

Removing Carbon Dioxide from the Atmosphere – Assessing the Technologies

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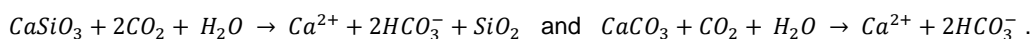
Current emission scenarios envisage the potential draw-down of around 810 Gt CO₂ from the atmosphere by 2100. This would require some 110×10^{12} kWh of reversible work, and the energy needed to drive the CO₂ capture processes would approach, and may even exceed, the energy gained in burning the fossil fuel in the first place. Negative Emission Technologies (NETs) would be needed at huge scale, motivating a search for novel, highly energy-efficient approaches. Separation processes such as CO₂ capture involve dissipation of energy in diffusion, the losses being greater when higher transfer rates are utilised to reduce equipment size. A process for generating power for air capture by humidifying dry air is analysed using an equivalent reversible process, which yields minimum utility requirements and maximum (reversible) efficiency. Comprehensive socio-economic and environmental assessments of NETs are needed. The Process Analysis Method provides a triple-bottom line sustainability assessment, but results are dependent on uncertain external factors such as the introduction of flue gas-CCS and the growth rate of renewables. The challenge for NETs becomes easier the faster the transition to a low-carbon economy occurs.

1. Introduction

The accumulation of greenhouse gases in the atmosphere can be reduced by cutting emissions, but elevated levels of CO₂ will persist for centuries (Lowe et al., 2009). Since climate models show that peak CO₂-induced warming depends mainly on cumulative emissions and not the emission pathway, later in this century we may wish to draw down CO₂ to counter unacceptable climate change. NETs are the methods proposed for this CO₂ removal. It is more efficient to capture carbon from flue gas, but even if applied quickly on a vast scale this on its own is not sufficient to reach policy targets - for example that agreed at Paris in 2015 (peak warming 1.5°C above pre-industrial temperatures). Figure 1 suggests the need for net-negative global emissions by 2090, so NETs must be introduced from at least 2040, to ramp up to the scale needed. The target is huge – to draw down 810 Gt of atmospheric CO₂ (range 440-1020 Gt) by the year 2100 (UNEP, 2017).

However, whilst it is relatively simple to build NETs into climate models, these are mostly new and often unproven technologies, certainly for the scale needed. For example the coupled system, BECCS, Bioenergy with Carbon Capture and Storage, takes CO₂ from the air by growing fuel crops, then removes it from the combustion process for compression and storage underground. It is the technology most commonly assumed in climate modeling work. However, producing biofuel at the scale required would create serious competition for land which currently supports food production or diverse natural ecologies (Boysen et al., 2017). And there are few operational applications of CCS at present, even for conventional power station flue gas.

An alternative to BECCS as a negative emission technology is Direct Air Capture (DAC), in which CO₂ is taken from the air by physical or chemical sorption taking place in some more or less conventional processing equipment. An example is described by Holmes and Keith (2012). There is an energy penalty per unit mass of CO₂ captured relative to capture from flue gas, and the volumes of gas to be treated are also much larger. A further series of NETs proposals suggests reacting atmospheric CO₂ with suitable minerals. This obviates the need for CO₂ storage. Typical reactions are



These reactions are a natural part of the carbon cycle, and can perhaps be stimulated to draw down more CO₂ more quickly by methods known as Enhanced Weathering. If the bicarbonates are washed into the sea, they join a carbon sink which is sixty times greater than that in the atmosphere, so have comparatively little effect. Various schemes have been suggested including spreading suitable mineral particles on agricultural land (which can also improve soil quality), and reacting CO₂ with mineral waste from mining. The extent to which such reactions can be used to “fix” CO₂ injected to underground storage is unclear at present. Other Negative Emission Technologies (see UNEP, 2017) include promoting the growth of algal bloom on the ocean (Ocean Fertilisation) and the use of Biochar (as adsorbent) on land. Afforestation and other Land-use management methods can draw down CO₂ and also have other beneficial side effects.

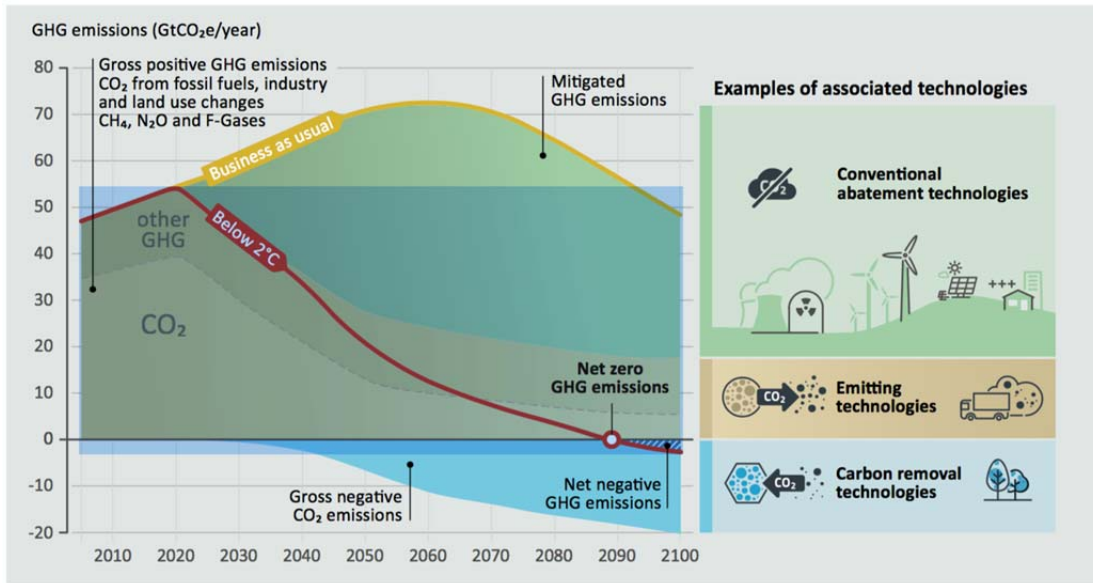


Figure 1. Emissions scenarios to 2100 showing the potential need for NETs. UNEP, 2017, Figure 7.2

2. Energy considerations in Direct Air Capture (DAC)

One of the major challenges in capturing CO₂ from the atmosphere is the work of separation that is needed, which is higher than for capture from flue gas. The reversible work needed to separate a flow of gas into pure carbon dioxide and a second “reject” stream which may contain some CO₂ and will contain all the other components in the feed can be calculated from the change in Gibbs free energy. The reversible work w_{rev} per mole of recovered CO₂ for feed and products at temperature T and constant pressure is given by

$$\frac{w_{rev}}{RT} = \ln \frac{1}{y_c} + \frac{1-\alpha}{\alpha} \ln \frac{1-\alpha}{1-\alpha y_c} + \frac{1-y_c}{\alpha y_c} \ln \frac{1}{1-\alpha y_c} \quad (1)$$

where y_c is mol fraction of CO₂ in the feed and α is the fraction of inlet CO₂ recovered in the pure CO₂ stream. With $\alpha = 1$ the reversible work required for taking CO₂ from air is 0.136 kWh/kg CO₂, at 293K. The reversible work is reduced by allowing some CO₂ to slip into the reject stream ($\alpha < 1$), though the benefit is slight as shown in Figure 2. Limiting the recovery of CO₂ to 10% only reduces the specific reversible work by about 10%, at the cost of having to process ten times as much air to capture the same amount of CO₂.

The standard enthalpy of formation of CO₂ is (-)2.484 kWh/kg, some 18 times w_{rev} for DAC from Eq (1). So it might seem that the energy cost of DAC, is comparatively low, perhaps to be supplied by burning fossil fuel. However w_{rev} is a work, not a heat, requirement. Separation processes that have been suggested for DAC include adsorption by particles and absorption in alkaline solvents such as amine solutions. These sorbents require regeneration, a process step involving heat input, so the sorption process functions as a separation engine, producing waste heat in addition to work of separation. The Carnot efficiency of such an engine, η_{Car} , can be estimated. For example for an amine treater, regenerating with low pressure steam at $T_H \sim 403K$, and removing heat in the overhead condenser and trim cooler at a mean temperature of $T_C \sim 343K$, $\eta_{Car} (= 1 - T_C/T_H)$ is 0.17 or $\sim 1/6$. Furthermore the Carnot efficiency refers to a reversible process. In practice, real equipment cannot avoid energy dissipated by friction and in transferring heat and mass across finite gradients. The efficiency of a real process might be perhaps a third to half the Carnot value, though this will depend on the process and the design choices made. The heat requirement of an actual DAC plant would then be around 12-

18 times w_{rev} , that is ~ 1.6 - 2.4 kWh/kg CO_2 . Thus the energy needed for DAC will approach, and may even exceed, the energy obtained by burning the fossil fuel in the first place (2.484 kWh/kg).

The validity of these estimates is supported by data for flue gas capture in power plants. The extra energy required for CCS in coal-fired plants is in the range 24-40%, and for natural gas in the range 11-22% (IPPC, 2005). With $\alpha = 1$, w_{rev} from Eq (1) and an overall efficiency of 1/12 - 1/18, we calculate the power loss for coal ($y_c=12\%$) and gas ($y_c=5\%$) fired power plants to be 23-34% and 15-22% respectively. Compression energy needed to transport CO_2 to underground reservoirs is neglected in this calculation – compressors are much more efficient than separation processes, and they add only a few percent to the power loss.

Capturing the target amount of 810 Gt CO_2 by 2100 needs about 110×10^{12} kWh of reversible work, which might consume say 1320 - 1980×10^{12} kWh of energy with conventional separation technology. In comparison, global primary energy consumption in 2016 was 155×10^{12} kWh (BP, 2017). These numbers drive the search for novel less energy-consuming separation processes to capture carbon dioxide – and should also motivate the use of very much less fossil fuel and the rapid transition to a low-carbon energy economy.

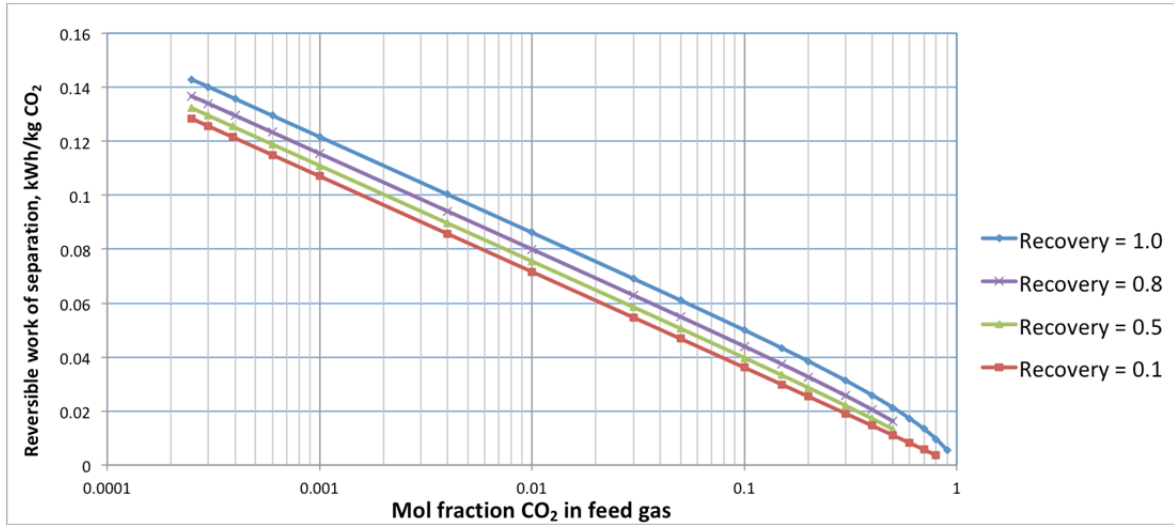


Figure 2. Reversible work of separating CO_2 from other gases. Concentration in air is currently 400 ppm; in flue gas generally ~ 3 -15%. Calculation for $T=293\text{K}$.

3. Diffusive dissipation losses in mass transfer during absorption

The development of better processes needs understanding of where inefficiencies arise. Both heat and mass transfer need to be optimised, for example using pinch analysis, since the energy they dissipate has to be supplied as extra heat or work. Here we consider losses in mass transfer. The force F per mol of a component with concentration c causing diffusion in the z -direction is the negative gradient of chemical potential:

$$F = -\frac{RT}{c} \cdot \frac{dc}{dz} \quad (2)$$

When the molecules move a small distance dz they do work $F \cdot dz$, which is dissipated by frictional resistance. The irreversible loss, per mol, when diffusing from c_1 to c_2 is equal to the work done which is

$$w_{irr} = -RT \int_1^2 \frac{dc}{c} = RT \ln \frac{c_1}{c_2} \quad (3)$$

This diffusive dissipation is exactly equal to the change (reduction) in Gibbs free energy. If, as is the case in an absorber, the component transfers from gas to liquid, there is diffusive dissipation in both phases: $RT \ln(p_b/p_i)$ in the gas and $RT \ln(c_i/c_b)$ in the liquid. Here p is the partial pressure, and subscripts b and i denote bulk and interface respectively. The interface will be locally at equilibrium, so that Henry's law $p_i = Hc_i$ applies there. Summing the two terms gives the total dissipation per mol diffusing as

$$w_{irr} = RT \ln \frac{p_b}{Hc_b} = RT \ln \frac{p_b}{p^*} = RT \ln \frac{y}{y^*} \quad (4)$$

where p^* ($=Hc_b$) is the partial pressure that would be in equilibrium with the actual bulk liquid composition, and y , y^* are the gas phase mol fractions corresponding to p_b and p^* . Over an element of absorber height in which

y changes by dy the diffusive dissipation rate is $\{RT \ln(y/y^*)\} G dy$, where G is the molar flow rate of gas. Over the absorber from top (T) to bottom (B) the total rate of diffusive dissipation is

$$W_{irr,tot} = w_{irr,tot} G (y_B - y_T) = RT \int_{y_T}^{y_B} \ln(y/y^*) G dy \quad (5)$$

If Henry's law with a constant value of H can be assumed to apply over the whole absorber (eg physical absorption in dilute systems), the ratio of slopes of equilibrium and operating line, the stripping factor S , will be constant, and by mass balance $dy^* = S dy$. Eq (5) then gives the total dissipation per mole transferred as

$$W_{irr,tot} = \frac{RT}{y_B - y_T} \left\{ \int_{y_T}^{y_B} \ln y dy - \frac{1}{S} \int_{y_T^*}^{y_B^*} \ln y^* dy^* \right\} = RT \left\{ \frac{y_B \ln y_B - y_T \ln y_T}{y_B - y_T} - \frac{y_B^* \ln y_B^* - y_T^* \ln y_T^*}{y_B^* - y_T^*} \right\} \quad (6)$$

a result independent of S . An indication of the height of absorber that is needed for a given degree of separation – the duty – is given by the number of overall gas phase mass transfer units, N_{OG} . For a constant stripping factor this is calculated from a well-known analytical result

$$N_{OG} = \frac{y_B - y_T}{(y - y^*)_{LM}} \quad (7)$$

where $(y - y^*)_{LM}$ is the log mean of $y - y^*$ between absorber bottom and top. Figure 3 shows N_{OG} for 90% recovery of CO_2 (i.e. $y_T/y_B = 0.1$) from air at 293K. Curves are plotted for values of y_B/y_B^* from 1.1 to 10 - as this parameter increases diffusive dissipation increases. As N_{OG} increases at constant y_B/y_B^* the operation moves closer to equilibrium and dissipation decreases, though a limit is reached as $y_T \rightarrow y_T^*$ (approach to pinch at the top), so adding further transfer units gives little benefit. From Eq (7) the minimum value of N_{OG} is $\ln(y_B/y_T)$, when back pressure from the solvent (i.e. y^*) is negligible. For this case $N_{OG,min}$ is $\ln 10 (= 2.3026)$.

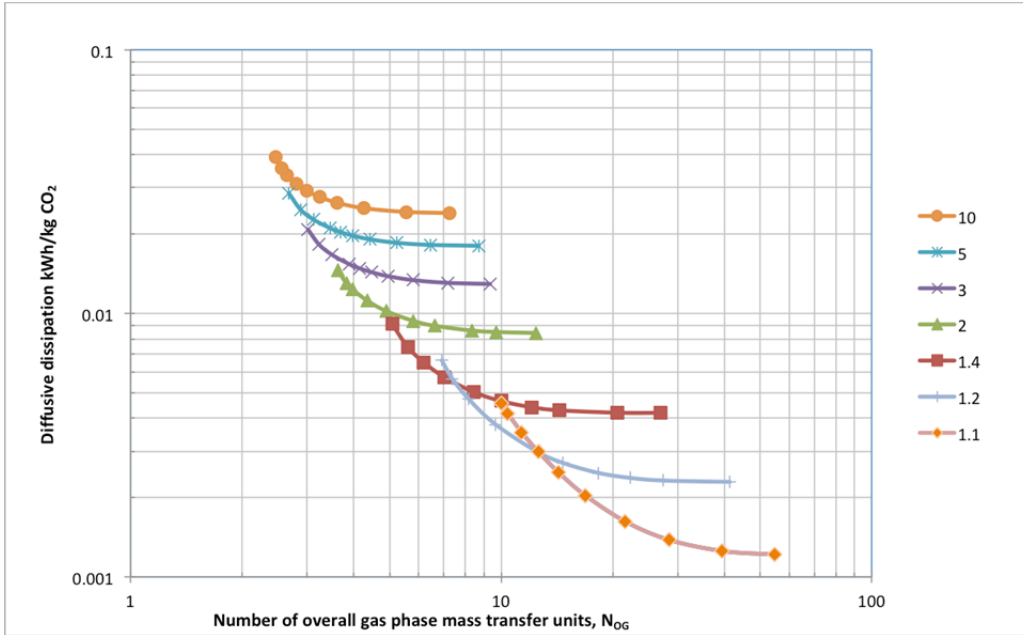


Figure 3. Diffusive dissipation in absorber, with $y_T/y_B = 0.1$ and parameter y_B/y_B^* . N_{OG} from Eq (7).

Column pressure drop is proportional to N_{OG} , and must be kept low to minimise compressor costs when processing large volumes of air. Diffusive dissipation losses are also incurred in the solvent regenerator. If a reactive solvent is used there is likely to be an approach to pinch in the middle of the column as the solubility decreases markedly at higher loading. This increases N_{OG} and gas and liquid will be far from equilibrium at the top of the regenerator, increasing diffusive dissipation losses.

4. A humidification engine to provide work of separation

Lackner (2013) suggested an ingenious scheme for generating the work of separation for DAC by evaporating water. Lackner's process involves a solid adsorbent, but its feasibility can be demonstrated by analysing a

reversible process with the same inlets (dry air and pure water) and outlets (humid air), as shown in Figure 4. Dry air at atmospheric pressure p_0 enters an isothermal reversible expansion turbine producing work w_{rev} , with outlet pressure $p_0 - p_{sat}$, where p_{sat} is the saturated vapour pressure of water at temperature T . The expanded dry air enters a reversible mixing chamber through a membrane which is permeable only to air (not water). Water vapour flows in through a membrane that only passes water (not air). The mixing chamber contains saturated humid air at (p_0, T) , which is exhausted to atmosphere. Heat q_{turb} is supplied to the turbine, equal in quantity to w_{rev} , to maintain isothermal conditions. Heat is also transferred to the water, q_{evap} , to provide latent heat of evaporation. Concentration and temperature gradients are infinitesimal, and there is no viscous dissipation. The thermal efficiency ($=w_{rev}/(q_{turb} + q_{evap})$) varies from 5.16% at 20°C to 5.53% at 50°C.

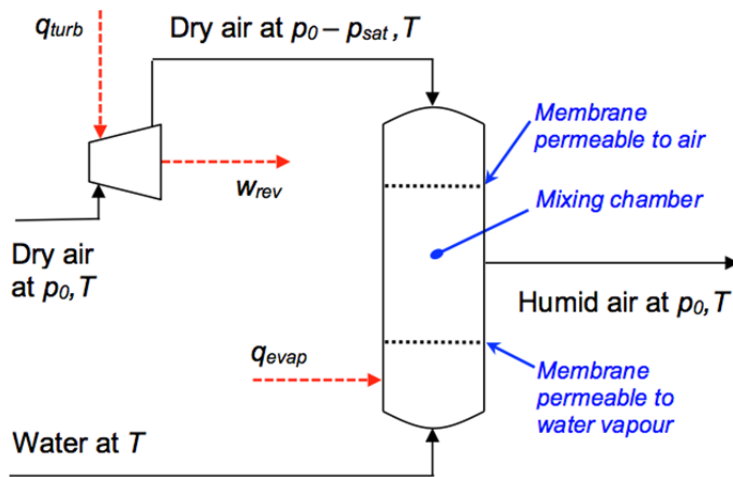


Figure 4. Notional reversible process to generate power by humidifying air

The reversible Lackner humidification engine (Figure 4) could supply power to a reversible separation process capturing CO₂ from air whose performance is given by Eq (1). The coupled process working at 20°C needs 3.67 kg water for every kg CO₂ captured, rising to 3.88 kg water at 50°C. But any practical embodiment would be far from reversible. Making assumptions for typical losses and driving forces suggests that the water requirement might be ten times the minimum (reversible) value – around 35 kg water per kg CO₂ captured.

5. General assessment

Removing greenhouse gases from the air at sufficient scale to affect the global climate (geoengineering) would be a vast undertaking. It raises questions of public policy, for which Rayner et al. (2013) suggested five basic principles. These include the regulation of geoengineering as a public good, and the disclosure of research with open publication of results. Independent assessment is proposed, to "...address both the environmental and socio-economic impacts of research, including mitigating the risks of lock-in to particular technologies or vested interests". Fourteen NETs were assessed by McLaren (2012), primarily to identify their potential, and major risks. However there has been little comprehensive independent assessment of the environmental and socio-economic impacts, because the technologies are not mature (technological "imaginaries" in many cases) and would be deployed over many decades against a political, environmental and economic background that is uncertain. Also tools for such assessments are not well developed.

A technique that can assess socio-economic and environmental impacts is the Process Analysis Method (PAM, see Darton, 2017), a triple-bottom line methodology which identifies the impact of system processes in the three domains: Human/social, Economic and Environmental as shown in Figure 5(a). Computer modelling is not required, and the method is based on a comprehensive description of activities within the system boundary. The structure of PAM is shown in Figure 5(b). In the Sustainability framework (step 4 in Figure 5(b)) impacts, issues and indicators are inventorised. This results in a set of indicators quantified as metrics, which measure the sustainability of the system. Applying the PAM to NETs shows the importance of defining deployment pathways and coupled energy and emissions scenarios as consistent background to the identification of impacts. For example, the timing and extent of the application of flue gas-CCS will be of major importance, as will the advance of renewables. These are uncertain factors, but it is clear that the challenge of NETs becomes easier the faster the transition to a low-carbon economy occurs.

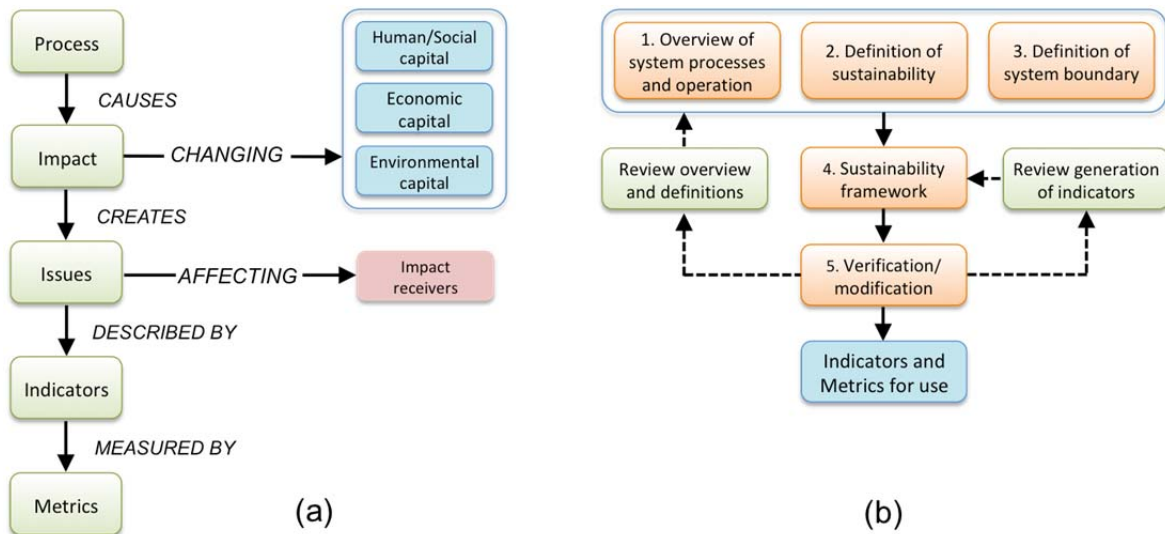


Figure 5(a) Chain of Cause and Effect; Figure 5(b) Structure of the Process Analysis Method. Darton, 2017

6. Conclusions

- Removing carbon dioxide from the atmosphere could become an important growing industry by 2040, with a target of capturing up to a trillion tons of CO₂ by the year 2100.
- CO₂ absorption processes need heat equivalent to around 12-18 times the reversible work of separation, mainly due to poor Carnot efficiency, but also frictional and diffusive dissipation.
- Energy dissipation due to diffusion in absorption or desorption can be reduced by operating nearer to equilibrium using more transfer units, but this incurs a pressure drop penalty. For CO₂ capture from air the trade-off will generally result in absorbers with low N_{OG} . Operation of a solvent regenerator close to equilibrium will often be hampered by an approach to pinch within the column.
- The generation of power to drive CO₂ capture by humidifying dry air as suggested by Lackner (2013) is shown to be possible, but has a low thermal efficiency - theoretical maximum about 5.5%.
- Tools are needed to enable comprehensive socio-economic and environmental assessments of NETs.

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