



Slicing the pie: how big could carbon dioxide removal be?

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The current global dependence on fossil fuels to meet energy needs continues to increase. If a 2°C warming by 2100 is to be prevented, it will become important to adopt strategies that not only avoid CO₂ emissions but also allow for the direct removal of CO₂ from the atmosphere, enabling the intervention of climate change. The primary direct removal methods discussed in this review include land management and mineral carbonation in addition to bioenergy and direct air capture with carbon capture and reliable storage. These methods are discussed in detail, and their potential for CO₂ removal is assessed. The global upper bound for annual CO₂ removal was estimated to be 12, 10, 6, and 5 GtCO₂/year for bioenergy with carbon capture and reliable storage (BECCS), direct air capture with reliable storage (DACS), land management, and mineral carbonation, respectively—giving a cumulative value of ~35 GtCO₂/year. However, in the case of DACS, global data on the overlap of low-emission energy sources and reliable CO₂ storage opportunities—set as a qualification for DAC viability—were unavailable, and the potential upper bound estimate is thus considered conservative. The upper bounds on the costs associated with the direct CO₂ removal methods varied from approximately \$100/tCO₂ (land management, BECCS, and mineral carbonation) to \$1000/tCO₂ for DACS (again, these are the upper bounds for costs). In this review, these direct CO₂ removal technologies are found to be technically viable and are potentially important options in preventing 2°C warming by 2100. © 2017 Wiley Periodicals, Inc.

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INTRODUCTION

Continuing to Emit CO₂ at Today's Rate Will Require a Backup Plan to Prevent 2°C Warming

Carbon dioxide removal (CDR) methods, also known as negative-emissions technologies (NETs), are strategies that allow for the removal of

CO₂ directly out of the atmosphere. Although it is widely accepted that the capture of CO₂ from air is, in most cases,^a significantly more expensive and energy-intensive than capture from more concentrated point sources, such as natural gas and coal-fired power plants, CDR may also be necessary to limit warming as fossil fuels continue to serve the majority of primary energy needs. According to the BP Statistical Review of World Energy for 2015, fossil fuels make up the majority (86%) of the world's primary energy consumption, as shown in Figure 1, with 2015 contributions of 30, 24, and 32% for coal, natural gas, and oil, respectively. As these trends have yet to flatten, let alone change direction, NETs and their potential to prevent global warming beyond 2°C are the focus of this review.

The IPCC clearly outlines that the optimal cost-effective path for limiting warming to 2°C by 2100

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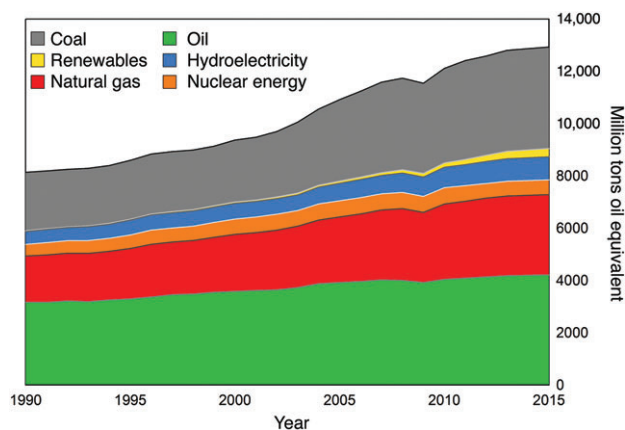


FIGURE 1 | Primary energy consumption worldwide (mt oil eq.) (Source attribution to BP Statistical Review of World Energy 2017¹. BP p.l.c. www.bp.com/statisticalreview)

(i.e., 450 ppm CO₂-eq) will require carbon capture and storage (CCS). More specifically, they report that the median mitigation costs may be up to 138% greater if CCS is not included in the portfolio of solutions and up to 64% greater if limited bioenergy is excluded. Furthermore, they report a 44% possible increase in median cost estimates if mitigation is delayed through 2050 and an additional 37% cost increase if it is delayed through 2100.² Unfortunately, CCS is not being scaled up as quickly as is required. Thus, it is likely that these incremental expenses will be realized within the century. For instance, there are 15 large-scale CCS projects operating today, representing a capacity of approximately 40 Mt CO₂ per year. Of these 15 projects, 4 are dedicated to the geological storage of CO₂, while the remaining 11 projects use the CO₂ for enhanced oil recovery (EOR).

Table 1 shows the estimated remaining fossil resources available in the Earth as of 2012.³ Conventional resources involve facile methods of development, e.g., drilling and recovery of oil and gas from highly permeable geological formations. By contrast, unconventional resources require specialized technologies, e.g., hydraulic fracturing, which can result in risks incurred by the developer and other stakeholders. Notable examples of unconventional resources include oil shales, natural bitumen or tar sands, heavy crude oil, coal-bed methane, tight-formation gas, and gas hydrates, i.e., methane trapped in crystalline water-based structures also known as clathrates. This latter category represents a vast untapped resource for methane recovery. However, clathrate natural gas stores are found primarily along the ocean floor, making economic recovery currently unfeasible.⁴ Additional resources include those yet undiscovered that are reasonably likely to exist based on current geological

TABLE 1 | Global Fossil Fuels in the Earth (Gt Oil Eq.) and Potential Future CO₂ Emissions (Gt)

	Oil	Natural Gas	Coal
Reserve			
Conventional	180	170	500
Unconventional	135	1600	
Subtotal	315	1770	
Resource			
Conventional	150	210	10,400
Unconventional	350	2910	
Subtotal	500	3120	
Additional resources	955	23,900 [†]	2800
Total	1770	4890	13,700
		28,790 [†]	
More Conventional Units			
Total	6.8	194,000	15,570
w/Additional resources	12.6	1,140,000 [†]	19,570
Units	Trillion barrels	Trillion cubic feet	Billion tons
Gt CO₂ if Oxidized			
Total	2970	10,580	38,900
w/Additional resources	5500	62,180	48,900

[†] Includes clathrates.

projections. While total fossil fuel resources increase as these additional categories are included, it is understood that the extent of recoverability generally declines as one moves from conventional to unconventional to additional resources.

Presented in more conventional units, the total oil reserve equates to 6.8 trillion barrels or nearly 200 years based on current annual consumption,⁵ while the non-clathrate reserve of natural gas (33,000 trillion cubic feet) could be used to produce 56.4 trillion MWh of energy. Full oxidation of these resources would result in catastrophic contributions to climate change, with an additional 2970, 10,580, and 38,900 GtCO₂ released for oil, natural gas, and coal, respectively.

Allen et al.⁶ estimated that the probability the globe will warm beyond 2°C is approximately 25% if cumulative emissions between 2000 and 2050 are on the order of 1000 Gt. Assuming that we, as a global society, continue our business-as-usual (BAU) practices, cumulative emissions will be on the order of 1800 Gt CO₂ during this time period, indicating

TABLE 2 | Comparison of Avoided Fossil Fuels to Prevent 2°C versus BAU Fossil Dependence

	800 Gt CO ₂	BAU 1800 Gt CO ₂	Existing Resources	Units
Oil	1.9	4.2	5.5	Trillion barrels
Natural gas	14,000	33,000	33,000	Trillion cubic feet
Coal	325	732	4800	Billions tons

the need to avoid approximately 800 Gt CO₂ to prevent warming beyond 2°C. Table 2 shows the equivalent amount of oil, natural gas, or coal that, if oxidized, would result in BAU emissions versus those that must be avoided to prevent warming beyond 2°C.⁶ Estimates are compared directly to the global oil, natural gas, and coal resources that are available today. Without CCS and CDR, these emission reductions translate to a decrease in fossil fuel dependence of 1.9 trillion barrels of oil, 14,000 trillion cubic feet of natural gas, or 325 billion tons of coal. The plausibility of such drastic targets becomes questionable when taking into consideration the fact that several emissions are already committed, i.e., CO_{2-eq} emissions are forecast for existing energy (and manufacturing) infrastructure over their remaining lifetimes.⁷

For example, just from 2010 to 2012, the global rate of increase of coal-based power capacity was 89 GW/year, a figure considerably higher than that observed over the previous two decades. Natural gas-generating capacity demonstrated a similar trend. A study carried out by Davis and Socolow⁸ showed that for just the plants coming online in 2012, assuming that the plants operate for an average of 40 years, they will cumulatively emit approximately 19 Gt CO₂ over the course of their lifetimes, compared to the 14 Gt CO₂ actually emitted from all fossil-based power plants in 2012. Thus, Davis and Socolow introduced the concept of commitment accounting for CO₂ based on existing infrastructure or that which may be built to assist in developing pathways to avoid exceeding 2°C. To meet the targets required to prevent 2°C will likely require the early retirement of some plants, retrofitting with CCS, and the inclusion of CDR to some extent. A study carried out by Gasser et al.⁹ further confirms the need to include CDR. Within their work, they focused on the 2.6 Representative Concentration Pathway (RCP2.6) adopted by the IPCC in its fifth Assessment Report (AR5),¹⁰ which represents a trajectory that would lead to a radiative forcing 2.6 W/m² by 2100. The RCP2.6 scenario projects a mean warming increase

of 1.0°C and likely range of 0.4–1.6°C between 2046 and 2065 and a mean warming of 1.0°C and likely range of 0.3–1.7°C between 2081 and 2100. This corresponds to the removal (or negative emissions) of 1.8–11 GtCO₂/year in their best-case scenario and 26–40 Gt CO₂/year in their worst-case scenario. Within this review, the various CDR approaches will be outlined, and their potential limits will be assessed and compared directly against these estimates.

It is interesting to note that the majority of the global emissions come from just a few countries, thereby highlighting the need for these countries to play a significant role in the mitigation of CO₂ emissions to prevent 2°C warming by 2100. In particular, the largest emitters are China, the United States, and India, with emissions in 2015 of 10.5, 5.3, and 2.3 GtCO₂, respectively.^b Figure 2 shows CO₂ emissions by country, organized by decreasing population (left to right). Naturally, highly populated countries typically lend to greater commodity manufacturing and power generation, yet the emissions per capita (column width) vary significantly, illustrating how several nations have a disproportionate contribution to global CO₂ emissions. It is important to recognize that if mitigation of CO₂ does not take place at a significant scale and soon in the top-emitting countries, then CDR will become even more important. More specifically, the results of mitigation strategies adopted by low-emitting countries will have minimal impact. For mitigation of CO₂ to prevent warming beyond 2°C by 2100, the United States, India, and China all must participate on a significant scale. Not only will CDR efforts become more crucial if these countries fail to act, but a significant benefit of CDR is the fact that efforts may involve both low- and high-emitting countries with results from each being potentially equivalent. Some examples that may lead to high-impact CDR in low-emitting regions include mineral carbonation in Oman¹¹ and reforestation efforts in China,¹² Brazil, and sub-Saharan Africa.¹³

CDR Approaches—What Are they and at What Pace May They Be Applied to Prevent 2°C by 2100?

Conventional CCS is unique from CDR; however, there are areas in which they overlap. Conventional carbon capture is the separation of CO₂ from the source from which it is emitted with the objective of preventing the CO₂ from entering the atmosphere. Examples include the separation of CO₂ from any exhaust source, e.g., coal- or natural gas-fired power plants or an industrial source such as from ethanol or hydrogen production. Once the CO₂ is separated,

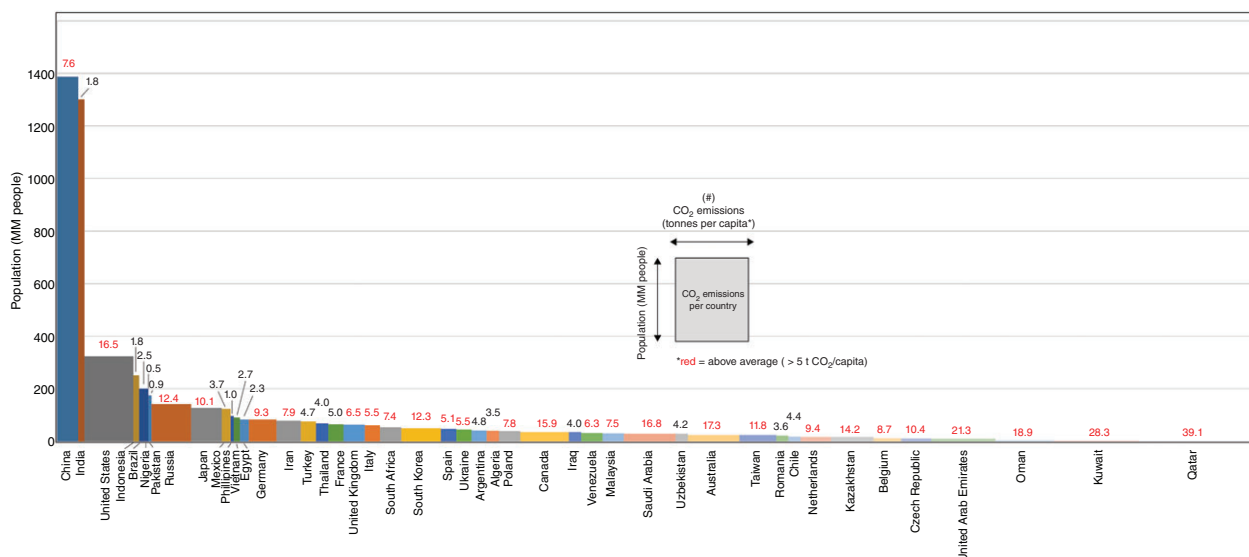


FIGURE 2 | Carbon dioxide emissions per country, sorted by decreasing country population (left to right). Area widths represent per capita emissions; numbers in red represent a surplus measured against the global average (five tonnes per capita).

it then requires compression for transportation to a utilization or storage opportunity, e.g., EOR or storage in a geological formation.

CDR, on the other hand, is the removal of CO₂ from the atmosphere after it has been emitted. It is widely accepted that the most cost-effective approach to implementing carbon capture is conventionally, i.e., through separation from the point source exhaust rather than from the air. The concentration of CO₂ in the exhaust from coal- and natural gas-fired power plants is 300× and 100× greater, respectively, than that of air (~400 ppm). Several prior studies concluded that the cost of separating CO₂ from air may be up to 10× more expensive than capture from a coal-fired power plant, assuming capture from coal exhaust is on the order of \$100/tCO₂.^{14–16} An additional difficulty with separating CO₂ from air is the outgassing that takes place by the ocean and the biosphere. For every ton of carbon removed from the atmosphere, the biosphere (land and ocean) will outgas, on average and in equal parts, half ton of carbon back into the atmosphere. Thus, to reduce the atmospheric concentration by one ton of CO₂ requires the removal of two tons in practice.¹⁷

Examples of NETs include land management (e.g., preventing deforestation, reforestation, afforestation, and tillage practices), accelerated weathering (land or ocean), direct air capture (DAC), and bioenergy. In the first two cases, CO₂ removal is directly coupled to its storage; however, with DAC and bioenergy, the compression and reliable storage of CO₂ make up a separate step that is required for effective removal of CO₂ from the atmosphere. In the case of

DAC and bioenergy coupled with CCS, termed DACS and BECCS, respectively, the research needs and pathway to deployment—in terms of storing the CO₂ reliably and on a timescale that positively impacts climate—are identical with those of conventional CCS approaches. There have been several studies that have focused on the limits associated with the various CDR approaches. For instance, a recent review by Fuss et al.¹⁸ estimates that the potential for CO₂ removal per year by 2100 for BECCS, DACS, land management, and accelerated weathering may be 3.67–12.1, 3.67–12.1, 5.5–14.67, and 0.73–3.67 GtCO₂/year, respectively. Many of these estimates were sourced from a similar review by Smith et al.¹⁹ and so are consistent with those findings. In addition, there was a similar review presented in a report on CDR approaches that was carried out by the National Academy of Sciences.²⁰ This report focused on the impact CDR may have and on what timescale for removing CO₂ from the atmosphere to prevent 2°C warming by 2100. These estimates were mostly consistent with the other reviews but did vary in the land management estimates. The variation of these estimates stems from the underlying assumptions based on available resources. For instance, to achieve 4 GtCO₂/year requires 320 Mha of land, while 12 Gt CO₂/year require 970 Mha of land. To what extent one adopts land management at the upper bound will depend in part on the extent to which bioenergy is adopted as a competition for land will exist between the two approaches. If BECCS is applied at 12 Gt CO₂/year, the land requirement will range between 380 and 700 hectares. If we consider land availability from the

terrestrial biosphere alone, there may not be adequate resources for all of the land-dependent approaches to be carried out at their upper limits of CO₂ removal. Not to mention there will be competition to grow food on some of the land as well. Although outside the scope of this review, there are a number of studies that have been carried out on marine biomass production,^{21–23} which may play a role in both land management and BECCS. It is anticipated that at the upper limits proposed in Fuss et al.¹⁸ and Smith et al.,¹⁹ such approaches will likely be required. In this review, we will carefully describe each of these CDR approaches and will outline the boundary conditions that will place limits on what their impact may be.

CDR METHODS REQUIRING RELIABLE STORAGE

Bioenergy

Given that sufficient solar irradiance, water, and nutrients are available, plants remove CO₂ from the atmosphere and temporarily fix the carbon within their biomass structure. Bioenergy has long been touted as a means to reduce greenhouse gas emissions, but when biomass energy is coupled with reliable storage, there is an opportunity for bioenergy to be included in the suite of CDR options.

The opportunity for BECCS deployment is regionally dependent. BECCS could make up a considerable fraction of the global energy supply, with estimates ranging from 50 to 675 EJ/year.²⁰ However, suitable land availability is a limiting factor for BECCS. The higher estimates for bioenergy potential are based on the assumption that climate change mitigation, and a price on carbon, will eventually result in a transition to both a lower carbon-intensive as well as a lower land-intensive diet. However, growing populations and increasing wealth are driving forces against transitioning diets. Less-extreme estimates for bioenergy production of 120–160 EJ/year, ramping up to 200–250 EJ/year by 2100, would be far from trivial, making up just over 35% of total energy production globally, which was approximately 555 EJ in 2013.²⁴ By some estimates, up to 100 EJ/year could be sourced from forestry practices and agricultural waste, meaning that the other half would require dedicated land for biomass cultivation.²⁵ If 10 tons of dry biomass can be produced per hectare, as estimated by Azar et al., 100 EJ/year of bioenergy would require 500 million hectares.²⁵

BECCS deployment can also be evaluated in tCO₂ of negative emissions. According to the emission pathways consistent with a 2°C scenario, Smith

et al.¹⁹ evaluated BECCS contribution to negative emissions to be approximately 12 GtCO₂/year by 2100²⁴. Furthermore, the limitation on BECCS for its CDR potential has been characterized by Kriegler et al., who found that the costs for CO₂ mitigation using BECCS increased dramatically above a removal rate of 12 GtCO₂/year, which was due to constraints on the supply of biomass as competition with agriculture for suitable land tightened.²⁶ Although values in EJ of bioenergy and in tons of CO₂ stored geologically are dependent variables, the conversion from one to another is not straightforward. Smith et al. evaluated BECCS carbon efficiency at 47% (2.11 tCO₂ stored biologically to store 1 tCO₂ geologically)¹⁹. According to the UK Bioenergy Strategy, in order to be considered sustainable, bioelectricity should achieve a 60% CO₂ emission reduction as compared to the EU mean electricity carbon intensity. Considering a power generation efficiency of 45%_{HHV}, this would translate into a limit on the biomass carbon footprint of 36 g CO₂/MJ of biomass. It is important to note that biomass supply chain emissions could be drastically higher when including land use change, potentially leading to a negative capture potential per MJ of biomass.²⁷ Now, if all of the CO₂ sequestered by the biomass is assumed to be released in the flue gas upon combustion, the amount of CO₂ sequestered per MJ of biomass would then depend on the postcombustion capture rate applied to the power facility, the biomass carbon content, the biomass heating value, and the biomass carbon footprint. Considering a capture rate of between 60 and 90%, biomass carbon content between 45 and 50%_{dry}, an HHV_{dry} between 18 and 20 MJ/kg, and a biomass carbon footprint between 0 and 36 g CO₂/MJ, the amount of CO₂ sequestered would be between 14 and 92 g CO₂/MJ. Hence, 1 EJ of biomass could capture between 14 and 92 MtCO₂/year, resulting in an annual requirement of between 130 and 860 EJ by 2100 to capture 12 GtCO₂/year.

In most cases, bioenergy must be coupled with CCS to qualify as CDR. The amount of energy, chemicals, and water required to produce, harvest, dry, process, and use bioenergy, and the resulting direct and indirect CO₂-eq emissions, put a strong limit on the quantity of CO₂ that can be stored using BECCS. For example, as shown in Figure 3, for switchgrass containing 2.11 tons of carbon, which is subsequently gasified and used for electricity production, only one ton of that carbon may be reliably stored.²⁸

An additional concern lies in the exhaustive and transparent accounting of greenhouse gas emissions with respect to direct and indirect land use

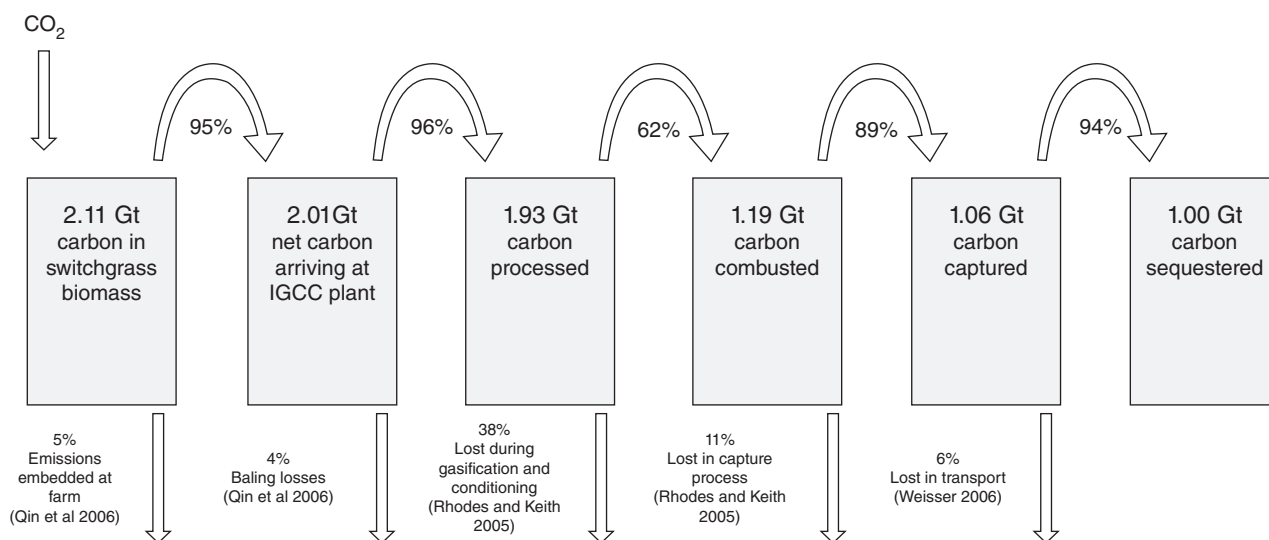


FIGURE 3 | An example using switchgrass that demonstrates for every 2.11 tonnes of carbon originally in the biomass, ultimately only one tonne is reliably stored. (Source from Ref 28 under creative commons license. Copyright 2013 Springer)

changes (ILUC).^{19,29,30} As defined by Fargione et al., direct land use changes encompass the resulting emissions from converting a particular land into an agricultural land for bioenergy. Land conversion emission factors are strongly dependent on the land type^{31,32} and can be negligible for marginal land and as high as over 3000 tCO_{2-eq}/ha for a peatland forest.³² ILUC can be understood as the emissions caused by the displacing of an activity, e.g., farming or grazing, when converting land for bioenergy. Emissions factors accounting for these effects are not only a function of land type but also highly sensitive to the activity displaced, region, time horizon, and socioeconomic conditions.^{33–35} According to Plevin et al., depending on those factors, ILUC could range from 10 to 340 gCO_{2-eq}/MJ of liquid biofuel. As a means of comparison, conventional gasoline emission intensity was estimated to be approximately 94 gCO_{2-eq}/MJ of combusted fuel. For solid biomass, this range of impact would need to be adapted, but it could potentially result in a biomass carbon footprint higher than 79 gCO_{2-eq}/MJ of electricity produced, the biomass sustainability criteria fixed by the Office of Gas and Electricity Market in the UK.³⁶ Some studies indicate that, on a transient basis, emissions resulting from land use changes would hardly be compensated by the CO₂ emissions reduction from displacing coal by biomass or only over a substantial time horizon,^{37–39} which, in the case of BECCS, would be longer than the useful life of a thermal power plant.

Ultimately, BECCS can be considered CDR only after a full life cycle analysis and careful, comprehensive accounting. Even so, the potential

magnitude for CO_{2-eq} removal via BECCS—12 Gt CO₂ annually before land restrictions lead to dramatic cost increases—has the potential to play a critical role in meeting international climate objectives.

Electricity Sector

According to the International Energy Agency (IEA), in 2012, about 370 TWh or 1.5% of global electricity was generated using biomass.⁴⁰ None of this generation employed CCS, so even this biomass-fired electricity was likely carbon positive. The IEA predicted that electricity from bioenergy could grow to 600 TWh by 2020.⁴¹ The IEA has also produced roadmaps projecting that bioenergy could contribute up to 3100 TWh of electricity production annually by 2050,⁴² although this should be considered an upper limit of what could be achieved technically, not a projection.

From a technical perspective, it has been reported that biomass can be successfully converted through pulverized coal cofiring or dedicated boilers providing modern technology is used.⁴³ Demonstrated in two units of the Drax thermal power plant in the UK since 2014,⁴⁴ dedicated biomass combustion for power generation is feasible on a large scale (660 MW) with no major change in the technology. Although technically feasible, these transformations may incur substantial additional capital and operating costs. Among potential capital expenditures, modifications to the existing equipment (grinder, boiler) as well as biomass supply chain facilities (handling, storing, and potentially processing) are required. In some cases, it may be a more economic approach to cofire coal and biomass, which could

also achieve negative greenhouse gas emissions if the biomass was properly sourced, and sufficient CCS was employed.

In Drax's example, capital investments of between 650 and £700M were reported to fully convert the plant to biomass firing. This amount included the conversion of the three 660 MW boilers, the delivery, storage and distribution infrastructure for the biomass, two pellets plants (900 kt/year) in the US as well as an export port facility, and additional investment to support compliance with European directives. However, no details as to how the budget was allocated were provided. Furthermore, biomass has different properties from coal that may also impact the power plant operating costs. Biomass storage in a nitrogen-rich atmosphere due to its high decomposition rate, as well as biomass lower grindability (1) and higher risk of boiler fouling during combustion (2), constitutes as many energy penalties, which in turn may impact the power plant operating and maintenance costs. Furthermore, as reported in their 2015 annual results, Drax imported over 90% of its pellets supply from North America,⁴⁵ with overall life cycle emissions certified to be less than 31.6 gCO₂/MJ of bioelectricity generated. This underscores the fact that local biomass availability might not be a constraint if BECCS were to be deployed on a global scale.

In the near term, the most economic approach to using bioenergy to produce electricity may be to combine bioenergy with coal in an existing system. There are also longer-term options, such as bio-dedicated integrated gasification and combined cycle (IGCC) power plants. In all cases, incorporating CCS with bioenergy could result in net negative emissions, depending on the sustainability of the biomass. The upper bound for the potential can be estimated using the power generation technologies that can incorporate biomass, as listed in Table 3.

The values in Table 3 cannot be added to predict a cumulative amount. First, some power plants are too far from CO₂ storage sites to be considered viable candidates for CCS. Second, not all power plants are within reasonable proximity to suitable, sustainable biomass sources. Finally, there is also the question of economic feasibility. As was already discussed, biomass limitation from land competition will strongly limit economic feasibility for bioenergy with CCS emissions reductions beyond 12 Gt/year annually. Instead, the values shown in Table 3 should be considered the upper technical bounds for the specific approaches listed, which could offer significant contributions to emissions mitigation in 2030 and 2050, but would not exceed a cumulative 12 Gt/year.

TABLE 3 | Power Plant Capacity and Potential for Incorporating Biomass⁴⁶

	Potential for Biomass (% Energy Basis)	CO ₂ Emissions Mitigation—Realizable Potential (Gt/year)
Pulverized coal	30% in 2030. 50% in 2050.	4.3 in 2030. 9.9 in 2050.
Circulating fluidized bed	100%	5.7 in 2030. 10.4 in 2050.
Integrated gasification combined cycle (IGCC)	30% in 2030. 50% in 2050.	4.3 in 2030. 9.9 in 2050.
Bio-dedicated IGCC	100%	5.7 in 2030. 10.4 in 2050.

Biomass fuel tends to have a higher moisture content (50% for raw wood chips against 9% for coal on average)⁴⁷ and, thus, an overall lower heating value. As a result, more biomass needs to be converted for a constant net power output, thereby further increasing the efficiency penalty on the power plant in addition to that already imposed by the capture system. The latter is a function of the power plant technology, capture technology, and capture rate but can be estimated to have at least 8.4% efficiency points for oxycombustion and 8.9% efficiency points for postcombustion⁴⁷ at 90% capture. With higher fuel cost and lower power generation efficiency, the marginal cost for a power plant employing BECCS is likely to be higher than other power generation options, hence limiting its dispatch priority in a global electricity market. However, considering that BECCS provides a service by removing CO₂ from the atmosphere, thereby avoiding future costs associated with climate change, incentives such as tax credits could be contemplated in order to improve BECCS competitiveness. For example, tax credits between \$30/tCO₂ and \$80/tCO₂ have been forecast by the Energy Information Administration (EIA) in different incentive scenarios,⁴⁸ and although global mechanisms are not yet in place, a legislative bill in the US is being put forward to bring the existing prices from \$10/tCO₂ to \$35/tCO₂ used for EOR and \$20/tCO₂ to \$50/tCO₂ in dedicated geological storage.⁴⁹

The International Energy Agency Greenhouse Gas Centre (IEA GHG) found that BECCS that was technically feasible—constrained only by resource availability and CO₂ storage capacity, not taking into account proximity—was approximately 10 Gt/year with the most viable options being CFB power

production and bio-dedicated IGCC. However, bio-IGCC is not currently being deployed at scale, and even coal-based IGCC projects are struggling technically and economically in the absence of major support. Thus, IEA GHG found that the *actual* realizable potential for BECCS for electricity was up to 2.3 Gt in 2030 and 3.2 Gt in 2050 (at a bioenergy utilization rate of 20 EJ/year).

Transportation Sector

Biomass may be gasified and converted via Fischer-Tropsch (FT) to produce liquid or gaseous fuels. Biomass-derived synthetic gas (syngas) can be prepared for FT processing via steam reforming to remove methane, plus subsequent water-gas shift activity to obtain the proper H_2/CO ratio (typically 1.7 for low-temperature FT over Fe-based catalysts).⁵⁰ Still, one of the major concerns of using biomass-derived syngas is contaminant control, the presence of which can poison the catalytic surface and reduce catalytic activity. For example, sulfur presence in biomass feedstock must be cleaned to sub-10 ppb levels; otherwise, irreversible poisoning of the catalytic surface may result.⁵¹ While this process can displace fossil fuels, it is not considered a CDR approach because on the combustion of the fuel, the carbon, in the form of CO_2 , is ultimately released into the atmosphere.

In the last decade, there have been studies focused on the use of membrane reactors for producing hydrogen via biofuel reforming for onboard applications.^{52,53} Potential benefits of using membrane technology include: (1) hydrogen production and separation in a single device; (2) production of a highly pure hydrogen stream (99.999% purity), which can be directly fed into a fuel cell for electricity generation; and (3) production of a concentrated CO_2 stream that may be reliably stored, thereby making the process CDR technology. In fact, the application of reactor technology to biofuel reforming may be a future CDR option for the transportation sector. Sjardin et al.⁵⁴ performed a technoeconomic analysis of small-scale membrane reactors for transportation, and their results showed that the cost for producing hydrogen and separating CO_2 with cryogenic separation is approximately \$50/t CO_2 , compared to the membrane approach, which was estimated at \$14/t CO_2 . Furthermore, costs for separation via the more conventional approach, pressure swing adsorption (PSA), have been estimated to range from \$7/t CO_2 ⁵⁵ to \$11/t CO_2 .⁵⁶

In some situations, biofuel production may be considered CDR even when it is not coupled with

geological CCS. For example, researchers found that low-input (i.e., minimal requirements for fertilizers, etc.) high-diversity (LIHD) grasslands are carbon negative on the order of about 4.4 Mg/hectare-year of CO_{2-eq} , that is stored in the soil and roots.⁵⁷ Importantly, LIHD bioenergy can be cultivated on land that is unsuitable for agriculture, eliminating the competition between agriculture and energy for land.⁵⁷ As the soil becomes more carbon-rich, the rate of uptake of carbon decreases. However, assuming that LIHD grasslands produced at a spatial density of 90 GJ/hectare-year are converted to biofuels via gasification and to electricity via Fischer-Tropsch processing, biofuels have the potential to displace 13% of current petroleum consumption and be slightly carbon negative.⁵⁷ While IEA GHG found that the realizable potential of biofuel could grow to 8 EJ/year in 2050, the actual negative potential for biofuels was 0.2 Gt CO_{2-eq} /year, which is limited by the eventual combustion of the biofuel.⁴⁶ Still, displacement of existing fossil fuels with some net negative CO_2 benefit is important.

Direct Air Capture

There have been several groups researching strategies and methods for the direct removal of CO_2 from the air. The separation methods considered thus far have focused on adsorption^{58–60} and absorption⁶¹ approaches, using solid sorbents and liquid solvents, respectively. A significant limitation of this approach is the lack of thermodynamic driving force for separation as CO_2 is extremely dilute in the atmosphere, i.e., 400 ppm. Due to this dilution, the sorbents and solvents rely on chemically binding CO_2 for effective removal, which increases the energy required for regeneration of the material for reuse. Although catalysts, such as carbonic anhydrase,^{62,63} and promoters, such as piperazine,⁶⁴ have been employed for conventional carbon capture from less dilute systems (i.e., exhaust from coal-fired power plants), these methods have yet to be explored for DAC applications.

An additional consideration with DAC is the need for decarbonized energy for running the DAC plant. Due to the high regeneration energy, in addition to the significant energy requirement for overcoming the pressure drop across a packed column, a low-emission (e.g., solar, wind or nuclear) energy source must be considered for this approach to be CDR. Therefore, when siting the placement of a DAC plant, available low-emission energy, such as wind, solar, or nuclear, must be considered. However, it should be noted that if these low-emission

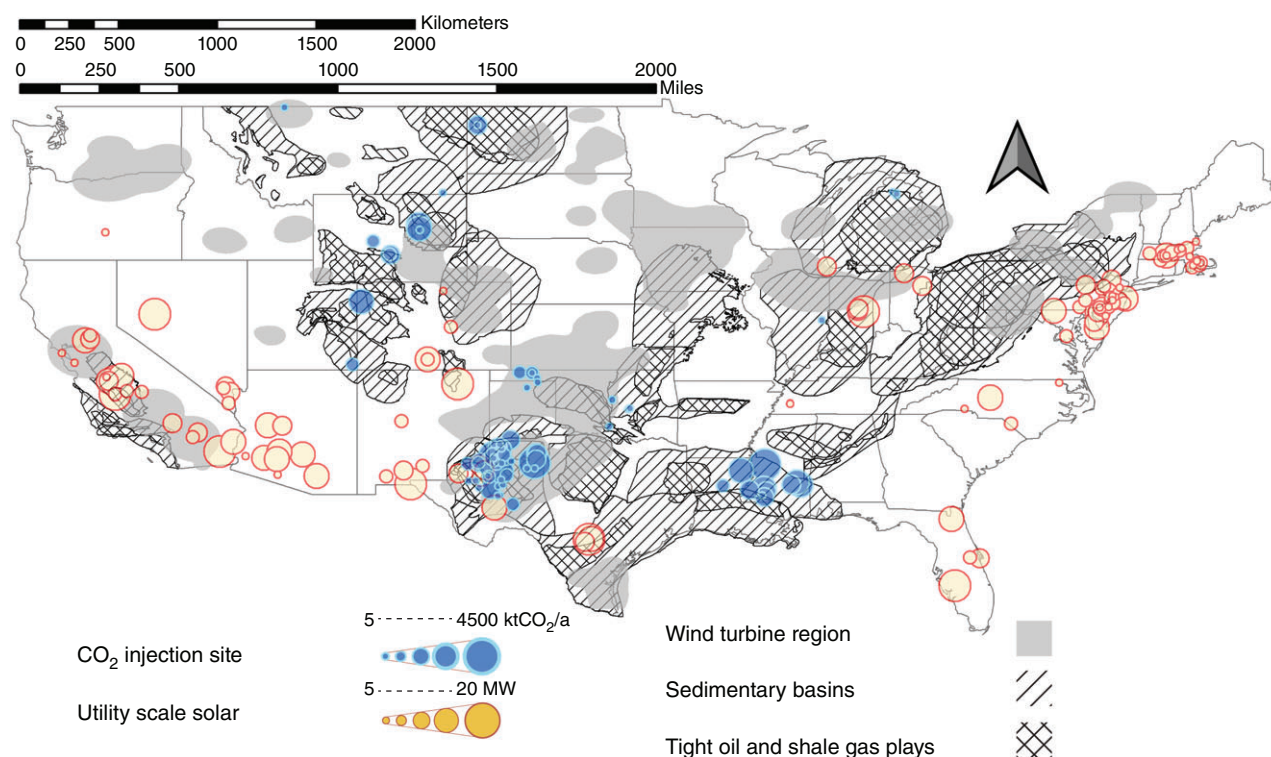


FIGURE 4 | Map of the U.S. showing opportunities for the placement of DAC plants, i.e., in regions where stranded wind or solar generation units overlap with reliable CO₂ storage opportunities.

energy sources are easily accessed by the electricity grid, then it would be more effective to avoid the CO₂ generation in the first place by replacing fossil-based electricity with wind or solar directly. Finally, DAC is only considered a CDR method if the CO₂ separated is reliably stored on a timescale that positively impacts climate. In fact, one of the few benefits of DAC is that one can place a DAC plant virtually anywhere, provided an adequate power supply is available. Ideally, DAC plants should be located near CO₂ utilization opportunities (e.g., EOR) or geological formations where the separated CO₂ can be reliably stored. It should be noted, however, that placing a DAC plant in a 'remote' location may lead to increased costs of construction and maintenance of the plant due to the transportation of construction materials and the likelihood of the population being low in the vicinity of the plant. Figure 4 shows an example of possible locations for future DAC plants in the US near both stranded wind or solar and utilization or reliable storage opportunities. It is important to note that priority should be placed on mitigating CO₂ as this would be a more cost-effective approach to reducing emissions. In this context, carbon-free energy, such as solar, wind, and nuclear, should first be considered for the replacement of coal- and natural gas-fired power

plants to avoid the emissions in the first place, rather than for providing energy to run a DAC plant.

Examination of the map in Figure 4 shows that there are regions in southern New York and Eastern Pennsylvania where utility-scale solar is available as a possible power source for DAC, with reliable storage potential residing in depleted oil and shale gas reservoirs or sedimentary basins located primarily in the neighboring region just to the west, where there are also wind turbine opportunities available for power. In southern to central California, another opportunity exists where solar and wind overlap with reliable CO₂ storage in depleted oil and gas reservoirs. The CO₂ may also be used for EOR opportunities in both of these regions as well, but it should be recognized that although CO₂ is stored to some extent in EOR, the ultimate goal is EOR, not CO₂ storage. For instance,⁶⁵ only 20–40% of the CO₂ injected for EOR is produced with the oil, separated, and reinjected for additional production. Finally, in regions of western Texas, where EOR is ongoing with existing CO₂ injection sites in place, there are both wind and solar opportunities in addition to CO₂ utilization and storage potential. Due to the lack of available similar global data used to generate Figure 4, it is difficult to determine global

estimates for DAC opportunities. Prior work of Fuss et al.¹⁸ and Smith et al.¹⁹ indicate global ranges of DACs of 3.67–12.1 GtCO₂/year. Again, future work will need to involve investigation of regions with overlapping low-emission energy sources combined with opportunities for reliable storage or usage on a timescale that positively impacts climate.

CDR METHODS WITH RELIABLE CO₂ STORAGE INCLUDED

Land Management

Deforestation, Reforestation, and Afforestation

In 2004, Stephen Pacala and Robert Socolow⁶⁶ published a landmark paper with a detailed proposal on how to solve the climate change problem over the next 50 years. Within this study, they investigated climate change mitigation scenarios based on climate stabilization wedges, such that one wedge is equal to an emissions reduction of 1 GtC/year at the end of 50 years, ultimately totaling 25 GtC. Several of the proposed wedges involved the repurposing of land in favor of forests or plantations. They estimated that with the reduction of clear cutting to zero, the reforestation or afforestation of approximately 250 million hectares in the tropics or 400 million hectares in the temperate zone, and the establishment of approximately 300 million hectares of plantations on nonforested land, would totally account for half of a wedge. In this section, we examine the current state of forests and the related opportunities for significant reductions in CO₂ from the atmosphere.

Loss of forest cover continues to pose a major threat in terms of mitigating carbon emissions. It has been reported that the forestry sector accounts for 17% of all CO_{2-eq} emissions,⁶⁷ with a global annual rate of

deforestation of 7 million acres⁶⁸ and with deforestation in the tropics alone emitting 1.1 billion tons of carbon (4.04 GtCO₂).⁶⁹ Although studies have shown that the uptake of carbon by established forests is consistently 9.2 ± 1.8 GtCO₂/year, this number may increase or decrease precipitously with the changing global forest landscape. Between 2000 and 2007, carbon emission losses from tropical forest degradation and deforestation resulted in a gain of 2.82 ± 0.45 GtC/year (10.35 ± 1.65 GtCO₂/year).⁷⁰ The Brazilian tropical forest's rate of disappearance, which peaked in 2004 at an alarming 2.74 million hectares per year, has since reduced to 1.1 million.⁷¹ Many countries depend on deforestation as a core element of their economy. For instance, Paraguay, Mongolia, and Zambia depend on timber and/or agriculture as a large percentage (i.e., 17–30%) of their GDP. Because of the slow uptake of atmospheric carbon in the first few years in new forests due to the S-shaped growth curve of trees, reforestation efforts must be carried out under the security of long-term preservation (20–30 years). Accounting for gains from additional carbon sequestered and socioeconomic benefits, there is more incentive for countries to invest in forests for the long term instead of logging for profits in the short term. For example, price growth rates for timber may barely exceed 1% in the next 60 years, even in high-demand situations;⁷¹ additionally, total ecosystem carbon and carbon sequestration both increase in the period after an initial disturbance, eventually plateauing at a point coinciding with the complete maturation of the forest, as shown in Figure 5. These disturbances include insects and disease, wildfire, partial cut harvest, timber stand improvement, plantation establishment, and grazing.⁷² However, prolonged disturbances offset the potential gains in carbon sequestration. For example, Canadian forests have been converted from a net sink to a net source due to increased salvage logging, pine beetle

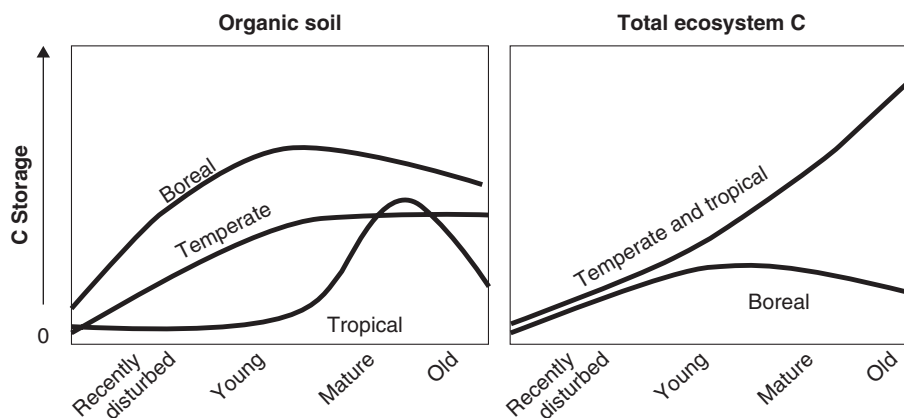


FIGURE 5 | Carbon storage in the organic soil (left) and the total ecosystem (right) as a function of forest type and age. (Adapted from Ref 72).

infestation, and several widespread wildfires. Estimates of annual emissions from these areas range from 3 to 400 MtCO₂ and are expected to last until 2022, when influence from mountain pine beetle infestation on GHG emissions is projected to cease.⁷³

As carbon storage is likely not the main goal for most landowners, especially in developing countries, there is a need for better land management and forestry practices worldwide. As the Kyoto Protocol exempts developing countries from its emissions reduction regulations, there must be guidelines in place to make reforestation/afforestation projects more appealing for developing countries. This can be accomplished through afforestation/reforestation (A/R) projects under the clean development mechanism (CDM), which is a program defined within the Kyoto Protocol that provides emissions reductions projects that result in certified emission reductions units that may be traded. Developing countries are particularly promising prospects because they have high availability of land and the need for future biomass.⁷⁴ Several studies have estimated that there are 750 million hectares suitable for CDM A/R,⁶⁸ which may ultimately sequester roughly 400 Gt CO₂ if all of the available land is utilized (10 times the global annual CO₂ emissions today).²⁸

The rate at which a forest can sequester carbon is largely dependent on its location. For example, boreal, temperate, and tropical forests have average sinks of 1.8 ± 0.3 , 3.0 ± 0.3 , and 4.4 GtCO₂/year, respectively. Although the boreal zone is the world's largest biome and has the largest effect on global temperature, complete deforestation of boreal forests would only increase global CO₂ concentration by 5 ppm in 150 years, compared to 110 and 299 for temperate and tropical forests, respectively.⁷⁵ The removal of tropical forests is strongly linked to evapotranspiration, which results in a decrease of clouds and darkens the planet. In a tropical forest, 56% of the carbon is stored in biomass and 32% in soil compared to 20% in biomass and 60% in soil in boreal forests. Therefore, deadwood and litter accumulation contribute significantly to the total carbon sink in boreal forests. Studies have also found that sawlog harvesting has large impacts on increasing soil carbon and nitrogen, whereas whole-tree harvesting caused slight decreases in temperate/tropical biomes.⁷⁶ There are many variables that could impact carbon storage, but the most influential include a loss of albedo in boreal zones and drought, fire, and deforestation in the tropics. Although removing external pressures from the system, such as high-impact harvesting, would lead to optimal results, there are other methods of forest recovery,

such as nutrient management, residue management, and utilization and better utilization of products from thinning, low-impact harvesting, optimizing rotation length, species or genotype selection, and forest biotechnology⁷⁷ that could potentially benefit the forest regeneration process. Through combined afforestation and reforestation efforts, the potential for CO₂ removal from the atmosphere ranges between 3 and 6 GtCO₂/year.^{28,78}

Genetic modification of trees to enhance their biotic and abiotic stress tolerance, improved wood properties, root mediation, and phytoremediation⁷⁹ could maximize their carbon storage potential. Transgenic trees could be less prone to damage from extreme temperatures, insects, and herbicide; could propagate through stem cuttings to meet increasing wood material demand, and could possess the ability to detoxify organic compounds. For example, poplar trees possess characteristics suitable for phytoremediation, such as fast growth, extensive root systems, and a high demand for water, and have been transformed using genetic coding to test resistance. This could also promote conservation tillage practices, which retain more atmospheric carbon in organic soils. Other biomass sources, such as switchgrass, are estimated to have twice⁸⁰ the soil carbon storage potential while utilizing half of the land area. Although the majority of the effects of transgenic biomass are secondary, it may transition into a viable CDR strategy with more time and experimentation.

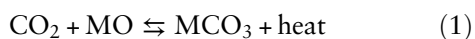
Agricultural Practices

Although demand for timber is a major reason for deforestation globally, it is not the sole reason. One of the aforementioned possibilities for disturbance, i.e., grazing, also contributes significantly to deforestation, especially in Latin American countries. In the past 40 years, over 40% of all forested land in Central America has been converted to pastures or cropland. There have been several measures implemented by countries in the region in an effort to impede the conversion from forest to pasture, with countries such as Costa Rica, Nicaragua, and Columbia spearheading the movement by creating what is known as a 'silvopastoral' system. This system is accomplished by planting trees, shrubs, and live fences on over 300 small farms. Since the start of the project, over 25,000 tons of CO₂ have been removed from the atmosphere in addition to increasing total payments to farmers, from \$63,000 to \$170,000.⁸¹ This is an example of combining regeneration of native forests and the provision of economically and socially valuable products. Another viable method that accomplishes both tasks is the introduction of plantations,

which can ‘catalyze’ the forest succession. Changes in understory microclimatic conditions, increased vegetative structural complexity, increased organic carbon in soil, and development of litter and humus layers that occur during the early years of plantation growth are the main factors contributing to its effectiveness. Positive effects generally increased in badly eroded and mined lands and decreased with increasing distance from native forests. There should be some consideration in deciding the catalytic species, with small-seeded and broadleaf forest species being the most likely candidates. Future research is required to understand and improve the design and implementation of these plantations, but the combination of economic and social benefits make plantations a promising option for increasing forest growth (Box 1).

Mineral Carbonation

As previously discussed, CO₂ in the atmosphere has the propensity to become absorbed over time into the biosphere (land and ocean). The mechanisms of absorption in each case are complex and vary considerably. A common mechanism of CO₂ uptake from the biosphere is through available alkalinity that leads to a reaction with CO₂ to form a stable carbonate mineral. Alkalinity—a measure of the buffering capacity of water—is associated with the presence of divalent cations of calcium and magnesium (Ca²⁺ and Mg²⁺). Carbon dioxide reacts with the available alkalinity via the following reaction:



where M = Ca²⁺ or Mg²⁺. Although this process is thermodynamically spontaneous, the kinetics are as prohibitively slow as a CO₂ mitigation strategy without anthropogenic acceleration.⁸⁴ The rate-limiting step involves the dissolution of naturally abundant silicate minerals to make the reactive divalent cations available for reaction with CO₂. Acceleration of this natural weathering process would lead to increased uptake of CO₂ in both the ocean and on land. In addition to slow-reaction kinetics, this process is limited by the lack of available alkalinity for CO₂ carbonation.

Land-Based Mineral Carbonation

There are two approaches to consider in terms of land-based mineral carbonation, i.e., naturally existing silicate minerals in the Earth’s crust and industrial by-products with high levels of available alkalinity. Examples of natural minerals include but

BOX 1

WHY BIOCHAR IS NOT CONSIDERED

Biochar refers to a broad class of products in which biomass (e.g., trees, grasses, crop residues) is combusted at moderately low temperatures (300–600°C) without oxygen through low-temperature pyrolysis. The pyrolysis process allows for the formation of charcoal, a relatively stable form of organic carbon, thereby slowing the inevitable oxidation and subsequent emission of CO₂ into the atmosphere due to decomposition when compared with adding the organic matter to the soil directly. Considering the energy inputs involved in the production of biochar, including field production, harvest operations, postharvest processing, and pyrolysis of feedstocks, the net energy output of pyrolysis optimized for energy for feedstock is more than the energy optimized for biochar (for switchgrass, it is 7.0 versus 5.3 MJ/ha·year).⁸² In fact, depending on the lifetime of biochar in the soil, if one were to cofire or burn the feedstock for energy production directly, the CO₂ emissions would be less than the route that involves biochar production and eventual oxidation and subsequent CO₂ release into the atmosphere. The residence time of biochar is largely dependent on the type of feedstock and the environment which the biochar inhabits. For very old biochar from the Amazon Dark Earths, the mean residence time was 4035 years at an annual temperature of 10°C. In contrast, biochar from fire-ravaged areas such as forests in Kenya and Zimbabwe were found to have mean residence lifetimes of decades or little as a few years. However, certain laboratory methods have determined the half-life of biochar to be around 60 years, with 80 being a possibility in optimum water conditions.⁸³ There is a general trend of decreasing rate of decomposition with increasing age of biomass feedstock, so there is a delay between the production of the biochar and the time it can be used effectively for carbon sequestration. Therefore, unless the feedstock for biochar can be carefully selected, it may be more optimal to oxidize the biomass for energy production at the beginning of its cycle. Hence, due to the potentially short timescale of biochar and the energy balance associated with its formation, it is unlikely that biochar is a feasible option for impacting climate and therefore is not considered in the portfolio of CDR methods discussed in this review.

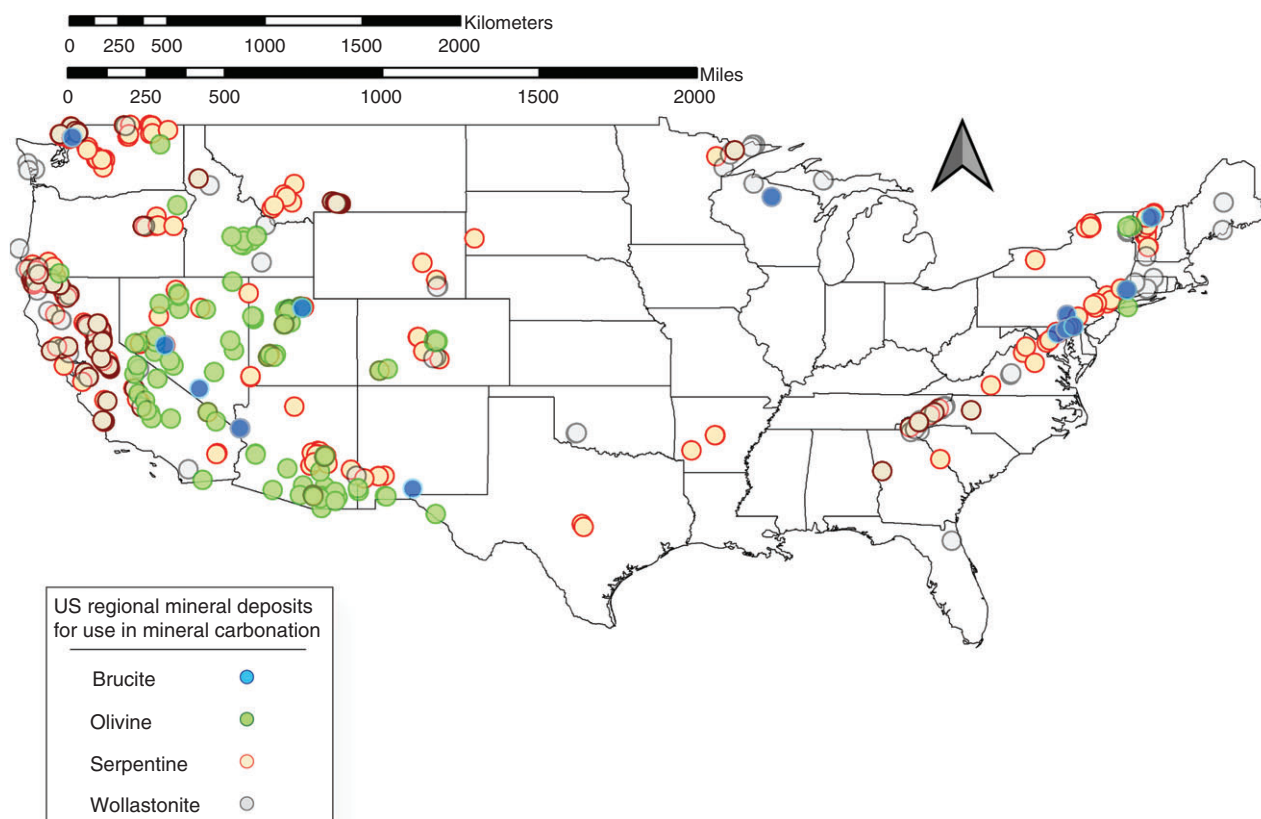


FIGURE 6 | Available deposits of common minerals for use in mineral carbonation of CO₂ in the US. (Source from United States Geological Survey 2016.)

are not limited to olivine,^{85–87} serpentine,^{88,89} brucite, and wollastonite.⁹⁰ On average, 2–4 tons of mineral are required to fixate one ton of CO₂.⁹¹ Figure 6 shows the availability of several mineral resources in the US. Globally, the potential for CO₂ storage through mineral carbonation is immense. For example, Power et al. predict that approximately 3×10^{10} tons of CO₂ could be stored via 100% carbonation of the peridotite in the Sultanate of Oman.⁹¹ Both *in situ* and *ex situ* mineral carbonation have been investigated, where in the first case, the CO₂ is injected into the formation, while in the latter case, the mineral is mined, transported, and reacted with CO₂ off-site. In the case of *in situ* mineral carbonation, CO₂ or aqueous mixtures containing CO₂ are injected into hydraulically fractured porous subsurface formations, e.g., peridotite or basalt.^{11,92} Using a typical dissolution rate for serpentine (i.e., 2.0×10^{-8} moles m⁻²s⁻¹), Cipolli et al.⁹² estimate that 33 g CO₂/kg serpentine per year may be mineralized at 60°C and a pCO₂ of 250 bar. Similarly, Paukert et al.⁹³ predict average uptake rates of 0.2–20 g CO₂/kg peridotite per year over 30 years for peridotite aquifers at 30–90°C and pCO₂ of 10 MPa. Carbonation in these models

reaches 100% after 30 years at 90°C. Limitations associated with *in situ* mineral carbonation have been outlined by Kelemen et al.⁹⁴ and consist primarily of compaction due to increasing of solid mass in the formation; precipitation in the pore space, which may limit subsequent penetration of CO₂; and covering of reactive surfaces through carbonate formation.

Ex situ mineral carbonation requires both mining and grinding of the mineral on the order of microns such that the dissolution and carbonate reaction occur on a significantly reduced timescale than what occurs in nature. Kohler et al.⁹⁵ determine that olivine spread in the river catchments of the Amazon and Congo (maintaining a pH of 8.2, i.e., no higher than the pH of seawater) could achieve mineralization of 1.8 and 0.4 GtCO₂, respectively, at a rate of 190g CO₂/m²/year over a combined area of 9.43×10^{12} m². Based on this approach, Kohler et al. estimate that, globally, up to 3.7 Gt CO₂/year may be achievable through land carbonation of olivine dispersed as a fine powder in humid tropical regions. It is important to consider, however, investigations associated with the impact that this scale of dispersion would have on the

tropical ecosystem, and related environmental impact studies are still in their infancy.

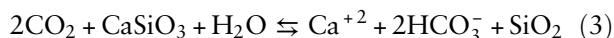
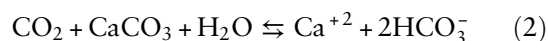
Enhancement of CO₂ uptake can be achieved via preinjection of heated fluids to the optimum temperature for carbonation (e.g., 185°C for olivine)⁹⁶ or from the addition of enhancement agents or catalysts. To give an indication of the scale required for these reactions, Kirchofer et al.⁹⁷ examined mineral carbonation of approximately 750 tCO₂/day using 10 micron-sized particles of olivine at 155°C, which requires an approximate reactor volume of 9000 m³. Additionally, to capture approximately 450 tCO₂/day through mineral carbonation using 100 micron-sized particles of fly ash at 75°C requires a reactor volume of just less than 18,000 m³. Larachi et al.⁹⁸ show that alkali metal impregnation can enhance the rate of chrysotile (Mg₃Si₂O₅(OH)₄) carbonation by a factor of up to 2.69, with a decreasing effect following the electropositivity of the doping atom (i.e., cesium > potassium > sodium > lithium). Gadikota et al.⁹⁹ have shown enhancements in olivine carbonation in the presence of 0.64M NaHCO₃. The mechanism of enhancement for this and other dissolved salts¹⁰⁰ remains debatable but could involve a buffering effect where the proper pH is maintained for enhanced dissolution of the ultra-mafic material, or there may be direct activation of the Mg–O bond, often considered the rate-limiting step in dissolution. Power et al.¹⁰¹ show evidence of the accelerated dissolution of chrysotile by one order of magnitude in the presence of acid-generating substances (e.g., metal sulfides) and microbial catalysts. The addition of cyanobacteria has also been linked to accelerated silicate dissolution (Mg²⁺ release) elsewhere.¹⁰² Organic anions, such as oxalate and citrate, have been shown to increase the extent of serpentine dissolution;¹⁰³ however, ultra-stable Mg-oxalate complexes have been reported,¹⁰⁴ which would preclude further carbonation of Mg²⁺(aq). Biomimetic agents modeled after the enzymatic activity of carbonic anhydrase have shown promise in facilitating carbonation;⁹⁶ however, these agents are relatively unstable and expensive, making their deployment at scale difficult.

Alkalinity may also be available as industrial by-products, some of which include fly ash from coal combustion, steel-making slag, electric arc furnace dust, and cement kiln dust. A number of studies have investigated the energy requirements and potential impact that these by-products could have on reliably storing CO₂ as carbonate. Kirchofer et al.⁹⁷ used an economic input–output life cycle assessment model to evaluate the CO₂ mitigation potential of various natural and industrial alkalinity sources, with cement

kiln dust showing the highest impact potential of 858 tCO₂/day. Furthermore, they argue that the most effective route to minimize energy-intensive material handling is to maximize the extent of reacted material. An analogous LCA treatment could reveal if the aforementioned enhancement agents prove similar benefit.

Ocean-Based Mineral Carbonation

On the timescale of thousands of years, the increase in sea water acidity caused by CO₂ absorption is mostly neutralized by the gradual natural dissolution of carbonate minerals situated in the seabed.^{105,106} Specifically, this neutralization occurs as a result of ions provided by carbonate and silicate-weathering reactions, which take place in the ocean sediments:



Each of these may react on the order of 1000 years, and reaction (3), in particular, may take up to hundreds of thousands of years in order to return the ocean-surface sediment silicate system to steady state.²⁰ This slow neutralization allows for the absorption of more CO₂ from the atmosphere without significantly altering the ocean pH.

Approaches have been proposed to accelerate these weathering reactions and to increase oceanic CO₂ uptake through the addition of alkalinity.¹⁰⁷ Kheshgi (1995)¹⁰⁷ and Rau and Caldeira (1999)¹⁰⁸ suggested carbonate minerals as the primary source of alkalinity to neutralize CO₂ acidity. Several studies have been performed to analyze the dissolution and precipitation kinetics of carbonate mineral in fresh water and sea water.^{109,110} It has been shown that although carbonate minerals and other alkaline compounds dissolve readily in the seawater surface (lab-scale), they do not dissolve so easily in ocean water owing to its oversaturation with respect to carbonate minerals.^{111,112} Moreover, the carbonate minerals do not precipitate due to kinetic limitations.¹¹⁰

The injection of lime (CaO) into the ocean¹¹³ is one technology under investigation to overcome this oversaturation effect. Lime is produced from the calcination of limestone (CaCO₃), an energy-intensive process requiring between 2.9 and 3.5 GJ/tCaO.¹¹⁴ However, magnesium carbonates decompose at lower temperatures, leading to slightly lower energy requirements for dolomitic

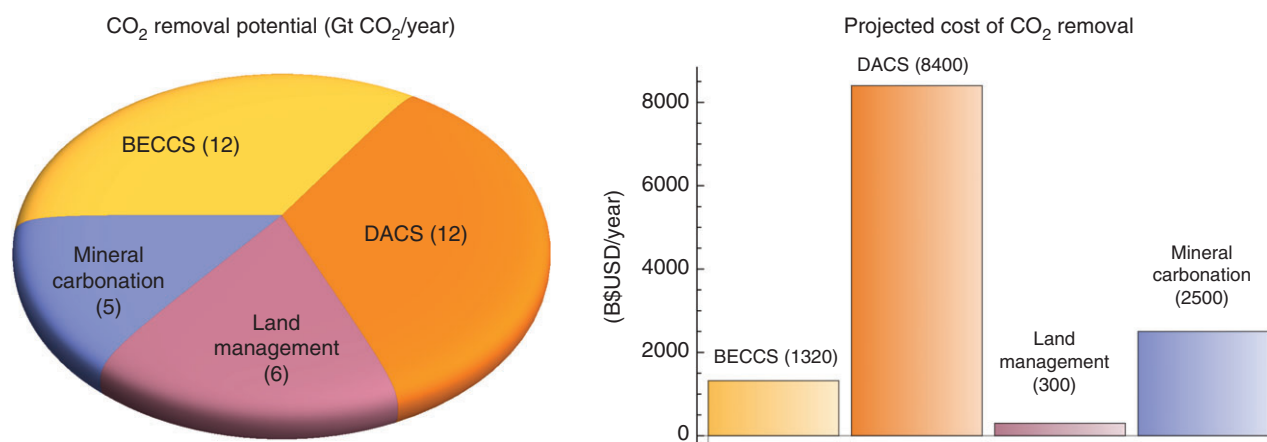


FIGURE 7 | Impact of various CDR strategies. Relative CO₂ removal potential per year (left) and projected cost of removal (right) using CDR cost estimates presented in Ref[20]. Though DACS and mineral carbonation have the potential for high impact, the low projected costs of BECCS and land management make these strategies more inviting to a first approach.

deposits (i.e., 3.0 GJ/ton CaO + MgO). Over the last decade, magnesium has attracted greater attention compared to calcium because of the abundant deposits of magnesium-rich minerals, such as serpentine, olivine, and peridotite, which are also characterized by high content of MgO. Moreover, the magnesium silicate is more reactive and therefore more suitable for mineral carbonation.¹¹⁵ Paquay and Zeebe found that between 2 and 10×10^{14} moles of alkalinity per year would need to be added to stabilize ocean pH above 8.0.¹¹⁶ Furthermore, although no direct damage to the aquatic ecosystem was found in the alkalinity models, indirect environmental consequences were noted, e.g., with the additional CO₂ generated in the production of lime.¹¹⁶

A primary benefit of this approach is its potential to reliably store a large amount of CO₂. However, although CO₂ storage by mineral carbonation seems to be feasible, research is currently focusing on mechanisms to reduce the costs of this approach. Specifically, calcium and magnesium are rarely available as binary oxides and are typically found in the form of calcium and magnesium silicates; therefore, these silicate minerals would need to be mined, processed, ground, and transported. The cost of *ex situ* mineral carbonation was reported in the National Academy of Sciences report on *Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration*,²⁰ and it was based on the LCA study of Kirchofer et al.⁹⁷ and includes the cost of mining, grinding, reaction, and transportation of the feedstocks and mineral carbonate product; it estimated an upper bound of \$1000/tCO₂ reliably stored.

CONCLUSION

Annual Global Potential of Each of the CDR Methods

The potential CO₂ removal from the atmosphere for each of the CDR methods considered in this review is demonstrated in the pie chart shown in Figure 7. In all cases considered in this review, the global upper bound was plotted with annual removal rates of 12, 12, 6, and 5 Gt CO₂/year for BECCS, DACS, land management, and mineral carbonation, respectively. Recalling the study by Gasser et al.,⁹ the upper bound of their worst-case scenario for CO₂ removal based on the RCP2.6 trajectory was approximately 40 GtCO₂/year. Collectively, all of the CDR methods considered in this review add up to a conservative 35 GtCO₂/year. The upper bound of their best-case scenario was approximately 11 GtCO₂/year, which may be achievable if action begins in the near term. In the case of DACS, global data supplying the overlap of low-emission energy sources and reliable CO₂ storage opportunities were unavailable, but estimates were taken from the reviews of Fuss et al.¹⁸ and Smith et al.¹⁹ Although costs of removing CO₂ from the atmosphere based on these various approaches was not the focus of this review, estimates from a recent report published by the National Academy of Sciences on *Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration*²⁰ were used to provide an upper bound in terms of costs for each of the CDR approaches if they are to be implemented at the removal rates discussed in this review. As shown in the bar chart of Figure 7, the more cost-effective CDR approaches are BECCS and land management, with DACS and mineral carbonation being the most

expensive. The following cost estimates were assumed for each approach. When a range was provided from literature references, the average was assumed for the generation of the bar chart of Figure 7. For BECCS, assuming that the cost of CO₂ separation and reliable storage are the same order of magnitude as conventional CCS, estimates are approximately \$100–120/tCO₂ in the absence of EOR or a revenue component. As stated previously in the review and in greater detail, initial BECCS plants may be more expensive than an 'nth' plant. This cost estimate is in fact higher than the mean reported in Smith et al.,¹⁹ i.e., ~\$40/CO₂. In the case of DACS, although costs range in the literature, an upper bound of \$1020/tCO₂ was assumed here, with \$20/tCO₂ estimated for reliable storage in a geologic formation. The range of costs reported in Smith et al. were \$400–\$600/tCO₂,¹⁹ which did not include the upper estimate of \$1000/tCO₂ from House et al.¹⁵ Land management approaches tend to be the most cost-effective CDR approaches, with an upper bound of \$100/tCO₂ estimated in the current work. Some estimates in the literature are as low as \$20/tCO₂ with upper estimates reported at \$100/tCO₂.^{20,117–119} It really depends on the land management approach applied. For instance, tillage practices may be low in cost, but their impact is not as great as some afforestation efforts, which may be higher in cost. The costs of mineral carbonation are highly dependent on whether carbonation is taking place in the ocean or on land. Ocean estimates are on the order of \$100/tCO₂, while land estimates depend on whether the mineral carbonation is *ex situ* or *in situ*. In the case of *ex situ*, estimates are approximately \$1000/tCO₂ due to the expense of mining, grinding, reaction, and transportation, while in the case of *in situ*, the impact may be smaller, but costs are lower with estimates of approximately \$100/tCO₂. Cost ranges reported in the literature for CDR range between \$20 and \$1000/tCO₂.^{19,20,120} The projected average costs of CO₂ removal for each approach were estimated at \$110, \$700, \$50, and \$500 per tCO₂ for BECCS, DACS, land management, and mineral carbonation, respectively.

Weighing the Risks of Climate Change versus Implementing CDR in Emergency Mode

There is a question as to whether the risks associated with climate change are greater than those resulting from the removal of CO₂ from the atmosphere on the timescale deemed essential to preventing 2°C of warming. Combining all of the CDR options considered in this review, an upper bound on the rate of CO₂ removal from the atmosphere is approximately

30–40 Gt CO₂/year, which is equivalent to a 1 ppm/year reduction in atmospheric CO₂. Recall the study by Allen et al., which discusses the need to remove or avoid 800 GtCO₂ by 2050 to prevent a 2°C warming. Also, recall that reducing the atmospheric concentration actually requires removal of double the amount of CO₂ from the atmosphere since the biosphere (land and ocean) will both offgas CO₂ as they reach equilibrium, indicating that 1600 GtCO₂ would have to be removed from the atmosphere. If we began implementing CDR at this scale today, that would lead to a removal of approximately 1000 GtCO₂ by 2050, which is inadequate. Society's BAU dependence on fossil fuels predicts cumulative emissions of 1800 GtCO₂ by 2050. Hence, in order to prevent 2°C warming, CDR would have to be applied in addition to other strategies, such as conventional CCS, replacement of fossil fuels with renewables, end-use fuel switching, etc.¹²¹ Thus, CDR is part of the broader mitigation effort.

Some risks may include application of some of these approaches at too great of a scale. Taking BECCS for instance, storing 9 GtCO₂/year requires approximately 500 million acres of arable land, and there are only 1530 million acres of arable land available worldwide. Clearly, if the scale of bioenergy were to be increased significantly, this would result in direct competition with food production. Aquaculture provides an important opportunity for increasing the amount of biomass available for BECCS, but a thorough quantification of the extent of this potential resource base is outside the scope of this study. There are also risks associated with the application of land management practices such as decreased biodiversity associated with reforestation of deforested land in addition to competition for land that may be used for agricultural production in the case of afforestation.²⁰ If society finds itself in crisis mode, there may be the temptation to apply CDR on a scale too great and too abrupt. Application at greater scales may come with unintended consequences, prohibitive costs, and could possibly result in scenarios that are riskier than those associated with warming.

NOTES

^a It is conceivable that, in some cases, slightly negative emissions that could be achieved by cofiring a small amount of biomass with coal at a power plant enabled with CCS could be on par with CO₂ capture from natural gas power plants in terms of \$/ton CO₂.

^b The 28 member states of the European Union (EU) collectively emitted 3.4 GtCO₂ over the same time period.

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