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# INCORPORATION OF HIGHER CARBON NUMBER ALCOHOLS IN GASOLINE BLENDS FOR APPLICATION IN SPARK-IGNITION ENGINES

**By**

**Kristina Marie Lawyer**

**A DISSERTATION**

**Submitted in partial fulfillment of the requirements for the degree of**

**DOCTOR OF PHILOSOPHY**

**In Mechanical Engineering – Engineering Mechanics**

**MICHIGAN TECHNOLOGICAL UNIVERSITY**

**2017**

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This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Mechanical Engineering – Engineering Mechanics.

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For Champie, Gail, Todd, my family, and my drag racing family;

Thank you for always believing in me.

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# TERMINOLOGY

| | |
|---|---|
| AFR | Air/Fuel Ratio |
| ASTM | ASTM International |
| BMEP | Brake Mean Effective Pressure |
| BOB | Blendstock for Oxygenate Blending |
| BTE | Brake Thermal Efficiency |
| C2-C8 | Carbon number of 2 through 8 |
| CAA | Clean Air Amendments |
| CO | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| CFR | U.S. Code of Federal Regulations |
| CTR at ANL | Center for Transportation Research at Argonne National Lab |
| DI | Direct Injection |
| DOHC | Dual OverHead Camshaft |
| E23 | Blend of 23 v% ethanol with gasoline |
| eth50, nprop50, etc. | 50/50 v% blend of BOB and ethanol, n-propanol, etc. |
| ECU | Engine Control Unit |
| EEE | A gasoline used for certification engine testing |
| EGR | Exhaust Gas Recirculation |
| EIA | U.S. Energy Information Administration |
| EPA | Environmental Protection Agency |
| ETBE | Ethyl Tertiary Butyl Ether |
| FID | Flame Ionization Detector |
| FTIR | Fourier Transform Infrared Spectroscopy |
| gpg Mn | Grains per gallon of manganese |
| HC | Hydrocarbons |
| HoV | Heat of Vaporization |
| LHV | Lower Heating Value |
| MFB5%, etc. | Crank angle at which 5%, etc. of the fuel/air charge has burned |
| MMT | Methylcyclopentadienyl Manganese Tricarbonyl |
| MON | Motor Octane Number |
| MTBE | Methyl Tertiary Butyl Ether |
| n-, t-, etc. | Isomer type of an alcohol |
| NA | Non-attainment Areas |
| NAAQS | National Ambient Air Quality Standards |
| $NO_x$ | Oxides of nitrogen |
| $O_2$ | Diatomic oxygen |
| Oxygenate | Substance that contains oxygen |



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| | |
|---|---|
| PD | Petroleum Displacement |
| RFG | Reformulated Gasoline |
| RFS/RFS2 | U.S. Renewable Fuel Standard |
| rpm | Revolutions per minute |
| ROHR | Rate of Heat Release |
| RON | Research Octane Number |
| RVP | Reid Vapor Pressure |
| SCR | Selective Catalyst Reduction |
| SI | Spark Ignition |
| SwRI | Southwest Research Institute |
| TAME | Tertiary Amyl Methyl Ether |
| U.S. | United States |
| v% | Percent by volume |
| VOC | Volatile Organic Compound |
| wt% | Percent by weight |
| WO | Winter Oxyfuel |



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# ABSTRACT

The 2007 U.S. Renewable Fuel Standard (RFS2) requires an increase in the use of advanced biofuels up to 36 billion gallons by 2022. Higher carbon number alcohols, in addition to cellulosic ethanol and synthetic biofuels, could be used to meet this demand while adhering to the RFS2 corn-based ethanol limitation. Alcohols of carbon numbers 2 through 8 are chosen based on their chemical and engine-related properties.

Blend comparison metrics are developed from automotive industry trends, consumer expectations, U.S. fuel legislation, and engine requirements. The metrics are then used to create scenarios by which to compare higher alcohol fuel blends to traditional ethanol blends. Each scenario details an overall objective and identifies chemical and engine-related properties that are crucial to meeting that objective as fuel criteria.

Fuel blend property prediction methods are adopted from literature and used to calculate both linear and non-linear properties of multi-component blends. Possible combinations of eight alcohols mixed with a gasoline blendstock are calculated and the properties of the theoretical fuel blends are predicted. Blends that meet all of a scenario's criteria are identified as suitable blends.

Blends of higher carbon number alcohols with gasoline blendstock are identified as optimal blends for each scenario if they meet all of the scenario's criteria and maximize either energy content, knock resistance, or petroleum displacement. Optimal blends are tested in a spark-ignition engine. The effect of higher carbon number alcohols as a fuel component on engine performance and emissions is examined.

Results suggest that combustion properties of blends of alcohols with carbon numbers from two to six are similar to those of the reference fuel at low and medium engine loads. Properties of blends of alcohols with carbon numbers from two to four are similar to those of the reference fuel even at high loads. However, due to their reduced knock resistance, the suitability of longer chain alcohols, specifically C5 and longer, as blending agents at increased levels is questionable.



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# 0 LITERATURE REVIEW

Chapter 0 details the Literature Review portion of the project, which includes an examination of U.S. legislation on automotive fuels, the use of alcohols and other oxygenates as spark-ignition engine fuel components, and the chemical and engine-related properties of higher carbon number alcohols.

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## 0.1 U.S. Fuel Legislation

A summary of legislation on spark-ignition (SI) engine fuels is provided here. This summary reviews only fuel use within the United States (U.S.) transportation sector and may not be pertinent when examining fuel use within other sectors or countries.

The key events in the history of alcohol and oxygenate use in SI automotive fuels in the U.S. are listed in Figure 0.1. In the figure, pieces of legislation are in italics. The use of alcohols and oxygenates in automotive engines dates back to the mid-1800s, but widespread use began in the 1970s with the U.S. oil crisis of 1973 [1]. The history of alcohols and oxygenates given here will focus on the 1970s to the present.

### 0.1.1 The Clean Air Act

The Clean Air Act (CAA), authored by the U.S. Environmental Protection Agency (EPA), was originally passed in 1963 and amended in 1970, 1977, and 1990. The CAA regulates air emissions from both stationary and mobile sources. The law created the National Ambient Air Quality Standards (NAAQS) and aimed to have every state meet the NAAQS by 1975. The amendments of 1977 and 1990 set new deadlines for the states that had yet to meet the NAAQS [2].

The CAA Amendments of 1990 had a large impact on the automotive industry through the regulation of vehicle emissions, fuels, and clean cars. The amendments set limits on tailpipe emissions of hydrocarbons, carbon monoxide, and nitrogen oxides of vehicles of model year 1994 and newer. Alcohol was blended with gasoline in cities with high carbon monoxide levels starting in 1992 and gasoline with lower aromatic levels was introduced in cities with high ozone levels beginning in 1995. Lastly, the 1990 amendments also started a Clean Car program in California which increased the use of gasoline substitutes [2].

### 0.1.2 Substantially Similar

Section 211(f)(1) of the CAA, also known as the Substantially Similar Rule, requires that automotive fuels and fuel additives to be used in vehicles of model year 1974 and newer have 'substantially similar' composition to the fuels and fuel additives utilized in the certification of any vehicle of model year 1975 and newer. This rule has been officially interpreted by the EPA many times since 1970, but generally means that the EPA's certification program has the ability to place limits on the chemical composition and physical properties of commercial gasoline, including the amount of alcohols and oxygenates that can be used [3].



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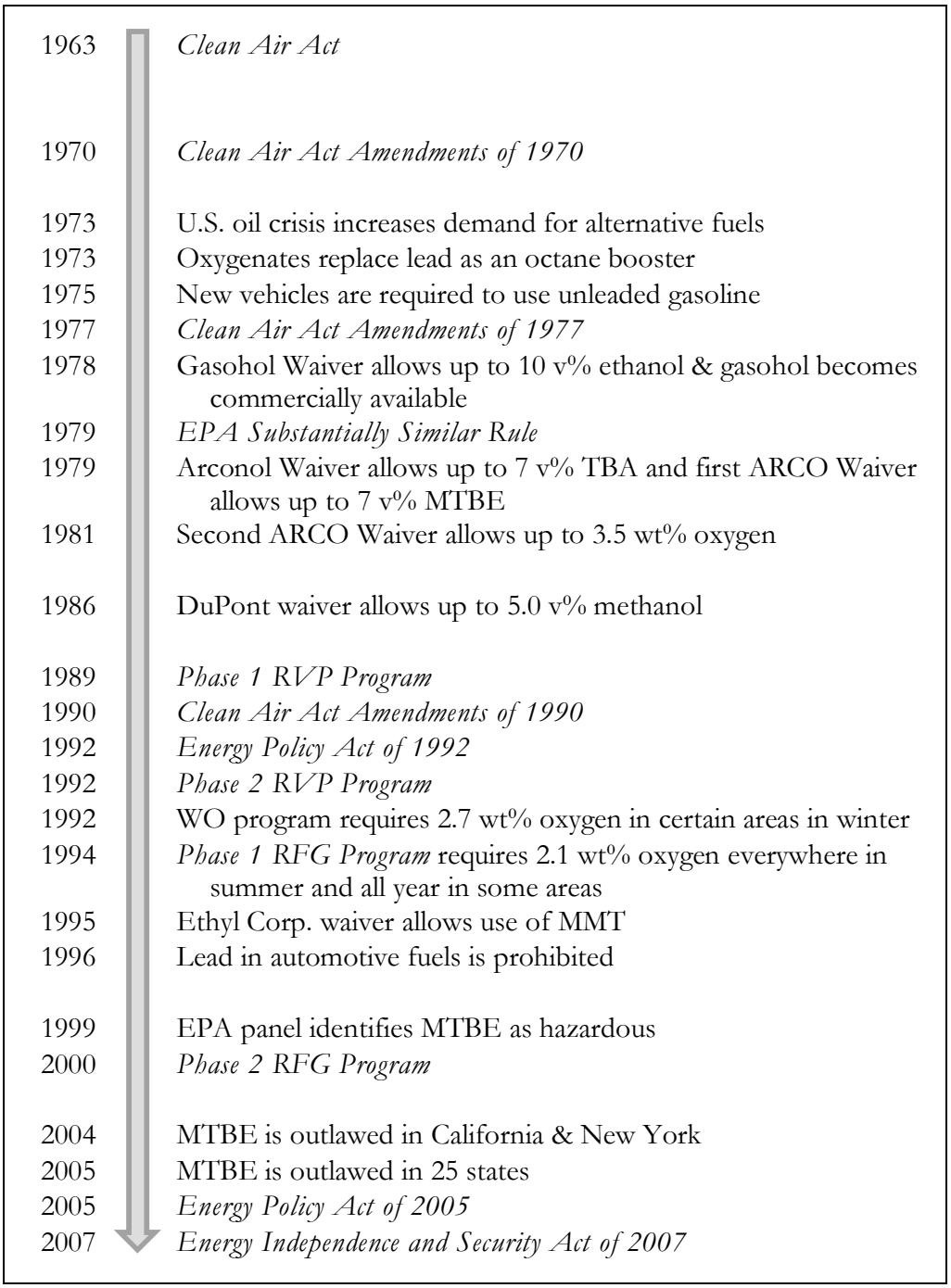


**FIGURE 0.1: CHRONOLOGICAL SUMMARY OF OXYGENATE USE IN AUTOMOTIVE SI FUELS IN THE U.S.**



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Since the passing of the Substantially Similar Rule in 1979, fuel waivers have been granted by the EPA to allow for commercial use of fuels that contain oxygenates. The Arconol Waiver, granted in 1979, allowed for the use of up to 7 v% tertiary butyl alcohol (TBA) in gasoline. Two waivers submitted by the ARCO Company, one in 1979 and one in 1981, allowed for up to 7 v% methyl tertiary butyl ether (MTBE) and up to 3.5 wt% oxygen content, respectively. The DuPont waiver, granted in 1986, increased the amount of allowable methanol in gasoline to 5 v% [4].

In addition to these waivers, manufacturers such as Texaco, Anafuel Unlimited, Synco 76 Fuel Corporation, Texas Methanol Corporation, Sun Refining and Marketing Company, and Ethyl Corporation were granted waivers for fuels of a proprietary mixture that contained oxygenates by the EPA between 1980 and 1995. The proprietary mixtures contained between 5 and 15 v% non-gasoline components but the exact oxygen content of the mixtures is not documented in the EPA waiver request. The Ethyl Corporation waiver, granted in 1995, allowed the use of 1/32 gpg Mn methylcyclopentadienyl manganese tricarbonyl (MMT) [4].

### 0.1.3 Required Use of Oxygenates

Oxygenates were first required in automotive fuel by the Winter Oxyfuel (WO) program in 1992 as a method of reducing carbon monoxide (CO) emissions in certain geographical areas throughout the country. The WO program required a minimum of 2.7 wt% oxygen in commercial gasoline sold in these areas during the winter months [5].

The Reformulated Gasoline (RFG) program was enacted in 1994 to reduce ozone-forming emissions during the summer months and to reduce nitrogen oxides ($NO_x$) and other toxic pollutants during the entire year in certain geographical areas. The RFG program requires commercial gasoline to contain a minimum of 2.1 wt% oxygen [5].

### 0.1.4 RVP Limitations

The EPA set limits on the Reid vapor pressure (RVP) of commercial gasoline sold during the summer ozone season to reduce volatile organic compound (VOC) emissions. The first phase of limitation, active from 1989 to 1991, required that automotive fuel have a RVP of 10.5, 9.5, or 9.0 psi depending upon geographical location and month [6].

Phase 2 of the RVP program took effect in 1992. This required an additional reduction in RVP, now limited to either 9.0 or 7.8 psi depending upon geographical location and month. In addition, a 1.0 psi RVP allowance is given to fuel blends that contain 9 to 10 v% ethanol. A process for obtaining exceptions to the 7.8 psi limit was also established,



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allowing for an area to be classified as an 'attainment area' provided it continues to meet NAAQS standards [6].

### 0.1.5 RENEWABLE FUEL STANDARD

The U.S. Renewable Fuel Standard (RFS) was authorized under the Energy Policy Act of 2005 and expanded in the Energy Independence and Security Act of 2007 with the intent of reducing greenhouse gas emissions. The 2007 update to the standard (commonly referred to as RFS2) mandates a yearly increase in the production of ethanol and advanced biofuels up to 36 billion ethanol-equivalent gallons in 2022. RFS2 limits corn-based ethanol to 15 billion gallons and requires the use of 1 billion gallons of biomass-based diesel, leaving 20 billion gallons to come from other advanced biofuels [7].

The volumetric RFS2 requirements are plotted in Figure 0.2 as an extension of historical U.S. ethanol consumption. Also plotted in the figure are the corresponding theoretical gasoline-ethanol blend levels of the historical data and RFS2 requirement. The theoretical blend level is the gasoline-ethanol blend that would be required to meet the consumption/requirement of that year and is based on Energy Information Administration (EIA) total consumption projections [8]. For example, the 2022 requirement of 36 billion gallons would require an alcohol blend level of approximately 28 v% if solely ethanol blends were being used to meet the requirement.

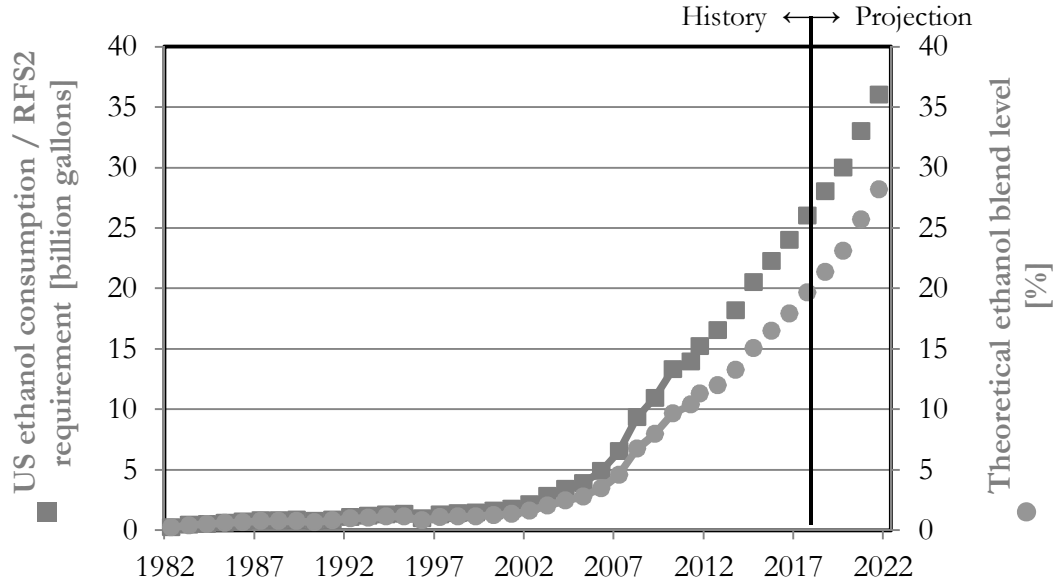


**FIGURE 0.2: U.S. ETHANOL CONSUMPTION, RFS2 REQUIREMENTS, AND THEORETICAL GASOLINE-ETHANOL BLEND LEVELS**

*Incorporation of Higher Carbon Number Alcohols in Gasoline Blends for Application in Spark-Ignition Engines* by Kristina Marie Lawyer

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### 0.1.6 MTBE

Methyl tertiary butyl ether (MTBE) has been a commercial gasoline additive since the 1970s. The first use of MTBE was as an octane booster in replace of lead in gasoline. Demand for MTBE grew through the 1980s as the demand for higher octane fuels increased. The WO program further increased demand of MTBE in the early 1990s and the RFG program kept demand high throughout the latter part of the 1990s. MTBE consumption reached 269,000 barrels per day in 1997 [5].

MTBE has the ability to increase fuel octane rating, but it is also water soluble and does not biodegrade easily which leads to build up in water reservoirs. In 1999, the EPA Blue Ribbon Panel on Oxygenates in Gasoline issued a report identifying the need to reduce the consumption of MTBE due to health concerns. California, New York, and 23 other states had prohibited the use of MTBE by 2004 [5]. The Energy Policy Act of 2005 left manufactures of MTBE vulnerable to lawsuits concerning water pollution which drove many to end production. Production of MTBE was down to 130 barrels per day in 2005 and 30 barrels per day in 2010. Production has remained around 30 barrels per day since 2010 [9].

### 0.1.7 ASTM STANDARDS

ASTM International is a not-for-profit organization that develops international engineering standards. ASTM standards are used by individuals, companies, and academic institutions around the world. There are multiple ASTM standards that apply to automotive fuels, such as D4814 (Standard Specification for Automotive Spark-Ignition Engine Fuel), D4806 (Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel), D5798 (Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines), D86 (Standard Test for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure), and D975 (Standard Specification for Diesel Fuel Oils). This project utilizes information from D4814 and D5798.

ASTM D4814 details vapor pressure and distillation requirements for fuels used in SI engines. Requirements vary depending on geographical location and month. The requirements for summer months throughout most of the country will be used in this project; this sets a maximum vapor pressure of 62 kPa (9.0 psi) and distillation points of 70°C (158°F), 77-121°C (170-250°F), 190°C (374°F), and 225°C (437°F) for 10 v%, 50 v%, 90 v%, and end point, respectively [10].



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ASTM D5798 details vapor pressure requirements for ethanol fuel blends to be used in flexible-fuel SI engines. These blends contain 51 to 83 v% ethanol. Requirements vary depending on geographical location and month. The requirements for summer months throughout most of the country will be used in this project; this sets a vapor pressure range of 38 to 59 kPa (5.5 to 8.5 psi) [11].

## 0.2 Alcohol Properties

In order to determine which alcohols could be viable components of automotive SI engine fuels, a database of chemical and engine-related properties of various alcohols needed to be generated. Alcohols of carbon numbers 2 through 8 were initially chosen for investigation. Two propanol isomers, four butanol isomers, eight pentanol isomers, 17 hexanol isomers, four heptanol isomers, and four octanol isomers were examined in addition to methanol and ethanol.

Some alcohol properties could be found in previous publications on engine testing and more could be found in chemical engineering databases. However, some properties, especially of heptanol and octanol, proved difficult to find. The pertinent properties are discussed here and again, in greater detail, in Chapter 2 while a list of all of the property values found are given in Appendix 7.2.

The skeletal structures of all 41 isomers are shown in Figure 0.3. The isomers are grouped by carbon number in the figure – the first row contains methanol, ethanol, and propanol; the second row contains the four butanol isomers; the third and fourth rows contain the eight pentanol isomers; rows five through nine contain the 17 hexanol isomers; row ten contains the four heptanol isomers; and row eleven contains the four octanol isomers. As illustrated in the figure, the n- isomer of each alcohol has a straight-chain structure and the iso- isomer is branched.

The knock resistance of each isomer is dependent upon its molecular bonds, as illustrated by their skeletal structures in Figure 0.3. Each black line in the skeletal structure represents a carbon atom. Longer carbon chains, such as 1-octanol, weaken the bond of the alcohol group. This results in lower knock resistance as the bonds would be more prone to breaking. Similarly, the closeness of the carbon atoms to the alcohol group in some of the isomers, such as tert-butanol, results in stronger bonds as compared to isomers that have carbon atoms that are more "stretched out" from the alcohol group, such as n-butanol.



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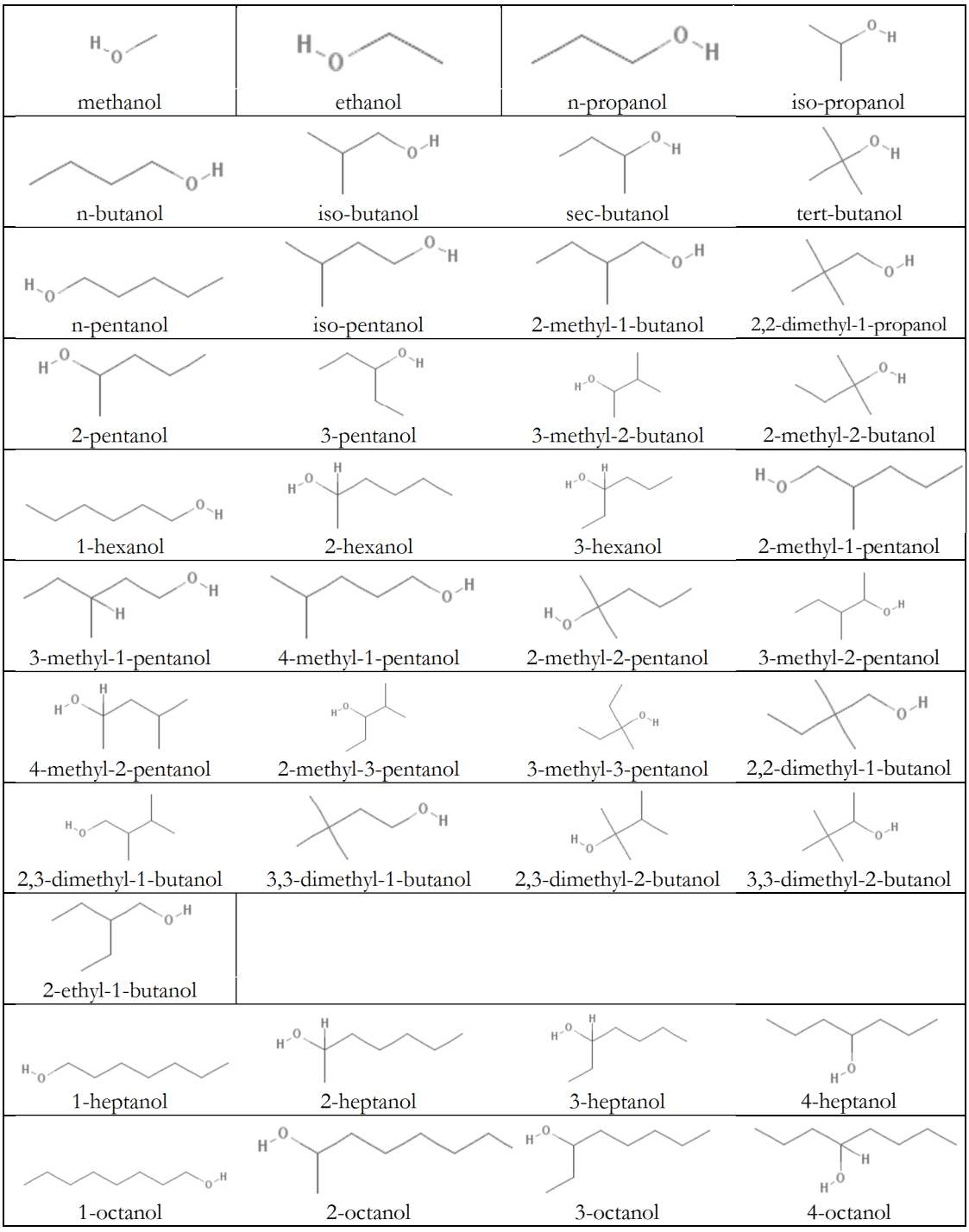


**FIGURE 0.3: CHEMICAL STRUCTURES OF ALCOHOLS OF CARBON NUMBER ONE THROUGH EIGHT**

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### 0.2.1 METHANOL

Methanol, $CH_3OH$, has a slightly higher density, much higher heat of vaporization (HoV), much lower energy content, much lower vapor pressure, and higher knock resistance than gasoline [12]. It has the highest knock resistance of all of the alcohol isomers because it has the shortest carbon chain, as illustrated in Figure 0.3.

Methanol is typically produced by steam-reforming natural gas and then feeding the product into a reactor with a catalyst. Other feedstocks can be used but natural gas is the most economical [13]. The oil crisis of the 1970s produced a need for alternative automotive fuels. Scientists and engineers were quick to propose methanol as an alternative fuel [14]. However, initial interest in methanol was for use as an octane booster rather than as an alternative fuel [15].

In 1979, the EPA Substantially Similar rule allowed for up to 2.75 percent by volume (v%) methanol to be combined with commercial gasoline. Fuel waivers increased the allowable methanol content to 4.75 v% in 1981 and then to 5.0 v% in 1986 [16]. Large scale use of methanol was severely reduced in 1989 by the EPA's fuel volatility regulations (Phase 1 RVP Program) which allowed vapor emissions waivers for ethanol blends but not for methanol blends [15].

Methanol was classified as an alternative fuel by the Energy Policy Act of 1992. Throughout the 1990s it was marketed in the U.S. automotive industry as a way to lower production costs, improve safety, and increase energy security. During this time, nearly 6 million gasoline-equivalent gallons of methanol were used annually in the form of 100 v% methanol and in blends of 85 v% with 15 v% gasoline. However, methanol use has declined dramatically since the 1990s and automotive manufacturers no longer design vehicles for methanol fuel [13].

In current years, methanol use in the automotive industry is limited to fuel cells and high performance applications. Hydrogen can be produced from methanol using an on-board reformer, making it a desirable fuel for fuel cell vehicles. Its higher knock resistance and HoV make it more desirable than gasoline as a high performance fuel. Despite its decreased use, there are still current efforts to utilize methanol to reduce emissions [17] and improve combustion efficiency [18].



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### 0.2.2 ETHANOL

Ethanol, which has a carbon number of two, has a slightly higher density, much higher HoV, lower energy content, much lower vapor pressure, and higher knock resistance than gasoline [12]. Despite its lower energy content and vapor pressure, ethanol is commonly blended with gasoline for use in SI engines because of its increased knock resistance. Recent research continues to examine the effects of ethanol, including its use in compression-ignition (CI) engines [19] and its compatibility with different materials used in automotive systems [20].

Some of the very first internal combustion engines were designed to run on ethanol and it has been utilized as an automotive fuel in varying quantities since the early 1900s. The Clean Air Act Amendments of 1990 required ethanol to be mixed with gasoline during the winter months in geographical areas that did not meet emissions standards. The Energy Policy Act of 2005, while not directly requiring the use of ethanol, again significantly increased ethanol consumption in the automotive sector [1].

Flexible fuel vehicles (FFVs), or FlexFuel vehicles, have also greatly increased the consumption of ethanol. FFVs are designed to utilize E85 which is a blend of 15 v% gasoline and 85 v% ethanol. Depending on the season and geographical location, E85 actually ranges from 51 to 83 v% [21]. In 2014 there were 3,320 light-duty FFVs and 485,500 fleet FFVs in the U.S. [22].

Fuel ethanol consumption from January 1981 until April 2016 is shown in Figure 0.4. Consumption remained around 10 trillion BTU (2,382,002 barrels) per month, or 120 trillion BTU (28,584,024 barrels) per year, throughout the latter half of the 1990s. In 2002, consumption had risen to approximately 14 trillion BTU (3,334,802 barrels) per month, or 171 trillion BTU (40,732,227 barrels) per year. Fuel ethanol consumption drastically increased between 2002 and 2011. In 2011, consumption had risen to approximately 89 trillion BTU (21,199,814 barrels) per month, or 1,065 trillion BTU (253,683,170 barrels) per year. From January 2012 to April 2016, monthly consumption has averaged 92 trillion BTU (21,914,414 barrels). The yearly consumption between 2012 and 2015 has gradually increased and averaged 1,105 trillion BTU (263,211,176 barrels) [23].

Most ethanol in the U.S. is produced through a dry-milling process that grinds starch- or sugar-based feedstocks and then ferments them into ethanol. Ethanol can also be produced from cellulosic feedstocks such as grass and wood through biochemical or thermochemical processes [24].



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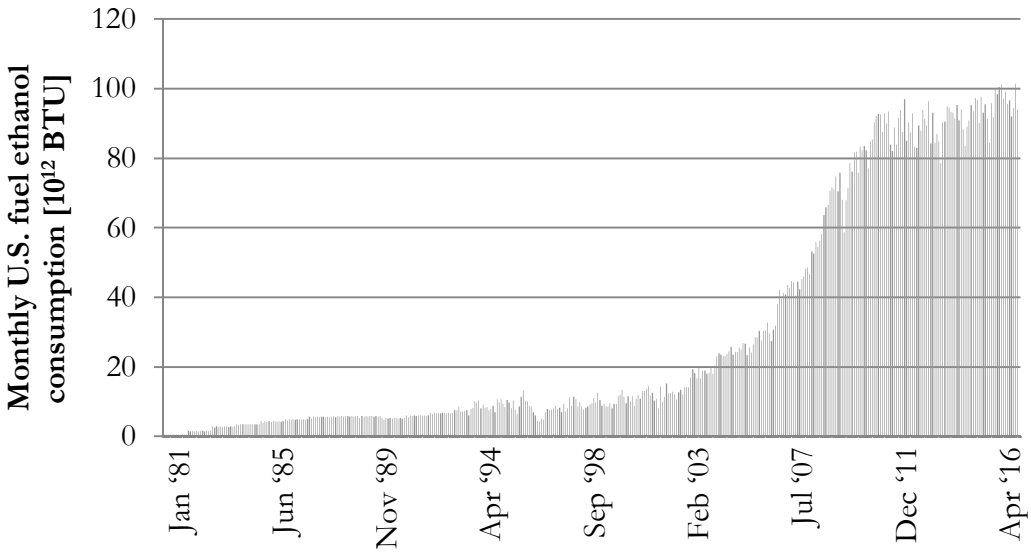


**FIGURE 0.4: MONTHLY U.S. FUEL ETHANOL CONSUMPTION**

### 0.2.3 PROPANOL

Propanol, $C_3H_7OH$, has a slightly higher density, much higher HoV, lower energy content, much lower vapor pressure, and higher knock resistance than gasoline [12]. N-propanol is currently used in the making of cosmetics, pharmaceuticals, perfumes, dyes, antifreezes, soaps, window cleaners, and other chemical products. Iso-propanol, or isopropyl alcohol, is a common household chemical [25].

Propanol is a by-product of the synthesis of methyl alcohol by high pressure during the propane/butane oxidation process. Over 1 billion pounds of propanol has been produced in the U.S. annually since 1990 [25].

Efforts to use propanol in gasoline blends for SI engines have shown it to reduce emissions while maintaining performance despite increased combustion durations [26]. Propanol fuel blends have also been shown to withstand durability testing in CI engines [27] and to reduce $NO_x$ emissions of selective catalyst reduction (SCR) systems [28].

### 0.2.4 BUTANOL

N-butanol and iso-butanol, which have a carbon number of four, have been studied thoroughly in SI engines over the last decade. Primarily driven by the need for automotive fuels that produce fewer emissions, the production, transportation, storage, physical and chemical properties, and combustion characteristics of butanol blended with gasoline have



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been examined by those in academia and industry. Multiple companies, such as DuPont and BP [29], Butalco [30], and Gourmet Butanol [31], have announced plans to develop butanol production methods.

In addition to industry support, biobutanol (butanol produced from renewable sources) qualifies as a renewable fuel under the Renewable Fuel Standard. There are two CAA provisions that allow the blending of biobutanol with gasoline for transportation fuel. The Fuel Quality Standard for Biobutanol, ASTM D7862, allows for butanol blends up to 12.5 v% with gasoline and the Octamix Waiver allows for a 16 v% biobutanol blend to be substituted for E10 [32].

Butanol can be produced from fossil fuels, but it is more commonly produced by fermenting a biomass feedstock such as sugar beets, sugar cane, corn grain, switchgrass, or wheat in a process nearly identical to the one used for ethanol production [32]. Current production of butanol in the U.S. is around 5 billion gallons per year. If made from corn, producing that quantity of butanol would require 20% of the U.S. corn crop but would only replace 1% of U.S. petroleum use. This suggests that corn-based butanol is not a long-term solution to the RFS2 requirements [33].

Compared to gasoline, butanol has higher oxygen content, lower hydrogen and carbon content, higher density, lower energy content, much lower vapor pressure, and higher HoV [12]. As illustrated in the skeletal structures shown in Figure 0.3, the increased chain length as compared to ethanol results in butanol's slightly lower knock resistance because the bonding of the alcohol group is weakened by the increased number of carbon atoms. Also shown in Figure 0.3, the knock resistance of the second and third isomers of butanol will have higher knock resistance because of the increased bond strength due to the carbon atoms being placed closer to the alcohol group [34].

Blending butanol with gasoline has been shown to reduce $NO_x$ emissions [35] and particulate emissions [36] in SI engines across multiple operating points (speeds and loads). In-depth engine testing has been done on butanol blends, including studies on fuel spray patterns [37] and the effects of butanol on lean-boosted engines [38]. Theoretical models of butanol's behavior as an engine fuel have been developed in addition to the numerous experimental studies done. For example, a kinetic oxidation mechanism was developed to aid in the study of the effect of ignition delay on butanol fuels [39].



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### 0.2.5 PENTANOL

Pentanol has been studied in CI engines during the past decade. Pentanol fuels have significantly different properties than neat gasoline with regard to ignition process and behavior in boosted conditions but they have proved to be a viable biofuel alternative [40]. While the use of pentanol as a fuel component is not directly addressed in current legislation or ASTM standards, any fuel containing pentanol would need to satisfy the Substantially Similar rule and applicable RVP requirements.

Compared to gasoline, pentanol has slightly higher density, much higher HoV, lower energy content, and much lower vapor pressure [12]. It is produced by hydrogenation of valeric aldehyde with sodium amalgam in quantities of over 10 million pounds annually in the U.S. since 1986. Pentanol is currently used as a lubricant additive, a processing aid, a solids separation agent, and as a solvent [41].

### 0.2.6 HEXANOL

Hexanol, $C_6H_{13}OH$, has a slightly higher density, higher HoV, lower energy content, much lower vapor pressure, and lower knock resistance than gasoline [12]. It has lower knock resistance than alcohols of carbon numbers 1 through 5 because of its elongated carbon chain, as illustrated in Figure 0.3. The long carbon chain reduces the strength of the alcohol group's bond making it easier to disassociate and lower in knock resistance.

Hexanol has a wide variety of both industry and consumer uses, such as: adhesives, lubricants, odor agents, paints, plasticizers, solids separation agents, solvents, hair care products, agricultural products, and textile products. It can be produced in a variety of ways including reaction and then hydrogenation of acetaldehyde and crotonaldehyde or by reducing ethyl caproate with sodium in absolute alcohol. Over 10 million pounds of hexanol has been produced in the U.S. annually since 1986 [42].

Hexanol as a fuel component has been studied in recent years. A fuel composed of 20 v% hexanol was tested for aeronautic application as part of the Alternative Fuels and Biofuels for Aircraft Development (ALFA-BIRD) project in Europe [43] and a blend of 15 v% n-hexanol was examined for its ability to reduce soot emissions in heavy-duty CI engines [44]. As compared to gasoline, hexanol has a slightly higher density, higher heat of vaporization, lower energy content, and much lower vapor pressure [12].



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### 0.2.7 HEPTANOL

Heptanol has not been widely studied as a substantial fuel component for use in SI engines but has been suggested as a fuel additive to improve ignition as far back as 1981 [45]. Heptanol has a slightly higher density, higher HoV, and slightly lower energy content than gasoline [12].

A distillation product of castor oil, enanthic aldehyde, is used to create heptanol through a reduction process. Around 75% of the heptanol is the U.S. is used as a plasticizer while the other 25% is used for anti-odor products such as deodorants and as a flavoring. Over 1 million pounds of heptanol was produced in the U.S. in 1994 but use has decreased since then [46].

### 0.2.8 OCTANOL

Octanol, which has a carbon number of eight, has also been studied recently as an automotive fuel component for use in CI engines as a method of reducing emissions [47] [48]. While the use of octanol as a fuel component is not directly addressed in current legislation or ASTM standards, any fuel containing octanol would need to satisfy the Substantially Similar rule and applicable RVP requirements.

Octanol has a slightly higher density, higher HoV, and slightly lower energy content than gasoline [12]. It also has significantly lower knock resistance than alcohols of any lower carbon number as it has the longest carbon chain. A longer carbon chain results in the weakening of the bond of the alcohol group. The long carbon chain of octanol is illustrated in Figure 0.3.

1-octanol can be synthesized from engineered microbes in a sustainable, bio-based method. However, because octanol is not currently used in large enough quantities to be comparable to U.S. fuel use, it is unknown if this production method could sustain the large demand of the automotive industry [49]. Currently 1-octanol is primarily manufactured for use in perfumes and 2-octanol is used as a raw material for flavorings, fragrances, paints, inks, and much more [50].



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# 1 INTRODUCTION

Chapter 1 provides an introduction to the project, including an overview of the use of oxygenates in SI engine fuels and of U.S. fuel regulations. This chapter also contains the project hypothesis and objectives.

Contents of this Chapter

1.1 Background
1.1.1 U.S. Fuel Regulations
1.1.2 Oxygenates as SI Fuel Components
1.2 Project Hypothesis
1.3 Project Objectives



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## 1.1 BACKGROUND

A brief history of the oxygenates used in spark-ignition (SI) engines in transportation vehicles in the United States (U.S.) is needed to fully understand this project. Within the scope of this project, 'oxygenate' is used to describe hydrocarbons that contain at least one oxygen atom.

### 1.1.1 U.S. FUEL REGULATIONS

The Clean Air Act Amendments of 1977 set the requirement that all oxygenates must be approved for use in automotive fuel by the U.S. Environmental Protection Agency (EPA). Alcohols and ethers are the primary oxygenates used in automotive fuels. The most common are: methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), and fuel ethanol. Methanol, isopropyl alcohol, n-butanol, t-butanol, tertiary hexyl methyl ether, tertiary amyl ethyl ether, and diisopropyl ether are also used [51].

The CAA Amendments of 1990 generated two automotive fuel programs: the Winter Oxyfuel (WO) program and the year-round reformulated gasoline (RFG) program. The WO program was implemented in 1992 and requires automotive fuels to contain at least 2.7% oxygen by weight (wt%) during the winter season in cities with high levels of CO. The RFG program, implemented in 1995, requires the use of reformulated gasoline in cities with high levels of smog. RFG contains at least 2.0 wt% oxygen and contains fewer pollutants than conventional gasoline [52] [53].

In recent years the use of oxygenates has increased as a means of reducing carbon monoxide (CO) and hydrocarbon (HC) emissions [54]. In addition, RFG sold in high pollution areas was required to contain a minimum of 2.1 wt% oxygen by 2000.

### 1.1.2 OXYGENATES AS SI FUEL COMPONENTS

Oxygenates have been used in the U.S. for 40 years to increase the volume and octane rating of automotive gasoline. The introduction of oxygenates was driven by the phasing-out of lead from gasoline that began in the 1970s. MTBE was the most common octane booster during this time. The use of MTBE was expanded in the late 1980s when states began requiring the use of oxygenates to reduce carbon monoxide (CO) emissions during the winter months.

Ethanol is currently the predominant oxygenate in transportation fuel. It is widely used as an alternative fuel for SI engines in blends of 10 percent by volume (v%) and 85 v%



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(known as E10 and E85, respectively) in gasoline. However, while there are more than 10 million vehicles in the U.S. which are capable of operating on E85, only a small fraction of these vehicles are actually fueled on the high-level ethanol blend due to availability and consumer behavior. Despite this, U.S. ethanol consumption averaged 850,000 barrels per day in 2011 [23].

RFS2 requires an increase in the use of advanced biofuels up to 36 billion gallons by 2022. While cellulosic ethanol and bio-derived synthetic hydrocarbons are likely candidates to fill the advanced biofuels portion of the RFS2 requirement, longer chain alcohols may also offer potential as advanced biofuels to displace gasoline for spark-ignition (SI) engine applications. Properties of these higher alcohols may, when blended in multi-component mixtures with a gasoline blendstock, create a fuel with improved blend properties such as higher petroleum displacement, improved knock resistance, or increased energy content.

There are many published studies concerning ethanol, n-butanol, and iso-butanol as fuel components. Studies comparing the engine-related properties of alcohols up to carbon number five have also been published [55], but there is a lack of comprehensive information concerning alcohols with carbon numbers higher than five as SI engine fuel components. Replacing gasoline with ethanol results in a substantial reduction in vehicle range, and high ethanol content blends can cause material compatibility issues and require adaptive engine calibrations. In addition, ethanol is fully miscible in water which requires blending at distribution sites instead of the refinery. Higher carbon number alcohols, on the other hand, have a higher energy density and lower affinity for water than ethanol, which could mitigate some of the above mentioned issues. However, little information is available on the combustion characteristics of a majority of the longer-chain alcohols.



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## 1.2 PROJECT HYPOTHESIS

This project aims to demonstrate that blends of alcohols up to carbon number six with gasoline blendstock can serve as a SI engine fuel with properties superior to those of traditional gasoline-ethanol blends.

In order to demonstrate this, alcohol isomers will be chosen for consideration based on their chemical and engine-related properties, metrics will be developed by which to compare fuel blends to traditional ethanol blends, promising blends will be identified based on their estimated chemical and engine-related properties, and promising blends will be tested in a SI engine for emissions and performance.



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## 1.3 PROJECT OBJECTIVES

This project consists of four phases: alcohol selection, comparison metric development, blend comparison, and blend testing, which correspond to the chapters in this document and are illustrated in Figure 1.1. Each phase consists of multiple project objectives which are listed here.

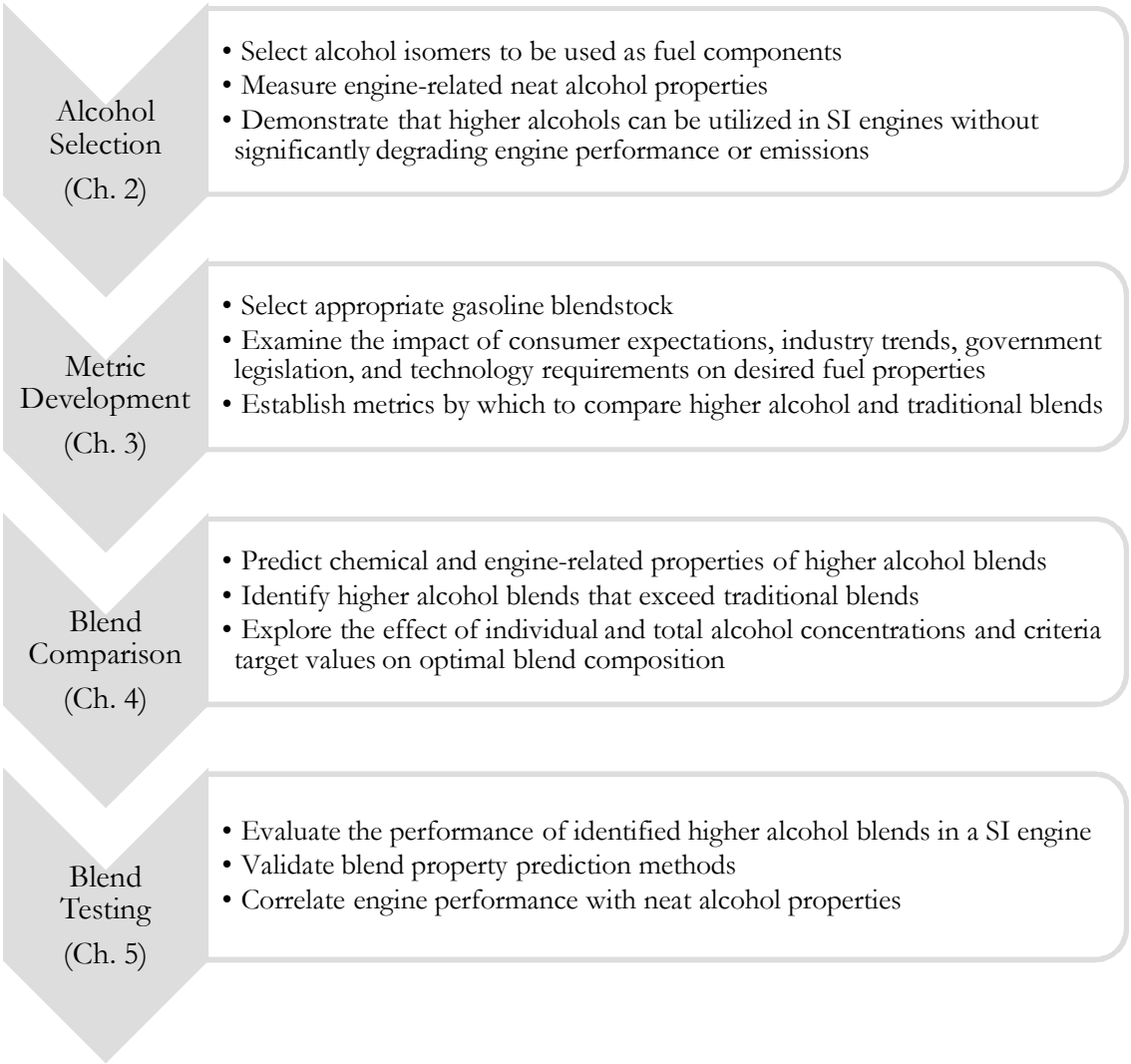


**FIGURE 1.1: PROJECT OBJECTIVES GROUPED INTO FOUR PHASES**



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Phase 1, Alcohol Selection, focused on a theoretical survey of higher alcohols as well as an experimental assessment of two-component blends of gasoline and higher alcohols. A state-of-the-art spark-ignited test engine setup in a dedicated engine test cell was used to evaluate the efficiency, emissions, and performance of the fuel blends. The test results include such basic metrics as engine efficiency, engine performance, and emissions characteristics. Combustion properties were also evaluated on the basis of in-cylinder pressure measurements. Several steady-state test points were chosen to best replicate automotive applications. The outcome of Phase 1 is detailed experimental data that allows for assessment of the potential of higher alcohols and their blends with gasoline as engine fuels.

Criteria for an objective assessment and their importance will be determined in Phase 2, Metric Development. These criteria will include, but are not limited to, evaporative behavior, vehicle range, and knock resistance. A suitable baseline for comparison will also be determined.

Phase 3, Blend Comparison, focuses on analytical work based on the experimental results from Phase 1. By using these data and information available in the literature, chemical properties of multi-component alcohol fuels will be predicted and promising blends will be proposed.

Phase 4, Blend Testing, will focus on experimental analysis of promising multi-component blends as determined from previous phases. The goal of this phase is to experimentally quantify the behavior associated with multi-component blends identified in Phase 3. Characterization will include engine performance and emissions, as well as overall vehicle fuel economy. Additional laboratory testing will be conducted to measure chemical properties of proposed multi-component blends.



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# 2 VIABLE ALCOHOL ISOMERS

**Alcohol Selection** | Metric Development | Blend Comparison | Blend Testing

Chapter 2 details the Alcohol Selection phase of the project, which includes the selection of alcohol isomers to be used as fuel components based on their chemical properties, the measurement of the neat engine-related properties of those isomers, and preliminary engine testing that demonstrates that the chosen isomers can be utilized in a SI engine without significantly degrading engine performance or emissions.

Contents of this Chapter

2.1 Chemical Properties
2.2 RON, MON, LHV, and RVP Measurement
2.3 Engine Testing of 50/50 Blends
2.3.1 Fuel Flowrate, BTE, and $CO_2$ Emissions
2.3.2 CO, HC, and $NO_x$ Emissions
2.3.3 Combustion Properties



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## 2.1 CHEMICAL PROPERTIES

This project began by examining isomers of ethanol, propanol, butanol, pentanol, hexanol, heptanol, and octanol (C2-C8). As listed in Table 2.1, two propanol isomers, four butanol isomers, eight pentanol isomers, 17 hexanol isomers, four heptanol isomers, and four octanol isomers were examined in addition to methanol and ethanol. Data on the most crucial chemical properties of each isomer was compiled. Key properties are presented here and a detailed dataset can be found in Appendix 7.2.

**TABLE 2.1: ISOMERS EXAMINED DURING ALCOHOL SELECTION**

| Carbon # | Isomer | Carbon # | Isomer |
|---|---|---|---|
| 1 | methanol | 6 | 4-methyl-1-pentanol |
| 2 | ethanol | 6 | 2-methyl-2-pentanol |
| 3 | n-propanol | 6 | 3-methyl-2-pentanol |
| 3 | iso-propanol | 6 | 4-methyl-2-pentanol |
| 4 | n-butanol | 6 | 2-methyl-3-pentanol |
| 4 | iso-butanol | 6 | 3-methyl-3-pentanol |
| 4 | sec-butanol | 6 | 2,2-dimethyl-1-butanol |
| 4 | tert-butanol | 6 | 2,3-dimethyl-1-butanol |
| 5 | n-pentanol | 6 | 3,3-dimethyl-1-butanol |
| 5 | iso-pentanol | 6 | 2,3-dimethyl-2-butanol |
| 5 | 2-methyl-1-butanol | 6 | 3,3-dimethyl-2-butanol |
| 5 | 2,2-dimethyl-1-propanol | 6 | 2-ethyl-1-butanol |
| 5 | 2-pentanol | 7 | 1-heptanol |
| 5 | 3-pentanol | 7 | 2-heptanol |
| 5 | 3-methyl-2-butanol | 7 | 3-heptanol |
| 5 | 2-methyl-2-butanol | 7 | 4-heptanol |
| 6 | 1-hexanol | 8 | 1-octanol |
| 6 | 2-hexanol | 8 | 2-octanol |
| 6 | 3-hexanol | 8 | 3-octanol |
| 6 | 2-methyl-1-pentanol | 8 | 4-octanol |
| 6 | 3-methyl-1-pentanol | | |



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Chemical properties deemed crucial and the reason for their importance are listed in Table 2.2. Many chemical properties impact engine performance: heat of vaporization and boiling point effect cold start behavior [56]; volumetric lower heating value determines the overall vehicle range; and octane number reflects the knock resistance of the fuel. Additional chemical properties play an important role in determining if a fuel could be a viable alternative to current fuels: melting point, vapor pressure, solubility, and toxicity effect storage requirements [57]; and production rate impacts availability and cost.

**TABLE 2.2: CRUCIAL CHEMICAL PROPERTIES OF ALCOHOL ISOMERS**

| Property | Reason for consideration |
|---|---|
| Heat of vaporization | Engine cold start performance |
| Lower heating value | Vehicle range |
| Boiling point | Engine cold start performance |
| Melting point | Storage issues |
| Vapor pressure | Storage and safety issues |
| Solubility | Fuel infrastructure requirements |
| Research octane number (RON) | Knock resistance |
| Motor octane number (MON) | Knock resistance |
| Toxicity | Danger of handling |
| U.S. annual production | Availability and pricing |

Data was compiled for all isomers of alcohols of carbon numbers two through six, and the four common isomers of alcohols of carbon numbers seven and eight. This resulted in 41 total isomers for initial consideration as SI engine fuel components. In order to narrow down the choice of alcohol isomers for preliminary engine testing, some isomers were excluded based on unfavorable chemical properties such as melting and boiling point. In addition, iso-hexanol was withdrawn from consideration because of its unusually high cost [58].



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Isomers fell within three categories with respect to the amount of information found in the literature about their chemical properties:

1. all information known;
2. most chemical properties (density, viscosity, etc.) known but no engine-related properties (RON, LHV, etc.) known; or
3. not enough information known to be properly assessed.

Examples of each of these 3 categories are given in Table 2.3 and a complete list is given in Appendix 7.2. Isomers that fell into information category three, 23 total, were withdrawn from the project because it is not likely that they are produced in large enough quantities to be a viable automotive fuel component.

**TABLE 2.3: ISOMER INFORMATION CATEGORIES AND AN EXAMPLE OF EACH**

| Property [12] | Category 1: Ethanol (& 3 other isomers) | Category 2: n-pentanol (& 12 other isomers) | Category 3: 3-heptanol (& 22 other isomers) |
|---|---|---|---|
| **Density [kg/m$^3$]** | 789 | 814 | 828 |
| **Dynamic viscosity [mPa-s]** | 1.2 | 3.33 | |
| **Heat of vaporization [kJ/kg]** | 919.6 | 647.1 | |
| **Lower heating value [MJ/kg]** | 25.541 | 34.74 | |
| **Boiling point [°C]** | 78 | 138 | 163.5 |
| **Melting point [°C]** | -112 | -78.5 | |
| **RVP [psi]** | 2.52 | 0.72 | |
| **Solubility [mol/100g of $H_2O$]** | Miscible | 0.03 | |
| **Stoichiometric AFR** | 9 | 11.76 | |
| **RON** | 107.4 | | |
| **MON** | 88.2 | | |
| **Toxicity (in rats) [mg/kg]** | 7060 | 210 | |
| **U.S. annual production [lb]** | > 1 billion | 10-50 million | |



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Figure 2.1 shows the boiling points of the alcohol isomers, plotted as a function of alcohol oxygen content (ethanol at 34.7 wt% through octanol at 15.7 wt%). Boiling point decreases with oxygen content, or increases with carbon number, due to increasing complexity in chemical structure (more carbon-carbon bonds). Iso-structures have lower boiling points than their corresponding n-structures (and sec- lower than corresponding iso-) because of a decrease in hydrogen bond strength.

The isomers of heptanol and octanol, which are circled in Figure 2.1, have boiling points above 150°C and therefore were withdrawn from consideration. Fuels with high boiling points can make engine operation undependable in cold environments [56]. The ASTM distillation specification for gasoline (D4814) requires at least 65% evaporation at 150°C [10].

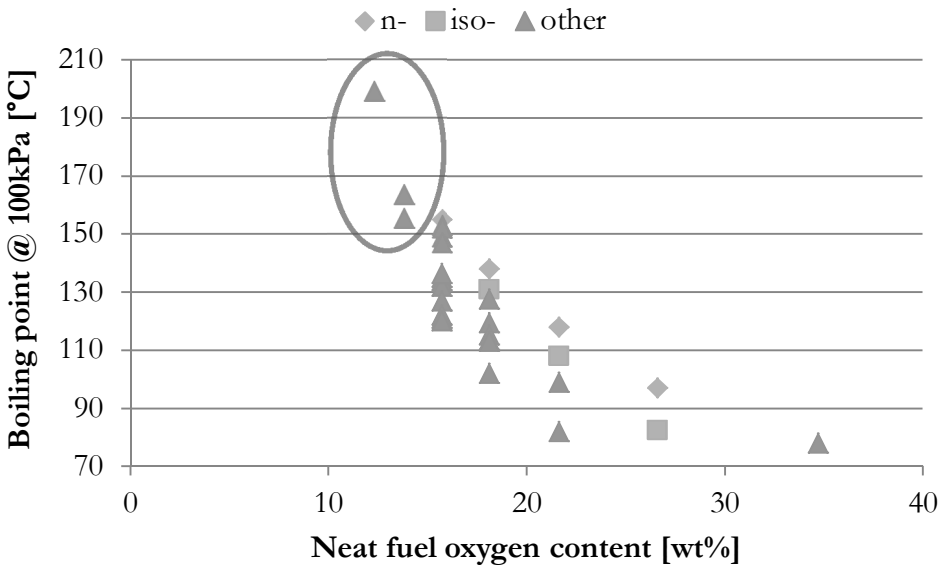


**FIGURE 2.1: BOILING POINT OF ALCOHOL ISOMERS**



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Figure 2.2 shows the melting points of the alcohol isomers, also plotted as a function of alcohol oxygen content. Tert-butanol, which is circled in Figure 2.2, has a melting point above 20°C and therefore was withdrawn from consideration. A melting point near room temperature could complicate storage of the fuel and make it incompatible with current fuel delivery infrastructure and vehicle fuel systems. The melting point of gasoline varies around -50°C [12].

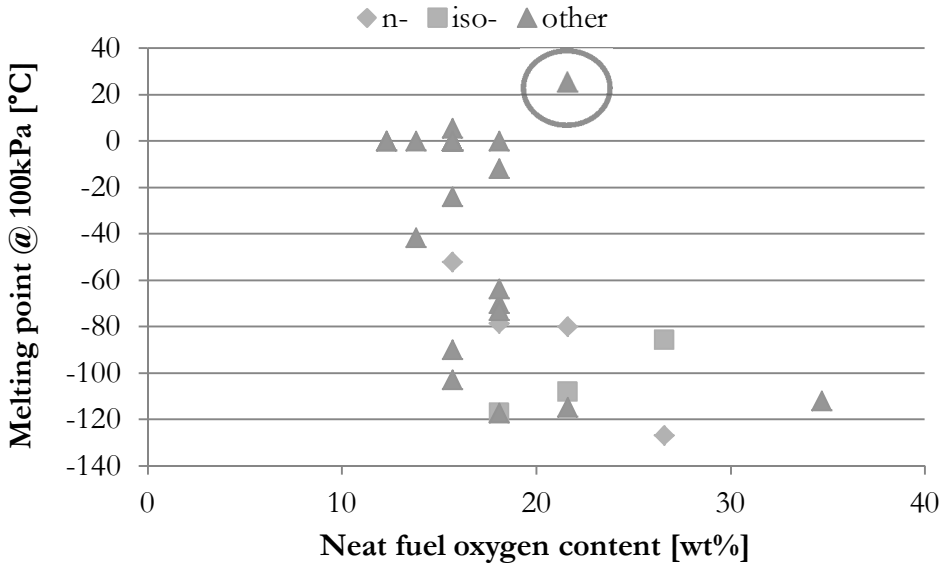


**FIGURE 2.2: MELTING POINT OF ALCOHOL ISOMERS**

Ultimately n- (straight) and iso- (branched) isomers of each alcohol through carbon number six (two isomers of each carbon number) were chosen for preliminary engine testing, with the exception of n-butanol since it has been previously studied by the author's colleagues. All isomers of alcohols with carbon numbers two through four were tested (except n-butanol for which previous data is used and tert-butanol which is a solid at room temperature), along with two common isomers of carbon number five and one of carbon number six. Isomers chosen are listed in Table 2.4.



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**TABLE 2.4: PROPERTIES OF SELECTED ISOMERS AND CERTIFICATION GASOLINE**

| Substance | Carbon # | Energy content[1] [MJ/kg] | Energy content of 50 v% BOB blend[2] [MJ/kg] | Density[3] [kg/m$^3$] | Oxygen content[4] [mass %] |
|---|---|---|---|---|---|
| **gasoline (EEE)** | | 43.0 | | 742 | 0 |
| **ethanol** | 2 | 25.5 | 33.9 | 789 | 34.7 |
| **n-propanol** | 3 | 30.2 | 36.3 | 803 | 26.6 |
| **iso-propanol** | 3 | 29.7 | 36.0 | 786 | 26.6 |
| **n-butanol** | 4 | 32.9 | 37.6 | 810 | 21.6 |
| **iso-butanol** | 4 | 32.7 | 37.6 | 802 | 21.6 |
| **n-pentanol** | 5 | 34.7 | 38.6 | 814 | 18.1 |
| **iso-pentanol** | 5 | 34.5 | 38.5 | 810 | 18.1 |
| **n-hexanol** | 6 | 36.0 | 39.2 | 814 | 15.7 |

[1] Values were measured using ASTM D240.
[2] Values are calculated from the LHV and density of the alcohol and of the BOB.
[3] [59] [60] [61]
[4] Values are calculated form molecular composition and molecular weight.

Denatured ethanol (96.5 v% ethanol, 2.4 v% gasoline, 1 v% water) was mixed with a blendstock for oxygenate blending (BOB) to make a 50/50 blend test fuel. All other isomers chosen for testing, listed in Table 2.4, were purchased from a chemical suppler at 98% or higher purity and then 50/50 splash blended with BOB to create a test fuel. While blending to match oxygen content [62] or vapor pressure are established methods of creating test fuels, blends of 50 percent by volume (v%) alcohol were chosen for this study so that the effects of high blend levels of each alcohol on combustion properties and engine emissions would be highlighted.

The energy content (lower heating value or LHV) of each neat substance and each alcohol blended 50 v% with BOB are given in Table 2.4 along with the density and oxygen content of each substance. Note that the energy content of all of the alcohols is lower than that of certification gasoline, and increases with increasing carbon number or decreasing oxygen content. Most of the alcohols have similar density, all of which are higher than that of certification gasoline.



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## 2.2 RON, MON, LHV, AND RVP MEASUREMENT

Testing for research octane number (RON), motor octane number (MON), lower heating value (LHV), and Reid vapor pressure (RVP) was done by Southwest Research Institute (SwRI) on the neat (not blended) alcohols listed in Table 2.4 so that reliable and consistent data was available for the remainder of the project. The results of this testing are detailed in Appendix 7.3 and plotted along with data for gasoline in Figure 2.3 through Figure 2.6.

Results are plotted as a function of neat fuel oxygen content so that identifying gasoline (zero oxygen) is less convoluted since it can have a range of carbon numbers. Note that the following plots are only meant to show trends for the single alcohols tested, therefore extrapolating based on oxygen content for other alcohols may not yield accurate information. Certification gasoline and a Blendstock for Oxygenate Blending, or BOB, are plotted along with the alcohols for reference. Certification gasoline has slightly different properties than pump gasoline, such as higher RON and MON and lower RVP [59].

Figure 2.3 and Figure 2.4 show the RON and MON of the alcohols as a function of neat fuel oxygen content. RON and MON are measures of a fuel's knock resistance. Both the isomer's chain length and location of carbon atoms affect the strength of molecular bonds and therefore the fuel's knock resistance. Straight chain alcohols (n- isomers) have secondary carbon-hydrogen bonds which are significantly weaker than the primary bonds found in branched chain (iso- isomers) alcohols, which makes them easier to autoignite. This results in the increase in RON and MON from the n- to the iso- structure shown in the figures. Alcohols with higher carbon numbers have longer chain lengths and a higher number of the weak secondary bonds, which results in a 30% decrease in RON and a 25% decrease in MON from n-butanol to n-hexanol.



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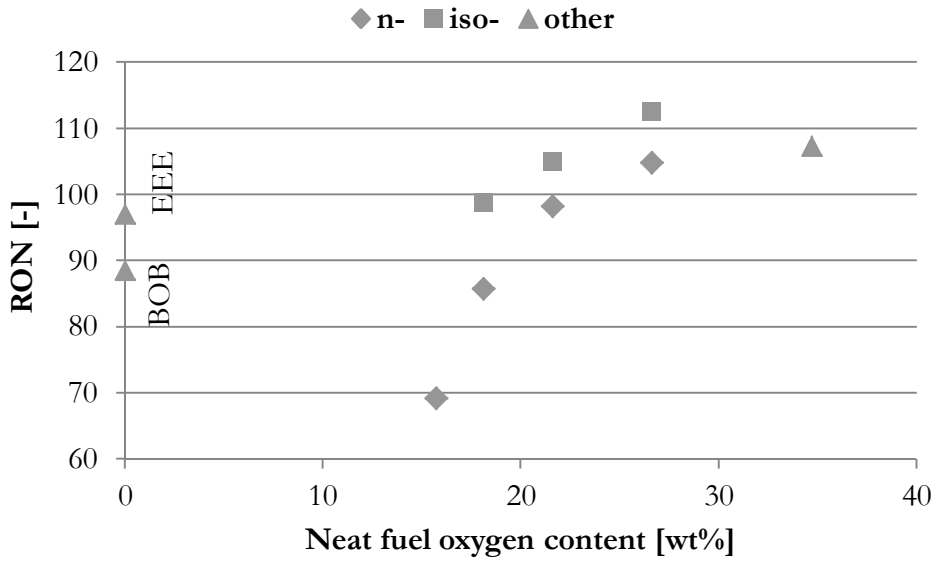


**FIGURE 2.3: RON OF NEAT ALCOHOLS**

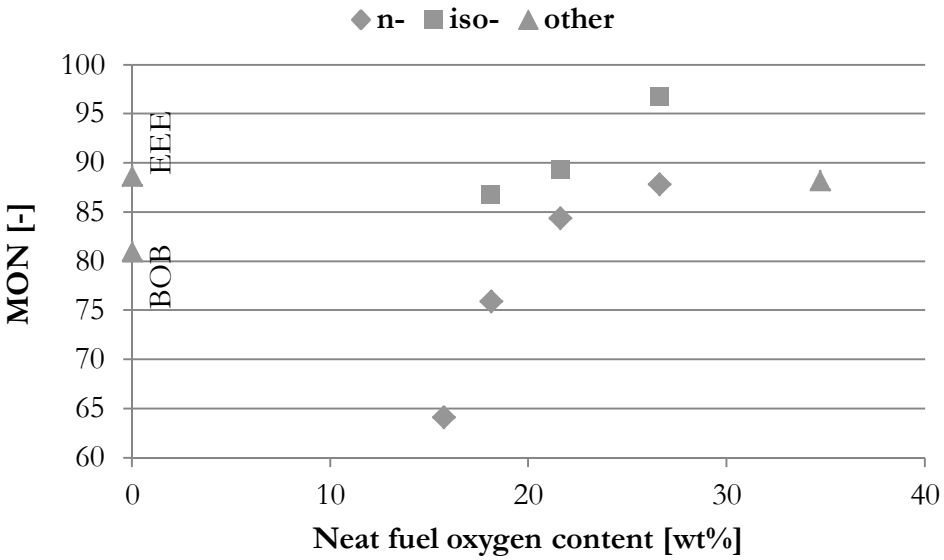


**FIGURE 2.4: MON OF NEAT ALCOHOLS**



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Figure 2.5 shows the lower heating value (energy content) of the neat alcohols as a function of oxygen content. Lower heating value (LHV) linearly decreases with increasing oxygen content. An isomer with a higher carbon number has more carbon-carbon bonds that are broken during combustion. An increase in the number of chemical bonds in addition to a lower mass percentage of oxygen increases the change in enthalpy during combustion which results in a higher heating value [12]. Note that the neat alcohols have LHV values between 16 and 40% lower than those of certification gasoline and BOB.

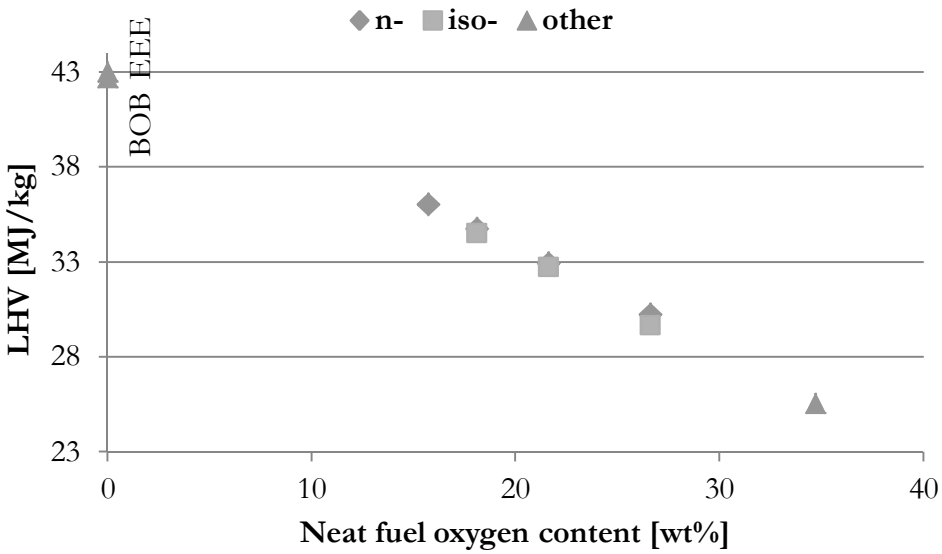


**FIGURE 2.5: LHV OF NEAT ALCOHOLS**



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RVP is plotted as a function of neat fuel oxygen content in Figure 2.6. RVP linearly increases with increasing oxygen content and all of the alcohols have much lower (between 57 and 95% lower) vapor pressure than certification gasoline and BOB. The test for RVP is only applicable for samples that exert pressures between 1.0 and 18.6 psi so the results for some of the alcohols may not be accurate [63].

RVP is related to boiling point and volatility. A higher RVP corresponds to a lower boiling point and increased volatility. RVP is a critical property for fuels since high RVPs will cause excess evaporative emissions and low RVPs will make the engine difficult to start in cold temperatures. ASTM standards require RVPs between 7.8 and 15.0 psi for gasoline, depending on geographical location and season [11].

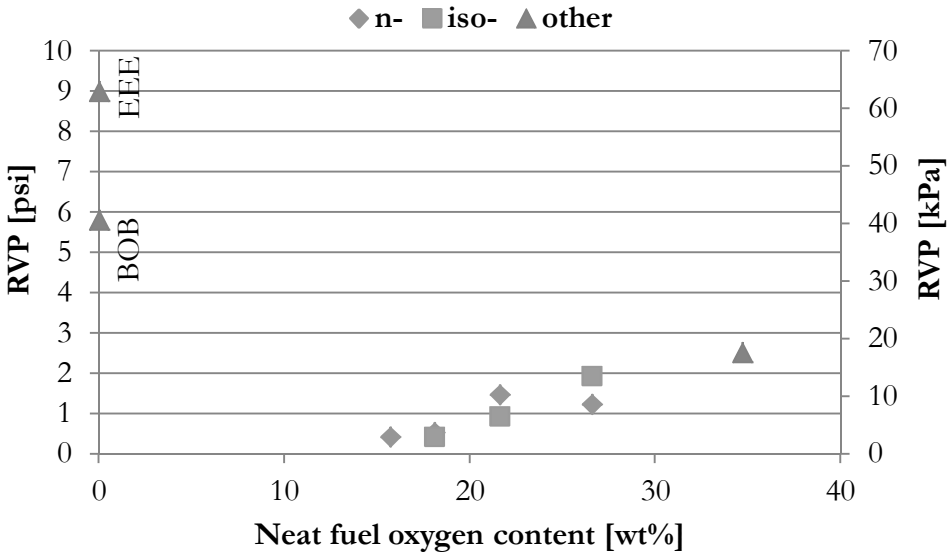


**FIGURE 2.6: RVP OF NEAT ALCOHOLS**



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In addition to the properties measured in laboratory analytical testing at SwRI, the heat of vaporization (HoV) of each of the alcohol isomers was examined. Figure 2.7 is a plot of HoV on a mass basis (left axis) and an energy content basis (right axis) of the neat alcohols as a function of oxygen content. The HoV of each alcohol by gasoline mass equivalent is calculated by multiplying the alcohol's HoV by the ratio of the LHV of gasoline to the LHV of the alcohol. This calculation normalizes HoV for different LHVs. HoV increases linearly with increasing oxygen content. All of the alcohols have higher (138 to 314%) HoV than EEE certification gasoline.

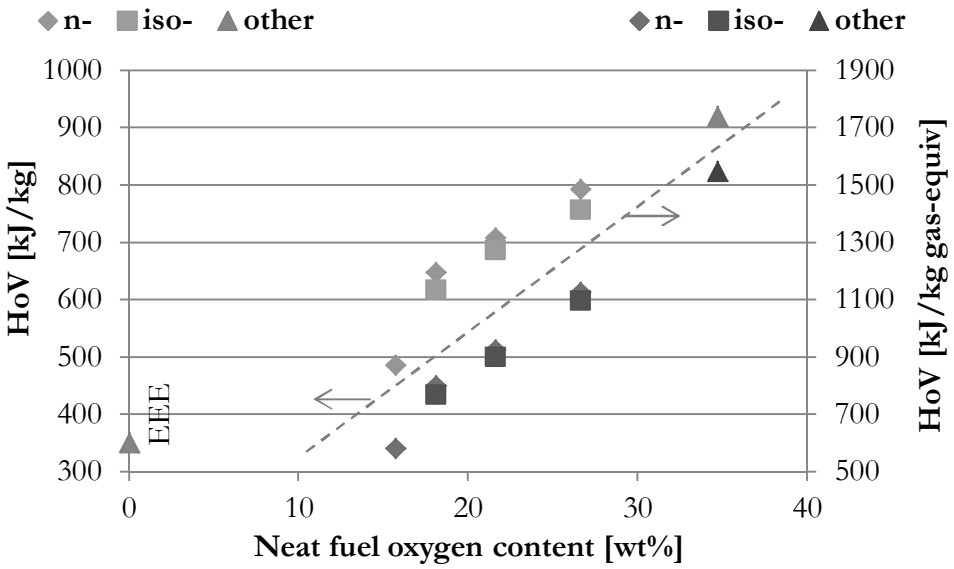


**FIGURE 2.7: HOV OF NEAT ALCOHOLS**

HoV is an important fuel property because of the charge cooling effect during fuel vaporization. Fuels with a higher HoV require more energy to change phase. When running at stoichiometric conditions, neat ethanol's charge cooling effect is about four times that of neat gasoline. Neat n-hexanol's charge cooling effect is about 165% that of neat gasoline. Increasing HoV coupled with decreasing stoichiometric AFR (captured by the gasoline equivalent HoV) as oxygen content increases results in lower cylinder temperatures because of the increasing charge cooling effect. The additional energy required to vaporize a fuel with a higher HoV results in a lower cylinder temperature during the compression stroke which leads to reduced temperatures throughout the entire engine cycle.



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## 2.3 Engine Testing of 50/50 Blends

Blends of 50 v% blendstock for oxygenate blending (BOB) and 50 v% of each alcohol listed in Table 2.4 were tested to identify any significant degradation in engine performance or emissions due to the high fraction of each alcohol. The blends tested and their properties are listed in Table 2.5. EEE certification gasoline was also tested for reference. Provided none of the test fuels exhibited a large increase in emissions or decrease in engine performance, each of the alcohols would be deemed viable engine fuel components and used throughout the remainder of the project.

**TABLE 2.5: PROPERTIES OF 50/50 BLEND FUELS USED IN ENGINE TESTING**

| Fuel | Oxygen [wt%] | LHV [MJ/kg] | Density [kg/m$^3$] | RON* [-] | HoV [kJ/kg] | RVP* [psi] | $AFR_s$ [-] |
|---|---|---|---|---|---|---|---|
| **EEE** | 0.0 | 43.0 | 742 | 97.1 | 351* | 9.0 | 14.7 |
| **eth50** | 17.8 | 33.9 | 771 | 103.8 | 642 | 6.3 | 12.0 |
| **nprop50** | 13.7 | 36.3 | 778 | 101.3 | 579 | 5.1 | 12.7 |
| **iprop50** | 13.6 | 36.1 | 769 | 107.1 | 558 | 5.5 | 12.7 |
| **nbut50** | 11.2 | 37.6 | 781 | 95.7 | 536 | 4.4 | 13.1 |
| **ibut50** | 11.1 | 37.6 | 777 | 100.5 | 524 | 4.4 | 13.1 |
| **npent50** | 9.4 | 38.6 | 783 | 86.6 | 505 | 4.2 | 13.4 |
| **ipent50** | 9.4 | 38.5 | 781 | 95.4 | 489 | 4.2 | 13.4 |
| **nhex50** | 8.2 | 39.2 | 783 | 75.7 | 421 | 4.2 | 13.6 |

*Values are calculated using the methods outlined in Section 4.1.

The oxygen content, energy content, density, calculated knock resistance, heat of vaporization, calculated vapor pressure, and stoichiometric air/fuel ratio of the 50/50 blends are listed in Table 2.5. RON and RVP are calculated as detailed in Section 4.1. In Table 2.5, three groups of fuels are highlighted: those with RON similar to EEE in dark gray (nbut50 and ipent50), those with RON significantly higher than EEE in light gray (eth50, nprop50, iprop50, and ibut50), and those with RON significantly lower than EEE in white (npent50 and nhex50). The LHV of all of the test fuels is lower than that of EEE, ranging from 9% (nhex50) to 21% (eth50) lower. The RVP of all of the fuels is also lower than that of EEE, ranging from 4.2 (nhex50) to 6.3 psi (eth50).

The 50/50 blend tests were run in a 2.4L Hyundai engine. The engine is a gasoline direct-injected (GDI), naturally aspirated (NA), spark-ignited (SI) 4 cylinder with exhaust gas



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recirculation (EGR) and knock detection systems. Details on the engine and the test equipment used can be found in Appendix 7.4.

The engine operating points chosen for steady-state engine testing are listed in Table 2.6 and illustrated in Figure 2.8 along with the test engine's peak performance curve. The worldwide mapping point (1500 rpm, 2.62 bar) was chosen to make comparing the results of this project to other projects more direct. The other four points were chosen to allow for same power, same speed, and same load comparisons as well as demonstrate the effects of high load and high speed. All tests were run at a stoichiometric air/fuel ratio. Emissions and combustion data was collected for 240 seconds at each operating point and then averaged.

**TABLE 2.6: ENGINE OPERATING POINTS FOR BLEND TESTING**

| Speed [rpm] | BMEP [bar] |
|---|---|
| 1500 | 2.62 |
| 1500 | 4.0 |
| 1500 | 8.0 |
| 3000 | 4.0 |
| 3000 | 8.0 |

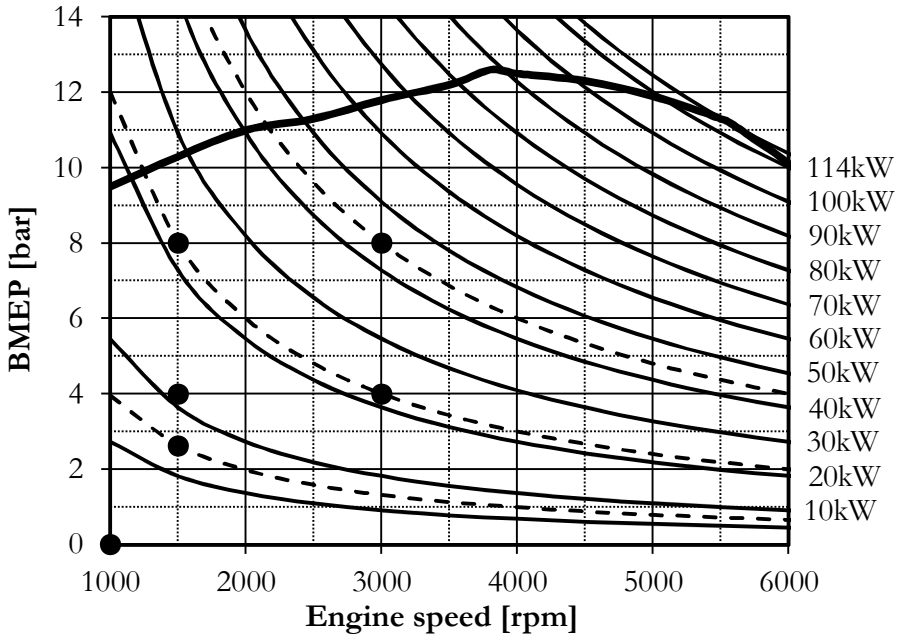


**FIGURE 2.8: ENGINE OPERATING POINTS**



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Engine testing results are plotted as a function of the blend oxygen content (values are listed in "Oxygen" column in Table 2.5). Note that increasing blend oxygen content (left to right on the x-axis in the plots) is decreasing carbon number for the alcohols (hexanol on the left at 8.2 to ethanol on the right at 17.8 wt%). EEE is shown at 0 wt% blend oxygen content. The n-hexanol blend does not appear in the 1500 rpm, 8 bar plots because the engine knocked too heavily for those tests to be completed.

Note that the following plots are only meant to show trends for the alcohols tested, therefore extrapolating based on oxygen content for other alcohols may not yield accurate information. Where two data points for a fuel at one operating point are shown, two test sessions were completed to help demonstrate the precision of the data.

### 2.3.1 Fuel Flowrate, BTE, and $CO_2$ Emissions

The fuel flowrate for each of the 50/50 blends is shown in Figure 2.9. As expected, fuel flowrate increases with increasing blend oxygen content at all engine operating points. The increase in flowrate is to compensate for the decrease in LHV and stoichiometric AFR as oxygen content increases.

Brake thermal efficiency (BTE) of each 50/50 blend at each engine operating point is plotted in Figure 2.10.. The plot is divided vertically by engine operating point. BTE is calculated using engine speed, engine torque, and the energy content of the fuel as shown in Equation 1. Nhex50 could not be run at 1500 rpm, 8 bar or at 3000 rpm, 8 bar because of engine knock. The LHV of each of the neat alcohols is used to calculate the LHV of each 50/50 blend.

$$BTE = \frac{engine\ speed * engine\ torque}{LHV * fuel\ flowrate} \quad \textbf{(1)}$$

Error is introduced into the BTE calculation from the measurement of each neat alcohol's LHV. The LHV measurement procedure mandates that a mass quantity of liquid fuel is combusted. The energy required to vaporize the liquid reduces the measured energy content of the fuel [64]. This causes an overestimation of efficiencies with higher heat of vaporization. The corrected BTE, which is calculated using the HoV and LHV from Table 2.5 according to Equation 2, is plotted in Figure 2.10 along with the raw BTE calculated with Equation 1.



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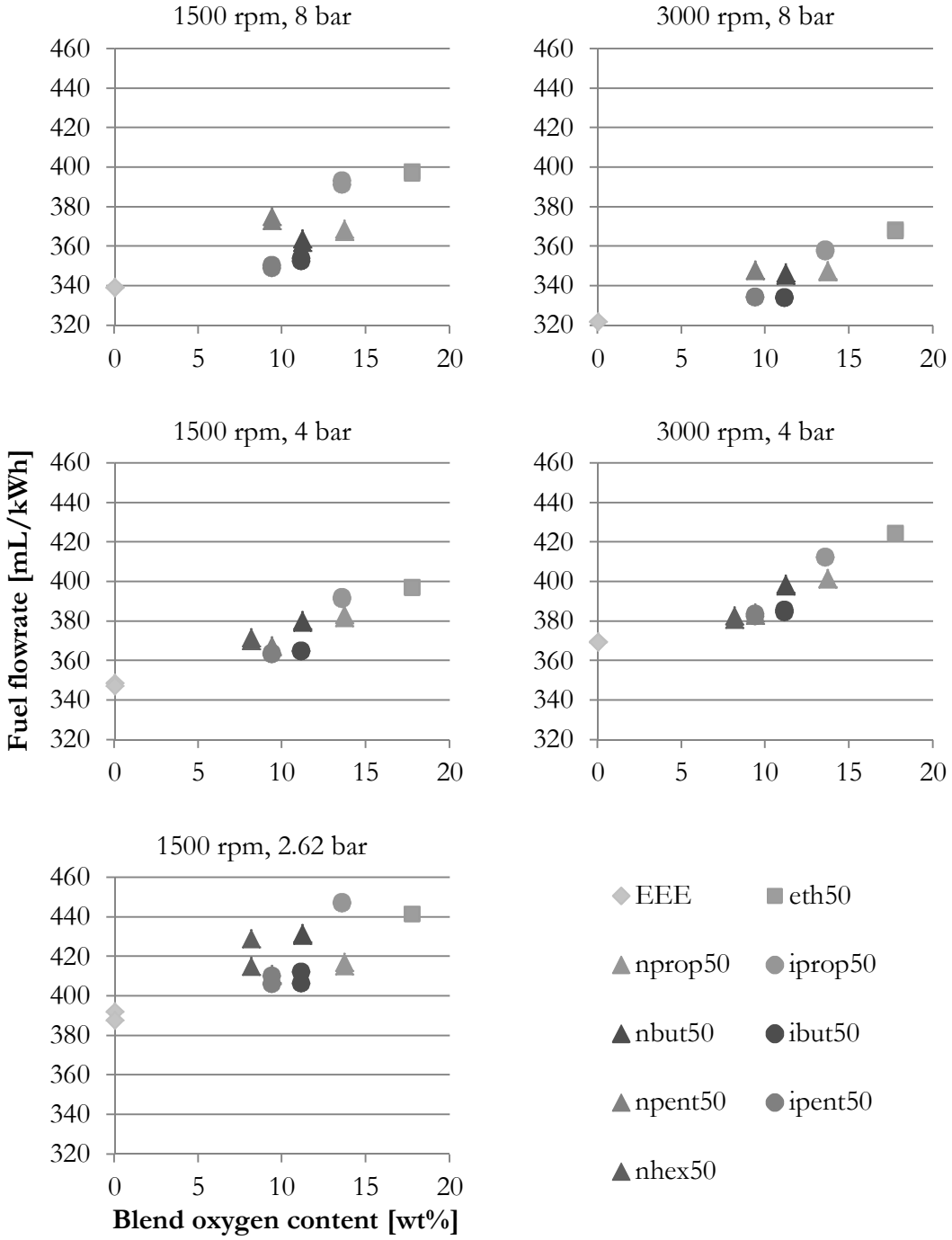


**FIGURE 2.9: FUEL FLOWRATE OF 50/50 BLENDS AT EACH OPERATING POINT**



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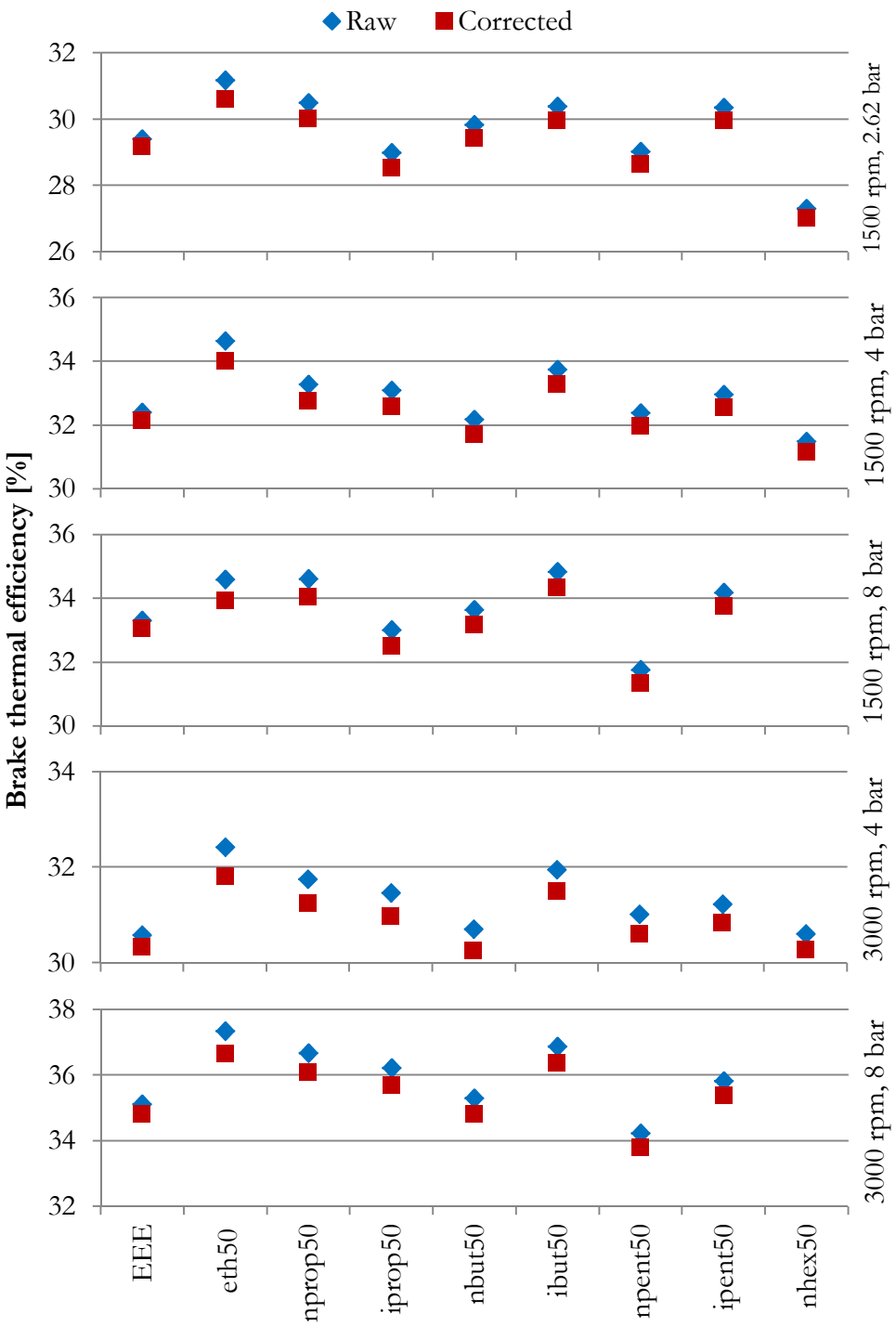


**FIGURE 2.10: BTE OF 50/50 BLENDS AT EACH OPERATING POINT**



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$$BTE_{corrected} = \frac{engine\ speed * engine\ torque}{(LHV + HoV) * fuel\ flowrate} \quad (2)$$

As shown in Figure 2.10, the differences between raw and corrected BTE numbers are not insignificant and decrease with increasing carbon number due to the decreasing HoV. The main factors influencing the remaining BTE differences are combustion phasing and heat transfer. Two categories of operating points have to be differentiated when analyzing BTE results: 1) knock-limited operation at medium and high engine load, and 2) non-knock-limited operation at low engine loads.

For example, npent50 shows significantly reduced efficiencies in knock-limited operation at the two 8 bar operating points which is mainly due to the retarded combustion phasing as a result of knock. Operating points that are not knock-limited, such as 3000 rpm, 4 bar also show differences in corrected BTE results. These differences are likely attributable to a combination of reduced wall heat transfer losses due to lower cycle temperature levels for blends with high HoV and more favorable combustion phasing at constant spark timing as a result of slower-burning velocities. This also explains the efficiency advantages of the slower-burning iso- isomers compared to their respective n- isomers.

$CO_2$ emissions are a result of complete combustion and are a function of BTE as well as the molecular hydrogen-to-carbon (H/C) ratio of the fuel. The H/C ratio of the tested fuels ranges from 1.87 for EEE to 2.35 for the eth50 blend. Thus, the strictly inverse trend of $CO_2$ emissions with BTE is shifted due to the changes in H/C ratio. The change in H/C ratio is estimated to result in a decrease in $CO_2$ emissions from gasoline to pure ethanol of approximately 3% [64]; thus the effect for eth50 compared to EEE would be approximately 1.5% with a further decrease in impact for higher carbon number alcohols.

Figure 2.11 compares the $CO_2$ emissions for all tested blends at each engine operating point. The majority of the blends have $CO_2$ emissions lower than those of EEE and $CO_2$ emissions generally increase with increasing carbon number among the alcohol fuels. This corresponds with BTE trends, while the H/C ratio impact diminishes with higher carbon number.



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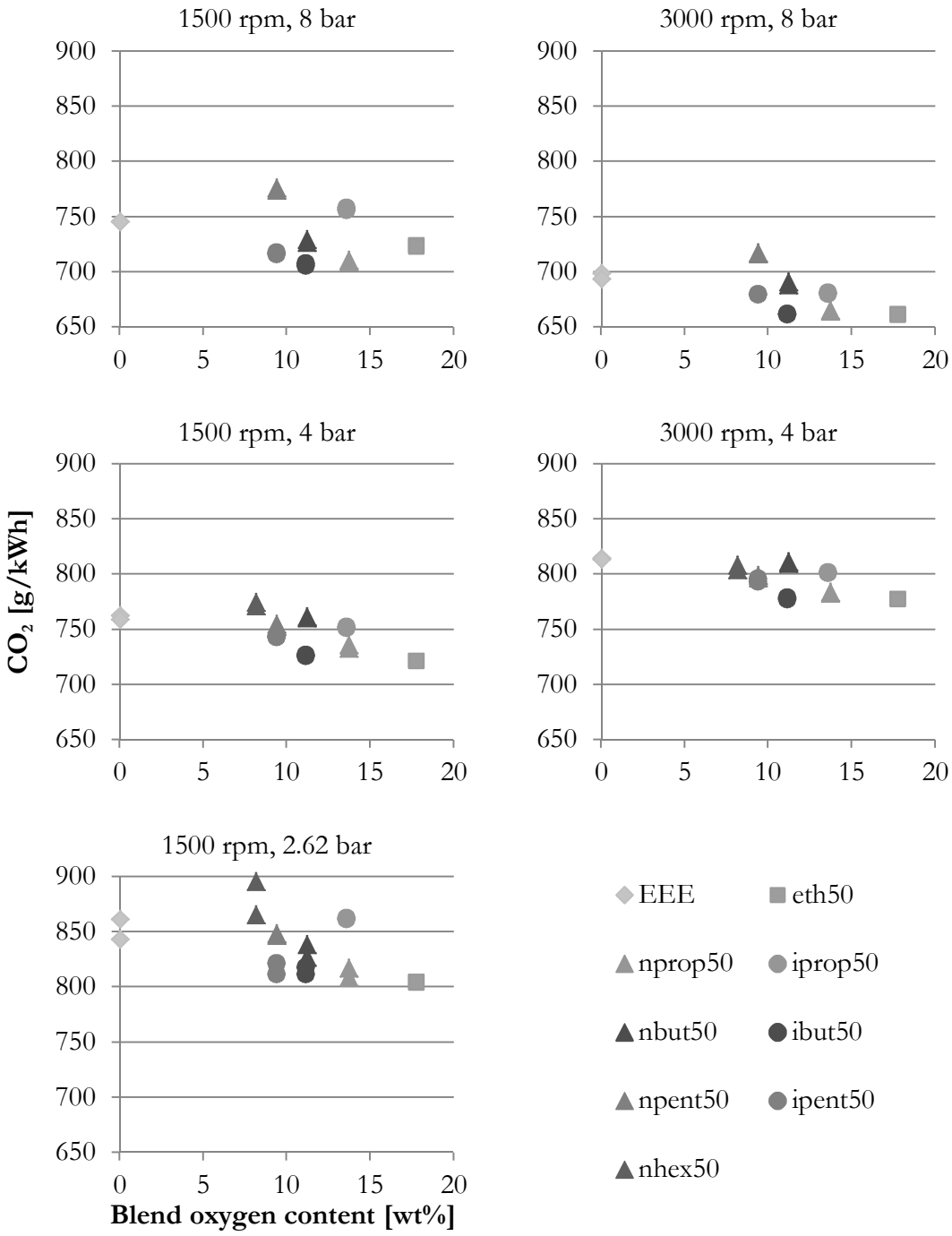


**FIGURE 2.11: $CO_2$ EMISSIONS OF 50/50 BLENDS AT EACH OPERATING POINT**



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### 2.3.2 CO, HC, AND $NO_X$ EMISSIONS

Figure 2.12 shows carbon monoxide (CO) emissions of each alcohol blend at each engine operating point as a function of blend oxygen content. CO emissions trends are inconsistent and of the same magnitude as that of EEE at each operating point. The smallest difference, 1.7%, is that of npent50 at 1500 rpm, 8 bar while the largest variation from EEE, 17.1%, is that of ibut50 at 3000 rpm, 4 bar.

Iprop50 and ipent50 generally have slightly higher CO emissions than their corresponding n- alcohol fuels, but ibut50 has lower emissions than nbut50. Therefore, it is difficult to find a definite trend in CO emissions based on isomer structure. There is also no apparent trend in CO emissions with alcohol carbon number.

Figure 2.13 shows the uncorrected hydrocarbon (HC) emissions of each alcohol blend at each engine operating point as a function of blend oxygen content. All of the alcohol blends have lower HC emissions that those of EEE at each engine operating point. HC emissions decrease with increasing blend oxygen content at all operating points.

CO and HC emissions are primarily controlled by the air/fuel ratio. Since all engine tests were run at tightly controlled stoichiometric conditions, neither CO nor HC emissions were expected to vary greatly from EEE. The HC emissions shown are not corrected for FID sensitivity[1] and therefore slightly underestimate the actual values.

$NO_x$ emissions of each alcohol blend at each engine operating point are shown in Figure 2.14 as a function of blend oxygen content. $NO_x$ emissions generally decrease with decreasing carbon number for most of the operating points. At all engine operating points, $NO_x$ emissions decrease with decreasing carbon number among the iso- isomers. $NO_x$ emissions of the n- isomers slightly increase with decreasing carbon number at each of the 1500 rpm operating points, but exponentially increase at 3000 rpm, 8 bar and slightly decrease at 3000 rpm, 4 bar.

[1] "FID sensitivity" refers to the ability of the Flame Ionization Detector (FID) emissions measurement system to correctly report HC emissions for a fuel that contains oxygen. Refer to SAE publication 2010-01-1571 for more information.



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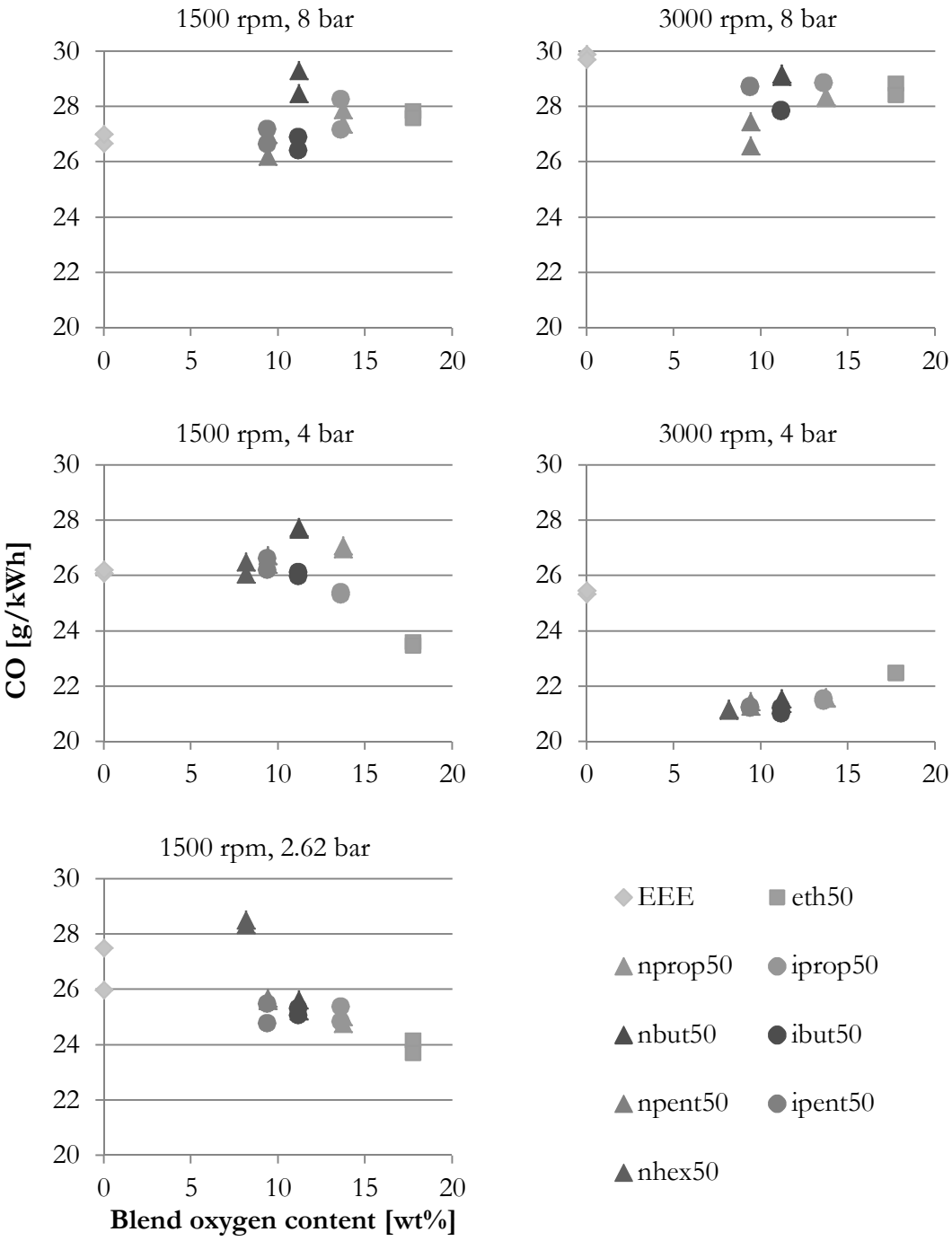


**FIGURE 2.12: CO EMISSIONS OF 50/50 BLENDS AT EACH OPERATING POINT**



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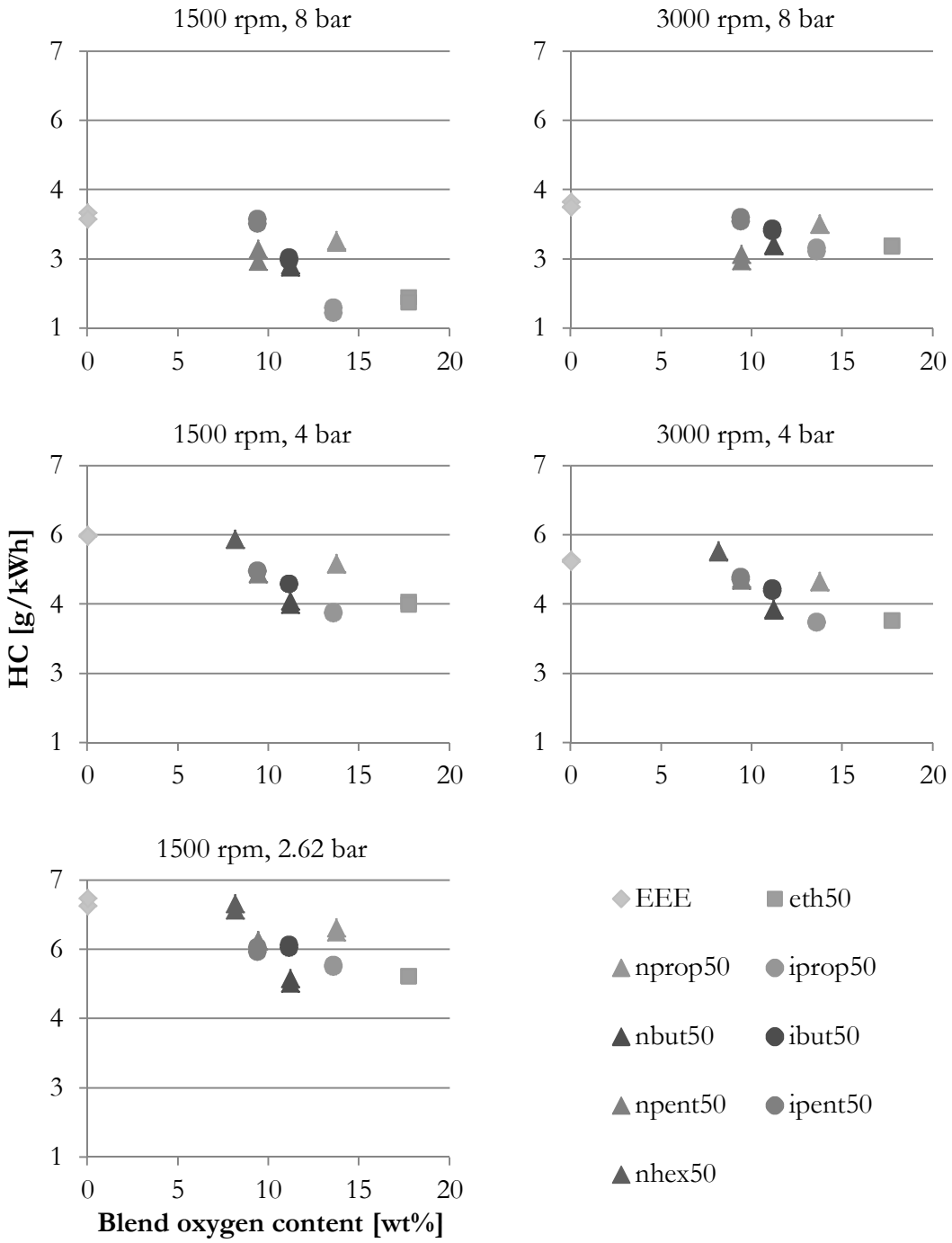


**FIGURE 2.13: HC EMISSIONS OF 50/50 BLENDS AT EACH OPERATING POINT**



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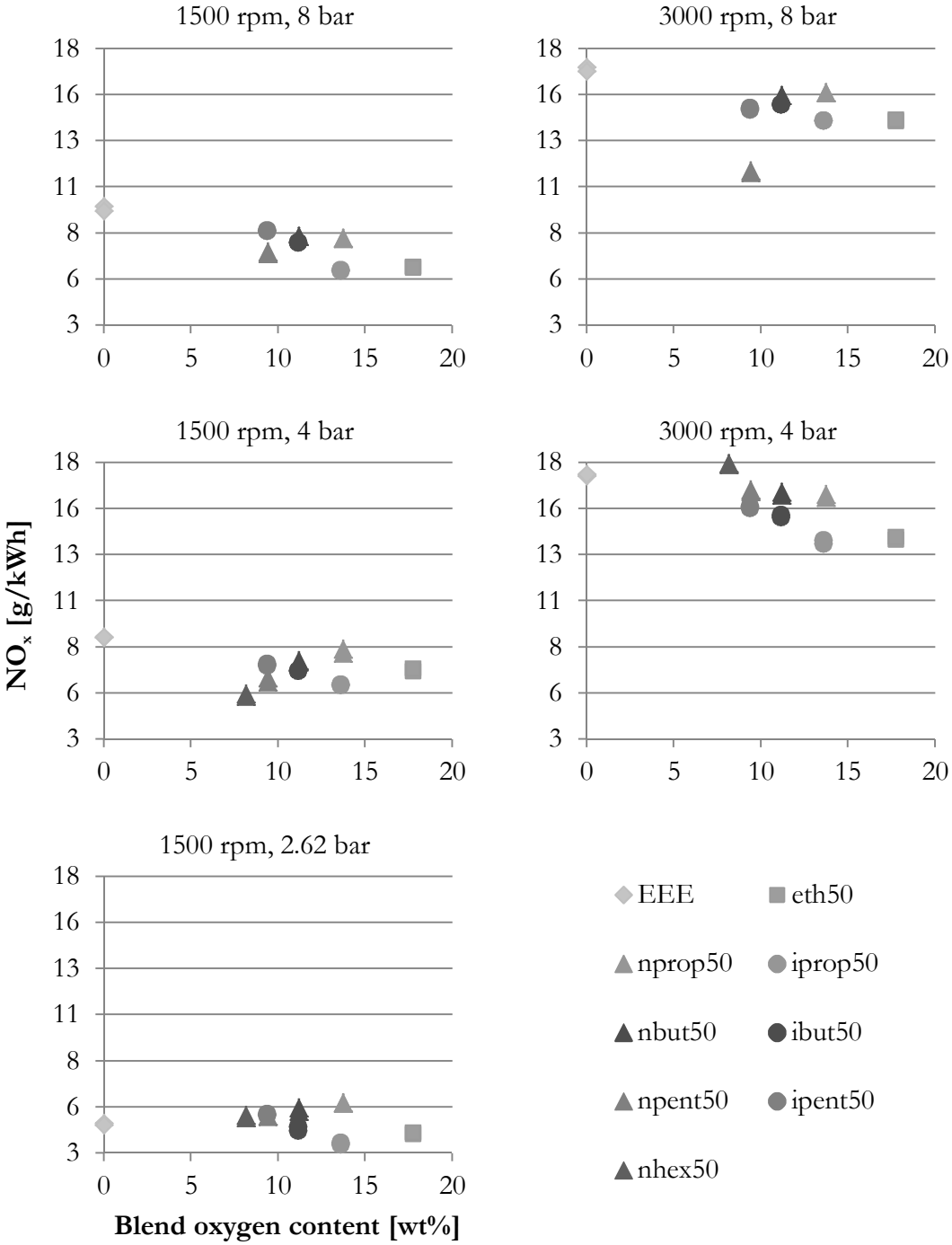


**FIGURE 2.14: $NO_X$ EMISSIONS OF 50/50 BLENDS AT EACH OPERATING POINT**



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$NO_x$ emissions are primarily driven by cylinder temperature. The higher fuel flowrate coupled with the higher HoV for fuels with increasing oxygen content results in lower cylinder temperatures and therefore lower $NO_x$ emissions. Most of the alcohol blends have $NO_x$ emissions lower than those of EEE at all of the engine operating points. These results are in agreement with other studies on high level blends of ethanol and butanol [65].

### 2.3.3 Combustion Properties

Combustion properties such as spark timing, knock occurrence, cylinder pressure, rate of heat release, and flame propagation rate of the 50/50 blends are examined here.

#### 2.3.3.1 Spark Timing

The spark timing change from EEE for each alcohol blend at each engine operating point is shown in Figure 2.15. At each operating point, 500 cycles were averaged for each cylinder. The average of all four cylinders was used to calculate the change in spark timing shown in the figure. Each fuel was run with stock ECU settings. The ECU retards the spark timing of each cylinder individually if knock is detected.

Spark timing was not retarded while testing ethanol, the propanols, or the butanols since they have a RON similar to that of EEE. Spark timing was retarded approximately 4 degrees for npent50 at 1500 rpm, 4 bar and 1500 rpm, 8 bar and approximately 10 degrees at 3000 rpm, 8 bar. Spark timing was retarded approximately 9 degrees for nhex50 at 1500 rpm, 4 bar. At low load the spark timing of npent50 and nhex50 are within 2° of EEE, but as load is increased the spark timing of npent50 and nhex50 are retarded compared to EEE.

The change in spark timing for npent50 and nhex50 suggests that knock resistance decreases with increasing carbon number and that iso- structures have higher knock resistance than n- structures. This is consistent with the RON and MON results illustrated in Figure 2.3 and Figure 2.4.



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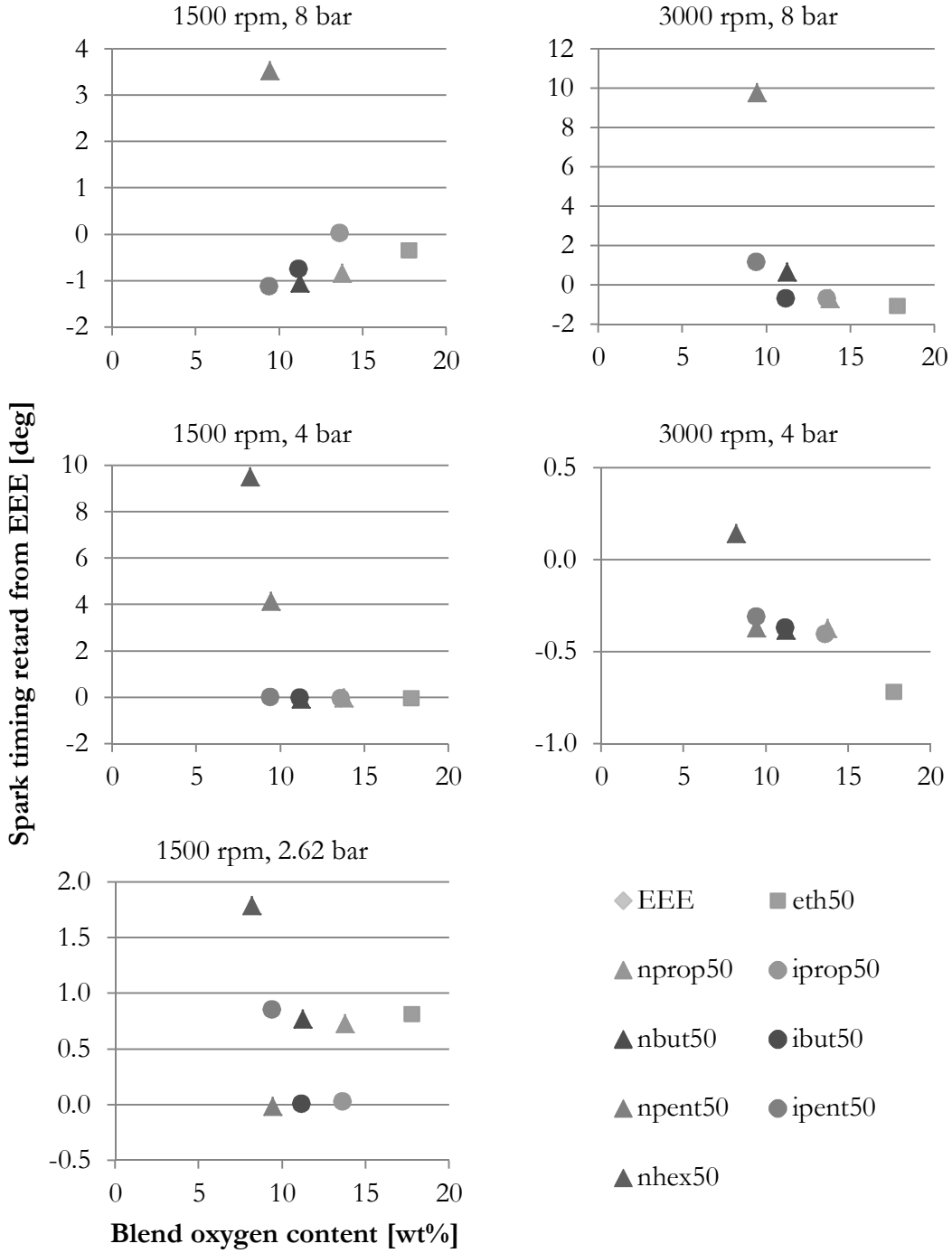


**FIGURE 2.15: SPARK TIMING RETARD FROM EEE GASOLINE FOR 50/50 BLENDS AT EACH OPERATING POINT**



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#### 2.3.3.2 KNOCK OCCURRENCE

To obtain a clearer quantification of the knocking behavior of the test fuels, further engine tests were conducted with the knock sensor disabled, eliminating the spark retard observed in earlier tests and using calibrated spark timing only. Test fuels were limited to EEE and 50 v% blends of ethanol, iso-propanol, iso-butanol, and iso-pentanol. Operating conditions were comprised of a sweep of engine load at 1500 rpm, across an approximate range of 4 to 8.5 bar BMEP.

Knocking behavior is quantified by analysis of high-speed cylinder pressure data. A sharp increase in cylinder pressure is characteristic of knock. Also, since knock is the autoignition of the end-gas mixture (fuel-air mixture ahead of the propagating flame), it generally occurs in the later stages of the combustion process. Therefore, the magnitude and location of the peak pressure rise rate (PPRR), the greatest increase in cylinder pressure per unit time within a cycle, is a clear indicator of knock.

Figure 2.16 shows the peak pressure rise rate as a function of when it occurs within the engine cycle for EEE, eth50, iprop50, ibut50, and ipent50. Cycles with high magnitude and later-phased PPRRs are considered to be knocking cycles. Cycles in the non-knocking region have earlier-phased PPRR with lower magnitudes compared to those in the knocking region.



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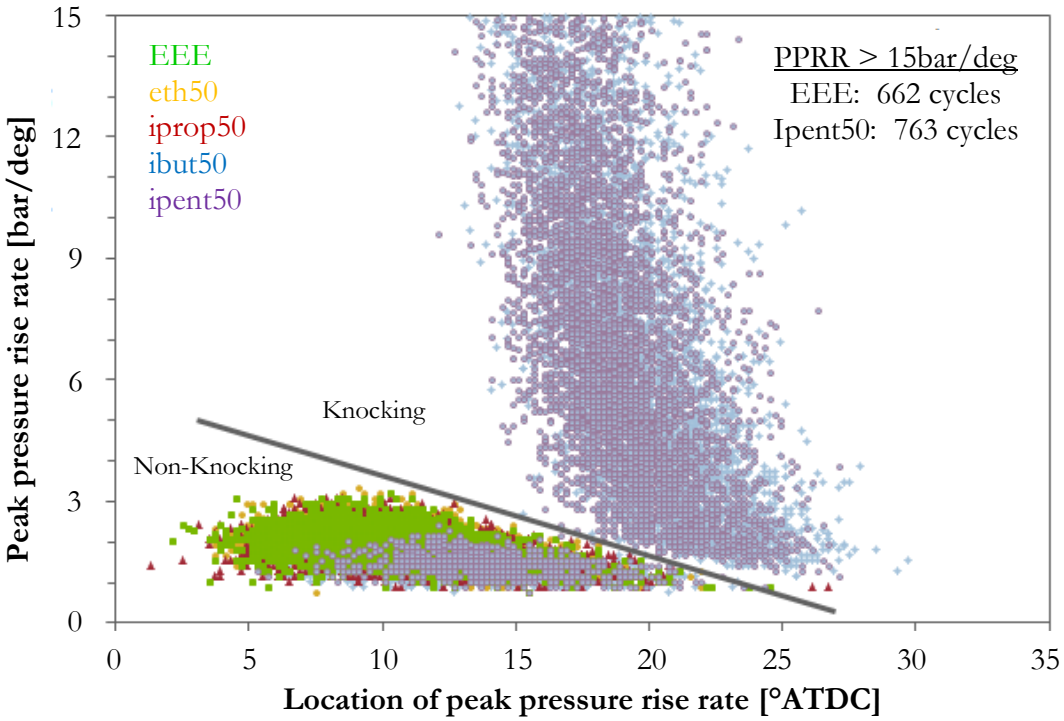


**FIGURE 2.16: CHARACTERIZATION OF KNOCK BASED ON LOCATION AND MAGNITUDE OF PPRR AT 1500 RPM**

Knock intensity trends with the magnitude of the PPRR (more severe knock yields higher PPRR) and with earlier phasing (earlier phasing suggests a greater quantity of end-gas mixture is autoigniting). A clear distinction between the knocking and non-knocking regions can be readily identified which allows cycle classification. This methodology was applied to all tested conditions in the load sweep to characterize the knock behavior across the range of conditions tested.

Knock prevalence, or the percentage of cycles identified as knocking, is shown as a function of load for each fuel in Figure 2.17. Data for this figure was measured at an engine speed of 1500 rpm and across a range of BMEP with both the EGR and knock sensor disabled. At each point, 1500 engine cycles were analyzed.

The blends of gasoline with ethanol, iso-propanol, and iso-butanol demonstrate almost no tendency to knock across the range of tested conditions; with less than 1% of cycles identified as knocking (this is not considered a significant number given the applied



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methodology). The iso-pentanol blend demonstrated comparable knocking behavior to the neat certification gasoline, with both fuels peaking around 75% knocking cycles.

A reduction from the peak level of knocking occurs at the very high load points and is tied to a retard in the calibrated spark timing. As identified in Figure 2.3 and Figure 2.4, the octane numbers (RON, MON) of ethanol (107, 88), iso-propanol (113, 97), and iso-butanol (105, 89) are greater than that of the certification gasoline (97, 89), which matches their observed knocking behavior. The octane numbers of iso-pentanol (99, 87) are close matches to the certification gasoline, as is the 50/50 blend's knock behavior. This suggests that trends of octane number, as measured on a CFR rating engine, generally correspond to observed knock behavior in the modern direct-injection test engine used in this study.

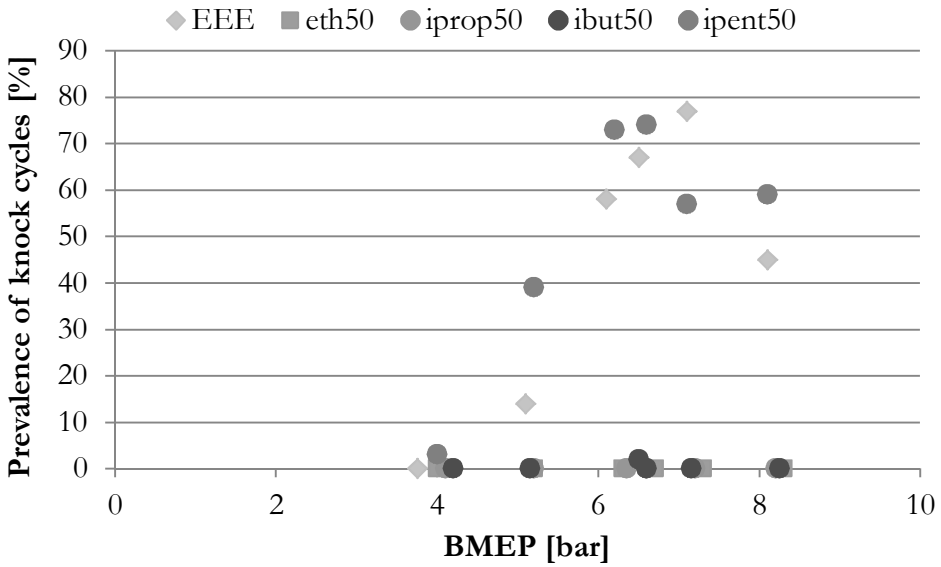


**FIGURE 2.17: PREVALENCE OF KNOCK FOR 50/50 BLENDS AT 1500 RPM**

#### 2.3.3.3 CYLINDER PRESSURE AND ROHR

A trace of average cylinder pressure and average rate of heat release (ROHR) for each of the fuels at 3000 rpm, 4 bar is shown in Figure 2.18. This engine speed and load chosen because each of the fuels could be run at equal spark timing, allowing for a direct comparison of cylinder pressure and ROHR. At this engine operating point, 500 cycles were averaged for each cylinder. The average of all four cylinders is shown in the figure.

The cylinder pressure traces show slight differences in the fuels. The peak cylinder pressures, from highest to lowest, are: nhex50 (32.7 bar), npent50, nbut50, nprop50,



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eth50, EEE, ipent50, ibut50, and iprop50 (30.5 bar). The fuels composed of n- isomer alcohols have the highest peak cylinder pressures while the iso- alcohol fuels have the lowest. The location of peak pressure moves slightly as the peak value decreases; from nhex50's peak at 11° to iprop50's peak at 13°. The ROHR traces show the same trends.

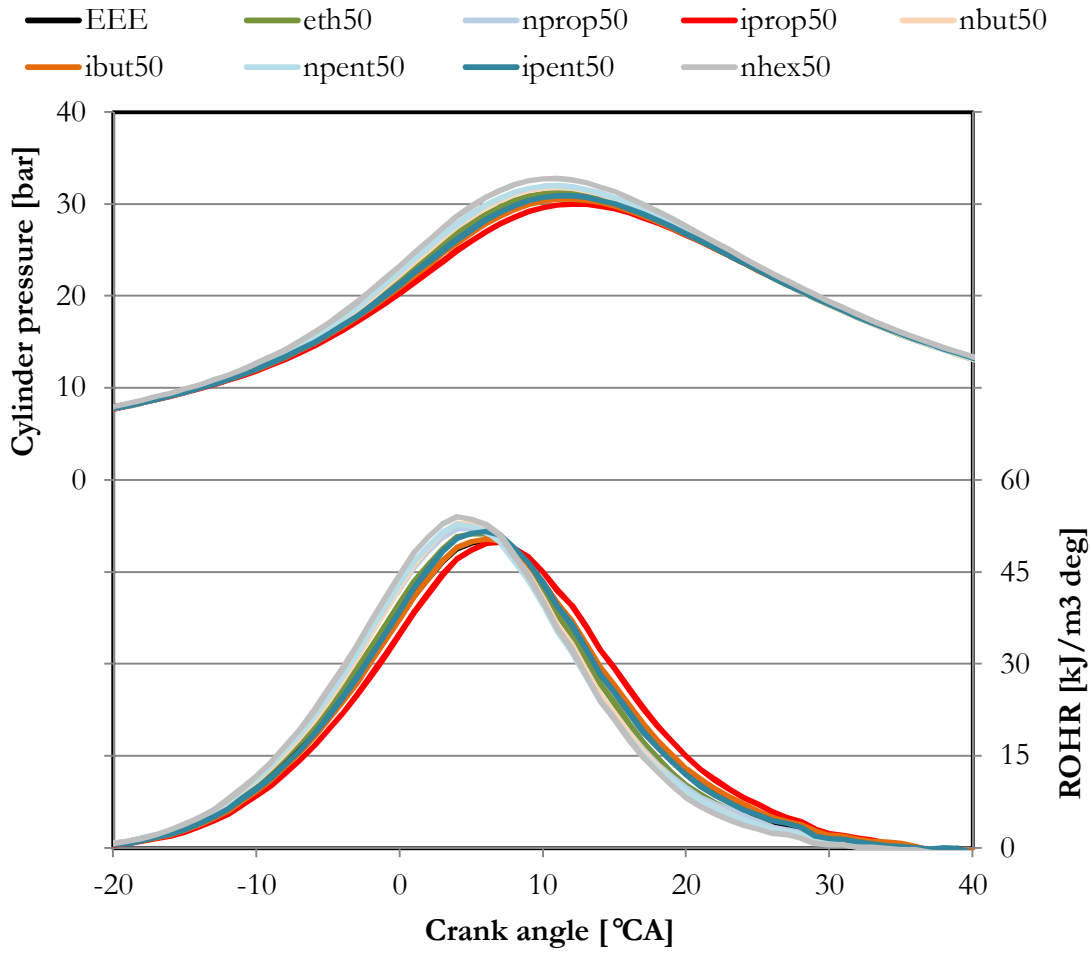


**FIGURE 2.18: AVERAGE CYLINDER PRESSURE AND ROHR FOR 50/50 BLENDS AT 3000 RPM, 4 BAR**

Higher flame speeds result in higher peak ROHR. While it is difficult to find a single source for the flame speeds of all of the alcohols used in this project, measured flame speeds of most of the alcohols from published studies are given in Table 2.7. Nhex50 has the highest flame speed while iprop50 has the lowest. Also, the n- isomer fuels have higher burn velocities than their corresponding iso- isomer fuels.



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**TABLE 2.7: LAMINAR FLAME SPEED OF STOICHIOMETRIC ALCOHOL/AIR MIXTURES AT SIMILAR P AND T**

| *Alcohol* | *Flame speed [cm/s]* |
|---|---|
| **ethanol** | 50 [66] |
| **n-propanol** | 46 [67] |
| **iso-propanol** | 44 [67] |
| **iso-butanol** | 56 [66] |
| **n-pentanol** | 62 [68] |
| **n-hexanol** | 61 [69] |

#### 2.3.3.4 FLAME PROPAGATION

The MFB50% location (point at which 50% of the fuel/air mixture has combusted) of each fuel at each operating point is plotted in Figure 2.19. At each operating point, 500 cycles were averaged for each cylinder. The average of all four cylinders is shown in the figure. The MFB50% location should be around 8 to 10° for maximum engine torque and efficiency [70].

At each operating point the MFB50% location for all of the fuels that have a RON similar to or greater than EEE (see Table 2.5) are approximately equal. The MFB50% of npent50 and nhex50 are approximately equal to the other fuels at low load (2.62 bar BMEP), but are retarded at medium and high loads (4 and 8 bar). In general, the iso- isomer fuels have more retarded MFB50% than the corresponding n- isomer fuels (which is in agreement with the trend of flame speed), although the differences are small at low and medium loads.



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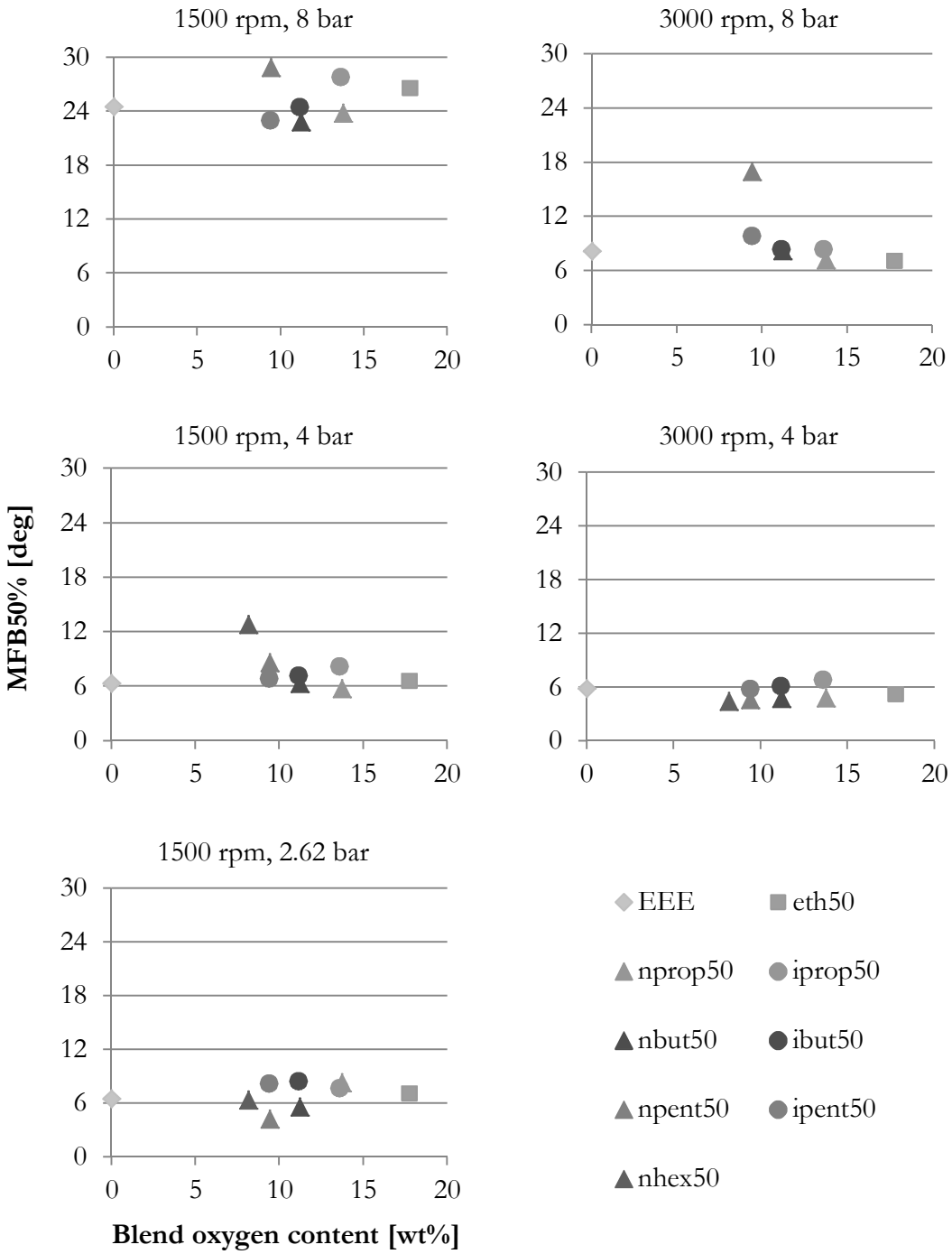


**FIGURE 2.19: MFB50% OF 50/50 BLENDS AT EACH OPERATING POINT**



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The spark timing, MFB10%, MFB50%, and MFB90% locations of each fuel at each operating point are plotted in Figure 2.20. The plot is divided vertically by engine operating point. For each operating point, fuels are plotted with increasing carbon number moving up the y-axis with EEE (blue diamond) at the bottom of all of the fuels and nhex50 (blue triangle) at the top. For each fuel, the left most point indicates spark timing, then MFB10%, MFB50%, and MFB90% points are plotted from left to right as a function of crank angle. The crank angle interval between each point is indicated with text.

The crank angle interval between spark and MFB10%, or the flame development angle, generally decreases with increasing carbon number among the alcohol fuels. For example, as shown in Figure 2.20, at the 1500 rpm, 4 bar operating point the flame development angle of eth50 (carbon number of two) is 29.9°, nprop50 (carbon number of three) is 29.3°, npent50 (carbon number of five) is 27.7°, and nhex50 (carbon number of six) is 25.9°.

Figure 2.20 also illustrates differences between the n- isomer fuels and the corresponding iso- isomer fuels of the same carbon number. The flame development angle of the iso- fuels is larger than the corresponding n- fuels at each operating point. Also, the 10-90% MFB duration for the iso- fuels is generally longer than that of the corresponding n- fuels.

While the range of average MFB90% locations is larger than the range of the other points, the average spark timing, MFB10%, MFB50%, and MFB90% of EEE, eth50, nprop50, iprop50, nbut50, ibut50, and ipent50 are approximately equal. Npent50 and nhex50 are significantly different because of engine knock. On average, the MFB10%, MFB50%, and MFB90% of iprop50 occur later than those of nprop50. Similarly, ibut50 occurs later than nbut50. The higher flame speed of the n- alcohol fuels results in higher peak ROHR and earlier MFB10%, MFB50%, and MFB90% locations.



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Points: Spark → MFB10% → MFB50% → MFB90%

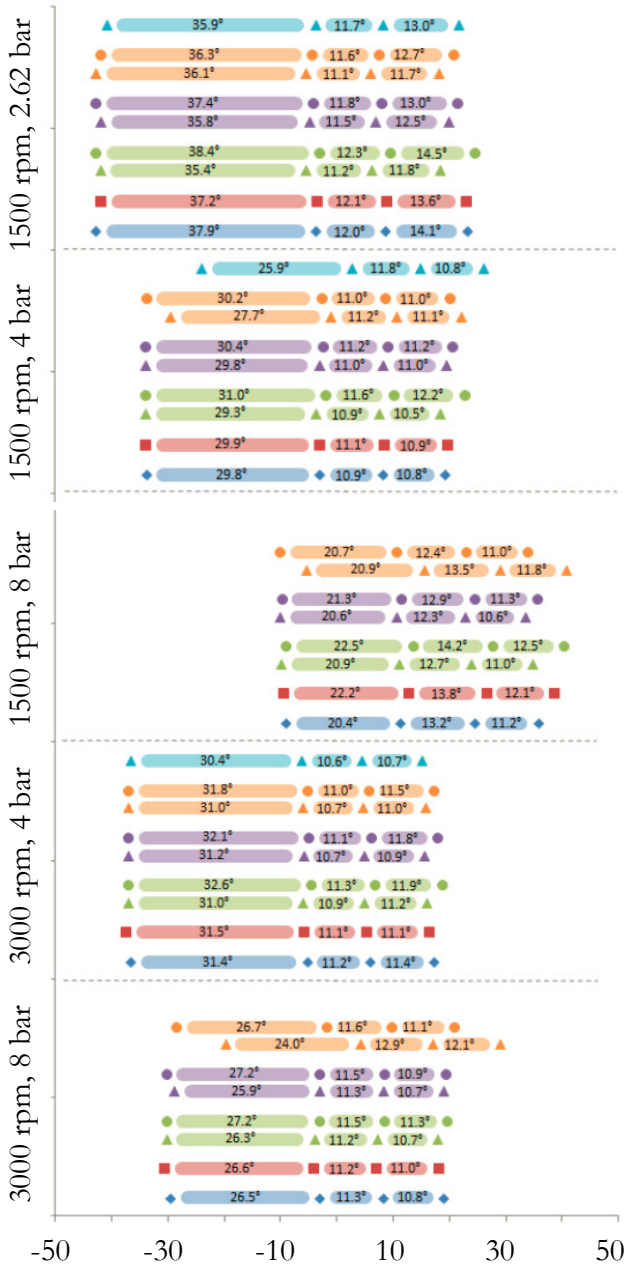


**FIGURE 2.20: SPARK TIMING, MFB10%, MFB50%, AND MFB90% OF 50/50 BLENDS AT EACH OPERATING POINT**



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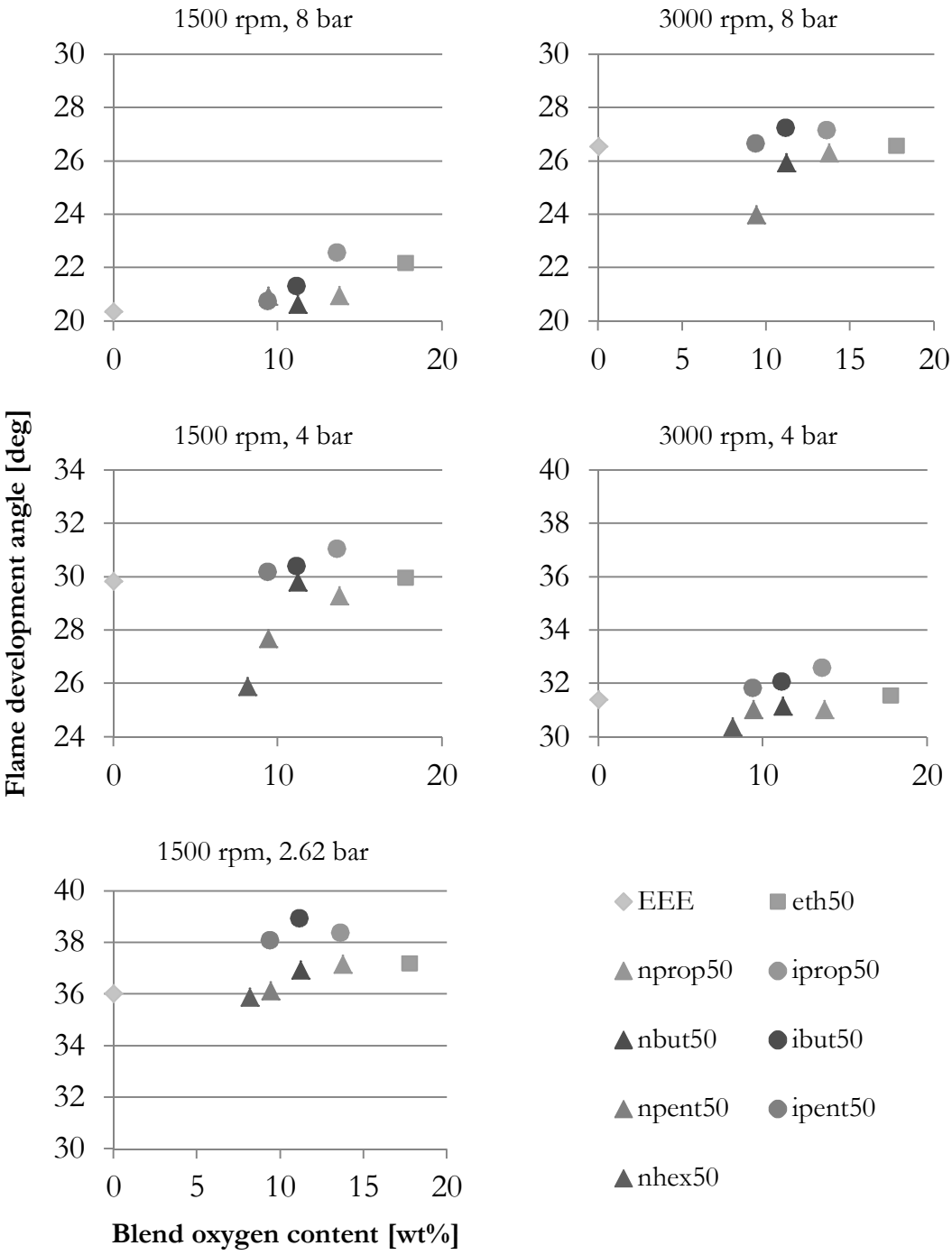


**FIGURE 2.21: FLAME DEVELOPMENT ANGLE OF 50/50 BLENDS AT EACH OPERATING POINT**



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# 3 BLEND COMPARISON METRICS

Alcohol Selection | **Metric Development** | Blend Comparison | Blend Testing

Chapter 3 details the Metric Development phase of the project, which includes the selection of criteria by which to compare multi-component blends to traditional ethanol blends, the selection of gasoline blendstocks to be used in multi-component blends, and the creation of three scenarios for which optimal blends would be identified.

Contents of this Chapter

3.1 Criteria
- 3.1.1 Industry Trends in Engine Technologies
- 3.1.2 Automotive Consumer Expectations
- 3.1.3 U.S. Fuel Legislation
- 3.1.4 Engine Requirements

3.2 Gasoline Blendstocks
- 3.2.1 Certification Gasoline
- 3.2.2 Blendstock for Oxygenate Blending (BOB)
- 3.2.3 Vapor Pressure Boosters

3.3 Fuel Scenarios
- 3.3.1 E10/E15 Alternate
- 3.3.2 RFS2 Fuel
- 3.3.3 E85 Alternate



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## 3.1 CRITERIA

If a multi-component gasoline-alcohol blend is to be a suitable alternative fuel, it would need to meet fuel property, engine emissions and performance, and production process criteria, as illustrated in Figure 3.1. The target values of each possible criterion could come from industry standards, government legislation, consumer expectations, or engine requirements. Some examples of target types and sources are listed in Table 3.1. For example, the total alcohol content of the blend would need to fall within a certain range to satisfy the RFS2 requirements.

**TABLE 3.1: EXAMPLE FUEL CRITERIA, CRITERIA TYPE, AND SOURCE FOR THE CRITERIA TARGET VALUE**

| Criterion | Type | Source |
|---|---|---|
| **Alcohol content** | Range | RFS2 requirements |
| **Distillation profile** | Range | ASTM D4814, ASTM D86 |
| **Vehicle range/LHV** | Min | Consumer acceptability |
| **Oxygen content** | Max | ASTM D4814 |
| **RON** | Min | Engine requirements |
| **RVP** | Range | ASTM D4814, ASTM D5798 |
| … | | |

In this project, fuel property considerations focus on energy content, oxygen content, petroleum displacement, and vapor pressure. The primary emissions and performance criterion is knock resistance. Production considerations, including cost, are not addressed in this project. A lack of information on large scale production of many of the higher carbon number alcohols makes cost estimation very difficult. In addition, only regulated emissions will be examined in this project.



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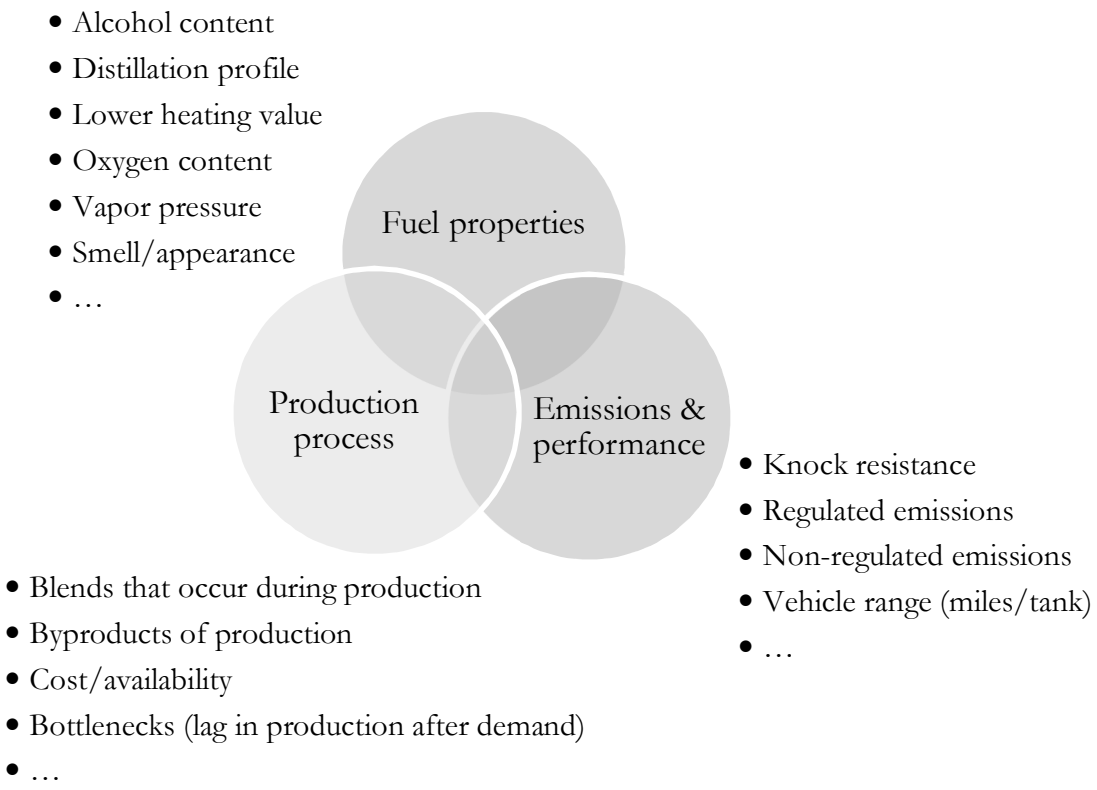


**FIGURE 3.1: TYPES OF BLEND COMPARISON CRITERIA**

### 3.1.1 INDUSTRY TRENDS IN ENGINE TECHNOLOGIES

In recent years the automotive industry has moved toward using smaller engines with turbochargers, direct-injection, and/or variable valve timing as a means of meeting emissions requirements without sacrificing performance. Fuels with higher octane rating are often required by these engines, or at least, can further increase the benefits of these advanced technologies. Therefore, demand for high octane (research octane number, or RON, of 100 or higher) fuels will likely increase in the near future [71].

In addition to providing a way to increase the octane rating of automotive fuels, alcohol blends can help automotive manufacturers meet regulated emissions requirements. The use of gasoline-alcohol blends have been shown to decrease carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxide ($NO_x$) emissions in spark-ignition (SI) engines [72].



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### 3.1.2 Automotive Consumer Expectations

One of the primary concerns of automotive consumers, other than the cost of fuel which is not addressed in the project, is the range of their vehicle (how many miles it can travel on one tank of fuel). Fuels with lower volumetric energy density will decrease vehicle range. Therefore, a minimum lower heating value should be maintained when identifying promising multi-component blends in this project.

The vapor pressure of a fuel plays a critical role in the ability of the engine to start in cold temperatures. To satisfy consumer expectations, the vapor pressure of any multi-component blend highlighted in this project should adhere to strict Reid vapor pressure (RVP) limits.

### 3.1.3 U.S. Fuel Legislation

Multiple vapor pressure considerations come from U.S. fuel legislation. The Environmental Protection Agency (EPA) E15 Waiver requires a vapor pressure below 62 kPa (9.0 psi). Section 211(h)(4) of the Clean Air Act Amendments allows the RVP of E10 to be 1 psi higher, but this would not apply to blends of alcohols other than ethanol [2].

### 3.1.4 Engine Requirements

ASTM D4814 details vapor pressure and distillation requirements for fuels used in SI engines. Requirements vary depending on geographical location and month. The requirements for summer months throughout most of the country will be used in this project; this sets a maximum vapor pressure of 62 kPa (9.0 psi) and distillation points of 70°C (158°F), 77-121°C (170-250°F), 190°C (374°F), and 225°C (437°F) for 10 percent by volume (v%), 50 v%, 90 v%, and end point, respectively [10].

ASTM D5798 details vapor pressure requirements for ethanol fuel blends to be used in flexible-fuel SI engines. These blends contain 51 to 83 v% ethanol. Requirements vary depending on geographical location and month. The requirements for summer months throughout most of the country will be used in this project; this sets a vapor pressure range of 38 to 59 kPa (5.5 to 8.5 psi) [11].

Engines in current production vehicles are designed to operate on E10 which has an oxygen content of 3.5 wt% and a RON of approximately 92 [73]. Vehicles of model year 2001 and newer can operate on E15 which has an oxygen content of 5.25 wt% and a RON of 94 [74].



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## 3.2 GASOLINE BLENDSTOCKS

The base of a multi-component blend, or the blendstock, plays a critical role in determining the properties of the blend. Two possible blendstocks for alcohol blends are EEE certification gasoline and a blendstock for oxygenate blending, or BOB. Additionally, BOB with an additive is typically used for high-level alcohol blends (≥ 50 v% alcohol). For this project, BOB will be used as the blendstock for blends with less than 50 v% alcohol and BOB+, BOB with 5 v% isopentane, will be used for blends of 50 v% or higher alcohol. Properties of each of these three blendstocks are given in Table 3.2.

**TABLE 3.2: PROPERTIES OF GASOLINE BLENDSTOCKS**

| | | EEE [59] | BOB [75] | BOB+ |
|---|---|---|---|---|
| **Density [kg/m$^3$]** | | 742 | 753 | 746 |
| **LHV [MJ/kg]** | | 43.0 | 42.7* | 42.9 |
| **HoV* [kJ/kg]** | | 351 | 351 | 351 |
| **RON [-]** | | 97.1 | 88.6 | 88.8 |
| **MON [-]** | | 88.7 | 81.0 | |
| **RVP [psi]** | | 9.0 | 5.8 | 6.5 |
| **Distillation points [°C]** | **5 v%** | 43.3 | 58.5 | 53.2 |
| | **10 v%** | 51.7 | 63.9 | 58.8 |
| | **20 v%** | 64.7 | 71.6 | 68.4 |
| | **30 v%** | 78.9 | 80.2 | 77.0 |
| | **40 v%** | 95.6 | 90.2 | 87.0 |
| | **50 v%** | 106.7 | 102.3 | 99.1 |
| | **60 v%** | 112.8 | 115.1 | 112.4 |
| | **70 v%** | 118.9 | 127.9 | 125.9 |
| | **80 v%** | 131.1 | 140.5 | 139.2 |
| | **90 v%** | 158.9 | 156.2 | 155.4 |
| | **95 v%** | 171.11 | 168.6 | 167.0 |

* Values were not reported, therefore a typical value found in the literature was used.

### 3.2.1 CERTIFICATION GASOLINE

Certification gasoline is used for benchmarking tests throughout the automotive industry. Multiple types of certification gasolines are available and all of them have tightly-controlled properties. The certification gasoline used in this project is an EPA Tier II EEE gasoline from Haltermann Solutions. The relevant properties of this EEE are listed in Table 3.2 and a more detailed listing of its properties can be found in Appendix 7.5.



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### 3.2.2 Blendstock for Oxygenate Blending (BOB)

Blendstocks for oxygenate blending, or BOBs, are used to create fuels that are blends of gasoline and alcohol(s). Many types of BOBs are available with properties suited to their application. The BOB used in this project is a RBOB, or regular blendstock for oxygenate blending, from Haltermann Solutions. The relevant properties of this BOB are listed in Table 3.2 and a more detailed listing of its properties can be found in Appendix 7.5.

### 3.2.3 Vapor Pressure Boosters

High-level alcohol blends (50 v% alcohol and higher) have significantly lower RVP than gasoline or low-level blends. A high-level blend composed of BOB and alcohol(s) would have too low RVP to be used in conventional SI engines. Additives are blended into high-level blends to boost the vapor pressure to an adequate level. Isopentane is one of many different additives that can be used.

Isopentane, $C_5H_{12}$, is a branched-chain alkane with five carbon atoms. It has a density of 620 kg/m$^3$, a lower heating value (LHV) of 48.9 MJ/kg [76], a RON of 93 [77], and a vapor pressure of 76.992 kPa (11.17 psi) [60]. Property values for a blend of 95 v% BOB and 5 v% isopentane were calculated using the methods outlined in Section 4.1. These values are listed in Table 3.2.



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## 3.3 FUEL SCENARIOS

Three scenarios were defined that specify criteria and targets for multi-component blends to meet. The first scenario, the E10/E15 Alternate Scenario, examines low-level blends and aims to identify a multi-component gasoline-alcohol blend with properties similar to those of currently approved fuels that could be used to increase the short-term use of higher alcohols in current engines. The RFS2 Fuel Scenario targets gasoline-alcohol blends that could theoretically satisfy the Renewable Fuels Standard, which mandates an ethanol-equivalent blend level of approximately 25 v%. The E85 Alternate Scenario targets high-level gasoline-alcohol blends and attempts to identify fuels with high knock resistance (RON ≥ 100) that reduce the range penalty of E85 when compared to gasoline.

The criteria chosen for these scenarios are based on industry standards, government legislation, consumer expectations, and engine requirements. Table 3.3 summarizes the criteria and targets for the three scenarios. The values listed in the table were calculated using the methods described in Section 4.1. For these calculations, ethanol was mixed with a BOB at blend levels of 10, 15, and 25 v%. The BOB has a LHV of 42.7 MJ/kg, density of 752.7 kg/m$^3$, RON of 88.6, RVP of 40 kPa (5.8 psi), and does not contain any oxygen.

**TABLE 3.3: CRITERIA AND TARGETS FOR FUEL DEVELOPMENT SCENARIOS**

| Criterion | E10/E15 Alternate | RFS2 Fuel | E85 Alternate |
|---|---|---|---|
| **Overall objective** | Increase short-term use of higher alcohols. | Meet RFS2 requirements. | Increase long-term use of higher alcohols. |
| **Alcohol content** | Low (10-20 v%) | Medium (17-50 v%) | High (51-90 v%) |
| **Blendstock** | BOB | BOB | BOB+ |
| **Oxygen content** | ≤ 5.25 wt% | | |
| **LHV** | ≥ 40.0* MJ/kg | ≥ 38.3* MJ/kg | ≥ 29.4* MJ/kg |
| **RON** | ≥ 92.4* | ≥ 92.4* | ≥ 100 |
| **RVP minimum** | 5.5 psi | 5.5 psi | 5.5 psi |
| **RVP maximum** | 9.0 psi | 15.0 psi | 8.5 psi |
| **PD** | ≥ that of E15 | ≥ that of E25 | ≥ that of E77 |

* Values are calculated using the methods outlined in Section 4.1.



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### 3.3.1 E10/E15 ALTERNATE

The objective of the E10/E15 Alternate Scenario is to identify multi-component blends that could be used in current SI engines and that offer higher petroleum displacement, knock resistance, and/or energy content than E10/E15 while adhering to industry standards and consumer expectations. These criteria and their values are summarized in Table 3.3.

Suitable blends in the E10/E15 Alternate Scenario would have total alcohol content under 20 v%, oxygen content under 5.25 wt% to meet the EPA E15 Waiver, and RON at least equal to that of E10 so that current engines can use the fuel without modification. Engines in current production vehicles are designed to operate on E10 which has an oxygen content of 3.5 wt% and a RON of approximately 92 [73]. Vehicles of model year 2001 and newer can operate on E15 which has an oxygen content of 5.25 wt% and a RON of 94 [74].

Blends should have LHV greater than or equal to that of E15 so that consumers will not notice a significant decrease in vehicle range. Blends would also need to meet or exceed the petroleum displacement of E15 so that previous efforts to meet RFS2 requirements are not mitigated.

Suitable blends in this scenario should meet the EPA E15 Waiver requirements so that they could be utilized without additional legislation. To do so, they must have a maximum RVP of 62 kPa (9.0 psi). Since a minimum RVP is not specified for low level blends, 38 kPa (5.5 psi) was selected based on specifications for blends containing 51 to 83 v% ethanol from ASTM D5798 [11].

### 3.3.2 RFS2 FUEL

The objective of the RFS2 Fuel Scenario is to identify blends that contain an ethanol-equivalent alcohol volume that meets the RFS2 requirement in addition to vapor pressure, knock resistance, and energy content criteria similar to those in the E10/E15 Alternate Scenario. These criteria and their values are also summarized in Table 3.3. Suitable blends for the RFS2 Fuel Scenario could be used in flexible-fuel engines and allow RFS2 compliance while maintaining the knock resistance and energy content of current fuels and adhering to industry standards and consumer expectations.

The minimum total alcohol content to meet RFS2 requirements varies from 17 to 25 v% depending on which alcohols are being used. Advanced engine technologies, such as



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gasoline direct-injection (GDI) and downsizing/turbocharging would benefit from increased knock resistance. However, calibrations for many vehicles are still based on regular grade gasoline; therefore the RON target in this scenario is the same as the E10/E15 Alternate Scenario. Suitable blends in the RFS2 Fuel Scenario should have LHV greater than or equal to E25 so that the range penalty is not increased.

ASTM standard D4814 provides the maximum RVP range, 54 – 103 kPa (7.8 – 15.0 psi), for a blend whose primary component is not an oxygenate. In absence of an actual lower RVP limit for fuels at this blend level, the RVP minimum is again set to 38 kPa (5.5 psi) based on ASTM D5798.

### 3.3.3 E85 Alternate

The objective of the E85 Alternate Scenario is to identify blends that utilize high levels of alcohols and have high knock resistance for advanced engine technologies, but that do not have the range penalty (lowered energy content) of E85. These fuels would be used in flexible-fuel vehicles or similar applications and would increase long-term use of higher alcohols.

Suitable blends in the E85 Alternate Scenario will have total alcohol content between 51 and 90 v%, and RON of at least 100. The RVP of suitable blends must fall between 38 and 58.6 kPa (5.5 and 8.5 psi) to meet ASTM standards. Blends should have LHV greater than or equal to that of E85. What is commonly called 'E85' is a gasoline-ethanol blend that ranges from 51 to 83 v% ethanol depending on geographic location and month [78]. For this project, E85 will be considered a blend of 23 v% BOB and 77 v% ethanol (a commonly found blend). This blend would have a LHV of 29.4 MJ/kg as calculated with the method outline in Section 4.1.



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# 4 HIGHER ALCOHOL BLENDS SUPERIOR TO TRADITIONAL ETHANOL BLENDS

Alcohol Selection → Metric Development → **Blend Comparison** → Blend Testing

Chapter 4 details the Blend Comparison phase of the project, which includes the prediction of chemical and engine-related properties of multi-component blends, the identification of optimal blends for each of the three fuel scenarios, examination of the effects of changing criteria target values on optimal blend composition, and the examination of the effects of changing total alcohol content on optimal blend composition.

Contents of this Chapter

4.1 Blend Property Prediction
- 4.1.1 Linear Properties
- 4.1.2 Distillation Profile
- 4.1.3 RON
- 4.1.4 RVP

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4.3 Target Value Sensitivity



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## 4.1 Blend Property Prediction

Both chemical and engine-related properties of gasoline-alcohol blends must be predicted in order to identify an optimal blend. For a fuel with a certain volumetric amount of each of the eight alcohols and the blendstock, it is desirable to be able to estimate the fuel's density, LHV, heat of vaporization (HoV), RON, distillation profile, and RVP. These properties are the most crucial when evaluating a fuel for customer satisfaction, engine requirements, meeting legislative requirements, and maintaining industry standards.

Some of these properties, including density, LHV, HoV, and oxygen content, are obtained with straightforward calculations if basic assumptions are made about the mixture. These calculations remain straightforward regardless of the number of components in the blend because they are linear combinations of the properties of the blend components. Other properties, like the distillation profile, RON, and RVP, are significantly more complicated to calculate.

### 4.1.1 Linear Properties

The density, oxygen content, HoV, LHV, and ethanol-equivalent of multi-component blends can be calculated using the volumetric concentration, v, of each component and the component's property values using Equations 3 through 7. In each equation, n is the total number of components in the blend (both alcohols and blendstock).

$$\rho_{blend} = \sum_{i=1}^{n} (v_i \rho_i) \tag{3}$$

$$oxygen_{blend} = \left[\sum_{i=1}^{n} (v_i \rho_i oxygen_i)\right] * (\rho_{blend})^{-1} \tag{4}$$

$$HoV_{blend} = \left[\sum_{i=1}^{n} (v_i \rho_i HoV_i)\right] * (\rho_{blend})^{-1} \tag{5}$$

$$LHV_{blend} = \left[\sum_{i=1}^{n} (v_i \rho_i LHV_i)\right] * (\rho_{blend})^{-1} \tag{6}$$



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$$eth\ equiv_{blend} = \left[\sum_{i=1}^{n}(v_i \rho_i LHV_i)\right] * (\rho_{eth} LHV_{eth})^{-1} \quad \textbf{(7)}$$

### 4.1.2 DISTILLATION PROFILE

The distillation profile of a multi-component gasoline-alcohol blend is a combination of the blendstock distillation profile and the boiling points of the alcohols [79]. Horizontal sections with width equal to each alcohol's volumetric concentration are merged into the blendstock's profile at each alcohol's boiling point as illustrated in Figure 4.1. The figure shows the distillation profile of an example blend that consists of 82 percent by volume (v%) BOB, 10 v% ethanol, and 8 v% iso-butanol.

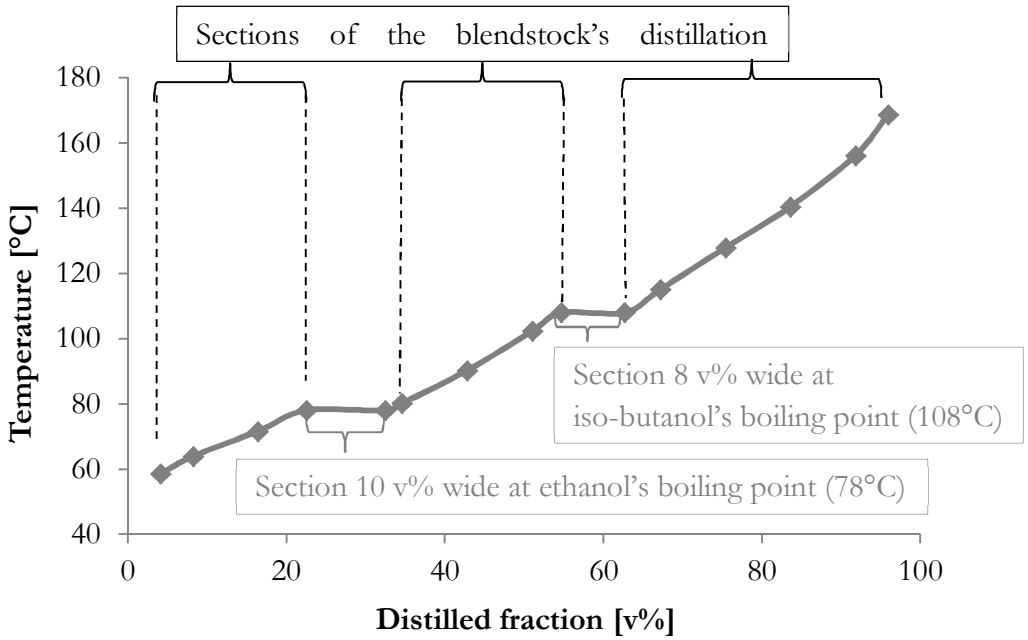


**FIGURE 4.1: DISTILLATION PROFILE OF 82 V% BOB, 10 V% ETHANOL, AND 8 V% ISO-BUTANOL EXAMPLE BLEND**

Knowledge of a blend's distillation profiles is required for the calculation of drivability index (DI). Drivability index is a method of evaluating a fuel's distillation parameters and behavior in low temperature environments. While DI alone is not an adequate predictor of gasoline-alcohol blend performance [80], it is an established methodology and regulated by ASTM standard D4814.



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According to the ASTM standard, DI is a function of the blend's 10, 50, and 90 v% distillation temperatures and volumetric ethanol content. When alcohols other than ethanol are present, the original equation has to be modified to properly predict a blend's DI. A modification has been proposed for butanol [56], but not for propanol, pentanol, or hexanol. Accordingly, no extra terms were added to the original equation for this project; instead the ethanol content parameter was replaced by total alcohol content, resulting in Equation 8.

$$DI_{blend} = 1.5T_{10} + 3T_{50} + T_{90} + 1.33v_{alc} \quad \textbf{(8)}$$

### 4.1.3 RON

Both research octane number (RON) and motor octane number (MON) are measures of a fuel's knock resistance. RON is indicative of a fuel's knock resistance at wide-open throttle and low and medium engine speeds. MON indicates a fuel's knock resistance at high-speed, high-load conditions [10]. Recent studies have shown that RON more accurately predicts the knock performance of a fuel in modern engines [81]. Therefore, this project will focus on predicting the RON of a multi-component blend.

Two methods of predicting blend RON are examined. The first is a linear combination of each blend component's mole fraction and blending octane number [82]. This method was used to predict the blend RON used in the process to determine the optimal blends detailed in Section 5.1. All predicted RON values given throughout this document were calculated by this method. The second is based on the molecular composition of all of the blend components [83]. The results of each are given here.

#### 4.1.3.1 Mole Fraction Method

RON of gasoline-alcohol blends is a non-linear function on a volumetric basis. One method for calculating the RON of a gasoline-alcohol blend is based on the molar fraction of each component in the mixture, x, and the blending octane number of each component on a molar basis, ON, as shown in Equation 9 [82]. In the equation, n is the total number of components in the blend (both alcohols and blendstock).

$$RON_{blend} = \sum_{i=1}^{n} (x_i ON_i) \quad \textbf{(9)}$$

Blending octane numbers are not available for all alcohols used in this study, but a comparison with available data [55] suggests that blending octane numbers based on molar



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concentrations are close to the pure component's RON value. Therefore this study assumes that each component's molar blending octane number is the measured RON at all molar concentrations. It is important to note that this method of calculating blend knock resistance has only been developed for blends of one alcohol with a gasoline blendstock, so it is unknown how accurately it will predict the RON of a multi-component blend.

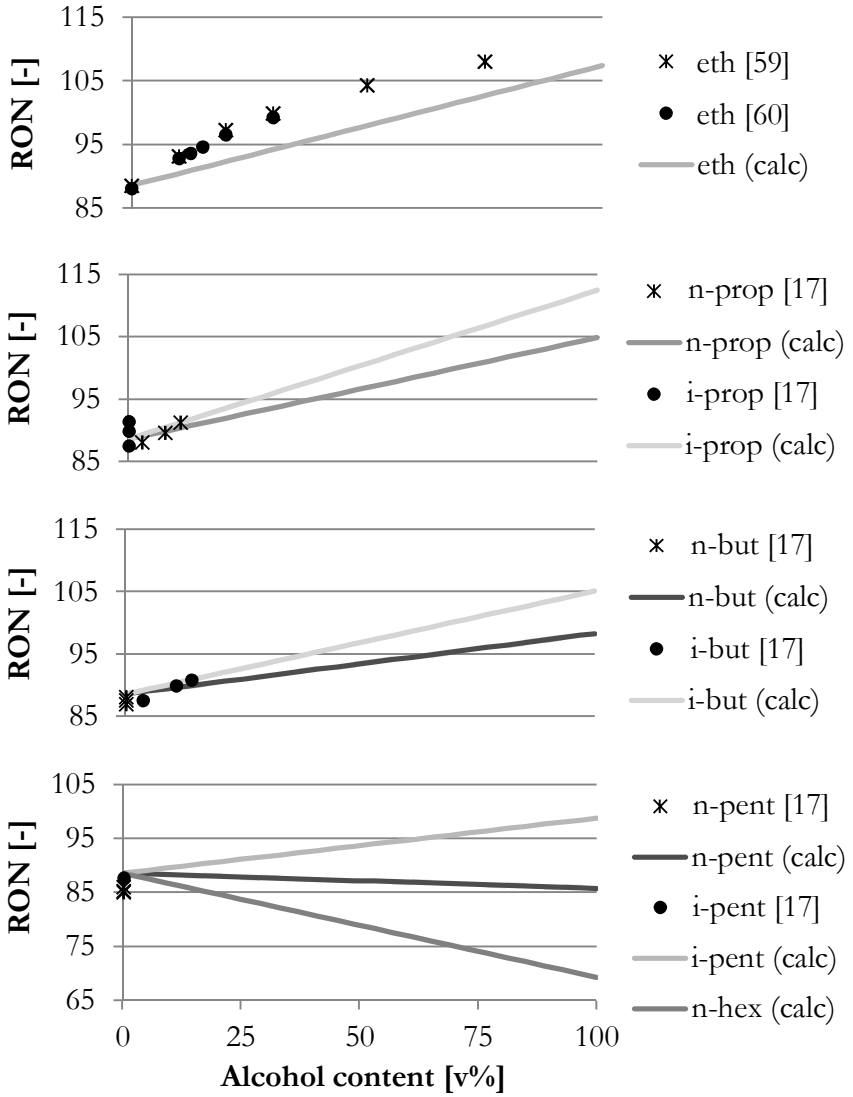


**FIGURE 4.2: PREDICTED RON VALUES FROM THE MOLE FRACTION METHOD COMPARED TO MEASURED VALUES FROM LITERATURE**



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Figure 4.2 compares the RON values calculated using Equation 9 to measured values found in the literature as a function of alcohol content when mixed with BOB. The calculated values over predict the RON values for iso-propanol, n-butanol, n-pentanol, and iso-pentanol. The calculated values agree well for n-propanol and iso-butanol. It is not known if this method accurately describes RON values for n-hexanol as no measured values could be found. The ethanol curve shown under predicts the RON value of the blend. In addition, it does not capture the arc of the measured values with increasing ethanol content.

This method of blend RON prediction is expected to contain some error. Linear models for the prediction of the octane number of a gasoline-alcohol blend tend to underestimate measured values [84]. However, 2nd-order prediction methods based on mole fraction require the use of the octane number of 50/50 molar blends of each of the alcohols with blendstock [82]. Because these octane numbers are not available for all of the alcohols used in this project, the 1st-order relationship must be used to predict the RON of multi-component blends if the mole fraction method is used.

#### 4.1.3.2 Molecular Composition Method

Another method of predicting blend RON is based on the molecular composition of each of the blend components. Molecular "lumps" are defined according to the classes listed in Table 4.1. Equation 10 is used to calculate blend RON, where $v_i$ is the volume fraction of molecule i, $\beta_i$ is the molecular parameter listed in Table 4.1, $ON_i$ is the pure octane number of molecule i, and P, O, N, and A stand for paraffins, olefins, naphthenes, and aromatics, respectively [83].

**TABLE 4.1: MOLECULAR CLASS, LUMPS, AND PARAMETERS FOR RON CALCULATION [83]**

| Class | Molecular Lumps | $\beta$ (RON) | $\beta$ (MON) |
|---|---|---|---|
| n-paraffins | $nC_4$-$nC_{12}$ | 2.0559 | 0.3092 |
| i-paraffins | $C_4$-$C_{12}$ mono-, di-, and trimethyl-i-parafiins | 2.0204 | 0.4278 |
| naphthenes | $C_5$-$C_9$ naphthenes | 1.6870 | 0.2821 |
| aromatics | benzene – $C_{12}$ aromatics | 3.3984 | 0.4773 |
| olefins | $C_4$-$C_{12}$ linear, branched, and cyclic olefins | 8.9390 | 10.000 |
| oxygenates | MTBE, TAME, EtOH | 3.9743 | 2.0727 |



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$$ON = \sum_{PONA} v_i \beta_i ON_i \left( \sum_{PONA} v_i \beta_i \right)^{-1} \quad \textbf{(10)}$$

BOB is modeled as 7 v% toluene, 7 v% xylene, 3 v% n-hexane, 0.5 v% benzene, and 82.5 v% 2,2,4-trimethylpentane for this method. These are average composition values as reported by the BOB manufacturer [75].

Measured RON values of 21 different two-component blends of $C_2$ through $C_5$ alcohols with a gasoline blendstock were found in literature [85] [55]. These values are compared with the predicted values from both the mole fraction and molecular composition methods in Figure 4.3. Blend numbers 1 through 5 in the figure are blends of ethanol ranging from 10 to 75 v% with BOB. Blend numbers 6 through 21 are blends of propanol, butanol, and pentanol ranging from 3 to 19 v% with BOB.

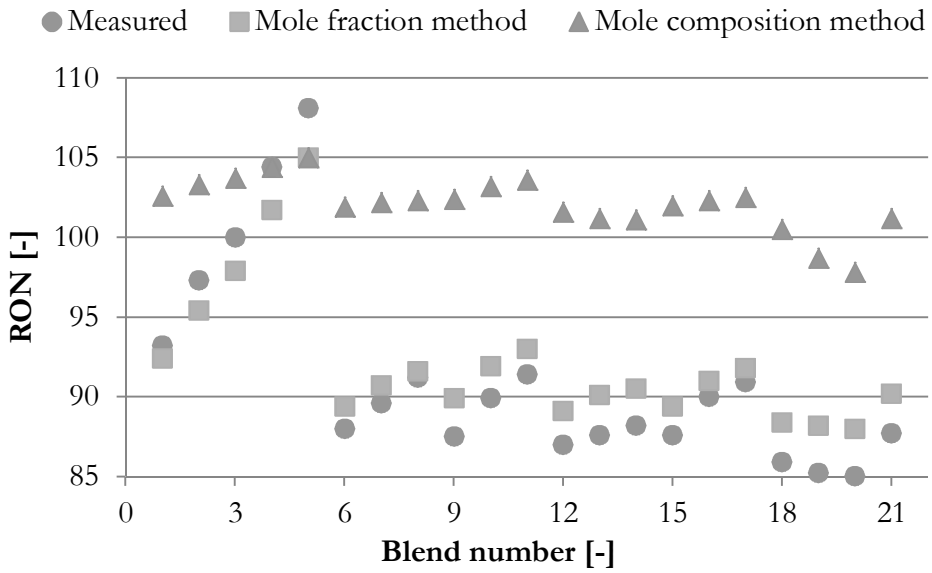


**FIGURE 4.3: PREDICTED RON VALUES FROM BOTH METHODS COMPARED TO MEASURED VALUES FROM LITERATURE**

Both prediction methods over predict RON for propanol, butanol, and pentanol blends (blend numbers 6 through 21 in Figure 4.3). The molecular composition method also over predicts RON for ethanol blends up to50 v% (blend numbers 1 through 4). The mole fraction method under predicts RON for ethanol at all blend levels and the molecular composition method under predicts for ethanol above 50 v% (blend number 5).



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Overall the mole fraction method is more accurate than the molecular composition method. The mole fraction method is within 3.5% of the measured RON value for all 21 blends while the molecular composition method is up to 17.0% different. The molecular composition method is fairly accurate for ethanol blends above 20 v% (within 6.2%), but is over 10% different than the measured RON value for all of the other blends.

### 4.1.4 RVP

The Reid vapor pressure (RVP) of a gasoline-alcohol blend is complicated to predict because of the azeotropic behavior of some of the alcohols. Short-chain alcohols, such as methanol and ethanol, have very pronounced peaks in RVP when mixed with a blendstock around 5 v% while the other alcohols do not exhibit this behavior [55]. Experimental data of the effect on blend RVP when more than one alcohol is mixed with a blendstock is not available for all possible combinations of the alcohols used in this project, therefore a method to estimate this behavior must be implemented.

Two methods of predicting the RVP of a multi-component blend were used. The first, extrapolating from measured data, was used to predict the blend RVP used in the process to determine the optimal blends detailed in Section 4.2. All predicted RVP values given throughout this document were calculated by this method. The second method, calculating vapor pressure from chemical activity coefficients, was done to investigate a possible way to more accurately predict RVP.

#### 4.1.4.1 Extrapolation Method

An array of multi-component blends was sent to SwRI for RVP testing. The results of these tests can be found in Appendix 7.3. Curves were fit to the experimental results of the two-component blends. Those curves were extrapolated for all two-component blends that were not tested. The curves used for RVP prediction are shown in Figure 4.4 (BOB blends) and Figure 4.5 (BOB+ blends). It is assumed that the low concentration RVP boost exhibited in the ethanol data diminishes with increasing carbon number and that all of the alcohols form the same general shape RVP curve when mixed with gasoline.



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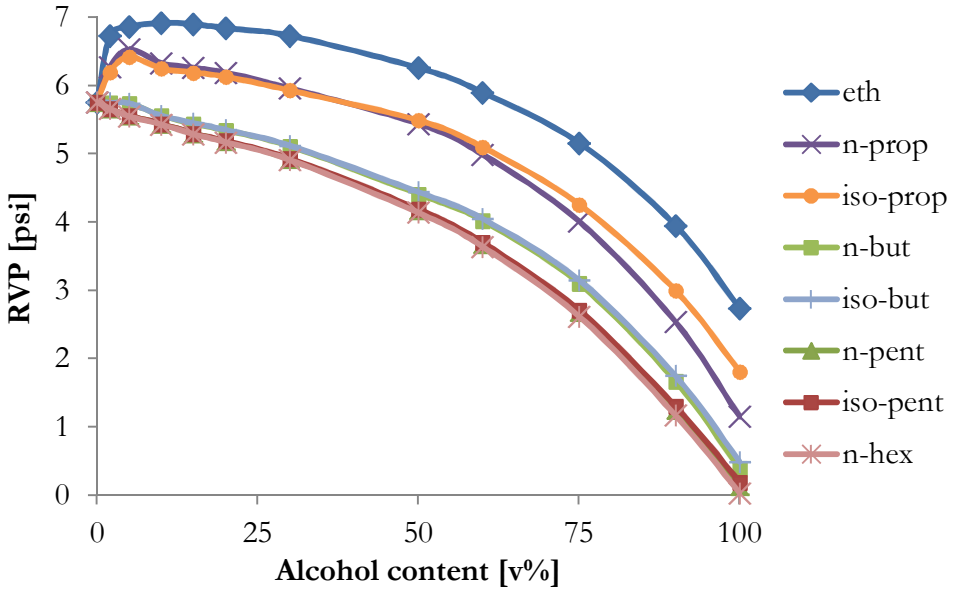


**FIGURE 4.4: CURVES USED TO PREDICT THE RVP OF BOB BLENDS**

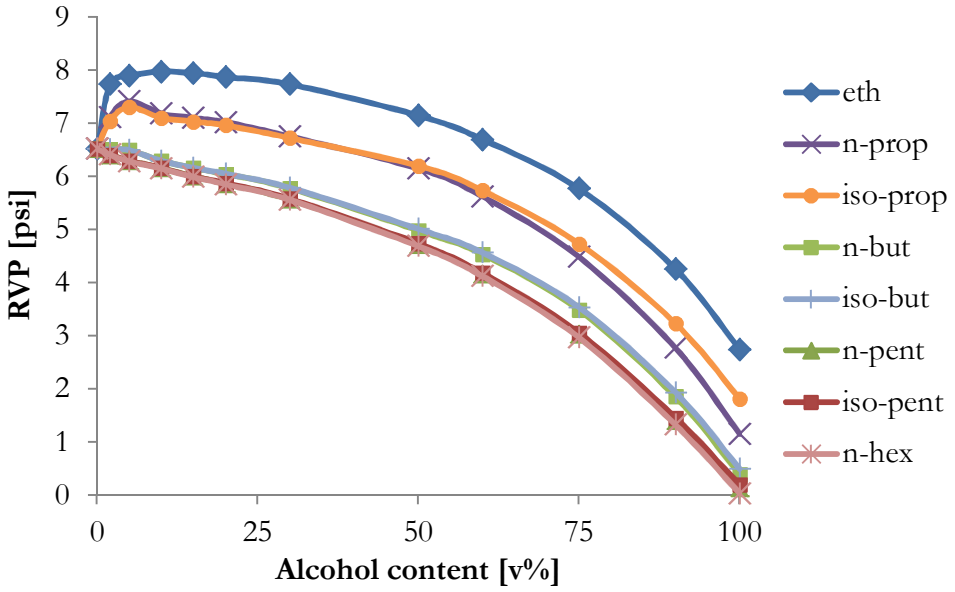


**FIGURE 4.5: CURVES USED TO PREDICT THE RVP OF BOB+ BLENDS**



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When more than one alcohol comprises the blend (three or more components in the blend), Equation 11 is used to calculate the RVP of the blend where $v_{alc}$ is the total volume fraction of alcohols in the blend, $v_i$ is the volume fraction of each alcohol, $RVP_i$ is each alcohol's RVP from either Figure 4.4 or Figure 4.5 at its volume fraction, and n is the total number of alcohols.

$$RVP_{blend} = \sum_{i=1}^{n} \left( \frac{v_i}{v_{alc}} RVP_i \right) \quad \textbf{(11)}$$

As shown in Figure 4.4 and Figure 4.5, low concentrations of ethanol increases the RVP of a gasoline-alcohol blend significantly. This RVP boost can cause E10 to have a vapor pressure outside of EPA fuel regulations. In response, the EPA issued an amendment to the Clean Air Act that allows E10 to have a RVP 1 psi (7 kPa) higher than stated by other regulations [2]. This RVP allowance is known as the "1 pound waiver" and only applies to a blend of 10 v% ethanol in gasoline.

#### 4.1.4.2 Activity Coefficient Method

Blend RVP can be calculated using the thermodynamic activity coefficients of the chemical groups that compose the fuel components [86]. Activity coefficients can be estimated using the UNIFAC method which accounts for the non-ideal solutions created when alcohols are mixed. A chemical group's activity coefficient is affected by both the group's concentration and the other types of groups that are present in the blend. This behavior requires a recalculation of each chemical group's activity coefficient for each different fuel blend, resulting in a computationally intensive procedure to predict the vapor pressure of many blends [87].

To utilize the UNIFAC method, the structural groups that comprise each of the fuel components must be identified. These are listed in Table 4.2. The group volume ($R_k$), surface area ($Q_k$), and interaction parameters ($a_{mn}$) of each structural group must also be identified. These are listed in Table 4.3 and Table 4.4 [87]. BOB and EEE are modeled as isooctane since their exact chemical composition is unknown.

Equations 12 through 22 detail the UNIFAC method used to calculate the activity coefficient of each fuel component [87]. The blend vapor pressure is then calculated using Equation 23. The activity coefficients must be recalculated for each change in composition (both changes in component and/or component quantity).



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**TABLE 4.2: STRUCTURAL GROUPS OF EACH FUEL COMPONENT [87]**

| Fuel Component | Molecular Formula | Structural Groups |
|---|---|---|
| **Isooctane** | $CH_3C(CH_3)_2CH_2CH(CH_3)_2$ | 1 $ACCH_3$, 4 $CH_3$, 1 $CH_2$, 1 CH |
| **ethanol** | $CH_3CH_2OH$ | 1 $CH_3$, 1 COH |
| **n-propanol** | $CH_3CH_2CH_2OH$ | 1 $CH_3$, 1 $CH_2$, 1 COH |
| **iso-propanol** | $(CH_3)_2CHOH$ | 2 $CH_3$, 1 CHOH |
| **n-butanol** | $CH_3CH_2CH_2CH_2OH$ | 1 $CH_3$, 2 $CH_2$, 1 COH |
| **iso-butanol** | $(CH_3)_2CHCH_2OH$ | 2 $CH_3$, 1 $CH_2$, 1 CHOH |
| **n-pentanol** | $CH_3(CH_2)_3CH_2OH$ | 1 $CH_3$, 3 $CH_2$, 1 COH |
| **iso-pentanol** | $(CH_3)_2CHCH_2CH_2OH$ | 2 $CH_3$, 2 $CH_2$, 1 CHOH |
| **n-hexanol** | $CH_3(CH_2)_4CH_2OH$ | 1 $CH_3$, 4 $CH_2$, 1 COH |

**TABLE 4.3: GROUP VOLUME AND SURFACE AREA PARAMETERS OF STRUCTURAL GROUPS [87]**

| Group | $R_k$ | $Q_k$ |
|---|---|---|
| **$CH_3$** | 0.9011 | 0.848 |
| **$CH_2$** | 0.6744 | 0.540 |
| **CH** | 0.4469 | 0.228 |
| **COH** | 1.2044 | 1.124 |
| **CHOH** | 0.9769 | 0.812 |
| **$ACCH_3$** | 1.2663 | 0.968 |

**TABLE 4.4: INTERACTION PARAMETERS OF STRUCTURAL GROUPS [87]**

| | $CH_3$ | $CH_2$ | CH | COH | CHOH | $ACCH_3$ |
|---|---|---|---|---|---|---|
| **$CH_3$** | 0 | 0 | 0 | 931.2 | 931.2 | 26.78 |
| **$CH_2$** | 0 | 0 | 0 | 931.2 | 931.2 | 26.78 |
| **CH** | 0 | 0 | 0 | 931.2 | 931.2 | 26.78 |
| **COH** | 169.7 | 169.7 | 169.7 | 0 | 0 | 92.61 |
| **CHOH** | 169.7 | 169.7 | 169.7 | 0 | 0 | 92.61 |
| **$ACCH_3$** | -15.84 | -15.84 | -15.84 | 856.2 | 856.2 | 0 |



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$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{12}$$

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \tag{13}$$

$$l_i = 5(r_i - q_i) - (r_i - 1) \tag{14}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{15}$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{16}$$

$$r_i = \sum_k v_k^i R_k \tag{17}$$

$$q_i = \sum_k v_k^i Q_k \tag{18}$$

$$\ln \gamma_i^R = \sum_k v_k^i \left[\ln \Gamma_k - \ln \Gamma_k^i\right] \tag{19}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right] \tag{20}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{21}$$

$$\Psi_{mn} = e^{-\frac{a_{mn}}{T}} \tag{22}$$

$$p_{blend} = \sum_i \gamma_i x_i p_i \tag{23}$$



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Of the 46 multi-component blends RVP tested at SwRI (listed in Appendix 7.3), 26 were composed of only one alcohol with blendstock (two-component blends). The other 20 blends were comprised of three to five components (two to four alcohols). The measured RVP values of those 20 blends are compared to the calculated RVP values using both the extrapolation and activity coefficient methods in Figure 4.6. The dashed lines in the figure indicate 5% error.

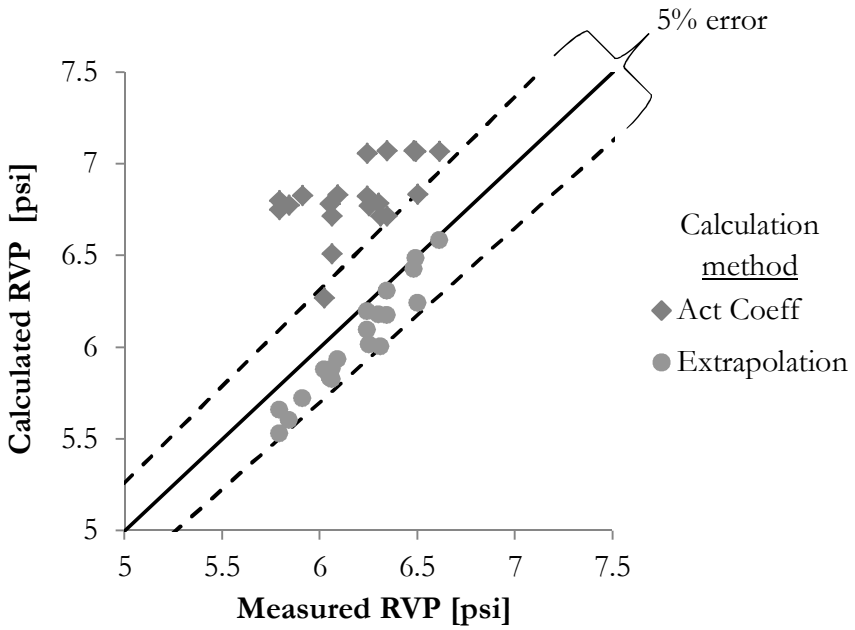


**FIGURE 4.6: COMPARISON OF MEASURED AND CALCULATED BLEND RVP FROM BOTH METHODS**

When using the extrapolation method, the calculated RVP of 19 of the 20 blends is within 5% of the measured value. Only 2 of the 20 blends are within 5% when using the activity coefficient method. Error is introduced into the activity coefficient method by having to model the gasoline blendstock as isooctane but it is unknown if that is the only source of error in the calculation. Further analysis cannot be made without knowing the exact composition of the BOB utilized.

Figure 4.7 compares the measured RVP of all 46 blends with the RVP calculated with the activity coefficient method by the number of components in the blend. The dashed lines in the figure indicate 10% error. Seventeen of the 26 blends (65%) that are comprised of 2 components are within 10% error. Ten of the 18 blends (56%) that are comprised of 3



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components are within 10% error. Each one of the five- and six-component blends are within 10% error.

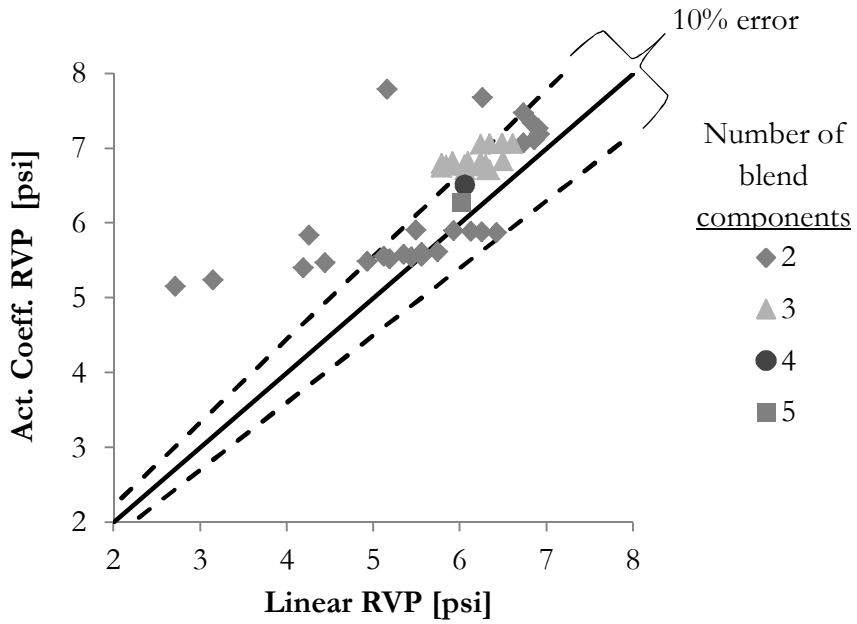


**FIGURE 4.7: COMPARISON OF MEASURED AND CALCULATED BLEND RVP FROM ACTIVITY COEFFICIENT METHOD**



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## 4.2 Optimal Blends

The blend property prediction methods described in Section 4.1 were used to calculate fuel properties of a large range of blends. The properties of each blend were compared to the criteria targets of each scenario to determine suitability and a scheme was developed by which to choose a set of optimal blends.

### 4.2.1 Selection Process

The process by which optimal blends were determined consists of the following steps: 1) generate a database of possible blends, 2) predict the chemical and engine-related properties of each blend, 3) identify which of the blends meet a scenario's criteria targets, 4) identify the three of those blends that have the highest energy content, knock resistance, and petroleum displacement, respectively.

#### 4.2.1.1 All Blends

A blend sweep using a 1 v% step width for the total alcohol content of the blend was used to create a database of possible blends. At each value of total alcohol content, many possible combinations of all eight alcohols were considered and each alcohol's content was varied by 10% of the total alcohol content. This method resulted in over one million possible blends.

Many blends do not meet one or more of the scenario's criteria targets and were immediately excluded from further consideration to generate a set of Suitable Blends, as illustrated in Figure 4.8. Blends were removed from consideration if they did not meet LHV, RON, oxygen content, or RVP criteria targets. This is detailed in the next section.

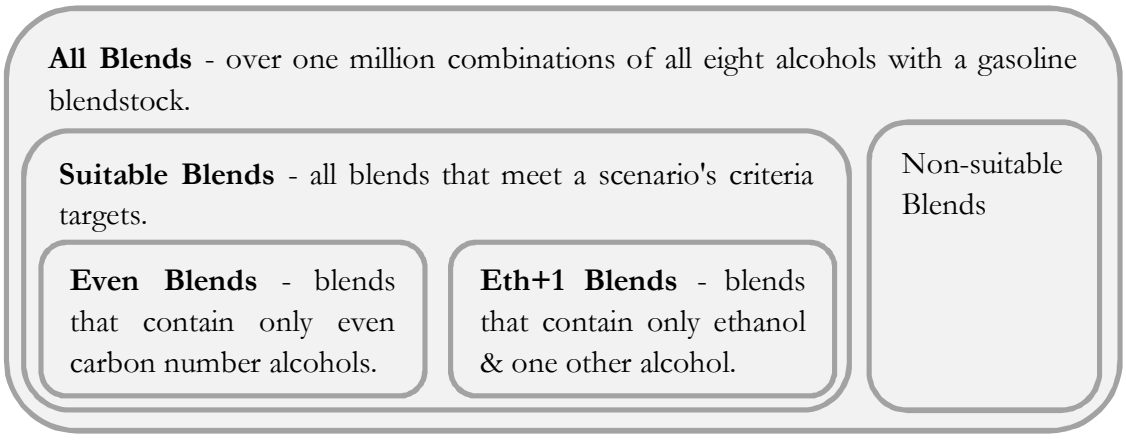


**FIGURE 4.8: SUBSETS OF ALCOHOL BLENDS**



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#### 4.2.1.2 SUITABLE BLENDS

Figure 4.9 shows LHV vs RON and oxygen content vs RVP of all of the blends that were considered for the E10/E15 Alternate Scenario colored by total alcohol content. Blends of total alcohol content between 10 and 25 v% were examined for this scenario. As expected, increasing total alcohol content decreases LHV. RON varies at each value of total alcohol content depending on which alcohols are present. As total alcohol content increases, oxygen content increases and RVP decreases.

Blends with RON below 92.4 and/or LHV below 40.0 MJ/kg are removed from consideration and are grayed out in the figure. Of the blends examined, 75.6% did not meet the minimum RON criterion and 9.6% did not meet the minimum LHV criterion. Blends with oxygen content higher than 5.25 wt% and/or RVP below 37.9 kPa (5.5 psi) are removed from consideration and are grayed out in the figure. Twenty percent of the blends exceeded the maximum oxygen content criterion and 25.0% did not meet the minimum RVP criterion.

Figure 4.10 shows LHV vs RON of all of the blends examined for the RFS2 Fuel Scenario colored by total alcohol content. Total alcohol content ranges from 17 to 50 v% in this scenario. Blends with RON below 92.4 and/or LHV below 38.3 MJ/kg are removed from consideration and are grayed out in the figure. Of the blends examined, 35.2% did not meet the minimum RON criterion and 26.1% did not meet the minimum LHV criterion. RON target non-attainment decreases and LHV target non-attainment increases in this scenario as compared to the E10/E15 Alternate Scenario because of the higher total alcohol content. Most of the alcohols have higher RON than the BOB and all of them have lower LHV.

The oxygen content and RVP of all of the blends that were examined for the RFS2 Fuel Scenario are also shown in Figure 4.10. Blends with RVP below 37.9 kPa (5.5 psi) are removed from consideration and are grayed out in the figure. Seventy two percent of the blends did not meet the RVP minimum. RVP minimum non-attainment is higher in this scenario because of the higher total alcohol content. All of the alcohols have a RVP much lower than the BOB.



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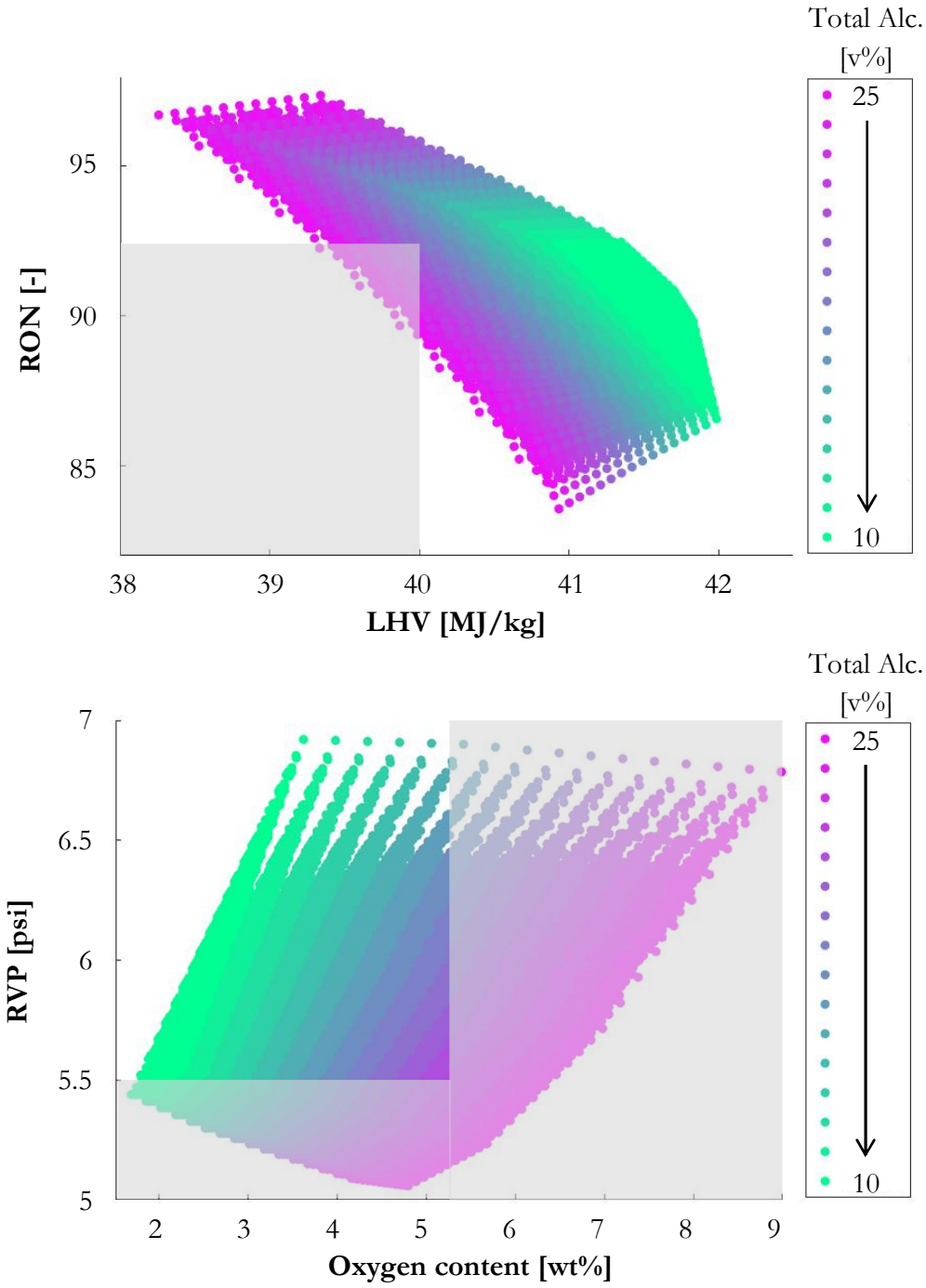


**FIGURE 4.9: LHV/RON AND OXYGEN/RVP OF ALL BLENDS EXAMINED IN THE E10/E15 ALTERNATE SCENARIO**



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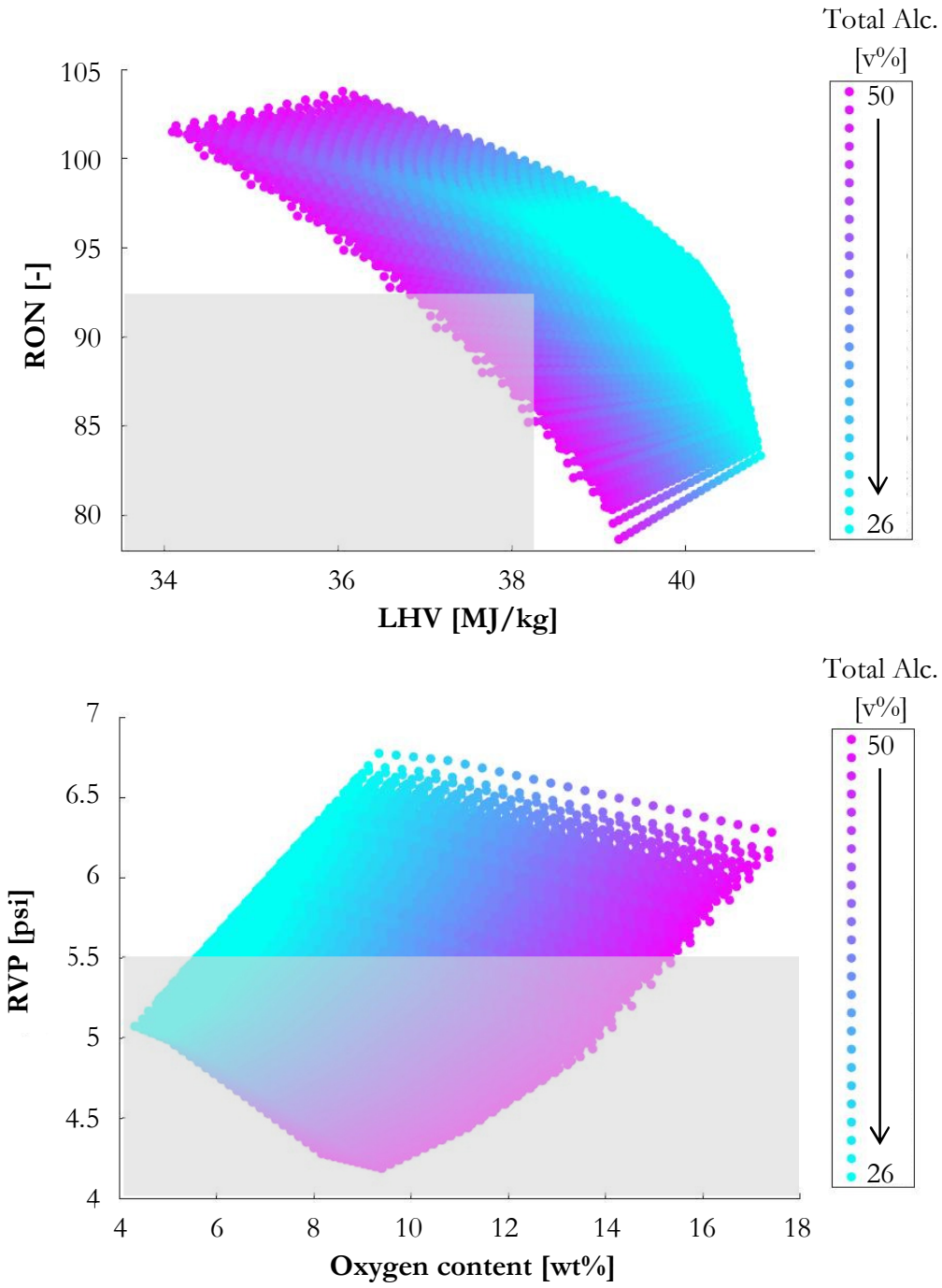


**FIGURE 4.10: : LHV/RON AND OXYGEN/RVP OF ALL BLENDS EXAMINED IN THE RFS2 FUEL SCENARIO**



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Figure 4.11 shows LHV vs RON and oxygen content vs RVP of all of the blends examined for the E85 Alternate Scenario colored by total alcohol content. Total alcohol content ranges from 51 to 90 v% in this scenario. Blends with RON below 100 and/or LHV below 29.4 MJ/kg are removed from consideration and are grayed out in the figure.

In each of the scenarios, the blend that is only blendstock with ethanol at each alcohol content value will have the highest oxygen content and RVP because ethanol has the highest oxygen content and RVP of the alcohols. Also, at low blend levels the addition of ethanol to a blendstock will increase the RVP although the RVP of neat ethanol is lower than that of neat blendstock [88]. This phenomenon causes the blendstock-ethanol blends to have significantly higher RVP than the other alcohol blends. In the oxygen content vs RVP plots, the top point of each colored triangle corresponds to the blend that is just ethanol with blendstock. The triangle shape is formed as the ethanol is replaced with other alcohols.

More information on the determination of suitable blends, including the percentage of examined blends at each total alcohol content value that did not meet each of the criteria targets, is examined in subsequent sections.

#### 4.2.1.3 Subsets of Suitable Blends

In addition to considering all suitable blends, two subsets were analyzed for each scenario. These are also illustrated in Figure 4.8. The first subset includes suitable blends that are composed of only even carbon number alcohols (ethanol, n- and iso-butanol, and n-hexanol). This limitation is based on production considerations that suggest that it might be more feasible to produce even number alcohols [89]. The second subset includes suitable blends that are composed of only ethanol and one other alcohol. These fuels could help ease the transition to fuels comprised of alcohols other than ethanol in the event of commercial deployment.

#### 4.2.1.4 Optimization

Within each subset of blends for a scenario (suitable blends, even blends, and eth+1 blends), the gasoline-alcohol mixtures with the highest LHV, RON, and petroleum displacement (PD) are identified as being the optimal blends. The choice of the blend with the highest LHV, RON, or PD as the overall most optimal would depend on application.



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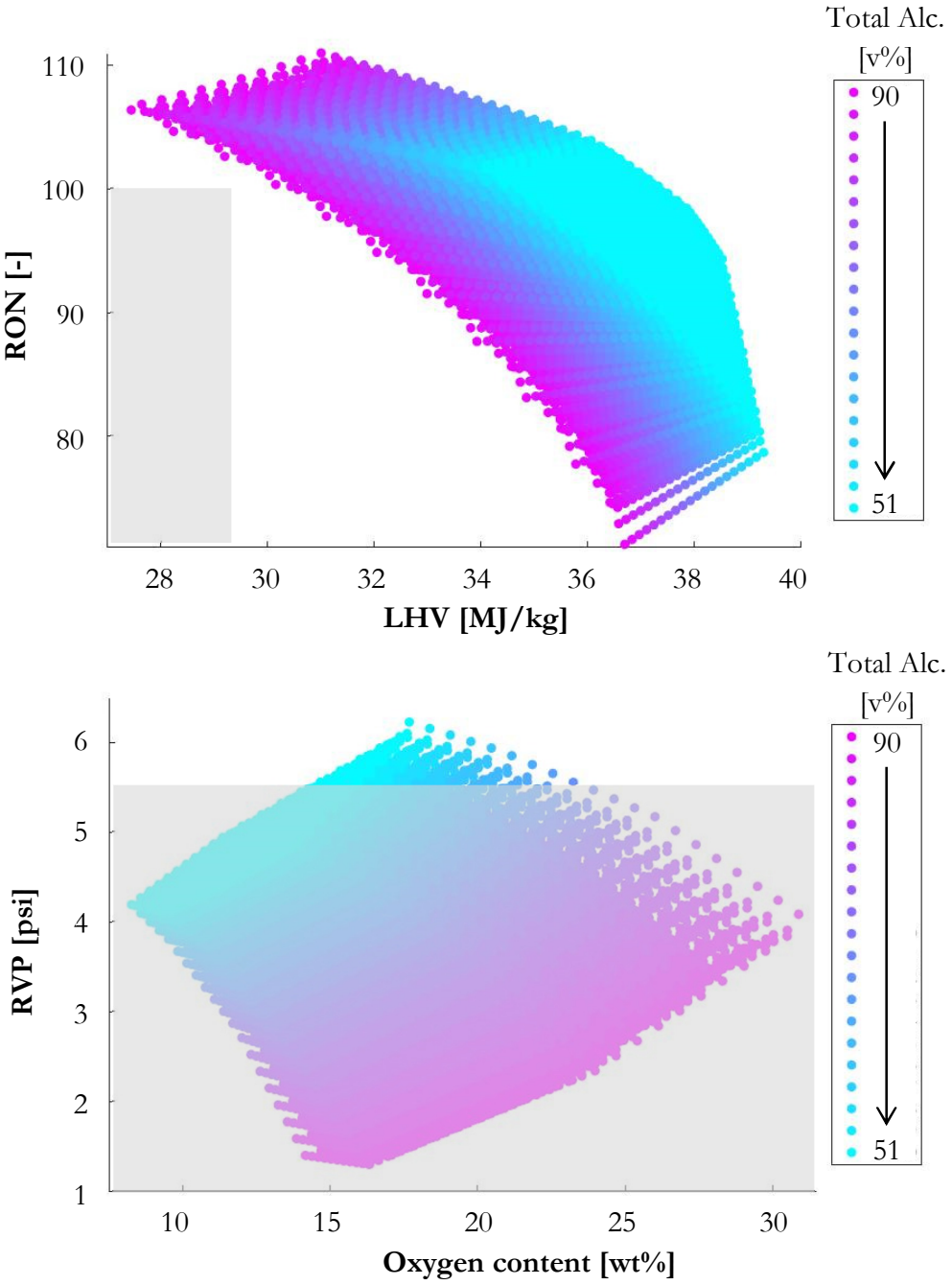


**FIGURE 4.11: LHV/RON AND OXYGEN/RVP OF ALL BLENDS EXAMINED IN THE E85 ALTERNATE SCENARIO**



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Blends with the highest LHV values could be fuels that meet vapor pressure and oxygen content regulations, engine knock resistance requirements, and maintain current levels of petroleum displacement while reducing the range penalty of ethanol blends. Blends with the highest RON values could be fuels that meet vapor pressure and oxygen content regulations, consumer expected vehicle range, and maintain currents levels of petroleum displacement while allowing for engine efficiency gains through higher knock resistance. Blends with the highest PD values could be fuels that meet vapor pressure, oxygen content, engine knock requirements, and consumer expected vehicle range while advancing efforts to meet the RFS2 requirement of 36 billion gallons of renewable fuels by 2022.

### 4.2.2 E10/E15 Alternate Scenario

The objective of the E10/E15 Alternate Scenario is to identify multi-component blends that could be used in current engines and offer higher petroleum displacement, knock resistance, and/or energy content than E10/E15 while adhering to industry standards and consumer expectations. Gasoline-alcohol blends that are suitable for this scenario will meet the criteria targets listed in Table 4.5.

**TABLE 4.5: CRITERIA, MOTIVATION, AND TARGET VALUES FOR THE E10/E15 ALTERNATE SCENARIO**

| Criteria | Motivation | Target |
|---|---|---|
| **LHVa minimum** | Meet RFS2 requirements | 3023 MJ/m$^3$ (E15) |
| **LHV minimum** | Meet consumer expectations | 40.02 MJ/kg (E15) |
| **RON minimum** | Utilize current engines | 92.4 (E10) |
| **RVP minimum** | Satisfy ASTM standards | 5.5 psi |
| **RVP maximum** | Satisfy EPA E15 waiver | 9.0 psi |
| **Oxygen maximum** | Satisfy EPA E15 waiver | 5.25 wt% |

#### 4.2.2.1 Criteria Non-attainment

The percentage of examined blends at each total alcohol content value that did not meet each of the criteria targets (minimum LHV, RON, and RVP and maximum oxygen content and RVP) for the E10/E15 Alternate Scenario is shown in Figure 4.12. Some blends failed to meet more than one criteria target, so the sum of the percentages, or non-attainment frequencies, at any one total alcohol content may be greater than 100%.

None of the blends with 10 v% total alcohol content are suitable because they do not meet the minimum ethanol-equivalent alcohol content criterion (LHVa min) of 3023



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$MJ/m^3$ (that of E15). Nearly 92% of the blends do not have suitable LHVa at the 11 v% total alcohol content level, but this percentage drops quickly to zero with increasing total alcohol content as shown in Figure 4.12. The maximum RVP criterion of 9.0 psi is not a factor in determining suitable blends at any total alcohol content value because of the low vapor pressures of each of the alcohols.

Non-attainment of the minimum LHV target does not occur at levels below 16 v% total alcohol content. At low total alcohol content the minimum LHV target does not disqualify any blends because of the high energy density of the BOB. Once the blend alcohol content is high enough for the minimum LHV target to have an effect, the percentage of blends disqualified by it grows rapidly with increasing total alcohol content.

At low total alcohol content, many of the blends do not meet the minimum RON target because the BOB has such a low RON. To meet the minimum RON requirement of 92.4, blends must contain at least 10 v% alcohols. As total alcohol content increases, the likelihood of RON target non-attainment decreases although blends with higher concentrations of pentanol and hexanol are still likely to fall short of the RON target.

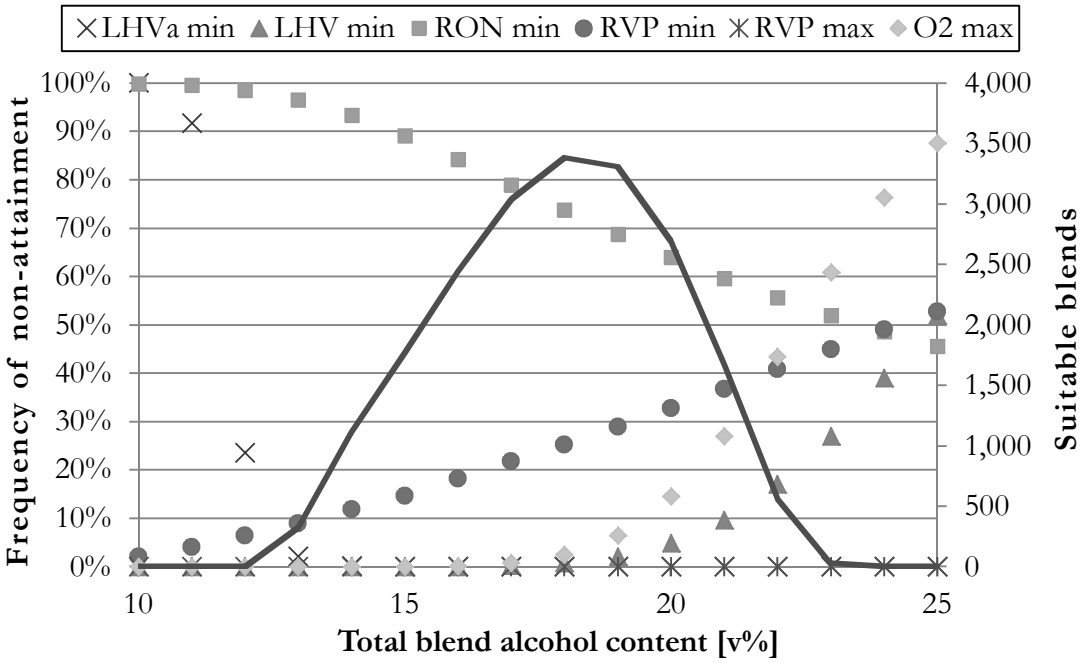


**FIGURE 4.12: CRITERIA NON-ATTAINMENT OF E10/E15 ALTERNATE SCENARIO**



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The RVP minimum criterion of 5.5 psi renders some blends unsuitable at each level of total blend alcohol content. At 10 v% total alcohol content, 2.2% of blends are unsuitable because they have a RVP less than 5.5 psi. The RVP minimum non-attainment frequency linearly increases with total alcohol content, to 52.8% at 25 v%. This is similar to the maximum oxygen content criterion which grows from 0.1% at 16 v% to 87.7% at 25 v%.

Figure 4.12 also shows the number of blends that are suitable for the E10/E15 Alternate Scenario for each level of total blend alcohol content. There are no suitable blends at 10, 11, 12, 24, or 25 v% total alcohol content. The low blend levels are not suitable mostly because they do not meet minimum RON requirements. The higher blend levels are not suitable because of a combination of not meeting the RVP or LHV minimums or surpassing the oxygen content maximum. The largest number of suitable blends occurs at 18 v% total alcohol content where 3386 of the 35196 possible blends of that alcohol content are suitable.

#### 4.2.2.2 Blend Property Assessment

Blends of alcohol(s) and BOB that met all scenario criteria targets were identified as suitable blends. The LHV and RON of all of the suitable blends of the E10/E15 Alternate Scenario are plotted in Figure 4.13. The figure is also colored by PD level, according to the legend shown. The suitable blend with the highest LHV is labeled #1A, the highest RON blend is labeled #1B, and the blend with the highest PD is labeled #1C. In addition, the reference fuels for the scenario are shown on the plot.

The density of points in the LHV/RON plot indicates that there are many suitable blends that have essentially equal LHV and/or RON. The compositions given in Figure 4.14 refer to the mathematically optimal blend but several other blends with slightly different compositions achieve practically identical properties. The compositions of several of the suitable blends are listed in Appendix 7.6 with their relevant properties.

The blend shown as #1A in Figure 4.13 yields the highest LHV in the E10/E15 Alternate Scenario, which is 41.2 MJ/kg as listed in Table 4.6. However, many other blends can satisfy the scenario criteria targets while essentially maximizing LHV. Of the suitable blends, 9.8% had a LHV within 1% of 41.2 MJ/kg. Blend #1B has a RON of 95.5 but another 968 blends, or 4.8% of all suitable blends, have a RON within 1% of 95.5.

There is a direct trade-off of LHV and RON among the suitable blends because LHV increases and RON generally decreases with increasing alcohol carbon number. Within each scenario, suitable blends with the highest LHV would be desirable for fuels that meet



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minimum knock resistance requirements yet provide an advantage over conventional gasoline-ethanol blends in vehicle range. Suitable blends with the highest RON would be desirable for fuels that meet customer expectations while increasing engine performance through higher knock resistance.

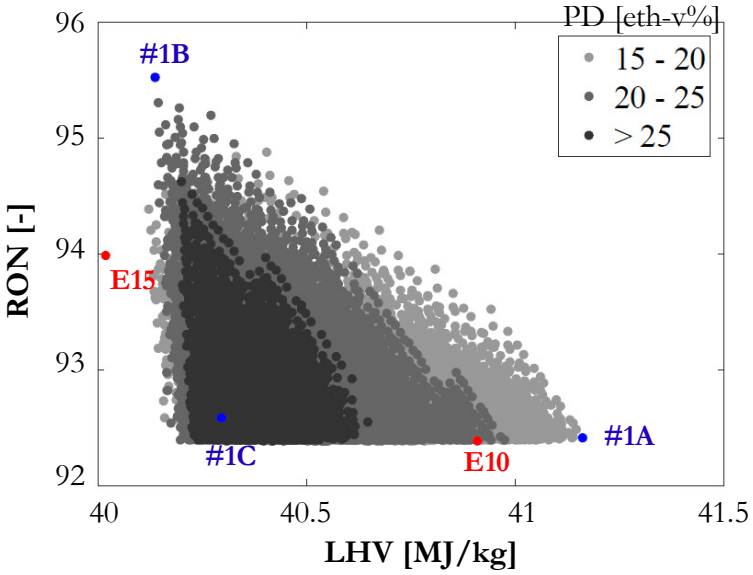


**FIGURE 4.13: LHV/RON CLOUD OF E10/E15 ALTERNATE SCENARIO SUITABLE BLENDS**

All of the suitable blends of the E10/E15 Alternate Scenario, represented in Figure 4.13, have a RVP between 37.9 and 62.1 kPa (5.5 and 9.0 psi), contain less than 5.25 wt% oxygen, have adequate knock resistance and energy content, and have the petroleum displacement of E15 or higher. Certain suitable blends exceed E10 in LHV or E15 in RON. However, because of the strong trade-off between LHV and RON, no blends are both higher than E10 in LHV and E15 in RON.

Figure 4.13 also shows the range of petroleum displacement of all of the E10/E15 Alternate Scenario suitable blends. Petroleum displacement, which is measured by ethanol-equivalent volumetric percent, generally increases with decreasing LHV and RON. The highest LHV blends are equivalent to E15 while the blends in the lower part of the LHV and RON ranges are equivalent to E28. E10 and E15 are also shown in the figure for reference.



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#### 4.2.2.3 Optimal Blend Composition

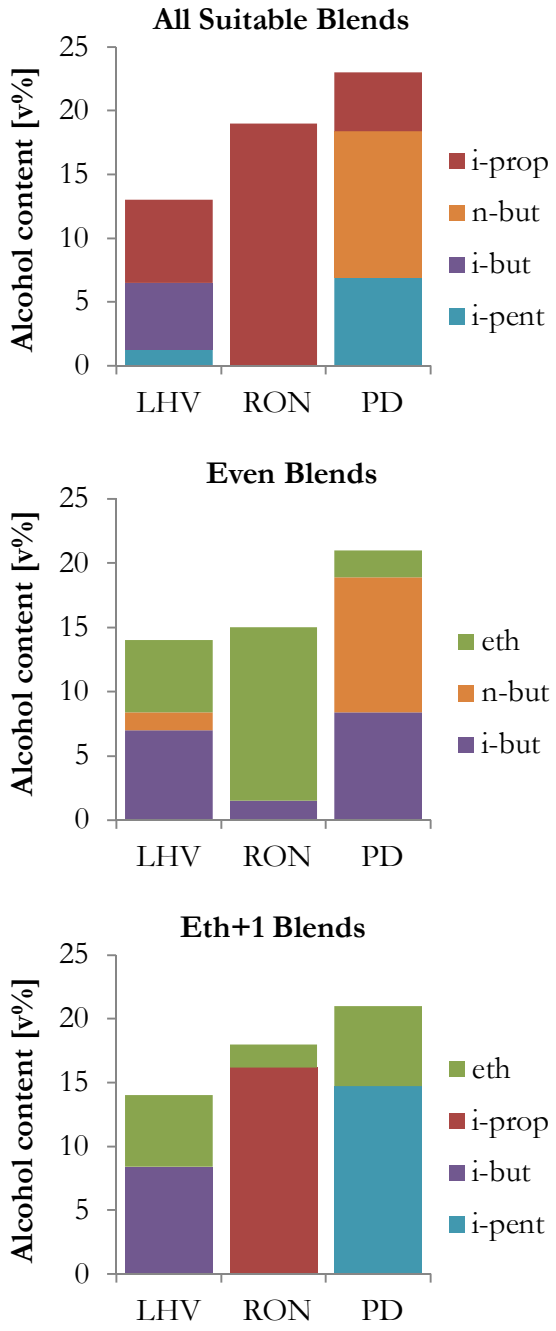


**FIGURE 4.14: COMPOSITION OF OPTIMAL BLENDS IN E10/E15 ALTERNATE SCENARIO**

The composition of each of the three optimal blends (highest LHV, highest RON, and highest PD) for each subset of suitable blends (All, Even, and Eth+1) for the E10/E15 Alternate Scenario is shown in Figure 4.14. The suitable blend with the highest LHV is comprised of 87.0 v% BOB, 6.5 v% iso-propanol, 5.2 v% iso-butanol, and 1.3 v% iso-pentanol. The suitable blend with the highest RON is comprised of 81.0 v% BOB and 19.0 v% iso-propanol. The suitable blend with the highest PD is comprised of 77.0 v% BOB, 4.6 v% iso-propanol, 11.5 v% n-butanol, and 6.9 v% iso-pentanol.

The even carbon number alcohols blend with the highest LHV is comprised of 86.0 v% BOB, 5.6 v% ethanol, 1.4 v% n-butanol, and 7.0 v% iso-butanol. The even carbon number alcohols blend with the highest RON is comprised of 85.0 v% BOB, 13.5 v% ethanol, and 1.5 v% iso-butanol. The even carbon number alcohols blend with the highest PD is comprised of 79.0 v% BOB, 2.1 v% ethanol, 10.5 v% n-butanol, and 8.4 v% iso-butanol.

The eth+1 blend with the highest LHV is comprised of 86.0 v% BOB, 5.6 v% ethanol, and 8.4 v% iso-butanol. The eth+1 blend with the highest RON is comprised of 82.0 v% BOB, 1.8 v% ethanol, and 16.2 v% iso-propanol. The eth+1 blend with the highest PD is comprised of 79.0 v% BOB, 6.3 v% ethanol, and 14.7 v% iso-pentanol.



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The energy content, knock resistance, and petroleum displacement for each of the nine optimal blends is given in Table 4.6 for the E10/E15 Alternate Scenario. In the table, blend #1A is the blend with maximum energy content (LHV), while #1B has maximum knock resistance (RON), and #1C has maximum petroleum displacement (PD). Each of these is given for the three data sets examined: all suitable blends (All), blends of only even number alcohols (Even), and blends that contain only ethanol and one other alcohol (Eth+1).

For each of the nine multi-component blends, the LHV, RON, and PD of the blend is given along with the percent improvement from the reference fuel. For example, the blend from the E10/E15 Alternate Scenario that is composed of only even number alcohols (Even) that has the highest LHV (#1A), which is 86 v% BOB, 5.6 v% ethanol, 1.4 v% n-butanol, and 7.0 v% iso-butanol as shown in Figure 4.14, has a LHV of 40.8 MJ/kg, a RON of 92.4, and a PD of 1.6 ethanol-v%. Its LHV is a 2.0% improvement from that of the reference fuel while matching RON and increasing PD by 10.5%.

A blend targeted at maximum energy content (#1A) provides a 2.9% increase in LHV while maintaining the RON of E10 and increasing PD by 7.4%. A blend targeted at maximum knock resistance (#1B) provides a 3.4% increase in RON while maintaining the energy content of E15 and increasing petroleum displacement by 46.6%. Finally, a fuel blend designed to maximize petroleum displacement results in a 100.8% increase in ethanol-equivalent alcohol content while maintaining RON and even slightly increasing energy content when compared to the reference fuels.

Similar knock resistance and energy content results can be achieved with blends that use only even carbon number alcohols but the potential to increase RON is limited when compared to blends that utilize all alcohols. Blends that use only ethanol and one other alcohol can achieve similar energy content and nearly equal knock resistance as blends of all alcohols, but the petroleum displacement gains are decreased because of the use of ethanol instead of a higher carbon number alcohol.

Compositions of these and several other promising blends, including those that utilize all alcohols as well as even alcohols only and blends of only ethanol and one other alcohol, are listed in Appendix 7.6 with their relevant properties.



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**TABLE 4.6: COMPARISON OF E10/E15 ALTERNATE SCENARIO OPTIMAL BLEND PROPERTIES TO REFERENCE FUELS**

| | | LHV [MJ/kg] | RON [-] | PD [eth-v%] |
|---|---|---|---|---|
| | **Baseline (fuel)** | 40.02 (E15) | 92.39 (E10) | 15.0 (E15) |
| **Blend #1A (max LHV)** | **All** | **41.2 (2.9%)** | 92.4 (0.0%) | 16.1 (7.4%) |
| | **Even** | **40.8 (2.0%)** | 92.4 (0.0%) | 16.6 (10.5%) |
| | **Eth+1** | **40.8 (2.0%)** | 92.6 (0.2%) | 16.5 (10.3%) |
| **Blend #1B (max RON)** | **All** | 40.1 (0.3%) | **95.5 (3.4%)** | 22.0 (46.6%) |
| | **Even** | 40.1 (0.3%) | **93.8 (1.5%)** | 15.5 (3.0%) |
| | **Eth+1** | 40.2 (0.4%) | **95.2 (3.0%)** | 20.6 (37.0%) |
| **Blend #1C (max PD)** | **All** | 40.3 (0.7%) | 92.6 (0.2%) | **30.1 (100.8%)** |
| | **Even** | 40.4 (0.9%) | 92.5 (0.1%) | **26.9 (79.6%)** |
| | **Eth+1** | 40.3 (0.7%) | 92.7 (0.3%) | **26.7 (78.0%)** |



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### 4.2.3 RFS2 FUEL SCENARIO

The objective of the RFS2 Fuel Scenario is to identify blends that contain an ethanol-equivalent alcohol volume that meets the RFS2 requirement in addition to vapor pressure, knock resistance, and energy content criteria similar to those in the E10/E15 Alternate Scenario. Gasoline-alcohol blends that are suitable for this scenario will meet the criteria targets listed in Table 4.7.

**TABLE 4.7: CRITERIA, MOTIVATION, AND TARGET VALUES FOR THE RFS2 FUEL SCENARIO**

| Criteria | Motivation | Target |
|---|---|---|
| **LHVa minimum** | Meet RFS2 requirements | 5038 MJ/m$^3$ (E25) |
| **LHV minimum** | Meet consumer expectations | 38.26 MJ/kg (E25) |
| **RON minimum** | Utilize current engines | 92.4 (E10) |
| **RVP minimum** | Satisfy ASTM standards | 5.5 psi |
| **RVP maximum** | Satisfy ASTM standards | 15.0 psi |

#### 4.2.3.1 CRITERIA NON-ATTAINMENT

The percentage of examined blends at each total alcohol content value that did not meet each of the criteria targets (minimum LHV, RON, and RVP and maximum RVP) for the RFS2 Fuel Scenario is shown in Figure 4.15. Some blends failed to meet more than one criteria target, so the sum of the percentages, or non-attainment frequencies, at any one total alcohol content may be greater than 100%.

None of the blends below 20 v% total alcohol content or above 37 v% are suitable for the RFS2 Fuel Scenario. The low level blends are not suitable because they do not meet the minimum alcohol content (LHVa min) or the minimum knock resistance (RON min) criteria. The high level blends are not suitable because they do not meet the minimum vapor pressure (RVP min) or minimum energy content (LHV min) criteria.

A large percentage of low level blends (79.0% of the blends with 17 v% total alcohol content) do not meet the minimum RON criterion, but this occurs less with increasing total alcohol content. Above 43 v% total alcohol content, less than 20% of the blends are disqualified because they do not meet the RON criterion.

The LHV minimum criterion is not of concern with low level blends as the BOB has a much higher energy content than all of the alcohols. No blends below 26 v% total alcohol content are disqualified by the minimum energy content criterion. However, as total



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alcohol content increases, the LHV minimum criterion disqualifies many blends (94.1% of blends with 50 v% total alcohol content).

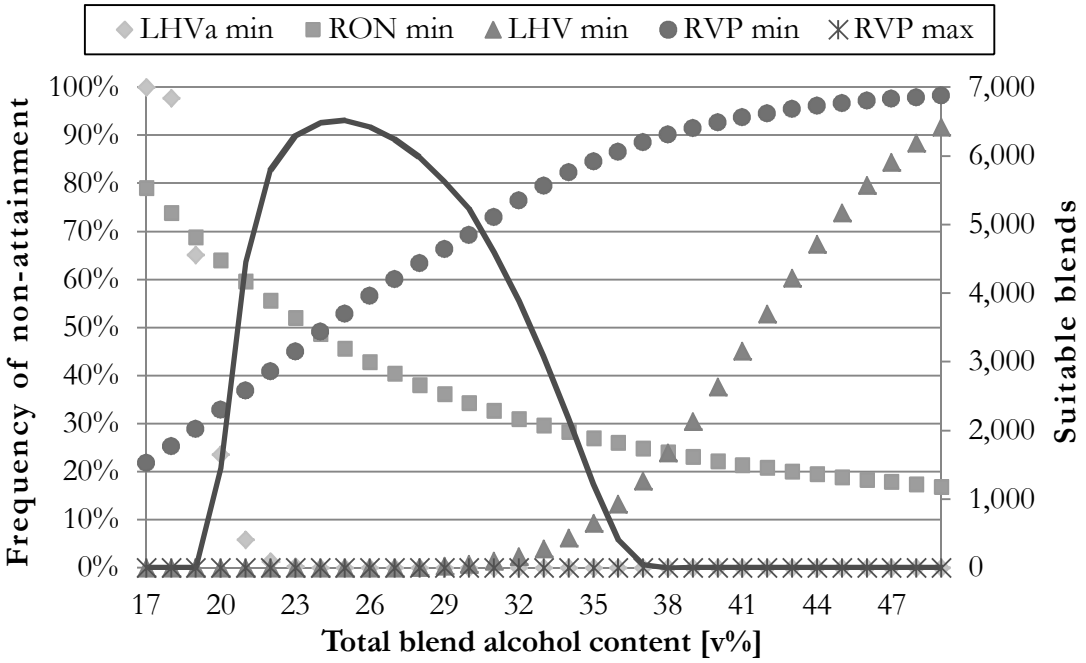


**FIGURE 4.15: CRITERIA NON-ATTAINMENT OF RFS2 FUEL SCENARIO**

The RVP minimum criterion of 5.5 psi renders some blends unsuitable at each level of total blend alcohol content. At 17 v% total alcohol content, 21.8% of blends are unsuitable because they have a RVP less than 5.5 psi. The RVP minimum non-attainment frequency increases with total alcohol content, to 98.5% at 50 v%. This is similar to the E10/E15 Alternate Scenario.

Figure 4.15 also shows the number of blends that are suitable for the RFS2 Fuel Scenario for each level of total blend alcohol content. There are no suitable blends at from 17 to 19 v% or from 38 to 50 v% total alcohol content. The largest number of suitable blends occurs at 25 v% total alcohol content where 6513 of the 35196 (18.5%) possible blends of that alcohol content are suitable. The number of suitable blends decreases rapidly with increasing or decreasing total alcohol content from 25 v%.



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#### 4.2.3.2 BLEND PROPERTY ASSESSMENT

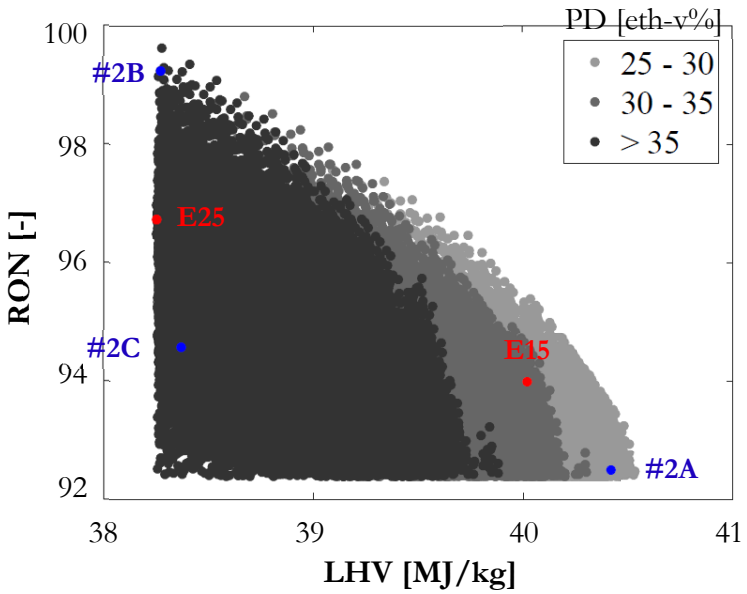


**FIGURE 4.16: LHV/RON CLOUD OF RFS2 FUEL SCENARIO SUITABLE BLENDS**

All of the suitable blends of the RFS2 Fuel Scenario, represented in Figure 4.16, have a RVP between 37.9 and 103.4 kPa (5.5 and 15.0 psi), adequate knock resistance and energy content, and have the energy-based ethanol-equivalent of E25 or higher. Based on the EIA total fuel consumption projections [8], E25 is the necessary blend level to satisfy the RFS2 requirements in 2022 [7]. Certain suitable blends exceed E15 in LHV or E25 in RON. But again, no blends are both higher than E15 in LHV and E25 in RON because of the LHV/RON trade-off among the alcohols.

The density of points in the LHV/RON cloud indicates that there are many suitable blends that have essentially equal LHV and/or RON. The compositions given in Figure 4.17 refer to the mathematically optimal blend but several other blends with slightly different compositions achieve practically identical properties. The compositions of several of the suitable blends are listed in Appendix 7.6 with their relevant properties.

The ethanol equivalence of the RFS2 Fuel Scenario suitable blends ranges from E25 to E46. Similar to the E10/E15 Alternate Scenario suitable blends, those with higher LHV have lower petroleum displacement. Petroleum displacement increases with decreasing LHV and slightly with decreasing RON. The RFS2 Fuel Scenario suitable blend with the highest LHV, RON, and petroleum displacement (PD) are shown as blend #2A, #2B, and



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#2C, respectively, in Figure 4.16. The composition of each of these blends is illustrated in Figure 4.17 and their properties are listed in Table 4.8. These blends are discussed in subsequent sections.

The blend shown as #2A in Figure 4.16 yields the highest LHV in the RFS2 Fuel Scenario, which is 40.6 MJ/kg as listed in Table 4.8. However, many other blends can satisfy the scenario criteria targets while essentially maximizing LHV. Of the suitable blends, 4.1%, or 3122 blends, had a LHV within 1% of 40.6 MJ/kg. Blend #2B has a RON of 99.6 but another 919 blends, or 1.2% of all suitable blends, have a RON within 1% of 99.6.



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#### 4.2.3.3 Optimal Blend Composition

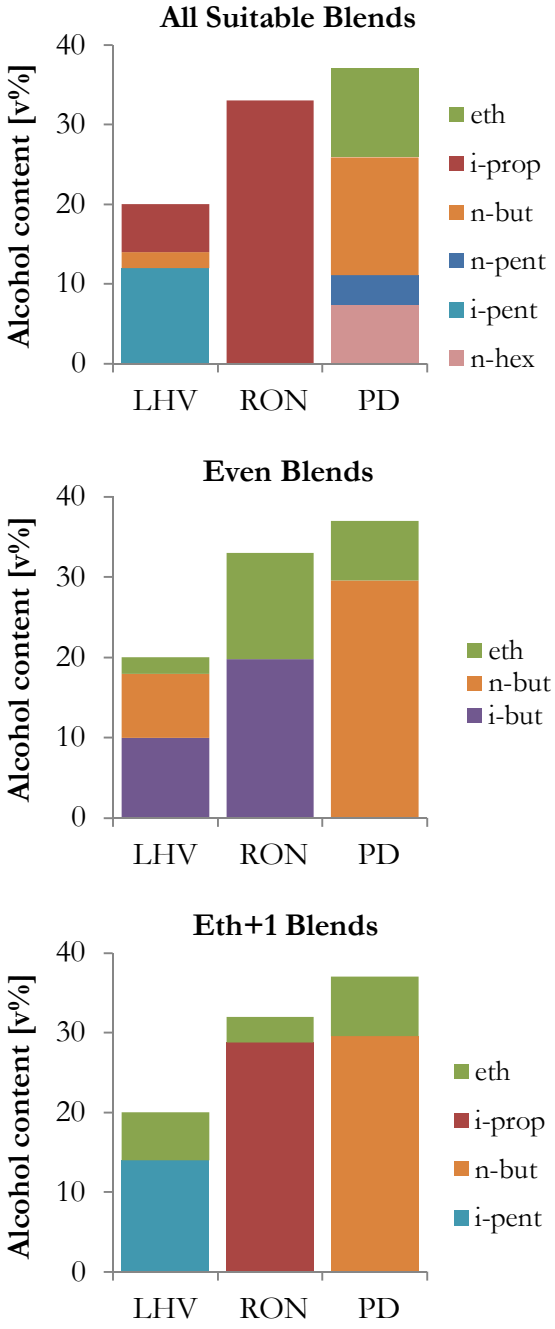


**FIGURE 4.17: COMPOSITION OF OPTIMAL BLENDS IN RFS2 FUEL SCENARIO**

The composition of each of the three optimal blends (highest LHV, highest RON, and highest PD) for each subset of suitable blends (all, even, and eth+1) for the RFS2 Fuel Scenario is shown in Figure 4.17. The suitable blend with the highest LHV is comprised of 80.0 v% BOB, 6.0 v% iso-propanol, 2.0 v% n-butanol, and 12.0 v% iso-pentanol. The suitable blend with the highest RON is comprised of 67.0 v% BOB and 33.0 v% iso-propanol. The suitable blend with the highest PD is comprised of 63.0 v% BOB, 11.1 v% ethanol, 14.8 v% n-butanol, 3.7 v% n-pentanol, and 7.4 v% n-hexanol.

The even carbon number alcohols blend with the highest LHV is comprised of 80.0 v% BOB, 2.0 v% ethanol, 8.0 v% n-butanol, and 10.0 v% iso-butanol. The even carbon number alcohols blend with the highest RON is comprised of 67.0 v% BOB, 13.2 v% ethanol, and 19.8 v% iso-butanol. The even carbon number alcohols blend with the highest PD is comprised of 63.0 v% BOB, 7.4 v% ethanol, and 29.6 v% n-butanol.

The eth+1 blend with the highest LHV is comprised of 80.0 v% BOB, 6.0 v% ethanol, and 14.0 v% iso-pentanol. The eth+1 blend with the highest RON is comprised of 68.0 v% BOB, 3.2 v% ethanol, and 28.8 v% iso-propanol. The eth+1 blend with the highest PD is comprised of 63.0 v% BOB, 7.4 v% ethanol, and 29.6 v% n-butanol.



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As listed in Table 4.5, the RFS2 Fuel blend with the highest LHV (#2A) exceeds that of the reference fuel (E25) by 6.2% while maintaining RON and increasing PD by 5.0%. A 5.8% improvement in LHV can be achieved when using only even number alcohols and a 5.6% improvement can be achieved with blends that are composed of only ethanol plus one other alcohol.

The RFS2 Fuel blend with the highest knock resistance (#2B) achieves a RON of 99.6 which is 7.8% higher than the reference fuel (E10) and even significantly exceeds the RON of E25 which is 96.7. At the same time, this blend improves PD by more than 50% while maintaining the energy content of E25. If only even carbon alcohols are used, the maximum achievable RON is 96.8 which is 4.8% above E10 and equivalent to E25. At the same energy content this even carbon alcohol blend improves the PD compared to E25 by 56%. The Eth+1 blend achieves a RON of 99.2 while maintaining LHV and increasing PD by 46%.

When targeting maximum PD (#2C) in the RFS2 Fuel Scenario, a blend based on selection from all alcohols can increase the ethanol-equivalent content by more than 86% while maintaining energy content of E25 and knock resistance equivalent to that of E10. When limiting the selection of alcohols to even carbon only, PD can still be improved by 86% while maintaining energy content. The knock resistance exceeds the base fuel but remains below that of E25. The Eth+1 blend achieve similar results with a PD of 46.6 ethanol v%, LHV of 38.4 MJ/kg, and RON of 94.6.

Detailed compositions of these and several other promising blends, including those that utilize all alcohols as well as even alcohols only and blends of only ethanol and one other alcohol, are listed in Appendix 7.6 with their relevant properties.



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**TABLE 4.8: COMPARISON OF RFS2 FUEL SCENARIO OPTIMAL BLEND PROPERTIES TO REFERENCE FUELS**

| | | LHV [MJ/kg] | RON [-] | PD [eth-v%] |
|---|---|---|---|---|
| | **Baseline (fuel)** | 38.26 (E25) | 92.39 (E10) | 25.0 (E25) |
| **Blend #2A (max LHV)** | **All** | **40.6 (6.2%)** | 92.6 (0.2%) | 26.2 (5.0%) |
| | **Even** | **40.5 (5.8%)** | 92.5 (0.2%) | 25.6 (2.5%) |
| | **Eth+1** | **40.4 (5.6%)** | 92.5 (0.1%) | 25.4 (1.7%) |
| **Blend #2B (max RON)** | **All** | 38.3 (0.0%) | **99.6 (7.8%)** | 38.2 (52.8%) |
| | **Even** | 38.3 (0.1%) | **96.8 (4.8%)** | 39.0 (56.0%) |
| | **Eth+1** | 38.3 (0.0%) | **99.2 (7.4%)** | 36.5 (46.2%) |
| **Blend #2C (max PD)** | **All** | 38.4 (0.4%) | 92.9 (0.5%) | **46.6 (86.6%)** |
| | **Even** | 38.4 (0.3%) | 94.6 (2.4%) | **46.6 (86.3%)** |
| | **Eth+1** | 38.4 (0.3%) | 94.6 (2.4%) | **46.6 (86.3%)** |



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### 4.2.4 E85 Alternate Scenario

The objective of the E85 Alternate Scenario is to identify blends that utilize high levels of alcohols and have high knock resistance, but do not have the range penalty (lowered energy content) of E85. Gasoline-alcohol blends that are suitable for this scenario will meet the criteria targets listed in Table 4.9.

**TABLE 4.9: CRITERIA, MOTIVATION, AND TARGET VALUES FOR THE E85 ALTERNATE SCENARIO**

| Criteria | Motivation | Target |
|---|---|---|
| **LHVa minimum** | Meet RFS2 requirements | 15517 MJ/m$^3$ (E77) |
| **LHV minimum** | Meet consumer expectations | 29.35 MJ/kg (E77) |
| **RON minimum** | Utilize advanced engines | 100 |
| **RVP minimum** | Satisfy ASTM standards | 5.5 psi |
| **RVP maximum** | Satisfy ASTM standards | 8.5 psi |

#### 4.2.4.1 Criteria Non-attainment

The percentage of examined blends at each total alcohol content value that did not meet each of the criteria targets (minimum LHV, RON, and RVP and maximum RVP) for the E85 Alternate Scenario is shown in Figure 4.18. Some blends failed to meet more than one criteria target, so the sum of the percentages, or non-attainment frequencies, at any one total alcohol content may be greater than 100%.

In this scenario, there are no suitable blends below 61 v% total alcohol content. This is largely due to the minimum alcohol content criterion which disqualifies all blends up to 55 v% total alcohol content. From 55 to 61 v% total alcohol content, a large percentage of blends do not meet the minimum alcohol content and/or the minimum knock resistance criteria. The effect of both of these criteria diminishes with increasing total alcohol content (the RON min criterion to 53.3% of blends at 90 v% and the LHVa min criterion to 0% at 77 v% total alcohol content).

Figure 4.18 also shows the number of blends that are suitable for the E85 Alternate Scenario for each level of total blend alcohol content. There are no suitable blends below 61 v% total alcohol content. The largest number of suitable blends occurs at 90 v% total alcohol content, the highest level examined, where 6684 of the 35196 (19.0%) possible blends of that alcohol content are suitable. The number of suitable blends quickly increases between 62 and 70 v%, then gradually increases to 90 v% total alcohol content.



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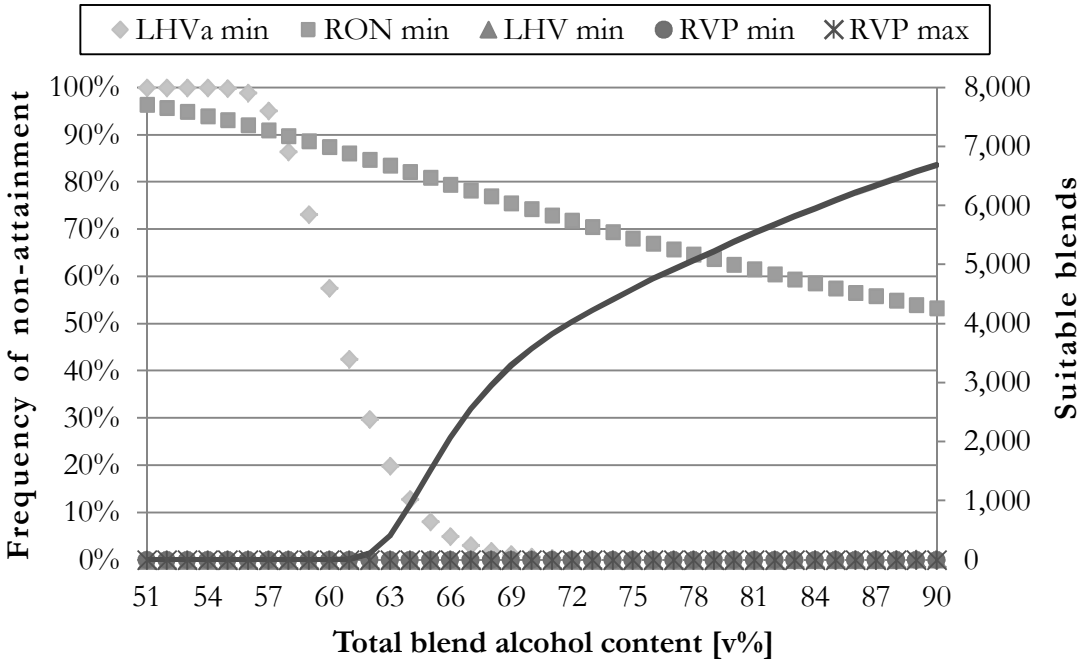


**FIGURE 4.18: CRITERIA NON-ATTAINMENT OF E85 ALTERNATE SCENARIO**

4.2.4.2 BLEND PROPERTY ASSESSMENT

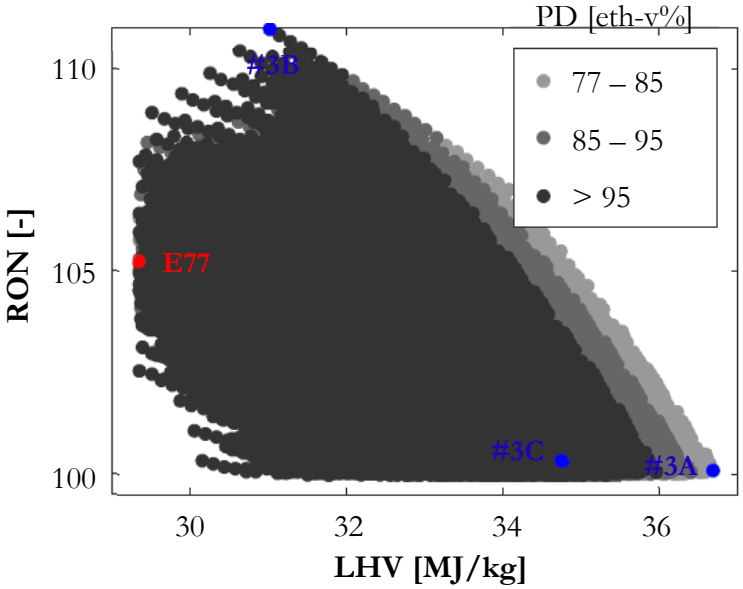


**FIGURE 4.19: LHV/RON CLOUD OF E85 ALTERNATE SCENARIO SUITABLE BLENDS**



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All of the suitable blends of the E85 Alternate Scenario, represented in Figure 4.19, have a RVP between 37.9 and 58.6 kPa (5.5 and 8.5 psi), adequate knock resistance and energy content, and have the energy-based ethanol-equivalent of E77 or higher. Certain suitable blends exceed E77 in LHV or in RON. But again, no blends are both higher than E77 in LHV and in RON because of the LHV/RON trade-off among the alcohols.

The density of points in the LHV/RON cloud indicates that there are many suitable blends that have essentially equal LHV and/or RON. The compositions given in Figure 4.20 refer to the mathematically optimal blend but several other blends with slightly different compositions achieve practically identical properties. The compositions of several of the suitable blends are listed in Appendix 7.6 with their relevant properties.

The ethanol equivalence of the E85 Alternate Scenario suitable blends ranges from E77 to E122. Similar to the suitable blends of the other two scenarios, those with higher LHV have lower petroleum displacement. Petroleum displacement increases with decreasing LHV and slightly with decreasing RON. The E85 Alternate Scenario suitable blend with the highest LHV, RON, and petroleum displacement (PD) are shown as blend #3A, #3B, and #3C, respectively, in Figure 4.19. The composition of each of these blends is illustrated in Figure 4.20 and their properties are listed in Table 4.10. These blends are discussed in subsequent sections.

The blend shown as #3A in Figure 4.19 yields the highest LHV in the E85 Alternate Scenario, which is 36.7 MJ/kg as listed in Table 4.10. However, many other blends can satisfy the scenario criteria targets while essentially maximizing LHV. Of the suitable blends, 0.5%, or 608 blends, had a LHV within 2% of 36.7 MJ/kg. Blend #3B has a RON of 111.0 but another 1293 blends, or 1.0% of all suitable blends, have a RON within 2% of 111.0.



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#### 4.2.4.3 Optimal Blend Composition

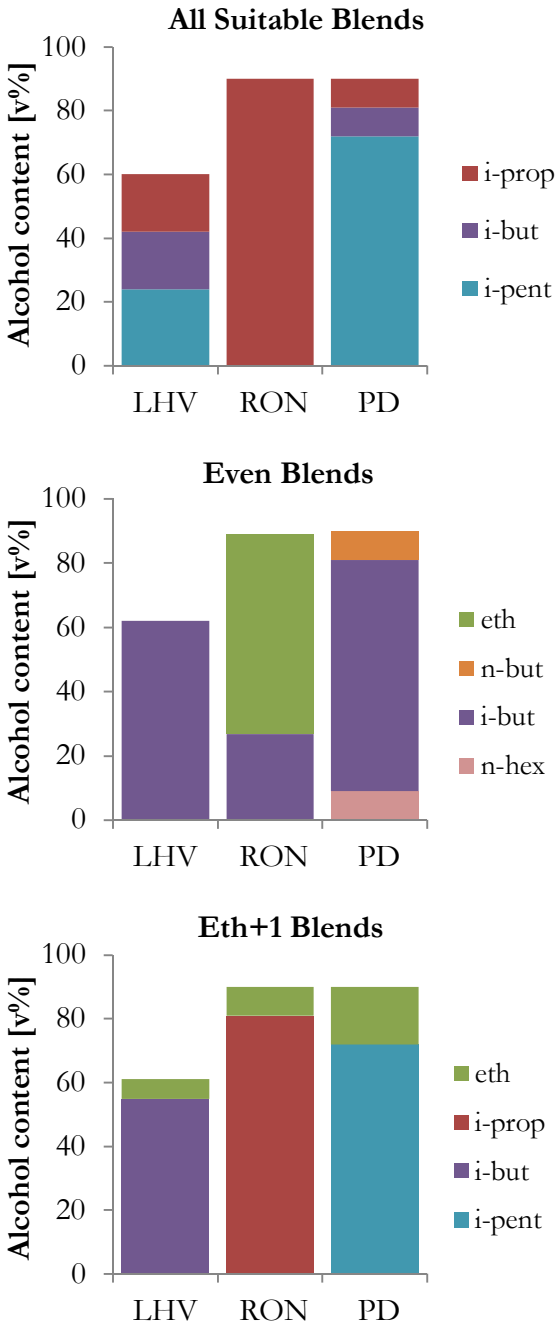


**FIGURE 4.20: COMPOSITION OF OPTIMAL BLENDS IN E85 ALTERNATE SCENARIO**

The composition of each of the three optimal blends (highest LHV, highest RON, and highest PD) for each subset of suitable blends (all, even, and eth+1) for the E85 Alternate Scenario is shown in Figure 4.20. The suitable blend with the highest LHV is comprised of 40.0 v% BOB+, 18.0 v% iso-propanol, 18.0 v% iso-butanol, and 24.0 v% iso-pentanol. The suitable blend with the highest RON is comprised of 10.0 v% BOB+ and 90.0 v% iso-propanol. The suitable blend with the highest PD is comprised of 10.0 v% BOB+, 9.0 v% iso-propanol, 9.0 v% iso-butanol, and 72.0 v% iso-pentanol.

The even carbon number alcohols blend with the highest LHV is comprised of 38.0 v% BOB+ and 62.0 v% iso-butanol. The even carbon number alcohols blend with the highest RON is comprised of 11.0 v% BOB+, 62.3 v% ethanol, and 26.7 v% iso-butanol. The even carbon number alcohols blend with the highest PD is comprised of 10.0 v% BOB+, 9.0 v% n-butanol, 72.0 v% iso-butanol, and 9.0 v% n-hexanol.

The eth+1 blend with the highest LHV is comprised of 39.0 v% BOB+, 6.1 v% ethanol, and 54.9 v% iso-butanol. The eth+1 blend with the highest RON is comprised of 10.0 v% BOB+, 9.0 v% ethanol, and 81.0 v% iso-propanol. The eth+1 blend with the highest PD is comprised of 10.0 v% BOB+, 18.0 v% ethanol, and 72.0 v% iso-pentanol.



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The E85 Alternate Scenario blend targeted at maximizing energy content (#3A) achieves a LHV of 36.7 MJ/kg exceeding that of the reference fuel (E77) by 25% while maintaining knock resistance and petroleum displacement. Slightly lower improvements can be achieved when limiting to even carbon alcohols only or to blends of only ethanol and one other alcohol.

The blend with the highest knock resistance (#3B) in the E85 Alternate Scenario achieves a RON of 111.0 exceeding the RON target by 11.0% while simultaneously increasing LHV by 5.7% and PD by more than 35%. If the alcohol selection is limited to even alcohols only, the maximum achievable RON is 105.8 which still significantly exceeds the RON target at constant energy content and a PD of 97.1. The Eth+1 blend achieves a similar RON of 110.4 with LHV 4.4% above the RON target and PD 33.5% above the reference fuel.

The E85 Alternate Scenario blend with the highest PD reaches an ethanol-equivalent content of 122 v% while meeting the RON target and increasing the LHV by 18.5%. When limited to even alcohols only, the maximum PD is reduced to 118.8 eth-v% at a RON of 100.7 and an improvement in LHV of 16.1%. Finally, when limited to Eth+1 blends, a PD of 117.9 eth-v% is reached while having a RON of 100.6 and LHV of 33.8 MJ/kg.

Detailed compositions of these and several other promising blends, including those that utilize all alcohols as well as even alcohols only and blends of only ethanol and one other alcohol, are listed in Appendix 7.6 with their relevant properties.



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**TABLE 4.10: COMPARISON OF E85 ALTERNATE SCENARIO OPTIMAL BLEND PROPERTIES TO REFERENCE FUELS**

| | | LHV [MJ/kg] | RON [-] | PD [eth-v%] |
|---|---|---|---|---|
| | **Baseline (fuel)** | 29.35 (E77) | 100 | 77.0 (E77) |
| **Blend #3A (max LHV)** | **All** | **36.7 (25.0%)** | 100.1 (0.1%) | 77.6 (0.8%) |
| | **Even** | **36.6 (24.7%)** | 100.0 (0.0%) | 80.8 (4.9%) |
| | **Eth+1** | **36.3 (23.5%)** | 100.3 (0.3%) | 77.7 (0.8%) |
| **Blend #3B (max RON)** | **All** | 31.0 (5.7%) | **111.0 (11.0%)** | 104.2 (35.3%) |
| | **Even** | 29.4 (0.2%) | **105.8 (5.8%)** | 97.1 (26.1% |
| | **Eth+1** | 30.6 (4.4%) | **110.4 (10.4%)** | 102.8 (33.5%) |
| **Blend #3C (max PD)** | **All** | 34.8 (18.5%) | 100.3 (0.3%) | **122.1 (58.5%)** |
| | **Even** | 34.1 (16.1%) | 100.7 (0.7%) | **118.8 (54.3%)** |
| | **Eth+1** | 33.8 (15.1%) | 100.6 (0.6%) | **117.9 (53.1%)** |



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### 4.2.5 General Trends

In all of the scenarios, and regardless of which blend property is being maximized, replacing alcohol blend components with alcohols of the same carbon number but different structure (for example, swapping iso-propanol for n-propanol) has negligible effect on the blend properties. For many cases, replacing one of the alcohol components with a different carbon number and/or structure alcohol also has negligible effect. This can be seen when comparing the composition of the five best blends when maximizing for each variable in each scenario, listed in the Appendix 7.6.

The largest gains from the use of higher alcohols are shown in the maximum PD blends of each of the scenarios. These blends increase petroleum displacement to 53 to 101% that of their reference fuel while matching energy content and knock resistance. These results demonstrate that higher carbon number alcohol blends could greatly increase the use of alternative fuels to meet the RFS2 standard while utilizing current engine technologies.

The ability of higher alcohols to increase the energy content of a blend increases with increasing total alcohol content. Improvements of only 2.0 to 2.9% were made in LHV for the E10/E15 Alternate Scenario which has blends of total alcohol content between 10 and 20 v%. LHV improvements of 5.6 to 6.2% occur in the RFS2 Fuel Scenario where blends have total alcohol content between 17 and 50 v%. The E85 Alternate Scenario, which has blends of total alcohol content between 51 and 90 v%, shows LHV gains of 23.5 to 25.0%.

Knock resistance can also be increased more with higher total alcohol content. RON gains for the E10/E15 Alternate Scenario, which has the lowest total alcohol content blends, are between 1.5 and 3.4%. RON gains in the E85 Alternate Scenario, which has the highest total alcohol content blends, are between 5.8 and 11.0%.



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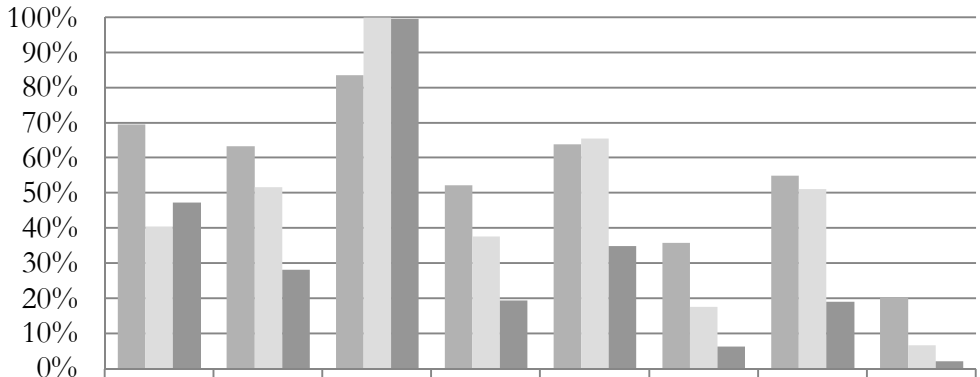
Figure 4.21, Figure 4.22, and Figure 4.23 illustrate the occurrence level of each alcohol in the suitable blends of each scenario. The percentages in the "LHV" row are for the blends with the highest LHV, percentages in the "RON" row are for the top RON blends, and percentages in the "All" row are for all suitable blends. For example, in the E10/E15 Alternate Scenario (Figure 4.21), ethanol appears in 70% of all suitable blends (row All) but only in 47% of the blends with the highest RON values (row RON) and 40% of the blends with the highest LHV values (row LHV). This means that ethanol can be used in many blends that satisfy the requirements of the scenario, but that ethanol is replaced by another alcohol when maximizing LHV or RON.




| | eth | n-prop | i-prop | n-but | i-but | n-pent | i-pent | n-hex |
|---|---|---|---|---|---|---|---|---|
| All | 70% | 63% | 84% | 52% | 64% | 36% | 55% | 20% |
| LHV | 40% | 52% | 100% | 38% | 65% | 18% | 51% | 7% |
| RON | 47% | 28% | 100% | 20% | 35% | 6% | 19% | 2% |

**FIGURE 4.21: ALCOHOL OCCURRENCE IN E10/E15 ALTERNATE SCENARIO SUITABLE BLENDS**



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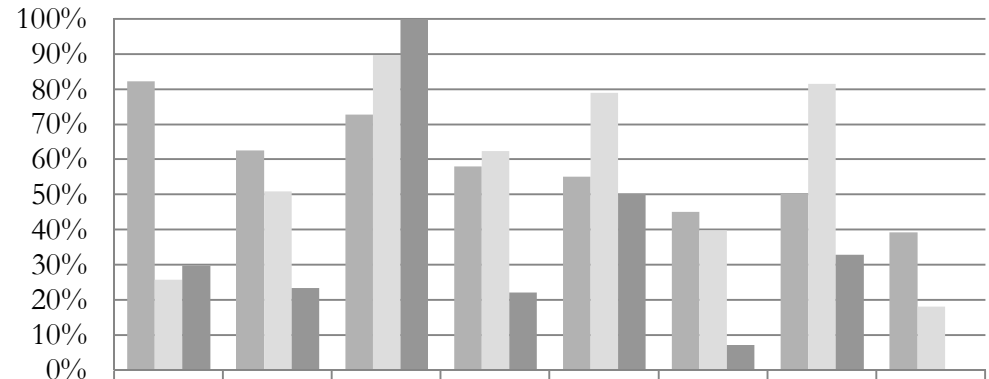


| | eth | n-prop | i-prop | n-but | i-but | n-pent | i-pent | n-hex |
|---|---|---|---|---|---|---|---|---|
| All | 82% | 63% | 73% | 58% | 55% | 45% | 50% | 39% |
| LHV | 26% | 51% | 90% | 62% | 79% | 40% | 82% | 18% |
| RON | 30% | 24% | 100% | 22% | 50% | 7% | 33% | 0% |

**FIGURE 4.22: ALCOHOL OCCURRENCE IN RFS2 FUEL SCENARIO SUITABLE BLENDS**

The alcohol occurrence figures show that iso-propanol is, overall, the most popular alcohol in each of the scenarios. Iso-propanol is used in 84%, 73%, and 77% of all of the suitable blends in the E10/E15 Alternate, RFS2 Fuel, and E85 Alternate scenarios, respectively. When maximizing for RON, iso-propanol becomes very dominant, occurring in 100% of the top RON blends in each of the three scenarios. Iso-propanol is dominant when maximizing for LHV as well, occurring in 90% or more of the top RON blends in each scenario.

Iso-butanol and iso-pentanol are also quite popular in each of the scenarios. Iso-butanol and iso-pentanol increase in popularity when maximizing for LHV. For example, 55% of all suitable blends in the RFS2 Fuel Scenario contain iso-butanol but 79% of the top LHV blends contain it. This correlates to the properties of neat alcohols shown in Figure 2.5.

The iso- structure of each alcohol is more popular than its n- structure in all of the scenarios. For example, n-butanol is used in 52% of all suitable blends, 20% of top RON blends, and 38% of top LHV blends in the E10/E15 Alternate Scenario while iso-butanol is used in 64% of all suitable blends, 35% of top RON blends, and 65% of top LHV blends. This trend is due to the slightly higher RON of the iso- structures while having the same LHV and PD as the n- structures.



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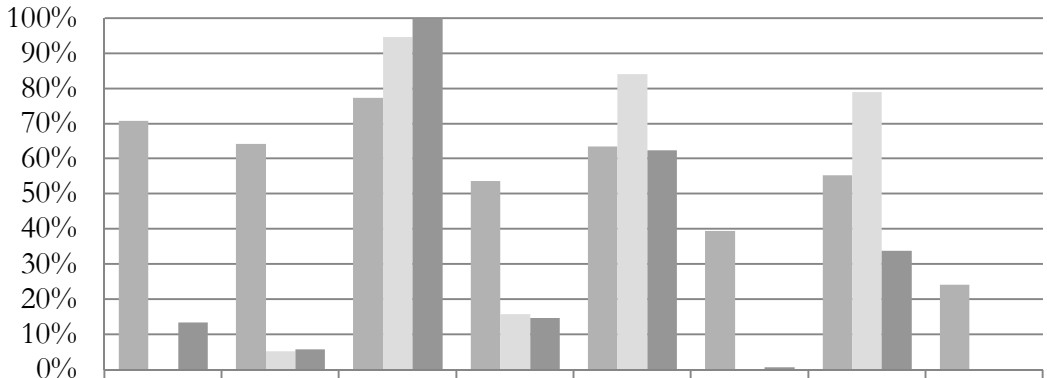
Low occurrence of the highest carbon number alcohols, pentanol and hexanol, was expected because of their low knock resistance. However, iso-pentanol was quite popular, being used in nearly the same percentage of blends as n-propanol in each scenario. In many cases, the higher LHV and PD of iso-pentanol made it a desirable blend component despite its lower RON.




| | eth | n-prop | i-prop | n-but | i-but | n-pent | i-pent | n-hex |
|---|---|---|---|---|---|---|---|---|
| All | 71% | 64% | 77% | 54% | 64% | 39% | 55% | 24% |
| LHV | 0% | 5% | 95% | 16% | 84% | 0% | 79% | 0 |
| RON | 13% | 6% | 100% | 15% | 62% | 1% | 34% | 0% |

**FIGURE 4.23: ALCOHOL OCCURRENCE IN R85 ALTERNATE SCENARIO SUITABLE BLENDS**



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## 4.3 TARGET VALUE SENSITIVITY

To explore how the criteria target values effect the composition of the optimal blends, the highest LHV suitable blend was identified for a sweep of RON target values while all other criteria targets remained the same. While the composition of only one top blend is plotted here, there are many blends that have very similar LHV and could therefore be considered the best blend. The plots in this section show the composition of the blend with either the highest LHV or RON for a certain value of the minimum LHV or minimum RON criteria target. The composition of each blend is read vertically at each x-axis value.

For example, to generate Figure 4.24, first the RON criteria target is set to 89 while all other criteria are as listed in Table 4.5. All of the blends that meet the criteria are sorted by LHV. The blend with the highest LHV that meets all of the criteria is 1.1 v% n-butanol, 5.5 v% iso-butanol, and 4.4 v% n-hexanol with BOB. These concentrations are all plotted at an x-axis value of 89. Then the RON criteria target is changed to 89.5 and the process is repeated.

The target value sweep plots, Figure 4.24 through Figure 4.29, also show the LHV and/or RON values of the reference fuel(s) for each of the scenarios as a black vertical line. For example, the two black vertical lines shown in Figure 4.24 are at 92.4, the RON of E10, and 94.0, the RON of E15.

Figure 4.24 shows the effect of RON target value on the best LHV blend composition in the E10/E15 Alternate Scenario. At a RON target of 92 (blend must have a RON of 92 or higher), the blend that has the highest LHV while meeting all of the other scenario criteria listed in Table 4.5 is 3.9 v% iso-propanol and 9.1 v% iso-butanol mixed with BOB. When the RON target increases to 95 the highest LHV suitable blend is 19 v% iso-propanol with BOB. The plot ends at the maximum RON achieved in the scenario, 95.5, with 19.0 v% iso-propanol with BOB (blend #1B).

As the minimum acceptable RON increases, the highest carbon number alcohols, which have poor RON, are replaced with those lower in carbon number. The same behavior is seen in the RFS2 Fuel Scenario, shown in Figure 4.26. At a RON target of 94, the top LHV blend is 6.3 v% iso-propanol and 14.7 v% iso-butanol with BOB. The maximum RON achieved in the scenario, 99.6, is a blend of 33 v% iso-propanol and BOB (blend #2B).



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In both the E10/E15 Alternate and RFS2 Fuel Scenarios, once the RON target is sufficiently high the optimal blend becomes just iso-propanol with BOB because iso-propanol has the highest RON of all of the alcohols. As the RON target continues to increase, the concentration of iso-propanol increases to meet the RON target until the amount of iso-propanol causes the blend to fail one of the other criteria. At that point there are no suitable blends and RON targets of that value or higher cannot be reached. This occurs at a RON target value equal to the maximum RON achieved in each scenario. Ethanol is not utilized in either scenario because iso-propanol has similar properties with higher RON.

Figure 4.25 shows the effect of LHV target value on the best RON blend composition in the E10/E15 Alternate Scenario. For LHV target values of 39.5 to 40.25 MJ/kg, the blend with the highest RON is 2.3 v% ethanol, 4.6 v% iso-propanol, 2.3 v% n-butanol, 11.5 v% iso-pentanol, and 2.3 v% n-hexanol mixed with BOB. As the value of the of LHV target increases past 40.25 MJ/kg, the higher number alcohols (pentanol and hexanol) are replaced with lower number ones (propanol and butanol).

The same general trend appears in the blends with the highest RON for each LHV target value for the RFS2 Fuel Scenario shown in Figure 4.27. At a LHV target value of 37 MJ/kg, the blend with the highest RON that still meets all of the other scenario criteria targets is 22.0 v% ethanol, 4.4 v% n-propanol, and 17.6 v% n-hexanol mixed with BOB. At a LHV target value of 39.5 MJ/kg, the blend with the highest RON is 12.0 v% iso-propanol, 9.0 v% n-butanol, and 9.0 v% n-hexanol mixed with BOB.



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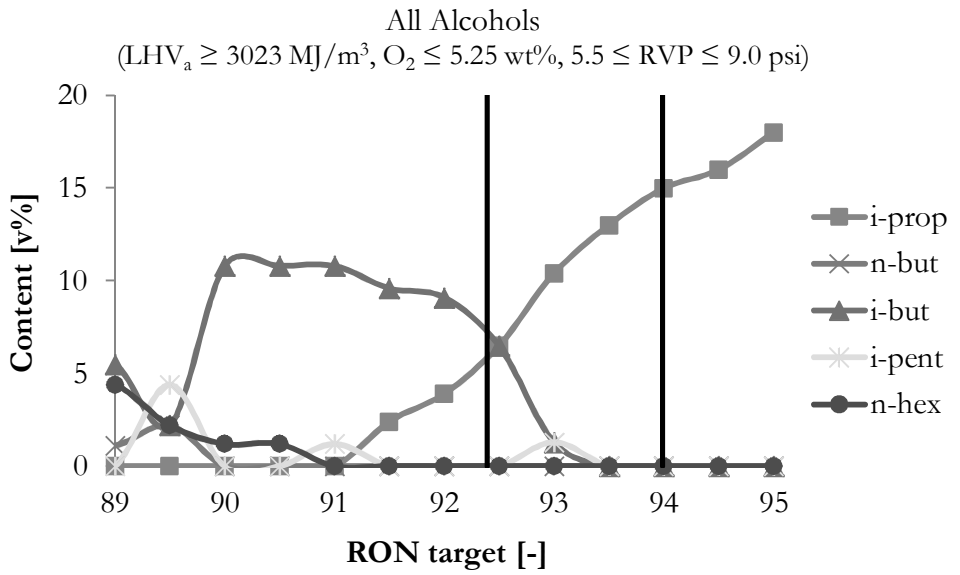


**FIGURE 4.24: EFFECT OF CHANGING RON TARGET VALUE ON OPTIMAL LHV BLEND FOR E10/E15 ALTERNATE SCENARIO**

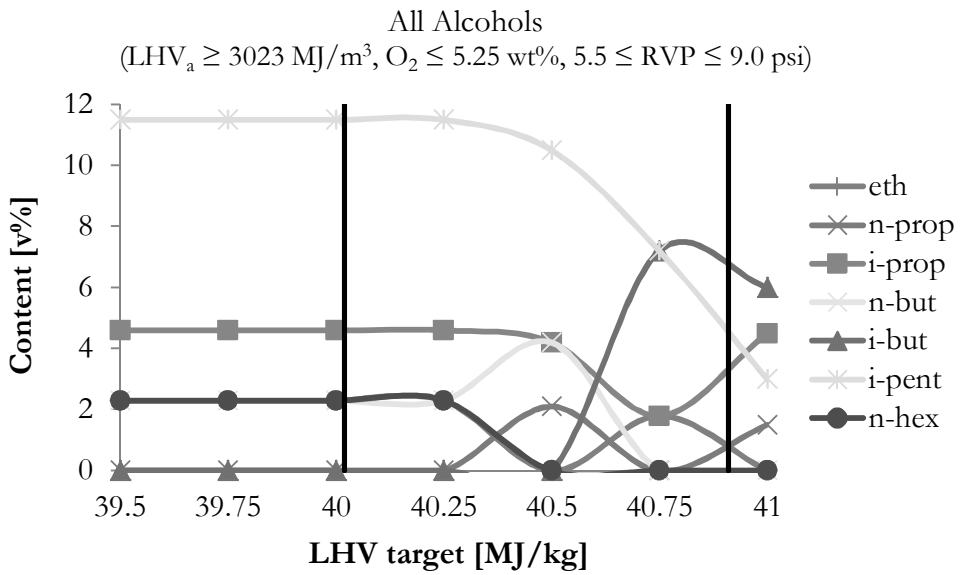


**FIGURE 4.25: EFFECT OF CHANGING LHV TARGET VALUE ON OPTIMAL RON BLEND FOR E10/E15 ALTERNATE SCENARIO**



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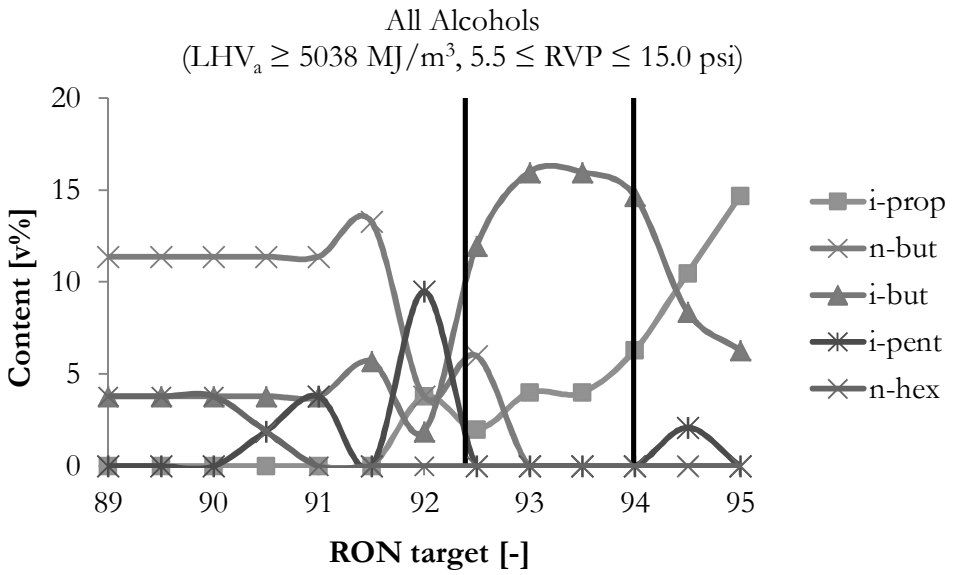


**FIGURE 4.26: EFFECT OF CHANGING RON TARGET VALUE ON OPTIMAL LHV BLEND FOR RFS2 FUEL SCENARIO**

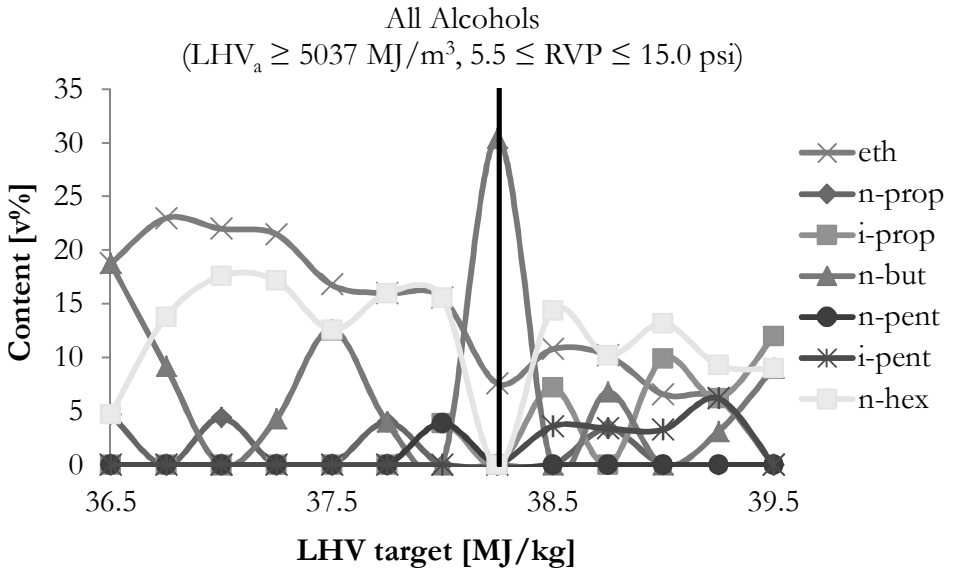


**FIGURE 4.27: EFFECT OF CHANGING LHV TARGET VALUE ON OPTIMAL RON BLEND FOR RFS2 FUEL SCENARIO**



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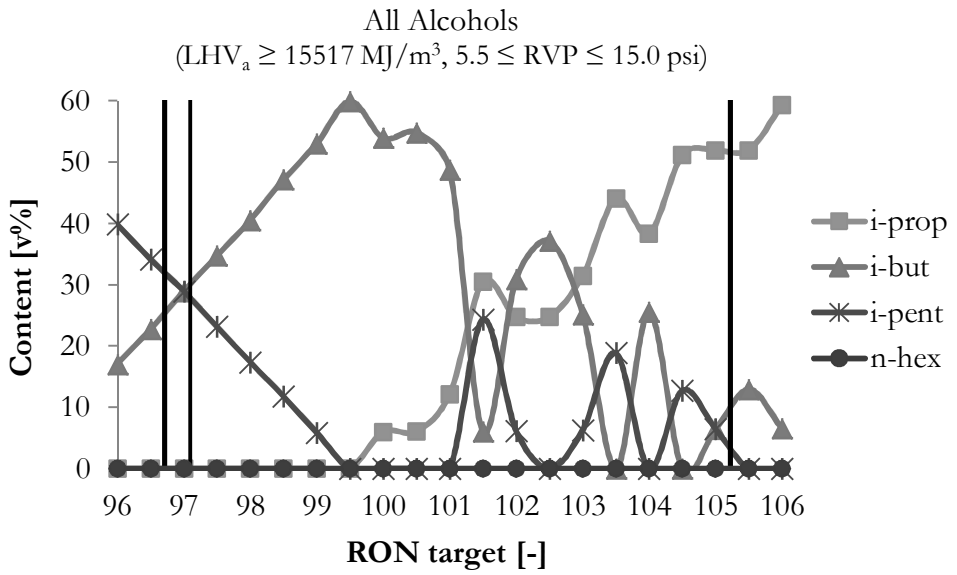


**FIGURE 4.28: EFFECT OF CHANGING RON TARGET VALUE ON OPTIMAL LHV BLEND FOR E85 ALTERNATE SCENARIO**

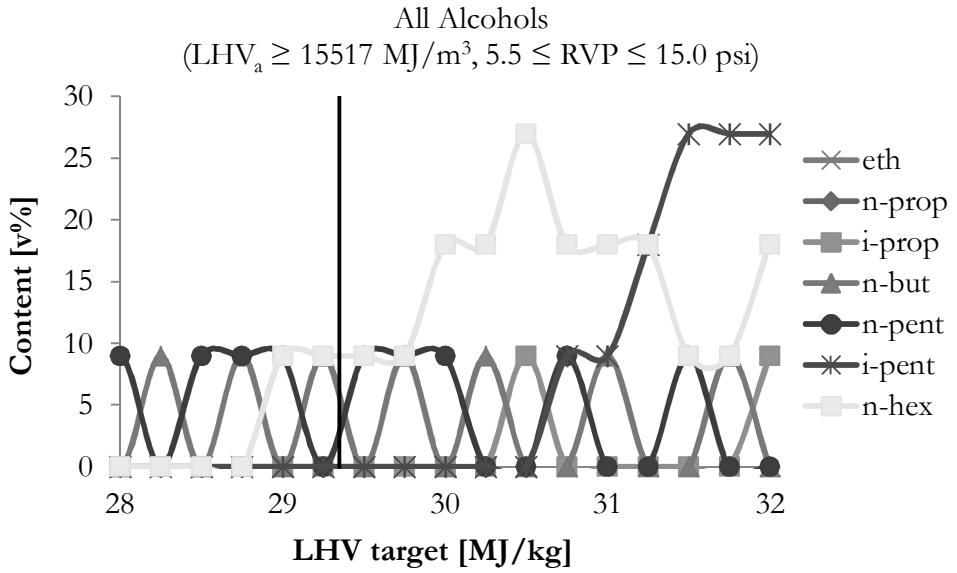


**FIGURE 4.29: EFFECT OF CHANGING LHV TARGET VALUE ON OPTIMAL RON BLEND FOR E85 ALTERNATE SCENARIO**



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# 5 Optimal Blend Performance

Alcohol Selection → Metric Development → Blend Comparison → **Blend Testing**

Chapter 5 details the experimental assessment of multi-component blends identified in Chapter 4. Multi-component blends selected to represent the optimal blends identified for each scenario were tested in a multi-cylinder gasoline direct injection (GDI) engine. Efficiency, emissions, and performance results collected from operating the engine on these blends are compared to baseline results gained with reference fuel (EEE), a blendstock for oxygenate blending (BOB), and several gasoline-ethanol blends.

Contents of this Chapter

5.1 Blends Tested
5.2 Combustion Properties
5.3 Emissions
5.4 Spark Timing Sweeps



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## 5.1 BLENDS TESTED

Since the calculations described in Chapter 4 were not yet complete before engine testing of multi-component blends was scheduled to occur, the exact optimal blends from each scenario could not be tested. Instead, multi-component blends were chosen based on preliminary calculations to represent the trends of the identified optimal blends for each scenario. The multi-component blends chosen for engine testing are summarized in Table 5.1 with their calculated RON value. In addition to testing 8 multi-component blends, EEE, BOB, and several gasoline-ethanol blends (E10, E15, E25, E50, and E77) were tested.

The Blend ID given in Table 5.1 correlates to the scenario and subset for which it would be the optimal blend. For example, blend "1A (all)" represents the blend from the E10/E15 Alternate Scenario that has the highest LHV ("A" signifies LHV optimization) of all suitable blends and blend "2B (even)" represents the blend from the RFS2 Fuel Scenario that has the highest RON ("B" signifies RON optimization) of the "even" subset of suitable blends.

**TABLE 5.1: MULTI-COMPONENT BLENDS USED IN ENGINE TESTING**

| Blend ID | BOB [v%] | eth [v%] | i-prop [v%] | i-but [v%] | i-pent [v%] | n-hex [v%] | RON [-] |
|---|---|---|---|---|---|---|---|
| **EEE** | | | | | | | 97.1 |
| **BOB** | 100 | | | | | | 88.6 |
| **E10** | 90 | 10 | | | | | 92.4* |
| **E15** | 85 | 15 | | | | | 94.0* |
| **E25** | 75 | 25 | | | | | 96.7* |
| **E50** | 50 | 50 | | | | | 101.7* |
| **E77** | 77 | 23 | | | | | 105.2* |
| **1A (all)** | 87 | | 6.5 | 5 | 1.5 | | 92.4* |
| **1B (all)** | 80 | | 18 | 2 | | | 95.6* |
| **2B (all)** | 67 | | 33 | | | | 99.6* |
| **1C (all)** | 77.5 | 2 | 9 | | 7 | 4.5 | 92.7* |
| **1B (even)** | 83 | 12 | | 5 | | | 94.0* |
| **2B (even)** | 69 | 15.5 | | 15.5 | | | 96.7* |
| **2C (all)** | 65.5 | 7 | 20.5 | | | 7 | 96.7* |
| **3A (all)** | 40 | | 18 | 18 | 24 | | 100.3* |

*Values are calculated using the methods outlined in Section 4.1.



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## 5.2 COMBUSTION PROPERTIES

Figure 5.1 shows the brake thermal efficiency (BTE) results for the blends from the E10/E15 Alternate Scenario. BOB and EEE are also shown in this plot for reference. BTE is defined as the power output of the engine divided by the fuel energy provided to the engine and is calculated with Equation 1. Therefore, differences in energy content of the different fuels used in these tests are already accounted. As can be seen, the achievable efficiencies are generally similar for all of the blends.

One of the main factors influencing the efficiency of a SI engine is the combustion phasing [90]. Figure 5.2 compares the combustion phases expressed as location of 50% of the fuel Mass Fraction Burned (MFB50%) for the blends from the E10E15 Alternate Scenario. The MFB50% point is the crank angle location at which half of the fuel in the combustion chamber has been consumed. As a general guideline, peak efficiency is typically achieved at a combustion phasing of MFB50% around 6 to 10 crank angle degrees after top dead center (°ATDC) [90].

The two 4 bar operating points show similar BTE and consistent combustion phasing in the optimal region (6-10°ATDC) for all of the blends. The efficiencies for blend 1A (all) are slightly below the other fuels. The two 8 bar operating points show uniform efficiencies for all fuels except BOB. This is due to the reduced knock resistance of BOB (RON of 88.6) compared to the other fuels.

Reduced knock resistance causes the engine control unit (ECU) to retard spark timing to avoid knock. This causes a delayed MFB50% location. The retarded spark timing also results in slower combustion which is apparent from the extended combustion duration for BOB at both of the 8 bar points as shown in Figure 5.7. Figure 5.2 also shows the retarded combustion phasing for all fuels at the 1500 rpm, 8 bar point. This is due to the engine's conservative ECU calibration to avoid knock which is most critical at low speed, high load conditions.

The largest variations in efficiency can be observed at the 1500 rpm, 2.62 bar operating point. This point was the first in the test sequence upon completion of the engine warm-up period. The differences between fuels at this point are likely due to slower combustion caused by slight differences in the engine thermal conditions and not necessarily attributable to a specific fuel. This hypothesis is also supported by the large errors bars in BTE on the first of the two data sets in Figure 5.1. This is particularly pronounced for BOB, E10, E15 and 1A (all) at 1500 rpm, 2.62 bar.



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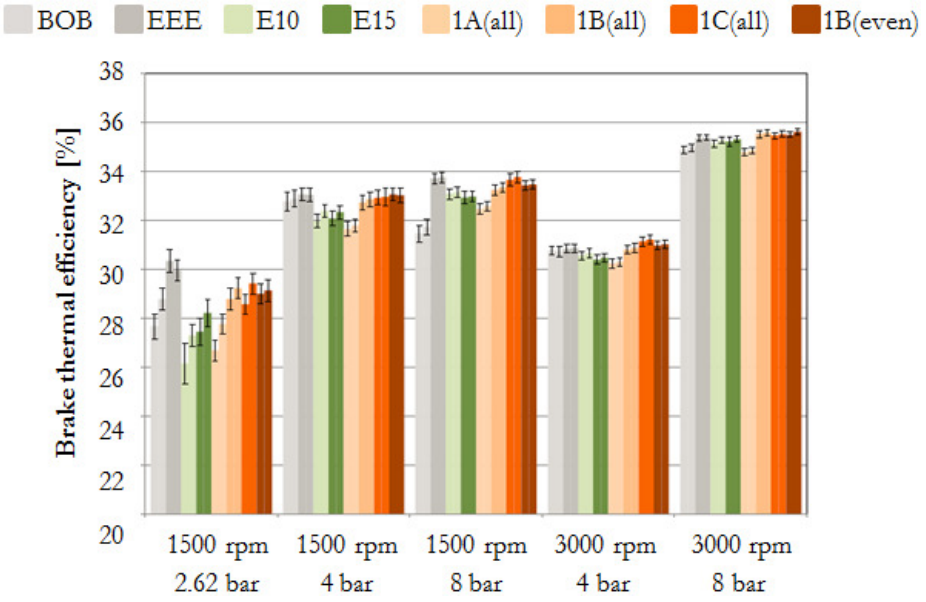


**FIGURE 5.1: BTE OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

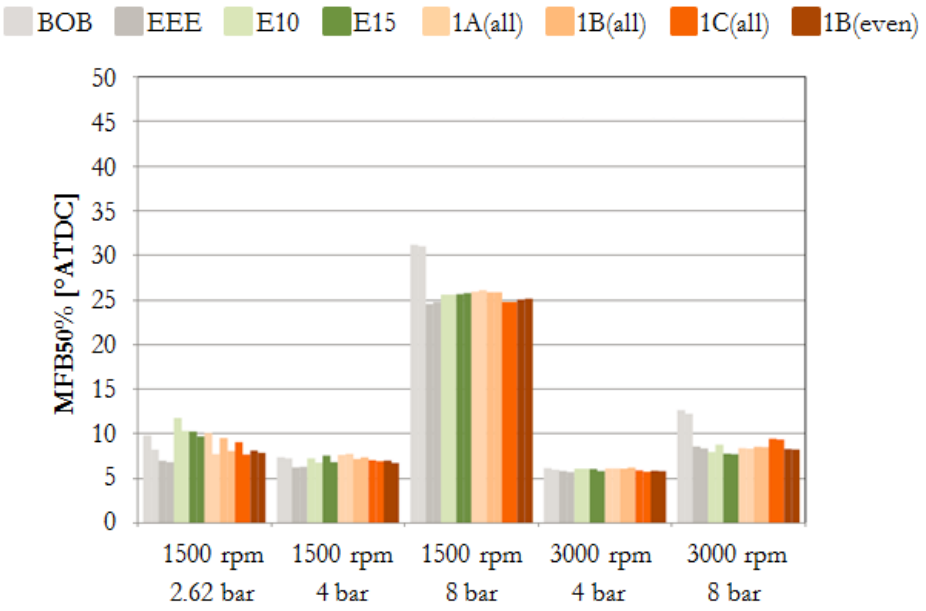


**FIGURE 5.2: MFB50% OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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Figure 5.3 and Figure 5.4 compare the BTE and combustion phasing (MFB50%) results for the reference fuels and blends for the RFS2 Fuel Scenario. Figure 5.5 and Figure 5.6 compare BTE and MFB50% results for the E85 Alternate Scenario. Both show similar results to those of the E10/E15 Alternate Scenario. The variations at the lowest load point (1500 rpm, 2.62 bar) are again more pronounced; in particular for the E10 and E15 reference fuels due to thermal conditions. Engine efficiencies at the higher load and speed points are consistent between the reference gasoline-ethanol blends and tested multi-component alcohol blends. Combustion phasing for the reference fuels and multi-component blends is consistent for all operating conditions and no knock related delay of combustion phasing beyond the base engine calibration is observed.



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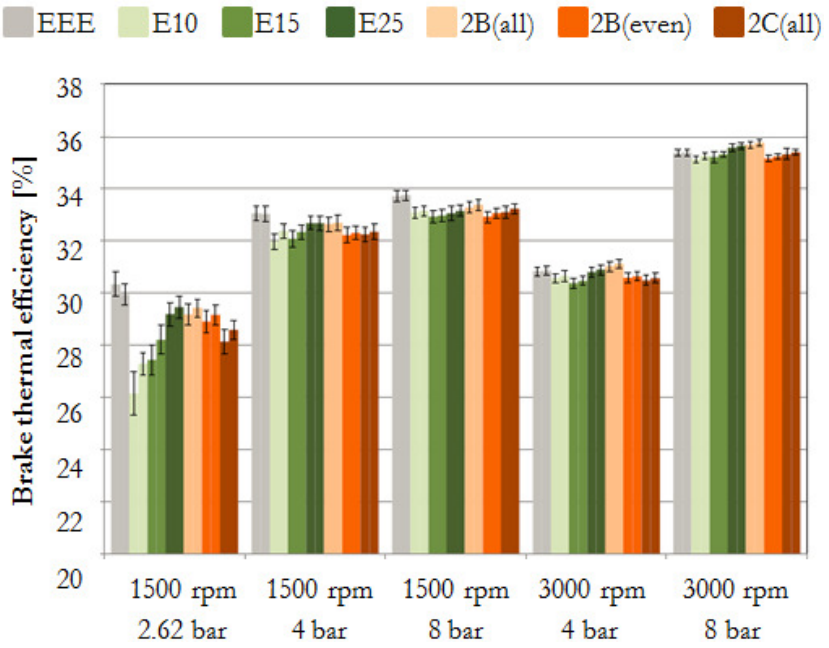


**FIGURE 5.3: BTE OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**

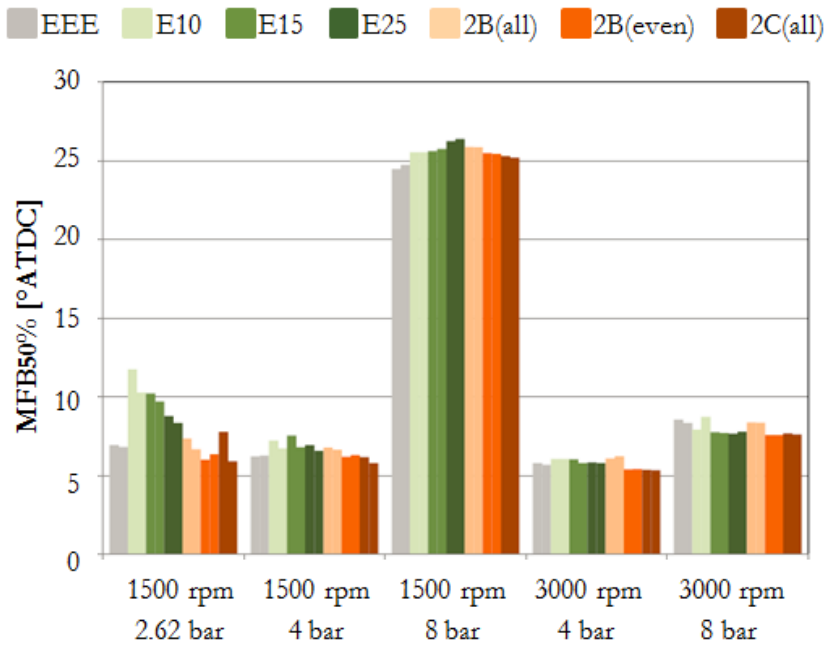


**FIGURE 5.4: MFB50% OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**



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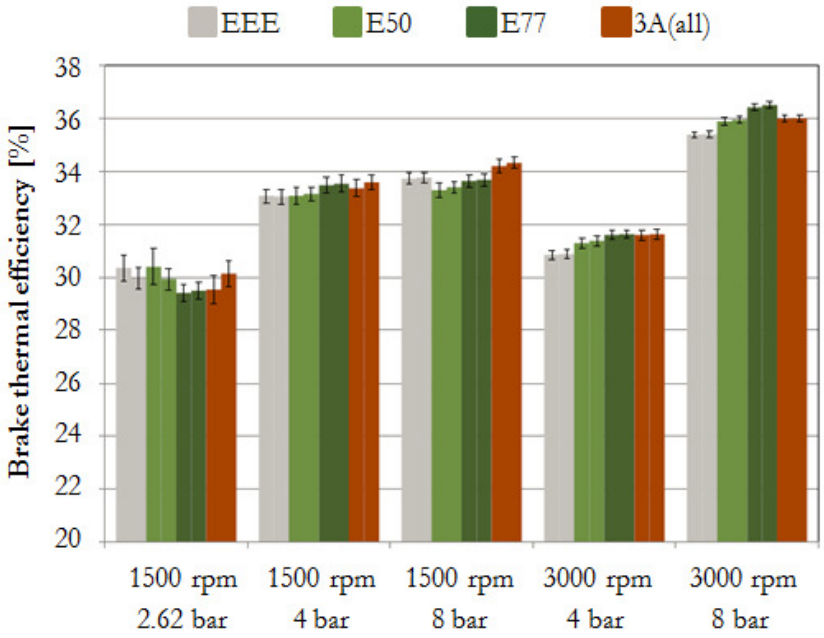


**FIGURE 5.5: BTE OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

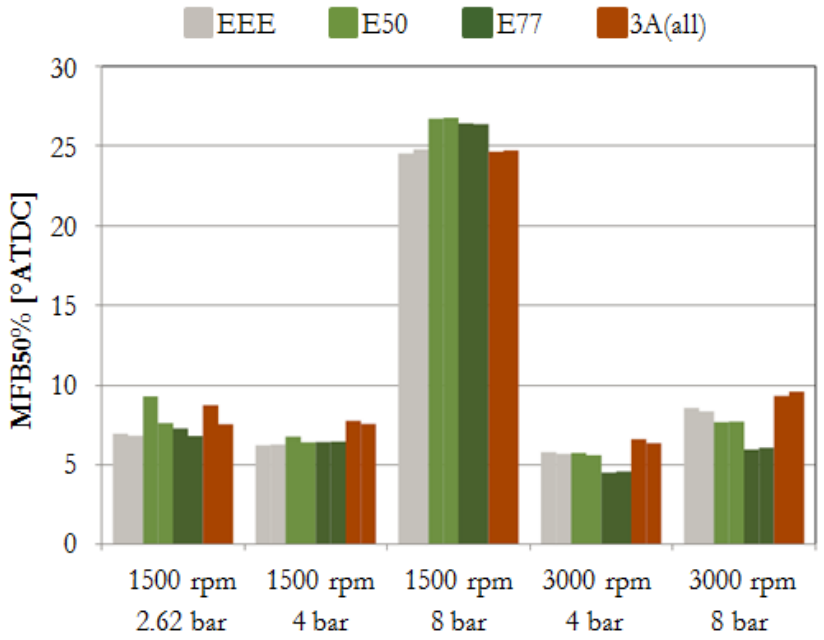


**FIGURE 5.6: MFB50% OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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The conclusion that the reference fuels and multi-component blends exhibit similar combustion behavior is further supported by the combustion duration and combustion stability plots. These are shown in Figure 5.7 and Figure 5.8 for the E10/E15 Alternate Scenario; Figure 5.9 and Figure 5.10 for the RFS2 Fuel Scenario; and Figure 5.11 and Figure 5.12 for the E85 Alternate Scenario. For each of the scenarios, combustion duration is consistent except at the 1500 rpm, 2.62 bar operating point due to the aforementioned differences in the thermal conditions. The thermal conditions also contribute to the slightly deteriorated combustion stability results shown at that operating point.

Combustion duration of each blend at each operating point is given in Figure 5.7, Figure 5.9, and Figure 5.11. Combustion duration is the difference between the crank angle location of MFB10% and MFB90%. A larger duration suggests a slower, less efficient combustion. Combustion stability is determined using the coefficient of variation (COV) of the Indicated Mean Effective Pressure (IMEP), shown in Figure 5.8, Figure 5.10, and Figure 5.12 for each blend at each operating point. COV is defined as the standard deviation of IMEP over a number of combustion cycles divided by the average IMEP. Reduced COV translates to more stable combustion. Typical COV values are below 5% [70].

Comparing the combustion duration and the combustion stability further supports the conclusion that combustion of reference fuels and the tested multi-component blends are similar under comparable operating conditions. Both combustion duration and COV are comparable for all fuels for comparable operating conditions. The increased combustion duration as a result of lower engine temperatures for the 1500 rpm, 2.62 bar (E10 and E15) case as well as the increased combustion duration due to delayed phasing for BOB at the two 8 bar points can be clearly seen in Figure 5.7. The resulting decrease in combustion stability is apparent in Figure 5.8. Similar results are shown for the other scenarios.



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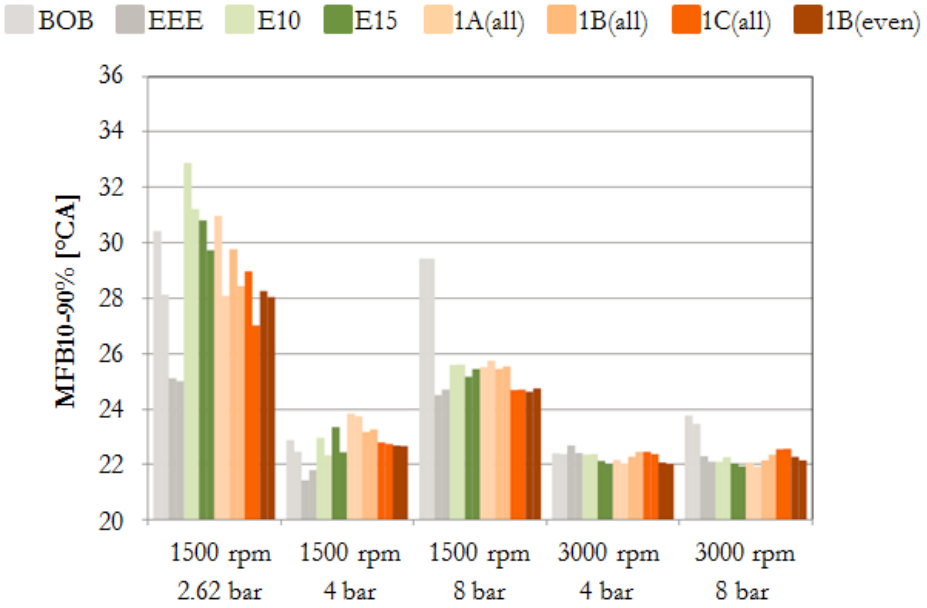


**FIGURE 5.7: COMBUSTION DURATION OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

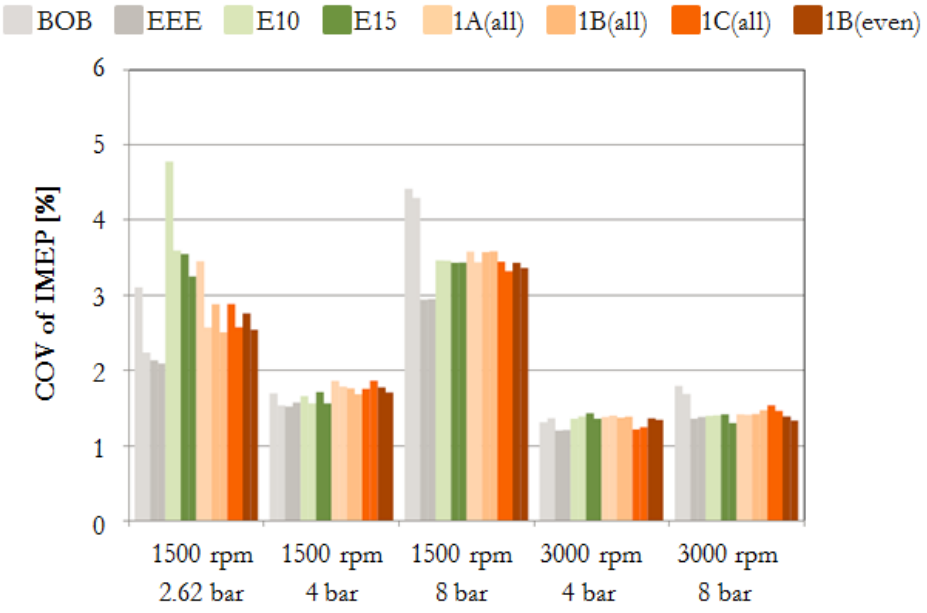


**FIGURE 5.8: COV OF IMEP OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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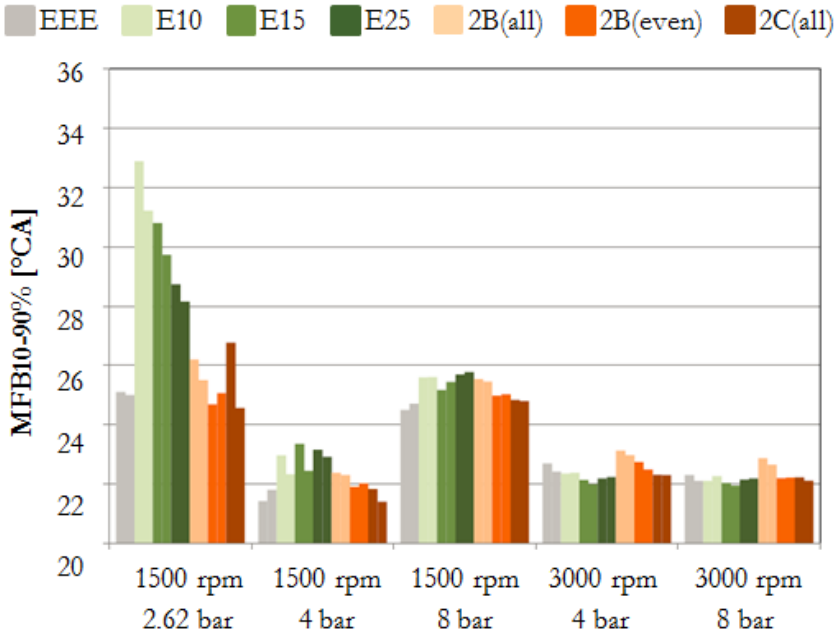


**FIGURE 5.9: COMBUSTION DURATION OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**

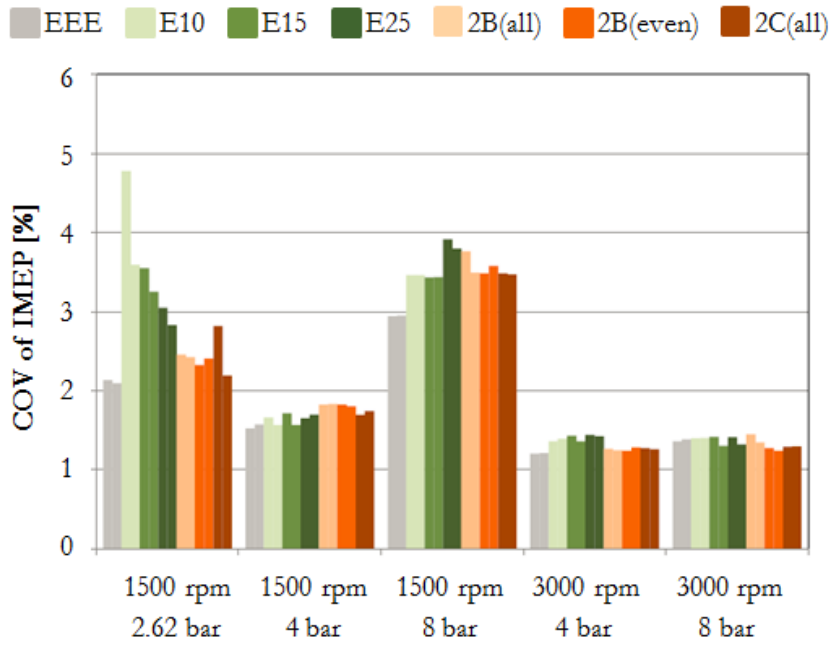


**FIGURE 5.10: COV OF IMEP OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**



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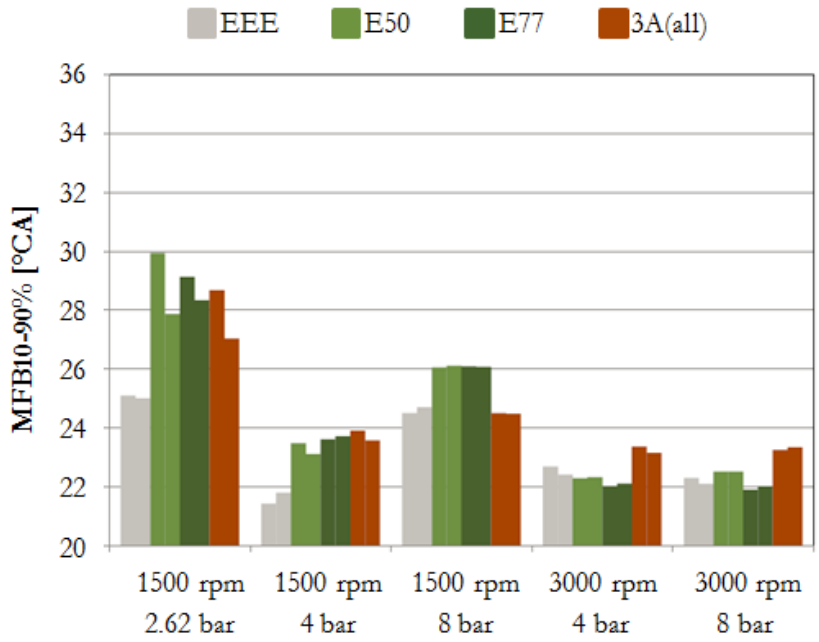


**FIGURE 5.11: COMBUSTION DURATION OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

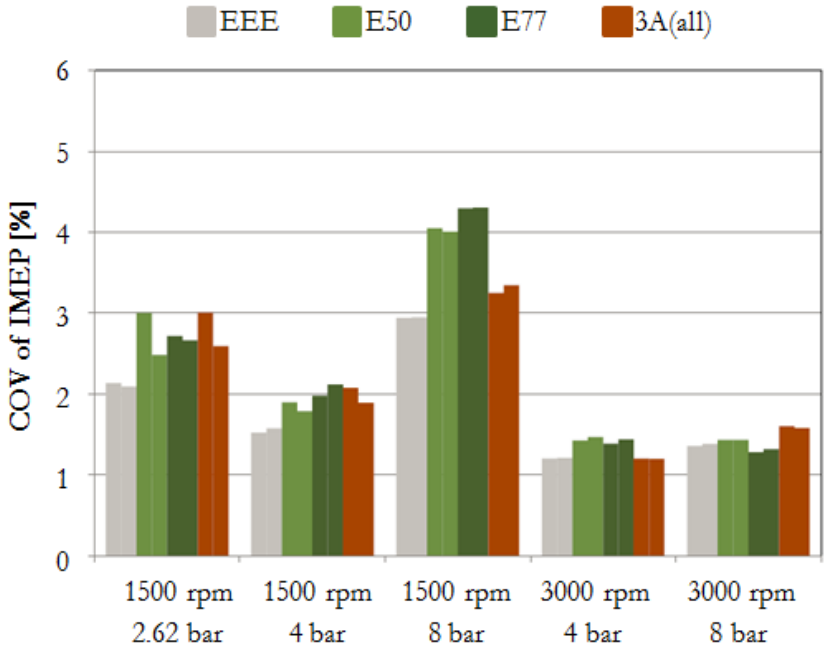


**FIGURE 5.12: COV OF IMEP OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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## 5.3 EMISSIONS

Figure 5.13, Figure 5.14, and Figure 5.15 show the carbon dioxide ($CO_2$) emissions for the reference fuels and blends for each of the three scenarios. $CO_2$ emissions are a result of complete combustion. The magnitude of $CO_2$ emissions depends on the engine efficiency as well as the hydrogen-to-carbon (H/C) ratio of the fuel [70]. Engine efficiency, shown in Figure 5.1, Figure 5.3, and Figure 5.5, does not vary significantly for the blends tested. The H/C ratio of gasoline (EEE and BOB) is 1.87, while the H/C ratios of the alcohol blends are between 2.05 and 2.1.

The increased H/C ratio of the alcohol blends favors the production of $H_2O$ over $CO_2$, and thus is not sufficient to dramatically change $CO_2$ emissions [70]. Therefore, $CO_2$ emissions are generally indirectly proportional to the engine efficiency results for each fuel. This inverse trend is most clearly visible with the increased $CO_2$ emissions of BOB at the 1500 rpm, 8 bar operating point.

Figure 5.16, Figure 5.17, and Figure 5.18 show the nitrogen oxides ($NO_x$) emissions for the reference fuels and blends for each of the three scenarios. $NO_x$ emissions are equal among the ethanol and multi-component alcohol blends and are generally lower than those for the EEE reference case likely due to increased heat of vaporization.

Nitrogen oxides are formed from the oxygen and nitrogen present in the air during combustion. $NO_x$ formation is strongly dependent upon cylinder temperature but is also dependent upon air-to-fuel ratio (AFR) [70]. As can be seen in the figures, $NO_x$ emissions are highly dependent on engine speed conditions. A general trend of slightly reduced $NO_x$ emissions with all alcohol blends compared to the EEE reference fuel can be observed which is likely due to the increased heat of vaporization which results in reduced cylinder temperatures. Differences between the blends are likely due to changes in combustion phasing rather than fuel composition itself [70].



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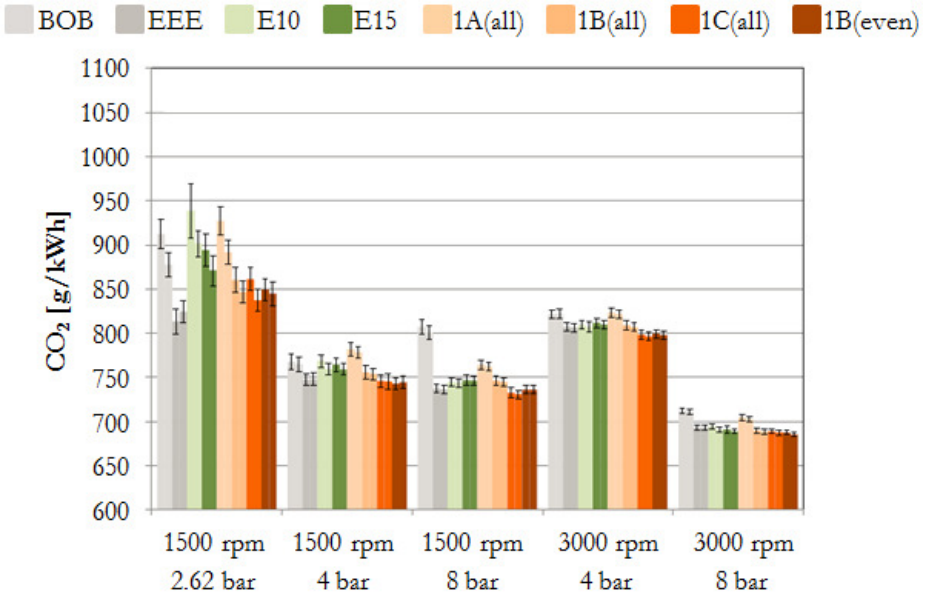


**FIGURE 5.13: $CO_2$ EMISSIONS OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

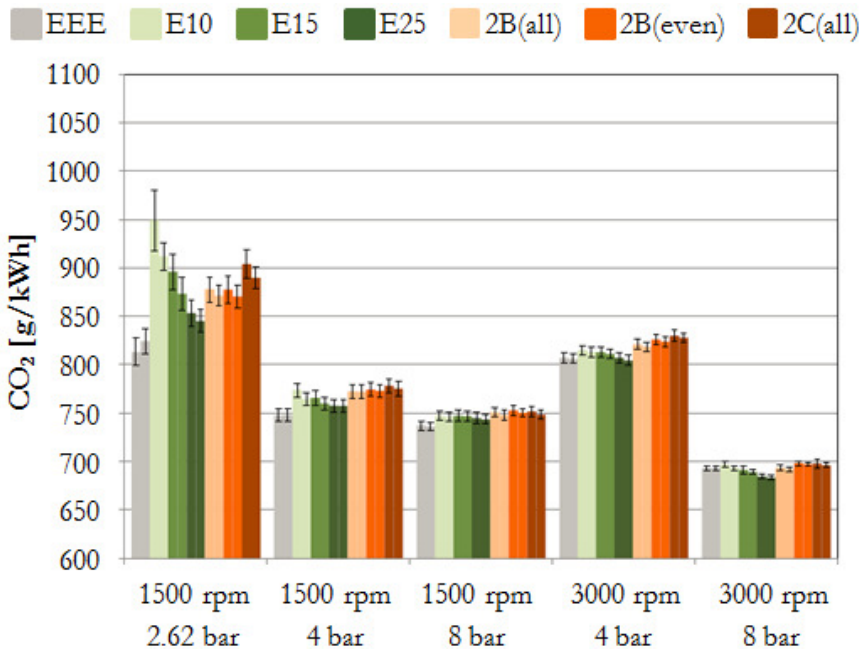


**FIGURE 5.14: $CO_2$ EMISSIONS OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**



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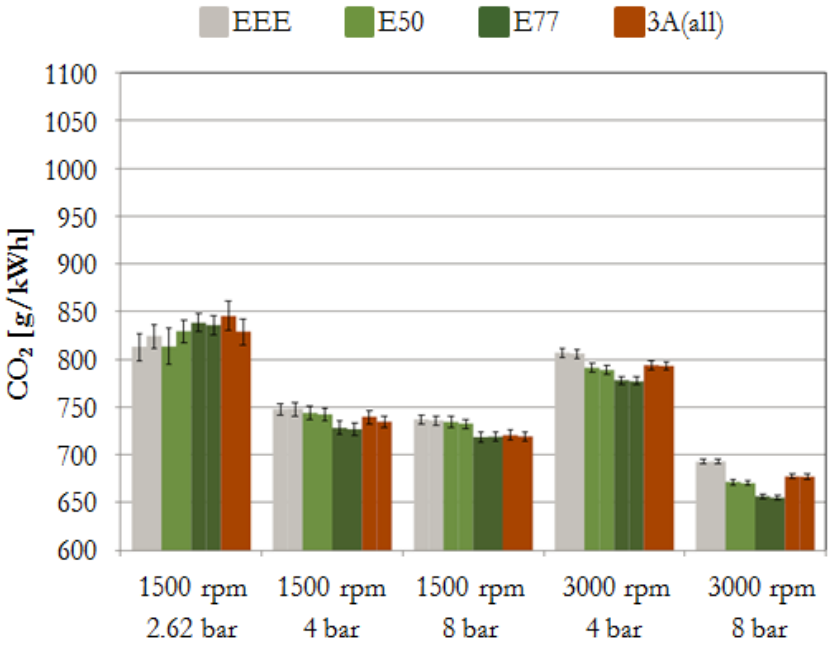


**FIGURE 5.15: $CO_2$ EMISSIONS OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

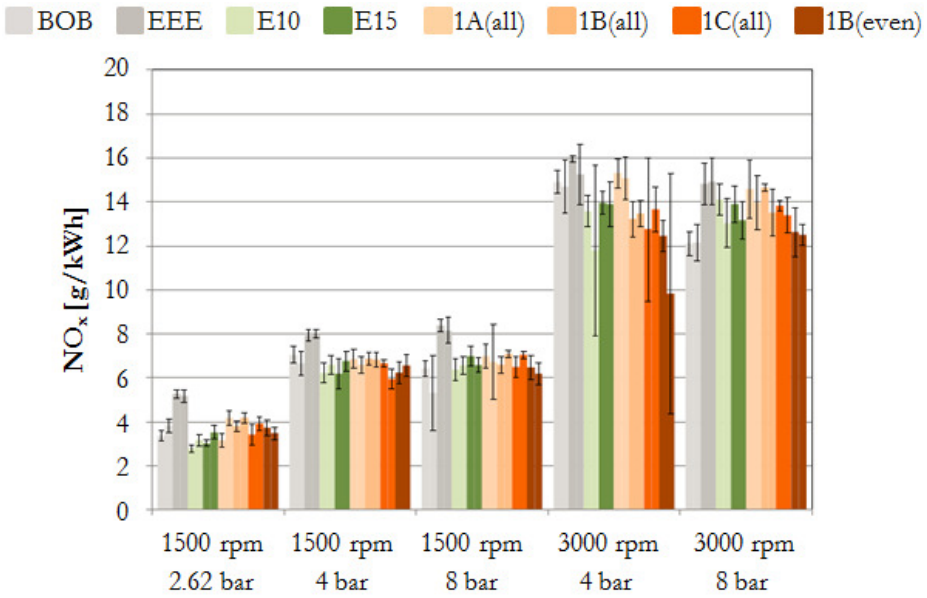


**FIGURE 5.16: $NO_X$ EMISSIONS OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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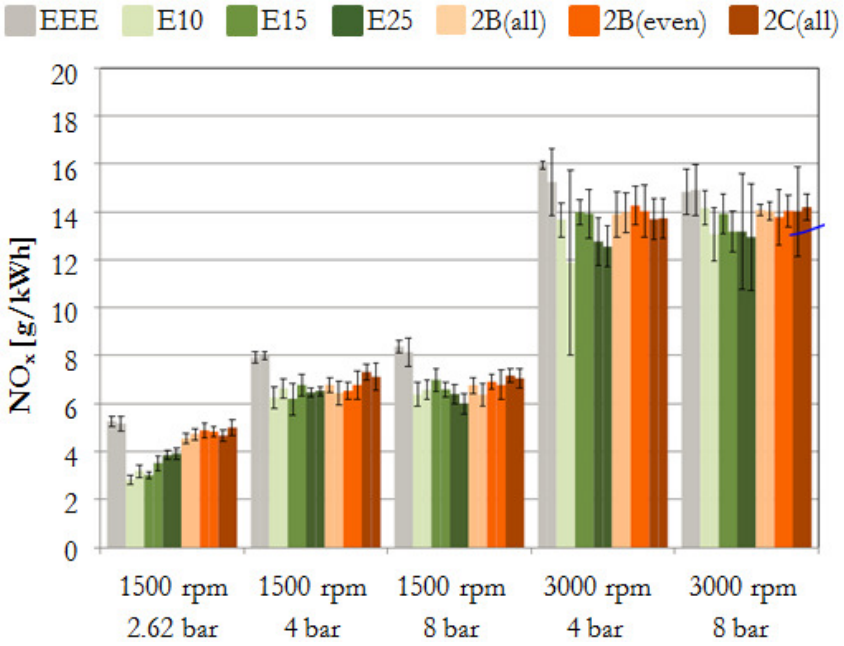


**FIGURE 5.17: $NO_x$ EMISSIONS OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**

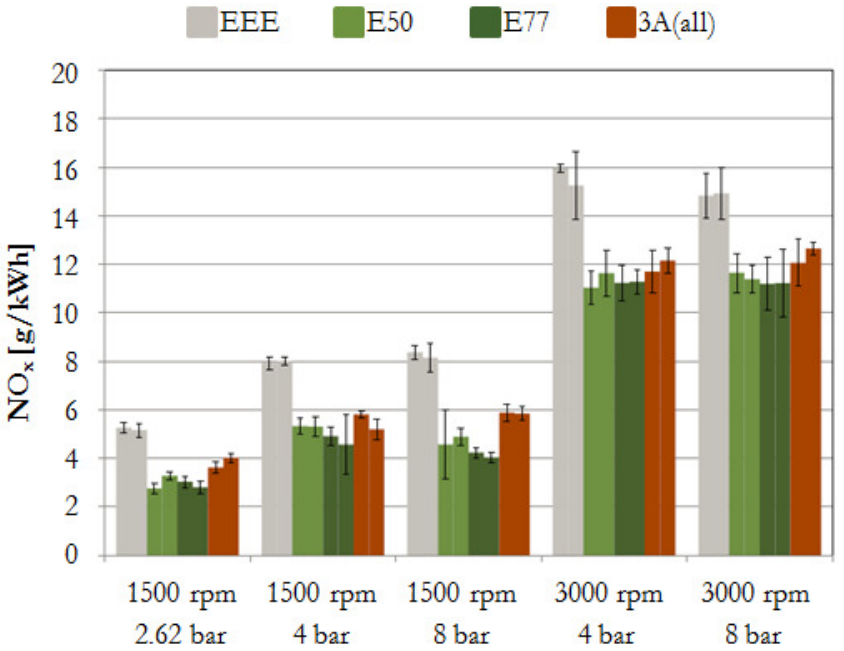


**FIGURE 5.18: $NO_x$ EMISSIONS OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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Figure 5.19, Figure 5.20, and Figure 5.21 show the carbon monoxide (CO) emissions for the reference fuels and blends for each of the three scenarios. CO emissions represent partially burned components and are strongly dependent on AFR. The Hyundai engine uses a closed loop feedback to tightly control AFR to stoichiometric conditions. CO emissions are relatively consistent for all of the blends because of the closely maintained AFR. No significant trends in CO emissions as a function of fuel properties were observed. Sensitivity to AFR is likely the dominant factor for the variability at certain load conditions.

Figure 5.22, Figure 5.23, and Figure 5.24 show the uncorrected hydrocarbon (HC) emissions for the reference fuels and blends for each of the three scenarios. HC emissions represent unburned fuel in the exhaust and are, just like CO emissions, highly dependent on AFR. Flame Ionization Detectors (FID), which were used to measure the amount of unburned hydrocarbon in the engine exhaust, are known to have reduced sensitivity to oxygenated hydrocarbon constituents [91]. When burning oxygenate blends in excess of 25 v%, the U.S. Code of Federal Regulations (CFR) requires measurement of the appropriate alcohols and aldehydes for certification-type testing [92].

As seen in the figures, HC emissions for the alcohol blends are generally equal or lower than those of the reference fuels. However, the differences are likely due to changes in FID analyzer sensitivity rather than actual changes in the concentration of unburned hydrocarbons. Given that the total alcohol concentration of the E10/E15 Alternate Scenario blends do not exceed 25 v%, a correction of the hydrocarbon emissions is not required. A correction would be required for blends from the RFS2 Fuel and E85 Alternate scenarios.



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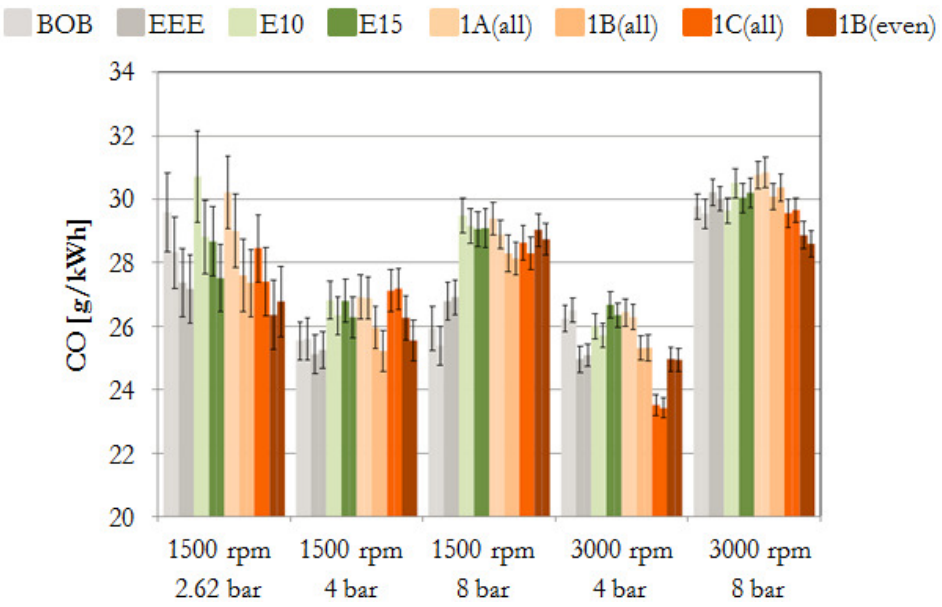


**FIGURE 5.19: CO EMISSIONS OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

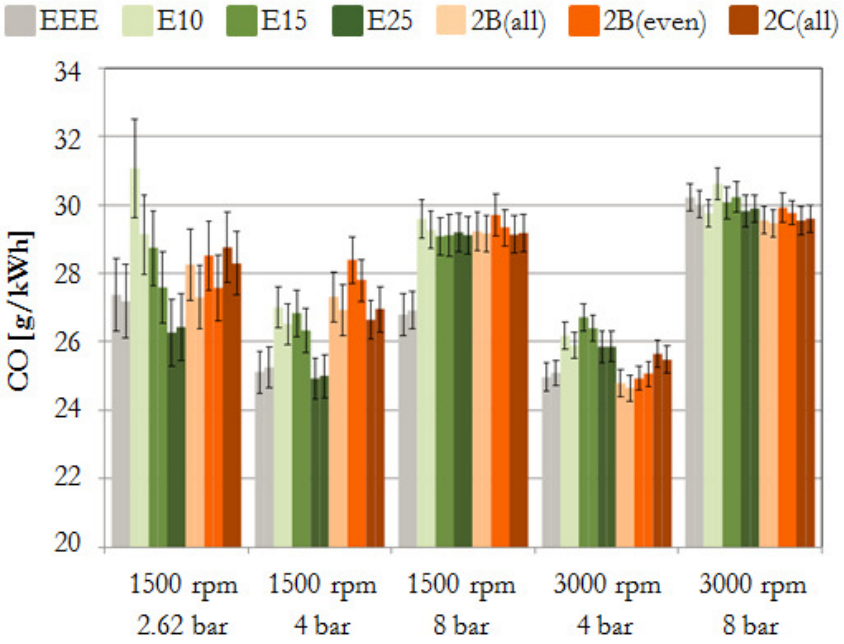


**FIGURE 5.20: CO EMISSIONS OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**



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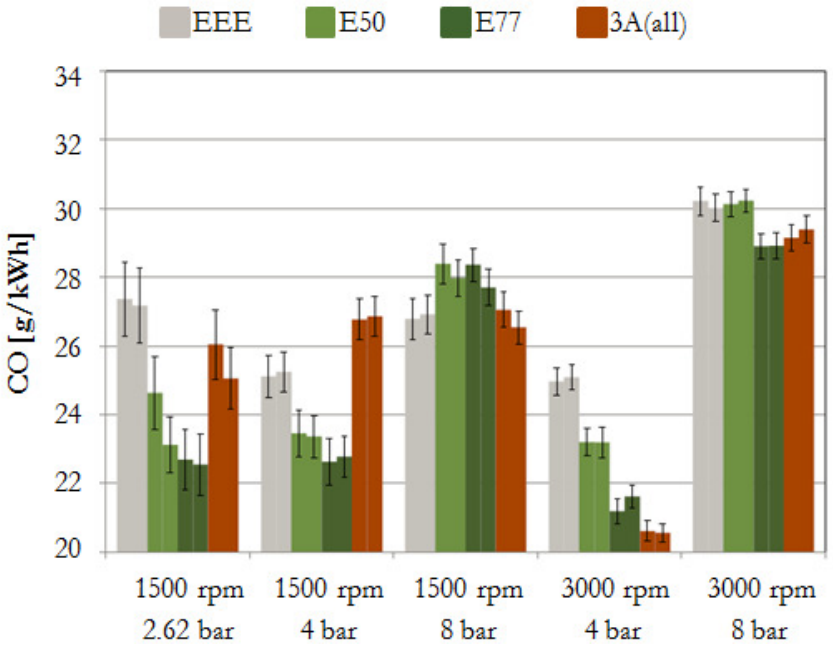


**FIGURE 5.21: CO EMISSIONS OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

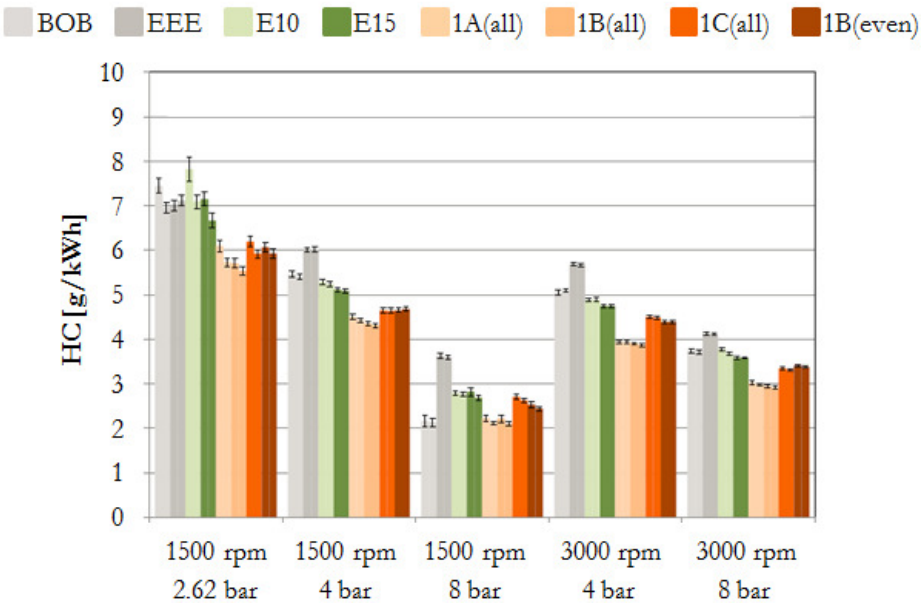


**FIGURE 5.22: UNCORRECTED HC EMISSIONS OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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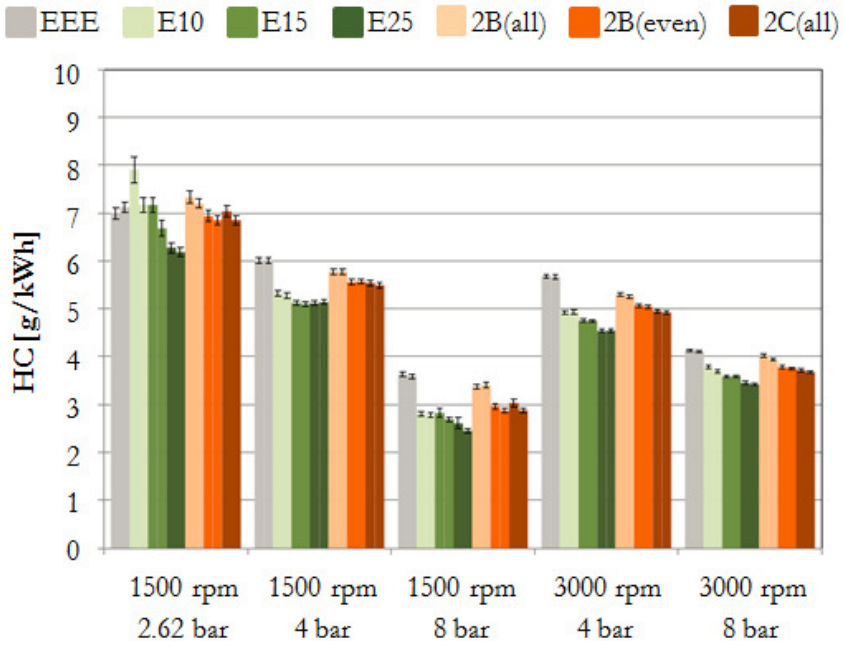


**FIGURE 5.23: UNCORRECTED HC EMISSIONS OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**

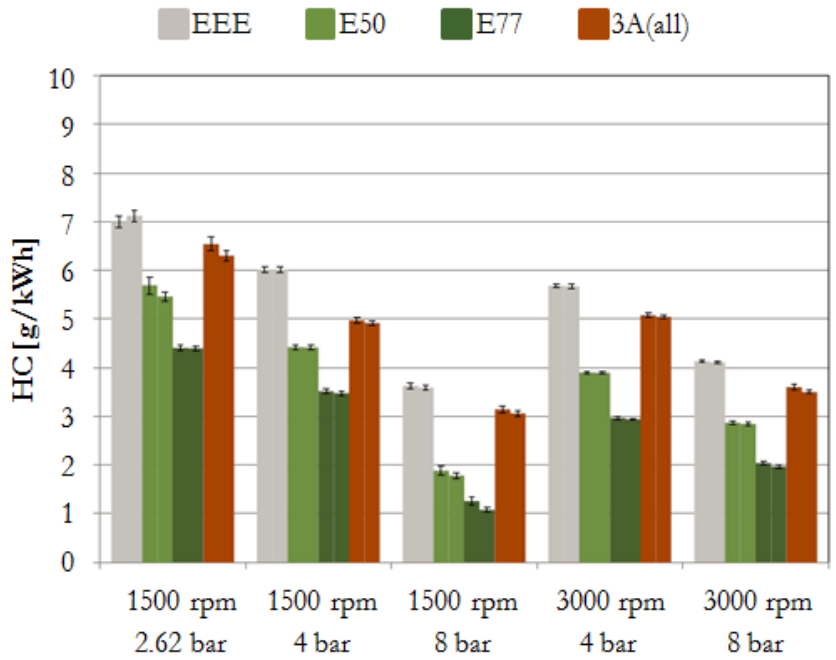


**FIGURE 5.24: UNCORRECTED HC EMISSIONS OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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## 5.4 SPARK TIMING SWEEPS

In addition to operating the engine at the predefined engine speed and load points listed in Table 2.6 with the stock ECU calibration, a spark sweep was performed to quantify each fuel's knock resistance characteristics. These tests were performed at 1500 rpm and constant throttle conditions resulting in an engine load of approximately 8 bar BMEP for the best torque conditions. Since neither throttle position nor fueling was adjusted when changing the spark timing, the actual engine load changes. This test most closely resembles a vehicle acceleration where fuel knock tendencies would limit engine performance and efficiency.

Spark timing was adjusted starting from very late phasing until either knocking combustion was encountered or peak efficiency (or peak torque) was exceeded. The spark timing at which the highest efficiency (or torque) is achieved is also known as Maximum Brake Torque (MBT) spark timing. Rather than plotting results as a function of spark timing, the combustion phasing is calculated from the measured pressure traces and results are plotted as a function of 50 % Mass Fraction Burned (MFB50%) location.

Figure 5.25 and Figure 5.26 show the results of the spark timing sweeps of the fuels associated with the E10/E15 Alternate Scenario. Figure 5.27 and Figure 5.28 pertain to the RFS2 Fuel Scenario and Figure 5.29 and Figure 5.30 pertain to the E85 Alternate Scenario. All three scenarios show similar trends.

BTE increases as the combustion phasing is advanced. The left-most point in each BTE plot (the point with the numerically lowest MFB50%) indicates the combustion phasing at which the knocking combustion limit is reached. A combustion event is counted as a knocking cycle if the peak magnitude of the hi-pass filtered (4000 Hz) cylinder pressure trace exceeds 0.2 bar. The RON of each fuel is indicated in the legend of each plot.



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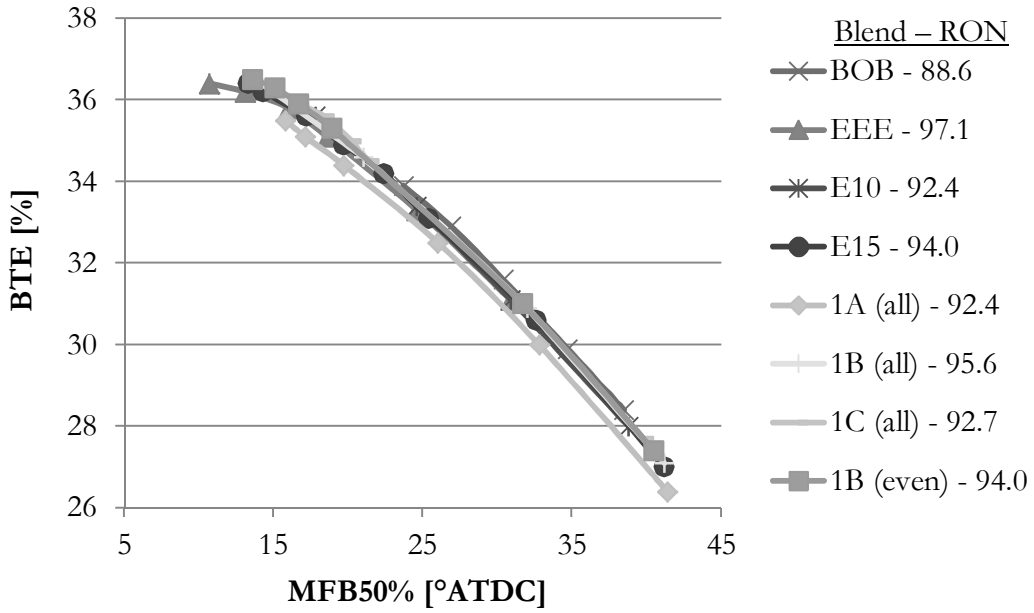


**FIGURE 5.25: MFB50% VS BTE OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

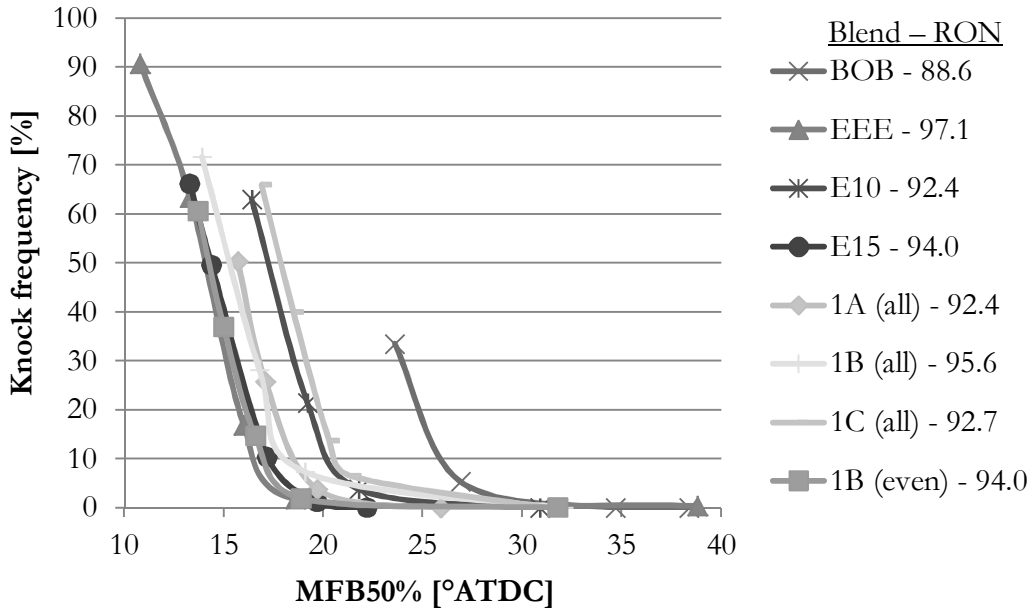


**FIGURE 5.26: MFB50% VS KNOCK FREQUENCY OF E10/E15 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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Due to the low knock resistance of BOB (88.6 RON), combustion phasing no earlier than 25°ATDC can be achieved resulting in a peak BTE of less than 34 % at this particular operating point (1500 rpm, 8 bar). The general trend of increasing efficiency with advanced combustion phasing is consistent for all of the blends, and all fuels show knocking combustion before the efficiency peak is achieved. Even the EEE reference fuel, which has the highest knock resistance of all of the blends in this scenario, is limited by engine knock.

Knock occurrence frequency is plotted against combustion phasing in Figure 5.26. As combustion phasing is advanced, the number of knocking cycles increases. While the knock-limited combustion phasing is higher for blends with higher RON, the order is not quite exactly as anticipated from the calculated RON values. The knock occurrence frequency of EEE, E15, and 1B (even) are almost identical although the calculated (as described in Section 4.1) RON values of E15 and 1B (even) are 94.0 and the RON of EEE is 97.1. A similar observation is made with blends 1A (all) and 1B (all).

Figure 5.28 shows the knock resistance of the RFS2 Fuel Scenario test blends compared to the respective reference fuels. The overall BTE trends observed as a function of combustion phasing are consistent for all of the blends. As noted previously, BOB, as well as E10 and E15, are limited by occurrence of knocking combustion before the efficiency peak is achieved. As illustrated by the flattening efficiency curve for E25, peak efficiency can be achieved with the higher level ethanol blend as well as the 2B (all) and 2B (even) blends.

When comparing the knock occurrence frequency trends, it is apparent that the 2B (all) and 2B (even) blends are similar to E25. While this is expected for the 2B (even) blend with a calculated RON of 94.1 (E25 has a calculated RON of 93.3), the higher calculated RON of the 2B (all) blend (96.5) is not reflected in the engine results. Additionally, blend 2C (all), which has a calculated RON of 93.5, performs similarly to EEE which has a RON of 97.1 and E15 which has a calculated RON of 91.4.

Figure 5.29 and Figure 5.30 show the efficiency trends and knock occurrence frequency as a function of combustion phasing for the E85 Alternate Scenario. The combustion phasing for both ethanol blends can be advanced well before MBT conditions without causing knock. Despite the almost identical calculated RON for the 3A (all) blend and E50, the observed knock resistance is not as high as the predicted value. In addition, the peak efficiencies with advanced spark timing reach 38% while the measured efficiencies



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with spark timing based on engine calibrations, shown in Figure 5.5, are limited to less than 34% with a combustion phasing of 25°ATDC.



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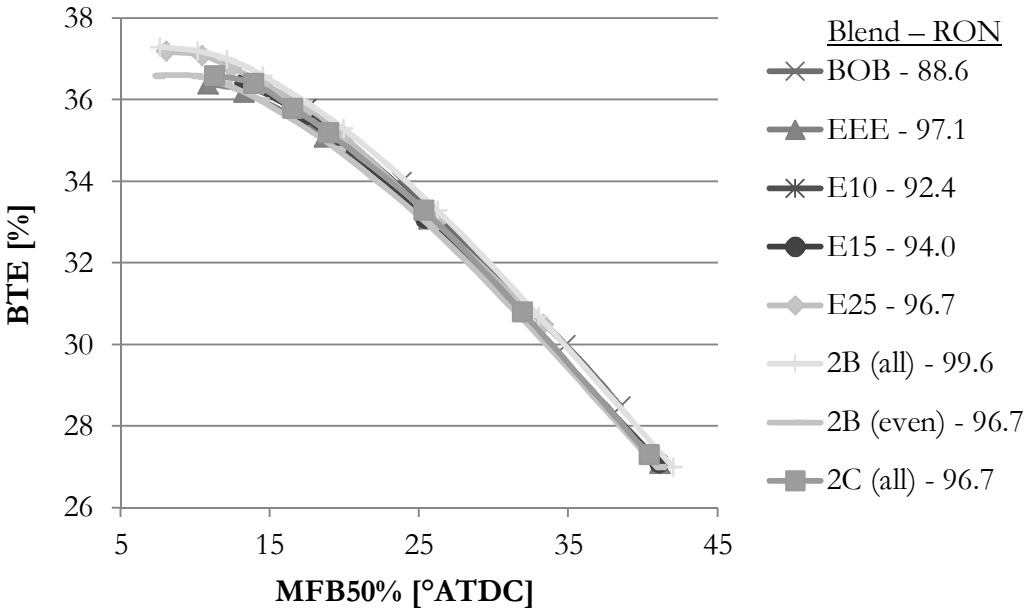


**FIGURE 5.27: MFB50% VS BTE OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**

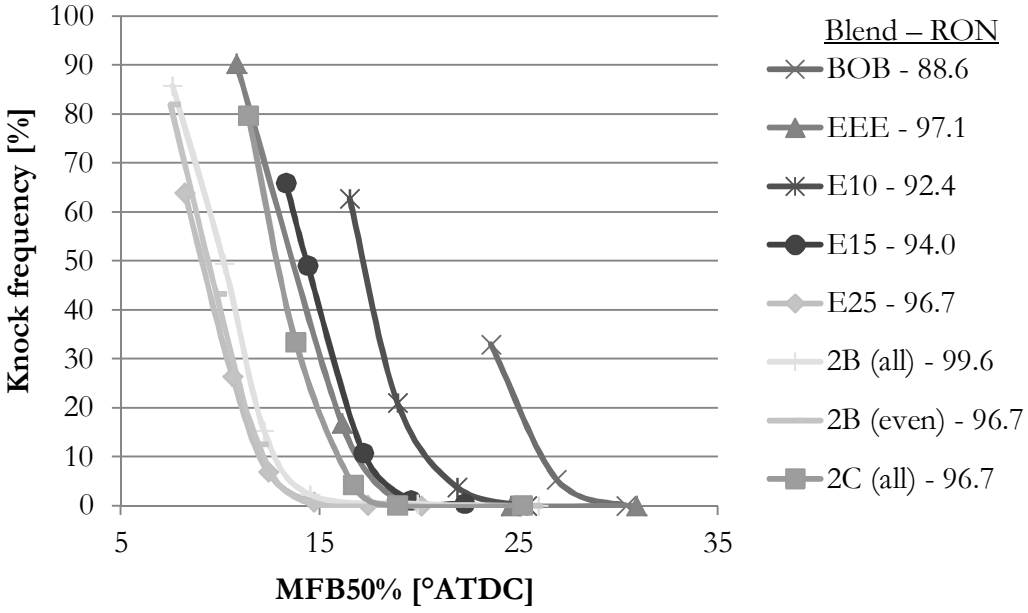


**FIGURE 5.28: MFB50% VS KNOCK FREQUENCY OF RFS2 FUEL SCENARIO MULTI-COMPONENT BLENDS**



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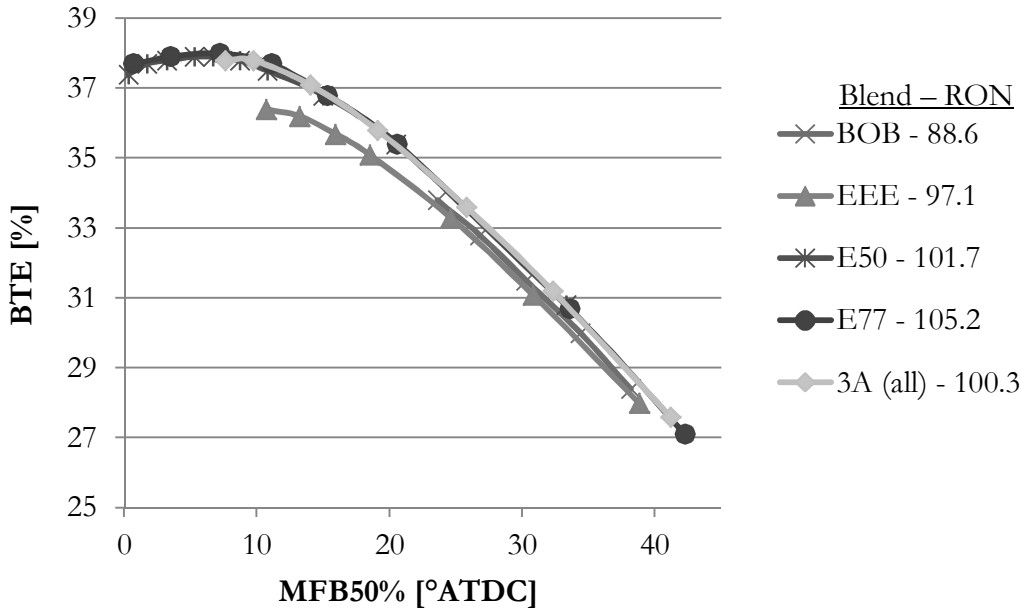


**FIGURE 5.29: MFB50% VS BTE OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**

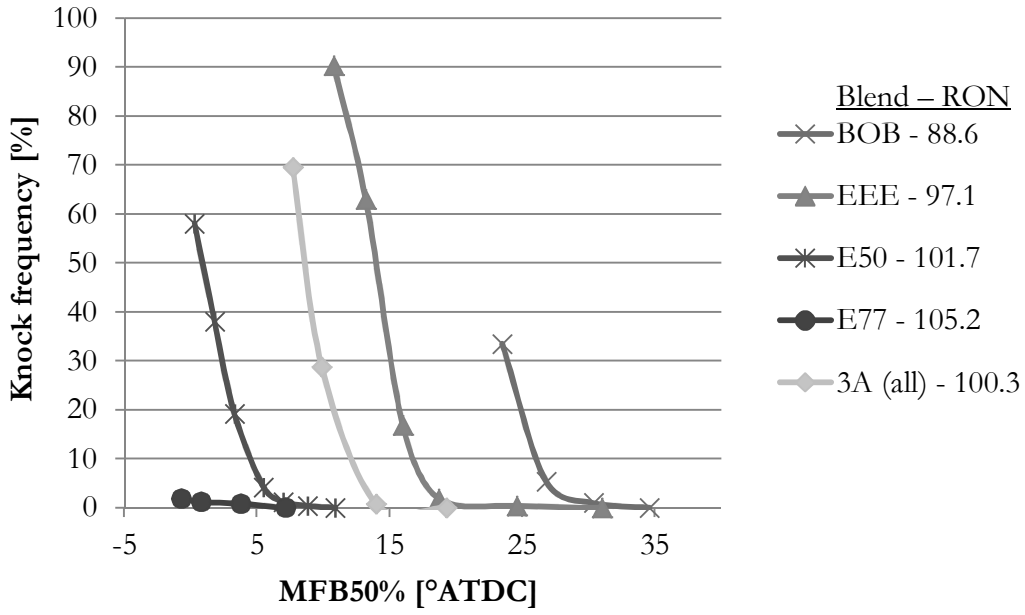


**FIGURE 5.30: MFB50% VS KNOCK FREQUENCY OF E85 ALTERNATE SCENARIO MULTI-COMPONENT BLENDS**



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# 6 PROJECT SUMMARY AND SIGNIFICANT FINDINGS

Chapter 6 contains a summary of each phase of the project: Alcohol Selection, Metric Development, Blend Comparison, and Blend Testing. An overview of the results of each phase is also given, including which alcohol isomers were chosen for testing, which metric were chosen by which to compare fuel blends, which blends were identified as optimal using the property prediction methods, and how those optimal blends behaved in a SI engine.

Contents of this Chapter

6.1 Alcohol Selection
6.2 Metric Development
6.3 Blend Comparison
6.4 Blend Testing



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## 6.1 ALCOHOL SELECTION

Ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, n-pentanol, iso-pentanol, and n-hexanol were 50/50 splash blended with a BOB to create eight test fuels. These fuels were tested in a SIDI engine along with certification gasoline at five steady-state test points.

At all operating points the spark timing for eth50, nprop50, iprop50, nbut50, ibut50, and ipent50 are within 2° of EEE. Npent50 and nhex50 have retarded spark timing at high loads because of engine knock. Nhex50 could not be tested at the high load operating points (8 bar BMEP) because of severe engine knock.

Cylinder pressure and ROHR traces show slight differences in the alcohol fuels. Fuels composed of the n- structure alcohols have the highest cylinder pressures and ROHRs. Peak cylinder pressure and ROHR decrease with decreasing carbon number of the alcohol constituent. Peak cylinder pressure and ROHR is related to the flame speed of the fuel, which is higher for the n- structure alcohol fuels as compared to the iso- structure fuels.

At each operating point the MFB50% location for eth50, nprop50, iprop50, nbut50, ibut50, and ipent50 are approximately equal. The MFB50% of npent50 and nhex50 are approximately equal to the other fuels at low load (2.62 bar BMEP), but occur later at medium and high loads (4 and 8 bar BMEP).

Engine efficiency generally decreases with increasing alcohol carbon number. The fuels composed of iso- structure alcohols tend to have higher efficiency than those composed of the n- structure alcohols of the same carbon number. At each operating point the efficiency of each alcohol fuel is within a few percent of EEE.

None of the alcohol fuels show a dramatic change from EEE in any of the emissions at any of the operating points. $CO_2$ emissions generally increase with carbon number among the alcohol fuels. All of the alcohol fuels have lower $NO_x$ and HC emissions than EEE at all operating points (with the exception of a few alcohols at low load).

While most of the alcohols in this study do not significantly degrade engine performance or emissions at a 50 v% blend level, the poor knock resistance of higher carbon number alcohols, specifically hexanol and n-pentanol, may render them inadequate as SI engine fuel components. However, the use of pentanol and hexanol in SI engine fuels at low blend levels could be advantageous in terms of boosting energy content or petroleum displacement.



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## 6.2 METRIC DEVELOPMENT

The RFS2 requires an increase in the use of advanced biofuels up to 36 billion gallons by 2022. Higher carbon number alcohols could be used in gasoline-alcohol blends to meet this demand. These alcohols can also improve the energy content, knock resistance, and/or petroleum displacement of gasoline-alcohol blends compared to traditional ethanol blends such as E10 while maintaining desired and regulated fuel properties.

The knock resistance, energy content, and vapor pressure of eight neat alcohols was measured and trends were identified. Knock resistance peaks at propanol (carbon number 3) and drastically decreases with increasing carbon number. Energy content is linearly related to carbon number, with hexanol (carbon number 6) being the highest and ethanol (carbon number 2) being the lowest. Vapor pressure is also linearly related to carbon number, but increases with decreasing carbon number.

A scenario approach was adopted to set criteria for identifying gasoline-alcohol blends that are potential alternative fuels. The scenario approach allows for an overall fuel objective to be defined and criteria targets specific to that objective to be chosen. Criteria target values are derived from industry standards, government legislation, consumer expectations, and engine requirements.

The objective of the E10/E15 Alternate Scenario is to identify multi-component blends that could be used in current engines and offer higher petroleum displacement, knock resistance, and/or energy content than E10/E15 while adhering to industry standards and consumer expectations. The objective of the RFS2 Fuel Scenario is to identify blends that contain an ethanol-equivalent alcohol volume that meets the RFS2 requirement in addition to most of the considerations referenced in the E10/E15 Alternate Scenario. The objective of the E85 Alternate Scenario is to identify high-level gasoline-alcohol blends with high knock resistance (RON $\geq$ 100) that reduce the range penalty of E85 when compared to gasoline.



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## 6.3 BLEND COMPARISON

Methods to predict the properties of multi-component gasoline-alcohol blends were adapted from literature. A blend's distillation profile is obtained from merging the blendstock's profile with the alcohols' boiling points and concentrations. The knock resistance of a blend can be estimated with the octane numbers and molar concentrations of each component. Vapor pressure is approximated from experimental data of ethanol blends and extrapolated for the other alcohols.

The property prediction methods were used to calculate the density, energy content (LHV), HoV, oxygen content, knock resistance (RON), RVP, distillation index, and ethanol equivalence of over one million blends. Blends that satisfied each of the three scenario's criteria were identified as suitable. Within each set of suitable blends, the blends that maximized energy content, knock resistance, and petroleum displacement were identified as optimal blends.

Optimal blends, those that maximize energy content, knock resistance, or petroleum displacement, were also found for two additional subsets of suitable blends: those that contain only even carbon number alcohols, and those that contain only ethanol and one other alcohol. In total, nine optimal blends were found for each of the three scenarios. All 27 optimal blends are listed in Table 6.1.

The largest gains from the use of higher alcohols are shown in the maximum PD blends of each of the scenarios. These blends increase petroleum displacement to 53 to 86% that of their reference fuel while matching energy content and knock resistance. These results demonstrate that higher alcohol blends could greatly increase the use of biofuels to meet the RFS2 standard while utilizing current engine technologies.

The ability of higher alcohols to increase the energy content of a blend increases with increasing total alcohol content. Improvements of only 2.0 – 2.9% were made in LHV for the E10/E15 Alternate Scenario, while improvements of 5.6 – 6.2% occur in the RFS2 Fuel Scenario, and gains of 23.5 – 25.0% occur in the E85 Alternate Scenario which has blends with higher total alcohol content (greater than 50 v%) than the blends of the other two scenarios (less than 50 v%).

Knock resistance can also be increased more with higher total alcohol content. RON gains for the E10/E15 Alternate Scenario, which has the lowest total alcohol content blends,



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are between 1.5 and 3.4%. RON gains in the E85 Alternate Scenario, which has the highest total alcohol content blends, are between 5.8 and 11.0%.

Additional calculations were done to examine the effects of the criteria target values on optimal blend composition. For example, the minimum RON target value for the E10/E15 Alternate Scenario was changed from 92.4 to 93 and the new optimal blends were found. This was repeated for a range of RON target values and then again for a range of LHV target values. Through this process, the effect of changing criteria target values on optimal blend composition can be seen.

As the minimum acceptable RON increases, the highest carbon number alcohols, which have poor RON, are replaced with those lower in carbon number. In each of the scenarios, once the RON target is sufficiently high the optimal blend becomes just iso-propanol with BOB because iso-propanol has the highest RON of all of the alcohols. As the RON target continues to increase, the concentration of iso-propanol increases to meet the RON target until the amount of iso-propanol causes the blend to fail one of the other criteria.

As the minimum acceptable LHV increases, the lower carbon number alcohols are replaced with higher ones because energy content increases with carbon number. This continues until the low RON of the higher alcohols causes the blends to fail the scenario's RON target.



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**TABLE 6.1: OPTIMAL BLENDS OF EACH SCENARIO**

| | | Subset of Suitable Blends | | |
|---|---|---|---|---|
| | | All | Even | Eth + 1 |
| E10/E15 Alternate Scenario | Max LHV | 87.0 v% BOB<br>6.5 v% iso-propanol<br>5.2 v% iso-butanol<br>1.3 v% iso-pentanol | 86.0 v% BOB<br>5.6 v% ethanol<br>1.4 v% n-butanol<br>7.0 v% iso-butanol | 86.0 v% BOB<br>5.6 v% ethanol<br>8.4 v% iso-butanol |
| | Max RON | 81.0 v% BOB<br>19.0 v% iso-propanol | 85.0 v% BOB<br>13.5 v% ethanol<br>1.5 v% iso-butanol | 82.0 v% BOB<br>1.8 v% ethanol<br>16.2 v% iso-propanol |
| | Max PD | 77.0 v% BOB<br>4.6 v% iso-propanol<br>11.5 v% n-butanol<br>6.9 v% iso-pentanol | 79.0 v% BOB<br>2.1 v% ethanol<br>10.5 v% n-butanol<br>8.4 v% iso-butanol | 79.0 v% BOB<br>6.3 v% ethanol<br>14.7 v% iso-pentanol |
| RFS2 Fuel Scenario | Max LHV | 80.0 v% BOB<br>6.0 v% iso-propanol<br>2.0 v% n-butanol<br>12.0 v% iso-pentanol | 80.0 v% BOB<br>2.0 v% ethanol<br>8.0 v% n-butanol<br>10.0 v% iso-butanol | 80.0 v% BOB<br>6.0 v% ethanol<br>14.0 v% iso-pentanol |
| | Max RON | 67.0 v% BOB<br>33.0 v% iso-propanol | 67.0 v% BOB<br>13.2 v% ethanol<br>19.8 v% iso-butanol | 68.0 v% BOB<br>3.2 v% ethanol<br>28.8 v% iso-propanol |
| | Max PD | 63.0 v% BOB<br>11.1 v% ethanol<br>14.8 v% n-butanol<br>3.7 v% n-pentanol<br>7.4 v% n-hexanol | 63.0 v% BOB<br>7.4 v% ethanol<br>29.6 v% n-butanol | 63.0 v% BOB<br>7.4 v% ethanol<br>29.6 v% n-butanol |
| E85 Alternate Scenario | Max LHV | 40.0 v% BOB+<br>18.0 v% iso-propanol<br>18.0 v% iso-butanol<br>24.0 v% iso-pentanol | 38.0 v% BOB+<br>62.0 v% iso-butanol | 39.0 v% BOB+<br>6.1 v% ethanol<br>54.9 v% iso-butanol |
| | Max RON | 10.0 v% BOB+<br>90.0 v% iso-propanol | 11.0 v% BOB+<br>62.3 v% ethanol<br>26.7 v% iso-butanol | 10.0 v% BOB+<br>9.0 v% ethanol<br>81.0 v% iso-propanol |
| | Max PD | 10.0 v% BOB+<br>9.0 v% iso-propanol<br>9.0 v% iso-butanol<br>72.0 v% iso-pentanol | 10.0 v% BOB+<br>9.0 v% n-butanol<br>72.0 v% iso-butanol<br>9.0 v% n-hexanol | 10.0 v% BOB+<br>18.0 v% ethanol<br>72.0 v% iso-pentanol |



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## 6.4 BLEND TESTING

Multi-component blends were chosen to represent the optimal blends of each scenario for each subset of suitable blends. They were then engine tested for combustion characteristics, emissions, and performance. EEE, BOB, E10, E15, E25, E50, and E77 were also tested as reference fuels. In addition to operating the engine at the predefined engine speed and load points with the stock calibration, a spark sweep was performed to quantify each fuel's knock resistance characteristics. These tests were performed at 1500 rpm at constant throttle conditions resulting in an engine load of approximately 8 bar BMEP for the best torque conditions.

As illustrated by combustion duration and combustion stability, the combustion of the reference fuels for each of the three scenarios and the multi-component blends for each scenario are similar under comparable operating conditions.

A general trend of slightly reduced NOx emissions with all alcohol blends compared to the EEE reference fuel can be observed; but this is likely due to the increased heat of vaporization which results in reduced cylinder temperatures. Differences between the blends are likely due to changes in combustion phasing rather than fuel composition itself. Overall, the emissions of multi-component alcohol blends from each scenario are comparable to the reference fuels for each scenario.

While the knock-limited combustion phasing is higher for blends with higher RON, the order is not quite exactly as anticipated from the calculated RON values. This occurs for each of the three scenarios and suggests that the RON prediction method utilized is not quite accurate.



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# 7 APPENDICES

Additional data and information pertaining to the project is provided here.

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## 7.1 Detailed Project Timeline

| | |
|---|---|
| **October '11** | Project begins and Kristina begins working at ANL.<br><br>"Determine whether a certain blend of gasoline with ethanol, as well as higher alcohols, could provide a fuel with properties superior to those of traditional gasoline-ethanol blends" is set as the project goal.<br><br>Literature review is conducted to find the chemical properties of alcohol isomers with carbon number 2 through 8.<br><br>The most important chemical and engine-related properties for this project are identified. |
| **November '11** | N- and iso- structures of alcohols through carbon number 6 are chosen for further investigation.<br><br>50/50 blends of each chosen alcohol are tested in a SIDI engine. |
| **December '11** | 50/50 blends of each chosen alcohol are tested in a SIDI engine. |
| **January '12** | 50/50 blends of each chosen alcohol are tested in a SIDI engine. |
| **February '12 – March '12** | Data analysis continued. |
| **April '12** | Phase 1 Progress Report submitted to the Iowa Corn Promotion Board (funder of the project work done at ANL). |
| **May '12 – November '12** | Data analysis continued. |
| **December '12** | Phase 2 Progress Report submitted to the Iowa Corn Promotion Board (funder of the project work done at ANL). |
| **January '13** | Data analysis continued. |
| **February '13** | Phase 3 Progress Report submitted to the Iowa Corn Promotion Board (funder of the project work done at ANL). |
| **March '13 – June '13** | Data analysis continued. |
| **July '13 – September '15** | Little progress is made as Kristina took a full-time job at Indiana State University and was given a teaching overload each semester. |
| **October '15 – November '16** | Drafts of dissertation chapters are produced and revised. |



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## 7.2 ALCOHOL ISOMER PROPERTIES

As detailed in Chapter 2, isomers fell within three categories with respect to the amount of information found in the literature about their chemical properties:

1. all information known;
2. most chemical properties (density, viscosity, etc.) known but no engine-related properties (RON, LHV, etc.) known; or
3. not enough information known to be properly assessed.

All of the isomers are listed by information category in Table 7.1.

**TABLE 7.1: ALCOHOL ISOMERS BY INFORMATION CATEGORY**

| Category 1 | Category 2 | Category 3 |
|---|---|---|
| ethanol | iso-propanol | 2,2-dimethyl-1-propanol |
| n-propanol | sec-butanol | 2-pentanol |
| n-butanol | tert-butanol | 3-pentanol |
| iso-butanol | n-pentanol | 3-methyl-2-butanol |
| | iso-pentanol | 2-methyl-2-butanol |
| | 3-methyl-1-butanol | 2-hexanol |
| | 2-methyl-1-butanol | 3-hexanol |
| | 1-hexanol | 2-methyl-1-pentanol |
| | iso-hexanol | 2-methyl-2-pentanol |
| | 1-heptanol | 3-methyl-2-pentanol |
| | 2-heptanol | 4-methyl-2-pentanol |
| | 1-octanol | 2-methyl-3-pentanol |
| | 2-octanol | 3-methyl-3-pentanol |
| | | 2,2-dimethyl-1-butanol |
| | | 2,3-dimethyl-1-butanol |
| | | 3,3-dimethyl-1-butanol |
| | | 2,3-dimethyl-2-butanol |
| | | 3,3-dimethyl-2-butanol |
| | | 2-ethyl-1-butanol |
| | | 3-heptanol |
| | | 4-heptanol |
| | | 3-octanol |
| | | 4-octanol |



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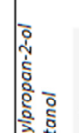
**TABLE 7.2: PROPERTIES OF ALCOHOLS OF CARBON NUMBER ONE THROUGH FOUR**

| *Alcohol* | *Methanol* | *Ethanol* | *Propanol* | | |
|---|---|---|---|---|---|
| *Formula* | *CH4O* | *C2H6O* | *C3H8O* | | |
| *Isomer* | | | *propan-1-ol* | *propan-2-ol* | |
| *AKA* | | | *n-propanol* | *isopropanol* | |
| |  |  |  |  | |
| *Density @ 25C & 100kPa, kg/m^3* | 792 | 789 | 803 | 786 | |
| *Dynamic Viscosity @ 20 or 25C, mPa-s* | 0.59 | 1.2 | 1.938 | 1.96 | |
| *Lower Heating Value, MJ/kg* | 19.93 | 25.541 | 30.236 | 29.679 | |
| *Heat of Vaporization, kJ/kg* | 1101.06 | 919.6 | 792.1 | 756.6 | |
| *Boiling Point @ 100kPa, C* | 65 | 78 | 97 | 82.5 | |
| *Melting Point @ 100kPa, C* | -97 | -112 | -127 | -85.8 | |
| *RVP, psi* | | 2.69 | 1.41 | 2.11 | |
| *Solubility @ 100kPa & 25C, mol/100g of H2O* | miscible | miscible | miscible | miscible | |
| *RON* | 109 | 107.4 | 104.9 | 112.5 | |
| *MON* | 89 | 88.2 | 87.8 | 96.7 | |
| *Anti-Knock Index (RON+MON)/2* | 98 | 97.8 | 96.35 | 104.6 | |
| *Toxicity (LD50 in rats), mg/kg* | 5628 | 7060 | 1870 | 5045 | |
| *US annual production, lbs* | > 1 billion | > 1 billion | 200 million | 1.45 billion | |

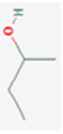
| *Alcohol* | *Butanol* | | | |
|---|---|---|---|---|
| *Formula* | *C4H10O* | | | |
| *Isomer* | *n-butanol* | *2-methylpropan-1-ol* | *2-butanol* | *2-methylpropan-2-ol* |
| *AKA* | *normal butanol* | *isobutanol* | *sec-butanol* | *tert-butanol* |
| |  |  |  |  |
| *Density @ 25C & 100kPa, kg/m^3* | 810 | 802 | 806 | 789 |
| *Dynamic Viscosity @ 20 or 25C, mPa-s* | 2.544 | 4.312 | 3.096 | |
| *Lower Heating Value, MJ/kg* | 32.928 | 32.749 | | |
| *Heat of Vaporization, kJ/kg* | 707.9 | 686.4 | 671.1 | |
| *Boiling Point @ 100kPa, C* | 118 | 108 | 99 | 82 |
| *Melting Point @ 100kPa, C* | -79.9 | -108 | -114.7 | 25.5 |
| *RVP, psi* | 1.64 | 1.11 | | |
| *Solubility @ 100kPa & 25C, mol/100g of H2O* | 0.11 | | | |
| *RON* | 98.3 | 105.1 | 105 | 103 |
| *MON* | 84.4 | 89.3 | 93 | 91 |
| *Anti-Knock Index (RON+MON)/2* | 91.35 | 97.2 | 99 | 97 |
| *Toxicity (LD50 in rats), mg/kg* | 790 | 2460 | 6480 | 3500 |
| *US annual production, lbs* | 1.33 billion | 1.8 billion | | |



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**TABLE 7.3: PROPERTIES OF ALCOHOLS OF CARBON NUMBER FIVE**

| Alcohol | Pentanol | | | |
|---|---|---|---|---|
| Formula | C5H12O | | | |
| Isomer | 1-pentanol | 3-methyl-1-butanol | 2-methyl-1-butanol | 2,2-dimethyl-1-propanol |
| AKA | n-pentanol | isopentyl alcohol | active amyl alcohol | neopentyl alcohol |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | 814 | 810 | 815 | 812 |
| Dynamic Viscosity @ 20 or 25C, mPa-s | 3.33 | 3.69 | 4.45 | |
| Lower Heating Value, MJ/kg | 34.74 | 34.528 | | |
| Heat of Vaporization, kJ/kg | 647.1 | 617.1 | | |
| Boiling Point @ 100kPa, C | 138 | 131 | 127.5 | 113.5 |
| Melting Point @ 100kPa, C | -78.5 | -117.2 | -70 | |
| RVP, psi | 0.72 | 0.6 | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | 0.08 | | | |
| RON | 85.8 | 98.8 | | |
| MON | 75.9 | 86.8 | | |
| Anti-Knock Index (RON+MON)/2 | 80.85 | 92.8 | | |
| Toxicity (LD50 in rats), mg/kg | 210 | 1300 | 3260 | |
| US annual production, lbs | 10-50 million | | | |

| Alcohol | Pentanol | | | |
|---|---|---|---|---|
| Formula | C5H12O | | | |
| Isomer | 2-pentanol | 3-pentanol | 3-methyl-2-butanol | 2-methyl-2-butanol |
| AKA | sec-amyl alcohol | diethyl carbinol | sec-isoamyl alcohol | tert-amyl alcohol |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | 812 | 815 | 818 | 815 |
| Dynamic Viscosity @ 20 or 25C, mPa-s | | | | 3.79 |
| Lower Heating Value, MJ/kg | | | | |
| Heat of Vaporization, kJ/kg | | | | |
| Boiling Point @ 100kPa, C | 119.5 | 115.3 | 113 | 102 |
| Melting Point @ 100kPa, C | -73 | -63.7 | -117.2 | -11.9 |
| RVP, psi | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | | | | 0.0011 |
| RON | | | | |
| MON | | | | |
| Anti-Knock Index (RON+MON)/2 | | | | |
| Toxicity (LD50 in rats), mg/kg | | | | 1000 |
| US annual production, lbs | | | | 1-10 million |



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**TABLE 7.4: PROPERTIES OF ALCOHOLS OF CARBON NUMBER SIX**

| Alcohol | | Hexanol | | | |
|---|---|---|---|---|---|
| Formula | | C6H14O | | | |
| Isomer | 1-hexanol | 2-hexanol | 3-hexanol | 2-methyl-1-pentanol | |
| AKA | | | | | |
| Density @ 25C & 100kPa, kg/m^3 | 814 | 826 | 819 | 826 | |
| Dynamic Viscosity @ 20 or 25C, mPa-s | 0.592 | | | | |
| Lower Heating Value, MJ/kg | 36.021 | | | | |
| Heat of Vaporization, kJ/kg | 486 | | | | |
| Boiling Point @ 100kPa, C | 155 | 148 | 135 | 149 | |
| Melting Point @ 100kPa, C | -52 | -90 | | | |
| RVP, psi | 0.6 | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | 0.0058 | 0.00587 | | | |
| RON | 69.3 | | | | |
| MON | 64.1 | | | | |
| Anti-Knock Index (RON+MON)/2 | 66.7 | | | | |
| Toxicity (LD50 in rats), mg/kg | 4590 | 2600 | | 1410 | |
| US annual production, lbs | 10-50 million | 1.8 million | | 1.8 million | |

| Alcohol | | Hexanol | | | |
|---|---|---|---|---|---|
| Formula | | C6H14O | | | |
| Isomer | 3-methyl-1-pentanol | 4-methyl-1-pentanol | 2-methyl-2-pentanol | 3-methyl-2-pentanol | |
| AKA | | isohexyl alcohol | | | |
| Density @ 25C & 100kPa, kg/m^3 | 824 | 813 | 835 | 831 | |
| Dynamic Viscosity @ 20 or 25C, mPa-s | | | | | |
| Lower Heating Value, MJ/kg | | | | | |
| Heat of Vaporization, kJ/kg | | | | | |
| Boiling Point @ 100kPa, C | 153 | 152 | 121 | 134 | |
| Melting Point @ 100kPa, C | | | -103 | 0 | |
| RVP, psi | | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | | | 0.000323 | 0.000186 | |
| RON | | | | | |
| MON | | | | | |
| Anti-Knock Index (RON+MON)/2 | | 1410 | | | |
| Toxicity (LD50 in rats), mg/kg | | | | | |
| US annual production, lbs | | 1.8 million | | | |



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**TABLE 7.5: PROPERTIES OF ALCOHOLS OF CARBON NUMBER SIX**

| Alcohol | Hexanol | | | |
|---|---|---|---|---|
| Formula | C6H14O | | | |
| Isomer | 4-methyl-2-pentanol | 2-methyl-3-pentanol | 3-methyl-3-pentanol | 2,2-dimethyl-1-butanol |
| AKA | isobutylmethylcarbinol | | | |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | 808 | 824 | 829 | 828 |
| Dynamic Viscosity @ 20 or 25C, mPa-s | 4.07 | | | |
| Lower Heating Value, MJ/kg | | | | |
| Heat of Vaporization, kJ/kg | 132 | 127 | 122 | 136.5 |
| Boiling Point @ 100kPa, C | -90 | | -24 | |
| Melting Point @ 100kPa, C | | | | |
| RVP, psi | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | 0.000147 | 0.000196 | 0.00044 | |
| RON | | | | |
| MON | | | | |
| Anti-Knock Index (RON+MON)/2 | | | | |
| Toxicity (LD50 in rats), mg/kg | 2600 | | | |
| US annual production, lbs | 1.8 million | | | |

| Alcohol | Hexanol | | | |
|---|---|---|---|---|
| Formula | C6H14O | | | |
| Isomer | 2,3-dimethyl-1-butanol | 3,3-dimethyl-1-butanol | 3,3-dimethyl-2-butanol | 2-ethyl-1-butanol |
| AKA | | | | |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | | 812 | | 833 |
| Dynamic Viscosity @ 20 or 25C, mPa-s | | | | |
| Lower Heating Value, MJ/kg | | | | |
| Heat of Vaporization, kJ/kg | | | | |
| Boiling Point @ 100kPa, C | | 120 | | 147 |
| Melting Point @ 100kPa, C | | 5.6 | | |
| RVP, psi | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | | 0.000232 | | |
| RON | | | | |
| MON | | | | |
| Anti-Knock Index (RON+MON)/2 | | | | |
| Toxicity (LD50 in rats), mg/kg | | | | |
| US annual production, lbs | | | | |



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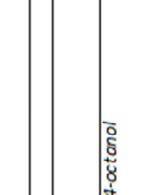
**TABLE 7.6: PROPERTIES OF ALCOHOLS OF CARBON NUMBER SEVEN AND EIGHT**

| Alcohol | Heptanol | | | |
|---|---|---|---|---|
| Formula | C7H16O | | | |
| Isomer | 1-heptanol | 2-heptanol | 3-heptanol | 4-heptanol |
| AKA | | | | dipropylcarbinol |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | 819 | 817 | 828 | 820 |
| Dynamic Viscosity @ 20 or 25C, mPa-s | | | | |
| Lower Heating Value, MJ/kg | | | | |
| Heat of Vaporization, kJ/kg | | | | |
| Boiling Point @ 100kPa, C | 175.8 | 159 | 163.5 | 155.4 |
| Melting Point @ 100kPa, C | -36 | | | -41.5 |
| RVP, psi | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | 0.0008 | | | |
| RON | | | | |
| MON | | | | |
| Anti-Knock Index (RON+MON)/2 | | | | |
| Toxicity (LD50 in rats), mg/kg | | | | |
| US annual production, lbs | | | | |

| Alcohol | Octanol | | | |
|---|---|---|---|---|
| Formula | C8H18O | | | |
| Isomer | 1-octanol | 2-octanol | 3-octanol | 4-octanol |
| AKA | isooctanol | hexylmethylcarbinol | | |
| |  |  |  |  |
| Density @ 25C & 100kPa, kg/m^3 | 834 | 820 | 836 | |
| Dynamic Viscosity @ 20 or 25C, mPa-s | 9.8 | | | |
| Lower Heating Value, MJ/kg | | | | |
| Heat of Vaporization, kJ/kg | | | | |
| Boiling Point @ 100kPa, C | 184.34 | 178.5 | 199 | |
| Melting Point @ 100kPa, C | -16 | -38.6 | | |
| RVP, psi | | | | |
| Solubility @ 100kPa & 25C, mol/100g of H2O | immiscible | immiscible | immiscible | immiscible |
| RON | | | | |
| MON | | | | |
| Anti-Knock Index (RON+MON)/2 | | | | |
| Toxicity (LD50 in rats), mg/kg | 5000 | 3200 | | |
| US annual production, lbs | 50-100 million | | | |

*Incorporation of Higher Carbon Number Alcohols in Gasoline Blends for Application in Spark-Ignition Engines* by Kristina Marie Lawyer

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## 7.3 Neat Alcohol Analytical Testing Results

### TABLE 7.7: TESTING RESULTS OF ETHANOL

| Ethanol | | *(SwRI Lab ID# oddb-4657)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 2.69 |
| | DVPE, psi | 2.52 |
| | CARVP, psi | 2.38 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 12170 |
| | MJ/kg | 28.308 |
| | cal/g | 6761.2 |
| | NET | |
| | BTU/lb | 10981 |
| | MJ/kg | 25.541 |
| | cal/g | 6100.3 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 107.4 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 88.2 |

### TABLE 7.8: TESTING RESULTS OF 1-PROPANOL

| 1-Propanol | | *(SwRI Lab ID# oddb-4655)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 1.41 |
| | DVPE, psi | 1.23 |
| | CARVP, psi | 1.07 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 14213 |
| | MJ/kg | 33.06 |
| | cal/g | 7896.2 |
| | NET | |
| | BTU/lb | 12999 |
| | MJ/kg | 30.236 |
| | cal/g | 7221.6 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 104.9 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 87.8 |



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## TABLE 7.9: TESTING RESULTS OF ISO-PROPANOL

| Iso-Propanol | | *(SwRI Lab ID# oddb-4656)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 2.11 |
| | DVPE, psi | 1.93 |
| | CARVP, psi | 1.78 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 13974 |
| | MJ/kg | 32.504 |
| | cal/g | 7763.5 |
| | NET | |
| | BTU/lb | 12760 |
| | MJ/kg | 29.679 |
| | cal/g | 7088.8 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 112.5 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 96.7 |

## TABLE 7.10: TESTING RESULTS OF 1-BUTANOL

| 1-Butanol | | *(SwRI Lab ID# oddb-4658)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 1.64 |
| | DVPE, psi | 1.46 |
| | CARVP, psi | 1.31 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 15387 |
| | MJ/kg | 35.791 |
| | cal/g | 8548.5 |
| | NET | |
| | BTU/lb | 14157 |
| | MJ/kg | 32.928 |
| | cal/g | 7864.8 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 98.3 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 84.4 |



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## TABLE 7.11: TESTING RESULTS OF 2-METHYL-1-PROPANOL

| 2-Methyl-1-Propanol | | *(SwRI Lab ID# oddb-4659)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 1.11 |
| | DVPE, psi | 0.92 |
| | CARVP, psi | 0.76 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 15312 |
| | MJ/kg | 35.615 |
| | cal/g | 8506.6 |
| | NET | |
| | BTU/lb | 14079 |
| | MJ/kg | 32.749 |
| | cal/g | 7821.9 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 105.1 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 89.3 |

## TABLE 7.12: TESTING RESULTS OF 1-PENTANOL

| 1-Pentanol | | *(SwRI Lab ID# oddb-4660)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 0.72 |
| | DVPE, psi | 0.53 |
| | CARVP, psi | 0.37 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 16177 |
| | MJ/kg | 37.628 |
| | cal/g | 8987.2 |
| | NET | |
| | BTU/lb | 14935 |
| | MJ/kg | 34.74 |
| | cal/g | 8297.4 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 85.8 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 75.9 |



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## TABLE 7.13: TESTING RESULTS OF 3-METHYL-1-BUTANOL

| 3-Methyl-1-Butanol | | *(SwRI Lab ID# oddb-4661)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 0.60 |
| | DVPE, psi | 0.41 |
| | CARVP, psi | 0.25 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 16086 |
| | MJ/kg | 37.416 |
| | cal/g | 8936.6 |
| | NET | |
| | BTU/lb | 14844 |
| | MJ/kg | 34.528 |
| | cal/g | 8246.8 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 98.8 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 86.8 |

## TABLE 7.14: TESTING RESULTS OF HEXYL ALCOHOL

| Hexyl Alcohol | | *(SwRI Lab ID# oddb-4662)* |
|---|---|---|
| ASTM D5191 | Vapor Pressure of Petroleum Products (Mini Method) | |
| | RVP, psi | 0.60 |
| | DVPE, psi | 0.41 |
| | CARVP, psi | 0.25 |
| ASTM D240 | Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter | |
| | GROSS | |
| | BTU/lb | 16736 |
| | MJ/kg | 38.928 |
| | cal/g | 9297.8 |
| | NET | |
| | BTU/lb | 15486 |
| | MJ/kg | 36.021 |
| | cal/g | 8603.5 |
| ASTM D2699 | Research Octane Number of Spark-Ignition Engine Fuel | |
| | RON | 69.3 |
| ASTM D2700 | Motor Octane Number of Spark-Ignition Engine Fuel | |
| | MON | 64.1 |



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## TABLE 7.15: RVP TESTING RESULTS OF ALCOHOL BLENDS

Southwest Research Institute
Petroleum Products Research Department
WO# 65303 Data Summary
For
Argonne National Laboratory
October 8, 2012

ASTM D5191 Vapor Pressure of Petroleum Products (Mini Method)

**Part I – Base Blend Components**

| | |
|---|---|
| EEE Gasoline | 8.74 |
| BOB Gasoline | 5.76 |
| Ethanol | 2.74 |
| Isopropanol | 1.81 |
| 1-butanol | 0.39 |
| Iso-butanol | 0.49 |
| 1-pentanol | 0.13 |
| Isopentyl Alcohol | 0.19 |
| 3-pentanol | 0.30 |
| 3-methyl-2-butanol | 0.46 |
| 1-hexanol | 0.03 |
| Isopentane | 19.22 |

**Part II – Mixtures of Alcohols with EEE Base Fuel**

| | |
|---|---|
| EEE gasoline w/Ethanol 2% | 9.54 |
| EEE gasoline w/Ethanol 5% | 9.67 |
| EEE gasoline w/Ethanol 10% | 9.57 |
| EEE gasoline w/Ethanol 15% | 9.53 |
| EEE gasoline w/Ethanol 20% | 9.35 |
| EEE gasoline w/Ethanol 30% | 9.10 |
| EEE gasoline w/Ethanol 50% | 8.30 |
| EEE gasoline w/Ethanol 75% | 6.19 |
| EEE gasoline w/1-butanol 10% | 8.28 |
| EEE gasoline w/1-butanol 20% | 7.80 |
| EEE gasoline w/1-butanol 30% | 7.46 |



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## RVP TESTING RESULTS OF ALCOHOL BLENDS (CONTINUED)

Southwest Research Institute
Petroleum Products Research Department
WO# 65303 Data Summary
For
Argonne National Laboratory
October 8, 2012

ASTM D5191 Vapor Pressure of Petroleum Products (Mini Method)

| | |
|---|---|
| EEE gasoline w/1-pentanol 5% | 8.29 |
| EEE gasoline w/1-pentanol 10% | 8.16 |
| EEE gasoline w/1-pentanol 20% | 7.81 |
| EEE gasoline w/1-pentanol 50% | 6.14 |
| EEE gasoline w/1-pentanol 75% | 3.71 |
| | |
| EEE gasoline w/isopentyl alcohol 5% | 8.28 |
| EEE gasoline w/isopentyl alcohol 10% | 7.99 |
| EEE gasoline w/isopentyl alcohol 20% | 7.69 |
| EEE gasoline w/isopentyl alcohol 50% | 6.17 |
| EEE gasoline w/isopentyl alcohol 75% | 3.9 |
| | |
| EEE gasoline w/3-pentanol 5% | 8.26 |
| EEE gasoline w/3-pentanol 10% | 8.07 |
| EEE gasoline w/3-pentanol 20% | 7.63 |
| EEE gasoline w/3-pentanol 50% | 5.96 |
| EEE gasoline w/3-pentanol 75% | 3.73 |
| | |
| EEE gasoline w/3-methyl-2-butanol 5% | 8.31 |
| EEE gasoline w/3-methyl-2-butanol 10% | 8.24 |
| EEE gasoline w/3-methyl-2-butanol 20% | 7.77 |
| EEE gasoline w/3-methyl-2-butanol 50% | 6.10 |
| EEE gasoline w/3-methyl-2-butanol 75% | 3.87 |
| | |
| EEE gasoline w/Ethanol/1-butanol 1.8/8.4% | 8.33 |
| EEE gasoline w/Ethanol/1-butanol 8.1/12.3% | 8.7 |
| EEE gasoline w/Ethanol/1-butanol 18.2/11.8% | 8.52 |



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## RVP TESTING RESULTS OF ALCOHOL BLENDS (CONTINUED)

Southwest Research Institute
Petroleum Products Research Department
WO# 65303 Data Summary
For
Argonne National Laboratory
October 8, 2012

ASTM D5191 Vapor Pressure of Petroleum Products (Mini Method)

**Part III – Mixtures of Alcohols with BOB Base Fuel**

| | |
|---|---|
| BOB gasoline w/Ethanol 2% | 6.73 |
| BOB gasoline w/Ethanol 5% | 6.86 |
| BOB gasoline w/Ethanol 10% | 6.92 |
| BOB gasoline w/Ethanol 15% | 6.9 |
| BOB gasoline w/Ethanol 20% | 6.84 |
| BOB gasoline w/Ethanol 30% | 6.73 |
| BOB gasoline w/Ethanol 50% | 6.26 |
| BOB gasoline w/Ethanol 75% | 5.16 |
| BOB gasoline w/Isopropanol 5% | 6.42 |
| BOB gasoline w/Isopropanol 10% | 6.25 |
| BOB gasoline w/Isopropanol 20% | 6.13 |
| BOB gasoline w/Isopropanol 30% | 5.93 |
| BOB gasoline w/Isopropanol 50% | 5.49 |
| BOB gasoline w/Isopropanol 75% | 4.26 |
| BOB gasoline w/Isobutanol 5% | 5.74 |
| BOB gasoline w/Isobutanol 10% | 5.56 |
| BOB gasoline w/Isobutanol 20% | 5.35 |
| BOB gasoline w/Isobutanol 30% | 5.12 |
| BOB gasoline w/Isobutanol 50% | 4.44 |
| BOB gasoline w/Isobutanol 75% | 3.15 |
| BOB gasoline w/Isopentyl alcohol 5% | 5.56 |
| BOB gasoline w/Isopentyl alcohol 10% | 5.44 |
| BOB gasoline w/Isopentyl alcohol 20% | 5.19 |
| BOB gasoline w/Isopentyl alcohol 30% | 4.93 |
| BOB gasoline w/Isopentyl alcohol 50% | 4.19 |
| BOB gasoline w/Isopentyl alcohol 75% | 2.71 |



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## RVP TESTING RESULTS OF ALCOHOL BLENDS (CONTINUED)

Southwest Research Institute
Petroleum Products Research Department
WO# 65303 Data Summary
For
Argonne National Laboratory
October 8, 2012

ASTM D5191 Vapor Pressure of Petroleum Products (Mini Method)

| | |
|---|---|
| BOB gasoline w/Isopentane 2% | 6.00 |
| BOB gasoline w/Isopentane 5% | 6.52 |
| BOB gasoline w/Isopentane 8% | 7.1 |
| BOB gasoline w/Isopentane 10% | 7.32 |
| BOB gasoline w/Ethanol/Isopropanol 5/5% | 6.61 |
| BOB gasoline w/Ethanol/Isopropanol 5/10% | 6.48 |
| BOB gasoline w/Ethanol/Isopropanol 5/15% | 6.34 |
| BOB gasoline w/Ethanol/Isopropanol 10/10% | 6.49 |
| BOB gasoline w/Ethanol/Isopropanol 10/20% | 6.24 |
| BOB gasoline w/Ethanol/Isobutanol 5/5% | 6.5 |
| BOB gasoline w/Ethanol/Isobutanol 5/10% | 6.09 |
| BOB gasoline w/Ethanol/Isobutanol 5/15% | 5.91 |
| BOB gasoline w/Ethanol/Isobutanol 10/10% | 6.24 |
| BOB gasoline w/Ethanol/Isobutanol 10/20% | 5.79 |
| BOB gasoline w/Ethanol/Isopentanol 5/5% | 6.3 |
| BOB gasoline w/Ethanol/Isopentanol 5/10% | 6.05 |
| BOB gasoline w/Ethanol/Isopentanol 5/15% | 5.84 |
| BOB gasoline w/Ethanol/Isopentanol 10/10% | 6.25 |
| BOB gasoline w/Ethanol/Isopentanol 10/20% | 5.79 |
| BOB gasoline w/Ethanol/1-hexanol 5/5% | 6.34 |
| BOB gasoline w/Ethanol/1-hexanol 5/10% | 6.06 |
| BOB gasoline w/Ethanol/1-hexanol 10/10% | 6.31 |
| BOB gasoline w/Ethanol/Isobutanol/isopentyl alcohol 5/5/5% | 6.06 |
| BOB gasoline w/Ethanol/Isopropanol/Isobutanol/isopentyl alcohol 5/5/5/5% | 6.02 |



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## 7.4 Engine, Dynamometer, and Test Cell Setup

The engine used for testing was a gasoline direct-injected, (GDI) four-cylinder Hyundai ThetaII shown in Figure 7.1. The naturally aspirated (NA) 2.4L spark-ignition (SI) engine was set up in an engine test cell and connected to an AC dynamometer with a range of temperature probes, fuel and air flow measurement sensors, exhaust emissions probes, and in-cylinder pressure transducers. The main engine specifications are summarized in Table 7.16.

**TABLE 7.16: MAIN SPECIFICATIONS OF HYUNDAI TEST ENGINE**

| Parameter | Value |
|---|---|
| **Bore** | 88 mm |
| **Stroke** | 97 mm |
| **Compression** | 11.3:1 |
| **Displacement** | 2.36 L |
| **Cylinder count** | 4 |
| **Rated power** | 147 kW at 6300 rpm |
| **Maximum torque** | 250 Nm at 4250 rpm |

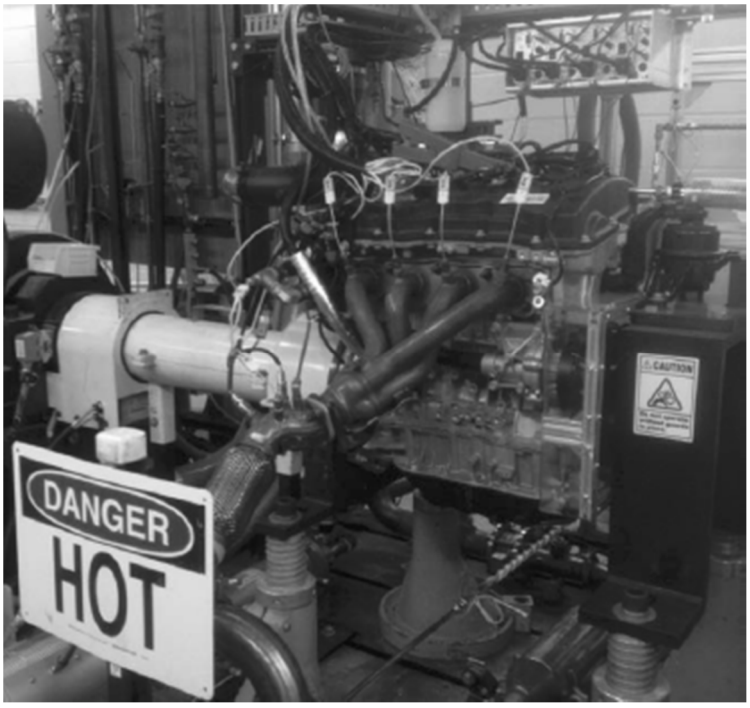


**FIGURE 7.1: HYUNDAI ENGINE USED FOR FUEL TESTING**



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The engine is equipped with an exhaust gas recirculation (EGR) system which was disabled for this project. The fuel trim in the engine control unit (ECU) was increased to adjust for the lower energy content of the alcohols. The engine is also equipped with a knock sensor and the ECU is calibrated to retard spark timing of each cylinder individually if knock is detected. To further understand the knock resistance of the fuels, a separate set of tests was run with the engine knock sensor disabled.

Pre-catalyst emissions data was collected using both a standard raw emissions bench (Horiba MEXA Model 7100D) as well as an FTIR analyzer (AVL SESAM-FTIR). The raw emissions bench uses separate analyzers to determine the level of $NO_x$, HC, CO, $CO_2$, and $O_2$ in the exhaust stream. Using a heated sample line, exhaust is fed to a heated oven that houses a heated flame ionization detector (FID Model FIA-725A) and a heated chemiluminescent detector (CLD Model CLA-720MA) for HC and $NO_x$ emissions measurements, respectively. CO, $CO_2$, and $O_2$ are measured using rack-mounted, cold analyzers (magneto-pneumatic for $O_2$ and non-dispersive infrared, NDIR, for CO and $CO_2$).

Each test fuel was run at the engine speed and load (BMEP) points listed in Table 7.17. These operating points were chosen to reflect common drive cycle operation and to allow for same load and same speed comparisons. Dynamometer data was collected for 120 seconds and cylinder pressure data for 500 engine cycles after allowing the engine to stabilize. Data was collected twice at each operating point at a frequency of 10 Hz. High-speed individual cylinder pressure data was taken with an AVL IndiModul system. In post-processing, data was averaged over the measurement interval for each of the two data sets and uncertainty ranges were calculated.

**TABLE 7.17: OPERATING POINTS FOR ENGINE TESTING**

| Speed [rpm] | Load [bar] |
|---|---|
| 1500 | 2.62 |
| 1500 | 4.0 |
| 1500 | 8.0 |
| 3000 | 4.0 |
| 3000 | 8.0 |



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## 7.5 BLENDSTOCK PROPERTIES

The fuel certificates (specification sheets) provided by the manufacturer for both the blendstock for oxygenate blending (BOB) and certification gasoline (EEE) used in this project are provided in this appendix.

**TABLE 7.18: PROPERTIES OF BOB**

Sales specification

FAX: (281) 457-1469

Johann Haltermann Ltd.

PRODUCT: Blendstock for Oxygenate Blending

| TEST | METHOD | UNITS | SPECIFICATIONS | | | Results |
|---|---|---|---|---|---|---|
| | | | MIN | TARGET | MAX | |
| Distillation - IBP | ASTM D86 | °C | | Report | | 39.6 |
| 5% | | °C | | Report | | 58.5 |
| 10% | | °C | | Report | | 63.9 |
| 20% | | °C | | Report | | 71.6 |
| 30% | | °C | | Report | | 80.2 |
| 40% | | °C | | Report | | 90.2 |
| 50% | | °C | | Report | | 102.3 |
| 60% | | °C | | Report | | 115.1 |
| 70% | | °C | | Report | | 127.9 |
| 80% | | °C | | Report | | 140.5 |
| 90% | | °C | | Report | | 156.2 |
| 95% | | °C | | Report | | 168.6 |
| Distillation - EP | | °C | | Report | | 189.5 |
| Recovery | | vol % | | Report | | 98.6 |
| Residue | | vol % | | Report | | 1.0 |
| Loss | | vol % | | Report | | 0.4 |
| Gravity | ASTM D4052 | °API | | Report | | 56.3 |
| Density | ASTM D4052 | - | | Report | | 0.8 |
| Reid Vapor Pressure | ASTM D5191 | psi | | Report | | 5.8 |
| Sulfur | ASTM D5453 | ppm | | Report | | 4.1 |
| Composition, aromatics | ASTM D1319 | vol % | | Report | | 34.6 |
| Composition, olefins | ASTM D1319 | vol % | | Report | | 1.4 |
| Composition, saturates | ASTM D1319 | vol % | | Report | | 64.0 |
| Research Octane Number | ASTM D2699 | | | Report | | 88.6 |
| Motor Octane Number | ASTM D2700 | | | Report | | 81.0 |
| R+M/2 | D2699/2700 | | | Report | | 84.8 |
| Sensitivity | D2699/2700 | | | Report | | 7.6 |



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**TABLE 7.19: PROPERTIES OF EEE**

RCVD. 3-
DRUMS
9/ /2011

**Product Information**

FAX: (281) 457-1469

Johann Haltermann Ltd.

**PRODUCT:** EPA TIER II EEE
FEDERAL REGISTER

**PRODUCT CODE:** HF0437

Batch No.: ZH1621LT30

Tank No.: 106

Date: 8/19/2011

| TEST | METHOD | UNITS | HALTERMANN Specs | | | RESULTS |
|---|---|---|---|---|---|---|
| | | | MIN | TARGET | MAX | |
| Distillation - IBP | ASTM D86 | °F | 75 | | 95 | 85 |
| 5% | | °F | | | | 110 |
| 10% | | °F | 120 | | 135 | 125 |
| 20% | | °F | | | | 148 |
| 30% | | °F | | | | 174 |
| 40% | | °F | | | | 204 |
| 50% | | °F | 200 | | 230 | 224 |
| 60% | | °F | | | | 235 |
| 70% | | °F | | | | 246 |
| 80% | | °F | | | | 268 |
| 90% | | °F | 305 | | 325 | 318 |
| 95% | | °F | | | | 340 |
| Distillation - EP | | °F | | | 415 | 398 |
| Recovery | | vol % | | Report | | 97.4 |
| Residue | | vol % | | Report | | 1.1 |
| Loss | | vol % | | Report | | 1.5 |
| Gravity | ASTM D4052 | °API | 58.7 | | 61.2 | 59.0 |
| Density | ASTM D4052 | kg/l | 0.734 | | 0.744 | 0.742 |
| Reid Vapor Pressure | ASTM D5191 | psi | 8.7 | | 9.2 | 9.0 |
| Carbon | ASTM D3343 | wt fraction | | Report | | 0.8647 |
| Carbon | ASTM E191 | wt fraction | | Report | | 0.8628 |
| Hydrogen | ASTM E191 | wt fraction | | Report | | 0.1349 |
| Hydrogen/Carbon ratio | ASTM E191 | mole/mole | | Report | | 1.862 |
| Stoichiometric Air/Fuel Ratio | | | | Report | | 14.601 |
| Oxygen | ASTM D4815 | wt % | | | 0.05 | None Detected |
| Sulfur | ASTM D5453 | wt % | 0.0025 | | 0.0035 | 0.0032 |
| Lead | ASTM D3237 | g/gal | | | 0.01 | None Detected |
| Phosphorous | ASTM D3231 | g/gal | | | 0.005 | None Detected |
| Silicon | ASTM 5184 | mg/kg | | | 4 | None Detected |
| Composition, aromatics | ASTM D1319 | vol % | | | 35 | 28 |
| Composition, olefins | ASTM D1319 | vol % | | | 10 | 1 |
| Composition, saturates | ASTM D1319 | vol % | | Report | | 72 |
| Particulate matter | ASTM D5452 | mg/l | | | 1 | 0.7 |
| Oxidation Stability | ASTM D525 | minutes | 240 | | | 1000+ |
| Copper Corrosion | ASTM D130 | | | | 1 | 1a |
| Gum content, washed | ASTM D381 | mg/100mls | | | 5 | 1.0 |
| Fuel Economy Numerator/C Density | ASTM E191 | | 2401 | | 2441 | 2425 |
| C Factor | ASTM E191 | | | Report | | 1.0080 |
| Research Octane Number | ASTM D2699 | | 96.0 | | | 97.1 |
| Motor Octane Number | ASTM D2700 | | | Report | | 88.7 |
| Sensitivity | | | 7.5 | | | 8.4 |
| Net Heating Value, btu/lb | ASTM D3338 | btu/lb | | Report | | 18489 |
| Net Heating Value, btu/lb | ASTM D240 | btu/lb | | Report | | 18202 |
| Color | VISUAL | | | Report | | Undyed |



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## 7.6 Blends Similar to the Optimal Blends of Each Scenario

As detailed in Chapter 4, many multi-component blends of slightly different composition have essentially equal properties including LHV, RON, and PD. The compositions of the top eight blends of each scenario and each subset of suitable blends are listed here with their relevant properties.



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## 7.6.1 E10/E15 Alternate Scenario

### 7.6.1.1 Suitable Blends

**TABLE 7.20: TOP 8 LHV SUITABLE BLENDS OF THE E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 87.0 BOB, 6.5 i-prop, 5.2 i-but, 1.3 i-pent | 758 | 41.2 | 400 | 3.23 | 92.4 | 5.80 | 642 | 16.1 |
| 87.0 BOB, 7.8 i-prop, 2.6 i-but, 2.6 i-pent | 758 | 41.1 | 400 | 3.25 | 92.5 | 5.9 | 642 | 16.0 |
| 87.0 BOB, 6.5 i-prop, 1.3 n-but, 5.2 i-but | 758 | 41.1 | 402 | 3.28 | 92.4 | 5.9 | 642 | 16.0 |
| 87.0 BOB, 6.5 i-prop, 6.5 i-but | 758 | 41.1 | 401 | 3.28 | 92.5 | 5.9 | 642 | 16.0 |
| 87.0 BOB, 1.3 n-prop, 7.8 i-prop, 3.9 i-pent | 758 | 41.1 | 401 | 3.27 | 92.4 | 5.9 | 642 | 16.0 |
| 87.0 BOB, 9.1 i-prop, 3.9 i-pent | 758 | 41.1 | 400 | 3.26 | 92.6 | 6.0 | 642 | 15.9 |
| 87.0 BOB, 1.3 n-prop, 6.5 i-prop, 3.9 i-but, 1.3 i-pent | 758 | 41.1 | 402 | 3.30 | 92.5 | 5.9 | 642 | 16.0 |
| 87.0 BOB, 1.3 n-prop, 7.8 i-prop, 1.3 n-but, 2.6 i-pent | 758 | 41.1 | 402 | 3.32 | 92.4 | 6.0 | 642 | 15.9 |



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**TABLE 7.21: TOP 8 RON SUITABLE BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 81.0 BOB<br>19.0 i-prop | 759 | 40.1 | 431 | 5.23 | 95.5 | 6.1 | 650 | 22.0 |
| 81.0 BOB<br>1.9 n-prop<br>17.1 i-prop | 759 | 40.1 | 432 | 5.24 | 95.3 | 6.1 | 650 | 22.1 |
| 81.0 BOB<br>17.1 i-prop<br>1.9 i-but | 759 | 40.2 | 430 | 5.14 | 95.3 | 6.1 | 650 | 22.3 |
| 82.0 BOB<br>18.0 i-prop | 759 | 40.3 | 427 | 4.96 | 95.2 | 6.2 | 648 | 20.8 |
| 82.0 BOB<br>1.8 eth<br>16.2 i-prop | 759 | 40.2 | 430 | 5.11 | 95.2 | 6.2 | 648 | 20.6 |
| 80.0 BOB<br>16.0 i-prop<br>2.0 i-but<br>2.0 i-pent | 760 | 40.2 | 431 | 5.24 | 95.1 | 6.0 | 651 | 23.9 |
| 81.0 BOB<br>17.1 i-prop<br>1.9 n-but | 759 | 40.2 | 430 | 5.15 | 95.1 | 6.1 | 650 | 22.3 |
| 81.0 BOB<br>17.1 i-prop<br>1.9 i-pent | 759 | 40.2 | 428 | 5.07 | 95.1 | 6.0 | 650 | 22.4 |



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**TABLE 7.22: TOP 8 PD SUITABLE BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 77.0 BOB, 4.6 i-prop, 11.5 n-but, 6.9 i-pent | 765 | 40.3 | 433 | 5.21 | 92.6 | 5.5 | 655 | 30.1 |
| 77.0 BOB, 4.6 i-prop, 9.2 n-but, 2.3 i-but, 2.3 n-pent, 4.6 i-pent | 765 | 40.3 | 433 | 5.21 | 92.5 | 5.5 | 655 | 30.1 |
| 77.0 BOB, 4.6 i-prop, 9.2 n-but, 2.3 i-but, 6.9 i-pent | 765 | 40.3 | 433 | 5.21 | 92.8 | 5.5 | 655 | 30.1 |
| 77.0 BOB, 2.3 eth, 2.3 i-prop, 6.9 n-but, 11.5 i-pent | 765 | 40.3 | 433 | 5.23 | 92.5 | 5.5 | 655 | 30.1 |
| 77.0 BOB, 2.3 n-prop, 4.6 i-prop, 6.9 n-but, 2.3 n-pent, 6.9 i-pent | 765 | 40.3 | 434 | 5.24 | 92.5 | 5.5 | 655 | 30.0 |
| 77.0 BOB, 2.3 n-prop, 4.6 i-prop, 6.9 n-but, 9.2 i-pent | 765 | 40.3 | 433 | 5.24 | 92.9 | 5.5 | 655 | 30.0 |
| 77.0 BOB, 6.9 i-prop, 4.6 n-but, 2.3 i-but, 6.9 i-pent, 2.3 n-hex | 764 | 40.3 | 428 | 5.17 | 92.6 | 5.5 | 655 | 30.0 |
| 77.0 BOB, 2.3 eth, 4.6 i-prop, 2.3 n-but, 11.5 i-pent, 2.3 n-hex | 764 | 40.3 | 428 | 5.20 | 92.4 | 5.5 | 655 | 30.0 |



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7.6.1.2 EVEN BLENDS

**TABLE 7.23: TOP 8 LHV EVEN BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 86.0 BOB, 5.6 eth, 1.4 n-but, 7.0 i-but | 759 | 40.8 | 414 | 3.94 | 92.4 | 6.1 | 643 | 16.6 |
| 86.0 BOB, 5.6 eth, 8.4 i-but | 759 | 40.8 | 414 | 3.94 | 92.6 | 6.0 | 643 | 16.5 |
| 85.0 BOB, 4.5 eth, 1.5 n-but, 9.0 i-but | 760 | 40.8 | 415 | 4.02 | 92.5 | 5.9 | 644 | 18.2 |
| 85.0 BOB, 4.5 eth, 10.5 i-but | 760 | 40.8 | 415 | 4.02 | 92.6 | 5.9 | 644 | 18.2 |
| 83.0 BOB, 1.7 eth, 1.7 n-but, 13.6 i-but | 761 | 40.8 | 416 | 4.10 | 92.5 | 5.6 | 647 | 21.7 |
| 83.0 BOB, 1.7 eth, 15.3 i-but | 761 | 40.8 | 415 | 4.10 | 92.6 | 5.6 | 647 | 21.6 |
| 84.0 BOB, 3.2 eth, 1.6 n-but, 11.2 i-but | 760 | 40.8 | 416 | 4.07 | 92.5 | 5.7 | 646 | 19.9 |
| 84.0 BOB, 3.2 eth, 12.8 i-but | 760 | 40.8 | 415 | 4.07 | 92.6 | 5.7 | 646 | 19.9 |



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**TABLE 7.24: TOP 8 RON EVEN BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 85.0 BOB<br>13.5 eth<br>1.5 i-but | 758 | 40.1 | 436 | 5.22 | 93.8 | 6.8 | 644 | 15.5 |
| 83.0 BOB<br>10.2 eth<br>6.8 i-but | 760 | 40.2 | 435 | 5.23 | 93.8 | 6.3 | 647 | 19.1 |
| 84.0 BOB<br>11.2 eth<br>4.8 i-but | 759 | 40.2 | 434 | 5.13 | 93.7 | 6.5 | 646 | 17.5 |
| 85.0 BOB<br>13.5 eth<br>1.5 n-but | 758 | 40.1 | 437 | 5.22 | 93.7 | 6.8 | 644 | 15.5 |
| 85.0 BOB<br>12.0 eth<br>3.0 i-but | 759 | 40.2 | 433 | 5.02 | 93.6 | 6.6 | 644 | 15.9 |
| 83.0 BOB<br>10.2 eth<br>1.7 n-but<br>5.1 i-but | 760 | 40.2 | 436 | 5.23 | 93.6 | 6.3 | 647 | 19.1 |
| 84.0 BOB<br>11.2 eth<br>1.6 n-but<br>3.2 i-but | 759 | 40.2 | 435 | 5.14 | 93.6 | 6.5 | 646 | 17.5 |
| 82.0 BOB<br>7.2 eth<br>10.8 i-but | 761 | 40.3 | 432 | 5.05 | 93.6 | 6.0 | 648 | 21.3 |



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**TABLE 7.25: TOP 8 PD EVEN BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 79.0 BOB, 2.1 eth, 10.5 n-but, 8.4 i-but | 764 | 40.4 | 433 | 5.06 | 92.5 | 5.6 | 652 | 26.9 |
| 79.0 BOB, 2.1 eth, 8.4 n-but, 10.5 i-but | 763 | 40.4 | 432 | 5.06 | 92.7 | 5.6 | 652 | 26.9 |
| 79.0 BOB, 2.1 eth, 6.3 n-but, 12.6 i-but | 763 | 40.4 | 432 | 5.06 | 92.9 | 5.6 | 652 | 26.9 |
| 79.0 BOB, 2.1 eth, 4.2 n-but, 14.7 i-but | 763 | 40.4 | 431 | 5.05 | 93.1 | 5.5 | 652 | 26.8 |
| 79.0 BOB, 2.1 eth, 2.1 n-but, 16.8 i-but | 763 | 40.4 | 431 | 5.05 | 93.3 | 5.5 | 652 | 26.8 |
| 79.0 BOB, 4.2 eth, 6.3 n-but, 8.4 i-but, 2.1 n-hex | 763 | 40.3 | 432 | 5.21 | 92.4 | 5.7 | 652 | 26.5 |
| 79.0 BOB, 4.2 eth, 4.2 n-but, 10.5 i-but, 2.1 n-hex | 763 | 40.3 | 432 | 5.21 | 92.6 | 5.7 | 652 | 26.5 |
| 80.0 BOB, 2.0 eth, 8.0 n-but, 10.0 i-but | 763 | 40.5 | 428 | 4.82 | 92.5 | 5.6 | 651 | 25.6 |



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7.6.1.3 ETH+1 BLENDS

**TABLE 7.26: TOP 8 LHV ETH+1 BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 86.0 BOB<br>5.6 eth<br>8.4 i-but | 759 | 40.8 | 414 | 3.94 | 92.6 | 6.0 | 643 | 16.5 |
| 85.0 BOB<br>4.5 eth<br>10.5 i-but | 760 | 40.8 | 415 | 4.02 | 92.6 | 5.9 | 644 | 18.2 |
| 83.0 BOB<br>1.7 eth<br>15.3 i-but | 761 | 40.8 | 415 | 4.10 | 92.6 | 5.6 | 647 | 21.6 |
| 86.0 BOB<br>1.4 eth<br>12.6 n-prop | 760 | 40.8 | 418 | 4.05 | 92.4 | 6.1 | 643 | 16.6 |
| 84.0 BOB<br>3.2 eth<br>12.8 i-but | 760 | 40.8 | 415 | 4.07 | 92.6 | 5.7 | 646 | 19.9 |
| 86.0 BOB<br>1.4 eth<br>12.6 i-prop | 757 | 40.7 | 412 | 3.98 | 93.8 | 6.3 | 643 | 16.0 |
| 86.0 BOB<br>2.8 eth<br>11.2 n-prop | 759 | 40.7 | 420 | 4.16 | 92.6 | 6.2 | 643 | 16.3 |
| 86.0 BOB<br>7.0 eth<br>7.0 i-but | 759 | 40.7 | 417 | 4.12 | 92.8 | 6.2 | 643 | 16.1 |



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**TABLE 7.27: TOP 8 RON ETH+1 BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 82.0 BOB<br>1.8 eth<br>16.2 i-prop | 759 | 40.2 | 430 | 5.11 | 95.2 | 6.23 | 648 | 20.6 |
| 83.0 BOB<br>1.7 eth<br>15.3 i-prop | 758 | 40.3 | 425 | 4.83 | 94.8 | 6.24 | 647 | 19.4 |
| 83.0 BOB<br>3.4 eth<br>13.6 i-prop | 758 | 40.3 | 428 | 4.98 | 94.8 | 6.31 | 647 | 19.1 |
| 83.0 BOB<br>5.1 eth<br>11.9 i-prop | 759 | 40.2 | 431 | 5.12 | 94.8 | 6.38 | 647 | 18.9 |
| 84.0 BOB<br>1.6 eth<br>14.4 i-prop | 758 | 40.5 | 421 | 4.55 | 94.5 | 6.25 | 646 | 18.3 |
| 84.0 BOB<br>3.2 eth<br>12.8 i-prop | 758 | 40.4 | 424 | 4.69 | 94.5 | 6.32 | 646 | 18.0 |
| 84.0 BOB<br>4.8 eth<br>11.2 i-prop | 758 | 40.3 | 426 | 4.82 | 94.5 | 6.39 | 646 | 17.8 |
| 84.0 BOB<br>6.4 eth<br>9.6 i-prop | 758 | 40.3 | 429 | 4.96 | 94.4 | 6.46 | 646 | 17.5 |



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**TABLE 7.28: TOP 8 PD ETH+1 BLENDS OF E10/E15 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 79.0 BOB<br>6.3 eth<br>14.7 i-pent | 763 | 40.3 | 430 | 5.08 | 92.7 | 5.7 | 652 | 26.7 |
| 80.0 BOB<br>6.0 eth<br>14.0 i-pent | 763 | 40.4 | 426 | 4.84 | 92.5 | 5.7 | 651 | 25.4 |
| 80.0 BOB<br>4.0 eth<br>16.0 i-but | 762 | 40.3 | 431 | 5.07 | 93.5 | 5.6 | 651 | 24.9 |
| 80.0 BOB<br>8.0 eth<br>12.0 i-pent | 762 | 40.2 | 432 | 5.18 | 93.0 | 5.9 | 651 | 24.7 |
| 81.0 BOB<br>1.9 eth<br>17.1 i-but | 762 | 40.6 | 423 | 4.57 | 93.0 | 5.5 | 650 | 24.2 |
| 81.0 BOB<br>3.8 eth<br>15.2 i-but | 762 | 40.4 | 427 | 4.82 | 93.3 | 5.7 | 650 | 23.6 |
| 81.0 BOB<br>7.6 eth<br>11.4 i-pent | 762 | 40.4 | 428 | 4.92 | 92.8 | 5.9 | 650 | 23.4 |
| 81.0 BOB<br>5.7 eth<br>13.3 n-but | 762 | 40.3 | 435 | 5.10 | 92.4 | 6.0 | 650 | 23.3 |



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## 7.6.2 RFS2 Fuel Scenario

### 7.6.2.1 Suitable Blends

**TABLE 7.29: TOP 8 LHV SUITABLE BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 80.0 BOB, 6.0 i-prop, 2.0 n-but, 12.0 i-pent | 763 | 40.6 | 418 | 4.41 | 92.6 | 5.5 | 651 | 26.2 |
| 80.0 BOB, 2.0 n-prop, 4.0 i-prop, 2.0 n-but, 2.0 i-but, 10.0 i-pent | 763 | 40.6 | 420 | 4.49 | 92.5 | 5.5 | 651 | 26.2 |
| 80.0 BOB, 8.0 i-prop, 10.0 i-pent, 2.0 n-hex | 762 | 40.6 | 416 | 4.45 | 92.4 | 5.6 | 651 | 26.0 |
| 80.0 BOB, 6.0 i-prop, 2.0 n-but, 2.0 i-but, 2.0 n-pent, 8.0 i-pent | 763 | 40.6 | 420 | 4.48 | 92.5 | 5.5 | 651 | 26.1 |
| 80.0 BOB, 6.0 i-prop, 4.0 n-but, 10.0 i-pent | 763 | 40.6 | 419 | 4.48 | 92.6 | 5.6 | 651 | 26.1 |
| 80.0 BOB, 6.0 i-prop, 4.0 i-but, 2.0 n-pent, 8.0 i-pent | 762 | 40.6 | 419 | 4.48 | 92.6 | 5.5 | 651 | 26.1 |
| 80.0 BOB, 6.0 i-prop, 2.0 n-but, 2.0 i-but, 10.0 i-pent | 763 | 40.6 | 419 | 4.48 | 92.7 | 5.5 | 651 | 26.1 |
| 80.0 BOB, 6.0 i-prop, 4.0 i-but, 10.0 i-pent | 762 | 40.6 | 418 | 4.48 | 92.9 | 5.5 | 651 | 26.0 |



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**TABLE 7.30: TOP 8 RON SUITABLE BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 67.0 BOB<br>33.0 i-prop | 764 | 38.3 | 489 | 9.03 | 99.6 | 5.8 | 668 | 38.2 |
| 68.0 BOB<br>32.0 i-prop | 763 | 38.4 | 485 | 8.76 | 99.4 | 5.9 | 667 | 37.0 |
| 67.0 BOB<br>3.3 n-prop<br>29.7 i-prop | 764 | 38.3 | 490 | 9.05 | 99.3 | 5.8 | 668 | 38.4 |
| 66.0 BOB<br>30.6 i-prop<br>3.4 i-pent | 765 | 38.3 | 488 | 9.02 | 99.2 | 5.7 | 670 | 40.1 |
| 68.0 BOB<br>3.2 eth<br>28.8 i-prop | 763 | 38.3 | 490 | 9.03 | 99.2 | 6.0 | 667 | 36.5 |
| 67.0 BOB<br>29.7 i-prop<br>3.3 i-but | 764 | 38.4 | 487 | 8.87 | 99.2 | 5.8 | 668 | 38.7 |
| 66.0 BOB<br>3.4 n-prop<br>27.2 i-prop<br>3.4 i-but | 765 | 38.3 | 492 | 9.15 | 99.1 | 5.7 | 670 | 40.0 |
| 66.0 BOB<br>27.2 i-prop<br>6.8 i-but | 765 | 38.4 | 488 | 8.97 | 99.1 | 5.6 | 670 | 40.3 |



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**TABLE 7.31: TOP 8 PD SUITABLE BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 63.0 BOB, 11.1 eth, 14.8 n-but, 3.7 n-pent, 7.4 n-hex | 772 | 38.4 | 493 | 9.22 | 92.9 | 5.5 | 674 | 46.6 |
| 63.0 BOB, 11.1 eth, 14.8 n-but, 3.7 i-pent, 7.4 n-hex | 772 | 38.4 | 492 | 9.22 | 93.3 | 5.5 | 674 | 46.6 |
| 63.0 BOB, 7.4 eth, 29.6 n-but | 772 | 38.4 | 505 | 9.33 | 94.6 | 5.5 | 674 | 46.6 |
| 63.0 BOB, 3.7 eth, 7.4 i-prop, 25.9 n-but | 771 | 38.4 | 500 | 9.19 | 95.4 | 5.5 | 674 | 46.5 |
| 63.0 BOB, 11.1 eth, 3.7 n-prop, 11.1 n-but, 11.1 n-hex | 772 | 38.4 | 490 | 9.32 | 92.8 | 5.5 | 674 | 46.4 |
| 63.0 BOB, 11.1 eth, 18.5 n-but, 7.4 n-hex | 772 | 38.3 | 495 | 9.36 | 93.4 | 5.6 | 674 | 46.4 |
| 63.0 BOB, 7.4 eth, 7.4 i-prop, 14.8 n-but, 7.4 n-hex | 771 | 38.4 | 491 | 9.22 | 94.2 | 5.5 | 674 | 46.3 |
| 63.0 BOB, 11.1 eth, 14.8 n-but, 3.7 i-but, 7.4 n-hex | 772 | 38.3 | 494 | 9.35 | 93.6 | 5.5 | 674 | 46.3 |



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7.6.2.2 EVEN BLENDS

**TABLE 7.32: TOP 8 LHV EVEN BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 80.0 BOB, 2.0 eth, 8.0 n-but, 10.0 i-but | 763 | 40.5 | 428 | 4.82 | 92.5 | 5.6 | 651 | 25.6 |
| 80.0 BOB, 2.0 eth, 6.0 n-but, 12.0 i-but | 763 | 40.5 | 428 | 4.82 | 92.7 | 5.6 | 651 | 25.6 |
| 80.0 BOB, 2.0 eth, 4.0 n-but, 14.0 i-but | 763 | 40.5 | 427 | 4.82 | 92.9 | 5.6 | 651 | 25.5 |
| 80.0 BOB, 2.0 eth, 2.0 n-but, 16.0 i-but | 762 | 40.5 | 427 | 4.81 | 93.1 | 5.5 | 651 | 25.5 |
| 80.0 BOB, 4.0 eth, 4.0 n-but, 10.0 i-but, 2.0 n-hex | 763 | 40.4 | 428 | 4.96 | 92.4 | 5.7 | 651 | 25.2 |
| 79.0 BOB, 2.1 eth, 10.5 n-but, 8.4 i-but | 764 | 40.4 | 433 | 5.06 | 92.5 | 5.6 | 652 | 26.9 |
| 79.0 BOB, 2.1 eth, 8.4 n-but, 10.5 i-but | 763 | 40.4 | 432 | 5.06 | 92.7 | 5.6 | 652 | 26.9 |
| 79.0 BOB, 2.1 eth, 6.3 n-but, 12.6 i-but | 763 | 40.4 | 432 | 5.06 | 92.9 | 5.6 | 652 | 26.9 |



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**TABLE 7.33: TOP 8 RON EVEN BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 67.0 BOB<br>13.2 eth<br>19.8 i-but | 767 | 38.3 | 498 | 9.18 | 96.8 | 5.7 | 668 | 39.0 |
| 70.0 BOB<br>18.0 eth<br>12.0 i-but | 765 | 38.3 | 499 | 9.16 | 96.8 | 6.1 | 664 | 33.6 |
| 69.0 BOB<br>15.5 eth<br>15.5 i-but | 766 | 38.3 | 496 | 9.05 | 96.7 | 5.9 | 666 | 35.7 |
| 74.0 BOB<br>23.4 eth<br>2.6 i-but | 762 | 38.3 | 498 | 8.99 | 96.7 | 6.6 | 659 | 26.8 |
| 73.0 BOB<br>21.6 eth<br>5.4 i-but | 763 | 38.3 | 497 | 8.97 | 96.7 | 6.4 | 660 | 28.6 |
| 72.0 BOB<br>19.6 eth<br>8.4 i-but | 764 | 38.3 | 496 | 8.93 | 96.7 | 6.3 | 662 | 30.5 |
| 68.0 BOB<br>12.8 eth<br>19.2 i-but | 767 | 38.4 | 493 | 8.91 | 96.6 | 5.7 | 667 | 37.8 |
| 71.0 BOB<br>17.4 eth<br>11.6 i-but | 765 | 38.4 | 494 | 8.86 | 96.6 | 6.1 | 663 | 32.5 |



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**TABLE 7.34: TOP 8 PD EVEN BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [M4J/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 63.0 BOB, 7.4 eth, 29.6 n-but | 772 | 38.4 | 505 | 9.33 | 94.6 | 5.5 | 674 | 46.6 |
| 63.0 BOB, 11.1 eth, 18.5 n-but, 7.4 n-hex | 772 | 38.3 | 495 | 9.36 | 93.4 | 5.6 | 674 | 46.4 |
| 63.0 BOB, 11.1 eth, 14.8 n-but, 3.7 i-but, 7.4 n-hex | 772 | 38.3 | 494 | 9.35 | 93.6 | 5.5 | 674 | 46.3 |
| 63.0 BOB, 14.8 eth, 3.7 n-but, 3.7 i-but, 14.8 n-hex | 771 | 38.3 | 485 | 9.38 | 92.4 | 5.5 | 674 | 46.1 |
| 64.0 BOB, 7.2 eth, 28.8 n-but | 772 | 38.5 | 501 | 9.08 | 94.4 | 5.6 | 672 | 45.3 |
| 64.0 BOB, 10.8 eth, 18.0 n-but, 7.2 n-hex | 771 | 38.4 | 492 | 9.11 | 93.2 | 5.6 | 672 | 45.1 |
| 64.0 BOB, 10.8 eth, 14.4 n-but, 3.6 i-but, 7.2 n-hex | 771 | 38.4 | 491 | 9.10 | 93.5 | 5.5 | 672 | 45.0 |
| 64.0 BOB, 10.8 eth, 10.8 n-but, 7.2 i-but, 7.2 n-hex | 771 | 38.4 | 490 | 9.10 | 93.8 | 5.5 | 672 | 45.0 |



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7.6.2.3 ETH+1 BLENDS

**TABLE 7.35: TOP 8 LHV ETH+1 BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 80.0 BOB<br>6.0 eth<br>14.0 i-pent | 763 | 40.4 | 426 | 4.84 | 92.5 | 5.7 | 651 | 25.4 |
| 79.0 BOB<br>6.3 eth<br>14.7 i-pent | 763 | 40.3 | 430 | 5.08 | 92.7 | 5.7 | 652 | 26.7 |
| 79.0 BOB<br>4.2 eth<br>16.8 i-but | 763 | 40.2 | 435 | 5.32 | 93.7 | 5.6 | 652 | 26.1 |
| 78.0 BOB<br>6.6 eth<br>15.4 i-pent | 764 | 40.2 | 433 | 5.32 | 92.8 | 5.6 | 654 | 28.0 |
| 79.0 BOB<br>8.4 eth<br>12.6 i-pent | 763 | 40.1 | 436 | 5.44 | 93.1 | 5.8 | 652 | 25.9 |
| 78.0 BOB<br>4.4 eth<br>17.6 n-but | 763 | 40.1 | 443 | 5.60 | 92.4 | 5.8 | 654 | 27.7 |
| 77.0 BOB<br>6.9 eth<br>16.1 i-pent | 764 | 40.1 | 437 | 5.56 | 93.0 | 5.6 | 655 | 29.2 |
| 78.0 BOB<br>4.4 eth<br>17.6 i-but | 763 | 40.1 | 439 | 5.57 | 93.9 | 5.6 | 654 | 27.3 |



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**TABLE 7.36: TOP 8 RON ETH+1 BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 68.0 BOB<br>3.2 eth<br>28.8 i-prop | 763 | 38.3 | 490 | 9.03 | 99.2 | 5.95 | 667 | 36.5 |
| 69.0 BOB<br>3.1 eth<br>27.9 i-prop | 763 | 38.4 | 486 | 8.76 | 99.0 | 5.98 | 666 | 35.4 |
| 69.0 BOB<br>6.2 eth<br>24.8 i-prop | 763 | 38.3 | 491 | 9.02 | 98.9 | 6.06 | 666 | 34.9 |
| 70.0 BOB<br>3.0 eth<br>27.0 i-prop | 763 | 38.5 | 481 | 8.48 | 98.7 | 6.01 | 664 | 34.3 |
| 70.0 BOB<br>6.0 eth<br>24.0 i-prop | 763 | 38.4 | 487 | 8.73 | 98.6 | 6.09 | 664 | 33.8 |
| 70.0 BOB<br>9.0 eth<br>21.0 i-prop | 763 | 38.3 | 492 | 8.98 | 98.5 | 6.17 | 664 | 33.3 |
| 71.0 BOB<br>2.9 eth<br>26.1 i-prop | 762 | 38.7 | 477 | 8.20 | 98.4 | 6.03 | 663 | 33.1 |
| 71.0 BOB<br>5.8 eth<br>23.2 i-prop | 763 | 38.6 | 482 | 8.44 | 98.3 | 6.11 | 663 | 32.7 |



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**TABLE 7.37: TOP 8 PD ETH+1 BLENDS OF RFS2 FUEL SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 63.0 BOB<br>7.4 eth<br>29.6 n-but | 772 | 38.4 | 505 | 9.33 | 94.6 | 5.5 | 674 | 46.6 |
| 64.0 BOB<br>7.2 eth<br>28.8 n-but | 772 | 38.5 | 501 | 9.08 | 94.4 | 5.6 | 672 | 45.3 |
| 65.0 BOB<br>7.0 eth<br>28.0 n-but | 771 | 38.6 | 497 | 8.84 | 94.3 | 5.6 | 671 | 42.9 |
| 65.0 BOB<br>10.5 eth<br>24.5 n-but | 771 | 38.3 | 504 | 9.2.9 | 95.0 | 5.7 | 671 | 42.9 |
| 66.0 BOB<br>6.8 eth<br>27.2 n-but | 771 | 38.7 | 493 | 8.59 | 94.2 | 5.6 | 670 | 42.8 |
| 67.0 BOB<br>3.3 eth<br>29.7 n-but | 771 | 39.1 | 482 | 7.91 | 93.4 | 5.5 | 668 | 42.6 |
| 66.0 BOB<br>13.6 eth<br>20.4 n-pent | 770 | 38.6 | 494 | 8.74 | 92.8 | 5.5 | 670 | 42.2 |
| 66.0 BOB<br>13.6 eth<br>20.4 i-pent | 769 | 38.6 | 487 | 8.73 | 95.5 | 5.5 | 670 | 41.9 |



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### 7.6.3 E85 ALTERNATE SCENARIO

#### 7.6.3.1 SUITABLE BLENDS

**TABLE 7.38: TOP 8 LHV SUITABLE BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 40.0 BOB+, 18.0 i-prop, 18.0 i-but, 24.0 i-pent | 797 | 36.7 | 549 | 13.06 | 100.1 | 4.2 | 645 | 77.6 |
| 40.0 BOB+, 12.0 i-prop, 36.0 i-but, 12.0 i-pent | 797 | 36.6 | 553 | 13.19 | 100.2 | 4.2 | 645 | 77.5 |
| 39.0 BOB+, 6.1 i-prop, 48.8 i-but, 6.1 i-pent | 797 | 36.6 | 556 | 13.33 | 100.1 | 4.0 | 647 | 79.1 |
| 39.0 BOB+, 24.4 i-prop, 36.6 i-pent | 797 | 36.6 | 548 | 13.14 | 100.1 | 4.2 | 683 | 79.0 |
| 40.0 BOB+, 6.0 i-prop, 54.0 i-but | 797 | 36.6 | 557 | 13.32 | 100.4 | 4.1 | 645 | 77.3 |
| 40.0 BOB+, 24.0 i-prop, 6.0 i-but, 30.0 i-pent | 796 | 36.6 | 548 | 13.13 | 100.3 | 4.3 | 645 | 77.2 |
| 38.0 BOB+, 62.0 i-but | 798 | 36.6 | 560 | 13.46 | 100.0 | 3.9 | 648 | 80.8 |
| 40.0 BOB+, 18.0 i-prop, 6.0 n-but, 18.0 i-but, 18.0 i-pent | 797 | 36.6 | 554 | 13.27 | 100.0 | 4.3 | 645 | 77.2 |



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**TABLE 7.39: TOP 8 RON SUITABLE BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 10.0 BOB+ 90.0 i-prop | 786 | 31.0 | 716 | 23.96 | 111.0 | 3.0 | 243 | 104.2 |
| 11.0 BOB+ 89.0 i-prop | 787 | 31.1 | 712 | 23.66 | 110.8 | 3.1 | 242 | 103.0 |
| 12.0 BOB+ 88.0 i-prop | 787 | 31.3 | 708 | 23.39 | 110.7 | 3.2 | 241 | 101.9 |
| 13.0 BOB+ 87.0 i-prop | 787 | 31.4 | 704 | 23.12 | 110.5 | 3.3 | 239 | 100.7 |
| 10.0 BOB+ 9.0 eth 81.0 i-prop | 787 | 30.6 | 731 | 24.66 | 110.4 | 3.1 | 484 | 102.8 |
| 10.0 BOB+ 81.0 i-prop 9.0 i-but | 788 | 31.3 | 709 | 23.47 | 110.4 | 2.9 | 351 | 105.5 |
| 14.0 BOB+ 86.0 i-prop | 787 | 31.5 | 699 | 22.86 | 110.3 | 3.3 | 238 | 99.6 |
| 11.0 BOB+ 8.9 eth 80.1 i-prop | 787 | 30.8 | 726 | 24.38 | 110.3 | 3.2 | 483 | 101.6 |



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**TABLE 7.40: TOP 8 PD SUITABLE BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 10.0 BOB+, 9.0 i-prop, 9.0 i-but, 72.0 i-pent | 805 | 34.8 | 609 | 17.38 | 100.3 | 1.5 | 636 | 122.1 |
| 10.0 BOB+, 36.0 i-but, 54.0 i-pent | 805 | 34.7 | 616 | 17.58 | 100.5 | 1.5 | 675 | 121.9 |
| 10.0 BOB+, 9.0 i-prop, 9.0 n-but, 9.0 i-but, 63.0 i-pent | 805 | 34.6 | 618 | 17.70 | 100.2 | 1.6 | 636 | 121.5 |
| 10.0 BOB+, 9.0 i-prop, 36.0 i-but, 45.0 i-pent | 804 | 34.6 | 616 | 17.70 | 100.9 | 1.6 | 698 | 121.3 |
| 10.0 BOB+, 45.0 i-but, 9.0 n-pent, 36.0 i-pent | 805 | 34.6 | 624 | 17.89 | 100.4 | 1.6 | 420 | 121.3 |
| 10.0 BOB+, 9.0 n-prop, 9.0 i-prop, 72.0 i-pent | 804 | 34.6 | 622 | 17.89 | 101.1 | 1.5 | 636 | 121.0 |
| 10.0 BOB+, 9.0 n-prop, 27.0 i-but, 54.0 i-pent | 805 | 34.5 | 625 | 18.03 | 100.3 | 1.5 | 658 | 121.0 |
| 10.0 BOB+, 9.0 i-prop, 18.0 n-but, 9.0 i-but, 54.0 i-pent | 805 | 34.5 | 626 | 18.02 | 100.1 | 1.8 | 636 | 120.9 |



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7.6.3.2 EVEN BLENDS

**TABLE 7.41: TOP 8 LHV EVEN BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 38.0 BOB+ 62.0 i-but | 798 | 36.6 | 560 | 13.46 | 100.0 | 3.9 | 648 | 80.8 |
| 37.0 BOB+ 63.0 i-but | 798 | 36.5 | 563 | 13.68 | 100.2 | 3.9 | 649 | 82.1 |
| 36.0 BOB+ 64.0 i-but | 798 | 36.4 | 567 | 13.89 | 100.3 | 3.8 | 651 | 83.4 |
| 35.0 BOB+ 65.0 i-but | 798 | 36.3 | 571 | 14.03 | 100.3 | 3.8 | 652 | 84.7 |
| 39.0 BOB+ 6.1 eth 54.9 i-but | 797 | 36.8 | 571 | 14.03 | 100.3 | 4.2 | 647 | 77.7 |
| 34.0 BOB+ 6.6 n-but 59.4 i-but | 799 | 36.2 | 575 | 14.33 | 100.1 | 3.8 | 653 | 86.2 |
| 34.0 BOB+ 66.0 i-but | 798 | 36.2 | 573 | 14.32 | 100.6 | 3.7 | 653 | 86.0 |
| 38.0 BOB+ 6.2 eth 55.8 i-but | 797 | 36.1 | 574 | 14.26 | 100.4 | 4.1 | 648 | 78.9 |



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**TABLE 7.42: TOP 8 RON EVEN BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 11.0 BOB+ 62.3 eth 26.7 i-but | 793 | 29.4 | 794 | 27.35 | 105.8 | 3.4 | 343 | 97.1 |
| 12.0 BOB+ 61.6 eth 26.4 i-but | 793 | 29.5 | 789 | 27.05 | 105.7 | 3.5 | 342 | 96.0 |
| 10.0 BOB+ 54.0 eth 36.0 i-but | 794 | 29.9 | 778 | 26.48 | 105.7 | 3.1 | 345 | 100.9 |
| 13.0 BOB+ 60.9 eth 26.1 i-but | 793 | 29.7 | 784 | 26.74 | 105.6 | 3.6 | 341 | 94.9 |
| 15.0 BOB+ 68.0 eth 17.0 i-but | 791 | 29.4 | 794 | 27.24 | 105.6 | 4.0 | 338 | 90.2 |
| 11.0 BOB+ 53.4 eth 35.6 i-but | 794 | 30.0 | 773 | 26.19 | 105.6 | 3.2 | 343 | 99.8 |
| 14.0 BOB+ 60.2 eth 25.8 i-but | 793 | 29.9 | 779 | 26.43 | 105.5 | 3.7 | 339 | 93.8 |
| 16.0 BOB+ 67.2 eth 16.8 i-but | 791 | 29.5 | 789 | 26.92 | 105.5 | 4.0 | 337 | 89.1 |



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**TABLE 7.43: TOP 8 PD EVEN BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 10.0 BOB+<br>9.0 n-but<br>72.0 i-but<br>9.0 n-hex | 803 | 34.1 | 637 | 18.93 | 100.7 | 1.8 | 437 | 118.8 |
| 10.0 BOB+<br>81.0 i-but<br>9.0 n-hex | 802 | 34.1 | 635 | 18.93 | 101.3 | 1.7 | 437 | 118.7 |
| 10.0 BOB+<br>54.0 n-but<br>36.0 i-but | 805 | 33.8 | 665 | 19.48 | 100.1 | 2.2 | 636 | 118.4 |
| 10.0 BOB+<br>45.0 n-but<br>45.0 i-but | 804 | 33.8 | 663 | 19.48 | 100.7 | 2.1 | 400 | 118.2 |
| 10.0 BOB+<br>36.0 n-but<br>54.0 i-but | 804 | 33.8 | 661 | 19.47 | 101.3 | 2.1 | 400 | 118.2 |
| 10.0 BOB+<br>27.0 n-but<br>63.0 i-but | 803 | 33.8 | 659 | 19.47 | 102.0 | 2.0 | 400 | 117.8 |
| 10.0 BOB+<br>18.0 n-but<br>72.0 i-but | 802 | 33.8 | 657 | 19.47 | 100.6 | 1.9 | 400 | 117.7 |
| 11.0 BOB+<br>8.9 n-but<br>71.2 i-but<br>8.9 n-hex | 803 | 34.2 | 634 | 18.73 | 103.2 | 1.8 | 435 | 117.5 |



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7.6.3.3 ETH+1 BLENDS

**TABLE 7.44: TOP 8 LHV ETH+1 BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 39.0 BOB+ 6.1 eth 54.9 i-but | 797 | 36.3 | 571 | 14.03 | 100.3 | 4.2 | 647 | 77.7 |
| 38.0 BOB+ 6.2 eth 55.8 i-but | 797 | 36.1 | 574 | 14.26 | 100.4 | 4.1 | 648 | 78.9 |
| 37.0 BOB+ 6.3 eth 56.7 i-but | 797 | 36.0 | 578 | 14.49 | 100.6 | 4.1 | 649 | 80.2 |
| 36.0 BOB+ 6.4 eth 57.6 i-but | 797 | 35.9 | 581 | 14.72 | 100.7 | 4.0 | 651 | 81.5 |
| 35.0 BOB+ 6.5 eth 58.5 i-but | 797 | 35.8 | 585 | 14.94 | 100.9 | 3.9 | 652 | 84.0 |
| 34.0 BOB+ 6.6 eth 59.4 i-but | 797 | 35.7 | 588 | 15.17 | 101.0 | 3.9 | 653 | 84.0 |
| 38.0 BOB+ 12.4 eth 49.6 i-but | 796 | 35.7 | 588 | 15.06 | 100.8 | 4.3 | 648 | 77.0 |
| 33.0 BOB+ 6.7 eth 60.3 i-but | 797 | 35.6 | 592 | 15.40 | 101.2 | 3.8 | 655 | 85.3 |



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**TABLE 7.45: TOP 8 RON ETH+1 BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 10.0 BOB+ 9.0 eth 81.0 i-prop | 787 | 30.6 | 731 | 24.66 | 110.4 | 3.120 | 484 | 102.8 |
| 11.0 BOB+ 8.9 eth 80.1 i-prop | 787 | 30.8 | 726 | 24.38 | 110.3 | 3.18 | 483 | 101.6 |
| 12.0 BOB+ 8.8 eth 79.2 i-prop | 787 | 30.9 | 722 | 24.11 | 110.1 | 3.27 | 482 | 100.5 |
| 13.0 BOB+ 8.7 eth 78.3 i-prop | 787 | 31.1 | 718 | 23.88 | 110.0 | 3.35 | 480 | 99.3 |
| 10.0 BOB+ 18.0 eth 72.0 i-prop | 787 | 30.3 | 745 | 25.39 | 109.9 | 3.20 | 484 | 101.3 |
| 14.0 BOB+ 8.6 eth 77.4 i-prop | 787 | 31.2 | 714 | 23.56 | 109.8 | 3.43 | 479 | 98.2 |
| 11.0 BOB+ 17.8 eth 71.2 i-prop | 787 | 30.4 | 741 | 25.11 | 109.7 | 3.28 | 483 | 100.2 |
| 15.0 BOB+ 8.5 eth 76.5 i-prop | 787 | 31.3 | 709 | 23.28 | 109.7 | 3.52 | 478 | 97.1 |



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**TABLE 7.46: TOP 8 PD ETH+1 BLENDS OF E85 ALTERNATE SCENARIO**

| Composition [v%] | Density [kg/m³] | LHV [MJ/kg] | HoV [kJ/kg] | $O_2$ [wt%] | RON [-] | RVP [psi] | DI [°C] | Eth. equiv. [v%] |
|---|---|---|---|---|---|---|---|---|
| 10.0 BOB+<br>18.0 eth<br>72.0 i-pent | 804 | 33.8 | 644 | 19.25 | 100.6 | 1.8 | 630 | 117.9 |
| 11.0 BOB+<br>17.8 eth<br>71.2 i-pent | 804 | 33.9 | 641 | 19.04 | 100.5 | 1.9 | 628 | 116.6 |
| 12.0 BOB+<br>17.6 eth<br>70.4 i-pent | 804 | 34.0 | 638 | 18.83 | 100.4 | 2.0 | 627 | 115.3 |
| 10.0 BOB+<br>9.0 eth<br>81.0 i-but | 800 | 33.1 | 674 | 20.63 | 104.2 | 2.0 | 561 | 114.6 |
| 10.0 BOB+<br>27.0 eth<br>63.0 i-pent | 802 | 33.0 | 671 | 20.72 | 101.6 | 2.1 | 630 | 114.4 |
| 13.0 BOB+<br>17.4 eth<br>69.6 i-pent | 804 | 34.1 | 635 | 18.62 | 100.3 | 2.1 | 626 | 114.0 |
| 11.0 BOB+<br>8.9 eth<br>80.1 i-but | 800 | 33.2 | 670 | 20.40 | 104.1 | 2.1 | 559 | 113.3 |
| 10.0 BOB+<br>18.0 eth<br>72.0 n-but | 804 | 32.6 | 710 | 21.79 | 100.0 | 2.8 | 591 | 113.3 |



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