Major Classification: Sustainability Science

Technoeconomic and life cycle analysis of catalytically converting wet ethanol into fungible fuel blendstocks

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JRH and CEW of Vertimass and BHD of ORNL haves a commercial interest in the subject of this paper.

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Abstract

Technoeconomic and life cycle analyses are presented for catalytic conversion of ethanol to fungible hydrocarbon fuel blendstocks, informed by recent advances in catalyst and process development. Whereas prior work toward this end has focused on three-step processes featuring dehydration, oligomerization, and hydrogenation, the consolidated alcohol dehydration and oligomerization (CADO) approach described here involves one-step conversion of aqueous ethanol to hydrocarbons and water over a metal-modified zeolite catalyst. During a 22-month project, liquid hydrocarbon yields were increased from 36% of theoretical to > 80%, cost of catalyst was reduced by an order of magnitude, and the process was scaled-up by 300-fold. Factors underlying catalyst cost reductions include use of doped commercial extrudates, > 5-fold decrease in metal concentrations, and a > 2-fold increase in catalyst life by modifying the silica to aluminum ratio. Based on these advances, the projected cost of ethanol conversion to fungible blendstocks was reduced by twelve-fold. Operating plus annualized capital costs for conversion of wet ethanol to fungible blendstocks are estimated at $2.00/GJ for CADO at its current state of development, and $1.44/GJ in the future – which is similar to the cost of purification to anhydrous ethanol ($1.46/GJ). Including the cost of ethanol from either corn or future cellulosic biomass but not production incentives, projected minimum selling prices for fungible blendstocks produced via CADO are competitive with conventional jet fuel when oil is $100/barrel, but not $60/barrel. For many of the existing production incentives, the projected minimum blendstock selling price is competitive with oil at $60/bbl.

Significance Statement

Decarbonizing heavy -duty transport sectors - i.e., aviation, ocean shipping, and long-haul trucking - is among the greatest challenges in moving to a sustainable economy and will likely require low-carbon liquid fuels. Ethanol can be produced from biomass feedstocks at lower cost than other liquid fuels and is currently produced in substantial volumes, but it cannot readily be used in today's jet and diesel engines. Conversion of wet ethanol to fungible hydrocarbon blendstocks at a similar cost per

GJ as production of anhydrous purified ethanol, projected here, represents a major advance and an opportunity to direct current and future biofuel production toward the applications for which they are most needed in order to stabilize the climate (<2°C).

Introduction

Global transportation sector greenhouse gas (GHG) emissions grew by 679 Megatonnes (Mt) CO_2e between 2011 and 2016 (1), more than any other sector, and recently surpassed electricity generation as the leading source of carbon emissions in the United States (2). Most analysts view electric vehicles in combination with low-carbon electricity generation as the leading option for decarbonizing the light-duty transport sector (3). For non-light-duty transport modes – including aviation, ocean shipping, and a significant fraction of long-haul trucking – on-board energy storage using batteries or hydrogen is much more challenging and continued use of energy-dense liquid hydrocarbon fuels is widely-anticipated (4,5,6). Even with aggressive reductions in travel growth, shifts to mass transport modes, strong efficiency improvements, and deep market penetration by vehicles running on electricity and hydrogen, liquid fuels are projected to be needed to meet about half of anticipated transport energy demand in 2075 (7). Fuels derived from plant biomass (biofuels) are widely regarded as the leading source for low-carbon liquid fuels (7,8).

Currently, one hundred billion liters of fuel ethanol are produced annually, accounting for over 98% of biologically-mediated production of liquid biofuels and supplying three quarters of biomass-derived liquid fuels of all kinds (9,10). The dominance of ethanol arises from production at near-theoretical thermodynamic yields, high titer, and low cost from easily-fermented carbohydrates in feedstocks such as maize, sugar cane, and sugar beets (11, 12). Commercial production of ethanol from cellulosic feedstocks is emergent but will require further technological advances to be cost-competitive (13, 14). Although an excellent fuel for spark-ignited engines (15), ethanol is not well suited for the jet and diesel engines in use today.

Decarbonizing the heavy-duty transport sector, including long-haul trucking, shipping, and aviation fuels, by using biofuels is being actively pursued via several strategies including producing fuel molecules other than ethanol from biomass (16-20), modifying engines to run on ethanol (21, 22), and producing ethanol as an intermediate followed by its conversion into a fungible hydrocarbon fuel (23-25). The latter approach is potentially attractive because of ethanol's low cost and large existing production capacity and is the focus here.

Most technologies for catalytic conversion of ethanol into hydrocarbons involve three steps prior to fractionation to meet fuel specifications: 1) ethanol dehydration to ethylene, 2) ethylene oligomerization to high molecular weight hydrocarbons, and 3) hydrogenation to saturate these oligomers to produce a finished renewable fuel that can be blended at high levels into conventional fuels. Chemistries and processes for converting ethanol into middle distillate fuels have recently been comprehensively reviewed (26) Published designs generally require inlet reactor temperatures > 400°C, pressures of 30 to 40 atm, and externally-supplied hydrogen. Companies such as LanzaTech in collaboration with Pacific Northwest National Laboratory (27) and Byogy Renewables (28) are pursing processes based on this concept. The ethanol conversion costs to jet fuel via such three-step approaches have been estimated at $3.38/GJ to $7.98/GJ ($0.11 to $0.26/L jet fuel) (29-33), with similar values for diesel. When combined with ethanol priced at between $17.4/GJ and $52.1/GJ ($0.37 to $1.11/L ethanol) together with reported yields, the range of jet fuel costs for the three-step process is $25.5/GJ to $86.7/GJ ($0.83 to $2.84/L) . For comparison, prices for petroleum-derived jet fuel in the United States have ranged from $7.9/GJ to $26.2/GJ ($0.26 to $0.80/L) over the last 5 years. Data from the literature are presented in the SI Appendix, **Table S1**.

An alternative approach involves one-step conversion of ethanol-water mixtures into hydrocarbon blendstocks and water over a metal-exchanged zeolite catalyst. A one-step conversion process in which dehydration and oligomerization of alcohols are accomplished in one reactor without addition of hydrogen was first proposed by Narula et al. (34). In their initial report on this technology, referred to here as consolidated alcohol dehydration and oligomerization (CADO), Narula et al. demonstrated complete conversion of ethanol, of which 36% was liquid (C5+) hydrocarbon using a laboratory powder catalyst and a reactor feed rate of 0.4 mL/hr. They also proposed a novel hydrocarbon pool mechanism describing reactions in which ethanol is directly converted into higher molecular weight hydrocarbons and water without intermediate production of ethylene. CADO offers low-cost potential relative to conventional catalytic upgrading approaches because it involves one processing step, can be carried out at near atmospheric pressure and 275 to 350°C, and does not require external hydrogen. However, liquid fuel yields reported previously have been low, catalyst, process development has been limited, and technoeconomic and life cycle analyses have not been reported.

Here we present recent advances in catalyst and process development for conversion of ethanol to fungible hydrocarbon fuel blendstocks via the CADO strategy. Current and projected costs of fungible blendstock production from ethanol vaporized from fermentation

broth are then compared to the cost of removing water from the same wet ethanol stream. Finally, we analyze the economics and life cycle greenhouse gas emissions for fungible blendstock production via CADO starting with a variety of current and future ethanol-production processes.

Results

Figure 1 summarizes the results of an intensive process development effort, including significantly increased liquid product yields compared to those previously-reported (Narula et al., 34). Optimization of operating conditions and catalyst formulations have increased liquid hydrocarbon yields from 36% of the theoretical maximum to > 80%. In addition to more than doubling liquid product yields, CADO has been progressively transitioned from powder to commercial catalyst formulations and supports that are industrially relevant. Finally, the cost of catalyst has been markedly reduced by 1) moving to doped commercial extrudates, 2) lowering metal concentrations from 6-10% reported previously (34), and 3) modifying the silica to alumina ratio to extend catalyst life in the presence of water.

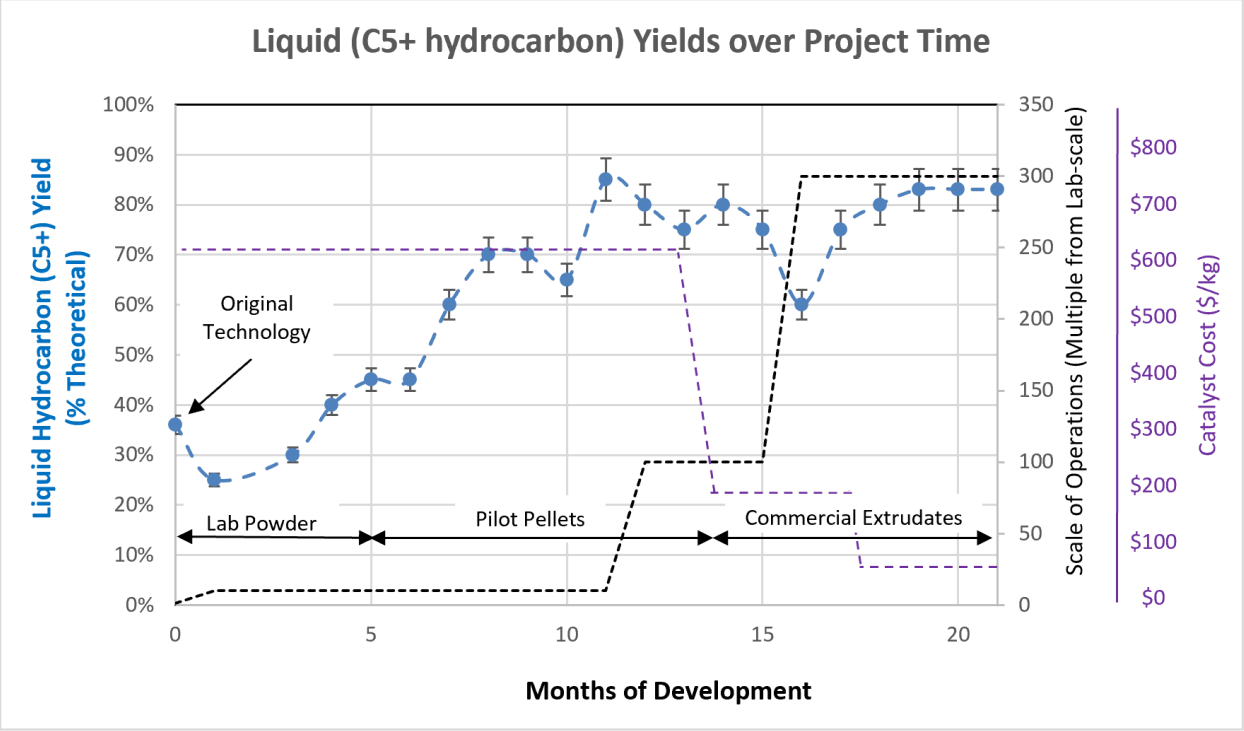


Figure 1. Increase in liquid hydrocarbon yields from consolidated alcohol dehydration and oligomerization (CADO) with research and development time and across increasing reactor scale of operation.

Figure 2 presents a representative catalytic run displaying liquid hydrocarbon products (C5+) along with tracking all other components (light components methane and ethylene shown here). The regeneration cycles are shown with dashed vertical lines generally after a day of operation though it is typical to extend run times until C5+ yields decrease below 70% before regeneration.

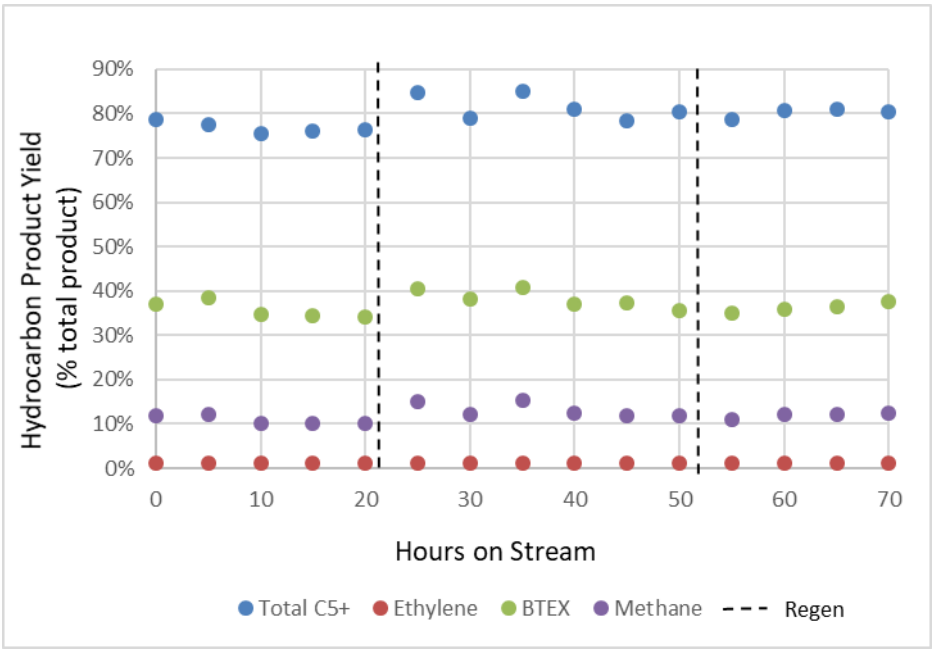


Figure 2. Catalytic consolidated alcohol dehydration and oligomerization run data with intermittent regenerations (dashed line)

Figure 3 presents the distribution of products obtained at the end of the project represented in **Figure 1** and **2**, including both the number of carbons and the breakdown of aromatics, aliphatics, and olefins. The product distribution obtained is concentrated in the C5 to C12 range, typical of gasoline blendstocks, with 40% by mass of the product distribution in the range typical of jet fuel (C7 to C16) and about 2% in the range typical of diesel (C10 to C20). Based on mechanistic considerations addressed in the discussion, we anticipate that this distribution can be shifted in the direction of higher molecular weight components. Noting that stoichiometric yields, market prices, and price supports are similar for gasoline, aviation fuel, and diesel (SI Appendix, **Table S2**), the analysis developed herein is presented in terms of fungible hydrocarbon fuel blendstocks, referred to as fungible blendstocks.

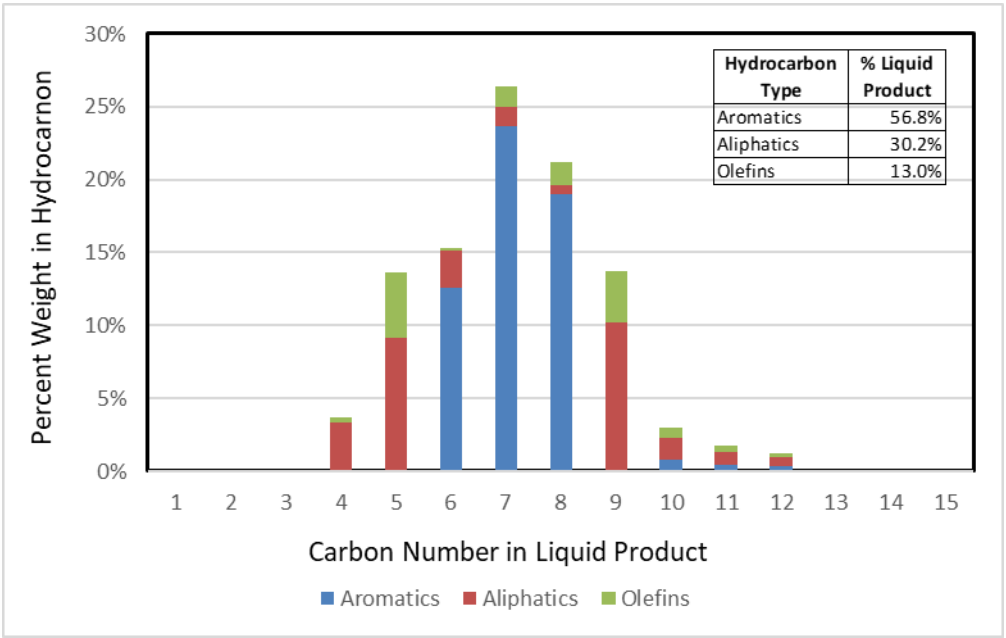


Figure 3. Current carbon number distribution of representative consolidated alcohol dehydration and oligomerization (CADO) hydrocarbon liquid product (gasoline range) and wet ethanol partial run data.

Comparative economic of converting wet ethanol vapor into anhydrous ethanol or fungible blendstocks. In an industrial facility producing ethanol with product recovery using distillation, a beer column separates ethanol-containing broth from fermentation into wet ethanol vapor exiting the top and water (as well as any solid residues) exiting the bottom. We assume that the concentration of this wet vapor is 40 wt.%, corresponding to a liquid feed concentration of approximately 6.4% wt (8.1% v/v), representative of a process producing second generation ethanol. Sensitivity of cost estimates to the concentration of ethanol leaving the beer column are expected to be small for CADO (for which CapEx is impacted) and somewhat larger for production of anhydrous ethanol from 40 wt.% ethanol vapor (for which OpEx as well as CapEx are impacted, particularly for the distillation steam). Costs are compared for converting wet ethanol vapor into either anhydrous ethanol or fungible blendstocks via CADO, assuming process configurations as outlined in **Figure 4**. Both cases are based on an annual ethanol production rate of 61 million gallons/year (231 million L/yr), typical of small ethanol plants in both the US and Brazil, and as assumed by the National Renewable Energy Laboratory (NREL) used in their technoeconomic analyses of cellulosic ethanol production (35).

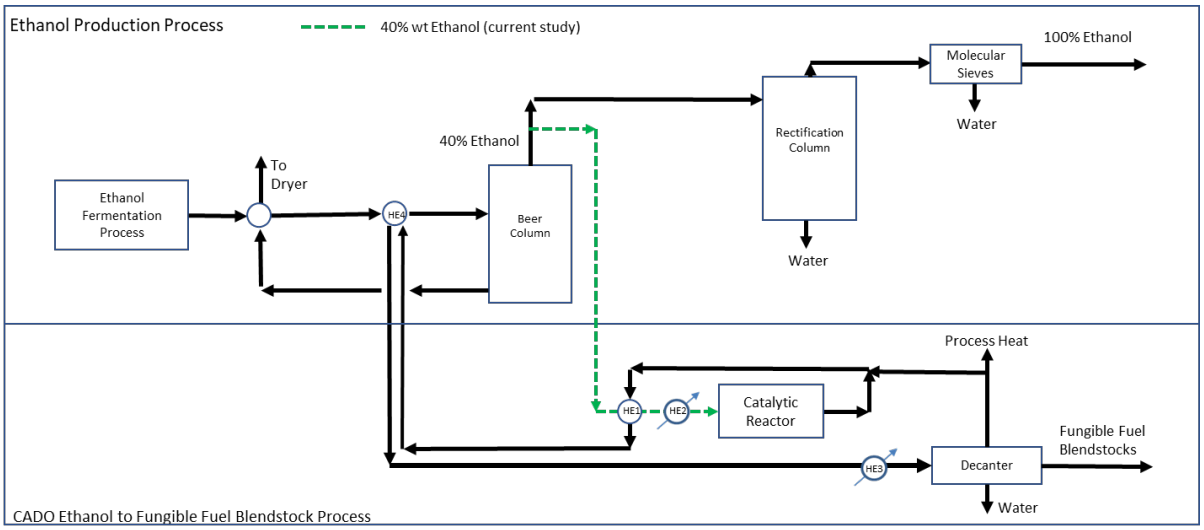


Figure 4. Block flow diagram illustrating 1) water removal from wet ethanol vapor above the feed tray to produce pure fuel grade ethanol or 2) consolidated alcohol dehydration and oligomerization (CADO) of the same wet ethanol to fungible blendstocks. HE refers to heat exchangers.

For the anhydrous ethanol case, wet ethanol vapor progresses to a rectifying column and then to molecular sieve dehydration. For CADO, wet ethanol vapor is fed to a catalytic reactor for conversion to liquid hydrocarbons, ethylene-free light gases, and water. This mixture is cooled to ambient temperature and fed to a three-phase separator from which water is drawn from the bottom, less dense liquid hydrocarbons from the middle, and non-condensable gases from the top. Most of the gas (~73% by mass) is recycled to the reactor for conversion to liquid fuels with the rest burned to reduce natural gas demand for process heat.

Operating Costs (SI Appendix, **Tables S3-S4**): The cost of producing fuel-grade ethanol from wet ethanol vapor is estimated using the 2011 NREL model (36). For conversion of wet ethanol into fungible blendstocks, current and future catalyst purchase prices of $70/kg and $30/kg, respectively, were estimated based on the NREL catalyst cost estimator (37) for current and future metal loadings and verified by consultation with a commercial catalyst manufacturer. A catalyst lifetime of 6 months was projected for laboratory powder and pilot pellets catalyst and extended to 9 months for current commercial and future catalysts based on half-lives estimated from 200-hour aging studies. An electricity price of $0.05/kWhr was applied, typical of the mid-western US. Catalyst replacement and electricity account for about 60% of operating costs. An additional cost of $1.85/1,000 Liters of treated water was included for chemical wastewater treatment additives to remove dissolved hydrocarbons. Catalyst disposal costs account for the cost of returning spent catalyst to the provider at a unit cost of $2000/tonne. Costs for insurance, taxes, and maintenance were used to be consistent with the NREL anhydrous ethanol model. Labor requirements for conversion of fungible blendstocks to ethanol are assumed to be similar to those for ethanol dehydration, since the unit operations involved are of comparable complexity. Labor was included although it is likely no additional personnel would be needed in that the operators responsible for running the rectification and

molecular sieves for ethanol dehydration would oversee operation of the catalyst bed (labor costs are comparable in SI Appendix, **Tables S4-S5**).

Capital Costs (SI Appendix, **Table S6**): Capital costs of $19.7 million for production of anhydrous ethanol from wet ethanol vapor were estimated using the NREL model adjusted to 2019 dollars (36). Capital costs were annualized by multiplying them by 0.15, corresponding to amortization over a 10-year period at a 12% interest rate. Based on this methodology, the annualized cost of capital contributes $0.031/L of anhydrous ethanol ($1.46/GJ LHV).

For production of fungible blendstocks from wet ethanol vapor, the major CADO equipment items are two catalytic reactors (to allow for catalyst regeneration), a 3-phase decanter, and four heat exchangers, with ancillary equipment includes pumps and load out systems. Fungible blendstock and water product storage tank requirements are assumed to be the same as for ethanol storage. The low concentrations of dissolved hydrocarbons (typically 600-1500 ppm) left in water from the decanter were from the water and sent to wastewater treatment. A compressor was included to provide the 0.417 MPa pressure needed to pass wet ethanol through the reactor, as well as a second compressor to recycle gases (compressors may not be required in cases where distillation is under pressure). The overall result was an estimated total installed capital cost of approximately $15.3 million, equivalent to $0.067/L of ethanol feed or $0.121/L of fungible blendstocks. Capital costs for processing via CADO were assumed, perhaps conservatively, to be the same for current and future technology. Applying the same 0.15 capital recovery factor as as for anhydrous ethanol, results in an annualized cost capital cost contribution of $0.018/L ($0.56/GJ LHV) for ethanol conversion to fungible blendstocks via CADO.

Figure 5 shows operating plus annualized capital costs for converting wet ethanol vapor into fungible blendstocks at four time points of the technology evolution history depicted in **Figure 1**, and also for projected future advances. Based on yields, catalyst costs, and lifetimes consistent with **Figure 1** and detailed in **Table S7 in** the SI Appendix. The cost of producing anhydrous ethanol from wet ethanol vapor is shown for comparison. It may be observed that the total conversion cost (operating plus annualized capital) was reduced 12.0-fold from the departure point established by Narula et al. (34). Current technology for fungible blendstock production via CADO exceeds that of ethanol distillation and dehydration by $0.54/GJ, or about $0.018/L. With anticipated future improvements, the total cost of fungible blendstock production from wet ethanol vapor via CADO is very nearly equal (within 3%) to that for ethanol distillation and dehydration to meet fuel grade requirements.

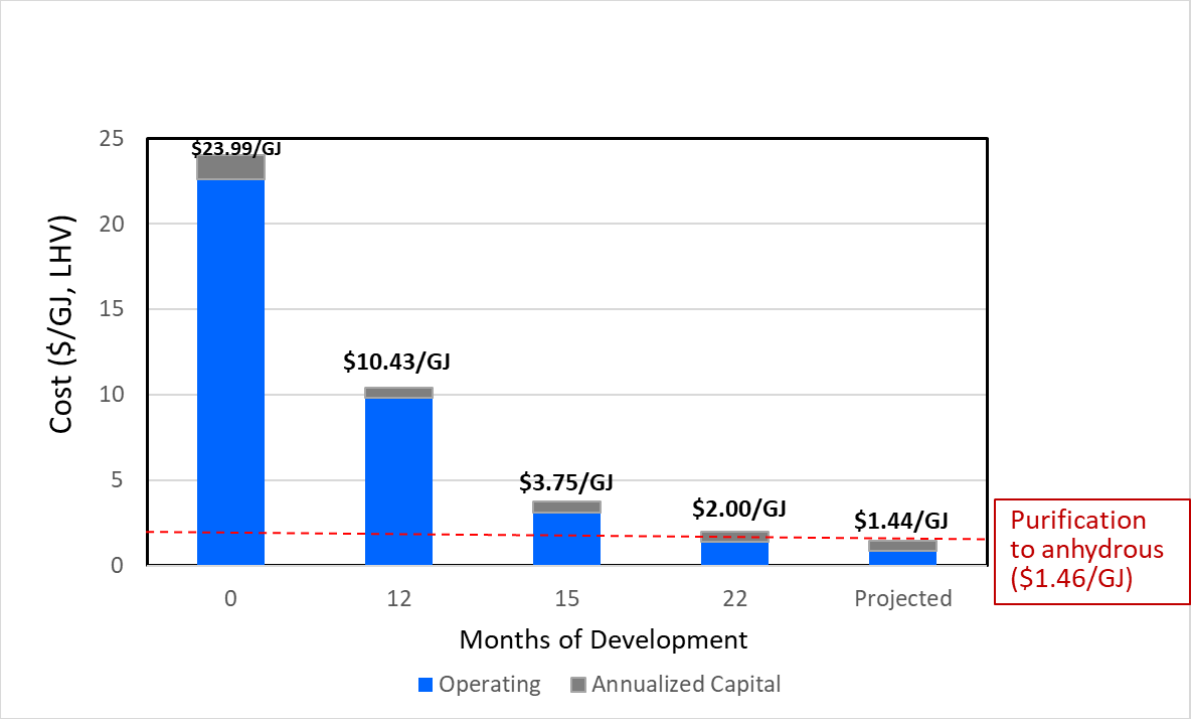


Figure 5. Migration of the total operating plus annualized capital cost for converting ethanol into fungible blendstocks via consolidated alcohol dehydration and oligomerization. The cost of ethanol is not included. Values are calculated based on lower heating values.

Economics and life cycle analyses including ethanol production

Economics: We evaluate the economic competitiveness of producing fungible blendstocks via current and future

CADO technology using ethanol derived from corn, sugar cane juice, corn stover by current and future cellulose conversion technology, and combined conversion of sugar cane juice and cellulosic feedstocks (bagasse and leaves) by current and future cellulose conversion technology.

Projected ethanol costs were calculated based on operating cost estimates from the sources cited plus an annualized capital cost determined by multiplying the total capital by 0.15,as noted above. Because biomass feedstock prices fluctuate (e.g., corn), average feedstock prices were applied, and processes were treated as greenfield facilities even though most US corn ethanol plants have been fully amortized. Costs of 40% ethanol vapor presented in **Table S5** of the SI Appendix were estimated by subtracting the cost of distillation and dehydration of this stream from the overall cost of making fuel grade ethanol.. The minimum blendstock product selling price (MBSP) was calculated from the ethanol cost, mass yield of fungible blendstock fuel per unit ethanol, and price of the ethanol-to-fungible blendstocks conversion as presented in **Figure 5** and SI Appendix **Table S7**). The projected MBSP was compared to historical wholesale prices of jet fuel when petroleum cost $60/bbl and $100/bbl (38). In particular, we found that jet fuel sells for ~19% more than petroleum on a volumetric basis – e.g., at wholesale oil prices of $76/bbl or $1.81/gal, wholesale jet prices were $2.15/gal or ~19% higher.

The results shown in **Table** 1 indicate that conversion of ethanol to hydrocarbon blendstock fuels can be competitive for several ethanol production platforms (current corn and cane sugar, cane cellulosic, and corn stover future) when crude oil is priced at $100/bbl but not at lower oil prices without some form of price support.

Table 1: Estimated operating plus annualized capital costs of fungible blendstocks made by consolidated alcohol dehydration and oligomerization (CADO) of ethanol produced from several biomass sources.

Ethanol Feedstock	Technological Maturity		Ethanol Selling Price ($/L)[a]				EtOH->Jet Fuel Conversion		Minimum Blendstock Selling Price MBSP ($/L)			
	Ethanol Production	**Ethanol --> Blendstock**	Prices 5 year & (current)	Projected	Est 40% EtOH Prices 5 year & (current)	Est 40% EtOH Projected	Yield (L Blend/L EtOH)	Cost ($/L Blend) [c]	From Ethanol [d]		From Petroleum[e]	
									@market	@projected price	$60/bbl	$100/bbl
FIRST GENERATION												
Corn Starch	Current	Current	0.46 (0.31)	------	0.429 (0.279)	------	0.487	0.065	0.95 (0.64)	------	0.48	0.80
		Projected	0.46 (0.31)		0.429 (0.279)		0.548	0.047	0.83 (0.56)			
Cane Juice	Current	Current	0.56 (0.41)		0.529 (0.379)		0.487	0.065	1.15 (0.84)			
		Projected	0.56 (0.41)		0.529 (0.379)		0.548	0.047	1.01 (0.74)			
SECOND GENERATION												
Cane Cellulosic	Current	Current	------	0.53	------	0.499	0.487	0.065	------	1.09		
	Projected	Projected		0.45		0.419	0.548	0.047		0.81		
Corn Stover	Current	Current		0.86		0.829	0.487	0.065		1.77		
	Projected	Projected		0.41		0.379	0.548	0.047		0.74		

[a] First generation (1G) corn starch and cane sugar prices are based on average market values over past 5 years (inflated by 1.5% average inflation (https://tradingeconomics.com/united-states/inflation-cpi) over past 5 years to obtain 2019$) and current market prices. Corn ethanol coproduct is DDGs and cane sugar co-product is electricity.

[b] Second generation (2G) sugarcane bagasse (named Cane cellulosic) and corn stover (estimate of minimum ethanol selling price) from respective sources updated to 2019$. OpEx includes feedstock and coproducts. Sugarcane (current and projected) (39), corn stover (current)(36), corn stover (projected)(40)

[c] Conversion costs from SI Appendix, **Tables S3-S4,** plus annualized capital costs

[d] Hydrocarbon price from ethanol based on minimum ethanol selling price/yield + conversion cost.

[e] Hydrocarbon price from petroleum based on oil cost per liter + 18.7% (average jet fuel premium over oil last 10 years) + (adjusted for 1.5% inflation over past 10 years)

Life-Cycle Analysis: Table 2 presents a breakdown of well-to-wheel (WTW) greenhouse gas emissions (GHG) for application of CADO to ethanol made from corn, cane sugar, cane cellulosic material, and corn stover. For ethanol produced by "first generation" processes involving easily-fermented feedstocks and established technology, overall GHG emissions for jet fuel production (used for comparison) are reduced compared to production from petroleum by 40% for corn starch and 69% for sugar cane juice. For ethanol produced by "second generation" processes which include conversion of lignocellulose via emergent technologies, GHG emissions are reduced by 69.6% for conversion of corn stover by current CADO and cellulosic technologies,, by around 80 % for combined conversion of sugar cane juice and cellulosic material by existing processes coupled with either current or future CADO technologies, and by 96% for corn stover with future conversion technology, each compared to GHG emissions for production of hydrocarbons from petroleum. The GHG emissions from application of CADO to corn starch ethanol

are slightly higher than those for application to sugar cane and corn stover ethanol because both of the latter have lower farm-related GHG emissions and can burn lignin to generate all the steam and electricity needed for making jet fuel via CADO while corn starch ethanol relies on fossil energy. The credit included in Table 2 (73 gCO_2e/ MJ of hydrocarbon fuel in this case) for recapture of carbon dioxide released during combustion by growing new plants (biogenic carbon) had a significant impact on keeping life-cycle GHG emissions low for fuels produced from biomass compared to fuel produced from fossil sources. The ethanol conversion values presented in **Table 2** were calculated using the Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model default information (Wang 2012, GREET 2018) (41, 42) for corn-based scenarios and the Virtual Sugarcane Biorefinery (Bonomi et al., 2016) (43) for sugarcane-based ones. However, these values were slightly modified to reflect energy savings for use of 40% ethanol, rather than anhydrous ethanol, as the CADO feedstock (Fig. 3). In particular, credits were taken for avoiding distillation energy to produce anhydrous ethanol from 40 wt.% ethanol, i.e., 25 GJ/hr (23.5 MMBtu/ hr, 0.0016 GJ/L) for natural gas, and 2.6 GJ/hr (710 kW, 0.00017 GJ/L) for electricity.

Table 2. Greenhouse gas emissions for production of jet fuel by application of CADO to ethanol made from starch, sugar, cane cellulosic material, and corn stover and by conventional production from petroleum.

From Ethanol						From Petroleum	
Ethanol feedstock	Conversion technology	Emission (gCO_2 e/ MJ of fungible blendstock)					
		Feedstock production and ethanol conversion	Catalytic conversion of ethanol	Jet fuel use	WTWa[e,f]	PTWa[g]	WTWa
First Generation						73.2	87.3
Corn starch [a]	Current	45.5	6.7	0.2	52.4 -40.0%		
Cane sugar [b]	Current	23.8	3.2	0.2	27.2 -68.8%		
Second Generation							
Cane cellulosic [b,c]	Current	14.5	3.2	0.2	17.9 -79.5%		
Cane cellulosic [b,c]	Projected	13.9	3.2	0.2	17.3 -80.2%		
Corn stover [d]	Current	23.2	3.2	0.2	26.6 -69.5%		
Corn stover [d]	Projected	0.13	3.2	0.2	3.53 -96.0%		

[a] Provided by Argonne National Laboratory - energy inputs for Corn Stover Base Case by the National Renewable Energy Laboratory: Technical Report NREL/TP-5100-47764 (36).

[b] Provided by Brazilian Bioethanol Science and Technology Laboratory based on Dias et al. (2016)(39).

[c] Cane cellulosic refers to an integrated first- and second-generation process in Brazilian context.

[d] Provided by Argonne National Laboratory based on previous study by Lynd et al. (40). Corn Stover Base Case based on National Renewable Energy Laboratory: Technical Report NREL/TP-5100-47764 (36).

[e] WTWa: well-to-wake which includes the full supply, production and use chain.

[f] Negative percent values represent percentage of GHG emission reduction compared to petroleum jet fuel.

[g] PTWa: pump-to-wake which includes combustion of fuel in an aviation system.

Values for catalytic conversion include emissions due to transportation and distribution of ethanol, estimated at 0.85 gCO_2e/MJ.

Impact of Production Incentives. We also investigated how the following production incentives influence the competitiveness of fungible fuel blendstocks made from the ethanol production processes considered in **Table 1**: 1) none, 2) a conservative shadow price of \$40/tonne CO_2 emissions avoided used by some multinationals including oil majors oil companies BP, Shell and Statoil for planning purposes (44),3) the threshold of \$100/tonne CO_2 avoided / sequestered used by the Griscom et al. in assessing 'natural' negative emission technologies (45), 4) Renewable Identification Numbers (RINs) applied under the United States Renewable Fuel Standard (D3 or D7 for cellulosic feedstocks, D5 for cane juice feedstocks, D6 for starch feedstocks) (46), and 5) values associated with the California Low-Carbon Fuel Standard (LCFS) (61). Documentation is provided in **Table S8** in the SI AppendixPayback period is calculated based on capital cost divided by net revenue, with net revenue defined as blendstock selling price plus production incentives minus the cost of ethanol and conversion costs).

Figure 6 presents the payback period associated with each ethanol production process and technological maturity, with blendstock selling price based on oil priced at either \$60 or \$100/bbl. With oil priced at \$60/barrel and no production incentives, none of the combinations of ethanol feedstocks and conversion technologies had positive net revenue. With oil prices at \$100/barrel but no production incentives, positive net revenue and payback periods < 3 years are realized for corn starch ethanol with either current or projected catalytic conversion, sugar cane juice ethanol with projected catalytic conversion, and corn stover ethanol with projected ethanol production and catalytic conversion technologies.

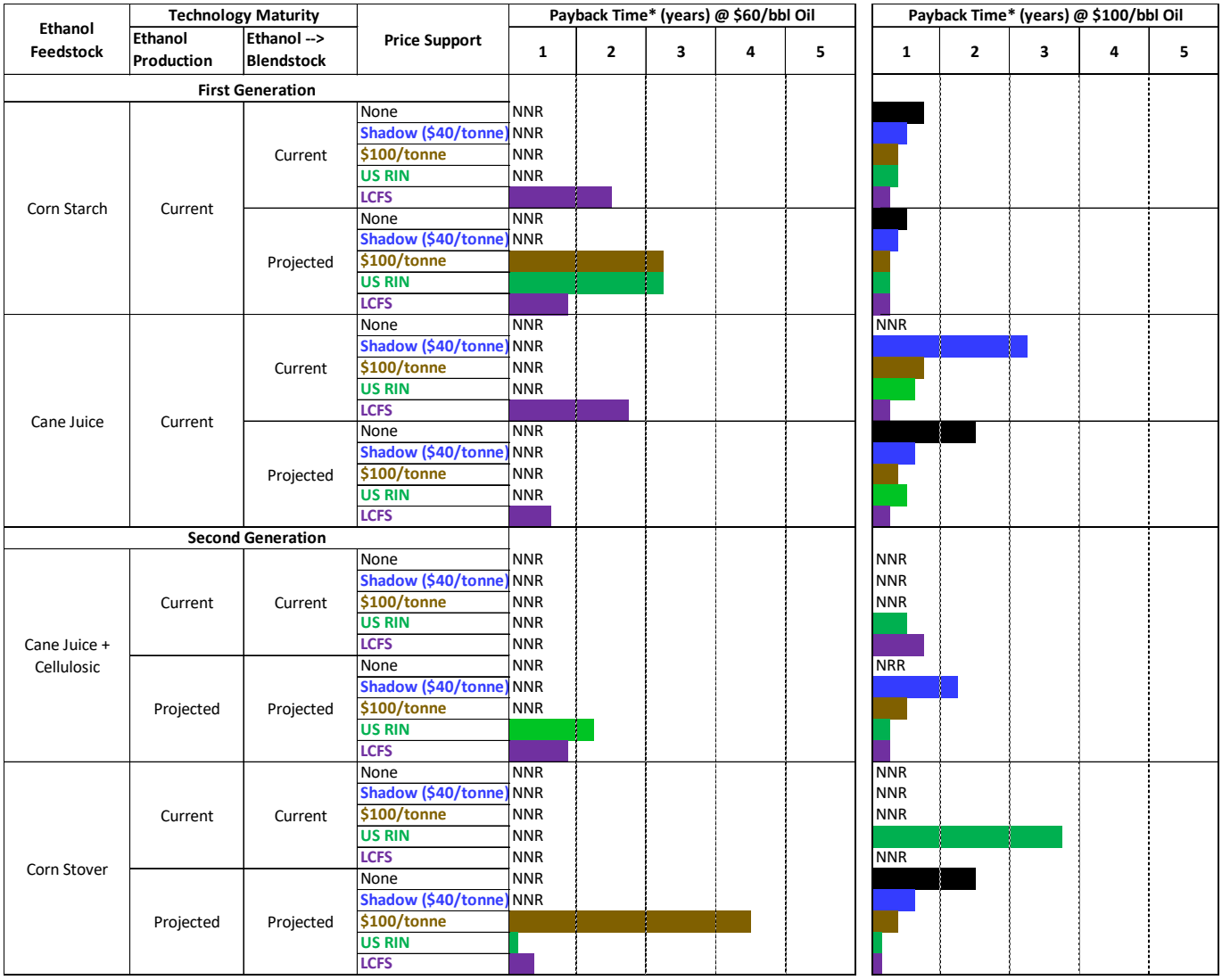


Figure 6. Effect of renewable fuel incentives (D6 RINs for corn starch ethanol, D5 RINs for cane juice ethanol, D3 or D7 RINs for cellulosic ethanol, and oil industry shadow price ($40/tonne CO_2 emissions avoided), $100/tonne CO_2 emissions avoided, and the California Low Carbon Fuel Standard (LCFS) on payback periods for production of hydrocarbon blendstocks by application of current CADO technology to wet ethanol (40wt%) made from corn starch and cane sugar and application of future CADO technology to conversion of wet ethanol as described in the text. NNR: negative net revenue.

The picture changes substantially with production incentives. With oil at $100/bbl, payback periods of < 3 years are realized for all technologies except for corn stover or with shadow or US$100/tonne production incentives for cane juice + cellulosic ethanol using current production and CADO technologies. US RINs also provide sufficient economic incentives to provide a < 2 year payback period with the exception of the corn stover (current) scenario, for which the payback period is estimated at 2.7 years. At $60/bbl oil price, an avoided carbon value of $40/tonne CO_2 ('shadow') is not sufficient to generate a positive net revenue and even at a carbon value of $100/tonne CO_2 avoided only corn starch projected and corn stover projected achieve payback periods of 2 years or less. With oil at $100/barrel and either the LCFS, the US RIN, or a CO_2 price of $100/tonne, payback periods of<2 years are realized for all combinations of ethanol production and conversion technologies except corn stover ethanol current production and conversion technology. We note that the payback period is more sensitive to improvements in second generation ethanol production technology than in improvements in catalytic conversion of ethanol.

Discussion

Carbohydrate conversion to ethanol via fermentation and catalytic conversion of that ethanol to fungible hydrocarbon blendstocks via a dehydration mechanism each realize energy efficiencies > 95%, and an overall energy efficiency for the two-steps combined of > 93% (SI Appendix, **Figure S1**) with energy efficiencies

demonstrated to achieve most of this potential. Given favorable thermodynamics, the main driver to be addressed is cost. Whereas the three-step process described in prior literature has been estimated to add $3.38/GJ to $7.98/GJ ($0.11 to $0.26/L jet fuel) to the cost of ethanol, the CADO process described herein is estimated to add $0.54/GJ ($0.018/L fungible fuel blendstocks) in its current state of development and no cost compared to the cost of anhydrous ethanol in the future based on modest anticipated cost reductions and future yield increases.

Actual and calculated selling prices for ethanol produced by current and foreseen processes including both first-generation and second-generation biomass feedstocks are in general equal to or greater than the selling price of petroleum-derived jet fuel on a $/GJ basis. Thus, even with high efficiency and low conversion costs, the selling price of ethanol-derived jet fuel or diesel will at best be equal to the cost of conventional jet fuel as presented in **Table 1**. With several current production incentives, production of fungible blendstocks via CADO from ethanol produced from several current and future biomass feedstocks and processes becomes cost-competitive (Fig. 5). Market willingness to pay a premium for low-carbon fungible blendstocks is strong in some locations and is likely to become more widespread over time. A 50% reduction in greenhouse gas emissions over the next two decades, only possible with low-carbon fuels, has been endorsed by both the aviation (47) and shipping (48) industries. Boeing is aware of 9 airlines who have signed off-take agreements for biomass-derived aviation fuels. Although current production of low carbon jet fuel is still low, it is expected to reach 2% of total projected demand by 2025.

We report here results from operation at a scale of up to 0.12 L ethanol processed/hr, but scale up to 2.0 L/hr is underway. A first commercial plant, for example processing 15 $x10^6$ L/yr ethanol, would require further scale-up by a factor of about 1000-fold, well within the range supported by experience for commercialization of processes based on gas-phase heterogenous catalysis (49-52). Thus, CADO is currently being operated at a scale that will support commercial implementation as the next step.

CADO has thus far made a distribution of products corresponding most closely to gasoline blendstocks (**Figure 3**). However, we hypothesize that this distribution can be shifted to ranges typical of aviation fuel (C7 to C16) and diesel (C10 to C20) by catalyst changes and/or further development based on such strategies as shifting catalyst pore size (53,54). Such changes/development are also known to impact the aromatics fraction (55, 56).

In its current state of development and taking into account aromatic content limits, we estimate that CADO-derived blendstocks could be blended at 20% with petroleum-derived jet fuel and somewhat more than that for gasoline, although verification and certification remain to be carried out. Using/blending low-carbon, biomass-derived hydrocarbons at yet higher levels could be enabled by a) improving CADO catalysts and processes, b) blending CADO-derived fuels with those derived from other processes that have lower aromatic content such as from Fischer-Tropsch (57) and LanzaTech processes (58), c) separating CADO-derived products into fractions desirable for a range of fuel and chemical applications, or d) combinations of the above. Given this range of possibilities, we do not include separation costs in this analysis. However, we also do not include revenue from chemical coproducts with higher value than fuels, which likely could be realized if a fractionation step were included.

The economics of an integrated greenfield plant producing partially-purified ethanol as an intermediate for subsequent conversion to fungible blendstocks via CADO, analyzed here, are somewhat more favorable than adding CADO as a bolt-on to an existing ethanol production facility. Although not large, this advantage arises because an integrated greenfield plant would not need to incur the cost to produce anhydrous ethanol. On the other hand, CADO has a low capital cost, CADO-mediated fungible blendstock could be quickly added to existing ethanol plants, thereby rapidly building low-carbon aviation fuel production capacity while realizing attractive investment returns and increasing product diversity for biofuel producers.

The 28% reduction in cost projected for future CADO derived fungible blendstocks to $1.44/GJ compared to the current estimate of $2.00 is less than the post-commercialization cost reductions observed historically for industrial processes and in particular processes based on gas-phase heterogeneous catalysis (59-60). As with all cost estimates, actual CADO costs can vary from those projected here due to such factors as location, time, and equipment costs.

Producing fungible hydrocarbon blendstocks at a similar cost per GJ as anhydrous ethanol, as foreseen here, represents a major advance and an opportunity to direct current and future biofuel production toward applications most needed in order to achieve climate stabilization.

Methods

TechnoEconomic Analysis (TEA) Methodology: Operating costs were based on mass and energy balances for wet ethanol to both fungible hydrocarbon blendstocks and anhydrous ethanol. For the consolidated alcohol dehydration and oligomerization catalytic conversion (CADO) approach, operating costs were estimated for waste water treatment, catalyst, electricity, waste disposal, insurance and taxes, and labor. It was assumed that all water from the process was directed to standard wastewater treatment at a cost of $1.85/1000 Liters

($7/1000 gallons). The reactor catalyst was assumed to be replaced at 6 and 9 month intervals for current ($70/kg) and future ($30/kg) CADO technology, respectively. The electricity unit cost of $0.05/kWh was taken to be representative of the Midwest where most U.S. ethanol is produced, with demand mainly to power compressors and pumps. Insurance and local taxes were calculated as 2.0% of Total Installed Capital (TIC), maintenance at 3.0% of TIC, and labor at 1.0% of TIC. For the wet alcohol conversion to anhydrous ethanol, mass and energy balances along with unit costs employed by NREL were utilized (36) along with the same factors for insurance and taxes, maintenance and labor, 2.0% TIC, 3.0% TIC, and 1.0% TIC, respectively.

Equipment sizes were calculated based on and energy balances and coupled with costs for similar equipment reported in NREL TP 47764 and Matche (http://www.matche.com/) to estimate capital costs. A 0.60 scale-up power was used to estimate the change in equipment costs with scale-up from the reference sizes reported by NREL, and installation factors comparable to NREL TP 47764 were implemented. Equipment costs were inflated at an average 1.5% (average yearly equipment inflation over the past 10 years) to 2019 values. Installation factors from NREL TP 47764 were used to estimate installed capital costs.

Life-cycle analysis (LCA) methodology: The GREET (Greenhouse Gas Regulated Emission and Energy used in Transportation) model developed by Argonne National Laboratory through funding by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (EERE) was applied to calculate life cycle GHG emissions of producing one MJ of hydrocarbons from corn starch and corn stover by current and advanced conversion technologies. Existing GREET results were used for conventional jet fuel production from fossil-derived sources (42). It was assumed that the fuel was produced and used in the US for corn, corn stover and petroleum feedstocks. Similarly, since most sugarcane ethanol is produced and used in Brazil, life cycle GHG impacts of ethanol production from cane juice and cane cellulosic by current and advanced conversion technologies were calculated using the Virtual Sugarcane Biorefinery model (43). Feedstock production included farming activities (e.g., fertilizer and pesticide applications), feedstock collection, and transportation to the biorefinery where ethanol was produced (conversion to ethanol in **Figure S2**). The second part of the analysis for ethanol conversion to hydrocarbons included the catalytic operation, product recovery, and hydrocarbon transportation, distribution, and storage. The system boundary also encompassed end-of-life of the CADO product, in this case, combustion for powering aviation. Details of the LCA input information are shown in **Table S9** of the SI Appendix.

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