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Economic and energetic analysis of capturing CO₂ from ambient air

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Capturing carbon dioxide from the atmosphere ("air capture") in an industrial process has been proposed as an option for stabilizing global CO₂ concentrations. Published analyses suggest these air capture systems may cost a few hundred dollars per tonne of CO₂, making it cost competitive with mainstream CO₂ mitigation options like renewable energy, nuclear power, and carbon dioxide capture and storage from large CO₂ emitting point sources. We investigate the thermodynamic efficiencies of commercial separation systems as well as trace gas removal systems to better understand and constrain the energy requirements and costs of these air capture systems. Our empirical analyses of operating commercial processes suggest that the energetic and financial costs of capturing CO₂ from the air are likely to have been underestimated. Specifically, our analysis of existing gas separation systems suggests that, unless air capture significantly outperforms these systems, it is likely to require more than 400 kJ of work per mole of CO₂, requiring it to be powered by CO₂-neutral power sources in order to be CO₂ negative. We estimate that total system costs of an air capture system will be on the order of \$1,000 per tonne of CO₂, based on experience with as-built large-scale trace gas removal systems.

direct air capture | gas separation economics | separation thermodynamics | concentration factor | Sherwood plot

Several researchers investigating chemical systems for capturing CO₂ from the air* have suggested that air capture could be a viable climate mitigation technology costing no more than a few hundred dollars per tonne of CO₂ avoided (1–3). It has been further argued (4) that air capture may be cost-competitive with more accepted climate change mitigation options like renewable power, nuclear power, and CO₂ capture and storage from large stationary sources (carbon capture and storage, CCS). Indeed, during visits to the Massachusetts Institute of Technology in the spring of 2009, the US President's Science Advisor, John Holdren, and Secretary of Energy, Steven Chu, each mentioned capturing carbon dioxide (CO₂) directly from the air as an option that may be needed for stabilizing global CO₂ concentrations and, thereby, global temperatures. To examine these claims, we have undertaken a series of analyses of the costs and energy requirements of air capture.

Instead of focusing on any particular proposed air capture system, we analyze the capture of CO₂ from air, where it has a concentration of approximately 0.04%, in the context of analogous industrial separation systems. Although the minimum thermodynamic work to separate CO₂ from air is not a prohibitive burden, separation systems themselves require significantly more energy than the thermodynamic minimum. This approach, which is independent of any particular air capture system or process, is motivated on the one hand by the utility of having a generic analysis, and on the other hand by the lack of literature regarding a detailed design of a particular capture process on which a detailed cost analysis could be based.

After a brief introduction to the history of CO₂ capture and separation processes, we review recently published designs of air capture systems. We then analyze the process of air capture

in five parts, without regard for a particular technology. In the first part of our analysis we start with the well-known Sherwood plot, which relates the market price of a substance to its initial dilution (5–7). Second, we analyze existing separation processes to estimate their second-law efficiencies (defined here as the ratio of minimum thermodynamic work to actual work expended) and relate them to the ratio of final concentration to initial concentration of the desired product (defined here as concentration factor). Based on our survey of second-law efficiency and concentration factor, in the third part of our analysis we develop our own cost and energy estimates for air capture systems. Fourth, we compare air capture systems to commercial SO_x and NO_x removal processes that operate at concentrations similar to that of CO₂ in air. This analysis is an extension of the Sherwood reasoning, which was also applied by Lightfoot and Cockrem (8), demonstrating that the actual work required to remove any type of trace gas from a mixed gas stream depends strongly on the initial trace gas concentration. Finally, we review the design trade-offs inherent in proposed air capture processes.

Absent radical technological breakthroughs, our analyses suggest that air capture is unlikely to be a practical CO₂ mitigation technology at carbon prices below \$1,000 per tonne of CO₂, and that it can only be viable (i.e., CO₂ negative) if powered by non-CO₂ emitting sources. In light of the present analysis, we find that many estimates in the literature appear to overestimate air capture's potential (1–3).

Background on CO₂ Removal from Air and Air Capture Proposals

In the 1930s, CO₂ was first commercially removed from ambient air in order to prevent the fouling of process equipment by dry ice formation in cryogenic air (i.e., N₂/O₂/Ar) separation plants (9). Modern air separation plants use molecular sieves for this purpose. Other applications of CO₂ removal from air include life support systems for spacecraft and submarines (10, 11). The technologies to purify air of CO₂ include, among others, reacting CO₂ with solutions of strong alkali, such as NaOH and KOH (12). These systems remove CO₂ from air, but do not produce highly concentrated streams of CO₂, which is more difficult and costly.

Climate change mitigation, on the other hand, requires not only that CO₂ be separated from air on a much larger scale than current commercial systems, but also that CO₂ be sequestered

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See Commentary on page 20277.

*This paper restricts its analysis to the proposed processes that chemically remove CO₂ from the atmosphere, sometimes termed "direct air capture." Biological approaches to air capture are briefly discussed in a section at the end of this paper.

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Table 1. Published air capture analyses

Refs.	Steps in proposed process	Cost, \$/tCO ₂	Energy required, * kJ/mol CO ₂	Second-law efficiency, [†] %
Keith (1)	NaOH scrubbing, causticization with lime, calcination, amine capture.	136	648 thermal and 31 work (total, 736 primary [†])	7.9
Baciocchi (24)	NaOH scrubbing, causticization with lime, thermal calcination in a proposed oxy-blown kiln. Option A uses standard technology for the precipitation and dewatering of the CaCO ₃ sludge; option B uses a prospective pellet reactor.	not reported	Option A: 515 thermal and 60 work (total, 686 primary [†]) Option B: 352 thermal and 53 work (total, 503 primary [†])	A: 10.0 B: 13.5
Nikulshina (34)	Aerosol-type carbonator using Ca(OH) ₂ , solar calciner, conventional slaker. Note that the alternative configuration with H ₂ production is not considered here.	solar calciner only, 176–220	2,485 thermal	2.4
Zeman (2)	NaOH scrubbing, causticization with lime, thermal calcination in a proposed oxy-blown kiln.	not reported	225 thermal and 104 work (total, 522 primary [†])	11.1
Stolaroff (35)	NaOH spray tower, proposal, and prototype. Does not include regeneration.	proposed spray tower only, 53–127 [§]	proposed spray tower only, 53–94 work [§] (150–270 primary ^{†§}) prototype spray tower only, 190–390 work (540–1,100 primary [†])	insufficient information
Mahmoudkhani (36)	Recover NaOH from Na ₂ CO ₃ through a hypothetical two-stage crystallization/precipitation followed by titanate process. Does not include capture system.	not reported	recovery cycle only, 150 enthalpy change	insufficient information
Lackner (14)	Filter with CO ₂ selective sorbent (resin). Air exchange, steam flush, compression.	220	38 work [¶] (110 primary ^{†¶})	50

For more details on each analysis, see *SI Appendix*.

*Does not include energy for CO₂ compression after capture for transport or storage purposes.

[†]Calculated in the current study based on the data provided in each publication.

[‡]Assuming a 35% efficiency of converting primary energy to work.

[§]Depends on the size of the tower and thus is the result of an optimization calculation.

[¶]Energy for compression of CO₂ to atmospheric pressure included for consistency, approximate energy for further compression removed (12 kJ/mol) (37).

for millennia, which—in the case of geologic sequestration—requires CO₂ to be concentrated from its ambient levels of approximately 400 ppm to high purity as well as compressed to typically 11–14 MPa to be efficiently transported and stored in geological formations (13).

Many of the air capture processes proposed in the literature (see Table 1) are categorized as chemical absorption (also referred to as chemical scrubbing), which is one of the primary processes envisioned for large-scale capture of CO₂ from power plant flue gases. The chemical absorption process uses a reactive solution to selectively absorb the CO₂ from a feed gas. After absorption, the CO₂-rich solution is processed by reversing the reaction such that a concentrated stream of CO₂ gas is produced, with the solvent regenerated for reuse. This “stripping” of CO₂ from the solvent typically requires the input of heat, which generally dominates the energy requirement of the capture process (13).

Table 1 summarizes the projected energy and dollar costs of air capture processes that have appeared in recently published technical analyses. The projected dollar costs are in the range of \$100–\$200/tCO₂—although the energy requirements vary widely, with most of those for NaOH scrubbing/lime causticization systems clustering around 500–800 kJ primary energy/mol CO₂.[‡] By contrast, a larger body of work has focused on systems to capture and purify CO₂ from coal-fired power plant flue gases, where the CO₂ concentration is approximately 12% by volume (“flue-gas capture”), approximately 300-fold higher than air. Estimates of avoided cost[§] for flue-gas capture using current-generation capture and compression technologies are in the range

of \$50–\$100/tCO₂ (15). The most developed flue-gas-capture solvents currently used for absorbing CO₂ from industrial gas streams are aqueous solutions of amines (16), particularly monoethanolamine. The primary energy required to strip CO₂ from the rich amine stream (115–140 kJ/mol CO₂; ref. 13) dominates the energy requirements of the process. The driving question of our study is how the energetics and costs will scale with input CO₂ concentration ranging from those found in air capture systems to those found in flue-gas-capture systems.

An Analysis in Five Parts

Part 1: The Sherwood Plot and the Cost of Separating Dilute Streams.

In 1959, Thomas K. Sherwood published the original version of what is now commonly referred to as a Sherwood plot (5). His graph revealed an empirical relationship between the market price of a metal and its typical concentration in the ore from which it is extracted, using mature separation technologies. Later versions by others include additional substances that are separated from dilute mixtures, such as pollutants and valuable organic compounds (17, 18). Recently, Dahmus and Gutowski developed such a plot to help assess material recycling potentials (7).

In all of these analyses, it is clear that the cost to separate a given substance from a mixture scales inversely with the initial concentration of that substance. Dahmus and Gutowski (7) interpret this result as related to material extraction and processing costs that scale with the amount of material processed, which we parallel to the amount of gas to be processed for capturing CO₂. In Fig. 1, we present the updated Sherwood plot from Grübler (6), which includes three categories of materials to be separated: metals, organics, and pollutants. A line with the form $P = A/C$, can be drawn through each set of separated materials, where P is the price (dollars per kilogram), C is the initial concentration of the input stream (i.e., mass of product per mass of mixture), and A is a separation constant with units (dollars per kilogram initial mixture). Dahmus and Gutowski observe that A is approximately \$1/kg of initial mixture (kg_i) for separating organics; approxi-

[†]The process described by Lackner (14), requiring 110 kJ primary energy/mol CO₂, is a clear outlier, and we treat it as such absent additional published data to evaluate the claimed efficiency.

[§]Avoided costs are based on the amount of avoided CO₂ emissions, defined as the amount of CO₂ captured minus the amount of CO₂ emitted by the capture process. Because avoided emissions are less than the amount of CO₂ captured, avoided costs (in dollars per tonne of CO₂ avoided) are greater than capture costs (in dollars per tonne of CO₂ captured). When analyzing the economics of climate change mitigation, one needs to use the avoided costs.

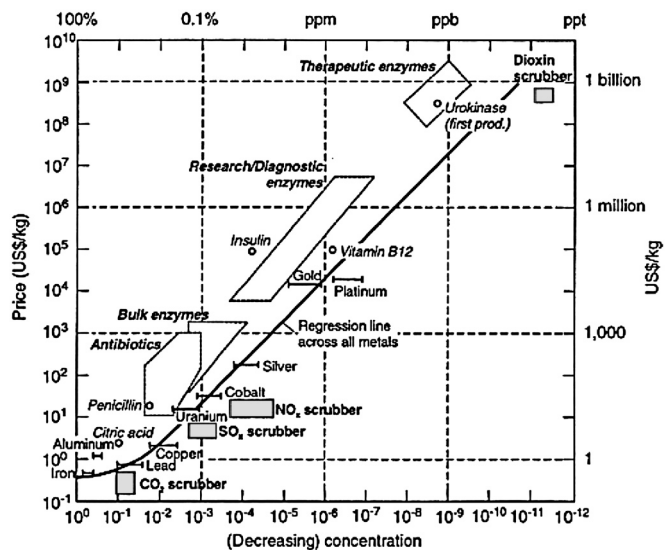


Fig. 1. A Sherwood plot showing the relationship between the concentration of a target material in a feed stream and the cost of removing the target material (6). For a more detailed look at the gas separation processes on this plot, see *SI Appendix*. [Reproduced from ref. 6 (Copyright 1998, Cambridge University Press).]

mately \$0.01/kg_i for separating metals; and approximately \$0.001/kg_i for separating pollutants from mixed gas streams (7).

We can use the estimated separation constant for separating pollutants from mixed gas streams (i.e., $A = \$0.001/\text{kg}_i$) to estimate the cost, per unit of CO₂, to separate CO₂ from a variety of mixed streams. For example, the CO₂-mole fraction of flue gas from a coal-fired power plant is about 12%, or order 0.1. Using Dahmus and Gutowski's constant and adjusting to 2008 dollars, we calculate that separating CO₂ from a coal-fired power plant will cost on the order of \$10/tCO₂. Most estimates suggest that capturing, but not compressing, a stream of CO₂ from a coal-fired power plant will cost closer to about \$30–\$60/tCO₂ (13, 19, 20) on a per tonne captured basis. When applied to CO₂ separation from a natural gas-fired power plant, the separation constant (7) indicates that the cost of CO₂ purification would be approximately \$25/tCO₂, which is also slightly lower than most reported values in the approximate \$50/tCO₂ range (13). Thus, using the separation constants derived by Dahmus and Gutowski (7) yields the correct order of magnitude.

Application of the separation constant to air capture would suggest a cost of about \$2,500/tCO₂. Just as types of materials scale (i.e., organics, metals, pollutants), according to Fig. 1, gases with similar chemical properties, such as acid gases, should also scale. For instance, after close inspection of Fig. 1, one can see that drawing a line through the cluster of acid gases (CO₂, SO_x, and NO_x) would result in a shallower slope than the \$0.001/kg_i cited. To better constrain the cost projection for air capture, we constructed a Sherwood plot for mixed acid gas stream separation only (*SI Appendix*). The projected cost was consistently larger than \$1,100/tCO₂ for air capture, whether different trace acid gas separation processes were included or not, indicating independence of separation cost on a particular process choice or process chemistry. Rather, as Lightfoot and Cockrem pointed out in 1987 (8), separation costs are more closely related to the “processing of valueless constituents.”

Part 2: Minimum Work and Second-Law Efficiency. The theoretical minimum work required to achieve a change in thermodynamic states is the net change in work potential (i.e., thermodynamic availability or exergy) of the system (21). The change in work potential is minimized when a flowing system undergoes a reversible isothermal, isobaric change (22). Therefore, the absolute

minimum work, W_{\min} , required for a given separation process is equal to the difference between the work potential of the product and feed streams, which is equal to the difference in stream exergy:

$$W_{\min} = \Delta\Psi_i, \quad [1]$$

where Ψ_i is the exergy of stream i . For the isothermal, isobaric processes that we are considering, the change in work potential equals the change in the Gibbs free energy. In the simple case of a separation of one feed stream (stream 1) consisting of n substances into two product streams (streams 2 and 3, as in Fig. 2), where all streams consist of ideal mixtures, the minimum work reduces to

$$W_{\min} = -RT \left(N_1 \sum_{k=1..n} X_{1,k} \ln X_{1,k} - N_2 \sum_{k=1..n} X_{2,k} \ln X_{2,k} - N_3 \sum_{k=1..n} X_{3,k} \ln X_{3,k} \right), \quad [2]$$

where N_j denotes the molar flow rate of stream j , and $X_{j,k}$ denotes the molar concentration of substance k in stream j . Note that for nonideal mixtures (i.e., real gases and solutions), we must account for the excess properties that depend on interactions between molecules.

According to Eq. 2, the theoretical minimum work required to separate a stream of air with 400 ppm CO₂ into one stream with 200 ppm CO₂ and a second stream of highly concentrated (i.e., 99% purity) CO₂, all at the same temperature and pressure, is about 20 kJ/(mol CO₂). No real process can operate by expending only the theoretical minimum work, because reversibility—the thermodynamic requirement to achieve minimum work—requires infinitesimal mass transport driving forces, which in turn require theoretical equipment of infinite size and cost. As such, the capital costs of processes designed to expend close to the minimum work are excessive.

The second-law analysis uses only work, whereas real capture processes may use a combination of heat and work. The minimum work analysis, however, is still valid for those systems because the heat is associated with work potential. For example, many amine capture systems use steam extracted from the turbine as their source of heat. That steam extraction results in a loss of power generation, which is the real work penalty associated with that heat. If one used fuel to generate the heat directly, it would most likely result in an even bigger work penalty because extracting steam from a turbine is a form of cogeneration, which tends to be more energy efficient than making low pressure steam from fuel directly (23).

Real-world separation processes typically achieve second-law efficiencies (η), defined as the ratio of minimum to actual power consumption, in the 5–40% range (see Fig. 3). For these processes, η is the result of a design strategy to minimize the net present value of total costs. That optimization involves balancing capital costs, which tend to increase with η , and operating costs, which tend to decrease with η .

Fig. 3 plots concentration factor (i.e., the ratio of the material's final concentration to its initial concentration) versus the second-law efficiency of several industrial separation processes. The data

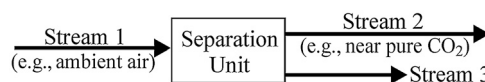


Fig. 2. Illustration of system under consideration. Mixed stream 1 enters the “black box separation unit,” where work is done to generate two product streams. In the case of air capture, stream 1 is air at ambient conditions; in the case of capture at a power plant, stream 1 is flue gas with approximately 12% CO₂, and so forth. Generally, stream 2 is high purity CO₂, and stream 3 is what is left.

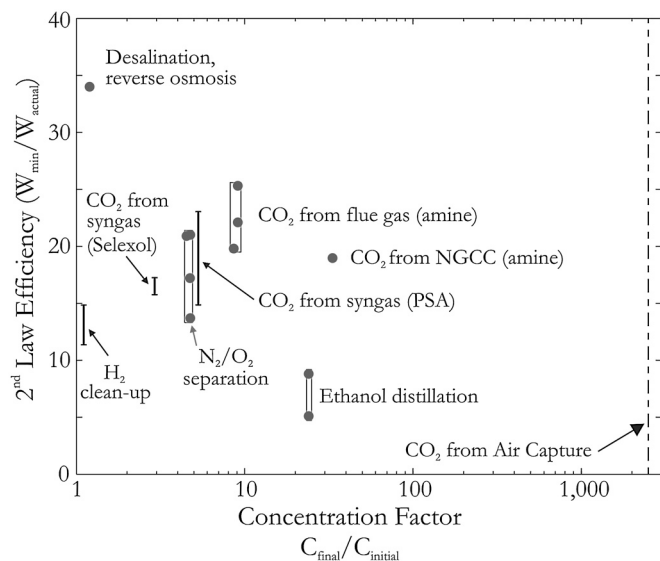


Fig. 3. Empirical relationship between the concentration factor of industrial separation processes vs. the achieved second-law efficiency of those processes. Processes include separation of impurities from H_2 after steam reforming and CO_2 removal (H_2 clean-up); separation of water from brine (desalination); separation of CO_2 from syngas in an Integrated Gasification Combined Cycle power plant [CO_2 from syngas (Selexol)]; separation of CO_2 from syngas after steam reforming [CO_2 from syngas (PSA)]; production of oxygen from air (N_2/O_2 separation); separation of CO_2 from coal power plant exhaust [CO_2 from flue gas (amine)]; separation of CO_2 from natural gas power plant exhaust [CO_2 from NGCC (amine)]; and separation of ethanol and water (ethanol distillation). Dots and boxes outline scatter in published reports, and lines indicate upper and lower bounds on calculations done on the basis of partial information in published reports. See *SI Appendix* for a technical explanation.

indicate that separation processes span a wide range of concentration factors and second-law efficiencies, but they never exhibit both high concentration factor *and* high second-law efficiency. That observation helps explain observations made by Sherwood et al. (5, 6) that the total costs scale with the concentration factor: As more material is processed, more work input is required for moving and arranging the additional material. The trend apparent in Fig. 3 suggests that, for air capture, the second-law thermodynamic efficiency is likely to be significantly below 10%. Indeed, unless a new technology is shown to substantially deviate from the efficiency frontier in Fig. 3, it is reasonable to assume

that the second-law efficiency of an air capture system could be below 5%. Rather than conflict with Baciocchi et al.'s projection of a process with 13.5% second-law efficiency (24) (see Table 1), this empirical projection is indicative of the difference in performance between detailed process design with process components that have yet to be developed (i.e., Baciocchi et al.'s process, ref. 24) and as-built commercial processes as shown in Fig. 3.

Part 3: The Cost of Power to Operate Air Capture of CO_2 . If we assume a second-law efficiency of 5% for air capture systems, 400 kJ/(mol CO_2) of work will be required to separate CO_2 from the air. As a reference, a power plant fueled by natural gas, the least carbon-intensive fossil fuel, produces about 400 kJ of work for each mole of CO_2 emitted (see Table 2). Therefore, if one powered an air capture system with 5% second-law efficiency this way, then no net CO_2 would be removed from the atmosphere. Under such circumstances, air capture systems would need to be driven by nearly CO_2 -free power sources, which are more expensive than today's mix of CO_2 and non- CO_2 emitting power sources.

Determining the cost of CO_2 -free work is not easy because the work can take many forms for different technological approaches. As an estimate, however, we use the Energy Information Agency's 2009 Levelized Cost of New Generating Technologies (25), which we have incorporated into Table 2.

Table 2 indicates that carbon-free electricity will have a cost of electricity (COE) in the 10–20 ¢/kWh range in the foreseeable future. If we use a price of 10 ¢/kWh, then just the cost of required CO_2 -free work is about \$253/t CO_2 for the air capture system. Because additional capital investment that is unrelated to the cost of CO_2 -free work (i.e., capture equipment, land, etc.) is required, the total cost of air capture will be substantially higher than just the cost of the work.

Using a range of η and COE, Table 3 (which does not include capital cost) indicates that air capture cost estimates (including capital) of \$100–\$200/t CO_2 (see Table 3) will not be realized unless the capture system is shown to significantly deviate from the trends observed in Fig. 3.

Part 4: Work Required to Remove Trace Gases from Mixed Gas Streams. In air, CO_2 is a trace gas (i.e., at 400 ppm, it is present at a very low concentration). Therefore, it is instructive to examine the thermodynamic work required to remove trace gases from mixed gas streams in commercial processes. We examined a class of processes that involve the removal of the trace gases by reaction (i.e., the trace gas is chemically transformed to eliminate it from the original stream). For example, the process for removing

Table 2. The financial costs of powering air capture in dollars per tonne of CO_2 avoided as a function of the second-law efficiency as well as the source of work (25)

Plant type	Total levelized cost, \$/MWh (30)	CO_2 intensity, t/MWh	Electricity produced per CO_2 emitted, kJ/mole	Costs of the work required for air capture, \$/(t CO_2 avoided)	
				$\eta = 0.05$	$\eta = 0.02$
Conventional coal	95	1	158	N/A*	N/A*
IGCC	103	0.9	176	N/A*	N/A*
IGCC with CCS	123	0.2	792	666	N/A*
Natural gas-fired					
Conventional combined cycle	84	0.4	396	N/A*	N/A*
Advanced combined cycle	80	0.4	396	N/A*	N/A*
Advanced CC with CCS	116	0.08	1,980	381	1,571
Advanced nuclear	110	0	CO_2 -free	286	715
Wind	142	0	CO_2 -free	369	923
Wind—offshore	230	0	CO_2 -free	598	1,495
Solar PV	396	0	CO_2 -free	1,030	2,574
Solar thermal	264	0	CO_2 -free	686	1,716
Biomass	107	0.2	792	580	N/A*
Hydro	115	0	CO_2 -free	299	748

Note, these costs do not include capital costs. IGCC, Integrated Gasification Combined Cycle; PV, photovoltaic.

*N/A, using these energy sources to power air capture will emit more CO_2 than captured, making air capture infeasible.

Table 3. Cost of power only (dollars per tonne of CO₂) for an air capture system as a function of η and the cost of carbon-free power

η	10 ¢/kWh, \$	15 ¢/kWh, \$	20 ¢/kWh, \$
0.01	1,263	1,894	2,525
0.025	505	758	1,010
0.05	253	379	505
0.10	126	189	253

SO₂ from flue gas results in the conversion of SO₂ into CaSO₃. Such chemical processes are thermodynamically favorable, meaning that the processes could, in principle, be used to do useful work. Yet, in practice, these processes require substantial inputs of thermodynamic work, and the work requirements of these processes result from losses associated with the handling of the non-reactive material contained in the mixed gas stream. As such, it is useful to extend our investigation of the energetic dependence on initial concentration to processes that involve the thermodynamically favorable removal of minority gas species from mixed gas streams. In doing so, we characterized a relationship between the actual work used by various separation processes and the initial concentration of the trace gas that is to be removed (Table 4). Note that the actual work required to remove these trace gases from flue gas increases as the initial concentration of the trace gas decreases.

The removal of NO_x from flue gas, in particular, is worth considering because the initial concentration of NO_x in flue gas is approximately equal to that of CO₂ in ambient air. Typical NO_x-removing selective catalytic reduction (SCR) systems can reduce on average 80% of the NO_x from the flue gas (26) through the injection of reactive ammonia into the flue-gas stream. The overall reaction between ammonia and NO_x across an SCR catalyst, typically comprised of supported vanadia, to form H₂O and N₂ is thermodynamically favorable, meaning that, in theory, no work is required to remove NO_x from flue gas. In practice, however, nearly 500 kJ of work is expended per mole of NO_x removed to power the fan/blower system due to increased pressure drop across monoliths of catalyst. Additionally, the SCR unit is placed just downstream of the boiler exit so that reaction kinetics of reduction are enhanced by the elevated temperature of the flue gas.

In addition to the concentration similarity between NO_x in flue gas and CO₂ in air, both the removal of NO_x from flue gas and the removal of CO₂ from air use “end-of-pipe” cleanup techniques, and they both involve reaction on a solid surface (catalyst for NO_x, absorbent for CO₂). As such, the removal of NO_x from flue gas by commercial systems should provide insight into the thermodynamic work required to remove CO₂ from air. It is important to note, however, that NO_x removal differs from air capture because, aside from the physical differences of the substances, NO_x removal is a thermodynamically favorable process; NO_x removal does not produce a concentrated stream of NO_x; and NO_x

Table 4. The work used by commercial processes to remove trace substances via reaction

Substance, sep. process	C _{initial} , molar	Required work, kJ/mol
SO ₂ from flue gas, wet FGD	1.2×10^{-3}	380
SO ₂ from flue gas, lime spray dryer	1.2×10^{-3}	240
NO _x from flue gas, SCR	3.5×10^{-4}	490
Hg from flue gas, activated carbon injection	9.9×10^{-10}	1.1×10^7

Calculated from Integrated Environmental Control Software (IECM). Assuming a 500-MW power plant burning Appalachian medium sulfur coal NO_x reduction involves an SCR unit with a 73.48% removal efficiency; work = 488.31 kJ/molNO_x. See <http://www.iecm-online.com> for further details and current public version of the IECM (2007) software. FGD, flue gas desulfurization.

removal benefits from the elevated temperature of the flue gas. Thus, all of the key differences between NO_x removal from flue gas and CO₂ removal from air indicate that air capture of CO₂ will require more thermodynamic work than NO_x removal. It is therefore very likely that CO₂ capture from air will require more thermodynamic work than the approximate 500 kJ/mol used for NO_x removal. As discussed in the prior section, an air capture process using greater than 400 kJ/mol is counterproductive unless powered by carbon-free energy.

Biomass Combustion with CCS. Notably, there is an alternative indirect pathway for air capture that may ultimately offer a reasonable CO₂ offset: a biomass-based combustion power plant with CO₂ capture. Powered by the sun, CO₂ is captured from the air via photosynthesis and stored in the biomass, along with the solar energy. Next, the biomass is harvested and combusted to produce power. The relatively concentrated CO₂ in the flue gas (about 10%) is captured and stored, while the excess carbon-free power is available for sale. The net result is that solar energy is used to capture CO₂ from the air for storage in geologic reservoirs with production of CO₂-free electricity. Estimates for the total cost of capturing CO₂ from this process are in the range of \$150–\$400/tCO₂ (27).

One drawback to this approach will be scale, because an estimated 180,000 square miles of arable land (roughly 6% of the land area of the contiguous United States) will be required to capture one billion metric tons of CO₂ per year (28, 29). Another concern is the life-cycle carbon balance. Greenhouse gas emissions may be associated with growing, harvesting, and transporting the biomass, as well as land-use changes associated with growing energy crops. To account for these “fugitive” emissions, they must be subtracted from the gross amount of CO₂ captured. The low end of the cost range above assumes no fugitive CO₂ emissions, whereas the high end assumes the fugitive emissions equal 50% of the gross amount captured (27).

It should be noted that this process for removing CO₂ from the air does not violate the empirical trend that the efficiency of systems that remove trace substances from mixtures tends to scale inversely with the initial concentration because photosynthesis operates with a first-law efficiency seldom better than 2% (30, 31). So, in the case of biomass combustion with CCS, the total system does the same amount of material handling as industrial air capture systems; in the former, nature, rather inefficiently, does some of the material handling.

Part 5: Design Trade-offs for Air Capture Systems. The 300-fold concentration difference of CO₂ in flue gas (12%) and air capture (0.04%) causes the minimum work to increase by only about a factor of three. As reported by Sherwood and others, however, the financial cost of separation tends to scale inversely to the initial concentration because of the large material handling requirements. Those large material handling requirements affect both the capital costs of the separation equipment as well as the process’s second-law efficiency. To better understand the empirical results presented above, this section looks at design trade-offs inherent in any CO₂ capture process based on traditional solvent/sorbent looping systems.

In the first step of any separation system, the air must be contacted with a solvent or sorbent to capture the CO₂. In conventional settings, contacting would be achieved by blowing the air through scrubber towers. To capture the same quantity of CO₂ as a flue-gas-capture plant, and assuming the same fractional CO₂ removal, an air capture plant would need to process 300 times the volume of gas. Given practical limits on gas velocities in traditional scrubbers (32), conventional scrubbers for air capture would need significantly greater cross-sectional areas, but unlike point-source scrubbers, may consist of an array of flat or short modules, rather than tall columns. In a conventional point-source

scrubbing system, the solvent or sorbent loading and regeneration must maintain the pace dictated by the flue-gas flow rates, which are on the order of 3,000 t/h for a conventional 500-MW power plant, whereas the air capture system flow requirements will be dictated by the desired capture rates. Without major design modifications from the conventional, the expense of blowing or fan power may drive the cost of such a plant far above the order of magnitude estimates of the current work. Therefore, the air capture system will likely have to rely on a sorbent or solvent configuration that requires minimal effort to flow air through the system.

Whether the air is contacted with a solvent or sorbent via traditional blowers and scrubbers, or via more passive means, in a looping system, the solvent or sorbent must then be regenerated. That raises another issue because the driving force (i.e., the partial pressure of CO₂) for sorption in air capture absorbers is 300-fold less than in flue-gas absorbers. As a result, if one were to use the same solvents or sorbents in air capture as in flue gas, the sorption rates would be much lower, requiring much larger contact surface areas. Therefore, it is likely that the air capture system may require more selective binding, which can take the form of greater accessible surface area, faster kinetics, minimum diffusion constraints to the active site of adsorption or reaction, and/or enhanced binding to a given surface site or chemical solvent; otherwise, both the rich and lean solvent loadings will be lower, requiring significantly more energy to be expended in order to regenerate the solvent to the lower lean loadings (27), further driving up the potential costs of direct air capture. Stronger binding, however, may not be the best route because it will come at the expense of increased solvent regeneration cost and power. It becomes clear that, if the design and implementation of direct air capture plants were to move forward at the costs estimated in this work, they would have to be quite unique to the traditional gas scrubbing systems of point-source CO₂ emissions.

It has been suggested that, unlike a power plant, where a high recovery factor (i.e., the fraction of CO₂ in the gas stream that is captured) of 80–90% is an essential design constraint for point-source CCS to be a meaningful mitigation tool, the recovery factor for an air capture plant need not be so high (1). A lower recovery factor, however, is not necessarily beneficial. For example, operating with a recovery factor of only 45% (vs. 90%) will necessitate processing twice as much air (to capture the same tonne of CO₂), doubling the gas handling disadvantage from 300:1 to 600:1.

Concluding Remarks

Our empirical analysis of energetic and capital costs of existing, mature, gas separation systems indicates that air capture processes will be significantly more expensive than mitigation technologies aimed at decarbonizing the electricity sector. Unless a technological breakthrough that departs from humankind's accumulated experience with dilute gas separation can be shown to "break" the Sherwood plot and the second-law efficiency plot—and the burden of proof for such a process will lie with the inventor—direct air capture is unlikely to be cost competitive with CO₂ capture at power plants and other large point sources.

Our assessment indicates that air capture will cost on the order of \$1,000/t of CO₂. Through 2050, it is likely that CO₂ emissions can be mitigated for costs not exceeding about \$300/t of CO₂ (33). However, at some point in time, air capture conceivably could be a useful tool to mitigate emissions from distributed sources, and may even be deployed to reduce atmospheric concentrations of CO₂ below current concentrations. Air capture for negative net CO₂ emissions would follow the decarbonization of our electricity system and other large anthropogenic point sources and assumes abundant and inexpensive non-carbon energy sources.

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