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Co-Optimization of Fuels & Engines

Top Ten Blendstocks Derived From Biomass For Turbocharged Spark Ignition Engines

Bio-blendstocks With Potential for Highest Engine Efficiency

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About the Co-Optimization of Fuels & Engines Project

This is one of a series of reports produced as a result of the Co-Optimization of Fuels & Engines (Co-Optima) project, a U.S. Department of Energy (DOE)-sponsored multi-agency project initiated to accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. The simultaneous fuels and vehicles research and development is designed to deliver maximum energy savings, emissions reduction, and on-road performance.

Co-Optima brings together two DOE Office of Energy Efficiency & Renewable Energy (EERE) research offices, nine national laboratories, and numerous industry and academic partners to make improvements to the types of fuels and engines found in most vehicles currently on the road, as well as to develop revolutionary engine technologies for a longer-term, higher-impact series of solutions. This first-of-its-kind project will provide industry with the scientific underpinnings required to move new biofuels and advanced engine systems to market faster while identifying and addressing barriers to commercialization.

In addition to the EERE Vehicle Technologies and Bioenergy Technologies Offices, the Co-Optima project team included 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.

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Abbreviations and Acronyms

Acronym	Definition
2-PE	2-phenylethanol
ABE	acetone/n-butanol/ethanol
BCF	bioconcentration factor
BETO	Bioenergy Technologies Office
Bgpy	billion gallons per year
bMON	blending motor octane number
BOB	blendstock for oxygenate blending
bRON	blending research octane number
bS	blending octane sensitivity
BSI	boosted spark ignition (or turbocharged)
CARBOB	California reformulated blendstock for oxygenate blending
cBOB	conventional winter blendstock for oxygenate blending
CFH	Central Fuel Hypothesis
CFR	cooperative fuel research
C-H	carbon-hydrogen
CO_2	carbon monoxide
Co-Optima	Co-Optimization of Fuels & Engines
DBE	double bond equivalent
DGS	distillers' grain with solubles
DI	direct injection
DIB	di-isobutylene
DISI	direct injection spark ignition

2,5-DMF	2,5-dimethylfuran
DOE	U.S. Department of Energy
E10	petroleum-derived gasoline containing 10% ethanol
EC	enzyme commission
EGR	exhaust gas recirculation
EtOH	ethyl alcohol
FFV	flex fuel vehicle
GC-MS	gas chromatography–mass spectrometry
GDI	gasoline direct injection
GGE	gallon of gasoline equivalent
GHG	greenhouse gas emissions
HC	hydrocarbon
HMF	hydroxymethylfuran
HoV	heat of vaporization
HPF	high performance fuel
IAB	isopropanol/acetone/n-butanol
IB	isopropanol/n-butanol
IBA	isobutanol
IBE	isopropanol/n-butanol/ethanol
IPA	isopropanol
LCA	life-cycle analysis
LD	light duty
LHV	lower heating value
LLNL	Lawrence Livermore National Laboratory
LSPI	low speed pre-ignition combustion (also known as superknock)

Mbpy	million gallons per year
2-MF	2-methylfuran
MFSP	minimum fuel selling price
MON	motor octane number
NOx	nitrogen oxides
NREL	National Renewable Energy Laboratory
OI	octane index
ORNL	Oak Ridge National Laboratory
PM	particulate matter
PMI	particulate matter index
PNNL	Pacific Northwest National Laboratory
R&D	research and development
RBOB	reformulated blendstock for oxygenate blending
RCM	rapid compression machine
RON	research octane number
RVP	Reid vapor pressure
S	octane sensitivity
sBOB	summer blendstock for oxygenate blending
SI	spark-ignition
S_L	laminar flame speed
SOT	state of technology
$T_{c,90}$	critical temperature of a catalyst where 90% of carbon monoxide, unburned hydrocarbons and nitrogen oxides are converted into less harmful gases
TEA	techno-economic analysis
UL	Underwriter's Laboratory

USDA	United States Department of Agriculture
VTO	Vehicle Technologies Office
YSI	yield sooting index

Executive Summary

Purpose

More efficient engines enabled by better fuels derived from biomass could increase the fuel economy of the light duty (LD) fleet by 10% over current technology and planned developments. This report identifies top LD boosted spark ignition (BSI) biofuel candidates for further development and commercialization identified using a fuel property basis. The BSI merit function was used to evaluate the performance of candidate bio-blendstocks in improving engine efficiency. This report is aimed at biofuel researchers looking to better understand the efficiency implications of biofuels under development, as well as engine researchers who are interested in future biofuels with properties that enable more efficient engine design and operation.

The Co-Optima team includes experts of from nine national laboratories: Argonne National Laboratory, Idaho National Laboratory, Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, the National Renewable Energy Laboratory, Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and Sandia National Laboratories. The team's expertise includes biofuel development, fuel property testing and characterization, combustion fundamentals, modeling and simulation from atomic scale to engine scale, and analysis.

- A tiered screening process efficiently and effectively screened hundreds of blendstocks.
- Ten blendstocks were identified with the potential to increase engine efficiency by 10% using the efficiency merit function.
- Six of the blendstocks were determined to have the fewest significant practical barriers to adoption and use.
- The blendstocks all have the potential to reduce greenhouse gas emissions by at least 60%.
- All of the top-performing blendstocks were determined to have the potential to be produced at a competitive cost.
- Co-Optima researchers identified barriers to adoption and key research gaps to be addressed in future research.

Findings

A tiered screening process was developed to efficiently screen potential blendstocks using small volumes initially, with more detailed screening conducted only for those which showed promise and for which no showstopper barriers (biodegradability, toxicity) were identified. More than 400 blendstocks were evaluated, including those derived from a broad range of production pathways. The majority of the blendstocks were single components, with a smaller number of simple mixtures and several complex thermochemical mixtures. Generally, the thermochemical mixtures did not provide target values of critical fuel properties and upgrading approaches to improve the properties of these mixtures were too complicated or required complex separations to implement. Several promising simple mixtures were identified and tested, and one of these mixtures made the final list of top blendstocks.

Maximizing BSI engine efficiency requires fuels with higher research octane number and higher-octane sensitivity, and increased heat of vaporization, along with low particular matter index (PMI; <2 leads to no merit function score decrease). While some properties blend in a linear fashion (heat of vaporization, PMI), autoignition properties blend in a complex manner that depends on the base fuel as well as the blendstock. Synergistic blending for octane and octane sensitivity increases the relative merit function impact of some blendstocks at a given blending level compared to that expected for linear blending.

Top Blendstocks

The blendstocks with the highest increase in merit function were: cyclopentanone, di-isobutylene, ethanol, a furan mixture (40/60 vol% mixture of 2-methylfuran and 2,5-dimethylfuran), a fusel alcohol blend, isobutanol, methanol, prenol, n-propanol, and isopropanol. Six of these were assessed to have the fewest significant practical barriers to adoption and use: di-isobutylene, ethanol, a fusel alcohol blend, isobutanol, n-propanol, and isopropanol. The top performing blendstocks with the fewest barriers to adoption include alcohols and an olefin (alkene). An additional fifteen blendstocks were identified which have potential to substantially improve engine efficiency, though not to the same level as for the top 10 blendstocks. These are: anisole, a bioreformate (an aromatic-rich mixture of species), 1-butanol, 2-butanol, 2-butanone, ethyl acetate, ethyl butanoate, methyl acetate, 3- or 4-methylanisole, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-pentanol, 2-pentanone, and propyl acetate. Several of these have significant practical barriers to commercial adoption, including the ketones, the esters and the aromatics.

The potential economic and environmental impacts of most of the top performing blendstocks were evaluated via techno-economic and lifecycle analysis. Additional analyses to evaluate environmental partitioning and biodegradability were also conducted. The findings of these analyses indicate that all of the top performing blendstocks have the potential to be produced at an acceptable cost with additional development and would reduce greenhouse gas emissions compared to petroleum-based fuels.

Barriers and Challenges

There are a number of outstanding challenges for the most promising blendstocks identified by Co-Optima. Foremost, only two (ethanol and isobutanol) are currently allowed in market fuels. Any new blendstocks would have to go through the normal fuel certification process. Second, the production cost of all of blendstocks identified is significantly higher than fuels on the market today; finding ways to value the enhanced fuel properties could help, along with process improvements. Third, fuel system and infrastructure compatibility, emissions impacts and health and safety impacts would have to be determined to be acceptable prior to the fuel certification process. Finally, the efficiency and environmental impacts must be confirmed in engine tests and more detailed analyses, along with opportunities for refinery integration.

1 Introduction

1.1 Purpose

Co-Optimization of Fuels & Engines (Co-Optima) focuses on developing new high-performance fuels that can boost engine efficiency and cut emissions when combined with advanced combustion approaches. One goal is to achieve a 35% improvement in LD vehicle fuel economy by 2030 (relative to a 2015 baseline), which is 10% beyond the improvements that will be realized with current fuels and planned engine-design improvements. Advanced turbocharged, or "boosted", spark ignition (BSI) engines with higher compression ratio have been identified that are capable of significantly improved efficiency, but new fuels are required to maximize benefits. There is an opportunity to exploit fuel properties and composition to enhance engine efficiency, particularly from biomass-derived fuels that may offer unique properties in addition to potentially low carbon-intensity.

To identify improved fuels, Co-Optima takes a fuel property-based approach based on two central hypotheses. The first, the Central Engine Hypothesis, states that there are engine architectures and strategies that provide higher thermodynamic efficiencies than are available from modern internal combustion engines and that new fuels are required to maximize efficiency and operability across a wide speed/load range. The second, the Central Fuel Hypothesis, states that if we identify target values for the critical fuel properties that maximize efficiency and minimize emissions for a given engine architecture, then fuels that have properties with those values (regardless of chemical composition) will provide comparable performance. This approach provides a basis for generalizing knowledge of engine behavior to evaluate potential fuels and their properties.

This report identifies the top biomass-derived fuel candidates identified by the Co-Optima initiative for blending with a petroleum base fuel. These are defined as those with the highest potential to increase boosted spark ignition engine efficiency and reduce greenhouse gas emissions with the fewest barriers to adoption.

This report also summarizes the resulting development and application of a screening methodology based on these hypotheses to identify candidate biomass-derived fuels (bio-blendstocks) for blending with a petroleum base fuel to identify those with the highest potential for increased efficiency and reduced environmental impact. The use of an efficiency "merit function" to quantify the potential for increased efficiency is a unique attribute of this approach (Miles 2018). The report also references analyses focused on identifying barriers to adoption, including techno-economics, life-cycle impacts, compatibility, and ability to meet current market requirements. A follow-up report will include the fuel property attributes, challenges and barriers, and research and development (R&D) needs for fifteen additional bio-blendstocks which exhibit high merit function scores, within three merit function points of the E10 premium comparator.

1.2 Background

This is the first systematic assessment of the suitability of a broad range of biomass-derived molecules and mixtures across many chemical families for use as BSI blendstocks. Past efforts to develop alternative liquid fuels derived from biomass have focused on cost including titer, rate and yield or conversion efficiency and selectivity for biochemical and thermochemical approaches, respectively. The decades of work on biofuels have led to the development and use of ethanol in large quantities, biomethane and bio-derived diesel fuels, including fatty acid methyl esters and hydrocarbons ("renewable diesel"). Many other chemistries have been explored, usually starting with the question, "what can I make efficiently?". Many fine books and reviews have been written regarding the conversion of biomass into complex mixtures, simple mixtures and single molecules. Despite this large body of work, advanced biofuels offering greater than 60% reduction in carbon emissions are still not widely used. A new approach to identify improved value propositions is needed, in addition to research, development and engineering focused on improving the techno-economics of known biofuel targets.

In more than a century of experience with hydrocarbon fuels from petroleum, we have developed a foundation for the development of new fuels and biofuels specifically. The properties required for boosted spark ignited engines are well-defined, with those factors that lead to high-efficiency refined within Co-Optima. There are databases with key fuel properties related to knock resistance (which results from the details of the autoignition kinetics on a particular pressure-temperature trajectory) for many hydrocarbon molecules, covering a range of chemical families including unbranched hydrocarbons (n-paraffins), branched hydrocarbons (iso-paraffins), cyclic hydrocarbons (naphthenes), and aromatics. There is also a wealth of literature focused on the behavior of these classes of molecules and their mixtures. Finally, there is a great deal of literature on the fuel properties and performance of alcohols, especially ethanol, methanol, and butanol. There are modest amounts of information on other oxygenates. Co-Optima cast a wide net to identify bio-blendstocks across a wide range of oxygenates and hydrocarbons, specifically looking to identify those that confer advantageous fuel properties for BSI.

To identify new or improved value propositions for new and existing biofuels, Co-Optima instead posed the questions: "What fuel do engines want?", "What fuel options work best?" and "What will work in the real world?". The answer to the first question is encapsulated in the efficiency merit function for LD BSI, described in detail by Miles (2018), and summarized later in this report. The answer to the question, "What fuel options work best?" is answered in this report, along with a partial answer to the final question, "What will work in the real world?". The merit function (Equation 1); a brief description of the terms in the merit function is provided in Section 1.3.

Additional Co-Optima publications are in development that will fully address the questions of impact and value of bio-blendstocks which can improve BSI engine efficiency. Key components of the answer to this question are the techno-economics (estimated cost of production), life-cycle impacts (carbon emissions, water use, fossil energy consumption, etc.), and fuel infrastructure and engine impacts (materials compatibility, emissions impacts, engine performance including phenomena such as low-speed pre-ignition/LSPI or "superknock").

The Co-Optima team includes experts in the conversion of biomass, in the details of fuel chemistry, fuel testing and combustion, engine experts, and in the development and application of techno-economic and life-cycle models.

1.3 Research Methodology and Approach

Co-Optima developed a three-tiered screening process, described in detail in Farrell, et al. (2017) which efficiently evaluated more than 400 candidate blendstocks, including single molecules, simple and complex mixtures. The final screening in the process focuses on the potential for increased efficiency using the BSI merit function (Miles 2018). In the final set of Co-Optima evaluations described in this report, an additional cohort of blendstocks was screened using the merit function. The new blendstocks were identified through the use of structure-property relationships and/or fuel property testing in the final half of the Co-Optima BSI efforts. In some cases, the blendstocks were evaluated as blended in an E10 base fuel (i.e., co-blended with 10 vol% ethanol), as synergistic effects were identified for some blendstocks (particularly some esters).

The updated version of the merit function depends on the values of six fuel properties of the blended fuel. These are:

- research octane number (RON)
- octane sensitivity (S)
- heat of vaporization (HoV)
- flame speed (S_L)
- particulate matter index (PMI)
- catalyst light-off temperature ($T_{c,90}$).

Other quantities required to calculate the merit function include the air-to-fuel ratio (AFR), density (to derive some quantities from volumetric mixing), and molar mass.

The merit function takes the form:

$$\begin{aligned} Merit = {} & \frac{(RON_{mix}-91)}{1.6} - K\frac{(S_{mix}-8)}{1.6} \\ & + \frac{0.085[ON/kJ/kg]\cdot((HoV_{mix}/(AFR_{mix}+1))-(415[kJ/kg]/(14.0[-]+1)))}{1.6} \\ & + \frac{((HoV_{mix}/(AFR_{mix}+1))-(415[kJ/kg]/(14.0[-]+1)))}{15.2} \\ & + \frac{(S_{L\,mix}-46[cm/s])}{5.4} \\ & - H\left(PMI_{mix}-1.6\right)\left[0.7+0.5\,(PMI_{mix}-1.4)\right] \\ & + 0.008\,{}^{\circ}C^{-1}\left(T_{c,90,conv}-T_{c,90,mix}\right) \end{aligned} \tag{1}$$

Octane index is a formalism relating autoignition resistance to RON and S via the equation:

$$OI = RON - K \cdot S \tag{2}$$

Where octane index (OI) is the octane index, RON and S as defined above, and K = Kalghati K-factor. The K-factor is engine-specific. In fact, the K-factor varies not just by engine, but also by engine operating condition. Following Szybist and Splitter (2017), we have used -1.25 as the basis for this analysis to represent a highly-boosted direct injection (DI) engine operating condition. We have also calculated the merit function score for K = -0.25, representing a low load condition, to make sure candidate bio-blendstocks were not high-performing under boosted conditions, but performing poorly under other operating conditions. The lower K value corresponds to conditions typical for legacy engines employing naturally aspirated port-fuel injection approaches.

On average, the largest contributors to merit function score were RON, S, and HoV. RON and S relate the potential efficiency improvements of the engine to the fuel's resistance to autoignition for engine operating with high compression ratio. High HoV produces cooling of the fuel-air mixture as the fuel evaporates ("charge cooling") in DI engines. High HoV fuels can provide a modest amount of additional efficiency.

Flame speed impacts dilution tolerance of exhaust gas recirculation (EGR). Flame speed depends on the specific composition of the base fuel (Farrell 2004; Szybist and Splitter 2017; Kolodziej et al. 2017a). Measurements focused on understanding flame speed impacts varied flame speed by 5–7 points and saw up to 1% increase in indicated thermal efficiency, although uncertainty remains in the impacts of flame speed. Given the small relative increase achievable with increased flame speed and the lack of measurements for the blended fuels containing candidate bio-blendstocks, the flame speed term was omitted in this analysis.

The majority of blendstocks examined saw no contribution to their score from the PMI term. However, blendstocks with high PMI saw a significant decrease in their merit function score due to the Heaviside function term used to estimate the decrease in efficiency for gasolines which generate large enough amounts of particulate matter (PM) to require a gasoline particulate filter to meet emissions requirements.

The catalyst light-off temperature term captures changes in the amount of fuel used to warm up emissions control catalysts during cold start. In modern vehicles, the majority of emissions occur during cold start, when the catalyst is too cold to convert the emitted pollutants (carbon monoxide/CO, non-methane organic gases/NMOG, and nitrogen oxides/NO_x) into less harmful gases (CO_2, H_2O, and N_2). Similar to the gaseous emissions, the majority of PM emissions are generated in the first 1–2 minutes of cold operation. While the delayed catalyst light-off may contribute to some of the semi-volatile organic compounds on the surface of the particles generated at cold-start, the cold surface of the combustion chamber and oil contribute to the increased particulate generated. Fuel contact with the cold walls prior to combustion and the temperature gradients within the chamber during combustion both facilitate the incomplete combustion of the fuel causing PM production. Since PM production is directly related to the fuel, changes in both the chemical and physical properties can influence the number and composition of the resulting PM.

Catalyst heating strategies are used to accelerate catalyst warm up, but these strategies rely on less efficient engine operation and result in a fuel penalty. The temperature at which a certain fraction of pollutants is converted over the catalyst, known as the catalyst light-off temperature, is a commonly used metric for catalyst activity. The temperature at which 50% of the emissions are converted is denoted as $T_{c,50}$, while the temperature at which 90% of the emissions are converted is denoted as $T_{c,90}$. Reducing (or increasing) the $T_{c,90}$ of the blended fuel by 125 °C would increase (or decrease) the engine efficiency by 1%. Changing fuel composition impacts exhaust speciation, and therefore can alter catalyst light-off temperatures. (Pihl et al. 2018) Synthetic exhaust flow reactor experiments conducted with an aged commercial three-way catalyst formulation using industry-developed evaluation protocols showed light-off temperatures can vary significantly for neat blendstocks: the difference between the highest and lowest measured $T_{c,50}$s was 90 °C, while the difference between the highest and lowest measured $T_{c,90}$s was 120 °C (Majumdar, et al., in press). However, when the blendstocks are mixed into more realistic fuel blends with petroleum-derived constituents, the measured light-off temperatures are all quite similar. The blend $T_{c,50}$s varied on the order of 10 °C (corresponding to a 0.08% theoretical change in fuel efficiency) while the blend $Tc,_{90}$s were within experimental error. Therefore, we have neglected this term in the merit function calculations.

Increasing RON and S provides the most straightforward pathway to increased efficiency. Although increasing RON is more easily achieved in real fuel, we note that each point of increase in S provides a larger benefit in a BSI engine designed for higher efficiency (given that our analysis assumed the absolute value of K is larger than 1). Figure 1 shows a series of hypothetical gasolines and their predicted efficiency increase in engines designed for such a fuel. The merit function indicates that gasoline with RON = 102 and octane sensitivity = 12 could achieve a 10% engine efficiency improvement – the Co-Optima target for light duty engines – over today's E10 regular fuel in an engine designed for these properties.

Details of the merit function calculations are provided in Section 2.

The analysis team evaluated the scalability and the economic and environmental viability of 24 bio-blendstocks produced from cellulosic biomass and, as a reference case, cellulosic ethanol. Dunn et al. (2018) report the results of these evaluations and Cai et al. (2018) provide detailed results for two bio-blendstocks, aromatic-rich hydrocarbons and isobutanol. Within these evaluations, the team evaluated the target cost, which is based on a modeled conversion process that considers the potential of the technology at full scale, and a state of technology cost, which reflects the current performance of the process. Other factors that were considered include whether the bio-blendstock could be used for other high-value purposes, such as in the chemical market, which could detract from their availability and use as a fuel, whether their economic viability depended on co-production of a valuable co-product, and whether any feedstock or intermediate compound in a bio-blendstock's production route would experience competition for other uses potentially limiting bio-blendstock production.

The research results presented in this report have several limitations. First, the research did not evaluate all possible molecules and mixtures. Furthermore, it does not identify all possible combinations of blendstocks with the fuel properties required to achieve engine efficiency targets. Finally, Co-Optima did not perform detailed techno-economic or life-cycle analyses (TEA and LCA, respectively) on all the blendstocks with the highest merit function scores. The relatively early stage of development of blendstock production prevented such an analysis for some candidates, while others were identified as particularly promising late in the evaluation process.

This report and companion journal articles describing the analysis outputs (including benefits and potential refinery integration implications) complete the Co-Optima efforts to identify fuel-engine combinations with the potential to significantly increase the efficiency of BSI engines. While other factors may determine whether a fuel with these characteristics could enter the marketplace, the Top 10 bio-blendstocks described herein could achieve the Co-Optima target efficiency blended into a petroleum base fuel, typically called a blendstock for oxygenate blending (BOB).

1.4 Overview of Content

The rest of the report is organized as follows. The details of the development and application of the tiered screening process are given in Section 2, along with a description of the set of candidates and their evaluation using the tiered screening process, including merit function calculations. Section 3 describes in some detail the ten bio-blendstocks with the highest merit function scores, including a brief summary of the characteristics, fuel properties, engine performance, challenges and barriers, and R&D needs. The merit function score details and datasheets for the ten bio-blendstocks in Section 4 are provided in Appendix A.

2 Evaluating Potential for Efficiency Increases Enabled by New Biofuels

2.1 Application of the BSI Merit Function

Co-Optima has taken the approach that biomass-derived fuels are likely to be blended into a petroleum base fuel in a manner similar to current market fuels such as E10 (10% ethanol blended into a petroleum base fuel). The Tier 1 and Tier 2 RON screening criteria (McCormick et al. 2017) ensure that all candidate bio-blendstocks exhibit a neat RON > 98, and that they increase the RON of the base fuel used for blend testing to >98 at a blending level of 30% or less. In order to differentiate the candidate bio-blendstocks, we have chosen to use the merit function score of an E10 premium as the bar that each candidate must clear to be selected for the final cohort.

The screening approach, therefore, evaluates the potential of biomass blended into a petroleum base fuel to increase engine efficiency. Candidate blendstocks were blended into a base fuel and then critical fuel properties were measured (particularly RON and S, with $T_{c,90}$ measured for many blendstocks as well). HoV blends linearly and literature values were used to estimate HoV contributions. PMI was determined from measured or estimated vapor pressure at 443 K and a simple calculation of the double bond equivalent (DBE). Methods to measure S_L require large amounts of fuel and were therefore not generally conducted (although ongoing research conducted by Co-Optima university teams is developing small volume flame speed testing capabilities). Details on each of these measurements and calculations are provided below.

In order to determine the merit function score on a consistent basis, the score should be calculated using the same BOB properties. However, the same BOB was not available for all measurements (and BOBs can change over time due to evaporative losses, etc., so measurements at different points in time would likely be slightly different). The petroleum BOB used to test candidates was either a four-component surrogate or one of several actual reformulated BOBs meeting California fuel specifications (CARBOB). Batch-to-batch variations led to small variations in the properties of each of the BOBs used for measurements of bio-blendstock blending performance. Co-Optima researchers therefore calculated the merit function in three BOBs representative of a range of fuel properties covering summer (sBOB), conventional winter (cBOB) and reformulated (rBOB) gasoline properties using an approach described below.

A few bio-blendstocks at a very early stage of research were only available in small volumes, so that only one or two RON and motor octane number (MON) measurements could be made. In these cases, a single blend level was used, typically 20%.

Some blendstocks were also tested co-blended with 10 vol% ethanol in the four-component surrogate BOB. Ethanol is likely to remain a key part of the nation's fuel mix given its current market penetration and performance advantages. Therefore, new bio-blendstocks may also be co-blended with ethanol, potentially leading to new and unexpected behavior. Synergistic blending of esters, for instance, was reported by Albrecht (2017). The blending RON (bRON) was determined by the changes in RON and MON compared to the E10 alone. This ensured the changes derived from blending in the ethanol are accounted for separately. The other fuel properties were also compared against the E10 properties. In all cases where co-blending was evaluated, the total bio-blendstock content was kept at or below 30 vol%, or 10 vol% ethanol plus 10 vol% or 20 vol% of the candidate bio-blendstock.

2.1.1 Calculating RON, MON, and S

Co-Optima researchers used an approach to determine an "effective blending RON". This approach calculated the blending RON and MON at each measured blend level (typically 10, 20, and 30 vol%). This bRON was used to calculate the fuel properties at the corresponding blend level.

The resulting bRON values were used to calculate the increase in RON and S expected when blended into the representative test BOBs. Some blendstocks exhibit synergistic blending. Synergistic blending means that bRON is greater than the sum of the pure-component RONs. The opposite effect is called antagonistic blending, where the bRON is less than the sum of the pure-component RONs. bRON can be calculated on a volumetric or molar basis. For commercial blending purposes, volumetric is more meaningful. For fundamental research, molar blending is more useful. All candidates presented here exhibited some level of synergistic blending in a BOB or E10.

2.1.2 Calculating HoV and PMI

HoV blends linearly. HoV values were determined from the literature value for the component(s) in the bio-blendstock and from the detailed hydrocarbon analysis for the BOBs.

PMI was calculated using the formula developed by researchers at Honda (Aikawa et al. 2010; Aikawa and Jetter 2014),

$$\mathrm{PMI} = \sum_{k=1}^{n} \left(\frac{DBE_k + 1}{VP_{|443K|_k}} \right) \times Wt_k \tag{3}$$

where k is each component of the fuel; and DBE is the double bond equivalent, $VP_{|443K|}$ is the vapor pressure at 443 K in kPa, and Wt_k is the weight percent for each component. The composition of the bioreformate was calculated from the detailed hydrocarbon analysis conducted by researchers at the National Renewable Energy Laboratory (NREL). Most blendstocks had no contribution from this term as their PMI was lower than 2. However, those with very low vapor pressure (i.e., 2-phenylethanol/2-PE and solketal) or high aromaticity (and therefore high double bond equivalent number) like anisole and methylanisole did see a reduction in their merit function score.

2.1.3 Fuel Properties

Table 1 describes the approach Co-Optima researchers took to determine the fuel properties used to determine the merit function score for each bio-blendstock. These values were used to calculate the merit function score in each of the three BOBs used for evaluation. The resulting merit function scores were compared to an E10 premium to evaluate whether a given bio-blendstock had the potential to improve performance compared to market fuels. In order to be considered for further evaluation, a bio-blendstock had to exceed the performance of an E10 premium benchmark.

Table 1. Fuel properties used to calculate merit function score and approach used in this evaluation.

Fuel Property	Approach
Research octane number (RON)	Calculated using bRON from measurements at each blending level
Octane sensitivity (S)	bRON and bMON were used to determine RON and MON at each blending level, and then S was calculated from its definition
Heat of vaporization (HoV)	Calculated using mass-based blending approach
Flame speed (S_L)	Neglected
Particulate matter index (PMI)	Taken from FPDB or calculated, scaled by weight for blends
Catalyst light-off temperature ($T_{c,90}$)	Neglected

2.1.4 *Candidate Blendstocks*

The fuel properties, including RON, MON, S, HoV, density, PMI and air-to-fuel ratio (AFR), for each candidate bio-blendstock for which a merit function score was calculated are shown in Table 2. This list includes candidates which were previously reported in Farrell et al. (2017) that passed through the Tier 2 screening, as well as additional bio-blendstocks that were identified and evaluated after Tier 2 screening had been completed.[1]

Table 2. Blendstock fuel properties for all blendstocks for which merit function calculated. RON and MON values were measured using neat blendstocks.

Blendstock	RON	MON	S*	HoV (kJ/kg)	Density (g/mL)	PMI	AFR
Methyl acetate	120***	120***	0	439	0.927	0.12	6.49
Isopropyl acetate	120***	120***	0	363	0.870	0.13	8.74
Ethyl acetate	118	120***	-2	400	0.895	0.19	7.79
Ethyl butanoate	115	106	9	369	0.874	0.43	9.45
2-Propanol	113	97	16	744	0.785	0.076	10.3
2,2,3-Trimethylbutane	112	101	11	288	0.695	0.13	15.1
2-Butanone	111	106	5	481	0.800	0.21	10.5
Fusel alcohol blend #2	110	98	12	648	0.835	4.5	11.0
Methanol	109	89	20	1174	0.786	0.045	6.43
Ethanol	109	90	19	919	0.789	0.063	8.94
Isobutyl acetate	109	112	-3	306	0.875	0.25	9.45
2-Butanol	107	93	14	671	0.806	0.14	11.1
Di-isobutylene	106	87	19	318	0.715	0.57	14.7
2-Pentanone	106	103	2	446	0.801	0.36	11.2
Isobutanol	105	90	15	685	0.802	0.17	11.1
1-Propanol	104	89	15	789	0.805	0.12	10.3
4-Methylanisole	104	92	12	377	0.969	5.7	11.2
2-Methylfuran	103	86	17	392	0.916	0.32	10.0
Bioreformate	103	89	14	372	0.829	5.2	13.9

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[1] This approach, termed the "leaky funnel", ensured new knowledge and understanding would permit the evaluation of new blendstocks after the initial tiered screening was completed. Prenol, the fusel alcohol blends and a number of other bio-blendstocks were included in this evaluation on that basis.

Blendstock	RON	MON	S*	HoV (kJ/kg)	Density (g/mL)	PMI	AFR
Methoxybenzene (anisole)	103	91	13	428	0.989	3.3	10.8
2-Methylfuran/2,4-dimethylfuran (40%/60%)	102	87	15	355	0.903	0.57	10.5
2-Methyl-1-butanol	102	88	14	614	0.816	0.3	11.7
Cyclopentanone	101	89	12	504	0.944	0.74	10.6
n-Butyl acetate	101	100	1	369	0.876	0.37	8.74
1,2-Isopropylideneglycerol	101	**	**	374	1.06	1.4	7..79
3-Methyl-1-butanol	99	87	12	550	0.808	0.3	11.7
2-Pentanol	99	91	8	608	0.805	0.24	11.7
2,4-Dimethyl-3-pentanone	99	93	6	363	0.804	0.62	12.0
Ketone mixture	99	100	0	355	0.903	0.57	11.6
1-Butanol	98	85	13	708	0.810	0.22	11.1
3-Methyl-2-buten-1-ol (prenol)	93	74	19	512	0.848	0.93	11.2
Fusel alcohol blend #5	**	**	**	677	0.826	3.4	10.9
Fusel alcohol blend #4	**	**	**	691	0.819	1.8	10.8
n-Propyl acetate	**	**	**	389	0.888	0.47	8.74
Cyclopentanol	**	**	**	511	0.949	0.7	11.2
3-Methylcyclopentanol	**	**	**	446	0.900	2.3	11.7
3-Methylcyclopentenone	**	**	**	386	0.913	6.0	11.2

RON = Research octane number; MON = motor octane number; S = octane sensitivity; HoV = heat of vaporization; PMI = particulate matter index; C = carbon; H = hydrogen; O = oxygen; MW = molecular weight; AFR = air-to-fuel ratio under stoichiometric conditions.

* Some values for S may appear different than RON – MON based on values in table due to rounding.

** Not measured as a neat fuel.

*** Maximum octane measurable.

The tiered screening process eliminated blendstocks with RON <98. One such blendstock, prenol, was added back into the candidate list when its “hyperboosting” phenomenon was discovered. Prenol’s neat RON is only 93, but it exhibits a high bRON in blends with a BOB. Prenol has the unusual property of increasing the RON of the mixture to a higher value than either the BOB or neat prenol. A detailed study of prenol autoignition behavior is ongoing. For more detail, see the more detailed description of prenol in Section 3.7.

2.1.5 BOB Properties

Table 3. BOB fuel properties for BOBs used in merit function calculations or fuel property measurements used to derive bRONs.

BOB	RON	MON	S	HoV (kJ/kg)	Density (g/mL)
Conventional Winter Premium BOB (cBOB)	94	87	6	347	0.73
CARBOB	85	81	4	340	0.73
Summer BOB (sBOB)	88	82	6	353	0.74
4-component surrogate BOB	90	85	5	344	0.73
4-component surrogate E10	96	88	8	406	0.73*
NREL BOB	88	81	7	345	0.74
NREL BOB #3	87	81	6	358	0.71
PNNL CARBOB #3	87	85	6	345*	0.74*
RBOB #1	85	80	5	345*	0.74*
RBOB #2	90	87	3	345*	0.74*
RBOB #3	85	83	2	345*	0.74*
RBOB #4	87	83	4	345*	0.74*
RBOB #5	85	80	5	345*	0.74*

RON = Research octane number; MON = motor octane number; S = octane sensitivity; HoV = heat of vaporization; C = carbon; H = hydrogen; O = oxygen; MW = molecular weight; AFR = air-to-fuel ratio under stoichiometric conditions; *estimated as no measurement of density and/or HoV was made.

Table 3 shows that a blendstock might be added to a BOB with a wide range of properties. The range of BOBs used in these tests make direct comparisons between bio-blendstocks tested at different times and by different laboratories very difficult. Thus, the blending RON approach was used to facilitate comparison of bio-blendstock performance. The HoV and density were not measured for some of the BOBs. By comparison with other petroleum fuels, it is clear that the estimated values are close to the values measured for other base fuels, and a standard value was used.

2.1.6 Blending RON

Table 4 shows the calculated bRON for all of the blendstocks in the various BOBs in which they were blended. Multiple measurements are shown for prenol in petroleum BOBs to show the variation in autoignition behavior that is due to the different properties and chemistry of the BOBs. Also shown are comparisons to measurements in E10 for some of the ethers, esters, and ketones. In these measurements, the bRON is calculated in comparison to the E10.

The furans have the highest blending RON, followed by a series of alcohols. The alcohol bRON is highest for the smallest molecular weight and decreases as chain length increases. Notably, the furans and alcohols increase MON only modestly. Prenol in particular shows very low bMON. The anisoles, di-isobutylene, and bioreformate all exhibit bRON greater than or equal to 120 as well. The ketones and esters show a somewhat lower bRON. Esters show a mix of behaviors – no change, modest increase in bRON, modest suppression of bMON – with the specific impact dependent on the bio-blendstock and the base fuel.

Synergistic blending increases the merit function score and provides the largest potential value to consumers and refiners – literally the largest bang for the buck. 2-methylfuran, methanol, ethanol, prenol, and anisole show the largest synergistic blending.

Table 4. Blending RON and MON values used in merit function calculations, derived from RON and MON measurements of blendstocks splash-blended in various BOBs.

Blendstock	BOB	bRON (10%)	bRON (20%)	bRON (30%)	bMON (10%)	bMON (20%)	bMON (30%)
2-Methylfuran/2,4-dimethyl-furan mixture	4CS	169	146	128	124	105	98
2-Methylfuran	4CS	166	142	127	125	108	102
Methanol	4CS	161	155	134	126	111	105
Ethanol	4CS	149	147	131	119	112	107
3-Methyl-2-buten-1-ol (prenol)	RBOB1	145	135	125	117	99	90
Prenol	RBOB4	143	130	119	103	91	85
Prenol	RBOB3	140	129	119	94	88	87
Prenol	RBOB2	137	126	118	79	82	83
Prenol (average)	N/A	135	126	117	95	88	85
Prenol	4CS	123	119	112	92	86	83
Prenol	RBOB5	122	116	111	85	84	82
4-Methylanisole	PC3	135	129	126	110	104	103
4-Methylanisole	PC3 + E10	126	124		101	103	
1-Propanol	4CS	133	130	124	105	102	99
Di-isobutylene	4CS	128	130	126	108	101	97
Anisole	4CS	128	125	124	113	107	104
Cyclopentanone	4CS	126	125	124	110	103	101
2-Propanol	NBOB3	123	122	124	106	105	105
Fusel alcohol blend #2	RBOB4	122	123	122	108	105	104
Fusel alcohol blend #2	PC3	121	123	121	96	97	96
Fusel alcohol blend #2	PC3 + E10	119	117		95	94	
Fusel alcohol blend #4	PC3	126	127	123	94	95	95
Fusel alcohol blend #5	PC3	128	126	123	90	95	94
Bioreformate	4CS	120	116	114	100	97	94
2-Butanol	4CS	117	120	117	102	102	101
Cyclopentanol	PC3 + E10	117	116		92	99	
2-Butanone	PC3 + E10	117	116		95	99	
2-Butanone	4CS	114	118	118	109	106	108
1,2-Isopropylideneglycerol	RBOB1 + E10	117	113	114	88	94	95
1,2-Isopropylideneglycerol	RBOB1	104	105	106	93	95	92
Isopropyl acetate	PC3 + E10	116	117		102	106	
2-Pentanone	4CS	116	116	113	110	110	109
2-Pentanone	PC3 + E10	113	113		97	102	
n-Propyl acetate	PC3 + E10	115	115		102	108	

Blendstock	BOB	bRON (10%)	bRON (20%)	bRON (30%)	bMON (10%)	bMON (20%)	bMON (30%)
n-Propyl acetate	PC3	111	111	111	104	103	104
Ethyl butanoate	4CS	113	114	116	110	108	105
Ethyl acetate	4CS	112	116	117	114	110	111
Ethyl acetate	4CS + E10	112	115		111	114	
Methyl acetate	4CS	108	116	117	103	107	106
Isobutanol	4CS	107	125	121	100	100	96
Isobutyl acetate	PC3 + E10	107	110		101	105	
Isobutyl acetate	RBOB1	98	104	106	104	108	110
2-Pentanol	4CS	107	105	104	96	97	95
2-Methyl-1-butanol	4CS	104	106	106	93	90	90
3-Methylcyclopentanol	PC3		105			92	
n-Butyl acetate	4CS	99	102	101	99	97	98
1-Butanol	4CS	98	103	102	99	86	87
2,2,3-Trimethylbutane	NBOB	96	99	105	90	96	96
3-Methyl-1-butanol	4CS	95	98	100	89	88	88
Ketone mixture	4CS	94	98	99	98	102	101
2,4-Dimethyl-3-pentanone	4CS	81	97	101	92	94	97

4CS = 4-component surrogate; 4CS + E10 = 4-component surrogate plus 10% ethanol; NBOB = NREL BOB used to measure 2,2,3-trimethylbutane; NBOB3 = NREL BOB #3 used for blending measurements; PC3 = PNNL CARBOB #3; PC3 + E10 = CARBOB #3 plus 10% ethanol; RBOB1 = SNL RBOB #1; RBOB4 = SNL RBOB #4. To improve readability, multiple results for a given blendstock were grouped together, in order of highest bRON at 10% blend level.

2.2 Merit Function Scores for K = -1.25

This section describes the merit function scores calculated for K = -1.25 for each of the three BOBs (sBOB, cBOB, rBOB) at blend levels of 10%, 20%, and 30%. Where the bRON for a given bio-blendstock could not be calculated due to a data gap, the data is left blank. For instance, those bio-blendstocks evaluated in E10 do not have a merit function score at 30% bio-blendstock due to the limit on the total bio-blendstock content. The bio-blendstocks are sorted from highest to lowest for merit function score for the 20%/sBOB blend first, 30%/sBOB blend second, and 20% cBOB third.

Table 5. Merit function scores for candidate bio-blendstocks evaluated under engine operating conditions corresponding to K = -1.25 (high load and high boost).

	10%			20%			30%		
Blendstock	cBOB	CAR-BOB	sBOB	cBOB	CAR-BOB	sBOB	cBOB	CAR-BOB	sBOB
Methanol	7.1	0.3	3.6	15.0	9.0	11.9	15.6	10.4	12.9
Ethanol	5.7	-1.1	2.2	12.2	6.2	9.1	12.8	7.5	10.0
Furan Mixture*	7.7	0.9	4.2	11.9	5.9	8.8	12.2	6.9	9.4
Prenol/average	5.7	-1.0	2.2	9.7	3.7	6.6	11.4	6.2	8.7
1-Propanol	4.4	-2.4	0.8	8.6	2.6	5.5	11.3	6.1	8.6
Diisobutylene	3.0	-3.8	-0.6	7.7	1.7	4.5	11.0	5.7	8.3

	10%			20%			30%		
Blendstock	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**
Fusel alcohol blend #4	3.4	-3.4	-0.1	7.8	1.8	4.7	10.8	5.5	8.0
2-Methylfuran	7.2	0.4	3.7	10.3	4.3	7.2	10.6	5.4	7.9
Cyclopentanone	2.8	-3.9	-0.7	6.5	0.6	3.4	10.4	5.1	7.6
Isobutanol	1.0	-5.8	-2.6	7.3	1.3	4.2	10.2	4.9	7.4
Fusel alcohol blend #5	3.4	-3.4	-0.1	7.3	1.3	4.2	10.1	4.9	7.3
2-Propanol	2.8	-3.9	-0.7	5.8	-0.2	2.7	9.7	4.4	6.9
Fusel alcohol blend #2/average	1.9	-4.8	-1.6	5.5	-0.6	2.3	8.2	2.9	5.4
Anisole	1.9	-4.8	-1.6	4.8	-1.2	1.7	7.9	2.7	5.2
2-Butanol	2.2	-4.5	-1.3	5.5	-0.6	2.3	7.5	2.3	4.8
Fusel alcohol blend #2/E10	2.1	-4.6	-1.4	4.9	-1.1	1.8			
Methyl acetate	0.8	-5.9	-2.7	3.7	-2.3	0.6	6.2	1.0	3.5
2-Butanone	1.1	-5.6	-2.4	4.7	-1.3	1.6	6.0	0.8	3.3
Ethyl butanoate	0.8	-5.9	-2.7	2.7	-3.3	-0.5	5.5	0.3	2.8
Bioreformate*	1.6	-5.2	-1.9	3.5	-2.5	0.4	5.4	0.2	2.7
2-Methyl-1-butanol	1.1	-5.6	-2.4	3.3	-2.7	0.2	5.2	-0.1	2.5
Ethyl acetate	0.5	-6.3	-3.0	2.9	-3.1	-0.2	4.9	-0.4	2.1
1-Butanol	-0.1	-6.9	-3.6	3.4	-2.6	0.3	4.6	-0.7	1.9
1,2-Isopropylideneglycerol	1.0	-5.7	-2.5	2.5	-3.5	-0.6	4.4	-0.8	1.7
4-Methylanisole	2.5	-4.3	-1.0	5.3	-0.7	2.1	4.4	-0.9	1.7
4-Methylanisole/E10	2.5	-4.3	-1.0	5.0	-1.0	1.9			
1,2-Isopropylideneglycerol/E10	3.2	-3.5	-0.3	4.7	-1.3	1.6			
Cyclopentanol/E10	2.9	-3.8	-0.6	4.7	-1.3	1.5			
2-Butanone/E10	2.7	-4.1	-0.9	4.6	-1.4	1.5			
Isopropyl acetate/E10	1.9	-4.8	-1.6	3.6	-2.4	0.5			
n-Propyl acetate	1.7	-5.1	-1.9	3.2	-2.8	0.1	4.3	-1.0	1.6
2-Pentanone/E10	1.9	-4.8	-1.6	3.2	-2.8	0.1			
2-Pentanone	1.2	-5.5	-2.3	2.9	-3.2	-0.3	3.4	-1.9	0.7
n-Propyl acetate/E10	1.8	-4.9	-1.7	2.8	-3.2	-0.4			
Ethyl acetate/E10	0.7	-6.1	-2.8	2.1	-3.9	-1.0			
2-Pentanol	1.3	-5.5	-2.2	1.9	-4.1	-1.3	3.1	-2.1	0.4
3-Methylcyclopentanol				1.6	-4.4	-1.6			
3-Methyl-1-butanol	0.0	-6.7	-3.5	1.4	-4.6	-1.7	2.9	-2.4	0.2
Isobutyl acetate/E10	0.7	-6.1	-2.8	1.2	-4.8	-1.9			
2-Methylcyclopentenone				1.0	-5.0	-2.1			
2,2,3-Trimethylbutane	-0.2	-6.9	-3.7	-0.3	-6.3	-3.4	2.1	-3.2	-0.7
Butyl acetate	-0.2	-6.9	-3.7	0.9	-5.1	-2.2	1.1	-4.2	-1.7
2,4-Dimethyl-3- pentanone	-2.3	-9.0	-5.8	-0.3	-6.3	-3.4	0.7	-4.6	-2.0

	10%			20%			30%		
Blendstock	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**
Isobutyl acetate	-0.8	-7.6	-4.3	-0.3	-6.3	-3.4	-0.4	-5.6	-3.1
Ketone Mixture*	-0.9	-7.6	-4.4	-1.2	-7.2	-4.4	-0.7	-6.0	-3.4

CARBOB = California reformulated BOB; cBOB = conventional winter blend BOB; sBOB = premium summer blend BOB

*Mixture compositions:

Furan mixture = 40wt% 2-methylfuran, 60wt% 2,5-dimethylfuran

Bioreformate = 1.5wt% paraffins, 8.0wt% isoparaffins, 69.8wt% aromatics, 5.1wt% naphthalenes, 11.9wt% olefins, 1.0wt% oxygenates, 2.7wt% unidentified by DHA with GC/MS; Aromatics average C9-C10

Ketone mixture = 42.5wt% 2-pentanone, 11.4wt% methyl-isobutylketone, 30.3wt% 4-heptanone, and 15.8wt% 2-heptanone.

The merit function is composed of four individual scores – RON, S, HoV, and PMI. The contribution to the merit function score for each blendstock in each BOB is slightly different. Figure 1 shows the contribution (positive and negative) for each of the blendstocks blended into the regular summer BOB at 20%.

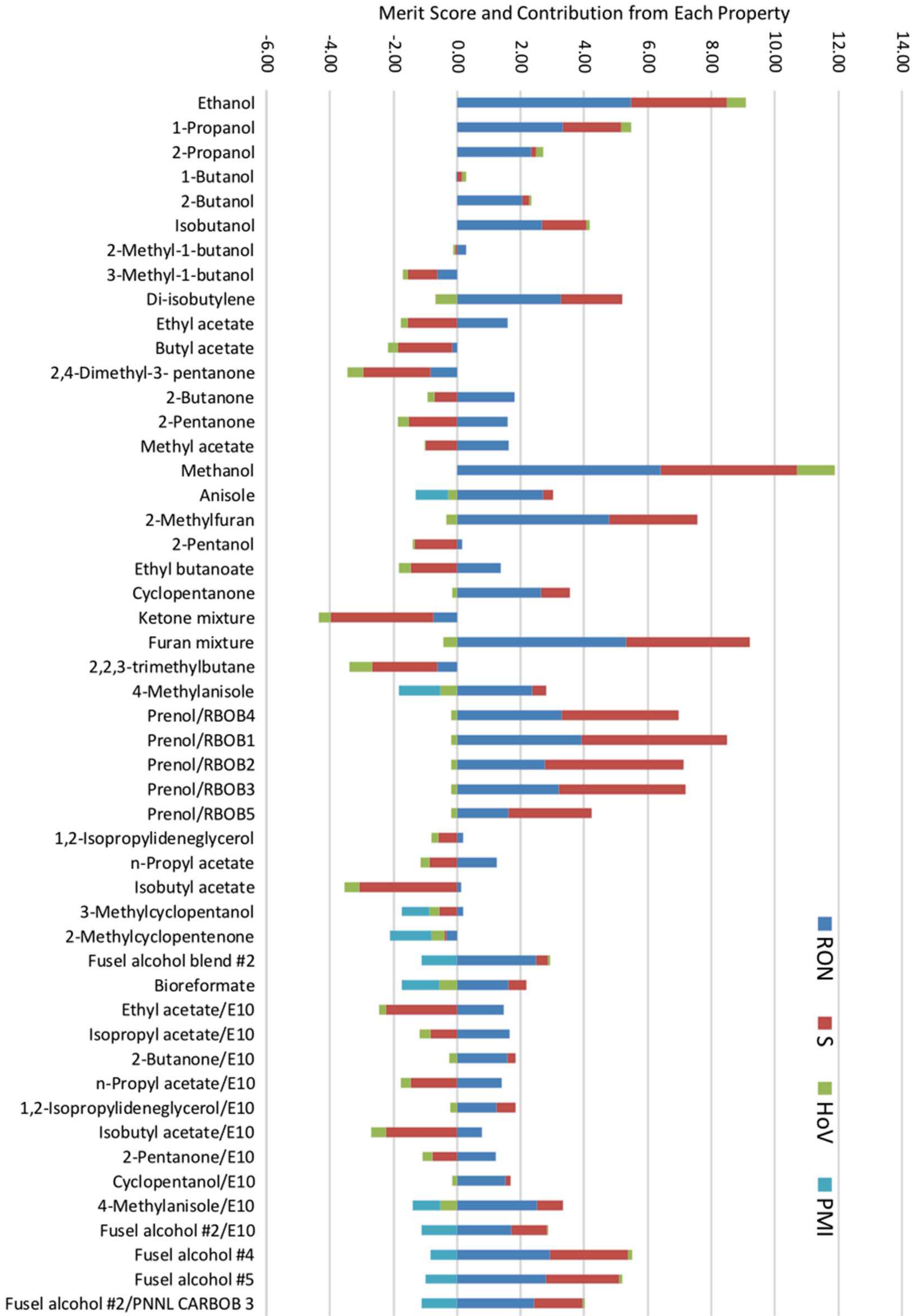


Figure 1. Merit function scores and contribution by fuel property for blendstocks blended into regular summer BOB at 20 vol% for an engine condition corresponding to K = -1.25 (highly-boosted conditions).

It is clear from Figure 1 that some blendstocks see large contributions from RON and others from S; in many cases the contributions are comparable. For a given blendstock at this engine operating condition, one point of increase in S leads to a higher merit function increase than one point in RON.

Only highly volatile blendstocks such as methyl acetate and the small alcohols exhibit large HoV contributions. The variability seen for prenol, which was tested in a number of reformulated BOBs, is indicative of the variability in fuel properties such as S in the base fuel, together with large non-linear blending effects which are, at this time, not easily estimated without conducting measurements.

2.3 Merit Function Scores for K = -0.25

The merit function score was also calculated for candidate bio-blendstocks using a K-factor value of -0.25, representing lower load (un-boosted conditions). The same caveats apply as for the K = -1.25 case. The bio-blendstocks are sorted from highest to lowest merit function score for the 20%/sBOB blend first, 30%/sBOB blend second, and 20% cBOB third.

Table 6. Merit function scores for candidate bio-blendstocks evaluated under engine operating conditions corresponding to K = -0.25 (low to moderate load and low boost).

	10%			20%			30%		
Blendstock	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**	**cBOB**	**CAR-BOB**	**sBOB**
Methanol	6.3	0.9	3.0	11.4	6.6	8.5	12.4	8.2	9.8
Ethanol	5.2	-0.2	1.9	9.6	4.8	6.7	10.5	6.3	7.9
1-Propanol	4.0	-1.4	0.7	6.9	2.1	4.0	8.8	4.6	6.2
Furan Mixture*	6.2	0.8	2.9	8.6	3.8	5.7	8.7	4.5	6.2
2-Propanol	3.2	-2.2	-0.1	5.5	0.7	2.6	8.3	4.1	5.8
2-Methylfuran	6.0	0.6	2.7	7.9	3.1	5.0	8.2	4.1	5.7
Cyclopentanone	3.2	-2.2	-0.1	5.6	0.8	2.7	8.1	3.9	5.5
Di-isobutylene	3.1	-2.3	-0.2	6.0	1.2	3.0	7.8	3.6	5.2
Isobutanol	1.9	-3.4	-1.3	6.0	1.2	3.0	7.8	3.6	5.2
Fusel alcohol blend #4	2.8	-2.6	-0.5	5.7	0.9	2.7	7.7	3.5	5.1
Fusel alcohol blend #5	2.9	-2.5	-0.4	5.3	0.5	2.4	7.3	3.1	4.8
Prenol/average	4.3	-1.1	1.0	6.5	1.7	3.6	7.3	3.1	4.7
2-Butanol	2.7	-2.7	-0.6	5.1	0.3	2.2	6.7	2.5	4.2
Anisole	2.3	-3.1	-0.9	4.4	-0.4	1.5	6.4	2.2	3.9
Fusel alcohol blend #2	2.0	-3.4	-1.2	4.4	-0.4	1.5	6.4	2.2	3.8
Methyl acetate	1.9	-3.5	-1.4	4.3	-0.5	1.4	6.3	2.1	3.7
2-Butanone	2.2	-3.2	-1.1	4.4	-0.4	1.4	6.2	2.0	3.7
Ethyl acetate	2.0	-3.4	-1.3	4.0	-0.8	1.1	5.8	1.6	3.3
1,2-Isopropylidene-glycerol/E10	2.8	-2.6	-0.5	4.1	-0.7	1.1	5.7	1.5	3.2
Ethyl butanoate	2.1	-3.3	-1.2	3.6	-1.2	0.7	5.6	1.4	3.0

	10%			20%			30%		
Blendstock	cBOB	CAR-BOB	sBOB	cBOB	CAR-BOB	sBOB	cBOB	CAR-BOB	sBOB
4-Methylanisole/E10	2.1	-3.3	-1.2	3.8	-1.0	0.9	5.4	1.2	2.9
n-Propyl acetate	2.4	-3.0	-0.9	3.7	-1.1	0.8	4.9	0.7	2.4
2-Pentanone	2.3	-3.1	-1.0	3.9	-0.9	1.0	4.8	0.6	2.2
2-Methyl-1-butanol	1.8	-3.6	-1.5	4.0	-0.8	1.1	4.4	0.2	1.9
Cyclopentanol/E10	2.8	-2.6	-0.5	4.3	-0.5	1.4			
2-Butanone/E10	2.7	-2.7	-0.6	4.3	-0.5	1.4			
Isopropyl acetate/E10	2.4	-3.0	-0.8	4.1	-0.7	1.1			
Fusel alcohol blend #2/E10	2.0	-3.4	-1.3	3.8	-1.0	0.9			
n-Propyl acetate/E10	2.4	-3.0	-0.9	3.7	-1.1	0.8			
Ethyl acetate/E10	2.1	-3.3	-1.2	3.7	-1.1	0.8			
2-Pentanone/E10	2.3	-3.1	-1.0	3.7	-1.1	0.7			
4-Methylanisole				3.5	-1.2	0.6	4.1	-0.1	1.5
1,2-Isopropylideneglycerol	1.7	-3.7	-1.6	2.8	-2.0	-0.1	4.1	-0.1	1.5
1-Butanol	1.3	-4.1	-2.0	3.1	-1.7	0.1	4.0	-0.2	1.4
Bioreformate*	1.7	-3.7	-1.6	2.9	-1.9	0.0	3.9	-0.3	1.4
2-Pentanol	2.0	-3.4	-1.3	2.7	-2.1	-0.2	3.7	-0.5	1.1
3-Methyl-1-butanol	1.1	-4.3	-2.2	1.9	-2.9	-1.0	2.9	-1.3	0.3
2,2,3-Trimethylbutane	0.8	-4.5	-2.4	1.2	-3.6	-1.7	2.7	-1.5	0.2
Isobutyl acetate	0.9	-4.5	-2.4	1.9	-2.9	-1.0	2.7	-1.5	0.2
Butyl acetate	1.2	-4.2	-2.1	2.1	-2.7	-0.8	2.6	-1.6	0.0
2,4-Dimethyl-3- pentanone	-0.2	-5.6	-3.5	1.2	-3.6	-1.8	2.2	-2.0	-0.3
Ketone Mixture*	0.8	-4.6	-2.5	1.2	-3.6	-1.8	1.8	-2.4	-0.8
Isobutyl acetate/E10	1.7	-3.7	-1.6	2.8	-2.0	-0.1			
3-Methylcyclopentanol				1.8	-3.0	-1.1			
2-Methylcyclopentenone				0.8	-3.9	-2.1			

Figure 2 shows the merit function calculation results for the same blending condition as shown in Table 6 for the same subset of blendstocks for a K value of -0.25.

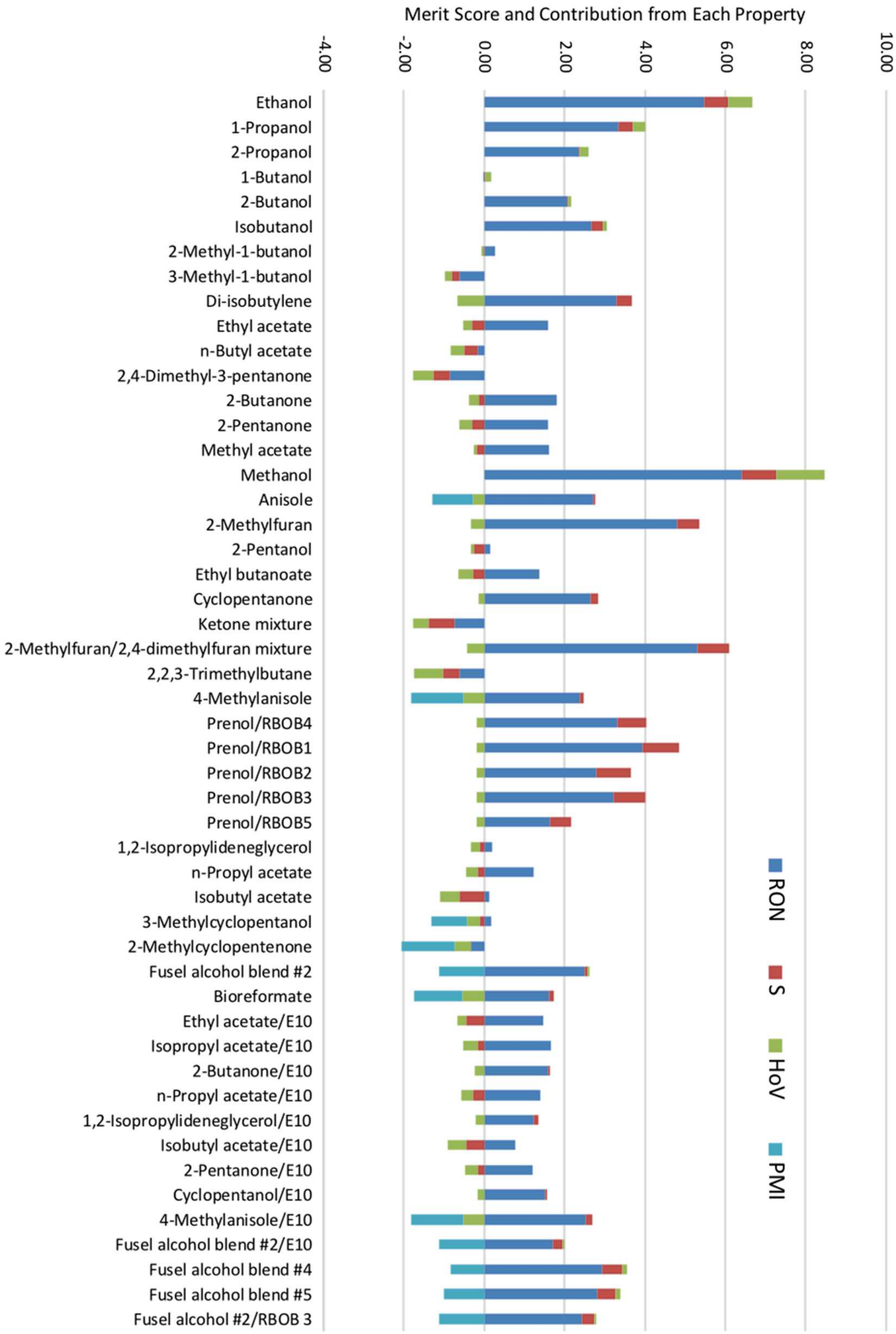


Figure 2. Merit function scores and contribution by fuel property for blendstocks blended into regular summer BOB at 20 vol% for an engine condition corresponding to K = -0.25 (moderate load conditions).

It is clear from Figure 2, that under low to moderate load, the primary contributor to efficiency is RON. Unlike under boosted conditions, the contribution due to S is small. Consistent with the K = -1.25 case, only highly volatile blendstocks such as methyl acetate and the small alcohols exhibit large HoV contributions.

2.4 Top 10 Bio-blendstocks Based on Merit Function Score

The 10 bio-blendstocks which exceed the score for E10 premium are shown in Figure 3. A brief description of each is provided in alphabetical order in this section, and detailed descriptions are provided in Section 3. Note that 2-methylfuran has a very high merit function score but is omitted from the Top 10. This is because a clear pathway to making this molecule from biomass was not identified within Co-Optima; a 60/40 mixture of 2-methylfuran (2-MF) and 2,5-dimethylfuran (2,5-DMF) does have a known production pathway and is included.

Cyclopentanone has high RON, moderate S and negligible HoV. Although most ketones do not exhibit appreciable S, the five-membered ring of cyclopentanone provides enough S to lead to a high merit function score when combined with the synergistic RON blending.

Di-isobutylene provides synergistic RON blending, with excellent S and slightly negative HoV. At higher blend levels, the synergistic RON blending is maintained, while the bMON decreases, leading to increased S proportional to blend level, even at 30%.

Ethanol has long been known to provide excellent autoignition resistance in the form of high RON with synergistic blending, excellent S and very high HoV. The merit function scores for ethanol were among the highest of the blendstocks tested.

The **furan mixture** – a 40/60 blend of 2-methylfuran and 2,5-dimethylfuran – has very strong synergistic RON blending at low blend levels, with the blending tending to more linear with increasing furan concentration. S is also very high at low blend levels, decreasing moderately at higher blend levels. HoV is slightly lower than the base fuel, leading to a small penalty in the merit function score. Overall, the furan mixture exhibited the highest merit function scores for some blend levels in some BOBs.

Given the components making up the **fusel alcohol blend**, it is not surprising that the fusel alcohol blend provides RON, S, and HoV in good measures. The three fusel alcohol blends reported herein differ in the relative amounts of the components. The merit function score for fusel alcohol blend #2 was only slightly higher score than 2-butanol due to the low volatility and high PMI of the 2-PE component. The 2-phenylethanol in fusel alcohol blends #4 and #5 comprises a smaller fraction of the mixture, leading to significantly smaller or no penalty from the PMI term.

Isobutanol exhibited very small synergistic blending RON at 10% (107 vs. 105 for neat isobutanol), but higher degrees of synergistic blending at higher concentrations (>120 at 20% and 30%). S also increased with blending level. The HoV contribution to the merit function score was modest but nonzero.

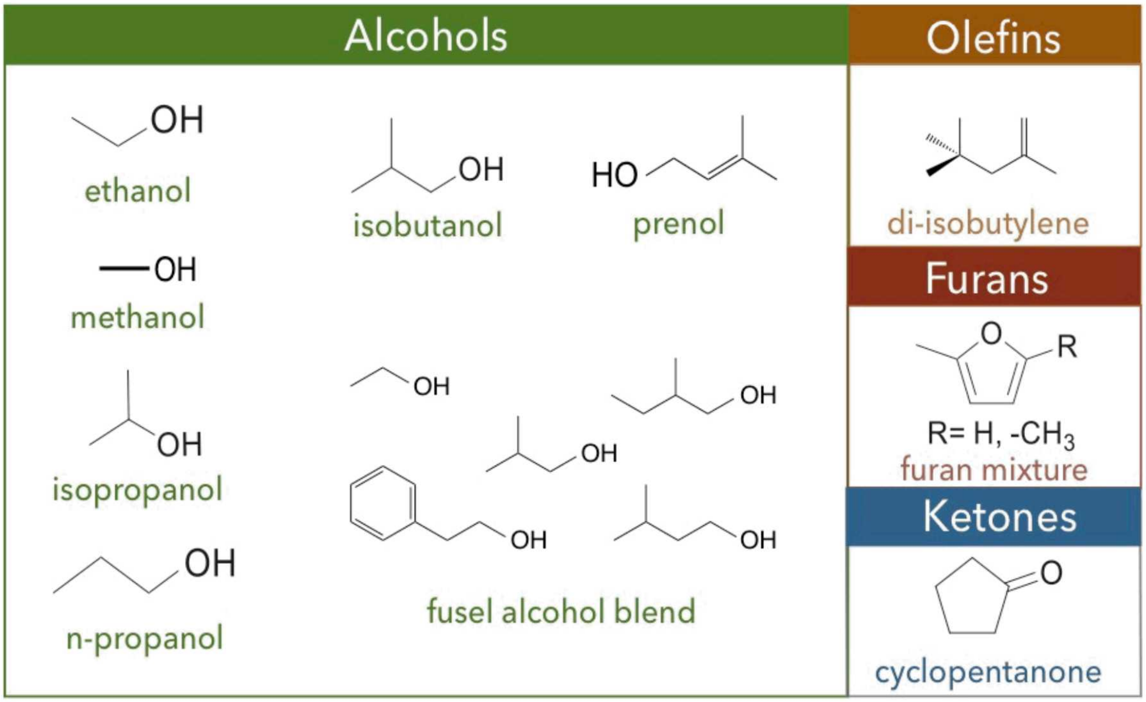


Figure 3. Ten bio-blendstocks with the highest potential engine efficiency based on merit function score. This evaluation is based solely on the ability to improve engine efficiency, as assessed through merit function values ≥ E10 premium (RON = 98) when blended in petroleum BOBs at levels up to 30% by volume.

Isopropanol exhibited synergistic RON and S blending that was essentially independent of concentration. The HoV contribution was lower than ethanol but still significant.

Methanol had the highest HoV contribution, high and synergistic RON blending, and excellent S. The S contribution peaked at blend level of 20%. The combination of these properties led to some of the highest merit function scores across the BOBs and blend levels.

Like isopropanol, **n-propanol** exhibited synergistic RON and S blending, but unlike isopropanol, the effect was larger at lower blending concentrations. Furthermore, n-propanol exhibited higher S. The HoV contribution was slightly higher than seen with isopropanol. Overall the merit function scores for n-propanol were higher than its C3 alcohol counterpart.

Prenol demonstrated synergistic RON blending, very high S and negligible HoV contribution. The high merit function scores are largely due to the very high S. By measuring prenol's blending behavior in a large number of reformulated BOBs, we are able to estimate the range of variability expected from variations in BOB chemistry. The bRON values at 10% prenol concentration varied from 122 to as high as 145, while blending S varied from 28 to 58. The differences decrease along with the degree of nonlinearity as prenol concentration increases.

Two bio-blendstocks with high scores were omitted – anisole and 2-methylfuran – as we did not find good routes to production starting with biomass. Single-component approaches and/or mixtures containing these components with other high potential components could be developed by enterprising researchers.

2.4.1 High Potential Bio-Blendstocks Within Three Merit Function Points of the Top 10

The merit function is not a precise evaluation tool, and the large variations in market fuel composition may lead to variations in the performance of a specific blendstock. The variability in individual blendstock merit function scores suggests a range of potential efficiency increases for a given blendstock. Therefore, other bio-blendstocks may be nearly as good as some of the Top 10 reported herein. An additional 15 blendstocks have been identified which have the potential to increase BSI engine efficiency nearly as much as the Top 10. Some of these additional bio-blendstocks were studied within Co-Optima to test fuel property hypotheses or to compare different chemical functionalities. The 15 bio-blendstocks are shown in Figure 4 with chemical structures.

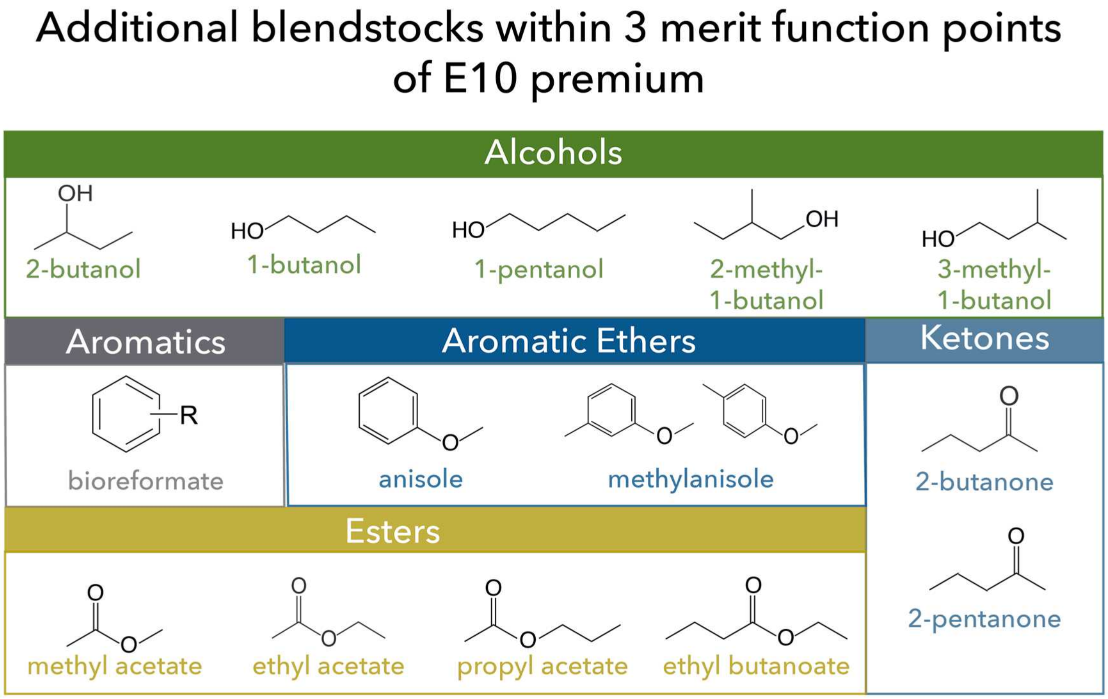
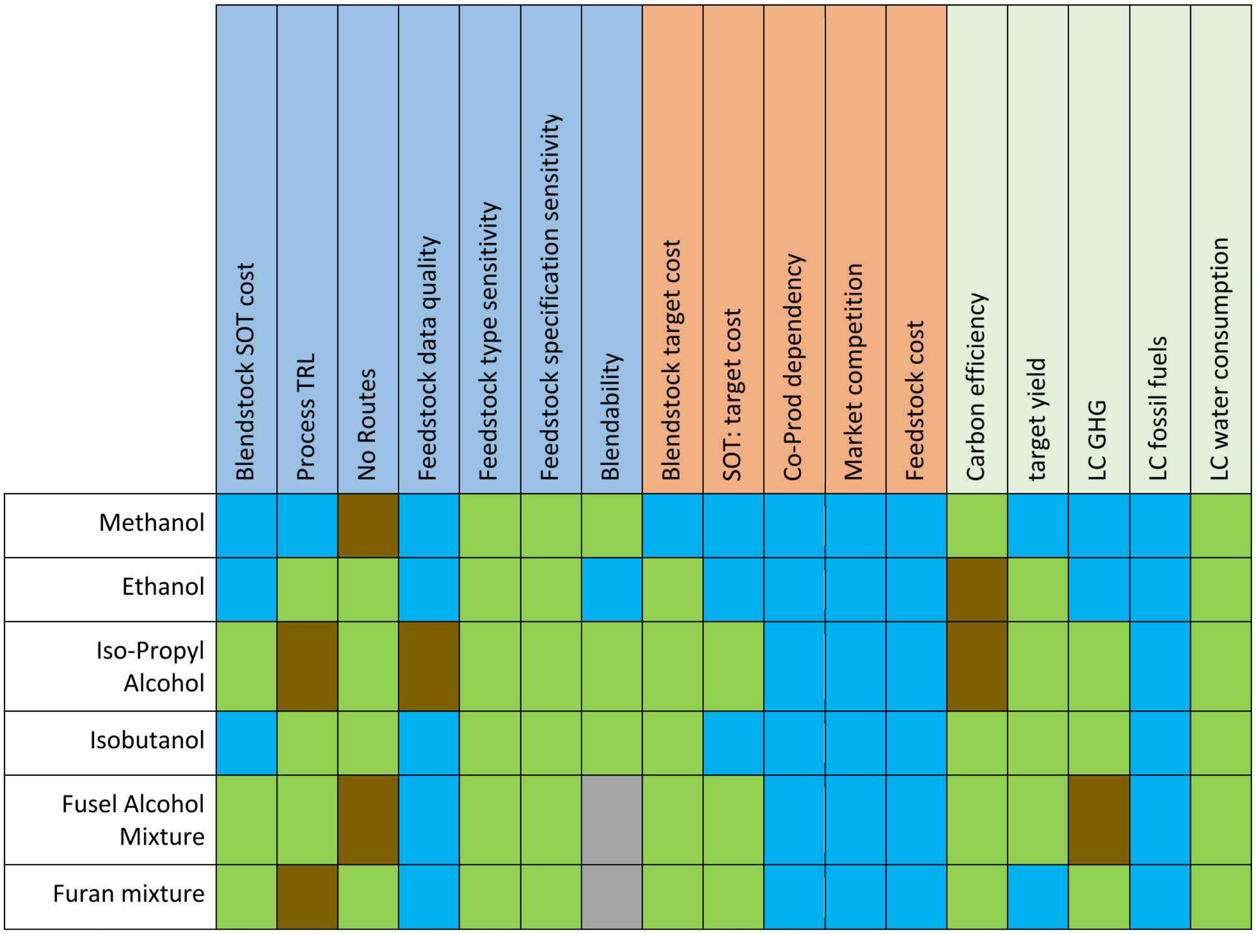


Figure 4. Fifteen additional blendstocks with merit function scores within three points of the score generated by E10 premium.

Several observations can be made regarding these blendstocks. First, the rest of the C4 and many C5 alcohols are included. Second, several other functional groups are represented – aromatic ethers, ketones, and esters – which are less developed as BSI fuel components, along with aromatics which are a major component of market gasolines. Co-Optima researchers identified significant technical barriers to adoption for some of these blendstocks, e.g., compatibility of ketones with infrastructure elastomers and plastics. Finally, the non-linear blending attributes of these blendstocks were less synergistic or essentially linear. Some of these (bioreformate, anisoles) would be expected to exhibit higher energy density, which would be an additional benefit for fuel economy.

2.5 Analysis of Bio-blendstock Economic and Environmental Factors

The analysis team conducted techno-economic and life-cycle analyses reported in Dunn et al. (2017). A summary of the results is shown in Figure 5 for the six candidates in the Top 10 which were evaluated. These analysis outputs were used to identify barriers, in addition to cost.



	Blendstock SOT cost	Process TRL	No Routes	Feedstock data quality	Feedstock type sensitivity	Feedstock specification sensitivity	Blendability	Blendstock target cost	SOT: target cost	Co-Prod dependency	Market competition	Feedstock cost	Carbon efficiency	target yield	LC GHG	LC fossil fuels	LC water consumption
Methanol	🟦	🟦	🟫	🟦	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟦	🟩	🟦	🟦	🟦	🟩
Ethanol	🟦	🟩	🟩	🟦	🟩	🟩	🟦	🟩	🟦	🟦	🟦	🟦	🟫	🟩	🟦	🟦	🟩
Iso-Propyl Alcohol	🟩	🟫	🟩	🟫	🟩	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟫	🟩	🟩	🟦	🟩
Isobutanol	🟦	🟩	🟩	🟦	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟦	🟩
Fusel Alcohol Mixture	🟩	🟩	🟫	🟦	🟩	🟩	▨	🟩	🟩	🟦	🟦	🟦	🟩	🟩	🟫	🟦	🟩
Furan mixture	🟩	🟫	🟩	🟦	🟩	🟩	▨	🟩	🟩	🟦	🟦	🟦	🟩	🟦	🟩	🟦	🟩

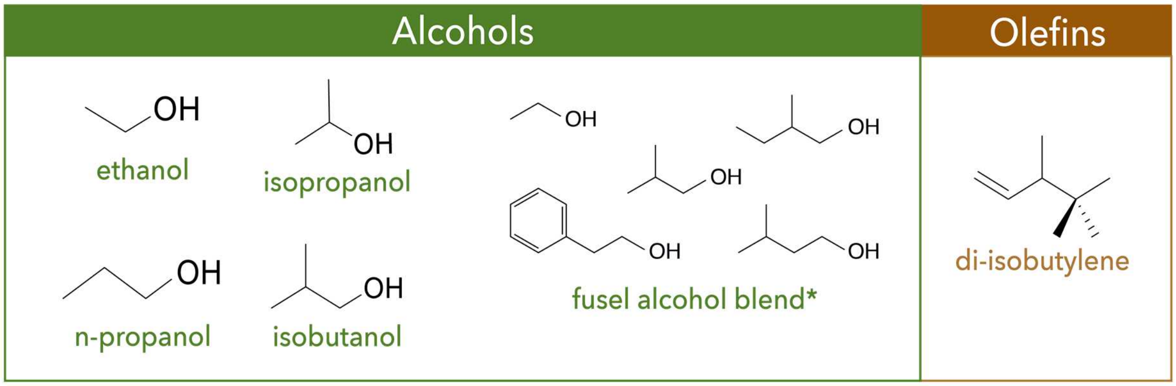
Note 1: Blue, green, and Brown boxes represent favorable, neutral, and unfavorable categorization respectively, and gray boxes indicate that insufficient data were available.

Figure 5. Bio-blendstocks screening results (Dunn et al. 2018).

The analyses that were completed are included in the detailed blendstock descriptions in Section 3, and public sources of information on the techno-economics of several additional blendstocks are also provided.

2.6 Top Six Blendstocks with Fewest Barriers to Adoption

The blendstocks listed and described in Section 2.4 were chosen without regard to barriers to adoption. Co-Optima has identified significant barriers to adoption for four of the blendstocks in the Top 10 list provided in Section 2.4 – cyclopentanone, methanol, prenol, and the 2-methylfuran/2,4-dimethylfuran mixture. The resulting list of six blendstocks with the highest potential efficiency increase and the fewest barriers to adoption are shown in Figure 6.



*Fusel alcohol blend: 57% isobutanol, 15% phenyl ethanol, 12% 3-methyl-1-butanol, 10% ethanol, 6% 2-methyl-1-butanol

Figure 6. Six bio-blendstocks with the highest potential engine efficiency gain and fewest barriers to market.

The limits on olefins imposed in some markets, which would also apply to di-isobutylene, are not included, nor is energy density, which would reduce the value of all of the lighter weight blendstocks. The barriers identified fall into four categories described in the following subsections.

2.6.1 Stability

Several of the candidate blendstocks were found to have issues with stability. Prenol passed the ASTM D525 (Standard Test Method for Oxidation Stability of Gasoline) in 20% blends with a petroleum BOB. However, the furan mixture and cyclopentanone did not pass, and prenol failed as a neat blendstock. Furthermore, the furans are known to polymerize under ambient conditions. For these blendstocks to be used in fuel, stabilizers would have to be used or developed.

2.6.2 Compatibility

Compatibility with all parts of the fuel distribution, storage, delivery, and use infrastructure is critical in reducing the potential cost of new bio-blendstock introduction. The majority of the Top 10 bio-blendstocks were estimated or determined to be compatible with a wide range of elastomers, plastics and metals in the fuel system. There are limits to compatibility for the small alcohols (particularly methanol and, to a lesser extent, ethanol). However, cyclopentanone was not found to be compatible with a range of materials, including fuel line materials. Additional work to eliminate these incompatibilities would be critical to adoption of cyclopentanone as a fuel.

2.6.3 Volatility and Distillation Properties

The impact of some components on final blend vapor pressure (particularly methanol and ethanol) currently limits the amount that can be used due to impacts on the Reid vapor pressure (RVP) (the vapor pressure at 100°F [Gaspar 2019; McCormick et al. 2017]). Co-blending can reduce these impacts and sealed gas tanks could also reduce the need for an RVP standard. Nonetheless, these blendstocks are currently limited in part due to volatility impacts.

The fusel alcohol blend also may face a barrier due to the extremely low vapor pressure of the 2-PE component. Despite the low level of the 2-PE in fusel alcohol blends (2–17 vol%), the very low vapor pressure at 443 K (estimated at 5.6 kPa by Ratcliff et al. 2016) leads to a high estimated impact on particulate matter formation. The overall impact of this low volatility on spray formation and combustion in the fusel alcohol blend requires further study.

2.6.4 Engine Impacts and Operability

Cyclopentanone exhibited a very high propensity to induce stochastic pre-ignition (low-speed pre-ignition or LSPI), a catastrophic form of knock of unknown origin (Jatana et al. 2018). A better understanding of the origin of this phenomenon and the mechanism by which cyclopentanone promotes LSPI could open the door to mitigation or avoidance strategies. For the time being, the high LSPI propensity is a large barrier to adoption and use of cyclopentanone in fuel.

2.7 Engine Investigations and Impacts

The majority of the engine investigations conducted within Co-Optima on boosted spark-ignition (BSI) have been conducted to better understand whether fuel properties are predictive of engine performance. This work supports the Central Fuel Property Hypothesis (CFPH), which states that if the right fuel properties are known, they are sufficiently descriptive of engine performance regardless of the composition of the fuel. Thus, the engine studies using the Co-Optima blendstocks fall into two main categories.

1. Determination of whether the CFPH is valid: For these studies, specific target fuel properties were matched with fuels of different chemistry, including the top Co-Optima blendstocks, to determine whether the CFPH holds true.
2. Investigations to determine the performance of individual fuel properties: In order to quantify the role of fuel properties as they relate to performance, such as in the efficiency merit function, the role of individual fuel properties must be better understood.

The studies associated with determining whether the CFPH holds true can be primarily associated with investigating whether the anti-knock metrics that we currently use are adequate. These studies include engine tests incorporating blends of many of the Top 10 bio-blendstocks including: ethanol, n-propanol, isopropanol, isobutanol, prenol, and di-isobutylene.

The main conclusion from the work is that, while some outliers exist, the CFPH does an adequate job at providing a first-pass estimate of the fuel property performance. In particular, the work performed within Co-Optima underscores the importance of octane sensitivity for knock resistance. Studies from Szybist et al. (2017), Szybist and Splitter (2018) and Vuilleumier et al. (2017a,b, 2018) concluded that, under boosted operating conditions, fuels with matched RON but lower octane sensitivity (S) underperformed fuels with higher octane sensitivity. These results are consistent with previous reported literature and confirm that the framework of the OI does a better job of predicting engine knock under boosted operating conditions than either RON or MON alone. While the kinetic basis for the OI was also confirmed within Co-Optima, both Szybist et al. (2017) and Vuilleumier et al. (2017a, 2017b, 2018) identified shortcomings or non-physical trends within the OI framework (Szybist and Splitter 2017). Typically, these outliers were most apparent when the engine operating conditions were unconventional (i.e., using a high intake manifold temperature). Nonetheless, they do show that this framework does have limitations. Further, Vuilleumier et al. (Vuilleumier 2018) found that, as conditions are further removed from the RON and MON test conditions, the error associated with predicting fuel quality using the OI framework increases.

For fuel properties associated with this framework, the fuel compositions investigated included ethanol, bioreformate, diisobutylene, isopropanol, n-propanol, isobutanol, and prenol (Szybist and Splitter 2017, 2018).

Investigations into the impacts of individual fuel properties on performance were also performed. Studies were conducted on the effect of flame speed (Kolodziej et al. 2017a; Szybist and Splitter 2016; Vuilleumier et al. 2018; Vuilleumier and Sjöberg 2017), the impact of heat of vaporization on knock, the impact on heat of vaporization on particulate matter, and the impact of heat of vaporization on the determination of octane number.

For flame speed effects, it was determined that the primary way in which flame speed impacts efficiency is through the dilution tolerance (Vuilleumier et al. 2018; Vuilleumier and Sjöberg 2017). While this has a measurable effect, the magnitude of this increase is small relative to other terms in the merit function (Miles 2018; Vuilleumier and Sjöberg 2017). The fuels used to investigate flame speed effects included methanol, ethanol, aromatics, isopropanol, and isobutanol. The flame speeds reported in the next sections are reported for stoichiometric conditions at an initial temperature of 298 K and a pressure of 1 atmosphere. Although the maximum flame speed is typically at slightly higher equivalence ratio (1.1–1.2), we have reported the stoichiometric value for consistency.

The impact of HoV on anti-knock properties was investigated in multiple ways. First, Sluder et al. (2016) and Kolodziej et al. (2017a) noted that when HoV was changed by splash blending ethanol and S was allowed to increase, it provided a performance benefit, but when RON and S were matched, higher HoV did not provide a performance benefit. Ratcliff et al. (2018) went on to show that even with matched RON and S, HoV could provide a performance benefit under some conditions where the intake manifold had an elevated temperature.

Next, a number of investigations were conducted to better understand how HoV impacts the RON determination itself (Hoth et al. 2018). It was found that when HoV was altered using ethanol, the factors that changed included intake manifold pressure, engine load, in-cylinder pressure, intake temperature, and equivalence ratio. Parametric investigations to better understand this showed that when these operating condition changes were corrected for, the impact of HoV was actually higher. Further investigations went on to show that fuel chemistry interactions with regards to RON rating were also important where toluene inhibited the octane boost produced by adding ethanol and isobutanol, as was seen when adding ethanol to paraffins.

Next, studies were conducted to understand the interaction between HoV and particulate matter emissions by Ratcliff et al. (2018). In particular, this investigation studied the interaction between ethanol and aromatics when generating particulate matter. Co-blending an aromatic having a boiling point of 191 °C with 30 vol% ethanol into a research gasoline increased particulate emissions from a gasoline direct injection (GDI) engine, compared to an ethanol-free blend with the same aromatic. The same comparison using a 153 °C boiling point aromatic revealed that co-blended ethanol reduced particulate emissions. Ethanol blending both concentrates aromatics in evaporating liquid droplets and increases evaporative cooling which extends droplet lifetime, thus leading to higher particulate emissions with the high boiling aromatic. A competing effect is ethanol's dilution of aromatics in the liquid fuel (mole % basis). For volatile aromatics which evaporate quickly, the dilution effect of ethanol dominates thus producing lower particulate emissions.

Finally, a study was conducted to investigate the effect of fuel composition on cold start emissions using an ethanol, an aromatic, and an alkylate fuel. It was found that the oxygenate fuels reduced particulate matter except in the case of an aromatic oxygenate (anisole).

2.8 Observations and Lessons Learned

Several key observations can be made regarding the merit function scores, blendstocks generally, and the potential for improved economic and environmental impacts.

First, one point of S increases efficiency more than one point of RON at the value of K used for the evaluation. However, no mechanism currently exists to move S into the marketplace. In order to obtain the benefit potentially available from increased S, an updated fuel specification including a minimum S requirement would be required. It is not straightforward to increase S in a fuel in the same way that it is for increasing RON. The complex interactions between the RON and MON of the fuel components and oxygenate bio-blendstock make understanding and predicting the nonlinearity of S blending more challenging than for RON. This is an active area of research in Co-Optima.

Similarly, there is no specification for HoV and thus no way to make sure a fuel has higher HoV or to value those that do. Only small alcohols provide significant HoV benefit due to the relatively large amount of hydrogen bonding that increases the amount of energy required to vaporize them, although there are other blendstocks which provide modest increases.

The PMI term in the merit function depends on the vapor pressure of the components of the blendstock at elevated temperature (443K). Various methods can be used to estimate this quantity for new materials which have not had a measurement made, but the uncertainty in this estimate is fairly high. The authors were able to generate estimates that differed by at least a factor of 3. For low volatility blendstocks with some level of unsaturation – aromatics, specifically – the difference in the merit function could be a point or more.

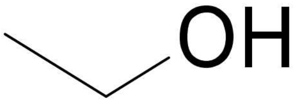
Finally, the emissions impacts of new blendstocks are not clear. Measuring catalyst light-off temperatures is a start, and more needs to be done in this area to reduce the risk of unintended consequences. Additional areas for work include measuring impacts on gaseous emissions and catalyst lifetime and developing a better understanding of cooperative emissions impacts (Burke et al. 2018).

3 Top 10 Boosted Spark Ignited Engine Biofuel Candidates

This section lists the candidate blendstocks with the highest merit function scores, organized by chemical family and alphabetically within chemical family. The merit function score for each of these candidates exceeded the score for E10 premium for at least one of the BOBs used in the merit function calculations.

3.1 Ethanol (ethyl alcohol)

Ethyl alcohol (ethanol)



CAS #		64-17-5
Formula		C_2H_5OH
RON		109
bRON at 20%		130
MON		90
S		19
HOV (kJ/kg)		918.6
LHV (MJ/kg)		26.84
PMI		0.063
YSI		10.3
S_L (298K; 1 bar; cm/s)		42
Water sol. @ 25 °C (g/L)		Miscible
Catalyst light off:	T_{50}	204 °C
	T_{90}	276 °C
LSPI propensity		Low

	RON	MON
Base BOB	90.3	84.7
10% EtOH	96.4	88.5
20% MeOH	100.9	89.5
30% MeOH	102.6	90.4

Ethyl alcohol (ethanol) has been known to be a good gasoline additive for decades. Ethanol is also a commodity chemical widely used in consumer products such as cosmetics, mouthwash, and hand sanitizer. It is most widely used as an additive to retail gasoline at 10% blend rate, known as E10. Spot prices in 2018 ranged from under \$1.25/gal to over \$1.50/gal. Most domestic ethanol is produced from fermentation of corn sugar in 208 plants in the United States. Other less mature methods continue to be developed, such as production from CO or CO_2. Ethanol can also be an intermediate product further converted to other biofuels or bioproducts such as the Vertimass or LanzaTech/Pacific Northwest National Laboratory (PNNL) processes (LanzaTech 2019) for converting ethanol to gasoline, diesel, or jet fuel. Ethanol can also be a feedstock for polymer production (API 2010; Makshina et al. 2014).

It exhibits excellent combustion properties, with high RON (109) and octane sensitivity (19). It blends nonlinearly providing a large RON boost at low blend levels. The RVP of denatured fuel-grade ethanol is low at 2.3 psi (API 2010) due to relatively high attraction between the polar ethanol molecules. However, at low blend rates in gasoline, this attraction is disrupted by dilution with the hydrocarbons and actually raises the RVP of the ethanol/gasoline blend by about 1 psi at 10% ethanol (actual RVP increase is dependent on the base gasoline and can range from 0.5 to 1.5 psi (API 2010). The lower heating value for ethanol is 26.84 MJ/kg. Ethanol is miscible with water. ASTM D4806 (2019) specifies the properties for fuel-grade ethanol, which generally contains about 2% hydrocarbons as denaturant and just under 1% water. To avoid separation of ethanol from gasoline due to water ingress, finished E10 blends need to stay below about 0.25% water (with the specific limit dependent on temperature) (Korotney 1995). Many studies have measured the laminar flame speed of ethanol, both pure and in mixtures with hydrocarbons (van Lipzig et al. 2011).

Ethanol has been used widely as a spark ignition engine fuel for decades, but domestic production and utilization were relatively modest until the early 2000s. Ethanol use grew dramatically with the phase-out of methyl-tertiary-butyl ether in the early 2000s and with the passage of the 2007 Energy Independence and Security Act (H.R.6. 2007) which established a new Renewable Fuel Standard requiring 36 Bgpy biofuel use by 2022, with 15 Bgpy being conventional corn ethanol. Domestic ethanol production grew slowly from the late 1970s to early 2000s, remaining below 2 Bgpy in 2000, but growing rapidly to 14 Bgpy by 2010. In 2017, the United States produced nearly 16 billion gallons of ethanol, consumed over 14 billion gallons, and exported over 1 billion gallons.

Co-Optima significantly advanced our understanding of the behavior of ethanol in fuels in several ways. First, additional information regarding the emissions behavior of ethanol/fuel blends was measured for cold start conditions and in the presence of large amounts of aromatics. New knowledge regarding the vapor pressure behavior was obtained, attributing the “ethanol plateau” to azeotrope-like behavior. Finally, a significant amount of engine testing using ethanol blends revealed the contributions of heat of vaporization on performance compared to octane.

3.1.1 Kinetic Model

The ethanol kinetic model was part of the base chemistry used in the Lawrence Livermore National Laboratory (LLNL) kinetic model. The ethanol kinetic model has been validated over a wide range of temperatures, pressures, and equivalence ratios with good agreement with experimental data. It has been validated using a variety of fundamental experimental data including 1) ignition delay times from shock tubes and rapid compression machines (RCMs), 2) speciation measurements from jet stirred reactors and flow reactors and 3) flame speeds from various experimental apparatuses.

The chemistry of alcohols relevant to autoignition in an engine has characteristic features. Alcohols scavenge reactive OH radicals which often abstract the hydrogen atom from the weak carbon-hydrogen (C-H) bond next to the OH group. The alcohol (hydroxyalkyl) radical produced reacts quickly with molecular oxygen to form an aldehyde and HO_2 radical. At conditions in internal combustion engines, the scavenging of OH leads to lower reactivity at lower temperatures, but at higher temperatures, the HO_2 radicals produced in the aforementioned reaction react with the fuel to form hydrogen peroxide (H_2O_2) which decomposes to two OH radicals that promote autoignition. These general mechanistic features apply to all alcohols described in this report.

3.1.2 Fuel Properties, Engine Tests, and Emissions Control Results

The U.S. Department of Energy (DOE) supported a $46M test program from 2007 through 2012 to evaluate mid-level ethanol blends in legacy vehicles and engines. With oversight and direction from the Vehicle Technologies Office (VTO) and the Bioenergy Technologies Office (BETO), Oak Ridge National Laboratory (ORNL), NREL executed a set of studies to examine the impact of increasing the motor gasoline ethanol content from 10% up to 15% or 20%. Through several pilot studies and larger subcontracted efforts, the Mid-Level Ethanol Blends Program examined legacy vehicles, non-automotive engines, materials, and the fueling infrastructure. In 2009 during this test program, Growth Energy and several ethanol producers filed a waiver application requesting that EPA permit E15 to be legally used in gasoline engines. In the fall of 2010 (75 FR 213 2010) and early in 2011 (76 FR 17 2011), EPA cited the DOE studies in its decisions to allow E15 into commerce. The partial waiver allowed for E15 to be used only in 2001 and newer light-duty vehicles and prohibited its use in vehicles older than 2001 and in non-automotive engine applications (such as motorcycles, lawn and garden equipment, and marine engines). The DOE Mid-Level Blends results showed that changes in emissions in the light-duty vehicles were consistent with prior blending studies. Aging vehicles increased emissions over time, as expected, but aging vehicles with increased ethanol levels did not affect aging differently than aging with ethanol-free gasoline. Small nonroad engines showed emissions and temperature changes consistent with fuel enleanment (which was expected due to the open-loop nature of the carbureted engines), including increased NOx and decreased CO emissions. Unintended clutch engagement was observed on some handheld engines due to increased idle speed (a safety concern with equipment such as chainsaws or brushcutters). Working closely with Underwriters Laboratories, compatibility of dispenser materials was examined, improving the understanding of materials/fuels interactions and led to development of new dispensers as well as retrofit kits for some existing dispensers (Bechtold et al. 2007; Knoll et al. 2009a,b; Shoffner et al. 2010; Sluder and West 2011a,b; Sluder et al. 2012b; West et al. 2012; Vertin et al. 2012; West and Sluder 2013; EPA et al. 2013; Sluder and West 2013a,b; Sluder et al. 2014; Zooubul et al. 2011; Hilbert 2011; Miers and Blough 2013; Boyce and Chapin 2010; Kass et al. 2011, 2012a,b, 2014a,b; Theiss et al. 2016; McCormick et al. 2017).

In 2014, BETO initiated a collaborative research program with ORNL, NREL, and Argonne National Laboratory to explore the potential benefits of using increased levels of ethanol to boost octane, reduce petroleum consumption, and minimize life-cycle greenhouse gas emissions while identifying the barriers to widespread adoption of a high-octane mid-level ethanol blend. The two-year study concluded that blends of 25–40% ethanol could provide vehicle efficiency improvements of 5–10% in vehicles designed for their use. Such blends could be used legally in the 20M Flex Fuel Vehicles on the road at the time providing these vehicles with measurable acceleration performance benefits (a potential marketing strategy) and lower well-to-wheel greenhouse gas emissions (GHG) emissions (up to 30% lower than from conventional E10 if ethanol were produced from cellulosic sources). Regulatory uncertainty, the need for retail investment, and expansion of biorefinery capacity were identified as potential limiting constraints. However, feedstock availability was not found to be a limiting factor. The study further found that neither technical nor materials obstacles were likely to prohibit high-octane mid-level ethanol blends, but new equipment compatible with the fuel would be required (Theiss et al. 2016).

Under the auspices of the Co-Optimization of Fuels and Engines Project, researchers have further explored the intricacies of ethanol blending, focusing on improved understanding of fuel properties. Much of this work is described in more detail in Section 2.7 and summarized below. For both categories of engine investigations, fuels containing ethanol were used extensively; ethanol is the most widely used biofuel. Thus, some of the investigations focused on understanding whether an ethanol-containing fuel behaved similarly to a non-ethanol containing fuel when they had matched properties. Other investigations focused on quantifying the role of an individual fuel property as it pertains to efficiency or emission effects.

Flame Speed

Ethanol was included in the fuels used to investigate flame speed effects, along with methanol, ethanol, aromatics, isopropanol, and isobutanol.

Heat of Vaporization

The investigations conducted to better understand how HoV impacts the RON determination relied on ethanol to a great extent (Hoth et al. 2018). These include investigations showing that fuel chemistry interactions reduced octane boost seen for ethanol in the presence of toluene in a paraffin fuel.

Blending

Ethanol has non-linear blending behavior for a number of fuel properties, which has both advantages and disadvantages. The properties most impacted by the non-linear blending behavior are the vapor pressure and the anti-knock rating.

When ethanol is added to a gasoline blend, the vapor pressure of the mixture increases to a level that is higher than either of the pure species (McCormick et al. 2017), and vapor pressure reaches a maximum at about 10% ethanol. This effect on gasoline vapor pressure is well-established, and to account for this and promote ethanol use, Congress granted a 1 psi RVP waiver to gasoline blends containing 10% ethanol (42 USC 7545). As part of the Co-Optima initiative, Abdollahipoor et al. (2018) explained that the non-linear increase in vapor pressure was a result of azeotropic-like interactions where the inter-molecular bonding mechanisms were being disrupted because ethanol is a highly polar molecule whereas most hydrocarbons are non-polar.

While there is an RVP waiver for 10% ethanol blends, no such legislative waiver exists for higher ethanol blends (even though these blends typically have a lower vapor pressure than E10). As a result, the RVP regulations currently serve as a barrier to the adoption of E15 and higher blend levels of ethanol.

While the non-linear blending behavior associated with ethanol is a barrier with regards to vapor pressure, the non-linear effect of ethanol on octane number is a major benefit. Ethanol was known to have non-linear blending effects on performance prior to the Co-Optima initiative. Szybist and West (2013) demonstrated that ethanol was able to upgrade natural gasoline, which is a low octane and low-cost liquid product of natural gas production, to the level where it outperformed premium grade gasoline (Szybist and West 2013). Anderson et al. (2010, 2012) explained that the effects of blending ethanol on octane are much more linear on a molar basis than on a volume basis, which explains much of the discrepancy. However, Foong demonstrated that both synergistic and antagonistic blending can occur with ethanol even on a molar basis, depending on the types of hydrocarbons in the blend (Foong et al. 2014).

Within Co-Optima, the non-linear blending of ethanol was quantified and compared with other promising bio-derived blendstocks (McCormick et al. 2017). In this study, ethanol was blended into a surrogate fuel formulation containing isooctane, n-heptane, toluene, and 1-hexene. Ethanol exhibited higher non-linear blending effects, behaving as though it had a RON of 148 at a 10% blend level if linear blending was experienced. In addition to an increase in RON with ethanol addition, the study also showed that ethanol addition increases octane sensitivity, which is important for additional knock resistance for boosted and downsized engines.

Emissions

Ethanol starts to light off over an aged commercial three-way catalyst at lower temperatures ($T_{c,50}$ 204 °C; $T_{c,90}$ 276 °C) than a four-component surrogate BOB ($T_{c,50}$ 247 °C, $T_{c,90}$ 284 °C). (Majumdar et al. in press). However, blends of the same BOB mixed with up to 30% ethanol light-off ($T_{c,50}$ 240 °C, $T_{c,90}$ 279 °C) at nearly the same temperature as the BOB without ethanol. Thus, even though ethanol is more catalytically reactive than other gasoline components, ethanol will likely neither help nor hinder compliance with NOx, NMOG, and CO regulations in realistic fuel blends.

Catalyst light-off of neat ethanol and a 10% ethanol blend surrogate was measured using a hydrothermally-aged commercial three-way catalyst in an exhaust flow reactor at ORNL. The reactor permits measurement of light-off behavior in a real automotive catalyst sample using an industry standard protocol with synthetic exhaust. The commercial application of the catalyst is the 2009 Chevrolet Malibu super ultra-low emission vehicle/partial zero emission vehicle. This catalyst is dual-zoned with a Pd-rich front zone and a Pd/Rh/CeO_2 rear zone. The E10 surrogate consisted of 10% ethanol, 25% toluene, and 65% isooctane (compounds common in gasoline that were also assessed individually for their light-off behavior). The $T_{c,90}$ of ethanol was measured to be 276 °C in this setup. Compared to other oxygenated organic compounds considered in the Co-Optima program, two- and three-carbon alcohols have lower light-off temperatures (Majumdar et al. in press).

The emissions from a 90 second cold-start idle test, which runs a transient that includes an ignition (key-on) event followed by a short idle, have been run repeatedly (Moses-DeBusk et al. 2017) on a forced-cooled, GDI start-cart engine to study the impact of different oxygenated fuel blends. Cold-start PM emission using a 30% ethanol-gasoline fuel blend, known as the Co-Optima E30 core-fuel, were compared with other oxygenated fuel blends, each containing 10% ethanol and 20% of another oxygenate blended into the same BOB as the E30 core-fuel. The Co-Optima alkylate and aromatic core-fuels, along with the E10 certification and EEE (E0 certification) fuels, were also run. The lowest PM emissions during this cold-start transient were with the E30 and alkylate Co-Optima core-fuels. Two of the other 30% oxygenate blended fuels that had similar PMI values (1.4) to the E30 had PM mass emissions that were very close to the level generated by the E30 and alkylate fuels. These fuels lowered the PM mass during this transient cold-start to about one quarter of the PM mass measured using the EEE fuel. Even at just 10% ethanol blending, the PM emissions were reduced by roughly 40% compared to the ethanol-free, EEE fuel.

Additional engine studies were conducted to understand the interaction between HoV and particulate matter emissions by Ratcliff et al. (2018). In particular, this investigation studied the interaction between ethanol and aromatics when generating particulate matter. Co-blending an aromatic having a boiling point of 191 °C with 30 vol% ethanol into a research gasoline increased particulate emissions from a GDI engine, compared to an ethanol-free blend with the same aromatic. The same comparison using a 153 °C boiling point aromatic revealed that co-blended ethanol reduced particulate emissions. Ethanol blending both concentrates aromatics in evaporating liquid droplets and increases evaporative cooling which extends droplet lifetime, thus leading to higher particulate emissions with the high boiling aromatic. A competing effect is ethanol's dilution of aromatics in the liquid fuel (mole % basis). For volatile aromatics which evaporate quickly, the dilution effect of ethanol dominates thus producing lower particulate emissions.

3.1.3 Conversion Routes from Biomass

Ethanol, a reference compound for other bio-blendstocks given its role as the primary biofuel in the United States, can be produced from cellulosic biomass thermochemically at demonstration scale or biochemically at commercial scale. In the former case, woody biomass-derived syngas is the intermediate. In the latter case, ethanol is produced via anaerobic fermentation of lignocellulosic sugars produced from a combination of acid pretreatment and enzymatic hydrolysis. For both conversion technologies, the ethanol is recovered via distillation. Both routes exhibit favorable process economics and technology readiness. Life-cycle GHG emissions and fossil fuel consumption are favorable for cellulosic ethanol whether it is produced thermochemically or biochemically. Domestic fuel ethanol is currently produced from corn at some 208 plants in the U.S., with total U.S. capacity exceeding 16 Bgpy. Cellulosic ethanol is being commercialized at the Poet facility in Emmetsburg, Iowa, using corn stover as a feedstock.

3.1.4 Economic, Scalability, and Environmental Effects

Ethanol, a reference compound for other bio-blendstocks given its role as the primary biofuel in the United States, can be produced from cellulosic biomass thermochemically, as shown at the demonstration scale, or biochemically, as demonstrated at the commercial scale. In the former case, woody biomass-derived syngas is the intermediate. In the latter case, ethanol is produced via anaerobic fermentation of lignocellulosic sugars produced from a combination of acid pretreatment and enzymatic hydrolysis. For both conversion technologies, the ethanol is recovered via distillation. Both routes exhibit favorable process economics and technology readiness. Life-cycle GHG emissions and fossil fuel consumption indicate cellulosic ethanol will meet the advanced biofuel criterion of at least 60% GHG emissions reduction whether it is produced thermochemically or biochemically.

3.1.5 Challenges and Barriers

The primary barriers to more widespread use of bio-derived ethanol at levels higher than 10 or 15% are infrastructure compatibility and the RVP waiver (discussed above). Significant progress has been made in building out mid-level blend dispensing capability through the USDA Biofuels Infrastructure Partnership (Press Release No. 0156.15 2015) and similar industry initiatives. As of late 2018, over 1600 stations were offering E15 (Growth Energy 2018). Thousands of E25-compatibile dispensers have been installed since Wayne Fueling systems announced in 2016 that all dispensers would be UL-listed for E25 (Wayne Fueling System 2016). While many of these E25-compatible dispensers were installed to dispense E10, with appropriate underground measures, they could readily be used for E15 or higher blends.

Water Solubility: Ethanol is miscible with water and forms an azeotrope, and thus cannot be distilled beyond 95% purity. Commercial ethanol plants use molecular sieves for the final drying step. Fuel ethanol is denatured by adding gasoline-range hydrocarbons. In the E10 fuel system care must be taken to maintain total water content below about 0.25% to avoid separation of the water and ethanol from the gasoline basestock. At higher ethanol levels, additional water can be tolerated, as shown in Figure 7.

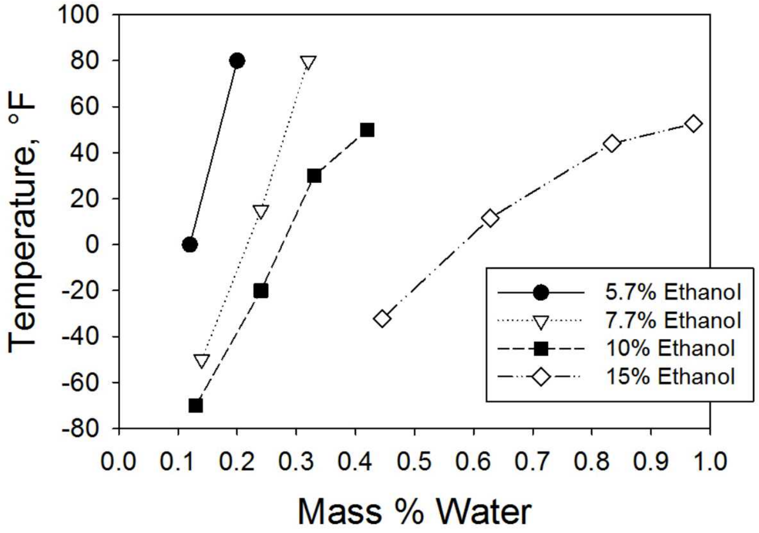


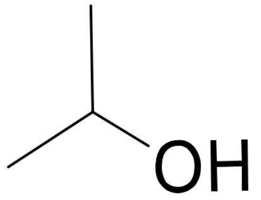
Figure 7. Water content of a hydrocarbon gasoline and various ethanol/gasoline blends as a function of temperature (Christensen and McCormick 2016).

3.1.6 R&D Needs

Ethanol has been in market fuels for decades now, and extensive additional research and development are not needed. Nonetheless, additional research to untangle subtle interactions may be warranted in some cases.

3.2 2-Propanol (isopropanol)

2-Propanol (isopropanol)



CAS #		71-23-8
Formula		C_3H_7OH
RON		109
bRON at 20%		122
MON		97
S		12
HOV (kJ/kg)		743.8
LHV (MJ/kg)		30.7
PMI		0.076
YSI		19.2
S_L (343K; 1 bar; cm/s)		44
Water sol. @ 25 ºC (g/L)		Miscible
Catalyst Light-Off:	T_{50}	203.9 °C
	T_{90}	219.2 °C
LSPI propensity		Low

	RON	MON
Base BOB	86.8	81.1
10% i-PrOH	90.6	83.7
20% i-PrOH	93.7	85.8
30% i-PrOH	97.7	88.1

2-Propanol, also known as isopropanol or IPA, has been known to be a good gasoline additive for decades. IPA is a commodity chemical widely used as a solvent, as a medical disinfectant, and as a "gas dryer" additive for automobile engines due to its affinity for water and good combustion properties. Spot prices vary around $3.50/gal for petroleum-derived IPA. It exhibits excellent combustion properties, with high RON (ranging from 109 to 114 depending on the source [Farrell et al. 2018; McCormick et al. 2017]) and octane sensitivity (12 to 17). It blends synergistically with a blending RON of 122 at a 20% blend level. The vapor pressure of IPA is lower than ethanol, and it has a 16% higher lower heating value. Like ethanol, it is miscible with water.

Co-Optima researchers have confirmed literature values of fuel properties for isopropanol and conducted blending studies to understand the degree of synergistic blending. Co-Optima researchers have also conducted a number of engine tests using IPA to evaluate the Co-Optima Central Fuel Hypothesis and understand impacts of flame speed and other fuel properties on efficiency.

3.2.1 Kinetic Model

The isopropanol kinetic model was taken from the literature and inserted into the LLNL kinetic model for high performance fuels (HPFs). The isopropanol kinetic model was verified to ensure that the simulated ignition delay times over a wide range of temperature, pressure, and equivalence ratio were the same as those predicted by the original published literature model; 95% of simulations were within a factor of 1.35. The kinetic model is also being validated using speciation data from the NREL flow reactor. The chemical mechanism features described for all alcohols in Section 3.1.1 apply here as well.

3.2.2 Fuel Properties, Engine Tests, and Emissions Control Results

IPA has been tested in engines in many different ways over the past decades. More recently, other groups have conducted engine tests in spark ignition engines with IPA as a means to optimize octane energy content (i.e., LHV), RVP, and emissions (Masum et al. 2014), including in alcohol and acetone/alcohol (Li et al. 2016; Nithyanandan et al. 2016) mixtures generated directly via microbial synthesis (described in Section 3.2.3). As a result of this extensive testing history, Co-Optima performed limited engine and fuel property tests of IPA and IPA blends at

10%, 20%, and 30% v/v in several base fuels. Flame speed measurements are reported in Veloo and Egolfopolous (2011) and included in the fuel property box. These results are summarized below.

Engine Tests

Isopropanol was included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis, as well as tests of the effect of flame speed on efficiency which determined the impact on dilution tolerance.

Emissions

Catalyst light-off tests revealed that isopropanol is the most catalytically reactive species of all the blendstocks and gasoline components evaluated, with light-off temperatures near 200 °C ($T_{c,50}$ 203 °C; $T_{c,90}$ 219 °C). However, it is likely that isopropanol will behave much like ethanol when blended to reasonable levels with a petroleum-based BOB, resulting in blend light-off temperatures close to that of the BOB.

3.2.3 Conversion Routes from Biomass

The production of isopropanol from petroleum is commercial, and therefore no additional production-related research was carried out under Co-Optima. Isopropanol has historically been produced by hydration of propene or hydrogenation of acetone. Acetone can be generated via fermentation or by, for instance, coupling ethanol (Ramasamy 2019) or CO_2 and CH_4 (Zhao et al. 2018; Connor and Liao 2009).

Isopropanol can be produced directly via microbial pathways including fermentation, either as the primary product or in mixtures with acetone and/or other small alcohols (see, for instance, Zhang et al. 2011 or Connor and Liao 2009, and references therein Zhang et al. 2011; Connor and Liao 2009; Hanai et al. 2007; Jojima et al. 2008; Inokuma et al. 2010). These mixtures include acetone/n-butanol/isopropanol (Chen and Hiu 1986), isopropanol/n-butanol/ethanol (LBE) (Lee et al. 2012; Dusséaux et al. 2013; de Vrije et al. 2013), isopropanol/n-butanol (IB) (Survase et al. 2011), or isopropanol/acetone/n-butanol (IAB) mixtures via fermentation. Use of these mixtures directly could potentially avoid the high recovery costs associated with the separation of individual components and removal of water. Of course, the acetone present in ABE mixtures has the potential to degrade elastomers in the fuel system, and therefore, IBE may have better potential as a high-octane additive.

3.2.4 Economic, Scalability, and Environmental Effects

The baseline design for isopropanol production is an aerobic conversion pathway, starting with lignocellulosic sugars produced through a combination of acid pretreatment and enzymatic hydrolysis. Isopropanol has the potential for economic viability although data and information regarding key process parameters were limited including the absence of conversion process data with real, rather than mock or pure sugar, feedstocks. Life-cycle GHG emissions and fossil energy consumption had the potential to be at least 60% less than conventional gasoline. According to U.S. Environmental Protection Agency (EPA), this bio-blendstock was approved as a registered gasoline additive.

3.2.5 Challenges and Barriers

Production and Separation: The primary technical barrier to the use of bio-derived isopropanol as a gasoline blendstock is in the state of technology for production from biomass. Hydration of propene generates an azeotrope with 12.1% water by weight, which requires azeotropic distillation using di-isopropyl ether or cyclohexane.

Water Solubility: Isopropanol is miscible in water and forms an azeotrope, similar to ethanol. It is therefore likely to behave in a similar fashion to ethanol in the fuel system. It should be compatible with ethanol-compatible materials and systems. Mixtures of IPA with other small alcohols and other oxygenates will likely be difficult and expensive to dry fully.

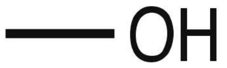
3.2.6 R&D Needs

Future efforts should focus on improving production techno-economics, determining the extent to which IBE and similar mixtures may be used directly as an additive, and optimizing mixtures containing IPA for fuel properties.

3.3 Methanol (methyl alcohol)

The potential for methanol as a gasoline additive has been known since the 1970s. It is a commodity chemical typically prepared from steam-reformed natural gas or coal with a market of ca. 30 billion gal/year. Spot prices have ranged from $0.50–2.50/gal from 2001 to 2018 (Methanex Historical Prices). Methanol's primary use is a chemical precursor to formaldehyde and acetic acid, which are then used in resins and plastics. More recently, methanol-to-olefins technology installations have emerged, especially in China, to generate ethylene and propylene for plastics. Methanol is used as a fuel blendstock in China and Europe, with specifications for low blend levels (1–15%) and high blend levels (85%). Many of its fuel properties are similar to ethanol: excellent combustion with a high pure-component RON (109) and high sensitivity (MON = 89), synergistic blending RON comparable to ethanol at 10–30% blend level, a reduced lower heating value compared to hydrocarbons (15.8 MJ/L vs ca. 30 for hydrocarbons), and miscibility with water (McCormick et al. 2017). The vapor pressure of methanol is higher than ethanol.

Methanol (methyl alcohol)



CAS #	67-56-1
Formula	CH_3OH
RON	109
bRON at 20%	143
MON	89
S	20
HOV (kJ/kg)	1173.5
LHV (MJ/kg)	20.09
PMI	0.045
YSI	6.6
S_L (cm/s)	42
Water sol. @ 25 ºC (g/L)	Miscible
Catalyst Light-Off: T_{50}	Not measured
T_{90}	Not measured
LSPI propensity	Low

	RON	MON
Base BOB	90.3	84.7
10% MeOH	96.4	88.5
20% MeOH	100.9	89.5
30% MeOH	102.6	90.4

Co-Optima performed a number of fuel property and engine tests to confirm literature values and allow direct comparisons of blending tests, and explore fuel property effects on engine performance, including understanding dilution tolerance.

3.3.1 Kinetic Model

The methanol kinetic model was part of the base chemistry used in the LLNL kinetic model for HPFs. The methanol kinetic model has been validated over a wide range of temperatures, pressures, and equivalence ratios. It has been validated with fundamental experimental data on ignition delay from shock tubes, RCMs, and on species measurements from jet stirred reactors and flow reactors. Predicted flame speeds at 1 atm and 358 K for stoichiometric methanol-air mixtures agree well with the experimental measurement from Ghent University. The chemical mechanism features described for all alcohols in Section 3.1.1 apply here as well.

3.3.2 Fuel Properties, Engine Tests, and Emissions Control Results

Methanol has been tested in engines in many different ways around the globe over the past 40 years (Landälv 2017). More recently, tests performed by Co-Optima in spark ignition engines have focused on octane enhancement, including non-linear blending, RVP, and emissions (McCormick et al. 2017).

Blending

A four-component surrogate BOB having RON 90.3 and MON 84.7 (AKI 87.5) was used for methanol blend studies (McCormick et al. 2017). Methanol has very high synergistic blending.

Engine Tests

Blends of ca. 10 and 20% methanol provided a slightly greater increase to RON than comparable 10 and 20% ethanol benchmark (McCormick et al. 2017). Similarly, enhancements to MON were comparable to ethanol over this range. At 30% methanol, only minor improvements were observed, and 30% ethanol provided a greater increase to RON and MON. These tests resulted in S values of about 8 and 12 at 10 and 20% methanol, respectively, leading to high merit function scores.

Methanol was also included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis, as well as tests of the effect of flame speed on efficiency which determined the impact of flame speed on dilution tolerance (Kolodziej et al. 2017a,b).

Emissions

Methanol has a very low propensity to form soot during combustion, with a PMI of 0.045 and a YSI of 6.6. The high vapor pressure of methanol leads to an increase in RVP and distillation curves in methanol-gasoline blends (McCormick et al. 2017). The effect of methanol blending on RVP exceeds that for ethanol. For example, for 10% methanol blended into a petroleum base fuel, the RVP was 2 psi greater than 10% ethanol. For a 10% methanol blend, the front end of the distillation curve was depressed significantly, and this was more pronounced for a 20% methanol blend, where a significant T50 depression was also observed. These data suggest that co-blending would be required to mitigate the increase in RVP (*vide infra*).

3.3.3 Conversion Routes from Biomass

The production of methanol from natural gas and coal is commercial and world-scale, and therefore no additional production-related research was carried out under Co-Optima.

Methanol can be made from virtually any carbon source via gasification to syngas ($CO + CO_2 + H_2$), syngas clean-up, and subsequent methanol synthesis over the commercially-employed $Cu/ZnO/Al_2O_3$ catalyst. Thus, a variety of renewable, alternative carbons sources have been investigated for this purpose, including biogas, biomass, municipal solid waste (MSW), and CO_2. With appropriate purification, biogas can integrate into existing steam reforming technology with natural gas (Abatzoglou and Boivin 2009; Chaemchuen et al. 2016). Detailed process designs for thermochemical conversion of biomass to methanol have been designed with associated TEA models, often considering downstream conversion of methanol to hydrocarbons (Tan et al. 2015, 2016; Philips et al. 2011). Operating at a 2000 tonne-dry-biomass/day scale, methanol production of 353,000 gal/day (129 million gal/year) can be achieved at a single facility. These process designs are comparable to MSW processes at a similar scale. Enerkem has commercialized MSW-derived methanol in Canada (Enerkem 2019). Similarly, conversion of CO_2 to methanol is well known, employing the same $Cu/ZnO/Al_2O_3$ catalyst (Lee et al. 1993), and has been promoted in the context of the "methanol economy" by George A. Olah and his colleagues (Olah 2005; Olah et al. 2009). This technology is currently commercially employed by Carbon Recycling International in Iceland with a nameplate capacity of ca. 1.3 million gal/year (CRI).

Unlike ethanol, biochemical production of methanol remains at the research stage, and is not practiced industrially. Research efforts are focused on methanotrophs, which can convert methane or CO_2 to methanol (Xin et al. 2004, 2007; Patel et al. 2016).

3.3.4 Economic, Scalability, and Environmental Effects

As noted above, methanol production capacity is world-scale from natural gas, but smaller-scale designs have been conceptualized and commercialized. It has been reported that up to 90% of the methanol production cost is due to feedstock cost, and when combined with advantages of economies of scale, the use of a low-cost feedstock at large scale is key to favorable overall economics (Iaquaniello et al. 2018). This results in less competitive production costs from alternative sources at smaller scales, such as biomass. Methanol production at the 2000-tonne-biomass/day scale was estimated to be ca. $3/gallon-gasoline-equivalent of energy, or approximately $1.50/gal of methanol ($500/tonne) (Tan et al. 2015, 2016). This is 1.5-4 times the cost of production from currently inexpensive natural gas (Broren et al. 2013). Similarly, a production cost of 355–544 euro/tonne was estimated for renewable methanol in Landalv (2017). However, production of methanol from MSW may provide an advantage in feedstock cost over biomass, where MSW represents a neutral or negative cost to the methanol plant (Ianquaniello et al. 2018). Despite higher production costs, there are significant environmental benefits to using biomass and other renewable carbon sources for methanol production. Process models have been used to estimate GHG emissions for methanol production from biomass and waste versus traditional natural gas (0.84 kg-CO_2/kg-MeOH). The estimated reduction in CO_2 emissions ranges from 24–55%, depending on feedstock (Ianquaniello et al. 2018; Biedermann et al. 2006).

Methanol can be produced thermochemically via a synthesis gas (syngas) intermediate. Production of syngas from biomass has been performed at a demonstration scale while methanol from syngas is produced commercially. Overall, the gasification route as evaluated using woody biomass as a feedstock has favorable process economics and technology readiness. For example, the target cost and state of technology (SOT) cost of this bio-blendstock are nearly equivalent and this bio-blendstock is produced directly from syngas (and not from a valuable chemical intermediate). In addition, competition for feedstock or intermediate compounds is not expected. Furthermore, life-cycle GHG emissions and fossil energy consumption could be more 80% lower than conventional gasoline. Although this alcohol could be produced via a number of pathways, including biologically, the scalability of this technology is limited because methanol is toxic to the fermenting microorganisms.

3.3.5 Challenges and Barriers

Physical Properties: Two major physical properties of methanol have limited its adoption as a fuel: low energy density resulting in low miles per gallon performance, and increased vapor pressure (Luque et al. 2008), which affects engine cold start especially for high methanol-gasoline blends (e.g., M85) without proper engine design (Bromberg and Cheng 2010; ACEA 2015; Dodge et al. 1998; Brusstar and Gray 2007).

Water Solubility: Methanol has a high affinity for water and will co-mingle with any water already present in a pipeline/tank. Additionally, the presence of water may lead to phase separation without the presence of a co-solvent, especially at colder temperatures (Bromberg and Cheng 2010, p.55).

Blend Vapor Pressure: The addition of methanol to gasoline, especially in the first 3% methanol, results in an increased vapor pressure of the mixture due to non-ideal mixing between methanol and gasoline components (ACEA 2015; Bromberg and Cheng 2010). This may be alleviated by the addition of co-solvent alcohols, such as ethanol or mixed alcohol blends, or by decreasing gasoline butane content (Methanol Institute 2016).

Corrosiveness and Toxicity: The existing engine fuel systems require modifications, similar to requirements for flex fuel vehicles designed for methanol in the past (Bromberg and Cheng 2010, p.56; Landalv 2017, pg. 66), to deal with the corrosiveness of methanol to certain elastomers (Schwartz 1984) and metals (Ingamells and Lindquist 1975). Similarly, refueling stations and distribution infrastructure needs to be constructed or retrofitted with methanol compatible materials (Landalv 2017) as outlined previously (Rawson et al. 1996; Methanol Institute 2016).

With respect to toxicity, methanol has similar or reduced toxicity as compared to gasoline through common routes of exposure (Bromberg and Cheng 2010, ch. VII). As methanol is water soluble it is more mobile during incidental spills than gasoline, however the environmental impact of a methanol spill may be lower due to faster bio-degradation than gasoline (Bromberg and Cheng 2010, ch. VII).

Co-solvent Requirement: Current EPA waivers require a co-solvent to combat issues with vapor pressure, phase separation, and material compatibility (Bromberg and Cheng 2010, p. 61) and the ASTM standard required by many states (ASTM D4814-18c 2019) requires equal parts of methanol and co-solvent, up to 2.75% of each, for gasoline blending.

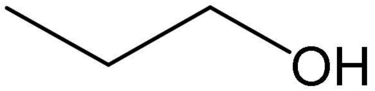
3.3.6 R&D Needs

As noted above and with references therein, thermochemical, large-scale production of methanol from fossil and renewable sources has few remaining research challenges. Rather, implementation of methanol into fuels requires fuel system/infrastructure modifications to enable widespread use, and for renewable production, the establishment of a low-cost feedstock to meet economic drivers and environmental goals.

3.4 1-Propanol (n-propanol)

1-Propanol is widely used in coatings industry as a medium-volatile alcohol for improving the drying characteristics of alkyd resins, electro-deposition paints, and baking finishes. It is used as a solvent in flexographic and other printing ink applications. Propanol is one of the key raw materials used in the cosmetics industry. Spot prices start at around $4.10/gal (Alibaba 2019). It exhibits good combustion properties, with RON of 104 and octane sensitivity of 15 (Christensen et al. 2011). It blends synergistically with an equivalent blending RON of 121.5 at 10% blend level into a suboctane BOB. The vapor pressure is lower than ethanol, and it has 16% higher lower heating value. Like ethanol, it is miscible with water (Chickos and Acree 2003; Andersen et al. 2010a).

1-Propanol (n-propanol)



CAS #	71-23-8
Formula	C_3H_7OH
RON	104
bRON at 20%	130
MON	89
S	15
HOV (kJ/kg)	788.7
LHV (MJ/kg)	30.8
PMI	0.118
YSI	16.2
S_L (343K; 1 bar; cm/s)	48
Water sol. @ 25 ºC (g/L)	Miscible
Catalyst Light-Off: T_{50}	206.8 ºC
T_{90}	247.9 ºC
LSPI propensity	Low

	RON	MON
Base BOB	90.3	84.7
10% n-PrOH	94.5	86.7
20% n-PrOH	98.0	88.1
30% n-PrOH	100.5	88.9

3.4.1 *Kinetic Model*

The n-propanol kinetic model was taken from the literature and inserted into the LLNL kinetic model for HPFs. The n-propanol kinetic model was verified to ensure the simulated ignition delay times over a wide range of temperature, pressure, and equivalence ratio were the same as those predicted by the original published literature model. 95% of simulations were within a factor of 1.27. The kinetic model is also being validated using speciation data from the NREL flow reactor. The chemical mechanism features described for all alcohols in Section 3.1.1 apply here as well.

3.4.2 *Fuel Property, Engine Test, and Emissions Control Results*

A number of fuel properties of 1-propanol were summarized in a NREL 2011 publication (Christensen et al. 2011). Co-Optima researchers performed additional engine and fuel property tests of 1-propanol and its blends at 10%, 20%, and 30% v/v in several base fuels. Laminar flame speed measurements are reported in several recent publications (Veloo and Egolfopolous 2011); the value given in the box is from Veloo and Egolopolous.

Flame speed data at a variety of elevated temperatures are available from literature sources (Galmiche et al. 2011; Beeckmann 2014; Veloo et al. 2010). The RVP of 1-propanol is slightly lower than IPA, and their blending behaviors with gasoline are similar (Andersen et al. 2010a).

Solubility and elastomer swelling tests conducted under Co-Optima established that 1-propanol does not pose significant compatibility issues with fuel infrastructure materials, except for SBR (styrene-butadiene rubber) and silicone elastomers (Kass and West 2017; Kass 2018).

Engine Tests

n-Propanol was included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis.

Emissions

n-Propanol has a very low propensity to generate soot, with a PMI of 0.118 and a YSI of 16.2. Catalyst light-off temperatures for neat n-propanol are relatively low ($T_{c,50}$ 206.8 °C, $T_{c,90}$ 247.9 °C). However, it is likely that n-propanol will behave much like ethanol when blended to reasonable levels with a petroleum-based BOB, resulting in blend light-off temperatures close to that of the BOB.

3.4.3 Conversion Routes from Biomass

The production of 1-propanol from petroleum is commercial, and therefore no additional production-related research was carried out under Co-Optima. 1-Propanol is industrially produced by reduction of propionaldehyde. Propionaldehyde is obtained by catalytic hydroformylation of ethylene using CO and hydrogen. Nakagawa et al. (2018) points out that in the latter case bioethylene can be used as a substrate for propionaldehyde production, and the usefulness of the bioethylene route to produce 1-propanol should be compared to that of the conventional process.

1-Propanol can be formed from various bio-feedstocks via microbial pathways along with other small alcohols (Zhang et al. 2011). Typically, low yields of 1-propanol are achieved, and such routes are not currently used for industrial 1-propanol production, though there have been research efforts to identify routes of its production from biomass-derived sources. These routes include hydrogenolysis of glycerol (by-product of biodiesel production) over heterogeneous catalysts (Zhu et al. 2012; Nakagawa et al. 2011; Tong et al. 2016) and microbial biosynthetic routes (Rodriguez et al. 2014; Shen and Liao 2008; Ammar et al. 2013; Walther and François 2016) with varied metabolic entries and stoichiometries.

Development of a route to convert propionic acid to propanol via a hybrid route is underway at NREL. No published data are available at the time of this writing.

3.4.4 Economic, Scalability, and Environmental Effects

Co-Optima analysts did not perform TEA or LCA on n-propanol, due to the limited information on production pathways from biomass. Research in the public domain has not been identified that provides analysis to understand economic, scalability, and environmental effects of producing this bio-blendstock

3.4.5 Challenges and Barriers

Water Solubility: 1-Propanol is miscible in water and forms an azeotrope, similar to ethanol. It is therefore likely to behave in a similar fashion to ethanol in the fuel system. It should be compatible with ethanol-compatible materials and systems. Mixtures of 1-propanol with other small alcohols and other oxygenates will likely be difficult and expensive to dry fully.

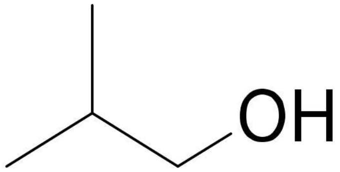
Production Routes: No economically viable pathways from biomass to 1-propanol have been developed that would enable its use as a fuel blendstock.

3.4.6 R&D Needs

1-Propanol has shown good combustion properties, however in order for it to be considered a viable bio-blendstock, economical pathways will need to be developed for its production from biomass. The absence of such pathways has been the main barrier for 1-propanol to be considered as transportation fuel. Therefore, future efforts should focus on improvements to production routes, including development of direct routes where 1-propanol is not a minor constituent and improve production techno-economics.

3.5 2-Methylpropan-1-ol (Isobutanol)

2-Methyl-1-Propanol (isobutanol)



CAS #	78-83-1
Formula	C_4H_9OH
RON	109
MON	90
S	19
HOV (kJ/kg)	508.0
LHV (MJ/kg)	33.5
YSI	26.2
PMI	0.168
S_L (343 K; 1bar; cm/s)	46
Water sol. @ 25 ºC (g/L)	85
Catalyst Light-Off: T_{50}	256 ºC
T_{90}	282 ºC
LSPI propensity	Low

	RON	MON
Base BOB	90.3	84.7
10% i-BuOH	91.9	86.2
20% i-BuOH	96.8	87.5
30% i-BuOH	99.2	88.1

Four-carbon alcohols have four isomers, with isobutanol (IBA) being the most common isomer for use in fuels. 1- and 2-butanol show very good performance, but not quite at the same level as IBA. Currently, IBA is more commonly used as a solvent and as a reactant in organic synthesis.

This slightly larger alcohol means more isobutanol must be blended into gasoline to achieve the same oxygen content as ethanol. To reach 2.7% oxygen in gasoline, one needs to blend 12.5% isobutanol. Other properties of IBA compare favorably to other alcohols. The low vapor pressure of IBA allows blenders to meet oxygenate blending requirements without the 1-psi waiver necessary for ethanol blending (EPA 2018). At low levels, IBA-gasoline blends show similar distillation curves to conventional gasoline (Anderson et al. 2010b). The low water solubility of isobutanol means it could be blended at the refinery gate and moved through common petroleum product pipelines.

3.5.1 Kinetic Model

The isobutanol kinetic model was taken from prior work by LLNL on the kinetic models on butanols and inserted into the LLNL kinetic model for HPFs. The isobutanol kinetic model was verified to ensure that the simulated ignition delay times over a wide range of temperature, pressure, and equivalence ratio were the same as those predicted by the original published literature model; 95% of simulations were within a factor of 1.65. The kinetic model is also being validated using speciation data from the NREL flow reactor. The chemical mechanism features described for all alcohols in Section 3.1.1 apply here as well.

3.5.2 Fuel Property, Engine Test, and Emissions Control Results

Anecdotal evidence exists that states isobutanol has been tested in spark ignition engines for many decades (Christensen 1936). Investigations into isobutanol as a gasoline blendstock have been on-going in recent years, including in marine and small engines. Several measurements of laminar flame speed are reported (Knorsch et al.2014; Veloo and Egolfopolous 2010; Liu et al. 2011); the value in the box is from Veloo and Egolfopolous (2011).

Stansfield et al. (2012) examined the impact of blending ethanol and/or IBA into a 2.0L Direct Injection Spark Ignition (DISI) engine. Blend ratios varied from IBA16 up to a flex-fuel-like

IBA68 and were compared to a conventional 95 RON baseline gasoline. The data shows that IBA16 had slightly higher fuel consumption over base gasoline on the NEDC (New European Driving Cycle) test cycle, although the penalty from the oxygenate was lower than for E10. This work also found IBA16 reduced emissions for HC, CO, NOx, and PM.

Karavalakis et al. (2014) studied the impact of higher IBA blends in a port-fuel injection flex fuel vehicle (FFV) and a GDI FFV. The blend was a 55% mixture of IBA in gasoline, which still met the summer gasoline specification in California. Testing was conducted on the light-duty FTP (Federal Test Procedure) and the Unified Cycle. Total hydrocarbon and non-methane hydrocarbon results showed statistically similar results for the higher IBA blends compared to conventional gasoline. No statistically significant changes were observed for CO and NOx using IBA55 on these test cycles.

Sileghem et al. (2015) also studied the use of neat IBA in a DISI engine. While the focus of this work was less on IBA, some interesting data is presented. The engine was tested at a constant load point and various speed conditions. Similar to the studies discussed above, the IBA lowered pollutant emissions in this on-road engine.

Utilization of IBA has been strong in the off-road and marine markets, due to the lower propensity for water uptake compared to ethanol. Wallner et al. (2014) studied the emissions of IBA16 on a 1.7L 4-stroke outboard motor. In contrast to the on-road engines discussed above, the outboard motor is open loop with no feedback control to the engine. Wide-open throttle curves and five steady-state power modes were tested with the IBA16 compared to indolene and E10. The wide-open throttle testing showed similar or slightly improved volumetric fuel consumption with the IBA16 compared to indolene. This result is believed to be due to sufficient improved brake thermal efficiency to offset the lower heating value of the IBA16. Although the IBA16 reduced CO emissions in this engine, HC and NOx emissions were increased. The increase was found mainly due to increased NOx emissions from the IBA16 in the open-loop engine. Alcohol, 1,3-butadiene, and aldehyde emissions increased with the IBA16 compared to the base indolene fuel. These results highlight the variability of emissions with different oxygenate fuels depending on engine technology.

Engine Tests

Isobutanol was included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis. Isobutanol was also used in the series of engine studies focused on determining the effects of heat of vaporization and flame speed.

Emissions

Catalyst light-off tests showed that isobutanol exhibits a two-stage light-off behavior, where it begins to convert over the catalyst at relatively low temperatures close to the smaller chain alcohols, but the conversion levels off at around 20%. Higher conversion levels require higher catalyst temperatures, and the measured light-off temperatures ($T_{c,50}$ 256 °C, $T_{c,90}$ 282 °C) are quite similar to that of a surrogate BOB. Not surprisingly, blends of up to 30% isobutanol in the surrogate BOB yield light-off temperatures nearly the same as the BOB without isobutanol.

3.5.3 Conversion Routes from Biomass

The commercial production of isobutanol from petroleum is through hydrogenation of isobutyraldehyde (Billing 2001). IBA is the lowest value product of the hydrogenation reaction. The production of isobutanol from biomass has been demonstrated commercially by Gevo through conversion of fermentable sugars from dry mill ethanol plants (Ryan undated). Butamax has published widely on IBA as well and is reportedly currently converting the Nesika 10 Mgpy corn ethanol plant in Kansas to IBA production (Nesika Energy 2019). Recent work has also explored the production of isobutanol from various microorganisms, though there are still significant challenges (Smith et al. 2010; Higashide et al. 2011; Baez et al. 2011).

3.5.4 Economic, Scalability, and Environmental Effects

Isobutanol can be produced biochemically from an herbaceous feedstock blend. This bio-blendstock has high potential for near-term commercialization. Importantly, EPA certification allows isobutanol blending levels up to 16.1%, which produces a final fuel with the same oxygen content (3.5%) and heating value as E10 (Kolodziej and Scheib 2012). The economic viability of isobutanol is generally good with a favorable target cost at a reasonable feedstock cost. The SOT and target case minimum fuel selling prices (MFSPs) were \$5.57/GGE and \$4.22/GGE, respectively. Cost reductions in the analysis are driven by yield increases or improvement in the utilization of lignin for higher value co-products (Cai et al. 2018). Isobutanol exhibits favorable GHG emissions with a potential GHG reduction of about 87% compared to conventional gasoline (Cai et al. 2018), in part, stemming from co-produced electricity. Lower process chemical requirements, higher isobutanol yield, and co-produced electricity are important drivers of life-cycle GHG emissions (Cai et al. 2018). However, isobutanol has a life-cycle water consumption of 0.7 L/MJ, which is significantly higher than that of petroleum gasoline (0.1 L/MJ). The most significant contributor to isobutanol's life-cycle water consumption is consumption of process chemicals (sodium hydroxide, sulfuric acid, and ammonia), which are water-intensive (Cai et al. 2018).

3.5.5 Challenges and Barriers

Production and Separation: Production of IBA from biomass has been done on a large scale by Gevo (Ryan undated) using a proprietary strain of yeast. Similar to the use of microorganisms to produce IBA, the toxicity of the isobutanol remains a significant issue driving novel separation technologies. Additionally, the Gevo process is dependent on a proprietary yeast strain, though it is likely other effective strains could be developed.

Cost: The largest barrier facing wider scale isobutanol use is the cost of production (Hewitt and Lakare 2016). Until cost parity is reached, the economic barriers remain significant. One benefit of IBA is there is no need for a 1-psi waiver in conventional gasoline blending. The proposed regulation to eliminate the need for this waiver could severely limit future markets for isobutanol by increasing the use of ethanol in areas previously limited by the vapor pressure created by ethanol (Heller 2018).

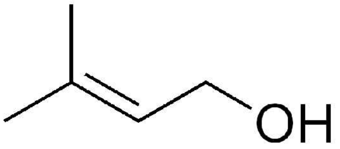
3.5.6 R&D Needs

Future efforts to improve production techno-economics, determine the extent to which IBE and similar mixtures may be used directly in as an additive, and optimize mixtures containing IPA for fuel properties.

3.6 3-Methyl-2-buten-1-ol (prenol)

3-Methyl-2-buten-1-ol, also known as prenol, is an unsaturated C5 alcohol typically used as a flavoring agent, or as an intermediate in the production of larger aromatic molecules. The demand for prenol in 2001 was between 6,000 and 13,000 tons (SIDS 2005). However, very little research on prenol for use as a blendstock in spark ignition engines was primarily due to its relatively low neat RON of 93.5 (Mack et al. 2014; NREL 2017). While this low neat RON seems to limit the potential of prenol as an anti-knock blending agent, recent results reported by Co-Optima researchers demonstrated high bRON of 122–145 at 10% v/v blend levels, with the value dependent on the chemistry of the BOB. Furthermore, Co-Optima researchers found that the measured RON of prenol-BOB blends surpass the neat RON value of 93.5 measured for prenol, with a measured 30% v/v prenol-BOB blend exhibiting a measured RON > 98 (Monroe et al. 2019). This effect has been noted in a variety of different base blendstocks with varying hydrocarbon composition. Research is ongoing to determine the mechanism behind this behavior and to determine which gasoline compositions maximize the effect. As is common for olefinic compounds, prenol has an octane sensitivity of 19 which leads to strong anti-knock performance at boosted conditions where both high RON and high S prevent knock. Prenol also has good energy density, modest water solubility, and low RVP. One area of concern for prenol is its oxidative stability. The internal double bond leads to measurable oxidation during testing. Emissions tests have been limited, but prenol is expected to demonstrate low soot production levels based on modeling efforts and comparison to similar molecules.

3-methyl-2-buten-1-ol
(prenol)



CAS #	556-82-1
Formula	C_5H_9OH
RON	93.
bRON at 20%	120
MON	74
S	19
HoV (kJ/kg)	512
LHV (MJ/kg)	34.0
YSI	47
PMI	0.93
S_L (298K; 1 bar; cm/s)	Not measured
Water sol. @ 25 ºC (g/L)	46.9 g/L
Catalyst Light-Off: T_{50}	Not measured
T_{90}	Not measured
LSPI propensity	Low

	RON	MON
Base BOB	90.3	84.7
10% prenol	94.0	85.5
20% prenol	96.7	84.9
30% prenol	97.4	84.0

3.6.1 Kinetic Model

The prenol kinetic model was developed under the Co-Optima initiative. It was validated using fundamental experimental data on speciation from a jet stirred reactor and from the NREL flow reactor. Additional experimental data are being acquired for validation including ignition delay times from a rapid compression machine by a university research collaborator. Also, experimental validation flame speed data will be acquired by researchers at the University of Central Florida under a Co-Optima competitive award. This additional validation data will be used to further improve the kinetic model. Prenol combines the characteristics of alcohols and alkenes. Prenol contains both a C=C double bond and an -OH moiety. This allows scavenging of OH radicals by both the allylic C-H bonds next to the double bond and by the alpha C-H bond next to the OH. These features give it a unique autoignition behavior when subjected to a temperature-pressure history in an internal combustion engine. Otherwise, the chemical mechanism features described for all alcohols in Section 3.1.1 apply here as well.

3.6.2 Fuel Properties

Co-Optima researchers have been developing structure-property relationships for prenol. The unique blending behavior seen for prenol has prompted the investigation of a wider range of olefinic alcohols as potential blending agents to increase engine efficiencies, especially at operating conditions where octane sensitivity becomes increasingly important.

Blending

The autoignition behavior of prenol blended into petroleum BOBs was investigated for a large number of base fuels; the results are discussed in detail by Monroe et al. (2019). This work showed that the synergistic RON blending measured for prenol is not unique to a specific BOB composition and can be increased or reduced by changing the BOB composition. The bRON varied from 122 to 145 in tests in seven BOBs including the four-component surrogate developed within Co-Optima. Preliminary results suggest that prenol also blends well with BOBs containing ethanol, with RON>99 at 20 vol% in E10, and interesting MON suppression behavior (bMON = 76 at 20% in an E10). Additionally, prenol also appears to blend well in combination with ethanol, as highlighted in Table 7. Blending prenol into the E10 blends leads to a slight decrease in the blending RON (~5) while the blending S values is slightly increased by about 5, compared to blending into the ethanol-free base fuel.

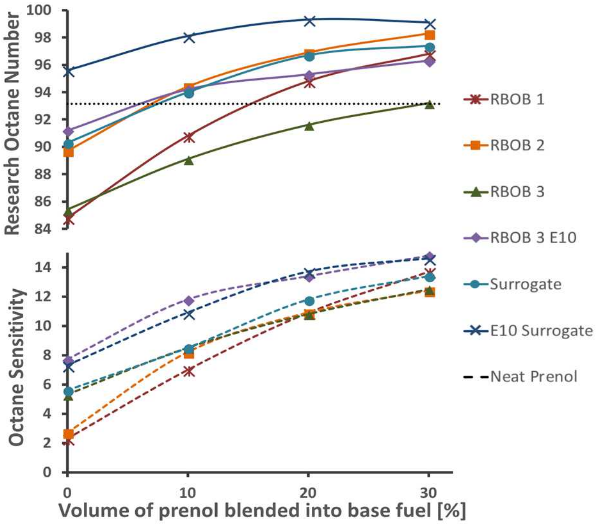


Figure 8. RON and S blending profiles for prenol blended into a variety of complex RBOB samples, the Co-Optima four-component surrogate and two of these with 10 vol% EtOH added (Monroe et al. 2019).

Table 7. Prenol blends in Surrogates and RBOBs with and without 10% ethanol.

	Volumetric blending RON			Volumetric blending octane sensitivity		
	10%	20%	30%	10%	20%	30%
Surrogate	127	122	114	35	37	32
Surrogate E10	121	114	107	43	39	32
RBOB	122	116	111	37	33	29
RBOB E10	121	112	108	49	36	31

Engine Tests

While a significant amount of effort has been put into prenol in cooperative fuel research (CFR) engines at RON and MON conditions, work is now underway to investigate prenol in engines that are more relevant to the vehicle fleet. Prenol was included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis.

Emissions

Emissions testing on prenol and prenol blends has been limited. Prenol has a predicted YSI of 47 ± 9 (Das et al. 2017). This suggests a relatively low propensity for prenol to soot, although more detailed research including emission measurements from on-road engines should be carried out. Additionally, detailed investigations into prenol's volatility, including RVP and distillation curves have yet to be conducted. Neat prenol has a boiling point of 140 °C, which could impact the fuel distillation curve at high blend volumes. Work is currently underway to measure emissions impacts.

3.6.3 Conversion Routes from Biomass

Prenol is produced industrially via a catalytic route developed as an intermediate in the production of citral (Hoelderich et al. 2007). Isobutene and formaldehyde are first reacted using a Brönsted acid catalyst via the Prins reaction to produce isoprenol (3-methylbut-3-en-1-ol). Isoprenol is then isomerized to prenol via double bond migration. The double bond migration is performed over modified Pd catalysts. Selenium is reported as a modifier in the patent literature (Rebafka 1982). The effect of selenium is reported to maintain Pd in an oxidized state active for the desired isomerization reaction while significantly depressing the hydrogenation activity associated with Pd^0. The reaction is carried out in an H_2 atmosphere to maintain the activity of the catalyst (Kogan et al. 2006).

Additionally, a significant amount of work has been done to investigate biological production of prenol. This has focused on dephosphorylation of intermediates in the isoprenoid pathways. While much of this work has targeted isoprenol, with some studies demonstrating titers of 2.5 g/L, reports suggest the possibility of selectively producing prenol over isoprenol (Monroe et al. 2019).

3.6.4 Economic, Scalability, and Environmental Effects

To the best of our knowledge, there are no techno-economic and life-cycle analyses for this bio-blendstock available in the literature. Although prenol is conventionally manufactured from petroleum-derived isobutene and formaldehyde, one study described a biosynthetic approach to selectively produce bio-derived prenol in engineered *E. coli* from renewable sources (Zheng et al. 2013). Analysis of this or other preferred routes should be undertaken in future research.

3.6.5 Challenges and Barriers

Production and Separation: While initial results for prenol look promising, significant work still needs to be done to demonstrate that prenol can be produced at the titers, rates, and yields that will make cost competitive with petroleum products. Potential issues around the acute oral and aquatic acute toxicity of prenol (4 and 3 rated hazards respectively according to Occupational Safety and Health Administration [OSHA] HAS ratings) should be considered in LCA assessments and potential market adoption.

Water Solubility: While prenol has significantly lower affinity to water than shorter chain length alcohol (methanol, ethanol, isopropanol), it is still water soluble up to 46.9 g/L which may restrict its ability to utilize existing petroleum infrastructure. Other C5 unsaturated alcohols (2-methyl-3-buten-2-ol) have been documented to form an azeotrope with water so it is likely that prenol will as well and this should be investigated further.

Reactivity: As is the case with all olefins present in complex gasoline mixtures, the internal double bond in prenol is reactive with other hydrocarbons as well as oxygen. Potential problems with long term storage of prenol should be investigated and accounted for in TEAs. 10% v/v prenol in gasoline blends were measured for oxidative stability via ASTM 525 and had an induction time of 141 minutes, below the limit of 240 minutes (ASTM D4814). Gum formation was measured via ASTM D873 to be 51 mg/100 mL. A blend of 20% prenol had an induction time of 85 minutes, well below the minimum, therefore higher blends may encounter stability related degradation during storage. For comparison, conventional gasolines typically produce gums from 5-20 mg/100mL after oxidation via ASTM D873, but do not produce an induction time within 24 hours on ASTM D525. Oxidation of prenol will likely require additional considerations for antioxidant additive use to prevent fuel quality degradation during storage and handling.

Blending Limit: Prenol would be limited in California to the 10% olefin blending limit without any changes in the regulation.

3.6.6 R&D Needs

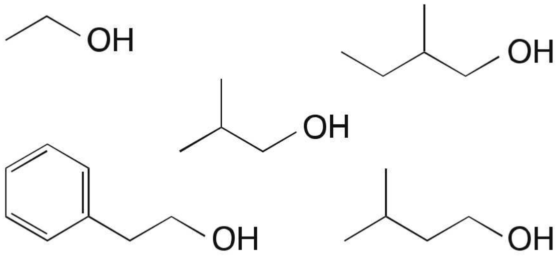
Several research needs were identified by the Co-Optima team. First, the most important R&D need is to determine the mechanism behind octane hyperboosting in prenol and determine whether this phenomenon is present in other blendstocks. Additionally, fuel properties such as distillation curves, vapor pressure effects, oxidation stability and toxicity issues must be more comprehensively determined if prenol is to be adopted into the market. Finally, more research is needed to demonstrate that prenol can be produced from sustainable sources at scale and at a cost that can be competitive in the marketplace, with favorable environmental impacts.

3.7 Fusel Alcohol Blend

Fusel alcohol is a term that is broadly used to refer to short-chained alcohols with carbon chains longer than that of ethanol. Fusel alcohols are most commonly thought of as undesired fermentation products in brewing or fuel ethanol production that microorganisms produce under environmental stress. Fusel alcohol mixtures can have a wide range of compositions, but this report highlights a particular mixture produced by a consortium of engineered bacteria designed to grown on low starch/high protein hydrolysate, as discussed further in Section 3.7.3. Three different variations of fusel alcohol blends based on fermentations of hydrolysates from different biomass sources were investigated and are discussed. Two of the mixtures (Blend #4 and Blend #5) were scored significantly higher than the third mixture (Blend #2) by the merit function. These mixtures are comprised of five different primary alcohols, all of which have been individually investigated as bio-blendstocks for BSI engines. The five alcohols are ethanol, isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-phenylethanol. The precise composition of the fusel alcohols depends on the production method, and the compositions of the three mixtures highlighted here can be seen in Table 10 from section 3.7.3.

The blend with the highest level of 2-phenylethanol has a higher PMI (4.5) which leads to a lower merit function score compared to the other blends. The values shown in the box are for blend #4 (see Table 8 in Section 3.7.3 for composition details by production method), which has a PMI below the merit function cutoff of two and the highest HoV of the fusel alcohol blends. The measured YSI varied from 32 (fusel alcohol blend #4) to 40 (fusel alcohol blend #5) to 51 (fusel alcohol blend #2), which follows the same trend as the 2-PE content. The octane and blending data are shown in Table 8, along with select fuel properties.

Fusel Alcohol Blend



CAS#		
	ethanol	64-17-5
	isobutanol	78-83-1
	2-methylbutan-1-ol	137-32-6
	3-methylbutan-1-ol	123-51-3
	2-phenylethanol	60-12-8

Component formulae	C_2H_5OH C_4H_9OH $C_5H_{11}OH$ $C_5H_{11}OH$ C_8H_9OH
RON	110
bRON at 20%	115
MON	98
S	12
HOV (kJ/kg)	691
LHV (kJ/kg)	35.4
YSI	32-51
PMI	1.8
S_L (cm/s)	Not measured
Water sol. @ 25 ºC (g/L)	Not measured
Catalyst Light-Off: T_{50}	Not measured
T_{90}	Not measured
LSPI propensity	Low

	RON	MON
Base BOB	87.4	85.2
10% fusels	91.3	86.1
20% fusels	95.3	87.2
30% fusels	98.2	88.2

[+] data calculated as a weighted average of each of the experimentally measured individual

These blends show synergistic RON blending as well as moderate octane sensitivity boosting which is in line with the literature on most short-chained alcohols. One of the strengths of the blends is the balance of properties from the different constituent molecules which are themselves good bio-blendstocks. Compounds like 2-phenylethanol were ruled out as biofuel candidates for BSI operation due to high boiling point, viscosity, and sooting tendency, but in this fusel alcohol blend those properties are mitigated by the other components in the mixture, while properties such as low RVP, high octane, and high energy density improve the performance of the mixture.

Table 8. Fusel alcohol blends blended into PNNL CARBOB #3 (RON = 87.4 and MON = 85.2) all show synergistic blending based on bRON and bMON.

	bRON (10%)	bRON (20%)	bRON (30%)	bMON (10%)	bMON (20%)	bMON (30%)
Fusel #2	121	123	121	96	97	96
Fusel #4	126	127	123	94	95	95
Fusel #5	128	126	123	90	95	94

The three different fusel alcohol mixtures were blended into reformulated blendstocks for oxygenated blending as well as E10 fuel mixtures. All three mixtures show synergistic RON blending and as well as synergistic S enhancement. The slight variation in composition of the mixtures can have a noticeable impact on both bRON and bMON values. The HoV is also affected, with Fusel Blend #4 having a >6% higher HoV than Fusel Blend #2. Additionally, PMI values are also variable and are driven by the mass% of 2-phenylethanol due to its high double bond equivalent and low vapor pressure. Limiting 2-phenylethanol concentration reduces the PMI penalty and can eliminate the penalty completely if kept to <9 vol %. Finally, LHV measurements of three of the fusel alcohol mixtures were consistent at 35.4 +/- 0.2 MJ/kg.

These results suggest that the composition of fusel alcohol blends can be further optimized to maximize the merit function score. This can be done by varying the feedstock used for bioconversion, optimizing pretreatment, changing fermentation process conditions, or by additional strain engineering. Each of these strategies is being investigated. The three versions of the fusel alcohol blends should be considered a starting baseline with significant room to improve the overall merit function score as well as the LCA and TEA outlook.

3.7.1 Kinetic Model

The fusel alcohol blend is comprised of six components, five of which are included in the LLNL kinetic model for HPs. The sixth component is 2-phenylethanol and is not currently available in the LLNL kinetic model. Since all the components in the fusel alcohol blend have an alcohol moiety, the kinetic mechanism features described for all alcohols in Section 3.1.1 generally apply here as well. A literature kinetic model for 2-phenylethanol is available. For the five component models that are available for the blend, the kinetic models for ethanol and isobutanol are discussed above in sections 3.1.1 and 3.5.1. The kinetic models for the two isopentanols were taken from the literature and inserted into the LLNL kinetic model for HPFs. The isopentanol kinetic models were tested to check that the simulated ignition delay times over a wide range of temperature, pressure, and equivalence ratio were the same as those predicted by the original published literature model, for example, 95% of simulations were within a factor of 1.41 (2-

methylbutan-1-ol) and 8.59 (3-methylbutan-1-ol). Because of the large difference seen for 3-methylbutan-1-ol, the present kinetic model predictions for this isopentanol are not quantitative and further work is needed to improve the model.

3.7.2 Fuel properties, Engine Test, and Emissions Control Results

The fusel alcohol blend has the benefit of being composed of molecules that have been extensively researched as bio-blendstocks in recent years. While this is often helpful, the blending behavior depends on the details of the inter-molecular interactions between the components as well as the hydrocarbons in the base fuel, and it is difficult to reliably make assumptions about a variety of combustion related fuel properties such as octane rating or flame speed. These more complex properties need to be measured for the blend and cannot be calculated simply as the sum of the various components.

Blend Fuel Properties

A potential advantage of a mixture of components with large difference in boiling points is in reducing impacts on fuel distillation properties. In order to determine these impacts, Co-Optima researchers measured distillation curves for the two most promising mixtures, Fusel Blend #4 and #5. The results are shown in Table 9. The T20 through T80 are lowered for both blends, but T10 and T90 are not dramatically affected. Further, the RVP was measured for a series of blends (Figure 9). Ethanol has been shown to increase vapor pressure of gasoline blends, while components like the isopentanols and 2-phenylethanol should reduce RVP values. Figure 9 shows that RVP blends for all three mixtures investigated are lower than the base fuel, and the measured RVP is highest in blends with the largest ethanol content, as expected.

Table 9. ASTM D86 test results for fusel alcohol blends #4 and #5 blended into BOB.

	Base Fuel	Fusel Blend #4			Fusel Blend #5		
		10%	20%	30%	10%	20%	30%
IBP	99.5	106.0	106.3	107.8	102.2	105.6	108.3
5	148.28	145.2	146.5	150.6	146.8	148.3	152.4
10	166.28	158.7	159.6	163.0	160.9	161.1	164.7
20	188.96	177.3	176.2	178.2	180.1	177.6	180.0
30	206.42	193.6	189.1	189.0	195.8	190.9	190.6
40	217.4	205.5	200.1	197.4	207.0	201.2	199.8
50	224.6	214.5	208.2	205.9	216.1	208.2	206.8
60	231.26	224.4	214.9	213.1	225.9	215.6	213.8
70	239.72	235.2	224.1	220.3	237.2	224.4	222.1
80	253.58	250.5	242.2	233.1	252.9	244.0	237.0
90	295.34	293.7	291.7	277.3	300.0	299.7	296.1
95	347.18	344.8	348.4	357.1	353.3	362.5	381.9
FBP	422.24	410.4	408.9	410.5	417.6	415.9	421.7
Recovered	98.7	98.0	97.7	98.4	98.4	97.8	98.2

Residue		1		1.1	1.1	1.0		1.1	1.1	1.1
Loss		0.3		0.9	1.2	0.6		0.5	1.1	0.7

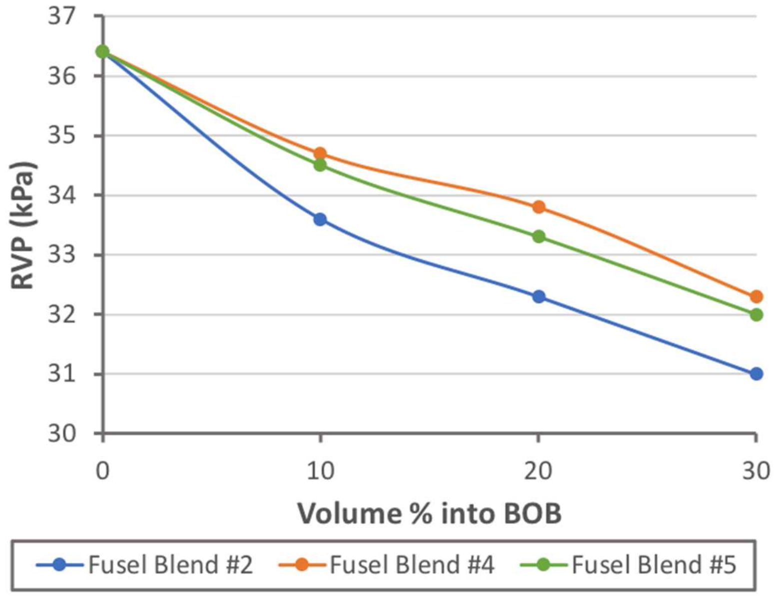


Figure 9. RVP of fusel alcohol blends blended into BOB. 2-PE has very low vapor pressure while ethanol has a high blending vapor pressure. This is consistent with these results where Fusel Blend #2 has the lowest blended RVP (highest 2-PE and lower EtOH content) while Fusel Blend #5 has the highest RVP (lowest 2-PE and higher EtOH content).

Engine Tests

Engine tests have been limited to CFR octane measurements, and none of the fusel alcohol blends has been run in more advanced research engines yet. Work in the coming years should give fusel alcohol blends a chance to be more thoroughly researched and possible engine efficiency gains to be better quantified.

Emissions

Emissions testing on the fusel blends have been limited. We have predicted and measured YSI and calculated PMI. Additional work measuring thermophysical properties, including RVP and distillation curves, have yet to be performed and should be high priority. 2-Phenylethanol is responsible for >90% of the PMI contribution and will therefore be the most problematic component for properties such as T90 and soot formation. The 2-PE content may need to be limited at the cost of octane performance or energy density.

3.7.3 Conversion Routes from Biomass

Fusel alcohols can be produced directly by microorganisms via the Ehrlich pathway. Fusel alcohol mixtures such as isopropanol/n-butanol/ethanol, isopropanol/n-butanol have been produced in a variety of engineered biocatalyst organisms, including *Clostridium* sp., *E. coli*, *Corynebacterium* sp., and yeast (Atsumi et al. 2008; Smith et al. 2010; Survase et al. 2011; Lee et al. 2012).

Fusel alcohols are comprised primarily of isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-phenylethanol as well as ethanol in Sandia's recently developed *Escherichia coli* bioconversion consortium (Liu et al. 2017). The *E. coli* consortium was engineered for the simultaneous conversion of the carbohydrate and protein fractions of mixed residual biomass into various fusel alcohols. In the consortium, one *E. coli* strain was modified for the conversion of hexose and pentose sugars; the second *E. coli* strain was modified for the utilization of the protein fractions of the biomass, each providing fusel alcohols as a reduced carbon fuel product (Liu et al. 2017; Huo et al. 2011; Wu et al. 2016). The consortium was demonstrated to utilize the pretreated biomass hydrolysates directly to produce fusel alcohols, without the need of adding any nutrient supplements. This *E. coli* consortium was subsequently demonstrated to produce fusel alcohols from various biomass feedstocks, including distillers' grain with solubles (DGS) which is the co-product form the 1st generation bioethanol industry, and different species of microalgae biomass. While isobutanol was the most dominant product, the compositions of the fusel alcohol mixture produced by the *E. coli* consortium varied when different biomass feedstocks were provided (Table 10).

Table 10. Compositions of fusel alcohol mixtures (vol%) produced from different biomass feedstocks by the *E. coli* consortium.

	Fusel alcohol compositions				
Biomass feedstock	**isobutanol**	**2-methyl-1-butanol**	**3-methyl-1-butanol**	**ethanol**	**2-phenyl-ethanol**
Glucose/xylose [Fusel Blend #2]	57%	6%	12%	10%	15%
Wastewater grown *Scenedesmus* obliquus microalgae [Fusel Blend #4]	57%	5%	11%	19%	8%
Distillers' grain with solubles (DGS) [Fusel Blend #5]	55%	5%	12%	17%	11%

3.7.4 Economic, Scalability, and Environmental Effects

Fusel alcohols can be made from biologically aerobically upgraded lignocellulose sugars which are produced from a combination of an acid pretreatment and enzymatic hydrolysis, like isopropanol. While preprocessing biomass to sugar and the associated yields have been demonstrated at the commercial scale, the final fermentation step to produce fusel alcohol remains at the bench scale. Factors that render this bio-blendstock potentially economically viable include a lack of dependence on value-added co-products and the absence of competition for end use of this bio-blendstock in other markets. One challenge this bio-blendstock faces is a high ratio of target cost to SOT cost, which indicates a significant amount of research and development is necessary to move its production to high technology readiness. A second challenge is that the fusel alcohol mixture has unfavorable life-cycle GHG emissions and does not achieve the threshold 60% life-cycle GHG reduction as compared to gasoline to be eligible as a cellulosic biofuel under EPA's Renewable Fuel Standard. Some of the key life-cycle GHG emissions drivers are electricity and ammonia consumption.

3.7.5 Challenges and Barriers

Production and Separation: It will be challenging to develop a robust fermentation process that produces the mixed fusel alcohols with constant compositions every batch. The costs associated with downstream refinement of the fusel alcohol mixture for various applications are not well characterized and will require additional investigation and demonstration.

Water Solubility: Isobutanol has a solubility of approximately 85 g/L in water. It has limited miscibility with water and does not absorb water from air, preventing the corrosion of engines and pipelines. 2-methyl-1-butanol, 3-methyl-1-butanol and 2-phenylethanol are only slightly soluble in water with a solubility of 28 g/L, 28 g/L and 22 g/L, respectively. Mixtures of fusel alcohols with different solubilities may cause difficulty in handling and processing.

Variability: Due to the variable compositions of the biomass, the compositions of fusel alcohol produced by microbial fermentation also vary when utilizing different biomass feedstocks. Fusel alcohol mixtures with different amounts of each fuel molecule may perform differently as blendstocks for gasoline.

3.7.6 R&D Needs

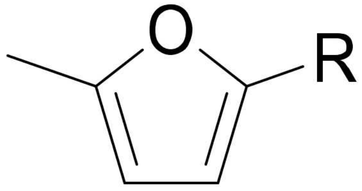
While there is a large body of work investigating fusel alcohols as bio-blendstocks for SI engine operation, more work is required for fusel alcohol blend and related mixtures. This includes additional work to evaluate octane boosting in a variety of different RBOBs as well as a more complete investigation of properties such as RVP and T90 to understand how this fuel mix might fit into existing fuel markets. The optimization of fusel alcohol mixtures via conversion processes under a variety of scenarios could identify blends with even better properties than those reported here. The product mixture can likely be driven to maximize or minimize specific properties, such as RON, but may come at the expense of other properties or yield. Finally, the rate, yield, and titers of the fusel alcohol products from engineered microorganisms need to be increased and scaled-up to industrial level to achieve market penetration.

3.8 Mixed Furan Derivatives (2,5-Dimethyl Furan and 2-Methyl Furan)

The furan derivates 2,5-DMF and 2-MF show promise as gasoline blendstocks due to their facile production from lignocellulosic sugars and promising fuel properties. 2,5-DMF can be produced from hexose sugars, while 2-MF can be produced from pentose sugars. Previous efforts have extensively evaluated the individual fuel properties of 2,5-DMF and 2-MF. Both 2,5-DMF and 2-MF show promising fuel properties for gasoline due to their high RON (2,5-DMF = 101, 2-MF = 103), energy density higher than ethanol (2,5-DMF = 30.1 MJ/L, 2-MF =28.5 MJ/L), and limited water solubility (2,5-DMF = 1.5 g/L, 2-MF = 3.4 g/L) (McCormick et al. 2017). However, neither 2,5-DMF or 2-MF is produced industrially from biomass due to the high process costs. The high cost is associated with the challenge of deconstructing lignocellulosic biomass to sugar monomers, as well as converting sugars to furan intermediates. Consolidated processing of lignocellulosic biomass to mixed hexose and pentose sugars streams shows promise for simplifying unit operations and reducing process cost when targeting mixed furan derivatives; however, this route and its resulting fuel properties have been far less studied.

Co-Optima contributed significantly to the understanding of methyl and dimethylfuran fuel properties, blending behavior, and stability. Building on previous work by Co-Optima researchers and the group in Aachen, the team expanded the understanding of fuel properties, stability, compatibility and combustion behavior.

2-MF/2,5-DMF at 40/60 mol%



R= H, -CH$_3$

CAS #	534-22-5/625-86-5	
Formula	C_5H_6O/C_6H_8O	
RON		102
bRON at 20%		146
MON		87
S		15
HOV (kJ/kg)		355
LHV (MJ/kg)		34.0
PMI		0.57
YSI		Not measured
S_L		Not measured
Water sol. @ 25 ºC (g/L)		2.2
Catalyst Light-Off:	T_{50}	276
	T_{90}	285
LSPI propensity	Low	

	RON	MON
Base BOB	90.3	84.7
10% furan mixture	98.0	88.5
20% furan mixture	101.4	88.7
30% furan mixture	102.0	88.9

3.8.1 Kinetic Model

The kinetic models for 2-MF and 2,5-DMF were taken from the literature and inserted into the LLNL kinetic model for high performance fuels. The 2-MF and 2,5-DMF kinetic models were verified to confirm that the simulated ignition delay times over a wide range of temperature, pressure, and equivalence ratio were the same as those predicted by the original published literature model; 95% of simulations were within a factor of 1.70 (2-methylfuran) and 1.77 (2,5-dimethylfuran). The 2,5-DMF kinetic model was validated using speciation data from the NREL flow reactor with good agreement between predicted and experimental species mole fractions.

3.8.2 Fuel Property, Engine Test, and Emissions Control Results

2,5-dimethyl furan (2,5-DMF)

CAS # 625-86-5		
RON		101.3
bRON at 20%		Not measured
MON		88.1
S		13.2
HOV (kJ/kg)		332
LHV (MJ/kg)		32.9
PMI		0.744
YSI		55
S_L (298K; 1 bar; cm/s)		37
Water sol. @ 25 ºC (g/L)		1.466
Catalyst Light-Off:	T_{50}	Not measured
	T_{90}	Not measured
LSPI propensity	Low	

2-methylfuran (2-MF)

CAS # 534-22-5		
RON		103
bRON at 20%		142
MON		86
S		17
HOV (kJ/kg)		358
LHV (MJ/kg)		31.2
PMI		0.316
YSI		42
S_L (298K; 1 bar; cm/s)		44
Water solubility (g/L)		3.41
Catalyst Light-Off:	T_{50}	Not measured
	T_{90}	Not measured
LSPI propensity	Low	

Based on the extensive history of testing 2,5-DMF and MF individually, Co-Optima performed fuel property and engine tests with a mixed furan blend (40/60 wt% 2-MF/2,5-DMF) in several base fuels. These results are summarized below.

Blending

Fuel properties including dry vapor pressure equivalent and autoignition properties (RON, MON, and S) for the furan mixture were measured in several BOBs, including the Co-Optima 4-component surrogate. These include measurements in E10, e.g., co-blended with ethanol. When blended into a petroleum BOB, mixed furans display favorable non-linear blending for RON and relatively modest increases in MON. The degree of nonlinearity decreases with increasing concentration more quickly than for ethanol. At 10%, the furan mixture had the highest blending RON of all blendstocks tested by Co-Optima. The blending RON of the furan mixture was higher at 10% than for 2-MF. Results were comparable to earlier work on oxygenate blending by Christensen et al. (2011), with slightly higher measured blending RON. Christensen et al. (2011) adjusted the blending volume to achieve comparable oxygen percentage, so the furan blend levels were slightly higher than in the Co-Optima measurements, which could account for these differences. BOB chemistry likely also plays a role (Somers et al. 2013a,b).

Engine Tests

The furans were subjected to limited engine tests, in large part due to the oxidative stability challenge identified during testing.

Emissions

Catalyst light-off tests showed that the furan mixture lights-off at temperatures ($T_{c,50}$ 276 °C, $T_{c,90}$ 285 °C) a bit higher than those measured for a surrogate BOB, and significantly higher than most of the other oxygenated blendstocks that were studied. In fact, the light-off behavior of the furans is closer to that of aromatic hydrocarbons, likely due to the aromaticity of the furan ring. Despite the aromaticity of the furans, the YSI of both components is modest (42 and 55) and the PMI is also low. Co-blending with E10 reduces the Reid vapor pressure by 1.5 psi compared to an equivalent ethanol blend by volume.

3.8.3 Conversion Routes from Biomass

Mixed furans can be produced through sequential chemical transformations of the cellulose and hemicellulose fraction of biomass. Initially, polymeric sugars must be hydrolyzed through enzymatic (Chen et al. 2016) or chemo-catalytical transformations (Carrasquillo-Flores et al. 2013) to generate hexose (e.g., glucose) and pentose (e.g., xylose, arabinose) sugar monomers. Glucose is unique in that it must first be isomerized to fructose using either enzymes (Bhosale et al. 1996; Li et al. 2017) or Lewis acid catalysts (Román□Leshkov et al. 2010), with the latter being intensely investigated with heterogenous materials due to the potential for lower cost and recyclability. Subsequently, dehydration reactions can transform the mixed hexose and pentose sugars into hydroxymethylfuran (HMF) and furfural, respectively (Caes et al. 2015). The dehydration of sugars to furans is typically promoted with Brönsted acid catalysts in a biphasic system, with side polymerization to humins and rehydration reactions to non-target products being the major concerns (Bhaumik and Dhepe 2016). Extensive research efforts have gone into facilitating the isomerization and dehydration steps with lignocellulosic-derived sugars, which remain a current bottleneck. Lastly, hydrogenolysis reactions over supported metal catalysts remove the pendant furan oxygen groups to transform HMF and furfural into 2,5-DMF and 2-MF, respectively (Chen et al. 2016). This final step has been fairly well demonstrated with high molar efficiency and catalytic stability.

3.8.4 Economic, Scalability, and Environmental Effects

Co-Optima researchers conducted fuel techno-economic and life-cycle analyses.

- Furfural, the furan precursor to 2-MF, is industrially available (with a predicted market size of $1.4B by 2022 according to public summaries of at least one market report [Allied Market Research 2016]). Furfural is currently 3 times more expensive than ethanol (1.2–2.1 $/L for furfural compared to 0.4 $/L for ethanol), making subsequent conversion to 2-MF impractical.
- Production of HMF, the furan precursor to 2,5-DMF, has only been demonstrated at the pilot scale and has yet to be produced at the commodity scale.

Production of this mixture is possible via both catalytic upgrading of sugars and pyrolytic pathways. The analysis team chose the catalytic conversion of sugars pathway as the representative pathway to conduct LCA because of increased data availability and higher projected yields. This pathway first employs a biomass deconstruction process (a combination of dilute acid pretreatment and enzymatic hydrolysis) then a thermochemical catalytic upgrading process. Factors contributing to potential economic viability of this bio-blendstock include a lack of dependence of price on a value-added co-product and a lack of competition for its use other than as a fuel. On the other hand, a high target-to-SOT cost ratio indicates extensive research and development is needed to advance the technology to a point of commercial deployment. This bio-blendstock was estimated to attain a 50% reduction in life-cycle GHG emissions and fossil energy consumption, which earned the bio-blendstock a neutral rating for these evaluation categories.

3.8.5 Challenges and Barriers

Human Health and Environmental Impacts: Concerns have been raised previously regarding the toxicity and environmental impacts of the furans. A more detailed look into the health and environmental impacts was therefore conducted and can be found in Alleman and Smith (2019). Their findings are summarized as follows.

The furans are very mobile in the environment and would predominantly partition into the vapor phase (troposphere), with minor amounts in the soil and ground water. EPI Suite predicts ready aerobic biodegradability for the furans, but no anaerobic biodegradability. Low water solubility and low persistence to bioaccumulation are predicted. Both furans show moderate acute toxicity compared to the other compounds in this report (generally predicted to be non- or slightly toxic). Much of the data for these compounds has been developed from structural activity relationships and/or animal and microbial system testing and extrapolated to human health impacts. These estimates are, at best, conservative. It is also worth noting that chronic exposures to chemicals can result in very different impacts than longer term, subchronic exposures, and additional information will need to be gathered as these novel bioblendstocks become more prevalent in fuels.

Production Costs: As expected for a chemical not currently in the marketplace for use as a fuel blendstock, conversion strategies are needed to improve yields and economics for producing HMF and furfural from lignocellulosic biomass.

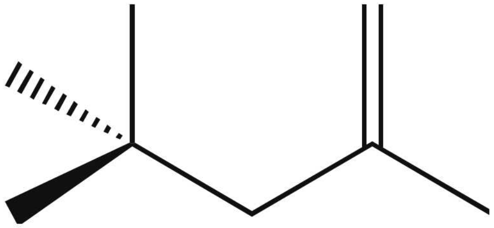
Stability: The most significant barrier to 2,5-DMF and MF implementation may be their poor storage stability. Gasoline blend tests with both compounds show significant formation of gums, peroxides, and polar reactive species that negatively impact storage stability, potentially making them nonviable (Christensen et al. 2018). Earlier work has also shown that MF blended into gasoline negatively impacts oxidation stability and results in higher injector deposits (Lange et al. 2011). Follow-on recommendations included the development and incorporation of suitable antioxidant additives to address this significant concern.

3.8.6 R&D Needs

Efforts to address these barriers are ongoing. Consolidated processing of hexoses and pentoses offers a near-term path to simplifying unit operations and reducing production costs. Targeted development of antioxidant additives to address gum and reactive species formation are warranted. Other coupling and chemical conversion strategies may also be an option to target more stable derivatives from furan intermediates as fuel products (Corma et al. 2012).

3.9 2,4,4-Trimethyl-1-pentene and 2,4,4-Trimethyl-2-pentene (di-isobutylene)

Di-isobutylene



CAS # 25167-70-8		
Formula		C_8H_{16}
RON		106
bRON at 20%		130
MON		87
S		19
HOV (kJ/kg)		318.2
LHV (MJ/kg)		44.3
PMI		0.574
YSI		68.5
S_L (298K; 1 bar; cm/s)		35
Water solubility @ 25 ºC		0.004 g/l
Catalyst Light-Off:	T_{50}	264
	T_{90}	275
LSPI propensity	Low	

	RON	MON
Base BOB	90.3	84.7
10% di-isobutylene	94.0	87.0
20% di-isobutylene	97.9	87.9
30% di-isobutylene	100.7	88.3

2,4,4-Trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene or mixtures of the two isomers are commonly known collectively as di-isobutylene (DIB). This eight-carbon olefin can be readily prepared by dimerization of isobutylene. DIB is a chemical intermediate for chemical products such as octylphenolic resins, octylated diphenylamine stabilizers for lubricants and rubbers, isononyl polymerization inhibitors and compressor fluids, sulfur additives for anti-wear lubricants and co-monomers. Isobutylene can be reduced to isooctane which is the primary component of aviation gasoline (Avgas). Spot prices vary around \$7.00–10.00/gal for petroleum-derived DIB. It exhibits excellent combustion properties, with high RON (106) and octane sensitivity (19). DIB blends linearly for RON with a blending RON of 90 at 10% blend level. It has 50% higher lower heating value (LHV) than ethanol. Unlike ethanol, it has very low miscibility with water.

3.9.1 *Kinetic Model*

The di-isobutylene kinetic model was improved under the Co-Optima initiative. Low temperature reaction pathways were added to the existing high temperature kinetic model and reaction rate constant estimates were improved. It is being validated with fundamental experimental data on ignition delay from shock tubes and RCMs; on species measurements from a jet stirred reactor and the NREL flow reactor; and with flame speed measurements from the University of Central Florida and Lund University. These validation data are being used to further improve and validate the kinetic model. Recently, laminar flame speed measurements have been reported elsewhere (Yin et al. 2019).

Di-isobutylene is an alkene whose molecular structure contains a C = C double bond and alkyl substitutions on the double bond which allows additional kinetic mechanism features such as addition of OH radicals to the double bond and the formation of relatively unreactive allylic radicals. The allylic radical mainly reacts with HO_2 to form a relatively reactive OH radical or can undergo termination reactions which inhibit reactivity. These features control its autoignition behavior when subjected to a temperature-pressure history in an internal combustion engine.

3.9.2 Fuel Properties, Engine Test Results, and Emissions Control Results

A detailed chemical kinetic mechanism for DIB was developed and demonstrated that the 2-pentene isomer of DIB ignites significantly faster than the 1-pentene isomer. In addition, the ignition delay times for blends were directly dependent on the proportions of each isomer. Although slower to ignite, the 1-pentene isomer is initially consumed nearly ten times faster than the 2-pentene isomer (Metcalfe et al. 2007).

An early study by Ford Motor Company found that DIB combusted more efficiently than isooctane, n-heptane, and toluene in a Labeco single cylinder research engine. At equivalence ratios above 1.0, DIB surprisingly produced less exhaust olefins than isooctane during combustion (Ninomiya and Golovoy 1969). A later study determined the NOx emissions to be higher for DIB than that of isooctane (Kaiser et al. 1993).

Co-Optima performed limited fuel property tests of DIB and DIB blends at 10%, 20%, and 30% v/v in several base fuels. These results are summarized below.

Blending

DIB has been blended at the 10%, 20%, and 30% levels with reformulated and conventional BOBs. In these cases, the RON blends linearly while the MON blends antagonistically leading to an increase in S as the blend level is increased (see Figure 10) with similar trends seen for both the RBOB and the cBOB.

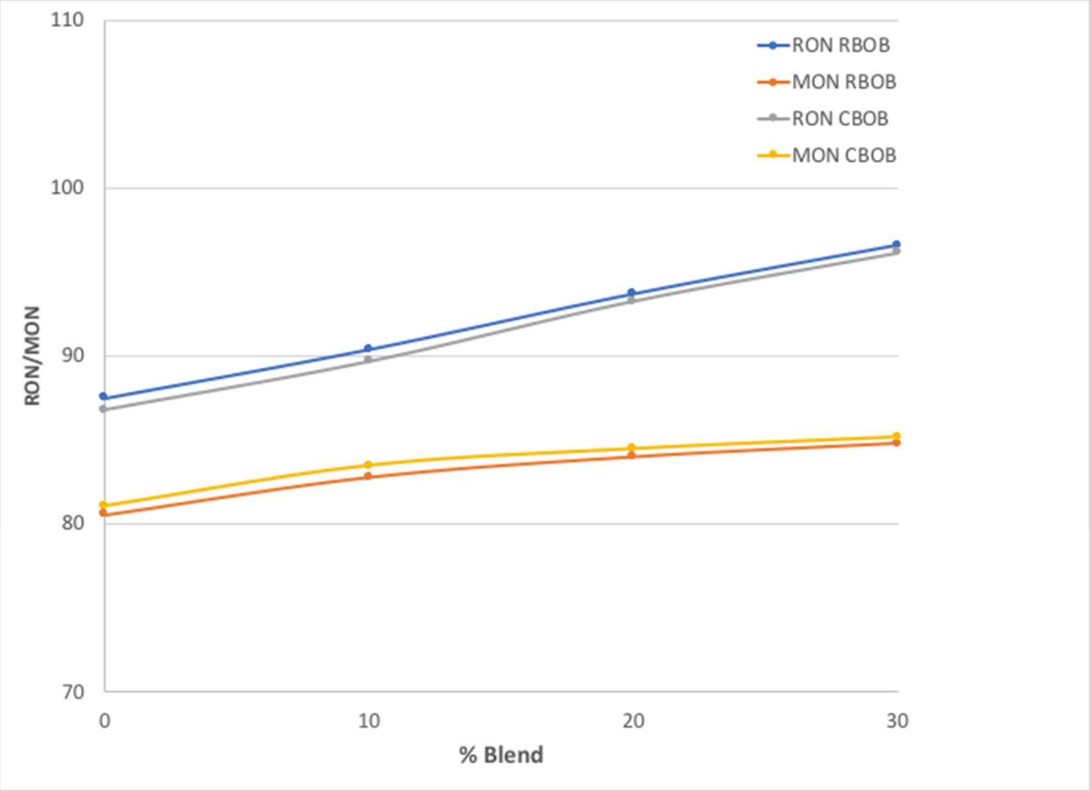


Figure 10. MON and RON blending linearity for di-isobutylene in two base fuels as a function of vol% di-isobutylene.

Engine Tests

Di-isobutylene was included in the engine tests focused on evaluating the validity of the Central Fuel Hypothesis, along with the studies aimed at understanding the effects of high S_L on dilution tolerance.

Emissions

Examination of the exhaust emissions from both a single component DIB fuel and as a blend with gasoline in a production spark ignition engine gave similar results to that of isooctane but with increased amounts of 2-methyl-1,3-butadiene and appreciable amounts of propene produced in the exhaust (Kaiser et al. 1993).

Catalyst light-off experiments showed that di-isobutylene starts to light-off at temperatures ($T_{c,50}$ 263 °C, $T_{c,90}$ 275 °C) slightly higher than those measured for a surrogate BOB. However, blends of up to 30% di-isobutylene in a surrogate BOB demonstrated light-off behavior very similar to the BOB itself. Thus, even though di-isobutylene is less catalytically reactive than other blendstocks and gasoline components, it will likely neither help nor hinder compliance with NOx, NMOG, and CO regulations in realistic fuel blends.

DIB produces relatively small amounts of soot, despite the double bond. The PMI of DIB is 0.5745 and the measured YSI is 68.5.

3.9.3 Conversion Routes from Biomass

Diisobutylene can be prepared through the dimerization of isobutylene using solid acid catalysts. Isobutylene can be synthesized from the bio-derived alcohols ethanol or isobutanol. Ethanol can be readily converted to acetone using basic catalysts (Murthy et al. 1988; Nakajima et al. 1994, 1987) and acetone can be selectively converted to isobutylene using a range of acidic zeolites (Chang and Silvestri 1977; Dolejsek et al. 1991; Hutchings et al. 1993). Ethanol can also be converted directly to isobutylene using nanosized $Zn_xZr_yO_z$ mixed oxides ~83% isolated yield at 450 °C in fixed bed flow reactors (Sun et al. 2011).

Industrially, Gevo Inc. dehydrate isobutanol to isobutylene for use as a precursor for isooctanes and jet fuel. Additionally, Lanzatech has processes to capture and convert CO or CO_2 to isobutylene which forms the basis for their C_8 to C_{12} jet fuel production. Global Bioenergies is also developing a microbial fermentation route to produce isobutylene directly from renewable resources.

3.9.4 Economic, Scalability and Environmental Effects

Research in the public domain has not been identified that provides analyses to determine economic, scalability and environmental effects of producing this bio-blendstock.

3.9.5 Challenges and Barriers

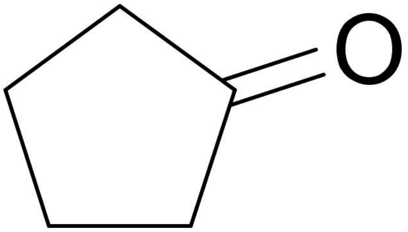
California limits the volume fraction of olefins allowed in fuel, with a cap limit of 10%, to reduce smog generation from fugitive emissions. This will ultimately limit the amount of DIB that may be included in gasoline.

3.9.6 R&D Needs

Due to the advanced commercialization of bio-derived DIB production, R&D needs are focused on improving large-scale production; these are currently being addressed by industry. To increase the amount of DIB that can be blended into gasoline, the limit in California would need to be changed, and the technical basis for such a change would need to be developed.

3.10 Cyclopentanone

Cyclopentanone



CAS #		120-92-3
Formula		C_5H_8O
RON		101
bRON at 20%		125
MON		89
S		12
HOV (kJ/kg)		504.0
LHV (MJ/kg)		32.0
PMI		0.744
YSI		22
S_L (423K; 1 bar; cm/s)		82
Water solubility @ 25 ºC		60.8 g/l
Catalyst Light-Off:	T_{50}	264
	T_{90}	281
LSPI propensity	High	

	RON	MON
Base BOB	90.3	84.7
10% cyclopentanone	93.7	87.2
20% cyclopentanone	97.3	88.3
30% cyclopentanone	100.5	89.4

Cyclopentanone is a cyclic ketone typically used as a synthetic intermediate to make fragrances, drugs such as cyclopentobarbitol, or pesticides. It is easily produced from the reaction of adipic acid with barium hydroxide at elevated temperatures (Thorpe and Kon 1925). It has only been very lightly studied as a potential fuel.

Co-Optima researchers conducted a number of fuel property, engine and compatibility tests on cyclopentanone, and developed a kinetic model explaining its combustion behavior (which is unusual for the ketones). Cyclopentanone has high RON, S, a moderately high HoV compared to gasoline, and a very high laminar flame speed.

3.10.1 *Kinetic Model*

The cyclopentanone kinetic model was developed under the Co-Optima initiative. It was validated using fundamental experimental data on ignition delays from shock tubes and rapid compression machines; on speciation data from a shock tube, a jet stirred reactor and the NREL flow reactor; and on flame speeds using two different methods (Bao et al. 2017; Vasu et al. 2019). The kinetic model shows that cyclopentanone's high flame speed is due to high yields of ethene that subsequently produce reactive vinyl radicals.

3.10.2 *Fuel Properties, Engine Test Results, and Emissions Control Results*

Blending

Cyclopentanone exhibits synergistic blending and enhances octane sensitivity. It is unusual among the ketones for both of these features, which is attributed to the presence of the five-membered ring. At a 30% blend level, the S of the blended fuel approaches that of neat cyclopentanone.

Engine Tests

Cyclopentanone was used for a number of engine studies in Co-Optima. Among these, Jatana and coworkers explored the dependence of distillation properties and flame speed on LSPI using neat gasoline, ethanol, 2-methyl-1-butanol, and cyclopentanone. Cyclopentanone was found to lead to more intense LSPI events than either of the alcohols, although all three had approximately the same event frequency.

Cyclopentanone exhibited compatibility issues in the Hansen solubility compatibility analysis, in exposure tests and in engine tests. The solubility analysis predicted significant compatibility issues with many elastomers, including fluorocarbons at mid-range blends and neoprene except at low blend levels. These predictions were confirmed in exposure tests conducted for cyclopentanone blended into an E10 base fuel, as demonstrated by large volume swell. These results are shown in Figure 11.

In engine tests, cyclopentanone dissolved the fuel line and led to seal leaks for at least one Co-Optima researcher (Szybist 2019).

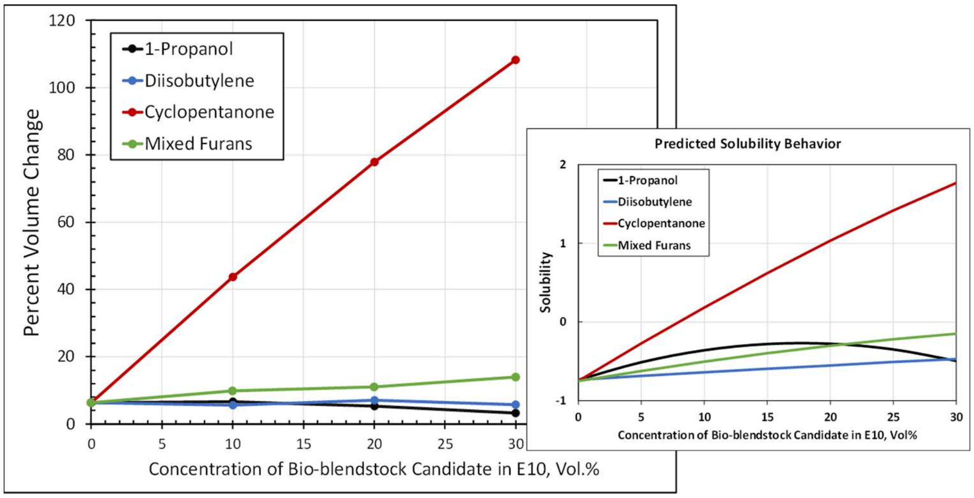


Figure 11. Percent volume change of fluorocarbon elastomer vs concentration of blendstock candidates in E10 (main figure), and Hansen solubility prediction (inset).

Emissions

Cyclopentanone has a low YSI and PMI, despite the presence of a five-membered carbon ring. Catalyst light-off experiments showed that cyclopentanone lights off ($T_{c,50}$ 264 °C; $T_{c,90}$ 281 °C) at temperatures slightly higher than a surrogate BOB. Interestingly, these light-off temperatures are much higher than those observed for all of the other ketones and esters that were evaluated. Additional emissions testing would need to be conducted to determine whether harmful partial oxidation products are produced during combustion.

3.10.3 Conversion Routes from Biomass

Cyclopentanone can be produced through a variety of thermochemical and biological processes. Thermochemically, cyclopentanone can be produced directly via pyrolysis as a minor product (Dermibas 2007; Resasco et al. 2018). Cyclopentanone can also be produced catalytically from furfural (a biomass-derived intermediate), selectively with very good yield using a variety of catalysts. Biochemical routes to cyclopentanone were uncovered using the retrosynthetic analysis tool by Whitmore and coworkers at Sandia National Laboratories as shown in Figure 12. The biochemical synthesis of cyclopentanone from biomass requires four enzymatic transformations from butyrate. Initially, butyrate is converted to valerate by transferring a methyl group on to butyrate. This can be catalyzed by a number of different methyltransferase enzymes (represented by the enzyme commission [EC] number EC 2.1.1.-). Valerate is synthesized to 5-hydroxypentanoate via the addition of an oxygen which can be performed by numerous monooxygenase enzymes (EC 1.14.13.-). Gluconolactonase (EC 3.1.1.17) transforms 5-hydroxypentanoate to 5-valerolactone and finally, 4-hydroxy-2-oxohexanoate aldolase catalytically transforms 5-valerolactone into cyclopentanone.

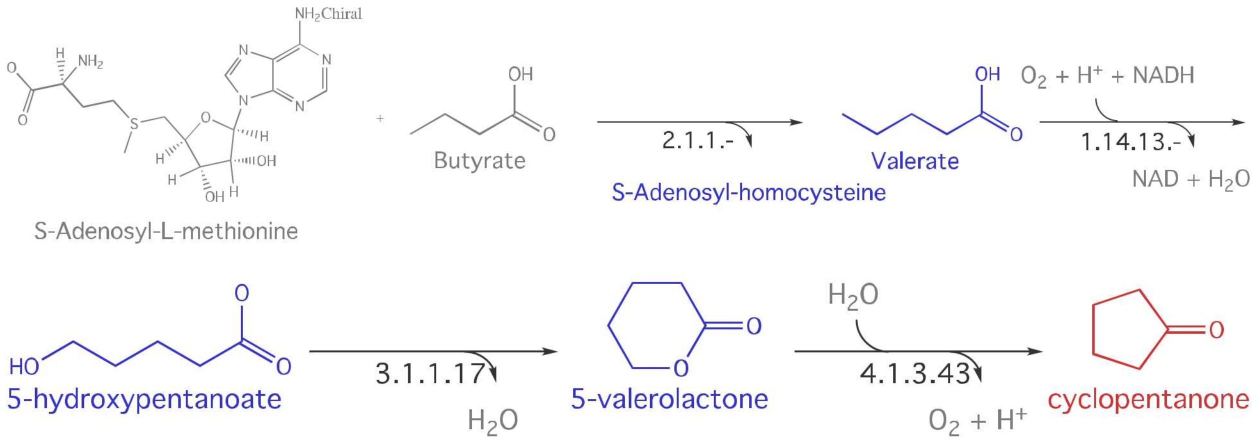


Figure 12. Biological production pathways for cyclopentanone from biomass discovered using retrosynthetic analysis.

3.10.4 Economic, Scalability, and Environmental Effects

Bio-based cyclopentanone can provide economic viability and potential reduction of fossil primary energy consumption and life-cycle GHG emissions compared to traditional cyclopentanone produced from adipic acid (Beck et al. 2018). In 2014, the market value of cyclopentanone was about $15 per kg produced with a global demand value of $100 million, and by 2020 this value is expected to grow to $130 million (Beck et al. 2018). Cyclopentanone is considered a great intermediate chemical that can be used in a variety of growing market products such as rubber chemicals, insecticides, pharmaceutical, perfumes, and electronics, which will affect its availability and use as a fuel. Kim and Han (2017) studied cyclopentanone production from lignocellulosic biomass. Their economic analysis showed that cyclopentanone could compete economically ($1.79/kg of cyclopentanone) with that produced by a petroleum-based process ($5 to $6/kg of cyclopentanone).

3.10.5 Challenges and Barriers

Despite the interesting and promising combustion behavior, Co-Optima researchers found a number of significant practical barriers to the commercial use of cyclopentanone as a fuel. These include stability, compatibility, LSPI, and production cost.

Cyclopentanone shows oxidation when tested as a 20% blend in a reformulated BOB using the ASTM D525 protocol with an induction time of 400 minutes. Testing in pure iso-octane leads to no observed oxidation, while testing in a hexane/iso-octane blend leads to observed oxidation. Thus, the presence of alkenes is required for cyclopentanone oxidation.

3.10.6 R&D Needs

Given the large number of barriers identified for cyclopentanone adoption as a market fuel, it is not clear if the promise of cyclopentanone is judged to be high enough to justify additional R&D.

Nonetheless, there are a number of areas where additional research could identify mitigation strategies for the identified barriers.

First, a fundamental understanding of LSPI must be developed to determine whether it is possible to devise a mitigation strategy to reduce cyclopentanone LSPI propensity. Second, a better understanding of the mechanism of oxidation in the presence of alkenes could provide the basis for a means to reduce or prevent oxidation and improve fuel storage potential. Finally, decreasing the cost of furfural, or alternatively, developing production methods from less expensive intermediates than furfural may be required to generate cyclopentanone at a competitive price (furfural is currently ~$5/gallon and decreasing). Currently, the compatibility issues do not have a simple solution beyond changing the materials used in the fuel supply, distribution, and use infrastructure to materials that are compatible. This would be an expensive proposition, which indicates an opportunity for innovation to devise an alternative technical solution.

4 Conclusions

The tiered screening process efficiently identified promising blendstocks from more than 400 candidates using small volumes, allowing targeted evaluations using larger volumes of material. The majority of the blendstocks were single components, with a smaller number of simple mixtures and several complex thermochemical mixtures. Generally, the thermochemical mixtures did not provide target values of critical fuel properties and upgrading approaches to improve the properties of these mixtures were too complicated or required complex separations to implement. Several promising simple mixtures were identified and tested, and one of these made the final list of top blendstocks.

Synergistic blending, e.g., blending that leads to a value above that expected from linear blending, for octane and octane sensitivity, increases the relative merit function impact of a given blendstock at a given blending level.

The merit function approach provided a strong foundation to evaluate blendstocks without conducting hundreds of expensive and time-consuming engine tests.

The ten blendstocks with the highest increase in merit function were: cyclopentanone, di-isobutylene, ethanol, a furan mixture (40/60 vol% mixture of 2-methylfuran and 2,5-dimethylfuran), a fusel alcohol blend, isobutanol, methanol, prenol, n-propanol, and isopropanol. Six of these were assessed to have the fewest significant practical barriers to adoption and use: di-isobutylene, ethanol, a fusel alcohol blend, isobutanol, n-propanol, and isopropanol. The top performing blendstocks with the fewest barriers to adoption include alcohols and an olefin (alkene).

An additional fifteen blendstocks were identified which have potential to substantially improve engine efficiency, though not to the same level as for the Top 10 blendstocks. These are: anisole, a bioreformate (an aromatic-rich mixture of species), 1-butanol, 2-butanol, 2-butanone, ethyl acetate, ethyl butanoate, methyl acetate, 4- or 5-methylanisole, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-pentanol, 2-pentanone, and propyl acetate. Several of these have significant practical barriers to commercial adoption, including the ketones, the esters, and the aromatics.

The potential economic and environmental impacts of most of the top performing blendstocks were evaluated via techno-economic and life-cycle analysis. Additional analyses to evaluate environmental partitioning and biodegradability were also conducted. The findings of these analyses indicate that all of the top performing blendstocks have the potential to be produced at an acceptable cost with additional development and would reduce greenhouse gas emissions compared to petroleum-based fuels.

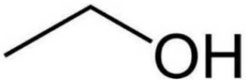
There are a number of outstanding challenges for the most promising blendstocks identified by Co-Optima. Foremost, only two (ethanol and isobutanol) are currently allowed in market fuels. Any new blendstocks would have to go through the normal fuel certification process. Second, the production cost of all of blendstocks identified is significantly higher than fuels on the market today; finding ways to value the enhanced fuel properties could help, along with process improvements. Third, fuel system and infrastructure compatibility, emissions impacts and health and safety impacts would have to be determined to be acceptable prior to the fuel certification process. Finally, the efficiency and environmental impacts must be confirmed in engine tests and more detailed analyses, along with opportunities for refinery integration.

Appendix A: Top 10 Bio-blendstock Datasheets

Nine of the Top 10 bio-blendstocks are included in this appendix. The fusel alcohol blend was not included, as several blends may be included and a single datasheet is not appropriate.

ETHANOL

Synonyms - ethyl alcohol
Molecular Formula: C_2H_6O
Molecular Weight: 46.10 g/mol
CAS# 64-17-5



Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	109	Hunwartzen, I. SAE Paper 82002, 1982
Motor Octane Number (MON)	90	Hunwartzen, I. SAE Paper 82002, 1982
Sensitivity	19	S = RON-MON
Heat of Vaporization	918.6 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-114.1°C	Scifinder Website
Boiling Point	78.5°C	Scifinder Website
Density	0.7893 g/cm^3 @20°C	Scifinder Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 2, no serious warnings
Rat LD50	10470 mg/kg
Flash Point	14°C
Lower Explosive Limit	3.3%
Upper Explosive Limit	19.0%
Autoignition Temperature	363°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	1.06 cSt @ 40°C	CRC Handbook
Lower Heating Value	26.84 MJ/kg	Owen, Keith and Trevor Coley, *Automotive Fuels Handbook*, 1990.
Yield Sooting Index	10.3	https://dataverse.harvard.edu
Surface Tension	22.0 dynes/cm @25°C	CRC Handbook
Water Solubility	1000g/L @25°C	Riddick et al, 1986

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
6.3 MPa	514.0 K	0.635	0.063

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

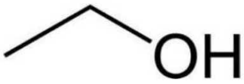
Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
15.8 MPa	8.8 MPa	19.4 MPa

* From Supplier Product Safety Data Sheet

ETHANOL

Synonyms - ethyl alcohol
Molecular Formula: C_2H_6O
Molecular Weight: 46.10 g/mol
CAS# 64-17-5



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	87.5	80.6
10% EtOH in RBOB	92.7	83.5
20% EtOH in RBOB	96.9	86.2
30% EtOH in RBOB	99.8	87.3
Conventional BOB	86.8	81.1
10% EtOH in CBOB	92.2	84.1
20% EtOH in cBOB	97.0	86.4
30% EtOH in cBOB	99.9	87.9

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	348, 373, 423	1	Knorsch Energy Fuels 28 (2014) 1446-1452
0.7-1.5	21	373	10	Beeckmann Fuel 117 (2014) 340-350
0.7-1.5	21	298, 358	1	Sileghem Fuel 115 (2014) 32-40
0.7-1.5	21	343	1	Veloo Combust. Flame 157 (2010) 1989-2004

Catalyst Light Off Temperature:

T50 (°C)	*T90 (°C)*	*Data Source*
204.0 ± 1.2	275.7 ± 4.1	DOE AMR 2017

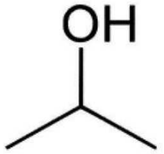
ISOPROPANOL

Synonyms – 2-propanol, isopropyl alcohol

Molecular Formula: C_3H_8O

Molecular Weight: 60.10 g/mol

CAS# 67-63-0



Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	113	Wallner, Proceedings of the FISITA, 2012
Motor Octane Number (MON)	97	Wallner, Proceedings of the FISITA, 2012
Sensitivity	16	S = RON-MON
Heat of Vaporization	743.8 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-88.5°C	Scifinder Website
Boiling Point	82.5°C	Scifinder Website
Density	0.7851 g/cm^3 @20°C	Scifinder Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 2, no serious warnings
Rat LD50	5045 mg/kg
Flash Point	12°C
Lower Explosive Limit	2.0%
Upper Explosive Limit	12.7%
Autoignition Temperature	399°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	2.04 cSt @ 25°C	Haynes, CRC Handbook
Lower Heating Value	30.70 MJ/kg	Christensen et al., Energy Fuels, 2011, 25, 4723-4733
Yield Sooting Index	19.2	https://dataverse.harvard.edu
Surface Tension	20.9 dynes/cm @25°C	Haynes, CRC Handbook
Water Solubility	Miscible @25°C	Riddick et al, 1986

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
4.8 MPa	508.0 K	0.669	0.0757

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
15.8 MPa	6.1 MPa	16.4 MPa

* From Supplier Product Safety Data Sheet

Co-Optimization of
Fuels & Engines

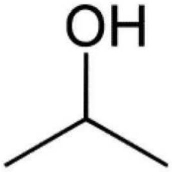
ISOPROPANOL

Synonyms – 2-Propanol

Molecular Formula: C_3H_8O

Molecular Weight: 60.10 g/mol

CAS# 67-63-0



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	87.5	80.6
10% 2-propanol in RBOB	90.6	83.3
20% 2-propanol in RBOB	94.2	84.9
30% 2-propanol in RBOB	97.6	87.5
Conventional BOB	86.8	81.1
10% 2-propanol in CBOB	90.6	83.7
20% 2-propanol in cBOB	93.7	85.8
30% 2-propanol in cBOB	97.7	88.1

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	343	1	Veloo Combust. Flame 157 (2010) 1989-2004

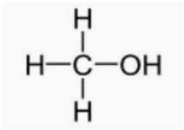
Catalyst Light Off Temperature:

T50 (°C)	*T90 (°C)*	*Data Source*
203.9 ± 0.1	219.1± 9.8	DOE AMR 2017

Co-Optimization of
Fuels & Engines

METHANOL

Synonyms - methyl alcohol
Molecular Formula: CH_4O
Molecular Weight: 32.04 g/mol
CAS# 67-56-1



$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	109	Anderson et al, 2010
Motor Octane Number (MON)	89	Anderson et al, 2010
Sensitivity	20	S = RON-MON
Heat of Vaporization	1,173.5 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-97.8°C	Scifinder Website
Boiling Point	64.7°C	Scifinder Website
Density	0.7864 g/cm^3 @20°C	Scifinder Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 1, causes organ damage
Rat LD50	1187 mg/kg
Flash Point	11°C
Lower Explosive Limit	6.0%
Upper Explosive Limit	36.0%
Autoignition Temperature	455°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	0.56 cSt @ 25°C	Haynes, CRC Handbook, Pub Chem website
Lower Heating Value	20.09 MJ/kg	Biomass Energy Databook, 2011
Yield Sooting Index	6.6	https://dataverse.harvard.edu
Surface Tension	22.1 dynes/cm @25°C	CRC Handbook
Water Solubility	Miscible @25°C	Riddick et al, 1985

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
8.1 MPa	512.0 K	0.564	0.045

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
14.7 MPa	12.3 MPa	22.3 MPa

* From Supplier Product Safety Data Sheet

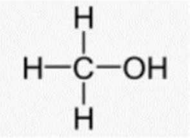
METHANOL

Synonyms - methyl alcohol

Molecular Formula: CH_4O

Molecular Weight: 32.04 g/mol

CAS# 67-56-1



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array}$$

Toxicology and Persistence Assessment:

Property	Value	Data Source
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	RON	MON
Surrogate BOB	90.3	84.7
10% MeOH in Surrogate	96.4	88.5
20% MeOH in Surrogate	100.9	89.5
30% MeOH in Surrogate	102.6	90.4

All RON and MON data was measured at the Colorado State Lab

Flame Speed Data:

Phi	O2 (mol%)	Temp_unburnt (K)	Pressure (bar)	Data Source
0.7-1.5	21	373	10	Beeckmann Fuel 117 (2014) 340-350
0.7-1.5	21	298, 358	1	Vancoillie Energy Fuels 26 (2012) 1557-1564
0.7-1.5	21	298, 358	1	Sileghem Fuel 115 (2014) 32-40
0.7-1.5	21	343	1	Veloo Combust. Flame 157 (2010) 1989-2004

Co-Optimization of Fuels & Engines

n-PROPANOL

Synonyms – 1-propanol
Molecular Formula: C_3H_8O
Molecular Weight: 60.10 g/mol
CAS# 71-23-8

Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	104	Christensen, 2011
Motor Octane Number (MON)	89	Christensen, 2011
Sensitivity	15	S = RON-MON
Heat of Vaporization	788.7 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-127.0°C	Scifinder Website
Boiling Point	97.2°C	Scifinder Website
Density	0.8053 g/cm^3 @20°C	Scifinder Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 1, eye damage
Rat LD50	8038 mg/kg
Flash Point	23°C
Lower Explosive Limit	2.2%
Upper Explosive Limit	13.7%
Autoignition Temperature	371°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	1.96 cSt @ 25°C	Pal et al, J. of Chem Thermodynamics, 2008
Lower Heating Value	30.80 MJ/kg	Christensen et al., Energy Fuels, 2011, 25, 4723-4733
Yield Sooting Index	16.2	https://dataverse.harvard.edu
Surface Tension	23.8 dynes/cm @25°C	Kirk-Othmer Encyclopedia of Chemical Tech
Water Solubility	Miscible @25°C	Riddick et al, 1986

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
5.2 MPa	537.0 K	0.622	0.1175

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

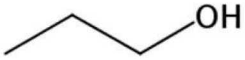
Dispersion	*Polarity*	*Hydrogen Bonding*
16.0 MPa	6.8 MPa	17.4 MPa

* From Supplier Product Safety Data Sheet

Co-Optimization of
Fuels & Engines

n-PROPANOL

Synonyms – 1-Propanol
Molecular Formula: C_3H_8O
Molecular Weight: 60.10 g/mol
CAS# 71-23-8



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	87.5	80.6
10% 1-propanol in RBOB	90.9	82.3
20% 1-propanol in RBOB	94.4	84.5
30% 1-propanol in RBOB	96.6	84.8
Conventional BOB	86.8	81.1
10% 1-propanol in cBOB	90.2	83.3
20% 1-propanol in cBOB	93.8	84.7
30% 1-propanol in cBOB	97.3	85.7

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	323, 373, 423, 473	1, 3, 5, 10	Galmiche Energy Fuels 25 (2011) 2013-2021
0.7-1.5	21	373	10	Beeckmann Fuel 117 (2014) 340-350
0.7-1.5	21	343	1	Veloo Combust. Flame 157 (2010) 1989-2004

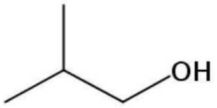
Catalyst Light Off Temperature:

T50 (°C)	*T90 (°C)*	*Data Source*
206.8 ± 0.7	247.9 ± 5.4	DOE AMR 2017

Co-Optimization of
Fuels & Engines

ISOBUTANOL

Synonyms - isobutyl alcohol,2-methyl-1-propanol
Molecular Formula: $C_4H_{10}O$
Molecular Weight: 74.10 g/mol
CAS# 78-83-1



Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	105	Christensen, 2011
Motor Octane Number (MON)	90	Christensen, 2011
Sensitivity	15	S = RON-MON
Heat of Vaporization	685.4 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-108°C	Alfa Aesar
Boiling Point	107.9°C	Alfa Aesar
Density	0.8018 g/cm^3 @20°C	CRC Handbook

Health and Safety* Information:

Property	*Value*
OSHA Hazard Category	Category 1, eye damage
Rat LD50	3350 mg/kg
Flash Point	28°C
Lower Explosive Limit	1.7%
Upper Explosive Limit	10.6%
Autoignition Temperature	415°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	3.87 cSt @ 20°C	Dow Chemical SDS
Lower Heating Value	33.2 MJ/kg	Christensen, Fuels Energy, 2011
Yield Sooting Index	26.2	https://dataverse.harvard.edu
Surface Tension	23.0 dynes/cm @25°C	Hahn, Pub Chem website
Water Solubility	85 g/L @25°C	Valvani, 1981

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
4.3 MPa	548.0 K	0.585	0.168

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
15.1 MPa	5.7 MPa	15.9 MPa

* From Supplier Product Safety Data Sheet

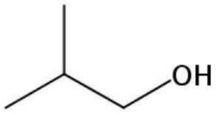
ISOBUTANOL

Synonyms - isobutyl alcohol,2-methyl-1-propanol

Molecular Formula: $C_4H_{10}O$

Molecular Weight: 74.10 g/mol

CAS# 78-83-1



Toxicology and Persistence Assessment:

Property	Value	Data Source
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	RON	MON
Reformulated BOB	87.5	80.6
10% i-BuOH in RBOB	90.0	82.2
20% i-BuOH in RBOB	92.6	83.3
30% i-BuOH in RBOB	95.3	84.6
Conventional BOB	86.8	81.1
10% i-BuOH in cBOB	89.5	82.9
20% i-BuOH in cBOB	92.5	84.2
30% i-BuOH in cBOB	95.1	85.3

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

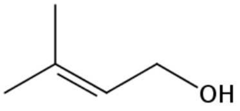
Phi	O2 (mol%)	Temp_unburnt (K)	Pressure (bar)	Data Source
0.7-1.5	21	348, 373, 423	1	Knorsch Energy Fuels 28 (2014) 1446-1452
0.7-1.5	21	353	1,2	Liu Proc. Combustion Inst. 33(2011) 995-1002
0.7-1.5	21	343	1	Veloo Proc. Combustion Inst. 33(2011) 987-993

Catalyst Light Off Temperature:

T50 (°C)	T90 (°C)	Data Source
255.8 ± 1.7	281.7 ± 1.1	DOE AMR 2017

PRENOL

Synonyms – 3-Methyl-2-butene-1-ol
Molecular Formula: $C_5H_{10}O$
Molecular Weight: 86.13 g/mol
CAS# 556-82-1



Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	93.5	Monroe et al, Fuel, 2019
Motor Octane Number (MON)	74.2	Monroe et al, Fuel, 2019
Sensitivity	19.3	S = RON-MON
Heat of Vaporization	512.0 kJ/kg @ 25°C	Predicted, ACD Labs
Melting Point	-59.3°C	Predicted, EPI Suite
Boiling Point	140.0°C	Scifinder Website
Density	0.8689 g/cm^3 @20°C	Scifinder Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 2, no serious warnings
Rat LD50	810 mg/kg
Flash Point	43°C
Lower Explosive Limit	2.7%
Upper Explosive Limit	16.3%
Autoignition Temperature	305°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	3.50 cSt @ 25°C	International Chemical Safety Cards
Lower Heating Value	34.04 MJ/kg	National Renewable Energy Laboratory
Yield Sooting Index	Not Available	Not Available
Surface Tension	26.4 dynes/cm @25°C	Predicted, ACD Labs
Water Solubility	40.9 g/L @25°C	Predicted, EPI Suite

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
4.6 MPa	573.0 K	Not Available	0.52

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
Not Available	Not Available	Not Available

* From Supplier Product Safety Data Sheet

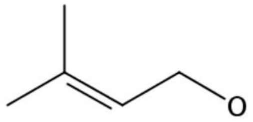
PRENOL

Synonyms - 3-Methyl-2-butene-1-ol

Molecular Formula: $C_5H_{10}O$

Molecular Weight: 86.13 g/mol

CAS# 556-82-1



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	84.8	82.5
10% Prenol in RBOB	90.8	83.8
20% Prenol in RBOB	94.8	83.9
30% Prenol in RBOB	96.8	83.1
Surrogate BOB	90.3	84.7
10% Prenol in Surrogate	94.0	85.5
20% Prenol in Surrogate	96.7	84.9
30% Prenol in Surrogate	97.4	84.0

All RON and MON data was measured at Southwest Research Institute, except RBOB data is from Monroe et al, Fuel, 2019.

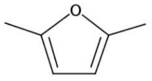
Flame Speed Data:

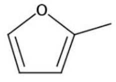
Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	428	1	UCF (paper in preparation)

Co-Optimization of
Fuels & Engines

FURAN MIX: 2,5-Dimethyl Furan/2-Methyl Furan (60/40 wt%)*

Synonyms – DMF and MF
Molecular Formulas: C_6H_8O/C_5H_6O
Molecular Weights: 96.13/82.10 g/mol
CAS#s: 625-86-5/534-22-5


2,5-dimethyl furan


2-methyl furan

Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	101/103	API Report
Motor Octane Number (MON)	88/86	API Report
Sensitivity	13 (DMF)	S = RON-MON
Heat of Vaporization	331/358 kJ/kg @ 25°C	Chickos and Acree, 2003 (DMF/MF)
Melting Point	-62.8°C/-87.5°C	Scifinder Website (DMF/MF)
Boiling Point	93.5°C/65°C	Scifinder Website (DMF/MF)
Density	0.895/0.916 g/cm^3 @20°C	Scifinder Website (DMF/MF)

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category (DMF/MF)	Category 2, no serious warnings
Rat LD50 (DMF)	1238 mg/kg
Flash Point (DMF/MF)	1°C/-6°C
Lower Explosive Limit (DMF)	3.3%
Upper Explosive Limit (DMF)	19.0%
Autoignition Temperature (DMF)	363°C

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	Not Available	Not Available
Lower Heating Value	30.1/28.5 MJ/L @ 20°C	Christensen at al., Energy & Fuels 2011
Yield Sooting Index	55 (DMF)	https://dataverse.harvard.edu
Surface Tension	22.0/25.5 dynes/cm @25°C	CRC Handbook/Predicted ACD Labs
Water Solubility	1.5/3.4 g/L @25°C	Predicted EPI Suite (DMF and MF)

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
3.7 MPa (DMF)	550.1 K (DMF)	0.510 (DMF)	0.744 (DMF)

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
15.8 MPa (DMF)	7.0 MPa (DMF)	4.8 MPa (DMF)

* From Supplier Product Safety Data Sheet

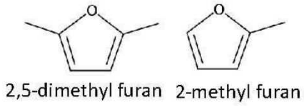
FURAN MIX: 2,5-Dimethyl Furan/2-Methyl Furan (60/40 wt%)*

Synonyms - DMF and MF

Molecular Formulas: C_6H_8O/C_5H_6O

Molecular Weights: 96.13/82.10 g/mol

CAS#s: 625-86-5/534-22-5



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation (DMF)	Possible Concern	Biowin Assessment

Blending RON and MON (60/40 wt% mixture):

Blend Level	*RON*	*MON*
Surrogate BOB	90.3	84.7
10% mix in Surrogate BOB	98.1	88.5
20% mix in Surrogate BOB	101.4	88.7
30% mix in Surrogate BOB	102.0	88.9

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	298,328,358,378,388, 398	1	Somers, Proc. Combust. Inst. 34 (2013) 225 (pure MF)
0.7-1.5	21	298,358	1	Somers, Combust. Flame 160 (2013) 2291 (pure DMF)

Catalyst Light Off Temperature (60/40 wt% mixture):

T50 (°C)	*T90 (°C)*	*Data Source*
276.1 ± 1.7	285.0 ± 1.0	DOE AMR 2017

*Data presented for each pure component unless otherwise noted. Value for DMF is listed prior to MF value. Furan Mixture is nominally 60/40 wt% DMF/MF.

Co-Optimization of Fuels & Engines

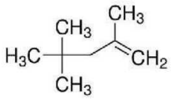
DIISOBUTYLENE

Synonyms – 2,4,4-trimethyl-1-pentene, isooctene

Molecular Formula: C_8H_{16}

Molecular Weight: 112.21 g/mol

CAS# 107-39-1



Key Fuel Properties:

Property	Value	Data Source
Research Octane Number (RON)	106	API Report
Motor Octane Number (MON)	87	API Report
Sensitivity	19	S = RON-MON
Heat of Vaporization	318.2 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-93.5°C	Scifinder Website
Boiling Point	101.4°C	Scifinder Website
Density	0.7150 g/cm^3 @20°C	Scifinder Website

Health and Safety* Information:

Property	Value
OSHA Hazard Category	Category 2, no serious warnings
Rat LD50	Not available
Flash Point	-5°C
Lower Explosive Limit	0.8%
Upper Explosive Limit	4.8%
Autoignition Temperature	391°C

Additional Properties of Interest:

Property	Value	Data Source
Viscosity	0.55 cSt @ 20°C	Sigma Aldrich SDS
Lower Heating Value	44.27 MJ/kg	NIST Website
Yield Sooting Index	68.5	https://dataverse.harvard.edu
Surface Tension	20.7 dynes/cm @20°C	US Coast Guard, Pubchem Website
Water Solubility	0.004 g/L @25°C	Predicted, EPI Suite

Critical Pressure	Critical Temperature	Acentric Factor	Particulate Matter Index
2.6 MPa	566.8 K	0.344	0.5745

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

Hansen Solubility Parameters:

Dispersion	Polarity	Hydrogen Bonding
14.7 MPa	1.1 MPa	1.4 MPa

* From Supplier Product Safety Data Sheet

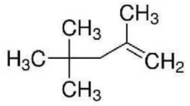
DIISOBUTYLENE

Synonyms – 2,4,4-trimehtyl-1-pentene, isooctene

Molecular Formula: C_8H_{16}

Molecular Weight: 112.21 g/mol

CAS# 107-39-1



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	No issues predicted	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	87.5	80.6
10% EtOH in RBOB	90.4	82.8
20% EtOH in RBOB	93.7	84.0
30% EtOH in RBOB	96.6	84.8
Conventional BOB	86.8	81.1
10% EtOH in CBOB	89.7	83.5
20% EtOH in cBOB	93.3	84.5
30% EtOH in cBOB	96.2	85.2

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7~1.5	21	348;373;423	1	UCF (paper in preparation)

Catalyst Light Off Temperature:

T50 (°C)	*T90 (°C)*	*Data Source*
263.7 ± 0.6	275.0 ± 9.9	DOE AMR 2017

Co-Optimization of Fuels & Engines

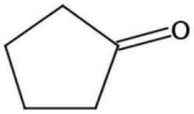
CYCLOPENTANONE

Synonyms – adipic ketone

Molecular Formula: C_5H_8O

Molecular Weight: 84.12 g/mol

CAS# 120-92-3



Key Fuel Properties:

Property	*Value*	*Data Source*
Research Octane Number (RON)	101	API Report
Motor Octane Number (MON)	89	API Report
Sensitivity	12	S = RON-MON
Heat of Vaporization	504.0 kJ/kg @ 25°C	Chickos and Acree, 2003
Melting Point	-51.3°C	Scifinder Website
Boiling Point	130.6°C	Scifinder Website
Density	0.9441 g/cm^3 @25°C	NIST Website

Health and Safety Information:*

Property	*Value*
OSHA Hazard Category	Category 2, no serious warnings
Rat LD50	2000 mg/kg
Flash Point	30°C
Lower Explosive Limit	Not Available
Upper Explosive Limit	Not Available
Autoignition Temperature	Not Available

Additional Properties of Interest:

Property	*Value*	*Data Source*
Viscosity	1.08 cSt @ 25°C	European Safety Sheet, EC# 204-435-9
Lower Heating Value	31.99 MJ/kg	NIST Website
Yield Sooting Index	22	https://dataverse.harvard.edu
Surface Tension	34 dynes/cm @25°C	Predicted, ACD Labs
Water Solubility	60.8 g/L @25°C	Predicted, EPI Suite

Critical Pressure	*Critical Temperature*	*Acentric Factor*	*Particulate Matter Index*
4.6 MPa	625.0 K	0.288	0.744

Yaws, C.L. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds: Physical, Thermodynamic and Transport Properties for 5,000 Organic Chemical Compounds. McGraw-Hill, 2003

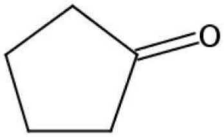
Hansen Solubility Parameters:

Dispersion	*Polarity*	*Hydrogen Bonding*
17.9 MPa	11.9 MPa	5.2 MPa

* From Supplier Product Safety Data Sheet

CYCLOPENTANONE

Synonyms – adipic ketone
Molecular Formula: C_5H_8O
Molecular Weight: 84.12 g/mol
CAS# 120-92-3



Toxicology and Persistence Assessment:

Property	*Value*	*Data Source*
Anaerobic Degradation	Possible Concern	Biowin Assessment

Blending RON and MON:

Blend Level	*RON*	*MON*
Reformulated BOB	87.5	80.6
10% EtOH in RBOB	90.1	82.8
20% EtOH in RBOB	93.0	83.8
30% EtOH in RBOB	96.0	84.8
Conventional BOB	86.8	81.1
10% EtOH in cBOB	88.9	82.9
20% EtOH in cBOB	89.6	83.1
30% EtOH in cBOB	96.0	85.1

All RON and MON data was measured at Southwest Research Institute

Flame Speed Data:

Phi	*O2 (mol%)*	*Temp_unburnt (K)*	*Pressure (bar)*	*Data Source*
0.7-1.5	21	428	1	UCF (paper in preparation)

Catalyst Light Off Temperature:

T50 (°C)	*T90 (°C)*	*Data Source*
264.0 ± 6.5	281.4 ± 8.0	DOE AMR 2017

References

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