PAPER

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Economics and global warming potential of a commercial-scale delignifying biorefinery based on co-solvent enhanced lignocellulosic fractionation to produce alcohols, sustainable aviation fuels, and co-products from biomass†

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Harnessing the natural diversity of plant biomass for producing economically and environmentally sustainable liquid fuels and high-value co-products entails the strategic integration of different technologies, each finely tuned for a unique biomass intermediate, to realize greater synergies in a co-processing schema known as biorefining. Presented here is a techno-economic and life cycle analysis of a hybrid biorefinery strategy that integrates several leading biochemical and catalytic processes to maximize the utilization of lignocellulosic biomass and produce commercially relevant biofuels and bioproducts. High fidelity computer models were assembled to evaluate the impact of feedstock and co-product selection on overall economics and global warming potential of the biorefinery. Central to this biorefinery model is the application of mild co-solvent enhanced lignocellulosic fractionation (CELF) pretreatment as the first step to non-destructively fractionate biomass into clean hemicellulose sugars, cellulose, and lignin intermediates that are funneled to a suite of downstream conversion technologies to yield alcohols, esters, carboxylic acids, and hydrocarbons as co-products. A multiparametric analysis of different process modalities using deterministic evaluation of experimental data and sensitivity analyses reveal the advantages of selecting a feedstock with higher carbon content (poplar wood instead of corn stover), the benefits of selecting a fuel alcohol product with higher yield and titer (ethanol instead of isobutanol) and the outcomes of selecting lignin fate (valorization vs. combustion). The application of supercritical methanol and a copper porous metal oxide catalyst to convert lignin to cyclic hydrocarbons, a component of sustainable aviation fuel (SAF), presents mixed outcomes: while this operation further improves carbon recovery from biomass, its inclusion in the biorefinery leads to a carbon footprint penalty in view of the use of methanol for lignin depolymerization. Nevertheless, the CELF biorefinery model demonstrated a possibility of supplying SAF to the market at competitive prices – as low as $3.15 per GGE (gallon of gasoline equivalent) – as well as carboxylic acids and esters.

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Broader context

Future efforts to decarbonize the U.S. economy pass through both the development of several biofuels and bioproducts and the deployment of large-scale biorefineries. It is thus imperative to act on several different fronts to maximize the potential of aiding the establishment of a true bioeconomy environment. This study provides a comprehensive economic and environmental analysis of next generation biorefineries based on a novel biomass deconstruction and fractionation method. The facilities yield a diverse product portfolio in the form of sustainable aviation fuel (SAF) to the hard-to-decarbonize aviation sector, of alcohols as "bridging fuels" for a low carbon economy, and biobased specialty chemicals to replace carbon-intensive, fossil-derived products in the market.

Introduction

Growing concerns over increased greenhouse gas (GHG) emissions arising from human activities and the unmetered consumption of fossil resources leading to profound effects on global climate change have prompted recent efforts by scientists and decision-makers to establish a progressively biobased economy.[1] An immediate and abundant source of lignocellulosic biomass, such as agricultural and forestry residues that do not compete with our food, can be utilized for supplying the growing demand for liquid fuels and chemicals to lead the way for a better carbon-managed future. Exciting progress in the development of new catalytic and biological conversion techniques can be fully realized within innovative biorefinery strategies if an efficient route for biomass deconstruction and fractionation can successfully achieve simultaneous access to its carbohydrate and lignin fractions. We analyze one such biorefinery concept that integrates both catalytic and biological processing to boost the total carbon utilization of biomass and evaluate the cost-competitiveness and environmental impacts of this method for producing biofuels and biochemicals from biomass.

Historically, conventional biorefining approaches have focused on primarily accessing biomass' carbohydrate fraction by using a sequential processing strategy that first aims to disrupt the biomass structure by employing an aqueous pretreatment step so that cellulolytic enzymes can more efficiently hydrolyze biomass' hemicellulose and cellulose fractions into monomeric pentose and hexose sugar syrups, respectively. Afterwards, the sugar syrups are then fermented to fuel ethanol that is to be blended into our existing gasoline infrastructure. Harsh pretreatment conditions or incomplete fractionation during pretreatment compromises the lignin,[2] preventing it from being utilized as a feedstock by leaving it suitable only for gross combustion to provide process heating. Although lignin burning offers lower-carbon process heating relative to fossil fuel-based heating, this method of eliminating lignin can have detrimental effects on biorefinery particulate emissions[3,4] and overall plant economics.[5]

Recently, advances in pretreatment technology have sought to increase the utilization of whole biomass and reduce the barrier to efficient biomass deconstruction and fractionation by employing water-miscible co-solvents capable of significantly enhancing separation of the lignin fraction while preserving the carbohydrate streams.[6] One such advancement is the co-solvent enhanced lignocellulosic fractionation (CELF) pretreatment, a dilute-acid process which promotes high recovery of pentoses, hexoses, and lignin while limiting their degradation.[7,8] CELF pretreatment uniquely employs tetrahydrofuran (THF) as a highly recyclable biomass-derivable aqueous co-solvent that has been shown to favorably interact with hemicellulose, cellulose, and lignin at milder temperatures (140–160 °C) by encouraging their solvation[9] and their clean fractionation[10] without having to resort to harsher reaction conditions that may cause undesired degradation of sugars and lignin.[11,12] For either agricultural[13] or forestry[14] biomass feedstocks, the reaction conditions of the CELF pretreatment process can be optimized to simultaneously produce separate intermediate streams of (1) enriched-cellulose solids (low lignin, low hemicellulose), (2) a concentrated pentose sugar (C5) liquor containing small amounts of water-soluble (WS) lignin (low lignin, low glucose), and (3) a high-purity precipitated water-insoluble (WIS) lignin (low sugars) known as CELF lignin.[15] Over 90% of the biomass lignin extracted during CELF is precipitated as WIS lignin, otherwise known as CELF lignin. Due to the high purity of each intermediate from CELF pretreatment, favorable conditions have been reported that support downstream biochemical,[16,17] thermochemical,[18,19] and catalytic[20,21] valorization pathways, which are able to harness the possibility of lower-cost operations with higher carbon concentrations and higher lignin quality to improve the carbon efficiency, energy intensity, and capital use fraction of a biorefinery. For these reasons, CELF was chosen as the first processing step in the biorefinery strategy of this study.

Once clean sugar and lignin intermediates are produced from biomass, different downstream conversion technologies could be tailored for each intermediate, enabling higher yields and greater robustness while eliminating the risk of performance loss from cross-contamination of other biomass components. How each biomass intermediate is processed will also define the overall plant design, mass and energy integrations, and the resulting portfolio of co-products. Biomass fractionation offers an ability to directly measure the economic and environmental impact of integrating different downstream conversion technologies when designing the biorefinery. This strategy also offers a high degree of process modularity aimed at helping to discover the most compelling case for 2nd generation biofuels, by calculating the feasibility of different feedstock compositions and downstream configurations that target different product types ranging from simple molecules up to longer carbon backbones, and market segments from energy carriers to specialty chemicals.

After CELF-pretreatment, the enriched-cellulose solids fractionated from biomass is configured to be directly fermented into either ethanol or isobutanol using a consolidated

bioprocessing (CBP) approach, which utilizes *Clostridium thermocellum*, a thermotolerant cellulolytic bacteria, to combine enzyme production, enzymatic hydrolysis of cellulose, and fermentation in a single fermentation vessel for simpler integrated processing while still allowing independent processing of other biomass streams. Although the CBP approach to alcohol fermentation is modeled similarly to simultaneous saccharification and fermentation (SSF) methods, CPB eliminates the need for the exogenous addition of cellulolytic enzymes providing potential economic and sustainability advantages to the biorefinery. We recognize both alcohols as "bridging fuels" to a low carbon economy, but also see them as highly relevant fuel intermediates for further upgrading to more advanced hydrocarbon fuels used in aviation and heavy-duty vehicles. Alcohol upgrading serves to supply paraffinic sustainable aviation fuel (SAF) fraction,[22–25] while lignin upgrading focuses on synthesizing olefinic or napthenic SAF fraction.[26–28] Apart from the practical applications of either ethanol or isobutanol, there is great interest in moving towards 2nd generation feedstocks over conventional crops, such as starch and sugarcane, in view of the forecast gains in terms of environmental impact.[29–31] Initial developments of CBP mostly targeted ethanol production[32–34] although other possibilities have been recently explored through the engineering or adaptation of genotypes from other microbial platforms.[35–37] To address the conversion of the pentose-rich syrup intermediate from CELF, a recently developed fed-batch fermentation strategy with *in situ* ester extraction using high molecular weight solvents (modeled as n-hexadecane) that utilizes genetically modified *Escherichia coli*[38,39] (or *C. thermocellum*) was implemented in the model for the high-efficiency production of the designer ester isobutyl acetate.[40–43]

For lignin valorization, a catalytic process known as athermic oxygen removal (AOR) was selected for implementation in these biorefinery models due to its effectiveness in converting lignin in one-pot to cyclic alcohols and cyclic hydrocarbons at high yields. AOR of WIS lignin utilizes supercritical methanol as both a solvent and hydrogen donor to support catalytic reductive chemistries over a relatively inexpensive copper porous metal oxide catalyst (Cu20PMO).[44,45] Owing to its name, AOR consists of tandem endothermic reformation of supercritical methanol to hydrogen and exothermic hydrodeoxygenation of biomass oxygenates in one pot, thus mitigating the potential exothermic runaway of hydrodeoxygenation while directly donating hydrogen towards reducing lignin. A single pass AOR reaction of WIS lignin has an 80% carbon yield towards cycloalkanes in the range of jet fuel.[44,45]

Finally, aerobic fermentation by *Pseudomonas putida* on the residuals after fermentation of the pentose-rich syrup by *E. coli* can be employed to produce dicarboxylic acids. The water-soluble (WS) residuals primarily contain low molecular weight lignin fragments that can be consumed by *P. putida* to produce muconic acid, a precursor to adipic acid, nylon, and polyethylene terephthalate.[46,47] All conversion platforms included in this study have been developed under the Center for Bioenergy Innovation's (CBI) scope, one of four national bioenergy research centers funded and led by the US Department of Energy (DOE).

This study represents a first of its kind effort towards a comprehensive understanding of a full-scale multi-product biorefineries established upon CELF pretreatment of two highly relevant 2nd generation bioenergy feedstocks: corn stover and poplar wood. A comparative analysis of the influence of feedstock selection over the economic and environmental performance of industrial facilities is also carried out, including selected sensitivities over economic parameters and the benefits of commercializing D3 renewable identification number (RIN) credits associated to cellulosic fuels. The main goal of this study is to provide a comprehensive analysis of different process configurations of a CELF-based biorefinery for efficient, economically feasible, and environmentally sustainable carbon conversion into biofuels and bioproducts. The techno-economic and life cycle analysis (TEA and LCA, respectively) also indicate the future potential for using CELF pretreatment for full exploitation of all fractions of biomass with results that could underpin the possibility of using alcohols as feedstocks for further catalytic conversion into SAF.

Results and discussion

Designing integrated biorefineries

We analyze the effect of three main variables over the performance of integrated biorefineries in this study: feedstock (poplar or corn stover), alcohol obtained from cellulose (ethanol or isobutanol), and lignin fate (conversion into cycloalkanes or combustion for energy generation). All scenarios consider the production of isobutyl acetate and muconic acid from pentoses and other residual carbon sources. With the compositions assumed in this study, poplar has higher total carbon content compared to corn stover (7.5%), which is further pronounced when considering only the constitutional carbohydrates and lignin fractions (23%). The forest feedstock is also advantageous in comparison to the agricultural biomass due to lower ash content (0.5% *vs.* 4.9%, respectively). Full biomass compositions can be found in the ESI† (Table S1, ESI†). Initial fractionation of biomass into its constituents (cellulose, lignin, and hemicellulose) is achieved using a CELF-based strategy, which employs THF as the co-solvent of choice, due to its theta-solvent behavior with lignin,[9] unique phase-behavior with water and cellulose,[12] high recoverability in commercial processes,[48] and the potential for it to be renewably produced from furfural.[49] Production of alcohols *via* CBP of CELF-derived cellulose considered different toxicity levels of ethanol and isobutanol towards the microorganism of choice, which in turn determines the maximum achievable titer in practice, assumed at 75 g L^{-1} for ethanol and 30 g L^{-1} for isobutanol. Such targets are ambitious but plausible targets of CBI within a 5–10-year timeframe. Finally, lignin is converted to cycloalkanes in a supercritical, methanol–laden environment using copper porous metal oxide as the catalyst, costed at around $2 per lb.[50] Fig. 1 summarizes the main individual sections considered in

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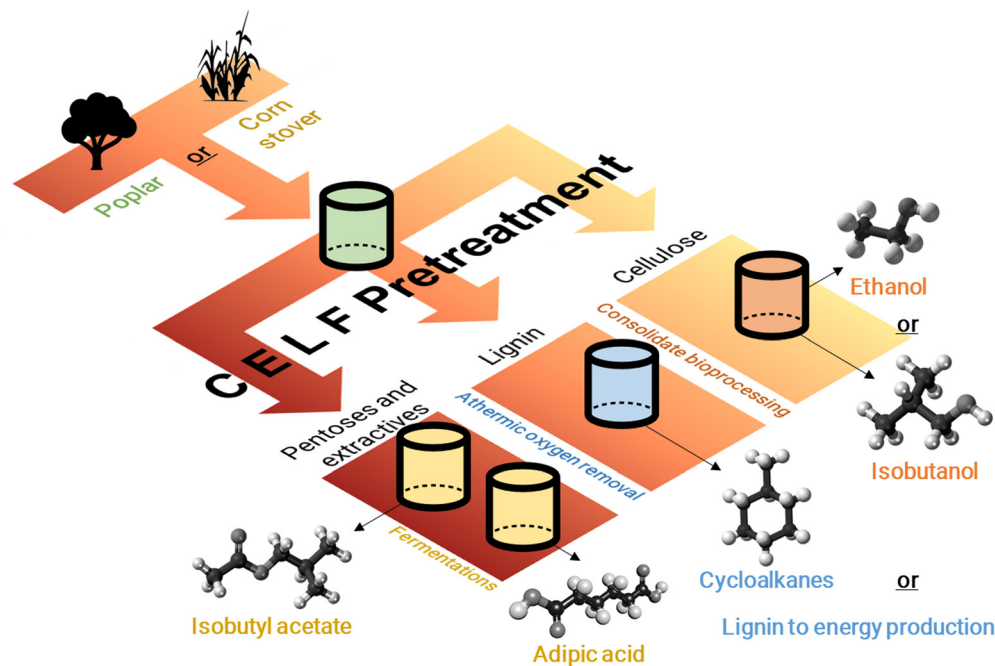
Fig. 1 Simplified diagram for the proposed CELF-based biorefineries outlining the mass integration strategy. CELF: co-solvent enhanced lignocellulosic fractionation.

the processing of biomass. More details on each step and full parameters considered in process modelling are presented in the ESI† (Table S2). CELF-based biorefineries were defined for a fixed biomass input of 2000 dry metric tons of biomass per day. Steady state operation of all biorefineries was simulated in the commercial software Aspen Plus V10 (AspenTech, Bedford MA) to retrieve the associated mass and energy balances for further TEA and LCA.

Non-fuel products include adipic acid and isobutyl acetate. Adipic acid has a significant market presence, with a worldwide annual consumption close to 3.0 million tonnes in recent years fueled mainly by the production of nylon 66 and by other minor non-nylon applications.[51] The process of fermentation to muconic acid and further upgrading to adipic acid has been chosen as a polishing step in this model to valorize WS lignin and other soluble organic compounds, thus preventing additional CO_2 generation in wastewater treatment. Another advantage lies in replacing a fossil-based compound with significant environmental impact due to the release of nitrous oxide during its production[52] with a biobased alternative. On the other hand, isobutyl acetate has a smaller global consumption, estimated at 200 thousand tonnes annually in the recent past,[51] mostly driven by its application as a solvent. Although already produced at industrial scale, we believe that an expansion of the isobutyl acetate market could occur as it becomes adopted as an alternative fuel additive or if further applications as an intermediate chemical in the industry are sought. Other esters could also be targeted for a greater portfolio diversification in nth-plant deployment scenarios to avoid oversupply of a single product. Short-chain ethyl esters, for instance, have already been touted as up-and-coming advanced biofuel alternatives[53–56] – such as

acetate esters,[38,39,41,42] lactate esters, and carboxylate esters[43,57–59] with different alcohol moieties that can be produced by engineered microorganisms, thus providing accessible functional diversity. Isobutyl acetate has been identified as a molecule with a potential high research octane number (RON).[60] While the industrial production of isobutyl acetate and other short-chain esters has historically relied on the Fischer esterification of fossil-based acids and alcohols,[61] a versatile platform for biosynthesis of such compounds could mean a shift in paradigm for their supply in large scale. In the biorefinery model depicted in Fig. 1, monomeric pentoses issued from CELF pretreatment of biomass are fermented into isobutyl acetate by *E. coli* using a fed-batch approach. The spent fermentation broth after isobutyl acetate recovery, still containing unused carbon in the form of constitutional and WS lignin is routed to the aerobic fermentation to muconic acid and further upgrading to adipic acid.[62]

Higher yields are favored over biomass solids loading in CBP to alcohols

Fig. 2 presents an initial evaluation and optimization of CBP fermentation of CELF-pretreated corn stover and poplar to ethanol with respect to ethanol yield, titer, solids loading. The calculations performed on experimentally available data indicate that although higher solids loadings during fermentation enable higher alcohol titers, leaner downstream operations, and lower relative energy requirements, the alcohol yield from fermentation remains the most important economic driver to the biorefinery's internal rate of return (IRR). Thus, optimum solids loadings of 20 wt% and 13 wt% for corn stover and poplar, respectively, were selected for the remainder of the biorefinery models – reflecting a decision to use operating
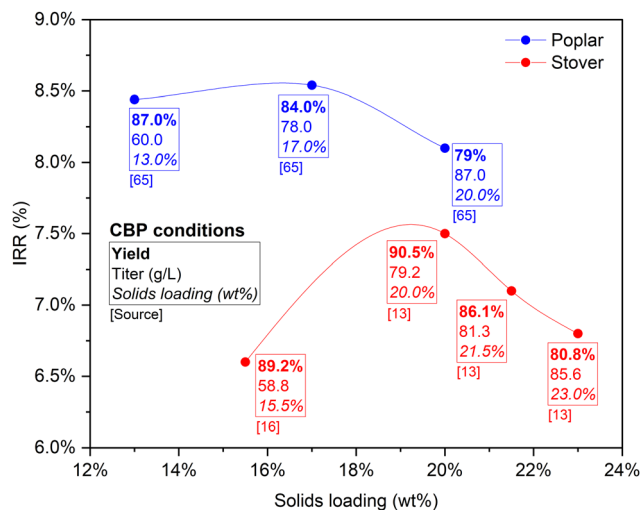
Fig. 2 SSF-informed preliminary analysis of the effect of solids loading in CBP of CELF-pretreated biomass over the economics of the CELF-based biorefinery. Parameters based on CELF studies in the literature.[13,16,65] CBP: consolidated bioprocessing; IRR: internal rate of return; SSF: simultaneous saccharification and fermentation.

parameters that maximize alcohol yields. Solids loading in CBP of CELF-derived cellulose to isobutanol was dialed down accordingly to 8.5% so as to reach a maximum titer of 30 g L^{-1} for this alcohol in comparison to ethanol (capped at 75 g L^{-1}). Although more advanced technologies for the recovery of isobutanol, such as the *in situ* removal of the alcohol,[63,64] could potentially allow for higher titers in the fermentation broth – these methods have not yet been demonstrated to improve CBP of CELF-derived cellulose.

CELF-based biorefineries favor feedstocks containing more available carbon for processing

The multiparametric study presented herein aims at probing the advantages of processing different feedstocks *via* CELF pretreatment and further converting their constituents to co-products, such as cycloalkanes and alcohols. We found that selecting poplar instead of corn stover as the primary feedstock for this biorefinery model yields superior economic, global warming potential (GWP), and carbon utilization efficiency indices (front *vs.* back facet of Fig. 3). Poplar provides better economic metrics even at feedstock price parity with corn stover, as the latter is *ca.* 20% more expensive than the former on a mass basis. The choice of alcohol type obtained *via* CBP also significantly affects the sustainability metrics of such plants, generally favoring ethanol over isobutanol in view of superior yields allowed by higher titer targets (75 g L^{-1} and 30 g L^{-1} for ethanol and isobutanol, respectively) and, therefore, total alcohol output (left *vs.* right facets of Fig. 3). Finally, while AOR of lignin to cycloalkanes helps boosting carbon utilization efficiency in CELF-based biorefineries, its supercritical nature and the consumption of externally sourced methanol contributes to mostly lower IRRs and higher GWPs for biorefineries that employ it (bottom *vs.* top facets of Fig. 3).

Results from the model suggest that processing of high-carbon feedstocks is naturally favored when CELF-based approaches are considered. Since CELF pretreatment of poplar solubilizes and recovers more lignin in comparison to corn stover, fuel slates obtained from the former feedstock yield more cycloalkanes than the latter. Combined fuel yield for poplar processing can attain 75.9 gallons of gasoline equivalent (GGE) per dry ton of feedstock, with a breakdown of 61% ethanol and 39% cycloalkanes; similarly, the highest fuel yield for corn stover processing is of 51.8 GGE per dry ton of feedstock (66% ethanol and 34% cycloalkanes). For comparison purposes, a recent biorefinery design based on a conventional pretreatment and enzymatic hydrolysis approach to process corn stover yields around 44 GGE per dry ton of corn stover of a renewable diesel blendstock composed of hydrocarbons, which require additional processing of intermediates to yield oxygen-free fuel.[62] For this feedstock and when converting lignin to cycloalkanes, the CELF approach provides a fuel yield benefit of 13–18% in comparison to conventional approaches.

Fig. 4 presents additional insights on the economic performance of the overall biorefinery and the economic contributions of each integrated processing step to produce ethanol and co-products from poplar. The economic advantages of implementing biomass fractionation using CELF pretreatment within a biorefinery can be seen in the cost breakdown analysis shown in Fig. 4a: the biorefinery can achieve the production of fuel ethanol at a competitive minimum fuel selling price (MFSP) of \$3.00 per GGE through the simultaneous co-production of isobutyl acetate, cycloalkanes, and adipic acid sold at their current market values. Fig. 4a also illustrates the impact of major economic drivers, such as the costs associated with feedstock and handling, the required inputs of raw materials, and the associated capital costs with the multiple processing trains within a single biorefinery. Fig. 4b showcases the effect of the nameplate capacity of poplar/ethanol biorefineries on the capital cost of a biorefinery, specifically at scales below the pre-defined 2000 dry metric tons per day. CELF has similar merits of other pretreatment methods[62] in terms of scalability, taking advantage of low temperature, low pressure, short residence times, and a semi-batch operation mode which allow for a simple dimensioning and fabrication of the equipment needed for pretreatment. In this way, the CELF pretreatment section accounts for between 8 and 10% of the total capital cost of a biorefinery independently of the plant's processing capacity, as detailed in the ESI† (Fig. S2). An additional analysis (Fig. 4c) depicts the potential losses in economies of scale when moving to smaller biorefineries, as could be expected based on the contribution of capital recovery charges towards the production of ethanol (Fig. 4a). It is noteworthy that the remainder of the study presented herein will rely on commercial-scale, *n*th-plant facilities processing 2000 dry metric tons of feedstock per day (as considered elsewhere in the literature[62]).

The stochastic analysis of the economic performance of CELF-based biorefineries indicates a probability distribution for IRR, as presented in Fig. 5 for twelve distinct economic
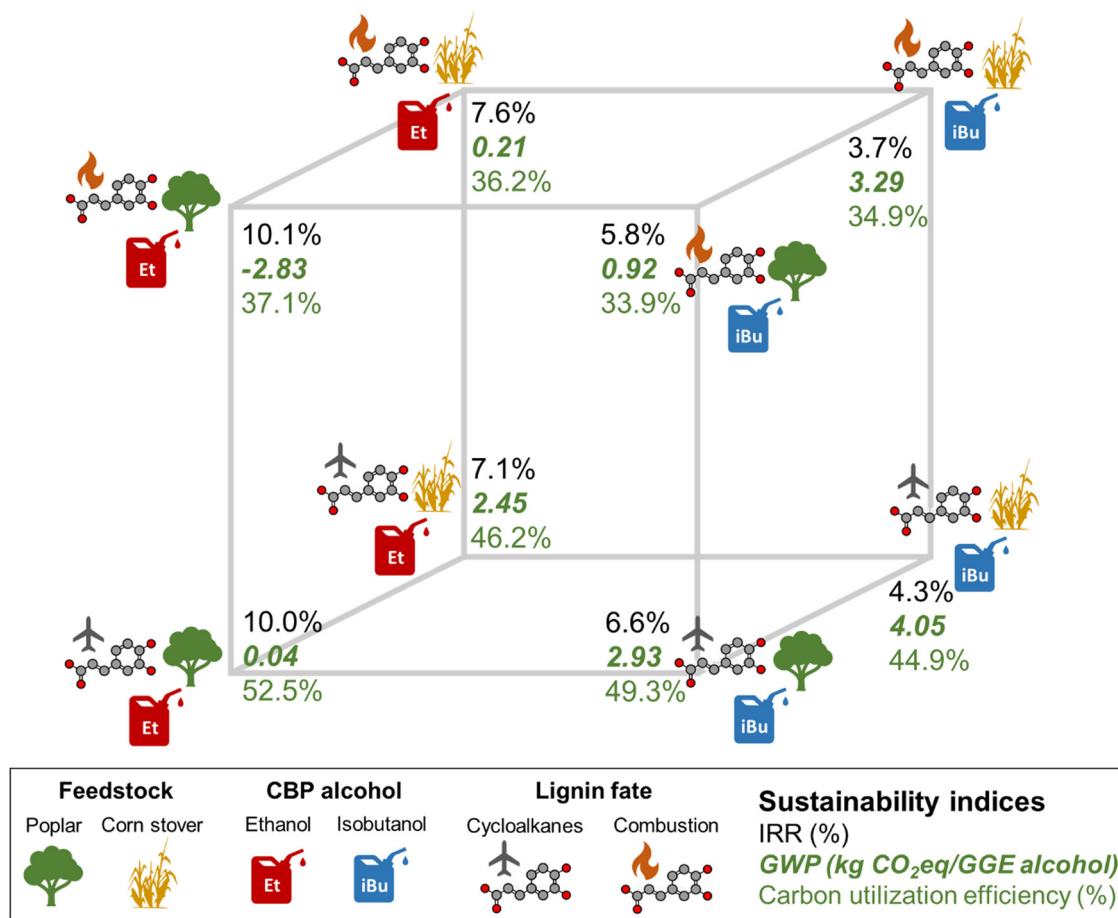
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Fig. 3 Sustainability indices of CELF-based biorefineries varying three major specifications: feedstock (poplar or corn stover), CBP alcohol (ethanol or isobutanol), and lignin fate (conversion into cycloalkanes *via* AOR or combustion). Carbon utilization efficiency is defined as the ratio between the amount of carbon recovered in products and the amount of renewable carbon entering the biorefinery. CBP: consolidated bioprocessing; GGE: gallon of gasoline equivalent; GWP: global warming potential; IRR: internal rate of return.

parameters, all of which have a contribution of $0.15 per GGE or higher to the MFSP of ethanol. Major factors impacting the economic performance of the industrial facilities are capital expenditures (CAPEX) and prices of the main products, such as alcohols, cycloalkanes, isobutyl acetate, and adipic acid. In the biorefinery configuration incorporating AOR processing of lignin, the selling price of SAF-grade cycloalkane fuels that are produced greatly influences the resulting plant economics (as depicted by Fig. 4a). In this work, we have assumed a conservative baseline selling price for the cycloalkanes of $0.83 per kg,[66] corresponding to the expected range of jet fuel export prices as these compounds will ultimately serve as a cloud point depressant of conventional jet fuel. If the trend of jet fuel continuously increases in price, beyond the upper limit considered in the sensitivity analysis, a CELF-based plant converting poplar into ethanol and with lignin processing through AOR would benefit from an increase of its IRR to 11.4% if cycloalkanes are sold at $1.00 per kg.[66] Alternatively, if cycloalkanes were to be priced as cyclic hydrocarbons for further chemical conversion at an estimated price of $1.50 per kg,[51] then the same biorefinery would see an estimated IRR of 15.5%. Independent of the feedstock of choice, a

higher fuel output through the conversion of both cellulose and lignin to alcohols and cycloalkanes, respectively, entails the emergence of a wider bell-shaped response curve than a biorefinery that burns lignin for energy generation. As exemplified for two specific biorefining strategies in Fig. 5, poplar processing with CELF pretreatment and further conversion into bioproducts has higher probabilities of attaining superior IRRs in comparison to corn stover (36% and 6% chances of achieving an IRR of 10% or higher, respectively). As further explored later in this study, the possibility of realizing extra revenues from RIN credit commercialization could largely improve the economics of any of the facilities presented in Fig. 3.

As an additional sensitivity analysis, we have carried out a single-point comparison between two biorefining configurations that convert corn stover to ethanol and to SAF-grade cycloalkanes: one of them with a CBP conversion of CELF-derived cellulose to ethanol that does not require adding exogenous cellulolytic enzymes and a second one with SSF that requires the addition of an on-site enzyme production section to hydrolyze cellulose to reducing sugars. At identical fermentation metrics (titer, yields, and solids loadings reported in ref. 13), an SSF-based biorefinery would achieve an IRR that

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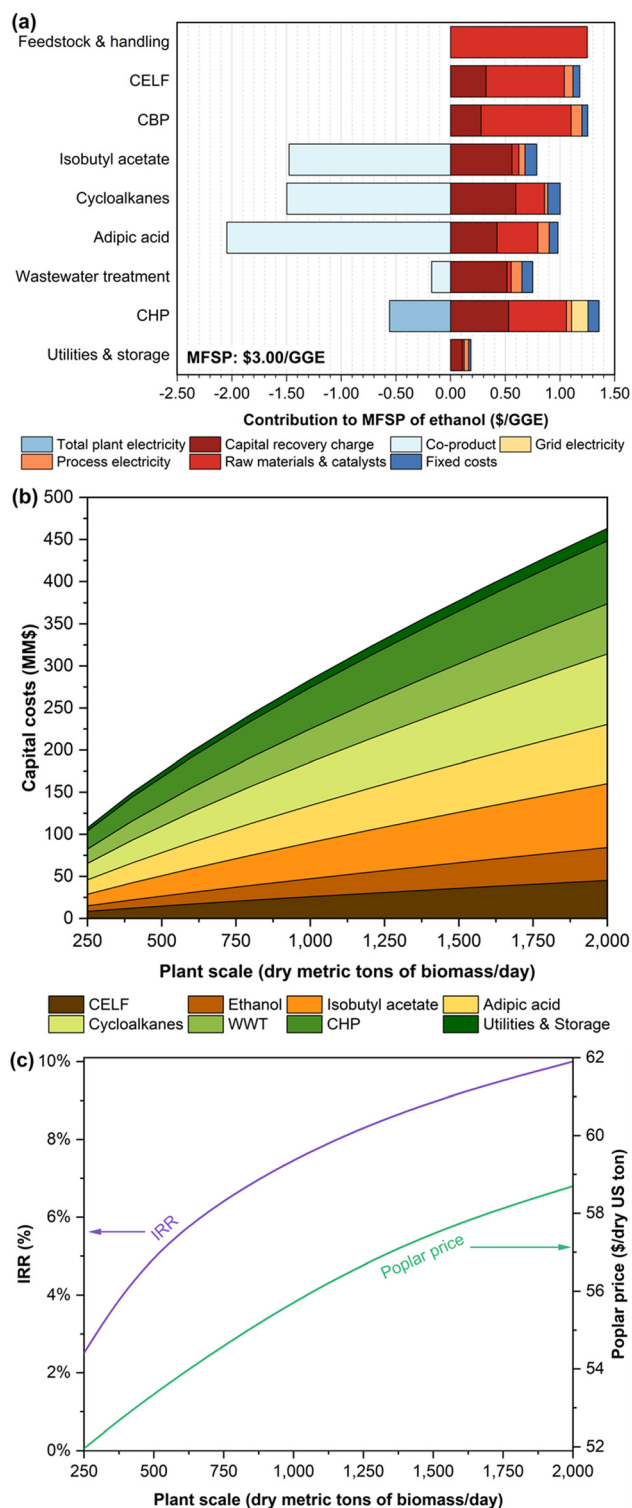*Energy Environ. Sci.*, 2024, **17**, 1202–1215 | **1207**

Fig. 4 Economic performance of a poplar/ethanol/lignin to cycloalkanes biorefinery. (a) Contribution of different biorefining sections to the MFSP of ethanol; (b) effect of plant scale on the capital cost of the biorefinery; and (c) effect of plant scale on both the economics of the biorefinery and on poplar price. CBP: consolidated bioprocessing; CELF: co-solvent enhanced lignocellulosic fractionation. CHP: cogeneration of heat and power. MFSP: minimum fueling selling price.

is 1.6 p.p. lower than that of a CBP-based plant. This performance could be alternatively measured by an MFSP of ethanol that is $0.50 per GGE higher for SSF than for CBP – $4.34 per GGE instead of $3.84 per GGE, respectively. The inclusion of a dedicated enzyme production module, simulated following the assumptions shown in ref. 62 and considering an enzyme loading of 10 mg of protein per g of cellulose, adds significantly to both CAPEX and operational expenses (OPEX) of a biorefinery. The results confirm our understanding that CBP is a more modern microbial fermentation chassis that outperforms a more traditional one (SSF) and clearly illustrate the benefits of in-cell enzyme production in the production of biofuels.

Poplar biorefining demands a thermal energy usage that is around 15% greater than that of corn stover, most likely due to the presence of a higher quantity of functional carbon in the former than in the latter. This, in turn, requires a non-negligible additional external energy input in the form of natural gas, but is then balanced when the processing facility adds value to the biomass as a whole and no fraction is deliberately routed to energy generation in combined heat and power (CHP) units. By combining the biorefining advantages enabled by the CELF pretreatment and the use of a less carbon-intensive energy source in the form of natural gas,[67] carbon utilization efficiency achieves a maximum of 46.2% for corn stover (cellulose to ethanol and lignin to cycloalkanes), while this number jumps to 52.5% when poplar is employed in an equivalent biorefinery configuration. It is important to note that these values represent actual carbon utilization of whole biomass to marketable fuels and co-products, excluding contributions from minor co-products that would be too economically challenging to further isolate. This plant design, combined with poplar utilization, surpasses a critical threshold of 50% renewable carbon utilization, an important performance target for biorefining. The calculation of the carbon recovery efficiency is presented in the ESI† (Table S3). Fig. 6 depicts the carbon flows for two flagship high-performance scenarios, namely the processing of poplar to ethanol and other co-products, with and without the conversion of lignin to cycloalkanes. The plots portray the ability of CELF to selectively deconstruct biomass and then funnel carbon into a slate of products through a series of conversion processes. It should be highlighted that the large output of CO_2 in either of the biorefining strategies could be leveraged through carbon capture and utilization technologies to further reduce the carbon footprint of such facilities.[68–70] Different technologies have been (and are) intensely researched to harness CO_2 in future biorefining setups, namely impregnation,[71,72] pressure-swing adsorption,[73,74] algae uptake,[75,76] methanation,[77,78] electrochemical conversion,[79–81] and gas fermentation.[82,83]

In CELF biorefineries, the fate of ash is similar to that in other biorefineries. In summary, ash that becomes soluble after the pretreatment step will be carried alongside the broth containing pentoses for the sequential production of isobutyl acetate and adipic acid. As ash remains inert during such conversion processes, virtually all of it will be present in the wastewater, which is sent to the wastewater treatment (WWT)
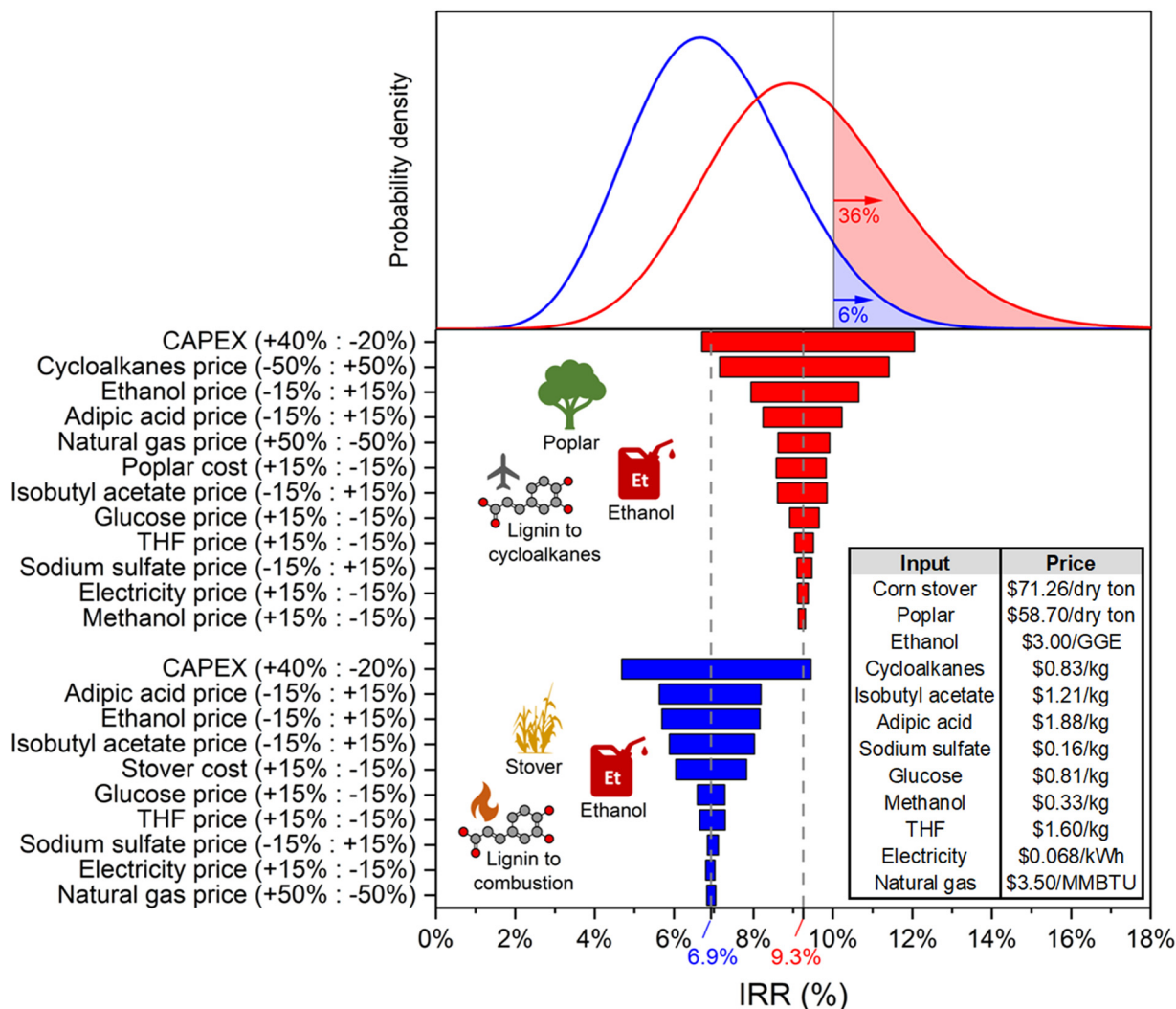
Fig. 5 Uncertainty analysis for CELF-based biorefineries: combined probability density (top) and tornado plots with the impact of varied parameters over IRR (bottom). Results are shown for the production of ethanol in biorefineries from corn stover (red) and poplar (blue). The inset box presents the base prices for all inputs to the analysis. CAPEX: capital expenditures; GGE: gallon of gasoline equivalent; IRR: internal rate of return; THF: tetrahydrofuran.

section. Finally, the digester sludge from WWT is routed to the CHP unit to be used as boiler fuel. The small portion of ash that is not solubilized in CELF pretreatment will remain with biomass solids and directly sent to the CHP unit if no previous processing (*e.g.*, AOR) is carried out. Independently of the pathway, biomass ash is ultimately recovered as boiler solid waste, after which it is disposed of at a modeled processed cost of $42 per t.

CBP ethanol is more suitable for conversion into SAF than isobutanol

Selected biorefining configurations could also supply alcohol-derived SAF to the market at competitive prices. Fig. 7 depicts the what-if analysis for facilities producing ethanol and iso-butanol *via* CBP, respectively. A recently developed single-step catalytic conversion of ethanol to SAF-grade hydrocarbons was considered,[22] while a conventional sequential approach of dehydration, oligomerization, and hydrogenation was chosen

for isobutanol.[84] As previously identified, the higher economic indices for the production of ethanol favor its use as a feedstock for further conversion into renewable jet fuel. The conversion of poplar-derived cellulose into ethanol and SAF could achieve a net zero operational margin at SAF prices of $3.15 per GGE, while the same analysis yield SAF prices around $3.75–4 per GGE for corn stover. When switching to isobutanol as the product of CBP, both the higher MFSPs and upgrading costs[84] make it a less advantageous feedstock for SAF, as break-even SAF prices would have to achieve $4.45 per GGE and $5.40 per GGE for poplar- and stover-based biorefineries that produce isobutanol instead of ethanol. Although other studies may indicate that the costs involved in the multi-step conversion of isobutanol to SAF are lower than those associated with ethanol,[85] these alternative assumptions would likely yield very similar results as shown in Fig. 7 due to the majority of the production cost of SAF being tied to the synthesis and recovery of the alcohol feedstock.
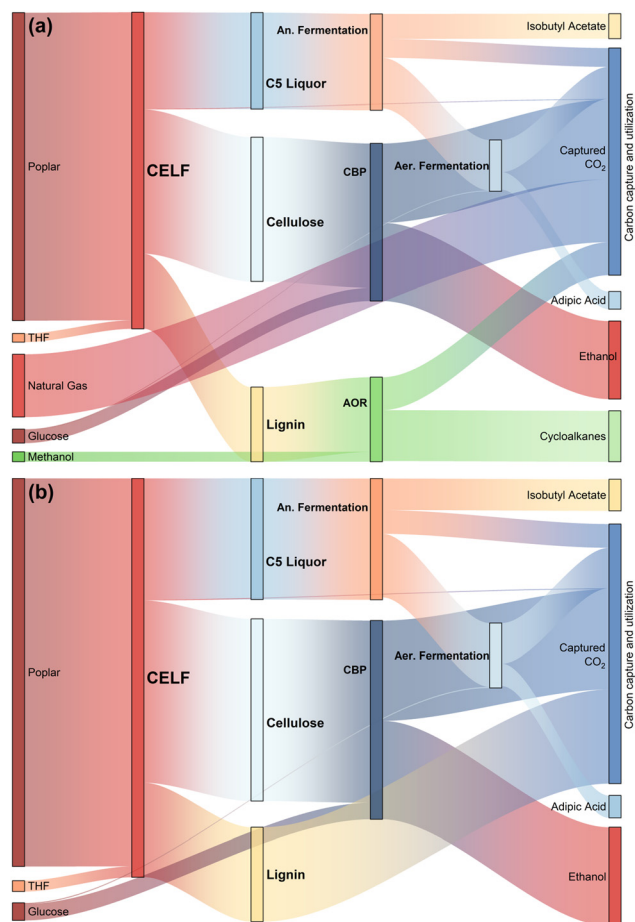
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Fig. 6 Carbon flow Sankey diagrams of CELF-based biorefineries processing poplar to ethanol and other co-products (a) with WIS lignin conversion to cycloalkanes and (b) with WIS lignin combustion for energy generation. Length of the bars is equivalent to carbon flow on a mass basis (poplar carbon input is of 39.9 t per h). Wastewater treatment and cogeneration of heat and power sections are omitted for simplification purposes. AOR: athermal oxygen removal; CBP: consolidated bioprocessing; CELF: co-solvent enhanced lignocellulosic fractionation; THF: tetrahydrofuran.

Fig. 7 Operational margins for SAF production from alcohols obtained in CELF-based biorefineries. SAF price calculated by adding an upgrading cost of $0.17 per GGE for (a) ethanol[22] and $0.54 per GGE for (b) isobutanol[84] to the respective alcohol MFSPs estimated for each biorefinery setup. GGE: gallon of gasoline equivalent; SAF: sustainable aviation fuel.

CELF-based biorefining supplies diverse low-carbon product portfolios

Producing ethanol as the primary CELF alcohol product results in lower overall impacts relative to isobutanol production (GWP is shown in Table 1 and CED in Table 2). This result is largely due to lower natural gas consumption in the ethanol-producing biorefineries, which leads to both lower cumulative energy demand (CED) and lower process-level emissions, which are both key components of GWP. The lowest-impact ethanol and isobutanol was produced by the poplar-to-alcohol biorefinery configuration that used lignin for energy generation purposes in the CHP units. The stover-to-alcohol biorefinery configuration that did convert lignin to cycloalkanes produced the highest-impact alcohol products.

Although the ethanol-producing biorefinery configurations outperform the isobutanol-producing configurations, all CELF bioref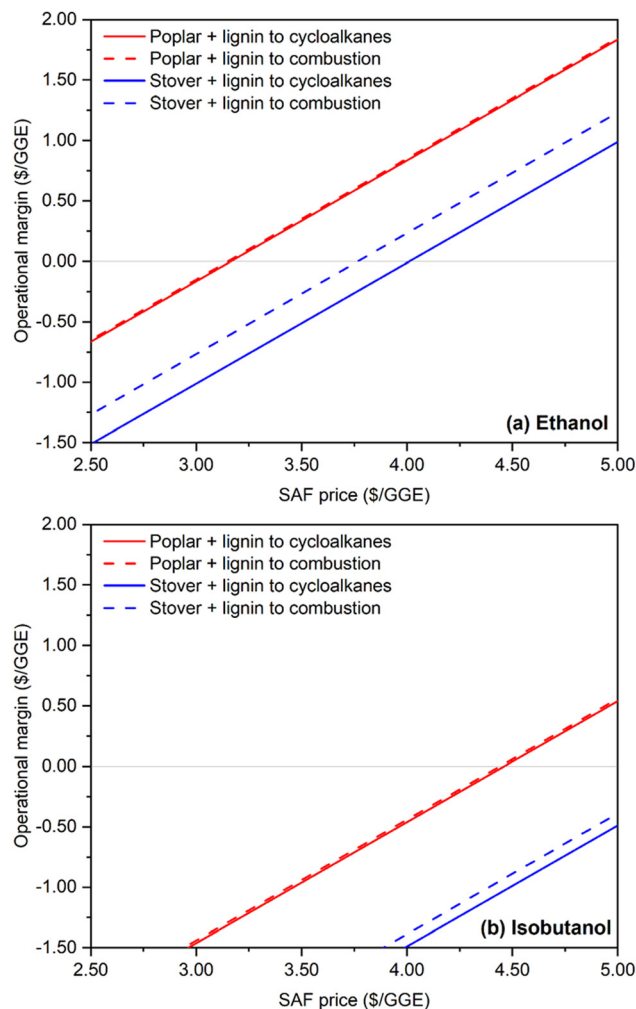inery configurations have substantially lower GWP impacts relative to the same product portfolios as produced using conventional technologies – either from fossil feedstocks or, for ethanol, from a biochemical stover conversion biorefinery

Table 1 Global warming potential (GWP) per gallon of gasoline equivalent (GGE) of alcohol product for the eight scenarios and both impact allocation methods: product mass and product economic value

Impact allocation method	Feedstock	Lignin fate	GWP (kgCO$_2$eq per GGE)	
			Isobutanol	Ethanol
Mass	Poplar	Cycloalkanes	2.93	0.04
	Poplar	Combustion	0.92	−2.83
	Stover	Cycloalkanes	4.05	2.45
	Stover	Combustion	3.29	0.21
Economic value	Poplar	Cycloalkanes	2.55	0.03
	Poplar	Combustion	0.78	−2.01
	Stover	Cycloalkanes	3.41	1.60
	Stover	Combustion	2.73	0.14

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Table 2 Cumulative energy demand (CED) per gallon of gasoline equivalent (GGE) of alcohol product for the eight scenarios and both impact allocation methods: product mass and product economic value

Impact allocation method	Feedstock	Lignin fate	CED (MJ per GGE)	
			Isobutanol	Ethanol
Mass	Poplar	Cycloalkanes	322	300
	Poplar	Combustion	320	276
	Stover	Cycloalkanes	297	265
	Stover	Combustion	295	234
Economic value	Poplar	Cycloalkanes	280	210
	Poplar	Combustion	272	196
	Stover	Cycloalkanes	250	173
	Stover	Combustion	245	153

(Fig. 8). This result indicates that the CELF biorefineries of this work offer a means of producing relatively lower-carbon product portfolios compared to the current state of technology

RIN credits can leverage the deployment of multiproduct biorefineries

While some of the biorefining strategies in Fig. 3 are able to achieve an IRR of 10% without any economic incentives, their economic performance could be greatly improved through the

commercialization of RIN credits associated with alcohol fuels and cycloalkanes. In comparison to the parameters varied in Fig. 5, D3 RIN credit price would have an even higher impact on the economics of CELF-based biorefineries, as this incentive would benefit alcohols and cycloalkanes alike. Fig. 9a and b indicate the variation of IRR with D3 RIN credits prices while also pinpointing the required credit price to achieve a minimum IRR of 10% for each of the biorefining strategies under scrutiny. In general, biorefineries which convert lignin to cycloalkanes are more sensitive to this incentive, represented by an overall higher slope of curves in Fig. 9a relative to Fig. 9b. As D3 RIN credits are computed based on the energy density of a biofuel (in comparison to that of a gallon of ethanol), this element is reflected accordingly in the study as isobutanol and cycloalkanes have energetic contents 25% and 79% higher than that of ethanol, respectively. All biorefineries could achieve an IRR of 10% with D3 RIN credit prices of, at most, $1.2 per gal. Fig. 9c presents the historical series for D3 RIN credit price between 2015 and 2021, which remains largely in the $0.60–3.15 per gal range. Based on this historical dataset, the analysis shows the probability of encountering specific D3 RIN credit prices in the market: 100% chance of being higher than $0.5 per gal, 88% probability of exceeding $1 per gal, and 70% chance of surpassing $1.5 per gal. This hints at the possibility of virtually all CELF-based biorefineries in this study being able
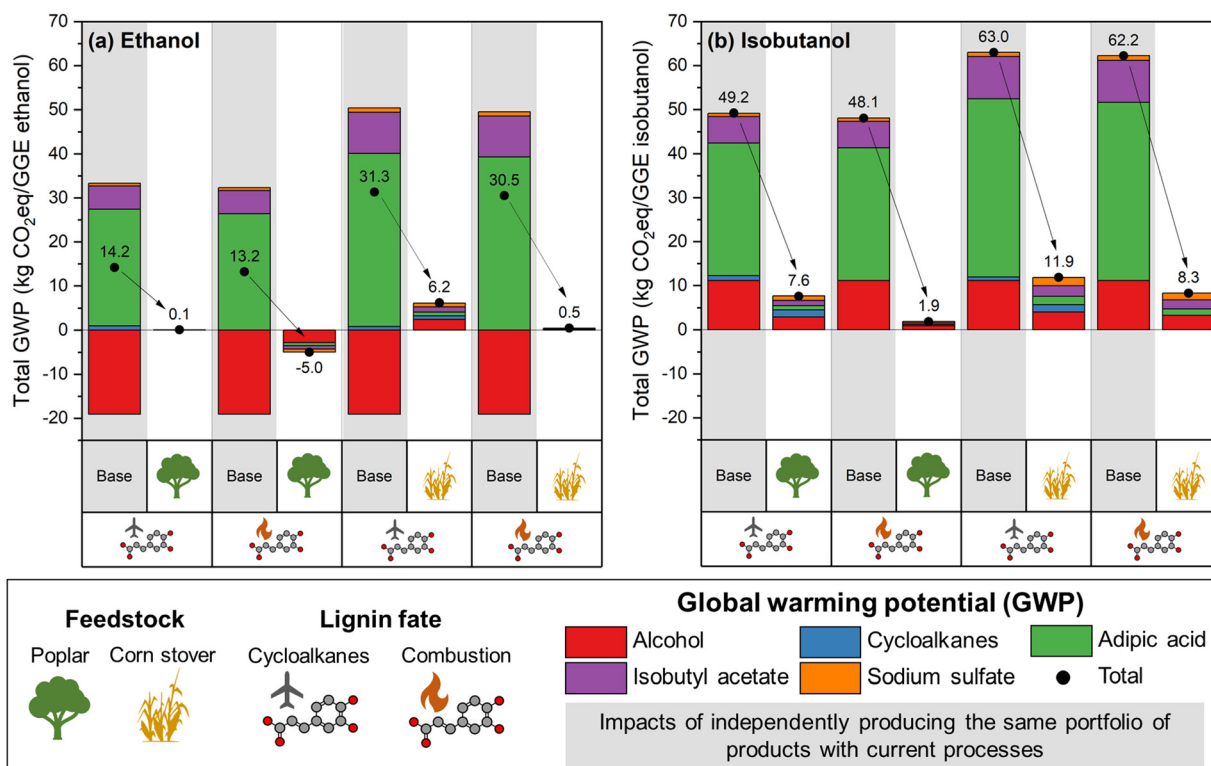

Fig. 8 Total global warming potential (GWP) of CELF biorefinery configurations producing (a) ethanol and (b) isobutanol. Breakdown of impacts is provided on a mass allocation basis. Overall, the ethanol-producing biorefineries have lower impacts per GGE of alcohol product, but all CELF biorefinery configurations offer substantial GWP savings when compared to producing the same portfolio of products independently using conventional processes/technologies.
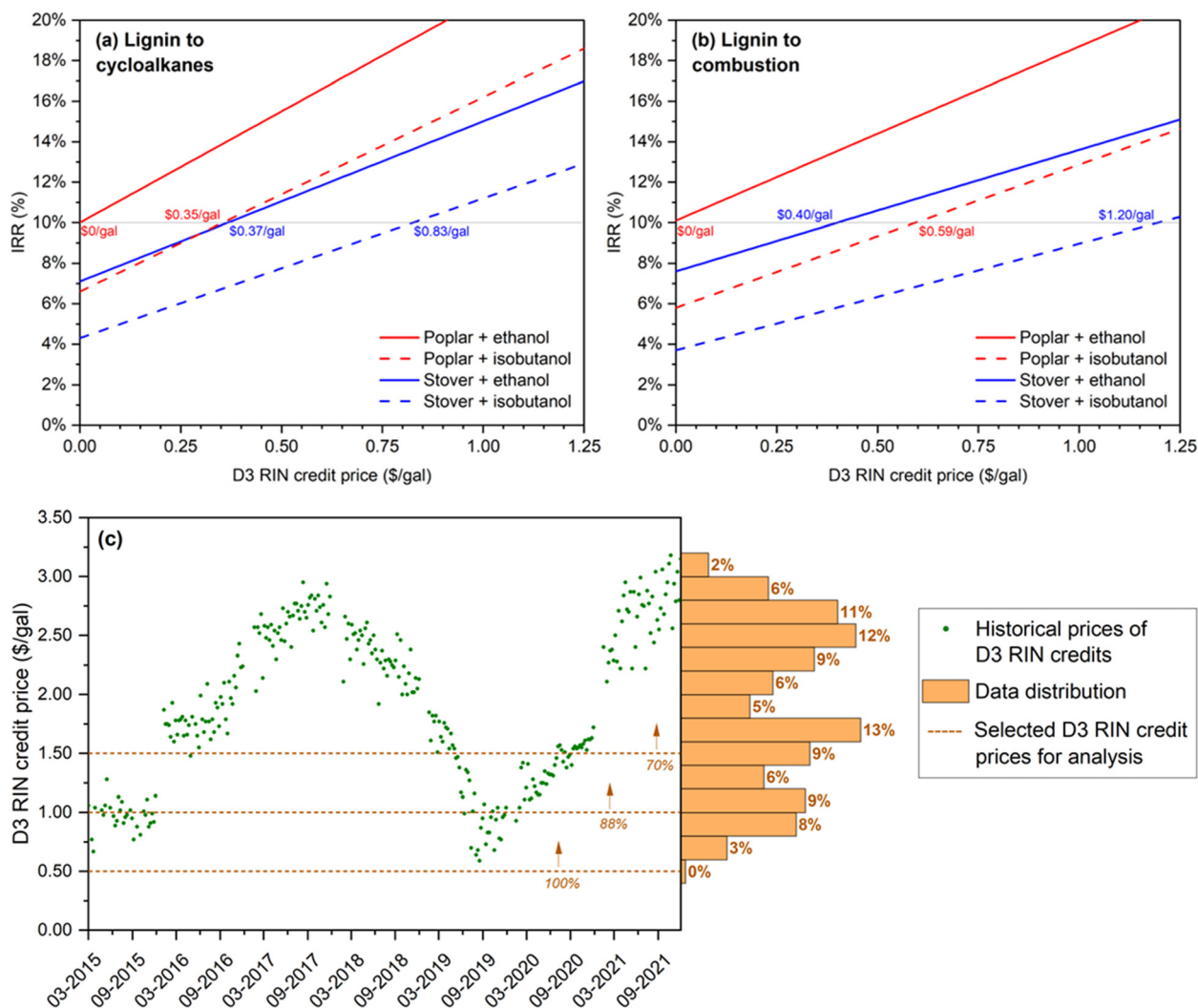
Fig. 9 Effect of D3 RIN credit prices over the economics of biorefineries (a) converting lignin to cycloalkanes and (b) burning lignin for energy generation. Historic D3 RIN credit price data is shown in (c). All D3 RIN credit prices are given in $ per gal of ethanol equivalent. IRR: internal rate of return; RIN: renewable identification number.

to achieve IRRs in excess of 10% if the credit price trends in recent years is maintained in the future.

Conclusions

This modeling study employs a multi-parametric TEA and LCA to evaluate the economic and environmental performance potential of a biomass-fractionating biorefinery that is configured to maximize biomass utilization. The biorefinery model utilizes CELF pretreatment to fractionate cellulose, hemicellulose, and lignin components and elucidates major cost drivers and environmental burdens for the commercial-scale production of sustainable aviation fuels, alcohol fuels, and co-products. Such facilities are able to simultaneously differentiate carbon into multiple products through a myriad of pathways and this biorefining approach rewards feedstocks with higher carbon content. Under the same analysis

conditions, ethanol appears as a more advantageous alcohol choice than isobutanol in CBP of CELF-derived cellulose and, in comparison to corn stover, poplar emerges as a competitive feedstock – one that could have a more innate flexibility in a future in which carbon credits are unclear. All configurations considered are highly benefited in terms of carbon footprint relative to current petrochemical or fossil-sourced molecules: for the best poplar case, the estimated GWP of ethanol is of -2.83 kg CO_2 per GGE, being also cost-competitive with current gas prices without the need for D3 RIN credits. Finally, the commercialization of D3 renewable identification number (RIN) credits could greatly boost the deployment of CELF-based plants: all analyzed facilities would achieve economic viability at a credit price below $1.20 per RIN, with poplar/ethanol biorefineries achieving an internal rate of return (IRR) of 10% without resorting to this incentive.

This study also presents the basis for more in-depth work aimed at providing feedback to different R&D teams to guide

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further experimental development, for which TEA/LCA is able to inform minimum performance thresholds to be attained in laboratory scale in a circular workflow model. The analysis also reveals that RIN credits positively support valorization of lignin to hydrocarbon fuels, increasing overall biorefinery competitiveness over simple lignin combustion.

Methods

Process simulation and techno-economic analysis

Process simulations were carried out using the Aspen Plus V10 software (AspenTech, Bedford, MA) to build integrated models of biorefineries converting 2000 dry metric tons of biomass per day (poplar or corn stover) into a suite of bioproducts through key technologies employed in parallel or sequentially. General modeling assumptions for biomass handling, CELF pretreatment, and the multiple processes included in the biorefineries presented herein are further detailed in the ESI† (Table S2). The effect of varying biomass recalcitrance between corn stover and poplar have not been considered in this study.[86] Simulations were then used to provide the pertinent mass and energy balances, which are required to estimate the associated capital expenditures (CAPEX) and operational expenses (OPEX). Multiple sources – internal databases, literature data, and patents – were used to determine such variables and all costs were deflated to 2016 US dollars. Finally, discounted cash flows (DCF) were established to gauge the economic performance of the industrial plants (parameters shown in the ESI,† Table S4). IRR was used as the main parameter for the biorefinery profitability comparison, which is a reasonable metric in view of the very large product portfolio of the biorefinery. We also solved for MFSP of alcohols as a possible additional economic metric of interest to researchers in the field. The ESI† contains detailed technical and economic indicators of the biorefineries under scrutiny (Tables S5–S7, ESI†). The economic performance analysis was complemented by an uncertainty analysis over the main relevant inputs, such as CAPEX, selected OPEX items, feedstock cost, and product selling price. The software @RISK 8.0 (Palisade, Ithaca, NY) was used to generate 10 000 stochastic simulations using Latin hypercube sampling. The complete variation ranges are presented in Fig. 5.

Feedstocks are delivered at plant's gate at $71.26 per dry ton (corn stover)[62] and $58.70 per dry ton (poplar, average price for trees with diameter at breast height [DBH] of 16 cm, following the methodology described in ref. 86). Other major inputs are: THF ($1.60 per kg), glucose ($0.81 per kg), natural-gas derived methanol ($0.33 per kg), and natural gas ($3.50 per MMBTU). On the products side, isobutanol and ethanol are set to be sold at $3.00 per GGE while branched cycloalkanes are considered freezing point depression blendstocks commercialized at twice the price of conventional A1 jet fuel ($0.83 per kg). Other products from the biorefinery include isobutyl acetate ($1.21 per kg), adipic acid ($1.88 per kg), and sodium sulfate ($0.16 per kg). The electricity surplus is sold at $0.057 per kW h, while electricity is imported from the grid at $0.068 per kW h.

D3 RIN credits, associated with cellulosic fuels, are applied to both fuels produced at the biorefinery (alcohols and cycloalkanes) in the associated sensitivity analysis.

Life cycle analysis

The scope of LCA in this work is farm-to-biorefinery-gate. Feedstock production is included in the system boundary, as is the production and transportation of all other biorefinery inputs. Impacts are quantified per GGE of the primary alcohol product, which may be isobutanol (0.268 GGE per kg) or ethanol (0.219 GGE per kg). The use phase of the various co-products is excluded from the system boundary. Allocation based on product mass and on product economic value is applied to divide total biorefinery impacts among the various co-products. 100 year global warming potential (GWP) calculated according to the IPCC 2013 method (v1.03) and cumulative energy demand (CED) are the impacts quantified. Biogenic carbon dioxide emissions from the biorefinery are included in the GWP calculation, as is carbon uptake by growing poplar and corn stover. Including these carbon flows avoids any assumption of carbon neutrality for the biomass feedstock and allows for the quantification of all carbon releases and uptake. Further details are given in the ESI.†

Abbreviations

AOR	Athermic oxygen removal
CAPEX	Capital expenditures
CBI	The Center for Bioenergy Innovation
CBP	Consolidated bioprocessing
CELF	Co-solvent enhanced lignocellulosic fractionation
CHP	Combined heat and power
DBH	Diameter at breast height
DCF	Discounted cash flow
DDA	Deacetylation and dilute acid
DMR	Deacetylation and mechanical refining
DOE	US Department of Energy
GGE	Gasoline gas equivalent
GHG	Greenhouse gases
LCA	Life cycle analysis
MFSP	Minimum fuel selling price
OPEX	Operational expenses
R&D	Research and development
RIN	Renewable identification number
RON	Research octane number
SAF	Sustainable aviation fuel
SSF	Simultaneous saccharification and fermentation
TEA	Techno-economic analysis
THF	Tetrahydrofuran
WIS	Water-insoluble
WS	Water-soluble

Conflicts of interest

None to declare.

Acknowledgements

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