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Technoeconomic and life-cycle analysis of single-step catalytic conversion of wet ethanol into fungible fuel blendstocks

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Technoeconomic and life-cycle analyses are presented for catalytic conversion of ethanol to fungible hydrocarbon fuel blendstocks, informed by advances in catalyst and process development. Whereas prior work toward this end focused on 3-step processes featuring dehydration, oligomerization, and hydrogenation, the consolidated alcohol dehydration and oligomerization (CADO) approach described here results in 1-step conversion of wet ethanol vapor (40 wt% in water) to hydrocarbons and water over a metal-modified zeolite catalyst. A development project increased liquid hydrocarbon yields from 36% of theoretical to >80%, reduced catalyst cost by an order of magnitude, scaled up the process by 300-fold, and reduced projected costs of ethanol conversion 12-fold. Current CADO products conform most closely to gasoline blendstocks, but can be blended with jet fuel at low levels today, and could potentially be blended at higher levels in the future. Operating plus annualized capital costs for conversion of wet ethanol to fungible blendstocks are estimated at \$2.00/GJ for CADO today and \$1.44/GJ in the future, similar to the unit energy cost of producing anhydrous ethanol from wet 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 per barrel but not at \$60 per barrel. However, with existing production incentives, the projected minimum blendstock selling price is competitive with oil at \$60 per barrel. Life-cycle greenhouse gas emission reductions for CADO-derived hydrocarbon blendstocks closely follow those for the ethanol feedstock.

low-carbon fungible fuel blendstocks | ethanol | heterogeneous catalysis

Global transportation sector greenhouse gas (GHG) emissions grew by 679 Megatonnes (Mt) CO₂e 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 reducing fossil carbon emissions from the light-duty transport sector (3). For nonlight-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 (4–6). 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, 100 billion liters of fuel ethanol are produced annually, accounting for over 98% of biologically mediated production of liquid biofuels in the United States 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 compression ignition engines in use today.

Reducing fossil carbon emissions in 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 (23–26). The latter approach is potentially attractive because of ethanol's low cost and large existing production capacity, and is the focus here.

This paper results from the Arthur M. Sackler Colloquium of the National Academy of Sciences, "Status and Challenges in Decarbonizing our Energy Landscape," held October 10–12, 2018, at the Arnold and Mabel Beckman Center of the National Academies of Sciences and Engineering in Irvine, CA. National Academy of Sciences colloquia began in 1991 and have been published in PNAS since 1995. From February 2001 through May 2019 colloquia were supported by a generous gift from The Dame Jillian and Dr. Arthur M. Sackler Foundation for the Arts, Sciences & Humanities, in memory of Dame Sackler's husband, Arthur M. Sackler. The complete program and video recordings of most presentations are available on the National Academy of Sciences website at <http://www.nasonline.org/decarbonizing>.

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Most technologies for catalytic conversion of ethanol into hydrocarbons involve 3 steps prior to fractionation to meet fuel specifications: 1) Ethanol dehydration to ethylene, 2) ethylene oligomerization to higher 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 (27). 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 (28), and Byogy Renewables (<http://www.byogy.com/technology>) are pursuing processes based on this concept. The ethanol conversion costs to jet fuel via such 3-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 3-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 y. Data from the literature are presented in *SI Appendix, Table S1*.

An alternative approach involves 1-step conversion of ethanol-water mixtures into hydrocarbon blendstocks and water over a metal-exchanged zeolite catalyst. A 1-step conversion process in which dehydration and oligomerization of alcohols are accomplished in 1 reactor without addition of hydrogen was proposed by Narula et al. (34). In their report on this technology, referred to here as consolidated alcohol dehydration and oligomerization (CADO), Narula et al. demonstrated complete conversion of anhydrous ethanol, of which 36% was liquid (C5+) hydrocarbon using a laboratory powder catalyst and a reactor feed rate of 0.4 mL/h. Narula et al. also reviewed previous ethanol-to-hydrocarbon work from the 1970s and investigated water/ethanol cofeeding, reporting that 10 to 100% ethanol concentration in water had no effect on conversion or product distribution. They also proposed a hydrocarbon pool mechanism describing reactions in which ethanol is directly converted into higher molecular weight hydrocarbons and water with minimal intermediate production of ethylene. CADO offers low-cost potential relative to conventional catalytic upgrading approaches because it involves 1 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 (TEA) and life-cycle analyses (LCA) 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 (40 wt% ethanol in water vapor). Finally, we analyze the economics and life cycle GHG emissions for fungible blendstock production via CADO starting with a variety of current and future ethanol-production processes.

Results

Fig. 1 summarizes the results of an intensive process development effort, including significantly increased liquid product yields compared to those previously reported (34, 35). Optimization of operating conditions and catalyst formulations have increased liquid hydrocarbon yields from 36% (“Original technology” in Fig. 1) of the theoretical maximum (0.609 g hydrocarbons/1.0 g of ethanol) 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

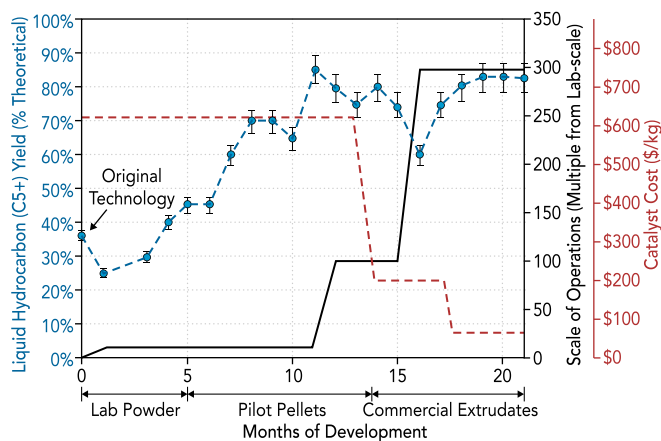


Fig. 1. Increase in liquid hydrocarbon yields from CADO with research and development time and across increasing reactor scale of operation (catalyst cost progression: 1) Expensive powdered and pilot catalysts at 6 to 10 wt% metal loading, 2) inexpensive commercial catalyst at 6 to 10 wt% metal loading, 3) commercial catalyst at <1 wt% loadings).

catalyst has been markedly reduced by 1) moving to doped commercial extrudates, 2) lowering metal concentrations from 6 to 10% reported previously (34, 35), and 3) modifying the silica-to-alumina ratio to extend catalyst life in the presence of water.

Fig. 2 presents a representative catalytic run displaying liquid hydrocarbon products (C5+) along with tracking all other components (light components methane and minimal ethylene shown here). The regeneration cycles are shown with dashed vertical lines generally after a day of operation, although it is typical to extend run times until C5+ yields decrease below 70% before regeneration. Note that ~40 wt% of liquid products are in the form of aromatic BTEXs (benzene, toluene, ethyl benzene, xylenes).

Fig. 3 presents the distribution of products obtained at the end of the project represented in Figs. 1 and 2, including both the carbon number 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 wt% 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.

Comparative Economic of Converting Wet Ethanol Vapor into Anhydrous (100%) 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 ~6.4 wt% (8.1 vol/vol%), representative of a process producing second-generation ethanol (36). Sensitivity of cost estimates to the concentration of ethanol leaving the beer column are expected to be small for CADO (for which capital costs [CapEx] is impacted) and somewhat larger for production of anhydrous ethanol from 40 wt% ethanol vapor (for which operating costs [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

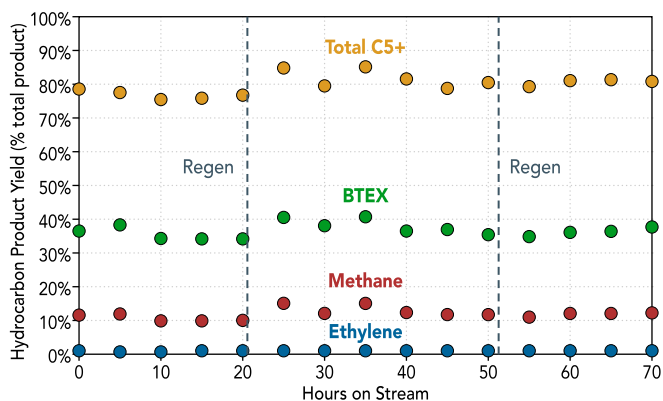


Fig. 2. Catalytic consolidated alcohol dehydration and oligomerization run data with intermittent regenerations (dashed line).

outlined in Fig. 4. Both cases are based on an annual ethanol production rate of 61 million gal/y (231 million L/y), typical of small ethanol plants in both the United States and Brazil, and as assumed by the National Renewable Energy Laboratory (NREL) in their TEA of cellulosic ethanol production (36).

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 3-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 and 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 mo was projected for laboratory powder and pilot pellets catalyst and extended to 9 mo for current commercial and future catalysts based on half-lives and extrapolation estimated from 200-h aging studies. Longer-term aging studies would increase the confidence of these estimates. An electricity price of \$0.05/kWh was applied, typical of the midwestern United States. Catalyst replacement and electricity account for about 60% of operating costs. An additional cost of \$1.85/1,000 L 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 \$2,000 per ton. Costs for insurance, taxes, and maintenance were used to be consistent with the NREL anhydrous ethanol model (36). 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 could oversee operation of the catalyst bed (labor costs are comparable in SI Appendix, Tables S4 and S5).

Capital Costs (SI Appendix, Table S6). CapEx of \$19.7 million for production of anhydrous ethanol from wet ethanol vapor were estimated using the NREL model adjusted to 2019 dollars (36).

CapEx were annualized by multiplying them by 0.15, corresponding to amortization over a 10-y 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 lower heating value [LHV]).

For production of fungible blendstocks from wet ethanol vapor, the major CADO equipment items are 2 catalytic reactors (to allow for catalyst regeneration), a 3-phase decanter, and 4 heat exchangers, with ancillary equipment including 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 to 1,500 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). A compressor is conservatively included in our design, although a back pressure-controlled flash system might well be used in practice for a greenfield plant. The overall result was an estimated total installed CapEx of approximately \$15.3 million, equivalent to \$0.067/L of ethanol feed or \$0.121/L of fungible blendstocks. CapEx for processing via CADO were assumed to be the same for current and future technology. Applying the same 0.15 capital recovery factor as for anhydrous ethanol, results in an annualized cost CapEx contribution of \$0.018/L (\$0.56/GJ LHV) for ethanol conversion to fungible blendstocks via CADO.

Fig. 5 shows operating plus annualized CapEx for converting wet ethanol vapor into fungible blendstocks at 4 time points of the technology evolution history depicted in Fig. 1, and also for projected future advances, based on yields, catalyst costs, and lifetimes, consistent with Fig. 1 and detailed in SI Appendix, Table S7. The cost of producing anhydrous ethanol from wet ethanol vapor is shown for comparison. The total conversion cost (operating plus annualized capital) was reduced 12-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 within 3% of that for ethanol distillation and dehydration to meet fuel grade requirements.

Economics and LCA, including Ethanol Production.

Economics. We evaluated the economic competitiveness of producing fungible blendstocks via current and projected CADO technology using ethanol derived from corn, sugar cane juice, and corn stover by current and future cellulose conversion

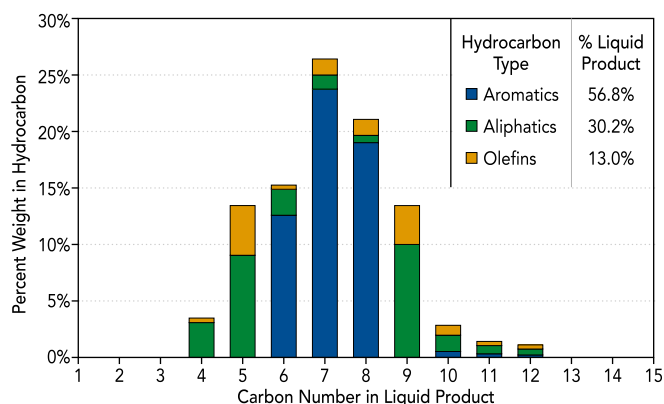


Fig. 3. Current carbon number distribution of representative CADO hydrocarbon liquid product (gasoline range).

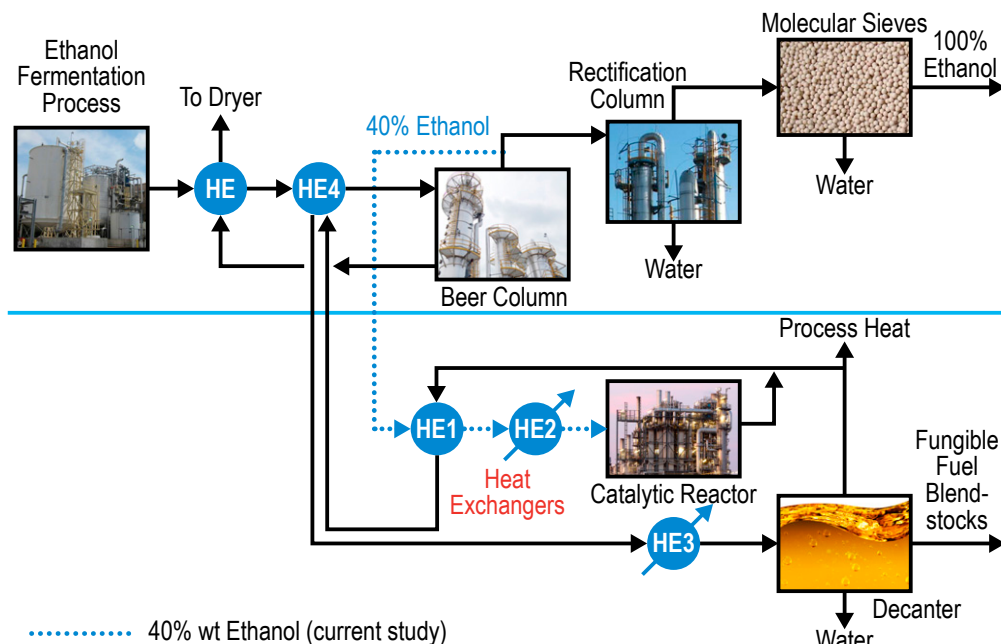


Fig. 4. Block flow diagram illustrating 1) water removal from wet ethanol vapor above the feed tray to produce pure fuel grade ethanol or 2) CADO of the same wet ethanol to fungible blendstocks. HE, heat exchangers.

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 OpEx 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 United States corn ethanol plants have been fully amortized. Costs of 40% ethanol vapor presented in *SI Appendix, Table S5* 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 Fig. 5 and *SI Appendix, Table S7*. The projected MBSP was compared to historical wholesale prices of jet fuel when petroleum cost \$60 per barrel (bbl) and \$100/bbl (38). In particular, we found that jet fuel sells for ~19% more than petroleum on a volumetric basis: For example, 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. *LCA*. Table 2 presents a breakdown of well-to-wheel GHG emissions 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 68.8% for sugar-cane juice. For ethanol produced by “second-generation” processes, which include conversion of lignocellulose via emergent technologies, GHG emissions are reduced by 69.5% 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 of 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 gCO₂e/MJ of hydrocarbon fuel in this case) for re-capture 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 (39, 40) for

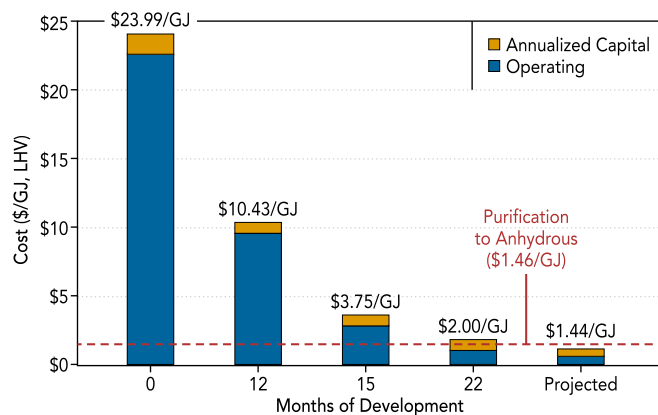


Fig. 5. Migration of the total operating plus annualized capital cost for converting ethanol into fungible blendstocks via consolidated alcohol dehydration and oligomerization. The cost of ethanol is not included. Values are calculated based on LHV.

Table 1. Estimated operating plus annualized capital costs of fungible blendstocks made by CADO of ethanol produced from several biomass sources

Ethanol feedstock	Technological maturity		Ethanol selling price (\$/L)*, †		EtOH→jet fuel conversion		MBSP (\$/L)					
	Ethanol production	Ethanol → blendstock	Prices		Est 40% EtOH prices	Est 40% EtOH projected	Yield (L blend/L EtOH)	Cost (\$/L blend) [‡]	From ethanol [§]		From petroleum [¶]	
			5 y and (current)	Projected					5 y and (current)	@ Market	@ Projected price	\$60/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	—	—

*First-generation (1G) corn starch and cane sugar prices are based on average market values over past 5 y (inflated by 1.5% average inflation [<https://tradingeconomics.com/united-states/inflation-cpi>] over the past 5 y to obtain 2019\$) and current market prices. Corn ethanol coproduct is distiller's dried grains and solubles and cane sugar coproduct is electricity.

†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) (41), corn stover (current) (36), corn stover (projected) (43).

‡Conversion costs from *SI Appendix, Tables S3 and S4*, plus annualized capital costs.

§Hydrocarbon price from ethanol based on minimum ethanol selling price/yield + conversion cost.

¶Hydrocarbon price from petroleum based on oil cost per liter +18.7% (average jet fuel premium over oil last 10 y) + (adjusted for 1.5% inflation over past 10 y).

corn-based scenarios and the Virtual Sugarcane Biorefinery (41–43) for sugarcane-based ones. However, these values were slightly modified to reflect energy savings for use of 40 wt% ethanol, rather than anhydrous ethanol, as the CADO feedstock (Fig. 4). In particular, credits were taken for avoiding distillation energy to produce anhydrous ethanol from 40 wt% ethanol: That is, 25 GJ/h (23.5 MMBtu/h, 0.0016 GJ/L) for natural gas and 2.6 GJ/h (710 kW, 0.00017 GJ/L) for electricity.

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/ton CO₂ emissions avoided used by some multinationals including major oil companies BP, Shell, and Statoil for planning purposes (44); 3) the threshold of \$100/ton CO₂ avoided/sequestered used by the Griscom et al. (45) in assessing "natural" negative emission technologies; 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, <https://www.epa.gov/renewable-fuel-standard-program/what-fuel-pathway>). Documentation is provided in *SI Appendix, Table S8*. Payback period is calculated based on CapEx divided by net revenue, with net revenue defined as blendstock selling price plus production incentives minus the cost of ethanol and conversion costs.

Fig. 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/bbl and no production incentives, none of the combinations of ethanol feedstocks and conversion technologies had positive net revenue. With oil prices at \$100/bbl but no production incentives, positive net revenue and payback periods <3 y 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.

The picture changes substantially with production incentives. With oil at \$100/bbl, payback periods of <3 y are realized for all technologies except for corn stover or with shadow or US\$100/ton production incentives for cane juice + cellulosic ethanol using current production and CADO technologies. United States RINs also provide sufficient economic incentives to provide a <2-y payback period with the exception of the corn stover (current) scenario, for which the payback period is estimated at 2.7 y. At \$60/bbl oil price, an avoided carbon value of \$40/ton CO₂ ("shadow") is not sufficient to generate a positive net revenue, and even at a carbon value of \$100/ton CO₂ avoided only corn starch-projected and corn stover-projected achieve payback periods of 2 y or less. With oil at \$100/bbl and either the LCFS, the United States RIN, or a CO₂ price of \$100/ton, payback periods of <2-y are realized for all combinations of ethanol production and conversion technologies except corn stover ethanol current production and conversion technology. Overall, less than a 5-y payback period can be realized for 11 scenarios at \$60/bbl, 24 at \$80/bbl (not included in Fig. 6), and 31 at \$100/bbl. 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 2 steps combined of >93% (*SI Appendix, Fig. S1*), with energy efficiencies demonstrated to achieve most of this potential. Given favorable thermodynamics, the main driver to be addressed is cost. Whereas the 3-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

Table 2. GHG 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

Ethanol feedstock	Conversion technology	From ethanol				From petroleum	
		Emission (gCO ₂ e/MJ of fungible blendstock)				PTWa	WTWa
		Feedstock production and ethanol conversion	Catalytic conversion of ethanol	Jet fuel use	WTWa*		
First generation						73.2	87.3
Corn starch [†]	Current	45.5	6.7	0.2	52.4		
					-40.0%		
Cane sugar [‡]	Current	23.8	3.2	0.2	27.2		
					-68.8%		
Second generation							
Cane cellulosic ^{‡,§}	Current	14.5	3.2	0.2	17.9		
					-79.5%		
Cane cellulosic ^{‡,§}	Projected	13.9	3.2	0.2	17.3		
					-80.2%		
Corn stover [¶]	Current	23.2	3.2	0.2	26.6		
					-69.5%		
Corn stover [¶]	Projected	0.13	3.2	0.2	3.53		
					-96.0%		

PTWa, pump-to-wake which includes combustion of fuel in an aviation system; WTWa, well-to-wake which includes the full supply, production, and use chain. Values for catalytic conversion include emissions due to transportation and distribution of ethanol, estimated at 0.85 gCO₂e/MJ.

*Negative percent values represent percentage of GHG emission reduction compared to petroleum jet fuel.

[†]Provided by Argonne National Laboratory for corn starch ethanol case.

[‡]Provided by Brazilian Bioethanol Science and Technology Laboratory based on Dias et al. (41).

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

[¶]Provided by Argonne National Laboratory based on previous study by Lynd et al. (43). Corn Stover Base Case based on National Renewable Energy Laboratory: Technical Report NREL/TP-5100-47764 (36).

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 dollar per gigajoule 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. 6). 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 GHG emissions over the next 2 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 capacity 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 per hour and scale up to 2.0 L/h is underway. A first commercial plant, for example processing 15 × 10⁶ L/y ethanol, would require further scale-up by a factor of about 1,000-fold, well within the range supported by experience for commercialization of processes based on gas-phase heterogeneous catalysis (49–51). 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 (Fig. 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 or further development based on such strategies as shifting catalyst pore size (52, 53). Such changes/development

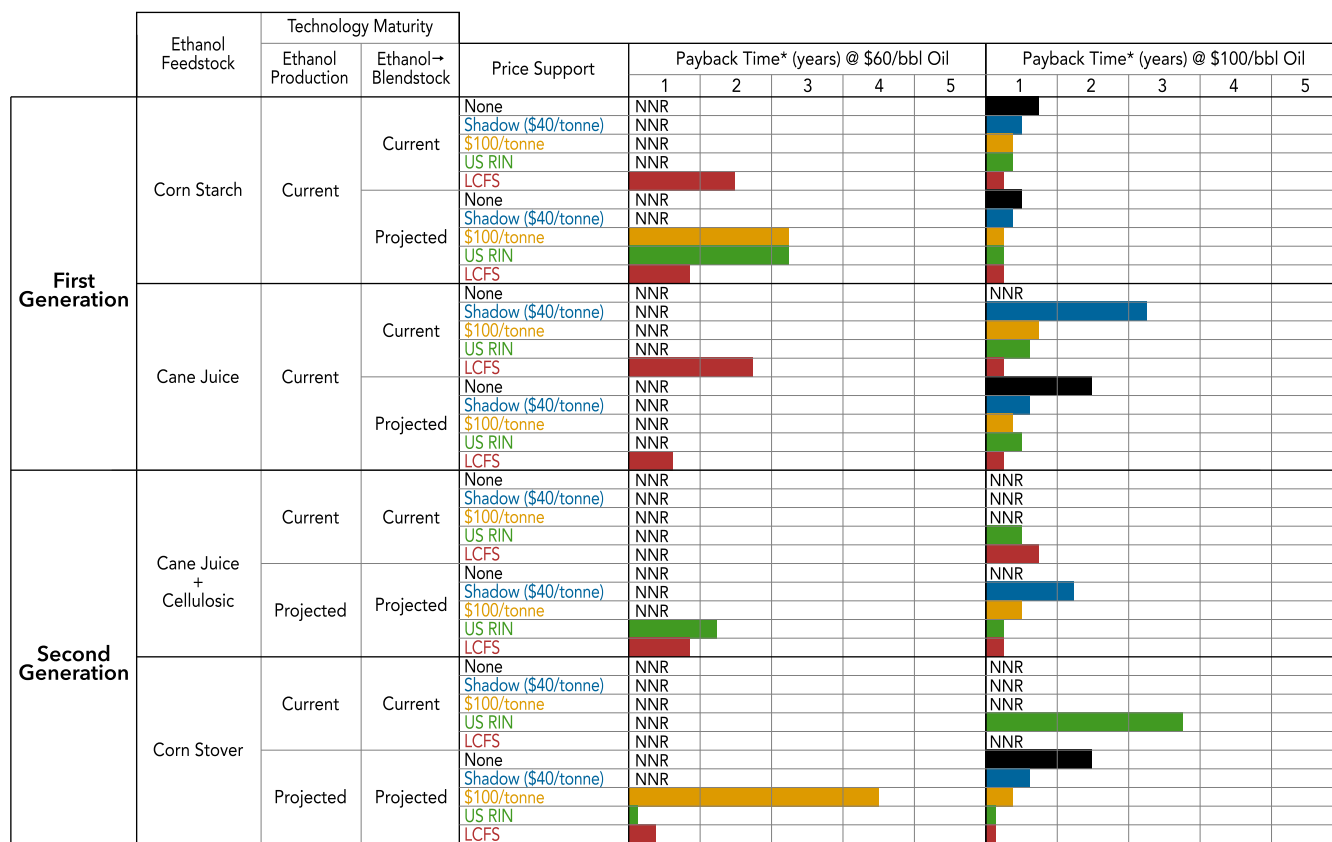
are also known to impact and reduce the aromatics content, a key variable for accessing other fuel and engine types (54, 55).

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 or blending low-carbon, biomass-derived hydrocarbons at yet higher levels could be enabled by: 1) Improving CADO catalysts and processes; 2) blending CADO-derived fuels with those derived from other processes that have lower aromatic content, such as from Fischer-Tropsch (56) and LanzaTech processes (28); 3) separating CADO-derived products into fractions desirable for a range of fuel (57) and chemical applications; or 4) combinations of the above.

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 is predicted to incur a low capital cost and CADO-mediated fungible blendstock could be added to existing ethanol plants, thus 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 postcommercialization cost reductions observed historically for industrial processes and in particular processes based on gas-phase heterogeneous catalysis (58, 59). 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 gigajoule as anhydrous ethanol, as predicted here, represents



* CapEx / Net Revenue Oil @ \$60/bbl & \$100/bbl NNR = Negative Net Revenue

Fig. 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/ton CO₂ emissions avoided), \$100/ton CO₂ emissions avoided, and the LCFS on payback periods for production of hydrocarbon blendstocks by application of current CADO technology to wet ethanol (40 wt%) 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.

a major advance and an opportunity to direct current and future biofuel production toward applications most needed to achieve climate stabilization.

Methods

Catalytic Conversion of Ethanol. A stainless-steel reactor (0.019-m inner diameter × 1.52-m high) was loaded with 30 g of either pilot powder pelletized catalyst (250 to 500 μm) or commercially doped Ga or V-ZSM-5 (1.6- to 3.- mm deep × 25-mm long) with 2 layers of quartz wool on the top and bottom of the catalyst bed. Ten thermocouples were used to measure the temperatures, starting from the inlet of the catalyst bed through the end of the catalyst bed equally spaced along its length. A tubular furnace was used to heat the catalyst bed to 350 °C and held for 30 min with nitrogen flush. Wet ethanol was pumped into the reactor and after stabilizing for 0.5 h, product analysis was performed by an on-line gas chromatograph (Agilent 6850). The transfer line between the reactor and the gas chromatograph was heated to around 250 °C to prevent condensation of heavy products. A capillary column, HP-Plot Q, was used, with a dimension of 30.0 m × 320 μm × 20.0 μm. The gas chromatograph was held at 50 °C for 3 min, ramped up to 250 °C at 15 °C/min, and then held for 35 min. A constant pressure of 9.51 psi was used, and the inlet temperature was 250 °C. Standards of benzene, toluene, p-xylene, ethylbenzene, and cumene were used to quantify aromatic compounds. Nitrogen (5 sscm) was used as internal standard for all of the analyses. For durability tests, the catalyst was regenerated by a 20-ccm airflow with temperature ramped up to 450 °C at 2 °C/min, held there for 15 min, then ramped up to 500 °C, and held there for 1 h before cooling back down for the next conversion run.

TEA Methodology. Operating costs were based on mass and energy balances for wet ethanol to both fungible hydrocarbon blendstocks and anhydrous ethanol. For the CADO catalytic conversion 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 L (\$7/1000 gal). 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 United States 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 y) to 2019 values. Installation factors from NREL TP 47764 were used to estimate installed capital costs.

LCA Methodology. The GREET model developed by the Argonne National Laboratory through funding by the US Department of Energy Office of Energy Efficiency and Renewable Energy was applied to calculate life-cycle GHG emissions of producing 1 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 (40). It was assumed that the fuel was produced and used in the United States 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 Sugar-cane Biorefinery model (41). Feedstock production included farming activities (e.g., fertilizer and pesticide applications), feedstock collection, and transportation

to the biorefinery where ethanol was produced (see conversion to ethanol in *SI Appendix, Fig. 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 *SI Appendix, Table S9*.

Data Availability Statement. Data beyond those presented in the paper and supplementary materials are openly available in Github at <https://github.com/johnrhannon/PNAS-2018-21684R>.

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