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Sun-to-Wheels Exergy Efficiencies for Bio-Ethanol and Photovoltaics

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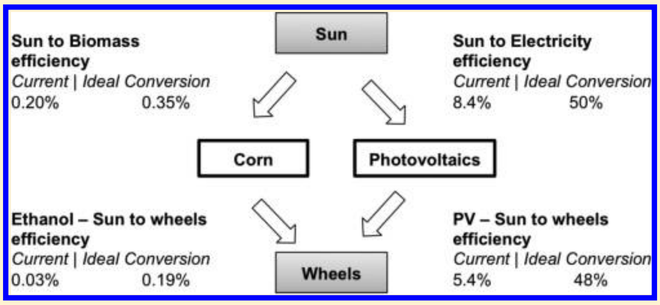
Supporting Information

ABSTRACT: The two main paths to power vehicles with sunlight are to use photosynthesis to grow biomass, converting to a liquid fuel for an internal combustion engine or to generate photovoltaic electricity that powers the battery of an electric vehicle. While the environmental attributes of these two paths have been much analyzed, prior studies consider the current state of technology. Technologies for biofuel and photovoltaic paths are evolving; it is critical to consider how progress might improve environmental performance. We address this challenge by assessing the current and maximum theoretical exergy efficiencies of bioethanol and photovoltaic sun-to-wheels process chains. The maximum theoretical efficiency is an upper bound stipulated by physical laws. The *current* net efficiency to produce motive power from silicon photovoltaic modules is estimated at 5.4%, much higher than 0.03% efficiency for corn-based ethanol. Flat-plate photovoltaic panels also have a much higher theoretical maximum efficiency than a C4 crop plant, 48% versus 0.19%. Photovoltaic-based power will always be vastly more efficient than a terrestrial crop biofuel. Providing all mobility in the U.S. via crop biofuels would require 130% of arable land with current technology and 20% in the thermodynamic limit. Comparable values for photovoltaic-based power are 0.7% and 0.081%, respectively.



INTRODUCTION

With concern over global warming and peak oil rising, the search for renewable transport fuels has begun. Biofuels and electricity from solar PV are two candidates currently being considered as successors to petroleum in vehicles. Corn has been the dominant resource for ethanol production in the United States, with corn-based ethanol being used as an additive in gasoline for some time. Conversely, electric vehicles have yet to evolve from niche utilization and solar power has yet to reach widespread adoption in the U.S. Societal expectations for renewable transport fuels are reflected in interventions to develop and promote them. Governments invest in research and development of biofuels and photovoltaic technologies. In many countries production mandates and/or subsidies support biofuel and photovoltaic development.

Government interventions to support technologies should be informed by analyses of their benefits and costs from environmental, economic, and social perspectives. A host of prior work assesses the environmental attributes of biofuels and photovoltaic panels, often using life cycle assessment (LCA). When applied to vehicles and their fuel chains, LCA is often referred to as a well-to-wheels analysis.[1,2] LCA and well-to-wheels analysis provide insights in the current state of a technology, for example the net energy payback and nutrient requirements for powering vehicles with corn-based ethanol.[3,4]

A major outcome of these prior assessments is recognition of the environmental impacts of biofuels.[3−5] Such work contributed to policy shifts such as the Renewable Fuel Standard, which calls for increased production of alternative biofuels other than corn-based ethanol.[6] California's Low Carbon Fuel Standard Program requires that the environmental benefits of a biofuel be quantitatively established.[7] For the photovoltaic pathway to mobility, nontrivial life cycle contributions from battery and photovoltaic production have been identified.[8,9] While a few environmental assessments have addressed trends, for example,[10] the focus has overwhelmingly been on characterizing temporal snapshots.

While current environmental impacts are certainly important, the potential for technological progress is also critical in policy formulation. For example, expectations for improved technologies to make alternative biofuels form the implicit foundation of the Renewable Fuel Standard. While forecasting is intrinsically uncertain, the shape of future technology is so important that it deserves much analytical attention.

How to approach technological forecasting methodologically? For economic traits, technology forecasting typically draws on approaches such as extrapolation of retrospective models (e.g., experience curves),[11] expert elicitation,[12] and scenario development.[13] These approaches can be applied to forecast environmental attributes.

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In this article, we explore a different direction, one motivated by the following question. Do physical laws impose bounds on technological progress relevant to their adoption? Given a function and technological approach to achieving this function, physical laws can impose nontrivial limits on efficiency. For example, the energy required to produce iron from iron ore cannot be reduced below 6.6 MJ/kg, the enthalpy of the chemical reaction.[14] The energy use in an integrated steel mill (currently ∼19MJ/kg) will never fall below the enthalpy limit. Shockley and Quiesser showed that the conversion efficiency of a single-junction silicon photovoltaic cell cannot exceed 30%.[15] While a technology will never reach its theoretical limit in practice, the limit provides an upper bound. If the upper bound has societal relevance, the rigor of the bound means the assertion *will always be true*, regardless of how much the technology improves. Physical laws thus provide a perspective distinct from conventional forecasting approaches.

We thus study the current and theoretical maximum of exergy efficiency of process chains to produce vehicle power from sunlight via biofuel and photovoltaic pathways. Exergy, discussed further in the next section, is a variant of energy that measures the capacity of a system to do work when brought into equilibrium with its environment. By process chain, we mean a sequence of processes that follow the exergy flow from incident sunlight to the wheels of a vehicle.

The system boundary of the process chains studied is shown in Figure 1. The stages included for the biofuel pathway are photosynthesis, industrial conversion (with and without coproducts), and the internal combustion engine. The stages of the PV pathway include the solar panel, electricity distribution, battery charging/discharging, and the electric powertrain. Corn-based ethanol and single-junction silicon-based photovoltaic modules are chosen to reflect current efficiencies. For theoretical maximum efficiency, we consider a more general C4-based plant and multijunction photovoltaic modules. Note that the biofuel path has the complication of producing coproducts, biomass not converted to fuel. We consider two cases: when coproducts such as corn stover are not utilized and when they are 100% utilized. In the last "wheels" step, we analyze only the power delivered to wheels, which does not account for air resistance or driving patterns. Such postwheel factors are safely neglected because they do not affect the comparison between biofuel and PV chains.

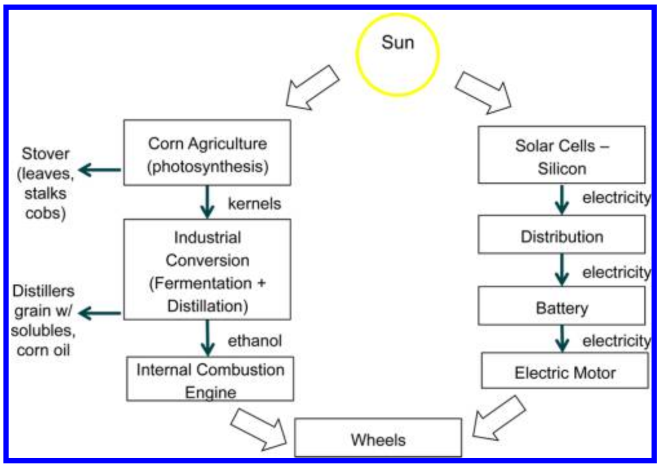

Figure 1. Biofuel and photovoltaic sun-to-wheels pathways.

Process chains need to be studied because selecting one stage (e.g., conversion of sunlight into biomass) has implications for later stages (e.g., chemical processing of biomass into fuels). The more holistic view yields insights that inform the choice of path and the areas of opportunity to improve efficiency for each path. It is important to emphasize that while this analysis draws on ideas from LCA, it is not LCA. One difference is that theoretical maximum efficiency does not depend on all processes in the supply chain, but on those processes that have a physical law limit under 100%. In addition, unlike assessments that characterize greenhouse gas emissions, exergy efficiency is not as sensitive to the boundary of included processes. This is because the exergy content of sunlight and fuels is contained within the numerator and/or denominator of each process step, reducing the importance of the supply chain.

The literature on theoretical efficiency limits generally focuses on individual processes.[14−16] From a methodological perspective, this is the second work to assess the theoretical maximum of process chains (as opposed to individual processes). The first example is a recent paper by the authors analyzing pathways to use natural gas to provide mobility.[17] From a case study perspective, current process chain efficiencies have been well studied, such as corn-based ethanol in refs 18−21. This is the first analysis of current and theoretical limits of sun-to-wheels paths.

Our methodological contribution beyond the prior gas-to-wheels analysis[17] is the development of theoretical limits for photosynthesis and photovoltaic stages. Photosynthesis and photovoltaic processes are complicated because their efficiency depends on a sequence of qualitatively different steps. First, geometrical factors such as leaf shape and flat plate vs rotating PV systems determine the amount of incident sunlight available to the conversion engine. Second, there is an efficiency factor for converting available sunlight to another form (e.g., ATP, DC electricity) and last, the initial form of energy is converted to a useful one (e.g., carbohydrates, AC electricity). Each step has different theoretical limits, thus one needs to analyze each separately. In this work we develop an approach to describe the theoretical maximum efficiency of each step.

Our scope only considers current and theoretical maximum exergy efficiencies. Efficiency is an important contributor to quantities of direct concern to society, for example, cost and carbon emissions, but it does not determine them. One must be careful in interpreting the societal implication of exergy efficiency, and we do so in later sections. Land use, however, is a quantity relevant to society that directly connects to efficiency. Therefore, we also analyze the effect of current and theoretical maximum efficiency on land use requirements.

■ MATERIALS AND METHODS

Exergy was chosen for this analysis because it properly accounts for the capacity of a system to do physical work.[22,23] First Law efficiency, often termed "energy efficiency", assumes that all forms of energy (kinetic, chemical, electric, heat, etc.) are equivalent. The capacity to derive useful work from a quantity of heat is, however, very different from the same amount of electricity. Exergy, or Second Law efficiency, describes how some forms of energy have a greater capacity to do useful work than others. Exergy, measured in units of energy, is thus defined as the maximum useful work that can be obtained when a system is brought to equilibrium with a reference environment.

While using energy instead of exergy would not result in qualitative changes to the results of this study, using exergy is

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Table 1. Description of the Two Types of Theoretical Limits Analyzed

	general description	bio-ethanol	PV
ideal conversion-step limit	conversion of available sunlight becomes "ideal," otherwise system same as current form	C4 limit to make biomass in current corn-type plant	ideal multijunction PV material in flat plate system with current derate factor
all steps ideal limit	all sunlight becomes available to ideal conversion, no losses	C4 limit with 100% absorbance, capturing all sunlight (e.g., biofilm on 2-axis tracking system)	ideal multijunction PV material in 2-axis tracking system with no derate losses.

important for future studies using the method when heat flows play a more critical role. The first step in this evaluation is defining a nonvariable reference environment. The reference environment used in this work is detailed in.[24] Electrical energy is considered pure exergy, and, therefore, the energy content of electricity is equal to its exergetic value. Heat exergy is defined as the maximum amount of work that can be obtained from the transfer of energy due to a temperature difference, quantified by the Carnot efficiency.[25] Additionally, the exergy of a substance can be separated into two components, physical and chemical. Physical exergy is how much work can be obtained by bringing a system to the temperature and pressure conditions of the reference environment. Similarly, chemical exergy is the amount of work that can ideally be obtained by bringing a substance into chemical equilibrium with its reference environment at constant temperature and pressure.

To illustrate why it is preferable to use exergy over energy efficiency, consider a fuel cell that converts 50% of input fuel exergy to electricity and 40% to utilized heat at 500C, with 10% wasted. The energy efficiency (first law) of the fuel cell is 90%. The exergy efficiency of the fuel cell is 50% + (1 − 273/773) × 40% = 76%. An improved fuel cell that converts 60% of fuel to electricity with 30% utilized 500C heat would have the *same* energy efficiency, because electricity and heat are treated as equivalent. The exergy efficiency of the improved fuel cell would be 60% + (1 − 273/773) × 30% = 79%, reflecting that producing more electricity should yield a higher efficiency.

Current Exergy Efficiency of a Process. The current exergy efficiency for an individual process with a set of *i* exergy inputs ($\mathrm{Ex}_i^{\mathrm{in}}$) and *j* outputs ($\mathrm{Ex}_j^{\mathrm{out}}$) is defined as

$$\text{current exergy efficiency} = \frac{\sum_j \mathrm{Ex}_j^{\mathrm{out}}}{\sum_i \mathrm{Ex}_i^{\mathrm{in}}} \tag{1}$$

The input exergy include the exergy of the fuel, as well as the process work associated with that step. The exergy of an output is determined by its chemical and physical exergy states, or, in the case of electricity, its exergy value is equal to its energy content. Additionally, only useful exergy is considered for the output exergy sum, and quantities such as discarded heat are not included.

Theoretical Maximum Exergy Efficiency of a Process. The definition is

$$\text{theoretical maximum exergy efficiency} = \frac{\sum_j \max \mathrm{Ex}_j^{\mathrm{out}}}{\sum_i \mathrm{Ex}_i^{\mathrm{in}}} \tag{2}$$

where the critical change from eq 1 is that current $\mathrm{Ex}_j^{\mathrm{out}}$ is replaced with the maximum value for an idealized version of the same process. For example, for a single-junction silicon photovoltaic module, the current efficiency of 14.5% is replaced with the theoretical multijunction panel efficiency limit of 86%.[26] We reiterate that the theoretical limit only provides an upper bound on the practical limit and does not inform how close the practical limit will approach the theoretical one.

The choice of specific exergy pathways and stages subjects the process to specific thermodynamic laws, affecting the total pathway efficiency. These thermodynamic laws may then be used to determine the total pathway efficiency. For example, constraining photosynthesis to the C4 route specifies a chain of biochemical reactions that can be thermodynamically analyzed. Future technological progress may remove the constraints that led to a theoretical limit.

Sunlight to Energy Carrier: A Multistep Process. While Figure 1 shows photosynthesis of biomass and photovoltaic production of electricity as single-step processes, in fact both are chains. The first step can be thought of as geometrical: A physical configuration of leaves or panels makes some fraction of incident sunlight available to conversion engines (chloroplast or p−n junction). In the next step, the conversion engine transforms light to an initial form (i.e., ATP or DC power), but needs further processing before arriving at its "useful" form (i.e., starch or AC power). The theoretical limit of such a multistep process depends on which steps are allowed to progress. Improving geometry, for example, by switching from fixed-plate PV panels to two-axis tracking is a different type of progress than improving the conversion step, for example, via a better photovoltaic material.

We address this complication of the thermodynamic limit by defining two types of theoretical maximum efficiency, as shown in Table 1. The Ideal Conversion-step limit assumes an idealized version of the main conversion step (photosynthesis, photovoltaic), leaving all other steps as they currently are. For example, the Ideal Conversion-Step limit for PV assumes the active PV in a flat plate system changes from its current value of 14.5% to its 86%-efficient theoretical limit. In the Ideal Conversion-step limit for biofuels, the corn plant has the same physical structure and capacity to capture sunlight and the efficiency of photosynthetic metabolism is increased to the C4 thermodynamic limit.

The All Steps Ideal limit assumes all conversion steps reach the theoretical limits. For the PV path, the All Steps Ideal limit assumes ideal (86% efficient) multijunction modules with two-axis tracking and no derate losses. For the biofuel path, the All Steps Ideal limit makes all sunlight available to chloroplasts (we imagine this would only be possible with biofilm grown on a 2-axis system) and idealized C4 photosynthesis that converts 100% of sunlight to kernels for fermentation.

Process Chain Efficiency. When there are is only a single exergy flow through a process chain, the exergy efficiencies of individual steps may be strung together in a process chain, separable by step, as shown in eq 3.

$$\text{path efficiency} = \frac{\mathrm{Ex}_{\mathrm{out}}^1}{\mathrm{Ex}_{\mathrm{in}}^1}\frac{\mathrm{Ex}_{\mathrm{out}}^2}{\mathrm{Ex}_{\mathrm{in}}^2 = \mathrm{Ex}_{\mathrm{out}}^1}\frac{\mathrm{Ex}_{\mathrm{out}}^3}{\mathrm{Ex}_{\mathrm{in}}^3 = \mathrm{Ex}_{\mathrm{out}}^2}\frac{\mathrm{Ex}_{\mathrm{out}}^4}{\mathrm{Ex}_{\mathrm{in}}^4 = \mathrm{Ex}_{\mathrm{out}}^3} = \frac{\mathrm{Ex}_{\mathrm{out}}^4}{\mathrm{Ex}_{\mathrm{in}}^1} \tag{3}$$

In this way, the product of the step efficiencies gives the total efficiency of the pathway. For example, consider the fuel cell

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Table 2. Comparison of Efficiency Components for Current Corn, The Theoretical Limit of the Solar Conversion Step Only and the Theoretical Limit of All Steps

	geometry factor (GF)	photosynthetic availability (PA)	conversion efficiency (CE)	partitioning efficiency (PE)	net efficiency (no coproducts)
current corn	7.3%[a]	44%[b]	7.8%[b]	80%[c]	0.20%
ideal conversion step limit	7.3%[a]	44%[b]	14%[b]	80%[c]	0.35%
all steps ideal limit	100%[d]	93%[b]	14%[b]	100%[d]	13%

[a]Derived from refs 16,28 [b]Derived from ref 16 [c]Derived from ref 28 [d]Assumed to be 100%

from before that converts 50% of fuel exergy to electricity hooked hooked up to an electricity distribution that is 90% efficient. If the excess heat is not utilized, the path efficiency is $0.5 \times 0.9 = 0.45$, or 45% system efficiency.

If there are multiple flows in a pathway such as coproducts or additional exergy inputs, the path efficiency is calculated differently. The efficiency is not separable and calculated with the basic definition in eq 1, considering the chain treated as a single integrated process:

$$\text{path efficiency} = \frac{\sum_1^j \mathrm{Ex}_{\mathrm{out}}^j}{\sum_1^i \mathrm{Ex}_{\mathrm{in}}^i} \qquad (4)$$

,where j is the number of exergy outputs and i is the number of inputs to the overall process chain. To illustrate this formula, consider a fuel cell/distribution system modified from the previous example: 100 units of natural gas input to the fuel cell yields 50 units of electricity and 40 units of utilized heat at 500 C. The distribution system requires inputs of 100 units of electricity and 5 units of exergy to construct and maintain infrastructure to output 90 units of electricity. If 100 units of natural gas exergy are input into the system, this implies $0.5 \times 5 = 2.5$ units of infrastructure energy are required. The exergy output of the system is $40 \times (1 - 273/773) = 26$ units of heat and $50 \times 0.9 = 45$ units of electricity. The path efficiency of the system is total exergy out/total exergy in = $(26 + 45)/(100 + 2.5) = 69\%$.

Sun-to-Biofuel Pathway. The biofuel sun-to-wheels pathway involves significant production of coproducts. The question of how to how to allocate benefits for coproducts continues to generate debate,[3] there is no unique positive choice. We address coproducts by considering two extremes: zero coproduct benefit and full 100% exergy value. Reality lies somewhere between these extremes, coproducts are used, but in lower value applications that do not merit their full exergy content (e.g., corn stover as a soil additive).

Photosynthesis. The first stage in the corn ethanol pathway is photosynthesis via growing corn. The exergy inputs for corn production are sunlight and agricultural inputs such as fertilizer, pesticides, herbicides, and seeds. The exergy outputs are kernels and stover. Corn stover includes leaves, stalks and corn cobs. The energy of sunlight varies by location; we assume the cornfield is located in Des Moines, Iowa. This location was chosen to provide an optimistic assessment of the corn pathway, while at the same time providing a relatively pessimistic assessment of the PV pathway.

Many studies have assessed the primary energy content of inputs to corn agriculture, which include the embodied energy of physical inputs (e.g., fertilizers) and energy consumed on-site (e.g., diesel, electricity). Chemical energy has an exergy quality factor close to 1, while the quality factor of electricity is equal to 1. It is also important to note that that agricultural inputs are less than 0.1% of the total exergy of the incoming solar radiation for a typical growing season of 120 days.[18,19] Agricultural inputs (e.g., fertilizer, diesel fuel) thus have little influence on exergy efficiency.

To identify the exergy content of outputs, we identify the average corn yield in Des Moines, Iowa to be 146 bushels/acre[27] (9.0 tons/hectare). Although stover is often not used as an exergy source, a second scenario the exergy content of all coproducts are credited to the stage efficiency. The quantity of stover produced is found using the ratio of stover to total plant mass (kernels + stover), based on USDA yield data.[28]

The net efficiency (E) of converting sunlight to biomass for ethanol production is given by the formula 5, adapted from[25]

$$E = \mathrm{GF} \times \mathrm{PA} \times \mathrm{CE} \times \mathrm{PE} \qquad (5)$$

.GF is the geometry factor, determined by canopy development and closure, leaf absorbance, canopy longevity, size, and architecture. PA represents the photosynthetic availability limited by light outside the photosynthetically active spectrum and reflected or transmitted light; CE is the conversion efficiency, which is the combined gross photosynthesis of all leaves within the canopy less all plant respiratory losses and photochemical inefficiency; and PE is the partitioning efficiency−the fraction of the total biomass exergy used as an input for ethanol production.[29,30] In the no coproducts case it is assumed that any biomass not used for ethanol production is wasted, and with coproducts included we assume the full exergy value of the coproducts in added to the exergy outputs of photosynthesis (eq 4).

Table 2 shows the photosynthetic efficiency for the current corn efficiency, Ideal Conversion-Step limit and the All Steps Ideal limit. References 16, 28, and 29 were used in developing the table. Details of the data sources and calculations can be found in the Supporting Information. To discuss the results, the Geometry Factor was found to be 7.3%, low compared to 75% for a PV fixed-plate system. In addition, much of the sunlight reaching a crop never reaches chloroplasts. In the All Steps Ideal limit we envision a hypothetical radically reconfigured plant equivalent to a PV 2-axis tracking system. The 56% loss in photosynthetic stage (PA = 44%) is mainly due to light frequencies outside the absorption band of chlorophyll. In the All Steps Ideal limit, we imagine some future pigments that would enable utilization of all light frequencies. Note in the conversion efficiency stage that improvement in C4 photosynthesis is reportedly locked in to around double current levels. The All Steps Ideal limit reflects a generalized C4 plant with perfect capture of sunlight to biomass, thus encompassing not only corn ethanol, but any biofuel from C4 photosynthesis (i.e., any cellulosic biofuel).

Industrial Conversion. Industrial conversion refers to converting biomass to ethanol and other coproducts. For the current corn system the input biomass is corn kernels. The harvested kernel is processed in dry or wet, in 2008 86% of ethanol was commercially produced using dry mills,[31] this share

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is expected to increase in coming years. In dry mills, harvested kernels undergo milling, cooking, fermentation, distillation, filtering using micro sieves, and denaturing. The result of the processes is 99.95% pure ethanol and three coproducts: dry distiller grain solids (DDGS), wet distiller grain solids (WDGS), and corn oil. The energy consumed in the dry mill is in the form of heat and electricity.

The current exergy efficiency of industrial conversion is primarily based on prior work.[31] The theoretical limit of industrial conversion is based on hypotheses for minimum exergy inputs required and maximum ethanol output. Results are that the current efficiency of industrial conversion is 47% without coproducts, 74% with full utilization of coproducts. The theoretical limit is 69% without coproducts, 88% with coproducts. See the Supporting Information section page S6 for details of data sources and calculations.

Internal Combustion Engine. Typically, U.S vehicles run on blends of ethanol and gasoline, with concentrations of ethanol varying between 5% and 10%. However, E100 technology for vehicles running purely on ethanol has already been demonstrated in Brazil. For the scope of our research and to facilitate comparisons with the solar PV pathway, we assume a vehicle running on pure ethanol. The current exergy efficiency of pure ethanol-based internal combustion engines varies between 28% and 34% for different engine speeds.[32,33] The efficiency is measured as a ratio of mechanical exergy delivered by the engine and the exergy of the fuel. For our calculation we used 34% to overestimate pathway efficiency. The mechanical exergy does not include the energy losses due to auxiliary units (e.g., fuel pumps, water pump and alternator), and, since the objective is to identify the work available at the wheels, losses due to auxiliary units and transmission are included, reducing the efficiency by 7%.[34]

The theoretical limit of any heat engine is limited by Carnot's Law, in which the efficiency is proportional to the temperature difference between the source and sink. The temperature limit is determined by the material components. While many materials, including ceramics and composites, can withstand temperatures of at least 900 °C, they have not been proved to be reliable application for IC engines yet. Theoretically, however, an engine could utilize such materials, providing an upper bound to our analysis at which the engine operates at 900 °C resulting in an efficiency of 74%. The efficiency loss due to the vehicle drivetrain is not included in the theoretical case, and air resistance and idling losses are not considered due to the fact that the system boundary ends with the power available to the wheels, not with the motion of the vehicle.

Solar PV Pathway. *Solar Modules.* To model a typical solar photovoltaic module, we use the PVWATTS program provided by the National Renewable Energy Laboratory (NREL) to define the system specifications of a module located in Des Moines, Iowa.[35] The derate factor accounts for efficiency losses from the inverter, transformer, wirings, system availability due to maintenance, shading, and age. We model the system using a crystalline-silicon PV module with 14.5% efficiency, fixed tilt of 41.5 degrees, array azimuth of 180 deg, and derate factor of 0.77.

Table 3 shows results for current and theoretical limits of PV panels, with two distinct theoretical limits defined as discussed in section 2.2. The result of 75% for the geometry factor for a fixed-axis system is based on the ratio of outputs of a 41.5 degree fixed tilt versus a two-axis tracking system in DesMoines.[35] Net efficiency is obtained by multiplying the geometry factor, the panel efficiency and the derate factor. We assume no curtailment of PV, which is reasonable for current small levels of PV adoption and in the theoretical limit. Integrating significant amounts of intermittent renewables into the grid is certainly a challenge, but one is outside the scope of an analysis of thermodynamic limits.

Table 3. Comparison of Efficiency Components for Current PV, the Theoretical Limit of the Solar Conversion Step Only and the Theoretical Limit of All Steps

scenario	geometry	geometry factor	panel efficiency	derate factor	net efficiency
current: flat plate single-junction Si	fixed plate	75%[a]	14.5%[a]	77%[a]	8.4%
ideal conversion-step limit	fixed plate	75%[a]	86%[b]	77%[a]	50%
all steps ideal limit	two-axis tracking	100%[c]	86%[b]	100%[c]	86%

[a]PVWATTS;[35] [b]Derived from ref 26 [c]Assumed to be 100%

Distribution. The distribution step in this process relates to the transmission of electricity from the PV module to the vehicle charging station. The current efficiency of this technology is around 92%,[36] with losses due to the resistance of the copper transmission lines and total distance covered. We assume the theoretical limit of the distribution system is 100% efficient.

Battery. The battery stage has two parts: the battery charger and the battery itself. The current technology, examined in,[37] limits the charging to an efficiency of 86% and vehicle battery discharge to 94% efficiency. The result is a current efficiency of 80% for the battery stage. With numerous research and development activities surrounding battery technology, batteries are likely to continue improving in performance and efficiency. The theoretical exergy efficiency for the battery charging and discharging step is primarily dependent on the specific chemistry of the battery and the length of time allowed for charging and discharging. Assuming the $Li/SOCl_2$ chemistry examined in[38] could theoretically be applied within an electric vehicle would result in a battery stage efficiency of 97%.

Electric Motor. The electric motor is powered by electricity provided from the battery bank. The batteries require a DC/AC conversion step, which is 97% efficient, before transmitting the power to the motor. The current motor to wheels efficiency is taken to be 90%, resulting in a step efficiency of 87%.[39,40] Theoretically, a DC motor would eliminate the need for a conversion step. Also, since electricity is pure exergy and motors are already testing with efficiencies near 100%, we assume a theoretical efficiency of 100% for this stage.

RESULTS

Exergy Efficiency. The current and theoretical exergy efficiencies of each stage are presented in Table 4. Since some stages of the biofuel pathway include coproducts, we identify the efficiency of the biofuel pathway with and without coproducts. Referring to eq 2, including coproducts as an additional exergy output of a given stage increases the numerator, and improves the stage's exergy efficiency.

Table 4 shows the total exergy efficiency of both pathways. The ethanol pathway efficiency is divided based on whether coproducts are included. When not including coproducts, the ethanol pathway has a current efficiency of 0.03%, with the potential to reach a theoretical maximum of 6.8%. When

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Table 4. Efficiencies of the (a) Biofuel Pathway with and without Co-Products and (b) Photovoltaic Pathway Where Ideal Conversion-Step Refers to a Maximal Efficiency Corn Plant and an Ideal Multi-Junction Photovoltaic Material in Current Flat Plate System, And All Steps Ideal Refers to Idealized Generic C4 Plant Collecting Full Sunlight or Idealized Multi-Junction Photovoltaic Material with Ideal 2-Axis Tracking System and No Derate Losses[a]

(a) Biofuel Pathway

	no coproducts			with coproducts		
stage	current	ideal conversion step	all steps ideal	current	ideal conversion step	all steps ideal
photosynthesis	0.20%	0.35%	13%	0.25%	0.44%	13%
industrial conversion	47%	69%	69%	74%	88%	88%
vehicle	27%	74%	74%	27%	74%	74%
total	**0.030%**	**0.19%**	**6.8%**	**0.15%**	**0.35%**	**9.4%**

(b) solar photovoltaic pathway

stage	current	ideal conversion step	all steps ideal
PV module	8.4%	50%	86%
distribution	92%	100%	100%
battery	80%	97%	97%
electric motor	87%	100%	100%
total	**5.4%**	**48%**	**83%**

[a]see section 2.3 for description of Ideal Conversion-Step and All Steps Ideal limits). Note that efficiencies do not multiply for the biofuel path (see eq 4).

coproducts are included, the current and theoretical maximum increase to 0.15% currently and 9.4% potential, respectively.

The current solar PV pathway converts 5.4% of the incident sunlight into exergy at the wheels, which has nearly achieved the theoretical maximum of the ethanol pathway, not including coproducts. Theoretically, the maximum exergy efficiency of the solar PV pathway could increase to 83%. Including life cycle or embodied energy in this analysis did not alter these results due to the magnitude of the incoming solar energy compared with all other energy inputs.

Land Use. Geyer and collaborators compare sun-to-wheels land requirements for bioethanol and photovoltaic paths for the current state of technology.[39] We do a similar type of calculation for both current state and theoretical limits. To build a context to interpret land use, we calculate the land area to provide 100% of personal vehicle mobility in the continental United States via solar power. The quantity of vehicle miles traveled in light duty vehicles in 2012 was 2.65 trillion miles in the 48 continental states.[41] We take the efficiency to convert power delivered to wheels to distance traveled as 3 miles/kWh, which assumes the biofuel vehicle is a hybrid. The total area of the 48 states is 7.6 million km^2, with 17% being arable.[42,43] When these data are combined with the efficiency results for current technologies (Table 4), providing all mobility via corn-based ethanol (0.03% efficiency) today would use 130% of arable land, while an ideal crop biofuel with no coproducts (0.19% system efficiency) would use 20% of arable land. An ideal crop biofuel with full exergy utilization of coproducts (0.35% system efficiency) would use 11% of arable land. For photovoltaic-based mobility, the figures are 0.7% of total land (assuming the systems can be put anywhere) for current technology and 0.081% of total land for ideal flat plate systems. These results strongly suggest that crop biofuels are too land intensive to be a dominant fuel source for mobility.

■ DISCUSSION

While it is well-known that the sun-to-wheels pathway for biofuel production is currently inefficient compared to PV, we have shown something new: Even with heroic efforts to improve the technology, the crop biofuel path will *always* be far less efficient than PV. An idealized crop-based biofuel with maximal photosynthetic efficiency and 100% utilization of coproducts can only achieve a system efficiency of around 0.35%. In comparison, current PV sun-to-wheels efficiency is already 5.4%. The main efficiency bottlenecks for biofuels are geometry that limits the channeling of incident light for conversion, the absorption band of chlorophyll, losses in the C4 biochemical cycle, and Carnot limits on combustion engines.

It is important to emphasize, however, that efficiency is by no means the sole determinant of what technology society should adopt. For important quantities such as net economic cost and carbon emissions per mile, efficiency plays an important role, but does not determine outcomes. Current biofuels enjoy a number of advantages over PV-based mobility, including lower capital costs and higher energy density for storage (liquid fuel vs battery). Society is faced with the challenge of gauging how different technology attributes will evolve and combine to deliver favorable outcomes. Our efficiency results inform future estimates of long-term costs and emissions, though such forecasts are beyond the scope of this work.

Efficiency does however play a formative role in determining the land-use requirements of solar-based mobility. Our results thus have direct and important implications for land-use. Providing all transportation fuel in the U.S. with C4 crop-based biofuel would require *at least* 20% of arable land, regardless of how much the technology improves. In the real world technologies do not reach their theoretical limits, so the real number would quite a bit higher. There should be a debate as to whether or not utilizing 20% of all arable land is acceptable. To us, the figure seems high and suggestive that crop-based biofuels should not be the cornerstone of sun-to-wheels based mobility. This said, we do not suggest abandoning crop-based biofuels. Given range limitations of electric vehicles, biofuels can make a critical contribution in meeting demand for long-distance trips. One vision to deliver 100% mobility via sun-to-wheels is to use Plug-In Hybrid Vehicles such that mobility demand for shorter trips is met with PV electricity, with biofuels supporting long distance trips.

Note that any C4 crop-based biofuel will have a thermodynamic limit close to the 0.19−0.35% range for corn-

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ethanol. Non-corn plants will have geometry factor of similar to corn as will the limit of the industrial conversion step for fuels other than ethanol. The "All Steps Ideal" limit for biofuels of 9.4% radically raises the bar due to two factors: Different geometry that allows plants full access to incident sunlight (analogous to 2-axis tracking system in PV) and capture of the full energy spectrum as opposed to the limited absorption band of chlorophyll. Different models of photosynthesis-based energy, for example, growing microalgae in reactors, show potential to improve geometry and conversion efficiencies, though naturally face their own challenges.[44] The approach developed here could be applied to provide insight into the potential of alternate paths to improve efficiency.

These methods are applicable to a variety of process chains for converting an energy source to an energy service. The question of how much a technology might improve from its current form is clearly a critical one. Our method makes it possible to analyze theoretical limits on efficiency. While limits are mathematically robust compared to forecasts, they require particular care in interpretation. We expect the approach has potential to yield useful insights when one or more steps in a process chain are strongly constrained by physical laws (e.g., C4 photosynthesis) or when choice of one stage leads to a later sequence of steps that cumulatively limit system efficiency (e.g., use of heat engine vs electrochemical process).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains details of data sources and calculations made to obtain results. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/es504377b.

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Notes

The authors declare no competing financial interests.

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