Assessment of reasonable opportunities for direct air capture

Jennifer Wilcox1, Peter C Psarras and Simona Liguori
Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO, United States of America
1 Author to whom any correspondence should be addressed.
E-mail: wilcox@mines.edu

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Abstract
This work explores the possibility of using CO2 captured directly from the atmosphere for several applications that require low to moderate purities. Comparisons of the minimum and real work for separating CO2 from air, natural gas combined cycle flue gas and pulverized coal combustion flue gas are proposed and discussed. Although it is widely accepted that the separation of CO2 from air to high purity is more energy-intensive than separating CO2 from more concentrated sources, this study presents select cases where the separation of CO2 from air to low and moderate purities is energetically equivalent with the work required for flue gas CO2 separation. These energetically-competitive cases are shown to be dependent on the percent capture and final CO2 purity desired. In particular, several technologies can be considered as CO2 utilization opportunities in which dilute CO2 may be an adequate feedstock. Specifically, this study is focused on enhanced oil recovery and microalgae cultivation technologies, which appear to be the most beneficial near-term applications for utilization of CO2 from direct air capture.

Introduction
Direct air capture (DAC) has received a great deal of attention in the mainstream due to its inherent appeal of the possibility of ‘going negative,’ that is, reversing society’s contribution to the increase in atmospheric CO2 concentrations associated with fossil fuel use since the Industrial Revolution, by removing CO2 directly from the atmosphere. The American Physical Society [1] reported on the feasibility of DAC using chemical absorption and estimated costs on the order of $600/tCO2, while House et al [2] carried out an investigation based upon a Sherwood analysis indicating costs on the order of $1000/tCO2. More recently, a report was published by the National Academy of Sciences [3] that lists DAC as one method of several that may be used to achieve negative emissions.

All of these studies agree that efforts should be focused in the near-term on mitigating or avoiding CO2 emissions in the first place. In 2004, Pacala and Socolow [4] published a pioneering study on what it would take for emissions to plateau through stabilization wedges that represent various mitigation strategies, i.e. increasing energy efficiency, carbon capture and storage, replacement of fossil fuels with renewables, etc. In 2011 [5], the trajectory was revisited and it was found that advances were not being made to reduce emissions, and that the trajectory was even worse than what was predicted in 2004. If as a global society, we fail to make progress toward mitigating emissions, then in 2100 we may find ourselves in a world that is 6 °C warmer than today, [6] which will have detrimental effects on human health, infrastructure and ports; in addition to food and water supplies. Depending on geography, some groups will surely be facing greater challenges than others.

It has been well established that the cost of separating CO2 increases with dilution. [2] That is, in the case of separating CO2 from the exhaust of a coal-fired power plant, the cost is less per mole of CO2 separated from a natural-gas-fired power plant, which is still less than the separation of CO2 directly from the atmosphere, each with approximate decreasing concentrations of 12%, 4%, and 0.04%, respectively. However, this is only the case if the percent capture and final CO2 purity are identical. In this study we define a parameter space for which the work required to capture CO2 from air is equivalent to separating CO2 from the exhaust of a natural-gas-fired power
plant. This parameter space exists at relatively low percent capture with corresponding low CO2 purities. We outline these parameters specifically and compare them against the work required for separating CO2 from more concentrated sources. The question then becomes; what applications exist for CO2 with purities less than 99.5%? These opportunities do exist, but are limited in number and scale.

Examples of CO2 utilization opportunities today include enhanced oil recovery (EOR), mineral carbonation, urea production, food and beverage, polymer processing, microalgae production, liquid fuels, and enhanced coal bed methane (ECBM) recovery. Most of these utilization opportunities, however, require high-purity CO2 as a feedstock. Examples in which the CO2 purity may be 50% or less include EOR, ECBM, microalgae production, mineral carbonation, and possibly liquid fuels. Of these opportunities, EOR is the only mature and commercially-available opportunity. The Global CCS Institute [7] reports that the cumulative global demand for EOR may be greater than 500 Mt up to 2020. In the EOR process, CO2 is injected into depleted oil fields, becomes miscible with some of the remaining residual oil, thereby decreasing its viscosity and allowing it to flow more freely to the production well. It is important to note that many of the studies that involve the use of dilute CO2 for EOR, include gas mixtures of N2 and CO2. These studies have shown that mixed-gas injection for EOR recovers only 80%–85% as much oil as pure CO2, but that the recovery process is quicker, which may lead to lower production costs [8]. In general, it is possible to use N2-diluted CO2 for EOR, and it may also result in greater viscosity reduction and higher oil swelling at an operating pressure typical for pure CO2 injection [9].

Another CO2 opportunity in which high purity is not necessary is for microalgae production, which has been described by the International Energy Agency (IEA) as an emerging use of CO2, with a potential of 300 MtCO2 yr⁻¹ [11]. There are several projects underway that use both air and exhaust gas streams as inputs for microalgae production and a number of companies that are interested in sourcing CO2 from petroleum processing or exhaust streams, in particular. Some of these include Trident Exploration Corporation and Menova, Eni Tecnologie R&D, and NRG Energy and Green Fuel Technologies. In addition, recent work of Moreira and Pires [12] has focused on microalgae growth with CO2 as a feedstock from both air and flue gas sources. Since flue gas streams contain ppm levels of acid gases such as NOx (NO and NO2) and SOx (SO2 and SO3), it is important to understand the effect that these gases may have on microalgae cultivation. In particular, SO2 has been shown to have a significant effect on growth rates and algal health. For instance, at SO2 concentrations greater than 400 ppm, the pH of the microalgae-containing medium may be reduced to less than 4 over the course of a day. However, studies by Matsumoto et al [13] have shown that the addition of NaOH to maintain a pH of 8 prevents decrease in microalgae growth. In terms of NOx tolerance, Zhao et al [14] showed that microalgae may tolerate NOx concentrations of 240 ppm and with a pH adjustment. In addition, Lackner et al have described the promise of algae-based fuel production using DAC CO2 as an input [15] and have worked to develop an anion exchange material coupled to humidity swing regeneration for the separation of CO2 followed by delivery to microalgae cultures [16].

In many of the microalgae cultivation processes, CO2 is absorbed by microalgae to produce biomass. The process of making oil from microalgae is expensive, so microalgae cultivation has historically been limited to high-value nutraceutical products, which represent a very small market. The costs of these products range from $60–$3500 per kg compared to a Phase I DARPA goal of $0.61 per kg (i.e. less than $2/gallon) [17]. The high cost of transforming the microalgae biomass to useful products may limit the impact that this opportunity could have. A recent study reported that maximum biomass production and rate of growth were obtained at a CO2 concentration of 35%, nearly three orders of magnitude higher than ambient CO2 at 0.04% [18]. In this study we compare the work required to separate CO2 from the atmosphere to the desired purities for EOR and microalgae cultivation technologies, which appear to be the most beneficial near-term applications for utilization of CO2 from DAC.

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2 Fuel combustion emissions and grid emission factors based on Australian life cycle data. LCA boundaries include CO2-e emissions associated with EOR operation (92%) and equipment/facilities (8%).

3 2011 US Dollars.
Methods for calculating minimum work, second-law efficiency, and real work

The laws of thermodynamics preclude the operation of any process at 100% efficiency; thus, there will always exist a quantifiable gap between the theoretical minimum work required to achieve a process (in this case, separation of a gas mixture), and the actual work required. The ratio of these two estimates is known as the second-law efficiency, \( \eta \), defined as:

\[
\eta = \frac{w_{\text{min}}}{w_{\text{real}}} \quad (1)
\]

and typically ranges from 5%–40% for real-world separation processes [2]. The theoretical minimum work is calculated from combined first and second laws of thermodynamics [17]:

\[
w_{\text{min}} = RT\left[\left(n_rCO_2\ln X_rCO_2 + n_e\ln X_e\right) + \left(n_pCO_2\ln X_pCO_2 + n_p\ln X_p\right) - \left(n_rCO_2\ln X_rCO_2 + n_e\ln X_e\right)\right] \quad (2)
\]

where \( n_rCO_2 \) and \( n_e \) represent the number of moles of CO\(_2\) and non-CO\(_2\) components in stream \( x \), respectively; likewise, \( X_rCO_2 \) and \( X_e \) represent the mole fractions of CO\(_2\) and non-CO\(_2\) components in stream \( x \), respectively.

For DAC, the input stream is treated as a binary mixture of CO\(_2\) and N\(_2\). Here, the input stream is characterized by a CO\(_2\) composition of 0.04 %, and an ambient temperature of 298.15 K; thus, the desired permeate stream CO\(_2\) purity and overall process CO\(_2\) percent capture can be achieved by manipulating the composition of the retentate and permeate streams. Minimum work values for separating CO\(_2\) from three different gas mixtures are shown in figure 1. In regions of outlet CO\(_2\) purities of less than 10% and for less than 60% capture, the minimum work for DAC is shown to be 8–10 kJ mol\(^{-1}\) CO\(_2\), which is similar to the minimum work required to separate CO\(_2\) from natural-gas-fired power plant exhaust for 90% capture to a final CO\(_2\) purity greater than 95%.

In the case of CO\(_2\) separation from natural gas exhaust, the minimum work increases reaching a maximum of approximately 14 kJ mol\(^{-1}\) CO\(_2\) for greater than 60% capture and outlet purities above 90%. In the case of CO\(_2\) separation from coal-fired power plant exhaust, where initial CO\(_2\) concentrations are on the order of 12%, the minimum work is less than 8 kJ mol\(^{-1}\) CO\(_2\) for higher purities and above 50% capture. The end purity (or outlet purity) is dictated by the specific CO\(_2\) application, where microalgal cultivation occupies the lower end with desired purities ranging between 5%–35%, followed...
by EOR with purities ranging from 50+%, followed by chemical processing and food and beverage processing, which requires high-purity CO2 as a feedstock, or International Society of Beverage Technologists (ISBT) grade, i.e. 99.9%.4

The real work required for the separation of CO2 from ambient air is unknown; thus, it is necessary to define a reasonable approach to the estimation of $\eta$ and real work for DAC based on similar, more thoroughly understood processes. Here, we use the Carnegie Mellon Integrated Environmental Control Module (IECM) [19] to determine the real work of CO2 separation (including compression) at variable percent capture for two distinct input streams, i.e. 4% CO2 for NGCC separation and 12% CO2 for PCC separation. An additional data point for DAC is included, based on results of the APS study of Socolow et al [1] These ‘real work’ projections are then compared to the minimum work calculated for NGCC and PCC processes to establish $\eta$ values as a function of exhaust composition, flow rate, and percent capture.

Real work projections for DAC were calculated by applying the estimated $\eta$ values to the theoretical minimum work under the same conditions (i.e. end purity and percent capture) as indicated in figure 1. The difference between the real work calculated for the DAC scenarios and the real work calculated for typical NGCC and PCC applications is quantified by subtracting the projected work for NGCC separation (91.6 kJ mol$^{-1}$ CO2) and PCC separation (28.5 kJ mol$^{-1}$ CO2), respectively, from the projected work for DAC separation. Real work for NGCC and PCC capture were calculated at identical conditions to the minimum work calculations: 333.15 K, 90% percent capture, 99.5% purity, and 4% and 12% CO2 flue composition for NGCC and PCC, respectively.

### Results

The second-law efficiencies of CO2 separation from the exhausts of PCC and NGCC power plants are shown as a function of percent capture and end purity in figure S1 available at stacks.iop.org/ERL/12/065001/mmedia. The second-law efficiencies, as described in greater detail in the methods section, were calculated from the ratio of the calculated minimum work and the real work, based upon available pilot-scale data sourced from IECM. Given that separation technologies for DAC to these final CO2 purities of interest do not exist today, this simple model was used to estimate second-law efficiencies for these unknown processes. Select, pertinent values are presented in table 1. Values presented in the upper half of table 1 were used in the multivariate regression analysis, whereas values in the bottom half of table 1 represent second-law efficiency predictions from this analysis for select DAC/utilization pairings. Because both the input stream purity and output stream purity serve as model inputs, it is sometimes more useful to describe them as a single ratio, $[\text{CO}_2]_{\text{out}}/[\text{CO}_2]_{\text{in}}$, or concentration factor, $C_f$. As

| $[\text{CO}_2]_{\text{in}}$ vol% | $[\text{CO}_2]_{\text{out}}$ vol% | Concentration Factor | Percent Capture (%) | Min Work (kJ mol$^{-1}$) | Second-Law Efficiency ($\eta$) | Real Work (kJ mol$^{-1}$) |
|-----------------------------|-----------------------------|---------------------|---------------------|--------------------------|-----------------------------|--------------------------|
| NGCCa 4 99.5 24.9 90 10.7 0.12 91.6 | NGCCa 4 99.5 24.9 80 10.4 0.11 92.5 | NGCCa 4 99.5 24.9 60 9.9 0.1 99 | PCCa 12.12 99.5 8.2 90 7.7 0.27 28.5 | PCCa 12.12 99.5 8.2 80 7.3 0.24 29.8 | PCCa 12.12 99.5 8.2 60 6.7 0.2 33.9 | DACb 0.04 99.5 2487.5 50 20 0.03 400 |
| DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 |
| DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 | DACb 0.04 99.5 2487.5 50 20 0.03 400 |

a Data obtained from the Carnegie Mellon Integrated Environmental Control Module (IECM). Ref. [20]
b Data obtained from [1]
c Second-law efficiency and real work calculated from regression analysis (method in SI).

4 The International Society of Beverage Technologists (ISBT) sets out quality guidelines for CO2 for use in food and beverage applications at 99.9% v/v CO2 minimum.
indicated in table 1, the second-law efficiency decreases with increasing concentration factor.

Figure 2 shows the projected real work for CO₂ separation from air, plotted as a function of end purity and percent capture. The difference between the real work for CO₂ separation from air versus exhaust streams is shown in figure 3 and identifies the parameter space where the energy penalty for DAC is most similar to that incurred in NGCC and PCC systems. This can be viewed as the energy premium (in kJ mol⁻¹) to separate CO₂ from ambient air over CO₂ separation from natural gas and coal exhaust streams.

**Discussion**

Within this study, real work estimates were presented for concentrating CO₂ from atmospheric conditions to concentrations that may be useful primarily for microalgae and EOR opportunities. This was achieved
by dividing the calculated minimum work (figure 1) by the extrapolated second-law efficiency (figure S1). As shown in table 1, the range of second-law efficiency values narrows as the concentration factor increases, i.e. as the desired final purity of CO₂ increases in the case of DAC. This trend in second-law efficiency is in agreement with the previous study by House et al [2].

In the case of CO₂ utilization opportunities for microalgae cultivation, the real work required for CO₂ separation from air is equivalent to that of removing CO₂ from the exhaust of a NGCC plant (assuming 90% capture and 99.5% purity) for greater than 40%–50% capture. For EOR applications, assuming a 50% purity CO₂ stream as a feedstock, the real work competes with CO₂ separated from natural gas exhaust at values above 80% capture. The real work parameter space is more limited when comparing between CO₂ separation from air versus the exhaust of a coal-fired power plant. For instance, the work requirements of CO₂ separation are competitive in the case of microalgae cultivation within 50%–60% capture. For EOR applications, the separation of CO₂ will always require more work than CO₂ separation from coal exhaust for conditions of 90% capture and 99.5% purity. Naturally, the optimal range for CO₂ utilization from DAC exists where the premium in energy of separation over NGCC and PCC is minimized. This is depicted as dark blue regions in figure 3, where the end purity falls between 0%–20% and the percent capture is in excess of 40%. Nine worked examples are provided in table 2 to better illustrate a direct comparison between the estimated real work involved in the separation from DAC versus fossil fuel exhaust streams to various utilization opportunities.

Although EOR and microalgae cultivation were the focus of this study, there may be other emerging CO₂ utilization opportunities that could tolerate dilute CO₂ as a feedstock. These may include, but are not limited to ECBM recovery, mineral carbonation, and liquid fuel synthesis. In ECBM, CO₂ is injected into coal seams where it preferentially adsorbs into the pores of the coal matrix, thereby displacing methane. This mechanism of enhanced recovery is very different than EOR. The Global CCS Institute reports that there may be significant opportunities for ECBM using CO₂ in China, with an estimated 140 Gt of CO₂ of storage following methane recovery [7]. In terms of both mineral carbonation and liquid fuel synthesis, CO₂ is a feedstock in a chemical reaction. Although prior investigations typically assume the CO₂ to be highly pure, [21, 22] this is not essential, provided that the gas in which it is diluted is not competing in the chemical reaction. If nitrogen is present in the gas mixture, for instance, since it is inert its reactivity will be negligible. However, since the reaction rate is directly proportional to the reactant concentration, the rate will decrease with decreasing CO₂ concentration, which may impact the capital costs of the operation.

Although we do outline possible opportunities for dilute CO₂ in this study and an estimate of the work required to concentrate CO₂ from air to various purities for several utilization opportunities, it is important to recognize the challenges that persist. For example, in the case of EOR, depending on the reservoir characteristics, on the order of 50%–70% of the CO₂ injected returns to the surface with the oil since the ultimate goal for EOR today in the absence of CCS subsidies or a carbon tax is not to sequester the CO₂, but to use it for enhanced recovery. In terms of microalgae cultivation, unlike EOR, it is not recognized today as a commercial-scale operation. It has been reported that commercial-scale systems will require in the range of 10–100 hectares, which would lead to CO₂ uptake of between 500 to 5 000 tCO₂ yr⁻¹. Again, as mentioned previously, to convert microalgae into biofuel, the costs need to be reduced nearly 100-fold from today's estimates. The primary market for biomass produced from microalgae today are high-priced nutraceutical products, which represents a very small market having the consequence of a nearly negligible impact on CO₂ utilization.

## Conclusions

There is no question that the separation of CO₂ from the air will always be more energy-intensive and costly than separating CO₂ from more concentrated sources, such as the exhaust streams of coal- and natural-gas-fired power plants; however, the increased energy and cost required for DAC will depend on the percent capture and final CO₂ purity desired. Several CO₂ utilization opportunities were considered in this study in which dilute CO₂ may be an adequate feedstock. These include, but may not be limited to EOR, microalgae cultivation, ECBM, mineral carbonation, and fuel synthesis. The most commercially advanced opportunity is EOR. Although it is evident that dilute

### Table 2. Estimated real work (kJ mol⁻¹) for separation of CO₂ in nine unique source-utilization pairings.

|                | 50% Capture | ISBT | 90% Capture |
|----------------|-------------|------|-------------|
|                | Algae       | EOR  | Algae       | EOR  |
| PCC            | –0.0°–11    | 17–39| –0.0°–10    | 15–29| 29+|
| NGCC           | –0.0°–52    | 66–108| 108+        | 61–95| 93+|
| DAC            | 216–440     | 493–635| 635+        | 308–399| 399+|

* Negligible work assumed for cases where [CO₂]outlet < [CO₂]inlet.
CO₂ may be used for EOR, one needs to be aware that recovery may decrease with increasing dilution. In addition, it was estimated that a downstream separation process for oxygen may likely increase the energy requirement for separation by approximately 10%, which would be required for EOR opportunities. Further, to date, EOR is not intended for reliable CO₂ storage and a large fraction of the CO₂ used in EOR is separated from the recovered oil at the surface for reuse. In terms of microalgae cultivation, although CO₂ purities between 5% and 35% may be adequate for sufficient microalgae production, the limiting factor is the conversion of the microalgae biomass to a marketable product in addition to handling the acid gases often present in exhaust streams. If DAC is to be implemented in the near-term, it will be important to identify further opportunities for using dilute CO₂ as a feedstock, whereby the energy required for concentrating CO₂ from the air is lower.

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