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# Environmental, Economic, and Scalability Considerations and Trends of Selected Fuel Economy-Enhancing Biomass-Derived Blendstocks

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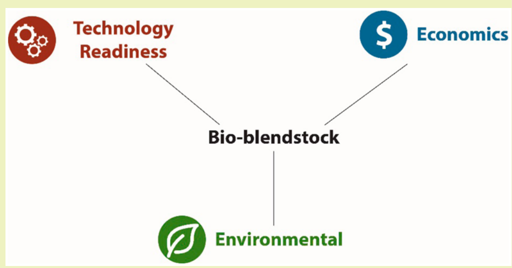
*Supporting Information*

**ABSTRACT:** Twenty-four biomass-derived compounds and mixtures, identified based on their physical properties, which could be blended into fuels to improve spark ignition engine fuel economy, were assessed for their economic, technology readiness, and environmental viability. These bio-blendstocks were modeled to be produced biochemically, thermochemically, or through hybrid processes. To carry out the assessment, 17 metrics were developed for which each bio-blendstock was determined to be favorable, neutral, or unfavorable. Cellulosic ethanol was included as a reference case. Overall economic and, to some extent, environmental viability is driven by projected yields for each of these processes. The metrics used in this analysis methodology highlight the near-term potential to achieve these targeted yield estimates when considering data quality and current technical readiness for these conversion strategies. Key knowledge gaps included the degree of purity needed for use as a bio-blendstock. Less stringent purification requirements for fuels could cut processing costs and environmental impacts. Additionally, more information is needed on the blending behavior of many of these bio-blendstocks with gasoline to support the technology readiness evaluation. Overall, the technology to produce many of these blendstocks from biomass is emerging, and as it matures, these assessments must be revisited. Importantly, considering economic, environmental, and technology readiness factors, in addition to physical properties of blendstocks that could be used to boost engine efficiency and fuel economy, in the early stages of project research and development can help spotlight those most likely to be viable in the near term.




**KEYWORDS:** *Techno-economic analysis, Life-cycle analysis, Biofuels*

## ■ INTRODUCTION

Fuel properties influence engine efficiency.[1,2] The primary focus of the Co-Optima initiative, a collaborative effort among nine U.S. Department of Energy National Laboratories, is to identify the fuel properties that will enable enhanced fuel economy, blended fuels with these properties, and engines that will work with these fuels toward increased efficiency and fuel economy. To date, the project has investigated potential biomass-derived blendstocks that could be blended with gasoline and used in spark ignition engines to reduce the energy consumption and emissions associated with the transportation sector. While many of the blendstocks considered could be produced from petroleum or natural gas feedstocks, this analysis has focused on biomass-derived blendstocks which may offer numerous technical, societal, and environmental benefits. Within Co-Optima, fuel properties, including boiling and freezing points, heat of vaporization, research octane number, solubility, ignition quality, corrosivity, toxicity, and heteroatom concentration, among other properties, of 400 biomass-derived potential blendstocks were evaluated. After this assessment, about 40 biomass-derived blendstocks exhibited favorable fuel properties.[3]

Not all of these 40, however, could be produced in the near term (∼15 years) economically and at scale. Further analysis was therefore needed to evaluate the economic and market viability and environmental impact of these bio-blendstocks. In the analysis herein, 24 of the bio-blendstocks—selected from the 40 to achieve diversity in chemical class, representativeness in conversion route (fermentation, thermochemical, and hybrid (with both biochemical and thermochemical attributes)), and

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sufficiently well-characterized conversion routes to enable a high-level techno-economic analysis (TEA)—were evaluated for these factors. We included cellulosic ethanol performance as a benchmark. Table S1 catalogues key physical property information on the 24 bio-blendstocks and ethanol.

The 24 selected bio-blendstocks listed in Table S1 include alcohols (8), esters (4), ketones (4), hydrocarbon mixtures (6), an alkane, and a furan blend. All Co-Optima bio-blendstocks have research octane numbers (RON) exceeding 98, a key enabler of enhanced fuel economy for spark ignition engines.[2] Ethanol, a biomass-derived octane enhancer, blended at a 10% volume in most gasoline in the United States, has been included as a reference case. While most of the ethanol in the market today is made from corn starch, this analysis considers cellulosic ethanol from municipal or agricultural waste, among other feedstocks, which offers additional benefits and is in the early stages of commercial production. It is important to note that other compounds derived from biomass or other feedstocks could offer desirable fuel properties. The 24 compounds and mixtures selected as case studies for the Co-Optima initiative are referred to herein as "Co-Optima bio-blendstocks."

In this paper, we evaluate these 24 Co-Optima bio-blendstocks for economic viability, scalability, and energy and environmental impact. While the influence of high-level ethanol blends on engine efficiency and the costs and environmental impacts of producing high-level ethanol blends have been investigated previously,[1,2] this is the first systematic study of other potential biomass-derived blendstocks that may improve fuel economy. This study does not recommend a specific blendstock be pursued or be included in gasoline at a specific blending level with or without ethanol. Rather, the aim is to identify whether these Co-Optima bio-blendstocks are viable to enter the market in a near-term time frame and to identify potential roadblocks to their commercialization and whether these can be overcome.

## ■ METHODOLOGY

While some of the Co-Optima bio-blendstocks (Table S1) are on the path to commercialization, many are just emerging or are still undergoing R&D at a range of scales. For these latter biomass-derived blendstocks, insights into how they may be produced are available only through the literature (academic and patent). For biomass-derived blendstocks in the commercialization pipeline (e.g., methanol-to-gasoline), more information may be available through company literature and presentations in addition to the literature. This nascent state of the industry translates into some uncertainty in establishing, for example, production costs based on process modeling. Therefore, the evaluation of these potential biomass-derived blendstocks is qualitative and based on thresholds. We developed 17 metrics (Tables 1−3) in the categories of economic viability, technology readiness (i.e., scalability), and environmental impact based on prior experience with cost, scalability, and environmental drivers of biomass conversion processes.[4−9] For each metric, we established three categories, or bins, into which each blendstock fell. When possible, these targets were based on regulatory thresholds (e.g., Renewable Fuel Standard requirements for GHG reductions) or previous analyses of mature (e.g., corn ethanol, gasoline) or emerging fuels. For example, the categories for the carbon efficiency metric were based on analyses of pyrolysis and gasification.[8,9]

**Table 1. Technology Readiness Metrics**

| Metric | Favorable | Neutral | Unfavorable | Approach |
|---|---|---|---|---|
| Co-Optima bio-blendstock production SOT cost | Falls in cluster of lowest cost pathways | Falls in cluster of moderate cost pathways | Falls in cluster of high cost pathways | Cost will be adopted from established target cases, published TEA data, and newly developed analysis. Costs compared on a $/GGE basis to take into account differing energy densities. |
| State of knowledge regarding conversion process and its technology readiness level (TRL) | Demonstration-scale (or larger) data available | Bench-scale data available | Notional, partly literature based | Conduct review of existing research and analyses, literature, and discussions with national laboratory researchers. |
| Number of viable routes to produce fuel or blendstock | >3 | 2−3 | 1 | Evaluate literature and discuss with national laboratory researchers. New viable routes are through a different conversion pathway (such as biochemical versus thermochemical designs) and are not changes to one particular design (such as a new catalyst). |
| Data quality regarding feedstock assumptions in process modeling | Experimental data only from real feedstocks | Experimental data are a combination of real feedstocks and mock feedstocks | Experimental data from mock feedstocks | Evaluate feedstock source in experiments used to inform process modeling. |
| Production process sensitivity to feedstock type | Feedstock changes result in minor variations in fuel yield/quality | Feedstock changes result in some variations in fuel yield/quality | Feedstock changes can cause significant variations in fuel yield/quality | When experimental data unavailable, use high-level mass balance to estimate. |
| Robustness of process to feedstocks of different specs | Changes in feedstock specifications minimally influences yield/quality | Changes in feedstock specifications moderately influences yield/quality | Changes in feedstock specifications greatly influences yield/quality | Examine experimental data for information on influence of specification changes (e.g., ash, hydrocarbon content) on yield and quality. |
| Blending behavior of blendstock with current fuels for use in vehicles | Current quality good enough for replacement | Current quality good enough for blend | Current quality in blend not good or unknown | Consider level of information regarding fuel quality of biomass-derived blendstock, such as whether it is known that it can be directly blended versus there is some limited knowledge about blending properties such as wide boiling range bulk properties. |



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Table 2. Economic Viability Metrics

| Metric | Favorable | Neutral | Unfavorable | Approach |
|---|---|---|---|---|
| Fuel production target cost | Falls in cluster of lowest cost pathways | Falls in cluster of moderate cost pathways | Falls in cluster of high cost pathways | Cost adopted from established target cases, published TEA data, and newly developed analysis. Costs compared on a $/GGE basis to take into account differing energy densities. |
| Ratio of SOT-to-target cost | <2 | 2−4 | >4 | See above approaches for developing SOT and target costs. |
| Percentage of product price dependent on co-products (i.e., chemicals, electricity, other blendstocks/fuels produced as co-product to Co-Optima fuel) | <30% | 30−50% | >50% | Evaluate with process models and techno-economic analysis. |
| Competition for the biomass-derived blendstock or its predecessor | Blendstock is not produced from, nor is itself, a valuable chemical intermediate. | Blendstock is produced from, or is itself, a raw chemical intermediate. | Blendstock is produced from, or is itself, a valuable chemical intermediate. | Evaluate market size for biomass-derived blendstocks and their predecessors in the production process (i.e., intermediates between feedstock and final blendstock product).[a] |
| Cost of feedstock (in US$2014) | Cost at or below target of $84/dry ton delivered at reactor throat[10,11] | Some uncertainty as to whether feedstock cost will be at or below $84/dry ton (e.g., < $100 ton[10,11]) | Feedstock cost at delivery to reactor throat likely to exceed $120/dry ton | Feedstock prices are based upon Idaho National Laboratory's feedstock cost analyses.[10,11] |

[a]It may be possible that competition for the bio-blendstock for multiple end uses could lead to more stable financing for biorefineries that would produce the bio-blendstock, but our primary focus in this analysis is availability as a bio-blendstock fuel, which could be compromised if there were competition with the chemicals market.

The metrics and bins developed were vetted with Co-Optima stakeholders including the project's External Advisory Board.

Notably, we considered two production cases for each potential blendstock. The first, called the state of technology (SOT) case, reflects the current performance of the conversion process. SOT key parameters, such as yield and selectivity, are lower than they would be when the technology is more mature. The second production case considered is called the target case, which is forward-looking and considers the potential of the technology at full scale. A process model for each case informed bio-blendstock cost estimates. (Detailed TEA and life-cycle analysis [LCA] assumptions are in the SI.) These process models generally were modifications of existing models.[4−9] The integration of these process models and economic evaluations, also described in previous studies,[4−9] produces an estimate of the cost per gasoline gallon equivalent (GGE) to produce the biomass-derived blendstocks. The overall designs are based on fully integrated, standalone facilities and include all supporting utilities and equipment required to operate the biorefinery. The financial assumptions align with recent process designs developed by both the National Renewable Energy Laboratory and Pacific Northwest National Laboratory.[4−9]

Technology readiness metrics (Table 1) were evaluated based on the SOT case. Given the emerging nature of the production of many of these compounds, production cost estimates should be viewed as the best understanding we can gain given the information that is available. For this reason, we did not rate the Co-Optima bio-blendstocks based on their absolute cost of production estimate, but rather on how their cost of production compared to other biomass-derived blendstocks in this analysis. A separate metric was included to reflect the state of knowledge regarding the production route considered and the source/quality of the baseline data. An unfavorable rating was assigned when process information was largely notional due to limited data availability.

We considered producing biomass-derived blendstocks from either a herbaceous biomass blend for the biochemical production routes or from a woody biomass blend for the thermochemical production routes (see SI). Within the technology readiness metrics, biomass feedstock influences were considered, including the state of knowledge regarding the effect of feedstock type and specifications on product yield and quality. The final technology readiness metric that was evaluated was the degree of biomass-derived product blending behavior with conventional gasoline given the information currently available. Importantly, the Co-Optima R&D projects are currently assessing the influence of blending levels on fuel properties[3] and working toward understanding the optimal blending levels for each Co-Optima biomass-derived blendstock.

Economic viability metrics (Table 2) take into account the target case and consider various aspects of process economics. First, we ranked the target cost for each blendstock through the ratio of the SOT cost to the target cost. This is a critical metric that assesses the amount of research and development required to cut processing costs. Furthermore, we considered the extent to which economic viability of the Co-Optima bio-blendstock depended upon the co-production of electricity (e.g., through lignin combustion), chemicals, or a co-produced blendstock (e.g., diesel). This was a minor effect given that only the n-butanol case has a chemical co-product. Nonetheless, this metric was included because a process heavily dependent upon co-products for viability may not be desirable. Swings in the


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**Table 3. Environmental Impact Metrics**

| Metric | Favorable | Neutral | Unfavorable | Approach |
|---|---|---|---|---|
| Efficiency of input carbon (fossil and biomass-derived) to Co-Optima bio-blendstock for the target case[a] | >40% | 30–40% | <30% | Based upon process modeling |
| Co-Optima bio-blendstock target case yield[a] (GGE/dry ton) | Falls in cluster of highest yielding pathways | Falls in cluster of moderate yielding pathways | Falls in cluster of lowest yielding pathways | Based upon process modeling |
| Life-cycle GHG emissions[b] | Likely to achieve a greater than 60% reduction in life-cycle GHG emissions as compared to conventional gasoline in 2015. | Could achieve a greater than 60% reduction in life-cycle GHG emissions as compared to conventional gasoline in 2015. | Unlikely to achieve a greater than 60% reduction in life-cycle GHG emissions as compared to conventional gasoline in 2015. | Estimate life-cycle GHG emissions, energy consumption, and water consumption of candidates with GREET model. Rely on preliminary TEA information, feedstock production data, and background GREET data (e.g., for electricity and natural gas). Develop baseline comparison for 2015 gasoline based on shares of feedstocks (e.g., oil sands, conventional crude) as in GREET1_2015. Water consumption thresholds based on corn ethanol and conventional gasoline. |
| Life-cycle fossil energy consumption[b] | Likely to use less fossil energy on a life-cycle basis than conventional gasoline in 2015. | Could use less fossil energy on a life-cycle basis than conventional gasoline in 2015. | Unlikely to use less fossil energy on a life-cycle basis than conventional gasoline in 2015. | |
| Life-cycle water consumption[b] | Likely to use less water on a life-cycle basis than 3 gal/GGE. | Could use less water on a life-cycle basis than 55 gal/GGE. | Could use more water on a life-cycle basis than 55 gal/GGE. | |

[a]In some cases, processes co-produce a blendstock/fuel, such as renewable diesel in the case of pyrolysis, which is not a Co-Optima bio-blendstock. The carbon efficiency results only estimate carbon efficiency to the bio-blendstock considered to have potential to improve fuel economy in light-duty, spark ignition engines. [b]Includes entire supply chain and system, including co-products of the biorefinery. It should be noted that biorefinery water consumption is not optimized in the high-level TEAs that were developed. Efforts to improve water economy could lower water consumption.



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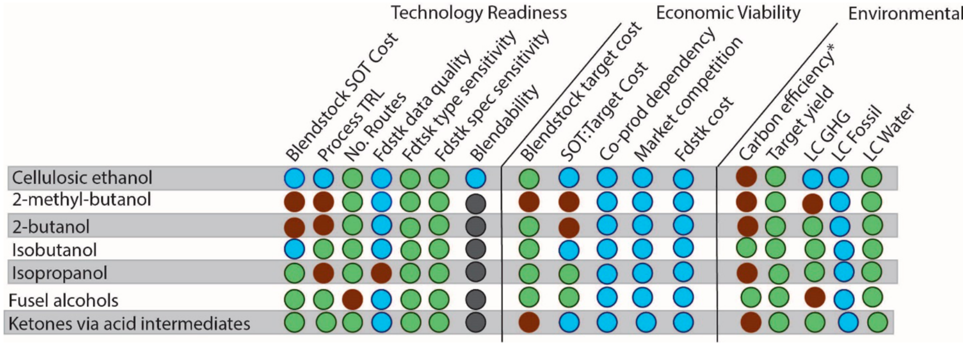


**Figure 1.** Biochemically produced Co-Optima bio-blendstocks screening results. Blue, green, and brown circles represent favorable, neutral, and unfavorable categorization as defined in Tables 1−3. Gray circles reflect a lack of information to categorize a given bio-blendstock for a certain metric. Cellulosic ethanol is included as a benchmark. *Carbon efficiency and target yields are for the Co-Optima blendstock for the target case.

market value of the chemical could prompt a producer to stop producing it along with the co-produced bio-blendstock. Additionally, if the bio-blendstock were produced from, or is itself, a valuable chemical intermediate, market factors could pull it to other uses. Most commodity chemicals have higher profit margins than fuel blendstocks, and production of biomass-derived fuel blendstocks could be challenged if competing with commodity chemicals. Finally, feedstock cost, an important process economics driver, was included as a metric.

The final group of metrics considered reflects the environmental impacts of the bio-blendstocks (Table 3). This part of the analysis aims to understand the impact that targeted bio-blendstocks could have on the reduction of greenhouse gas (GHG) emissions, water consumption, and air pollution when compared to traditional fossil fuels production. To evaluate life-cycle energy and environmental impacts of the biomass-derived blendstocks, we incorporated material and energy flows from process models into Argonne National Laboratory's Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model (2015 release) and carried out an LCA of each biomass-derived blendstock. Additional data sources included feedstock processing and logistics from Idaho National Laboratory's analyses[10,11] and feedstock production data from GREET.[12]

## ■ RESULTS AND DISCUSSION

Figure 1 contains the screening results for Co-Optima bio-blendstocks that are produced biochemically. Biochemical ethanol is included as a comparison case since commercialization of this bio-blendstock spanned a decade, whereas many of the bio-blendstocks in this analysis are at a much earlier point in the commercialization process. Furthermore, because they are produced from sugars, market competition is not expected to be a significantly challenging factor for economic viability. With a goal to produce Co-Optima fuels with limited reliance on co-products for economic viability, all bio-blendstocks were rated favorably if they were minimally dependent on a co-product in this regard. Feedstock costs, assumed to be equivalent to those developed by Idaho National Laboratory,[10,11] are favorable for all bio-blendstocks. All bio-blendstocks offer life-cycle reductions in fossil fuel compared to fossil-derived comparable compounds.

The analysis yielded insights into process sensitivity to feedstock type and specifications. Given that biochemical processes use microorganisms that prefer certain substrates and are sensitive to impurities, these factors are important for biochemical processes, and all bio-blendstocks received a neutral rating. Life-cycle water consumption was uniformly neutral across all biochemically produced bio-blendstocks. Biochemical processes, which are fermentation-based, can use significant amounts of water. Ultimately, water intensity may be determined by the design and effectiveness of separation technologies, purification requirements, and supporting systems, such as the approach to producing combined heat and power.

Examining technology readiness metric results, 2-methyl butanol and 2-butanol both exhibited unfavorable SOT costs of production that were higher than other Co-Optima bio-blendstocks considering today's technology. As the information used to develop the process models from these compounds was purely literature-based, demonstration-scale data, when available, may improve these metrics.

Regarding feedstock data quality, for the most part, process modeling data for biochemical processes relied on experiments with corn stover as the feedstock. In the case of isopropanol, however, the feedstock was glucose. The experimental data underpinning process modeling for isopropanol may therefore not reflect results from cellulosic feedstocks.

Economic viability metric evaluations raised some unfavorable ratings. 2-Methyl butanol and 2-butanol both received unfavorable ratings for the ratio of SOT-to-target cost. 2-Methyl butanol and ketones via acid intermediates had a higher targeted cost when compared to other biochemical pathways. However, other bio-blendstocks produced thermochemically or through a hybrid process exhibited higher target costs than these two bio-blendstocks.

A number of unfavorable metrics also arose in the environmental category. Three Co-Optima bio-blendstocks demonstrated unfavorable carbon efficiency. The target case carbon efficiency metric reflects carbon in the Co-Optima bio-blendstock product only; it does not take into account co-produced non-Co-Optima blendstocks and chemicals. Target yield and target carbon efficiency were not always rated identically for a given bio-blendstock because, in our evaluation of target yield, we assigned favorable ratings to bio-blendstocks produced in similarly high yields. A second, lower cluster of yields were assigned a neutral rating, and the lowest cluster of yields received unfavorable ratings. This approach, which did not use specific thresholds, avoided separating bio-blendstocks with yields that were only slightly above or below a given threshold value. In general, life-cycle GHG emissions were not always strongly related to target yields because process material


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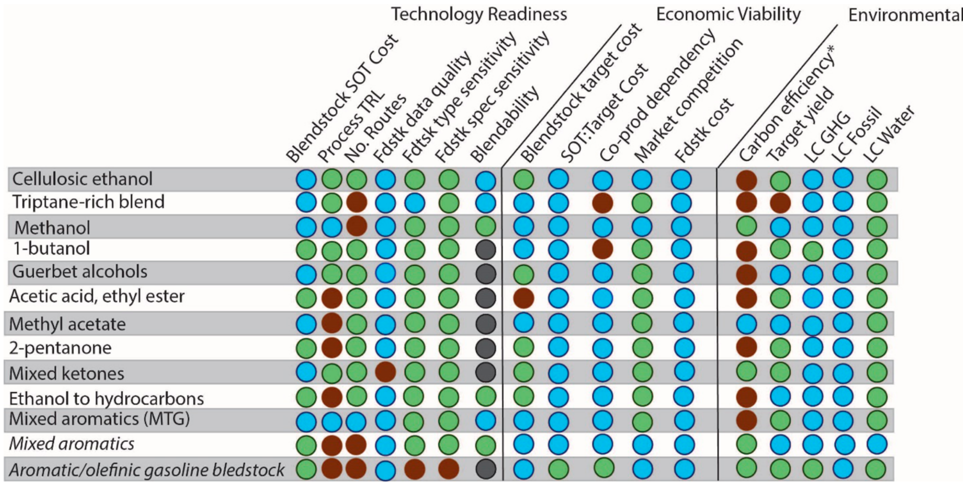


**Figure 2.** Thermochemically produced bio-blendstocks screening results. Blue, green, and brown circles represent favorable, neutral, and unfavorable categorization as defined in Tables 1−3. Gray circles reflect a lack of information to categorize a given bio-blendstock for a certain metric. Cellulosic ethanol is included as a benchmark. Italicized bio-blendstocks are produced via pyrolysis. Other bio-blendstocks are produced via indirect liquefaction. *Carbon efficiency and target yields are for the Co-Optima blendstock for the target case.

and energy intensity, in addition to co-products, have a stronger influence on life-cycle GHG emissions results than yield. 2-Methyl butanol and fusel alcohols had unfavorable life-cycle GHG emissions. In the latter case, electricity and ammonia consumption are key life-cycle GHG drivers; fusel alcohol yields are relatively high compared to other alcohols. On the other hand, isobutanol (anaerobically produced) exhibited favorable GHG emissions stemming in part from an electricity co-product assumed to displace national-grid-derived electricity.

Overall, isobutanol was considered to have the highest potential for near-term commercialization (with ongoing efforts by companies such as Butamax and Gevo working to scale up these processes on commodity sugars) of the Co-Optima bio-blendstocks in Figure 1. Isobutanol had the most favorable evaluation of these biochemically derived Co-Optima bio-blendstocks with similar performance to cellulosic ethanol. U.S. Environmental Protection Agency (EPA) certification allows isobutanol blending levels up to 16.1%,[13] which produces a final fuel with the same oxygen content (3.5%) and heating value as E10. All other compounds had at least one unfavorable rating generally concentrated in the technology readiness metrics; many biochemical pathways are still in the early stages of development to the best of our knowledge. For example, a 2-butanol processing cost driver is the cost of liquid−liquid extraction to meet high purity expectations. If lignin were converted to co-products in the process to produce 2-butanol, or any of these biochemically derived blendstocks (rather than combusting them to produce heat and power), the process economics for this compound could improve, although there may be a corresponding decline in environmental performance.

Figure 2 contains the screening results for bio-blendstocks that are produced thermochemically by gasification (i.e., indirect liquefaction) or pyrolysis. Thermochemically produced cellulosic ethanol is included as a reference case. Enerkem is developing thermochemically produced ethanol from waste feedstocks.[20] As with the biochemically produced bio-blendstocks, all thermochemically produced blendstocks were rated favorably for feedstock cost and life-cycle fossil energy consumption.

All but two thermochemically produced bio-blendstocks exhibited some variation in technology readiness metrics depending on feedstock type and specifications. Generally, high-temperature thermochemical processes handle feedstock variations fairly well. Of the thermochemical processes, lower-temperature pyrolysis processes exhibit more sensitivity to feedstock ash content and organic chemical composition. Impurities can affect downstream catalysis steps in any thermochemical process. The triptane-rich bio-blendstock, modeled as produced from gasification, exhibited little sensitivity to feedstock variations. On the other hand, the process to upgrade pyrolysis-derived sugars to an aromatic/olefinic gasoline blendstock shows significant yield variations when nonwoody, higher-ash feedstocks are used and the specifications of the feedstock significantly influence the product yield.

Seven thermochemically derived Co-Optima bio-blendstocks exhibited favorable SOT costs of production. The remaining thermochemically derived compounds were rated neutral. As indicated by several unfavorable ratings in the TRL category, demonstration- or pilot-scale data for producing these compounds can be scarce. In the case of ethyl acetate, methyl acetate, and 2-pentanone, information regarding production of the mixed alcohol intermediate is from the demonstration scale, while the Chemical Process Economics Program yearbook,[14] literature, or personal correspondence is the basis for informing models of the remaining process stages. Information regarding the two pyrolysis routes comes entirely from the literature. For these two pathways, the number of routes to produce the bio-blendstock is limited to one, resulting in an unfavorable rating for the number of routes. Methanol is produced from a single feedstock in this analysis: syngas. This alcohol could be produced biologically, but it exhibits toxicity to fermenting microorganisms that limits the scalability of this type of production route.

For all thermochemically derived pathways, we considered a woody blend feedstock in process modeling. In the case of mixed ketones, however, only bench-scale data from ethanol were available, so this bio-blendstock received an unfavorable rating for feedstock data quality, although it should perform similarly to cellulosic ethanol.

Concerning blending these bio-blendstocks into gasoline, routes that produce nonoxygenated hydrocarbon blendstocks


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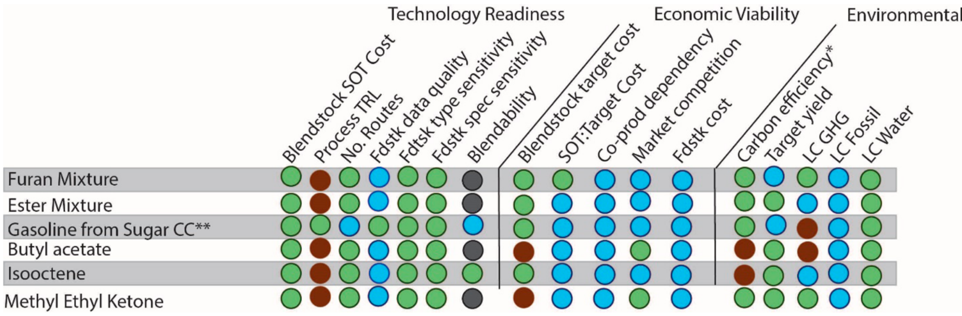


**Figure 3.** Screening results for bio-blendstocks produced via hybrid biochemical−thermochemical routes. Blue, green, and brown circles represent favorable, neutral, and unfavorable categorization as defined in Tables 1−3. Gray circles reflect a lack of information to categorize a given bio-blendstock for a certain metric. *Carbon efficiency is for the Co-Optima blendstock for the target case. **CC denotes catalytic conversion.

are likely to be directly blendable such as the triptane-rich blendstock. Mixed aromatics produced via the methanol-to-gasoline route should be directly blendable as long as impurities are sufficiently low concentration. For example, benzene must be less than 1.3% by volume of gasoline per EPA regulations.[15] With more stringent standards, California is permitted to have even lower benzene levels and caps them at 1.1% by volume.[16] Although EPA does not have a maximum limit on aromatics, which include benzene, toluene, ethylbenzene, xylenes, $C_9$ and heavier, and total aromatics, in California, total aromatics are limited to 35% by volume.[17]

The economic viability of Co-Optima bio-blendstocks in Figure 2 is generally good. Bio-blendstock target costs are either favorable or neutral with the exception of ethyl acetate. Importantly, the ratio of the SOT cost to the target cost was favorable for all but one of these bio-blendstocks, indicating that perhaps the amount of research and development to move these compounds toward commercial scale could be manageable. This could also reflect that the conversion downstream of syngas has been well developed commercially for several pathways via fossil feedstocks. Thermochemically produced bio-blendstocks showed greater potential to have an element of market competition that caused many of them to receive neutral ratings for this metric. The triptane-rich blend, for example, is produced via methanol, which can be used as a fuel or chemical and can have a fair element of market competition. The methanol-to-gasoline pathway also relies on methanol as an intermediate between biomass and the final product. 1-Butanol, the Guerbet mixture of alcohols, 2-pentanone, mixed ketones, and ethyl acetate are produced via a raw ethanol intermediate. Methyl acetate is produced from raw methanol and acetic acid intermediates.

Two thermochemically derived bio-blendstocks that we considered in this analysis exhibit unfavorable dependence on co-products. The triptane-rich blendstock is a high-octane (>98 RON) portion of an overall fuel stream produced in a gasification process, and this portion of the total energy product output of the process is heavily dependent on the majority of fuel product that has a RON below 98. 1-Butanol is co-produced with other alcohols. Feedstock costs again are uniformly favorable across bio-blendstocks because we assumed a single feedstock cost.

Examining the environmental metrics, although the target case carbon efficiency for many of the Co-Optima bio-blendstocks was low, life-cycle GHG emissions tended to be favorable or neutral.

Overall, methanol and methanol-to-gasoline—subject to commercialization efforts—received the most favorable ratings of the various thermochemically derived bio-blendstocks. Most unfavorable ratings for these pathways fall in the technology readiness metric group, and the overall target case carbon efficiency tends to be unfavorable. Thermochemical ethanol serves as a point of comparison in Figure 2, but this route is not fully commercialized and has an unfavorably rated carbon efficiency and many neutral ratings. It should be noted that the baseline gasification designs are energy self-sufficient and burn biomass rather than relying on imports of natural gas or electricity for these designs. Carbon efficiency could be boosted if such imports were assumed; however, further analysis would be required to understand the impact on sustainability metrics.

The aromatic/olefinic gasoline blendstock via pyrolysis-derived sugars/upgrading had the greatest number of unfavorable ratings in Figure 2. Limited information was available regarding the SOT for sugars recovery and upgrading. Very preliminary experimental work suggested that hydro-treating the mostly lignin fraction may be difficult.[21] Furthermore, feedstock quality (such as high ash or low lignin fraction) has a significant effect on yield. Ash also poses challenges to catalyst maintenance.

Five bio-blendstock candidates were evaluated based on process models that incorporated biochemical and thermo-chemical elements (Figure 3). For example, routes to the furan mixture, ester mixture, and gasoline produced via the catalytic conversion of sugars considered in this analysis first employ an enzymatic hydrolysis step followed by a thermochemical step. The route to isooctene begins with fermentation that produces isobutanol, which is subsequently catalytically converted to isooctene. Production of butyl acetate proceeds through biological conversion in two separate fermentation trains. One train produces ethanol; the other produces isobutanol. Subsequent conversion and catalysis steps produce butyl acetate. Thermochemical gasification produces syngas, which is first biologically upgraded to produce a 2,3-butandiol intermediate, then dehydrated to yield methyl ethyl ketone.

For each of these hybrid routes, the SOT cost of production received a neutral rating. Production information for these compounds tended to be from the literature for relevant feedstock types. The multiple conversion routes to each of these bio-blendstocks tended to be robust regarding feedstock types and specifications. Whereas gasoline produced from sugar catalytic conversion would be blendable with gasoline and isooctene should be similarly blendable as long as impurities are low, the blending behavior of other bio-blendstocks is not clear at this point.

Target costs for these bio-blendstocks could be high, but these were paired with somewhat high SOT costs yielding


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relatively favorable ratios of SOT-to-target costs. For these particular blendstocks, this latter metric may not yield the most important insight compared to the individual target costs. Overall, co-product dependency for these bio-blendstocks was low. Notably, the pathway to methyl ethyl ketone that we considered goes through 2,3-butanediol, which is a potentially valuable intermediate. For this reason, we assigned a neutral rating to the market competition metric for methyl ethyl ketone. The butyl acetate pathway proceeds through valuable intermediates ethanol and isobutanol.

Environmental metrics aside from life-cycle fossil energy consumption were mostly neutral. The carbon efficiencies of isooctene and butyl acetate pathways, however, were relatively low, and the life-cycle GHG emissions of gasoline from catalytic sugar conversion and butyl acetate were high.

Overall, all bio-blendstocks produced via hybrid biochemical and thermochemical technologies had one or more unfavorable ratings. Many were in the environmental metric category. One reason for high GHG emissions in the gasoline from the catalytic conversion of the sugar pathway is the use of significant quantities of hydrogen that was assumed in process modeling to be sourced from natural gas steam-methane reforming. Alternative design options could allow for internally sourced hydrogen, although Co-Optima bio-blendstock yield would decline and the production cost would likely rise as hydrogen was purchased from a vendor.[5] On the other hand, the high GHG emissions associated with butyl acetate are driven by the relatively low yield of this compound in the process modeling. If these compounds (or any included in this analysis that can be produced by multiple technologies) were produced through an alternative route, the analysis results might be different. For example, the furan mixture could be produced through pyrolytic pathways.

## ■ CONCLUSIONS

This analysis highlighted several key overarching themes. First, based on our current understanding of these pathways, feedstock considerations are not insignificant but are also not roadblocks provided feedstocks are available at sufficient levels and reasonable cost. Second, yields of bio-blendstocks in biochemical, sugar-based routes may be relatively lower than bio-blendstock yields in thermochemical processes because, in biochemical routes, the lignin fraction of the feed is not available for bio-blendstock production. On the other hand, thermochemical routes tend to mimic those that would be used if the candidate were a chemical, which consist of many steps. If the impurity level were known for various thermochemically produced bio-blendstocks, then the carbon usage could be optimized and economic and environmental metrics may improve. Additionally, the quality of these fuel mixtures is uncertain regardless of the conversion pathway. The impact that the composition of these streams has on the fuel properties (including octane) for these further-looking target cases is also uncertain. Also, the results suggest that new synthesis routes that focus on fuel rather than chemical-grade production are needed. Routes that proceed through an ethanol intermediate could produce a high-octane component. Such bolt-on technologies for converting ethanol to a different high-octane bio-blendstock is motivated in part by the infrastructure challenges ethanol faces and current blending limits, which may be altered in the future.

Another key issue identified in this analysis is the uncertainty about the blending level of many of these bio-blendstocks. Any oxygenate that had not been certified (i.e., all except isobutanol and reference case ethanol) or tested (e.g., methanol underwent limited testing) was noted as having unknown blending behavior. Higher alcohols were expected to behave at least as well as ethanol, but if no testing had been performed, a bio-blendstock received an unknown rating. Ongoing work within the Co-Optima initiative will address these data gaps.

This analysis presented several challenges. First, the emerging nature, or the limited public information, of the technology precluded a robust quantitative evaluation of the Co-Optima bio-blendstocks. With time, technology maturation, and increased information disclosure, it will become viable to increase the robustness and quantitative nature of this type of analysis. For example, corn ethanol plants routinely participate in surveys that publish information regarding yield and energy consumption,[18] and this may become the norm for other biorefineries over time. Second, balancing the importance of technology readiness, economic, and environmental metrics is a challenge, although some have developed methodologies to handle this balancing quantitatively.[19] The qualitative approach we adopted makes possible the identification of options that are not likely viable, at least in the near term. For example, 2-methyl butanol exhibited unfavorable SOT cost, ratio of target-to-SOT cost, target case Co-Optima bio-blendstock carbon efficiency, and GHG emissions. This bio-blendstock is an inadvisible choice for targeted efforts toward development in the near term. This method can also flag Co-Optima bio-blendstocks with few barriers toward deployment, such as the methanol-to-gasoline route. Future work will refine several of the process modelings, TEAs, and LCAs involved in this screening process and consider alternative screening techniques. The current screening analysis, however, was instrumental as a supplement to a physical-property-based screening of Co-Optima bio-blendstocks, allowing the initiative to check for roadblocks that could arise in even the most promising of blendstocks if only properties were considered. The current harmonized assessment between fuel and engine developers and analysts yields a robust approach to identify/develop a renewable transportation fuel that can potentially decrease the overall fossil energy consumption and improve the environmental impact and economic viability of the transportation sector.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b02871.

Fuel properties of bio-blendstocks considered in this study, biomass feedstock assumptions, high-level process information for production of bio-blendstocks. (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

| | |
|---|---|
| BETO | Bioenergy Technologies Office |
| CC | catalytic conversion |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| GGE | gasoline gallon equivalent |
| GHG | greenhouse gas |
| GREET | Greenhouse gases, Regulated Emissions, and Energy use in Transportation |
| LC | life cycle |
| LCA | life-cycle analysis |
| MTG | methanol-to-gasoline |
| RON | research octane number |
| SOT | state of technology |
| TEA | techno-economic analysis |
| TRL | technology readiness level |
| VTO | Vehicle Technologies Office |

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