

ANALYSIS

View Article Online
View Journal | View IssueCite this: *Energy Environ. Sci.*,
2022, 15, 2679

Analysis of alternative bioenergy with carbon capture strategies: present and future†

Caleb H. Geissler ^a and Christos T. Maravelias ^{*ab}

Biomass can be converted *via* fermentation, pyrolysis, gasification, or combustion to a variety of bioenergies, and each conversion technology generates streams with different flows and CO₂ concentrations that can undergo carbon capture. We use system-wide optimization models to determine the conversion technologies and level of carbon capture that lead to the minimum breakeven cost of fuel for a range of capacities and sequestration credits. We investigate how the optimal systems depend on constraints, such as energetic biorefinery self-sufficiency; and parameters, such as biomass availability. Pyrolysis to gasoline/diesel with hydrogen purchase produces liquid fuel for the lowest cost when energy purchase is allowed, with flue gas capture incentivized at sequestration credits of \$48–54 per Mg CO₂. With increasing sequestration credits, gasification to gasoline/diesel with carbon capture becomes optimal. When all bioenergies are considered, the cost per forward motion of electricity and hydrogen is lower than for liquid fuels because of the higher efficiency of electric motors and hydrogen fuel cells. We find that while gasification to electricity results in the greatest greenhouse gas mitigation under the current energy production mix, gasification to hydrogen is expected to result in the greatest mitigation in the future as the energy production mix changes.

Received 23rd February 2022,
Accepted 9th May 2022

DOI: 10.1039/d2ee00625a

rsc.li/ees

Broader context

Bioenergy with carbon capture and sequestration (BECCS) is expected to be pivotal in global warming mitigation. BECCS systems include conversion technologies such as fermentation to ethanol, pyrolysis to gasoline/diesel, gasification to gasoline, combustion to electricity, and gasification to electricity or hydrogen. However, it is not yet clear which of these different conversion technologies with integrated carbon capture has the greatest economic and CO₂ mitigation potential. Accordingly, we determine the cost-optimal BECCS strategy under a wide range of scenarios and assumptions. Looking into the future, we present the expected mitigation potential of the most promising BECCS strategies through 2050.

1 Introduction

Given the continued fossil fuel-based emissions and the worsening effects of climate change, effective methods of greenhouse gas (GHG) mitigation and carbon dioxide removal (CDR) are needed.¹ While bioenergy can result in some net emissions due to farming inputs, transportation, and other material consumption, it typically results in significantly lower emissions than the fossil fuels it replaces² and, importantly, can result in net-negative emissions if the CO₂ generated at the biorefinery is captured and sequestered underground in secure geological storage. Thus, bioenergy with carbon capture and sequestration (BECCS) can both mitigate fossil fuel usage and actively remove CO₂ from the atmosphere. For these

reasons, BECCS features prominently in many pathways found by the Intergovernmental Panel on Climate Change that limit global warming to 1.5 °C above pre-industrial levels.¹

The most common biofuel in the United States is currently ethanol, typically made by fermenting the sugars in corn grain. However, this results in competition between food and fuel in terms of both corn use and in terms of the cropland used to grow the corn.³ For this reason, significant research has been performed on using nonfood crops such as grasses and woody biomass,^{4,5} and growing these crops on land not suitable for food crop production, often referred to as marginal lands.^{2,6,7}

There have been many technoeconomic analyses that focus on one specific fuel and conversion technology, such as the conversion of biomass to ethanol *via* fermentation,^{3,8–13} gasoline/diesel *via* pyrolysis^{14–16} or gasification,^{17,18} hydrogen *via* gasification,^{19–21} and electricity *via* either direct combustion²² or gasification and combustion.^{23–25} Some of these studies also include carbon capture in their analyses.^{9,11–13,20,21,24,25} However, the results of these studies can be difficult to directly

^a Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA. E-mail: maravelias@princeton.edu

^b Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ee00625a>



compare because of the wide array of process, economic, and environmental assumptions they are based on. Some researchers have directly compared multiple conversion technologies, but typically without considering carbon capture. For example, Anex *et al.*²⁶ and García-Velásquez and Cardona²⁷ compared the economics of pyrolysis to gasoline/diesel, gasification to gasoline/diesel, and fermentation to ethanol. The studies that do include carbon capture are Muratori *et al.*,²⁸ who compared fossil fuels and biomass to power or liquid fuels, and Yan *et al.*²⁹ and Sanchez and Callaway³⁰ who both compared direct combustion and integrated gasification and combustion.

However, some questions remain open. First, each conversion technology is typically studied with either no carbon captured, or with capture from one source. However, some conversion technologies have multiple CO₂ streams with varying concentrations and pressures that would have different costs and energy requirements of capture. For example, a biorefinery using fermentation has potential CO₂ capture sources in the nearly pure CO₂ released from fermentation, the biogas generated from anaerobic digestion of wastewater, and the flue gas from solid residue combustion.⁸ Second, comparisons across multiple BECCS systems have been carried out at a fixed capacity. Importantly, as the capacity increases, the capital and fixed costs per unit of fuel decrease, but the average cost of transporting the feedstock to the biorefinery increases.^{13,31} The capital and fixed costs of biorefineries based on different conversion technologies scale differently, so the optimal conversion technology and fuel may change as the capacity changes. The optimal capacity of a biorefinery producing ethanol has been studied before with³² and without^{33,34} carbon capture, but no studies have examined the optimal capacity of a biorefinery using pyrolysis or gasification. Third, estimations of GHG mitigation of BECCS systems are based on the current state of technologies for calculating the benefit for mitigating electricity or hydrogen production. An important consideration however is the expected evolution of technologies used for electricity and hydrogen production, and therefore the evolution of the GHG benefit for mitigating them.

To address these open questions, we compare the economic and environmental performance of biorefineries using fermentation, pyrolysis, gasification, or combustion. Biorefineries using each conversion technology have multiple conversion and configuration options (*e.g.*, biorefineries using pyrolysis can either purchase hydrogen or produce it onsite) and carbon capture options. We use optimization, under varying inputs (*e.g.*, sequestration credit, capacity, biomass availability), to identify the cost-optimal strategy, which is defined by the conversion technologies, fuel output, types of purchased energy inputs, and streams which undergo carbon capture.

In this paper, after introducing our methods and assumptions, we start, in Section 3.1.1, with results for the first biorefineries that would likely be built: pioneer plants producing liquid fuels. For these pioneer plants, which have higher costs and lower performance because of their novelty, we present how the cost-optimal strategy changes as a function of carbon incentive and biorefinery capacity. After many of these plants have been built, future plants (*n*th plants) will no longer have overdesign of

equipment or reduced performance. For these *n*th plants that produce liquid fuels, we discuss cost-optimal strategies, how representative biorefinery strategies are affected by changes in key cost parameters, and GHG emissions of biorefineries that have energy inputs other than biomass (Section 3.1.2) or are energetically self-sufficient (Section 3.1.3). In Section 3.1.4, we present how *n*th plants utilizing fermentation may benefit from lignin valorization. In Section 3.2.1, we consider biorefinery strategies that produce electricity or hydrogen in addition to those producing liquid fuels, and identify cost-optimal biorefinery strategies when costs are normalized to forward motion in vehicles. For these optimal strategies, we then present, in Section 3.2.2, the expected total GHG mitigation into the future as the emissions associated with fuel generation change.

2 Methods

We first present background and assumptions on biomass growth and transportation, biorefinery conversion technologies, and carbon capture. We then discuss the method of economic evaluation we use, and the structure of the optimization model we develop to analyze BECCS systems.

2.1 Feedstock and supply chain modeling

We assume switchgrass is the feedstock for strategies using fermentation, while poplar is the feedstock for strategies using thermochemical conversion methods, based on the choice of feedstock in the literature.^{8,16,18} As a baseline, we assume average yields of 10 Mg km⁻² and 13 Mg km⁻² for switchgrass and poplar, respectively, but consider a range of yields based on average land availability and productivity in the US Midwest (see S9 in the ESI[†]).^{6,35} To mitigate drastically increasing costs of delivering biomass from farms to the biorefinery at large distances, processing depots can pretreat and/or densify the biomass close to the farms. The densified biomass can then be transported to the biorefinery by either truck or rail with lower variable costs (\$/(km Mg)), though the processing depot incurs additional costs.^{36–38} We use a model developed by Ng *et al.* that assumes a uniform spatial distribution of biomass, and allows biomass to be transported to the biorefinery directly *via* truck, or first to a depot *via* truck and then to the biorefinery by either truck or rail, choosing the cost-optimal transportation method at each distance.³¹ Even with depots, we assume a maximum biorefinery capacity of 30 000 Mg feedstock day⁻¹. While biorefineries of this size do not exist today, previous analyses suggest that if bioenergy were to be adopted widely, then biorefineries of this size would not be unreasonable.¹³ Using this bound also allows us to include results for nearly any biorefinery capacity that might be feasible. Assumed transportation cost and energy requirements, and feedstock growth parameters are available in Tables S2.1 and S2.2 in the ESI[†].

2.2 Conversion technologies

Schematics of the conversion technologies considered, the fuel outputs, and the streams from which carbon can be captured



are shown in Fig. 1. More detailed information on carbon flows, fuel yields, and cost parameters can be found in the ESI.†

2.2.1 Fermentation. The sugars in biomass are biologically converted to ethanol, while the solid residues, consisting mostly of lignin, are combusted to generate heat and electricity. To overcome biomass recalcitrance, researchers have developed different pretreatment technologies, such as dilute acid, ammonia fiber expansion, γ -valerolactone, extractive ammonia, and copper-catalyzed alkaline hydrogen peroxide.³⁹ As a baseline, we use the process conditions and equipment costs in the report by National Renewable Energy Laboratory (NREL) where dilute acid (DA) is used as pretreatment.⁸ We then add the possibility of carbon capture from the three different CO₂ sources: fermentation, biogas, and flue gas. The cost, energy, and process parameters used, and the relative carbon flows between process units are available in the ESI,† in Table S5.1 and Fig. S7.1, respectively.

2.2.2 Pyrolysis. Biomass is first converted into vapor, a portion of which can be condensed into bio-oil, with the non-condensable gases combusted to generate heat and electricity. The bio-oil is then upgraded by hydrotreating and hydrocracking, which requires hydrogen. That hydrogen can either be purchased, or a portion of the non-condensable gases can be reformed into hydrogen. We use the baseline parameters of technoeconomic analyses performed by NREL researchers.^{16,40} Cost, energy, and process parameters used are available in the ESI,† in Table S5.2 and carbon flows are depicted in Fig. S7.2.

Pyrolysis also leads to biochar production along with bio-oil and non-condensable gases. While biochar can be utilized to sequester carbon in soil and for soil remediation, there is still significant uncertainty on its effect on yields, herbicides/pesticides, soil stability, toxicity, and long-term storage potential.⁴¹ Instead, by combusting the biochar, additional heat and/or electricity can be produced, resulting in a credit for selling excess electricity.¹⁶ For

sequestration credits that incentivize carbon capture, the carbon from the combusted biochar can be captured and sequestered, which along with the GHG mitigation from generating electricity results in greater GHG mitigation than administering biochar to soil. For these reasons, we do not consider carbon sequestration in biochar, and instead we include the potential for capture of the carbon in the flue gas generated from the combustion of the biochar. Similarly, we do not consider sequestration of bio-oil because this prevents the production of fuels, and this study is focused on systems that produce bioenergy.

2.2.3 Gasification. Biomass is gasified into syngas, which, after cleaning, can be converted to a wide range of liquid fuels, such as diesel and gasoline, isobutane, dimethyl ether, or methanol. The conversion process generates a fuel gas that is combusted to meet the heat and electricity demands of the biorefinery, and releases flue gas. Reports by NREL have identified gasoline production *via* methanol and dimethyl ether intermediates as a promising option, so that is the focus of this paper.¹⁸ In the NREL system, CO₂ is released as part of syngas cleaning, and in the flue gas from fuel gas combustion. The CO₂ from syngas cleaning is already pressurized to 3.5 bar, and is quite pure at 99% CO₂.

Alternatively, the syngas can undergo steam reforming and water-gas-shift to generate hydrogen, which is purified with pressure swing adsorption (PSA). The remaining gases after PSA and some of the clean syngas may be combusted to meet heat and/or electricity demands.⁴² Another alternative is to combust the syngas, after cleaning, to generate electricity. When either hydrogen or electricity is produced, there is no carbon in the final fuel, and therefore the vast majority (>90%) of the carbon in the feedstock can potentially be captured at the biorefinery.³⁵ The cost, energy, and process parameters used for gasification and conversion to each fuel are available in

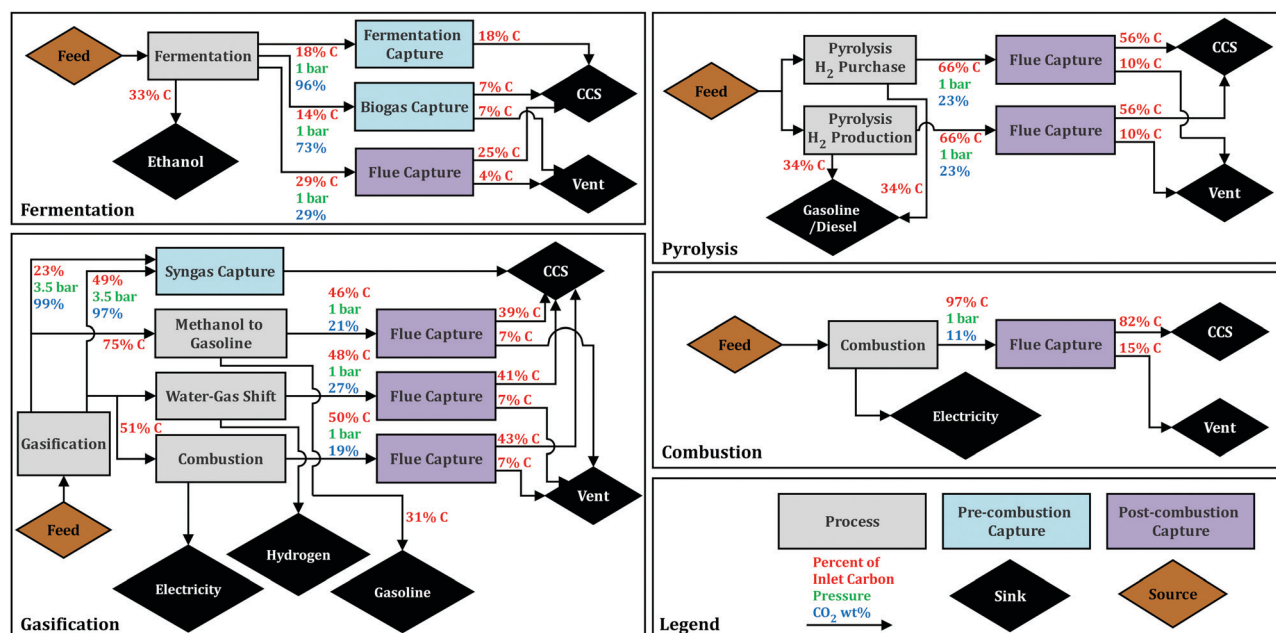


Fig. 1 Conversion technologies, fuel outputs, and carbon capture options considered in this paper.

Tables S5.2 and S5.3, and the relative carbon flows are in Fig. S7.3–S7.5 in the ESI.†

2.2.4 Direct combustion. One of the simplest ways to convert biomass to a useful fuel is to directly combust it (without gasification) and generate electricity. This conversion technology has lower capital costs than integrated gasification and combustion, but also has lower electricity efficiency.²⁹ Here, like for pyrolysis, we consider only one point source of carbon capture: flue gas. Process parameters used for direct combustion are available in Table S5.3 and relative carbon flows are in Fig. S7.6 in the ESI.†

2.3 Carbon capture and emissions

2.3.1 Carbon capture technology. We assume that carbon capture from biogas and flue gas is performed using monoethanolamine (MEA) absorption, as it is the current typical industrial capture technology.⁴³ We assume a fixed capture rate of 85% of CO₂ in flue gas based on the literature.^{44,45} Given that advances are being made in new capture technologies, such as membrane separation⁴⁶ and new solvents for CO₂ absorption,⁴⁷ we also consider the general effect of energy and capital requirements of the capture technology on the cost of carbon capture in Fig. S8.1 in the ESI.† The CO₂ released from fermentation and syngas is highly pure and therefore requires only dehydration prior to compression and sequestration.^{17,48}

2.3.2 Carbon incentives. Minimizing costs means that carbon capture will not be selected unless financial incentives are applied. There are a number of economic policies that can incentivize carbon capture and that have been examined in the context of biorefineries, such as a carbon tax, carbon pricing with cap-and-trade systems, or a sequestration credit.^{49,50} We apply a sequestration credit and investigate how different credit amounts affect the fuel cost and optimal strategy.⁵¹

2.3.3 GHG emissions. For the GHG balance, our analysis encompasses emissions and sequestration associated with growth and harvesting of the feedstock, transportation, and biorefinery operation, shown in Fig. 2. Emissions from fertilizers, chemicals, seed, fuel consumption, N₂O emissions and sequestration from soil CH₄ oxidation and soil organic carbon (SOC) changes are taken from Gelfand *et al.*³⁵ Emissions from materials consumed at the biorefinery are taken from the US life cycle inventory database.⁵² We also consider the emissions mitigated by replacing electricity, hydrogen, and liquid fuels. All emissions are normalized to carbon dioxide-equivalent (CO₂e). We do not include emissions from transporting the final fuel product. The parameters for emissions are available in Table S2.1 in the ESI.† We use forecasts developed by the U.S. Energy Information Administration and by the Net Zero America project for future energy production mixes and emissions.^{53,54}

We consider two different sets of emissions. The first set is direct emissions, which are GHGs either emitted or sequestered within the bounds of our system, for example from biomass growth and carbon sequestration. The second set is indirect emissions, which are emissions incurred or mitigated, such as by the consumption or displacement of liquid fuels, hydrogen, or electricity.

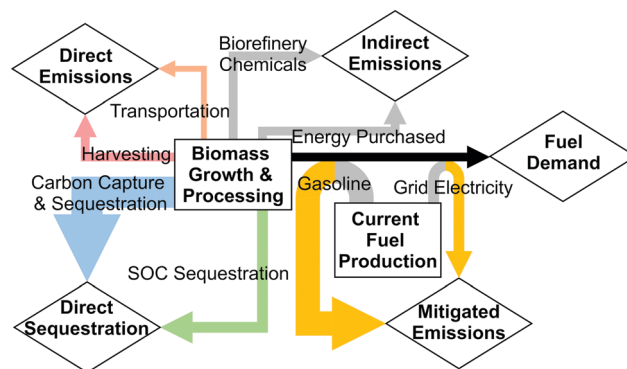


Fig. 2 Schematic of sources of direct emissions, direct sequestration, and indirect and mitigated emissions for a biorefinery producing gasoline and electricity. (Orange: transportation emissions, red: harvesting emissions, blue: sequestration of carbon captured at biorefinery, green: SOC sequestration, gray: indirect emissions, yellow: mitigated emissions).

2.4 Economic analysis

Economic assumptions and cost data for all strategies are given in Tables S3.1, S3.2 and S5.1–3 in the ESI.† For first-of-a-kind (pioneer) plants, we use an existing method to adjust capital investment and plant performance to account for equipment overdesign and reduced performance associated with new plants.⁵⁵ A discussion of the method and parameters we assume for each technology are available in Section S4 in the ESI.†

We calculate the breakeven price, or the price required to obtain a zero net present value (NPV), also known as the minimum fuel selling price (MFSP). All costs are indexed to 2017 US dollars, and the breakeven cost is reported per gallon gasoline-equivalent (GGE). When used for transportation, electricity, hydrogen, and liquid fuels require different engines with different efficiencies, so the breakeven cost is normalized to \$(/GJ forward motion) for comparisons amongst strategies producing different fuels. We assume net efficiencies of 30% for internal combustion engines, 80% for electric motors, and 50% for hydrogen fuel cells/electric motors.

2.5 Optimization

We identify a strategy as the combination of conversion technology $t \in \mathbf{T}$, type(s) of energy inputs purchased $e \in \mathbf{E}$, type of fuel output $f \in \mathbf{F}$, and source(s) of carbon capture $c \in \mathbf{C}$. The elements of these sets are given in Table 1. We abbreviate strategies as Technology.EnergyPurchased.FuelType.Carbon-CaptureSources. For example, pyrolysis to liquid fuels with hydrogen purchase and carbon capture from flue gas is abbreviated as Pyr.H2.Liq.Flu. A dash for energy purchased

Table 1 Set elements for biorefinery strategies

Set	Set elements
T	<i>Fer, Pyr, Gas, Comb</i>
E	<i>–, Elec, H2, H2Elec</i>
F	<i>Liq, H2, Elec</i>
C	<i>–, Fer, FerBio, FerBioFlu, Syn, Flu, SynFlu</i>



means that no energy is purchased, and the same for carbon capture.

The optimization problem is formulated as a mixed-integer nonlinear programming (MINLP) model, and the formulation and notation are shown in S1 in the ESI.[†] Binary variables are used for conversion technology and carbon capture selections and for logical restrictions (*e.g.*, only one strategy may be chosen), while continuous variables are used for material, energy, and cash flows. The model is implemented in GAMS 36.2.0 and solved using a global optimization solver – BARON.⁵⁶

We choose to minimize the cost of fuel production as the objective function. While the proposed framework could be utilized to study BECCS systems with different objective functions, that may focus on different economic or environmental performance metrics, the primary purpose of BECCS systems is to produce fuel with net-negative emissions, or at least significantly lower emissions than current petroleum-based fuels. Furthermore, if we select carbon sequestration, or another purely environmental metric, as an objective function, there would be a single strategy that would be optimal regardless of sequestration credit, and likely independent of biorefinery capacity. For these reasons, we minimize the breakeven cost of fuel production to determine biorefinery strategies that are most economically viable, and are therefore most likely to be implemented. We account for the environmental performance of these BECCS strategies with the inclusion of a sequestration credit that governments may apply to weight the importance carbon capture and sequestration.

3 Results and discussion

We first present results for pioneer plants producing liquid fuels before doing the same for plants based on mature technologies, referred to as n^{th} plants. We analyze the impact of requiring energetic self-sufficiency, and the role that lignin valorization may play in biorefineries using biological conversion. In Section 3.2, we consider all bioenergies, analyze the costs normalized to forward motion in vehicles, and present the expected GHG mitigation under different future scenarios.

3.1 Liquid fuels

3.1.1 Pioneer plant analysis. First, we consider a pioneer plant producing liquid fuels. Pioneer plants typically have high capital costs and low performance due to equipment overdesign and lack of experience with the process. The increase in capital costs and decrease in performance is a function of parameters such as the number of new processes and their complexity.⁵⁵ We consider fermentation, pyrolysis, and gasification to liquid fuels, and carbon capture from any source. If the energy demand for the optimal amount of carbon capture exceeds the heat and electricity generated at the biorefinery, electricity may be purchased from the grid. The dependence of the optimal strategy, and its breakeven cost, on the capacity of the biorefinery and the sequestration credit applied is illustrated in Fig. 3. The GHG balances of the different optimal strategies are shown in Fig. 4.

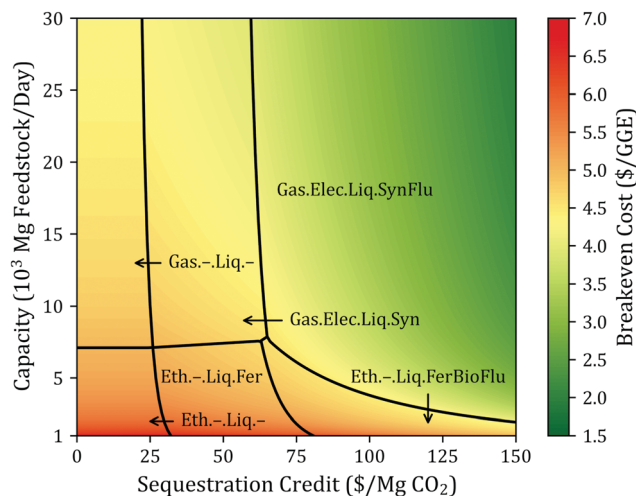


Fig. 3 Breakeven cost of liquid fuel from a pioneer plant as a function of sequestration credit and biorefinery capacity. Solid black lines show boundaries of where a specific biorefinery strategy is chosen.

Fermentation has the highest technological maturity among the studied conversion technologies and is optimal at low capacities. At higher capacities, reduced capital costs due to economies of scale favor gasification. The CO_2 released from both fermentation and syngas cleaning is very pure, so carbon capture is incentivized at sequestration credits of only \$24–33 per Mg CO_2 . Flue gas capture is incentivized at credits of \$60–80 per Mg CO_2 , depending on the capacity and conversion technology. Gasification results in the largest CO_2 emissions at the biorefinery, so strategy Gas.Elec.Liq.SynFlu results in more carbon capture than any other biorefinery strategy producing liquid fuels and purchasing electricity, making it increasingly favorable as the sequestration credit increases. No strategy using pyrolysis is optimal for pioneer plants due to the relatively low technological maturity of pyrolysis compared to fermentation and gasification, and because strategies utilizing pyrolysis can only capture carbon from relatively dilute flue gas.

3.1.2 n^{th} plant analysis. In contrast to the pioneer plant, for the n^{th} plant analysis, all biorefineries are assumed to operate at peak capacity and have no overdesign of equipment. For the remainder of the paper, all analyses are performed on n^{th} plants. In this section, electricity may still be purchased to increase the amount of carbon capture if such a decision is optimal.

The breakdown of how different costs contribute to the breakeven price, and the sensitivities of the breakeven costs to changes in feedstock farm price, transportation cost, and electricity price are shown in Fig. 5. For several representative strategies, we include the breakdown and sensitivities for no carbon capture and the maximum amount of carbon capture that can be achieved with energy purchase. The switchgrass transportation cost is higher than its farm price, so the breakeven price is slightly more sensitive to the transportation than the farm price. The opposite is true for poplar, which has a much higher farm price than transportation cost, resulting in high sensitivity of the breakeven cost of pyrolysis or gasification strategies to changes in the farm price. Electricity is never sold



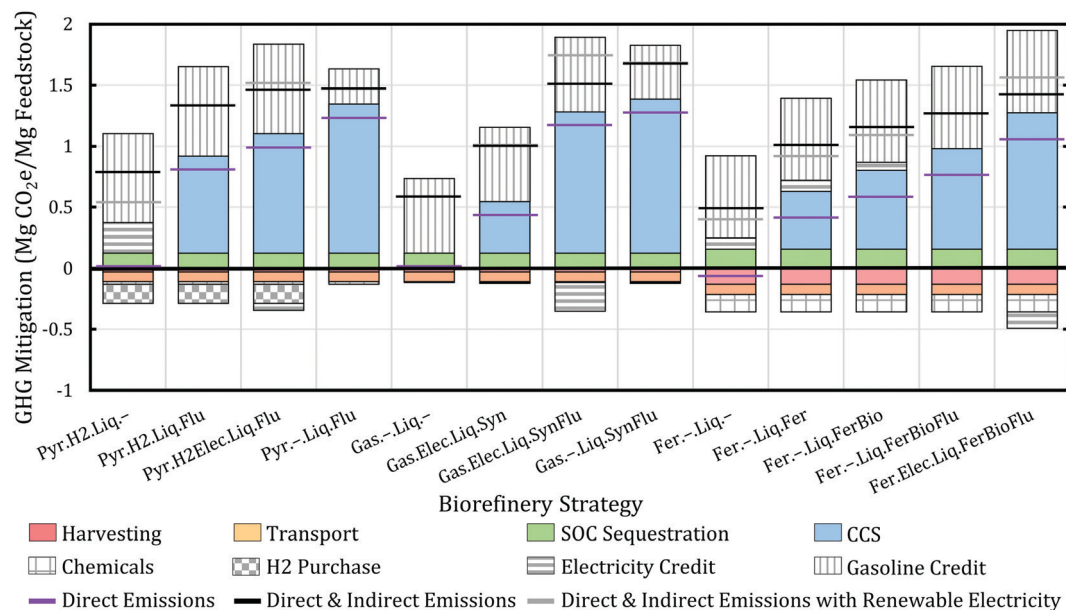


Fig. 4 Mitigated GHG emissions per mass feedstock for biorefinery strategies in Sections 3.1.1–3.1.3 processing 2000 Mg feedstock per day. GHG mitigation refers to the net GHG reduction in the atmosphere for the case of direct emissions, and to the combination of GHG reduction in the atmosphere and GHG emissions incurred or displaced by chemical/fuel consumption or production in the case of direct and indirect emissions.

in any strategy using gasification, so increasing the electricity price either does not affect, or increases, the breakeven price. Depending on the amount of carbon capture, electricity may be either purchased or sold in strategies using fermentation or pyrolysis, so an increase in electricity can either increase or decrease the breakeven cost of fuel production.

The breakeven cost as function of sequestration credit and biorefinery capacity is shown in Fig. 6A. With no, or a low, sequestration credit, strategy Pyr.H2.Liq.- produces liquid fuel at the lowest cost. At higher capacities, economies of scale reduce the capital cost per unit fuel produced. At sequestration credits of \$48–54 per Mg CO₂, strategy Pyr.H2Elec.Liq.Flu becomes optimal, which notably requires the purchase of electricity. Similar to the case of pioneer plants, at high sequestration credits, Gas.Elec.Liq.SynFlu is the optimal strategy.

3.1.3 Energetically self-sufficient biorefineries. As seen in the previous section, many economically optimal solutions involve either the purchase of electricity to increase CO₂ capture rate or, in the case of biorefineries using pyrolysis, the purchase of hydrogen to increase yield. However, purchasing external energy relies on the existing energy infrastructure and may limit where a biorefinery can be built. Furthermore, using grid electricity, a significant portion of which is produced by fossil fuels, can reduce the renewability of the process and incur a GHG emission penalty for the CO₂ generated during electricity production.⁵³ If renewable electricity were available, a strategy for which energy is purchased will no longer have the GHG emission penalty from the electricity production. However, an energetically self-sufficient biorefinery will still result in greater GHG mitigation. As an example, consider

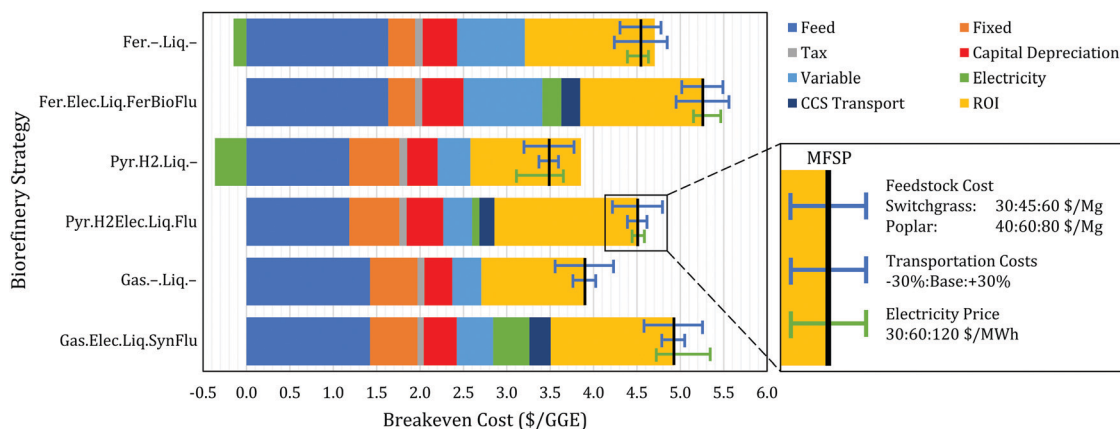


Fig. 5 Sensitivity analyses of feedstock cost, transportation cost, and electricity price on breakeven price of n^{th} plant biorefinery strategies processing 2000 Mg feedstock per day into liquid fuels.



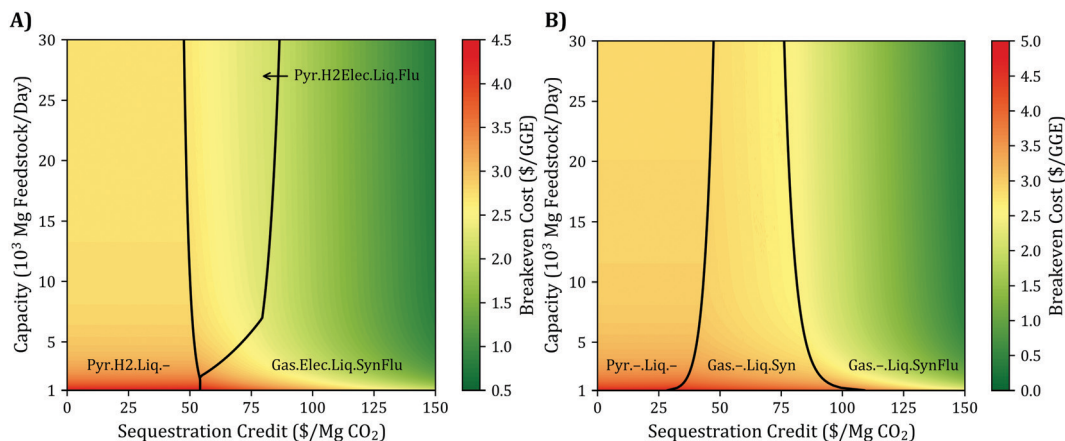


Fig. 6 Breakeven cost of liquid fuel from an n^{th} plant as a function of sequestration credit and biorefinery capacity. Solid black lines show boundaries of regions where a specific biorefinery strategy is chosen. (A) Energy purchase allowed, (B) energetic self-sufficiency enforced.

strategy Gas.-.Liq.SynFlu. If 0.392 MW h per Mg feedstock of renewable electricity were purchased, the liquid fuel yield would be maximized, leading to an additional mitigation of 0.064 Mg CO₂e per Mg feedstock. However, that clean electricity could instead be used to displace fossil liquid fuels, which would mitigate 0.335 Mg CO₂e per Mg feedstock (for details of these calculations, see S11 in the ESI†). For these reasons, we consider the effect of sequestration credit and biorefinery capacity on the optimal strategy when energetic self-sufficiency is enforced in an n^{th} plant. If there is insufficient excess heat or electricity at the biorefinery to capture carbon, some of the feedstock may be combusted to supply the energy, at the expense of decreased fuel yield. The results are shown in Fig. 6B.

Similar to the case when energy purchase is allowed, pyrolysis is the optimal conversion technology at low or no sequestration credits. The cost of carbon capture from syngas is low, so as the sequestration credit increases, Gas.-.Liq.Syn becomes the optimal strategy. However, biorefinery strategies using pyrolysis benefit more from increasing capacity because they have a higher capital cost than gasification strategies; therefore, as the capacity increases, a higher sequestration credit is needed to incentivize changing to strategy Gas.-.Liq.Syn. At sequestration credits of \$76–108 per Mg CO₂, Gas.-.Liq.SynFlu becomes the optimal strategy. The credit required to incentivize flue capture with energetic self-sufficiency is higher than when energy purchase is allowed because some of the feedstock is burnt to supply the increased heat and electricity demand of carbon capture, which decreases fuel yield.

3.1.4 Lignin valorization in biorefineries using fermentation.

To achieve energetic self-sufficiency, enforced in the previous section, waste streams or off-gas are combusted. However, one distinction of the biological platform is that it can leave a lignin-containing stream relatively intact, which can be converted into value-added chemicals rather than combusted to generate electricity.⁵⁷ NREL researchers have also examined the potential conversion of off-gases from pyrolysis into by-products, but these byproducts can only be produced in relatively small quantities (<3% by mass of the dry feedstock).⁴⁰ Meanwhile, because around 15% of switchgrass consists of lignin, NREL projects that

by 2030, 12% of the mass of the feedstock could be converted into valuable byproducts.⁵⁸ Since this higher potential yield of byproducts makes biorefineries utilizing fermentation more suitable for and sensitive to byproduct conversion, we focus on byproducts only in biorefineries using fermentation.

We examine the effect of energy requirement of the production and sale of an unspecified byproduct on the cost of ethanol production in an energetically self-sufficient biorefinery with a 2000 Mg feedstock/day capacity and no sequestration credit. The energy requirement includes both heat and electricity requirements, with the electricity requirement normalized to the heat required to produce that electricity with an assumed turbo-generator efficiency of 38%, with 50% of the inlet heat to the turbogenerator able to be recovered to meet heating demands. The profit accounts for revenue from the sale of the byproduct minus the operating costs of the lignin valorization process. The results of this analysis are shown in Fig. 7. We find that at profit margins greater than \$1 per kg byproduct, the benefits of lignin valorization can lead to a lower breakeven fuel cost than strategy Pyr.-.Liq.-, which has the lowest fuel production cost among all other energetically self-sufficient strategies considered.

3.2 All bioenergies

We simultaneously consider the production of liquid fuels as in Section 3.1, the production of hydrogen *via* gasification, and the generation of electricity *via* either direct combustion or with integrated gasification and combustion. While purchasing hydrogen or electricity can reduce the capital cost required to generate them on-site from biomass, it reduces the renewability of the biorefinery because it requires fossil resources. If energy purchase is allowed, then a number of questions arise: How much external energy purchase is allowed? If natural gas is purchased to meet all heat and electricity demands, can then electricity be sold to the grid? Can these facilities still be considered biorefineries (when they use fossil energy)? Furthermore, in the case of a power plant with carbon capture, heat and electricity are not purchased to meet the energy demands of carbon capture, rather, the yield is reduced as some heat and electricity generated on-site are used for carbon capture. To keep our analyses consistent



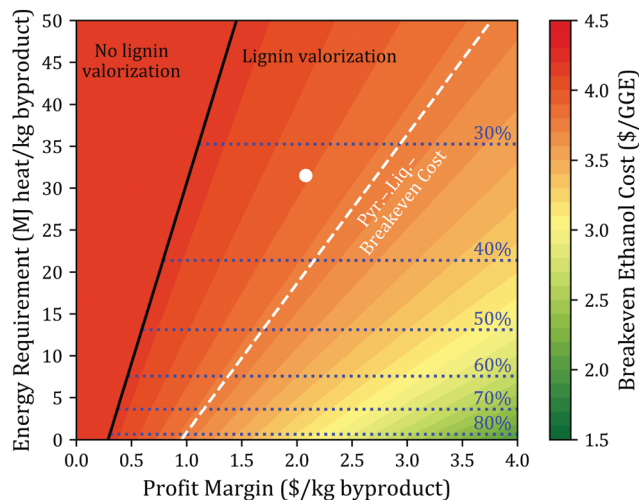


Fig. 7 Effect of profit margin and energy requirement of lignin conversion on the breakeven cost of ethanol production in a biorefinery processing 2000 Mg day^{-1} . Dotted blue lines denote lignin utilization rate for a given energy requirement. The solid black line indicates the boundary where lignin valorization is selected. The dashed white line shows the breakeven cost of strategy Pyr.-Liq.-. The white dot corresponds to the projected 2030 profit margin and energy requirement of converting lignin to adipic acid.⁵⁸

with such power plants, in the remainder of the paper we assume that biorefineries are built to produce bioenergy (as liquid fuels, electricity, hydrogen, *etc.*), and therefore may not purchase energy. Instead, biorefineries may combust a portion of the biomass feedstock to generate additional heat or electricity to meet carbon capture energy demands at the cost of fuel yield, if such a decision is optimal.

3.2.1 Economic analysis. We examine how sequestration credits and capacity determine the economically optimal strategy. As mentioned in the Methods section, different bioenergies are associated with different engine efficiencies, so we minimize the breakeven cost per unit energy of forward motion (\$ per GJ forward motion). The results are shown in Fig. 8.

When costs are normalized to forward motion, gasification to either electricity or hydrogen is always optimal due to the higher efficiencies of electric motor and H_2 fuel cells. At higher sequestration credits, such that carbon capture is incentivized, strategies producing electricity or hydrogen have the additional advantage of being able to capture nearly all the carbon in the feedstock, while the carbon captured in liquid fuels strategies is limited because a significant fraction of the inlet carbon ends up in the fuel. For electricity production, even though integrated gasification and combustion has higher capital costs than direct combustion, its higher electricity yield makes it preferable.

At low credits and capacities, Gas.-H2.- is the optimal strategy. As the capacity increases, the higher capital costs of gasification to electricity become less significant and the higher production of energy compared to gasification to hydrogen (6.3 vs. 5.3 GJ forward motion per Mg feedstock) makes strategy Gas.-Elec.- optimal. As the sequestration credit increases, capture from syngas is incentivized for gasification to both

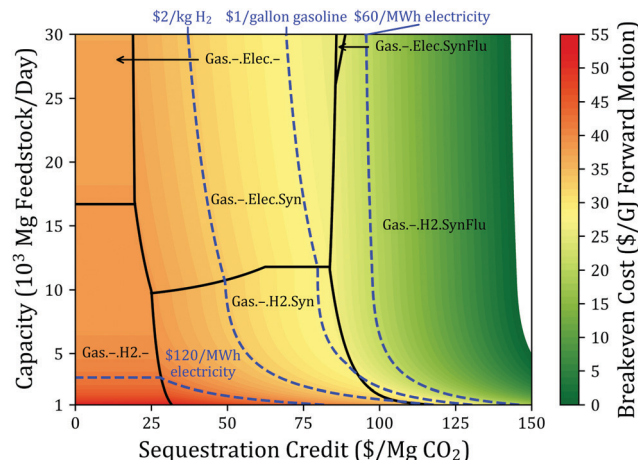


Fig. 8 Effect of sequestration credit and biorefinery capacity on break-even fuel cost. Black lines indicate transition to a new strategy. Blue dashed lines indicate contour lines for different example fuel prices.

electricity and hydrogen, as both strategies include a high-purity CO_2 stream. However, the two strategies have different CO_2 concentrations in the flue gas they generate (29% for gasification to hydrogen, 19% for gasification to electricity). The higher concentration of CO_2 in flue gas for gasification to hydrogen means that less energy is required, reducing the cost of capture, and making strategy Gas.-H2.SynFlu optimal once flue capture is incentivized.

3.2.2 Current and future GHG mitigation. To examine future GHG mitigation, direct and indirect emissions and sequestration/mitigation must be considered. Direct emissions are assumed to be constant over the 30 year period. However, mitigated emissions (*e.g.*, from the replacement of grid electricity), change over time as the production mix of electricity changes. Therefore, estimates of the future production mix of electricity and hydrogen are needed. We consider two scenarios: one base case scenario based on current policies⁵³ and one based on reaching net-zero GHG emissions by 2050 with high rates of electrification.⁵⁴ The corresponding production mixes and GHG emissions of electricity and hydrogen are given in Tables S6.1 and S6.2 in the ESI.†

We present here the GHG mitigation of the biorefinery strategies that were found to be economically optimal in the previous section: gasification to hydrogen or electricity. The expected mitigation over time of strategies producing liquid fuels can be found in the Fig. S10.1–S10.3 in the ESI.† The balance of direct and indirect GHG emissions and mitigation using electricity and hydrogen production mixes estimated by the U.S. Energy Information Administration's 2020 Annual Energy Outlook are shown in Fig. 9A. In 2020–2045, gasification to electricity is expected to result in greater GHG mitigation than gasification to hydrogen with the same amount of carbon capture. This is because the electricity produced displaces grid electricity, which has higher average GHG emissions per unit energy than hydrogen. Over time, electricity is projected to be produced by an increasing percentage of renewable sources which means that the electricity GHG emissions, and therefore mitigated emissions for displacing grid electricity, decrease



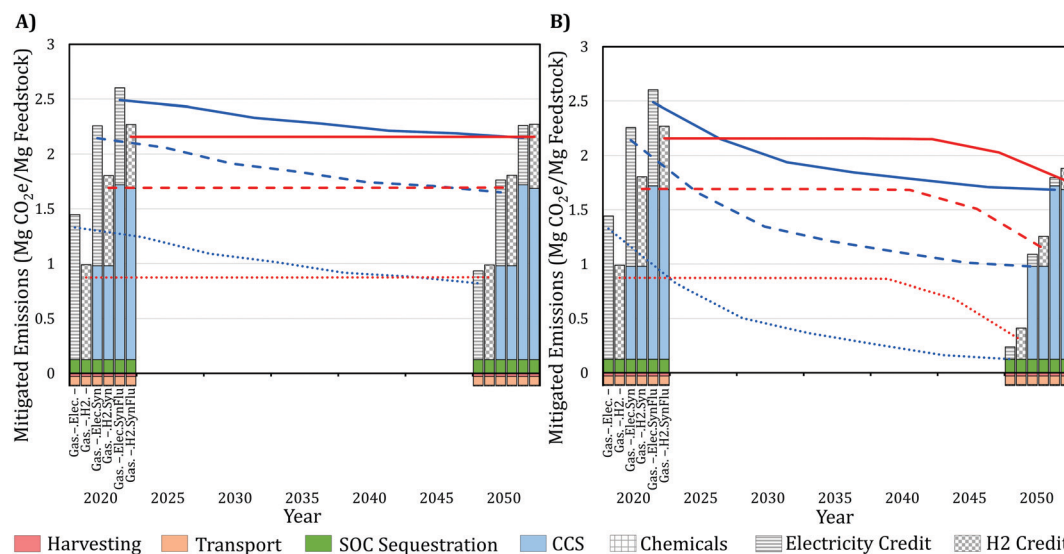


Fig. 9 GHG mitigation of a 2000 Mg feedstock per day biorefinery using gasification to hydrogen or electricity through 2050 based on (A) the U.S. Energy Information Administration's 2020 Annual Energy Outlook and (B) the Net Zero America project's 'E+' scenario of high electrification.

over time. On the other hand, hydrogen is projected to be produced primarily by steam methane reforming, and the small fraction of hydrogen produced *via* hydrolysis uses grid electricity, so the GHG emissions of hydrogen production are expected to remain relatively constant over time.⁵³ Thus, in the year 2050, gasification to hydrogen is expected to result in greater GHG mitigation than gasification to electricity. Over 30 years, we expect gasification to electricity to result in greater GHG mitigation than gasification to hydrogen for any level of carbon capture (160 kgCO₂e more mitigation per Mg feedstock for no capture, 170 kgCO₂e more for syngas capture, and 140 kgCO₂e more for syngas and flue capture).

Fig. 9B shows the GHG mitigation balance for the high electrification scenario. Solar and wind are projected to become the primary sources of electricity (55% of electricity produced by wind and 31% by solar in 2050), which quickly reduces the GHG emissions of grid electricity. Therefore, producing electricity from biomass gasification and combustion has lower GHG mitigation in the high electrification scenario relative to the base case scenario in Fig. 9A. Even with high electrification, hydrogen production by electrolysis is not projected to occur in significant quantities until 2040. Together, lower emissions from grid electricity and still high emissions from hydrogen mean that in the high electrification scenario, gasification to hydrogen is expected to result in much greater GHG mitigation than gasification to electricity (300 kgCO₂e more mitigation per Mg feedstock for no capture, 280 kgCO₂e more for syngas capture, and 180 kgCO₂e more for syngas and flue gas capture).

4 Conclusions

We studied the economics and GHG mitigation potential of various BECCS strategies using system-wide models. We performed sensitivity analyses by solving thousands of optimization problems with

varying parameter values. For strategies that produce liquid fuels, we found that fermentation to ethanol is optimal for lower-capacity pioneer plants, while pyrolysis to gasoline/diesel with hydrogen purchase is the cost-optimal strategy at low sequestration credits for nth plants. The optimal strategy changes as the sequestration credit and capacity increase, with gasification to gasoline/diesel being favored at high sequestration credits for both pioneer and nth plants. When all bioenergies are considered, gasification to either hydrogen or electricity is always the cost-optimal strategy when costs are normalized to forward vehicle motion, and also have higher GHG mitigation potential than liquid fuel production because there is no carbon in the fuel produced. With the current mix of electricity and hydrogen, gasification to electricity with carbon capture from both syngas and flue gas results in the greatest GHG mitigation, but in the future that will likely change. Gasification to hydrogen is expected to have the highest GHG mitigation of all strategies by 2040 in the base case scenario, and the highest GHG mitigation by 2025 in the high electrification scenario.

Author contributions

Caleb H. Geissler: Conceptualization, data curation, formal analysis, investigation, methodology, resources, software, validation, visualization, writing – original draft, writing – review & editing. Christos T. Maravelias: conceptualization, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, validation, writing – review & editing.

Nomenclature

BECCS	Bioenergy with carbon capture and sequestration
CCS	Carbon capture and sequestration
CDR	Carbon dioxide removal
CO ₂ e	Carbon dioxide equivalent



DA	Dilute acid
GGE	Gallon gasoline equivalent
GHG	Greenhouse gas
MEA	Monoethanolamine
MFSP	Minimum fuel selling price
MINLP	Mixed-integer nonlinear programming
NPV	Net present value
NREL	National Renewable Energy Laboratory
PSA	Pressure swing adsorption
SOC	Soil organic carbon

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This material is based upon work supported by the Great Lakes Bioenergy Research Center, U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under Award Number DE-SC0018409.

References

- Intergovernmental Panel on Climate Change, Global Warming of 1.5 °C, 2018.
- M. Fajardy and N. Mac Dowell, *Energy Environ. Sci.*, 2017, **10**, 1389–1426.
- F. K. Kazi, J. A. Fortman, R. P. Anex, D. D. Hsu, A. Aden, A. Dutta and G. Kothandaraman, *Fuel*, 2010, **89**, S20–S28.
- H. J. Huang, S. Ramaswamy, W. Al-Dajani, U. Tschirner and R. A. Cairncross, *Biomass Bioenergy*, 2009, **33**, 234–246.
- G. R. Sanford, L. G. Oates, P. Jasrotia, K. D. Thelen, G. P. Robertson and R. D. Jackson, *Agric., Ecosyst. Environ.*, 2016, **216**, 344–355.
- I. Gelfand, R. Sahajpal, X. Zhang, R. C. Izaurralde, K. L. Gross and G. P. Robertson, *Nature*, 2013, **493**, 514–517.
- M. Fajardy, S. Chiquier and N. Mac Dowell, *Energy Environ. Sci.*, 2018, **11**, 3408–3430.
- D. Humbird, R. Davis, L. Tao, C. Kinchin, D. D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton and D. Dudgeon, Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: Dilute-acid pretreatment and enzymatic hydrolysis of corn stover, NREL/TP-5100-47764, 2011, DOI: [10.2172/1013269](https://doi.org/10.2172/1013269).
- A. Laude, O. Ricci, G. Bureau, J. Royer-Adnot and A. Fabbri, *Int. J. Greenh. Gas Control*, 2011, **5**, 1220–1231.
- S. Kim, B. E. Dale, M. Jin, K. D. Thelen, X. Zhang, P. Meier, A. D. Reddy, C. D. Jones, R. C. Izaurralde, V. Balan, T. M. Runge and M. A. Sharara, *GCB Bioenergy*, 2019, **11**, 871–882.
- H. B. Carminati, R. F.-D. de Milão, J. L. de Medeiros and O. Q.-F. de Araújo, *Appl. Energy*, 2019, **254**, 113633.
- S. Bello, Á. Galán-Martín, G. Feijoo, M. T. Moreira and G. Guillén-Gosálbez, *Appl. Energy*, 2020, DOI: [10.1016/j.apenergy.2020.115884](https://doi.org/10.1016/j.apenergy.2020.115884).
- S. Kim, X. Zhang, A. D. Reddy, B. E. Dale, K. D. Thelen, C. D. Jones, R. C. Izaurralde, T. M. Runge and C. T. Maravelias, *Environ. Sci. Technol.*, 2020, 10797–10807, DOI: [10.1021/acs.est.0c01097](https://doi.org/10.1021/acs.est.0c01097).
- M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard and D. D. Hsu, Techno-economic analysis of biomass fast pyrolysis to transportation fuels, NREL/TP-6A20-46586, 2010.
- M. B. Shemfe, S. Gu and P. Ranganathan, *Fuel*, 2015, **143**, 361–372.
- A. Dutta, A. H. Sahir, E. C. Tan, D. Humbird, L. J. Snowden-Swan, P. Meyer, J. Ross, D. Sexton, R. Yap and J. Lukas, Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: Thermochemical research pathways with *in situ* and *ex situ* upgrading of fast pyrolysis vapors, NREL/TP-5100-62455, 2015.
- R. M. Swanson, J. A. Satrio, R. C. Brown, A. Platon and D. D. Hsu, Techno-economic analysis of biofuels production based on gasification, NREL/TP-6A20-46587, 2010.
- E. C. Tan, M. Talmadge, A. Dutta, J. Hensley, J. Schaidle, M. Bidy, D. Humbird, L. J. Snowden-Swan, J. Ross, D. Sexton, R. Yap and J. Lukas, Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons via indirect liquefaction: Thermochemical research pathway to high-octane gasoline blendstock through methanol/dimethyl ether intermediates, NREL/TP-5100-62402, 2015.
- M. Muresan, C. C. Cormos and P. S. Agachi, *Chem. Eng. Res. Des.*, 2013, **91**, 1527–1541.
- T. Detchusanand, K. Im-orb, P. Ponpesh and A. Arpornwichanop, *Energy Convers. Manage.*, 2018, **171**, 1560–1572.
- N. Sunny, N. Mac Dowell and N. Shah, *Energy Environ. Sci.*, 2020, **13**, 4204–4224.
- T. Morató, M. Vaezi and A. Kumar, *Renewable Sustainable Energy Rev.*, 2020, **134**, 110154.
- E. D. Larson, H. Jin and F. E. Celik, *Biofuels, Bioprod. Biorefining*, 2009, 174–194.
- M. Li, A. D. Rao and G. Scott Samuelsen, *Appl. Energy*, 2012, **91**, 43–50.
- G. Zang, J. Jia, S. Tejasvi, A. Ratner and E. Silva Lora, *Int. J. Greenh. Gas Control*, 2018, **78**, 73–84.
- R. P. Anex, A. Aden, F. K. Kazi, J. A. Fortman, R. M. Swanson, M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard, A. Platon, G. Kothandaraman, D. D. Hsu and A. Dutta, *Fuel*, 2010, **89**, S29–S35.
- C. A. Cardona and C. A. García-vel, *Energy*, 2019, **172**, 232–242.
- M. Muratori, H. Khesghi, B. Mignone, L. Clarke, H. McJeon and J. Edmonds, *Int. J. Greenh. Gas Control*, 2017, **57**, 34–41.
- L. Yan, L. Wang, Z. Wang, Y. Cao and B. He, *J. Cleaner Prod.*, 2021, **285**, 125424.
- D. L. Sanchez and D. S. Callaway, *Appl. Energy*, 2016, **170**, 437–444.
- R. T.-L. Ng and C. T. Maravelias, *Appl. Energy*, 2017, **205**, 1571–1582.
- C. H. Geissler and C. T. Maravelias, *Appl. Energy*, 2021, **302**, 117539.



- 33 M. Wright and R. C. Brown, *Biofuels, Bioprod. Biorefining*, 2007, **1**, 191–200.
- 34 J. Leboireiro and A. K. Hilaly, *Biomass Bioenergy*, 2013, **54**, 158–169.
- 35 I. Gelfand, S. K. Hamilton, A. N. Kravchenko, R. D. Jackson, K. D. Thelen and G. P. Robertson, *Environ. Sci. Technol.*, 2020, **54**, 2961–2974.
- 36 P. L. Eranki, B. D. Bals and B. E. Dale, *Biofuels, Bioprod. Biorefining*, 2011, **5**, 621–630.
- 37 P. Lamers, M. S. Roni, J. S. Tumuluru, J. J. Jacobson, K. G. Cafferty, J. K. Hansen, K. Kenney, F. Teymouri and B. Bals, *Bioresour. Technol.*, 2015, **194**, 205–213.
- 38 L. Chai and C. M. Saffron, *Appl. Energy*, 2016, **163**, 387–395.
- 39 R. T.-L. Ng, P. Fasahati, K. Huang and C. T. Maravelias, *Appl. Energy*, 2019, **241**, 491–503.
- 40 A. Dutta, C. Mukarakate, K. Iisa, H. Wang, M. Talmadge, D. Santosa, K. Harris, F. Baddour, D. Hartley, H. Cai, L. Ou, J. Schaidle and M. Griffin, Ex situ catalytic fast pyrolysis of lignocellulosic biomass to hydrocarbon fuels: 2020 state of technology, NREL/TP-5100-80291, 2021.
- 41 A. Tisserant and F. Cherubini, *Land*, 2019, **8**, 179.
- 42 P. Spath, A. Aden, T. Eggeman, M. Ringer, B. Wallace and J. Jechura, Biomass to hydrogen production detailed design and economics utilizing the Battelle Columbus Laboratory indirectly-heated gasifier, NREL/TP-510-37408, 2005.
- 43 A. Kiani, K. Jiang and P. Feron, *Front. Energy Res.*, 2020, **8**, 1–13.
- 44 J. Kim, T. A. Johnson, J. E. Miller, E. B. Stechel and C. T. Maravelias, *Energy Environ. Sci.*, 2012, **5**, 8417–8429.
- 45 T. Dreher, C. Dugan, T. Harkin and B. Hooper, *Energy Procedia*, 2011, **4**, 5549–5556.
- 46 H. Zhai and E. S. Rubin, *Environ. Sci. Technol.*, 2013, **47**, 3006–3014.
- 47 R. F. Zheng, D. Barpaga, P. M. Mathias, D. Malhotra, P. K. Koech, Y. Jiang, M. Bhakta, M. Lail, A. Rayer, G. A. Whyatt, C. J. Freeman, A. J. Zwoster, K. K. Weitz and D. J. Heldebrant, *Energy Environ. Sci.*, 2020, **13**, 4106–4113.
- 48 D. L. Sanchez, N. Johnson, S. T. McCoy, P. A. Turner and K. J. Mach, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 4875–4880.
- 49 E. Tvinnereim and M. Mehling, *Energy Policy*, 2018, **121**, 185–189.
- 50 S. A. Haji Esmaeili, A. Sobhani, J. Szmerekovsky, A. Dybing and G. Pourhashem, *Appl. Energy*, 2020, **277**, 115606.
- 51 Internal Revenue Service, Section 45Q, [https://uscode.house.gov/view.xhtml?req=\(title:26section:45Qedition:prelim\)](https://uscode.house.gov/view.xhtml?req=(title:26section:45Qedition:prelim)).
- 52 NREL (National Renewable Energy Laboratory), U.S. life cycle inventory database, <https://www.nrel.gov/lci/>.
- 53 U.S. Energy Information Administration, Annual Energy Outlook 2020, 2020.
- 54 E. D. Larson, C. Greig, J. Jenkins, E. Mayfield, A. Pascale, C. Zhang, J. Drossman, R. Williams, S. Pacala, R. Socolow, E. Baik, R. Birdsey, R. Duke, R. Jones, B. Haley, E. Leslie, K. Paustian and A. Swan, *Net-Zero America: Potential Pathways, Infrastructure, and Impacts Interim Report*, Princeton, NJ, 2020.
- 55 E. W. Merrow, K. E. Phillips and C. W. Myers, *Understanding Cost Growth and Performance Shortfalls in Pioneer Process Plants*, Rand Corporation, 1981.
- 56 M. Tawarmalani and N. V. Sahinidis, *Math. Program.*, 2005, **103**, 225–249.
- 57 K. Huang, P. Fasahati and C. T. Maravelias, *iScience*, 2020, **23**, 100751.
- 58 R. Davis, A. Bartling and L. Tao, Biochemical conversion of lignocellulosic biomass to hydrocarbon fuels and products: 2020 state of technology and future research, NREL/TP-5100-79930, 2021.

