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1,3-Propanediol from Fossils versus Biomass: A Life Cycle Evaluation of Emissions and Ecological Resources

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Despite the popularity of life cycle assessment (LCA) for understanding the broader implications of technological alternatives, it faces challenges due to difficulties in defining the analysis boundary, uncertain data, and ignoring the role of ecological goods and services. The latter natural capital is essential for sustainability but is only considered partially in conventional LCA. Accounting for ecological resources introduces the challenge of how to aggregate resources of widely varying qualities such as sunlight, wood, water, and coal. Methods based on mass, energy, and exergy have been proposed and are evaluated in this work. In addition, this work aims to analyze three LCA techniques with different system boundaries: conventional process-based LCA, hybrid economic input−output LCA (EIO-LCA), and hybrid ecologically based LCA (Eco-LCA). These three methods are applied to the case study of 1,3-propanediol (PDO) produced via fossil-based and bio-based feedstocks. The results of this study indicate that a hierarchical set of metrics can be useful for gaining insight into the role of ecosystem resources in a life cycle. Among aggregation methods, ecological cumulative exergy consumption seems to provide meaningful results, but more empirical studies are needed. It is also determined that bio-based PDO is more attractive than fossil-based PDO because of less nonrenewable resource consumption and greenhouse gas emissions. However, bio-based PDO does rely more on land, water, and fertile soil. By determining the impact of making the current PDO demand entirely from corn, it is found that the consumption of natural resources relative to national consumption is very low. While producing PDO alone from corn may have a negligible impact in terms of emissions and resource use, switching other products to bio-based will have an additive effect, increasing the strain on some ecological goods and services. These impacts should be addressed before promoting the large scale production of bio-based products.

Introduction

Many of the materials that are used in common products, from plastics and adhesives to lubricants and coolants, are derived from fossil feedstocks. Although fossil-derived materials use a significantly smaller portion of fossil feedstocks compared to fuels and electricity,[1] producing these products using methods that use less energy and cause lower environmental impact may be a positive step in improving the sustainability of industrial processes. For example, polymers derived from biomaterials are more easily recycled than polymers that serve the same function but are derived from fossil feedstocks.[2] Therefore, if producing a biomaterial reduces emissions and energy consumption, multiple recycles will have an additive effect, creating much larger reductions.

Whether bio-based products are "better" from a life cycle point of view is not clear. Studies as far back as 1996[3] have realized the complexity of the issue and have attempted to analyze the life cycle of bio-based products. Many studies that attempt to quantify the life cycle impacts of bio-based products have shown that while these products result in a reduction of some unwanted categories (such as greenhouse gas emissions, energy consumption, etc.), they often result in an increase in other unwanted categories.[2,4−10] A recent U.S. EPA case study compared conventional versus bio-based motor oil, wall insulation, asphalt coatings, transformer oils, and general purpose cleaners.[4] It did not detect any general trend among the individual case studies; for example, it was found that bio-based motor oil may reduce greenhouse gas (GHG) emissions compared to conventional motor oil but bio-based wall insulation appears to increase GHG emissions compared to conventional insulations. This indicates that bio-based products are not inherently better from a life cycle point of view, as it depends on the specific product or process as well as the impact category of interest.

Although these studies claim to look at bio-based products from a life cycle perspective, most are limited in scope. Many studies focus only on emissions and their impacts[4,7,8] or emissions and consumption of some nonrenewable resources[2] while ignoring the role of ecosystem goods and services such as land use, water consumption, carbon sequestration, and soil erosion. Emissions and fuel consumption are important in analyzing the life cycle of a product or process, but ecosystem goods and services consumption is also significant because all processes rely on them directly or indirectly.[11,12] Processes that may look appealing from an emissions or energy standpoint may not be feasible if they heavily exploit ecosystems beyond their carrying capacity. Some studies do examine land requirements for bio-based polymers and energy. For example, Dornburg et al.[13] calculate the amount of energy consumed and GHG emissions *per unit of land used* as a basis of comparison between products produced from different biological feedstocks. So although this study accounts for land use by determining which technology has the lesser impact for a given amount of land usage, it is on an intensive basis, which does not reveal the extensive or overall impact of the technologies. Therefore, if land is a limiting resource, it is not captured via an intensive basis. Also, this study is still too narrow since it does not account for the numerous other ecological goods and services. Lynd and Wang[14] lay out a framework for comparing bio-based products

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to fossil-based products and potentially accounting for natural resource consumption but do not explore this in detail. Because bio-based products are heavily reliant on ecosystem goods and services, it is imperative to account for them when performing a life cycle assessment (LCA). Not doing so neglects an extremely important aspect and could even encourage environmentally harmful decisions. Examples of this are plentiful throughout history, where treating ecosystems as "infinite" or "free" has caused severe deterioration of many essential ecosystem services.[15]

Various efforts have been made to account for the role of ecological resources in a life cycle. In conventional LCA, methods used to quantify resource consumption include approaches such as Abiotic Depletion Potential[16,17] and Surplus Energy.[18,19] However, these methods only focus on some ecological resources, making them of limited use for a comprehensive analysis. Other efforts are based on representing resources in terms of their mass, energy, or exergy. Among these, material flow analysis focuses on mass,[20] net energy analysis on fuel value,[21] and cumulative exergy consumption[22] and emergy analysis[11] on exergy. These methods define various aggregate metrics for reducing dimensionality by combining the raw data to facilitate comparison between alternatives and decision making. An implicit assumption made in aggregating different quantities in a common unit is that they are substitutable. Thus, aggregating resources in terms of their mass implies that a resource can be replaced by the same mass of another resource. Clearly, this assumption is often violated since one kilogram each of water, biomass, or coal is not substitutable. Similar challenges exist in energy and exergy based methods[23,24] and also in assessing the impact of emissions.

Conventional LCA has addressed the substitutability assumption in impact assessment by representing various emissions in terms of their impact in different categories such as global warming, ozone depletion, and eutrophication, with each category represented via a common numeraire. For example, emissions such as N_2O, CH_4, CFCs, and CO_2 are represented in CO_2 equivalents to create a single number for the global warming potential. This approach has been widely studied and is now standardized.

For resource accounting, the approach of emergy or ecological cumulative exergy consumption (ECEC) analysis attempts to address the resource quality and substitutability issue by representing all resources in terms of a common numeraire: solar equivalent joules. This approach considers the network of ecological processes needed to produce natural resources to represent each resource in terms of solar energy. For example, if producing one joule of biomass exergy requires 50 000 joules of solar exergy, then one joule of biomass is equal to 50 000 solar equivalent joules. This approach, pioneered by H. Odum,[11] is appealing but faces challenges due to inadequate understanding about ecological networks.[25] Other aggregation methods have also been suggested, but there is little agreement on the appropriate approach.[23,26−28]

This study analyzes the life cycle of 1,3-propanediol (PDO), produced using fossil feedstocks and biological feedstocks. PDO has many industrial applications as an additive and as a polymer precursor for plastics and fiber manufacture.[29] A joint venture between DuPont and Tate & Lyle, DuPont Tate & Lyle BioProducts, has been formed to manufacture PDO from corn-derived glucose via fermentation.[30] The company has indicated that this biological route is more environmentally friendly and consumes less energy than the fossil fuel route over the life cycle.[31] However, their life cycle study seems to be narrowly focused on nonrenewable energy and GHGs and is not available in the public domain. Anex and Ogletree[2] have completed a life cycle study of PDO to compare the fossil and biomass routes. Although this study has been published, the underlying data are not publicly available. Also, it is a conventional process LCA study with primary emphasis on emissions and their impact and consumption of some nonrenewable fuels. It does not provide insight into the reliance of the two PDO pathways on other ecological resources that could be limiting and does not consider thermodynamic aggregation methods.

There are multiple goals of this study. First, verifying the results from Anex and Ogletree's study on PDO[2] is important to ensure their results are reproducible. Also, adding to the database of available literature also helps to improve the overall comprehensiveness of bio-based product LCA. However, the more meaningful reason for performing this study is to extend the conventional life cycle thinking of biomaterials from emissions and energy consumption to include ecological resources and compare different aggregation methods. Also, this study compares LCA results based on three different system boundaries and implications of the results toward decision and policy making. Studies involving LCA often do not touch on these topics but instead perform the LCA and present the results without adequate insight into the reasons behind choosing particular methods or the deeper implications of choosing one alternative over another. This study aims to break this trend and analyze the broader and significant results that LCA can give. Instead of using conventional LCA techniques that focus mostly on emissions and energy, the scope of this LCA is extended to include thermodynamic methods to account for the reliance on ecological resources. The goal of using the *ecologically based LCA* (Eco-LCA) approach[32] is to account for the vast array of life cycle impacts that bio-based and fossil-based technologies may have to determine which, if any, is the better alternative. From a decision making standpoint, shedding light on some of the less discussed impacts of biotechnology should provide a stronger scientific basis for a more educated dialogue about bio-based products. Finally, this work performs LCA with different boundaries corresponding to process model based and hybrid LCA. This provides insight into the variation of the results with the boundary and corresponding challenges in interpreting and improving LCA.

The rest of this paper first includes a brief background of LCA, exergy, and related methods. Approaches and data sources used in this research are then discussed along with details about their use. The Results and Discussion section presents the various quantities and trends obtained through the research and how they can be interpreted from multiple points of view. Finally, the Conclusions section states the general significance of the research and presents recommendations for further study on the topic. A Supporting Information section is available separately that presents all raw data and other figures that are not included in the main article.

Background

Boundary Selection in LCA. Despite the large body of literature on LCA, the challenge of selecting the analysis boundary still remains, and there is no general agreement on which method is superior in accurately capturing the full environmental implications of a product or service.[33] In general, LCA can be lumped into three categories based on how the boundary is selected: process model based, economic model based, and hybrid methods.

Process LCA. The advantage of process model based LCA, or "Process LCA" is the detailed process level data that it uses;

the disadvantage is the selection of cutoff rules or boundary selection. Because including every process connected in the life cycle of a product or service would be overwhelmingly complicated, it is necessary to choose a boundary that would, in theory, include all the important processes and exclude the ones that are negligible to the overall result. However, boundaries are often chosen in a seemingly arbitrary way, sometimes on the basis of rules of thumb, or chosen simply for convenience.[33] Because of this, boundary selection can be a problem: processes that are outside of the boundary may be more significant than assumed, and ignoring them can skew the results.[34]

Economic Model Based LCA. LCA approaches at this scale rely on input−output economics,[35] which uses a static, linear equilibrium model of the economy by dividing it into discrete sectors and treating it as a network, with the connection between sectors being money in the form of actual cash or goods and services. By using linear network algebra techniques, the model can determine the effect of stimulating certain sector(s) by means of a purchase of a good or service throughout the entire economic network.[36] For example, if a ton of steel was purchased from a steel mill, the input−output model would give the direct and indirect effect of that purchase on every sector of the economy. Economic model based LCA extends Leontief's input−output economic model by augmenting the economic activity with emissions and resource data for each sector on a per dollar basis, and therefore life cycle impacts can be determined. The Economic input−output LCA (EIO-LCA) model developed at Carnegie Mellon is most popular among economic model based LCA methods.[36] The input−output model alleviates the boundary selection problem encountered in Process LCA by incorporating the entire economy as the boundary.[37] However, despite the comprehensiveness of economic model based LCA, it has two main disadvantages. First, it lumps the economy into a finite number of sectors, which introduces aggregation errors. For instance, the model does not distinguish between two products in the same economic sector even if they are manufactured differently. Second, it considers monetary flow to be a proxy for physical flow, which is true only if prices are homogeneous, which is often not the case in reality. This implies that all sectors pay the same price for a good or service from another sector. Also, the EIO-LCA model neglects ecosystem goods and services which are consumed through the life cycle and gives only emissions and energy consumption information. This last shortcoming is overcome by the Eco-LCA model at the economy scale, which is described in more detail in the next subsection.

Hybrid Methods. Hybrid LCA combines models at the economy and process scales with the intention of getting the best of both approaches. In a hybrid approach, details about the process such as emissions and energy usage are combined with input−output data to capture upstream emissions and energy use. The goal is to combine the comprehensiveness of the economic model based LCA with the detailed process information used in process model based LCA to create an LCA model that is likely to be more complete and accurate.

The easiest way to perform a hybrid LCA is via a "process sum hybrid" or "tiered hybrid" approach, which adds the results based on process models with those from the economic model when the latter supplies goods to the former. This differs from "integrated hybrid", which accounts for the fact that processes at the process level may also be part of an economic sector that is already being accounted for at the economy scale. It does this by removing the portion of the economic sector that is represented on the process scale to avoid double counting. However, it requires more information and is often difficult to implement. It has been suggested that the error in not performing an integrated hybrid is often minor.[38,39]

Choosing the LCA method that will give the most accurate and meaningful results is not obvious. The International Organization for Standardization (ISO) has outlined a basic methodology for performing LCA using a primarily process-based approach,[33] but this introduces the problem of possible narrow boundary selection. There is also support for input−output models because they are generally more comprehensive and can be combined with process data to form hybrid analysis, but this introduces the problem of aggregation errors and the errors of assuming a linear, static model of the economy. Instead of choosing one method over another, it may be worthwhile to use all of the methods when performing LCA and draw comparisons between them, and this is the approach adopted in this work.

Assessment and Evaluation in LCA. Emissions and Their Impact. Traditional LCA assessment focuses on emissions and their impact. Although results pertaining to specific emissions may be of interest, it is hard to draw conclusions from a LCA in terms of emissions using disaggregated data. This is why methods exist for aggregating emissions data that aim to combine the data into more manageable and physically meaningful metrics. These are so-called "midpoint indicators", as they aggregate data into potential impacts such as global warming potential, as opposed to "end point indicators" that aggregate data into categories such as cases of cancer or asthma. End point indicators, such as the Eco-indicator 99 method, use impact models to calculate the potential damage emissions may have.[40] Although these are meaningful and important, it is also vital to account for the goods and services that nature provides to completely specify the full LCA of a product or service.

Resource Use. Resources may be accounted via physical units such as mass, energy, and exergy. Among these, exergy is appealing because of its thermodynamic rigor and ability to account for resource use in both industrial and ecological systems. It can be applied to LCA by considering the cumulative exergy consumed in the life cycle. This has been done in two ways in existing methods. Industrial cumulative exergy consumption (ICEC) accounts for exergy consumption in industrial processes in the life cycle and has been developed and used in engineering.[22] ECEC also accounts for exergy consumption in ecological processes needed to make the natural resources consumed by industrial processes. In other words, it is expanding the boundary from the industrial scale to the ecological scale. This can be equivalent to the concept of emergy[41] developed by systems ecologists.[11] These physical quantities can be used to define aggregate metrics such as a renewability index (RI) and physical return on investment (ROI), as shown by the following equations.

$$\mathrm{RI} = \frac{X_{\mathrm{in}}^{\mathrm{renewable}}}{X_{\mathrm{in}}^{\mathrm{total}}} \tag{1}$$

$$\mathrm{ROI} = \frac{X_{\mathrm{out}}^{\mathrm{product}}}{X_{\mathrm{in}}^{\mathrm{processing}}} \tag{2}$$

Here, X represents the selected resource, which could be money, energy, or even mass. Renewability index is the fraction of resources consumed needed to make a product that are renewably sourced. Return on investment is similar to the monetary return on investment and is the ratio of the value of the product to the amount consumed in producing that product. It is important to note that return on investment only includes resources consumed in processing the product, which does not include the feedstock. This is because this quantity is supposed to give insight on the value of a product compared to the resources required in addition to what was already there in the raw materials. For example, when considering the return on energy investment for gasoline production, it does not make sense to consider the energy in the crude oil in the denominator of eq 2 but rather only the energy consumed to refine the crude into gasoline because this is what was truly "consumed" to make the gasoline. Similarly, "net energy" is the difference between the energy of the product and the processing energy. This point, however, is often misunderstood.[42] Although RI and ROI may provide valuable insight, it is important to use them in tandem with more disaggregated quantities to avoid coming to conclusions based on a metric that could hide vulnerabilities seen only in more detailed, disaggregated data.

Among the physical methods for resource accounting, only ECEC takes the substitutability assumption into account in an explicit manner by representing all resources in solar equivalents, as described in the introduction. A hierarchical approach[32] presents the data at different levels of aggregation, from the detailed raw data about resource use through to the higher level of aggregation. This way, aggregated metrics can be used while still keeping the more detailed data in sight to avoid losing information.

These ideas are included in the recently developed approach of Eco-LCA.[32] This approach is meant to complement and extend conventional LCA and proposes a hierarchical aggregation scheme to quantify the role of resources. This natural resource oriented approach shows vulnerabilities and drawbacks of a particular product or process by determining the impact on the often ignored natural capital of the Earth. The main feature of Eco-LCA is that it focuses on consumption of ecological resources and uses various physical quantities such as mass, energy, and exergy for comparing and aggregating industrial and ecological flows. Like conventional LCA, Eco-LCA can also be applied to the process or economy scales, and a 1997 Eco-LCA model of the U.S. economy has been developed.[35] The present study develops a hybrid Eco-LCA model of the PDO pathways.

Allocation. Another important aspect of life cycle assessment and evaluation involves allocation. Allocation becomes important when a particular process results in multiple co-products. For example, in the wet milling of corn (one of the upstream processes for bio-based PDO production), multiple products are formed: dry germ, gluten feed, gluten meal, and starch.[43] Attributing all of the process requirements and emissions to one of the products may be unfair. Allocation remains controversial; it is not a widely accepted theory, and various methods exist on how exactly to allocate.[44] Two of the more common methods of allocation are market value-based and mass-based allocation.[45] In market-based allocation, the relative market values of the co-products are used as weighting factors for allocation. In the case of corn wet milling, if the starch product represented 90% of the total product stream value, then 90% of all the process requirements and emissions would be attributed to starch. In mass-based allocation, the same is true, but this time the relative mass of the co-products is the weighting factor. System expansion is another method for allocation, which is suggested by the ISO 14041 LCA standard.[46] This involves expanding the LCA boundary to include the processes that consume the co-products generated. Although this eliminates the need for fractional allocation, it introduces more complexity into the LCA because additional processes need to be considered.

Methods and Data Sources

Process Information and Assumptions. Two different routes of producing PDO are considered in this study. The first is a fossil-based production route, where syngas (a mixture of H_2 and CO) is reacted with ethylene oxide (EO) over a catalyst to form PDO.[47] The second route is a bio-based process, where glucose is fermented by a genetically modified strain of *E. coli* to produce PDO.[2] There is a third route based on acrolein, but it is not considered in this study because it is less economically attractive than the EO/syngas or bio-based processes and has a lower yield compared to the EO/syngas process.[48]

The functional unit for this study is 1 kg of PDO, and the scope is from "cradle-to-gate", meaning nothing is considered after the PDO leaves the factory "gate". This is because the end use of the PDO is independent of the method used to produce PDO given that the PDO is of the same grade and quality. A key assumption for the bio route is that the corn farming, wet milling, and PDO production facilities are all located close to each other. Therefore, transportation of corn from the farm to the mill and transportation of mill products to the PDO facility are neglected. This is a reasonable assumption because Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model has shown that only a small amount of the total energy consumed for corn farming and transportation is by transportation of the corn to the mill.[49] Also, this model assumed a fixed distance from the farm to the mill; in reality, this distance could be highly variable, and calculating transportation energy would therefore be highly variable as well. For the fossil-based route, it is assumed that the PDO facility is located on a refinery in Louisiana, so all necessary fossil fuel feedstocks are essentially available onsite. Therefore, no transportation of these feedstocks to the PDO facility is considered. For both the bio-based and the fossil-based routes, building materials for the various production facilities as well as materials for equipment and machinery are also neglected. This is because it would be very tedious and involve many assumptions to determine the amounts of these materials needed.[2,8,50] Such information at the aggregate economy level could be approximated via the relevant economic sector, but here it is assumed that their contribution to the overall life cycle will not be significant.[51] Another assumption is that the catalyst production is ignored for the fossil-based PDO production phase. This is because a reasonable approximation for the amount of catalyst needed per unit of PDO was not available. Also, the catalyst manufacturing phase for the EO and syngas processes, which was included in this study because the information was readily available, represents a very small fraction of the total life cycle impacts, so ignoring it only for the PDO process should also have a negligible impact.

Since both the bio-based and the fossil-based PDO processes are relatively new, much of the process level information, such as emissions and energy consumption, is proprietary and therefore difficult to find. For the fossil-based route, general patent information, reaction stoichiometry, engineering design assumptions, and CHEMCAD[52] process simulation software were used to model the process. For the bio route, process information was taken from a study on the LCA of PDO.[2] Figures 1 and 2 show the process details for fossil-based and bio-based PDO, respectively. Further details on the process variables used in each process can be found in the Supporting Information.

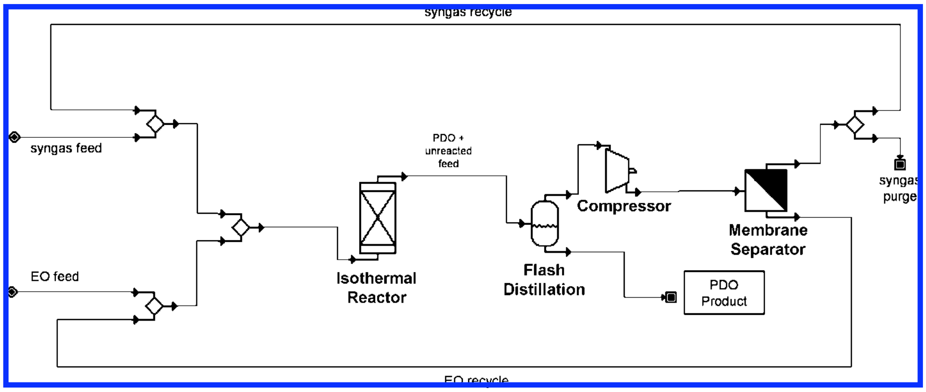

Figure 1. Process flowsheet for fossil-based PDO.

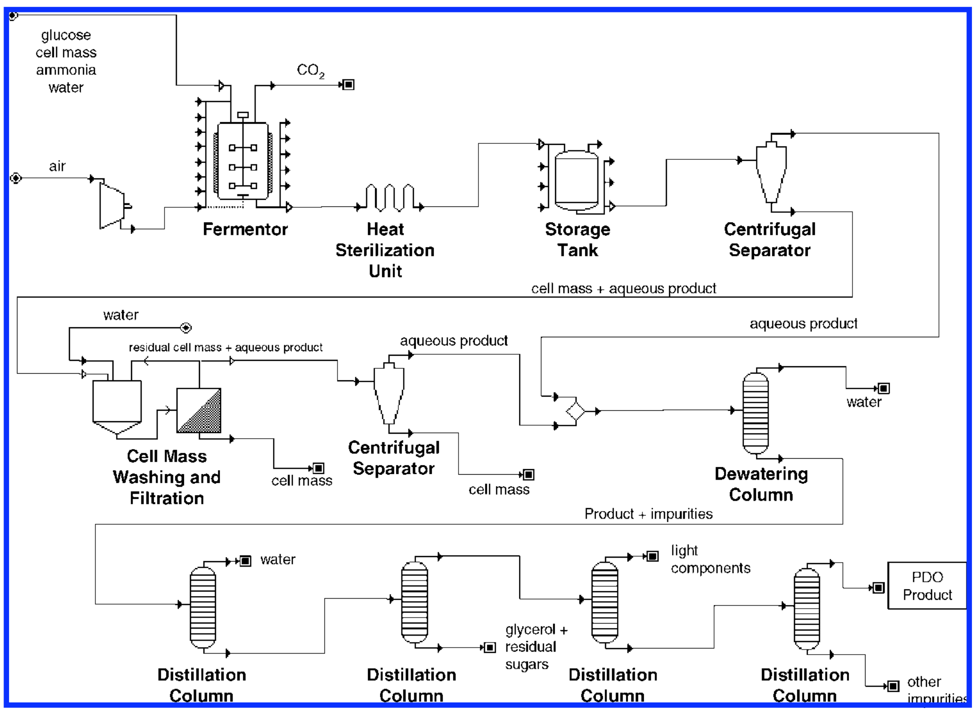

Figure 2. Process flowsheet for bio-based PDO.[2]

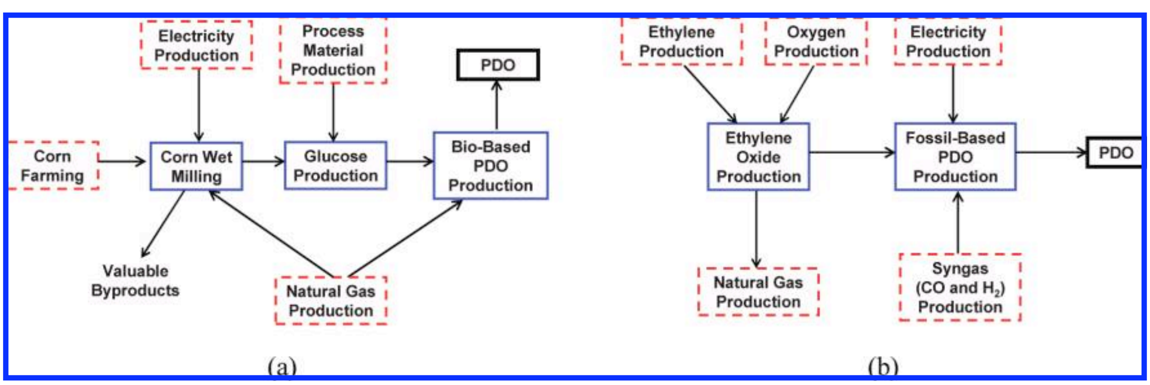

Figure 3. Process LCA boundary illustrating (a) bio-based and (b) fossil-based PDO. Process model based LCA for dashed boxes was done via SimaPro.

Methods for LCA of PDO. To access the life cycle impacts of producing PDO, three different methods were used: process LCA, hybrid EIO-LCA, and hybrid Eco-LCA. The process LCA was performed independently of the hybrid LCA, meaning the process LCA is not contained within the hybrid LCA. This is to demonstrate how an LCA can be performed in multiple ways and how this influences the results. Figures 3 and 4 show the LCA boundary for process LCA and both hybrid LCAs, respectively, for both bio-based and fossil-based PDO. In these figures, arrows indicate the flow of material. Some of the flows for natural gas appear to be going outward; this is because, in those processes, there is a large amount of heat given off as a result of the exothermic nature of the reaction. This can be captured in the form of steam, which is ordinarily produced

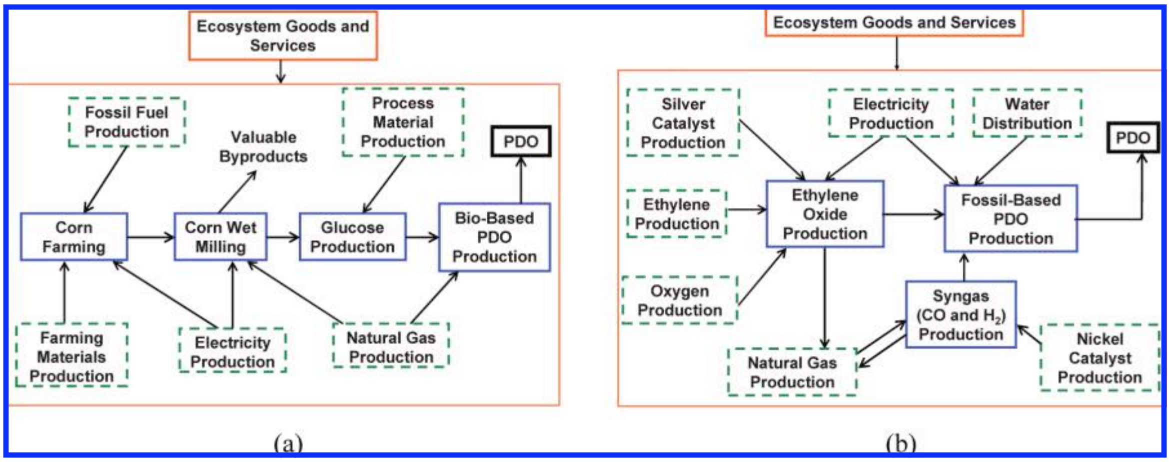

Figure 4. Hybrid LCA boundary illustrating (a) bio-based and (b) fossil-based PDO. Data for the life cycle of the dashed boxes was obtained from the economy scale LCA model.

from natural gas.[43] Therefore, a "credit" was given in the form of natural gas for the processes that generated excess steam.

SimaPro LCA software[53] was used to model the LCA of the processes with dashed lines, whereas process information available in literature was used to model the processes with solid lines. SimaPro does account for processes upstream from those outlined in dashes, albeit in a process based LCA fashion. Wherever possible, models based on U.S. technology were used within SimaPro; however, some processes only had models based on European technology. In this case, they were used as a substitution for U.S.-based models. The reason that information from literature was needed to model the processes with solid lines is that SimaPro did not have a model for these.

Figure 4 shows the hybrid LCA boundaries for bio-based and fossil-based PDO. EIO-LCA stops at the economy level, whereas Eco-LCA extends the boundary to include ecosystem goods and services. This study used the 1997 491-sector model of the U.S. economy for input−output LCA which is currently the most recent model available in the EIO-LCA and Eco-LCA models. The technique for hybrid LCA is to keep extending the boundary until a process is reached that can be well represented by an economic sector. For instance, corn farming can be found within a sector in EIO-LCA. However, it may be part of a highly aggregated sector that may or may not represent corn farming accurately. Because there is plenty of literature available on corn farming, it can be combined with economic model based LCA to capture the upstream effects of the materials and energy needed in corn farming. The results at each level were summed to capture the total life cycle.

For this study, mass- and market-based allocation were considered using a mass fraction of 0.667 (based on the fact that the milling product stream mass is 66.7% starch) and a market fraction of 0.652 (based on the fact that the milling product stream value is 65.2% starch).[43] Because the market and mass fractions are essentially identical, only mass-based allocation is presented because they give virtually identical results. The system expansion approach for allocation was not used because of its complex nature.

Aggregation Methods for Emissions and Resources. For this study, the Centre for Environmental Studies (CML), University of Leiden, baseline method was chosen, which characterizes emissions into 10 categories or metrics.[54] Midpoint indicators were chosen for this study to avoid the controversial nature of end point indicators and because they rely less on model predictions. Resource aggregation was accomplished using the techniques of net energy, ICEC, and ECEC as well as metrics based on these quantities.

Data Sources. This section will briefly overview data sources used in this study. More details can be found in the Supporting Information.

Process LCA. Databases in packages such as SimaPro have models for corn farming, natural gas production, electricity production, and various process material production; they do not have models for corn wet milling, glucose production, or PDO production. Similarly for the fossil-based process, SimaPro has models for all processes except EO production and PDO production. To fill in the gaps of missing process information, various data sources were needed. In the case of EO, a common chemical engineering encyclopedia provided process level information on emissions and raw material and energy requirements.[55] This is how the amounts of ethylene, oxygen, and utilities are determined for EO production. For fossil-based PDO production, chemical engineering simulation using CHEMCAD[52] was performed to estimate emissions and raw material and energy requirements.

For the bio-based route, process information was needed for corn wet milling and glucose production. Since these are common processes, plentiful information is available on both of these. For corn wet milling, an extensive study[43] was used to determine all process requirements such as raw materials and energy. For glucose production, an NREL study[56] was used to determine processing chemicals needed to convert starch into glucose. For this process, emissions and energy consumption were ignored because very little processing energy is required for starch hydrolysis.[56]

Hybrid LCA. For the hybrid methods, process information is obtained in the same way as in the process LCA. However, processes that are in the "Economy Level" of Figure 4 need to be in terms of the producer price to use the economic model based LCA tools. Price information for energy flows is readily available via the Energy Information Administration,[57] which supplies official energy statistics for the United States. Material prices are less readily available, but resources do exist, such as *ICIS Pricing* and other miscellaneous publications. The problem with price information is that in reality, prices fluctuate (sometimes significantly), but the input−output models rely on the assumption that prices are static. Whenever possible, average prices were used and the price fluctuations were treated as sensitivities in the data. Details on the exact sources of pricing can be found in the Supporting Information.

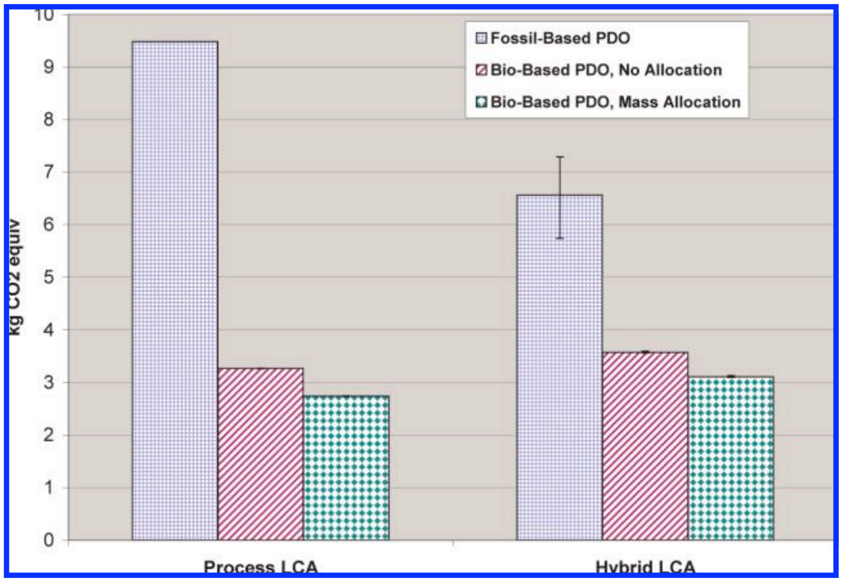

Figure 5. Global warming potential for bio-based and fossil-based PDO.

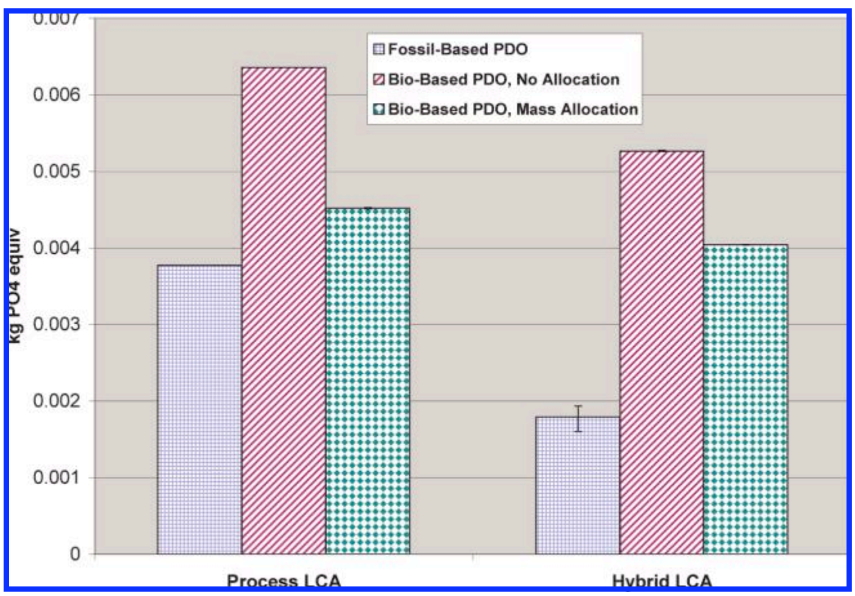

Figure 6. Eutrophication potential for bio-based and fossil-based PDO.

Emissions and energy consumption for fuels that are burned in the "Process Level" processes in Figure 4 are calculated using emissions and enthalpy values from the Argonne National Laboratories GREET model.[49] Emissions not resulting from fuel combustion are estimated through process level data found in literature, as mentioned in the section on Process LCA. Exergy and emergy consumption values are calculated using thermodynamic data available in literature.[11,22,58,59]

Results and Discussion

The results for the Eco-LCA portion of this research can be reproduced through a software tool that is under development.[60]

LCA Results. This section contains results from the three LCA methods as applied to PDO. The "sensitivity bars" in the figures for hybrid LCA arise because there is a range of values that can be found as a result of variations in the prices of products such as electricity.[57]

Emissions. The emissions considered in this study are so-called "conventional" air pollutants and GHGs. Phosphorus and nitrogen emissions to water are considered only for the corn farming process in bio-based PDO, because fertilizer runoff is a significant pollution source in farming. Figures 5 and 6 show the midpoint metrics of global warming potential (GWP) and eutrophication potential for fossil-and bio-based PDO. The remainder of the CML midpoint metrics as well as the disaggregated emissions can be seen in the Supporting Information.

Note that all of the LCA methods used in this study report emissions data beyond what is considered here. These emissions are not considered because of a couple of factors. First, EIO-LCA reports over 500 different emissions but does not include a tool that can combine these releases into midpoint indicators. Therefore, accounting for every emission that EIO-LCA reports can be extremely tedious. SimaPro, on the other hand, has built-in capabilities to automatically characterize and aggregate the many emissions that are reported. Second, while both EIO-LCA and SimaPro provide vast emissions data, both methods do not report the same data. Therefore, for a fair comparison of LCA

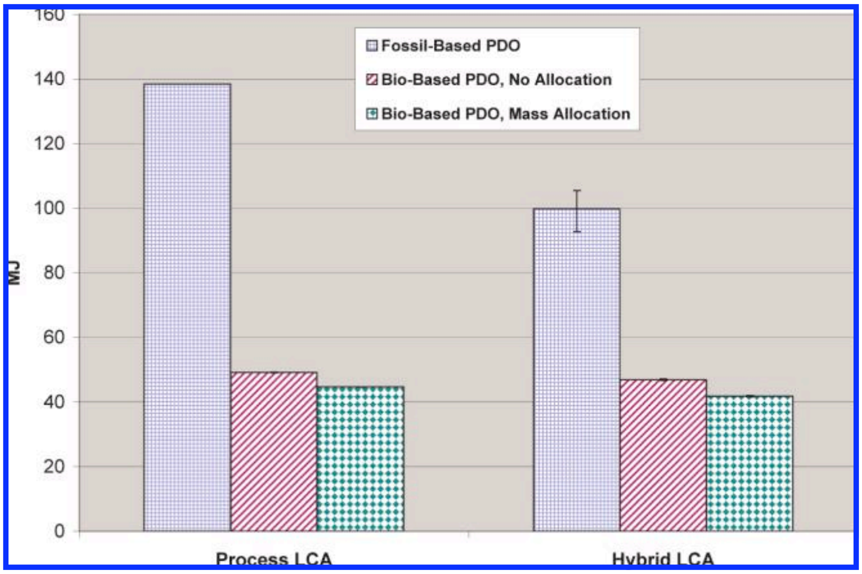

Figure 7. Fossil fuel consumption for bio-based and fossil-based PDO.

results for different boundaries, only the conventional air pollutants and GHGs are considered since these are included in both SimaPro and EIO-LCA.

Energy Consumption. Figure 7 shows the results of energy analysis applied to PDO. All three LCA methods indicate that bio-based PDO uses less fossil fuels over its life cycle than fossil-based. EIO-LCA and Eco-LCA give essentially the same results; however, process LCA gives nearly a 40 MJ higher value for fossil fuel consumption in the fossil-based PDO.

Compared to the LCA results of DuPont[31] and Anex and Ogletree,[2] Figures 5 and 7 predict nearly a 50% reduction in GHG emissions and over 50% reduction in fossil fuel consumption for bio-based PDO compared to fossil-based PDO, whereas DuPont and Anex and Ogletree predict a 20% and 40% decrease in GHG emissions and fossil fuel consumption, respectively. The reason for this discrepancy is not clear because both studies do not reveal specifically the data used. For example, the study by Anex and Ogletree take information for the fossil-based PDO process from a private consulting firm and therefore the data is not publicly available. Also, their LCA boundary for the fossil-based process may be different than the one used in this study. However, this study and those by DuPont and Anex and Ogletree give the same trend which is that bio-based PDO emits less GHGs and consumes less fossil fuels compared to fossil-based PDO.

Resource Consumption. Up to this point, process LCA, EIO-LCA, and Eco-LCA have all given the same types of results. The additional insight from Eco-LCA becomes apparent when resource consumption is considered and explored via various physical aggregation schemes.

For resource consumption as applied to PDO, two scenarios are considered. The first case is the increase or decrease in resource consumption if a unit of PDO produced via fossil fuels was replaced by a unit of bio-based PDO. This can be seen in Figure 8. In this figure, anything above the *x*-axis corresponding to the *y*-value of unity in Figure 8 indicates that bio-based PDO consumes more of that particular resource than fossil-based PDO. The reverse is true for anything below the *x*-axis corresponding to the *y*-value of unity. This figure shows that bio-based PDO will increase consumption of resources such as fertile soil, agricultural land and water, and natural gas. It will also return more detritus that forms soil, sequester more CO_2 via farming, and reduce the consumption of many minerals, crude oil, and other resources.

The second scenario considered is what would happen if the current national consumption of PDO was made entirely from the bio-based route. The current PDO demand is approximately 45.4 million pounds.[61] Figure 9 shows the fraction of national consumption of ecological resources that would be consumed under this situation, which is quite small. If the projected 2014 PDO demand of 145 million pounds[62] was produced entirely from the bio route, the trend is nearly identical with little change. This figure can be seen in the Supporting Information.

Cumulative Exergy Consumption Analysis. Another important aspect of Eco-LCA is its ability to account for ecological resources via their exergy and emergy. Figure 10 shows the ICEC for bio-based and fossil-based PDO. This figure indicates that bio-based PDO consumes approximately seven times more ICEC than fossil-based PDO. However, most of this ICEC is renewable; in fact, the nonrenewable part is virtually invisible on the graph. This result is counterintuitive and misleading and is due to the assumption of substitutability between resources in terms of their exergy. This conveys the limitation of ICEC for analyzing systems that use a wide variety of resources. Taking away the renewable ICEC from Figure 10 gives a different perspective, as seen in Figure 11. Now it becomes clear that fossil-based PDO consumes approximately twice the amount of nonrenewable ICEC as bio-based PDO. Taking into account DeWulf's assumption that only 2% of solar exergy is consumed for photosynthesis,[26] Figure 12 shows how the total ICEC changes. Now, fossil-based PDO consumes more total ICEC *and* nonrenewable ICEC than bio-based PDO. The reason is that a large portion of the renewable ICEC for bio-based PDO is sunlight compared to fossil-based PDO, so taking away 98% of sunlight ICEC for bio-based PDO is a much larger decrease than for fossil-based PDO. Figure 13 shows the ECEC, which represents the ecological support required for these processes. Fossil-based PDO requires more ecosystem support, mainly due to the large reliance on fossil resources. Note that, as a result of the quality correction in this approach, the contribution of renewables is greatly diminished.

Renewability index and return on investment defined for ECEC, ICEC, and ICEC using DeWulf's sunlight assumption are shown in Figures 14 and 15 ("NR" stands for nonrenewable).

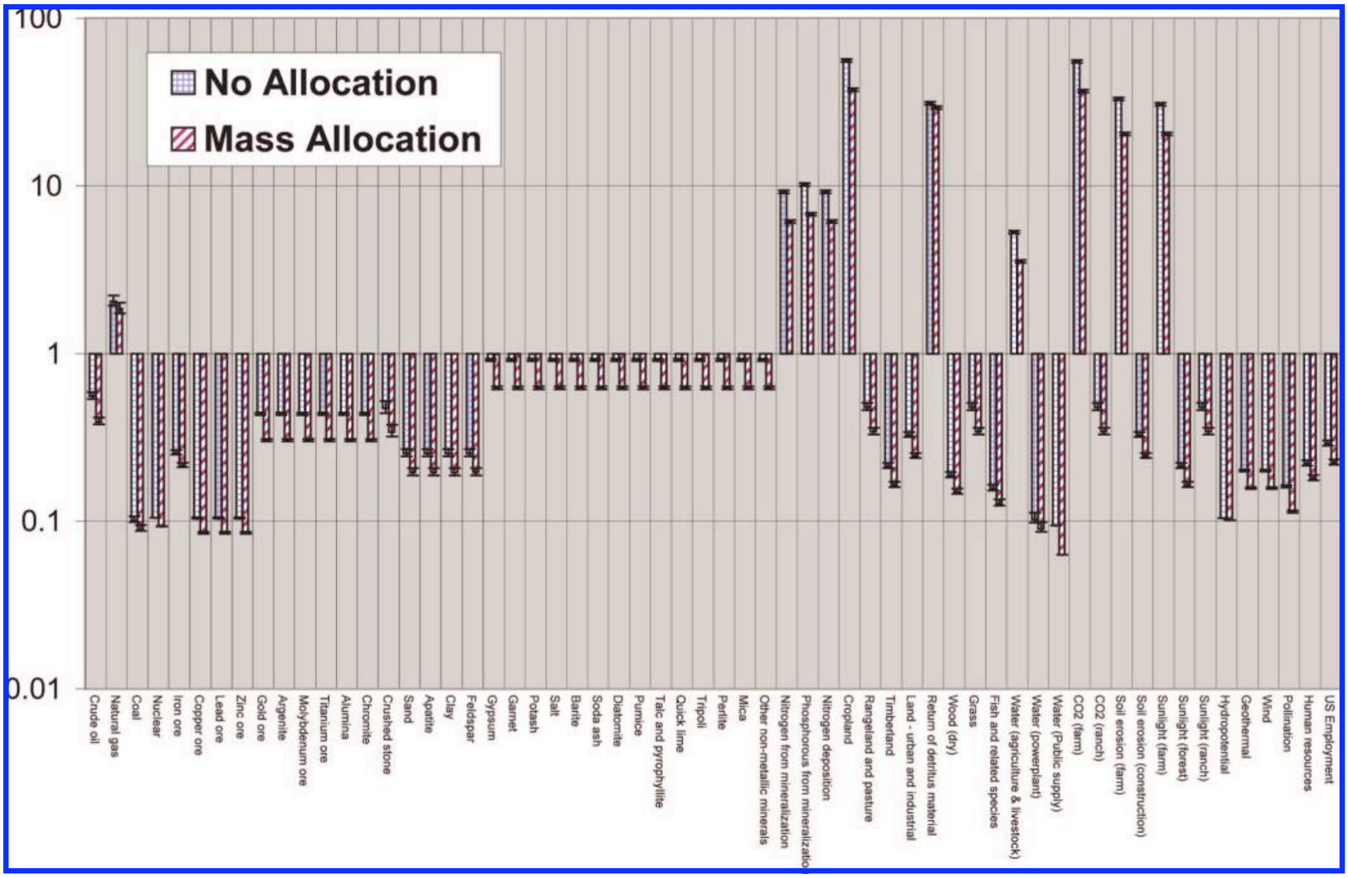

Figure 8. Ratio of bio-based PDO to fossil-based PDO.

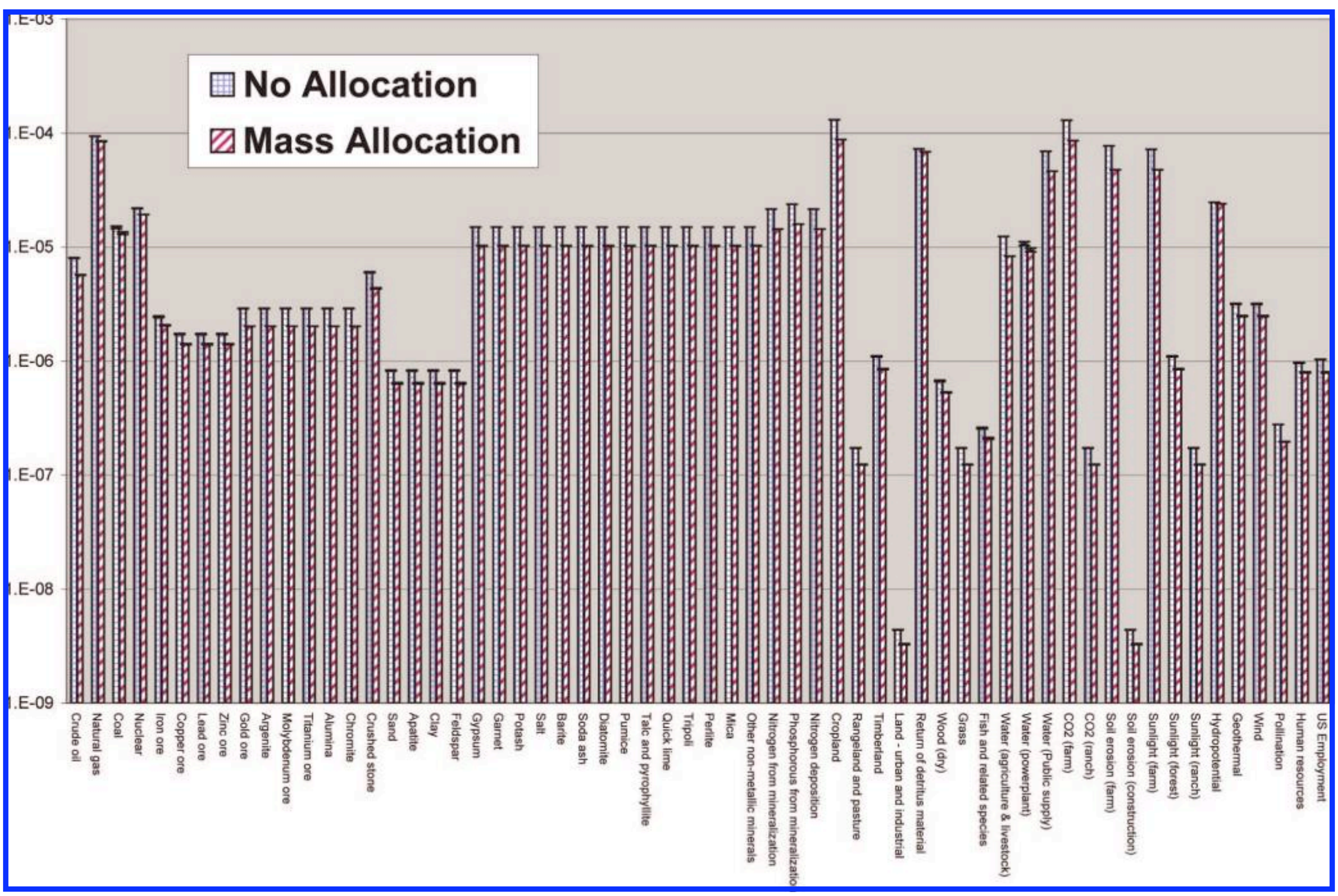

Figure 9. Fraction of national consumption if current PDO demand was made from the biological route.

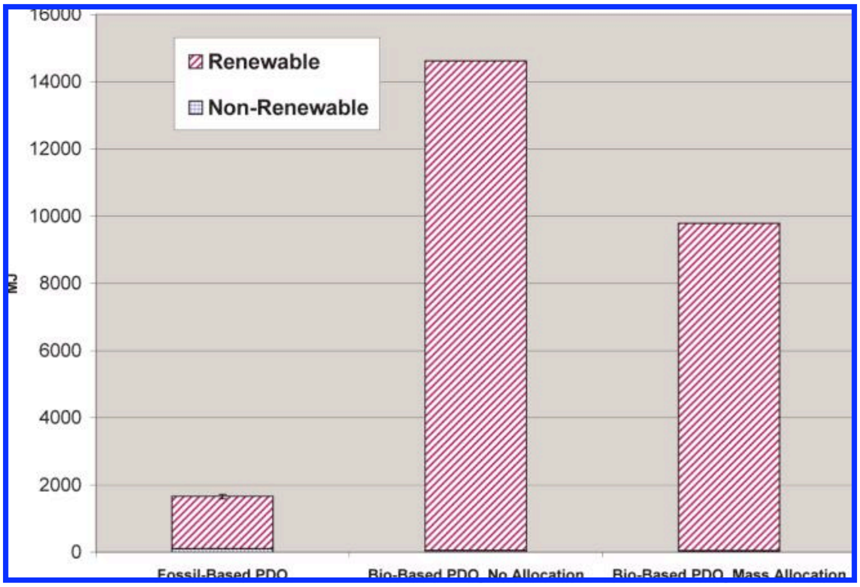

Figure 10. ICEC for bio-based and fossil-based PDO.

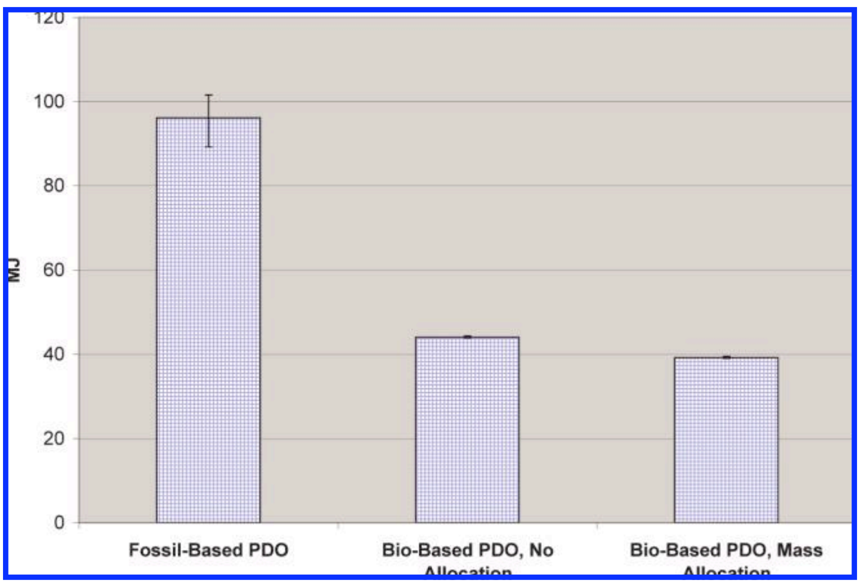

Figure 11. Nonrenewable ICEC for bio-based and fossil-based PDO.

In the renewability index figure, ICEC analysis indicates that both fossil fuel and bio-based PDO have a high renewability index, with the value approaching one. This is due to the sunlight issue that was discussed earlier in this section. Because there is an extremely large portion of ICEC from sunlight, which is renewable, the ratio defined by eq 1 is dominated by sunlight. Therefore, regardless of feedstock, the renewability index will be close to one. Correcting for sunlight using DeWulf's method alleviates this problem but still indicates a high renewability index for fossil-based PDO, which is counterintuitive since fossil feedstocks are inherently nonrenewable. Using ECEC to calculate the renewability index dramatically decreases the value. In all three cases, bio-based PDO has a higher renewability index, which seems logical because of the renewability of the feedstock. However, it is not dramatically higher, mostly because of the intensive processing that goes into converting biomass into a useable product, which involves fossil fuel consumption and other nonrenewables. It is also because bio-based PDO increases the consumption of natural gas.

Figure 15 also gives different results depending on the type of data used to make the calculation. ROI based on ICEC gives a small value for both fossil-based and bio-based PDO with fossil fuel being slightly higher. ICEC using DeWulf's method gives a completely different trend and indicates that the ROI for bio-based is much higher than the fossil-based PDO. This is because sunlight makes up a large portion of the exergy consumed in the bio-based production route, and only accounting for 2% of this causes the return to increase. Considering only the return on nonrenewable exergy also indicates that the bio-based route is superior. The fact that the ROI is less than one does not mean that the production routes are not thermodynamically feasible; since PDO is a material and not a fuel, it is expected that the thermodynamic value of PDO is to be less than the thermodynamic value of the resources required to produce the PDO. ROI based on ECEC is slightly different than that based on ICEC. This quantity can never be less than one because the ECEC of PDO is always larger than the processing ECEC, so it is not possible to have a denominator in eq 2 greater

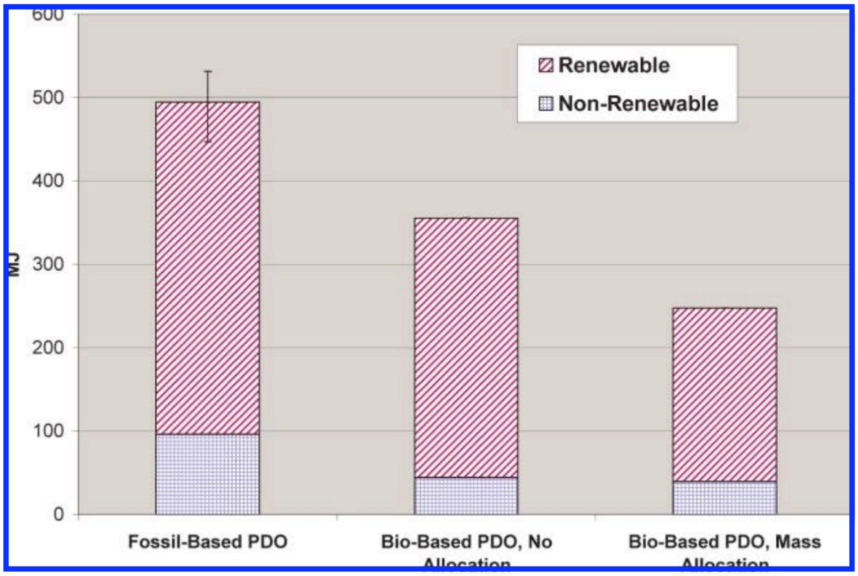

Figure 12. ICEC for bio-based and fossil-based PDO, using DeWulf's correction for sunlight.

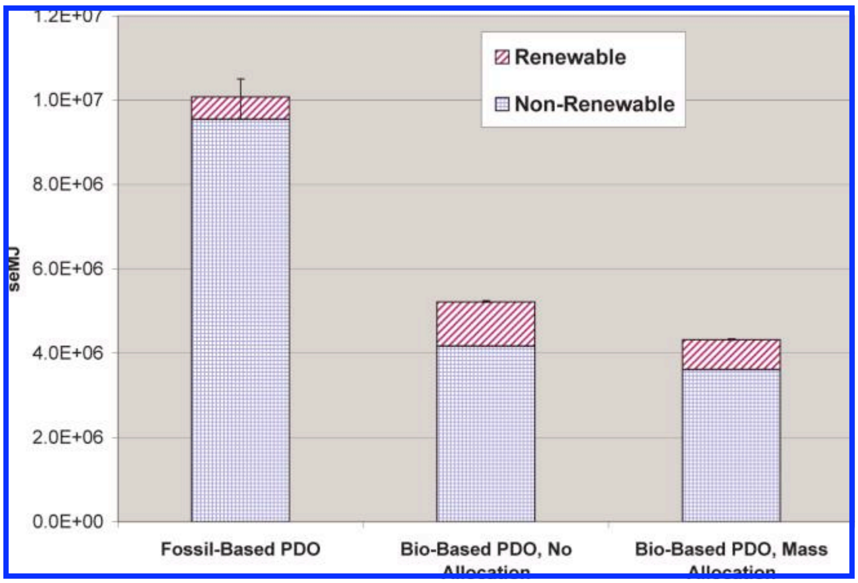

Figure 13. ECEC for bio-based and fossil-based PDO.

than this quantity. ROI based on ECEC gives values of about 1 for both fossil-based and bio-based PDO, which is near the lowest possible value. This is because feedstock ECEC makes up a very small portion of the total ECEC in the life cycle, so processing ECEC is very close to the total ECEC consumed. Return on nonrenewable ECEC shows bio-based PDO to be slightly better than fossil fuel PDO.

Sources of Uncertainty. When presented with LCA results or performing an LCA, there are always inherent sources of uncertainty and error that can arise. When calculating process variables, such as the amount of feedstock needed and energy requirements, there are certain "best practice" assumptions that need to be made because data is not readily available. For the production of PDO both from fossil fuels and biomass, little information is known other than patent literature. Therefore, estimation or simulation of the process is necessary to get values for process variables. This introduces uncertainty because it may or may not accurately represent the process as it stands in real life. Emissions data often has to be estimated or even ignored for certain processes because of the lack of available data. As stated in the section "Boundary Selection in LCA", LCA at both process and economy scales is dependent on process models and price information, respectively, both of which are dynamic and approximated. This is the nature of LCA, as it is often based on approximations and educated guesses to fill in missing information. Further improvement of life cycle inventories and publicly available data will undoubtedly make LCA a more accurate tool. As it stands now, it is the best method available to capture and quantify the life cycle of a product or process. Taking into account broader impacts is a step in the right direction to improving the sustainability of industrial processes.

Discussion of LCA and Aggregation Methods. The three LCA methods used here do accomplish the goal of capturing the broader impacts of a particular process that are neglected when considering the process alone, albeit in different ways and in varying degrees of scope. Process LCA and hybrid EIO-LCA give essentially the same type of results, namely, emissions and energy (net fossil fuel consumption) data. As applied to the PDO study, they also give very similar trends upon aggregation, which is that bio-based PDO creates less GHG emissions but creates more eutrophication potential. In terms

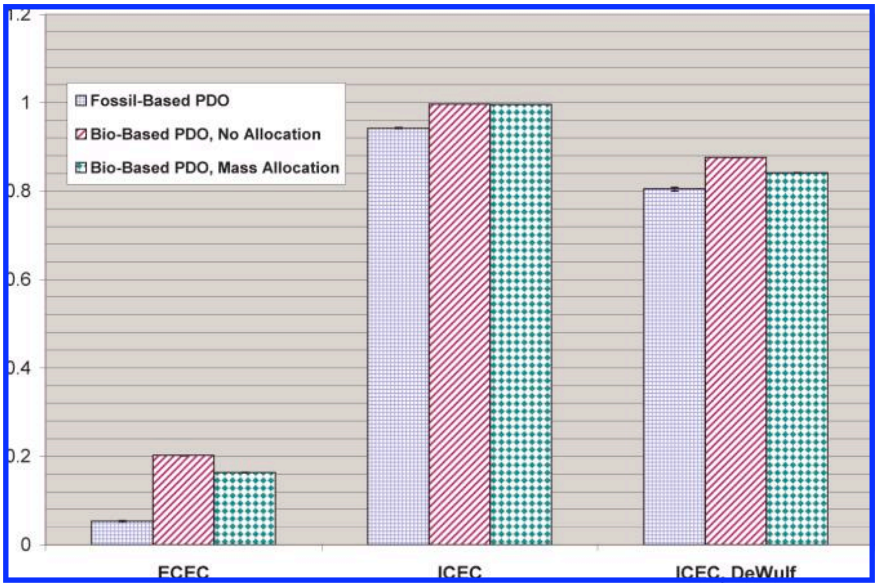

Figure 14. Renewability index.

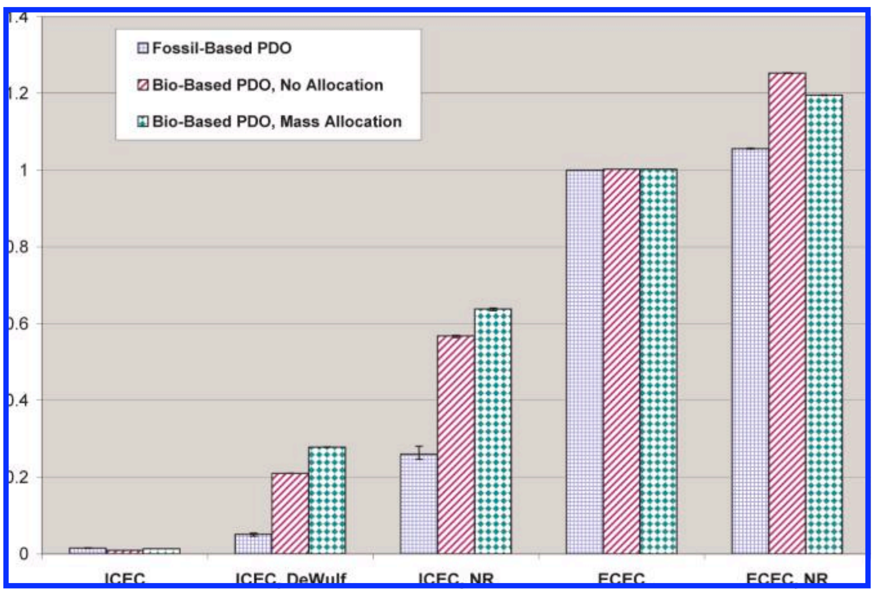

Figure 15. Return on exergy/emergy investment.

of net fossil fuel consumption, all three LCA methods indicate that bio-based PDO uses less fossil fuels over the life cycle.

Comparing the results of process LCA with those of the hybrid LCA, Figure 7 shows that that process LCA indicates nearly 40% larger fossil fuel consumption than hybrid LCA for fossil-based PDO. This difference is not seen for bio-based PDO. As a result of the inherent complexity of the two life cycle methods and the data that each one uses, it is difficult to pinpoint the exact reason for this large difference. Even so, this issue has been looked into in more detail to determine why process and input−output LCA can give much different results.[34] It has been shown that fuel consumption in the electricity generation economic sector is underestimated by input−output models. The cause of this may be the price homogeneity assumption of input−output analysis, which assumes that the price of a certain commodity is the same throughout the economy. However, sectors such as electricity generation are known to get a "discount" on fuels such as coal, and therefore the price homogeneity assumption is violated and the model will give lower values for the amount of fuels needed for electricity generation[34] because the model equates a monetary discount to a physical discount. Since fossil-based PDO uses a large amount of electricity, there is a large discrepancy between process and input−output methods due to the underestimation of fuel consumption in the electricity generation sector. The discrepancy between process and input−output methods is not seen in bio-based PDO because these processes use significantly less electricity, so the effect is not as noticeable.

Other than a few discrepancies, the three LCA methods seem to be, in general, fairly similar in terms of final results. Which one, if any, is superior and should be used over the others is not obvious unless the goals for the LCA are considered. For overall robustness and completeness of results, hybrid Eco-LCA may be superior over process LCA and hybrid EIO-LCA. This is because it combines the elements present in those two LCAs, namely, emissions and energy consumption, and extends them to account for energy quality and resource consumption. If anything has become apparent in the past decade, it is that neglecting the role of ecosystem goods and services can have catastrophic effects. Therefore, it is imperative to consider the stresses a process places on these goods and services instead of only considering emissions and energy consumption. For PDO production, looking only at emissions and energy consumption indicates that bio-based PDO is the better alternative. However, Eco-LCA takes this a step further and provides additional insight into the ecological aspects that is not available via other methods.

However, sometimes the goal of an LCA is to get results efficiently and with a minimal time commitment. Hybrid studies are generally more time-consuming and involved than process LCA due to the need for additional data and lack of appropriate tools. For process LCA, using commercial software such as SimaPro makes performing an LCA fairly straightforward and fast, although the unavailability of data may make performing a process LCA more involved for certain studies. Therefore, there is a tradeoff when choosing an LCA method. For a faster LCA, process LCA performed with commercial software is usually the fastest of the three methods. However, completeness, robustness, *and* efficiency are often desired. For this reason, further development of software for hybrid LCA is recommended to aid in performing faster LCAs using these methods.

Aggregation methods shown throughout this paper are important in understanding "big picture" consequences of both PDO production routes. The disadvantage of these aggregation methods is that they lose the fine grained detail of the disaggregated data. For example, Figure 14 indicates that bio-based PDO is more renewable than fossil-based PDO. However, since this is an aggregated metric, the information of the vulnerabilities of bio-based PDO is completely absent, which is seen in the disaggregated data of Figure 8. The more appropriate approach is to use both the disaggregated and the aggregated data in tandem to draw conclusions. This way, the ease of interpretation inherent in aggregated metrics is always presented with the disaggregated data in the background so that both can be used to supplement each other.

Even with the loss of information issue aside, there are still other problems created when aggregate metrics are presented. More specifically, the question of which metrics make sense to use for interpretation of LCAs is not easily answered. There is the choice of using ICEC, ECEC, and their variants as the basis for the calculation of the renewability index and return on investment. This study shows that ECEC seems to provide the most meaningful aggregate results and is best at considering substitutability between resources. Unfortunately, ECEC is also not without challenges and controversy. Hence, more empirical studies like the one in this article are needed for gaining insight into the pros and cons of various aggregation methods.

Another important result of this study is the role of allocation. In general, whether the results are allocated or not does not seem to have an impact on the overall conclusions of this study. This is significant because the issue of allocation is a subjective decision in current LCA methodology. However, it is still important to consider both allocated and unallocated results because there may be cases where allocation could play a larger role in the results of an LCA, such as in a process that produces a vast array of co-products and is also highly resource intensive (for example, crude oil refining). In the case of corn derived PDO, the starch makes up a large portion of the co-products involved in corn wet milling, so allocating the impacts of that process to starch does not significantly reduce the overall impact of accounting for corn wet milling.

Decision Making. Given the results of this study, it does not mean that all PDO production should shift from fossil-based to bio-based because Figures 8 and 9 show that there are some vulnerabilities of bio-based PDO production, namely, land use, water use, soil erosion, and nutrient runoff. Even though at the projected 2014 demand bio-based PDO seems to consume a very small fraction of these resources, the current trend of converting traditional fossil-based products to bio-based would have an additive effect, so the strain on these resources would increase. Coupling this with the increasing interest in producing larger fractions of the nation's fuel supply from biomass, a scenario in which these resources become scarce is not far fetched. From a decision making point of view, it is extremely important to take into account ecosystems because of their deteriorating state[15] and crucial role in ensuring sustainability. Since all living things depend on ecosystems, GHG emissions and fossil fuel consumption will be meaningless quantities if there are not enough natural resources to go around. For this reason, it is recommended to proceed with caution when exploring and promoting the possible switch from fossil-based products to bio-based products. Bio-based products may help in reducing air pollution and GHGs while using renewable resources, but they must be developed and used carefully to avoid immense negative impacts on the ecological infrastructure.

Another concern when proposing using a foodstuff such as corn for industrial or nonfood purposes is the "food for materials" issue. It has been suggested that food products should never be used for industrial purposes, because it could have negative impacts on society such as food shortages and food price increases. In the case of corn, this may be a legitimate concern, because a plethora of foods are corn-based. Tapping into the corn industry for other uses may cause this to happen, and because land is limited, sustaining both a food industry and industrial products industry on corn alone may not be feasible. Other potential feedstocks such as municipal solid waste (MSW) and cellulosic feedstocks such as switchgrass may provide a better alternative to corn-based bioproducts,and should be evaluated via life cycle studies.

Conclusions

The trends found in this study are similar to those found with biofuels, which are that biomaterials may reduce GHGs and fossil fuel consumption but they place a larger stress on ecosystems than their fossil-based equivalent. These stresses are determined by the Eco-LCA approach, which goes beyond conventional LCA methods by including energetic quality and ecosystem goods and services consumed through the entire life cycle. These results suggest caution before large scale development of corn-based PDO. In fact, this should be the case with all bio-based products since they rely heavily on ecosystem goods and services and have the potential to deplete these resources if not carefully engineered. Not accounting for the life cycle emissions and reliance on natural capital may present an even larger problem than the looming fossil fuel depletion and climate change, which is the continued degradation of our planetary resources and life supporting services.

Acknowledgment

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Supporting Information Available: Fictional LCA example, additional information about the thermodynamic methods used and process variables, additional figures, process LCA details, and hybrid EIO-LCA details. This material is available free of charge via the Internet at http://pubs.acs.org.

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