LETTER

Flawed analysis of the possibility of air capture

In the article entitled "Economic and energetic analysis of capturing CO_2 from ambient air," House et al. (1) drew an analogy between air capture and other gas separation processes. It concludes that (*i*) "unless air capture significantly outperforms these systems, it is likely to require more than 400 kJ of work per mole of CO_2 " and (*ii*) "costs of air capture systems will be on the order of \$1,000 per tonne of CO_2 " (1).

The underlying logic in this conclusion is clearly circular because the key phrase is "unless" and is flawed in making a connection between energy used and cost. Furthermore, the article does not claim or prove that any fundamental law of thermodynamics or physics prevents the air capture system from outperforming the specific processes used for comparison, or that it cannot take considerably less than 400 kJ/mol of work. In fact, the notion of minimum work does not apply to the capture of CO₂, because the capture process is exothermic. This is a basic flaw in using a second law of thermodynamics analysis to compare CO₂ capture (air or flue gas) with analogous types of physical separation processes. From this perspective, we point out that the only fundamental difference between air capture at 400 ppm and flue gas capture at 10% is the well-known entropy difference of about 10 kJ/mol associated with concentrating the CO_2 (2). Furthermore, this implies that beyond that difference, there is no fundamental reason why CO₂ capture from relatively clean air at ambient temperatures need be more costly (or less costly) than flue gas capture of CO_2 from contaminated and hot flue gas.

There is one area of work and cost that could be an energy and cost problem for CO_2 from ambient air. That is the work required to move the large amount of air, about 2,500-fold or more than CO_2 captured, over a contactor containing a sorbent that will exothermally capture the CO_2 . A straightforward analysis will show that for this exothermic process, the work is related to the pressure drop in the contactor. In the well-studied parallel channel monolith contactors used in automobile catalytic converters to remove mono-nitrogen oxides chemically, pressure drops of 100 Pa have adequate surface area to capture a specific component effectively from the input gas stream. At this pressure drop, the work required is easily shown to be less than 6 kJ/mol.

Although additional energy will clearly be needed to liberate the CO_2 from sorbent, it is the same to the first order for both air and flue gas capture and can be in the form of cheap heat and not the expensive carbon free electricity used by House et al. (1).

For all the above reasons, we assert that the circular logic in the article fails to describe the energy and costs of air capture. Furthermore, there is no fundamental reason beyond the 10 kJ/mol why air capture need be more costly than flue gas capture. Given its other potential climate and economic benefits compared with flue gas capture, it certainly warrants effort to pursue economically viable approaches.

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^{1.} House KZ, et al. (2011) Economic and energetic analysis of capturing CO₂ from ambient air. *Proc Natl Acad Sci USA* 108:20428–20433.

Lackner K (2009) Capture of carbon dioxide from ambient air. Eur Phys J Spec Top 176: 93–106.

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LETTER

Reply to Realff and Eisenberger: Energy requirements of air capture systems

We strongly disagree with the statement made by Realff and Eisenberger (1) that the approach we used in our analysis of the energy requirements and of "air capture" systems is circular (2). On the contrary, our analysis is linear:

- *i*) We calculated the minimum work based on fundamental thermodynamics.
- *ii*) We then estimated second-law efficiencies using a large amount of empirical data from real processes.
- iii) We estimated the energy costs based on market prices.

The statement by Realff and Eisenberger (1) that "the notion of minimum work does not apply" is wrong. By definition, all air capture processes start with ambient air and produce a concentrated stream of CO₂, as well as a CO₂-depleted airstream. As shown in our paper (2), one can precisely calculate the difference in exergy between these two end points. This exergy difference is the minimum work required by any air capture process. The fact that proposed air capture processes may have exothermic steps has absolutely no impact on the minimum work requirement; if there is an exothermic step in the process and that energy is not recovered, as is generally true for CO₂ absorption processes, that lost energy becomes a source of process inefficiency. Furthermore, if all the energy in the exothermic step were harnessed and used to drive another step in the process, and if there were no other irreversible losses through friction, for example, that air capture system would require work input exactly equal to the minimum work.

We also understand that the exergy required by the process can be supplied in many forms. To keep our analysis straightforward, we chose to supply the exergy with carbon-free electricity. This has the benefits of (i) not having to worry about how much CO₂ is released by our energy source and (ii) easily determining its market price. We understand that there may be niche opportunities to provide this exergy at reduced prices. If air capture is to be deployed on a scale large enough to address climate change, however, it will need to pay market prices rather than niche prices. The idea that there are vast amounts of exergy available in the form of "cheap heat" is just not true.

Although we agree that "there is no fundamental reason" for air capture second law efficiencies to be lower than those for flue gas capture, we feel we present a very strong empirical case that it is so. This analysis relies on data from real processes that incorporate a large amount of engineering experience.

In our paper, we documented an empirical relationship between the second-law efficiency of separation systems and the concentration factor of those systems. It is physically possible for a new technology to break that empirical relation; however, until demonstrated experimentally, there is no reason to believe that the relation will not hold for air capture systems.

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^{1.} Realff MJ, Eisenberger P (2012) Flawed analysis of the possibility of air capture. *Proc Natl Acad Sci USA* 109:E1589.

House KZ, et al. (2011) Economic and energetic analysis of capturing CO₂ from ambient air. Proc Natl Acad Sci USA 108:20428–20433.