Carbon-Negative Biofuel Production

Seungdo Kim*[1,2], Xuesong Zhang[3,4], Ashwan Daram Reddy[5], Bruce E. Dale[1,2], Kurt D. Thelen[1,6], Curtis Dinneen Jones[5], Roberto Cesar Izaurralde[5,7], Troy Runge[8], Christos Maravelias[8,9]

[1]Great Lakes Bioenergy Research Center, Michigan State University, 164 Food Safety and Toxicology Building, East Lansing, MI 48824,

[2]Chemical Engineering and Materials Science, Michigan State University, 3815 Technology Boulevard, Lansing, MI 48910,

[3]Joint Global Change Research Institute, Pacific Northwest National Laboratory, 5825 University Research Court, Suite 3500, College Park, MD 20740,

[4]Earth System Sciences Interdisciplinary Center, 5825 University Research Court, Suite 4001 College Park, MD 20740, USA

[5]Department of Geographical Sciences, University of Maryland, 2181 Samuel J. LeFrak Hall, 7251 Preinkert Drive, College Park, MD 20742,

[6]Department of Plant, Soil and Microbial Sciences, Michigan State University, 1066 Bogue Street, East Lansing, MI 48824,

[7]Texas AgriLife Research and Extension, Texas A&M University, Temple, TX 76502,

[8]Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, 1552 University Avenue, Madison, WI 53726

[9]Department of Chemical and Biological Engineering, University of Wisconsin - Madison, 1415 Engineering Dr., Madison, WI 53706

*** Correspondence to:** kimseun@egr.msu.edu

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Abstract

Achieving the 1.5°C limit for global temperature increase relies on large-scale deployment of carbon dioxide removal (CDR) technologies. In this article, we explore two CDR technologies: soil carbon sequestration (SCS), and carbon capture and storage (CCS) integrated with cellulosic biofuel production. These CDR technologies are applied as part of decentralized biorefinery systems processing corn stover and unfertilized switchgrass grown in riparian zones in the Midwestern United States. Cover crops grown on corn-producing lands are the SCS approach chosen, and biogenic CO_2 in biorefineries is captured, transported by pipeline and injected into saline aquifers. The decentralized biorefinery system using SCS, CCS or both can produce carbon-negative cellulosic biofuels ($\leq$ -22.2 gCO_2 MJ^{-1}). Meanwhile, biofuel selling prices increase by 15-45% due to CDR costs. Economic incentives (e.g., cover crop incentives and/or a CO_2 tax credit) can mitigate price increases caused by CDR technologies. Combining different CDR technologies in decentralized biorefinery systems is the most efficient method for greenhouse gas (GHG) mitigation, and its total GHG mitigation potential in the Midwest is 0.16 $GtCO_2$ $year^{-1}$.

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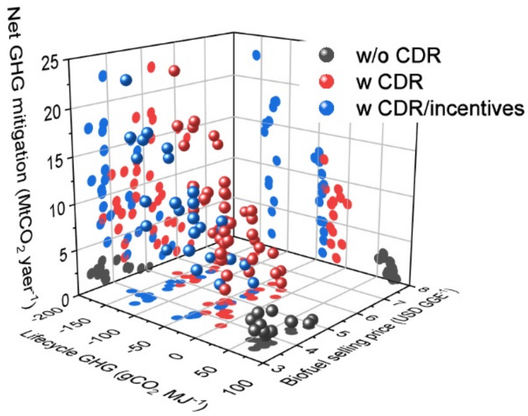

Introduction

Biofuels derived from cellulosic feedstocks (e.g., corn stover, switchgrass, miscanthus, poplar, energy sorghum, wood residues, etc.) are alternative liquid fuels that displace petroleum transportation fuels. The lifecycle greenhouse gas (GHG) emissions of cellulosic biofuels are generally less than those of petroleum fuels; hence cellulosic biofuels can reduce GHG emissions by displacing petroleum fuels[1-4]. The GHG avoidance potentials by biofuels derived from corn stover in the United States Midwest are about 2-16 $MtCO_2$ $year^{-1}$ [4].

The IPCC Special Report on Global Warming of 1.5°C[5] estimated a remaining carbon budget of 420 (65th percentile of transient climate response to cumulative emissions of carbon)-580 (50th percentile) $GtCO_2$, excluding additional Earth system feedbacks such as permafrost thawing, to limit global temperature increase below 1.5°C. CO_2 emissions from FFI (fossil-fuel combustion and industry processes) and AFOLU (agriculture, forestry and other land use) are expected to be 650-1270 $GtCO_2$ for the period 2018-2100 (5th-95th percentile range; median: 950 $GtCO_2$)[5]. Thus CO_2 emissions exceeding the remaining carbon budget must be removed from the atmosphere via carbon dioxide removal (CDR) technologies to achieve the 1.5°C target[5-9]. CDR technologies include afforestation and reforestation (AR), soil carbon sequestration (SCS), ocean fertilization (OF), biochar (BC), enhanced weathering of minerals (EW), bioenergy combined with carbon capture and storage (BECCS), and direct air capture and storage (DACCS)[5-8, 10]. Particularly, BECCS and AFOLU-related CDR (e.g., AR and SCS) can play a major role in achieving the 1.5°C target[5]. Annual sequestration rate of BECCS amounts to 0-1, 0-8, and 0-16 $GtCO_2$ $year^{-1}$ in 2030, 2050, and 2100, respectively, while the annual sequestration rate of AFOLU-related CDR is 0-5, 1-11, and 1-5 $GtCO_2$ $year^{-1}$ in 2030, 2050, and 2100, respectively[5].

The cost of CO_2 capture from ethanol fermentation in ethanol plants ranges from 20 to 175 USD tCO_2^{-1} [7].

Since avoided GHG emissions by cellulosic biofuels do not remove CO_2 directly from the atmosphere, CDR technologies (e.g., SCS, and carbon capture and storage (CCS)) must be integrated with biofuel production to achieve the 1.5°C target. Here, we explore CDR technologies within a cellulosic biofuel production system, with a particular focus on SCS and CCS technologies, in order to quantify the effects of CDR technologies on biofuel selling price, the lifecycle GHG emissions of biofuel, and the total GHG mitigation. The total GHG mitigation is defined as the sum of GHG avoidance (avoided GHG emissions by displacing petroleum fuel and grid electricity by biofuel production) and net CO_2 removal (net GHG removed from the atmosphere by biofuels). The biorefinery system under investigation is the decentralized depot-based biorefinery (DDB) system, in which very large biorefineries are located adjacent to coal-fired power plants in large urban areas to take advantage of existing transportation systems. It is assumed that biorefineries operate independently of adjacent coal-fired power plants. Therefore, there is no exchange of material and energy between biorefineries and adjacent coal-fired power plants. Demand for transportation fuel in large urban areas adjacent to DDBs can reduce the cost of transportation and distribution of biofuels. Depot facilities that pretreat and pelletize cellulosic biomass are located at existing grain elevators and supply pretreated pellets to decentralized biorefineries[11-13]. Feedstock supply chains for the individual biorefineries are determined by minimizing their biofuel selling prices.

Cellulosic feedstock in the DDB system is corn stover and unfertilized switchgrass grown in riparian buffer zones in the Midwestern United States. We assumed that biorefineries and depot facilities are able to process corn stover and switchgrass together. Switchgrass has long been used in riparian buffers[14-16]. Riparian buffers are strips of grasses, shrubs or trees grown along rivers, streams, lakes and wetlands, and provide the following ecosystem services: slowing and absorbing flood water, trapping and redistributing sediments, cycling nutrients, filtering chemical pollutants, maintaining fish and wildlife habitats, and supporting the food web for biota[17]. The potential of switchgrass grown in riparian areas as feedstock for biofuel production has been studied[15, 18, 19]. Ha and Wu[15] show that the conversion of low-productivity land in watershed land areas to switchgrass production for biofuel can effectively improve water quality by reducing suspended sediment and nutrient run-off.

Winter rye grown as a cover crop within a corn-soybean rotation is used as a CDR technology (SCS). Planting cover crops can sequester carbon as soil organic carbon (SOC) at a rate of about 0.32±0.88 MgC ha^{-1} $year^{-1}$ and can limit soil organic carbon (SOC) losses caused by corn stover removal[3, 20-24]. Other benefits of cover crops include nutrient replenishment, attenuation of soil compaction, reduction of soil erosion and so forth. However, cover crop costs range from 82 USD ha^{-1} to 173 USD ha^{-1}, depending on seeding rate and seed cost[24]. Singer et al.[25] showed that about 56% of farmers participating in the survey would plant cover crops if a cost-sharing incentive was available.

CCS technology has been practiced in ethanol plants in the United States to capture CO_2 from fermentation. The CO_2 captured in ethanol plants in Kansas (Arkalon and Bonanza) has been used for enhanced oil recovery (EOR), and their capture capacities are 0.30 and 0.16 $MtCO_2$ $year^{-1}$, respectively[26]. In contrast to these EOR applications, within the Illinois Basin-Decatur Project (IBDP) the ADM corn ethanol plant captured about one million metric tons of CO_2 from fermentation during 2011 to 2014 and injected it into a deep saline reservoir in the Mt. Simon Sandstone Formation in the Illinois Basin (https://www.netl.doe.gov/node/5914). The total CO_2

capture cost in the IBDP is 31.76 USD tCO_2^{-1} [27]. Based on experiences from the IBDP, an industrial-scale demonstration project (Illinois Industrial Carbon Capture and Storage Project) has begun to capture about a million tons of carbon dioxide (CO_2) per year from a corn-based ethanol plant (https://netl.doe.gov/node/2254). Sanchez et al.[28] estimated that about 27 $GtCO_2$ $year^{-1}$ arising from fermentation in 216 existing biorefineries in the United States could be captured and compressed for under 25 USD tCO_2^{-1}. The projected CO_2 capture cost in cellulosic biorefineries is 32-70 USD tCO_2^{-1} [29], estimated from the CO_2 capture cost in other systems (e.g., coal-fired power plant, etc.).

Unlike most previous studies on biofuels with CCS[29, 30, 31], in which only high-purity CO_2 streams from fermentation are captured, in this analysis CO_2 streams in flue gas from the boiler in the cogeneration facility and CO_2 streams from fermentation are captured. Carbon in flue gas from the boiler in the cogeneration facility accounts for 53 mol% of the total carbon output in the cellulosic biorefinery (including biofuel), equivalent to about 77-78% of the total CO_2 captured in these decentralized depot-based biorefineries (see SI Figure S1). Low purity CO_2 in flue gas must be captured by absorbents, then released as a purified gas and compressed, while CO_2 from fermentation is simply dehydrated and compressed.

Six biorefinery system scenarios using different CDR technologies and economic incentives are investigated in this study (see Table 1). The economic incentives studied are cover crop incentive payments such as the Environmental Quality Incentives Program (EQIP) in the United States and a tax credit for CO_2 sequestration. The EQIP provides an incentive of 68 USD ha^{-1} for planting grasses or cereal grains as cover crops in 2013 (https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/stelprdb1082778.pdf). The United States also offers a tax credit for carbon dioxide sequestration of 50 USD per metric ton of CO_2

captured and permanently stored, and 35 USD per metric ton of CO_2 captured and used in enhanced oil recovery or natural gas development operations in the year 2026 (https://uscode.house.gov/view.xhtml?req=(title:26%20section:45Q%20edition:prelim)). This CO_2 tax credit (45Q) is only available for the first 12 years of operation. To qualify for the CO_2 tax credit, the facility must begin construction by January 1, 2024. Neither CDR technologies nor economic incentives are integrated with biofuel production in the reference scenario (denoted by "A"). Feedstock supply chains for the individual biorefineries in the reference scenario are first determined to calculate minimum biofuel selling price (MBSP), lifecycle GHG emissions, and total GHG mitigation. The feedstock supply chains in other scenarios follow the same supply chains determined in the reference scenario to estimate the effects of CDR technologies.

Table 1 Biorefinery system scenarios in the decentralized depot-based biorefinery system. (CCS: carbon capture and storage; N/A: not applicable)

Scenario	Cover crop	CCS	Incentive for cover crop	Carbon tax credit
A	No	No	N/A	N/A
A1	No	Yes	N/A	No
A2	No	Yes	N/A	Yes
B	Yes	No	No	N/A
B1	Yes	Yes	No	No
B2	Yes	Yes	Yes	Yes

Materials and methods

Cellulosic feedstock production

Corn stover is collected within corn-soybean rotations under historical tillage management practices. The Environmental Policy Integrated Climate (EPIC) model is used to estimate the county-level grain yield, SOC changes in a corn-soybean rotation, and the quantity of corn stover removed per hectare[2, 32]. The county-level information is aggregated from the pixel-level results (56×56 m) using a 50-year time horizon. The removal rate of corn stover is 66% (a practical maximum) in all scenarios. No other stover removal rates are considered in the analysis. The effects of different stover removal rates on GHG emissions associated with SOC losses per Mg of dry corn stover are probably insignificant[33]. Negative environmental effects of using a high corn stover removal rate in the analysis would be significantly mitigated by planting cover crops.

For winter rye (as a cover crop) simulation, we add winter rye planting and killing operations into the existing corn-soybean cropping systems in the Midwest. The planting and killing dates were designed following the scenario used by Feyereisen et al.[34]. The planting date for winter rye is 2 days after corn or soybean harvesting, while the killing date is set as 7 days before corn or soybean planting for the next year. Fertilizer is not applied during winter rye growing season. When no corn residue is removed, EPIC simulates an average yield of 2.12 dry Mg ha^{-1} $year^{-1}$ of winter rye over the entire Midwest, and the simulated county-level winter rye yields range between 1.2 and 6.1 dry Mg ha^{-1} $year^{-1}$. The range of rye yields compares favorably with the estimated range of county-level winter rye yields by Feyereisen et al.[34], which vary from less than 2 dry Mg ha^{-1} $year^{-1}$ in the northern states to ca. 6 dry Mg ha^{-1} $year^{-1}$ in the more southern states of the Midwest. The EPIC simulations show that corn stover collection with planting cover crops can increase SOC level by 0.17±0.17 MgC ha^{-1} $year^{-1}$, while corn stover collection without planting cover crops can reduce SOC by 0.26±0.25 MgC ha^{-1} $year^{-1}$.

The EPIC model is also used to simulate switchgrass production across the 12-state Midwest for a 60-year period from 1991 through 2050. A 10-year spin-up period modeled as grassland precedes the planting of switchgrass in the year 2001. Unfertilized simulations are performed with the aboveground biomass harvested each November. Fertilized (56 kg N $ha^{-1}year^{-1}$)

simulations are also performed for validation purposes. The growing season is governed by location-specific heat unit values, which are adjusted based on switchgrass maturity estimates from Behrman et al.[35] and historical climate data. Additional steps are taken to summarize EPIC results for 150-foot (45.7 meters) wide riparian zones surrounding streams and rivers in the Midwest, a maximum riparian buffer width to reduce runoff into streams, among other environmental benefits[36]. The riparian zones are defined using stream and river features from the National Hydrography Dataset (https://www.usgs.gov/core-science-systems/ngp/national-hydrography/national-hydrography-dataset?qt-science_support_page_related_con=0#qt-science_support_page_related_con). Croplands, forest and urban areas are excluded in the riparian zones for switchgrass production. EPIC site results were clipped to areas within 150-feet of this stream dataset and summarized for each county. Although some riparian areas may not be suitable for biofuel production due to accessibility and economic feasibility, we assume that all the riparian areas are available to biofuel production to estimate the maximum biofuel production potential in the Midwest. County-level fertilized switchgrass yields simulated by the EPIC model are adequately predicted compared to yields estimated in the 2016 U.S. Billion-Ton Report[37]: R^2=0.69 (see SI Figure S2). Fertilized switchgrass yield is on average 24% higher than unfertilized switchgrass yield, similar to results from field experiments[38, 39]. Overall, fertilized switchgrass cultivation in the riparian buffer zones reduces the SOC by about 5% of the initial SOC, similar to the overall change estimated by Qin et al.[40].

Decentralized depot-based biorefinery (DDB) system

Corn stover and unfertilized switchgrass are baled in the biomass production areas and transported by truck to depot facilities, where baled cellulosic biomass is pretreated via the ammonia fiber expansion (AFEX™) technology[41], and then pelletized[42]. The pretreated corn stover and switchgrass pellets are transported by either truck or railroad to DDB. Depot facilities are assumed to be located at existing grain elevators[11-13]. It is assumed that 100% of farmers within the collection radius supply baled cellulosic feedstock to a depot facility owned by farmers. Sensitivity analyses are performed to quantify the effects of farmer participation rate and riparian area availability on the system. Over 1600 depot facilities (at grain elevators) are potentially available to participate in DDBs, and could process 107 Tg of dry cellulosic feedstock per year in the Midwest. The mass fraction of corn stover in the cellulosic feedstock processed in depot facilities is about 0.9. An average depot size is 185±31 dry Mg day^{-1}, and an average collection radius is about 13±2.2 km. The depot sizes and the collection radii depend on cellulosic biomass density (dry Mg $(km^2)^{-1}$). It is assumed that cellulosic biomass is evenly distributed within a county.

Fifteen coal-fired power plants in the Midwest are selected as candidate DDB sites based on the total population within an 80-km radius of the coal-fired power plant (see SI Table S1). Kim and Dale[11] modified the Aspen Plus model developed by the National Renewable Energy Laboratory (NREL)[43] for DDB. This modified Aspen Plus model is used to estimate mass and energy balances in this analysis. Ethanol yield in the biorefinery depends on the feedstock composition. Corn stover composition is available in the Aspen Plus model developed by NREL[43], while switchgrass composition is estimated based on values from literature[44-49]. Ethanol yield is 56.2 gasoline gallon equivalent (GGE) dry Mg^{-1} (213 gasoline liter equivalent (GLE) dry Mg^{-1}) for pretreated corn stover pellets and 55.0 GGE dry Mg^{-1} for pretreated switchgrass pellets. For a 50/50 mixture of pre-processed corn stover and switchgrass pellets, the ethanol yield is 55.6 GGE dry Mg^{-1}. In contrast to ethanol yield, excess electricity is 5.4 kWh GGE^{-1} (1.4 kWh GLE^{-1}) in the DDB processing pretreated corn stover pellets and 5.9 kWh GGE^{-1} in the DDB processing pretreated switchgrass pellets when a CO_2 capture facility is not integrated. The high lignin content in pretreated switchgrass pellets slightly reduces ethanol yield, but also increases excess electricity production.

The CO_2 capture facility in the biorefinery is comprised of the following units: CO_2 absorber, CO_2 stripper, absorbent purification, triethylene glycol (TEG) dehydration, and compressor[50]. The CO_2 capture process consumes about 2.5 MJ of steam per kg of CO_2 captured and 0.15 kWh of electricity per kg of CO_2 captured[50]. The energy consumed by the CO_2 capture facility changes the energy generation system in biorefineries. The thermal energy generated by burning solid residue and biogas in the DDB is assumed to provide sufficient thermal energy to the carbon dioxide capture facility as well as the biorefinery process. However, producing more thermal energy in the biorefinery reduces the amount of electricity generated by the cogeneration facility, which then is not sufficient to operate both the biorefinery process and the CO_2 capture facility. Therefore, grid electricity is used to operate some units in the CO_2 capture facility. As a result, there is no excess electricity, that is, no electricity is exported to the grid in biorefineries with the CO_2 capture facility.

CO_2 is emitted in the following portions of the decentralized depot-based biorefinery: enzyme production, fermentation/recovery, cogeneration, and wastewater treatment (see SI Figure S1). The fraction of carbon dioxide in the stream from fermentation/recovery is about 97 wt%. Carbon dioxide in this stream is dehydrated and compressed, but no CO_2 absorber and associated units are required. Unlike the stream from the fermentation/recovery facility, the less-concentrated CO_2 in the flue gas stream from the cogeneration facility is captured by CO_2 absorber and associated units, and then dehydrated and compressed. A sensitivity analysis investigates the case of capturing only high-purity CO_2 stream from fermentation/recovery in the

CO_2 capture facility. CO_2 streams from the enzyme production and the wastewater treatment facilities are not captured. In the wastewater treatment facility, CO_2 is released into the atmosphere. The stream from the enzyme production facility contains low purity CO_2 and is not an economical candidate for capture.

Economic values

The costs of corn stover collection and growing the cover crop are estimated based on field experiment data at the W.K. Kellogg Biological Station in Michigan and at the Arlington Agricultural Research Station in Wisconsin. The cost of field operations per hectare is assumed to be constant regardless of biomass yield and farm size because there is not enough information on the size of individual farms. We also make conservative assumptions about the cover crop, namely: 1) no economic incentives for growing cover crop and 2) no cover crop is grown unless corn stover is collected. Thus, when planting cover crops, the farm gate price of corn stover includes cover crop costs in the following corn and soybean season (e.g., seed, herbicides, planting, etc.) along with the corn stover collection costs. The farm gate price of switchgrass is based on field experiment data from these two stations and literature[51-53]. Land rental rates for the riparian zone are also included in the farm gate price of switchgrass and are assumed to be equal to the county-level rental rates for pasture. The 2013 county-level rental rates for pasture in the National Agricultural Statistics Service (https://www.nass.usda.gov/) are used in the analysis and range from 12.36 to 191.51 USD ha^{-1}. A mass-weighted average farm gate price of corn stover without planting cover crops is 38.74±3.98 USD dry Mg^{-1}, while a mass-weighted average farm gate price of corn stover with planting cover crops is 73.53±21.68 USD dry Mg^{-1}. A mass-weighted average farm gate price of unfertilized switchgrass is 42.67±13.92 USD dry Mg^{-1}.

The operating costs at depot facilities are estimated from the literature[11]. We assume that depot facilities sell pretreated pellets at the same price (i.e., mass-weighted average price) regardless of biomass types. The minimum biofuel selling price (MBSP) in biorefineries without CCS is estimated by a regression equation based on the modified Aspen Plus model[11]. The cost year is 2013. Truck and rail transport costs are calculated based on literature[52, 54]. Energy prices in 2013 (e.g., electricity, natural gas, etc.) are obtained from the US Energy Information Administration (https://www.eia.gov/outlooks/aeo/).

We estimate the costs of the CO_2 capture facility in the biorefinery based on National Energy Technology Laboratory (NETL) reports[50, 55] even though the NETL report focused on CO_2 capture in coal-fired boiler systems. The mass fraction of CO_2 in flue gas in the boiler in DDB (18%) is similar to that from a coal-fired boiler (20%[50]). The CO_2 capture facility costs in the biorefinery include total capital investment (e.g., CO_2 absorber, stripper, absorbent purification, dehydration, compressor, and etc.), material costs (e.g., make-up absorbent, TEG, caustic soda, and etc.), and operating costs (i.e., electricity). The labor costs of the CO_2 capture facility are not included because it is not clear whether additional personnel are required for the CO_2 capture facility. A scaling factor of 0.6 is applied to the total equipment cost (see SI Figure S4). The effects of a different scaling factor on total cost of CO_2 capture equipment and biofuel selling price are investigated in a sensitivity analysis. The method used in the NREL repot[43] is applied to calculate total capital investment, which includes total equipment cost, indirect costs (e.g., prorated expenses, field expenses, home office & construction fee, project contingency, other costs (start-up, permits, etc.), etc.), and working capital. Detailed information is presented in the Supporting Information (see SI Table S2). Pipeline transport distances are measured on a map based on natural gas pipelines (https://www.eia.gov/naturalgas/archive/analysis_publications/ngpipeline/index.html). Pipeline transport and storage costs are calculated in spreadsheet models developed by NETL[56, 57]. Storage sites are not specified in this analysis, and state weighted average storage costs are used. The storage costs ranges from 6.63 to 1008 USD tCO_2^{-1} (see SI Tables S3 and S4).

Lifecycle GHG emissions

GHG emissions associated with the biofuel production system are calculated by the life cycle approach based on one MJ of biofuel. The system boundaries in the GHG calculations include all GHG emissions from cellulosic feedstock production to biofuel combustion including cellulosic feedstock production, transportation and storage of baled feedstock, the depot facility, transportation of pretreated pellets, the decentralized depot-based biorefinery, transportation and distribution of biofuel, combustion of biofuel, relevant upstream processes, avoided grid electricity (if applicable), and pipeline transport and CO_2 injection if applicable (see SI Figure S3). Excess electricity in the biorefinery without CCS is assumed to displace the grid electricity in the state where the biorefinery is located, resulting in GHG credit from avoided grid electricity. The 2016 electricity fuel mix[58] is used to calculate the GHG emissions of materials, transportation, and energy productions. The effects of the electricity fuel mix on the lifecycle GHG emissions are investigated in a sensitivity analysis. The GHG emissions associated with material, transportation, and energy production are calculated based on unit process data from US Life cycle inventory Database (https://www.nrel.gov/lci/) and Ecoinvent version 3.4 (https://www.ecoinvent.org/database/database.html). Greenhouse gas in the analysis includes CO_2, CH_4 and N_2O, and the 100-year time horizon global warming potentials are used in the analysis.

The GHG emissions of cellulosic feedstock includes GHG emissions of fertilizers (if applicable), agrochemicals (if applicable), diesel, seed (e.g., switchgrass and winter rye), carbon released (or sequestered) from SOC changes, and N_2O emissions. Carbon stock loss due to land conversion from riparian zones to switchgrass production is also included in the GHG emissions of switchgrass. It is assumed that grasses are planted in the riparian zones before converting to switchgrass production. Due to lack of data, the state-level carbon stocks in grassland[59] are used to estimate carbon losses of aboveground biomass with a 50-year time horizon. The agronomic inputs and the fuel usage for corn stover collection, cover crop culture and switchgrass production are based on the field experiment data at the two experimental stations. Similar to the farm gate price calculations, fuel use per hectare for field operations is assumed to be constant regardless of yield and farm size. SOC changes are estimated based on the results from the EPIC simulations. N_2O emissions are estimated by the Tier 1 method in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories[60]. The system expansion allocation method is used to assign the environmental burdens to corn stover. The GHG emissions of corn stover therefore include GHG emissions of diesel used in collecting and baling corn stover, GHG emissions of the replacement nutrients required, carbon emissions from SOC changes due to corn stover removal, and changes in N_2O emissions by corn stover removal. When cover crops are planted, the GHG emissions associated with the cover crop in both corn and soybean growing years are assigned to corn stover.

The process data at the depot facility are obtained from literature[11] and the biorefinery process data are estimated based on the mass and energy balances calculated in the modified Aspen Plus model. GHG emissions of transportation and distribution of biofuel are estimated based on the Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) Model[61].

GHG emissions of biofuel combustion are obtained from literature[62]. The amount of energy and materials used in the CO_2 capture facility, pipeline transport and injection in saline aquifers is estimated based on the NETL reports[50, 56, 57, 63, 64]. The materials used in the CO_2 capture units (i.e., CO_2 absorber, stripper, absorbent purification) are ion exchange resin, caustic soda, and amine-based absorbent[50]. The NETL report[50] listed the total cost of the materials used. To estimate GHG emissions associated with these materials, the amount of make-up absorbent is assumed to be equal to the amount of make-up monoethanolamine (MEA) in the MEA system for coal-fired power plant[55]. Since the amine-based absorbent is not specified in the NETL report[50], it is assumed to be MEA. Caustic soda is used for ion exchange resin regeneration, and the amount of caustic soda is obtained from a U.S. patent[65]. Based on the quantities of MEA and caustic soda, and the prices of each material[43, 55, 66], the amount of ion exchange resin can be estimated.

Supply chain

Feedstock supply chains for the individual biorefineries in the reference scenario are determined by minimizing their biofuel selling prices under the constraint of biorefinery size (see SI). It is assumed that the size of any DDB should be greater than 3,000 dry Mg day^{-1}. A depot facility is assumed to supply pretreated pellets to one DDB. The road distances between depot facilities and DDBs are obtained from mapping software (https://www.caliper.com/maptovu.htm). It is assumed that the railroad distance is equal to about 1.3 times the road distance[54]. The sequence of the supply chains follows the energy demand-oriented approach[11]. For example, the first biorefinery is located in the highest gasoline consumption area (Chicago) among the urban areas considered here, the second biorefinery is located in the second highest gasoline consumption area (Detroit), and so on. When a candidate biorefinery does not meet the biorefinery size constraint, this candidate site is ignored, and supply chain optimization moves to the next candidate biorefinery.

Results & discussion

Reference scenario and its supply chain

Thirteen biorefineries out of 15 candidate biorefineries are established through feedstock supply chain analysis (see SI Figure S5). Candidate biorefineries adjacent to coal-fired power plants in Jasper County, Missouri and Clay County, Minnesota process less than 3000 Mg of dry pretreated pellets per day, which does not meet the biorefinery size constraint, and thus are excluded in the DDB system. The mean annual biofuel production in the individual biorefineries is 0.45±0.22 billion GGE $year^{-1}$ (1.71±0.85 billion GLE $year^{-1}$). The projected biorefineries in Chicago, Detroit, Minneapolis, and Milwaukee are very large, over 0.60 billion GGE $year^{-1}$. The DDB system in the Midwest can annually produce 5.9 billion GGE (22 billion GLE) of biofuels derived from about 105 Tg of dry pretreated pellets (i.e., corn stover and switchgrass). Due to limited land areas in the riparian zones, the mass fractions of switchgrass in the pretreated pellets processed in DDBs are 0.03-0.29. Higher fractions of switchgrass in the pretreated pellets are seen in Kansas, where corn stover availability is lower than other states.

Lifecycle GHG emissions of biofuels in scenario A are 51.6-79.6 gCO_2 MJ^{-1} with an energy-weighted average of 67.2±7.7 gCO_2 MJ^{-1}. Producing the pretreated pellets is the largest GHG emission source (83.7±4.0 gCO_2 MJ^{-1}) in biofuel production in the DDB system. Emissions associated with SOC changes in the cellulosic feedstock production and combustion of natural gas in depot facilities are the major GHG contributors with emissions of 27.6±1.9 and 24.6 gCO_2 MJ^{-1}, respectively. GHG credits for the excess electricity in the biorefineries are 31.1±7.6 gCO_2 MJ^{-1} (see Figure 1). Biofuel selling prices in scenario A are 3.37-5.09 USD GGE^{-1} (0.89-1.35

USD GLE^{-1}). The delivered feedstock cost (78% of biofuel price) is the main contributor to the biofuel selling price, followed by the cost of glucose. Glucose is used to produce enzymes in the biorefinery, amounting to 0.57 kg GGE^{-1}. The credit for the excess electricity is 0.32 USD GGE^{-1}, accounting to 8% of biofuel price (see SI Figure S6). The biofuel selling prices in the four largest DDBs (in Chicago, Detroit, Minneapolis, and Milwaukee) are below 3.70 USD GGE^{-1}. The lowest biofuel selling price is in the Chicago area biorefinery, 3.37 USD GGE^{-1}.

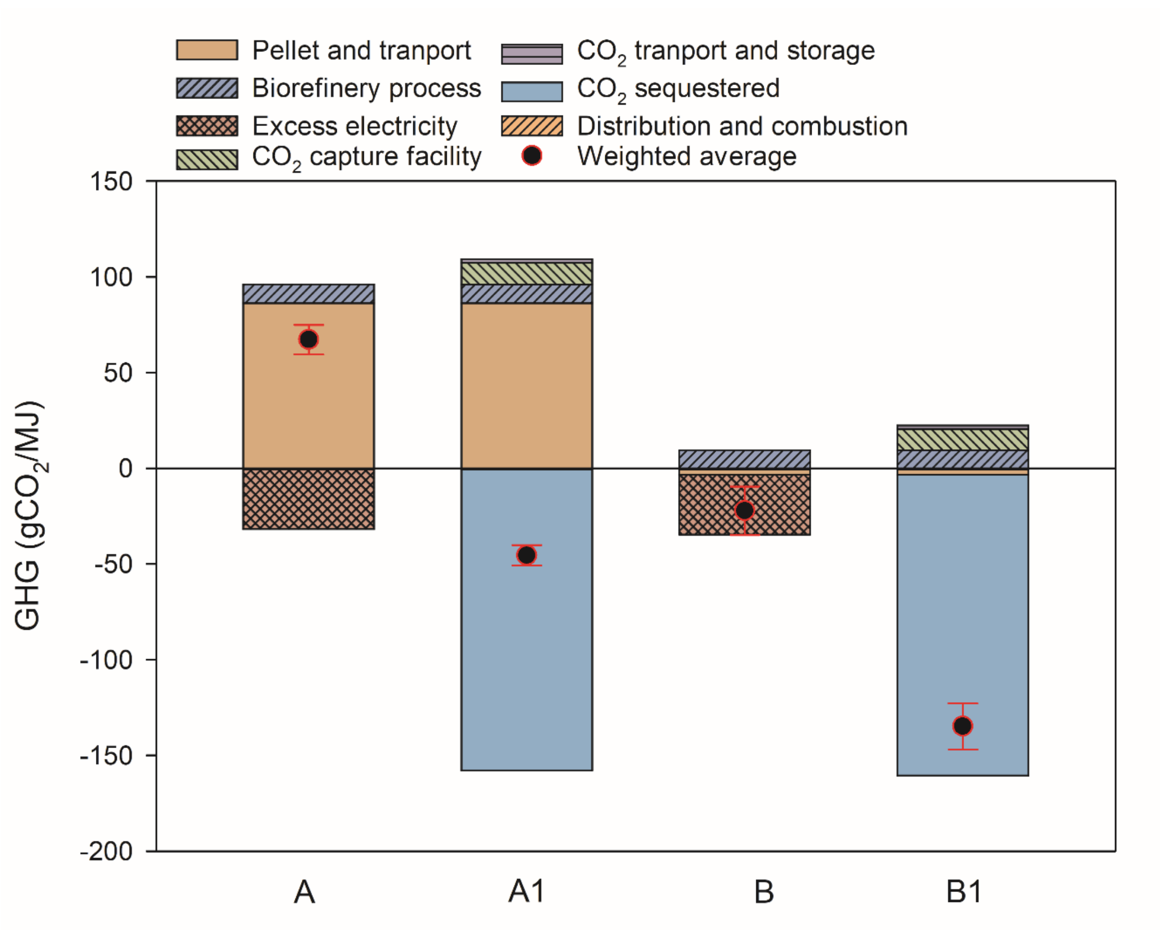

Figure 1. Lifecycle GHG emissions of biofuels (Excess electricity: GHG credit for the excess electricity; Biorefinery process: GHG of materials used in the biorefinery (e.g., glucose, corn steep liquor, etc.))

Soil carbon sequestration (cover crop)

Using cover crops as a CDR technology in the decentralized depot-based biorefinery system (scenario B), all the biorefineries are able to produce carbon-negative biofuels, and the lifecycle GHG emissions of biofuels range from -0.8 to -40.7 gCO_2 MJ^{-1} for an energy-weighted average of -22.2±12.7 gCO_2 MJ^{-1}. Cover crops compensate for SOC losses induced by corn stover removal and also sequester soil organic carbon in amounts ranging from 57.2 to 97.7 gCO_2 MJ^{-1}. Cover crops in the DDB system can remove about 0.01 Gt of carbon per year from the atmosphere, equivalent to about 1-4% of the annual sequestration rate of AFOLU-related CDR. However, cover crops produced without any economic incentives raise biofuel selling prices by 11-19% (39-89 cents per GGE) compared to the biofuel prices in scenario A. In scenario B, the volume-weighted average biofuel selling price is 4.41±0.54 USD GGE^{-1}, while a volume-weighted average biofuel selling price in scenario A is 3.84±0.42 USD GGE^{-1} (see Figure 2). The cover crop costs are assigned to corn stover, resulting in a 1.8-fold increase in the farm gate price of corn stover compared to the corn stover price in scenario A. As a result, the delivered feedstock cost in scenario B is 3.57±0.49 USD GGE^{-1}, higher than that for scenario A (3.00±0.37 USD GGE^{-1}). If farmers receive a cover crop incentive of 68 USD ha^{-1} from EQIP, growing cover crops results in only a slight increase in the biofuel selling price (3.91±0.49 USD GGE^{-1}).

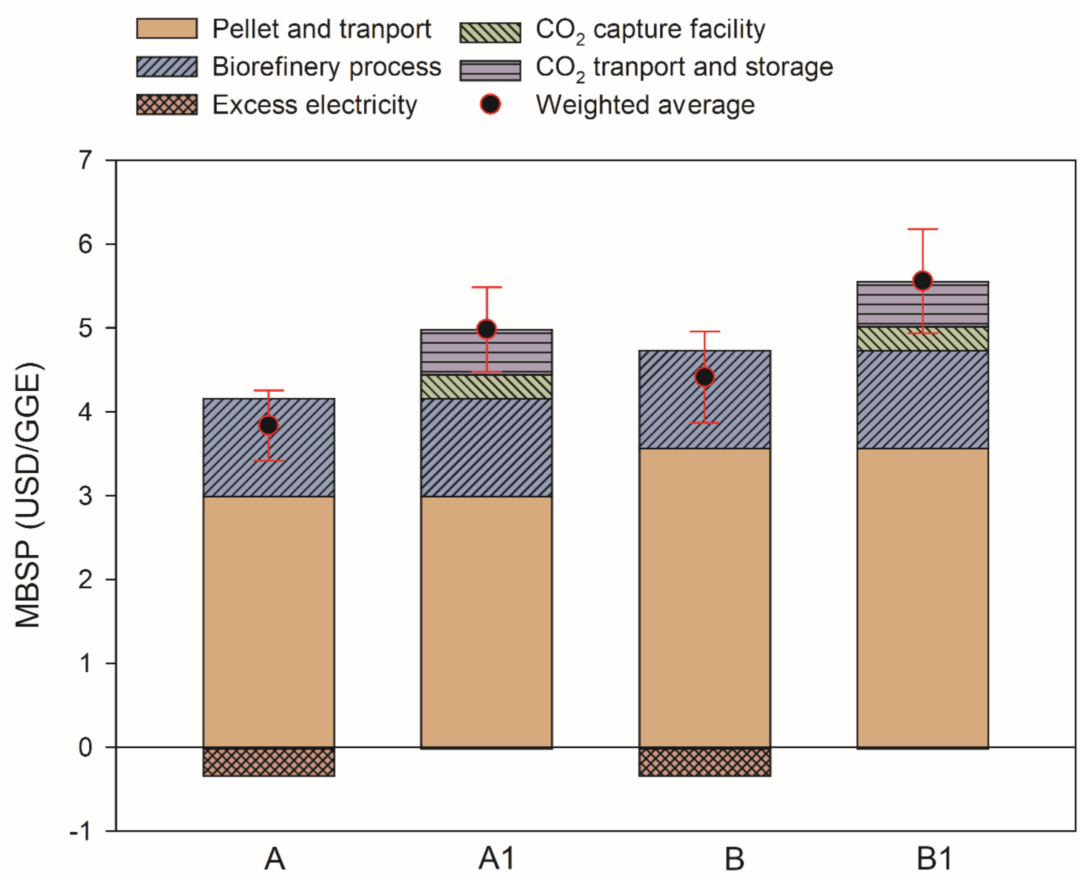

Figure 2. Minimum biofuel selling prices (MBSP) (Excess electricity: credit for the excess electricity; Biorefinery process: material cost, capital, labor, etc.))

Carbon capture and storage

About 159 gCO_2 per MJ of biofuel in decentralized depot-based biorefineries (DDB) can be captured in scenarios A1 and B1, equivalent to 1.3-14 MtCO_2 year^{-1} in the individual biorefineries. However, the GHG emissions associated with the CO_2 capture facility are about 11.3±1.4 gCO_2 MJ^{-1} (see Figure 1), including 5.8±1.4 gCO_2 MJ^{-1} from external electricity consumed in the CO_2 capture facility and 5.5±0.01 gCO_2 MJ^{-1} from chemicals used in the CO_2 capture facility (i.e., amine-based absorbent makeup, ion exchange resin and caustic soda for carbon dioxide absorption, triethylene glycol for dehydration, and etc.). GHG emissions associated with electricity consumed in pipeline transport and CO_2 injection in saline aquifers are about 1.9±0.4 gCO_2 MJ^{-1}. The overall GHG emissions associated with CCS in the DDB system are thus 13.2±1.4 gCO_2 MJ^{-1}. Overall GHG emissions associated with biofuel production, CCS, and CO_2 injected in saline aquifers (~157 gCO_2 MJ^{-1}, including CO_2 losses during transport and injection) are negative in all the DDBs. The lifecycle GHG emissions of biofuel with carbon capture and storage range from -38.1 to -56.1 gCO_2 MJ^{-1} in scenarios A1-2 and from -121.4 to -159.1 gCO_2 MJ^{-1} in scenarios B1-2 (see SI Tables S5 and S6).

The CO_2 capture cost in the biorefinery ranges from 13.4 to 29.6 USD tCO_2^{-1}, depending on the biorefinery size, that is, on the amount of CO_2 captured. A mass-weighted average CO_2 capture cost is 15.2±2.6 USD tCO_2^{-1}. Although CO_2 in flue gases stream from the boiler in the cogeneration facility is included in the CO_2 capture facility along with CO_2 from fermentation, the CO_2 capture costs of most biorefineries estimated here are lower than the CO_2 capture costs of the cellulosic biorefinery estimated in literature[29]. These reduced CO_2 capture costs result from economies of scale provided by the very large biorefineries which are in turn made possible by a pellet-based decentralized depot system.

An average pipeline transport cost is 5.3±4.4 USD tCO_2^{-1}, while an average storage cost is 23.4±7.1 USD tCO_2^{-1}. The CCS cost in the DDB system thus ranges from 33.1 to 66.8 USD tCO_2^{-1}. The CCS technology in the DDB system raises the biofuel selling prices by 0.94-1.57 USD GGE^{-1}. The biofuel selling prices in the DDB with CCS are 4.62-6.46 USD GGE^{-1} in scenario A1 and 5.17-7.36 USD GGE^{-1} in scenario B1 (see SI Tables S5and S6). Volume-weighted average biofuel selling prices are 4.98±0.50 USD GGE^{-1} in scenario A1 and 5.56±0.62 USD GGE^{-1} in scenario B1 (see Figure 2).

The tax credit for carbon dioxide sequestration of 50 USD tCO_2^{-1} is equivalent to 0.93 USD GGE^{-1} in scenarios A1 and B1. Applying this carbon dioxide tax credit, the CCS technology increases biofuel selling prices in scenario A2 by 0.3-17% compared to biofuel prices in scenario A. Applying both carbon dioxide credit and cover crop incentive (EQIP) in scenario B1, biofuel selling prices in scenario B2 decline by 21-28%. Volume-weighted average biofuel selling prices are 4.05±0.50 USD GGE^{-1} in scenario A2 and 4.12±0.57 USD GGE^{-1} in scenario B2 (see Figure 3). The break-even CO_2 tax credit, that is, a tax credit sufficient to offset the CCS cost, ranges from 51 to 85 USD tCO_2^{-1} in scenario A1, depending on the biorefinery size (see SI Figure S7).

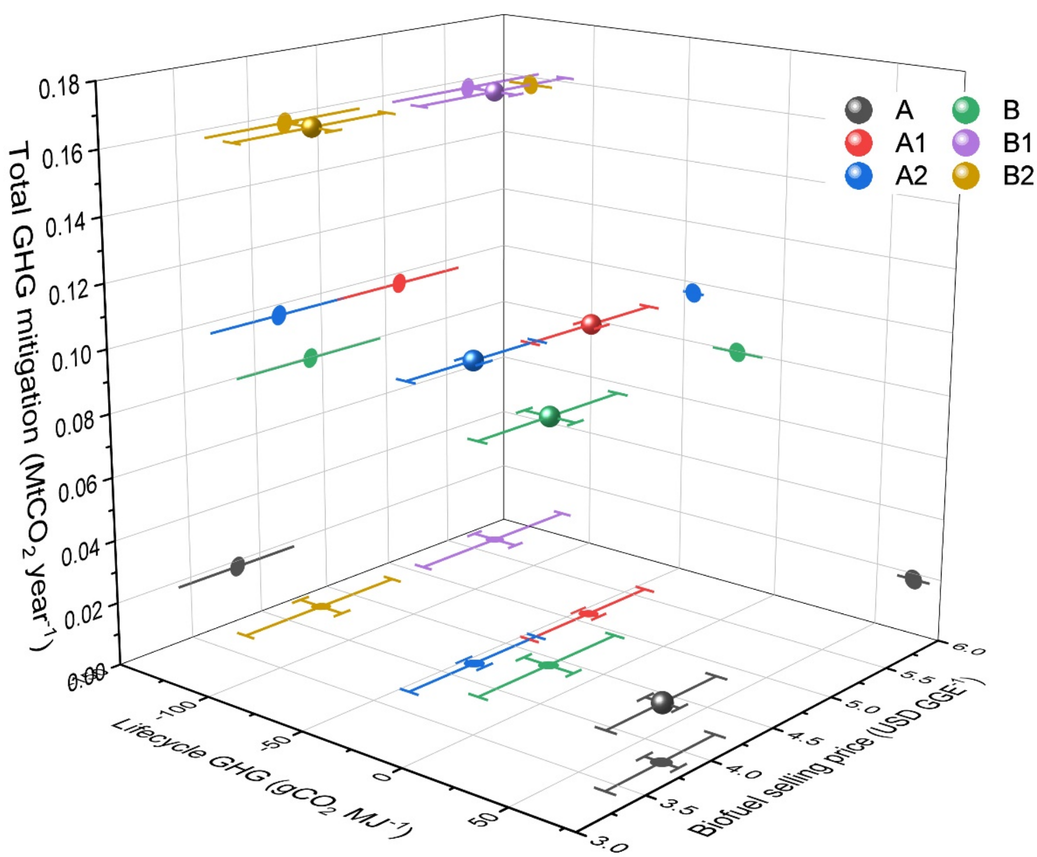

Figure 3. Biofuel selling price, lifecycle GHG and total GHG mitigation.

Total GHG mitigation

GHG mitigation in the DDB system without CDR technologies is equivalent to the GHG avoidance by displacing gasoline and grid electricity, amounting to 18.0 $MtCO_2$ $year^{-1}$ in scenario A. Using cover crop as a CDR technology in the DDB system (scenario B), the total GHG mitigation in scenario B is 79.6 $MtCO_2$ $year^{-1}$ (from GHG avoidance), 4-fold greater than that in the DDB system without CDR technologies (scenario A). The total GHG mitigation in the DDB using a CCS system is 96.4 $MtCO_2$ $year^{-1}$ in scenarios A1-2 and 157.4 $MtCO_2$ $year^{-1}$ in scenarios B1-2 (see Figure 3). The net CO_2 removal via biofuel combustion is 33% of the total GHG mitigation in scenarios A1-2 and 59% in scenarios B1-2. In the scenarios studied here, the total GHG mitigations in scenarios A1-2 and B1-2 are equivalent to 13-21% of the total GHG emissions from passenger cars in the United States in the year 2017[67]. The annual total GHG mitigation in the DDB system with CCS accounts for 1-31% of the global mitigation potential for BECCS (500-16000 $MtCO_2$ $year^{-1}$) estimated by literature[5, 7].

Sensitivity analysis

Low farmer participation in biofuel production can reduce the total ethanol production and increase the biofuel selling prices due to loss of economies of scale (small-scale biorefineries). However, the farmer participation rates do not significantly change the weighted life cycle GHG emissions. In contrast to the lifecycle GHG emissions, total GHG mitigation is greatly affected by the farmer participation rate because farmer participation rates directly determine total biofuel production (see SI Tables S7-9). Lowering the availability of riparian areas can reduce biofuel production and total GHG mitigation. In contrast, the effects of availability of riparian areas for biofuel production on biofuel selling price and lifecycle GHG emissions are not significant because the overall fraction of switchgrass processed in the biorefinery systems is small (about 10%).

When only the high-purity CO_2 stream from fermentation is captured, the CO_2 capture cost is reduced by 50-60% compared to the case of capturing CO_2 streams from both fermentation and the boiler (see SI Figure S8), thereby also reducing biofuel selling prices by 12-20%. However, when economic incentives (i.e., cover crop incentives and/or a CO_2 tax credit) are applied, the differences in biofuel selling prices between the two cases (CO_2 from fermentation versus CO_2 from fermentation and boiler) are small because of the relatively small amount of CO_2 sequestered (about 4.2 $kgCO_2$ GGE^{-1}). Without planting cover crops, the DDB system is not able to produce carbon-negative biofuel when capturing only high-purity CO_2 streams from fermentation (see SI Figure S9). Capturing only high-purity CO_2 streams from fermentation reduces the total GHG mitigation by 45-75%, and the total GHG mitigations in scenarios A1-2 and B1-2 are 24.4 $MtCO_2$ $year^{-1}$ and 86.0 $MtCO_2$ $year^{-1}$, respectively.

Due to the operation of the depot facilities, the DDB system without CCS consumes electricity at a rate of about 2.1% of the total electricity consumption in the Midwest. Integrating CCS technology with the cellulosic biorefinery can increase the electricity consumption of the DDB system by 53-60%. New power plants would likely be built to meet the power demand of CCS facilities, and their energy sources would be natural gas (44%) and renewable resources (56%, i.e., hydro, geothermal, solar, wind)[13]. Such electricity would be marginal electricity. When the CCS facilities in the DDB system consume marginal electricity, the life cycle GHG emissions in scenarios A1-2 and B1-2 are -49.4 ± 4.8 gCO_2 MJ^{-1} and -138.8 ± 11.7 gCO_2 MJ^{-1}, respectively. Using marginal electricity in the CCS facilities increases the total GHG mitigation by 3% in scenarios A1-2 (99.2 $MtCO_2$ $year^{-1}$) and 2% in scenarios B1-2 (160.1 $MtCO_2$ $year^{-1}$) (see SI Figure S10).

The size of some CO_2 capture facilities analyzed here is 3-4 times larger than that of the coal-fired power plants used as a reference in the cost calculations. For very large CO_2 capture facilities, the equipment cost would increase linearly with size due to equipment size limitations. If the scaling factor for large CO_2 capture facilities is 1 (linear increase), the mass-weighted average CO_2 capture cost in scenarios A1-2 increases by 16% (equivalent to 2.46 USD tCO_2^{-1}) compared to 0.6, but the volume-weighted average biofuel selling price increases only by about 1% in scenarios A1 and A2, respectively (see SI Figure S11).

Discussion

The CO_2 capture cost in the biorefinery depends greatly on the amount of carbon captured (see SI Figure S8). Thus very large biorefineries are favored over smaller ones. Using baled feedstock is therefore a significant obstacle to large-scale biorefineries in the centralized biorefinery system. Biorefineries using baled feedstock are limited in size to less than about 2,000 dry Mg day^{-1} [43] because of biomass transport costs. About 0.73 Mt of CO_2 per year can be captured in a centralized biorefinery of 2,000 dry Mg day^{-1}, and the CO_2 capture cost is about 43 USD $MgCO_2^{-1}$, which is much greater than the average cost in the DDB system. When only the CO_2 stream from fermentation is captured in a centralized biorefinery of 2,000 dry Mg day^{-1} (0.17 Mt of CO_2 per year), the CO_2 capture cost is about 25 USD $MgCO_2^{-1}$. From an economic standpoint, decentralized biorefinery systems based on pellets are much better suited to CCR technology than the smaller centralized systems.

Another potential economic advantage of the decentralized biorefinery system is that a biomass pellet-based biorefinery system can be located adjacent to power plants that are usually far distant from the cellulosic feedstock production areas. Most centralized biorefineries would be located near feedstock production areas. Long distance feedstock transportation is probably not practical in the bale-based centralized system. Sharing the CO_2 capture facility between the decentralized biorefinery and the adjacent power plant can reduce the capital and pipeline transport costs, resulting in a 7% reduction in both capital and transport costs on the biorefinery side due to economies of scale. CO_2 emissions from adjacent coal-fired power plants in the DDB system considered in this analysis account for 58% on average of the total CO_2 captured in the biorefineries. Another reason for co-locating the biorefinery with a power plant is that the power plants are in or near urban areas, and thus the cost of distributing biofuel to the consumers can be reduced.

Decentralized biorefineries with CDR technologies can provide carbon-negative biofuels, but these biofuels are more expensive than biofuels without CDR technologies. Economic incentives (i.e., cover crop incentives, and/or a CO_2 tax credit) can mitigate price increases due to CDR technology. Federal economic incentives cost 5.5 and 8.4 billion USD annually in scenarios A2 and B2, respectively. The total GHG mitigation per dollar of economic incentives is 17.7 $kgCO_2\ USD^{-1}$ in scenario A2 and 18.8 $kgCO_2\ USD^{-1}$ in scenario B2. In other words, scenario B2 uses the economic incentives somewhat more efficiently than does scenario A2 in terms of total GHG mitigation versus economic incentives. In addition to federal economic incentives, the California Low Carbon Fuel Standard (LCFS) provides credit for cellulosic biofuel at a rate of 200 USD per metric ton of carbon dioxide reduced (https://ww3.arb.ca.gov/regact/2019/lcfs2019/isor.pdf). The LCFS credits for scenarios A1, B, and B1 are 3.25, 2.70, and 5.57 USD GGE^{-1}, respectively, resulting in a 65-97% decrease in biofuel selling prices. The LCFS credits in scenario B2 are greater than biofuel selling prices, implying that CCS technology integrated with cover crops in biofuel production is more profitable. Therefore, combining different CDR technologies (i.e., cover crop and CCS) in decentralized biorefineries is economically efficient for GHG mitigation.

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Supporting information.

Description of objective function, Information on coal-fired power plants, Supply chain results, Sensitivity analysis results, System boundary (PDF)

Author contributions.

S.K., B.E.D. designed research; S.K., X.Z., A.D.R., K.D.T. performed research; S.K., B.E.D., X.Z., A.D.R. analyzed data; S.K., B.E.D., X.Z., A.D.R., C.D.J., K.D.T., R.C.I., T.R., C.M. wrote the paper.

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Author contributions.

S.K., B.E.D. designed research; S.K., X.Z., A.D.R., K.D.T. performed research; S.K., B.E.D., X.Z., A.D.R. analyzed data; S.K., B.E.D., X.Z., A.D.R., C.D.J., K.D.T., R.C.I., T.R., C.M. wrote the paper.

Figure Legends and Tables

Figure 1. Lifecycle GHG emissions of biofuels (Excess electricity: GHG credit for the excess electricity; Biorefinery process: GHG of materials used in the biorefinery (e.g., glucose, corn steep liquor, etc.))

Figure 2. Minimum biofuel selling prices (Excess electricity: credit for the excess electricity; Biorefinery process: material costs, capital, labor, etc.)

Figure 3. Biofuel selling price, lifecycle GHG and total GHG mitigation.

Table 1. Biorefinery system scenarios in the decentralized depot-based biorefinery system. (CCS: carbon capture and storage; N/A: not applicable)