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# Estimation of the Fuel Efficiency Potential of Six Gasoline Blendstocks Identified by the U.S. Department of Energy's Co-Optimization of Fuels and Engines Program

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## Abstract

Six blendstocks identified by the Co-Optimization of Fuels & Engines Program were used to prepare fuel blends using a fixed blendstock for oxygenate blending and a target RON of 97. The blendstocks included ethanol, n-propanol, isopropanol, isobutanol, diisobutylene, and a bioreformate surrogate. The blends were analyzed and used to establish interaction factors for a non-linear molar blending model that was used to predict RON and MON of volumetric blends of the blendstocks up to 35 vol%. Projections of efficiency increase, volumetric fuel economy increase, and tailpipe $CO_2$ emissions decrease were produced using two different estimation techniques to evaluate the potential benefits of the blendstocks. Ethanol was projected to provide the greatest benefits in efficiency and tailpipe $CO_2$ emissions, but at intermediate levels of volumetric fuel economy increase over a smaller range of blends than other blendstocks. A bioreformate surrogate blendstock was projected to provide the greatest increase in volumetric fuel economy and the lowest increase in efficiency. Tailpipe $CO_2$ emissions for blends of the bioreformate surrogate were higher at all blend levels compared to the baseline E10 fuel.

## Introduction

Increasingly stringent fuel economy standards in the coming decade have resulted in renewed interest in increasing the anti-knock performance of fuels as a means of enabling higher compression ratio in spark-ignited engines. [1-9] The relationship between fuel anti-knock performance, engine compression ratio, and efficiency has been known for many years. [10-12] That is, increasing fuel anti-knock performance as measured by the research octane number (RON) and motor octane number (MON) allows increase of the engine compression ratio without an accompanying increase in the incidence of knock. Increasing compression ratio improves engine efficiency. [13,14]

More recently, the octane index (OI) concept has been introduced to describe the added benefit of octane sensitivity (OS) for knock prevention in modern engines under certain circumstances. [15-19] OS is the mathematical difference between RON and MON. Isooctane is defined as having RON and MON of 100, and thus an OS of 0. Fuels that exhibit higher levels of OS do so because they have less significant negative-temperature-coefficient kinetic behavior than isooctane. [20] MON test conditions cause a relatively high in-cylinder temperature at a given in-cylinder pressure. RON conditions at the same in-cylinder pressure result in lower in-cylinder temperature relative to MON conditions. Historically, these two sets of test conditions bracketed conditions encountered in typical engines. However, in many modern turbocharged engines, the in-cylinder temperature at a given in-cylinder pressure is often lower than those experienced in the RON test. This difference gives rise to the use of the term "beyond RON" to describe these conditions. Under MON conditions, OS greater than zero detracts from knock resistance, while at RON conditions OS has no impact on knock resistance. However, in "beyond RON" conditions, OS contributes additional knock resistance beyond what would be expected for a given value of RON. Since engines operate over a range of conditions, the OS benefit to knock resistance varies even for a given engine. Thus, the concept of OI was introduced. OI is RON minus the product of OS and the K-factor. The K-factor is a measure of the importance of OS to knock resistance at a given engine condition. At MON conditions K = 1, while at RON conditions K = 0. "Beyond RON" conditions have negative values of K. For negative K values, increasing OS causes OI to increase, reflecting greater knock resistance. This relationship is shown in equation 1.

*Equation 1*

$$OI = RON - K * S$$

Szybist et al. have subsequently explained that engine operation "beyond RON" means that the lower temperature and higher pressure (relative to RON conditions) in-cylinder pressure-temperature trajectory shifts from a region of where ignition delay is predominately dependent on pressure to a region of temperature dependence. [21-23] While the K factor does not convey the full complexity of differences in kinetic behavior, it remains a useful metric to rank the relative importance of differences in kinetic processes at a given engine operating condition.

The U.S. Department of Energy's Co-Optimization of Fuels & Engines Program (co-optima) has been investigating fuel blendstocks that can potentially be used to increase fuel anti-knock performance

while also potentially offering properties that enable further improvements to engine efficiency and greenhouse gas emissions. [24] The Co-optima fuel screening process focused on three tiers of evaluation. Tier 1 evaluations focused on whether a compound can be used as a fuel, and if so, whether it is likely to have fuel properties that are desirable for a spark-ignited engine. Other properties, including toxicity, peroxide-forming potential, and so on, were also evaluated in Tier 1. Tier 2 screening of a smaller list of candidate compounds focused on blending those compounds to establish metrics such as vapor pressure, blending octane, distillation temperatures, and other properties of fuel blends. [25] Tier 3 evaluations that are currently ongoing focus on engine studies with fuels blended using eight candidate blendstocks: ethanol, n-propanol, isopropanol, isobutanol, diisobutylene, aromatic mixtures, cyclopentanone, and furan mixtures. [26]

## Fuel Blends with Co-Optima Tier 3 Blendstocks

Gage Products of Ferndale, Michigan was contracted to manufacture gasoline blends using six co-optima Tier 3 blendstocks. These blendstocks included ethanol, n-propanol, isopropanol, isobutanol, diisobutylene, and a bioreformate surrogate. Diisobutylene is a blend of two isomers: 2,4,4 trimethyl-1-pentene and 2,4,4 trimethyl-2-pentene. The bioreformate surrogate was formulated from petroleum feedstocks to approximate the chemical makeup of anticipated bioreformate formulations. The compounds present in the bioreformate surrogate at greater than 0.5% by weight are shown in Figure 1. More than 95% of the blendstock (by weight) consisted of substituted mono-aromatics with carbon numbers between 7 and 11. Toluene was the most prevalent single compound in the bioreformate surrogate, with a weight fraction of 16.9%.

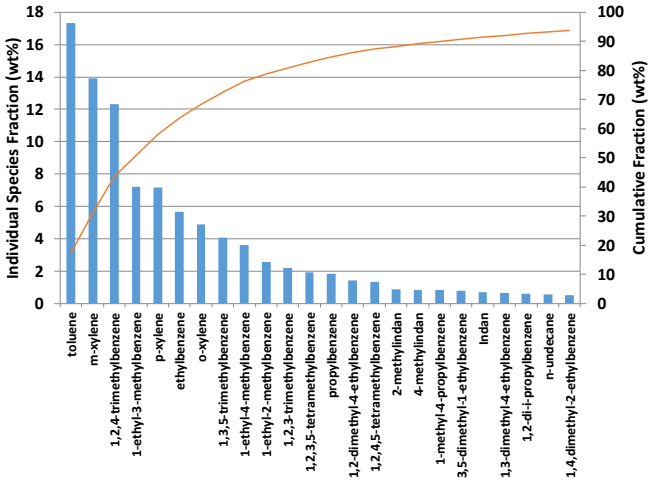


*Figure 1. Compounds present in the bioreformate surrogate blendstock at greater than 0.5 weight percent.*

The fuel blends were constrained to use the same hydrocarbon base and to have 97 RON. This blend strategy was used in recognition of the fact that new fuels successfully entering the marketplace will most likely be used in combination with a hydrocarbon base that is very similar to blendstocks for oxygenate blending (BOBs) already in wide use. Other blend properties (including the volumetric blending fraction of the tier 3 blendstock) varied to accommodate the fixed hydrocarbon base and finished RON constraints. The hydrocarbon base for the present study was also produced by Gage Products to approximate the properties of a retail regular-grade BOB. The hydrocarbon base will hereafter be referred to as a BOB as a convenience, though two of the fuel blends do not contain oxygenates. Figure 2 shows the prevalence of chemical families in the BOB as a function of their carbon number.

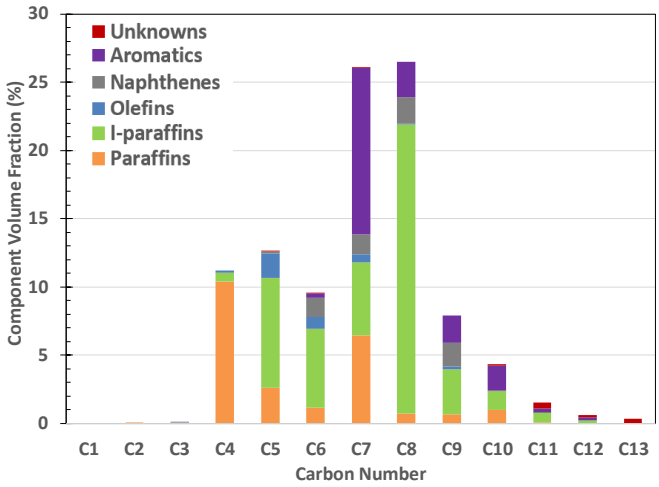


*Figure 2. Prevalence of chemical families in the BOB by carbon number.*

Measurements of RON and MON were conducted per applicable ASTM standards at two laboratories. [27,28] Figure 3 shows the average RON, MON, and octane sensitivity (OS) of the finished fuels and the BOB. The fuels achieved a RON slightly in excess of the target, but generally in good agreement with one another. The spread in average RON from maximum to minimum was less than 1 octane number (ON) and 1.1 ON for MON for the finished fuels. Although OS varied with blend fraction, when the fuels were constrained to a fixed RON and BOB, the OS values for the fuels were also quite similar. OS for the blends varied over a range of 2.55 ON. Isobutanol produced the lowest OS while diisobutylene produced the highest OS.

Figure 4 shows the volumetric blend fraction for the finished fuels. In each case, the blend fraction was determined by analysis of results from a detailed hydrocarbon analysis. [29] Achieving well-matched RON and sensitivity ratings with the differing blendstocks required greater variability in the required blend fraction. The ethanol-blended fuel required the lowest volume of blendstock at just over 21%. Blends with isopropanol and n-propanol required 27.5 and 27.7 volume percent, respectively. The other blendstocks required over 30 volume percent to achieve the RON target, with the bioreformate surrogate requiring the highest fraction (38.8%).

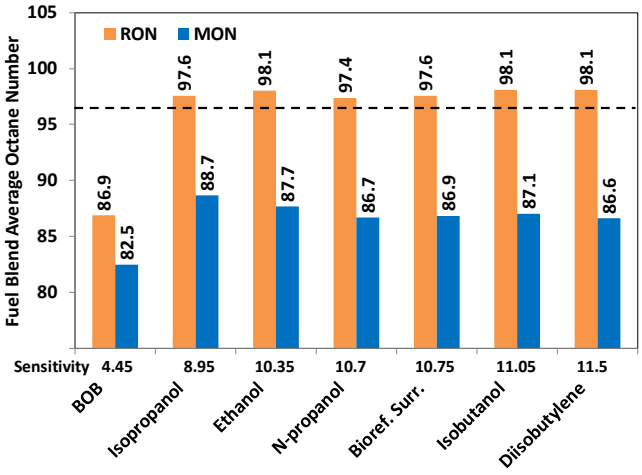


*Figure 3. RON, MON, and OS for the finished fuel blends. OS values are the horizontal values at the base of the bar chart. The dashed line shows the target RON value.*

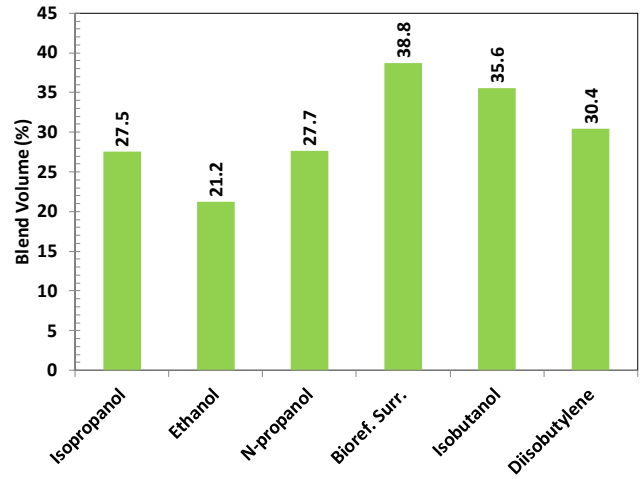


*Figure 4. Volumetric blending fractions for the finished fuels.*

Tables 1 and 2 show the distillation characteristics and driveability ratings for the BOB and finished fuels. The range of specifications from ASTM D4814 is also shown for each temperature. [30] The T90 and endpoint temperatures for all fuels fall within the specified ranges. The only T50 that was out of specification was for the bioreformate surrogate blend. The T10 temperatures for all fuels fell within specification for at least one vapor pressure class. ASTM D5188 measures the temperature at which the vapor to liquid volume ratio equals 20. Specification of this temperature within D4814 helps to protect against vapor lock in vehicle fuel systems. The temperature at which the vapor to liquid ratio equals 20 varied, but no fuels had a value less than the 35 °C minimum temperature required for protection class 6. Several fuels would meet the minimum temperature of 54 °C for the greater level of vapor lock protection offered by class 1. Reid vapor pressure (RVP) results indicate that the BOB was produced from wintertime refinery streams (consistent with the time of purchase of these fuels) as it has an RVP of 11.72 pounds per square inch. The ethanol blend had a slightly elevated RVP compared to the BOB of 11.74. The other fuel blends had lower RVPs. These results indicate that these fuel blends would meet the maximum RVP requirement of 15 pounds per square inch (PSI) during the winter months.

*Table 1. Distillation characteristics for the BOB and finished fuel blends.*

| | D86 Distillation Temperatures | | | |
|---|---|---|---|---|
| | T10 °C | T50 °C | T90 °C | Endpoint °C |
| BOB | 46 | 101 | 141 | 198 |
| Isopropanol | 54 | 78 | 131 | 190 |
| Ethanol | 49 | 72 | 133 | 191 |
| N-propanol | 55 | 88 | 129 | 192 |
| Bioref. Surr. | 64 | 124 | 168 | 197 |
| Isobutanol | 60 | 98 | 108 | 188 |
| Diisobutylene | 61 | 102 | 125 | 188 |
| Class C-E Specification | 50 - 60 MAX | 66 MIN - 116 MAX | 185 MAX | 225 MAX |
| Class AA-B Specification | 65 - 70 MAX | 66 MIN - 121 MAX | 190 MAX | 225 MAX |

Driveability index is a rating that is intended to control distillation parameters that can affect cold-start and warm-up driveability. This index is a function of the T10, T50, and T90 temperatures as well as the ethanol content of the fuel. [30] Ethanol content is included because it has a significantly different heat-of-vaporization (HOV) compared to non-oxygenated hydrocarbons. Numerically higher values of driveability index can indicate greater likelihood of cold-start and warmup issues, and thus maximum acceptable values of the index are specified for each vapor class. The other alcohols included in the current study have lower HOVs than ethanol. This fact suggests that their contribution to the driveability index should be smaller than that of ethanol at a fixed blend level. Since no specific term has been proposed for these alcohols, the index was calculated both with and without the ethanol term included to bracket the potential range of values of the index. The only fuel blend to exhibit a driveability index outside of specification limits was the bioreformate surrogate blend.

*Table 2. T(V/L=20), driveability index, and RVP for the BOB and finished fuel blends. The driveability index for the oxygenate blends was calculated both with and without the ethanol term to estimate the range of potential values.*

| | D5188 T(V/L=20) °C | Driveability Index* °C | D5191 RVP PSI |
|---|---|---|---|
| BOB | 49 | 514 | 11.72 |
| Isopropanol | 54 | 445 - 482 | 10.55 |
| Ethanol | 49 | 424 - 452 | 11.74 |
| N-propanol | 57 | 476 - 513 | 10.18 |
| Bioref. Surr. | 70 | 634 | 7.67 |
| Isobutanol | 61 | 491 - 538 | 9.36 |
| Diisobutylene | 64 | 522 | 8.71 |
| Class C-E Specification | 35 Min | 569 - 586 MAX | |
| Class AA-B Specification | 35 Min | 591- 597 MAX | |

Figure 5 shows the volumetric heating value for the BOB and finished fuel blends. These values were calculated from the measured density (by D4052) and gravimetric heating value (by D4809). The heating value is shown both for the total blend and for the BOB contribution to enable subsequent life-cycle analysis of these fuels. The blends that include oxygenates decline in heating value compared to the BOB, as expected, with the ethanol blend resulting in the lowest volumetric heating value of the oxygenated fuels. Interestingly, the N-propanol blend exhibits a marginally higher

volumetric heating value than the isobutanol blend, although the difference in heating value between these two blends is within the repeatability specification for the D4809 analysis. Figure 6 shows the $CO_2$ intensities for the BOB and finished fuels. These quantities are also shown as the total for the blend and the BOB contribution. $CO_2$ intensity is calculated from the carbon content of the fuel and the fuel density. They do not include any $CO_2$ associated with fuel production, making these values "tailpipe" $CO_2$ values rather than source-to-wheels values.

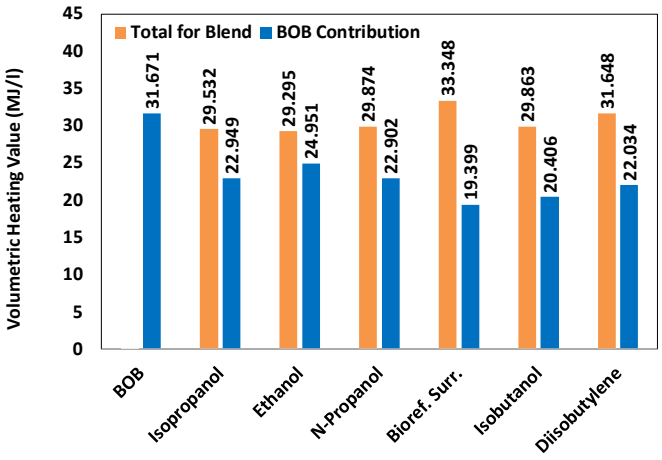


*Figure 5. Volumetric heating values for the BOB and finished fuel blends.*

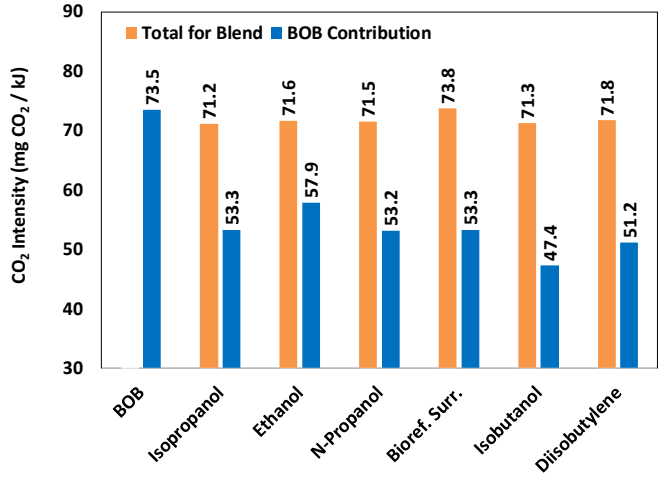


*Figure 6. $CO_2$ intensities for the BOB and finished fuels.*

## Modeling Varying Blend Levels

The blends manufactured by Gage Products allowed comparison of these blendstocks at one RON value. A model was constructed to estimate the RON improvement offered from each blendstock as a function of volumetric blending fraction to expand the comparison to multiple blending and RON levels. The non-linear molar blending model proposed by Anderson et al. for ethanol blending was adopted for this purpose. [31,32] Anderson et al. postulate that the molar blending model should be valid for other oxygenated compounds but noted that little data was available on the behavior of other compounds in blends. [32] Use of the molar blending model requires inputs of the molecular weight, density, RON, and MON of each blendstock and the BOB. RON, MON, density, and molecular weight for each of the blendstocks were taken from values included in the co-optimization of fuels and engines fuel property database and in a previous report by researchers at the National Renewable Energy Laboratory. [33,34] RON, MON, and density of the BOB were obtained by analyses conducted for the current project. Detailed hydrocarbon analysis (DHA) using the procedure in ASTM D6730 was conducted for each of the fuels and the BOB. The DHA results for the BOB provided the mass-fraction-weighted average molecular weight of the BOB (93.442 kg/kmol) for use in the molar blending model. The molecular weight of the BOB was lower than the range of values (98.6 – 103.8 kg/kmol) measured by Anderson et al. [31] The lower value for the BOB in the present study may result from the use of wintertime refinery streams that had higher volatility, as the BOB had a higher RVP than those used by Anderson et al. [31]

The RON and MON results for each fuel blend were used to establish values of the combined interaction factors for modeling each blendstock. Specifically, the values of the interaction factors were selected so that the blending model correctly predicted the measured RON and MON values for each of the fuel blends that were produced by Gage Products. Table 3 shows the interaction factor values that were calculated for each blendstock for the BOB used in this study. The interaction factors for ethanol in the present study were 0.56 for RON and 1.42 for MON. Anderson et al. report values of 0.45-0.48 for RON and 0.94-1.21 for MON. Although the isoparaffin (46.599 vol%) and paraffin (22.176 vol%) content of the BOB for the present study falls within the range reported by Anderson et al., it has lower aromatic content (19.401 vol%). This difference is one potential explanation for the increased values of the interaction factors for RON and MON. Another possible explanation is that the specific molecular makeup of the isoparaffins in the BOB for the present study was sufficiently different to result in a different combined interaction factor.

Figures 7 and 8 show the predicted RON and MON, respectively, for these blendstocks at different volumetric blending fractions with the BOB. Blending model results are shown by the lines, with the points indicating the values for the blends that were produced by Gage Products. Ethanol was the most effective of the study blendstocks at improving the RON rating of the blend, as it achieves a higher RON value at all blend levels up to 35 vol%. N-propanol and isopropanol were comparable RON boosters, as might be expected. Isobutanol was the least effective octane booster of the alcohols in the study. Overall, the bioreformate surrogate was the least effective RON improver in this study. The greatest MON increases at up to 35 vol% also occurred with ethanol blending. At blend levels over 15%, the MON increases from isopropanol diverged from n-propanol, and nearly reached the value attained by ethanol. N-propanol and isobutanol had similar MON increase trends with blending fraction. The smallest predicted increases in MON occurred with bioreformate blending. All of RON and MON trends are in agreement with the single-point values for each blendstock attained through physical blending of fuels as outlined previously.

*Table 3. Interaction factors for non-linear molar blending modeling of the blendstocks.*

| | Interaction Factor | |
|---|---|---|
| | RON | MON |
| Ethanol | 0.563514 | 1.415285 |
| N-propanol | 0.937929 | 1.274536 |
| Isopropanol | 0.71926 | 0.122896 |
| Isobutanol | 0.772484 | 0.852959 |
| Diisobutylene | 1.633374 | 3.36289 |
| Bioref. Surr. | 0.482016 | -0.31676 |

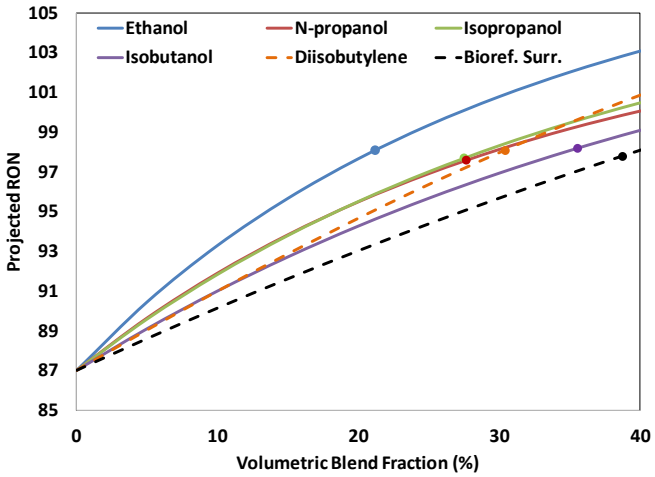


*Figure 7. Projected RON values for the blendstocks at a range of volumetric blending fractions.*

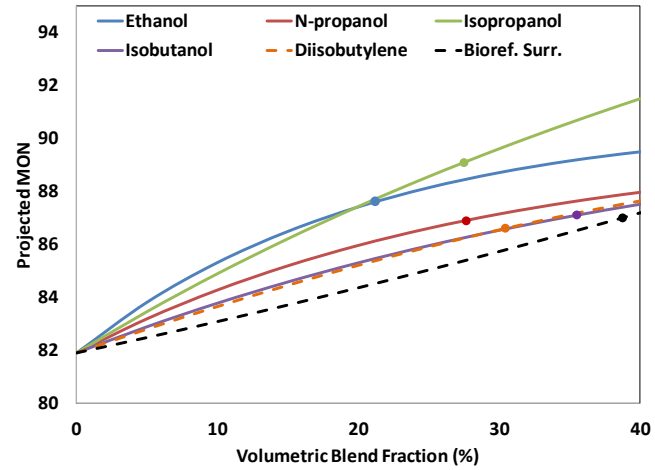


*Figure 8. Projected MON values for the blendstocks at a range of volumetric blending fractions.*

## Estimating Potential Efficiency, Fuel Economy, and Tailpipe $CO_2$ Improvements

Two models were used to estimate potential efficiency improvements that may be gained through increasing octane ratings using these blendstocks. The model developed collaboratively by researchers at Ford Motor Company, General Motors, and Fiat Chrysler Automobiles (henceforth referred to as the Leone et al. model) for estimating vehicle efficiency, fuel economy, and tailpipe $CO_2$ emissions impacts associated with increasing fuel octane rating was used for the present study. [35] The DOE co-optimization of fuel and engines program also developed a merit function to describe the anticipated efficiency benefit of new fuels. The merit function was initially influenced by the work of Leone et al. but was further developed to support the needs of the co-optimization program. [36]

### *Projections Using the Leone et al. Model*

The model proposed by Leone et al. projects fuel efficiency improvement based upon CR increase that is enabled through RON increase. There are also additional terms in the model. The first of these terms captures additional, non-octane related benefits of ethanol blending. The second captures efficiency improvements from engine downsizing. This term is needed because maximum output torque increases as CR increases, potentially leading to comparisons between engines of unequal performance. Retaining a fixed maximum output torque by marginally downsizing the engine resolves this issue and can result in further efficiency improvement. [35] Equations 2 and 3 show the calculations for efficiency increase from CR and the total efficiency increase for the Leone et al. model. The recommendations of Leone et al. to use a requirement of 3 RON numbers increase beyond 91 RON per unit of CR increase beyond 10.0 and a downsizing factor of 1.1 were used for the present study to estimate the CR enabled by increasing octane rating of the fuel for turbocharged engines. RON values from the fuel blending model discussed previously were used to support this analysis. Figure 9 shows the CR enabled by increasing RON through blending of ethanol and bioreformate surrogate. The other blendstocks were omitted from this graph to enhance its legibility. Ethanol blends are projected to enable greater CR values at blends of up to 35% than all other blendstocks in this study. For example, at 15 vol% blends, ethanol is projected to enable a CR of 11.6 compared 10.2 for the bioreformate surrogate. Other blendstocks in the study enabled CRs that fell between those of ethanol and the bioreformate surrogate blends.

*Equation 2*

$$\Delta\eta_{CR} = -0.207\% \; x \; (CR_{new}^2 - CR_{base)}^2 + 6.44\% \; x \; (CR_{new} - CR_{base})$$

*Equation 3*

$$\Delta\eta_{total} = 100\% \; x \left( \left( 1 + \frac{F_{downsize} \; x \; \Delta\eta_{CR}}{100\%} \right) \left( 1 + \frac{\Delta\eta_{ethanol}}{100\%} \right) - 1 \right)$$

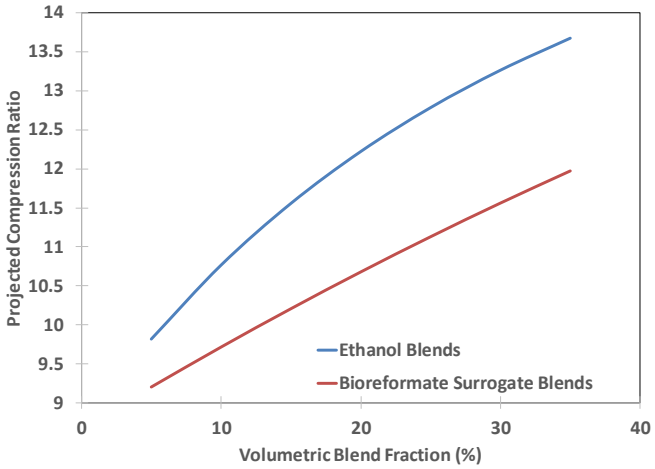


*Figure 9. Projected CRs for ethanol and bioreformate surrogate blending.*

The Leone et al. model recommends that projected engine efficiency be increased by 0.5% for each 10 vol% ethanol blending beyond the baseline value of 10 vol%. This recommendation is based on a study executed by Jung et al. that investigated benefits of ethanol blending in part-load conditions where knock did not limit engine efficiency. [37] Jung et al. identified several effects that derived from the relatively high heat of vaporization of ethanol. For the current study, the 0.5% improvement per 10 vol% ethanol blending was adjusted for the other alcohols by multiplying the 0.5% improvement for ethanol and the ratio of the heat-of-vaporization (HOV) of a stoichiometric mixture of each alcohol compared with that of ethanol. This scaling process results in efficiency gains of 0.28% for n-butanol, 0.27% for isopropanol, and 0.18% for isobutanol at 10 vol% blend levels. The two non-oxygenated blendstocks were assumed to have similar HOV to the BOB, such that no additional improvement associated with HOV occurred.

Figure 10 shows the projected efficiency improvements offered by blends using the co-optima blendstocks. The curve for ethanol blends crosses zero at a blend level of about 6% and shows a potential efficiency benefit of about 1% at a 10 vol% blend. This occurrence is a result of the fact that blends with 10% ethanol in the fuel marketplace often have a RON of greater than 91, since the refiners must meet a minimum anti-knock index (AKI) of 87, but at a maximum of 10 vol% ethanol. Thus, 91 RON often occurs at an ethanol level slightly lower than 10 vol% to assure regulatory compliance. In this case, the RON value projected for a 10 vol% ethanol blend in the BOB was 93.3. The projected AKI for the blend was 89.3, indicating that this blend would be a mid-grade fuel instead of a regular-grade fuel. Thus, it is logical that this blend should provide a small improvement in efficiency compared to the baseline case. At blend fractions greater than 15 vol%, all the blendstocks are projected to provide an efficiency benefit. The trends show that ethanol provides the greatest projected efficiency improvement and the bioreformate surrogate the lowest improvement at blend levels less than 35 vol%.

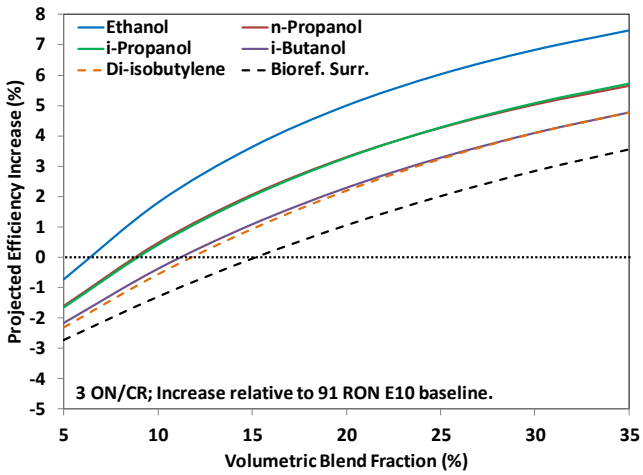


*Figure 10. Projected efficiency increases for the blendstocks using the Leone et al. model.*

Next, the projected efficiency improvements were used in combination with the volumetric heating values of the fuel blends to project potential impacts to vehicle fuel economy. The measured volumetric heating values for the blends that were physically produced were used to establish the changes in heating value as a function of blend level for each blendstock. This was accomplished by assuming the impact of the blendstock on the finished fuel heating value was linear and scaling based on the measured values. These heating values were then used to calculate the effect of projected efficiency increases for each blendstock on volumetric fuel economy using equations provided in Leone et al. [35] Projected fuel economy impacts are shown in Figure 11. Although the bioreformate surrogate was projected to produce the lowest efficiency improvements, it is projected to provide the greatest volumetric fuel economy improvements. This difference is due to the relative changes that the blendstocks impose on the volumetric heating value of the finished fuels. Ethanol blending is projected to offer a volumetric fuel economy increase at blend levels from 5 vol% to just over 25 vol%. The remaining blendstocks are projected to offer a volumetric fuel economy benefit at blend levels from 5% vol% to over 35 vol%. N-propanol has the highest potential volumetric fuel economy benefit of the alcohols for blend levels up to 25 vol%, at which point isobutanol provides a greater benefit.

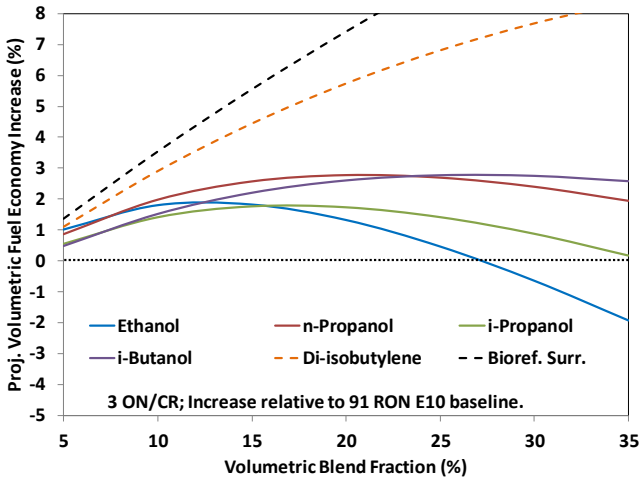


*Figure 11. Projected volumetric fuel economy impacts for the blendstocks at up to 35 vol% levels using the Leone et al. model.*

Tailpipe (or tank-to-wheels) $CO_2$ emissions projections for the fuels were calculated using measured values for the fuel blends, scaled linearly to establish energy-based tailpipe $CO_2$ intensities for a range of volumetric blends. As with the fuel economy projections, equations provided by Leone et al. were used to project tailpipe $CO_2$ emissions impacts for volumetric blends of the blendstocks. These results are shown in Figure 12. The trends in $CO_2$ emissions decreases are consistent with the projected efficiency increases for each blendstock, with the exception of the bioreformate surrogate. Even though the bioreformate surrogate offered efficiency increases at blend levels over 15 vol%, the projected tailpipe $CO_2$ emissions increase relative to the E10 baseline at all blend levels. This outcome is a result of the increases in $CO_2$ intensity for blends with the bioreformate surrogate. As was observed with projected efficiency increase values, the greatest improvement in tailpipe $CO_2$ emissions is provided with ethanol blending.

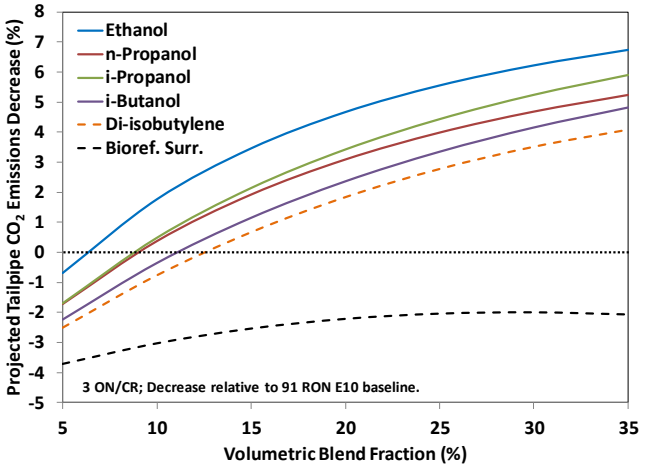


*Figure 12. Projected tailpipe $CO_2$ emissions decreases for the blendstocks at up to 35 vol% levels using the Leone et al. model.*

## *Projections Using the Co-Optima Merit Function*

The co-optima merit function was developed to provide estimates of the potential engine efficiency impacts of blendstocks under investigation by the co-optima program. Although the merit function was influenced by the Leone et al. model, it differs in several ways. The first difference is in the use of the octane index (OI) rather than RON as the enabler for higher CR. The merit function incorporates OS in addition to RON by adding an OS term with a recommended K factor of -1.25. [36] HOV is included in a different manner in the merit function but has a magnitude of impact that is comparable to that proposed by Leone et al. [35] The merit function downsizing term is the more aggressive 1.2 value reported by Leone et al, rather than the 1.1 value that is recommended. There are also added terms in the merit function to include the effects of laminar flame speed, particulate formation propensity, and catalyst light-off effects. [36] For the current study, these additional terms are neglected because their impacts are small relative to those of OI and HOV and to provide a straightforward comparison with the predictions of the Leone et al. model. The merit function as used for computations in the current study is shown in Equation 4.

*Equation 4*

$$Merit = \frac{(RON_{mix} - 91)}{1.6} - K\frac{(S_{mix} - 8)}{1.6} + \frac{0.085 * \left(\frac{HOV_{mix}}{AFR_{mix}+1} - \frac{415}{14.0+1}\right)}{1.6} + \frac{\frac{HOV_{mix}}{AFR_{mix}+1} - \frac{415}{14.0+1}}{15.2}$$

Figure 13 shows the efficiency improvements projected by the merit function. The merit function predicts ethanol blending to provide a 1.4% benefit at 10 vol%, which is comparable to the 1.8% projected by the Leone et al. model and discussed previously. The merit function projects higher efficiency gains for the blendstocks compared to the Leone et al. model as volume fractions increase. Differences between the two models are blendstock specific and range from a maximum of 4.5% for 35 vol% ethanol to minimum of 1.5% for 35 vol% bioreformate surrogate. Ethanol remains the blendstock with the highest projected efficiency benefit at all blend levels and the bioreformate surrogate remains the blendstock with lowest projected efficiency improvements. The merit function projects marginally higher efficiency gains for n-propanol compared to isopropanol and improved efficiency gains for diisobutylene compared with isobutanol. The Leone et al. model projected that the two propanol isomers would yield similar efficiency gains and that diisobutylene and isobutanol would also yield similar efficiency gains.

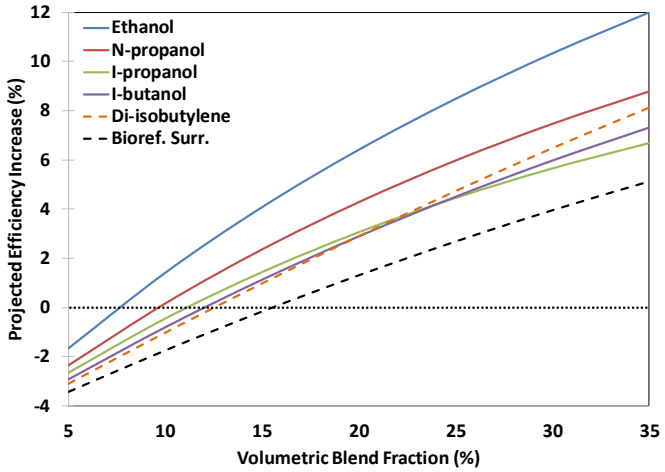


*Figure 13. Efficiency improvements projected by the merit function for the blendstocks at up to 35 vol% levels.*

The efficiency improvement projections provided by the merit function and values for volumetric heating value and energy-based $CO_2$ intensity were also used to calculate volumetric fuel economy and tailpipe $CO_2$ emissions impacts by using the equations provided by Leone et al. These results are shown in Figures 14 and 15, respectively. The efficiency increases projected by the merit function are sufficiently high that all blendstocks, including ethanol, are projected to provide volumetric fuel economy benefits at blend fractions of 35% and greater. The merit function projections indicate that the bioreformate surrogate provides the greatest potential volumetric fuel economy improvements all blend levels. N-propanol provides the greatest potential fuel economy benefits of the alcohols studied. Ethanol blending provides the greatest tailpipe $CO_2$ reductions, with the bioreformate surrogate blends projected to cause

tailpipe $CO_2$ increases at all blend levels. The other blendstocks provide potential tailpipe $CO_2$ reductions at blend levels above 10-12 vol%.

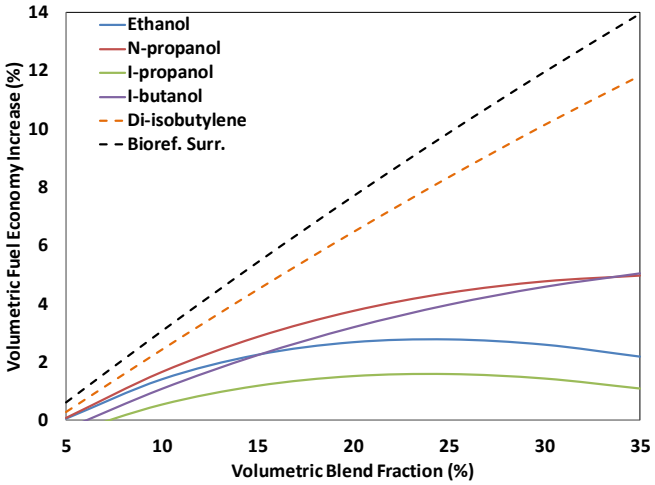


*Figure 14. Merit function projections of volumetric fuel economy improvements for the blendstocks at up to 35 vol%.*

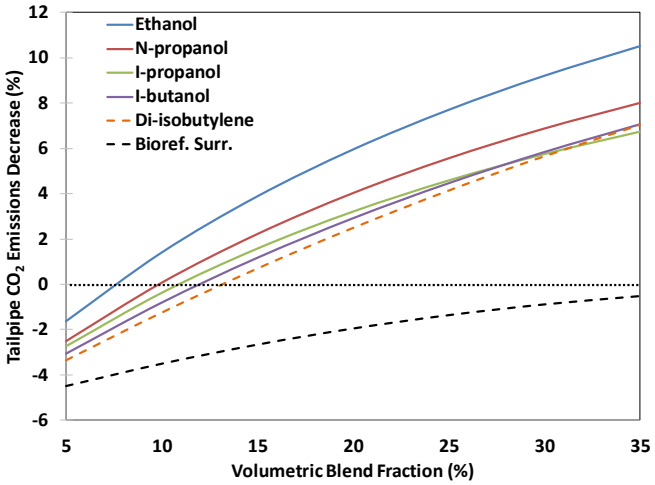


*Figure 15. Merit function projections of tailpipe $CO_2$ decreases for the blendstocks at up to 35 vol%.*

## Comparing Results for the Blendstocks

Energy consumption and $CO_2$ emissions associated with production of these blends are outside the scope of the current study. Nevertheless, these upstream impacts are an important part of a complete assessment of the potential benefits or disbenefits of these fuels. The comparisons among the blendstocks in this study are based on their impacts on vehicle operation.

Both modeling approaches project that ethanol blending provides the greatest potential improvements in efficiency and tailpipe $CO_2$ emissions at a given volumetric blend level. Increasing ethanol blend fraction above 10 vol% can also provide improved volumetric fuel economy, though other blendstocks can provide greater volumetric fuel economy benefits, and over a wider range of blending fractions. The two models differ in their prediction of volumetric fuel economy impacts of ethanol at levels greater than 25 vol%, with the Leone et al. model projecting volumetric fuel economy decreases above that level.

N-propanol and isopropanol exhibited the second highest potential for efficiency improvement at a given volumetric blend level. The Leone et al. model projects them to be essentially equivalent in this regard, while the co-optima merit function projects n-propanol to exhibit a greater efficiency improvement than isopropanol at blend levels up to 35 vol%. The gains in efficiency for n-propanol are approximately 2/3 of the gains projected for ethanol at the same blend fraction. Both models agree that n-propanol exhibits the highest volumetric fuel economy increase of the alcohols in the study up to at least 20 vol%. The tailpipe $CO_2$ improvements offered by both propanol isomers are similar, with Leone et al. model projecting more improvement for isopropanol at blend levels greater than 10 vol%. The merit function projects greater CO2 emissions improvements for n-propanol compared with isopropanol at all blend levels. The $CO_2$ improvements for n-propanol were approximately 2/3 of those offered by ethanol at the same blend level.

Isobutanol blends exhibited about 60% of the projected efficiency and tailpipe $CO_2$ benefits of ethanol blending and marginally less volumetric fuel economy benefit compared to n-propanol at up to 25 vol%. At higher blend levels isobutanol had marginally higher potential volumetric fuel economy gains compared with n-propanol. The Leone et al. model projects this crossing point at about 25 vol%, with the co-optima merit function projecting it at about 35 vol%. Based on these results, it is difficult to postulate a fuel efficiency or greenhouse gas argument in favor of pursuing isobutanol blending based on these results. However, isobutanol blends may exhibit other potential advantages outside the scope of this study.

The Leone et al. model projects the efficiency improvement offered by diisobutylene as comparable to that of isobutanol at all blend levels, while the co-optima merit function projects a gradual improvement that brings the benefit to nearly the same level as for n-propanol at high blend levels. Both models project diisobutylene to provide the second highest potential benefits in terms of volumetric fuel economy. Fuel economy benefits are substantially higher than those offered by n-propanol but are not as high as those offered by the bioreformate surrogate. Tailpipe $CO_2$ emissions impacts from diisobutylene blending are projected to be lower than the alcohols for blend levels less than 30 vol%, but to be similar to benefits offered by isobutanol above 30 vol%. As with isobutanol, is it difficult to postulate a fuel efficiency or greenhouse gas argument for pursuing diisobutylene blending based on these results. Additionally, high olefin content in gasoline is frequently associated with gum formation and ground level ozone formation, presenting another challenge for this blendstock. [38,39]

The bioreformate surrogate was projected to have the lowest energy efficiency benefits and the highest volumetric fuel economy benefits of the blendstocks. However, this blendstock is projected to increase tailpipe $CO_2$ emissions at all blend levels. Both models agree on these projected outcomes.

Comparison of the benefits of the blendstocks at a fixed RON level is also informative. Table 4 shows the projected impacts to energy efficiency, volumetric fuel economy, and tailpipe $CO_2$ emissions for the blendstocks at RON levels of 95, 97, and 100. At 95 RON, there is relatively little differentiation in the potential efficiency gains offered by the blendstocks, with the projected improvements ranging from 2.4% to 3.1%. Blendstock effects become more important as RON level increases. This increased blendstock importance is largely because of HOV effects that become more pronounced at higher blend levels. The Leone et al. model is more conservative than the merit function, but both models project significant

*Table 4. Projected engine efficiency, volumetric fuel economy, and tailpipe $CO_2$ benefits of the blendstocks at three RON levels.*

| | Ethanol | n-Propanol | Isopropanol | Isobutanol | Diisobutylene | Bioref. Surr. |
|---|---|---|---|---|---|---|
| **Projected Engine Efficiency Increase (%)** | | | | | | |
| **95 RON** | | | | | | |
| Leone et al. | 3.1 | 2.9 | 2.9 | 2.8 | 2.4 | 2.4 |
| Co-optima Merit | 3.3 | 3.7 | 2.6 | 3.7 | 3.3 | 3.3 |
| **97 RON** | | | | | | |
| Leone et al. | 4.6 | 4.3 | 4.3 | 4.1 | 3.6 | 3.6 |
| Co-optima Merit | 5.6 | 6.1 | 4.4 | 6.0 | 5.4 | 5.2 |
| **100 RON** | | | | | | |
| Leone et al. | 6.4 | 6.1 | 6.0 | 5.8 | 5.0 | 5.0 |
| Co-optima Merit | 9.3 | 9.9 | 7.1 | 9.6 | 8.7 | 7.8 |
| **Projected Volumetric Fuel Economy Increase (%)** | | | | | | |
| **95 RON** | | | | | | |
| Leone et al. | 1.9 | 2.7 | 1.8 | 2.7 | 6.0 | 9.9 |
| Co-optima Merit | 2.1 | 3.5 | 1.4 | 3.6 | 6.8 | 10.9 |
| **97 RON** | | | | | | |
| Leone et al. | 1.5 | 2.7 | 1.4 | 2.7 | 7.2 | 12.4 |
| Co-optima Merit | 2.6 | 4.4 | 1.6 | 4.6 | 9.1 | 14.1 |
| **100 RON** | | | | | | |
| Leone et al. | 0.0 | 1.4 | -0.2 | 1.9 | 8.6 | 15.8 |
| Co-optima Merit | 2.7 | 5.0 | 0.8 | 5.6 | 12.4 | 19.0 |
| **Projected Tailpipe $CO_2$ Emissions Decrease (%)** | | | | | | |
| **95 RON** | | | | | | |
| Leone et al. | 3.0 | 2.8 | 3.1 | 2.9 | 2.0 | -2.0 |
| Co-optima Merit | 3.2 | 3.5 | 2.7 | 3.7 | 2.8 | -1.1 |
| **97 RON** | | | | | | |
| Leone et al. | 4.3 | 4.0 | 4.4 | 4.2 | 3.1 | -2.1 |
| Co-optima Merit | 5.3 | 5.6 | 4.6 | 5.9 | 4.8 | -0.5 |
| **100 RON** | | | | | | |
| Leone et al. | 5.9 | 5.7 | 6.2 | 5.8 | 4.2 | -2.8 |
| Co-optima Merit | 8.4 | 8.9 | 7.2 | 9.1 | 7.5 | 0.0 |

improvements at all RON levels compared to the baseline case of 91 RON. Differences in projection between the two models are less than 1% at 95 RON but increase to 3-5% at 100 RON.

All of the blendstocks were projected to improve volumetric fuel economy at RON levels 95 and 97. All blendstocks with the exception of isopropanol were also projected to provide improvements at 100 RON. The alcohols provided smaller improvements than diisobutylene and the bioreformate surrogate. This effect is due largely to their reduced heating value compared to the baseline. The differences among the alcohols were small relative to the difference between the alcohols and the non-oxygenated blendstocks. Differences in projection between the two models were again less than 1% at 95 RON and increased with RON level.

All of the blendstocks except the bioreformate surrogate were projected to provide reductions in tailpipe $CO_2$ emissions. The trends in tailpipe $CO_2$ emissions reduction generally followed those observed for efficiency improvement. The bioreformate surrogate was projected to exhibit increased tailpipe $CO_2$ emissions, with the Leone et al. model projected greater levels of increase compared to the Co-optima merit function. Increases projected by both models ranged from 0 – 2.8% depending on RON level.

## Conclusions

- Blends of 6 blendstocks identified by the co-optimization of fuels and engines program were produced using a fixed BOB and a 97 RON target for the finished blends. Volumetric blend fractions varied from 21 vol% (ethanol) to 38.8 vol% (bioreformate surrogate). When blended to the

same RON, there was only minor variation in the OS of the blend.

- Measured properties of the blends indicated that only one of the fuels, the bioreformate surrogate blend, would have fallen outside of ASTM distillation specifications for a wintertime fuel blend.
- A nonlinear ethanol molar blending model was adopted and expanded to include the 5 additional blendstocks by using measured RON and MON of the BOB and blends with each blendstock to establish values for interaction factors for each blendstock. The model enabled RON and MON estimation for a range of volumetric blend fractions for each blendstock.
- The two models provided different magnitudes but similar trends in projections of the efficiency and fuel economy increases as well as tailpipe $CO_2$ emissions decreases for the six blendstocks at a range of volumetric blend fractions.
- Ethanol blending provided the largest potential benefits in terms of fuel efficiency increase and tailpipe $CO_2$ decrease, but did not provide the greatest magnitude of volumetric fuel economy benefit or the largest range of volumetric blending fractions at which a volumetric fuel economy benefit was obtained.
- Blending using a bioreformate surrogate provided the largest projected volumetric fuel economy increases, but the smallest projected efficiency improvements. Tailpipe $CO_2$ emissions for this blendstock were projected to increase relative to the E10 baseline fuel.
- N-propanol blending was projected to offer about 2/3 of the efficiency and tailpipe $CO_2$ benefits projected for ethanol at the same blend level but provided greater volumetric fuel economy benefit over a wider range of volumetric blend fractions.
- Comparing the blendstocks at fixed RON levels (rather than by volumetric blend fractions) demonstrated that the differences among the blendstocks were small at 95 RON but increased with RON.
- In general, the Leone et al. model provides more conservative projections of potential improvements than the co-optima merit function.

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## Disclaimer

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## Definitions/Abbreviations

| | |
|---|---|
| **AKI** | Anti-knock index |
| **ASTM** | ASTM International |
| **BOB** | Blendstock for oxygenate blending |
| **Co-optima** | Co-optimization of fuels and engines program |
| **CR** | Compression ratio |
| **DHA** | Detailed hydrocarbon analysis |
| **DISI** | Direct injection spark ignition |
| **DOE** | U.S. Department of Energy |
| **E10** | Blend containing 10 volume% ethanol |
| **HOV** | Heat of vaporization |
| **OI** | Octane index |
| **OS** | Octane sensitivity |
| **PSI** | Pounds per square inch |
| **RVP** | Reid vapor pressure |
| **MON** | Motor octane number |
| **RON** | Research octane number |
| **T10** | 10% Distillation recovery temperature |
| **T50** | 50% Distillation recovery temperature |
| **T90** | 90% Distillation recovery temperature |
| **Vol%** | Volume percentage of a blend |