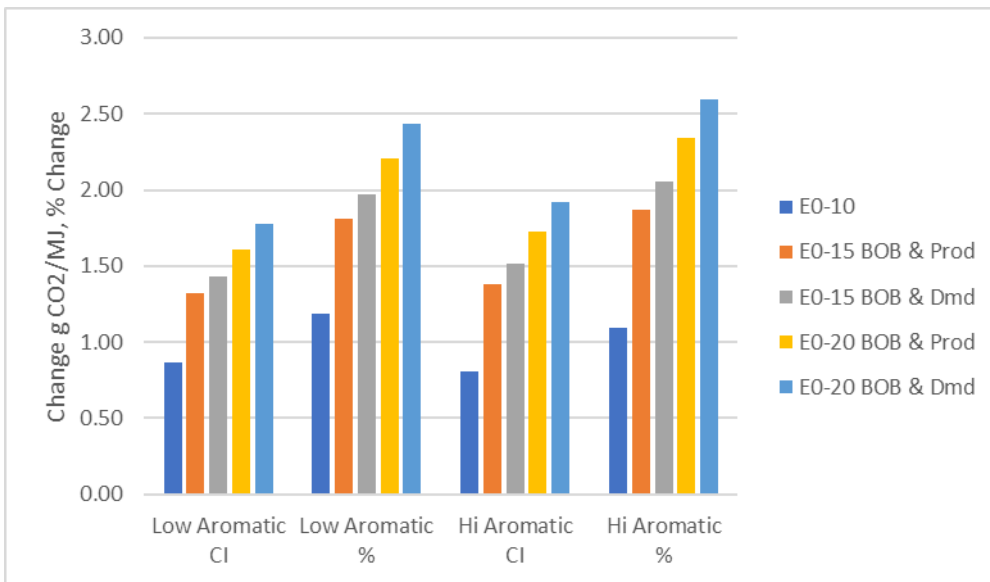
Figure 11: CI Reduction versus Ethanol in absolute terms and in percent

Figure 11 also confirms for blending scenarios that any error or offset in the fuel composition that is measured will not affect appreciably the differential effects of the blending.

The reduction in gasoline blend carbon intensities with increasing ethanol addition in the above blending scenarios, as well as that demonstrated in the Figure 1 surrogate blend cases, appear small in terms of percentage reduction from the base E0 fuel (i.e., 1.4 to 3.0 percent reduction, as in Table 2). However, the

carbon intensity reductions are realized across the entire final gasoline volume so the impact per unit volume of ethanol on CO_2 emissions is far greater than the above percentage reduction in gasoline carbon intensity.

Particulate Matter Index of Blends

The analysis of ethanol blending scenarios discussed above was expanded to examine the corresponding impacts on gasoline and refinery stream PMI. Gasoline PM emissions have taken on new importance as diesel PM emissions from new vehicles have been curtailed by the use of particulate filters (Platt et al., 2017). Aromatics in gasoline have for some time been a focus of emission studies for both toxicity and particulate matter (PM) emissions. More recently focus on aromatics has moved to specific heavier aromatics and in particular those constituents which, when included, result in higher gasoline PM emissions. The Honda Predictive Model Index (PMI) has been shown to be a reliable indicator of the propensity of gasoline to produce PM emissions (Aikawa et al., 2010). Other PM predictive models have been proposed (Chapman et al., 2021; Crawford et al., 2021), but are not considered in this report.

PMI values were calculated for each of the category of chemical species discussed above. As with the case of carbon intensity, PMI values of aromatics are higher than other gasoline species but the difference between PMI for aromatics and other compounds is far more significant than differences in CI.

Figure ES-2 (in the Executive Summary) shows the PMI values for gasoline chemical species of refinery components as well as that for ethanol and representative current market gasoline. PMI of the pool of aromatics is an order of magnitude higher than other species. Within the aromatic group the heavy complex aromatics are roughly 4 times higher than the average PMI of mono aromatics. Unlike in the case of carbon intensity, ethanol PMI is well below that of most other gasoline compounds.

When gasoline octane is lowered at the refinery in anticipation of ethanol addition, the chemical species shift from the higher PMI aromatics to lower PMI hydrocarbon species and ethanol, reducing the overall gasoline PMI. The ethanol, with its own, low PMI, also contributes to lowering the PMI of the final blend. The impacts of ethanol blending on PMI for the cases defined above are shown in Figures 12 (set 1 scenarios) and Figure 13 (low and high aromatic scenarios).
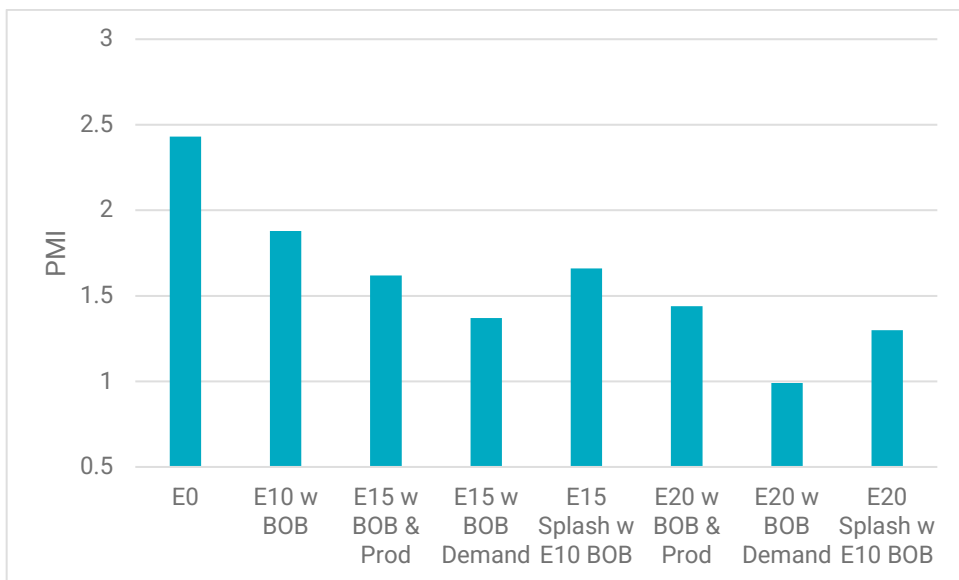
Figure 12: PMI Values Set 1 Scenarios
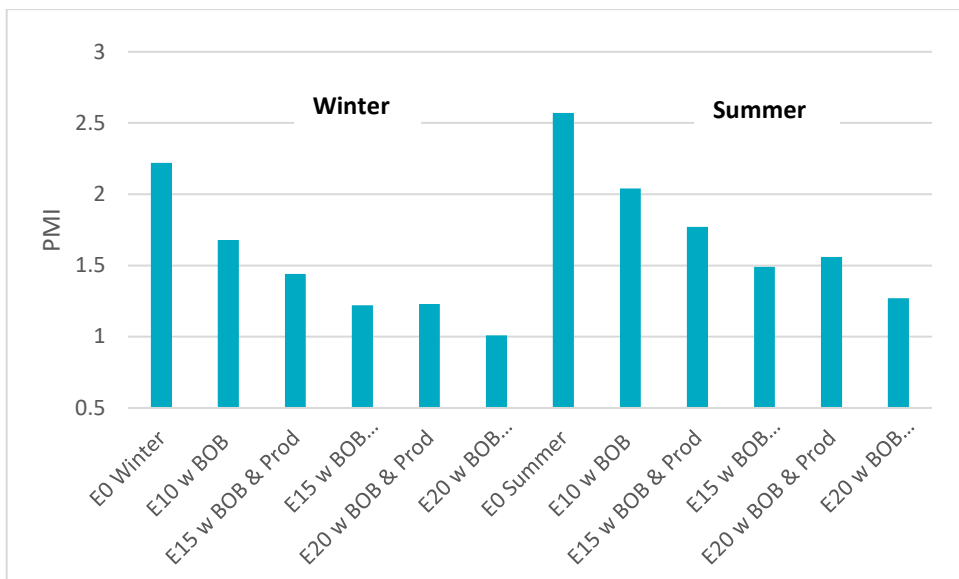
Figure 13: PMI Values for Set 2 and Set 3 (Low and High Aromatic) Scenarios

The reduction in PMI with ethanol addition is far greater than the change in carbon intensity. Also, as in the case of carbon intensity, the set 1 case and the low and high aromatics show similar trends of PMI reduction. What is different with PMI versus carbon cases is the trend with the BOB blending where gasoline production is reduced as ethanol is added such that demand is met with no expansion of gasoline exports. In these cases, refinery FCC gasoline, as well as other streams is reduced. However, the reduction in FCC gasoline is proportionately larger because of undercutting gasoline to distillate to reduce volume. The undercutting

reduces the concentration of the very heavy, high PMI streams resulting in significant PMI reduction. This lower gasoline production case results in a PMI 16 percent below the higher production case.

95 RON Grade Blend

Increased knock resistance offers a pathway for engine design that enables higher engine efficiency (Stein et al., 2013; Syzbist et al., 2021; Miles, 2018). A 95 RON minimum specification has been discussed amongst stakeholders to enable introduction of higher efficiency vehicles, which would also offer reduced GHG footprints. There are several approaches for accommodating the 95 RON such as marketing a new grade of gasoline to moving all gasoline to a minimum 95 RON product.   The appropriate approach would be dictated by available infrastructure, level of ethanol used, capability of refining to increase octane and business decisions by stakeholders. Regardless, outside of infrastructure issues, the primary implications of the RON requirement will be its effect on refinery octane requirements. The change in octane requirement would in turn impact carbon intensity and PMI of final gasoline.

Refiners cannot meet a pool 95 RON without substantial investment and/or without a large increase in ethanol blending. Assuming adequate infrastructure, refiners could produce a portion of the pool at 95 RON minimum, with the producible volume depending on the level of ethanol used. For insight into the implications of a 95 RON requirement and the role of ethanol on gasoline producibility and carbon intensity/PMI impacts, gasoline bending scenarios incorporating 95 RON were examined, similar to those discussed in the previous sections. The specific scenarios presented below (and in Appendix B) were designed to assess the refining industry's ability to provide a 95 RON gasoline grade and the impact of its production and associated ethanol blending on carbon intensity and PMI. All the scenarios assumed a separate 95 RON grade would be made with the current premium grade volume and octane remaining unchanged and the portion of regular grade not upgraded to 95 RON remaining at current octane levels. The scenarios also assumed refineries would continue to produce the same overall gasoline volume. As ethanol volumes increased, any surplus gasoline production would be exported.

The first set of cases estimated the volume of 95 RON which could be produced with 10 percent ethanol and without refinery gasoline octane investment. The initial cases then examined carbon intensity and PMI impacts under the same RON 95 volume but with 15 percent and 20 percent ethanol in the gasoline pool. The 15 percent and 20 percent ethanol cases also assumed an E15 and an E20 BOB were produced by refiners. Finally, the 95 RON capability was estimated assuming 15 and 20 percent ethanol splash blended on the E10 BOB.

The second set of cases was similar but started with an assessment of the volume of 95 RON which could be produced with 15 percent ethanol in the domestic gasoline pool. The impact of increasing ethanol to 20 percent (with an E20 BOB) on the carbon intensity and PMI was then assessed as well as the 95 RON capability. Figure 14 shows the percent of the regular gasoline pool that could be upgraded to 95 RON at different levels of ethanol blending. About 23 percent of the regular gasoline pool can be produced at 95 RON with ethanol use at

E10 and premium gasoline and the remaining regular gasoline at current market octane levels. At 15 percent ethanol the portion of 95 RON that can be produced increases to 44 percent. All regular gasoline can be upgraded to 95 RON with 20 percent all blending.
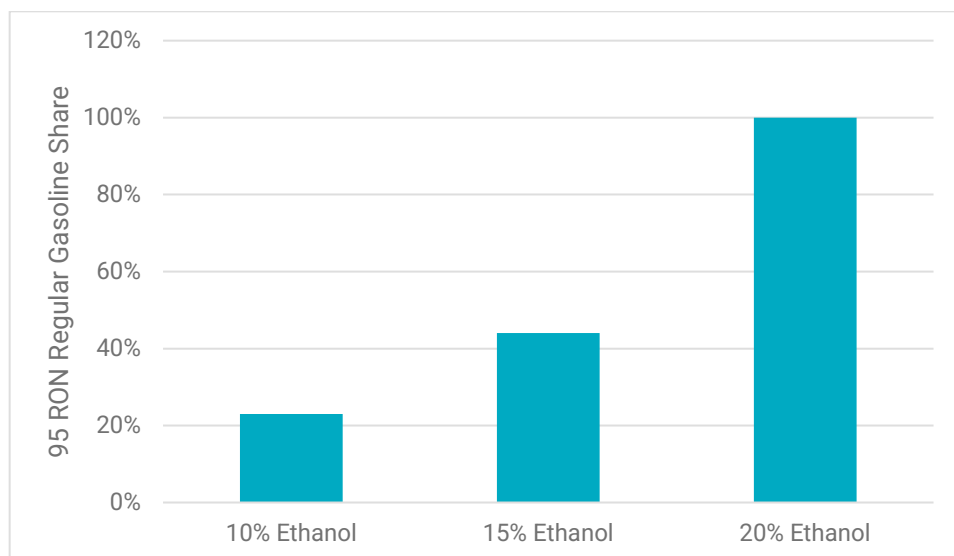
Figure 14: 95 RON Production Capability vs Ethanol Content

Figure 15 shows the impact of the 95 RON grade and ethanol use on fuel-based CI. The first two bars display the impact of 95 RON with no change in ethanol, i.e., gasoline pool at E10. Production of 23 percent of the regular pool at 95 RON and E10 increases carbon intensity by 0.2 percent. The incremental octane requirement is met with higher refinery severity and higher aromatics. With ethanol blending increased to 15 and 20 percent CI is reduced by 0.9 percent and 1.3 percent, respectively. With E15, the 95 RON increases to 44 percent and the carbon intensity is 0.3 percent below the E10 case with only 23 percent 95 RON. At 20 percent ethanol, the RON pool can be increased to 100 percent with the carbon intensity 0.6 percent below the E10 case producing only 23 percent 95 RON.

The CI advantages of the high RON ethanol blending shown in Figure 18 are reflective of the fuel-based calculations. Insofar as the increased RON would enable more efficient engine designs (Szybist, 2021), there would be further in-use reduction of CO_2 emissions associated with increased vehicle fuel economy.
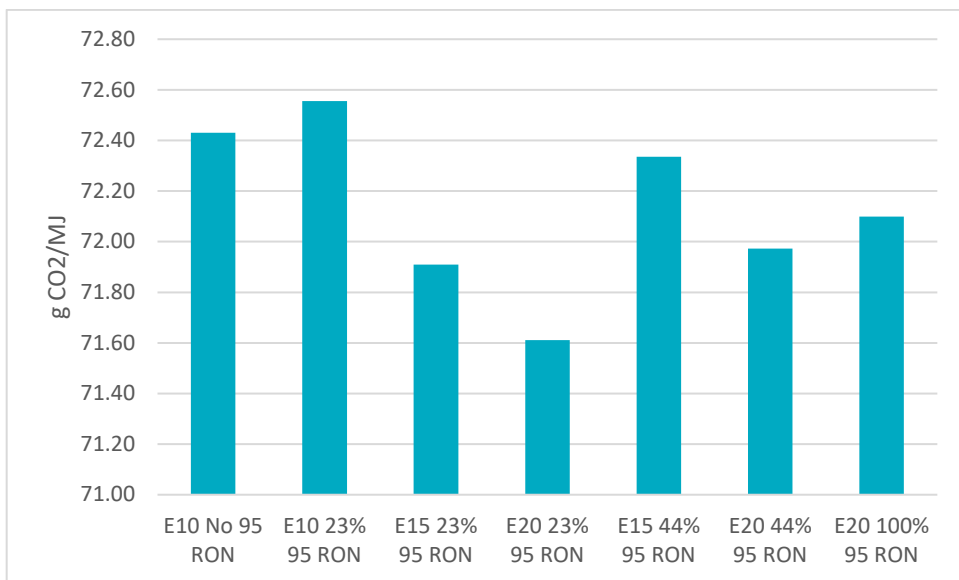
Figure 15: Impact of Ethanol and 95 RON on Carbon Intensity

Implications of 95 RON and ethanol on PMI averaged across all gasoline production was also assessed for the above cases. Figure 16 shows PMI for the 95 RON and the E10. E15, and E20 cases with different market penetration of 95 RON gasoline. General PMI trends are similar to the carbon intensity trends, but the magnitude of PMI change is larger. For example, the reduction in PMI for the 23% RON case going from 10 percent to 20 percent ethanol was 1.3 percent. The PMI reduction for these cases is 23 percent.

Figure 16: Impact of Ethanol and 95 RON on PMI

Refining Impact of Reduction in Fuel CI

Ethanol blending and the associated octane enhancement allow refineries to adjust refining operations and refinery level gasoline quality (BOB), resulting in the lower CI fuel discussed above. In addition to their impact on the fuel quality and CI, these operational changes will have a secondary impact on CO_2 emissions apart from that related to the final gasoline combustion. The lower octane refinery operations result in a lower refinery fuel consumption and an adjustment to the refinery hydrogen balance, both with CO_2 implications. While these secondary impacts do not play a role in the CO_2 emissions from the gasoline itself, they do play a role in overall CO_2 emissions inventory immediately upstream of fuel use, and are deserving of review.

As refinery octane is lowered, refinery process throughput is reduced and/or adjusted, generally resulting in lower refinery energy requirements. The reduction in refinery energy will have a direct impact on refinery fuel combustion CO_2 emissions and, in some cases, on CO_2 emissions from outside utilities providing energy (electricity and steam) to refineries. The reduction in refinery energy requirements will be most pronounced in those cases where incremental refinery gasoline production in reduced in response to product volume supplied in the form of ethanol and overall refinery utilization can be lowered.

From the hydrogen side, the impact of lowering refinery octane will result in an increase CO_2 emissions. The refinery gasoline reformer will produce less hydrogen as octane is lowered which must be replaced to satisfy refinery desulfurization needs. The hydrogen replacement will for the most part be generated via methane reforming (at the refinery or merchant hydrogen facilities), resulting in incremental CO_2 emissions.

The impacts of ethanol levels on refinery processing/blending and on potential CO_2 emissions were examined through a literature search and separate computation using the output from the gasoline blend model. Studies reported in literature vary in their approach to accounting for changes in refinery energy and are not always applicable to the scenarios examined here. Some consider changes in the overall refinery energy balance including raw material input and product output. This approach likely captures overall fuel CO_2 impacts, but does not separately quantify refinery fuel and processing impacts. Other studies have quantified changes in refinery energy use but do not appear to properly account for changes in hydrogen production/consumption. The gasoline blend model used for the above carbon intensity analysis quantifies refinery processing levels and reformer throughput and severity. This output was used to calculate changes in refinery fuel requirements and hydrogen supply and, in turn, changes in refinery CO_2 emissions. Literature sources were used as a check on calculated changes in fuel and hydrogen balances.

The impact of ethanol blending on refinery fuel and hydrogen CO_2 emissions for the initial cases discussed above are summarized in Figure 17 shows change in daily CO_2 for the blend scenarios. Increasing ethanol blend levels lowers refinery energy and lowers CO_2 emissions as shown, but with a more than offsetting increase in CO_2 emissions from incremental hydrogen production requirements. The net is a small net increase in CO_2

emissions (from the refinery or supplying utility/hydrogen source) as more ethanol is used. The net increase small relative to overall refinery fuel and hydrogen related emissions, but is not insignificant.
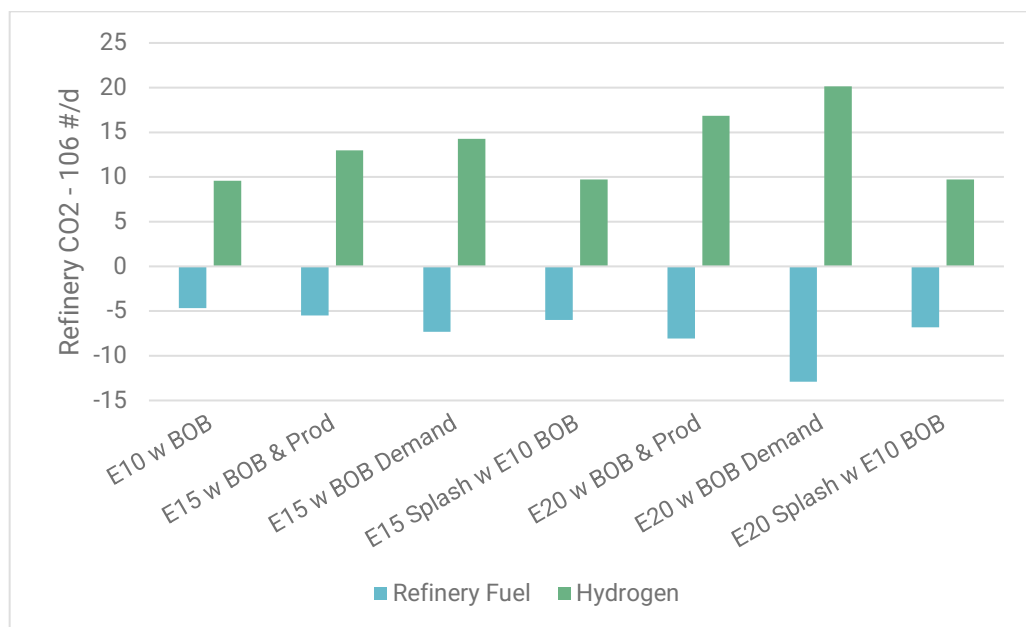
Figure 17: Refinery Fuel and Hydrogen Production CO_2 *Emissions vs Ethanol Blending*

To put the refinery fuel and hydrogen emissions in perspective, Table 3 compares the previously reported gasoline CI values with an adjusted value considering refinery fuel and hydrogen. The adjusted values were calculated by adding the net daily change in grams of refinery fuel/hydrogen CO_2 emissions (change versus the E0 baseline) to the calculated CO_2 gasoline emissions (based on CI) and dividing the sum by the daily MJ of gasoline. The adjusted values shown do not reflect potential gasoline CO_2 emissions, but provide a basis for understanding the magnitude of refinery emissions.

| | Gasoline CI | | Adjusted for Refinery Emissions | |
	CO_2 CI g/MJ	CO_2 CI % vs E0	CO_2 CI g/MJ	CI Reduction % vs E0
E10 w BOB	72.48	-1.41%	72.68	-1.136%
E15 w BOB & Prod	71.88	-2.23%	72.18	-1.824%
E15 w BOB Demand	71.75	-2.40%	72.04	-2.012%
E15 Splash w E10 BOB	72.24	-1.74%	72.39	-1.538%
E20 w BOB & Prod	71.53	-2.70%	71.86	-2.253%
E20 w BOB Demand	71.28	-3.04%	71.58	-2.632%
E20 Splash w E10 BOB	72.08	-1.95%	72.19	-1.802%

CI and PMI for Market Fuels

The variability of properties of market fuels was considered for further review of gasoline CI and is illustrated in Table 3. Texas summer regular fuels from a survey were ranked by aromatic content. The fuel representing the 25th percentile of aromatic content amongst the 2020 Texas summer regular fuels (ERG, 2020) was identified, and grouped with the two fuels with immediately smaller aromatic fractions, and the two with immediately larger aromatic fractions. Similar groups of five fuels were centered on the 50th and 75th percentiles. Average properties for each group of five fuels are also shown in Table 3. DHA (D6729 method) was used to determine the aromatic order of the fuels, and in all cases the ASTM D5769 yielded lower aromatic values than D6729.

Although the aromatic levels vary little within each group, Fuel 22 has substantially higher D6550 olefin content and a lower content of iso-paraffins than others in the 25th percentile group. However, both the CI and PMI values of Fuel 22 are similar to the average values for the group. Fuel 23 (the 25th percentile fuel itself) had the greatest disagreement between the two aromatic determinations D5769 and D6729), and a high PMI value uncharacteristic of the group. The PMI of fuel 23 was higher than for three of the five fuels in the 50th percentile group, and two fuels in the 75th percentile group, attesting that the relationship between PMI and total aromatic content is approximate. Both the carbon: hydrogen ratio and the CI varied little and tracked one another. C:H ratio was very similar within all three groups of fuels. CI rose as aromatic content rose, as expected, and CI varied less than 0.5% within each group. There were substantial differences between DHA (D6729) olefin content and D6650 olefin content.

	Aromatics, DHA, Vol%	Aromatics, D5769, Vol%	Ethanol, DHA, Vol%	Ethanol, D5599, Vol%	Olefins, DHA, Vol%	Olefins, D6550, Vol%	Iso-Paraffins, DHA, Vol%	Specific Gravity	mCO₂/mFuel	MJ/kg	C:H Ratio	CI (g CO₂/MJ)	PMI
25th Ave	20.3	17.5	7.7	9.54	7.21	10.29	41.0	0.773	2.951	40.7	0.514	72.5	1.36
21	20.0	17.7	7.9	9.52	7.28	8.83	41.7	0.762	2.993	41.3	0.512	72.4	1.18
22	20.2	17.6	8.6	9.46	8.42	15.34	35.0	0.798	2.855	39.3	0.517	72.6	1.33
23	20.2	16.3	8.1	9.45	7.07	8.92	44.0	0.764	2.977	41.1	0.513	72.4	1.77
24	20.6	18.5	7.0	9.54	7.03	9.13	41.8	0.768	2.981	41.1	0.514	72.4	1.37
25	20.7	17.2	7.1	9.72	6.28	9.21	42.4	0.776	2.952	40.7	0.514	72.4	1.13
50th Ave	24.7	21.7	7.3	9.57	7.70	9.25	35.6	0.776	2.984	40.8	0.532	73.0	1.67
44	24.4	21.1	6.8	9.50	7.68	8.55	42.2	0.782	2.960	40.5	0.528	72.9	1.82
45	24.5	22.7	7.8	9.77	11.20	12.46	28.5	0.771	3.000	41.0	0.534	73.1	1.62
46	24.7	21.0	7.0	10.16	4.09	5.58	36.0	0.776	2.988	40.9	0.533	73.0	1.83
47	24.8	21.3	6.1	8.96	7.81	10.06	36.7	0.786	2.960	40.6	0.531	72.9	1.46
48	24.9	22.4	8.6	9.45	7.74	9.59	34.8	0.766	3.014	41.2	0.531	73.1	1.61
75th Ave	29.2	26.4	8.1	9.52	6.61	8.40	32.4	0.777	3.017	41.0	0.54	73.6	1.79
66	29.0	26.5	8.3	9.37	4.76	5.60	31.8	0.773	3.029	41.1	0.543	73.7	1.64
67	29.0	27.1	8.2	9.33	9.02	11.63	26.4	0.776	3.016	40.9	0.550	73.7	1.95

	Aromatics, DHA, Vol%	Aromatics, D5769, Vol%	Ethanol, DHA, Vol%	Ethanol, D5599, Vol%	Olefins, DHA, Vol%	Olefins, D6550, Vol%	Iso-Paraffins, DHA, Vol%	Specific Gravity	mCO₂/mFuel	MJ/kg	C:H Ratio	CI (g CO₂/MJ)	PMI
68	29.1	26.3	8.6	9.50	7.09	9.10	35.1	0.777	3.008	40.9	0.543	73.5	1.90
69	29.3	26.5	8.0	9.57	5.93	6.42	32.5	0.774	3.030	41.1	0.543	73.7	1.69
70	29.5	25.5	7.2	9.81	6.25	9.23	36.1	0.783	3.002	40.9	0.544	73.4	1.78

Table 4: Summary of properties of gasoline with 25th, 50th, and 75th percentiles of aromatic content. in the survey.

Relationships for Market Fuels

The Texas fuel surveys (ERG, 2017 and 2020) provide DHA on E10 gasoline across the state and provide a sound database for examining relationships between CI, PMI and fuel properties. CI is influenced very strongly by the aromatic content, because aromatics are the species that differ most in CI from both other hydrocarbon species and from ethanol. Further, the Texas fuels are all nominally 10% ethanol by volume, and typical of summer blends. For each Texas regular E10 fuel, full DHA data were used to determine CI from carbon content and from published or modeled LHV. Figure 18 shows that a linear relationship exists between CI and total aromatic content (vol%) for Texas regular grade gasoline, and that a 10% change in aromatic content causes a 3% rise in CI. Based on the best fit in Figure 18, a reasonable tradeoff ratio between ethanol and aromatic content would suggest that a 10% change in ethanol would produce a decrease of about 2.4% in CI due to the 8% aromatic reduction but would see a corresponding increase of about 0.5% due to the ethanol addition, yielding a slightly higher net CI reduction than the 1.41% deduced from modeling in the body of the report. However, as noted in that section of the report, the production volume of E0 was reduced from the E10 volume because of real-world refinery production limitations so the potential change in aromatic levels and CI may be slightly understated.
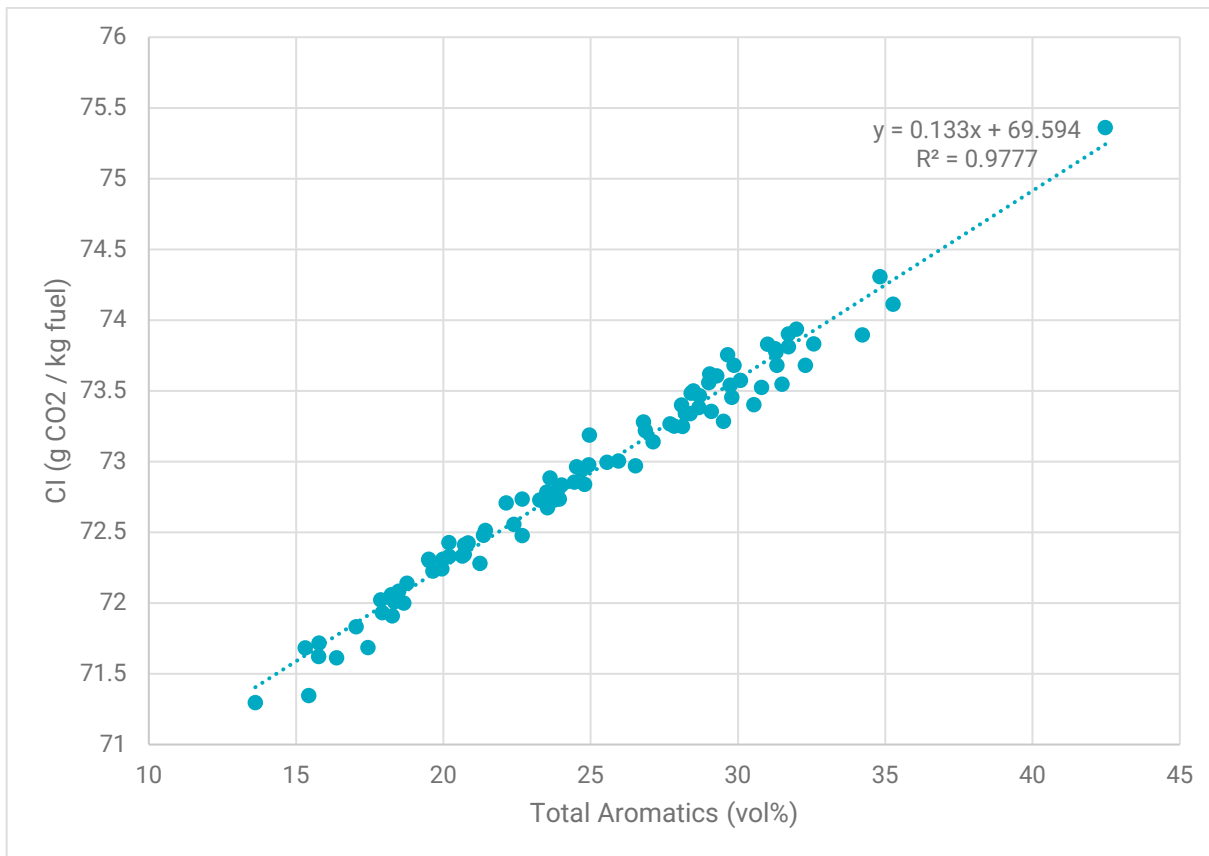
Figure 18: Relationship between CI and aromatic content of the fuel.

Aromatic content is also associated with the high carbon to hydrogen ratio of the benzene ring. Figure 19 shows that the CI values of the E10 summer fuels predict their C:H ratios closely, with a very similar correlation coefficient to that for the CI-aromatic relationship.
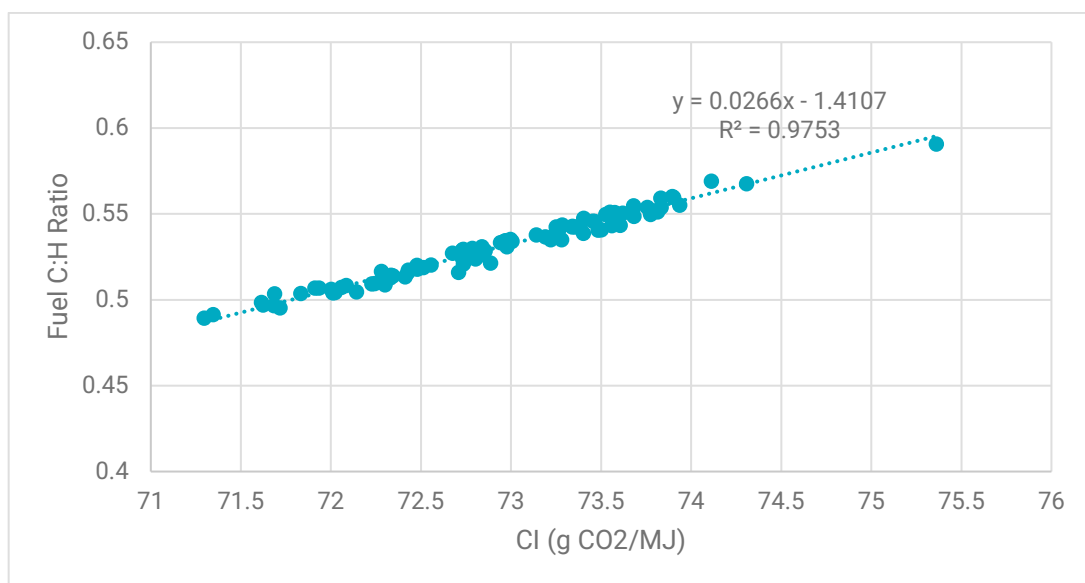
Figure 19: CI is an accurate predictor of the carbon to hydrogen ratio for the summer E10 fuels

Although the CI is closely correlated with the C:H ratio, its relationship to the fraction of paraffins (both normal and iso-paraffins) in the gasoline is not as good, as shown in Figure 20. Scatter can be attributed to the varying composition of the remainder of the gasoline, where olefins and napthenes offer higher C:H ratios than aromatics. CI decreases as paraffinic content of the gasoline increases, but scatter exists due to the varying mix of olefins, napthenes, and aromatics in the remainder of the fuel. Ethanol content varied little from 10% by volume in the Texas summer fuels.

Noting that aromatics were more dense than other species, and that the quantity of ethanol in the gasoline varied little, CI was also compared to the specific gravity (sg) of the gasoline blends, as shown in Figure 21. However, there was not a strong correlation between CI and the sg of the Texas fuels.
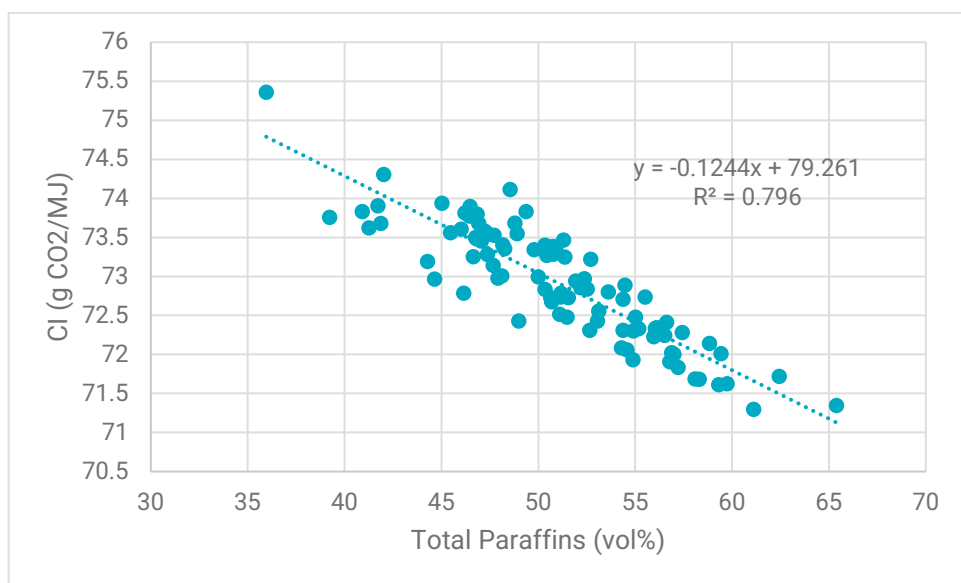
Figure 20: CI versus percent of normal and iso-paraffins in Texas summer fuels.
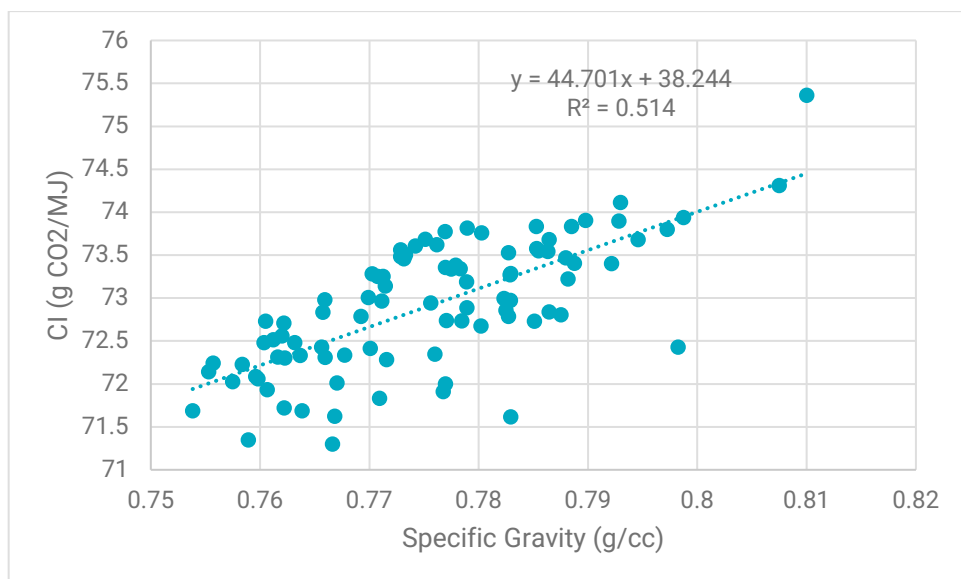
Figure 21: CI versus specific gravity of Texas gasoline blends

Some scatter is expected in the plot between CI and total aromatic content (Figure 18) because the C:H ratio for single ring aromatics varies with molecular weight. For example, alkyl benzenes, and even indan and indene, have lower C:H ratios than benzene. However, PMI is more sensitive to the molecular weight of aromatics, and hence is affected by the distribution of those molecular weights in the fuel, as well as the overall aromatic content. In the Fuel Blending Guide (Clark et al., 2020 & 2021) and in experimental fuel formulation by Sobotowski et al. (2015), the importance of the distribution between heavy and light aromatics is recognized.

Figure 22 shows that the relationship between PMI and aromatic content is approximate. In consequence, there is also scatter in the plot of PMI versus CI, as shown in Figure 23
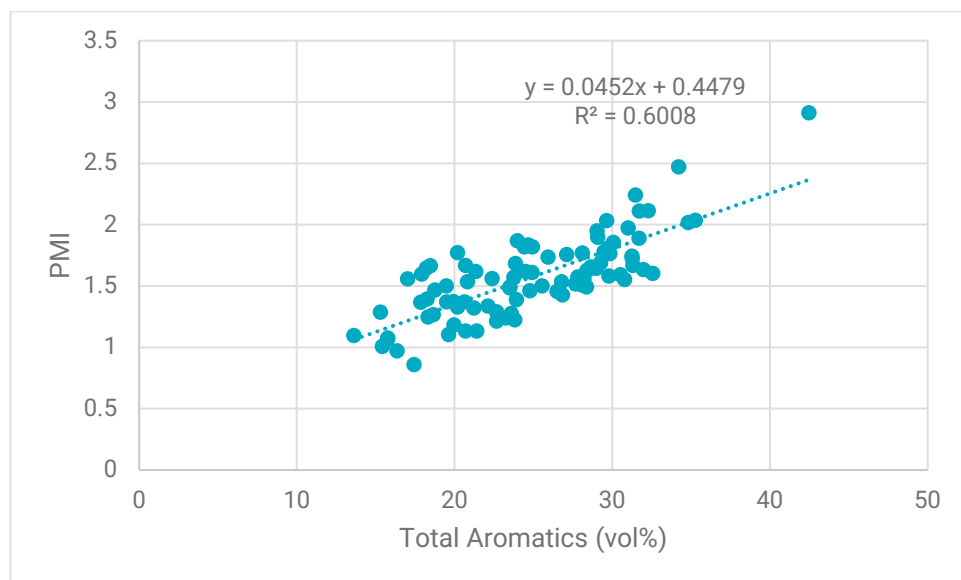
Figure 22: PMI versus aromatic content for Texas fuels.
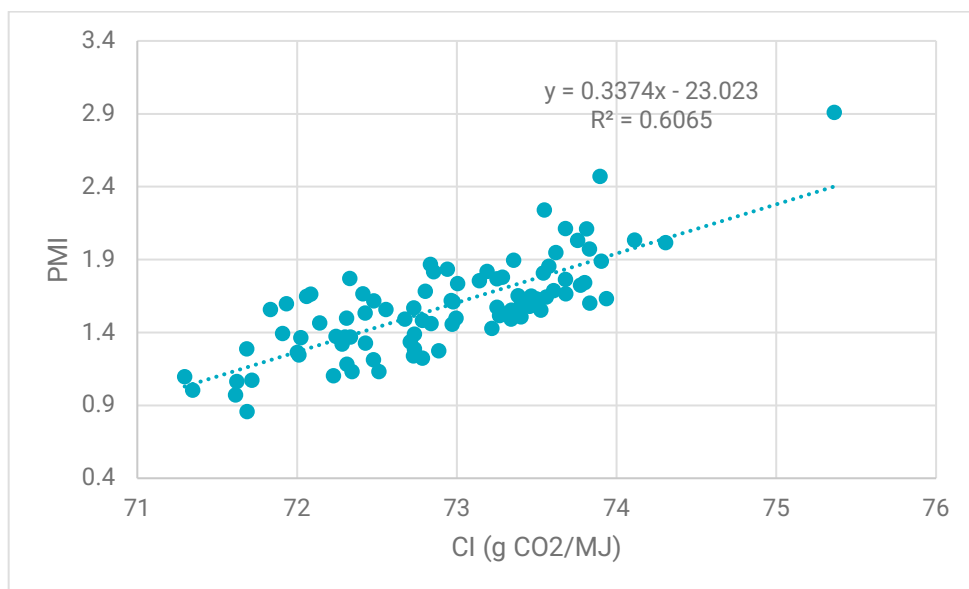
Figure 23: PMI versus CI for Texas fuels

There have been several indices proposed as improvements to PMI for PM prediction (Aikawa et al., 2010; Chapman et al., 2016; Shi et al., 2018; Zhao et al., 2019; Leach et al., 2019). Recently, Crawford et al. (2021) have reported a new approach, and include ethanol content in the prediction. Chapman et al. (2021) have

provided a review of trends in indices as a measure of gasoline quality. Literature has also sought to predict PM in terms of distillation measures of heaviest components (Butler and Sobotowski, 2021; Tahtouh et al., 2019) or distillation fractions. The relationships between PMI and fuel descriptors are examined below.

Figure 24 shows that there is an increasing trend of PMI with respect to T90 for the Texas summer fuels, but the correlation is poor. This may be attributed to the varying fraction of aromatics in the final stages of distillation, and to the varied presence of lighter aromatics that contribute to the PMI but are not associated with T90. In Figure 25 the product of T90 and aromatic content is shown to have slightly better prediction of PMI than either T90 or aromatic content alone, but it is insufficiently accurate to represent an economical predictor. Figure 26 shows that T80 offers only slight improvement of PMI prediction over T90.
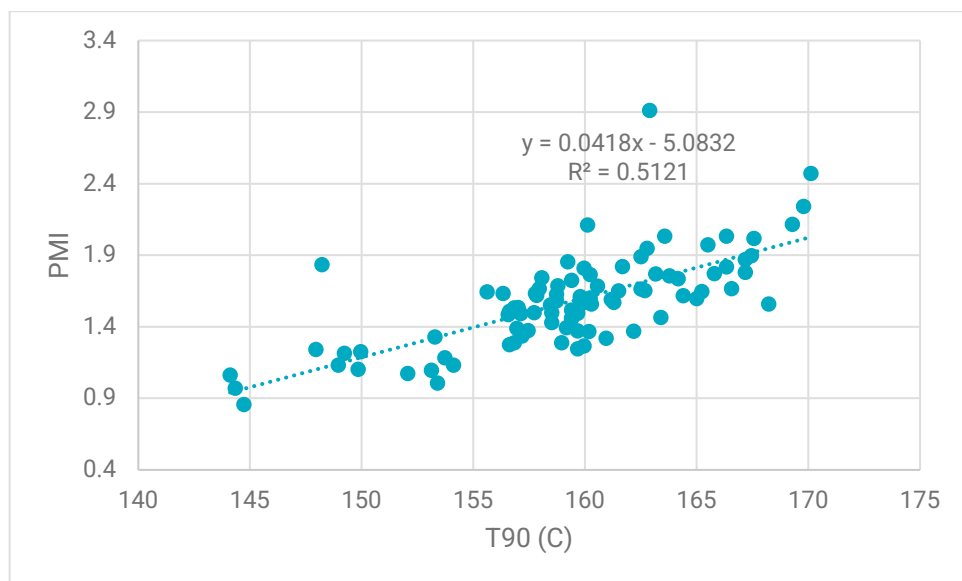
Figure 24: PMI compared with distillation T90 for Texas summer fuels.
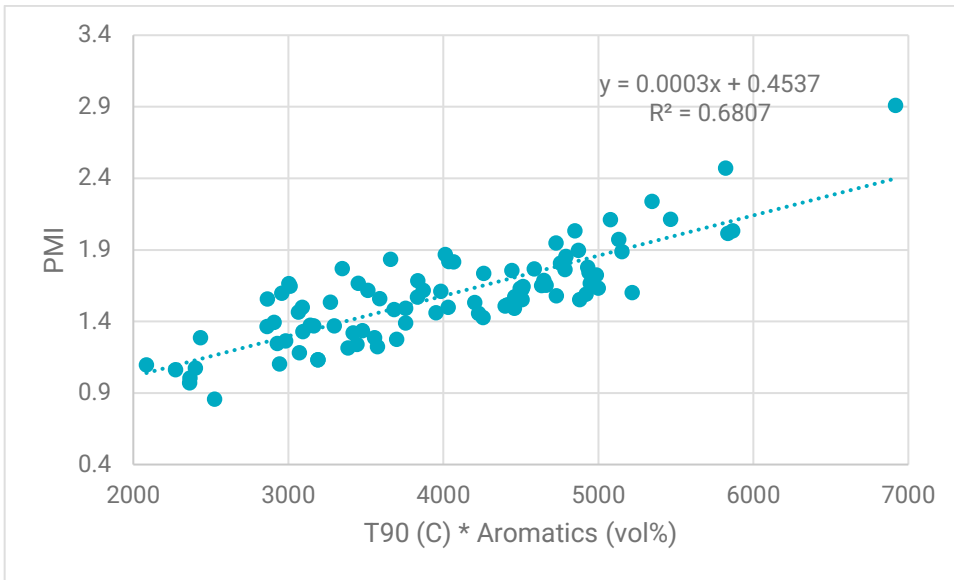
Figure 25: PMI compared with the product of aromatic content and T90 for Texas summer fuels.
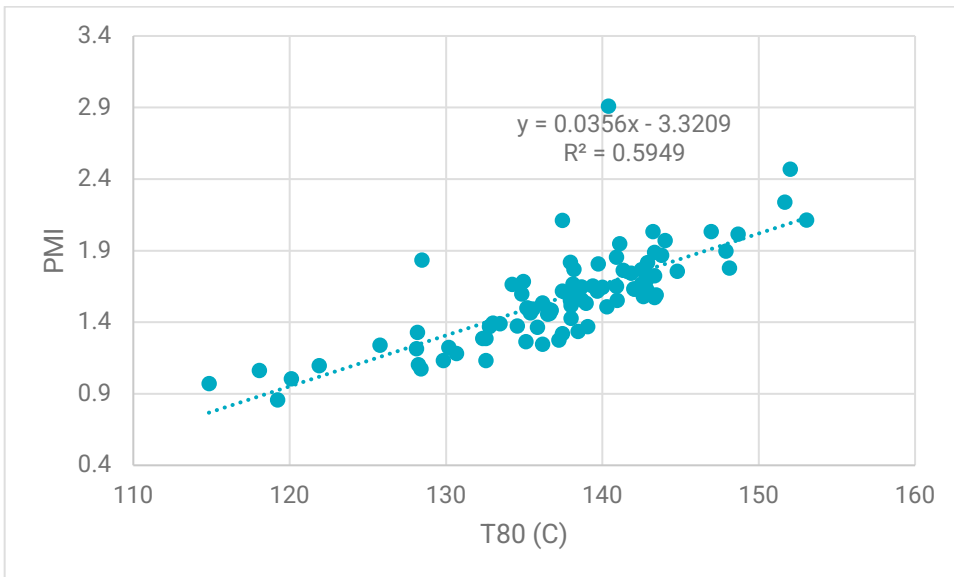
Figure 26: PMI relationship with T80 for Texas summer fuels.

Tailpipe CO₂ Production and the R-Factor

When a vehicle is operated on two different fuels under the same operational circumstances, it will consume a quantity of energy associated with each fuel. If the vehicle uses less total energy for one of the fuels, it is using the heat of combustion of that fuel more efficiently, and that difference can be expressed through a measure termed the R-factor. This is the primary topic of the section below. If the R-factor is unity, then the same amount of energy is used from each fuel. The energy ratio is readily related to the mass ratio between the fuels,

using the LHV, which has units of energy/mass. In turn, the volume ratio between the fuels is found by using the two values for density or specific gravity. Since each fuel has a CI, the relative amounts of CO_2 for each fuel can be found from the energy use, assuming that all of the carbon in the fuel is burned or catalyzed to form CO_2. With modern closed crankcase engines, CO_2 cannot escape from the engine except via the tailpipe. Likewise, the mass fraction of carbon in each fuel can be used together with the mass of fuel that is burned to deduce the relative CO_2 quantities. In reality, the CO_2 is lower than computed from fuel use, because some fuel carbon is emitted as CO, THC and organic species. The fate of those other species from a greenhouse gas perspective is complex, as discussed earlier in this report.

In practice, the fuel energy is not measured directly. The fuel consumed may be measured directly by volume or mass, or determined from measurement of total carbon (primarily CO_2) in the exhaust. It is possible that the measured CO_2 ratio does not match the carbon ratio in the exhaust precisely if the two fuels produce comparatively different fractions of unburned fuel, CO, or other hydrocarbons. "While the R factor was established to account for changes in the volumetric heating value of different fuels, this change is generally accompanied by changes to other fuel properties that may have an impact on fuel economy." (Sluder et al., 2014) Further, the R-factor between two selected fuels may also be influenced by the vehicle choice and the test schedule that is used. As one example, one fuel may have a higher or lower anti-knock behavior than the other. This may not affect the R-factor in a light load test cycle such as the FTP or even the EPA Highway Cycle, while real world driving or a higher load cycle such as the US06 may elicit ignition timing differences between the two fuels. The fuel with more retarded timing that is employed for knock avoidance would have a disadvantage with respect to fuel efficiency, but that disadvantage may not be elicited in light load use.

Philosophically, the quantity of an environmental pollutant produced is often considered as a ratio to the useful work that is done. Light duty vehicle emissions are expressed in units of mass/distance traveled. Commercial vehicle and stationary engine emissions are expressed a ratio to the shaft work done by the engine, or more rarely as a ratio to ton-miles of useful transportation. CI is expressed in units of carbon or CO_2 mass/LHV. For light duty vehicles there is a regulatory need to determine the CO_2 mass/mile as well as the fuel economy. Translation requires a measure of the vehicle efficiency in terms of energy used per mile. This also may be couched in terms of volumetric fuel consumption and volumetric energy content of the fuel, which can be determined from LHV and fuel density.

When two fuels are compared in light duty vehicle use, the volumetric fuel consumption (vehicle fuel economy) may not change in proportion to the volumetric heating value of the fuel. Adopting units of miles per gallon and BTU (per gallon) for a "fuel 2" that is compared to a baseline "fuel 1," an R factor is defined as "the ratio of the percent change in fuel economy to the percent change in volumetric heating value (VHV) for tests conducted using two differing fuels" (Sluder et al. 2014).

$$R = [(mpg2 - mpg1)/mpg1]/[(VHV2-VHV1)/VHV1]$$

If LHV is employed as a mass-based energy measure, a density or specific gravity correction is required to yield the volumetric energy basis:

$$R = [(mpg2 - mpg1)/mpg1]/[(LHV2(sg2/sg1)-LHV1)/LHV1]$$

The existence of an R-factor that is not unity also implies that adjustment may be needed in modeling CO_2 that is produced, based upon the LHV and carbon content of the fuel. A distance-based CO_2 value (g/mile) will require adjustment in sympathy with the inverse fuel economy adjustment (1/mpg), provided that the combustion efficiencies of the two fuels are the same. However, the correction may not be precisely inversely proportional due to differences in fuel CI and completeness of combustion. The R-factor has been applied historically to adjust EPA certification data as certification fuels have been redefined. Traditionally this was to assure continuity in fuel economy data (for CAFE), but now CO_2 GHG emissions are also of importance. For the fuel economy R-factor, the EPA basis is the certification fuel (Indolene) used in 1975. In 1976 the EPA reviewed the effect of gasoline properties on fuel economy (EPA, 1976). The EPA provided an adjustment R-factor of 0.6 in 1986 and has recently provided a new factor to address Tier 3 certification fuel, as discussed below. Fuel economy decrease due to oxygenated fuels and RFG was presented as being in lock-step with energy content in a later report (EPA, 1995). A distinction should be drawn between establishing an R-factor to distinguish two defined certification fuels from the more general use of an R-factor to compare two fuels based on their energy content. It is likely that the actual fuel compositions affect the R-factor in addition to the energy contents of the fuels.

When CO_2 emissions are considered rather than fuel economy, there are three separate factors that can cause the CO_2 emissions at the tailpipe per unit distance traveled to differ between two fuels, namely:

- Since the LHV, specific gravity and carbon content may all differ, the fuel CI may differ, whether expressed in volumetric or mass-based terms.
- The vehicle may use one fuel more efficiently than the other. This is a corollary of the R-factor.
- The vehicle may emit more of the carbon of one of the two fuels as other carbon species, including unburned fuel, other hydrocarbons, particulate matter and non-methane organic gases. If the measure is defined at the tailpipe, the ultimate fate of these other species is not relevant. However, those other species are considered in computing fuel economy.

The low R factor value of 0.6 that was used for over three decades may be attributed to legacy vehicle technology that did not adjust stoichiometry precisely. The 0.6 value was determined for, and applied to, a very small VHV difference between the baseline fuel and the Tier 2 fuel, so that any inaccuracy of measurement or fuel analysis at that time had small consequences. The Tier 2 fuel that was introduced to replace the earlier indolene had a higher volumetric energy content, so the 0.6 factor was associated with a rise in fuel economy (in mpg), although that rise was small.

Chevron (2009) presented a plot of data from Hochhauser et al. (1993) to show the effect of varying volumetric heating value (108 to 118 BTU/gallon) on the fuel economy of two fleets, one of 1984-85 vehicles, and one of 1989 vehicles. Data were strongly correlated with best fit lines. The lines suggest that the average R-factor was slightly less than unity: Hochhauser et al. (1993) found it to be about 0.93. This value implied that fuel economy was only slightly less impacted by a reduction in the fuel LHV than proportionality would suggest. Chevron observed that this proportionality showed that "heating values can be used as surrogates for actual fuel economy measurements when considering the effect of gasoline composition on fuel economy." Clearly the technology of the two test fleets was not representative of designs that predominate in the current on-road fleet.

Sluder and West (2013) presented a review of the R-factor and reported on EPA processing of EPAct data (EPA, 2013a, 2013b) that yielded R-factors of 0.82 to 0.86 for the LA92 cycle. They also reported on the use of prior data from catalyst studies at two sites (West et al., 2012) to determine R-factors using the FTP. Sluder et al. (2014) published these findings along with findings from a third study that used the LA92 (Knoll et al., 2009). All three studies had changes in fuel energy content as a result of ethanol addition to the petroleum fuel, where 20% ethanol addition reduced the energy content by 7% to 8%. All subject vehicles were port fuel injected. Sluder et al. (2014) reported that data from both the EPAct study and the Immediate Effects study (Knoll et al., 2009) suggested that the R-factor for only E15 and E20 fuels (relative to a baseline fuel) was higher than for only E10 fuels. Overall R-factors were computed for all fuels, regardless of ethanol content. The EPAct data showed variability of vehicle responses, with R-factors ranging from 0.83 to 1.0. There were also variations from phase to phase of the LA92. A summary of test fleet averaged results is presented in Table 5.

Study	Fuels	Cycle	R factor
Immediate Effects Study	All Fuels	LA92 Weighted	0.911
Immediate Effects Study	E10 Fuels	LA92 Weighted	0.768
Immediate Effects Study	E15 Fuels	LA92 Weighted	0.859
Immediate Effects Study	E20 Fuels	LA92 Weighted	1.105
EPAct Study	All Fuels	LA92 Weighted	0.921
EPAct Study	E0 Fuels	LA92 Weighted	0.811
EPAct Study	E10 Fuels	LA92 Weighted	0.834
EPAct Study	E15 & E20 Fuels	LA92 Weighted	1.185
Catalyst Study	All Fuels	FTP Weighted	0.935
Catalyst Study	E10 Fuels	FTP Weighted	0.946
Catalyst Study	E15 Fuels	FTP Weighted	0.936
Catalyst Study	E20 Fuels	FTP Weighted	0.929

Table 5: A summary of the results presented by Sluder et al. (2014)

The results shown in Table 5 arise from studies with different fuels and blending protocols. Sluder et al. (2014) additionally cautioned the reader that uncertainties in the fuel analyses exist and propagate possible error into the computed R-factors. They also discussed some questionable results that can be excluded from the catalyst

study and that resulted in a small increase in the R factor. Although there is no equitable way to average all of these data, a simple average for all fuels yields an R factor of about 0.92.

Sluder (2019) re-addressed the R-factor, discussing the likelihood that ethanol effects may exist separately from fuel heating value effects. Sluder examined other causes for changes in fuel economy, addressed effects such as engine efficiency variations that work in parallel with a fuel heating value change, and concluded that "[c]onfounding factors that accompany a change in fuel heating value make it very difficult to correctly assess R-factor values through experimentation." It was observed that these confounding factors may have the same level of influence on the R-factor as the heating value change. Further, from the analysis of Sluder et al. (2014), a single value may not be sufficient to address vehicle to vehicle differences in response to a heating value change.

In the Coordinating Research Council (CRC) E94-2 study, directly measured CO_2 differences for twelve GDI vehicles were reported between eight gasoline blends, having high PMI, low PMI, high AKI, and low AKI, and with 0% and 10% ethanol content. The E10 was found to have 0.5% higher CO_2, but this is readily attributed to the fact that all fuels in the E94-2 had the same target aromatic content, and aromatics are the prime contributor to elevated CI. As presented above, there is a market fuel expectation that aromatics are removed from the fuel as ethanol is added.

A study by Wu et al. (2019) of proposed E10 use in China compared a "China 5" E0 (RON = 96.2, 33.1% aromatics by volume, 15% MTBE by mass) with a 93 RON E10 having a reduced aromatics content of 20.9% and 0.75% MTBE. A low olefin E10 was also studied. Seven PFI and two GDI vehicles were used with the Worldwide Test Cycle. The low aromatic fuel contained 1.5% less carbon on an equivalent heating basis (i.e. 1.5% lower CI). CO_2 reduction s ranged from 1.1 to 4.7% with a 3.1% average. The two GDI vehicles averaged 4%. The LHV of the two fuels were similar noting the MTBE loading in the E0: 41.91MJ/kg for the E0 and 41.87% for the E10. The 0.6% increase in volumetric fuel consumption for the E10 was not found to be significant, and the energy-based consumption varied between vehicles.

The EPA conducted a new study specifically to address CO_2 emissions and fuel economy changes associated with the current move from Tier 2 to Tier 3 certification fuel (EPA, 2018a). Tier 2 certification gasoline contained no ethanol and could have a high octane rating with a maximum of 35% aromatics. In contrast, Tier 3 certification fuel has been specified to contain 9.6% to 10% of ethanol by volume. It has a maximum aromatic content of 25%, with a defined distribution of aromatics by weight, and with an AKI of 87 to 88.4. In the comparative study, the EPA used a Tier 2 fuel with an AKI of 92.6 and an aromatic level of 32.3. The octane rating difference was reversed between the two fuels in comparison to a splash blend, such as in the catalyst study (West et al., 2012). The Tier 3 fuel contained 10.15% ethanol (which was within the measurement allowance from 10%) and 25.4% aromatics, with an AKI of 87.25. The Tier 2 fuel had a heat of combustion of 18,529 BTU/lb, and the Tier 3 fuel was 17,889 BTU, lb, 3.6% lower. The Tier 3 fuel had a 1.3% lower CI (based on energy content) than the Tier 2 fuel.

The EPA study used 11 cars and light trucks, three with PFI engines and the remainder with GDI engines, with model years from 2013 to 2016 and odometer readings typical of a year or less of driving. These vehicles, although predominantly GDI, may not be fully representative of future GDI technology, as manufacturers seek to craft injection strategies that will reduce PM from GDI vehicles (Short et al., 2017). Manufacturers are also likely to increase engine downsizing and boosting and employ selective electric hybridization to improve fuel efficiency (Isenstadt et al., 2016; Lutsey et al., 2017; Conway et al., 2018). The vehicles were driven over repeat runs of the FTP and the Highway Fuel Economy Test (HFET). Fuel economy was measured using a carbon balance that considered CO_2, CO and methane and non-methane organic gases, thereby avoiding questions of combustion efficiency.

The fleet results were averaged to yield a CO_2 reduction of 1.78% for the FTP and 1.02% for the HFET. The corresponding reductions in fuel economy were 2.29% and 2.98%. One vehicle was found to have unexpected octane response effects, leading to higher CO_2 and lower fuel economy. It is not clear whether other vehicles may have been impacted less visibly by the reduction in octane rating that occurred simultaneously with the inclusion of ethanol in the Tier 3 fuel. There were substantial differences in measured response to the fuel change between vehicles and between the FTP and HFET.

Based on the study results the EPA proposed to adjust CO_2 data measured using oxygenated Tier 3 certification fuel to match Tier 2 fuel expectations "by multiplying by a factor of 1.0166 to produce the expected CO_2 performance had the vehicle been tested over the same test cycles while operating on Tier 2 fuel." (Federal Register, 2020). The fuel economy R-factor was referenced to the original indolene test fuel, or, equivalently, to a "0.6" correction of the Tier 2 fuel economy (NPRM, 2020). It was determined that fuel economy for CAFE standards should be adjusted using an R-factor of 0.81 (NPRM, 2020). This R-factor of 0.81 would be relative to the original 1975 reference fuel used for the Tier 2 fuel R-factor. Published comments (Gaiser, 2020) provide deeper history relating to the R-factor and show disagreement with several aspects of the proposed rule.

Between the Tier 2 and Tier 3 fuels, the average fuel economy was 2.98% lower for the HFET and 2.29% lower for the FTP. The volumetric fuel energy content was 2.77% lower for the Tier 3 fuel. Therefore, the relative R-factor between the Tier 2 fuel (as a baseline) and the Tier 3 fuel for the HFET was 1.08, and for the FTP was 0.82. These values are compatible with the range of results from the three studies (including EPAct) reported by Sluder et al. (2014). The EPA study predominantly employed GDI vehicles, whereas the prior studies were for PFI vehicles. The three PFI vehicles in the EPA study had higher differences for the FTP cycle than the GDI vehicles, but not for the HFET.

The Tier 2 and Tier 3 fuels differed in ethanol content by 10.15%, and in aromatic content by 8.5%. This ethanol-aromatic tradeoff (a factor of -0.84) is in good agreement with the modeled market regular summer fuel compositions presented in this report but does not correspond to the small reduction in aromatics associated with the E0 to E10 adjustment factors (-0.202 and -0.22) in EPA documents for MOVES 2014b (EPA, 2018b) and MOVES 3 (EPA 2020) respectively.

The literature suggests that the effect of fuel changes on fuel efficiency extends beyond the one dimensional measure of heating value, and that certification fuels do not necessarily reflect the composition or behavior of market gasoline. As one example, Liu et al. (2012) compared the droplets and burning characteristics of indolene and a regular grade market gasoline in a dedicated apparatus. They concluded that "Indolene and gasoline were found to display remarkably similar droplet evaporation rates. However, the sooting dynamics were substantially different." In addition, fuels that are splash blended from an E0 gasoline (not a BOB), as in the catalyst study (West et al., 2012) or that are match blended, as in the EPAct study, may not represent the relative behaviors of market fuels. Further, driving activity influences engine speed and load, and alter fuel effects conclusions (Clark et al., 2019). The R-factor adjustments for fuel economy, and its counterpart CO_2 adjustment, are therefore circumstantial, not invariant, and are not well documented for real on-road operation. Yan et al. (2013) observed that "uncertainties in the net GHG effect of ethanol, particularly when used in a low-level blend with gasoline, are considerably larger than previously estimated." However, if the combustion of higher ethanol blends results in higher combustion efficiency, and if the R-factor is less than unity relative to E0, this implies that ethanol blends offer a slightly greater in-use greenhouse gas reduction than is computed from the fuel CI alone.

Figure 27 shows the CO_2 g/mile relationships between the FTP and the higher speed HFET. The lack of strong correlation may be attributed to several causes, but the accuracy of emissions measurement would limit the ability to determine small differences quantitatively without averaging a large number of runs. Figure 27 also suggests that data may not describe accurately the relative performance across a broad range of operation. For all vehicles in the EPA "Tier 3" study, the average FTP CO_2 reduction of 1.78% exceeds the 1.34% CI reduction alone, but the HFET value of 1.02% is lower. These measured values become 1.85% and 1.20% if the Acura, disadvantaged by the octane reduction, is excluded. It is unknown whether any other vehicles may have been affected to a lesser degree by the adverse octane change. Although the vehicles were intended for operation on regular fuel, feedback control of ignition timing for knock avoidance is likely to be affected by an absence of knock detection when higher octane fuel is used. This effect may be limited due to the low power demand of the FTP and modest power demand of the HFET, but current control culture is to use low engine speed and raise engine load even at low road load. The EPA value of 1.66% for Tier 2 to Tier 3 CO_2 adjustment certainly exceeds the 1.34% difference for fuel-based CI, but also includes any CO_2 reductions due to CO, and THC in the tailpipe. The oxygenated Tier 3 fuel yielded lower CO distance specific emissions.
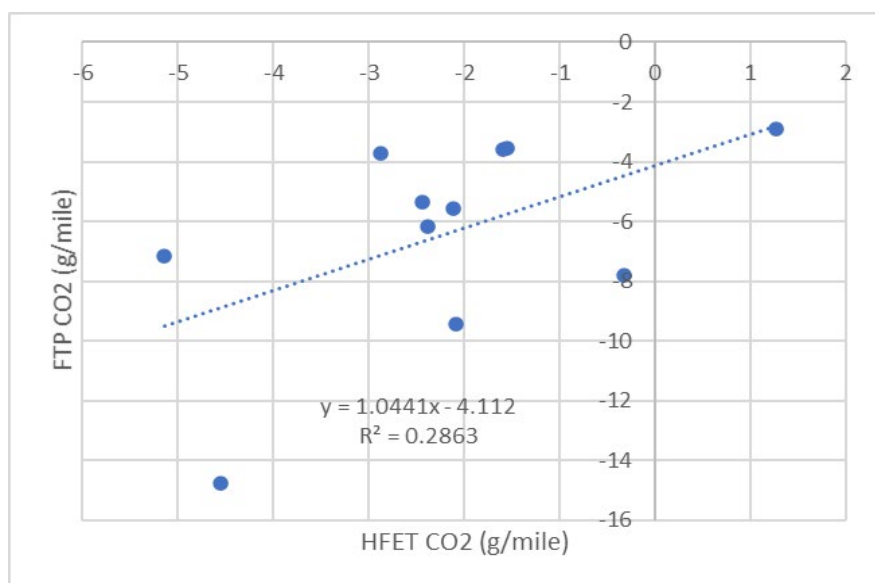
Figure 27: Comparison of fuel effects on CO_2 between the FTP and HFET

If the true on-road R-factor is less than unity and if CO_2 is reduced by more than the CI ratio of fuels, national implication for both fuel efficiency and CO_2 reduction is favorable for ethanol use. However, the use of E10 Tier 3 certification fuel will be obligatory. If the beneficial Tier 3 fuel reduction margin of 0.19 for the 0.81 R-factor is used to correct (reduce) the measured fuel economy value to yield a certification value, it places a burden on the engine or vehicle manufacturer to raise the measured fuel economy by other means for CAFE compliance. The same is true for the CO_2 certification. Since the measured R-factor evidently varies between vehicles (EPA, 2018a) and between test schedules (See Figure 27), it implies that the CO_2 and fuel economy corrections are statistically uncertain, engine dependent, or both and are not well represented by an average correction. Further, it is not clear that a single R-factor would be applicable across all compliant Tier 2 and Tier 3 certification fuels. Present study results (EPA, 2018a) are for one blended Tier 2 fuel and one blended Tier 3 fuel.

The present headroom for engine efficiency improvement is marginal without elevated fuel knock resistance for high load, low engine speed operation (see Miles, 2018; Sjoberg et al., 2017; Szybist et al., 2021). For market fuels ethanol content and gasoline energy content are not fully coupled and AKI will not describe knock margins adequately. Szybist and Splitter (2018) conclude that "the complex chemistry leading to knock cannot readily be accounted for with metrics such as RON, AKI, or OI" (OI is the octane index). In real world on-road application, these margins will cause minor mis-estimation of fuel economy, since it is unlikely that ethanol content and BOB properties unite to yield a simple and unequivocal relationship between engine efficiency and energy content.

Conclusions

TTW CO_2 reduction for ethanol blends may be examined from either a fuel-based perspective or a vehicle exhaust inventory perspective. Fuels are typically characterized using CI, calculated as a ratio of carbon in the fuel, or carbon dioxide production potential, per unit of mass-based LHV in the fuel. Ethanol has both a reduced carbon content and a reduced LHV relative to petroleum species and enjoys a CI that is slightly lower than that of typical petroleum gasoline, and slightly higher than for paraffins in the fuel. Aromatics in the fuel have a far higher CI, in sympathy with their low C:H ratio. Both aromatics and ethanol serve to raise the octane rating of a gasoline blend.

CI may be calculated by employing DHA and summing the weighted CI contributions of each species in the fuel, or otherwise by grouping components with similar CI and using a simpler summation. Total fuel LHV and carbon content analyses can also yield CI. Generally, variability of fuel analysis has a small effect on conclusions when considering fuels that are intentionally blended or splash blended, but caution is needed in comparing CI of two unrelated fuels, analyzed in different ways, due to measurement variability. C:H ratio was found to be a good correlational estimator of CI for market gasoline blends.

Refinery modeling, economic considerations, availability of feedstocks and examination of gasoline properties support the conclusion that as ethanol is blended into gasoline, so aromatics are reduced to maintain a constant octane rating. The primary refinery option for lower octane is through lower severity or throughput for the gasoline reformer. This in turn reduces both gasoline aromatic content and carbon intensity. The reduction of aromatics in preparing a BOB for E10 and higher ethanol blends results in a net reduction in CI for market fuels. While the actual percentage reduction in CI of 10 percent and higher ethanol blends is not large, the TTW reductions are applied to a large source. This reduction opportunity applies to nearly all US gasoline consumption of about 135 billion gallons/year, requiring 13.5 billion gallons of ethanol to achieve that goal.

The 135 billion gallons of gasoline consumed represents 715 billion pounds of carbon annually. This yields 1.3 billion short tons of CO_2 from vehicle exhaust. From the fuel-based CI data in Table 1, and from detailed refinery modeling, a reversion from very high E10 penetration to an increased aromatic E0 gasoline would therefore raise the US CO_2 inventory by 18.3 million tons per year. Conversely, just from fuel CI, a move to E20 would double the benefit over E0. Taking into account vehicle efficiency effects embodied in the EPA 1.66% value for moving from E0 to E10 suggests that E10 currently offers a TTW reduction of over 21.6 million tons annually.

CI reductions for ethanol blending were demonstrated for a three-component mixture of ethanol, toluene and iso-octane, and more detailed gasoline modeling was extended to cover a variety of scenarios and E10, E15 and E20 blends. Scenarios included maintaining current refinery production and increasing exports to compensate for incremental ethanol, adjusting refinery production down to meet domestic demand and keep base E10 case exports constant, and splash blending E15 and E20 using an E10 BOB. CI reduction relative to E0 ranged from 1.41% for E10 to 3.04% for E20 with a dedicated BOB under the scenario of adjusting refinery production to

meet demand. Employing a higher or lower E0 aromatic basis did not alter conclusions appreciably. Although not a part of TTW emissions, modeling of immediate upstream hydrogen demand at the refinery suggested a sufficiently small increase in CO_2 emissions that the bulk of the TTW gains would be preserved in a WTW scenario. It is important that the TTW benefits presented in this report are recognized quantitatively in WTW analyses.

The TTW reductions discussed above are more modest than the WTT GHG emissions effects discussed in the literature, but they are quite certain. In contrast the cited WTT emissions changes vary widely, with US government sources varying from 21 to 39% reductions, and with far greater variation in the broader literature, due to the disparate factors and assumptions such as those related to plant source, agricultural practices, methods and energy of production and soil effects.

The modeling demonstrating aromatic reduction resulting from ethanol addition is in strong contrast to the MOVES 3 Fuel Wizard scenario presented by the EPA for a high alkylate E0 (EPA, 2018b). Such a scenario would demand new refinery infrastructure and attractively priced feedstocks that are unlikely to become available. Aromatic reduction, explained in this report, not only favors CI but also lowers PMI, with implied reduction of tailpipe PM 2.5 production. Gasoline exhaust PM is considered a major health care concern and has gained greater visibility as a result of GDI adoption and the relative improvement of diesel exhaust PM reduction. PMI is not directly correlated with CI, because the weight and structure of the aromatic components have a more complex effect on PMI, but efforts to reduce CI have favorable PMI effects.

Measurements of CO_2 from vehicles operated on a dynamometer provide information both on the fuel CI and on the reaction of the engine to properties of the fuel other than LHV. In particular, recent model year GDI engines with high compression ratios will take advantage of a fuel with superior in-use knock resistance to improve efficiency. CO_2 is reduced by the small amount of unburned fuel, other hydrocarbons, particulate matter and non-methane organic gases that are present in the exhaust downstream of the catalyst. The more efficient use of fuel is related to the R-factor, which is employed to assure constancy of fuel economy data over time as certification fuel specifications are changed. The change from the first indolene used to the present Tier 3 E10 certification fuel is proposed by the EPA to have an R-factor of 0.81, implying that the engine does not show the full penalty of the reduced LHV of the E10. However, there is difference or uncertainty in comparing fuel economy numbers from separate test runs. Data from other programs have shown variation in engine reaction to LHV changes, suggesting that the cause for fuel economy change is not one dimensional in LHV.

Appendix A: Review and Analysis of US Refining Operations

This appendix describes the review and analysis of U.S. refining operations and gasoline quality intended to provide a complete understanding of the real-world relationship between refining, gasoline and ethanol blending, gasoline composition and gasoline quality. The products of the analysis were:

- a gasoline blend model capable of characterizing trends in gasoline volume and detailed quality parameters over time and with changes in ethanol blend levels,
- quantification of the impacts of E10 ethanol blending on aromatics content, and
- review of MOVES3 Fuel Wizard ethanol-aromatics development.

Refining and Gasoline Blending Review: Gasoline Blend Model Development

The review/analysis included U.S. Energy Information Administration (EIA) refinery operating data, refinery capacity data, literature, and database references for detailed estimates of blend component yields and qualities. The review also relied on EPA and other literature estimates of final gasoline quality. The first step in the model development was to examine refining and gasoline production and quality over a period of increasing ethanol blending. The period 2006 through 2019 was selected for calibrating and testing the model because it represented expansion of ethanol use from 3.0 percent to 9.8 percent, could be compared to the final gasoline quality estimated in EPA's online Public Data on Gasoline Fuel Quality Properties and their "Fuel Trends Report", and included gasoline production and quality representative of recent history. The period 2006-2014 was particularly of value because it represented the larger portion of change in ethanol blending and did not have a large variation in gasoline production. During 2017-2019 ethanol blending did not change substantially but refiners significantly expanded refinery gasoline production and exports.

Starting from EIA supply/demand data a gasoline balance was constructed to quantify refinery gasoline (non-California) production, gasoline imports (BOB and finished), exports, supply provided from California and gasoline supplied to the market. Figure A.1 provides a summary of gasoline supply and production over the period. Refinery production remained relatively constant through 2013/14 and then increased along with an increase in exports.
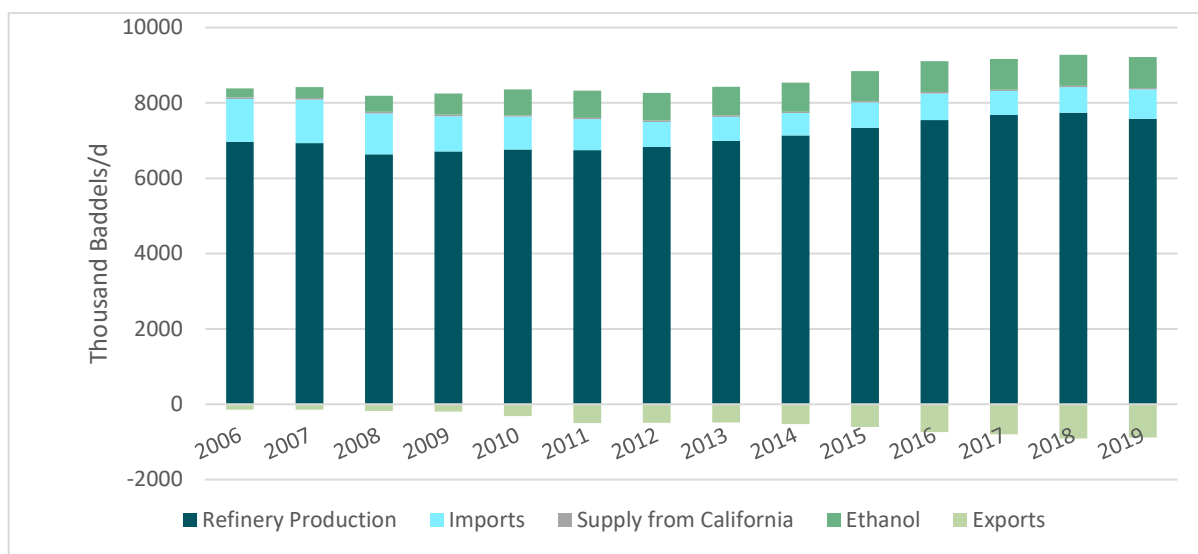
Figure A.1: U.S. Gasoline Volume Balance, 2006-2019 (Source: EIA)

An octane balance was then developed to track changes in refinery produced octane. Marketed octane was estimated from various reported values and the pool octane established using EIA reported values for premium-regular grade ratios. Gasoline imports were characterized as final gasoline and BOB with octane assumed consistent with U.S. market gasoline or the corresponding E10 BOB. Export octane was estimated based on EIA's export destinations and available internal Transport Energy Strategies' database of octane and type of gasoline imported by the receiving countries. Finally, the octane contribution of ethanol was calculated, and the refinery octane derived. The refinery octane was that required to balance octane considering market quality and the contribution of imports, exports, and ethanol.

Figure A.2 shows the trend in octane sources over time. Market octane increased through 2008, declined in 2009 and then after rebound remained relatively constant between 2010 and 2016. The difference between refinery and market octane is provided by ethanol (not shown). Refinery octane requirements fell significantly between 2006 and 2012 as ethanol addition increased from 3.0 percent to 9.5 percent. Also of interest is that refinery gasoline production fell between 2006 and 2011; for every barrel of additional ethanol blended, refinery gasoline production declined by about 0.5 barrels. After 2011, refineries expanded exports and refinery gasoline production increased by nearly 12 percent between 2011 and 2016.

A final adjustment was made to calculated refinery octane requirement to account for changes in gasoline benzene and sulfur requirements. Lowering the allowable level of benzene and sulfur results in lower octane of some of the refinery blend components. This octane requires replacement through refinery processing to meet the above refinery required octane. Figure A.2 includes a refinery adjusted octane line (dashed line) reflecting the impact of benzene and sulfur requirements. Refineries must raise the octane of affected gasoline components to maintain the required refinery octane. Refineries produce BOB at the lower refinery octane shown in Figure A.2 but use additional processing to raise the octane of individual components so that this

refinery octane can be maintained. This effectively increases actual refinery produced octane requirement (from the lower refinery octane in Figure A.2 to the higher dashed line level).
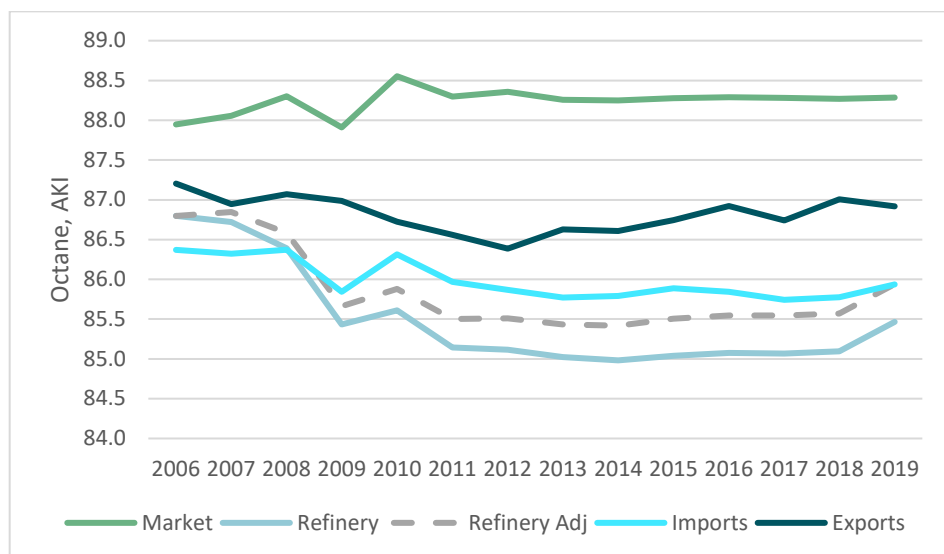
Figure A.2: U.S. Gasoline Market, Refinery, Import and Export Octane, 2006-2016 (Source: Transport Energy Strategies)

Having established refinery production volume and octane, EIA refinery data along with literature sources were used to estimate production and quality of individual refinery gasoline blend streams. EIA data include throughput for the refinery FCC and reformer processing. Capacity data are reported for alkylation and isomerization processes. Together these four streams represent more than 75 percent of refinery produced gasoline blend streams. For the FCC and reformer, a range of gasoline component yields can be estimated based on literature and process technology data and for reformers on octane and yield correlations. For alkylation and isomerization, gasoline yields correspond to throughput (with alkylation throughput being defined on alkylate gasoline production as opposed to butane input) and capacity utilization was estimated based on past literature estimates, EPA estimates for Tier 3 analysis and input from technology vendors.

Butane makes up an additional 5 to 6 percent of gasoline and its use was estimated based on gasoline volatility. All of these data resources served as input along with gasoline reformer octane/yield correlations to create a blending model capable of replicating refinery production and octane as well as market volume and quality.

Each refinery gasoline stream was characterized by chemical species groupings based on various literature and technology vendor data. A representative average gasoline quality was then specified based on EPA quality data and other available sources. The weighted average qualities of the gasoline streams were then compared against the representative final gasoline. There was close but not full agreement between the two, so small adjustments were made in component qualities until the weighted average blend matched the finished gasoline.

The chemical species characterizations were added to the model so that, in addition to gasoline volume and octane, the model calculated aromatics, olefin, paraffin and naphthene of refinery gasoline production and final market gasoline. As shown in Figure A.3, the model was able to match reported properties closely. The only significant deviation is for 2019 aromatics and olefin data from the EPA online data. However, the 2019 data are questionable and not consistent with the historic online data reported[1].
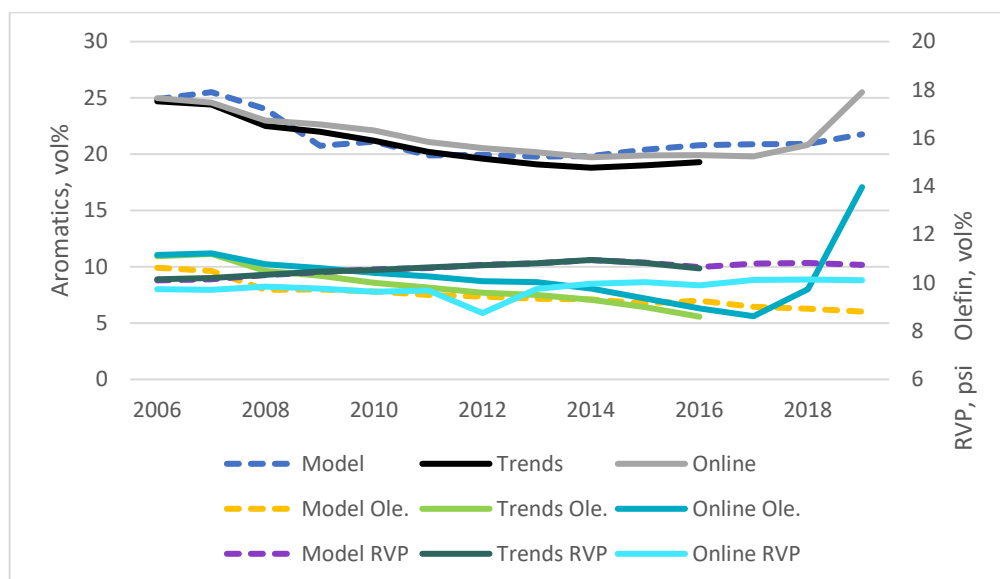
Figure A.3: Calculated versus Reported Gasoline Properties, 2006-2016 (Source: Transport Energy Strategies and EPA Fuel Trends Report: Gasoline 2006-2016)

Figure A.4 reviews reported and calculated aromatics and illustrates the strong relationship between ethanol blending and the aromatic content of the final gasoline blend. During the period of high incremental ethanol penetration (2006-2012/13), ethanol blend share increased 6.5 percent with a reported decline in aromatic content of 4.6 to 5.4 percent and a model calculated decline of 5.0 percent. Thereafter gasoline aromatics (reported and calculated) began a slight upward trend while ethanol penetration continued to increase slightly. The increase in aromatics was the result of higher overall gasoline production and a slightly higher required refinery octane (increase in market octane and higher-octane requirements of gasoline exports). Other than for 2019, the model provides good correlation with reported data. As mentioned above the 2019 data reported by EPA are questionable and not consistent with historic data.

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[1] An aromatic increase of this magnitude is highly unlike without a corresponding change in octane or available blend streams. Furthermore, an olefin increase of this magnitude would require a large corresponding change in FCC gasoline which did not occur. A large increase in olefin is not consistent with a large increase in aromatics.
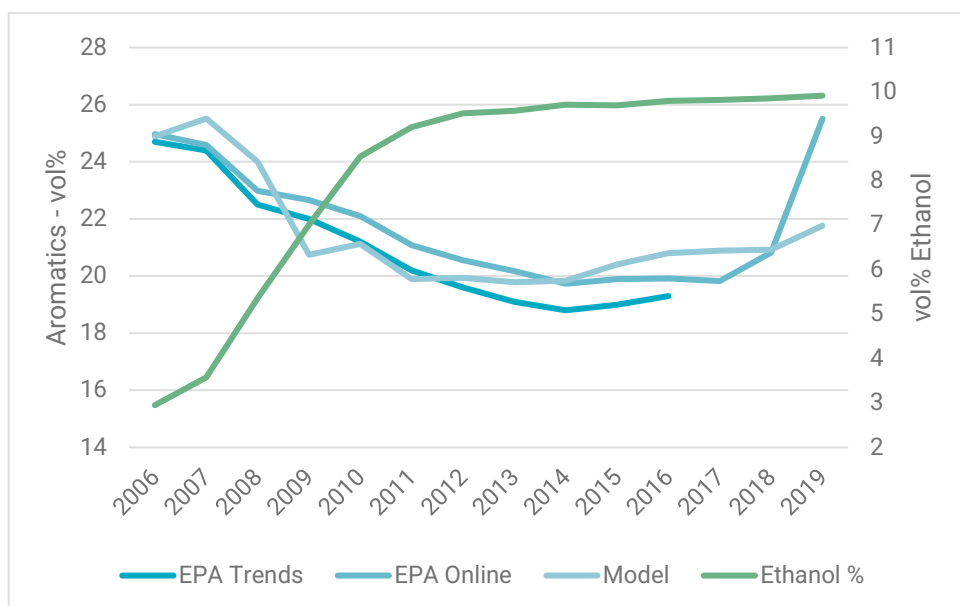
Figure A.4: Calculated versus Reported Gasoline Properties, 2006-2016 (Source: Transport Energy Strategies and EPA Fuel Trends Report: Gasoline 2006-2016)

The trend in gasoline aromatics is a function of refinery octane requirements. The primary source of incremental octane is from the refinery reformer. Higher gasoline octane requires more and/or higher severity (octane) gasoline reformer output (reformate). Reformer octane is created by conversion of lower octane paraffin and naphthene to higher octane aromatics. Therefore, as refinery octane requirements are increased (or decreased) gasoline aromatics increase (or decline)[2]. As ethanol blending is increased, refinery octane requirements are reduced and thus aromatics decline. Figure A.5 illustrates the relationship between refinery octane and aromatics. As the refinery octane from Figure A.2 (adjusted for benzene and sulfur requirements) declines due to incremental ethanol blending (Figure A.4) aromatics decline as well. A reduction in refinery octane of 1.4 to 1.5 (2006 to 2012/13) yields the 4.6 to 5.4 percent change in aromatics referenced above. Again, the 2019 reported EPA Online aromatics are questionable.

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[2] Alkylation and Isomerization also provide for octane adjustment but far less so. Alkylation economics are dictated by gasoline and LPG prices versus octane enhancement and therefore typically play a small role in octane adjustment. Isomerization capacity is relatively low and thus will likewise play a minor role in octane adjustment.
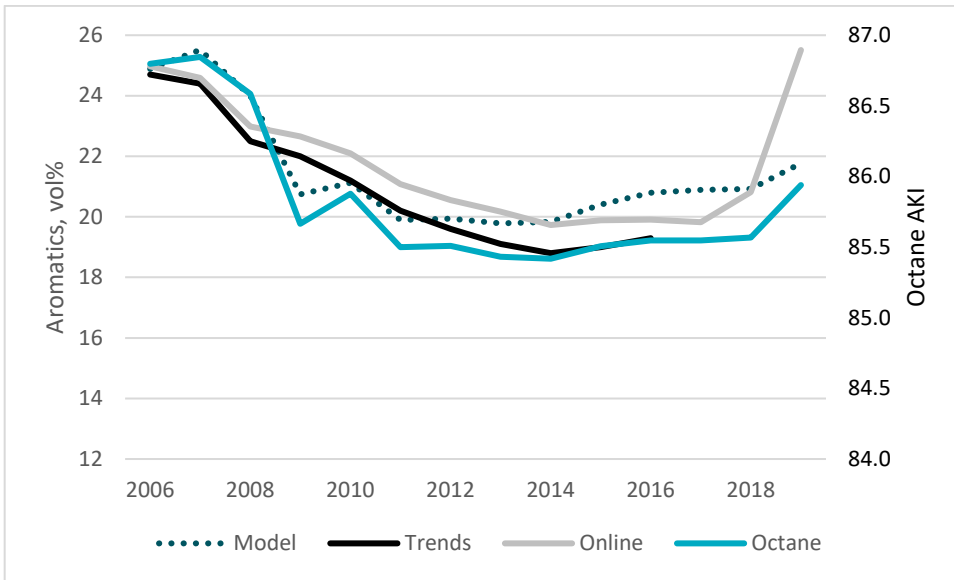
Figure A.5: Refinery Octane Requirement versus Final Gasoline Aromatics (Source: Transport Energy Strategies and EPA Fuel Trends Report: Gasoline 2006-2016)

E10 blending vs Aromatics: Blending Model Output v. Market Data and MOVES2014 Modeling

Market data and model calculations discussed above focus on ethanol blending at levels of 3.0 to 9.9 percent. The full impact of E0 to E10 will be even higher than these values. As noted above, the model calculations showed that aromatic content decreased 5 percent when ethanol blending levels increased 6.5 percent. However, that calculation was based on required refinery octane including additional octane requirements for lower sulfur and benzene. When the impacts of sulfur and benzene are not included, the aromatics reduction increases to 6.0 percent. Extrapolating this to a full 10 percent increase in ethanol (E0 to E10), the change in aromatics is estimated at 9.2 percent. To further quantify the E0 to E10 impact on aromatic levels, the model was run with no ethanol in 2006 and 10 percent ethanol in 2012/13 and the calculated difference in aromatics for the 10 percent ethanol addition was 9.0 percent.

Actual data for 2006 to 2012/13 show a reduction in aromatics of 4.6 percent (Online data) to 5.4 percent (EPA, 2017). Extrapolating these values to a 10 percent change in ethanol results in an aromatic decrease of 7.1 to 8.2 percent. If the impact of lower sulfur and benzene are considered the change in aromatics is 8.6 to 9.7 percent.

Analysis used by EPA in support of MOVES2014 also provides insight into the impact of 10 percent ethanol on aromatic content. In support of the MOVES2014 Fuel Wizard, EPA conducted a series of refinery model runs to estimate the change in aromatics (and other properties) associated with increased ethanol blending. Although reported as the adopted relationship for E0 to E10, the modeling analysis presented in the Tier 3 Regulatory Impact Analysis represented a case where ethanol was increased from an average of about 6.2 percent to 10

percent. The increase in gasoline production was close to the increased ethanol volume and therefore not significantly different than 2006 to 2012/13 volume trends. The EPA model runs also included constant sulfur and benzene levels.

Figure A.6 compares the EPA model results for percent ethanol versus aromatics to the model results presented in Figures A2 and A.3. The model discussed above shows a greater aromatic reduction with increasing ethanol than EPA analysis, but the differences are not large. The EPA analysis results in a 3.1 percent change in aromatics when ethanol was increased from 6.2 percent to 10 percent. Extrapolating this to a change in ethanol blending of 10 percent yields 8.2 percent reduction in aromatics for E0 to E10.
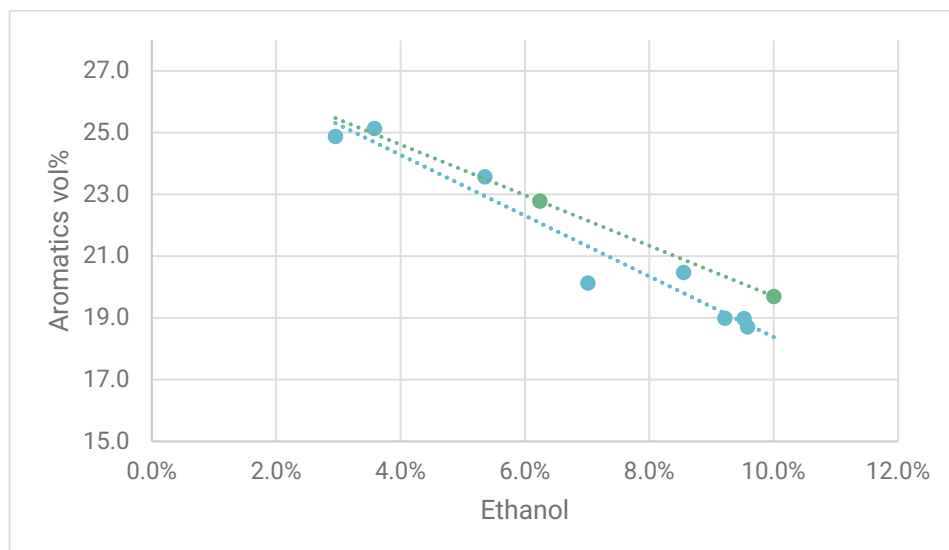
Figure A.6: Ethanol vs Aromatics, EPA MOVES Runs and Model Calculated Aromatic Content (Source: Transport Energy Strategies and EPA Tier 3 Regulatory Impact Analysis)

To summarize, the blending model, actual market aromatics data and EPA's Tier 3 modeling all support the finding of a reduction in aromatic content between 8.2 and 9.7 percent for E0 versus E10. The average for all sources, summarized in Table A.7, is an 8.9 percent reduction.

	Reduction in Aromatic Content
Model 2006-2013 Calculated, Extrapolated	9.2%
Model Calculated E0-E10	9.0%
Actual EPA Trends Data Extrapolated[1]	9.7%
Actual EPA Online Data Extrapolated[1]	8.6%
EPA Tier 3 Modeling Extrapolated	8.2%
Average of Above	**8.9%**

Table A.7: Aromatic Reduction for E0 to E10 from Modeling Analysis and Actual Data (Source: Transport Energy Strategies and EPA Tier 3 Regulatory Impact Analysis)

MOVES3 Ethanol – Aromatics Relationship

MOVES3 included an update of the adjustment factors used for ethanol blending. EPA relied on the results of refinery linear program analysis in revising downward the aromatic reduction for E0 to E10 and E15. Unfortunately, the modeling approach is far from representative of real-world gasoline blending or refining and the modelling in some cases fails to address issues EPA hoped to address with the updated analysis.
In its report describing the update, "Fuels Supply Defaults: Regional Fuels and the Fuel Wizard in MOVES3 (EPA, 2020)", EPA explained that actual data were not used for estimating the effect of ethanol blending on gasoline properties (as suggested by stakeholders) because "other market changes were also at play and their impacts are overlaid upon and confound the effects of increasing ethanol use". However, as discussed below, the market changes listed by EPA could be addressed without modeling, would not have a significant impact on the ethanol-aromatics relationship and/or were not all addressed through their modeling analysis.

Phase in of sulfur and benzene regulations. The impact of these factors could be handled with an adjustment as referenced in the previous sections. Furthermore, these factors reduce the impact of ethanol on aromatics so real-world aromatic reduction would be greater than reported, not lower as concluded in the modeling analysis.

MTBE Phase-out. MTBE was essentially phased out by 2006 (less than 1 percent in 2006 and negligible thereafter).

Rising crude prices, expansion of light hydrocarbons favoring alkylation as octane source over reforming. Crude-light hydrocarbon prices fluctuated over the period and did at times provide high alkylate margins. However, the economics of alkylation are driven by conversion of LPG streams to gasoline, not by octane. While the gasoline-LPG prices fluctuated over the period, they were the same in 2016 as in 2006. The prices did not impact choice of octane processing (alkylation vs reforming). Despite the highly favorable alkylation economics over the 2006-2016 period, there was only a 3.8 percent capacity increase, versus a 9 percent increase during the previous 10 years when the pricing incentives were far less. Note as highlighted below, the real-world expansion of alkylation capacity has grown at less than 1 percent annually as opposed to the 75+ percent growth concluded through EPA's modeling.

Reduced gasoline hydrocarbons relative to diesel. The gasoline to diesel ratio had no impact on ethanol-aromatic relationships. In fact, over the period, gasoline production expanded more than diesel. In contrast, EPA's modeling results showed a reduction in gasoline with no reduction in diesel production.

The modelling approach used to support the revised Wizard adjustments represents an unrealistic scenario outside the realm of real-world refining and blending. Furthermore, the reported output of the analysis raises questions as to the appropriateness or validity of the modelling itself. The shortcomings are discussed below.

Volume of gasoline exports. It is unrealistic to assume export volume must continue while refinery gasoline supply and octane must be increased. As the model indicates, refiners would have to invest to replace the domestic volume and octane. So essentially the analysis requires a higher level of investment to maintain exports, which is an unlikely scenario. The MathPro report (Appendix to the MOVES 3 Fuel Wizard report, EPA, 2020) states that positing certain volume reductions in exports without supporting modeling could be viewed as arbitrary. However, it is more arbitrary and/or inappropriate to assume constant exports when the cost of producing gasoline is increasing. The reported cost of conventional gasoline for the E0 case averages $5 per barrel above the reference case ($12 per barrel in the summer). The cost increase would likely make U.S. gasoline uncompetitive in the global market and export volumes would decline.

Constraints on properties of RFG and exports. Constraining RFG and export properties while making substantial changes in the remainder of the pool creates an unrealistic constraint, particularly when the changes in operation and blending are as dramatic as in the modeling scenario. Refiners have and use flexibility through logistic options, product exchanges, etc., to shift blend components and optimize blending as economics and markets dictate.

Alkylation feed. The source of feed for the alkylation is questionable. The report states that catalyst options were permitted in the model to produce additional light olefin for alkylation. This is a feasible option, although not likely to the extent modeled. But the level of alkylation expansion would also require around 700 thousand b/d of isobutane. The report states that isobutane purchases increased significantly, but the reported increase (in the supporting tables) is less than 100 thousand b/d. No other source of isobutane is identified.

Butane price. The analysis assumes no increase in butane price because the supply of butane from NGL production could increase significantly. As noted above, the supporting tables show only a small isobutane increase, insufficient for the alkylation expansion. If the tables incorrectly reported the butane purchases and model purchases were at the required volume of about 600 thousand b/d, then the assumption that there would be no price impact is questionable. The incremental NGL production forecast from 2017 to 2020 (AEO 2017) was 840 thousand b/d. The isobutane available from that increment is less than 100 thousand b/d. Even if all the normal butane were also used (isomerized to isobutane at an investment and operating cost) the total incremental butane supply would be less than 150 thousand b/d, far less than the required volume. Butane supplies are likely inadequate and certainly could not be secured with without a substantial price increase.

Alkylate investment. The extent of alkylation investment concluded is highly unlikely, particularly when there is some level of spare reforming capacity. The modeling projects a 75 percent increase in capacity. Capacity expansion has averaged under 1 percent annually. Completion of this level of alkylation addition would require at least 5 or 6 years. Gasoline demand will be declining over time and will be lower by at least 5 percent by the

time these facilities would be completed. Refiners will be reluctant to invest in this declining market, and certainly would avoid an investment in a 75 percent capacity increase.

Other issues. There are other issues that would likely impede the level of alkylation investment concluded by EPA. Both sulfuric and hydrofluoric acid alkylation processes have been under scrutiny because of acid handling and release concerns. Organizations have expressed concern about sulfuric acid transport to and from refineries. Even greater opposition has been voiced in opposition for HF units because of release concerns. Initiatives in some areas have even threatened to shut down existing facilities. If the alkylation facilities were to be built, most would likely have to be sulfuric acid based (or perhaps may use new solid or ionic technologies which are in early stages of commercialization). A 75 percent capacity increase would increase the sulfuric acid market by more than 5 percent, likely impacting price. More significantly, sulfuric acid regenerating capacity is already operating at near capacity. The capacity increase projected by the model would increase regeneration capacity requirements by about 50 to 75 percent.

Appendix B: DHA of Gasoline and Blends

Appendix A described development of a gasoline blend model for calculation of gasoline aromatic, paraffin, naphthenic and olefin content, and the impact of ethanol blending on gasoline properties. The model also included octane and RVP of gasoline components with the ability to produce final gasoline meeting these market specifications for these parameters. This Appendix discusses expansion of that model to include detailed DHA analysis of gasoline and gasoline blend streams and as well as PMI characterization. It also describes ethanol blending cases analyzed with the DHA and PMI data incorporated into the model.

Gasoline and Gasoline DHA Characterization

Gasoline species (aromatics, olefins, etc.) vary considerably from batch to batch or refinery to refinery and the chemical composition within a species category will also exhibit variation. As gasoline supplies are comingled through the distribution system, variation is reduced but not eliminated. The market variation is illustrated in the following example of gasoline quality from the 2017 Texas summer gasoline survey (ERG, 2017). Figure B.1 shows gasoline quality for average aromatic content along with aromatics for the 25 quartile and the 75 percent quartiles. The aromatic content of the 25 percent quartile is around 4.5 percent below the average and the 75 percent quartile is about 4.5 percent higher. Within species variation is less, but in some cases significant. Figure B.2 shows variation in types of aromatics and paraffin. Aromatic variation is small but variation in percentage of paraffin type is about two thirds as large as variation in total paraffin (from Figure B.1).
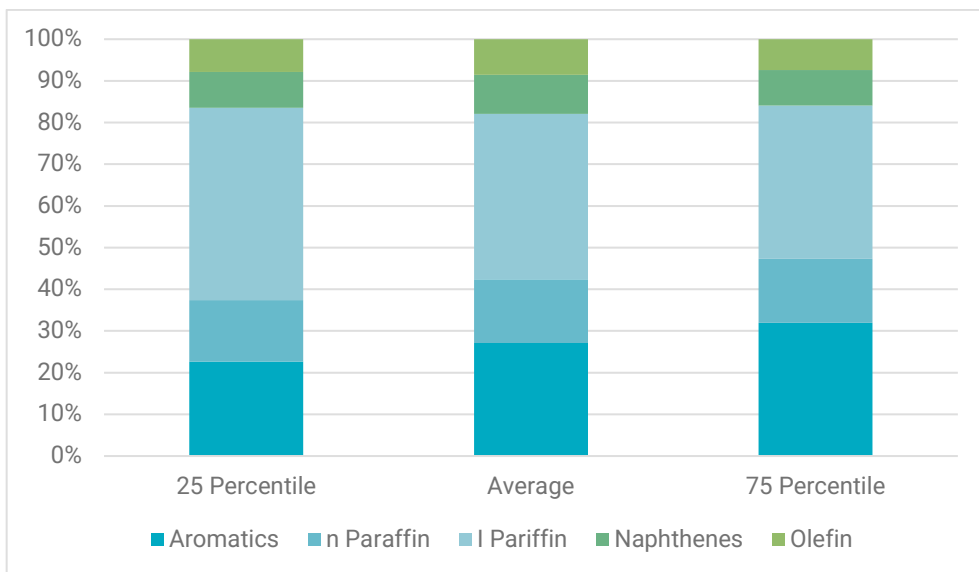
Figure B.1: Variation in Gasoline Species from Texas Survey Data
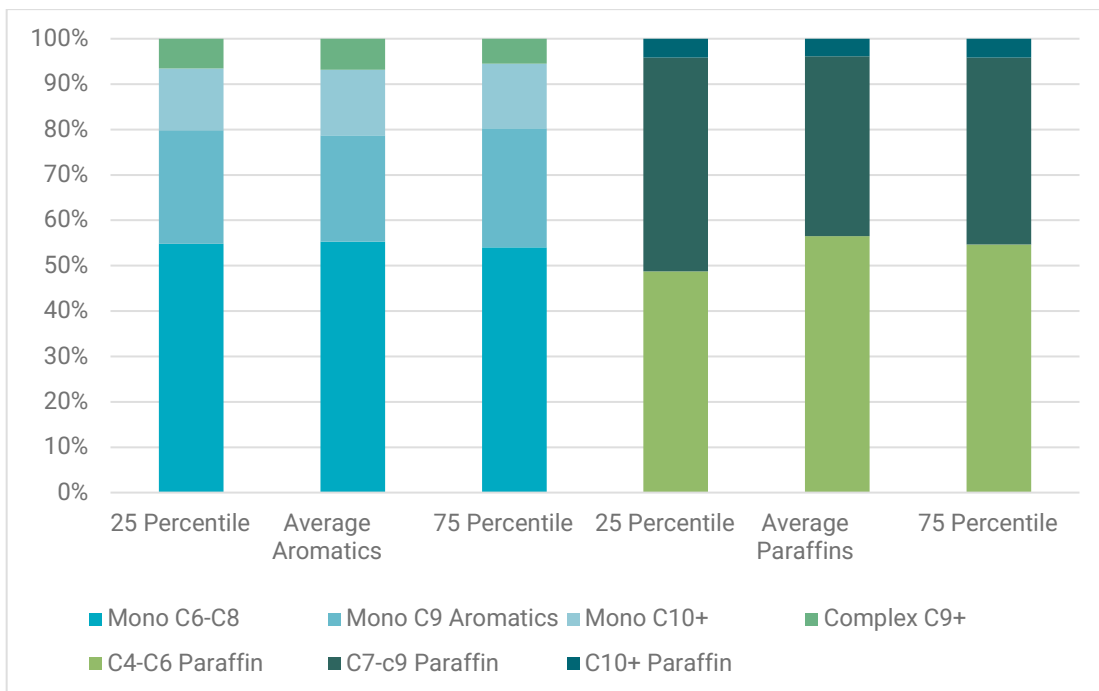
Figure B.2: Variation in Aromatic and Paraffin Species from Texas Survey Data

The variation in composition of real-world gasolines and issues associated with testing accuracy and chemical property data place some limitations on full characterizing DHA of average or representative gasoline in the marketplace. However, analysis of the relationship between carbon intensity or PMI and ethanol blends involves the differences in properties between gasoline at two ethanol blend levels. In looking at differences, the

limitations of absolute inaccuracy of a specific reference gasoline will have significantly reduced impact on the validity of analysis.

The average gasoline qualities used for development of the gasoline blend model and discussed in Appendix A were further defined in terms of individual chemical species or groups of species within the categories of aromatics, paraffin, naphthene and olefin. The speciation relied on several literature sources with much focus on the Texas data (ERG, 2017). The species were aggregated into grouping based on carbon number and/or aromatic ring structure. Chemical configuration groupings were selected where there were significant carbon intensity or PMI differences in these configurations versus other compounds in the group with the same carbon number. Consideration was also given to the estimated quantity of species in gasoline and refinery gasoline blend streams.

In addition to gasoline properties and characterization of aromatic, paraffin, naphthene and olefin, the expanded model also calculated the chemical content according to individual detailed species defined above and shown in Table B.3. Values for specific gravity, carbon content, energy content (LHV) and PMI were assigned to each species allowing for computation of carbon intensity and PMI of gasoline blends considered in the ethanol blend analyses. Table B.3 lists the species groupings included in the model along with selected properties for each.

As was done for the overall categories of species (discussed in Appendix A), speciation was made for representative average market gasoline and for individual refinery gasoline blend streams. The weighted average qualities of the gasoline streams were then compared against the representative final gasoline. There was close but not full agreement between the two, so small adjustments were made in component qualities until the weighted average blend matched the finished gasoline.

	Specific Gravity	Carbon Fraction	LHV BTU/#	CI g CO_2/mg Joule	PMI
AROMATICS					
Benzene	0.884	0.923	17256	84.3	0.72
C7 (Mono)	0.872	0.913	17421	82.6	1.21
C8 (Mono)	0.872	0.906	17465	81.7	2.37
C9 (Mono)	0.883	0.900	17645	80.4	4.47
C10 (Mono)	0.880	0.896	17615	80.1	7.26
C11+ (Mono)	0.915	0.892	17490	80.3	18.10
C9 Indane	0.965	0.915	17327	83.2	8.02
C10+ Indane Group[1]	0.917	0.909	17450	83.0	13.60
Naphthalene	1.025	0.938	16674	86.7	27.83
C11+ Naphthalenes	1.000	0.930	16898	84.3	64.48
n-PARAFFIN					
C4	0.584	0.828	19495	66.9	0.02
C5	0.631	0.833	19335	67.9	0.05
C6	0.664	0.837	19233	68.6	0.09
C7	0.688	0.840	19155	69.1	0.18

	Specific Gravity	Carbon Fraction	LHV BTU/#	CI g CO_2/mg Joule	PMI
C8	0.707	0.842	19096	69.5	0.34
C9	0.722	0.844	19054	69.8	0.62
C10	0.735	0.845	19018	70.0	1.10
C11+	0.745	0.846	19006	70.1	2.34
I-PARAFFIN					
C4	0.563	0.828	19440	67.1	0.01
C5	0.625	0.833	19303	68.0	0.03
C6	0.665	0.837	19284	68.4	0.07
C7	0.688	0.840	19094	69.3	0.14
C8	0.718	0.842	19080	69.5	0.26
C9	0.725	0.844	19068	69.7	0.44
C10	0.742	0.845	19048	69.9	0.72
C11+	0.748	0.846	19038	70.0	1.38
NAPTHENE					
C5	0.750	0.857	18825	71.7	0.12
C6	0.768	0.857	18796	71.8	0.22
C7	0.770	0.857	18745	72.0	0.39
C8	0.779	0.857	18710	72.2	0.61
C9	0.786	0.857	18720	72.1	1.06
C10	0.822	0.857	18725	72.1	1.49
C11+	0.825	0.857	18720	72.1	3.49
OLEFIN					
C4	0.618	0.857	19255	70.1	0.04
C5	0.655	0.857	19133	70.6	0.09
C6	0.676	0.857	19036	70.9	0.17
C7	0.698	0.857	19020	71.0	0.32
C8	0.719	0.857	18976	71.2	0.64
C9	0.734	0.857	18969	71.2	0.94
C10	0.745	0.857	18940	71.3	1.52
C11+	0.755	0.857	18916	71.4	2.70
Ethanol	0.787	0.522	11573	71.0	0.06

Table B.3: Model Species and Species Properties

Ethanol Blending Cases

Several cases were developed to project average and range of carbon intensity and PMI for historic and future gasolines at varying ethanol blend levels. Additional cases were then developed to examine carbon intensity and PMI with higher gasoline market octane and again at varying ethanol blend levels. The first set of cases was established starting with a representative annual average current E10 gasoline (Table B.4). Gasoline properties, CI and PMI were calculated with the blend model for the E10 and a comparable E0 gasoline. The model was then used to examine the impact of ethanol blend levels at 15 and 20 percent for three gasoline production options. The blend options assumed for the initial scenarios are defined in Table B.5 which also provides the assumed refinery production volume. The first blend option assumed that refineries would continue to produce the same volume of refinery gasoline (BOB plus export volume) as in the E10 reference, but

they would produce an E15 or E20 BOB. The additional ethanol supply would result in an additional surplus over domestic demand and the surplus would be exported. The second option assumed that refineries would reduce gasoline production to balance demand including the incremental ethanol supply and again with an E15 or E20 BOB. Exports would remain the same as in the reference E10 case. The final option assumed that E15 or E20 would be produced by splash blending 15 and 20 percent ethanol with the reference case E10 BOB. The assumed refinery production volume was set at the average of the high-low volumes for the E15 and E20 BOB options.

	Initial Average Gasoline	Low Aromatic Winter Gasoline	High Aromatic Summer Gasoline
Octane, AKI	88.3	88.3	88.3
RVP, psi	10.8	12.5	8.0
Aromatics, vol%	21.7	18.6	24.1
Olefin, vol%	8.9	8.2	9.7
Paraffin, vol%	52.1	56.3	48.4
Naphthene, vol%	7.3	6.9	7.8
Ethanol, vol%	10.0	10.0	10.0

Table B.4: Gasoline Properties, Average E10 and Low and High Aromatics

A second set of cases was established to examine effects of ethanol blending on CI and PMI over a range of gasoline aromatic content. These cases were intended to determine whether high or low aromatic blends in the market would respond differently to changing ethanol than an average quality gasoline. The low aromatic case was represented by a winter gasoline that also included higher-than-average non-aromatic content high-octane components. The high aromatic case was a summer gasoline with a lower portion of non-aromatic high-octane components. Properties of the high and low aromatic E10 gasolines are included in Table B.4. The model was run with E15 and E20 blended with the appropriate BOB under the same refinery production volumes as above. The splash blend option was not examined.

	Refinery Production Thousand b/d
E10 representative of current market quality	7660
E0 meeting current market quality without ethanol[1]	7520
E15 BOB produced w/ volume at E10 BOB plus export level	7660
E15 BOB w/ BOB volume adjusted incremental ethanol supply	7390
E15 splashed blended on E10 BOB	7530
E20 BOB produced w/ volume at E10 BOB plus export level	7660
E20 BOB w/ BOB volume adjusted incremental ethanol supply	7110
E20 splashed blended on E10 BOB	7390

¹ E0 case not able to meet refinery volume of E10 case because of octane loss

Table B.5: Blend Option Scenarios and Gasoline Production Volumes

A final set of cases was developed to examine the effects of ethanol blending where the gasoline market included a minimum 95 RON grade. The 95 RON specification has been discussed amongst stakeholders to enable introduction of higher efficiency vehicles. There are several approaches for accommodating a 95 RON grade (such as shifting all premium to 95 RON, converting all grades to 95 RON, or producing a separate, midgrade type 95 RON). The appropriate approach would depend on available infrastructure, level of ethanol used and capability of refining to increase octane.

Refiners cannot meet a pool 95 RON without substantial investment and/or without a large increase in ethanol blending. Assuming adequate infrastructure, refiners could produce a portion of the pool at 95 RON minimum, with the producible volume depending on the level of ethanol used. For the first set of 95 RON cases, a portion of the pool was designated as 95 RON and the remainder of the domestic pool would continue to be 87 regular grade and 92/93 AKI premium grade. Exports were assumed to continue at current octane. Refinery production was specified at the high and low volumes in Table B.5. Finally, the 95 RON share of the domestic pool was set at a level estimated to be comfortably within the current octane capability of refineries and with 10 percent ethanol in the pool. Comparable E15 and E20 cases assumed the same 95 RON market share but with the higher ethanol blending. These initial cases provided an estimate of the maximum share of 95 RON grade which could be produced, and quantified the impact of the 95 RON production on carbon intensity and the ability of higher ethanol to offset the increase in carbon intensity.

The second set of higher-octane cases started with E15 and a higher 95 RON share corresponding to a level estimated to be comfortably within the current octane capability of refineries and with 15 percent ethanol in the pool. A comparable E20 case was run as above. These cases provided insight into the maximum 95 RON which could be produced at the higher ethanol levels. The cases then quantified the impact on carbon intensity and the ability of higher ethanol to offset the increase in carbon intensity. Finally, a case was run with the entire domestic gasoline pool (premium and regular) produced at 95 RON and ethanol was increased to the point where refinery octane requirements were comfortably within the current octane capability of refineries. This latter case provided an estimate of ethanol blending required for a 95 RON pool and insight into carbon intensities.

Appendix C: Examples of Differences in Fuel Composition Measurements

The 2020 survey of Texas gasoline (ERG, 2020) reported total aromatics determined using ASTM D5769. Total aromatics were also computed by summing the aromatic components in the DHA found using ASTM D6729. Differences between the two methods exist, as shown in Figure C-1. Projection of changes in CI as a result of

change in the composition of a fuel is reasonably reliable, but comparison of CI of two fuels when their composition is determined by different methods is less reliable. PMI is more sensitive to aromatic content than CI, particularly for aromatics with high molecular weights.
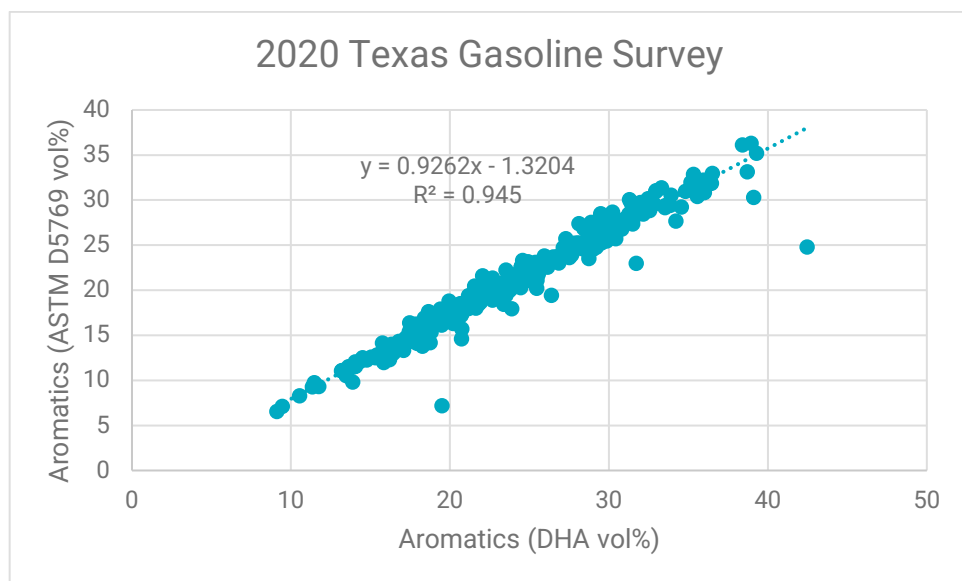
Figure C-1: Differences in measured aromatics using two different methods for the Texas 2020 gasoline survey.

In the prior Texas survey (ERG, 2017) ASTM D1319 was employed to determine aromatic fraction rather than D5769. Difference between The D1319 data and summed aromatic DHA are shown in Figure C-2. Note that the best fit slope is far from unity. Differences are also found for olefins, as shown in Figures C-3 and C-4. There is less variation between D1319 and DHA data (Texas 2017 data for olefins) than between D6550 and DHA data (Texas 2020 data for olefins).
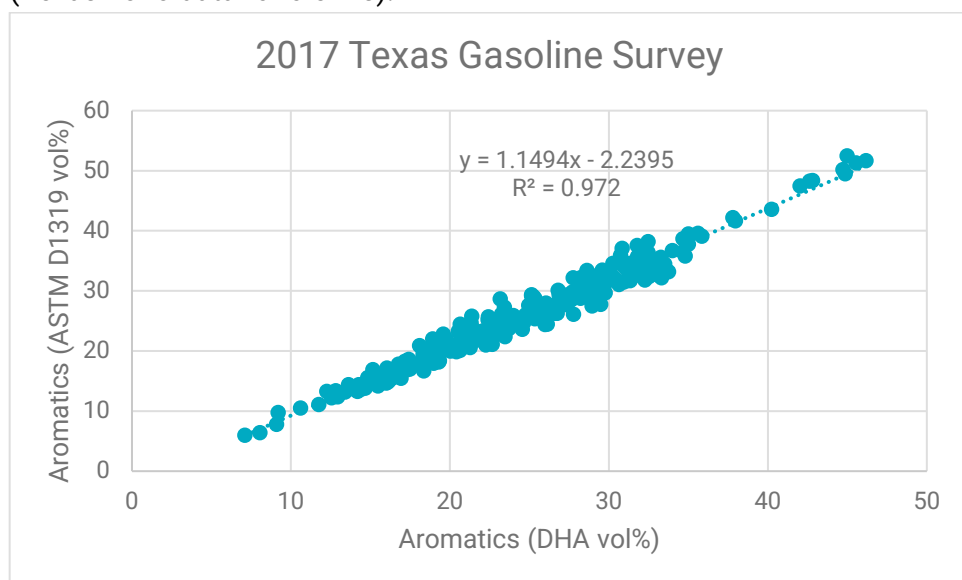
Figure C-2: Differences in measured aromatics using two different methods for the Texas 2017 gasoline survey.

2020 Texas Gasoline Survey

$y = 1.1486x + 0.8622$
$R^2 = 0.857$

Olefins (ASTM D6550 vol%) — vertical axis
Olefins (DHA vol%) — horizontal axis
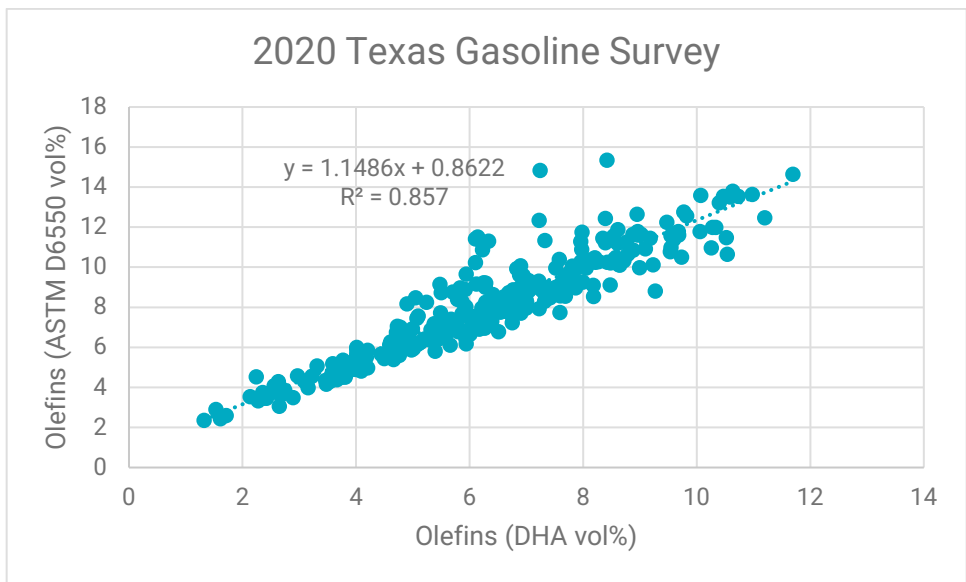
Figure C-3: Differences in measured olefins using two different methods for the Texas 2020 gasoline survey.

2017 Texas Gasoline Survey

$y = 1.2977x - 0.7006$
$R^2 = 0.9561$

Olefins (ASTM D1319 vol%) — vertical axis
Olefins (DHA vol%) — horizontal axis
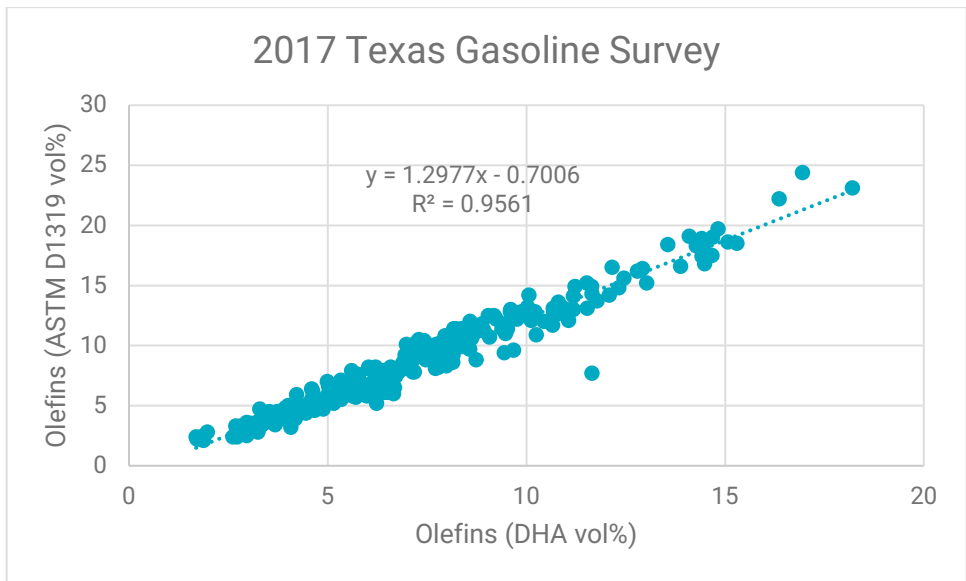
Figure C-4: Differences in measured olefins using two different methods for the Texas 2017 gasoline survey.

These differences are not unique to the Texas data. Figure C-5 shows D1319 and D6729 for the fuels used in the EPAct (2013) study. The EPAct used fuels with a low aromatic content of about 15% and a high content of about 35%.
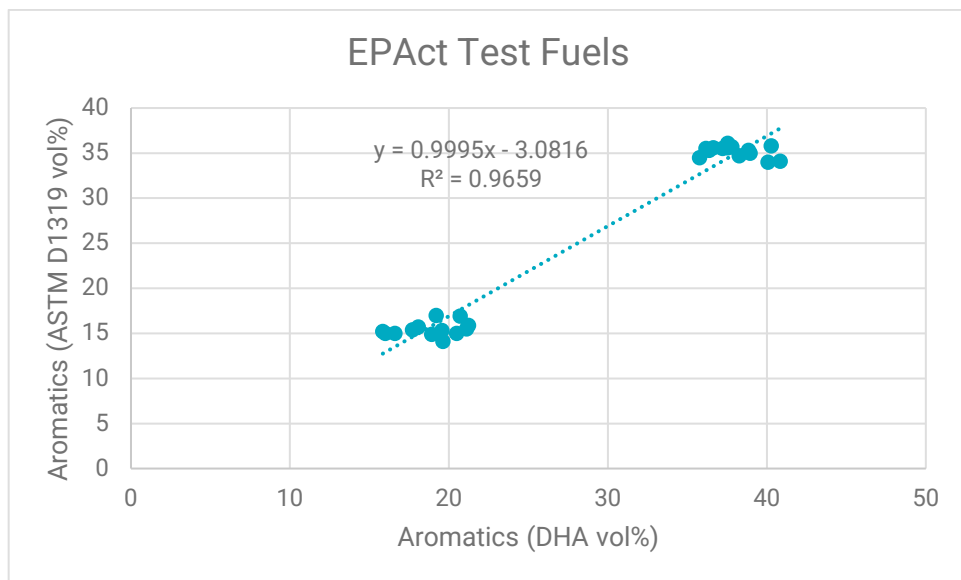
Figure C-5: Differences in measured aromatics using two different methods for the EPAct study fuels.
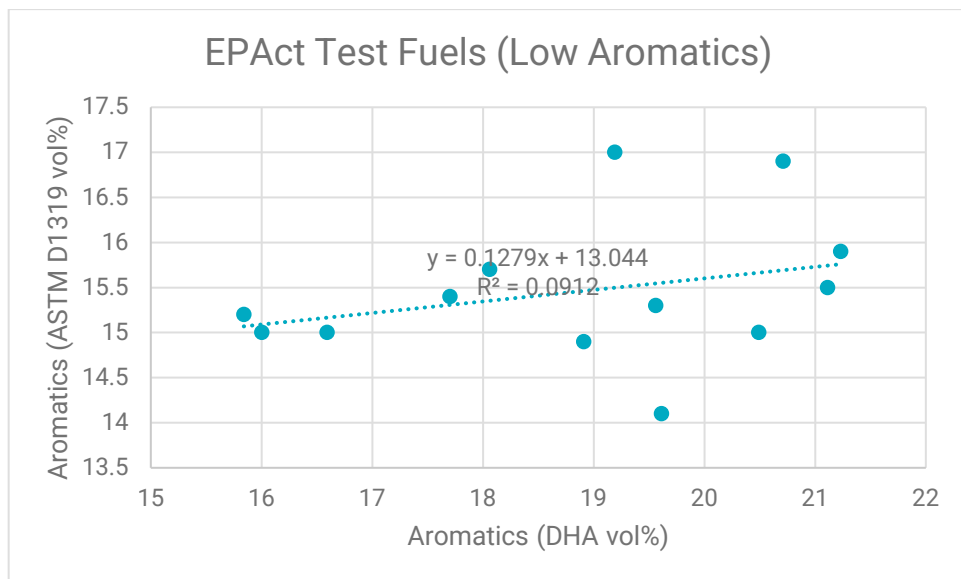
Figure C-6: Differences in measured aromatics for the low aromatic content EPAct fuels.

Appendix D: Determination of Lower Heating Values of Hydrocarbon Species

Estimating Lower Heating Values for Gasoline-Ethanol Fuel Mixtures

Prediction of carbon intensity (CI) for gasoline-ethanol fuels based on detailed hydrocarbon analyses (DHA) requires both the chemical formula and the lower heating value (LHV) for individual fuel components. Chemical formulas for the individual components are readily available but LHVs may only be available for select components and vary depending on source.

DHA data are available from several Texas Commission on Environmental Quality (TCEQ) surveys including the 2020 Summer Fuel Study conducted by the Eastern Research Group (ERG - TCEQ Contract No. 582-19-90502) (ERG, 2020). In this study ERG collected regular, mid-grade and premium fuel samples from 91 gas stations in the state of Texas which then underwent detailed analyses by the Southwest Research Institute (SWRI) including standard fuel properties (distillation, vapor pressure, oxygenate concentration, etc.) as well as DHA on both volume and mass basis. The SWRI database utilized in the study includes 447 individual fuel constituents including paraffins, aromatics, oelfins, oxygenates, and napthalenes with the CAS number, chromatography elution time, group (paraffin, aromatic, etc.), carbon and hydrogen numbers, double bond equivalency, boiling point and vapor pressure at 170 C.

COMPONENT	TIME	CASNO	GROUP	Carbon number	Hydrogen number	DBE	B.P	V.P @ 170degC (kPA)
Propane	7.391	74-98-6	P	3	8	0	-42.05	14475
i-Butane	8.616	75-28-5	I	4	10	0	-11.72	6682
Isobutene	9.41	115-11-7	K	4	8	1	-6.90	5949
Butene-1	9.45	106-98-9	K	4	8	1	-6.25	5857
1,3 BUTADIENE	9.755	106-99-0		4	6	2	-4.40	5551
n-Butane	9.799	106-97-8	P	4	10	0	-0.50	5108
t-Butene-2	10.275	624-64-6	K	4	8	1	0.88	4945
2,2-Dimethylpropane	10.397	463-82-1	I	5	12	0	9.50	4043
c-Butene-2	10.996	590-18-1	K	4	8	1	3.72	4626
Ethanol	12.752	64-17-5	X	2	6	0	78.29	1581

The SWRI database was provided as an electronic spreadsheet and accompanied the full ERG dataset made available to the public.

Carbon intensity for individual fuels required calculation of both the carbon dioxide (CO_2) mass contribution of each constituent as well as their contribution to energy produced during combustion. Calculation of CO_2 contributions was relatively straightforward and involved multiplying the carbon number by the molecular weight of CO_2 and dividing the result by the product of the carbon number, hydrogen number and, in the case of oxygenates, oxygen number and their respective molecular weights. For example, complete combustion of on mole of ethanol (C_2H_5OH – 46.07 g/mole) would produce 88.02 grams of CO_2 (2 x 44.0095 g/mole) resulting in a CO_2 mass ratio of 1.91 (88.02 g CO_2 / 46.07 g ethanol). Calculation of the CO_2 contribution of ethanol using a fuel DHA would involve multiplying the fuel mass percentage of ethanol by the CO_2 mass ratio for ethanol. The CO_2 mass ratio for the fuel is calculated by summing the product of each constituents mass percentage by their respective CO_2 mass ratios.

Mass percentages of each individual component from a fuel DHA are multiplied by their lower heating values and summed to calculate fuel energy per unit mass (e.g. MJ/kg, BTU/lb). For a fuel containing ethanol at 10% by mass, the energy contribution from ethanol, based on a lower heating value of 11,573 BTU/lb (26.90 MJ/kg), would be 1,126 BTU/lb. This contribution would be summed with the contributions from the other fuel constituents to arrive at an energy per unit mass value for the fuel.

LHVs are available for only a select number of constituents from the SWRI DHA database. GPA Midstream Standard 2145-16: Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas and Natural Gas Liquids Industries includes LHVs for 187 liquid hydrocarbons. Many of these cross-reference with the SWRI DHA database. However, some cross references between the SWRI and GPA databases are difficult owing to the differences in chemical naming conventions used. For example, cis-1,2,trans-1,4-1,2,4-trimethylcyclohexane, which is listed in the GPA database with a LHV of 43.76 MJ/kg, can also be named:

cis-1,2,4-Trimethylcyclohexane
c,t,t-1,2,4-TRIMETHYLCYCLOHEXANE
Cyclohexane, 1,2,4-trimethyl-, cis
(1S,2R,4R)-1,2,4-trimethylcyclohexane
(1R,2S,4S)-rel-1,2,4-TriMethylcyclohexane
CIS,TRANS,TRANS-1,2,4-TRIMETHYLCYCLOHEXANE
cis-1,2,cis-1,4-1,2,4-Trimethylcyclohexane
Cyclohexane, 1,2,4-trimethyl-, (1R,2S,4S)-rel-
Cyclohexane, 1,2,4-trimethyl-, (1alpha,2alpha,4alpha)-

A best effort was made to cross-reference hydrocarbons where different naming schemes were used.

Since a complete database of LHVs is not available, an accurate determination of gasoline energy per unit mass based on DHA is not possible. For example, GPA 2145-16 LHV data were only available for constituents

representing 67.8% of the mass for a sample of from the ERG (2020) survey (sample 61787, regular E10 gasoline). In addition, the GPA data included LHVs for only a single oxygenate (ethanol). Since LHV values for only two-thirds of the sample were available, a method to estimate the LHV for non-oxygenate SWRI fuel constituents was developed using constituent LHVs from GPA Std. 2145-16 and their respective carbon mass ratios.

Figure D.1 shows plot of lower heating values from GPA 2145-16 versus CO_2 mass ratios for 104 constituents which cross reference with the SWRI database.

$$y = -15.507x + 92.238$$
$$R^2 = 0.95$$

(C * 44.010) / (C * 12.0101 + H * 1.0078)
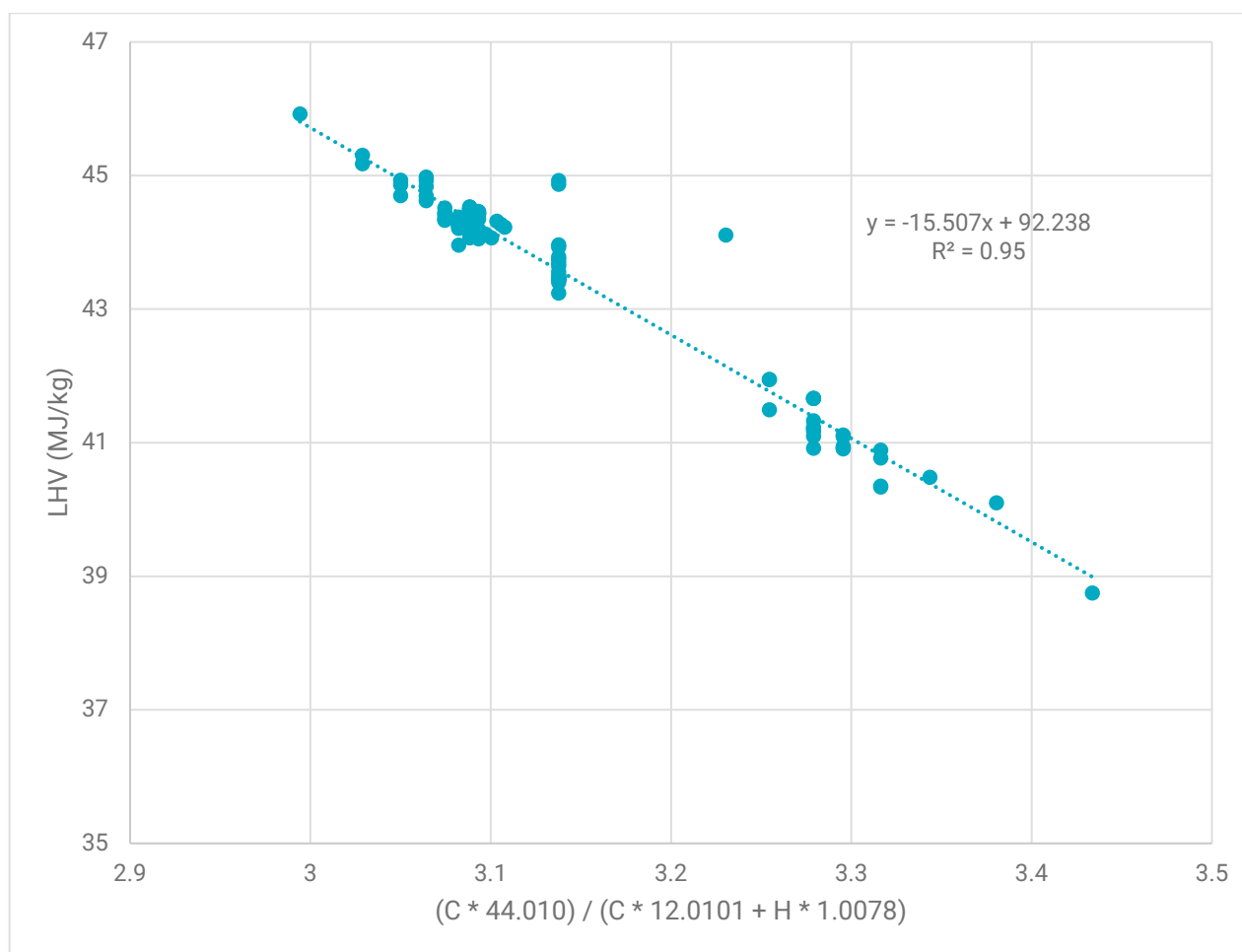
Figure 1: Least squares regression model with CO2 ratio (g CO2 / g fuel) as the independent variable and lower heating value as the dependent variable for hydrocarbons in the GPA database.

GPA Name	SWRI Name	CO_2 (g CO_2/g)	NHV (BTU/lbm)	NHV (MJ/kg)	g CO_2/MJ	Predicted NHV (MJ/kg)
propane	Propane	2.994	19760	45.96	65.15	45.81
i-butane	i-Butane	3.029	19440	45.21	66.99	45.27
n-butane	n-Butane	3.029	19495	45.34	66.80	45.27
i-pentane	i-Pentane	3.050	19303	44.90	67.93	44.94
n-pentane	n-Pentane	3.050	19335	44.97	67.82	44.94
n-hexane	n-Hexane	3.064	19233	44.73	68.50	44.72
n-heptane	n-Heptane	3.074	19155	44.55	69.01	44.56
n-octane	n-Octane	3.082	19096	44.41	69.40	44.44
n-nonane	n-Nonane	3.088	19054	44.32	69.69	44.35
n-decane	n-Decane	3.093	19018	44.23	69.93	44.27
butene-1	Butene-1	3.138	19307	44.90	69.87	43.58
2-methyl-1,3-butadiene	2-Methyl-1,3-Butadiene	3.230	18980	44.14	73.18	42.14
pentene-1	Pentene-1	3.138	19333	44.97	69.78	43.58
cyclopentane	Cyclopentane	3.138	18825	43.78	71.66	43.58
2,2-dimethylpropane	2,2-Dimethylpropane	3.050	19235	44.74	68.17	44.94
benzene	Benzene	3.380	17256	40.13	84.23	39.82
methylcyclopentane	Methylcyclopentane	3.138	18917	44.00	71.31	43.58
cyclohexane	Cyclohexane	3.138	18676	43.44	72.23	43.58
2,2-dimethylbutane	2,2-Dimethylbutane	3.064	19294	44.87	68.28	44.72
2,3-dimethylbutane	2,3-Dimethylbutane	3.064	19332	44.96	68.15	44.72
2-methylpentane	2-Methylpentane	3.064	19202	44.66	68.61	44.72
3-methylpentane	3-Methylpentane	3.064	19355	45.02	68.07	44.72
toluene	Toluene	3.344	17421	40.52	82.52	40.39
1,1-dimethylcyclopentane	1,1-Dimethylcyclopentane	3.138	18693	43.48	72.17	43.58
1t,3-dimethylcyclopentane	1t,3-Dimethylcyclopentane	3.138	18710	43.52	72.10	43.58
1c,3-dimethylcyclopentane	1c,3-Dimethylcyclopentane	3.138	18701	43.50	72.14	43.58
1t,2-dimethylcyclopentane	1t,2-Dimethylcyclopentane	3.138	18696	43.48	72.16	43.58
1c,2-dimethylcyclopentane	1c,2-Dimethylcyclopentane	3.138	18722	43.54	72.05	43.58
methylcyclohexane	Methylcyclohexane	3.138	18782	43.68	71.82	43.58
ethylcyclopentane	Ethylcyclopentane	3.138	18904	43.97	71.36	43.58
2,4-dimethylpentane	2,4-Dimethylpentane	3.074	19085	44.39	69.26	44.56
2,2,3-trimethylbutane	2,2,3-Trimethylbutane	3.074	19077	44.37	69.29	44.56
3,3-dimethylpentane	3,3-Dimethylpentane	3.074	19079	44.37	69.28	44.56
2-methylhexane	2-Methylhexane	3.074	19106	44.44	69.19	44.56

GPA Name	SWRI Name	CO_2 (g CO_2/g)	NHV (BTU/lbm)	NHV (MJ/kg)	g CO_2/MJ	Predicted NHV (MJ/kg)
3-methylhexane	3-Methylhexane	3.074	19119	44.47	69.14	44.56
3-ethylpentane	3-Ethylpentane	3.074	19125	44.48	69.12	44.56
ethylbenzene	Ethylbenzene	3.316	17594	40.92	81.04	40.81
p-xylene	p-Xylene	3.316	17364	40.39	82.12	40.81
m-xylene	m-Xylene	3.316	17358	40.37	82.14	40.81
o-xylene	o-Xylene	3.316	17545	40.81	81.27	40.81
1,1,3-trimethylcyclopentane	1,1,3-Trimethylcyclopentane	3.138	18840	43.82	71.60	43.58
1,1-dimethylcyclohexane	1,1-Dimethylcyclohexane	3.138	18606	43.27	72.50	43.58
3t-Ethylmethylcyclopentane	3t-Ethylmethylcyclopentane	3.138	18693	43.48	72.17	43.58
3c-Ethylmethylcyclopentane	3c-Ethylmethylcyclopentane	3.138	18700	43.49	72.14	43.58
2t-Ethylmethylcyclopentane	2t-Ethylmethylcyclopentane	3.138	18697	43.49	72.15	43.58
ethylcyclohexane	Ethylcyclohexane	3.138	18800	43.73	71.76	43.58
2,2,4-trimethylpentane	2,2,4-Trimethylpentane	3.082	18916	44.00	70.06	44.44
2,2-dimethylhexane	2,2-Dimethylhexane	3.082	19024	44.25	69.66	44.44
2,5-dimethylhexane	2,5-Dimethylhexane	3.082	19030	44.26	69.64	44.44
2,4-dimethylhexane	2,4-Dimethylhexane	3.082	19043	44.29	69.59	44.44
2,2,3-trimethylpentane	2,2,3-Trimethylpentane	3.082	19043	44.29	69.59	44.44
3,3-dimethylhexane	3,3-Dimethylhexane	3.082	19040	44.28	69.60	44.44
2,3,4-trimethylpentane	2,3,4-Trimethylpentane	3.082	19050	44.31	69.56	44.44
2,3-dimethylhexane	2,3-Dimethylhexane	3.082	19058	44.33	69.54	44.44
2-methylheptane	2-Methylheptane	3.082	19049	44.30	69.57	44.44
4-methylheptane	4-Methylheptane	3.082	19062	44.34	69.52	44.44
3,4-dimethylhexane	3,4-Dimethylhexane	3.082	19061	44.33	69.52	44.44
3-ethylhexane	3-Ethylhexane	3.082	19066	44.34	69.51	44.44
3-methylheptane	3-Methylheptane	3.082	19059	44.33	69.53	44.44
i-propylbenzene	i-Propylbenzene	3.295	17683	41.13	80.13	41.14
n-propylbenzene	n-Propylbenzene	3.295	17692	41.15	80.09	41.14

Table 1: Lower heating values and carbon dioxide intensities for cross-referenced hydrocarbons (GPA and SWRI databases)

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
Propane	2.99	45.92	45.81	-0.2%

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
i-Butane	3.03	45.17	45.27	0.2%
Isobutene	3.14		43.58	
Butene-1	3.14	44.87	43.58	-2.9%
1,3 BUTADIENE	3.25		41.77	
n-Butane	3.03	45.30	45.27	-0.1%
t-Butene-2	3.14		43.58	
2,2-Dimethylpropane	3.05	44.70	44.94	0.5%
c-Butene-2	3.14		43.58	
3-Methylbutene-1	3.14		43.58	
i-Pentane	3.05	44.86	44.94	0.2%
Butyne-2	3.25		41.77	
Pentene-1	3.14	44.93	43.58	-3.0%
2-Methylbutene-1	3.14		43.58	
n-Pentane	3.05	44.93	44.94	0.0%
2-Methyl-1,3-Butadiene	3.23	44.11	42.14	-4.4%
t-Pentene-2	3.14		43.58	
3,3-Dimethylbutene-1	3.14		43.58	
c-Pentene-2	3.14		43.58	
2-Methylbutene-2	3.14		43.58	
1t,3-Pentadiene	3.23		42.14	
1,3-Cyclopentadiene	3.33		40.62	
2,2-Dimethylbutane	3.06	44.84	44.72	-0.3%
Cyclopentene	3.23		42.14	
4-Methylpentene-1	3.14		43.58	
Cyclopentane	3.14	43.75	43.58	-0.4%
2,3-Dimethylbutane	3.06	44.92	44.72	-0.4%
4-Methyl-c-pentene-2	3.14		43.58	
2-Methylpentane	3.06	44.62	44.72	0.2%
4-Methyl-t-pentene-2	3.14		43.58	
3-Methylpentane	3.06	44.98	44.72	-0.6%
2-Methylpentene-1	3.14		43.58	
Hexene-1	3.14		43.58	
2-Ethylbutene-1	3.14		43.58	
n-Hexane	3.06	44.69	44.72	0.1%
t-Hexene-3	3.14		43.58	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
t-Hexene-2	3.14		43.58	
2-Methylpentene-2	3.14		43.58	
3-Methylcyclopentene	3.21		42.39	
3-Methyl-c-pentene-2	3.14		43.58	
c-Hexene-2	3.14		43.58	
3,3-Dimethylpentene-1	3.14		43.58	
Methylcyclopentane	3.14	43.96	43.58	-0.9%
2-Pentene, 4,4-dimethyl-	3.14		43.58	
2,4-Dimethylpentane	3.07	44.35	44.56	0.5%
2,3,3-Trimethylbutene-1	3.14		43.58	
2,2,3-Trimethylbutane	3.07	44.33	44.56	0.5%
C6 - Naph-Olefin - 2	3.21		42.39	
3,5-Dimethylcyclopentene	3.20		42.56	
Benzene	3.38	40.10	39.82	-0.7%
1-Methylcyclopentene	3.21		42.39	
C6-Diolefin-1	3.21		42.39	
3-Methylhexene-1	3.14		43.58	
5-Methylhexene-1	3.14		43.58	
Cyclohexane	3.14	43.40	43.58	0.4%
3,3-Dimethylpentane	3.07	44.34	44.56	0.5%
1-Pentene, 2,3-dimethyl-	3.14		43.58	
1,1-Dimethylcyclopentane	3.14	43.44	43.58	0.3%
2-Methyl-c-hexene-3(1)	3.14		43.58	
4-Methylhexene-1	3.14		43.58	
Dimethyl pentadiene	3.20		42.56	
4-Methyl-t/c-hexene-2	3.14		43.58	
2-Methylhexane	3.07	44.40	44.56	0.4%
Cyclohexene	3.21		42.39	
3-Methylhexane	3.07	44.43	44.56	0.3%
1t,3-Dimethylcyclopentane	3.14	43.48	43.58	0.2%
1c,3-Dimethylcyclopentane	3.14	43.46	43.58	0.3%
1t,2-Dimethylcyclopentane	3.14	43.45	43.58	0.3%
2-Ethylpentene-1	3.14		43.58	
C7 - Iso-Olefin - 2	3.14		43.58	
3-Ethylpentane	3.07	44.44	44.56	0.3%

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
2,2,4-Trimethylpentane	3.08	43.96	44.44	1.1%
Heptene-1	3.14		43.58	
C7 - MonoNaph - 1	3.14		43.58	
3-Methyl-c-hexene-3	3.14		43.58	
t-Heptene-3	3.14		43.58	
2-Methylhexene-1	3.14		43.58	
n-Heptane	3.07	44.51	44.56	0.1%
c-Heptene-3	3.14		43.58	
2-Methyl-2-hexene	3.14		43.58	
3-Methyl-t-hexene-3	3.14		43.58	
t-Heptene-2	3.14		43.58	
3-Methyl-c-hexene-2	3.14		43.58	
3-Ethylpentene-2	3.14		43.58	
Cyclopentene, 1,5-dimethyl-	3.20		42.56	
2,3-Dimethylpentene-2	3.14		43.58	
3-Methyl-t-hexene-2	3.14		43.58	
2-Pentene, 3,4-dimethyl-, (Z)-	3.14		43.58	
3-Ethylcyclopentene	3.20		42.56	
Methylcyclohexane	3.14	43.65	43.58	-0.1%
1c,2-Dimethylcyclopentane	3.14	43.51	43.58	0.2%
1,1,3-Trimethylcyclopentane	3.14	43.78	43.58	-0.4%
2,2-Dimethylhexane	3.08	44.21	44.44	0.5%
C8 - Naph-Olefin - 1	3.19		42.69	
1,4-Pentadiene, 2,3,4-trimethyl-	3.19		42.69	
Ethylcyclopentane	3.14	43.93	43.58	-0.8%
2,2,3-Trimethylpentane	3.08	44.25	44.44	0.4%
C8 - Naph-Olefin - 2	3.19		42.69	
C8 - IsoOlefin - 1	3.14		43.58	
2,5-Dimethylhexane	3.08	44.22	44.44	0.5%
2,4-Dimethylhexane	3.08	44.25	44.44	0.4%
1c,2t,4-Trimethylcyclopentane	3.14		43.58	
3-Heptene, 2-methyl-	3.14		43.58	
3-Heptene, 4-methyl-	3.14		43.58	
1,3-Cyclopentadiene, 1,2-dimet	3.27		41.50	
3,3-Dimethylhexane	3.08	44.24	44.44	0.4%

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
2,6-Dimethylheptene-1	3.14		43.58	
1t,2c,3-Trimethylcyclopentane	3.14		43.58	
2,3-Dimethyl-1-hexene	3.14		43.58	
2,3,4-Trimethylpentane	3.08	44.27	44.44	0.4%
1-Ethylcyclopentene	3.20		42.56	
Toluene	3.34	40.48	40.39	-0.2%
2,3,3-Trimethylpentane	3.08		44.44	
4-methyl-2-heptene	3.14		43.58	
3-Ethyl-3-Hexene	3.14		43.58	
C8-Napht-Olefin	3.19		42.69	
Cyclohexene, 1-methyl-	3.20		42.56	
C8 - Diolefin - 1	3.19		42.69	
2,3-Dimethylhexane	3.08	44.29	44.44	0.4%
1c,2c,4-Trimethylcyclopentane	3.14		43.58	
3-Methyl-3-ethylpentane	3.08		44.44	
C8 - IsoOlefin - 4	3.14		43.58	
2-Methyl-3-ethylpentane	3.08		44.44	
3,4-Dimethylhexane	3.08	44.29	44.44	0.3%
2-Methylheptane	3.08	44.27	44.44	0.4%
1c,2t,3-Trimethylcyclopentane	3.14		43.58	
4-Methylheptane	3.08	44.30	44.44	0.3%
1-c,2-t,4-trimethyl cyclopent	3.14		43.58	
C8 - Naph-Olefin - 3	3.19		42.69	
C8 - IsoOlefin - 5	3.14		43.58	
1,3-dimethyl-t-cyclohexane	3.14		43.58	
3-Methylheptane	3.08	44.29	44.44	0.3%
C8 MonoNaph - 1	3.14		43.58	
3-Ethylhexane	3.08	44.31	44.44	0.3%
1-Heptene, 2-methyl-	3.14		43.58	
1,1-Dimethylcyclohexane	3.14	43.24	43.58	0.8%
2,2,5-Trimethylhexane	3.09	44.07	44.35	0.6%
C8 - IsoOlefin - 7	3.14		43.58	
3c-Ethylmethylcyclopentane	3.14	43.45	43.58	0.3%
2t-Ethylmethylcyclopentane	3.14	43.45	43.58	0.3%
3t-Ethylmethylcyclopentane	3.14	43.44	43.58	0.3%

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
1,1-Methylethylcyclopentane	3.14		43.58	
i-Propylcyclopentane	3.14		43.58	
C8 - Naph-Olefin - 4	3.19		42.69	
C8 - IsoOlefin - 8	3.14		43.58	
1t,3-Dimethylcyclohexane	3.14		43.58	
C8 - Diolefin - 2	3.19		42.69	
5-Methyl-3-heptene	3.14		43.58	
t-Octene-4	3.14		43.58	
Octene-1	3.14		43.58	
t-Octene-3	3.14		43.58	
n-Octane	3.08	44.38	44.44	0.2%
C9-Isoparaffin-x	3.09		44.35	
t-Octene-2	3.14		43.58	
C8 - MonoNaph - 3	3.14		43.58	
C8-IsoOlefin-9	3.14		43.58	
3-Heptyne, 5-methyl-	3.19		42.69	
2,6-Dimethyl-3-heptene	3.14		43.58	
C8-Naph-olefin-4	3.19		42.69	
2,3,3-Trimethylhexene-1	3.14		43.58	
2,3,4-Trimethylhexane	3.09	44.50	44.35	-0.3%
C8 - IsoOlefin - 10	3.14		43.58	
2,3,5-Trimethylhexane	3.09	44.14	44.35	0.5%
Cyclopentane, 1-ethyl-2-methyl	3.14		43.58	
C8 - Naph-Olefin - 5	3.19		42.69	
C9 - IsoOlefin - 1	3.14		43.58	
1,4-Dimethyl-1-cyclohexene	3.19		42.69	
C8-Naph-olefin-6	3.19		42.69	
n-propyl Cyclohexane	3.14		43.58	
1c,2-Dimethylcyclohexane	3.14		43.58	
2,4-Dimethylheptane	3.09	44.48	44.35	-0.3%
2,3-Dimethyl-3-heptene	3.14		43.58	
Ethylcyclohexane	3.14	43.69	43.58	-0.2%
2,6-Dimethylheptane	3.09	44.46	44.35	-0.3%
3,5-Dimethyl-3-heptene	3.14		43.58	
2,2,3-Trimethylhexane	3.09	44.15	44.35	0.4%

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
n-Propylcyclopentane	3.14		43.58	
1-Ethyl-2-Methylcyclopentene	3.19		42.69	
2,5-Dimethylheptane	3.09	44.48	44.35	-0.3%
2-Methyloctene-1	3.14		43.58	
1,1,4-Trimethylcyclohexane	3.14	43.47	43.58	0.3%
1,1,3-Trimethylcyclohexane	3.14	43.56	43.58	0.1%
C9 Naph-Olefin -1	3.19		42.79	
3-Heptene, 2,6-dimethyl-	3.14		43.58	
1c,2t,4t-Trimethylcyclohexane	3.14		43.58	
Ethylbenzene	3.32	40.88	40.81	-0.2%
3-Heptene, 4-ethyl-	3.14		43.58	
C9 - IsoOlefin - 2	3.14		43.58	
C9 - MonoNaph - 4	3.14		43.58	
C9 - MonoNaph - 1	3.14		43.58	
2,3-Dimethylheptane	3.09	44.50	44.35	-0.3%
m-Xylene	3.32	40.34	40.81	1.2%
2,4-Dimethylheptene-1	3.14		43.58	
p-Xylene	3.32	40.35	40.81	1.1%
4-Ethylheptane	3.09		44.35	
C9-IsoOlefin-3	3.14		43.58	
3,5-Dimethylheptane	3.09	44.50	44.35	-0.3%
3,3-Diethylpentane	3.09		44.35	
2-Methyloctene-2	3.14		43.58	
4-Methyloctane	3.09	44.53	44.35	-0.4%
2-Methyloctane	3.09	44.51	44.35	-0.4%
C9 - Olefin - 1	3.14		43.58	
C9 - NaphOlefin - 2	3.19		42.79	
Heptane, 3-ethyl-	3.09		44.35	
C9-isoolefin	3.14		43.58	
3-Methyloctane	3.09	44.53	44.35	-0.4%
1c,2t,4c-Trimethylcyclohexane	3.14		43.58	
C9 - NaphOlefin - 3	3.19		42.79	
o-Xylene	3.32	40.77	40.81	0.1%
C10 - Isoparaffin - 2	3.09		44.27	
Cyclohexane, 1,2,4-trimethyl-,	3.14		43.58	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
C10 - IsoParaffin - 1	3.09		44.27	
Cyclohexane, 1-ethyl-4-methyl-, trans-	3.14		43.58	
Cyclopentane, 1-methyl-2-propy	3.14		43.58	
Nonene-1	3.14		43.58	
trans-1,3-Diethylcyclopentane	3.14		43.58	
C10 - MonoNaph - 1	3.14		43.58	
C9 MonoNaph - 6	3.14		43.58	
2,2,4-trimethylheptane	3.09		44.27	
t-Nonene-3	3.14		43.58	
trans-4-Nonene	3.14		43.58	
c-Nonene-3	3.14		43.58	
C10 - IsoOlefin - 1	3.14		43.58	
2,3-Dimethylheptene-2	3.14		43.58	
t-2-Methyloctene-3	3.14		43.58	
n-Nonane	3.09	44.28	44.35	0.2%
t-Nonene-2	3.14		43.58	
3,7-Dimethyloctene-1	3.14		43.58	
1,1-Methylethylcyclohexane	3.14		43.58	
1-ethyl-4-t-methylcyclohexane	3.14		43.58	
i-Propylbenzene	3.30	41.09	41.14	0.1%
2,3-Dimethyloctane	3.09	44.42	44.27	-0.3%
1-Methyl-2-propyl-cyclopentan	3.14		43.58	
C10-IsoOlefin-4	3.14		43.58	
C10-isoparaffin-x	3.09		44.27	
C10 Iso-olefin - 5	3.14		43.58	
C10-MonoNaph-1	3.14		43.58	
C9-Naphtheno-olefin-5	3.19		42.79	
2,2-Dimethyloctane	3.09	44.35	44.27	-0.2%
C10 Iso-olefin - 6	3.14		43.58	
C9-NaphthenoOlefin-6	3.19		42.79	
1,2,3,5-t-Tetramethylcyclohex	3.14		43.58	
2,5-Dimethyloctane	3.09		44.27	
1,2,3,5-c-Tetramethylcyclohex	3.14		43.58	
2,7-Dimethyloctane	3.09		44.27	
2,4-Dimethyloctane	3.09		44.27	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
C10-IsoOlefin-7	3.14		43.58	
2,6-Dimethyloctane	3.09		44.27	
3,6-Dimethyloctane	3.09	44.42	44.27	-0.3%
C10 Isoparaffin -1	3.09		44.27	
n-Propylbenzene	3.30	41.11	41.14	0.1%
C10-n-Olefin	3.14		43.58	
3-Methyl-5-ethylheptane	3.09		44.27	
C10 - IsoOlefin - 8	3.14		43.58	
1-Methyl-3-ethylbenzene	3.30		41.14	
1-Methyl-4-ethylbenzene	3.30		41.14	
2,3-Dimethyl-2-octene	3.14		43.58	
1,3,5-Trimethylbenzene	3.30	40.91	41.14	0.6%
2-Methylnonane	3.09	44.05	44.27	0.5%
5-Methylnonane	3.09	44.07	44.27	0.5%
4-Methylnonane	3.09	44.44	44.27	-0.4%
2,2,6-Trimethyloctane	3.10		44.21	
1-Methyl-2-ethylbenzene	3.30		41.14	
3-Ethyloctane	3.09	44.46	44.27	-0.4%
C10-IsoOlefin-12	3.14		43.58	
Heptane, 2,2,3,5-tetramethyl-	3.10		44.21	
3-Methylnonane	3.09	44.44	44.27	-0.4%
C11-Isoparaffin-1	3.10		44.21	
C10-IsoOlefin -15	3.14		43.58	
C11-Isoparaffin-2	3.10		44.21	
C10 - IsoParaffin - 5	3.09		44.27	
1,2,4-Trimethylbenzene	3.30	40.91	41.14	0.5%
C10 - MonoNaph - 2	3.14		43.58	
t-Butylbenzene	3.28		41.39	
1t-Methyl-2-n-propylcyclohexan	3.14		43.58	
i-Butylcyclohexane	3.14		43.58	
2,3,3-trimethyloctane	3.10		44.21	
3-Nonene, 3-methyl-, (E)-	3.14		43.58	
3-Ethyl-3-methylheptane	3.09		44.27	
i-Butylbenzene	3.28		41.39	
C11-Isoparaffin-3	3.10		44.21	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
4-Methyldecane	3.10		44.21	
n-Decane	3.09	44.19	44.27	0.2%
3-Decene	3.14		43.58	
sec-Butylbenzene	3.28	41.33	41.39	0.2%
1,2,3-Trimethylbenzene	3.30	40.94	41.14	0.5%
1-Methyl-3-i-propylbenzene	3.28		41.39	
C11 Isoparaffin-4	3.10		44.21	
1-Methyl-4-i-propylbenzene	3.28		41.39	
Indan	3.35		40.26	
2,5,6-Trimethyloctane	3.10		44.21	
C11-Isoparaffin-5	3.10		44.21	
C11-Isoparaffin-6	3.10		44.21	
Indene	3.41		39.36	
3-Ethylnonane	3.10		44.21	
n-ButylCyclohexane	3.14		43.58	
1-Methyl-4-n-propylbenzene	3.28		41.39	
C11-Isoparaffin-7	3.10		44.21	
1,3-Diethylbenzene	3.28	41.66	41.39	-0.7%
1-Methyl-3-n-propylbenzene	3.28		41.39	
Nonane, 3,7-dimethyl-	3.10		44.21	
1,4-Diethylbenzene	3.28	41.66	41.39	-0.7%
n-Butylbenzene	3.28		41.39	
1,3-Dimethyl-5-ethylbenzene	3.28		41.39	
C11-Isoparaffin-9	3.10		44.21	
1,2-Diethylbenzene	3.28	41.66	41.39	-0.7%
C11-Isoparaffin-8	3.10		44.21	
C11- Isoparaffin-10	3.10		44.21	
1-Methyl-2-n-propylbenzene	3.28		41.39	
C11 - IsoOlefin - 1	3.14		43.58	
C11- Isoparaffin - 12	3.10		44.21	
C9 - Aromatic - 1	3.30		41.14	
C11- Isoparaffin-11	3.10		44.21	
C11- IsoParaffin - 13	3.10		44.21	
C11 - IsoParaffin - 15	3.10		44.21	
1,4,Dimethyl-2-ethylbenzene	3.28		41.39	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
1,3-Dimethyl-4-ethylbenzene	3.28		41.39	
2-Methylindan	3.33		40.62	
2-Methylindan(1)	3.33		40.62	
C11 - IsoParaffin - 14	3.10		44.21	
1,2-Dimethyl-4-ethylbenzene	3.28	41.18	41.39	0.5%
C11-MonoNaphthene-2	3.14		43.58	
1,3-Dimethyl-2-ethylbenzene	3.28	41.22	41.39	0.4%
5-Undecene	3.14		43.58	
2-Undecene, (E)-	3.14		43.58	
1-Ethyl-3-i-propylbenzene	3.27		41.60	
1-Methyl-4-t-butylbenzene	3.27		41.60	
1,2-Dimethyl-3-ethylbenzene	3.28	41.22	41.39	0.4%
n-Undecane	3.10	44.12	44.21	0.2%
1-Ethyl-4-i-propylbenzene	3.27		41.60	
C11 - Aromatic - 1	3.27		41.60	
1,2,4,5-Tetramethylbenzene	3.28	40.91	41.39	1.2%
C11 - Aromatic - 2	3.27		41.60	
1H-Indene, 2,3-dihydro-1,2-dim	3.31		40.90	
1,2,3,5-Tetramethylbenzene	3.28	41.09	41.39	0.7%
C12 - IsoParaffin - 1	3.10		44.16	
C12 - IsoParaffin - 2	3.10		44.16	
C11 - Aromatic - 3	3.27		41.60	
5-Methylindan	3.33		40.62	
1,2-Di-i-propylbenzene	3.25		41.77	
1-methyl-4-(1-methylpropyl)be	3.27		41.60	
C11 - Aromatic - 4	3.27		41.60	
2,4-diethyl-1-methylbenzene	3.27		41.60	
C11 - MonoNaph - 5	3.18		42.94	
4-Methylindan	3.33		40.62	
1,4-diethyl-2-methylbenzene	3.27		41.60	
Benzene, 1-methyl-4-(2-methylp	3.27		41.60	
1-Ethyl-2-n-propylbenzene	3.27		41.60	
s-Pentylbenzene	3.27		41.60	
n-Pentylbenzene	3.27		41.60	
C12 - Isoparaffin - 3	3.10		44.16	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
tert-Pentylbenzene	3.27		41.60	
1-Methyl-2-n-butylbenzene	3.27		41.60	
C11 - Aromatic - 7	3.27		41.60	
C12 - IsoParaffin - 4	3.10		44.16	
1,4-Di-i-propylbenzene	3.25		41.77	
C11 - Aromatic - 9	3.27		41.60	
C12-Aromatic-1	3.25		41.77	
Naphthalene	3.43	38.75	38.99	0.6%
1-t-Butyl-3,5-dimethylbenzene	3.25	41.49	41.77	0.7%
4,7-Dimethyl Indane	3.31		40.90	
C12-Isoparaffin-6	3.10		44.16	
C11 - Aromatic - 10	3.27		41.60	
1,1-Dimethyl Indane	3.31		40.90	
Dimethyl Indane - 1	3.31		40.90	
Dimethyl Indane - 2	3.31		40.90	
1t-Butyl-4-ethylbenzene	3.25		41.77	
1,3-Di-n-propylbenzene	3.25		41.77	
C11 - Aromatic - 11	3.27		41.60	
1,1,3-Trimethyl Indane	3.30		41.14	
n-Dodecane	3.10	44.07	44.16	0.2%
C11 - Aromatic - 12	3.27		41.60	
1-ethyl-2,4,5-trimethylbenzen	3.27		41.60	
Naphthalene, 1,2,3,4-tetrahydr	3.31		40.90	
C3-Indane-1	1.56		67.98	
C11 - Aromatic - 13	3.27		41.60	
1,3,5-trimethyl-2-propylbenze	3.25		41.77	
C11 - Aromatic - 14	3.27		41.60	
1,3,5-Triethylbenzene	3.25	41.94	41.77	-0.4%
C11 - Aromatic - 15	3.27		41.60	
C2 Indane - 1	3.31		40.90	
C12 - Aromatic - 1	3.25		41.77	
C12 - Aromatic - 4	3.25		41.77	
C12 - Aromatic - 2	3.25		41.77	
C12 - Aromatic - 3	3.25		41.77	
C12 - Aromatic - 5	3.25		41.77	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
C3-Indane-2	3.30		41.14	
4,7-DimethylIndane	3.31		40.90	
n-Hexylbenzene	3.25		41.77	
C12 - Aromatic - 7	3.25		41.77	
C12 - Aromatic -8	3.25		41.77	
Diimethyl Indene - 2	3.36		40.18	
Dimethyl Indane - 3	3.31		40.90	
C12 - Aromatic - 10	3.25		41.77	
C12-Aromatic-9	3.25		41.77	
C13 - IsoParaffin - 1	3.10		44.12	
Dimethyl Indane - 4	3.31		40.90	
Trimethyl Indane - 1	3.30		41.14	
Trimethyl Indane - 2	3.30		41.14	
Trimethyl Indane - 3	3.30		41.14	
1,2,4-Triethylbenzene	3.25	41.94	41.77	-0.4%
Pentamethylbenzene	3.27		41.60	
C13 - IsoParaffin - 2	3.10		44.12	
Trimethyl Indane - 4	3.30		41.14	
2-Methylnaphthalene	3.40		39.45	
C12 - Aromatic - 11	3.25		41.77	
C12 - Aromatic - 11(1)	3.25		41.77	
n-Tridecane	3.10	44.31	44.12	-0.4%
1-Methylnaphthalene	3.40		39.45	
C13-Isoparaffin-4	3.10		44.12	
Methylnaphthalene	3.40		39.45	
5-Ethyltetralin	3.30		41.14	
Trimethyl Indane - 8	3.30		41.14	
6-Methyl Tetralin	3.31		40.90	
C3 Indane - 4	3.30		41.14	
C13-Isoparaffin-5	3.10		44.12	
C13 - Aromatic - 1	3.25		41.91	
C3-Indene	3.34		40.48	
1-Methyl-3-Hexylbenzene	3.25		41.91	
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	3.30		41.14	
C13 - Aromatic - 2	3.25		41.91	

Component	grams CO_2/gram Component	GPA LHV (MJ/kg)	Predicted LHV (MJ/kg)	Prediction Error
C14-Isoparaffin-1	3.11		44.08	
C12 - Aromatic - 12	3.25		41.77	
C14-Isoparaffin-2	3.11		44.08	
C3Benzothiophene-1	3.30		41.14	
C13 - IsoParaffin - 6	3.10		44.12	
C14 - IsoParaffin - 3	3.11		44.08	
Biphenyl	3.42		39.13	
Tetramethyl Indene - 1	3.34		40.48	
C14 - IsoParaffin - 4	3.11		44.08	
C14 - IsoParaffin - 5	3.11		44.08	
C13 - IsoParaffin - 7	3.10		44.12	
2-Ethylnaphthalene	3.38		39.82	
C3 Indane - 6	3.30		41.14	
n-Tetradecane	3.11	44.27	44.08	-0.4%
Dimethylnaphthalene-3	3.38		39.82	
Dimethylnaphthalene-4	3.38		39.82	
C4-Indane-2	3.28		41.33	
Dimethylnaphthalene-5	3.38		39.82	
C3-Indane - 7	3.30		41.14	
Dimethylnaphthalene - 6	3.38		39.82	
C14-Isoparaffin-7	3.11		44.08	
Dimethylnaphthalene-6	3.38		39.82	
1c,4-Dimethylcyclohexane	3.14		43.58	
n-Pentadecane	3.11	44.23	44.05	

Table 2: Predicted lower heating values for hydrocarbons in the SWRI database.

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