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Research Article

Identification of Key Drivers of Cost and Environmental Impact for Biomass-Derived Fuel for Advanced Multimode Engines Based on Techno-Economic and Life Cycle Analysis

Pahola Thathiana Benavides, Andrew W. Bartling, Steven D. Phillips, Troy R. Hawkins,* Avantika Singh, George G. Zaimes, Matthew Wiatrowski, Kylee Harris, Pralhad H. Burli, Damon Hartley, Teresa Alleman, Gina Fioroni, and Daniel Gaspar

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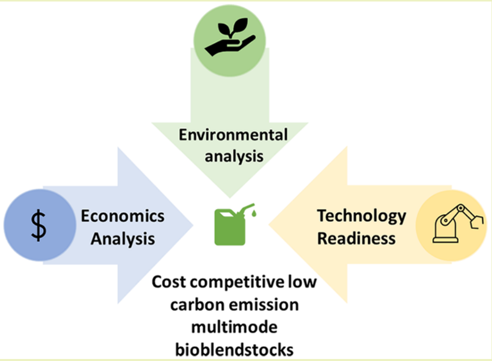

ABSTRACT: Early stage research and development are needed to accelerate the introduction of advanced biofuel and engine technologies. Under the Co-Optima initiative, the U.S. Department of Energy is leveraging capabilities from its nine national laboratories and more than 35 university and industry partners including advanced computational tools, process design, data analysis, and economic and sustainability modeling tools to simultaneously design fuels and engines capable of running efficiently in an affordable, scalable, and sustainable way. In this work, we conducted techno-economic analysis (TEA) and life cycle assessment (LCA) to understand the cost, technology development, and environmental impacts of producing selected bioblendstocks for advanced engines such as multimode (MM) type engines at the commercial scale. We assessed 12 biofuel production pathways from renewable lignocellulosic biomass feedstocks using different conversion technologies (biochemical, thermochemical, or hybrid) to produce target co-optimized biofuels. TEA and LCA were used to evaluate 19 metrics across technology readiness, economic viability, and environmental impact and for each ranked on a set of criteria as favorable, neutral, unfavorable, or unknown. We found that most bioblendstocks presented in this study showed favorable economic metrics, while the technology readiness metrics were mostly neutral. The economic viability results showed potentially competitive target costs of less than \$4 per gasoline gallon equivalent (GGE) for six candidates and less than \$2.5/GGE for methanol. We identified 10 MM bioblendstock candidates with synergistic blending performance and with the potential to reduce greenhouse gas (GHG) emissions by 60% or more compared to petroleum-derived gasoline. The analysis presented here also provides insights into major economic and sustainability drivers of the production process and potential availability of the feedstocks for producing each MM bioblendstock.

KEYWORDS: *Biofuels, Multimode, Techno-economic analysis, Life cycle analysis, Technology readiness, Economic viability, Environmental impacts*

INTRODUCTION

The transportation sector in the United States (U.S.) plays an important role in the energy market. Twenty-eight percent of the total energy is used to move people or goods around the U.S. or about 28 quadrillion British thermal units according to the EIA.[1] This sector also contributes 28% of the total greenhouse gas (GHG) emissions generated in the U.S.[2] A bioderived fuel (or biofuel) can be considered as a low-carbon intensity liquid fuel that can alleviate the emission burdens in the transportation sector. Production of domestic biofuel allows diversification of transportation energy options and lower transportation sector emissions and can stimulate the domestic bioeconomy. However, it is critical to understand the economic and environmental impacts of emerging biofuel pathways to assess their viability and potential for commercialization. Research conducted in the Co-Optimization of Fuels & Engines (Co-Optima), a U.S. Department of Energy (DOE) sponsored consortium project that includes nine DOE laboratories and numerous university and industry partners,[3] aims to explore how innovations in biofuels and engines can enhance vehicle performance and fuel economy while simultaneously reducing emissions. Co-Optima research focuses on bioblendstocks that can be added to fuel to dramatically improve fuel properties, reduce emissions, and co-optimize performance with engine technologies.[3] These

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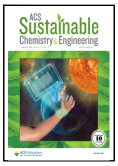


bioblendstocks can be produced from a wide variety of domestic resources, including nonfood biomass such as forestry and agricultural waste, using combinations of conversion technologies from biochemical and thermochemical, or a combination of both also known as a hybrid conversion technology, and a variety of fuel upgrading scenarios.

This paper is part of a series of papers that discuss the economic, environmental, and scalability viability of bioblendstocks that are designed based on properties that enable improvement in the engine fuel economy.[4−6] To determine which biofuel candidates are likely to be viable in terms of affordability, sustainability, and state of technology, we conducted techno-economic analysis (TEA) and life cycle analysis (LCA). TEA and LCA are methodologies used to assess economic and environmental impacts, respectively; LCA, however, is associated with all stages of the life cycle of biofuels studied here. In this paper, we focused the analysis on bioblendstocks designed for multimode (MM) engine types. Multimode engines can use two or more combustion strategies, including conventional stoichiometric spark-ignited (SI) combustion and advanced compression ignition (ACI). Mazda's SPCCI combustion system is an example of ACI.[7] Stoichiometric SI combustion provides high power density and is moderately efficient at high engine load but provides lower efficiency at low and intermediate load conditions that make up most of real-world driving.[8] Advanced compression ignition (ACI) and lean SI combustion modes and engine technologies hold promise to increase efficiency and cut emissions under these low to mid loads where stoichiometric SI combustion provides relatively low efficiency. Engines that utilize boosted SI (BSI) for high loads where it is most efficient and ACI/lean SI modes under other conditions are also known as multimode (MM) engines.[9]

For this analysis, 12 production pathways for producing MM bioblendstocks were considered. The list of bioblendstock candidates and their production pathways selected for this analysis are presented in Table S1 of the Supporting Information (SI). These bioblendstocks encompass a variety of structures, chemical functional groups, and properties such as linear and branched alcohols (2-butanol, isopropanol, isobutanol, n-propanol, prenol mixture, propanol−ethanol mixture, ethanol, and methanol), furans (2,5-dimethylfuran and 2-methylfuran mixture), and olefins (di-isobutylene). Some of these bioblendstocks have been investigated in the literature to assess economic and sustainability performance in diverse applications from biofuel to bioproducts. For instance, Tao et al.[10] previously reported the production design, economics, and environmental implication of producing cellulosic isobutanol, comparing the results to cellulosic ethanol and n-butanol. The authors showed that economics will be influenced by having high fermentation yields (xylose and glucose yield to isobutanol) of about 85%. Panjapakkul and El-Halwagi[11] described the synthesis, process design, and economics of producing biobased isopropanol, widely used as a solvent and chemical, from different production pathways. Gogar- et al.[12] conducted TEA of high-yield production of furans from mixed-sugar hydrolysates via a novel hybrid enzyme−chemo−catalytic process and estimated a minimum fuel selling price (MFSP), the price required to achieve a net present value of zero for a biorefinery, of about $1.42 per kg, which according to the authors is a promising price point for industrially high-value added chemical products. However, studies evaluating production economics, state of technology development, and environmental impacts at once are limited. Accordingly, in this paper, we focus on the assessments of the mentioned candidates for fuel application, as all of them are prioritized based on target fuel properties in support of MM combustion approaches for light-duty vehicle use. We also present details on the economic and environmental drivers that could provide research direction for future analysis and help in the deployment and development of these bioblendstocks. In this paper, we first introduce all MM bioblendstocks evaluated and describe the selection process. We then describe the methodology of our TEA and LCA and the different metrics used to assess economic viability, state of technology, and environmental impacts. Then, we present the results in the Results and Discussion section and discuss the drivers that influence the economics, GHG emissions, and water consumption metrics as well as opportunities to mitigate their impacts. We also expand on the potential market for these bioblendstocks looking at feedstock availability and production potential. Finally, we present the conclusions of this work.

■ METHODOLOGY

In collaboration with other Co-Optima teams, namely, high-performance fuels (HPF) and fuel property (FP) teams, we selected 10 bioblendstock candidates for TEA/LCA evaluation. The selected pathways were chosen from a larger group of potential bioblendstocks based on multiple criteria including the potential to meet favorable MM fuel properties. Because MM engines need to be able to operate in both ACI and BSI modes, most of the fuel properties that were defined for BSI still apply; therefore, we used a similar screening approach used for both BSI[13] and mixing controlled compression ignition.[14] The MM candidates, which are gasoline-like fuels, were screened based on a fuel property database that fulfilled characteristics including being liquid at room temperature and boiling in the gasoline range temperatures (<165 °C), not being be a carcinogen or reproductive toxin (such as benzene), having a research octane number (RON) greater than 98, and being biodegradable (e.g., better than methyl *tert*-butyl ether). In addition, with exception of diisobutylene, all these selected candidates are oxygenates offering high synergistic RON and S (octane sensitivity of the fuel). More information regarding fuel properties of the selected MM bioblendstocks is presented in Supporting Information Section S2. For the down selection, we also considered a diverse set of production methods, chemical structures, and feedstocks. Seven of these bioblendstock candidates (2-butanol, isopropanol, furan mixture, isobutanol, diisobutylene, ethanol, and methanol) were previously highlighted in a Co-Optima publication[4] that presented economic and sustainability screening analysis for 24 BSI bioblendstock pathways. Allthough in this analysis, economic assumptions were updated to be consistent with recent reports,[15] and sustainability metrics were updated to the most recent GREET model.[16] In addition, TEA and LCA were conducted for four new pathways: n-propanol, a 50:50 mixture of prenol and isoprenol, two variants of a diisobutylene-rich blendstock, and a propanol−ethanol mixture. Details of these new production pathways are presented in Supporting Information Section S3.

As it is presented in previous work,[4,6,18] we developed a set of metrics across three categories such as technology readiness, economic viability, and environmental impact and classified them as favorable, neutral, unfavorable, or unknown. The latter is used in limited cases where lack of information prevents categorization of the bioblendstock for a specific metric. We also considered two production cases to reflect the state of technology for each blendstock: *baseline case*, which represents the current performance of the process, and the *target case*, which is forward looking and reflects the potential of the technology at full scale.[4] The baseline key parameters, such as yield and selectivity, are lower than they would be when the technology is more mature. TEA and LCA were used to assess these metrics across the different categories. TEA begins with a thermodynamically rigorous process model developed in Aspen Plus or CHEMCAD software using a typical scale of 2000 dry metric tons/day biomass feed, with resultant energy and material balance results from the process model used for economic analysis. Capital expenditures (CAPEX) and operational expenses (OPEX) were estimated with the aid of multiple sources (internal databases, literature data, discussion with Co-Optima researchers, and patents). Discounted cash flows (DCFs) are then established to assess the economic performances of the different biorefineries. The main output from DCFs is the minimum fuel selling prices (MFSP) of MM bioblendstock candidates. The MFSP is the "breakeven" value that produced fuel must be sold at to achieve a net present value of zero across the biorefineries lifetime assuming a 10% nominal internal rate of return. Valorization of lignin, a residual product of the biorefinery process, was not included for biochemically produced pathways. This was chosen to keep comparisons consistent based on only the merits of the fuel production process, rather than conflate with high-*co*-product credits. For LCA, we used the GREET (Greenhouse gases, Regulated Emissions, and Energy use in Technologies) model to estimate life cycle GHG emissions, fossil fuel consumption (FFC), and water consumption for all Co-Optima bioblendstock pathways presented here.[16] The LCA system boundary that considers the biomass feedstock supply chain, biorefinery operations, transportation, and end use of the MM bioblendstocks is presented in Figure S6 of Supporting Information Section S4. Life cycle inventories (LCI) for fuel conversion and upgrading were informed by the results of material and energy balance also used in the TEA, while feedstock processing and logistical data were based on Idaho National Laboratory design cases 2022 projection.[19,20] Details of the feedstock processing and logistics data were described in previous analysis.[4,21] Multiple conversion technologies were considered including fermentation, pyrolysis, liquefaction, and hybrid technologies. Cellulosic and nonfood feedstocks were investigated including herbaceous- (corn stover) and woody-based feedstocks (forest residue). Some of the pathways generate electricity as a coproduct in addition to the bioblendstock. The electricity was coproduced via combustion of lignin using combined heat and power (CHP), which was enough to supply the electricity needs of the biorefinery. For the net electricity exported to the grid, we used the energy method to allocate the emissions and energy burdens between the bioblendstock product and the surplus electricity generated using the relative product output ratios based on their energy contents as the allocation basis.

Table 1 describes the metrics used to assess the technology readiness level of the selected MM bioblendstocks. Six metrics were selected for this category including establishing the process modeling data source, feedstock type sensitivity, robustness to feedstock changes, blending behavior with current fuels, and testing of the blendstock toward certification.

Table 1. Technology Readiness Metrics

Metric	Favorable	Neutral	Unfavorable
Process modeling data source	Demonstration-scale (or larger) data available, includes detailed process analysis from literature	Bench- or pilot-scale data available	Notional, yields, and conversion conditions estimated partly from research-based literature
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
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
Blending behavior of bioblendstock 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
Bioblendstock underwent testing toward certification	Yes	Limited	None
Bioblendstock blendable only in limited levels because of current limits	No limit	Blendable at high levels	Significant limit

Table 2. Economic Viability Metrics Classification

Metric	Favorable (+)	Neutral (0)	Unfavorable (−)
Co-Optima bioblendstock production baseline cost	Falls in cluster of lowest cost pathways (<\$4/GGE)	Falls in cluster of moderate cost pathways (\$4/GGE−\$7/GGE)	Falls in cluster of highest cost pathways (>\$7/GGE)
Fuel production target cost	Falls in cluster of lowest cost pathways (<\$4/GGE)	Falls in cluster of moderate cost pathways (\$4/GGE−\$5.5/GGE)	Falls in cluster of highest cost pathways (>\$5.5/GGE)
Ratio of baseline-to-target cost	<2	2−4	>4
Percentage of product price dependent on coproducts[a]	<30%	30−50%	>50%
Competition for the bioblendstock or its predecessor[b]	Bioblendstock is not produced from, nor is itself, a valuable chemical intermediate	Bioblendstock is produced from, or is itself, a raw chemical intermediate	Bioblendstock is produced from, or is itself, a valuable chemical intermediate
Cost of feedstock (in U.S.\$2016)	Cost at or below target of \$84/dry ton delivered at reactor throat	Cost between \$84/dry ton and \$120/dry ton	Feedstock cost at delivery to reactor throat likely to exceed \$120/dry ton

[a] For example, compared to chemicals, electricity, other bioblendstocks/fuels produced as coproducts to co-Optima fuel. [b] It may be possible that competition for the bioblendstock for multiple end uses could lead to more stable financing for biorefineries that would produce the bioblendstock, but our primary focus in this analysis is availability as a bioblendstock fuel, which could be compromised if there were competition with the chemicals market.

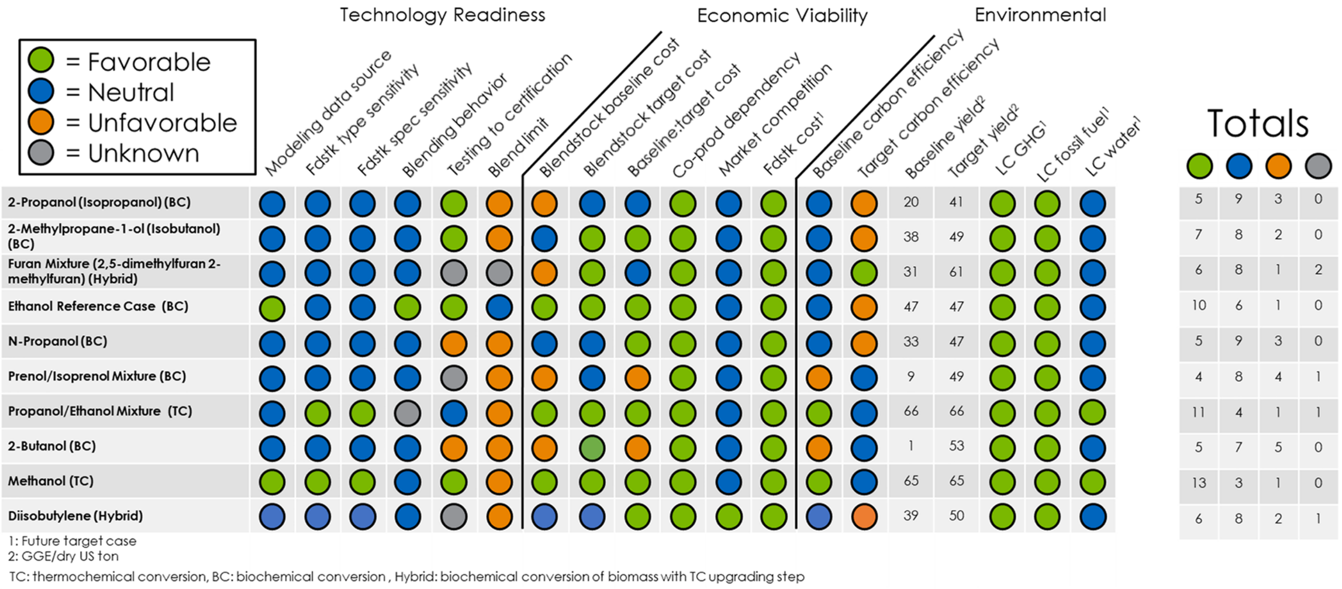
Table 3. Environmental Metrics Classification

Metric	Favorable	Neutral	Unfavorable
Baseline: Efficiency of input carbon (fossil and biomass-derived) to Co-Optima bioblendstock	>30%	10−30%	<10%
Target: Efficiency of input carbon (fossil and biomass-derived) to Co-Optima bioblendstock	>40%	30−40%	<30%
Baseline: Co-Optima bioblendstock yield (GGE/dry ton)[a]			
Target: Co-Optima bioblendstock yield (GGE/dry ton)[a]			
Target: Life cycle GHG emission reduction compared to conventional gasoline fuel[a]	Likely to achieve a greater than 60% reduction in life cycle GHG emissions	Could achieve a greater than 60% reduction in life cycle GHG emissions.	Unlikely to achieve a greater than 60% reduction in life cycle GHG emissions
Target: Life cycle fossil energy consumption reduction to conventional gasoline fuel[b]	Likely to use less fossil energy on a life cycle basis than conventional gasoline	Could use less fossil energy on a life cycle basis than conventional gasoline	Unlikely to use less fossil energy on a life cycle basis than conventional gasoline
Target: Life cycle water consumption (gal/GGE)[b,c]	Likely to use less water on a life cycle basis than 6 gal/GGE	Could use less water on a life cycle basis than 42 gal/GGE	Could use more water on a life cycle basis than 42 gal/GGE

[a] Baseline and target yields are not ranked into favorable, neutral, or unfavorable bins because it is difficult to compare based on highest and lowest yields when feedstocks (oils, dry or wet feedstocks) and conversion technologies are so different across the pathways. [b] Developed from baseline comparison for 2020 gasoline based on shares of feedstocks (e.g., oil sands, conventional crude) as in GREET2020. [c] Water consumption thresholds are based on conventional gasoline (6 gal/GGE) and corn ethanol (42 gal/GGE) to the determine the lower and upper bound values.

For processing the modeling data source, indicative of technology readiness level (TRL), we conducted a review to obtain information based on existing research and analyses, published literature, and discussions with national laboratory researchers. When experimental data were unavailable, we relied on high-level mass balance to estimate values. While there may be many parts of a process that are proven industrially, favorability was ranked by the lowest TRL portion of the process, typically fermentation titers, rates, and yields or reactor catalyst conversion extents. To understand process robustness, this screening analysis considered the impact of changing feedstocks (woody or herbaceous feedstocks) on process performance. Finally, the metrics in Table 1 considered the quality of the final biofuel to evaluate if the biofuels would be compatible with current engines, blending behaviors, and testing toward certification. Testing for certification is based on approval as a fuel or fuel additive by the U.S. EPA.[22]

When considering the economic metrics (presented in Table 2), the focus was on where a proposed process could improve compared to the current baseline and developing cost projections of the potential economic viability of the pathway. The cost values for these pathways were evaluated with process modeling and TEA and were adopted from established target cases, published TEA data, and newly developed analysis. All bioblendstocks evaluated were normalized on a lower heating value (LHV) basis against gasoline to yield a gasoline gallon equivalent (GGE) basis. The use of a per GGE basis provides a consistent comparison between costs and other metrics for produced bioblendstocks which may have different densities and volumetric energy bases. A key metric in the analysis was the estimate of the MFSP of both baseline and targeted designs. The production costs are estimates given available information and are subject to change as technology develops and more research is conducted. Similarly, while some processes such as ethanol are more mature, others are at a much earlier stage of research and may encounter unforeseen challenges in scaling up making estimation of true MFSP difficult. As such, we do not report MFSP here but rather report a qualitative favorability based on clustering and comparing pathways relative to each other. Favorable were those in the lowest cost pathways. Neutral were those approximately in the middle. Unfavorable were those in the highest cost pathways. To understand how far each target case was from the baseline, we included the metric of baseline-to-



🟢 = Favorable
🔵 = Neutral
🟠 = Unfavorable
⚪ = Unknown

	Technology Readiness						Economic Viability						Environmental							Totals			
	Modeling data source	Fdstk type sensitivity	Fdstk spec sensitivity	Blending behavior	Testing to certification	Blend limit	Blendstock baseline cost	Blendstock target cost	Baseline:target cost	Co-prod dependency	Market competition	Fdstk cost[1]	Baseline carbon efficiency	Target carbon efficiency	Baseline yield[2]	Target yield[2]	LC GHG[1]	LC fossil fuel[1]	LC water[1]	🟢	🔵	🟠	⚪
2-Propanol (Isopropanol) (BC)	🔵	🔵	🔵	🔵	🟢	🟠	🟠	🔵	🔵	🟢	🔵	🟢	🔵	🟠	20	41	🟢	🟢	🔵	5	9	3	0
2-Methylpropane-1-ol (Isobutanol) (BC)	🔵	🔵	🔵	🔵	🟢	🟠	🔵	🟢	🟢	🟢	🔵	🟢	🔵	🟠	38	49	🟢	🟢	🔵	7	8	2	0
Furan Mixture (2,5-dimethylfuran 2-methylfuran) (Hybrid)	🔵	🔵	🔵	🔵	⚪	⚪	🟠	🟢	🔵	🟢	🔵	🟢	🔵	🟢	31	61	🟢	🟢	🔵	6	8	1	2
Ethanol Reference Case (BC)	🟢	🔵	🔵	🟢	🟢	🔵	🟢	🟢	🟢	🟢	🔵	🟢	🔵	🟠	47	47	🟢	🟢	🔵	10	6	1	0
N-Propanol (BC)	🔵	🔵	🔵	🔵	🟠	🟠	🔵	🔵	🟢	🟢	🔵	🟢	🔵	🟠	33	47	🟢	🟢	🔵	5	9	3	0
Prenol/Isoprenol Mixture (BC)	🔵	🔵	🔵	🔵	⚪	🟠	🟠	🔵	🟠	🟢	🔵	🟢	🟠	🔵	9	49	🟢	🟢	🔵	4	8	4	1
Propanol/Ethanol Mixture (TC)	🔵	🟢	🟢	⚪	🔵	🟠	🟢	🟢	🟢	🟢	🔵	🟢	🟢	🔵	66	66	🟢	🟢	🟢	11	4	1	1
2-Butanol (BC)	🔵	🔵	🔵	🔵	🟠	🟠	🟠	🟢	🟠	🟢	🔵	🟢	🟠	🔵	1	53	🟢	🟢	🔵	5	7	5	0
Methanol (TC)	🟢	🟢	🟢	🔵	🟢	🟠	🟢	🟢	🟢	🟢	🔵	🟢	🟢	🔵	65	65	🟢	🟢	🟢	13	3	1	0
Diisobutylene (Hybrid)	🔵	🔵	🔵	🔵	⚪	🟠	🔵	🔵	🟢	🟢	🟢	🟢	🔵	🟠	39	50	🟢	🟢	🔵	6	8	2	1

1: Future target case
2: GGE/dry US ton

TC: thermochemical conversion, BC: biochemical conversion , Hybrid: biochemical conversion of biomass with TC upgrading step

Figure 1. Screening results for bioblendstocks for multimode engines. The bioblendstocks listed are produced via biochemical (BC), thermochemical (TC), and hybrid production pathways. Green, blue, and orange circles represent favorable, neutral, and unfavorable classification, respectively, as defined in Tables 1−3. Gray circles reflect a lack of information to categorize a given bioblendstock for a certain metric. GGE = gasoline gallon equivalent.

target cost ratio. Additional metrics focused on quantifying the dependence of the proposed process economics on coproducts, as commodity market price changes for coproducts could result in large swings in the MFSP. Additionally, consideration was given to uses of the final fuel or its intermediates outside of the fuels market, particularly if either were, for example, used as a commodity chemical or chemical intermediate. Commodity chemicals are likely to have a higher profit margin than fuels and could be challenged if competing in this space. Feedstock prices are based upon Idaho National Laboratory's feedstock cost analyses for conversion-ready feedstock delivered to the conversion reactor throat.[19,20]

Finally, Table 3 presents the environmental metrics evaluated for the MM bioblendstocks studied in this paper. These metrics not only evaluate the efficiency and yields of a process based on process modeling but also the impacts that the bioblendstocks will have on the reduction of GHG emissions, fossil energy use, and water consumption. Carbon efficiency is calculated based on the amount of carbon from primarily input feedstock and other carbon-containing inputs that end up in the final product or that were burned to provide process heat (e.g., natural gas). Baseline and target yields were included for reference but not ranked on favorability due to different comparative bases between pathways and energy density of feedstocks. GHG emission reduction, fossil energy consumption, and water consumption were all evaluated for the target cases only. Their values include the entire supply chain and system, including coproducts of the biorefinery. GHG emissions were a percent reduction compared relative to conventional petroleum-derived gasoline. GHG emission reductions were favorable if bioblendstocks could achieve advanced biofuel emission reduction targets of at least 60%. Water consumption was compared on a gallon per unit energy basis (GGE).

RESULTS AND DISCUSSION

Results for the screening of the Co-Optima MM bioblendstock pathways against technology readiness, economic viability, and environmental metrics are presented in Figure 1. All the fuels considered had high merit function scores, using the BSI formula. The high scores indicate that the candidate fuels have beneficial combustion and environmental properties and warrant further consideration. Columns represent the criteria described in Tables 2 and 3, while rows represent all the MM bioblendstocks included in this analysis. The results presented in this figure are categorized and compared based on favorability for each metric. Cellulosic ethanol (biochemical) is included as a benchmark but is itself a viable MM fuel candidate. Although the original list of MM bioblendstocks presented in Table S1 included three diisobutylene pathways, the results presented in Figure 1 only include bioblendstock candidates that met the advanced biofuel criteria of greater than 60% reduction in life cycle GHGs compared with conventional gasoline on an energy basis.

Most technology readiness metrics were categorized as neutral. Information for process modeling was based on bench-scale experiments except for ethanol and methanol which are already commercial pathways; therefore, the modeling data source was favorable for these two pathways. For most of the pathways, the fuel production process was minimally affected by feedstock type and specification. The gasification-based technologies considered were favorable because the technology is commercially developed for a wide range of feedstocks with significant variations in mineral matter content and speciation (e.g., coal versus biomass). The ash contents of some herbaceous feedstocks can be high and impact yield primarily because on a mass basis less convertible material is fed to the process. Slagging can be an issue in some reactor types.[23] However, in the gasifiers used for our analysis (indirectly heated steam gasification), slagging is not typically a problem because the temperatures are lower than with oxygen-blown gasifiers, and olivine is used for the bed media to avoid solid

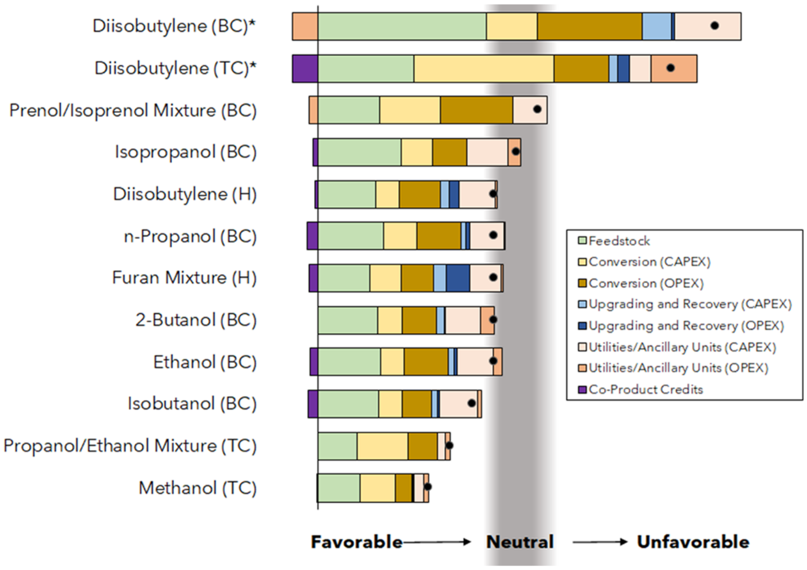


Figure 2. Cost breakdown for selected multimode bioblendstocks. The values presented here are described for major process operations and capital and operational expenses. CAPEX refers to capital expenditures, while OPEX refers to the operating expenses. BC, biochemical; TC, thermochemical; H, hybrid.

eutectic formation, possible with silica and potassium mixtures, that tend to defluidize fluidized bed reactors. Only the propanol−ethanol mixture blending behavior was classified as unknown for blending behavior, although it is expected to be favorable with measurement in progress. Blending behavior was neutral for most bioblendstocks as most are currently approved fuel additives, while testing toward certification was favorable for four candidates (isopropanol, isobutanol, ethanol, and methanol) as permitted oxygenate/fuel additives in some states. However, the furan mixtures and prenol−isoprenol mixture were categorized as unknown. As discussed by Kolodziej and Scheib,[23] blending isobutanol with gasoline (up to 12.5 vol%) produces a similar gasoline at 2.7% O_2 content, which is acceptable by engine manufacturers; therefore, the U.S. EPA waiver (211b) could potentially allow isobutanol blending levels up to 16.1%, which produces a final fuel with the same oxygen content (3.5%) and heating value as an ethanol 10% blend (E10).[17] Finally, there are legal restrictions for blending these fuels such as limits on oxygenates (1-butanol, isopropanol, isobutanol, prenol, propanol/ethanol mixture) and olefins (prenol, diisobutylene). The ethanol reference case is well known with blending levels as high as E85.

In terms of economic readiness metrics, most of the metrics fell in the favorable category. Baseline and target costs were compared relative to each other. Three pathways fell at or below \$4/GGE for baseline cases (ethanol, propanol/ethanol mixture, and methanol), while for target cases production costs improved significantly with six pathways showing the potential to achieve a fuel selling price of \$4/GGE or less. Although routes produced biochemically did not include the valorization of lignin to coproducts to provide a conservative estimate of MFSP, this could be an alternative to reduce the MFSP of these biofuels. The level of research and development required to reach target cost (baseline: target cost ratio) were mostly favorable, although 2-butanol and prenol−isoprenol have higher barriers to achieve target case costs due to limitations in baseline fermentation yields. The percentage of product price dependent on coproducts was favorable for all bioblendstocks, while market competition for either the produced fuel or feedstock fell in the neutral category for most bioblendstocks. MM fuels such as small alcohols are widely used as industrial and laboratory solvents, chemical intermediates, or antiseptics which may create market pull away from the fuels market. For the final economic metric, the feedstock costs were uniformly favorable across bioblendstocks due to the use of lower-cost lignocellulosic biomass feedstocks.

Most of the environmental metrics for MM bioblendstocks candidates fell between the favorable and neutral bins, especially in the case of methanol and propanol−ethanol pathways. Carbon efficiency (baseline/target) is a key challenge for these pathways with values ranging from 5.5% to 33%. Baseline case carbon efficiency was neutral for most candidates. The 2-butanol pathway had the lowest carbon efficiency (5%) in the baseline case; however, it improved to 31% in the target case due to projected improvements in fermentation yield. In contrast, the propano−ethanol mixture and methanol have the highest baseline carbon efficiency (33%) and the highest yield among all bioblendstocks as they are produced using thermochemical indirect liquefaction to synthesis gas, capable of utilizing most of the biomass carbon instead of just carbohydrates in cases of fermentation and high conversion efficiency during alcohol synthesis. Target case carbon efficiency was unfavorable for most blendstocks (<40%). Only the furan mixture had favorable target case carbon efficiency which was improved from 21% in the baseline case to 40% in the target case. As previously mentioned, Figure 1 only reports the pathways with a favorable GHG emission reduction greater than 60% compared to conventional gasoline. The lowest GHG emissions value was obtained by methanol (10 gCO_2e/MJ), representing an 89% reduction compared to conventional gasoline. Fossil energy consumption was favorable in all presented pathways with more than 54% reduction in fossil fuel consumption compared to conventional gasoline. Finally, water consumption was neutral for most of the pathways but favorable for methanol and the propanol−ethanol mixture, showing reductions of 31% and 39%, respectively, compared to water used to produce

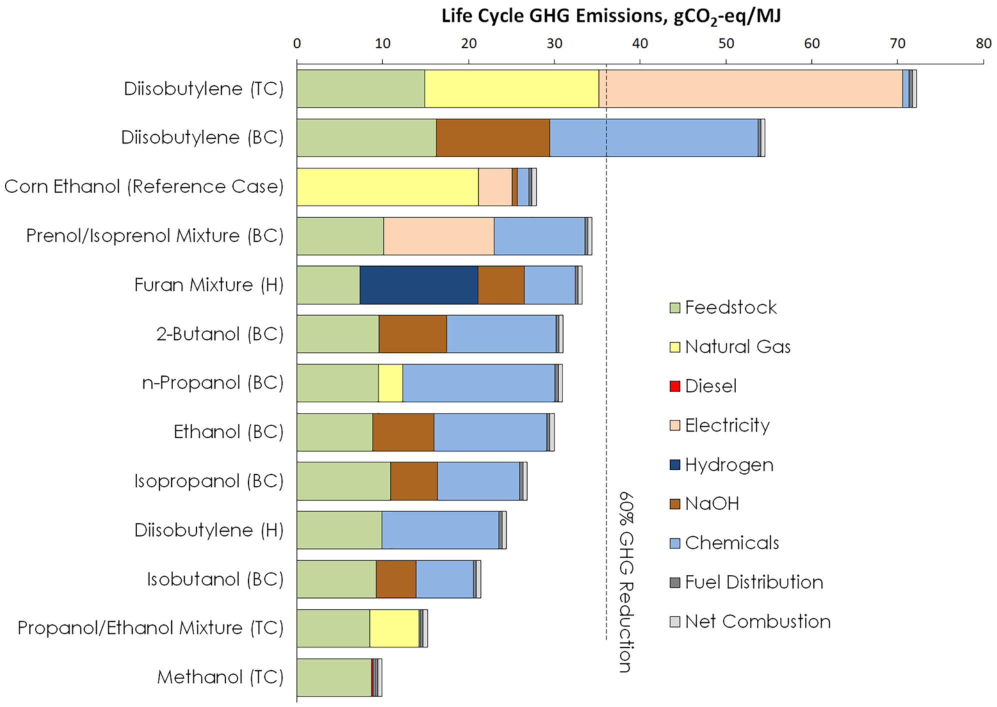


Figure 3. Life cycle greenhouse gas emissions breakdown for selected multimode bioblendstocks. The life cycle greenhouse gas emissions results for the 10 MM bioblendstocks presented in Table S1. This figure also includes corn ethanol as a reference case. BC, biochemical; TC, thermochemical; H, hybrid.

petroleum gasoline. Water used in the bioblendstock production process and water used upstream in the production of chemicals used in the biorefinery were the largest contributors to the total water use metrics for all the pathways studied here. Section 4 of the Supporting Information presents the water consumption breakdown for all the pathways and some additional discussion related to this metric.

Economic drivers for the MM bioblendstock are shown in Figure 2. Feedstock and conversion costs are key contributors to the MFSP of all MM bioblendstocks representing between 25% to 40% of costs for all the pathways. The feedstock used in biochemically produced diisobutylene had the biggest impact in diisobutylene MFSP, while for the thermochemically produced diisobutylene the CAPEX for the conversion process was the biggest contributor to the MFSP. Biochemically produced alcohols had similar MFSPs and cost breakdowns due to nearly identical enzyme production and pretreatment processes, although upgrading processes and recovery costs were relatively small. On the other hand, thermochemically produced methanol and the propanol−ethanol mixture maintained a larger proportion of costs attributed to conversion which was offset by higher overall product yields resulting in lower MFSPs.

Figure 3 describes the key drivers that influence the life cycle GHG emissions for all the pathways studied in the paper, including the three routes for diisobutylene as described in Table S1. Pathways for ethanol produced from corn starch and corn stover via biochemical conversion are also shown to provide a comparative basis. Details of the corn starch pathway can be found at Argonne[16] and for the corn stover pathway are presented at Dunn et al.[4] Carbon dioxide emissions during engine combustion were omitted from the figure as they are canceled by the uptake of carbon dioxide during the growth of the biomass feedstock. As shown in Figure 1, 10 of the 12 MM pathways showed favorable life cycle GHG emissions (>60% reduction). GHG emissions reductions varied from 20% for thermochemically produced diisobutylene to 89% for methanol compared to those of conventional diesel. Two diisobutylene pathways (BC and TC) did not achieve the 60% GHG emission reductions. In the biochemical pathway, the major contributor to the GHG emissions was the chemicals used during the conversion process, while in the thermochemical pathway it was energy usage during conversion. The chemicals involved in the biochemical pathway were related to the material used during the fermentation process, for example, ammonia and diammonium disulfate which served as the source of nitrogen and phosphorus fermentation nutrients, in addition to corn steep liquor, glucose, and lime. For the thermochemical pathway of diisobutylene, about 50% of the GHG emissions are due to electricity consumption used to power gas compressors in the high-pressure catalytic synthesis of ethanol, while 28% comes from natural gas consumption to provide process heating. These energy inputs are similar for the other thermochemical processes that are based on ethanol production and upgrading, but the diisobutylene carbon efficiency is lower than in the other pathways due to the production and loss of CO_2 in the conversion mechanism that reduces the yield of desired product. Figure 2 also presents that material and energy contributions were very similar among biochemical pathways showing that the major contributor was the chemical usage during fermentation processes or the caustic (NaOH) used for pH control in wastewater treatment. For most of these biochemical pathways, the process was largely energy independent (diisobutylene BC, furan mixtures, 2-butanol, ethanol BC, isopropanol, isobutanol) due in part to combustion of lignin for heat and electricity. The prenol−isoprenol mixture and n-propanol pathways, however, do require electricity and natural gas inputs. Thermochemical

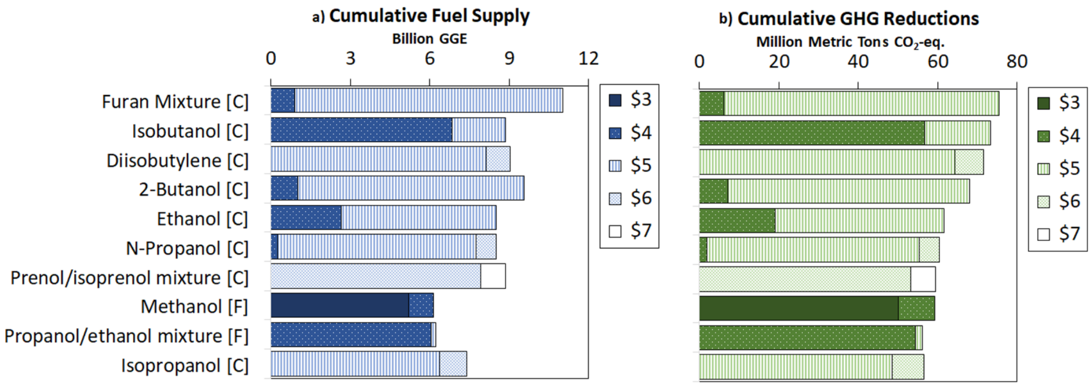


Figure 4. (a) Cumulative fuel supplies for MM bioblendstocks at a range of price levels. (b) Cumulative GHG emission reductions. C, corn stover-based pathways; F, forest residue-based pathways.

pathways show slightly different breakdowns between each pathway. For the diisobutylene TC pathway, the major contributor was the energy inputs, and for methanol and the propanol−ethanol mixture the feedstock played a primary role. Although these last two pathways met the advanced biofuel criterium of 60% GHG emissions reduction, the feedstock contribution of methanol represented 88% of the total GHG emission, while for the propanol−ethanol mixture this contribution was 56%. Figure S7 of the SI describes additional details of emissions during feedstock processing and logistics for the two main feedstocks used in this analysis.

The potential for the MM blendstocks to reduce transportation greenhouse gas emissions is fundamentally limited by the supply of feedstocks for their production. Therefore, in this analysis, we also consider the potential availability of the feedstocks for producing each MM bioblendstock analyzed here. Although in this paper the production of each MM bioblendstock was modeled based on either corn stover or forest residue biomass (See Table S1 of the SI), we also consider energy crops such as switchgrass and miscanthus and whole tree (poplar, pine, willow, and eucalyptus) biomass to provide a more complete estimate. While conversion of these additional biomass resources would vary to some degree from base case assumptions, for the purpose of this simplified calculation, it is assumed the conversion operations, TEA, and LCA for corn stover and forest residue can be used as proxies to estimate bioblendstock supplies and life cycle greenhouse gas emissions. Total cumulative supply of corn stover, switchgrass, and miscanthus is used to estimate the supply curves for the bioblendstocks originally modeled based on corn stover, and the total cumulative supply of forest residue and whole tree biomass is used to estimate the supply curves for methanol and the propanol−ethanol mixture originally modeled based on forest residue. For details on the feedstock supply curves estimations, please refer to SI Section S7. Figure 4a shows the cumulative fuel supply (billion GGE) for the MM bioblendstocks at different MFSP ranges (i.e., \$3−\$7 per GGE), while Figure 4b shows the cumulative GHG emission reductions relative to petroleum gasoline (92 gCO_2-eq/MJ). For these estimates, it is assumed that the life cycle carbon intensity of the fuels produced from the alternate feedstocks are the same as those for the original calculations based on corn stover and forest residue. This is a simplification as the carbon intensity of switchgrass and miscanthus will differ to some degree from corn stover. However, these differences are relatively small for the purposes of this analysis, while there are significant other uncertainties related to specific conditions of switchgrass and miscanthus production at various scales. For comparison, the GREET estimates for carbon intensities for ethanol produced from corn stover, switchgrass, and miscanthus are 10, 14, and −4.2 gCO_2-eq./MJ, respectively.[16] The differences in these estimates incorporate land use change effects such as changes in soil organic carbon and other considerations which have a high degree of uncertainty.[16] For these reasons, assuming the same life cycle carbon intensity for ethanol from switchgrass and miscanthus is reasonable for these rough estimates, and results should be interpreted with this in mind. These figures were generated by using the GHG emissions shown in Figure 3 and the target yields reported in Figure 1 (also summarized in SI Section S7). The calculation of bioblendstock supplies at different MFSPs is based on the estimates of delivered feedstock costs at the reactor throat described in SI Section S7. As the TEA models for this study were performed at a screening level, the effect of changes in feedstock price on MFSP was calculated using the TEA model for each bioblendstock. For instance, the MFSPs were calculated for a range of feedstock prices, e.g., \$50, \$71, and \$100/dry US ton. For all models presented here, the relationship between MFSP and feedstock cost was perfectly linear ($R^2 = 1$), and so the slope and intercept of the relationship between feedstock price and MFSP were used to perform the estimates presented in this analysis.

The results of this analysis show that significant volumes of MM bioblendstocks could be produced with lignocellulosic biomass feedstocks at MFSP values of about \$5/GGE. Figure 4a shows that cumulative supply for bioblendstocks produced from corn stover, switchgrass, and miscanthus ranges from 11 billion GGE, based on a lower heating value, for the furan mixture at an MFSP of approximately \$5/GGE (using a U.S.2016\$ cost basis), to 7 billion GGE for isopropanol at roughly the same MFSP. The MFSPs for methanol and the propanol−ethanol mixture produced from forest resources were slightly lower (\$3−4/GGE), as well as a lower biofuel supply due to less biomass being available compared to the lignocellulosic biomass feedstock pathways. Combined with differences in the supply of forest residue and whole tree biomass, we estimated production volumes of roughly 6 billion GGE in both cases at MFSPs of roughly \$4/GGE for methanol and \$5/GGE for the propanol−ethanol mixture. One important assumption is that we did not consider competing uses for the biomass; the results presented here are the maximum amount of fuel that could be produced from the total available feedstock in the U.S. Estimates of cumulative GHG reductions reached 50−75 million metric tons CO_2-eq. across the pathways evaluated at MFSPs ranging from $3−7/GGE. These values were estimated considering the replacement of conventional gasoline with each multimode bioblendstock and the differential life cycle GHG emissions. Having the lowest estimated MFSP among bioblendstocks evaluated, methanol achieved a GHG reduction of roughly 50 million metric tons of CO_2-eq. at about the $3/GGE MFSP price point and roughly 60 million metric tons of CO_2-eq. at about the $4/GGE price point. GHG reductions above 60 million metric tons CO_2-eq. were only achieved by the bioblendstocks produced from corn stover, switchgrass, and miscanthus due to their larger supply.

CONCLUSIONS

This analysis presented economic, scalability, and sustainability considerations for 12 bioblendstock production pathways for bioblendstocks suitable for use in MM engines. The pathways were selected from a variety of renewable feedstocks and conversion technologies including seven biochemical conversions, three thermochemical conversions, and two hybrid production pathways as well as biochemically produced ethanol as a reference case. The economic metrics were favorable for most of the bioblendstocks. Under the baseline case, three pathways offered the potential of fuel selling price of $4/GGE or less, and this number increased to six pathways because of the potential of technology improvement under the target case. The feedstocks were available at scale for a reasonable cost, although they played a key role in reducing MFSP as it is the major driver for estimating the biofuel cost. Most of the conversion technologies analyzed here were robust and only moderately affected by the variations in feedstock quality. Technology readiness was mostly neutral for the MM bioblendstocks. We found that most pathways had bench-scale data available for process modeling assumptions, and the blendstock quality is sufficient for blending with current fuels for use in vehicles. However, blend limits for oxygenates and olefins were a barrier affecting most of the bioblendstocks. In terms of environmental metrics, it was found that all 10 bioblendstock were able to achieve more than 60% GHG emission reduction relative to petroleum gasoline. From the three options to produce diisobutylene, the hybrid pathway with a 73% reduction in GHG emissions was the only pathway able to achieve the target 60% threshold, while biochemically and thermochemically produced diisobutylene only reduced GHG emissions by 20% and 40%, respectively, compared to conventional petroleum gasoline. The GHG emissions of the latter pathways were affected by the amount of sodium hydroxide used for feedstock pretreatment in the biochemical case and electricity demand during the conversion process in the thermochemical case. In general, we found that feedstock, sodium hydroxide, and chemical consumption were primary contributors to the GHG emissions of the analyzed bioblendstocks, while feedstock and conversion costs are key contributors to the MFSP of all MM bioblendstocks representing between 25% to 40% of costs for all the pathways. Although the intention of this work was not to choose the best or worst pathways, we found through this analysis that methanol and the propanol−ethanol mixture may offer the fewest barriers to adoption as they had the highest number of favorable metrics falling mostly into the economic viability and environmental performance. However, these bioblendstocks have lower supply potential with estimated volumes of roughly 6 billion GGE for MFSPs $4/GGE for methanol and $5/GGE for the propanol−ethanol mixture compared to the lignocellulosic-based pathways with estimated volumes from 7 to 11 billion GGE for isopropanol and furan mixtures, respectively, at an MFSP of about $5/GGE.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00944.

> List of multimode bioblendstock pathways, characteristics of bioblendstock pathways selected for multimode engines, LCA boundary assumptions, high-level process descriptions for bioblendstock production, water consumption and feedstock procession breakdowns, and feedstock supply estimations (PDF)

AUTHOR INFORMATION

Corresponding Author

Troy R. Hawkins − *Systems Assessment Group, Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, United States;* orcid.org/0000-0001-6897-175X; Email: thawkins@anl.gov

Authors

Pahola Thathiana Benavides − *Systems Assessment Group, Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, United States;* orcid.org/0000-0002-8253-7877

Andrew W. Bartling − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States;* orcid.org/0000-0002-6236-0031

Steven D. Phillips − *Energy Processes and Materials Division, Pacific Northwest National Laboratory, Richland, Washington 99354, United States*

Avantika Singh − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States*

George G. Zaimes − *Systems Assessment Group, Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, United States*

Matthew Wiatrowski − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States;* orcid.org/0000-0002-0658-7178

Kylee Harris − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States*

Pralhad H. Burli − *Operations Research and Analysis, Idaho National Laboratory, Idaho Falls, Idaho 83415, United States*

Damon Hartley − *Operations Research and Analysis, Idaho National Laboratory, Idaho Falls, Idaho 83415, United States;* orcid.org/0000-0002-3115-8527

Teresa Alleman − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States;* orcid.org/0000-0001-8302-7767

Gina Fioroni − *National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States;* orcid.org/0000-0003-1916-1763

Daniel Gaspar − *Energy Processes and Materials Division, Pacific Northwest National Laboratory, Richland, Washington 99354, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acssuschemeng.2c00944

Notes

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■ ABBREVIATIONS:

ACI	Advanced compression ignition
ANL	Argonne National Laboratory
BC	Biochemical conversion
BETO	Bioenergy Technologies Office
BOB	Blendstock for oxygenate blending
BSI	Boosted spark ignition
CHP	Combined heat and power
CAPEX	Capital expenditures
EIA	Energy Information Administration
DCF	Discounted cash flows
DOE	U.S. Department of Energy
FFC	Fossil fuel consumption
FP	Fuel property
GHG	Greenhouse gas
GGE	Gasoline gallon equivalent
GREET	Greenhouse gases, Regulated Emissions, and Energy use in Technologies
H	Hybrid
HPF	High-performance fuels
INL	Idaho National Laboratory
LCA	Life cycle analysis
LCI	Life cycle inventory
LHV	Lower heating value
MSFP	Minimum fuel selling price
MM	Multimode
NREL	National Renewable Energy Laboratory
OPEX	Operational expenses
PNNL	Pacific Northwest National Laboratory
RON	Research octane number
S	Octane sensitivity
SI	spark ignited
TEA	Techno-economic analysis
TRL	Technology readiness level
TC	Thermochemical conversion
U.S. EPA	United States Environmental Protection Agency
VTO	Vehicle Technologies Office

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