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Research Article

Environmental, Economic, and Scalability Considerations of Selected Bio-Derived Blendstocks for Mixing-Controlled Compression Ignition Engines

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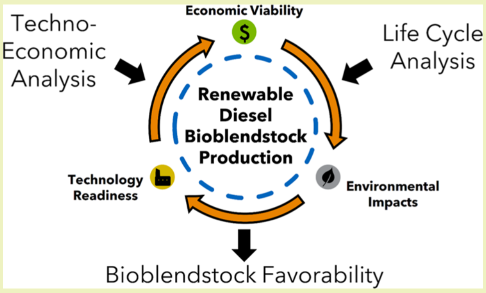

ABSTRACT: Economic and environmental favorability are vital considerations for the large-scale development and deployment of sustainable fuels. Here, we have conducted economic and sustainability analyses of pathways for producing bioblendstocks optimized for improved combustion for mixing-controlled compression ignition (MCCI) engines. We assessed 25 pathways for the production of target fuels from renewable feedstocks and conducted techno-economic analysis (TEA) and life cycle analysis (LCA) to determine which bioblendstock candidates are likely to be viable given a slate of 19 metrics evaluating technology readiness, economic viability, and environmental impacts ranking each metric as either favorable, neutral, unfavorable, or unknown across a range of screening criteria. Among the results, we found that the economic metrics were largely favorable for most of the bioblendstocks. Of the near-term baseline cases, eight pathways offered the potential of a minimum fuel selling price (MFSP) of less than \$5/gallon of gasoline equivalent (GGE). In comparison, under future target case scenarios, there is potential for seven pathways to reduce their fuel selling price to less than \$4/GGE. Biochemically-based pathways struggled to achieve favorable target case MFSP under the processing approach taken here, but further economic improvements could be achieved when lignin valorization is included. Most of the conversion technologies were determined to be robust in that they would be minimally affected by the feedstock specifications and variations. However, given the early stage of development for most of the pathways, blending behavior and testing for regulatory limits are key data gaps as knowledge of how many of these bioblendstocks will perform when blended with existing fuels and how much can be added while still meeting fuel property specifications is still being assessed. Twelve pathways showed significant reductions in life cycle greenhouse gas (GHG) emissions greater than 60%, and 15 showed favorable fossil energy use reductions compared to conventional diesel fuel. Energy-intensive processes and the use of GHG-intensive chemicals such as sodium hydroxide contribute significantly to GHG emissions. Results from these analyses enable researchers and industry to assess the potential viability of MCCI bioblendstocks.

KEYWORDS: *techno-economic analysis, life cycle analysis, biofuels, renewable diesel*

■ INTRODUCTION

Society needs cost-effective, clean, and low-carbon powertrains. The supply chains, freight, and other services that rely on transportation networks share a set of criteria requiring long-range applications capable of rapid re-energizing, of sufficiently low weight, and a compact size required for roadways and existing shipping infrastructure. Currently, much of this need is met by compression ignition engines burning petroleum-derived diesel fuels. While this mode of operation has time-tested advantages of being cost-effective, high efficiency, durable, long range, and as easy to re-energize as a trip to the pump, they are disadvantaged in their current paradigm that the combustion of conventional, petroleum-derived diesel leads to emissions of carbon dioxide, soot, and nitrogen oxides into the atmosphere. While efforts are underway to reduce these emissions through electrification or fuel cell technologies, these too have disadvantages to their wide-scale adoption in their current form. Significant cost, weight, and space required for batteries to power larger vehicles still bring a significant hurdle to their adoption in

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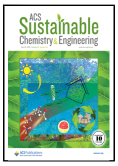

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shipping fleets. In addition, the time required to recharge batteries to provide sufficient additional range is much slower than refueling a tank and may hinder longer-range applications. Fuel cells offer additional challenges with a lack of infrastructure for hydrogen supply, a lower energy density than liquid fuels, and production of hydrogen itself, which most commonly employs steam methane reforming, which is both carbon- and energy-intensive, or electrolysis that currently requires significant electricity to produce in quantities required for large-scale application. Therefore, there remains a need for low-carbon, sustainable liquid fuels compatible with the existing infrastructure that can be leveraged by compression ignition engines.

The United States Department of Energy's (DOE) Co-Optimization of Fuels & Engines (Co-Optima) initiative, a consortium of 9 national laboratories and over 20 university and industrial partners, explores how simultaneous innovations in fuels and engines can boost fuel economy and vehicle performance while simultaneously reducing emissions. Using a tiered screening approach, Co-Optima aims to identify promising fuel candidates that meet a set of specified property criteria depending on the combustion mode. Recently, research within Co-Optima has focused on fuel production and the benefits of deploying bioblendstocks for mixing-controlled compression ignition (MCCI) engines for the medium-duty (MD) and heavy-duty (HD) sectors. To be considered, these fuel candidates should possess diesel-like attributes such as high cetane number, high energy density, and cold weather performance but be advantaged with reduced soot formation, low sulfur, low toxicity, and improved operability. The results of this screening are a downselection from thousands of potential fuel candidates to a list of those most promising from a fuel property standpoint.[1] The Co-Optima Consortium builds on and expands concepts developed by the tailor-made fuels from the biomass program at Aachen University, which also predicted engine fuel performance based on fuel properties[2] and identified potential pathways for bioblendstock production.[3]

In addition to the identification of bioblendstock candidates with promising fuel properties, Co-Optima also aims to understand the socioeconomic and environmental implications of wide-scale adoption of bioblendstocks into the fuel market. Technological readiness for producing the bioblendstock from renewable feedstocks, economic viability, and environmental impacts are considered. To that end, in collaboration with fuel property experts within Co-Optima, we identified a down-selected list of those fuels meeting early tier favorable MCCI fuel property criteria to then conduct techno-economic analysis (TEA) and life cycle analysis (LCA) for a potential commercial-scale process. Downselection criteria were based on blendstocks that could utilize existing modeling efforts to accelerate analysis, those blendstocks with data available either from literature or from experimental results from within the Co-Optima initiative, blendstocks with the most favorable properties for MCCI engines and to provide a comprehensive overview, and blendstocks that were diverse in chemistry, production methods, and starting feedstocks. We conducted an in-depth analysis of 23 pathways maintaining identical economic assumptions such as tax rate, cost year, and chemical costs. Two of these pathways produced from waste feedstocks, hydroprocessed esters and fatty acids (HEFAs) produced from yellow grease and renewable diesel via hydrothermal liquefaction (HTL) of wet wastes produced from swine manure were adapted from pathways previously evaluated in detail by Ou et al.[4] We also include for reference two additional pathways meeting MCCI fuel property criteria: farnesane based on a pathway evaluated by Davis et al.[5] and traditional fatty acid methyl ester (FAME) biodiesel based on market analysis. The 25 evaluated pathways fall into three overarching conversion themes. Biochemically-based pathways utilize fermentation at some point in the process, either directly to the final desired bioblendstock or to a chemical intermediate where subsequent catalytic upgrading steps and separations yield the desired fuel. Thermochemical pathways employ heat and pressure to break down biomass feedstocks into either syngas via indirect liquefaction or a biocrude via HTL. Subsequent catalytic steps then yield the final desired fuel. Finally, catalytic/hybrid pathways lumped together pathways that do not necessarily break down feedstock or convert the chemical backbone extensively but may rearrange or modify the starting feedstock. Pathways that utilize fat, oil, and grease (FOG) feedstocks, such as FAME biodiesel, fall into this category. A detailed summary of all conversion pathways is given in the Supporting Information. Evaluated bioblendstocks were chemically diverse in structure and functional groups, including hydrocarbons, alcohols, esters, ethers, and dioxolanes, and also represent both relatively pure compounds and mixtures. Feedstocks were also diverse, including both herbaceous and woody lignocellulosic biomass, algae, fats/oils/greases (FOGs), and wastes such as swine manure, food waste, and yellow grease. This diversity may allow for the identification of trends and may provide insights into novel MCCI bioblendstock production pathways even without in-depth modeling analysis.

This article is part of a series of works aiming to understand the economic, environmental, and scalability considerations of fuels identified within Co-Optima. Previous studies were conducted in the light-duty (LD) sector for boosted spark ignition engines leading to the identification of those most promising with the least barriers to entry.[6,7] Recently, work has been published on the top MCCI bioblendstocks based on fuel property screening and TEA and LCA.[8] Here, we expand upon the analysis efforts, providing a more comprehensive view and additional insights into the cost and environmental drivers for evaluated pathways.

■ METHODS

Selection of candidates for TEA and LCA began with a large number of candidates identified through several different means (literature, computation, experimental work). A tiered screening process established a list of potential blendstocks possessing fuel properties offering performance improvements when used as blends with diesel fuel in MCCI engines. While a detailed explanation of these criteria and methods is described elsewhere,[1,8] fuel candidates offered emissions or operability performance advantages such as a high cetane number, adequate low-temperature operability, and reduced sooting tendency. Furthermore, reductions in energy density compared to conventional diesel fuel (energy density is decreased by the presence of oxygen as well as reduced aromatic content), low toxicity, and compatibility with existing fuels and fuel infrastructure were weighed against the potential performance advantages. Such criteria eliminated, for example, ketones due to issues in material compatibility with fuel distribution and storage systems combined with limited or no emission performance advantage and upgraded pyrolysis oils due to a high aromatic content and low cetane number.

Detailed TEA methods used for these analyses are reported elsewhere;[9] here, we provide a brief overview. After literature review and discussion with subject matter experts, a process for converting

Table 1. Technology Readiness Metrics Classification

Metric	Favorable	Neutral	Unfavorable
Process modeling data source	Demonstration-scale (or larger) data available; this includes detailed process analysis from the literature	Bench-scale data available	Notional, yields, and conversion conditions estimated partly from the 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 specifications	Changes in feedstock specifications minimally influence yield/quality	Changes in feedstock specifications moderately influence yield/quality	Changes in feedstock specifications greatly influence yield/quality
Blending behavior of bioblendstock with current fuels for use in vehicles	Current quality good enough for replacement (i.e., drop-in)	Current quality good enough for blend	Current quality in blend not good or unknown
Bioblendstock underwent testing toward certification	Yes	Limited	None
Bioblendstock will be blendable only in limited levels because of current regulatory limits	No limit	Blendable at high levels	Significant limit (i.e., on aromatics)

feedstock to bioblendstock is developed and material and energy balances are calculated using thermodynamically rigorous process simulation software such as Aspen Plus or CHEMCAD. The resultant material and energy flows are then imported into a Microsoft Excel spreadsheet where equipment and raw material flows are automatically scaled and costed, and all other process economic considerations are accounted for assuming *n*th plant economics. A discounted cash flow rate of return analysis is then conducted, solving for the minimum fuel selling price (MFSP) required to achieve a net present value of zero across the entirety of the biorefinery lifetime, assuming a nominal 10% internal rate of return. To provide a consistent comparative basis for all bioblendstocks evaluated, all MFSPs are normalized to an energy basis based on lower heating value (LHV) compared to conventional gasoline[10] and do not include any credits under the renewable fuel standard program. Finally, a life cycle inventory of material and energy inputs and outputs to the biorefinery is generated for each process to be used for LCA.

We use LCA to estimate greenhouse gas (GHG) emissions, fossil fuel consumption (FFC), and water consumption for all Co-Optima MCCI bioblendstock pathways discussed in this paper. To conduct the LCA, we used the GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies) model developed at Argonne National Laboratory.[10] The LCA system boundary considers the biomass feedstock supply chain, biorefinery operations, transportation, and end use of the MCCI bioblendstocks (Figure S1). The feedstock processing and logistical data were obtained from Idaho National Laboratory design cases 2022 projection.[11,12] The biorefinery operation (fuel conversion and upgrading) inputs were based on the results of material and energy balance used in the TEA. Finally, feedstock production data, upstream processing information for chemicals and energy used during the production process, transportation, and logistics of the final bioblendstock were all leveraged from the GREET model. Because of the variety of pretreatment, conversion technologies, and feedstock type, some of the pathways analyzed in this paper produced different coproducts in addition to the MCCI bioblendstock. Therefore, different methods to allocate the emission and energy burdens between products were selected depending on the type of products. For example, if the coproducts were energy products such as electricity, naphtha, or hydrogen, the emission and energy burden were allocated according to the product's energy value. If the coproduct was a chemical with significant market value such as glycerol, the allocation chosen was market allocation. We also used the displacement method that provides credits assuming, for example, that the sodium sulfate recovered in the wastewater treatment area of the biorefinery will be displacing conventional sodium sulfate production. Details on the coproduct list for each pathway can be found in Table S1.

Metrics Development. The 25 bioblendstocks we evaluated, identified under Co-Optima as having fuel properties amenable to MCCI combustion modes, fall under various research, development, and/or production scale. While some are currently produced commercially (e.g., FAME biodiesel), others to date have only been studied in the lab or even may only be postulated. Despite reports for several of the evaluated MCCI bioblendstocks giving a detailed account of vetted process assumptions and analysis results,[5,13−15] even with the most recent data available through the literature, patents, research ongoing under Co-Optima, or discussion with the academic and industry subject matter experts, there remains unquantifiable uncertainty in mapping process simulation and subsequent economic and environmental analysis to what may eventually be a commercial-scale process. To reflect this uncertainty in our analysis, we chose to qualitatively present results of our screening based on favorability criteria either determined based on cutoffs for otherwise quantitative results or through subjective measures of favorability. We developed a total of 19 metrics, spanning three overarching themes: technology readiness, economic viability, and environmental considerations. Each metric was ranked as either favorable, neutral, or unfavorable based on screening criteria, or unknown if data was unavailable to appropriately bin the metric.

Six technology readiness metrics aim to determine bioblendstock technology readiness level (TRL), process robustness, and consider fuel and regulatory properties of the bioblendstock, rather than its production process. A summary of technology readiness screening criteria is given in Table 1. The process modeling data source serves as a proxy for estimating technology readiness level (TRL). Process simulations developed using data from a demo- or commercial-scale processes are likely to have greater fidelity to a commercial-scale process than analysis using bench-scale or notional data where unforeseen scale-up challenges may exist. Process sensitivity to feedstock type and process robustness to feedstocks of different specifications are important considerations in process deployment. For example, if a process can only use a very specific feedstock produced only in a small area of the country, that may limit the total disruption and limit range. A process that can use almost any feedstock with little variation in fuel yield or quality would be deployable over a larger region. Similarly, a production process more sensitive to changes to feedstock specifications such as ash content or carbohydrate content would be less favorable than a process that can continue to maintain similar yields and process reliability across differences in feedstock lots or composition. While feedstock availability may also be considered in evaluating the total disruption potential of a bioblendstock and pathway favorability, this analysis is focused on biorefineries at the individual level and total feedstock availability was not ranked in this analysis. Finally, within technology readiness, three metrics evaluate fuel properties and regulatory elements. Blending behavior evaluates whether the bioblendstock can be considered a drop-in or near-replacement of current diesel-range fuels. A drop-in fuel could feasibly have wide deployment in the near-term while a bioblendstock that is only suitable for blending in limited fractions could face blend walls. Favorability was also given to bioblendstocks that are currently an approved fuel additive and those that may be blended in high quantities despite regulatory limits such as aromatic content, oxygenate content, or otherwise, regardless of how well it may perform in an engine. The essence of co-optimization is that engines and fuels are developing together. Regulations will need to evolve to accommodate progress away from the status quo. Such changes may affect the favorability of these final two metrics as time progresses. However, we attempted to categorize based on the current understanding as of the writing of this report.

Six economic viability metrics aim to identify cost potential for MCCI bioblendstocks and evaluate additional market considerations. A summary of economic viability metrics is given below and summarized in Table 2. MFSP was determined for two production routes for each bioblendstock pathway, a baseline and a target case. The baseline case evaluates the current technology performance benchmarks assuming a commercial-scale production process using available experimental and literature data for process parameters such as process yield, productivity, conversion extent, separation extents, or others. While there is a possibility for unforeseen difficulties in process scale-up making a true estimation of baseline MFSP with a high degree of certainty challenging, the baseline case provides a comparison point from which to evaluate the improvement potential of a pathway toward achieving a target case. The target case provides an optimistic scenario for a bioblendstock pathway by evaluating the process using best-case assumptions for process conversions, productivity, titers, yields, etc. For example, this could include thermodynamic equilibrium approaches for catalysts or theoretical metabolic yields for biological fermentation. When possible, assumptions for target case process parameters were vetted with subject matter experts for each respective pathway. Similar to the baseline case, target case assumptions are an approximation and may not capture unforeseen scale-up challenges. Thus, given the uncertainty in the estimation of MFSP, especially for pathways with low technology readiness levels, we only report a qualitative assessment of MFSP with favorability based on clusters of the lowest cost, median cost, and highest cost pathways. Table 2 provides a range of MFSPs that could be expected for each cost cluster.

Taking the baseline: target MFSP ratio provides context when evaluating a bioblendstock's technology readiness level or the amount of research and development required to achieve the target case. A high ratio hints that more research will be required versus a low ratio approaching unity; thus, a low ratio is favorable for this metric. This implies that a process already at the commercial scale would have a ratio equal to 1. Coproduct dependency evaluates how reliant the MFSP is on the sale of additional outputs of the biorefinery, such as the sale of excess electricity to the grid or additional fuels and chemicals produced in the biorefinery. While coproducts may help improve process economics and provide a buffer for market volatility in fuel prices, if the process is too heavily reliant on coproducts to achieve a target MFSP and the market for the coproduct itself changes, this could negatively impact fuel production, process profitability, or lead a biorefinery to stop producing a bioblendstock entirely. Thus, the low dependency of coproducts on the MFSP was considered favorable in this analysis. For biochemical pathways, previous reports have shown the potential for a significant reduction in MFSP if lignin streams are valorized to coproducts such as adipic acid.[13] However, such conversion pathways are themselves at an early stage of research, and the inclusion of a lignin conversion train may convolute the economics of a fuel pathway. To provide a conservative estimate of the cost of fuel production, lignin was assumed to be burned for process heat and electricity, rather than upgraded to coproducts. The last two economic viability metrics evaluate the market competition and feedstock cost. If the bioblendstock is produced from a valuable chemical intermediate with uses elsewhere, there may be market competition away from the fuel market. As the commodity fuel market is likely to have a lower profit margin than the chemical market, favorability was given to bioblendstocks that do not have uses elsewhere. Finally, the given feedstock can significantly influence biorefinery economics, and lower-cost feedstocks were considered more favorable than their more expensive counterparts.

Seven metrics were used to assess the environmental impact of producing the MCCI bioblendstocks, as summarized in Table 3. These metrics include the carbon efficiencies and yields of the baselines and target cases, and the reduction of GHG emissions, FFC,

Table 2. Economic Viability Metrics Classification

Metric	Favorable	Neutral	Unfavorable
Bioblendstock production baseline cost	Falls in the cluster of lowest cost pathways (≤\$5/GGE)	Falls in the cluster of moderate cost pathways (\$5/GGE−\$7/GGE)	Falls in the cluster of highest cost pathways (≥\$7/GGE)
Bioblendstock production target cost	Falls in the cluster of lowest cost pathways (≤\$4/GGE)	Falls in the cluster of moderate cost pathways (\$4/GGE−\$5.5/GGE)	Falls in the 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 (i.e., chemicals, electricity, other bioblendstocks/fuels produced as coproduct to Co-Optima fuel)	<30%	30−50%	>50%
Competition for the biomass-derived bioblendstock or its predecessor	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 US\$2016)	Cost likely to be at or below target of \$84/dry ton delivered at the reactor throat	Cost likely to be between \$84/dry ton and \$120/dry ton delivered at the reactor throat	Cost likely to exceed \$120/dry ton delivered at the reactor throat

Table 3. Environmental Metrics Classification

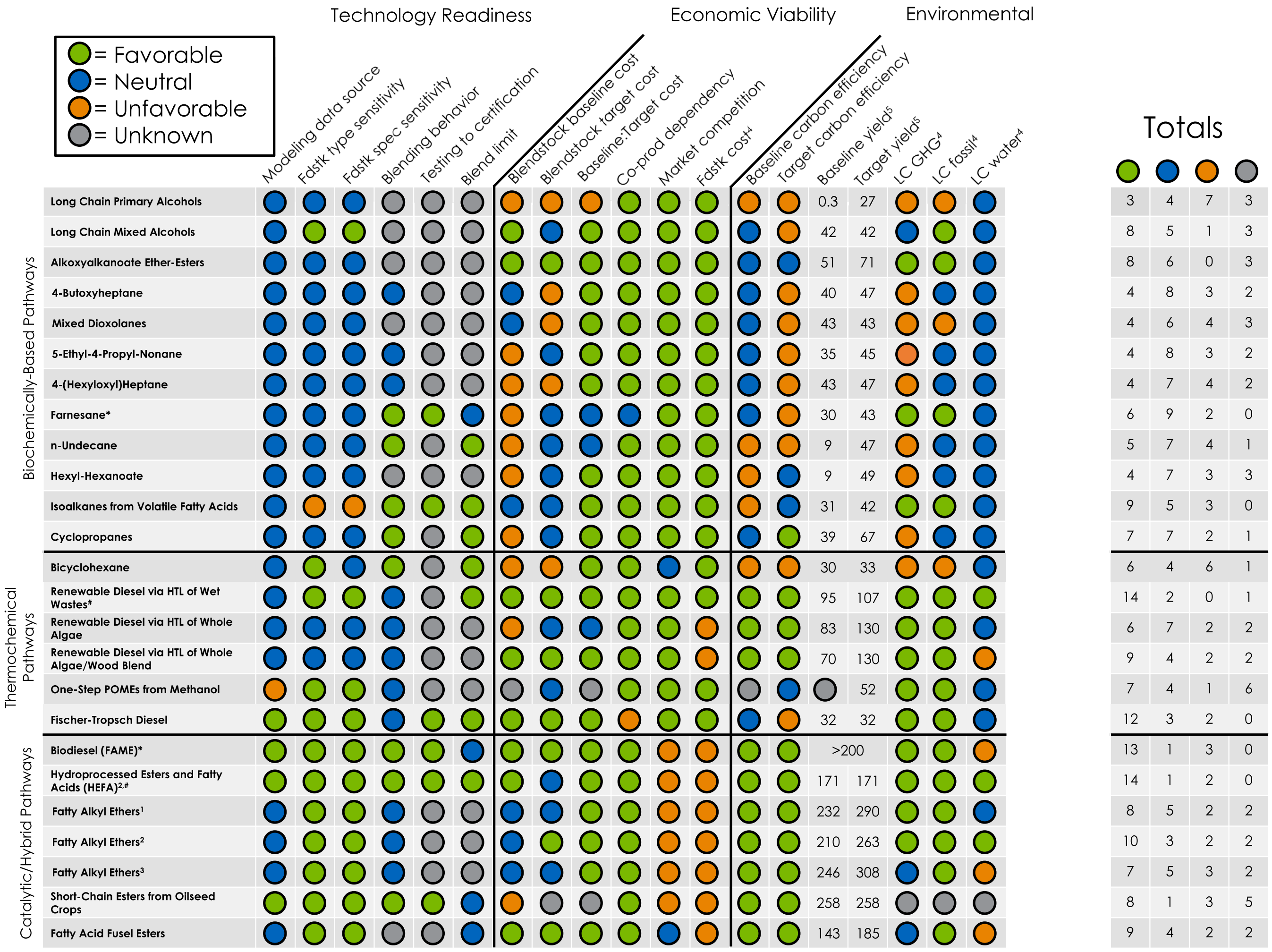
Metric	Favorable	Neutral	Unfavorable
Baseline: Conversion efficiency of input carbon (fossil- and biomass-derived) to Co-Optima bioblendstock	>30%	10−30%	<10%
Target: Conversion efficiency of input carbon (fossil- and biomass-derived) to Co-Optima bioblendstock	>40%	30−40%	<30%
Baseline: Co-Optima bioblendstock yield (GGE/dry ton)[a]			
Target: Co-Optima bioblendstock yield (GGE/dry ton)[a]			
Target: Life-cycle GHG emission reduction compared to conventional diesel fuel	≥60%	50−60%	<50%
Target: Life-cycle fossil energy consumption reduction compared to conventional diesel fuel	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	≤3 gal/GGE	3 gal/GGE−55 gal/GGE	>55 gal/GGE

[a] Baseline and target bioblendstock yields were included for reference but were not categorized due to differences in feedstock and conversion technologies.

and water consumption relative to petroleum diesel. Carbon efficiency is evaluated gate-to-gate across the conversion process and assesses the amount of carbon from primarily input feedstock and other carbon-containing inputs that end up in the final bioblendstock. Although baseline and target yields were included as a reference, they were not classified within the three bins because the wide variation in feedstocks and conversion technologies may not offer a direct comparative basis. For example, FOG feedstocks are relatively energy-dense and require minimal processing compared to whole lignocellulosic biomass feedstocks and will intrinsically have higher yields that are not inherently reflective of conversion technology. GHG emission reduction, FFC, and water consumption were all evaluated for the target cases only using the GREET model[10] and compared relative to conventional petroleum-derived fuel (conventional diesel) also reported in the GREET model. We evaluated the life cycle GHG emissions for each MCCI bioblendstock pathway, which include not only the tailpipe emissions but also the upstream emissions resulting from biomass cultivation, feedstock transportation, biofuel production, and biofuel distribution. Biogenic CO_2 emissions are considered carbon neutral and not accounted for in the calculation of life cycle (LC) GHG emissions. Emissions of other GHGs (i.e., CH_4 and N_2O) are also tracked in addition to CO_2 and included in the reported life cycle GHG emissions. GHG emissions were calculated based on the 100-year global warming potentials for CO_2, CH_4, and N_2O emissions, which are 1, 30, and 265 kg CO_2-eq./kg emissions, respectively.[10] Therefore, the life cycle GHG emissions are reported in terms of grams of CO_2 equivalent (CO_2e) per MJ of MCCI bioblendstocks. GHG emission reduction was favorable if bioblendstocks could achieve advanced biofuel emission reduction targets of at least 60%. Thresholds for neutral and favorable water consumption were based on corn ethanol and conventional diesel requirements, respectively, on the basis of fuel energy content. It should be noted that biorefinery water consumption is not optimized in some aspects of the high-level TEAs that were developed; therefore, efforts to improve the water economy could lower water consumption.

Criteria air pollutant emissions are outside the scope of this study. While it is worth noting that MCCI bioblendstocks may bring other environmental benefits such as reduced tailpipe emissions of criteria pollutants such as particulate matter (PM) and nitrogen oxides (NO_x), these metrics are highly dependent on engine/combustion characteristics and are further altered by emission control systems and are therefore challenging to generalize in a study such as this one. The fuels included in this analysis were screened for sulfur content and therefore are expected to have low sulfur oxide emissions and acidification potential. Given the already low sulfur content in diesel fuel and interactions with the emission control system, it is also challenging to generalize sulfur oxide emissions, but they would be expected to be low for the bioblendstocks presented here.[16]

These metrics and others such as eutrophication would be relevant to consider in the next steps as efforts may be made to commercialize MCCI bioblendstock production from selected feedstocks. Eutrophication and induced land use change are important considerations for agricultural feedstocks. Many of the pathways here use waste feedstocks such as forest residues, wastewater sludge, and food waste, which would not compete with other agricultural land uses and do not require fertilization. Similarly, corn stover is a byproduct of corn grain production and studies have shown that it can be harvested at levels around 30% without causing loss of soil organic carbon. Here, we assume that algae could be grown on marginal land unsuitable for other agricultural production; however, microalgae production does require some nutrient inputs. Pathways relying on oil are generally modeled here based on soybean oil as there is already an abundant supply. LCA metrics would improve for similar pathways relying on waste vegetable oil, but supplies of these waste resources are limited. Soybean oil is an agricultural commodity that has received much attention. Here, we incorporate induced land use change estimates for soybean based on the GREET/carbon calculator for land use and land management change from biofuel production[17] estimates as well as the supply chain effects of fertilizer production. Cuphea oil is a novel



🟢 = 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[4]	Baseline carbon efficiency	Target carbon efficiency	Baseline yield[5]	Target yield[5]	LC GHG[4]	LC fossil[4]	LC water[4]	🟢	🔵	🟠	⚪
Biochemically-Based Pathways	Long Chain Primary Alcohols	🔵	🔵	🔵	⚪	⚪	⚪	🟠	🟠	🟠	🟢	🟢	🟢	🟠	🟠	0.3	27	🟠	🟠	🔵	3	4	7	3
	Long Chain Mixed Alcohols	🔵	🟢	🟢	⚪	⚪	⚪	🟢	🔵	🟢	🟢	🟢	🟢	🔵	🟠	42	42	🔵	🟢	🔵	8	5	1	3
	Alkoxyalkanoate Ether-Esters	🔵	🔵	🔵	⚪	⚪	⚪	🟢	🟢	🟢	🟢	🟢	🟢	🔵	🔵	51	71	🟢	🟢	🔵	8	6	0	3
	4-Butoxyheptane	🔵	🔵	🔵	🔵	⚪	⚪	🔵	🟠	🟢	🟢	🟢	🟢	🔵	🟠	40	47	🟠	🔵	🔵	4	8	3	2
	Mixed Dioxolanes	🔵	🔵	🔵	⚪	⚪	⚪	🔵	🟠	🟢	🟢	🟢	🟢	🔵	🟠	43	43	🟠	🟠	🔵	4	6	4	3
	5-Ethyl-4-Propyl-Nonane	🔵	🔵	🔵	🔵	⚪	⚪	🟠	🔵	🟢	🟢	🟢	🟢	🔵	🟠	35	45	🟠	🔵	🔵	4	8	3	2
	4-(Hexyloxyl)Heptane	🔵	🔵	🔵	🔵	⚪	⚪	🟠	🟠	🟢	🟢	🟢	🟢	🔵	🟠	43	47	🟠	🔵	🔵	4	7	4	2
	Farnesane*	🔵	🔵	🔵	🟢	🟢	🔵	🟠	🔵	🔵	🔵	🟢	🟢	🔵	🟠	30	43	🟢	🟢	🔵	6	9	2	0
	n-Undecane	🔵	🔵	🔵	🟢	⚪	🟢	🟠	🔵	🔵	🟢	🟢	🟢	🟠	🟠	9	47	🟠	🔵	🔵	5	7	4	1
	Hexyl-Hexanoate	🔵	🔵	🔵	⚪	⚪	⚪	🟠	🔵	🟢	🟢	🟢	🟢	🟠	🔵	9	49	🟠	🔵	🔵	4	7	3	3
	Isoalkanes from Volatile Fatty Acids	🔵	🟠	🟠	🟢	🟢	🟢	🔵	🔵	🟢	🟢	🟢	🟢	🟠	🔵	31	42	🟢	🟢	🔵	9	5	3	0
	Cyclopropanes	🔵	🔵	🔵	🟢	⚪	🟢	🟠	🔵	🟢	🟢	🟢	🟢	🔵	🟢	39	67	🟠	🔵	🔵	7	7	2	1
Thermochemical Pathways	Bicyclohexane	🔵	🟢	🔵	🟢	⚪	🟢	🟠	🟠	🟢	🟢	🔵	🟢	🟠	🟠	30	33	🟠	🟠	🔵	6	4	6	1
	Renewable Diesel via HTL of Wet Wastes#	🔵	🟢	🟢	🔵	⚪	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	95	107	🟢	🟢	🟢	14	2	0	1
	Renewable Diesel via HTL of Whole Algae	🔵	🔵	🔵	🔵	⚪	⚪	🟠	🔵	🔵	🟢	🟢	🟠	🟢	🟢	83	130	🟢	🟢	🔵	6	7	2	2
	Renewable Diesel via HTL of Whole Algae/Wood Blend	🔵	🔵	🔵	🔵	⚪	⚪	🟢	🟢	🟢	🟢	🟢	🟠	🟢	🟢	70	130	🟢	🟢	🟠	9	4	2	2
	One-Step POMEs from Methanol	🟠	🟢	🟢	🔵	⚪	⚪	⚪	🔵	⚪	🟢	🟢	🟢	⚪	🔵	⚪	52	🟢	🟢	🔵	7	4	1	6
	Fischer-Tropsch Diesel	🟢	🟢	🟢	🔵	🟢	🟢	🟢	🟢	🟢	🟠	🟢	🟢	🔵	🟠	32	32	🟢	🟢	🔵	12	3	2	0
Catalytic/Hybrid Pathways	Biodiesel (FAME)*	🟢	🟢	🟢	🟢	🟢	🔵	🟢	🟢	🟢	🟢	🟠	🟠	🟢	🟢	>200		🟢	🟢	🟠	13	1	3	0
	Hydroprocessed Esters and Fatty Acids (HEFA)[2,#]	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🔵	🟢	🟢	🟠	🟠	🟢	🟢	171	171	🟢	🟢	🟢	14	1	2	0
	Fatty Alkyl Ethers[1]	🔵	🟢	🟢	🔵	⚪	⚪	🔵	🔵	🟢	🟢	🟠	🟠	🟢	🟢	232	290	🟢	🟢	🔵	8	5	2	2
	Fatty Alkyl Ethers[2]	🔵	🟢	🟢	🔵	⚪	⚪	🔵	🟢	🟢	🟢	🟠	🟠	🟢	🟢	210	263	🟢	🟢	🟢	10	3	2	2
	Fatty Alkyl Ethers[3]	🔵	🟢	🟢	🔵	⚪	⚪	🔵	🔵	🟢	🟢	🟠	🟠	🟢	🟢	246	308	🔵	🟢	🟠	7	5	3	2
	Short-Chain Esters from Oilseed Crops	🟢	🟢	🟢	🟢	🟢	🔵	🟠	⚪	⚪	🟢	🟠	🟠	🟢	🟢	258	258	⚪	⚪	⚪	8	1	3	5
	Fatty Acid Fusel Esters	🔵	🟢	🟢	⚪	⚪	🔵	🟢	🟢	🟢	🟢	🔵	🟠	🟢	🟢	143	185	🔵	🟢	🟠	9	4	2	2

1: Feedstock is 60:40 mix of soybean oil and yellow grease
2: Feedstock is 100% yellow grease
3: Feedstock is 100% soybean oil
4: Future target case
5: GGE/dry US ton

Figure 1. Summary of screening results for the evaluated MCCI bioblendstock pathways. Results are categorized and compared based on favorability for each metric. Green, blue, and orange circles represent favorable, neutral, and unfavorable categorization, respectively, as defined in Tables 1−3. Routes produced biochemically do not include the valorization of lignin to coproducts. *, pathways based on previous analysis or market research, which may have economic assumptions that differ from other pathways evaluated; #, adapted from analysis by Ou et al.;[4] GGE, gasoline gallon equivalent; HTL, hydrothermal liquefaction; LC, lifecycle; and POME, polyoxymethylene dimethyl ether.

feedstock that could cause induced land use change; however, as it is not yet produced at a large scale, little data was available for its production. Further exploration of the eutrophication potential and induced land use change of specific feedstocks should be completed prior to commercialization of certain presented here.

■ RESULTS AND DISCUSSION

Figure 1 compiles the results for the technology readiness, economic viability, and environmental screening. The columns correspond to the criteria described in Tables 1−3, while each row provides the results for the different MCCI candidates. Pathways were lumped into their overarching conversion pathways, as described in the Methods section (more details for each pathway may be found in the Supporting Information).

Due to the early stage of research for evaluated pathways, technology readiness metrics for Co-Optima MCCI bioblendstocks were predominantly either neutral or unknown, with notable exceptions given to catalytic/hybrid pathways where favorable metrics were most common. For this reason, the process modeling data source was predominantly based on bench-scale data and thus neutral. Only three pathways, Fischer−Tropsch diesel, FAME, and HEFA, are already produced at the demo scale or larger and considered favorable. Short esters from oilseed crops, while not itself produced commercially, follow an identical conversion route to FAME and are thus also considered favorable, although feedstock agronomics for cuphea oil is still uncertain. Only one-step POMEs from methanol were based on theoretical thermodynamic equilibrium via an oxidative synthesis route, although To et al. have previously demonstrated one-step reductive synthesis routes from methanol.[18] Given the low calculated thermodynamic equilibria limit for the reductive synthesis route, the oxidative synthesis route was evaluated instead. Feedstock type and specification sensitivity were also predominantly favorable or neutral depending on the overarching conversion route. FOG feedstocks from catalytic/hybrid pathways were favorable in this regard as they can typically be readily interchanged between various oil-producing crops such as canola, soybean, or corn oils, animal sources such as tallow, or waste feedstocks such as yellow grease provided sufficient preprocessing or upstream cleanup is performed. Similarly, hydrothermal or indirect liquefaction can use several types of feedstocks to break down into biocrude or syngas, although there is some sensitivity to the lipid content where algae are used as a feedstock. Biochemically-based pathways were slightly more sensitive as lignocellulose-derived sugars are the primary biomass components to be converted to fuels. If the feedstock is more recalcitrant or has a lower carbohydrate content, this could negatively impact fuel yields, and so these pathways were predominantly neutral. Isoalkanes from volatile fatty acids (VFAs), where food wastes are used instead of lignocellulose, were the most sensitive to changes in lipids, carbohydrates, and protein contents and the only unfavorable pathway for these metrics.

The low TRL for MCCI bioblendstock pathways also manifests itself through limited knowledge of blending behavior and regulatory aspects for the fuel. Unlike many potentially bio-derived gasoline-range fuels and additives such as methanol, ethanol, propanols, and butanols, which are already approved fuel additives, diesel-range MCCI bioblendstocks typically lacked this information, and unknown categorization was frequently observed for many of these metrics. Notable exceptions were FAME biodiesel, HEFA, and Fisher−Tropsch diesel, which are already approved fuels and additives, blendable in high amounts in certain engines, and have minimal regulatory barriers for blending—achieving mostly favorable metrics in this regard. Fischer−Tropsch diesel achieved a neutral rating for blend behavior; however, the initial modeling basis by Tan et al. used in this analysis did not include isomerization of the diesel-range fuel produced in the process leading to concerns over cloud point if this blendstock was highly pure.[15,19] Adding isomerization to this process could lead to a favorable metric in this category although impacts on fuel yields, economics, and environmental considerations would need to be accounted for. The remaining bioblendstocks were largely considered favorable in blend behavior and regulatory limits if they were branched hydrocarbons or hydrocarbon mixtures and neutral if the blendstock contained oxygen, had some fuel property testing performed within Co-Optima or externally, or if internal discussions with fuel property experts led to minimal concerns over blend behavior. While at the time of this report, the state of testing to certification was primarily unknown, this should be revisited later as more information becomes available.

Overall, a majority of economic viability metrics fell in the favorable bin. Baseline and target costs were mixed across favorability due to categorization being based on cost clusters. In total, eight pathways achieved favorable baseline costs (< \$5/GGE) and seven pathways achieved favorable target costs (<\$4/GGE), with notable trends emerging depending on the overall conversion pathway. Costs tended to be highest for biochemically-based conversion routes and lower for thermochemical and catalytic/hybrid routes. For example, 7 of the 12 evaluated biochemical pathways in the baseline case and 4 in the target case had unfavorable MFSPs when focused on carbohydrate valorization alone. This contrasts with thermochemical and catalytic/hybrid routes where only three MFSPs from baseline cases (bicyclohexane, renewable diesel via HTL of whole algae, and short-chained esters from oilseed crops) and one MFSP from target cases (bicyclohexane) reached unfavorable categorization. Alkoxyalkanoate ether esters were the only biochemically-based pathway able to achieve favorable categorization in the target case due in part to higher metabolic yields for the fermentation pathway, helping to reduce capital and operational costs once normalized to an energy yield basis. It was also among the lowest cost pathways in the target case across all conversion routes along with renewable diesel via HTL of wet wastes, fatty acid fusel esters, and Fischer−Tropsch diesel falling near or below approximately \$3.5/GGE. The baseline-to-target cost ratio was favorable for most pathways, indicating lower levels of research and development required to achieve the target case.

Two routes, one-step POMEs from methanol and short-chain esters from oilseed crops, did not have a baseline or target cost, respectively, due to lack of information. POMEs, as described above in the Metrics Development section, did not have baseline data available for the oxidative synthesis route, and thus it is unknown where a baseline cost may lie. However, target case assumptions with a 75% approach to theoretical equilibrium led to an MFSP between \$4 and \$4.5/GGE. If a greater approach to equilibrium is achieved or if residence time could be reduced, target costs could potentially fall below \$4/GGE and be considered favorable. Short-chain esters from oilseed crops follow a similar conversion route to conventional biodiesel using more typical FOG feedstocks such as soybean oil. In this respect, the conversion route could be considered commercial. However, the use of a more novel feedstock, cuphea oil, leads to uncertainty in agronomics and target feedstock costs as opposed to processing costs and strategy at the biorefinery as is more typical with other pathways evaluated and information on feedstock cost is limited as cuphea is not yet a commercial crop. A report by Gesch et al. estimated that to cover production costs, a cuphea price of \$1830/metric ton of harvested seed would be required.[20] While other production, transportation, and processing costs are likely to bring this cost higher once delivered to the biorefinery, using this as a baseline feedstock cost estimate led to an MFSP of approximately \$16/GGE. The future cultivation and commercial potential of cuphea oil remain uncertain, so MFSP was not ranked for the target case. However, a neutral rating target cost of \$5.5/GGE could feasibly be achieved if cuphea oil could be produced and delivered to the biorefinery at a feedstock price of approximately \$1200/ton or less.

While the MFSP takes into account all costs within the boundary of the biorefinery and expresses them as a \$/GGE price, a single categorization may not provide all necessary economic insights into challenges or advantages of any particular bioblendstock. The MFSP may also be broken down into contributions of each major processing area of the biorefinery, which can provide a more holistic view and identify major cost contributors to focus on in accelerating research and development. For each pathway evaluated under Co-Optima, we determined contributions of feedstock, conversion, upgrading and recovery, utilities/ancillary units, and coproduct credits to the target case MFSP, shown in Figure 2. The feedstock costs include all applicable upstream feedstock logistics, including growth, harvest, preprocessing, and transportation to the biorefinery. Conversion costs include breaking down biomass into more usable forms such as sugars, syngas, or biocrude. In biochemically-based pathways, this also includes fermentation into the final blendstock or intermediate. Upgrading and recovery account for downstream operations after primary feedstock conversion, for example, hydrotreating, distillation, ketonization, or final bioblendstock cleanup prior to sale. Utilities/ancillary units are any biorefinery areas not

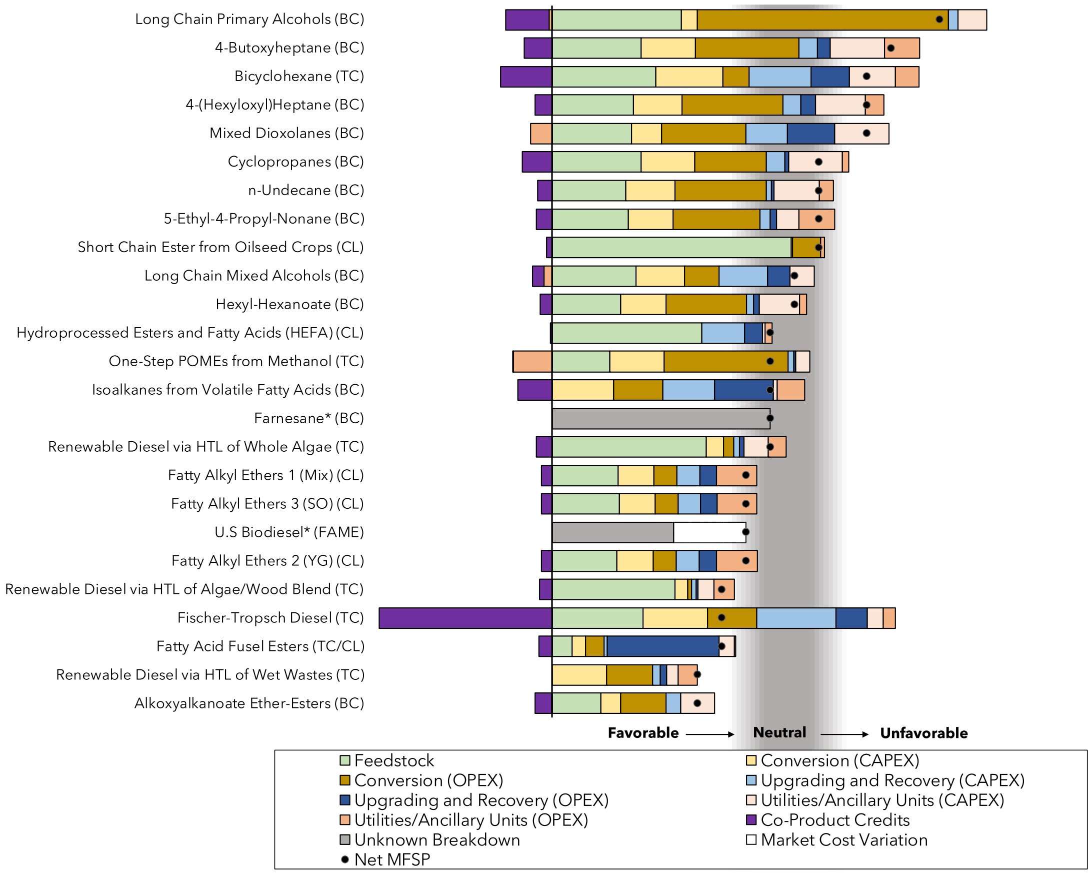


Figure 2. Cost breakdown of target case MFSP, normalized on a \$/GGE basis for evaluated bioblendstocks. Costs were broken down by the overall biorefinery process area and divided into capital (CAPEX) and operational (OPEX) costs. The gray vertical bar in the plot indicates a neutral net MFSP categorization, while those to the left and right indicate favorable and unfavorable MFSP categorizations, respectively. *Farnesane and U.S. biodiesel, taken from earlier reports and/or market research, were not broken down but included for reference based on MFSP reported. Short-chain esters from oilseed crops are plotted for reference with an assumed feedstock cost required to achieve a neutral categorization of ~\$5.5/GGE or less (approximately \$1200/dry U.S. ton). BC, biochemically-based pathways; TC, thermochemical pathways; and CL, catalytic/hybrid pathways.

directly involved in bioblendstock production or purification but are necessary for most large-scale processes such as wastewater treatment, heat and power generation, and utilities. Finally, coproduct credits include any coproduced fuel, chemical, electricity, or other recovered costs that could offset the production costs of the bioblendstock. Conversion, upgrading and recovery, and utilities/ancillary units were also broken down into the contribution of capital costs, such as process equipment and depreciation, and operational costs, such as raw materials. While the intention of our screening analysis is to provide a higher-level overview of process feasibility, approximate production costs, and comparative assessment, we do not report MFSP here, and no cost axis is included in the figure. Rather, the pathways are plotted compared to one another, sorted by the overall approximate MFSP.

For all pathways except for those produced from wastes such as isoalkanes from volatile fatty acids and renewable diesel via HTL of wet wastes, feedstock contributed significantly to MFSP. This was particularly apparent in pathways with more expensive feedstocks such as algae or FOG where in the case of HTL of whole algae, feedstock cost made up over half of net MFSP. This also echoes the results of the favorability screening, where all pathways that use these feedstocks fell into the unfavorable category of feedstock cost as opposed to lignocellulosic feedstocks, which were all favorable. However, the ease of processing and energy density of FOG and algae helped offset this expense. Despite feedstock costs of upwards of \$600/dry ton, these pathways still maintained favorable or neutral target costs. In addition to cost, market competition for FOG feedstocks is also much higher than lignocellulosic biomass or wastes. FOG finds uses in food, cosmetics, soap production, and even existing biodiesel fuel markets. Bicyclohexane was rated as neutral, as the aromatic intermediate used in its production finds uses industrially. MCCI bioblendstocks themselves are not expected to have many established uses outside of the fuel markets.

Potential exists to reduce feedstock costs through the use of waste feedstocks. Isoalkanes from volatile fatty acids follow a similar recovery/upgrading strategy as 5-ethyl-4-propyl-nonane where short-chain carboxylic acids are upgraded to the target blendstock via ketonization, condensation, and hydrodeoxygenation. These intermediate fatty acids are derived from the anaerobic digestion of food waste rather than fermentation of lignocellulose-derived sugars, eliminating feedstock costs typically associated with lignocellulosic biomass. However, the availability of food waste is much more limited than corn stover and could reduce the total national production potential. A similar trend in feedstock trade-offs can be observed for HTL pathways. Changing from an algae-only pathway to an algae/wood or wet-waste pathway reduces MFSP through different mechanisms. For example, blending with wood reduces net feedstock costs compared with an algae-only approach but maintains advantages of the high lipid content of algae, which keeps conversion costs relatively low. Conversely, the wet-waste pathway has a near-zero feedstock cost but the highest conversion costs among the three HTL pathways. While there remain advantages in utilizing waste feedstocks, these trade-offs should be considered.

Along with feedstock costs, conversion costs, specifically OPEX, were highest for the evaluated biochemically-based pathways and one-step POMEs from methanol, making up the largest proportion of MFSP for these pathways. These were primarily due to sodium hydroxide used in biomass pretreatment and glucose used in enzyme production, assumed here to be integrated on-site in keeping with the published reference cases.[13] For example, in the 5-ethyl-4-propyl-nonane pathway, sodium hydroxide and glucose add \$0.74/GGE and \$0.26/GGE, respectively, to MFSP. Reducing sodium hydroxide, either overall or through the use of less expensive bases such as sodium carbonate, and reducing glucose use through reduced enzyme loadings could bring down both conversion costs and MFSP for these pathways.[21] One-step POMEs from methanol also had high conversion OPEX, but these costs were due to large amounts of catalyst that would be required to achieve the reaction extents at the residence time specified in the POME synthesis reactor.

Lastly, within economic viability metrics and the cost breakdown was, with the exception of Fischer−Tropsch diesel, the relatively small contribution of coproducts to the overall MFSP. These were primarily due to the export of excess produced electricity, sodium sulfate salts recovered from wastewater treatment, or other minor side products produced in fermentation or catalytic steps. Fischer−Tropsch diesel has the largest proportion of coproduct credits and was the only unfavorable pathway for this metric due to coproduced naphtha-range fractions and wax. While we only consider the diesel-range fuels amenable for MCCI combustion engines for this analysis, if the energy content of the entirety of the Fischer−Tropsch fuel is considered, then coproduct dependency for this pathway would be greatly diminished. Importantly, lignin valorization was not included for biochemically-based pathways, but rather lignin was routed to process boilers for the generation of heat and electricity, which could have significant implications for process economics for these pathways. For example, the pathway for producing 5-ethyl-4-propyl-nonane was previously evaluated by Davis et al. with the inclusion of a lignin conversion train yielding an adipic acid coproduct.[13] This showed the potential for significant coproduct offsets reducing MFSP to below \$2.5/GGE. While the current state of technology indicates a net increase in MFSP with lignin valorization,[21] if these design targets could be met, given identical biomass deconstruction strategies for biochemically-based pathways using lignocellulosic feedstocks, the same coproduct offsets could be applied to all of these pathways, reducing MFSP and increasing favorability.

Finally, environmental impact metrics were approximately equally distributed across favorability. Carbon efficiency, which assesses the amount of carbon converted from feedstock to product, was favorable for most of the thermochemical pathways, except for long-chain mixed alcohols and Fischer−Tropsch diesel, and all catalytic/hybrid pathways. Fischer−Tropsch carbon efficiency only considered the diesel-range fraction, but carbon efficiency would increase markedly if the naphtha and wax coproducts were included. The highest carbon efficiencies were obtained by short-chain esters from oilseed crops (>91%) and fatty alkyl ether pathways (>75%). Carbon efficiencies of renewable diesel via HTL of wet wastes were also favorable, with values greater than 49%. Thermochemical and catalytic/hybrid pathways resulted in higher yields than biochemical pathways, especially the catalytic/hybrid pathways, due to a higher energy density in the yellow grease feedstocks. Twelve bioblendstock pathways show a significant reduction in GHG emissions, and 13 show favorable fossil energy consumption reduction compared to conventional diesel fuel. Most of the unfavorable GHG emission reduction fell in the biochemical pathways due to the significant amount of sodium hydroxide used that is required mostly during feedstock pretreatment; however, biochemical alkoxyalkanoate ether-esters, farnesane, and isoalkanes from volatile fatty acids (VFAs) were able to achieve more than 60% GHG emission reduction. Water consumption was favorable for only three pathways. Pathways using soybean oil feedstocks were more water-intensive than waste or lignocellulosic pathways because of the significant water demand involved in the soybean production (Figure S2).

Figure 3 presents the contributors to the life cycle GHG emissions in terms of gCO_2-eq/MJ for all pathways considered in this study. It should be noted that CO_2 from fuel combustion is omitted from the figure because it originates from biogenic carbon, which was taken up or would have been emitted from the biomass and waste feedstocks used for fuel production. Feedstock production, sodium hydroxide (NaOH), and chemicals are the biggest drivers of the GHG emissions and the highest for biochemically-based pathways due to significant contributions from both sodium hydroxide used in pretreatment and chemicals used during the enzyme production and fermentation processes. Recent analysis has indicated significant GHG emission reduction by reducing sodium hydroxide uses in pretreatment using sodium carbonate, a less GHG-intensive alkali material, in the biomass deacetylation (alkali extraction) pretreatment step. However, this strategy is not considered in this analysis.[21,22] For thermochemical and catalytic/hybrid pathways, feedstocks or the energy input were key GHG drivers. However, several pathways, regardless of the conversion technology used, were energy-independent due in part to either the combustion of lignin that supplies to the biorefinery energy demand or energy provided by the input biomass feedstock.

As previously mentioned, this analysis included a variety of renewable feedstocks from traditional biomass used in biofuel production such as corn stover, forest residue, soybean oil, yellow grease, and algae to less traditional feedstocks such as cuphea oil, wet wastes, and food wastes. Carbon intensity for each of these feedstocks is shown in Figure S3. Different feedstocks can be used to produce the same bioblendstocks. For instance, the HTL process can utilize several types of feedstocks and due to the use of water as a solvent, it is particularly suitable for processing wet feeds such as algae or wet wastes.[14,22−24] All of the HTL pathways evaluated here showed GHG emission reduction greater than 60% compared to conventional diesel. We also evaluated multiple MCCI bioblendstocks produced through carboxylic acids, volatile fatty acid intermediates produced via fermentation such as 5-ethyl-4-propyl-nonane, 4-butoxyheptane, *n*-undecane, 4-(hexyloxyl)heptane, hexyl-hexanoate, and mixed isoalkanes from VFAs. Biochemically-based pathways using corn stover feedstocks were unable to achieve greater than 60% GHG

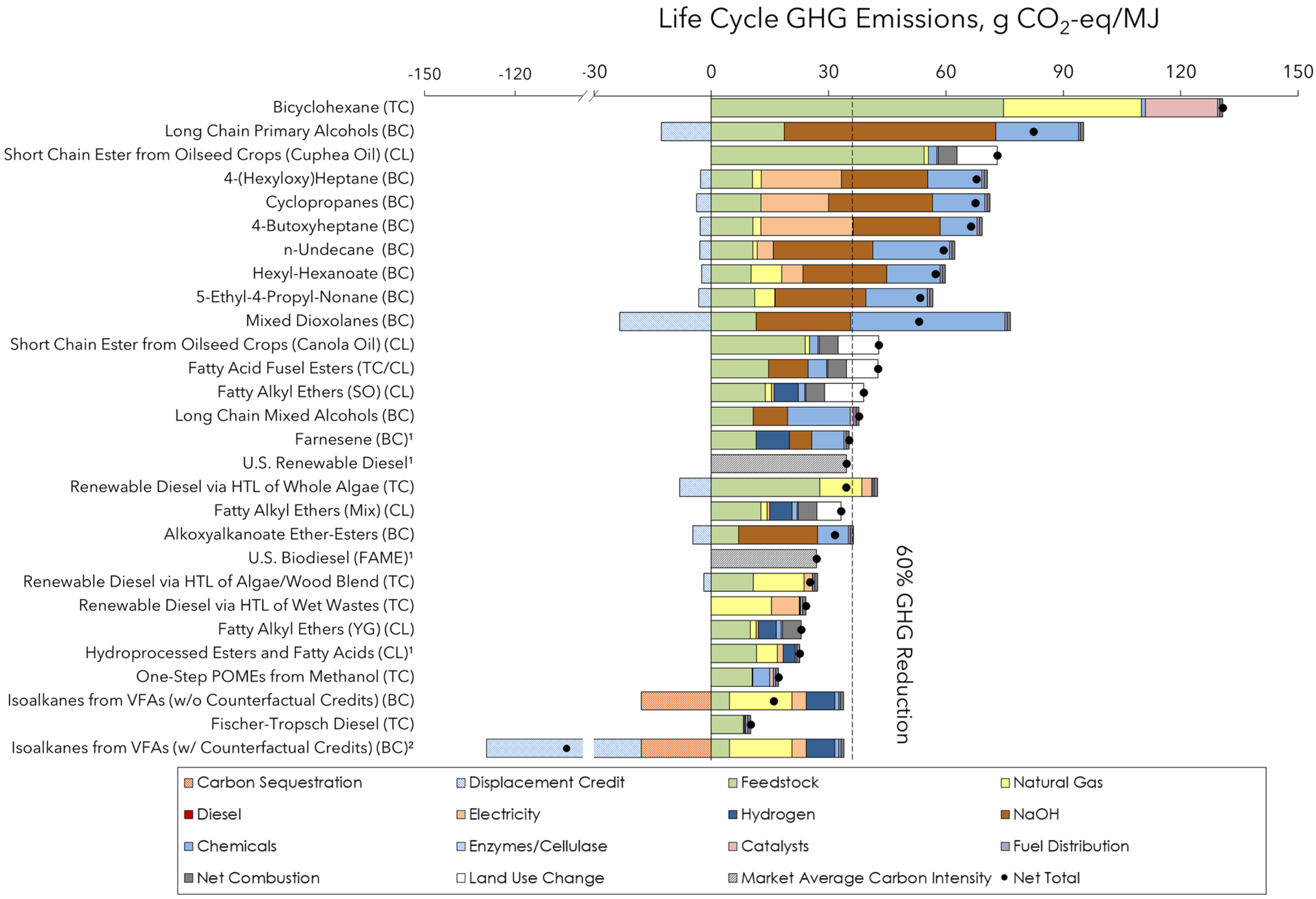


Figure 3. Life cycle greenhouse gas emission breakdown for MCCI bioblendstocks. The vertical dashed line corresponds to a 60% GHG emission reduction from conventional diesel. 1GHG emissions of these pathways are from either an earlier study or the average of market fuels such as the U.S renewable diesel and the U.S. biodiesel market values as a reference case. 2The negative GHG emissions from the "isoalkanes from volatile fatty acids" pathway is due to the credits of avoided emissions from landfill of the food waste feedstock. BC, biochemically-based pathways; TC, thermochemical pathways; and CL, catalytic/hybrid pathways.

emission reduction due to GHG-intensive biomass deconstruction process (deacetylation and mechanical-refining). In contrast, when food waste was used as a feedstock to produce the isoalkanes VFAs, GHG emissions dropped sharply. This bioblendstock reports favorable GHG emissions under the two LCA approaches considered to account for different business-as-usual management of food waste. The first approach (w/ counterfactual credits) gives credit for the avoided emissions from the food waste landfills. This approach is appropriate when the food waste is diverted from landfill for producing MCCI bioblendstocks. This study uses the same assumptions as adopted by Lee et al. to estimate the GHG emissions from food waste landfilling,[25] which amounts to 241 kg CO_2e/wet ton food waste, and translates to a counterfactual credit of 119 g CO_2e/MJ of MCCI bioblendstocks produced from food waste. Large credits for avoided emissions associated with food waste and manure feedstocks are commonly reported by LCA studies, such as those used to certify pathways under California's Low Carbon Fuel Standard.[26] The second approach (w/o counterfactual credits) does not consider such credits. This approach can be applied when the incumbent management practice of food waste is not landfill disposal. Instead, food waste used for MCCI bioblendstock production is diverted from other usages such as feeding animals. Both approaches include the environmental burdens associated with food waste collection and transportation. The carbon in the food waste is considered biogenic in both approaches. These approaches give different LCA results ranging from negative GHG emissions of −103 gCO_2e/MJ with the first approach to 16 gCO_2e/MJ with the second approach, compared to those of petroleum diesel (91 gCO_2e/MJ). We applied the carbon sequestration credits in both approaches due to the solid waste stream produced as a byproduct of this process. The solid residue stream remaining after the arrested anaerobic digestion process contains 46% of carbon and is disposed of by landfilling. It is assumed that the solid residue stream has similar carbon stability to regular anaerobic digestate because it is generated from the arrested anaerobic digestion process. Therefore, 20% of carbon in the solid waste is eventually sequestered. In addition, a small amount of CH_4 (0.05 g CH_4/kg C landfilled) is emitted during landfilling of the solid waste, which are accounted for in both approaches.[10,27] The rest of the carbon within the solid residue stream is emitted as CO_2.

Among other pathways that achieved significant GHG emission reduction (greater than 60%) are the Fischer−Tropsch Diesel, one-step POMEs from methanol, and HEFA. Fischer−Tropsch diesel, already a commercial process and approved as a fuel additive capable of using less costly and more abundant lignocellulosic feedstocks,[19] could achieve about 89% GHG emission reduction compared to petroleum diesel. Feedstock production (forest residue) and chemicals used during conversion were the major drivers of the GHG emissions from the POME pathway; however, this pathway could achieve about 81% of GHG emission reduction. HEFA could achieve nearly 75%. Hydrogen and energy consumption in hydroprocessing are the main contributors to GHG emissions.[4]

Life cycle GHG emission reduction for fatty alkyl ether pathways ranges from 57% (soybean-based) to 75% (yellow grease-based). The major difference between these pathways is the emission burdens allocated to the feedstock upstream production. Soybean oil production is more energy- and resource-intensive than yellow grease. For yellow grease, minimal impacts are assigned as it is a waste from restaurant operations. However, the emissions and energy consumption of yellow grease collection and transportation within a 50 mile range were included in the calculation. For pathways using soybean oil, canola oil, and cuphea oil, we considered the effects of the indirect land use change (iLUC) to account for the GHG emissions resulting from the change in the land types and its carbon cycle due to increased biofuel production causing expansion of agricultural production. The inclusion of iLUC increases the GHG emission associated with the feedstock production. We leverage the information for iLUC already studied in the previous work and assume that canola oil and cuphea oil will have the same impact due to the lack of information for their two feedstocks.[28]

Environmental metrics of short-chain esters from oilseed crops were challenging to estimate. For example, life cycle GHG emissions and fossil energy consumption could vary significantly depending on the feedstock assumption used for the analysis. The GHG emissions and fossil fuel consumption of this pathway are 53 and 77%, respectively, less than conventional petroleum diesel, assuming if cuphea oil can be produced in a similar way as canola oil and the equivalent upstream emissions are used. However, using the estimation of cuphea oil upstream emissions, these reductions will decrease to 20% less GHG emissions and 44% less fossil energy consumption compared to those of petroleum diesel. The availability of data on cuphea farming is limited because cuphea is not a commercial crop yet. Gesch et al. compared the budgets and production yields for the production of cuphea, corn, and soybean in an attempt to commercialize cuphea.[20] Therefore, the energy consumption and material usage of cuphea farming were estimated from the average data of corn and soybean farming reported by Gesch et al., using the ratios of the energy and material usage of corn/soybean farming to those of cuphea farming. For more details of the assumption of cuphea production estimation, see Table S2. Similar to MFSP, additional reductions in emissions could be achieved through the valorization of lignin to coproducts. Previous work by Huq et al. showed that 4-butoxyheptane has the potential to reduce GHG emissions when lignin is converted to adipic acid product by 50−271% relative to petroleum diesel, depending on the coproduct treatment used.[29] Among all of the MCCI bioblendstock presented in this paper, bicyclohexane has the greatest GHG emissions (131 gCO2e/MJ) due to a carbon-intensive feedstock (clean pine), a significant amount of natural gas input, and catalyst requirement.

Availability of feedstocks to scale production is a key consideration for these MCCI bioblendstocks to have a significant impact on the market. While quantitative feedstock supply analysis was outside the scope of this study, we did consider scalability when selecting pathways. The feedstocks used by these pathways are listed in Table S1 and include forest residues, corn stover, soybean oil, microalgae, wastewater sludge, food waste, yellow grease, and cuphea oil. These feedstocks were selected for various reasons including the availability of sufficient supply as well as to include a variety of options for the analysis. Forest residues and corn stover are examples of waste biomass, which could be provided in large volumes.[30] They are also representative of woody and lignocellulosic feedstocks, which could be substituted with other similar biomass from other sources such as other wood wastes (woody) and energy crops such as switchgrass and miscanthus (lignocellulosic). Soybean oil is already produced at a large scale, although its expansion as a fuel feedstock could bring concerns related to competition for productive land as mentioned previously. While microalgae could potentially be produced at a very large scale on marginal/unproductive land, further research is needed to reduce its cost. Wastewater sludge and food waste are examples of relatively abundant biomass resources, although at a smaller scale than the woody or lignocellulosic feedstocks. These pathways could potentially be extended to other abundant wet-waste resources such as manure. Yellow grease is an example of a waste product with a low-carbon intensity that potentially faces competition for a limited supply. Cuphea oil is a novel feedstock included to highlight its promising properties for producing short-chain esters, but work is still needed to understand its potential to be cultivated efficiently and at a significant scale.

■ CONCLUSIONS

This process to screen the candidate bioblendstocks against 19 metrics has provided insights into the technology readiness, economic viability, and environmental considerations of the MCCI bioblendstock pathways studied in this report. We found that most technology readiness metrics were neutral to unknown. Challenges for most bioblendstock pathways are in the blending behavior and testing for regulatory limits as most MCCI bioblendstocks are at a low TRL. Therefore, more analyses and testing on blendability and potential regulatory limits are needed for these candidates. Most of the conversion technologies are robust and will be minimally affected by the feedstock specifications and variations, although biochemically-based pathways will be modestly affected by biomass recalcitrance and carbohydrate content of starting feedstocks. Overall, economic metrics were predominantly favorable for most of the bioblendstock candidates and further economic and environmental improvements could be realized in biochemically-based pathways when lignin valorization or other coproduct opportunities are included. However, only seven pathways currently show the potential for $4/GGE or less. Finally, environmental impact metrics were mixed across favorability ratings. Biochemically-based pathways were challenged in carbon efficiency due to only using the carbohydrate fraction of biomass feedstock. Energy-intensive processes and the use of GHG-intensive chemicals such as sodium hydroxide contribute significantly to the GHG emissions of these pathways. Overall, 12 pathways showed the potential to achieve greater than 60% GHG emission reduction compared to conventional diesel, and three pathways had favorable water consumption.

The pathway with the most favorable ratings is renewable diesel via HTL of wet wastes; however, the availability of waste feedstocks (e.g., pig manure) for this pathway could limit its ability to be scaled up to serve a large fraction of transportation fuel use. Similarly, the highly rated fatty alkyl ethers may be limited by the availability of the yellow grease feedstock. Feedstock availability continues to be explored within projects supported by the U.S. Department of Energy's Bioenergy Technologies Office.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00781.

> Description of coproduct allocation methods, estimation of cuphea oil farming inventory, LCA boundary assumptions, bioblendstock water usage, feedstock carbon intensity, and high-level process descriptions for bioblendstock production (PDF)

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Notes

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