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Production Cost and Carbon Footprint of Biomass-Derived Dimethylcyclooctane as a High-Performance Jet Fuel Blendstock

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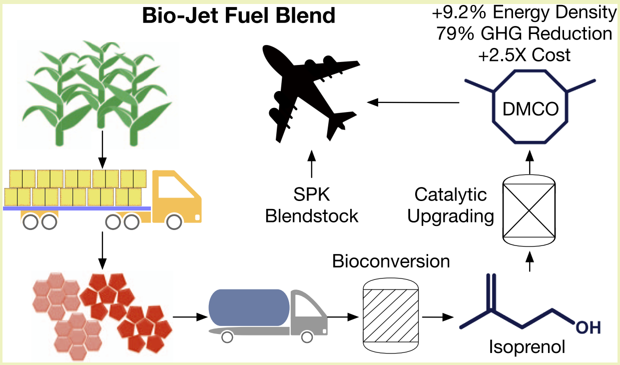

ABSTRACT: Near-term decarbonization of aviation requires energy-dense, renewable liquid fuels. Biomass-derived 1,4-dimethylcyclooctane (DMCO), a cyclic alkane with a volumetric net heat of combustion up to 9.2% higher than Jet A, has the potential to serve as a low-carbon, high-performance jet fuel blendstock that may enable paraffinic bio-jet fuels to operate without aromatic compounds. DMCO can be produced from bio-derived isoprenol (3-methyl-3-buten-1-ol) through a multistep upgrading process. This study presents detailed process configurations for DMCO production to estimate the minimum selling price and life-cycle greenhouse gas (GHG) footprint considering three different hydrogenation catalysts and two bioconversion pathways. The platinum-based catalyst offers the lowest production cost and GHG footprint of $\$9.0$/L-Jet-A$_{eq}$ and 61.4 gCO$_{2e}$/MJ, given the current state of technology. However, when the supply chain and process are optimized, hydrogenation with a Raney nickel catalyst is preferable, resulting in a $\$1.5$/L-Jet-A$_{eq}$ cost and 18.3 gCO$_{2e}$/MJ GHG footprint if biomass sorghum is the feedstock. This price point requires dramatic improvements, including 28 metric-ton/ha sorghum yield and 95−98% of the theoretical maximum conversion of biomass-to-sugars, sugars-to-isoprenol, isoprenol-to-isoprene, and isoprene-to-DMCO. Because increased gravimetric energy density of jet fuels translates to reduced aircraft weight, DMCO also has the potential to improve aircraft efficiency, particularly on long-haul flights.

KEYWORDS: *biomass sorghum, ionic liquid, lignocellulosic sugar, isoprenol, sustainable aviation fuel, technoeconomic analysis, life-cycle assessment*

1. INTRODUCTION

The aviation industry is difficult to decarbonize in part because of aircraft weight constraints and the difficulty of developing batteries with sufficient pack-level specific energy.[1] Energy-dense liquid fuels are likely to play an important role in fueling large aircraft for the foreseeable future, and numerous routes have been developed to produce bio-based blendstocks suitable for use in Jet A.[2,3] However, bio-jet fuel uptake is limited by a few key factors: first, currently available bio-jet blendstocks are paraffinic, and Jet A relies on aromatic blendstocks to ensure O-ring/seal swelling;[4] second, the properties of bio-based blendstocks are not sufficiently advantageous to catalyze demand in early adopter markets that value performance over cost.[2,5] The ability to appeal to early adopters that prioritize performance over cost is essential, as bio-jet fuels have not yet reached cost parity with Jet A (if policy support is excluded from the calculation).[2] While paraffins present in hydroprocessed esters and fatty acids (HEFA) and other more mature bio-jet fuels provide modest increases in the gravimetric net heat of combustion, they cannot currently serve as a one-to-one replacement for Jet A. The aromatic compounds typically added for O-ring/seal swelling, however, present downsides: these molecules initiate the formation of carcinogenic polyaromatic hydrocarbons[6] and reduce the net heat of combustion for the overall fuel blend. In this paper, we evaluate the cost and environmental tradeoffs of producing a bio-derived, energy-dense naphthene potentially capable of replacing these aromatic constituents: 1,4-dimethylcyclooctane (DMCO).

Cyclic alkanes such as DMCO have been shown to achieve acceptable swelling of nitrile O-rings at a 30% blending level, as compared to a conventional jet fuel with 8% aromatics.[4] DMCO's cyclic structure and chain branching lend the molecule exceptional fuel properties, including a density of 0.827 kg/L (6.7% higher than Jet A), a gravimetric net heat of

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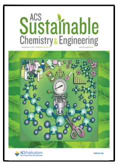

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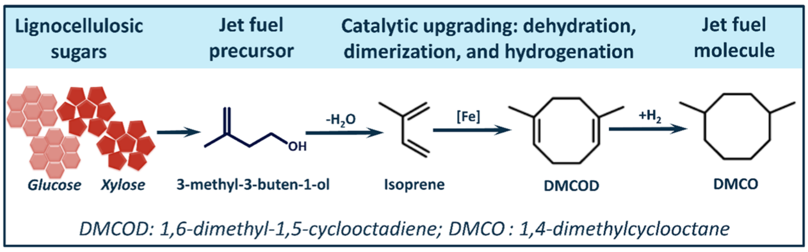

Figure 1. Overview of 1,4-dimethylcyclooctane (DMCO) synthesis processes from the biomass-derived glucose and xylose. This figure is consistent with the isoprenol-to-DMCO conversion process reported in a prior study.[6]

combustion of 43.82 MJ/kg (2.4% higher than Jet A), and a volumetric net heat of combustion of 36.22 MJ/L (9.2% higher than Jet A).[6] Additional properties of DMCO and their comparison with commercial jet fuels, including Jet A, Jet A-1, and Jet B, are documented in the Supporting Information (SI), Table S1. Ultimately, the success of this advanced jet fuel blendstock will depend on the cost of production, its ability to reduce greenhouse gas (GHG) emissions relative to petroleum-derived jet fuel, and use-phase benefits associated with its favorable fuel properties.

DMCO can be catalytically produced from isoprene in two steps: dimerization and subsequent hydrogenation (Figure 1).[6] There are numerous routes to produce the precursor isoprene; it is the monomer of natural rubber and can also be produced from sugars in *Escherichia coli* through the MVA or MEP pathways.[7,8] However, the volatile isoprene product is challenging to recover and purify for downstream conversion; it is also highly flammable, which increases the risk of fire or explosion in an aerobic bioreactor. To avoid this issue, isoprene can also be produced from the dehydration of isoprenol (3-methyl-3-buten-1-ol) and this is the route explored further in this paper.[9,10] Other isoprene production methods are documented in the SI, S2. Isoprenol can be biologically produced from plant-derived sugars using microbes such as *E. coli*.[11,12] *E. coli* metabolizes sugars, such as glucose and xylose, resulting in isoprenol yields from 10.5 to 22.3 g per 100 g of glucose using different biosynthetic pathways including the mevalonic acid (MVA) pathway and 5-methyl erythritol phosphate (MEP) pathway.[12,13] This highest demonstrated isoprenol yield to-date reached 55% of the maximum stoichiometric theoretical yield, which is 40.9 g isoprenol per 100 g of glucose.[14] The detailed costs, life-cycle GHG emissions, and water footprint for microbial production of isoprenol from biomass sorghum are documented in a recent study.[14] As noted in that study, isoprenol is also potentially interesting as a platform chemical for use in multiple markets; it is easily transportable in liquid form and, in addition to its potential for conversion to isoprene, it can also be used directly as a gasoline blendstock.[14]

As noted, isoprenol is a convenient bio-based intermediate, some or all of which may be dehydrated to produce isoprene. Recently, researchers dimerized isoprene into 1,6-dimethyl-1,5-cyclooctadiene (DMCOD) using earth-abundant iron-based catalysts (Figure 1).[6,15] They obtained an isolated DMCOD yield of 92% at a catalyst-loading rate of 0.025 mol %. DMCOD requires subsequent hydrogenation in the presence of a catalyst to produce DMCO (Figure 1). The same group has demonstrated an isolated yield of DMCO from DMCOD of 85 wt % with PtO_2 catalyst.[6] In more recent work, researchers have demonstrated DMCOD-to-DMCO yields of 97, 75, and 94 wt %, respectively, with three different metal catalysts—PtO_2, Raney nickel, and 10%Pd/C. These results are encouraging, but overall production cost and life-cycle GHG reduction potential relative to petroleum fuels will determine the degree to which DMCO can be successful as a jet fuel blendstock. This study provides a detailed technoeconomic analysis (TEA) and life-cycle GHG inventory for bio-based DMCO production using biomass sorghum as a feedstock. We explore two different biosynthetic routes to the isoprenol precursor—the MVA and MEP pathways—and three different hydrogenation catalysts—10%Pt/C, Raney nickel, and 10%Pd/C. Although PtO_2 was used for experimental research, commercial production would likely use a cheaper carbon-supported platinum catalyst (10%Pt/C) so our model relies on the assumption that the carbon-supported platinum catalyst achieves comparable performance. We identify parameters with the greatest impact on cost and GHG footprint and identify potential avenues to reducing the minimum selling price to \$0.66/L (\$2.50/gal) and achieving at least a 70% GHG reduction relative to the conventional jet fuel. These targets are based on the cost and GHG emission reduction targets for low-carbon drop-in biofuels set by the United States Department of Energy.[16]

2. METHODS

2.1. Process Model for DMCO Production. Lignocellulosic biofuel production can rely on an integrated process, in which biomass is shipped to large biorefineries and converted on-site to final fuels and products, or biomass can be deconstructed to sugar at decentralized facilities known as depots and then sent for downstream conversion at more centralized production facilities. This study considers separate sugar production depots, which can ship lignocellulosic sugars to large-scale biorefineries for downstream conversion to fuel. The modeled DMCO production facility utilizes 1000 bone-dry metric tons (bdt) of lignocellulosic sugar per day (more detail on biorefinery economies of scale are provided in the SI, Figure S1). This strategy allows for a decoupling of the sugar production process from downstream biological conversion and upgrading, thus enabling biorefineries to source sugar from different sources depending on availability and price. Although this paper focuses on lignocellulosic sugars derived from biomass sorghum, the modeled DMCO production facilities could choose to source some or all of their sugars from first-generation feedstocks. In the baseline analysis, the biorefinery is colocated with the sugar production facility (the supply distance of sugar is zero). However, we also explore scenarios in which sugar must be shipped longer distances from remote depot facilities, which results in higher transportation costs and emissions.

The lignocellulosic sugar considered in this study is derived from field-dried biomass sorghum via a one-pot high-gravity ionic liquid (cholinium lysinate, [Ch][Lys])-based biomass deconstruction process.[17] The incoming sugar composition for the baseline scenario is 70% glucose and 30% xylose.[18] This sugar composition was determined using a separate sugar model based on the current state-of-the-art biomass sorghum-to-sugar conversion rate.[18] At present,

Table 1. Major Input Parameters Associated with DMCO Production Stages under Different Scenarios[a]

parameter	unit	current state of technology (SOT)	improved MVA or MEP pathway	optimal future case
Lignocellulosic Sugar Feedstock				
cost of sugar[b]	\$/t	618.5	618.5	220.9
glucose[b]	%	70.4	70.4	61.60
xylose[b]	%	29.6	29.6	38.40
impacts from SOC sequestration[b,21,22]	$kgCO_{2e}/kg$	−0.11	−0.11	−0.11
carbon footprint of sugar excluding SOC[b]	$kgCO_{2e}/kg$	0.17	0.17	0.08
Bioconversion				
solid loading rate[22]	wt %	25	25	25
bioreactor power consumption[2,23]	kW/m^3	0.56	0.56	0.11
bioconversion time[12]	h	63	36	36
glucose utilization[12]	%	44	95	98
xylose utilization[c,12]	%	39.6	85	95
Recovery and Separation				
recovery of isoprenol[c]	%	95	95	98
Catalytic Upgrading				
isoprenol-to-isoprene conversion rate[9,10]	%	95	95	98
dimerization catalyst-loading rate	wt %	0.13[d]	0.13[d]	0.0013[c]
dimerization catalyst-loading cost[c,24]	\$/kg	10.26	10.26	7.14
isoprene-to-DMCOD isolated yield[6]	%	97	97	98[c]
Hydrogenation with 10%Pt/C				
10%Pt/C catalyst loading[d]	wt %	0.75	0.75	0.75
10%Pt/C catalyst cost[24]	\$/kg	261.3	261.3	231.8
DMCOD-to-DMCO isolated yield	wt %	97[d]	97[d]	98[c]
Hydrogenation with Raney Ni				
Raney Ni catalyst loading[d]	wt %	0.43	0.43	0.43
Raney Ni catalyst cost[24]	\$/kg	14.5	14.5	10.5
DMCOD-to-DMCO isolated yield	wt %	75[d]	75[d]	98[c]
Hydrogenation with 10%Pd/C				
10%Pd/C catalyst loading[d]	wt %	1	1	1
10%Pd/C catalyst cost[24]	\$/kg	316.2	316.2	279.8
DMCOD-to-DMCO isolated yield	wt %	94[d]	94[d]	98[c]
Bioconversion Reactor (Stoichiometry)				
MVA pathway: maximum pathway-dependent theoretical yield of isoprenol = 31.87/100 g of sugar				
1.5 glucose + 2 oxygen = 1 isoprenol + 4 CO_2 + 4 H_2O				
1.8 xylose + 2 oxygen = 1 isoprenol + 4 CO_2 + 4 H_2O				
MEP pathway: maximum pathway-dependent theoretical yield of isoprenol = 38.25/100 g of sugar				
1.25 glucose + 0.5 oxygen = 1 isoprenol + 2.5 CO_2 + 2.5 H_2O				
1.5 xylose + 0.5 oxygen = 1 isoprenol + 2.5 CO_2 + 2.5 H_2O				

[a]MVA = mevalonic acid pathway; MEP = 5-methyl erythritol phosphate pathway; SOC = soil organic carbon; DMCOD = 1,6-dimethyl-1,5-cyclooctadiene; and DMCO = 1,4-dimethylcyclooctane. [b]Determined in a separate sugar model (SI, Figure S2). [c]Assumed for analysis in this study. [d]Experimental data obtained from Naval Air Warfare Center Weapons Division, China Lake, California.

about 2500 bdt of biomass sorghum is required to produce 1000 bdt of lignocellulosic sugar. Our recent studies[14,18] documented the detailed modeling parameters and assumptions associated with the sugar production process, and the results are documented in Table 1 and SI, Figure S2. Briefly, the sugar model is based on an estimated sorghum bale supply cost of \$125/bdt and associated GHG emissions of 112 $kgCO_{2e}$/bdt at the pretreatment reactor throat, which are consistent with our recent study.[19] The structural carbohydrate and lignin contents of biomass sorghum for the baseline sugar model were estimated at 52 and 22%, respectively.[14] In the optimal future case, which represents the most favorable possible feedstock composition, the total carbohydrate content in biomass was increased to a maximum of 70% and the lignin fraction was reduced to 9.8%.[14] In the current state of technology (SOT) scenario, we considered experimentally determined glucose and xylose yields of 75.8 and 60.7%, respectively, at an IL loading rate of 5% and enzyme loading rate of 30 mg protein/g-glucan.[18] Although this paper considers dry sorghum, a recent study has shown that using ensiled sorghum can increase sugar yields at lower IL loading and may be preferable in some cases.[18] For the optimal future case, the sugar yield was increased to 93% of the theoretical yield, and IL and enzyme loading rates were reduced to 2.5% and 10 mg protein/g-glucan, respectively.[14,18]

Once delivered to the biorefinery, the lignocellulosic sugar is routed to the aerobic bioconversion reactor for isoprenol production. The basic unit operations involved in isoprenol production do not vary depending on the choice between MVA and MEP biosynthetic pathways; titer, rate, and yield variations between these pathways will primarily impact the sizing and residence time for the bioconversion reactor.[7] Full details of the isoprenol production process from biomass sorghum feedstock are documented in our recent study.[14] Air is supplied using a compressor to meet the required oxygen for the cell redox balancing, which varies depending on the biosynthetic pathway (Table 1). The bioconversion reactor is operated at 30 °C for 63 h.[12] Table 1 summarizes glucose and xylose utilization rates and the reaction stoichiometry for each pathway considered in this study. An important note is that isoprenol production has so far been demonstrated only in hosts that utilize glucose. However, we adjust the SOT scenario to account for the likelihood that, in a commercial-scale operation, a co-utilizing strain would be used to convert both glucose and xylose. We use a slightly lower xylose utilization (10% lower than glucose), which is consistent with typical co-utilizing strains. Additionally, we calculate the production cost and carbon footprint of DMCO if only glucose is utilized as an alternative scenario. Following bioconversion, the solid fraction, including cell mass, is separated using a decanter centrifuge and routed to the on-site energy generation unit, and the liquid fraction is sent to the isoprenol recovery and separation unit. Isoprenol is recovered through a distillation and decantation system, and the product is further purified using a subsequent distillation. The overall isoprenol loss during the recovery and separation process is assumed to be 5%. After recovery and separation, isoprenol is routed to the catalytic upgrading unit and the remaining liquid fraction is delivered to the wastewater treatment unit.

In the catalytic upgrading unit, isoprenol is dehydrated to produce isoprene, which is subsequently dimerized to DMCOD, and DMCOD is hydrogenated to produce DMCO. In this unit, isoprenol is first mixed with steam (20 vol % at 150 °C) and catalytic dehydration is carried out using phosphoric acid (15 wt % based on the whole slurry).[10] The yield of isoprene is assumed to be 95% of the theoretical yield.[10] Isoprene is recovered via condensation, where 3% of isoprene is lost during the process. The isoprene recovered after the dehydration process is delivered to the dimerization reactor.

The dimerization of isoprene is carried out in the presence of an iminopyridine iron dihalide catalyst, $[(^{Me}PI)FeCl(\mu\text{-}Cl)]_2$, at room temperature for 24 h.[6] The reaction is activated by adding a MeMgCl solution. The isolated yield of DMCOD is 92 wt %.[6] This alkene can be hydrogenated to form DMCO in the presence of one of three different metal catalysts: PtO_2 (or 10%Pt/C), Raney nickel, and 10% Pd/C. Excess hydrogen is recovered and 91% of the recovered hydrogen is recycled back to the hydrogenation unit. The DMCO is purified using distillation and then stored on-site. The waste hydrogen is routed to the on-site energy generation unit and other wastes from the catalytic upgrading unit are delivered to the wastewater treatment unit. Additional details of the catalytic upgrading of isoprene into DMCO is available elsewhere.[6,19,20] Table 1 summarizes the key operating parameters and ranges explored in this study.

The wastewater treatment, on-site energy generation, and utility stages considered in this study (Figure 1) are consistent with previously published technoeconomic analyses.[23,25] Supplemental natural gas is added to the boiler because the fuel generated from the unutilized sugars (biogas produced through on-site anaerobic digestion) and the waste hydrogen is not sufficient to meet the heat and electricity demands of the facility. The lignin fraction of biomass is separated and combusted at the sugar production facility to generate process steam and electricity, and thus it is not available for combustion at the DMCO production facility modeled here. Cost and carbon credits from the lignin-fired electricity generation are accounted for in the standalone sugar model, which are reflected in the sugar production cost and associated GHG emissions (Table 1).

2.2. Analysis of Minimum Selling Price and Life-Cycle Greenhouse Gas Emissions.

The minimum selling price of DMCO is determined using the standard discounted cash flow rate of return analysis, which is consistent with previous studies.[14,23] Briefly, the capital and operating costs are determined based on the process model developed in SuperPro Designer after the rigorous material and energy balancing and sizing of the process equipment. The baseline equipment purchase costs are gathered from recent technoeconomic analyses.[2,23,25] The SuperPro model captures changes in the material flows, equipment size and quantity, and corresponding changes in the capital and operating costs. We considered an internal rate of return (IRR) of 10%, plant lifetime of 30 years, and plant operating hours of 7920 h (330 days/year and 24 h/day).[14,23] The income tax is assumed to be 21%[8] to accurately reflect the most recent corporate tax rate.[23]

The carbon footprint of DMCO is determined using the Bio-Cradle-to-Grave (BioC2G) model used in previous studies.[26] The model uses a hybrid process-based/input-output-based life-cycle inventory approach and most emission factors (SI, Table S3) are, where possible, harmonized with Argonne National Lab's Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET) model. The material and energy balances for fuel production are obtained from the SuperPro model serve as the main input to the LCA model. The GHG emissions impact vector of process chemicals were gathered from widely used LCA databases.[27−29] We use the U.S. electricity mix for the sugar production facility and DMCO biorefinery. Carbon footprints of the selected metal catalysts were determined by building their separate production process models and using all of the direct/indirect inputs to the model. The resulting carbon footprints are documented in the SI, Table S3. The carbon footprint of tetrahydrofuran (THF)[30] is used for MeMgCl because it is available as a solution in THF (3.0 M in THF). Life-cycle energy use (total and fossil-only) are documented in the SI, Table S3. We use a higher heating value for DMCO of 46.3 MJ/kg and a functional unit of 1 MJ.

2.3. Scenario and Uncertainty Analysis.

Each part of the conversion process, from the breakdown of biomass to sugars, to biological conversion of sugars to isoprenol, and final conversion to DMCO are all under active research and development. We address this changing technological landscape through scenario analysis. The current yield scenario reflects the current SOT for isoprenol yields via the most common MVA pathway, as well as the SOT for all other components of the supply chain and conversion process.[12,13] To reflect the potential outcome of ongoing efforts in engineering MVA and MEP biosynthetic pathways to improve the titer, rate, and yield of isoprenol,[31−33] we also present future scenarios based on 95% of the pathway-dependent maximum theoretical yield of isoprenol. Apart from the glucose and xylose utilization rates, aeration rate, and bioconversion time, other input parameters remained the same for these different product yield scenarios (Table 1). In the optimal future case, we modeled the minimum selling price and life-cycle GHG footprint of DMCO considering 95−98% of the theoretical yield and otherwise optimized performance for each stage of the process, including biomass composition/cost, deconstruction, bioconversion, and upgrading (Table 1).

Within each scenario, there are sources of uncertainty that will impact the minimum selling price and life-cycle GHG footprint of DMCO (SI, Table S2). Our analysis includes single-point sensitivity analysis and stochastic uncertainty analysis using Monte Carlo simulation. The single-point sensitivity analysis was performed by modeling all inputs with a uniform probability distribution and varying them individually. For the Monte Carlo simulations, probability distributions were assigned to each parameter. Baseline, minimum, and maximum values used to model input parameters are summarized in the SI, Table S2. For this uncertainty analysis, sugar composition, sugar utilization, and the DMCOD-to-DMCO conversion rate considered for each scenario (Table 1) were kept constant. Other inputs were modeled based on their probability distributions, including uniform, triangular, and lognormal (SI, Table S2). For the optimal scenario, an ideal value assigned for each parameter (Table 1) was considered as a baseline value, which resulted in positively skewed probability distributions of most of the key inputs. The simulation ran for 5000 Monte Carlo trials.

2.4. Fuel Cost Savings in a Hypothetical Commercial Flight.

Fuel consumption of an aircraft over the flown distance was determined using the Breguet range equation illustrated in previous studies.[34,35] The main inputs to the Breguet range equation can be obtained from a payload range diagram of an aircraft, which is presented in the SI (Figure S3). The payload range diagram provides the maximum possible take-off mass based on the planned flight distance. Other inputs to the Breguet range equation, including aircraft characteristics (SI, Table S5) as well as density and lower heating values of conventional jet fuel and DMCO, are summarized in the SI (Table S1). A previous study[34] documented the detailed methods and illustrated each calculation step with an example. Briefly, the Breguet range equation provides fuel consumption per passenger per 100 km flight distance over the flown distance. The fuel cost is determined considering the fuel consumption over the range obtained from the Breguet range equation and the prices of Jet A and DMCO. We considered the projected prices (2020 U.S. Dollars) of conventional jet fuel at the refinery gate in 2050 of \$0.42/L, \$0.73/

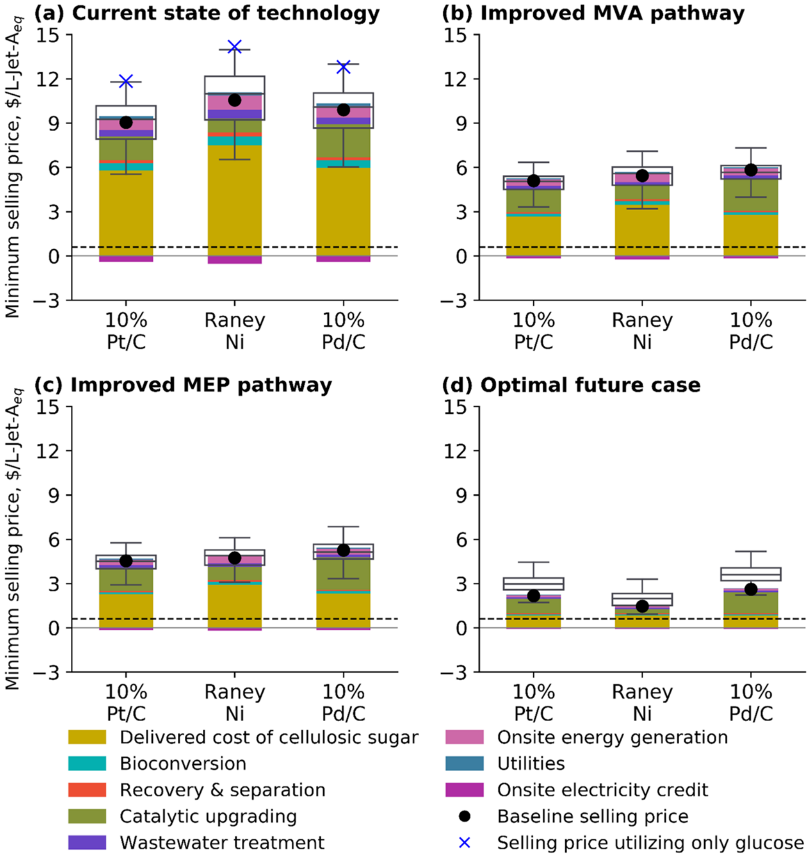

Figure 2. Minimum selling price of DMCO under different scenarios: (a) current state of technology (SOT) with the MVA pathway; (b) improved MVA pathway with 90% of the theoretical isoprenol yield; (c) improved MEP pathways with 90% of the theoretical isoprenol yield; and (d) optimal future case with the MVA pathway. The catalytic upgrading costs estimated in this study of \$0.3−1.5/L-Jet-A$_{eq}$ is similar to the alcohol-to-jet fuel upgrading cost reported in prior study of \$0.1−1.8/L-Jet-A$_{eq}$.[38] The horizontal dashed lines represent the last 10 year (2009−2018) average selling price of the conventional jet fuel of \$0.6/L-Jet-A at the refinery gate.[37] The box and whisker plots show the results of Monte Carlo simulations.

L, and \$1.22/L, which correspond to the low, reference, and high oil prices.[36] Fuel cost savings over conventional jet fuel were determined by considering the optimal selling price of DMCO at the biorefinery gate of \$1.46/L-Jet-A$_{eq}$. We consider an example flight from San Francisco (SFO), USA to London (LHR), UK (a distance of 4664 nautical miles or 8638 km) to illustrate the total fuel savings over the entire flight range. Additionally, the impacts of policy incentives on the fuel cost saving were determined considering California's Low Carbon Fuel Standard (LCFS) credit and the Renewable Fuel Identification Number (RIN) values. These credits reduce the minimum selling price of DMCO. The LCFS (assigned based on carbon intensity) and RIN values (for D3 category fuels) considered in this study are summarized in the SI, Table S4.

3. RESULTS AND DISCUSSION

3.1. Minimum Selling Price of DMCO. Figure 2 depicts the minimum selling prices of DMCO under current and potential future scenarios, including improved isoprenol yields and optimal conditions for other processes. Broadly speaking, DMCO results in a higher minimum selling price than paraffinic bio-jet fuels currently on the market, such as HEFA synthetic paraffinic kerosene (SPK), alcohol-to-jet SPK, or Fischer−Tropsch SPK. Improvements at each step of the process will be required to reach the lowest possible cost, excluding policy incentives, of \$1.5/L-Jet-A$_{eq}$. Optimizing the titer, rate, and yield for isoprenol is an important first step. Research in recent years on isoprenol biosynthesis has mainly focused on different MVA pathways, including the native and IPP-bypass MVA pathways, to improve titer, rate, and yield.[6,10] The experimentally demonstrated isoprenol yield via the MVA pathway, on average, of 14/100 g of sugar[12] and the overall isoprenol-to-DMCO conversion rates of 51−66 wt %[6,10] result in a minimum selling price of DMCO of \$9.0, \$11, and \$9.9/L-Jet-A$_{eq}$ with 10%Pt/C, Raney nickel, and 10%Pd/C catalysts, respectively (Figure 2a). These current state-of-the-art selling prices of DMCO are increased by 29−34% when only glucose is utilized (Figure 2a) because isoprenol production utilizing xylose or lignocellulosic hydrolysate is not fully demonstrated. Based on the Monte Carlo simulation results, the likelihoods of achieving minimum selling prices at or below these values are in the range of 45−48% (Figure 2a). Variation in minimum selling price across the catalyst options is the result of differing isoprenol-to-DMCO conversion rates and the catalyst-loading rates and unit costs (Table 1). The minimum selling prices corresponding to the current state-of-the-art are still an order of magnitude higher than the last 10 year (2010−2019) average price of jet fuel at the refinery gate of \$0.6/L-Jet-A.[37] The lignocellulosic sugar costs and catalytic upgrading processes are responsible for 80−83% of the total DMCO production cost, so reducing sugar costs, improving isoprenol yield, and increasing DMCO yields from DMCOD are particularly critical to reaching cost competitiveness (Figure 2a).

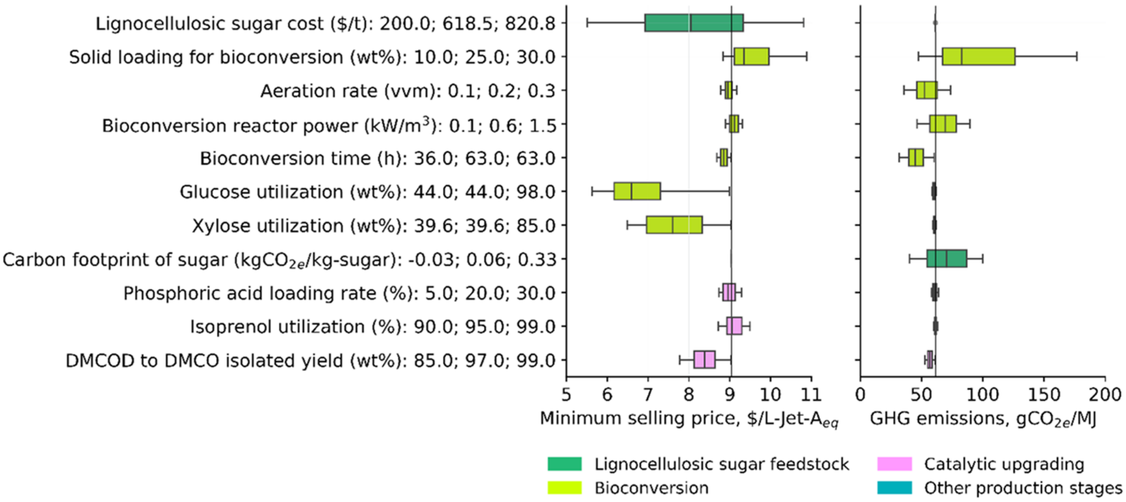

Figure 3. Most significant process parameters requiring additional research and development efforts. DMCOD: 1,6-dimethyl-1,5-cyclooctadiene. This is a representative case considering the current SOT and the 10%Pt/C catalyst for the hydrogenation process.

Both the MVA and MEP pathways could be considered for isoprenol synthesis in the future to improve the sugar to DMCO conversion rate. The MEP biosynthetic pathway results in a 9.7−13% lower selling price of DMCO relative to the MVA pathway when both pathways are improved to achieve 90% of the theoretical yield (Figure 2b,c). The MEP pathway has an advantage because of its 20% higher theoretical isoprenol yield from both glucose and xylose relative to MVA, and a lower oxygen requirement for the cell redox balancing (Table 1). However, the MEP pathway is difficult to control relative to the MVA pathway because any imbalances in the supply of glyceraldehyde 3-phosphate and pyruvate greatly decrease the pathway performance.

The pathway-dependent selling prices of DMCO (Figure 2b,c) at 90% of theoretical isoprenol yield suggest that focusing solely on improving the titer, rate, and yield of isoprenol is not sufficient to achieve a market-competitive price for DMCO. Further optimization of the MVA pathway to achieve 96.7% of the pathway-dependent theoretical yield (Table 1) or 75.4% of the stoichiometric maximum theoretical yield of 40.9 wt % is required. This high biological yield is considered assuming that the engineered *E. coli* strain directs most lignocellulosic sugars to isoprenol and CO_2 production (Table 1) and only 2% of lignocellulosic sugar to the cell mass growth, similar to *Z. mobilis*.[23] Additionally, optimal values of major process parameters (Table 1) are required. In particular, improving the isoprenol-to-DMCO conversion rate to 77% and reducing lignocellulosic sugar production cost to $221/bdt result in a minimum selling price of DMCO in the range of $1.5−2.6/L-Jet-$A_{eq}$ (Figure 2d). Based on the Monte Carlo simulation, the likelihoods of achieving these optimal prices (Figure 2d) are 22% with Raney nickel, 8% with 10%Pt/C, and 7% with 10% Pd/C catalysts. These likelihoods can be increased by optimizing and/or fixing (assuming no variability) the key cost drivers (Figures 3 and S5), including lignocellulosic sugar production cost, solids loading rate, glucose and xylose utilization, and the isoprenol-to-DMCO conversion rate at their optimal values. For comparison, a prior review[38] reported a sugar-to-hydrocarbon fuel (jet fuel precursor) production cost in the range of $1−2.4/L-Jet-$A_{eq}$ with an average value of $1.5/L-Jet-$A_{eq}$. The actual jet fuel cost would be higher because not all hydrocarbons are usable as jet fuel. The results from other past studies[2,35] considering different biochemical and thermochemical jet fuel conversion pathways are in the range of $0.6−9.8/L-Jet-$A_{eq}$ and the calculated average value is $2.1/L-Jet-$A_{eq}$. This average selling price of bio-jet fuel is close to the optimal selling price of DMCO estimated in this study; however, these studies all rely on different assumptions, including feedstock types and delivered costs, conversion processes, and biorefinery configurations.

Although, under the current SOT, the 10%Pt/C catalyst achieves the lowest DMCO minimum selling price, this route may not have the greatest long-term potential. If all three catalysts can achieve comparable isoprenol-to-DMCO conversion rates, the Raney nickel-based hydrogenation process results in the lowest DMCO production cost because of the lower catalyst-loading rate and cost relative to other catalysts considered in this study (Table 1). This highlights the importance of achieving a near-theoretical yield of DMCO with a cheap metal catalyst at a low catalyst-loading rate.

Another area of incremental improvement is the delivered cost of sugar, which is the single most influential parameter in determining the minimum selling price of DMCO (Figure 3). Biorefineries could source commercial sugars, including dextrose, beet sugar, and cane sugar; however, price of these sugars can be higher than lignocellulosic sugars by as much as a factor of 2 (SI, Figure S4). A low-quality commercial sugar could likely be sourced a lower cost relative to the sugars included in the SI, Figure S4, although the impact of different quality sugars on isoprenol yield and downstream separations costs remains unknown and will require further testing. There are many opportunities to reduce the production cost of lignocellulosic sugar as well. The lignocellulosic sugar cost of $221/bdt in the optimal future case could be reduced to $213/bdt by minimizing the transportation of the engineered biomass sorghum, selecting a sorghum variety with high carbohydrate content (70 wt %) and low lignin (9.8 wt %),[18] and optimizing yields and process conditions for sugar production. Field trial and compositional analysis data suggests that these are achievable, particularly in some high-yielding nonphotoperiod sensitive sorghum varieties.[39] These improvements result in a $1.4/L-Jet-$A_{eq}$ minimum DMCO selling price if the Raney nickel-based hydrogenation process is used. In this case, the sugar depot would need to be located near the

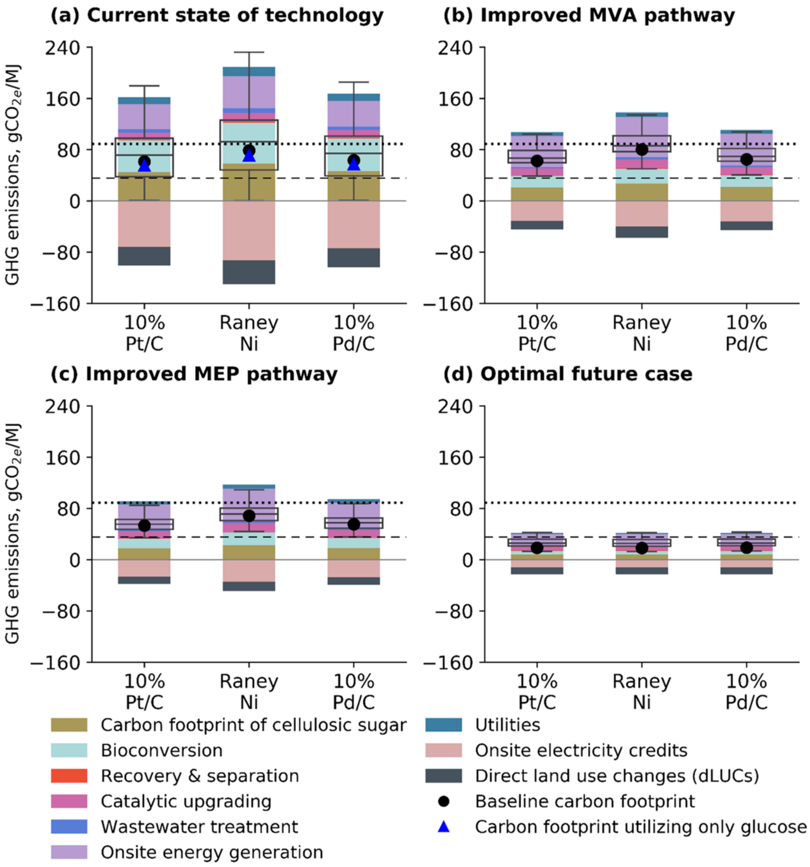

Figure 4. Greenhouse gas footprint of DMCO under different scenarios: (a) current SOT with MVA pathway; (b) improved MVA pathways with 90% of the theoretical isoprenol yield; (c) improved MEP pathways with 90% of the theoretical isoprenol yield; and (d) optimal future case with the MVA pathway. The horizontal dotted and dashed lines, respectively, represent the carbon footprint of conventional jet fuel and the anticipated carbon footprint of 60% reduction relative to the conventional jet fuel. The box and whisker plots show the results of Monte Carlo simulations.

sorghum field (trucking distance of 33 km or ∼20 miles) and sugar yield must be increased to 98% of the theoretical yield at a low IL loading rate of 2.5 wt % and an enzyme loading rate of 7 mg of protein per g of glucan (SI, Figure S2). We find that, for each \$0.01/kg decrease in sugar cost, the minimum selling price of DMCO is reduced by 3.7−11.9 cents/L-Jet-A_{eq} depending on the specific technological scenario (yield, residence time, upgrading yields). However, reducing the sugar supply cost is a challenge for a remote biorefinery as the sugar supply cost increases with transportation distance. Concentrated sugar (20% moisture content) transportation by truck is estimated to cost 7.6 cents per bone-dry metric-ton per km traveled. This sugar supply cost has the potential to increase the minimum selling price of DMCO by 2.8−7.4 cents/L-Jet-A_{eq} per 100 km increase in the supply distance from the sugar depot to the biorefinery. These basic guidelines can be used to evaluate tradeoffs between purchase cost and increasing transportation distance. Of course, long-distance transportation costs can be reduced by mode-switching to rail or marine transport.

It is clear from our results that even the aggressive process-level improvements considered here (Tables 1 and S2) are not sufficient to reach parity with the last 10 year average selling price of jet fuel[37] of \$0.6/L-Jet-A. This means that replacing Jet A with 100% DMCO will come at a substantial cost. However, if replacing petroleum-derived jet fuel is a priority and paraffinic bio-jet fuels require a blendstock like DMCO to achieve the necessary specifications (at, for example, a 30% blend to avoid the use of petroleum-derived aromatics), it is conceivable that DMCO could garner a premium, particularly in markets where its high energy density is valuable. Although not considered in this study, lignin valorization can be a viable route to improving the economics of advanced biorefineries,[2,23] and depending on the value of the lignin (either sold as a coproduct or converted on-site), this may further reduce the minimum selling price for lignocellulosic sugars. Another option for increasing the value derived from lignocellulosic biomass is to accumulate bioproducts in planta, either through plant breeding or engineering efforts.[40] Policy supports tied to biofuels' ability to mitigate GHG emissions is the most viable near-term option for making these fuels cost competitive.

3.2. Greenhouse Gas Footprint of DMCO Production.

In every biomass sorghum-based scenario analyzed, DMCO achieves GHG emissions savings relative to conventional jet fuel. In fact, counterintuitively, GHG savings are less dependent on overall yields than the costs (which are sensitive to yields) for two reasons: first, the sorghum biomass feedstock is expected to sequester carbon in the soil, resulting in a relatively low GHG footprint per unit of lignocellulosic sugar and consequently a modest GHG benefit from increased sugar-to-fuel yields; second, unutilized sugar from the bioconversion reactor is not wasted, but instead converted to biogas in the facility's anaerobic digester (which in turn reduces the need for on-site combustion of natural gas). Although some of the sugar not converted to isoprenol may instead go to side products, including CO_2 and H_2O, or cell mass, the underlying assumption is that nongaseous products will be available to microbes for conversion in the anaerobic digester. When combined, these mechanisms have a dampening effect on the GHG footprint.

For the current SOT scenario, the soil organic carbon (SOC) sequestration potential of biomass sorghum, on average, of −0.46 metric tons of CO_{2e}/ha[21,22] and electricity generated on-site offsets a portion of on-site energy demand (Figure 4a). In Figure 4, thermal and electrical energy demand in each stage are accounted for the positive bars, based on the use of natural gas for combined heat and power, and offset credits (shown in negative bars) are applied based on the amount of bio-based heat and power available to offset natural gas needs. The result is DMCO GHG footprint values that are 31, 11, and 28% lower than Jet A with 10%Pt/C, Raney nickel, and 10%Pd/C catalysts, respectively. The variations across the three cases are driven by DMCOD-to-DMCO conversion rates with the selected catalysts (Table 1). The GHG footprint of DMCO production using the current SOT scenario is, surprisingly, decreased by only 10% if xylose remains unutilized (Figure 4a) because the xylose-containing wastewater boosts biogas generated on-site, thus reducing natural gas input to the boiler. For the current SOT, the likelihood of achieving a reduction in the GHG footprint relative to Jet A is in the range of 43−44%. When the isoprenol yield is increased to 90% of the theoretical yield, the carbon footprint of DMCO—relative to the current SOT scenario—is increased by 1−2% for the MVA pathway (Figure 4b) and is reduced by 9−12% for the MEP pathway (Figure 4c). This is simply a result of the MVA pathway's lower theoretical yield (31.87/100 g of sugar) and the fact that unutilized sugars were providing a cobenefit because of their downstream conversion to biogas. In contrast, the MEP pathway achieves a net GHG benefit when it reaches 90% of its higher theoretical yield (38.25/100 g of sugar) (see Table 1).

Net GHG contributions from sugar feedstock production and bioconversion to isoprenol can be reduced from 28 to 20% and 31 to 13% of the total emissions, respectively, when these processes are fully optimized. To reduce the GHG footprint of lignocellulosic sugars, sugar yields must be improved to (>90%) using low ionic liquid (2.5%) and enzyme (10 mg protein/g-glucan) loadings (Table 1). Importantly, the lower bioconversion time of 36 h in the optimal case reduces on-site electricity consumption to operate the aerobic bioconversion reactor (including agitation and sparging) (Figure 4a,d). However, the carbon footprint contribution from the on-site energy generation stage to the total GHG emissions is increased from 24 to 42% when the DMCO production process is improved from the current SOT (Figure 4a) to the optimal future case (Figure 4d). Essentially, as the conversion efficiency improves, less unconverted sugar remains in wastewater, thus reducing biogas yield during anaerobic digestion. With less biogas generated for use in the boiler, more external energy (natural gas) is required to meet the heat and electricity demands of the facility. In an integrated biomass-to-biofuel facility, more lignin and other organics are available for conversion and changes in biogas yield will have a smaller relative effect on heat/electricity generation potential, while a facility utilizing a relatively clean sugar stream does not have access to those renewable sources of energy. Despite these tradeoffs, the optimal case does result in a net reduction in the carbon footprint of DMCO by 79% relative to conventional jet fuel (Figure 4d). Based on the Monte Carlo simulation, the likelihood of achieving this optimal carbon footprint reduction is 15% (Figure 4d). As noted previously, additional improvements that reduce the energy input of bioconversion per unit of isoprenol produced will shrink the final GHG footprint of DMCO; this can include increased solids loading rate during bioconversion, decreasing the aeration rate (if the yield is held constant) (Figures 3 and S5). Procuring lignocellulosic sugars with a lower GHG footprint and increasing the DMCOD-to-DMCO conversion rate are also viable strategies. For comparison, past studies[2,38] reported that GHG emission reductions of different bio-jet fuel molecules (paraffins and naphthenes) relative to the conventional jet fuel are in the range of 57−105%.

There is considerable uncertainty about how the sugar depot model would be implemented in practice and the distances that sugar would need to be transported. These distances will not only impact the cost but also GHG emissions. We find that the GHG footprint of sugar is increased by 0.17 gCO_{2e}/kg-sugar/km of the supply distance if sugar is transported via a conventional diesel-powered truck. These transportation emissions will increase the carbon footprint of DMCO by 4.4 gCO_{2e}/MJ/100 km of the supply distance for the current state of the technology and by 1.7 gCO_{2e}/MJ/100 km of the supply distance for the optimal future case (because of higher yields in the optimal case). Mode shifting from truck to rail can allow facilities to source sugar from a larger radius with minimal impact on emissions. The use of advanced fuel cell hybrid electric or fully electric trucks is another option for minimizing transportation emissions.[41,42] Eliminating the use of natural gas for the boiler in favor of renewable resources, such as hog fuel (wood residue and sawmill wastes) or biogas sourced from dairy digesters, can also further reduce the GHG footprint of DMCO. For the optimal future case, we find that switching from natural gas to hog fuel increases the likelihood of a 79% reduction in GHG emissions relative to conventional fuel from 15 to 57%. Sourcing electricity from renewable resources, either through strategic siting of facilities in renewables-dominated regions or through special purchase agreements with the local utility, is yet another option that may become increasingly attractive for facilities wishing to earn policy incentives for GHG mitigation.

4. COST OF CARBON MITIGATION AND USE-PHASE IMPACTS OF DMCO

Reaching DMCO selling prices competitive with conventional Jet A requires policy incentives. For the optimal future case, depending on the metal catalysts used for the hydrogenation process, the calculated cost of carbon mitigation (absent any supplemental policy support) is \$331−786/t-CO_{2e} to achieve a minimum selling price of DMCO equal to \$0.6/L-Jet-A_{eq} (10 year average price of conventional jet fuel at the refinery gate).[37] Renewable DMCO can qualify as D3 "cellulosic biofuel" under the Renewable Fuel Standard (RFS), as it achieves a carbon intensity reduction of at least 60% relative to petroleum fuel, resulting in Renewable Identification Numbers (RINs) worth an average value in 2020 of \$1.32/RIN (which is equal to a gallon of ethanol-equivalent fuel) (SI, Table S4). Average RIN values alone do not enable DMCO to reach cost parity with Jet A even if the Raney nickel-based hydrogenation process is used and the full process is optimized. In this case, RIN values would need to be at least \$1.94, which is higher than the average 2020 value but lower than the current price in

2021 of \$2.39/RIN. Alternatively, a lower RIN value of \$0.78/RIN (minimum value in 2020, SI, Table S4) is acceptable if DMCO is sold into a market where a Low Carbon Fuel Standard (LCFS) provides supplemental support, as is the case in California. If the RIN value is near the average of \$1.32, an LCFS credit of \$106.7/t-CO_{2e}, which is lower than typical California LCFS values (\$141−219/t-CO_{2e})[43] is sufficient to achieve cost parity.

So far, the energy density advantage of DMCO has not been incorporated in these calculations, except to adjust to Jet A_{eq} values on a higher heating value basis as needed. However, a 9.2% higher volumetric net heat of combustion relative to conventional Jet A does offer use-phase advantages for aviation in addition to the previously discussed blending opportunities with paraffinic biofuels such as HEFA-Jet. The higher energy density of DMCO provides additional value to commercial aviation by increasing aircraft range and efficiency. Considering an extreme case of 100% drop-in replacement of conventional jet fuel with DMCO, an airline could save 46.5 L of fuel per passenger (10.3% reduction relative to Jet A) in a typical international flight from San Francisco (SFO), USA, to London (LHR), UK. However, without policy supports, this efficiency advantage does not compensate for the 16% higher selling price for DMCO relative to the projected jet fuel price in 2050 of \$1.22/L (2020 U.S. dollars) (see Figure 5). This highlights the importance of either lignin valorization (not considered in this work) or policy incentives for making renewable jet fuel competitive with the petroleum counterpart. Assuming a high jet fuel price in 2050 of \$1.22/L-Jet A (2020 U.S. dollars), airlines can save fuel cost over the entire flight range when 100% DMCO is utilized and DMCO biorefineries receive RINs or LCFS credits (Figure 5). Compared to a low oil price scenario, DMCO requires a combination of California LCFS and Federal RINs to outperform Jet A on a cost basis. Independent of the economics, we find that replacing Jet A with DMCO produced through a fully optimized supply chain and conversion process can save 0.14 $kgCO_{2e}$ per passenger per km traveled.

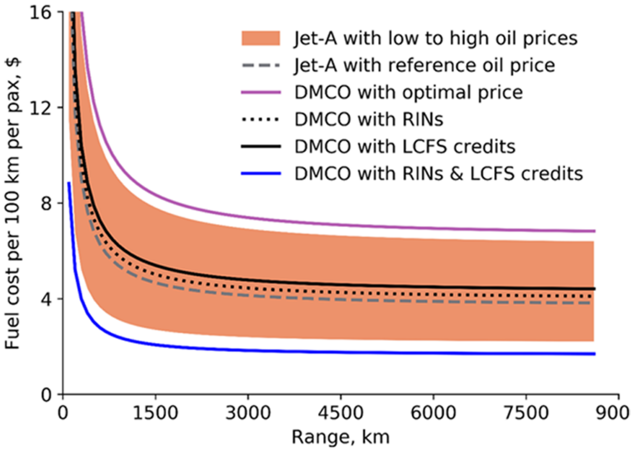

Figure 5. Fuel cost savings over the range of aircraft per 100 km per passenger (Pax). This analysis includes the projected conventional jet fuel prices (2020 U.S. dollars) in 2050 of \$0.42/L, \$0.73/L, and \$1.22/L with low, reference, and high oil prices.[36] This analysis includes the average LCFS and RIN credits of \$199.07/t-$CO_{2e\text{-avoided}}$ and \$1.32/RIN (for D3), respectively (SI, Table S4).

5. CONCLUSIONS

Our results highlight that DMCO, because of its high volumetric heat of combustion and ability to substitute for petroleum-derived aromatic jet fuel molecules, may play an important role in transitioning toward sustainable aviation fuels. A DMCO-HEFA blend could replace Jet A. DMCO production is, however, less mature than some of the simpler routes to paraffinic bio-jet fuels and even at its most mature state; it is unlikely to reach costs competitive with current Jet A prices. The SOT scenario for DMCO production represents research that is still early stage, with work falling into technology readiness level (TRL) 3 for most components of the process. This means that the proof-of-concept work has been done and, in some cases, limited optimization of the individual processes has occurred. However, the work is still occurring at a small scale and thus scale-up and commercialization would likely result in considerable performance improvements. Practical experience indicates that the transition to larger-scale demonstrations alone can increase yields relative to small-scale experiments.[44] The current ionic liquid-based biomass deconstruction process releases more than 75% of the theoretical glucose from the field-dried biomass and more than 90% of the theoretical glucose from ensiled biomass, while xylose yields are typically in the 60−70% range.[18] Further process intensification and scale-up will be required to reach glucose and xylose yields of 90−95% of the theoretical yield while simultaneously lowering solvent and enzyme loading.

Once low-cost lignocellulosic sugars are available for conversion, strain engineering will be critical to reach at least 95% of the biological maximum isoprenol yield at a compressed bioconversion time of 36 h and a sugar loading rate of at least 20 wt %. Oxygen required for cell redox balancing could further be reduced by improving the biosynthetic pathway; this strategy can bring the life-cycle GHG footprint down because the aeration rate substantially reduces the electricity demand for the facility. The dimerization and hydrogenation stages require additional research to ensure a high yield and selectivity with a low metal catalyst loading, which will reduce the upfront catalyst and catalytic upgrading costs. Prior studies[6,45] reported that the use of a heterogeneous catalyst could further improve selectivity and activity for the dimerization process relative to the homogeneous system. Those prior results suggest that the development of a heterogeneous catalyst with a long lifetime could reduce costs, particularly when paired with a transition to a continuous process (which further reduces capital costs, energy demand, and processing time relative to the batch process) for DMCOD synthesis. Our results indicate that, while DMCO is unlikely to be the lowest-cost bio-jet fuel available, this molecule serves a potentially unique purpose in the portfolio of sustainable aviation fuel blendstocks available. Provided further scale-up, process intensification, and system optimization can be employed to reduce costs and emissions, DMCO may be important to enabling a 100% renewable aviation sector.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03772.

Properties of 1,4-dimethylcyclooctane (DMCO) and commercial jet fuels; process modeling inputs; carbon footprint of process chemicals and electricity; biorefinery size; lignocellulosic sugar production cost and associated greenhouse gas emissions; inputs to the Breguet range equation; and sensitivity analysis (PDF)

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Notes

The authors declare no competing financial interest.

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