U.S. DEPARTMENT OF ENERGY
Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

## Co-Optimization of Fuels & Engines

# Fuel Blendstocks with the Potential to Optimize Future Gasoline Engine Performance

**Identification of Five Chemical Families for Detailed Evaluation**

January 2018

# About the Co-Optimization of Fuels & Engines Initiative

This is one of a series of reports produced as a result of the Co-Optimization of Fuels & Engines (Co-Optima) initiative, a Department of Energy (DOE)–sponsored effort initiated to simultaneously investigate advanced engine designs and the enabling fuel properties. This first-of-its-kind effort is designed to provide American industry with the scientific underpinnings needed to maximize vehicle performance and efficiency and leverage domestic fuel resources, leading to greater transportation energy affordability, reliability, and security.

Co-Optima brings together DOE's Office of Energy Efficiency & Renewable Energy (EERE), 9 national laboratories, 13 universities, and numerous industry and government stakeholders in a collaboration exploring solutions with potential for near-term improvements to the types of fuels and engines found in most vehicles currently on the road, as well as to the development of revolutionary engine technologies for a longer-term, higher-impact series of solutions.

In addition to the EERE Vehicle Technologies and Bioenergy Technologies Offices, the Co-Optima team includes representatives from the National Renewable Energy Laboratory and Argonne, Idaho, Lawrence Berkeley, Lawrence Livermore, Los Alamos, Oak Ridge, Pacific Northwest, and Sandia National Laboratories. More detail on the project—as well as the full series of reports—can be found at www.energy.gov/fuel-engine-co-optimization.

## Availability

This report is available electronically at no cost from SciTech Connect: http:/www.osti.gov/scitech.

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# Report Contributors and Roles


### Lead Author

John Farrell, National Renewable Energy Laboratory (NREL)

### Co-Lead Authors

John Holladay, Pacific Northwest National Laboratory (PNNL)

Robert Wagner, Oak Ridge National Laboratory (ORNL)

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*DOE Office of Energy Efficiency and Renewable Energy*
Steven Chalk, Deputy Assistant Secretary for Transportation

*Bioenergy Technologies Office*

Jonathan Male, Director

Alicia Lindauer, Technology Manager

Borka Kostova, Technology Manager

*Vehicle Technologies Office*

Michael Berube, Director

Gurpreet Singh, Program Manager, Advanced Engines and Fuels

Kevin Stork, Technology Manager

Mike Weismiller, Technology Manager

The national laboratory project management team consisted of:

John Farrell (Technical Monitor), National Renewable Energy Laboratory

John Holladay, Pacific Northwest National Laboratory

Chris Moen, Sandia National Laboratories

Robert Wagner, Oak Ridge National Laboratory

This report was reviewed by:

Jennifer Dunn, Argonne National Laboratory

Robert McCormick, National Renewable Energy Laboratory

Paul Miles, Sandia National Laboratories

James Szybist, Oak Ridge National Laboratory

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# Abbreviations and Acronyms

| | |
|---|---|
| AKI | antiknock index |
| ASTM | ASTM International / ASTM Association for Testing Materials |
| BETO | Bioenergy Technologies Office |
| BOB | blendstock for oxygenate blending |
| CARB | California Air Resources Board |
| cBOB | conventional gasoline blending components |
| Co-Optima | Co-Optimization of Fuels & Engines |
| DOE | U.S. Department of Energy |
| E10 | blend of 90% gasoline and 10% ethanol |
| HoV | heat of vaporization |
| MON | motor octane number |
| rBOB | reformulated blendstock for oxygenate blending |
| RON | research octane number |
| RVP | Reid vapor pressure |
| S | octane sensitivity |
| SI | spark ignition |
| SOT | state of technology |
| TRL | technology readiness level |
| VTO | Vehicle Technologies Office |

# Executive Summary

A systematic study of more than 400 potential blendstocks from 14 chemical families has provided new insights into the relationship between fuel properties and chemical families, providing valuable guidelines for identifying new fuels for boosted spark-ignition (SI) engines. This report describes the process and interim results of this study.

The blendstock identification and evaluation activities have explored a broad and diverse range of chemical functional groups and production routes. Assessment criteria include physical property and high-level health-impact assessments, ability to improve boosted SI engine efficiency, and the potential to be introduced commercially in the 2025–2030 time frame.

Research into fuel property impacts on engine efficiency and performance has been guided and informed by an engine efficiency “merit function” that relates changes in the values of key fuel properties to improvements in engine efficiency. The current boosted SI merit function includes the following properties: research octane number (RON), octane sensitivity (S), heat of vaporization (HoV), laminar flame speed, particulate matter index, and catalyst light-off temperature.

Much of the efficiency benefit from boosted SI engines comes from mitigating engine knock at high load. Higher values of RON, S, HoV, and flame speed all mitigate knock and allow engines to operate at higher compression ratios and boost levels that further benefits efficiency. Heat of vaporization and flame speed confer charge cooling and dilution tolerance benefits, respectively, and the particulate matter index and catalyst light-off temperature affect engine efficiency indirectly through requirements for emissions controls and management.

The merit function formalism reveals that fuel property impacts are more complex than reflected by traditional thinking that focuses solely on increasing RON. It allows the relative contributions of key fuel properties to be quantified, identifying those properties most important for conferring efficiency benefits. The merit function formalism shows that fuel properties can be “traded off,” that is, a fuel can still provide the same efficiency as a fuel with higher RON if it has (for example) appropriately higher S. These and additional insights can potentially transform the development of a new SI fuel specification into an opportunity to conduct a multidimensional optimization exercise that identifies optimal solutions not previously envisioned, providing valuable flexibility to fuel providers.

Two fuel properties—RON and S—contribute the majority of the efficiency benefits. HoV can contribute small improvements, but only small alcohols (four carbon atoms or fewer) increase HoV when blended with petroleum blendstocks; the other fuel properties included in the merit function are relatively less effective. The only chemical family that can increase all three major fuel properties is small alcohols. Many cycloalkanes, ketones, aromatics, alkenes, and furans can confer meaningful increases in RON and S. Iso-alkanes, ethers, and esters primarily contribute higher RON.

Merit function values are also strongly dependent on the composition of the base fuel to which the blendstocks are combined to produce fuels meeting commercial specifications. This understanding could help identify value propositions for blendstocks with relatively low RON

(e.g., mid-90s) but high S, which could be combined with other blendstocks to yield the desired overall properties, providing fuel providers more flexibility in meeting a new boosted SI fuel performance specification.

Based on the interim results, eight representative blendstocks from five chemical families are currently undergoing detailed investigation: alcohols (ethanol, iso-propanol, n-propanol, and iso-butanol); ketones (cyclopentanone); furans (a 40:60 mixture by weight of methylfuran:2,4-dimethylfuran); alkenes (di-isobutylene); and high-aromatics mixtures. These blendstocks encompass a broad range of structures and properties but this list should not be viewed as final or limiting. Blendstocks within these five chemical families could be added or removed as more data and information become available.

Current efforts are refining the fuel property data and blending models and focusing on key science questions, such as the nature of non-linear octane blending. Higher-fidelity analyses are also being conducted on the state of technology and environmental, economic, and market impacts of the blendstocks, using improved input data to quantify model output and uncertainty. Refinery integration studies are assessing the impact of new blendstocks on economics and product balance for model refineries. Results are being shared with external stakeholders and market decision makers with the goal of facilitating a comprehensive and consistent comparison of the benefits and tradeoffs of new blendstock options and engine operating approaches that can be brought to market in the 2025–2030 time frame.

# 1 Introduction

The U.S. Department of Energy's (DOE's) Co-Optimization of Fuels & Engines (Co-Optima) initiative is conducting the early-stage research and development needed to accelerate the market introduction of advanced fuel and engine technologies. The research includes both spark-ignition (SI) and compression-ignition combustion approaches as well as multi-mode operation that includes combinations of SI and compression-ignition combustion approaches. Target applications include the entire on-road fleet (light-, medium-, and heavy-duty vehicles). The initiative's major goals include (1) improving light-duty vehicle fuel economy 10% beyond the projected results of existing research and development efforts, which when combined represent a total improvement of more than 35% in relation to a 2015 baseline; (2) improving heavy-duty fuel economy by up to 4%, representing up to $5 billion savings in annual fuel costs; (3) providing the market pull for up to 25 billion gallons/year of domestically sourced fuel; (4) identifying lower-cost pathways to reduce emissions; and (5) leveraging diverse U.S. fuel resources.

Co-Optima's coordinated engine and fuels research and analysis are providing the framework for the co-development of fuel and engine technologies that offer the greatest combination of efficiency, performance, and fuel diversification. This report documents results from Co-Optima's near-term light-duty vehicle research focused on direct injection, boosted SI engines, and the fuel properties needed to optimize performance of those engines.[1]

A key objective of Co-Optima's research is to identify new blendstocks that enhance current petroleum blending components, increase blendstock diversity, and provide refiners with increased flexibility to blend fuels with the key properties required to optimize advanced internal combustion engines. This report identifies eight representative blendstocks from five chemical families that have shown the potential to increase boosted SI engine efficiency, meet key fuel quality requirements, and be viable for production at commercial scale by 2025–2030.

Co-Optima's research approach is based on the following two hypotheses.

- *Engines Hypothesis*—New engine architectures and combustion strategies can provide higher thermodynamic efficiencies than those that are currently delivered by commercially available internal combustion engines, but new fuels are required to maximize efficiency and operability across a wide range of speeds and loads.
- *Fuels Hypothesis*—Fuels that meet target values for the properties identified as critical to maximizing efficiency and emissions performance of a given engine architecture will provide comparable performances regardless of chemical composition.

Co-Optima's fuel property-based approach is identifying the technical fuel requirements from a composition-agnostic perspective, allowing the market to define the best means to blend and

[1] Efforts are currently underway to investigate the suitability of the boosted SI merit function to describe efficiency improvements possible from multimode operation, in which the engine operates under homogeneous SI conditions at high load, but utilizes compression ignition and/or lean SI combustion under partial load. These multimode strategies have the potential to contribute higher efficiency than boosted SI operation relying on homogeneous SI throughout the drive cycle, but might require an expanded merit function to fully represent the efficiency impacts.

provide these future fuels. In support of this objective, a systematic study is being conducted to identify a diverse set of blendstocks that meet a broad range of performance and fuel quality targets.

While blendstocks are being considered that can be produced from a wide variety of fossil and renewable resources, a targeted effort is focused on identifying options that can be sourced from domestic biomass. Blendstocks sourced from cellulosic biomass and similar renewable non-food and surplus waste resources can provide a number of technical, societal, and environmental benefits. These include the potential to increase U.S. jobs, support rural economies, reduce stresses on the environment, enhance energy security, affordability, and reliability by diversifying energy resources to make transportation fuels, and expand U.S. science and engineering leadership. Co-Optima is developing the comprehensive and consistent set of data on blendstock production, fuel properties, and engine performance that is required for a detailed assessment of the benefits of sourcing blendstocks from biomass versus conventional resources, and to identify areas where further research and development are needed.

The major deliverables of Co-Optima's fuels and engines research include data; tools; knowledge from state-of-the-art experiments; high-fidelity simulations; and integrated, comparative, systems-level analyses of economic, environmental, state of technology, and market factors. This information is being shared with stakeholders and market decision makers to facilitate a consistent and comprehensive comparison of the benefits and tradeoffs of new blendstock options and engine operating approaches. These Co-Optima activities will provide industry with information required to make investment decisions, break down communication barriers, and bring new fuels and engines to market sooner.

Research into fuel property impacts on engine efficiency and performance has been guided and informed by an engine efficiency merit function that relates changes in the values of key fuel properties to improvements in engine efficiency.[2] The current boosted SI merit function (Miles 2017) includes the following properties: research octane number (RON), octane sensitivity (S),[3] heat of vaporization (HoV), flame speed, particulate matter index, and catalyst light-off temperature. Much of the efficiency benefit comes from mitigating engine knock at high load. Higher values of RON, S, HoV, and flame speed all mitigate knock and allow engines to operate at higher compression ratios and boost levels. HoV and flame speed confer charge cooling and dilution tolerance benefits, respectively. The particulate matter index and catalyst light-off temperature affect engine efficiency indirectly through requirements for emissions controls and management.

Co-Optima's blendstock identification and evaluation activities explore the diversity of chemical functional groups and production routes using a tiered process: screening (Tier 1), blendstock survey (Tier 2), and detailed blendstock evaluation (Tier 3). The representative blendstocks identified as meeting Tier 2 performance and fuel quality criteria are reported here.

[2] Note that engine efficiency gains, captured in the merit function, are not the same as fuel economy gains, which depend on fuel energy density and vehicle powertrain design choices.
[3] Octane sensitivity is the difference between RON and the motor octane number (MON), i.e., S = RON – MON.

Tier 3 activities are underway to assess whether, when blended with petroleum blendstocks, the Tier 3 blendstocks can: (1) significantly increase merit function values and allow boosted SI and multimode engines to operate at high efficiency, (2) meet key fuel-quality specifications, and (3) potentially be introduced into the commercial fuel market at scale in the 2025–2030 time frame. Tier 3 efforts are focused on providing the experimental data, simulation results, tools, and analyses to assess the tradeoffs of various options to inform stakeholders and market decision makers.

# 2 Expanding Boosted SI Blendstock Options: High-Level Blendstock Screening and Survey

Over the past several decades, the engine and fuels community has developed a comprehensive understanding of how fuel properties impact SI engine efficiency and performance. A broad body of literature exists that describes how the chemical families represented in today's fuels—aromatics, normal and iso-paraffins, olefins, naphthenes (cycloparaffins), and alcohols[4]—affect engine operation and emissions controls. However, increasing transportation fuel use, shifting demand between gasoline and diesel, continuing changes to crude supply, increasingly stringent fuel economy and emissions requirements, and social drivers are motivating fuel providers to search for new blendstock options that can provide performance advantages and market benefits.

While the blendstocks that compose today's fuels represent a diverse set of chemical families and possess a broad range of properties, a large number of potential blendstocks remain unutilized, in part because they lack the comprehensive and consistent set of fuel property and engine-performance data required to assess their potential. Such blendstocks are principally oxygenates but also include select hydrocarbons. One of the Co-Optima objectives is to narrow the gap in understanding of these potential blendstocks versus traditional blendstocks. Although these blendstocks could all be produced from a variety of feedstocks—including natural gas and petroleum—Co-Optima is developing a detailed understanding of the cost, market, and environmental implications and benefits of producing these blendstocks from domestic biomass to facilitate a detailed comparison of tradeoffs versus fossil-based production routes.

The comprehensive blendstock assessment activities utilize a tiered process: screening (Tier 1), blendstock survey (Tier 2), and detailed blendstock evaluation (Tier 3).[5] The Tier 1 screening considered 470 blendstocks representing 14 chemical families (*see* Table 1). These 14 chemical families are listed in the box to the right. The Tier 1 blendstocks represent hydrocarbons and oxygenates that have known production pathways from biomass and can be blended into liquid fuels in the gasoline or diesel boiling range.[6] The Tier 1 assessment involved a high-level physical property and health impact assessment to identify blendstocks that provide adequate fuel-ignition quality and meet key fuel-quality specifications. This screening yielded a refined set of 41 blendstocks that meet the following requirements.

Fourteen chemical families considered in Tier 1 blendstock screening:

1. Normal paraffins
2. iso-Paraffins
3. Olefins
4. Aromatics
5. Naphthenes
6. Alcohols
7. Ketones
8. Simple and volatile fatty acid esters
9. Furans
10. Ethers
11. Multi-ring aromatics
12. Aldehydes
13. Fatty esters
14. Carboxylic acids

[4] The only alcohols currently present in U.S. fuels sold at retail stations are ethanol and iso-butanol.

[5] While the three-tiered blendstock evaluation described here is specific to boosted SI engines, the same approach is being applied to the other Co-Optima research projects (e.g., mixing controlled compression ignition, kinetically controlled combustion).

[6] Gaseous fuels are outside the scope of the Co-Optima initiative.

- Melting point ($T_M$) and boiling point ($T_B$): $T_M < -10°C$ and $20°C < T_B < 165°C$
- Solubility: soluble in hydrocarbon fuel (e.g., soluble at 30% blend level)
- Corrosivity: Pass initial literature review
- Toxicity: No Category 1 or Category 2 toxins (e.g., acutely toxic, known or suspected carcinogens and teratogens)
- Fuel handling/safety: No known rapid peroxide formers or oxidative instability (must meet ASTM International Standard D525 requirement in the gasoline standard, D4814)
- Biodegradation: Reject if anaerobic biodegradability is the same or worse than methyl tert-butyl ether and solubility in water >10,000 milligrams per liter
- Ignition quality: RON of 98 or higher.

Table 1. Summary of Co-Optima Tiered Assessment Criteria for Boosted SI Blendstocks

| | **Tier 1: High-Level Screening** | **Tier 2: Blendstock Survey** | **Tier 3: Detailed Blendstock Evaluation** |
|---|---|---|---|
| # Blendstocks | > 470 | 41 | 8 |
| # Chemical Families | 14 | 10 | 5 |
| Approach | • Conduct broad screening analysis to identify wide range of potential blendstocks<br>• Assess potential based on existing data or estimates of ignition quality and fuel quality<br>• Consider properties of neat blendstock | • Measure blendstock properties and compare against performance criteria<br>• Conduct high-level state of technology, economic, environ-mental, and market assessments<br>• Review and refine list of suitable blend-stocks based on potential to meet fuel quality specs, increase engine efficiency, and achieve market impact in 2025–2030 time frame<br>• Consider properties of blendstock blended into petroleum blendstocks | • Conduct detailed measurements of fuel properties and develop improved blending models<br>• Conduct detailed state of technology, economic, environmental, and market assessments<br>• Conduct engine tests to confirm performance<br>• Conduct emissions control experiments to assess impact<br>• Confirm potential to meet fuel economy targets<br>• Consider properties of blendstock blended into petroleum blendstocks |

Note: The tiered assessment approach involves high-level screening of blendstock properties (Tier 1), followed by blendstock survey (Tier 2), and detailed blendstock evaluation (Tier 3).

In the Tier 2 blendstock survey stage, Co-Optima researchers focused on the 41 blendstocks shown in Table 2. In contrast with Tier 1—which focused on properties of the individual blendstocks—Tier 2 and Tier 3 focus on properties of the blendstocks combined with various petroleum blendstocks to assess the performance that would be achieved with fuels meeting market requirements. The blendstocks have been characterized both neat and as blended fuels at levels of up to 30% into blendstocks known as "BOBs," or blendstocks for oxygenate blending.[7] Key properties of the blendstocks have been measured (McCormick et al. 2017) and entered into a publicly available fuel property database.[8] These properties include merit function properties (e.g., RON, motor octane number [MON], S, HoV), as well as fuel-quality properties important for assessing performance in blended fuels (e.g., Reid vapor pressure [RVP], distillation, oxidative stability). Computational approaches based on machine learning and group contribution tools were used in the screening process to complement experimental measurements and identify new blendstock options. More detailed discussions of these activities are available in McCormick et al. (2017) and Whitmore et al. (2016). Other Tier 2 activities expanded the team's understanding of combustion kinetics (Zhou et al. 2016) for representative hydrocarbon and oxygenate blendstocks and surrogates, and of how a fuel's molecular structure affects important physical and chemical properties.

Through a broad range of analyses, the attributes of these blendstocks were assessed using metrics describing the state of technology, environmental performance, economics (Dunn et al. 2017), and compatibility with plastics and elastomers commonly used in vehicles and infrastructure equipment (Kass and West 2017). The 23 metrics shown in Table 3 were used to assess the Tier 2 blendstocks (Farrell and Holladay 2017, Dunn and Biddy 2017, Longman 2017).

Because many of the 41 Tier 2 blendstocks are chemically similar, a representative subset of 20 blendstocks was identified for the initial analyses, based on several practical considerations: (1) they have a clear production pathway from biomass; (2) they cover the chemistry/functional group space of the Tier 2 blendstocks; (3) they provide a systematic variation of structure within a chemical family; and (4) they avoid duplication of similar compounds with similar production pathways. To support these analyses, concerted efforts were carried out to identify viable production pathways from biomass for the Tier 2 blendstocks, and retrosynthetic analyses identified the most promising pathways from which these blendstocks can be produced from biomass (Gaspar 2017).

[7] BOBs are gasoline blending components intended for blending with oxygenates (typically ethanol) to produce finished conventional motor gasoline. Conventional gasoline blending components (cBOB) and reformulated blendstock for oxygenate blending (rBOB) are the two base gasoline stocks that are mixed with ethanol at the terminal racks. "CARBOB" is an example of a special rBOB formula mandated by the State of California.

[8] A comprehensive fuel-property database was established and is being maintained as the repository of fuel-property data for the Co-Optima blendstocks, both "neat" and blended in finished fuels. This database is publicly accessible and available at https://fuelsdb.nrel.gov/fmi/webd#FuelEngineCoOptimization.

Table 2. List of Tier 2 Boosted SI Blendstocks

| | Alcohols (9) |
|---|---|
| 1 | Methanol |
| 2 | Ethanol |
| 3 | 1-Propanol |
| 4 | iso-Propanol |
| 5 | 1-Butanol |
| 6 | 2-Butanol |
| 7 | iso-Butanol |
| 8 | 2-Methylbutan-1-ol |
| 9 | 2-Pentanol |

| | Ethers |
|---|---|
| 10 | Anisole |

| | Esters (13) |
|---|---|
| 11 | Methyl acetate |
| 12 | Methyl butanoate |
| 13 | Methyl pentanoate |
| 14 | Methyl isobutanoate |
| 15 | Methyl-2-methylbutanoate |

| | Esters (13) |
|---|---|
| 16 | Ethyl acetate |
| 17 | Ethyl butanoate |
| 18 | Ethyl isobutanoate |
| 19 | iso-Propyl acetate |
| 20 | Butyl acetate |
| 21 | 2-Methylpropyl acetate |
| 22 | 3-Methylpropyl acetate |
| 23 | Mixed esters |

| | Ketones (9) |
|---|---|
| 24 | 2-Butanone |
| 25 | 2-Pentanone |
| 26 | 3-Pentanone |
| 27 | Cyclopentanone |
| 28 | 3-Hexanone |
| 29 | 4-Methyl-2-pentanone |
| 30 | 2,4-Dimethyl-3-pentanone |
| 31 | 3-Methyl-2-butanone |
| 32 | Ketone mixture |

| | Furans |
|---|---|
| 33 | 2,5-Dimethylfuran/ 2-methylfuran |

| | Branched alkanes |
|---|---|
| 34 | 2,2,3-Trimethylbutane |

| | Alkenes |
|---|---|
| 35 | Di-isobutylene |

| | Multicomponent Mixtures (6) |
|---|---|
| 36 | Methanol-to-gasoline |
| 37 | Ethanol-to-gasoline |
| 38 | Bioreformate via multistage pyrolysis |
| 39 | Bioreformate via catalytic conversion of sugar |
| 40 | Mixed aromatics via catalytic fast pyrolysis |
| 41 | Aromatics and olefins via pyrolysis-derived sugars |

Table 3. Metrics used to Assess State of Technology, Environmental Performance, Economics, and Market Barriers of Co-Optima Blendstocks

| Technology Readiness | Environmental | Economics | Market |
|---|---|---|---|
| SOT – Fuel production | Carbon efficiency | Target cost | Geographic factors |
| SOT – Vehicle use | Target yield | Needed cost reduction | Vehicle compatibility |
| Conversion TRL level | Life-cycle greenhouse gas | Co-product economics | Infrastructure compatibility |
| Feedstock sensitivity | Life-cycle water | Feedstock cost | Regulatory requirements |
| Process Robustness | Life-cycle fossil energy use | Alternative high-value use | |
| Feedstock quality | | | |
| No. of viable pathways | | | |

SOT = state of technology; TRL = technology readiness level
Technology readiness, environmental, and economic analyses only focused on bio-route.
Market metrics apply to either petroleum- or bio-derived blendstocks.

# 3 Transition from Tier 2 Blendstock Survey to Tier 3 Detailed Blendstock Evaluation

At the end of the Tier 2 blendstock survey, Co-Optima researchers evaluated data on the 41 Tier 2 blendstocks, identified chemical functional groups that conferred desired fuel properties when blended into petroleum BOBs, and identified a smaller set of blendstocks for more detailed analysis, allowing the team to focus efforts on the blendstocks with the greatest potential to meet the Co-Optima performance and timing goals. The Tier 3 efforts already underway include detailed characterization, engine experiments, modeling, and analyses, and they are providing the data, tools, and knowledge necessary for stakeholders to conduct a comprehensive and consistent comparison of the benefits and challenges of introducing new blendstocks to market.

The evaluation considered three criteria: (1) ability to improve engine efficiency, as assessed through merit function values ≥ E10 premium (RON = 98) when blended in petroleum BOBs at levels of up to 30% by volume; (2) ability to meet current critical fuel-quality requirements (RVP, distillation, and oxidative stability) when blended into petroleum BOBs (or at least have viable pathways identified to meet these requirements; and (3) whether there are any "showstopper" barriers to introducing these blendstocks commercially at scale by 2025–2030.[9] Each criterion is described in more detail below. Blendstocks that meet all three criteria were selected for Tier 3 evaluation (*see* Figure 1).

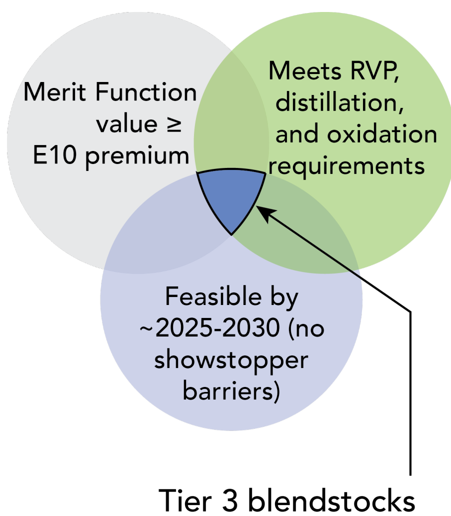


**Figure 1. Evaluation criteria for Tier 3 blendstocks**

## 3.1 Efficiency Improvement Potential: Merit Function Values

Using blend data and models developed during Tier 2 activities, merit function values were calculated for each blendstock splash-blended at levels of 10%, 20%, and 30% by volume in six diverse BOBs representing a range of properties.[10] The properties of these BOBs are shown in

[9] Here, "commercially available" is defined as being produced at the level of 4 billion gallons per year.
[10] Merit function values are calculated based on the properties of the finished fuel, rather than on those of the BOBs or blendstocks (Miles 2017).

Table 4. These include one premium grade and two regular grade BOB (Chupka et al. 2015), labeled Conventional, CARB, and Summer in Table 4, and three BOBs (Prakash et al. 2017) with the same RON but different MON (and hence S) values, labeled F1, F2, and F3 in Table 4.

Table 4. Properties of the Six BOBs Used to Evaluate Merit Function Values for the Tier 2 Blendstocks

| Name | Conventional | CARB | Summer | F1 | F2 | F3 |
|---|---|---|---|---|---|---|
| Grade | Premium Winter | Reformulated Regular | Regular | Low-S Regular | Regular | High-S Regular |
| RON | 93.7 | 84.8 | 87.9 | 85.7 | 85.7 | 85.7 |
| MON | 87.3 | 80.8 | 81.9 | 83.5 | 77.9 | 72.4 |
| AKI (RON+MON)/2 | 90.5 | 82.8 | 84.9 | 84.6 | 81.8 | 79.1 |
| S (RON-MON) | 6.4 | 4.0 | 6.0 | 2.2 | 7.8 | 13.3 |
| HoV (kJ/kg) | 346.7 | 340.3 | 352.8 | 345.0 | 345.0 | 345.0 |
| Density (g/mL) | 0.727 | 0.732 | 0.737 | 0.730 | 0.730 | 0.730 |

AKI = antiknock index
CARB = California Air Resources Board

The blended fuels were evaluated without added ethanol.[11] 11 Merit function values were calculated using K = –1.25, which is representative of knock-limited operating conditions for boosted SI engines.12 Merit function values were compared to the value achieved by an E10 premium fuel (i.e., the conventional premium BOB in Table 4 blended with 10% ethanol, yielding a finished fuel RON=98). Calculation results are included in Appendix A.

The chemical families with blendstocks having the highest merit function values are:

- Small alcohols: methanol, ethanol, n- and iso-propanol, and iso-butanol
- Furan compounds: a mixture of methyl- and dimethyl furan
- Highly branched olefins: di-isobutylene
- A cyclic ketone: cyclopentanone.

A common attribute of these blendstocks is the ability to confer high RON and high S to the fuel. There are blendstocks from other families that have high RON, such as branched alkanes and esters, but do not achieve high enough merit function values for use in boosted SI engines, primarily because of their low S.

## 3.2 Fuel Quality Requirements: Reid Vapor Pressure, Distillation, and Oxidative Stability

The Tier 2 blendstocks were evaluated as blends in a petroleum BOB at levels of 10%, 20%, and 30% by volume (McCormick et al. 2017). These blends were then subjected to RVP (ASTM

[11] Ethanol-containing blends will be studied during Tier 3 evaluations.

D323), distillation (ASTM D86), and oxidative stability (ASTM D525) testing and assessed against the following criteria.

1. RVP: Meets RVP limit for Class A gasoline in BOB without 1-psi waiver.[12]
2. Distillation: Ensure that end point and critical distillation points are not adversely impacted (e.g., T10 maximum for cold start, T90 for lube oil dilution[13]).
3. Oxidative stability: Meets current gasoline specs (ASTM D525).

Blendstocks that have significant difficulty meeting current key fuel-quality specifications could increase costs to fuel providers and could require a lengthier fuel-approval process, which is not compatible with the targeted 2025–2030 commercial introduction timing. Blendstocks that did not meet the fuel specification were not eliminated from Tier 3 consideration if viable mitigation paths were identified. The results of these measurements are summarized in Table 5.

Table 5. Summary of Results from Assessment of Fuel-Quality Requirements for Select Tier 2 Blendstocks

| | RVP | | | Distillation | | | 20% |
|---|---|---|---|---|---|---|---|
| Blendstock | 10% | 20% | 30% | 10% | 20% | 30% | Oxid. Stab. |
| Methanol | | | | | Fails T50 (low) | Fails T50 (low) | |
| 2,5-Dimethylfuran/2-methylfuran | | | | | | | |
| Ethanol | | | | | | | |
| 2-Propanol | | | | | | | |
| 1-Propanol | | | | | | | |
| Cyclopentanone | | | | Fails T10 | Fails T10 | Fails T10 | |
| Isobutanol | | | | | | | |
| Diisobutylene | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2-Butanol | | | | | | | |
| 2-Butanone | | | | | | | |
| Methyl acetate | | | | | | Fails T50 (low) | |
| Ethyl acetate | | | | | | | |
| Anisole | | | | Fails T10 | Fails T50 (high) | Fails T50 (high) | |
| Ethyl butanoate | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2-Methylbutan-1-ol | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2-Pentanone | | | | | | | |
| 1-Butanol | | | | Fails T10 | Fails T10 | Fails T10 | |
| Butyl acetate | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2,4-Dimethyl-3-Pentanone | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2-Pentanol | | | | | | | |
| Ketone Mixture | | | | Fails T10 | Fails T10 | Fails T10 | |
| 2,2,3-Trimethylbutane | | | | | | | |

The color coding in this table reflects the following results and technical assessment.

- Green: Blends up to 30% meet gasoline specifications.

[12] Depending on the state and month, gasoline RVP may not exceed 9.0 psi or 7.8 psi. The U.S. Environmental Protection Agency provides a 1.0-psi RVP allowance for gasoline containing ethanol at 9 to 10 volume percent. For more details, see https://www.epa.gov/gasoline-standards/gasoline-reid-vapor-pressure.
[13] T10 is the temperature where 10 percent by weight of the gasoline has evaporated. T90 is the temperature where 90 percent by weight of the gasoline has evaporated.

- Yellow: Blends do not meet specification, but feasible mitigation paths have been identified.
- Red: Blends do not meet gasoline specification, and no feasible paths to mitigating challenges are evident in the 2025–2030 time frame.

Three blendstocks were assigned red ratings:

- Methanol: RVP and distillation[14]
- Methyl acetate: RVP and distillation
- Anisole (methoxybenzene): distillation.[15]

Based on these results, these blendstocks are not being assessed as part of Tier 3 evaluations.

The only blendstock with high merit function values that is not being evaluated in Tier 3 is methanol. The other blendstocks mentioned above—methyl acetate and anisole—had merit function values less than E10 premium. Although cyclopentanone and the furan mixture show evidence of oxidation in ASTM D525, discussions with fuel providers indicated that potential mitigation paths are feasible. Additional Tier 3 work is assessing their oxidation behavior in more detail.

## 3.3 "Showstopper" Barriers

### Potential for Market Introduction by 2025–2030

Results from the state of technology, environmental, economic, and compatibility assessments were reviewed to identify blendstocks that could reasonably be expected to be commercially available in the 2025–2030 time frame. Consistent with the focus of the state of technology, environmental, and economic analyses on bio-derived blendstocks, these assessments are meant to prioritize efforts away from blendstocks that have fundamental challenges to near-term introduction.

Of the blendstocks identified above that meet the merit function and fuel quality criteria, none was eliminated from consideration for Tier 3 evaluation based on the "showstopper" barrier criteria. This is not to suggest that commercial introduction of fuels with these blendstocks will be easy, but rather that there are pathways identified that are plausible based on the high-level Tier 2 analyses and are being considered in more detail as part of Tier 3. More details are provided in Dunn et al. (2017).

[14] There are other considerations that contributed to the decision to omit methanol from Tier 3 evaluation: corrosion, infrastructure and vehicle compatibility, energy density (methanol's very low energy density makes it exceedingly challenging to meet Co-Optima's fuel economy targets), and toxicity.

[15] This decision also recognized that anisole was included as a representative oxygenated aromatic that could be derived from upgraded biomass pyrolysis oil. Because most of the molecules that would be present in upgraded pyrolysis oil are higher in molecular weight than anisole, the impact on distillation would be even greater.

# 4 Results, Insights, and Ongoing Efforts for the Boosted SI Project

## 4.1 Results

Evaluation of the Tier 2 survey results has identified blendstocks from five chemical families that, when blended with petroleum BOBs, have the potential to (1) increase the efficiency of advanced boosted SI engines, (2) meet key fuel-quality requirements (or have viable mitigation pathways identified), and (3) be commercially available at scale by 2025–2030. Because the Tier 2 blendstock survey activities were by necessity conducted at a fairly high level, the Tier 3 blendstocks are considered representative and are not a set of specific blendstocks recommended for commercial use.

General conclusions from the survey of the 41 Tier 2 blendstocks include the following.

- Alcohols: Alcohols generally impart high RON, S, and HoV when blended into representative BOBs. Branched alcohols provide greater benefits versus unbranched (e.g., iso-butanol versus n-butanol). Tier 3 evaluations are yielding additional measurements on alcohols and mixtures (ethanol, iso-propanol, n-propanol, and iso-butanol).
- Esters: Many ester blendstocks have both high RON and high MON, but low S. Additionally, esters demonstrate antagonistic octane blending, that is, blending esters into BOBs results in a sub-linear increase in RON (in contrast with alcohols, which typically exhibit super-linear RON blending). For these reasons, no esters are included as Tier 3 blendstocks, although studies are planned to develop a detailed, molecular-level understanding of the octane blending behavior of esters.
- Ketones: Many impart high RON and S, in particular the highly branched isomers. Tier 3 evaluations include one ketone—cyclopentanone.
- Ethers: Anisole provides high RON and S, but has deleterious effects on distillation. Tier 3 research does not include studies of ethers or methyl phenols.
- Furans: The 40:60 mixture (by weight) of methylfuran: 2,4-dimethylfuran provides high RON and S, and blends of the furan mixture yielded some of the highest merit function values of all the Tier 2 blendstocks. Tier 3 efforts include further study of various furan mixtures with a particular emphasis on fully characterizing their oxidative stability performance.
- iso-Alkanes: Branched alkanes can have high RON and MON, but generally possess very low S, lowering the merit function value. Although highly branched iso-alkanes can be valuable as BOB enhancers, this chemical family is not included in Tier 3 evaluations.
- Alkenes: Di-isobutylene (a mixture of three parts 2,4,4-trimethyl-1-pentene and one part 2,4,4-trimethyl-2-pentene) provides high merit function values, reflecting its high RON and S. Other branched alkenes in the $C_7$–$C_9$ range likely confer similar performance benefits, and Tier 3 is further evaluating branched olefins.
- Aromatics: No experimental results were generated with Tier 2 aromatics and complex mixtures containing high levels of aromatics (blendstocks 36–41 in Table 2) because

sufficient quantities were not available at the time of these investigations. However, aromatics and complex mixtures are included in Tier 3 evaluations, and commercially produced samples of representative blendstocks are being procured.

The blendstocks that are being evaluated in Tier 3 are shown in Figure 2.

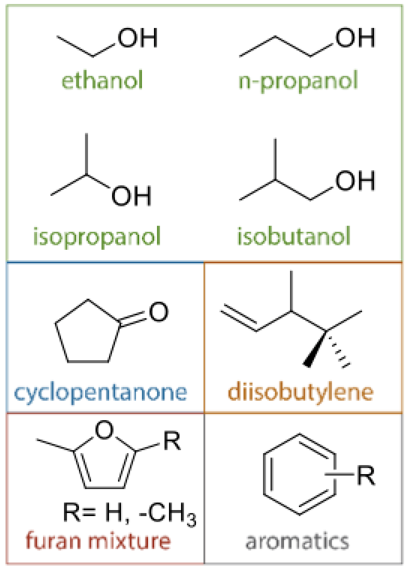


**Figure 2. Eight representative blendstocks identified for Tier 3 evaluation**

## 4.2 Insights

The Tier 2 survey has yielded several important insights that are being further developed during Tier 3 evaluations. First, two properties—RON and S—account for 85%–95% of the merit function values for the Tier 3 blendstocks. Contributions from HoV are small in general because the HoV values for most blendstocks do not differ significantly from HoVs for petroleum BOBs. Contributions from the particulate matter index are generally very small (note that data for flame speed and catalyst light-off temperature were not available for all blendstocks and thus were not included in the current assessment).

Although a relatively small number of blendstocks have the ability to provide substantial boosts in RON when blended with representative BOBs, fewer are able to simultaneously provide the large increases in S that together contribute to high merit function values. The chemical families (functional groups) that contribute high S include olefins, furans, aromatics, ketones, and smaller alcohols. Octane blending is non-linear, and some chemical families contribute smaller RON benefits to the blended fuel than indicated by the blendstock RON. Esters fall into this category, and in fact demonstrate antagonistic blending (i.e., the increase in RON is sub-linear, in contrast with alcohols where octane blending with common BOBs is super-linear).

The Tier 2 results also demonstrate the importance of BOB properties on achieving high merit function values. In particular, the merit function values of Tier 2 blendstocks in BOB F1 (RON = 85.7, S = 2.2) are significantly lower than those from BOB F3 (RON = 85.7, S = 13.3). This finding has important implications for fuel providers looking to meet future fuel requirements utilizing the broadest range of diverse blendstocks. Additionally, this understanding could help identify value propositions for blendstocks with relatively low RON (e.g., mid-90s) but high S, which could be co-blended with Tier 3 blendstocks and petroleum BOBs, giving fuel providers more flexibility in meeting a new boosted SI fuel performance specification.

It is worth highlighting the insights afforded by the merit function approach to correlating fuel properties to SI engine efficiency. The merit function formalism has revealed that fuel property impacts are more complex than reflected by traditional thinking that focuses solely on increasing RON. First, as illustrated in Figure 3, it allows the relative contributions of key fuel properties to be quantified, identifying those properties most important for conferring efficiency benefits. More specifically, a unit increase in RON has the greatest impact on efficiency, followed by S and HOV. The merit function formalism also shows that fuel properties can be "traded off," that is, a fuel can still provide the same efficiency as a fuel with higher RON if it has (for example) appropriately higher S. Recent revisions to the merit function (Miles 2017) have also highlighted the complexity of fuel property impacts under low-speed operation (through their role in promoting stochastic pre-ignition) as well as on cold start. These insights can potentially transform the development of a new SI fuel specification into an opportunity to conduct a multidimensional optimization exercise that identifies optimal solutions not previously envisioned while providing valuable flexibility to fuel providers.

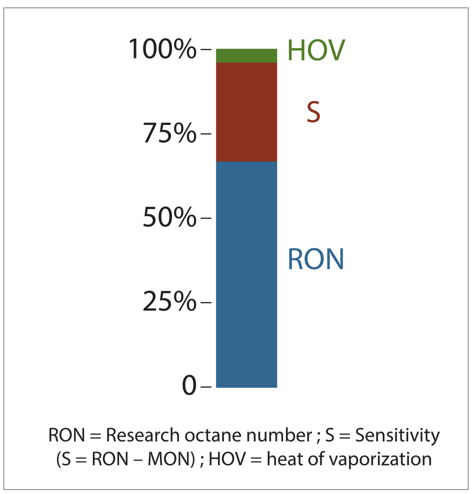


**Figure 3. Average contribution to merit function for the eight highest-scoring Tier 2 blendstocks (*see* Appendix A)**

## 4.3 Ongoing Activities: Co-Optima Boosted SI Research and Analysis

Tier 3 research and analysis efforts are providing a more thorough evaluation of the eight representative blendstocks from the five chemical families identified in Tier 2. The Tier 3 blendstock list covers a broad range of structures and properties and should not be viewed as final or limiting. Blendstocks within these five chemical families might be added or removed as more data and information become available. For example, although di-isobutylene has been identified as a Tier 3 blendstock, other branched olefins and mixtures of branched olefins might perform as well or better. Similarly, other alcohols and/or ketones that merit Tier 3 evaluation also could be identified, as could blends of Tier 3 blendstocks identified above. There are no plans to narrow this list further, consistent with the Co-Optima goal of providing data, tools, and knowledge to stakeholders and not recommending market solutions. However, Tier 3 efforts will include exploration of illustrative solutions that could inform industry and markets in the development of implementation plans and market adoption approaches.

Tier 3 efforts are building on the insights discussed in the preceding section through experiments and simulations focused on developing a better understanding of how molecular composition impacts fuel properties. These efforts are also helping to refine the fuel property data and blending models, focused on key science questions such as the nature of non-linear octane blending. Additionally, the initial blends studied in Tier 2 used non-ethanol-containing BOBs to identify blending effects with conventional petroleum-based fuel components. Additional data are being collected with splash blends into representative E10 fuels to identify a molecular-level understanding of blending effects with ethanol-containing fuels.

Expanding on the insights generated around the importance of BOB properties, opportunities to tailor BOB properties to the individual Tier 3 blendstocks are being explored to identify the value proposition associated with changes to the BOB. Engine tests are being carried out to validate merit function predictions, assess the potential of Tier 3 blendstocks to meet the Co-Optima fuel economy targets, and identify how fuel property impacts differ under multimode operation. Emissions control experiments are assessing performance of the Tier 3 blendstocks versus conventional gasoline and identifying impacts on efficiency and durability. Uncertainty analyses are also underway on the merit function to help assess differences between blendstocks and to identify experiments and simulations needed to improve the team's understanding of how key fuel properties impact boosted SI operation.

Higher-fidelity analyses are also being conducted on the state of technology, environmental, economic, and market impacts of the blendstocks, using improved input data to quantify model output and uncertainty. Refinery integration studies are assessing the impact of Tier 3 blendstocks on economics and product balance for model refineries. More-detailed studies are being carried out on fuel compatibility with vehicles and infrastructure.

Results from Tier 3 studies are being shared with external stakeholders with the goal of providing a comprehensive and consistent assessment of the key barriers and research needed to bring these blendstocks to the market in the 2025–2030 time frame.

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# Appendix A. Calculation Results of Merit Function Scores for Select Tier 2 Blendstocks in Six BOBs at Levels of 10%–30% by Volume

See Section 3.1 for details on the calculations. The color coding in Table A.1 reflects the following.

- Green: Meets or exceeds merit function score of 98 RON E10 premium (5.7; see merit function score for ethanol under the 10% cBOB [conventional gasoline blending components] column below).
- Yellow: Merit function score is within one unit of 98 RON E10 premium.
- Red: More than one merit function unit lower than 98 RON E10 premium. (The red box defines blendstocks that have the greatest ability to achieve high merit function scores, as discussed in Section 3.1).

Table A.1. Calculation Results of Merit Function Scores for Select Tier 2 Blendstocks in Six BOBs at Levels of 10%–30% by Volume

| | 10% | | | 20% | | | 30% | | | 10% | | | 20% | | | 30% | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blendstock | cBOB | CARBOB | sBOB | cBOB | CARBOB | sBOB | cBOB | CARBOB | sBOB | F1 BOB | F2 BOB | F3 BOB | F1 BOB | F2 BOB | F3 BOB | F1 BOB | F2 BOB | F3 BOB |
| 2,5-Dimethylfuran/2-methylfuran | 8.6 | 1.9 | 5.1 | 12.8 | 6.8 | 9.6 | 12.9 | 7.7 | 10.2 | 1.1 | 5.1 | 9.0 | 6.1 | 9.6 | 13.1 | 7.1 | 10.2 | 13.2 |
| Methanol | 7.1 | 0.3 | 3.6 | 15.0 | 9.0 | 11.9 | 15.6 | 10.4 | 12.9 | (0.4) | 3.5 | 7.4 | 8.4 | 11.9 | 15.3 | 9.8 | 12.9 | 15.9 |
| Ethanol | 5.7 | (1.1) | 2.2 | 12.2 | 6.2 | 9.1 | 12.7 | 7.5 | 10.0 | (1.8) | 2.1 | 6.0 | 5.6 | 9.1 | 12.5 | 6.9 | 10.0 | 13.0 |
| 1-propanol | 4.4 | (2.3) | 0.9 | 8.5 | 2.6 | 5.4 | 11.6 | 6.4 | 8.9 | (3.0) | 0.9 | 4.8 | 1.9 | 5.4 | 8.8 | 5.8 | 8.9 | 11.9 |
| Diisobutylene | 2.9 | (3.8) | (0.6) | 7.7 | 1.7 | 4.5 | 11.0 | 5.7 | 8.3 | (4.5) | (0.6) | 3.3 | 1.0 | 4.5 | 8.0 | 5.2 | 8.2 | 11.2 |
| Isobutanol | 1.0 | (5.8) | (2.6) | 7.3 | 1.3 | 4.2 | 10.2 | 4.9 | 7.4 | (6.5) | (2.6) | 1.3 | 0.6 | 4.1 | 7.6 | 4.4 | 7.4 | 10.4 |
| Cyclopentanone | 2.8 | (3.9) | (0.7) | 6.5 | 0.6 | 3.4 | 10.4 | 5.1 | 7.6 | (4.6) | (0.7) | 3.2 | (0.1) | 3.4 | 6.8 | 4.6 | 7.6 | 10.6 |
| Isopropanol | 4.0 | (2.7) | 0.5 | 7.2 | 1.2 | 4.1 | 9.8 | 4.6 | 7.1 | (3.4) | 0.5 | 4.4 | 0.6 | 4.1 | 7.5 | 4.0 | 7.1 | 10.1 |
| 2-Butanol | 2.2 | (4.5) | (1.3) | 5.4 | (0.5) | 2.3 | 7.5 | 2.3 | 4.8 | (5.2) | (1.3) | 2.6 | (1.2) | 2.3 | 5.7 | 1.7 | 4.8 | 7.8 |
| Anisole | 1.9 | (4.8) | (2.6) | 4.8 | (1.2) | 1.7 | 7.9 | 2.7 | 5.2 | (5.6) | (1.6) | 2.2 | (1.8) | 1.7 | 5.1 | 2.1 | 5.2 | 8.2 |
| 2-Butanone | 1.1 | (5.6) | (2.4) | 4.0 | (2.0) | 0.9 | 6.0 | 0.8 | 3.3 | (6.4) | (2.4) | 1.4 | (2.6) | 0.9 | 4.3 | 0.2 | 3.3 | 6.3 |
| Methyl acetate | 0.8 | (5.9) | (2.7) | 3.7 | (2.3) | 0.6 | 6.2 | 1.0 | 3.5 | (6.7) | (2.7) | 1.1 | (2.9) | 0.6 | 4.0 | 0.4 | 3.5 | 6.5 |
| Ethyl butanoate | 0.8 | (5.9) | (2.7) | 2.7 | (3.3) | (0.5) | 5.5 | 0.2 | 2.8 | (6.6) | (2.7) | 1.2 | (4.0) | (0.5) | 3.0 | (0.3) | 2.7 | 5.8 |
| 2-Methylbutan-1-ol | 1.1 | (5.6) | (2.4) | 3.3 | (2.7) | 0.2 | 5.2 | (0.1) | 2.5 | (6.3) | (2.4) | 1.5 | (3.4) | 0.1 | 3.6 | (0.6) | 2.4 | 5.4 |
| Ethyl acetate | 0.5 | (6.3) | (3.0) | 2.9 | (3.1) | (0.2) | 4.9 | (0.4) | 2.1 | (7.0) | (3.1) | 0.8 | (3.7) | (0.2) | 3.2 | (1.0) | 2.1 | 5.1 |
| 1-Butanol | (0.1) | (6.9) | (3.6) | 3.4 | (2.6) | 0.3 | 4.6 | (0.7) | 1.9 | (7.6) | (3.7) | 0.2 | (3.2) | 0.3 | 3.7 | (1.2) | 1.8 | 4.8 |
| 3-Methylbutan-1-ol | (0.0) | (6.7) | (3.5) | 1.4 | (4.6) | (1.7) | 2.9 | (2.4) | 0.2 | (7.5) | (3.5) | 0.3 | (5.2) | (1.7) | 1.7 | (2.9) | 0.1 | 3.2 |
| Butyl acetate | (0.2) | (6.9) | (3.7) | 0.9 | (5.1) | (2.2) | 1.1 | (4.2) | (1.6) | (7.7) | (3.7) | 0.1 | (5.7) | (2.2) | 1.2 | (4.7) | (1.7) | 1.3 |
| 2,4-Dimethyl-3-Pentanone | (2.3) | (9.0) | (5.8) | (0.3) | (6.3) | (3.4) | 0.7 | (4.5) | (2.0) | (9.7) | (5.8) | (1.9) | (7.0) | (3.5) | (0.0) | (5.1) | (2.1) | 1.0 |
| 2-Pentanone | 1.2 | (5.5) | (2.3) | 2.8 | (3.1) | (0.3) | 3.4 | (1.8) | 0.7 | (6.2) | (2.3) | 1.6 | (3.8) | (0.3) | 3.1 | (2.4) | 0.6 | 3.7 |
| 2-Pentanol | 1.3 | (5.5) | (2.2) | 1.9 | (4.1) | (1.3) | 3.1 | (2.1) | 0.4 | (6.2) | (2.3) | 1.6 | (4.8) | (1.3) | 2.2 | (2.7) | 0.4 | 3.4 |
| Ketone Mixture | (0.9) | (7.6) | (4.4) | (1.2) | (7.2) | (4.4) | (0.7) | (6.0) | (3.4) | (8.3) | (4.4) | (0.5) | (7.9) | (4.4) | (0.9) | (6.5) | (3.5) | (0.5) |
| 2,2,3-Trimethylbutane | (0.2) | (6.9) | (3.7) | (0.3) | (6.3) | (3.4) | 2.1 | (3.2) | (0.7) | (7.7) | (3.7) | 0.2 | (6.9) | (3.4) | 0.0 | (3.8) | (0.7) | 2.3 |

Note: Conventional gasoline blending components (cBOB) and reformulated blendstock for oxygenate blending (rBOB) are the two base gasoline stocks that are mixed with ethanol at the terminal racks. “CARBOB” is an example of a special rBOB formula mandated by the State of California.

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