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Sustainable development of biorefineries: integrated assessment method for co-production pathways

Biorefineries for coproducing bioenergy and bioproducts have developed to replace petroleum refineries. This study presents a coincident feasibility assessment method that concentrated on the following challenges found from a thorough analysis of literature data: system boundaries, technological level, allocation, environmental concerns and uncertainty. The feasibility assessment method for sustainable development of biorefineries is validated by simultaneously performing TEA, LCA and UA on 10 biorefinery pathways to bioproducts integrated with bioethanol. The future realization of selected technology paths and products on the market makes it an economically and environmentally sustainable biorefinery.

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Sustainable development of biorefineries: integrated assessment method for co-production pathways†

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Biorefining is a promising technology for coproducing bioenergy and bioproducts to increase the benefit and sustainability relative to petroleum-driven products. Although several feasibility studies with certain valuations or materials have been conducted, a thorough analysis of the integration of bio-base products with sustainable bioenergy production is needed. This study conducts a comprehensive investigation of recently published feasibility studies on biorefining. Five challenges are found to be particularly important: system boundaries, technological level, allocation, environmental concerns, and uncertainty. A case study on 10 biorefinery pathways to bioproducts integrated with bioethanol (bioEtOH) is examined *via* a coincident feasibility assessment that concentrated on the proposed issues, as well as on certain technological, economic, and environmental aspects. When 25% of bioEtOH was replaced by furandicarboxylic acid (FDCA), 15.3–16.7 MJ of FDCA per gasoline gallon equivalent (GGE) of bioEtOH is produced, leading to economic mitigation potentials of US$2.40–2.48 per GGE.

Broader context

Biorefining has developed to replace petroleum refining having global warming and resource depletion issues. Given many decision makers have had to define proper criteria to evaluate the feasibility of emerging biorefinery technology, the following challenges are faced: (1) analysis of potential biobased coproducts: the number of published studies reporting the use of feasibility assessment methods in the field of biorefinery produced bioenergy has been rising but thorough analysis and comparisons adding a value range of a broad selection of bio-based products to their assessment are lacking, (2) technology complexity for biobased pathways: the coproduction technology has been technically possible at lab and even pilot scales, but the development of more new, versatile, bio-based materials and pathways will incrementally grow the biorefinery size and complexity, and (3) uncertainty of evaluation measures: biorefineries producing multiple outputs increase the difficulty of allocating economic viability or environmental impacts to one main from various outputs, resulting in an increase of uncertainty in valuation. Thus, our findings will allow decision makers to understand the methods involved in coincidentally evaluating and enhancing the potential of all biorefinery technologies if the future realization of selected technology paths and products on the market is economically and environmentally sustainable.

Introduction

Biorefining is an integrated process in which conversion and separation technologies are used to convert almost all types of biomass to bioenergy and biochemicals.[1–3] Biofuels as bioenergy are mainly used in the transportation sector and are produced at a commercial scale; however, most biofuels still cannot be produced profitably at the current price of oil.[4] Fig. S1 (ESI†) shows U.S. fuel prices (gasoline and bioethanol [bioEtOH]) and bioEtOH production in the 2000s. Recent price gaps between fuels and the slowing down of growth in production have revealed the limitations of government regulation and financial support in the expanding biofuels sector, which do not reflect the heterogeneity of preferences and the motivations of key actors.[5] In addition to mandates and promotion policies, the coproduction of value-added products represents a promising approach for reducing biofuel production costs. The average bioEtOH price over the past five years was 20% higher than the average price of gasoline.[6] The coproduction of biochemicals has the potential to reverse this trend by increasing overall profitability. When biochemical production replaces 25% of bioEtOH production, the bioEtOH price can be 3–69% lower than the gasoline price range.[4] In addition, biofuels and biochemicals carry smaller

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environmental impacts than petroleum-based products. If the carbon credits resulting from a reduction in greenhouse gas (GHG) emissions are considered revenue, this can affect the overall profitability of the coproduction pathway.[7–9] Coproduction technology is technically possible at a lab scale and even at pilot scales. Commercial biorefineries using starch-based feedstock (corn, sugarcane, grain, *etc.*) biomass have been already operated to produce valuable chemicals such as organic acids, alcohols, *etc.*[10] While the scale of commercial biorefineries (70 000–450 000 tonnes [t] per year of product) is smaller than oil refineries, biorefineries using lignocellulosic biomass will be developed in a similar pattern to starch-based biorefineries. For instance, Cargil-Dow, which can produce 140 000 t per year of polylactic acid (180 000 t per year of lactic acid) from starch, is developing a technology for lactic acid production using corn stover.[10]

However, the development of new, versatile, bio-based production materials and pathways incrementally grows the size and complexity of the biorefinery process, which results in an increase of uncertainty in valuations. Therefore, it is difficult to predict which type of emerging biorefinery will eventually prove to be technically, economically, and environmentally viable at an industrial scale. Conducting rigorous biorefinery feasibility assessments is essential to overcoming these barriers and uncertainties. The economic and environmental potential of bio-based products produced with biorefinery technology were estimated through a techno-economic assessment (TEA)[11,12] and life cycle assessment (LCA),[13,14] respectively. These methods are based on experimental and simulated data and are reliable analytical tools for evaluating various products and processes. In addition, an uncertainty assessment (UA) using mathematical techniques was applied to reflect uncertainty in the results.[15] These methods provide decision makers in the commercialization process with feasibility data to help determine the most promising coproduction pathways and also suggest avenues (*e.g.*, new research directions, bottlenecks) for accelerating the commercialization of the technology.

The number of published studies that report on the use of feasibility assessment methods in the field of biorefinery bioenergy production is increasing; however, thorough analysis and comparisons that add a value range of a broad selection of bio-based products to the assessment are lacking (Fig. 1). Accordingly, this study aims to identify the critical factors that may be important in a coincident feasibility assessment of new biorefinery technologies and alternative bioproducts. To this end, an overview of the typical feasibility assessment methods (TEA, LCA, and UA) used in the design and management of biorefineries is given and the limitations of each method in satisfying its own specific requirements are identified (see Feasibility assessment methods for biorefinery coproducing: a review). In addition, the similarities and differences between the feasibility assessment methods are presented. The analysis in this study opens the possibility of combining the three methods (TEA, LCA, and UA) to overcome their limitations and chart a way forward (see the Method section: a coincident feasibility assessment compensating limitations and combining methodologies). Based on this approach, potential bio-based coproduction pathways, with classified publications according to the given criteria, are selected and analyzed with the described methodology as illustrative case studies throughout this study (see Analysis of potential bio-based coproducts: case studies). We present 10 biorefinery pathways that are comparable at present, namely bioproduct pathways (adipic acid [AdA], caprolactam [CaL], pentanediol [Diol], phthalic anhydride [PAN], and furandicarboxylic acid [FDCA] with a lower technology readiness level [TRL], integrated with the production of bioEtOH *via* enzymatic or nonenzymatic sugar production from lignocellulosic biomass, with a higher TRL [see Analysis of potential bio-based coproducts: case studies]). Specifically, the impact of four different factors is compared and contrasted: (1) energy yield (EY), (2) economic potential (EP), (3) mitigation potential (MP), and (4) economic mitigation potential (EMP).

Feasibility assessment methods for biorefinery coproducing: a review

Numerous feasibility studies have been conducted to measure the research and development of coproduction pathways (Tables S1 and S2, ESI†). The relevant publications are assessed and compared in terms of (1) the feasibility assessment methodology applied, (2) the corresponding main decision factors addressed, (3) the corresponding performance index to be measured, and (4) the type of bioproduct being considered. As Fig. 1 shows, despite the high interest in individual feasibility studies, few studies have applied two or more assessment methods simultaneously. It is clear that the TEA of coproduction pathways has certain limitations, such as the consideration of MP and uncertainty. LCA also has some limitations, such as the need to determine the functional unit, consider the technological level, and select the byproduct allocation method.

When conducting a TEA study, it is necessary to determine the markets for alternative coproducts and the TRL for new biorefineries. The economic viability of bioenergy (fuel, heat, electricity) directly depends on the selling price of any coproducts, but the markets from biorefineries are often poorly defined or are of limited size, which leads to high uncertainty in relation to cost estimates. For example, the production cost of bioEtOH using corn stover increased from US$0.63 to US$2.43 per gallon when the market price of 1,5-diol decreased from US$2000 to US$1000 per t.[16] In general, the TRL of new biorefineries is low, and it is difficult to predict whether or not a biorefinery will work on scale-up at a high TRL. Although a number of studies have considered the TRL for conducting TEA, there are few standardized approaches available for estimating cost growth with unexpected problems (introducing additional processing steps including environmental aspects and risk identification, and decreasing plant performance) for low-TRL technologies, which means that uncertainty is also high.

In the LCA of a multi-product biorefinery, in which several products are produced in similar volumes, functional unit selection can be challenging in terms of the aggregation of

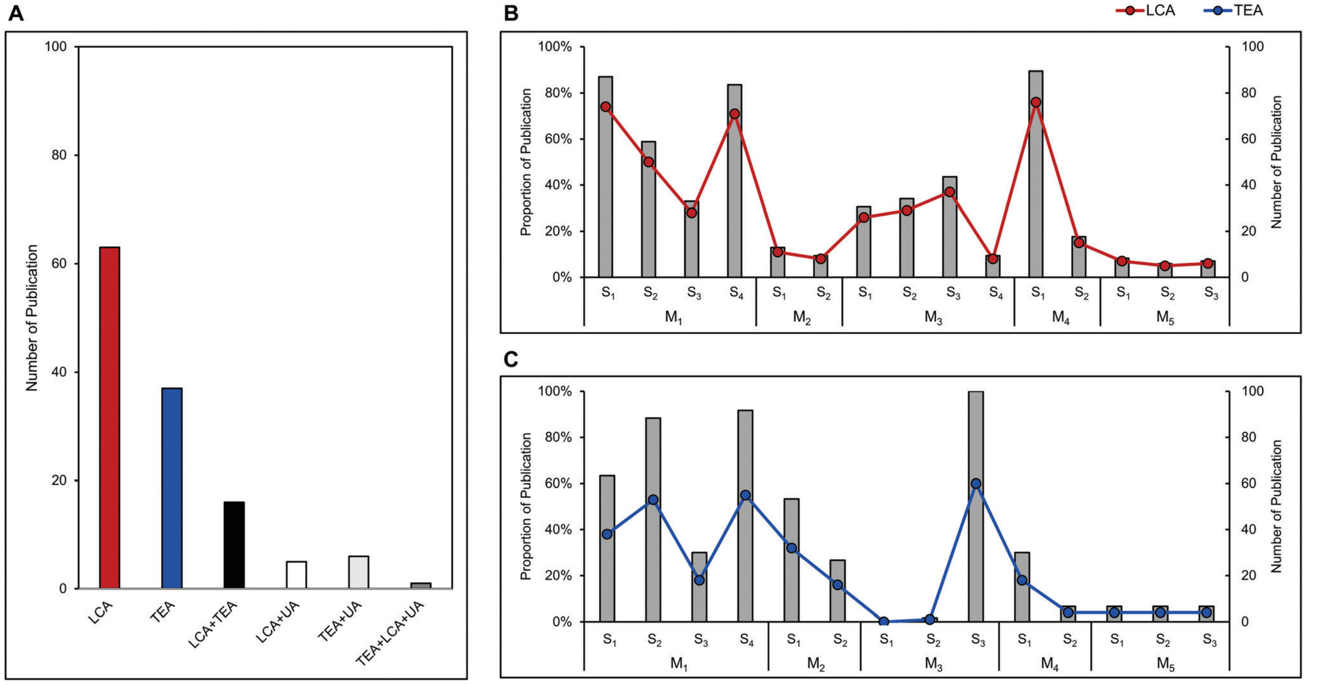

Fig. 1 Trends in research on coproduction pathways over the last six years (2014–2019). (A) The graph shows the number of papers published annually in the last six years. Papers containing keywords related to coproduction and feasibility assessment were searched for using Google Scholar. The keywords were common—biofuel, biochemical, and coproduct; LCA—life cycle assessment; TEA—economic analysis; and UA—uncertainty analysis. (B) LCA studies on specific categories of feasibility assessments. (C) TEA studies considering specific categories of feasibility assessments. In (B and C), the line and bar charts indicate the number and proportion of publications in each category, respectively. Categories considered in each scenario are as follows: M1 (system boundary), M2 (technological level), M3 (allocation), M4 (environmental aspect), and M5 (uncertainties). Each main category included the following detailed categories: M1—s1 (conversion), s2 (separation), s3 (disposal), and s4 (feedstock); M2—s1 (capital cost growth) and s2 (plant performance reduction); M3—s1 (mass-based allocation), s2 (energy-based allocation), s3 (economic-based allocation), and s4 (credit-based allocation); M4—s1 (global warming potential) and s2 (fossil depletion); M5—s1 (uncertainty in feedstock price), s2 (uncertainty in utility price), and s3 (uncertainty in product yield).

the results of the environmental impacts allocated to particular coproducts through partitioning based on a particular attribute, such as mass, energy, or market value. As an alternative, a functional unit can be defined through the expansion of the system boundaries to reflect all the bioproducts within a system; here, credit is received for the environmental burden that each product avoids or is replaced by producing each particular bioproduct. In such cases, coproduction with higher value bioproducts may require other combined unit processes, such as product separation, waste disposal, and feedstock handling. This can all affect the uncertainty of the overall environmental impacts associated with the main bioenergy or bioproduct. For example, GHG emissions arising from the biochemical conversion of bioEtOH to jet fuel using eucalyptus for feedstock range from 6.1 to 13.1 g CO_2 eq. per MJ, depending on the attributional partitioning allocation procedure that is applied.[17] Another challenge in the LCA of a biorefinery involves the timing of process variables (materials and energy consumed or emissions generated during the process), particularly in relation to the TRL. Unlike TEA, most LCA studies overlook the effect of production loss that inevitably occurs under coproduction pathways over time with a low TRL. This means that uncertainties still remain without its use, resulting in a time difference between the uptake and release of CO_2, which affects the overall environmental impact.

Few studies have simultaneously performed TEA, LCA, and UA on the coproduction pathway. In addition, these studies are limited to presenting the economic and environmental feasibilities determined by TEA and LCA. In some cases, conflict exists between economic and environmental feasibility, which causes confusion among decision makers. For example, producing bioEtOH and ethylene from lignocellulosic biomass creates lower GHG emissions than fossil-based products, while having a higher selling price than fossil-based products.[18] If the economic and environmental indicators could be integrated and presented as a single indicator, errors associated with decision making could be reduced.

Analysis of potential bio-based coproducts: case studies

Lignocellulosic biomass can be used for the production of sugars (glucose and xylose) *via* enzymatic or catalytic hydrolysis processing, and the sugars can be upgraded to a wide variety of bioenergy and bioproducts *via* fermentation or catalysis.[19,20] Lignocellulosic biomass based processing technologies generally have the drawbacks of a lower TRL and consequently have greater difficulty in assessing costs and environmental impacts compared with corn- and starch-based crops.[21] This study selected an ideal case for applying the proposed methodology to an attractive technology with a low TRL for the production of bio-based energy and products discussed in the roadmap, both currently and in the longer term. In terms of bioEtOH as bioenergy, two enzymatic and catalytic hydrolysis processing pathways were considered. Each bioEtOH production pathway is matched with five bio-based coproducts: AdA, CaL, Diol, PAN and FDCA. The bio-based coproduction pathways were selected with regard to the following criteria: (1) a current or future market size of at least 100 000 t per year, (2) a significant substitution potential of bio-based products to replace their petrochemical reference products with a well-known GHG emission intensity, and (3) availability of sufficient data derived from the conceptual design developed in the literature. Especially, the market size of the coproduct is a major factor related to the reliability of the feasibility study. When the market size is too small, uncertainty in the market price and sales potential of the coproduct will be significant. If the production scale is near the scale of the existing market, the results of the feasibility study could be invalid due to conflicts with market economics. The market size of each coproduct is shown in Table S3 (ESI†).

A simplified flowchart of the selected bio-based coproduction pathways, including the main platform chemicals and processing steps, is shown in Fig. 2. Further information is provided about the technical details of the processing pathways in the ESI† (Section S4: process description).

Using the method proposed in the Methods section (a coincident feasibility assessment compensating limitations and combining methodologies), assessments were performed for 10 biorefinery pathways, and the effect of the major limitations of each assessment methodology is identified in each scenario (Table 1). Fig. 3 presents a schematic diagram of the biorefinery pathways and the results of the feasibility assessments for each scenario. To enable a comparison among the different bio-based coproduction pathways, a uniform approach and assumptions were applied: a portion (25%) of bio-based products is produced from lignocellulosic biomass, with the remaining portion as bioenergy. As a performance index for the assessment methodology, EY, EP, global warming potential (GWP),

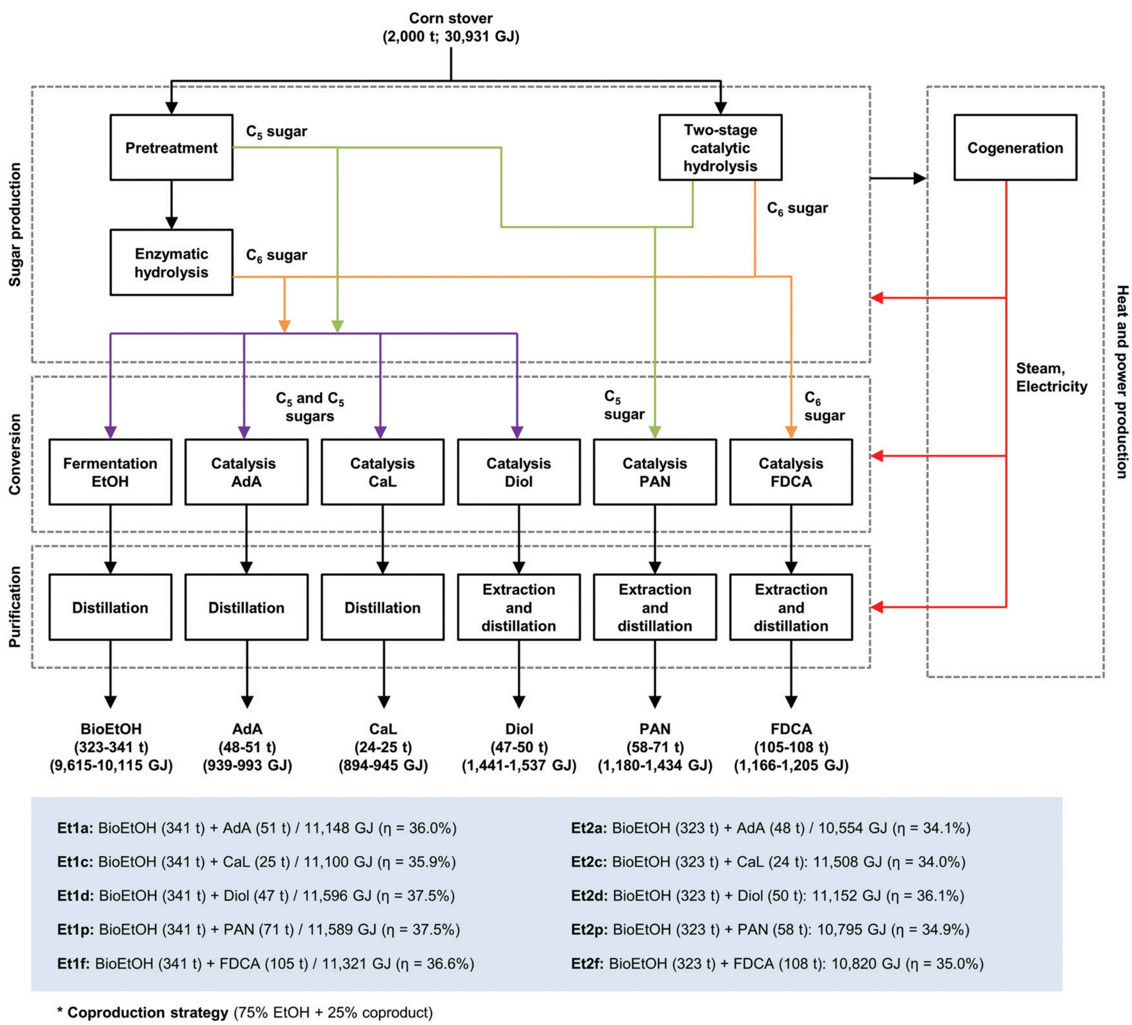

Fig. 2 Simplified flowchart of selected bio-based coproduction pathways presenting major processes with the production and energy flow of feedstock and products. There are 10 coproduction pathways that produce a portion (25%) of bio-based products from lignocellulosic biomass, with the remaining portion (75%) of bioenergy. The production and energy flow were calculated based on a coproduction pathway processing 2000 t of corn stover per day.

Table 1 Categories of feasibility assessment for coproduction pathways. Each category is defined to identify the change in results when overcoming each constraint of the feasibility assessments. Categories considered in each scenario are as follows: M1—system expansion (TEA and LCA), M2—pioneer plant analysis (TEA and LCA), M3—credit-based allocation (LCA), M4—mitigation potential (TEA), and M5—uncertainties (TEA and LCA). The results for each category are shown in Fig. 3

	Base	M1	M2	M3	M4	M5
System boundary	X	O	O	O	O	O
Technological level	X	X	O	O	O	O
Allocation	X	X	X	O	O	O
Environmental aspect	X	X	X	X	O	O
Uncertainty	X	X	X	X	X	O

and EMP were expressed in GJ, US$ per GGE, kg CO_2 eq. per GGE, and US$ per GGE, respectively.

Based on the different glucose and xylose to target product carbon yields in each pathway and the energy input of lignocellulosic biomass, the energy output of products for each pathway was estimated. The energy contents of the biofuels produced by enzymatic hydrolysis followed by fermentation (Et_1) were about 10 115 GJ per 2000 t of corn stover, which was higher than the catalytic hydrolysis based pathway (Et_2) (9615 GJ per 2000 t of corn stover) due to the 3.0% higher total sugars production. In the catalytic upgrading pathway to diol, PAN, and FDCA with Et_1 or Et_2, a high energy content of the bioproduct (1166–1537 GJ per 2000 t of corn stover) was produced. This led to about 3.8–5.0% more EY, which is the ratio of the energy output to energy input.

In the case of coproducts with higher values, the energy potentials above are finally converted into mass potential expressed in terms of tonne produced from conversion of one tonne dry corn stover. FDCA production (105–108 t per 2000 t of corn stover) is 1.5–4.5 times compared to the other coproducts (24–71 t per 2000 t of corn stover). This suggests that the coproduction of bioEtOH and FDCA could be a more feasible pathway.

Changes in EP and GWP per GGE of EtOH in each scenario are shown in Fig. 3. Laboratory-scale experimental studies on biorefineries, which are mainly focused on conversion technology, have previously demonstrated the potential of bio-based processes (base). In the base case, the EPs of Et1f and Et2f are US$0.76 and −1.06, and the GWPs are 3.12 and 1.17 kg CO_2 eq. To provide reliable feasibility results, the cost and environmental burden of conversion and separation processes after scaling up must be estimated. After the extension of the system boundary (M1), the EPs of Et1f and Et2f increased by 89% (US$0.68) and 128% (US$1.36), and the GWPs increased by 8% (0.26 kg CO_2 eq.) and 20% (0.23 kg CO_2 eq.). As Et2f includes more separation processes for sugar extraction and organic solvent separation than Et1f, the rates of increase in EP and GWP for Et2f were larger than those for Et1f. Biorefinery processes that utilize large amounts of solvents for solubilizing biomass are important because the energy requirements of the separation process can have a significant impact on the techno-economic and environmental feasibilities. In addition, some LCA studies have compared products based on the mass of the target ingredient for products with different purities, without considering the separation process. However, such methods could be inappropriate.

Biorefinery processes include many types of undemonstrated equipment for conversion and separation processes and can have problems that arise from processing solids, as well as impurity issues, among others. This can lead to a significant rise in production cost resulting from an increase in capital investment and a reduction in plant performance. When pioneer plant analysis is applied to Et1f and Et2f (M2) based on relatively immature technology, the EP of EtOH in Et2f (US$3.15) increases to higher than that of Et1f (US$3.11). The main reason for the inversion of EP is the high capital cost of the separation process in Et2f. This makes Et2f more affected by capital cost growth than Et1f. The reduction in plant performance affects the environmental burden as well as the production cost. This reduces the amount of EtOH produced over the lifetime of the plant (20 years) to 98% of the designed value. The GWP of Et1f and Et2f increases by 2% (0.07 and 0.03 kg CO_2 eq., respectively).

In general, multiple products are produced simultaneously in biorefineries, and the impact allocation of major products is important in LCA. Some methods for allocating environmental impacts are based on mass, energy, and price, but do involve some limitations. If the mass or energy of the main products is much lower than the byproducts, the impact of the main product can be under-allocated. In addition, in price-based allocation, the environmental impacts can depend on the price change, which is not reasonable. For this reason, a credit-based allocation method is recommended, as it reflects the environmental impact of byproducts as an emission reduction or increase compared to the emissions from existing production methods. When credit-based allocation, which assumes that a coproduct from a biorefinery replaces a fossil fuel-based coproduct, is applied to the two pathways (M3), the GWPs of Et1f and Et2f decrease by 74% (2.56 kg CO_2 eq.) and 148% (2.12 kg CO_2 eq.), respectively. This is similar to fixing the revenue of byproducts in TEA to determine the EP of a major product and is considered an appropriate allocation method in that it can effectively present the environmental impacts of the major product.

To date, most TEAs have focused on estimating process costs, which consist of capital and operating costs. However, as preventing environmental damage caused by investment projects has grown in importance, the costs arising from environmental aspects have increased. Relative emission reductions and increases can be converted into a MP based on the environmental impacts through LCA. The environmental cost is calculated using the MP of the two cases and the carbon price (US$60 per t CO_2 eq.).[7] Because the CO_2 emissions of Et1f and Et2f (0.89 and −0.69 kg CO_2 eq.) are lower than the emissions for gasoline (11.20 kg CO_2 eq.), the environmental costs are considered revenue. When the environmental aspect is reflected in the TEA (M4), the EMPs of Et1f and Et2f are decreased by 20% (US$0.63) and 24% (US$0.75). In the future, environmental costs may be incurred from existing traditional environmental damage, such as GWP, water pollution, and air pollution, as well as from new sources of environmental damage, such as fine dust and plastic, among others. Therefore, it

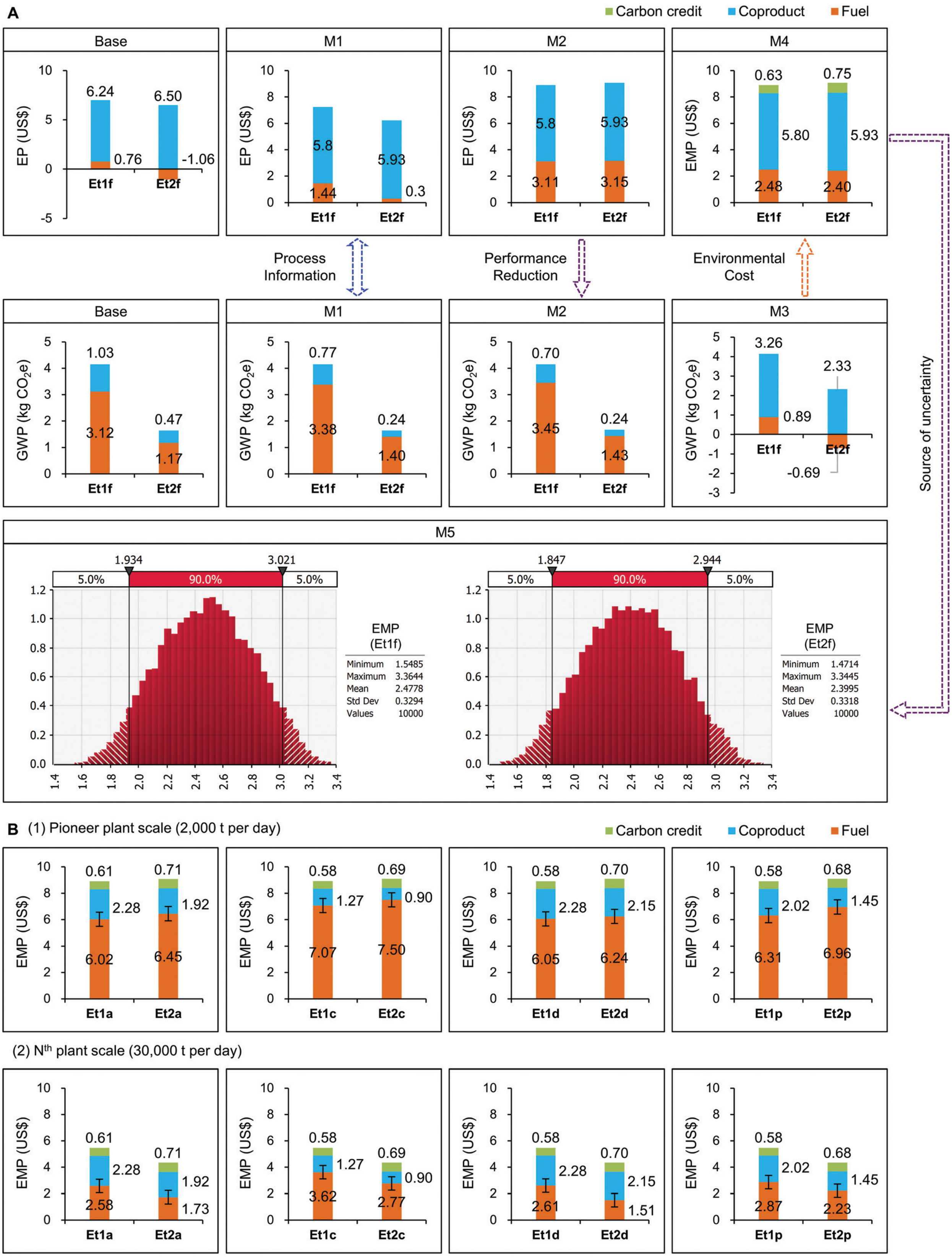

Fig. 3 Results of the feasibility assessments for the coproduction pathways. (A) Results of feasibility assessments for the Et1f and Et2f pathways. The graphs represent the EP, EMP, and GWP of the two pathways in each scenario. Base case—EP and GWP of bioEtOH, excluding the separation process; M1—system expansion (TEA and LCA), M2—pioneer plant analysis (TEA and LCA), M3—credit-based allocation (LCA), M4—mitigation potential (TEA), and M5—uncertainties (TEA and LCA). See Sections S5–S7 (ESI†) for additional details of these results. (B) EMPs of the remaining coproduction pathways by plant scale (Et1a, Et2a, Et1c, Et2c, Et1d, Et2d, Et1p, and Et2p).

will be increasingly necessary to consider the environmental aspects of TEA.

UA with a Monte Carlo simulation can identify a reliable techno-economic and environmentally feasible range.[22] Possible price and environmental impact ranges are obtained by considering uncertainty in the input variables. Considering uncertainty in the corn stover price and carbon credit, the possible EMP ranges are shown in M5 of Fig. 3A. Reflecting uncertainty in the corn stover and carbon prices, the possible EMP ranges with 90% confidence are US$1.93–3.02 (Et1f) and US$1.85–2.94 (Et2f). In the real world, there are many sources of uncertainty as well as raw materials, which makes UA useful as a final step in feasibility studies. After consideration of the fundamental constraints, the overall rates of change in the EMP of the two pathways are +226% (Et1f) and +326% (Et2f), while the overall rates of change in the GWP of the two pathways are −71% (Et1f) and −159% (Et2f). In terms of GWP and EMP, Et2f appears to be the more feasible option based on the assessment results. Whereas the EMPs of the above pathways (Et1f and Et2f) are in the range of fossil-based gasoline (US$2.13–3.65), the EMPs of the remaining pathways (US$6.02–7.50; Fig. 3B) are out of the gasoline price range. The scale of the biorefinery needs to change from 2000 t per day to 30 000 t per day, which is the scale at which oil refineries operate.[23] When the biorefinerys are operated at a pioneer plant scale for 2000 t per day of corn stover, the FDCA coproduction pathway can compete with fossil fuels. On the other hand, an increase of the processing rate to oil refinery scale (30 000 t per day of corn stover) through economies of scale can significantly decrease the production cost. On the N^{th} plant scale (oil refineries), the EMPs for the other pathways could decrease to US$1.51–3.62 per GGE, which are in the range of fossil fuels. This means that developing improved conversion technologies to increase the processing scale with higher product yields is required for commercialization of coproduction strategies.

Consequently, the results suggest that the omission of certain factors could act as an obstacle to choosing a more feasible biorefinery strategy. Recently, integrated biorefinery strategies that produce various types of products (fuels, chemicals, and utilities) from various types of feedstock have been developed to improve economic feasibility. Overcoming constraints by combining both methodologies in further biorefinery strategies of increasing complexity will be essential for providing reliable results to decision makers.

Conclusions

The coproduction of biofuels and biochemicals, which could improve overall profitability compared with biofuel-only production, has become the most popular approach in the commercialization of biorefineries. The analysis in this paper revealed a comprehensive way to evaluate and compare the feasibility of coproduction strategies producing different chemicals. Feasibility assessments, which quantify the techno-economics and environmental impacts of coproduction strategies based on experimental and simulated data, are required to provide feasibility data to decision makers and have implications for the commercialization of biorefinery technologies, such as bottlenecks, as well as providing new research directions to other researchers. However, feasibility data obtained from individual assessment methods that have fundamental constraints resulting from the characteristics of coproduction strategies, such as technological immaturity and complexity, can be misinterpreted. Further analysis revealed significant changes in the TEA and LCA results for a biorefinery with consideration of fundamental constraints. This suggested that the appropriate handling of key issues (determining the system boundary, reflecting technological immaturity, selecting the impact allocation method in LCA, considering environmental aspects in TEA, and considering uncertainty) can help produce estimated costs or environmental impacts that are closer to the actual values.

From a methodological perspective, this analysis also illustrated the value of combining elements or the results of TEA, LCA, and UA to provide reliable results to policy or decision makers. In the comprehensive method, TEA and LCA can provide each other with performance reductions based on the technological level and environmental costs based on the environmental burden of technology, respectively. Variations caused by external factors can be reflected by UA based on Monte Carlo simulations.

This study is the first step towards using a combined method for consistent comparisons of a large variety of coproduction biorefinery strategies from the twin perspectives of techno-economics and environmental impacts. Although further discussion on the adequacy or reliability of the key information exchanged between the assessment methods is required, a comprehensive method that comprises TEA, LCA, and UA represents an important direction for future research.

Methods

EP of fuels

Average U.S. retail fuel prices per GGE data were taken from clean city alternative fuel price reports from the U.S. Department of Energy.[24] These data included price data for fossil fuels and biofuels from 2000 to 2018, and this study used five years of data (2014–2018) to find the average (US$2.64 [gasoline] and US$3.17 [bioEtOH]), minimum (US$1.98 [gasoline] and US$2.45 [bioEtOH]), and maximum (US$3.70 [gasoline] and US$5.03 [bioEtOH]) prices of fuels. The U.S. fuel EtOH production data are taken from the U.S. Renewable Fuel Association.[25] The carbon credit was calculated based on carbon price data taken from the World Bank[7] and CO_2 emissions data taken from the U.S. Environmental Protection Agency[26] and International Energy Agency.[4] The carbon price range needed to achieve the target temperature of the Paris Agreement was US$40–80 per t CO_2 eq., and the average price is US$60 per t CO_2 eq.[7] The CO_2 emission of gasoline was 11.2 kg CO_2 per GGE (average), while the CO_2 emission of bioEtOH was 8.0 kg CO_2 per GGE (average), 3.1 kg CO_2 per GGE (minimum), and 11.9 kg CO_2 per GGE (maximum).[26] The CO_2 reduction of biochemicals relative to their petroleum-derived equivalents was also used to calculate the carbon credit.[4]

When 25% of bioEtOH production was replaced by six biochemicals (acetic acid, acrylic acid, AdA, butanol, CaL, and ethyl lactate), the possible EP of bioEtOH in the coproduction strategy was estimated. The production of each product was determined based on the higher heating value. The revenue of the biochemicals was calculated based on the production and price of each chemical.

Literature review of trends in research on coproduction pathways

This study investigated LCA, TEA, and UA studies on biofuel and biochemical coproduction pathways. We determined five main categories (M1–M5), which consisted of 2–4 subcategories (s1–s4). Papers containing common keywords (biofuel, biochemical, coproduct) and specific keywords related to feasibility assessments (LCA, economic analysis, uncertainty analysis) were searched for using Google Scholar. Papers published during the last six years (2014–2019) were classified by main and subcategories. The details of the literature review are presented in the ESI† (Section S2: literature reviews of feasibility research on coproduction pathways).

A coincident feasibility assessment compensating limitations and combining methodologies

A number of feasibility studies on biorefineries based on each methodological framework have been conducted, as shown in the section Feasibility assessment methods for biorefinery coproducing: a review; however, five fundamental constraints can distort the results: (1) determining the system boundary in both TEA and LCA; (2) reflecting technological immaturity in both TEA and LCA; (3) selecting the impact allocation method in LCA; (4) considering environmental aspects in TEA; and (5) considering uncertainty in both TEA and LCA. Fig. S2 (ESI†) presents a coincident feasibility assessment framework that compensates for limitations and combines the methodologies proposed in this section.

There are five main phases of TEA. The first phase is the estimation of technological maturity. Pioneer plant analysis enables estimations of cost growth and plant performance reduction for low-TRL technologies to be made.[27] Information on the technological level and knowledge is passed to the second phase (goal, scope, and scenario definition) of TEA and can also be utilized to determine the functional unit and system boundary in the first phase of LCA. Furthermore, the effect of low TRLs can be reflected as a plant performance reduction in the second phase (inventory analysis) of LCA. In the second phase of TEA, the goal of a TEA is frequently to present economic criteria and use technological factors to estimate the net present value, return on investment, and internal rate of return, which together represent the profitability of a biorefinery. Scope and scenario definitions determine the target pathway, assessment system boundaries, data collection method, and assessment method. The third phase of TEA is inventory analysis, where various data are collected by considering the scope and scenario defined in the second phase. Process variables (*e.g.*, materials and energy amounts, equipment size) and economic variables (*e.g.*, material and energy prices) are collected by searching the literature and developing a simulation model using the commercial tool Aspen Plus (Fig. S2B, ESI†). The inventory analysis phase exists in LCA as well as TEA, and the process information can be exchanged between the two assessment methods to improve the reliability of the assessment results. The fourth phase of TEA is the cost and benefit assessment. Based on the collected process and economic variables, the total production cost, consisting of capital and operating costs, is estimated by creating a cash flow table in Excel (Fig. S2B, ESI†). The benefit (EP) of the developed process is subsequently assessed by comparing the total cost and revenue obtained from products. As shown in Fig. S2 (ESI†), the environmental aspect of the overall process can lead to additional costs or revenues. The third phase (impact assessment) of LCA can provide a cost and benefit assessment phase with quantified environmental impacts that can be converted into a MP. The accuracies of the cost estimates differ at the TRL stage of each coproduction pathway and introducing pioneer plant analysis could be a promising solution to this problem. In addition, conducting UA could be another option for ensuring the accuracy of the estimates. A source of uncertainty in costs is collected in this phase and sent to the UA, which provides the TEA with a distribution of possible costs by statistical methods using the commercial tool @RISK (Fig. S2B, ESI†). The fifth phase of TEA is interpretation. In this phase, validation of the results and the identification of techno-economic issues, such as techno-economic feasibility, major cost drivers, and techno-economic bottlenecks, are conducted. This phase provides a new research direction in terms of commercialization for other researchers.

The basic logic for LCA is defined by ISO14040/14044, and there are four main phases of LCA.[28] The first phase of LCA is the goal and scope definition. The goal of LCA is to present environmental criteria that consider damage to human health, ecosystems, and resource availability by estimating GWP and fossil depletion, which represent the environmental impacts of biorefineries.[29] Although the logic of LCA is similar to TEA, the scope definition, including the assessment system boundaries, data collection method, functional unit, and impact assessment method, of LCA is more complicated because various options depend on the researcher. Considering the current TRL of target technology could help determine more reasonable functional units and system boundaries that are more suitable for the practical application of LCA, and the information on current TRL of target technology can be obtained in the first phase (estimation of technological maturity) of TEA. The second phase of LCA is inventory analysis. The main objective of this phase is to collect the input and output of materials and energy during the process and normalize the data based on the unit process and functional unit of LCA.[30] While process information is exchanged between LCA and TEA, the importance of some information differs. In TEA, which considers plant construction and maintenance as a major factor, equipment size and operating conditions are two of the main variables. On the other hand, LCA commonly focuses on the materials and energy consumed or generated during the process, the levels of which are significantly higher than those caused by construction and maintenance. This creates a difference in the range of the dataset between TEA and LCA. The first phase (estimation of technological maturity) of TEA provides information on plant performance reduction due to low TRLs. In LCA, the normalization of total variables during the plant lifetime based on the total production considering the plant performance reduction that inevitably occurs under coproduction pathways with low TRLs could be a solution to this problem. The third phase of LCA is impact assessment, which consists of characterization, normalization, and weighting. Firstly, in the characterization step, specific impact categories are selected, and the environmental burden of substances is quantified as an environmental impact using a characterization factor based on different physical properties using the commercial tool GREET (Fig. S2B, ESI†). The quantified impact can then be used to estimate the MP, and this information can help calculate the overall cost and revenue of a coproduction pathway, considering any environmental aspects in the fourth phase (cost and benefit assessment) of TEA. Normalization can then be performed to effectively communicate the LCA results to nonexperts. The score obtained from the characterization is divided by a reference situation, such as the average annual environmental load per person. Finally, the weighting step creates a single score (MP) from the results of various impact categories, which multiplies the score of each impact category by a weighting factor. In the impact assessment phase, in contrast to characterization, normalization and weighting are not essential steps. The source of uncertainty in relation to the environmental impact collected in this phase is sent to UA, and this phase produces a distribution of possible environmental impacts from UA using @RISK (Fig. S2B, ESI†). The fourth phase of LCA is interpretation. The results of the LCA are validated, and environmental issues such as environmental feasibility, major environmental drivers, and environmental bottlenecks are identified. LCA is widely applied today; for example, it is used to support environmental product declarations and make public policy.

There are two main phases of UA. The first phase of UA is the preparatory data assessment. The goal of this step is to identify sources of uncertainty and collect sample data used in the statistical analysis. Large sample datasets, such as price fluctuation trends or environmental emissions, should be collected to apply statistical methods used to calculate data and modeling uncertainties subject to random variation. Sample data for the estimation of economic and environmental uncertainties are collected during the fourth phase (cost and benefit assessment) of TEA and the third phase (impact assessment) of LCA, respectively. The second phase of UA is the identified uncertainty quantification, which involves estimating the individual uncertainties identified in the previous step based on the large sample dataset. Important statistical information, including the mean, standard deviation, confidence interval, and probability distribution, is obtained in this step using mathematical techniques such as first-order error propagation (Gaussian method) or a Monte Carlo simulation in @RISK (Fig. S2B, ESI†). Finally, the statistical information on the economic and environmental impacts is used to reflect the uncertainty in each assessment method and aggregate the assessment results into a final score, EMP, ranging for certain confidence intervals.

Abbreviations

AdA	Adipic acid
bioEtOH	Bioethanol
CaL	Caprolactam
Diol	Pentanediol
EMP	Economic mitigation potential
EP	Economic potential
Et1a	Enzymatic hydrolysis based bioEtOH and AdA production pathway
Et1c	Enzymatic hydrolysis based bioEtOH and CaL production pathway
Et1d	Enzymatic hydrolysis based bioEtOH and Diol production pathway
Et1f	Enzymatic hydrolysis based bioEtOH and FDCA production pathway
Et1p	Enzymatic hydrolysis based bioEtOH and PAN production pathway
Et2a	Catalytic hydrolysis based bioEtOH and AdA production pathway
Et2c	Catalytic hydrolysis based bioEtOH and CaL production pathway
Et2d	Catalytic hydrolysis based bioEtOH and Diol production pathway
Et2f	Catalytic hydrolysis based bioEtOH and FDCA production pathway
Et2p	Catalytic hydrolysis based bioEtOH and PAN production pathway
EY	Energy yield
FDCA	Furandicarboxylic acid
GGE	Gasoline gallon equivalent
GHG	Greenhouse gas
GWP	Global warming potential
LCA	Life cycle assessment
MP	Mitigation potential
PAN	Phthalic anhydride
t	Tonnes
TEA	Techno-economic assessment
TRL	Technology readiness level
UA	Uncertainty assessment

Conflicts of interest

There are no conflicts to declare.

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