Energy and Mass Balances Related to Climate Change and Remediation

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Abstract

The goal of this paper is to provide a forum for a broad interdisciplinary group of scientists and engineers to see how concepts of climate change, energy, and carbon remediation strategies are related to quite basic scientific principles. A secondary goal is to show relationships between general concepts in traditional science and engineering fields and to show how they are relevant to broader environmental concepts. This paper revisits Fourier's early mathematical derivation of the average temperature of the Earth from first principles, i.e. an energy balance common to chemical and environmental engineering. The work then uses the concept of mass balance to critically discuss various carbon remediation strategies. The work is of interest to traditional scientists/engineers, but also it is potentially useful as an educational document in advanced undergraduate science or engineering classes.

Keywords

Climate model, carbon capture and storage, carbon utilization

1. Introduction

From artists to engineers, how does an instructor best prepare students for issues they will face related to climate change, energy supply, and the nexus of these two issues? Future public policy decisions may well be in the hands of those without a strong scientific background. Meanwhile, as many science and engineering undergraduates are developing the technical background to tackle these challenges, they may miss out on many aspects

of a broader education that will put future solutions in context. To “engineer a sustainable future”, our undergraduates will need a broad contextual understanding of energy usage, energy supply, carbon dioxide emissions, and environmental ramifications of technology. Yet, topics regarding energy and the environment are much broader than are typically covered in disciplinary science and engineering courses, and although these topics are suitable for electives, the scientific concepts of many electives may be diluted to accommodate a broader audience. Meanwhile, technical papers are often so highly specialized that they may be nearly incomprehensible to those outside the immediate field, at least without a significant investment of time to understand the background literature.

Over the past three years, we have written a textbook, *Science of Earth, Climate and Energy*,¹ which is targeted to a general (non-scientific) audience. In undertaking such a task, i.e. writing such a very broad overview that introduces the underlying scientific concepts that govern these processes on a level accessible to a non-scientifically minded citizen, the authors often found in their discussions that many of the “basic” concepts should not be taken as “assumed basic knowledge” to all authors. This is perhaps surprising, given that the authors of this book come from quite closely related disciplines (i.e. physics and chemical engineering), and even had collaborated on a number of scientific papers. If such a small subset of scientists occasionally found difficulty in communicating in each other’s “basic language”, surely the same could likely be said for a larger subset of scientists from even more divergent fields. Moreover, in asking colleagues to review the book draft, and/or discussing basic tenets that came to light in its writing, the authors often received comments from “expert” colleagues indicating that

48 they had learned something new, or seen something from a new perspective. Surely such
49 dialogue on such an important topic has merit beyond the narrow community of educators
50 that would be teaching from a general education textbook. The purpose of this paper is to
51 repurpose the basic premises found within this general education textbook to a broader
52 technical community, including scientists and engineers that are expert within their
53 individual disciplines, but perhaps have become too focused to see the broader
54 applicability of their disciplinary science. The paper has the additional purpose of serving
55 as an introductory manuscript for advanced undergraduates to learn how issues of energy
56 and the environment are grounded in basic fundamental principles. Too often, in an effort
57 to communicate difficult concepts to the general public, some of these basic tenets may
58 become lost and not at all transparent to disciplinary scientists and engineers.

59 Anthropogenic climate change is a politically charged subject, as it has considerable
60 implications regarding how we use energy, which in turn, affects every facet of our
61 society and economy. Much attention and heated debate have been drawn to the so-called
62 “hockey stick” graph,² which, when published in 1998, showed a long-term “global
63 warming” phenomenon. Indeed, the seven warmest years on record are all recent: 1998,
64 2005, 2009, 2010, 2013, 2014 and 2015; the present year, 2016, thus far, exceeds *all*
65 records. The hockey stick graph is but one aspect of much more detailed reports of the
66 Intergovernmental Panel on Climate Change (IPCC) which was established by the United
67 Nations in 1988 to study climate change. However, the hockey stick graph is perhaps the
68 one piece of information that is distilled from these reports to communicate a complex
69 topic to the general public, including policy makers, the media, and even scientists in
70 other fields. Although suitable to communicate a complex topic to the general public, the

hockey stick graphs presents an observational relationship without a detailed mechanistic understanding of the phenomenon. In many of these same public policy forums, it is often mentioned that the science of climate change is ‘settled’, in that there exists an overwhelming consensus among scientists that human activities are responsible for these changes, with fossil fuel emissions believed to be the proverbial “smoking gun”. For many scientists outside the direct field, those that lack the time to dig deeply into complex models, this perhaps stand at odds with one’s ideal notion that no scientific law is ever ‘proven’. Certainly, an observational relationship without mechanistic understanding does not represent scientific ‘proof’ by traditional definitions of scientific study, because that is never possible (as exemplified by Newton’s laws, which were replaced in the 20th Century by relativity and quantum mechanics). In this paper, we attempt to provide this mechanistic understanding with a “derivation” of climate and climate change, using basic scientific principles. This leads to a discussion of how that temperature varies over time, which is one of the characteristics associated with the much discussed “climate change”. Using a similar approach, we then analyse the carbon mass flux through the environment, and use this as a starting point to discuss various carbon remediation strategies that have been proposed.

2. An Energy Balance on the Earth

Calculations of the Earth's temperature were first carried out in the early 19th Century by the mathematical physicist Joseph Fourier.^{3,*} Similar to the consideration below, these led to a result that was much colder (35 °C or 63 °F) than the actual temperature of the Earth. As a result, Fourier's theory was not accepted, however plausible was his methodology. This discrepancy was corrected some 40 years later, when John Tyndall discovered experimentally that gases like CO₂ and H₂O play an essential role in controlling climate.⁴ This modification later came to be known as the *greenhouse effect* and highlights the critical role played by atmospheric gases in warming a planet. Subsequent generations of scientists have explored these basic ideas with increasingly sophisticated models. Notable among these early pioneers was Svante Arrhenius, who was able to explain, in principle, both those periods when our Earth is comfortably warm and the colder periods, like the Ice Ages. Fourier's simple model, with later adaptations by Tyndall and others, is presented below as a first-order approximation of the energy balance on the Earth, showing how the composition of the atmosphere is used to determine a planet's temperature from first principles.

2.1 Energy In

The Sun's radiation (light) is by far the most important source of energy input for our Earth. Fig. 1 presents the *spectral irradiance*[†] of the Sun, defined as the amount of light that arrives at the Earth per second, per unit wavelength, as a function of wavelength. The

* Fourier's calculation was carried out in the spirit of that presented here, but differ because the correct solar spectrum was not known until it was derived by Max Planck in 1900 (on the basis of experimental data).

† A java applet showing the spectrum of radiation emitted as a function of the source temperature is found at <http://phet.colorado.edu/en/simulation/blackbody-spectrum>.

peak intensity of the Sun's radiation lies within the visible region of the electromagnetic spectrum, ranging from 400 to 700 nm, as shown by the shaded region in Fig. 1. The vision of most animals (not living underground or deep in the ocean) is particularly sensitive to the wavelength region provided in greatest abundance by our Sun. In particular, human vision has evolved so that it can detect only wavelengths from 400 to 700 nm.

Figure 1: Intensity of radiation, as a function of wavelength, arriving at the Earth from the Sun (solid curve) and that emitted by the Earth (dashed curve). The Earth's emission curve (centred on 10 μm) has been multiplied by a factor of 3 million. The shaded area represents the visible region of the spectrum, centered on 0.5 μm. From Cole et al., *Science of the Earth, Climate and Energy*,¹ and used with permission.

There is negligible energy loss of the Sun's energy as it radiates outward through the near vacuum of space. Thus, the rate of energy emission of the Sun, E (energy/time), is essentially a constant.[‡] However, as with any source of energy, it disperses as it spreads outwards. The relationship between the energy emitted and the flux $J(r)$ in radial coordinates is:

$$E = J_o(r_o) * (4 \pi r_o^2) = J(r) * (4 \pi r^2) \quad [1]$$

[‡] The solar radiation exhibits an 11 year solar cycle of variation, of relative magnitude about 0.1%, known from hundreds of years of sunspot observations.

Where r_o is taken as the radius of the Sun (~432,000 miles), and r is some arbitrary distance away from the Sun. The flux at the surface of the Sun is related to its temperature (T_s) via the Stefan-Boltzmann Law:

$$J_o(r_o) = \sigma T_s^4 \quad [2]$$

Here σ is the *Stefan-Boltzmann constant*, with a value of $5.67 \times 10^{-8} \text{ W}/(\text{m}^2\text{-K}^4)$. Combining Eqns. 1-2, the flux from the Sun at any radial position is given by:

$$J(r) = \sigma T_s^4 * (r_o / r)^2 \quad [3]$$

The distances in our solar system are vast. The Earth's diameter is over 100-fold smaller than that of the Sun, and the distance between the Sun and Earth (93 million miles) is over 11,000 times that of the Earth's diameter. Thus, the rays emitted by the Sun may be taken to be of nearly parallel incidence upon arrival at the Earth. One will note that the rays strike one point on the Earth directly from above, while no radiation strikes the side of the Earth experiencing night time. The global *average* solar radiation per unit area equals the flux from the Sun times its cross-sectional area at the equator ($A_E = \pi r_E^2$) divided by the surface area of the Earth ($A_S = 4\pi r_E^2$). Dividing A_E by A_S leads to a factor of $1/4$, meaning that the average energy flux to the Earth is equal $1/4^{\text{th}}$ that of the energy flux incident at the Equator:

$$J_{\text{in,avg}} \sim J(r) * A_E / A_S = \sigma T_s^4 * (r_o / 2 r)^2 = 340 \text{ W} / \text{m}^2 \quad [4]$$

In the above equation, the temperature of the Sun's corona,[§] T_s , is known to be 5,800 K from *Wien's displacement law*, which relates the observed maximum intensity

[§] The corona is the outermost region of the sun, the source of the radiated energy we observe. Radiation from the Sun's interior is at much smaller wavelengths (because the interior is several hundred times hotter than the corona) but that radiation does not penetrate through this outer layer.

wavelength of electromagnetic radiation (i.e. Fig. 1) to the temperature of its source; a value of $\lambda_{\max}$ of $\cong 0.5 \mu\text{m}$ (see Fig. 1) has been used.

In addition to the Sun's radiation, a number of other cosmic sources transfer small amounts of energy to the Earth. The *solar wind* is a stream of particles emitted by the Sun, consisting of energetic electrons and protons which travel to Earth.** The Earth also receives very small amounts of radiant energy from stars and from our Moon. *Cosmic rays* are energetic particles from outside of the solar system, which were critically important in producing the planet we stand upon because they include atoms heavier than carbon, which are extremely rare in the universe. However, these sources convey a negligible amount of energy relative to that transferred by the Sun.

On the surface of the Earth, there arise a number of factors that contribute to temperature fluctuations, including the so-called El Niño (La Niña) events, which unbury (bury) surface heat below the ocean surface. These effects tend to average out over decade-long periods; furthermore, the model discussed here considers only the average temperature of the Earth, such that these “mixing events” provide only spatial but no appreciable temporal variations.

Geothermal energy, including volcanic activity, is a result of radioactive decay within the Earth's core, slow densification of the Earth, and the resulting friction between subsurface rocks. On average, the geothermal energy flux is roughly 75 mW/m^2 at the surface, about 0.03% of the solar energy flux arriving at the Earth's surface. Due to its small relative magnitude, geothermal energy is ignored in the development of the simple model.

** This stream can be “detected”, either directly or indirectly, through its disruptive effects on communications on Earth (due to solar storms), through the aurorae (polar lights) and through the tails of comets (which always point away from the Sun).

2.2 Energy Out

Like the Sun, the Earth emits energy into space via electromagnetic radiation, although this fact is not well known to nonscientists. As before, the flux of radiant energy emitted from the Earth's surface, J_{out} , is given by the Stefan-Boltzmann relation:

$$J_{\text{out}} = \sigma T_P^4 \quad [5]$$

Where T_P is taken as the average temperature of the planet. Clearly, the Earth's temperature has large spatial and temporal variations, but for the sake of developing a simple model, we first consider only the Earth's global average temperature, ignoring temporal and spatial variations (consistent with the preceding treatment of the incident energy).

It comes as a surprise to many that the Earth emits electromagnetic radiation. As the Earth's surface is about 20 times^{††} colder than the Sun's surface, the wavelengths of the Earth's radiation lie in the infrared region, centred on a wavelength about 10 μm (See Fig. 1), invisible to the naked eye. The intensity of the radiation of the Earth is also much less than ($\sim 1/3,000,000^{\text{th}}$) that of the Sun, as shown in Fig. 1.

2.3 Energy Balance

The energy balance on the Earth can be written as follows:

$$\Delta E_{\text{earth}} = E_{\text{in}} - E_{\text{out}} \quad [6]$$

^{††} The Sun's corona (which produces the light we see) is about 5,800 K, while we are at about 290 K. The Sun's interior at millions of K, but that super-hot radiation doesn't make it outside the Sun, but mostly gets absorbed in the interior.

Here ΔE_{earth} is the net rate of energy accumulation of the Earth, E_{in} is the incident solar radiation, and E_{out} is the radiant energy emitted by the Earth back into space. These two variable are defined in terms of flux by Eqs. 4-5 (with $E = J * \text{Area}$).

As a first step, we consider the *steady state approximation*, such that $\Delta E_{\text{earth}}=0$. To justify this approximation, we note that the temperature of the Earth has varied only a few degrees over the half-million year period for which we have a good temperature record.⁵

The steady state approximation is then:

$$E_{\text{in}} \sim E_{\text{out}} \quad [7]$$

Using the average solar incidence defined above, and considering the flux to/from the Earth at a fixed radial distance, leads to:

$$T_P = T_S * (r_o / 2 r_P)^{1/2} \quad [8]$$

This equation predicts the temperature of the Earth to be 278 K, slightly less than temperature records showing the average temperature to be 289 K. Given the fair number of approximations, this estimate seems to be fairly good, but like Fourier's original model, the temperature is too cold.

Generalizing Eq. 8 to other planets yields average temperatures of 450 K for Mercury, 322 K for Venus, 278 K for Earth, and 223 K for Mars. Notably, Eq. 8 predicts the average temperature of the planets should decrease with increasing distance from the Sun. However, the corresponding actual surface measurements are 440 K, 737 K, 288 K, and 208 K. The experimentally determined values do not correlate with distances from the Sun: Venus is the hottest planet, even though Mercury is the closest to the Sun. This discrepancy suggests that a key feature in the model, is yet to be considered. The origin of this discrepancy is *the greenhouse effect*.

2.4 The Greenhouse Effect

Gardeners and vegetable growers in northern latitudes are likely to be familiar with the wonders of a greenhouse, which permits plants to grow year-round. These plants are beneficiaries of the *greenhouse effect*, by which the temperature inside a greenhouse is much warmer than the ambient temperature outside. Also familiar is the analogous phenomenon of the interior of a car in the summer sun: with its windows closed, the interior becomes significantly warmer than the outside environment. The reason for this phenomenon is that the walls of a greenhouse and the windows of a car allow most inbound solar radiation to enter, but prevent most outward-bound radiation from passing out, essentially acting as a *one-way door*, trapping the energy inside the greenhouse or car so as to warm the interior.

The windows of a greenhouse and car are able to act this way because the incident radiation is at a very different wavelength than that of the thermal radiation inside the body and because the transmission properties of the glass are strongly dependent upon the wavelength. Consider, for example, Fig. 2, which shows the fraction of incident radiant energy that is transmitted through a typical glass window, as a function of the radiation's wavelength. One sees that more than 80 per cent of the visible light ($400\text{ nm} < \lambda < 700\text{ nm}$) passes through the glass. In contrast, the transmittance of thermal radiation, with a wavelength typically exceeding $2,500\text{ nm}$ falls to nearly zero. A simple energy balance analysis of the greenhouse or the car (ignoring convective flow of air due to ventilation) would show energy coming in, but little or no energy coming out.

Figure 2 Transmission percentage of electromagnetic radiation through AZO glass (zinc oxide with added aluminium) as a function of wavelength. In the visible light region (400-700 nm), about 80% of the radiant energy is transmitted; the transmission drops to 0% at wavelengths >2500 nm. From adapted from Cole et al., *Science of the Earth, Climate and Energy*,¹ as adapted from Ref. 40; used with permission.

The atmosphere blanketing the Earth behaves in a remarkably similar manner, allowing incident solar radiation in the visible region largely to pass through, while absorbing a fraction of the thermal infrared radiation emitted by the Earth back into space. The wavelength at which a particular gas absorbs radiation is dependent upon its molecular structure and the frequencies at which it vibrates. Gases that absorb in the infrared region of the electromagnetic spectra trap the Earth's emitted infrared radiation, essentially serving as a blanket of the Earth. Gases that absorb in the infrared region include carbon monoxide (CO), methane (CH₄), nitrous oxide (N₂O), ozone (O₃), water (H₂O), and carbon dioxide (CO₂). This is illustrated in Fig. 3: the solid line represents the energy flux that would occur if there were no greenhouse effect; one will note the various greenhouse gases that absorb this radiation, decreasing the energy flux at certain wavelengths. The contribution of these gases to the greenhouse effect depend upon their concentration and relative abundance in the atmosphere, and whether or not they are condensable and how they influence cloud formation and humidity.⁷

Figure 3 The Greenhouse effect: gases absorb infrared radiation, decreasing the spectral flux at the top of the atmosphere (shaded region) relative to that expected from a blackbody emission at 294 K (red curve). Courtesy of G. Schmidt.

243

244 Due to the greenhouse effect, the simple energy balance presented above must be

245 modified to account for the fraction of the radiation that is ‘trapped’ by the greenhouse

246 gases. This fraction of transmission is captured in an “f factor”, which is determined by

247 the composition of the atmosphere, and the molecular absorbance of the gases in the

248 atmosphere. The anomalous trends discussed above for Venus is due to the composition

249 of its atmosphere, which is almost 96.5% by volume carbon dioxide, a greenhouse gas.

250 Its presence results in a much higher temperature (741 K) than that predicted based solely

251 on its distance to the Sun (322 K).

252 Just as the Earth’s atmosphere may trap some of the Earth’s irradiation, its cloud cover

253 may block some of the Sun’s radiation from reaching the Earth. The incident energy due

254 to the Sun is modified accordingly by taking into account the Earth’s *albedo* (α) which

255 represents the fraction of the total solar radiant energy incident on the Earth that is

reflected back into space. The value of α is determined from satellite photographs^{††} and measurements of solar intensity reaching the Earth's surface.

The incident Solar irradiation and the fraction of Earth's irradiation transmitted are modified in the development of the energy balance above, by multiplying each term by the fraction of energy transmitted, i.e. $(1-\alpha)$ for incident radiation and $(1-f)$ for outgoing radiation, respectively. This modification leads to:

$$T_p' = T_p * \{(1-\alpha_{\text{planet}})/(1-f_{\text{planet}})\}^{1/4} \quad [9]$$

In a hypothetical situation in which a planet lacks any atmosphere and reflects no incident light from the Sun, both α_{planet} and f_{planet} are zero, and Equation 9 reduces to Equation 8. Inserting the currently accepted average values into this equation (i.e. $f=0.4$ and $\alpha=0.3$)¹, this equation yields the result $T_{\text{earth}} = 289 \text{ K}$, which is consistent with the Earth's average temperature today.

2.5 Energy Imbalance or Non-Steady State.

The equations above incorporated the steady state approximation. One should recognize that a small deviation from steady state can yield a non-negligible accumulation of energy over sufficiently long time. Beyond the scope of this document, precise quantification of the net energy flows to and from the Earth include many of the so called negligible terms above, including the radioactive decay of matter within the Earth and especially the significant consequences of volcanic eruptions. Such complex accounting actually leads to an *imbalance* of the energy terms. The difference between E_{in} and E_{out} in Eq. 6, is less than 1/2% of the individual terms that are retained. *Although small, the "error" in the*

^{††} The albedo varies both temporally and spatially. It is higher than 0.3 at places where the sky is cloudy (or the ground is covered by ice) while it is somewhat lower under desert conditions of a dry, impurity-free atmosphere.

approximation given in Eq. 7 corresponds to the phenomenon of global warming (or cooling).

2.6 Modern Climate Models

The preceding model is a so-called one parameter, scalar description of the Earth's energy balance, in that the sole variable is the Earth's average temperature. During the last half-century of intense study, the vast increase in relevant data and the growing concern about the environment have stimulated the development of much more sophisticated models. These characterize the temperature as a function of three spatial variables: latitude, longitude and altitude (or depth below the ocean surface). There is in addition the time variable, so high quality models are truly four-dimensional. Built into each model is a vast body of empirical information, as well as a solid theoretical foundation, based on the equations of fluid dynamics. These latter laws describe wind and ocean currents, which are influenced by the time-dependent, nonuniform temperatures and pressures, as well as the Earth's rotation and fluctuations in solar radiation. At a more local level, the models must characterize variables such as clouds, mountains, glaciers, forestation, lakes and volcanic eruptions. At the truly microscopic level, a model needs to account for variations in atmospheric composition, since it affects the greenhouse behaviour.

The development of such models is a gargantuan task, posing great challenges for both human computation and the accumulation of observational data used to test models' predictions. The Intergovernmental Panel on Climate Change (IPCC) is an international program which assesses these models in terms of the observational data. The IPCC reports present a continual growth in confidence in its findings that human actions are significant causes of climate change, i.e., anthropogenic climate change. While every

significant group of scientists in this field has issued a statement endorsing the IPCC findings, there remain scientists who do not subscribe to this consensus view.

3. The Carbon Cycle

Carbon is an essential element of life, and the carbon cycle characterizes the changing state of the carbon atom. In brief, photosynthesis converts inorganic carbon dioxide (CO_2) in the atmosphere to sugars, carbohydrates, and other organic molecules that form the basic building blocks of plants. Animals eat these plants, using the carbohydrates for fuel and further converting these organic building blocks into more complex biological molecules. As they breathe, the animals take in oxygen, which reacts with the sugars to create the CO_2 that is released to the atmosphere. When the animal eventually decays, the carbon remaining in the animal's molecules is converted back to CO_2 , and the cycle repeats.

Quantitative representation of the carbon cycle (Fig. 4) as a 'mass flow diagram' shows both the reservoirs for carbon in the environment, as well as the mass flux between reservoirs. In addition to the simple description of the carbon cycle in the preceding paragraph, one will note flux to/from the ocean, which includes both organic (such as algae, phytoplankton, and sea life) and inorganic carbon (such as dissolved CO_2). Although the total amount of carbon on Earth is fixed, the amount in any given reservoir may change with time. One will note that the reservoirs in the diagram are not at steady state, as there is generally a mismatch between the mass flows in and out of any given reservoir.

For example, consider the atmosphere, which has 780 GT (gigatons) of carbon. This carbon is very dilute, at a concentration of 0.04% (400 ppm) CO_2 and trace (~1-2 ppm)

323 amounts of methane. Natural flows of carbon to/from the atmosphere tend to be close to
 324 steady state, i.e. photosynthesis exceeds that of decomposition and respiration by just 2%,
 325 and the flow to the ocean exceeds that from the ocean by ~2%. The anthropogenic carbon
 326 flows include the combustion of fossil fuels and changes in land usage, at 6.3 and 1.6
 327 GT/year, respectively. There is a net 3.2 GT/year flow of carbon into the atmosphere,
 328 which is dominated by anthropogenic flows.
 329 Importantly, the flow of carbon from fossil fuels to the atmosphere is a one-way path (the
 330 stream denoted 'FF' in Fig. 4). This is due to the mismatch between the time in which the
 331 fossil fuels were formed (i.e. millions of years) versus the time in which they have been
 332 extracted and utilized (i.e. 100-200 years). If one were to redefine the 'active system' as

Figure 4: Mass flow diagram of the carbon cycle, showing the relative size of the carbon reservoirs (the boxes) and the flow of carbon between the boxes. Data is from the 1990s, and all values represent gigatons (billions of tons) of carbon per year. From Cole et al., *Science of the Earth, Climate and Energy*,¹ adapted from Ref. 41; used with permission.

the region enclosed by the dotted line in Fig. 4, this one-way flux into the new system virtually ensures that the carbon concentration in the other reservoirs will continually increase due to non-steady state conditions. This net influx from the FF stream explains the 2% excess in natural flows out of the atmosphere, as noted in the preceding paragraph. Fig. 4 suggests that 6.3 GT/year of anthropogenic carbon flow need to be removed in a hypothetical carbon storage (CS) stream to return the ‘active system’ to steady state. However, these are 1990 numbers, and the increase in CO₂ concentrations in the atmosphere has already led to climate change, for reasons discussed in Section I. Detailed modelling suggests that several GT of CO₂ have to be extracted from the ‘active system’ to limit warming to 2 °C; more pessimistic estimates suggests tens of GT per year must be removed.⁸ As there is uncertainty in these numbers, the discussion below treats the “CS stream” as a variable referring to the carbon that must be removed from the system to return to steady state conditions.

4. Remediation Strategies: Reducing the Flux of Carbon to the Environment

The goal of this section is to consider several routes by which the hypothetical CS stream may significantly offset the fossil fuel (FF) stream (as illustrated in Fig. 4). The concepts discussed are ranked in tiers, based on the authors’ perceptions of priority, including (Tier 1) direct displacement of the FF stream and reduced consumption via energy efficiency measures; (Tier 2) alternate routes to use fossil fuels with decreased CO₂ emissions; and (Tier 3) remediation strategies that have been proposed to remove CO₂ from the atmosphere directly. The ranking of these strategies is based on the ‘mass balance’ vantage point outlined above, in particular, the relative fluxes and concentrations in Fig. 4. Specifically, one may note that removing the CS stream from any of the carbon

reservoirs may return to the ‘active system’ to steady state (albeit perhaps with a rebalance between the internal reservoirs).

4.1 Tier 1A. Stop/Reduce the Carbon Flux.

4.1.1 Carbon-Free Electricity. The most direct means to reduce the FF stream is to make it obsolete, replacing the dependence on fossil fuels with carbon-free energy sources, such as renewables or nuclear energy. Renewable energy includes hydroelectric energy, energy derived from wood and biomass, wind energy, geothermal energy, and solar energy. How the renewables are used in the economy are illustrated in Fig. 5, with the current relative importance reflecting the various sectors of the U.S. economy (as an example).

For the purposes of this discussion, the most important aspect of renewables is their carbon-neutrality. Hydroelectric power provides 16% of the electricity generated in the world (about 3,500 terawatt-hours in 2010).⁹ After a large capital investment to build a dam,^{§§} the facility produces virtually carbon free energy over its lifetime (excluding maintenance considerations). The energy payback periods of wind and solar energy sources are estimated to be 8 months¹⁰ and just over a year,¹¹ respectively, with variations of these estimates based on the assumptions in various life cycle analyses. Given that the lifetimes of these systems are much longer than their payback periods, the *energy* benefits for investing in these devices seems clear. Biomass can replace fossil fuels in centralized combustion facilities with minimal equipment changes, although this does lead to certain logistical challenges because of its low energy density. Although biomass combustion

^{§§} Hoover Dam, for example was built in 1936 at a cost of \$49 million, roughly \$700 million in today’s US dollars. The Three Gorges Dam in China was built in 2008 at a reported cost of \$37 billion US dollars. The difference in cost can be attributed in part to size: Hoover Dam is 1350 MW, versus 22,5000 MW for the Three Gorges Dam.

Figure 5 Schematic showing how various renewable energy sources are used. The areas of items on the left are proportional to their relative importance in the U.S. energy portfolio in 2016. From Cole et al., *Science of the Earth, Climate and Energy*,¹ and used with permission.

produces carbon emissions, these are offset by the CO₂ taken up by the biomass during the process of photosynthesis. Thus, biomass has the potential to be carbon neutral, provided that sustainable agricultural process are used that have minimal carbon emissions.¹² If combined with carbon capture and storage (see below), displacing fossil fuel combustion with biomass has the *potential* to produce negative carbon emissions without a major overhaul of existing facilities, especially if waste biomass is used.¹³

4.1.2 Carbon-free transportation. The transportation sector comprises 34% of the world's primary energy consumption,⁹ with ~90% of this energy supplied by petroleum. An estimated 40% of the world carbon emissions are from the transportation sector.¹⁴ Capturing CO₂ emissions from mobile sources is likely to be an insurmountable logistical

challenge, and thus the only likely feasible solution to offset emissions from the transportation sector is to seek alternative fuels or alternative vehicles.

The only primary energy source that has the potential to offset petroleum *directly*, without carbon emissions in *today's* vehicles is biomass-derived fuel. Today, ethanol and biodiesel are the predominant biofuels. Biodiesel^{***} is produced by chemical rearrangement of the fatty acids present in oils (like soybean, canola and sunflower oils, animal fat or recycled cooking grease) by reaction with an alcohol that splits the fatty acid into two smaller pieces. Ethanol is generally derived from the *fermentation of cellulosic biomass*, i.e. the sugars and starches present in corn, switchgrass, and sugarcane. Both ethanol and biodiesel are generally mixed with petroleum fuels to increase performance in engines, although the amount depends upon the type of engine. There has been a dramatic increase in the use of ethanol over the past decade, particularly in the United States and Brazil, two countries which use twice the combined total of ethanol fuels of all of the other nations of the world combined. The regional applicability of the use of ethanol is due to a combination of land availability and government policies, as well as technological feasibility and economic factors. For example, in the United States, corn-producing states have lobbied Congress to mandate the inclusion of some ethanol in conventional gasoline mixtures, partly rationalizing this legislation in terms of reduced imports of foreign oil. Similarly, in Brazil, lacking any domestic oil supply, the government has encouraged the use of all-ethanol vehicles, resulting in a higher percentage of its energy from biomass than that of any other country in the world.

^{***} Biodiesel should be differentiated from the use of unprocessed vegetable and waste oils in diesel engines. Use of unprocessed waste vegetable oils generally requires modification of the mechanics of the diesel engine for *legal* operation.

Ethanol-blended gasoline in the U.S. typically contains about 10% ethanol, whereas *flexible fuel vehicles* (such as those found in Brazil) are able to run on blends containing about 85% ethanol.

Production of cellulosic ethanol is energy intensive, as biological fermentation is typically low yield and requires subsequent energy-intensive separation of an azeotropic water-ethanol mixture. Thus, the carbon neutrality of biofuels has been the subject of debate, and is often dependent upon how the energy input of agricultural processes are accounted for in the life cycle assessment.¹² Moreover, “burning our food supply” raises ethical concerns.

It would be much more desirable to use waste biomass instead of a food crop to produce a fuel, and this problem lies at the food-water-energy nexus. Whereas biological fermentation converts readily digestible sugars (such as those present in food) to alcohol, metabolic engineering of microorganism that feed on [indigestible] lignin is in the research stage. Yet, even ethanol is not an ideal fuel for today’s automobile, and a true “drop in” biofuel would be significantly lower in oxygen content, so that blending with petroleum would not be required. Thermal pyrolysis to convert biomass to bio-oils has been proposed as a means to develop such drop in biofuels, but water must be removed from the resulting biphasic bio-oil, which is an energy-intensive and carbon inefficient separation as a great deal of carbon is lost to the aqueous stream. Development of a “drop in” biofuel that has performance comparable to that in today’s automobile represents a significant research challenge.

Electric vehicles provide a virtually carbon-free alternative to the internal combustion engine, provided that the electricity source is dominated by carbon-free sources. Growth

431 in the use of renewable forms of electricity and electric charging stations makes this an
432 increasingly viable scenario. Research to extend battery range, lifetime, and weight will
433 extend the range of today's electric vehicles, and make this an increasingly attractive
434 option for consumers. However, replacing all internal combustion engines with electric
435 vehicles will put a considerable demand on the existing electricity infrastructure. Methane
436 and hydrogen fuel cells have also been proposed, and have been the subject of
437 considerable government research funding across the world. In principle, hydrogen may
438 be produced from electrolysis of water powered by renewable energy, and 'renewable'
439 methane may be produced via anaerobic digestions. A hydrogen-powered transportation
440 fleet has a number of technical hurdles to overcome, including a fueling infrastructure,
441 safe on-board storage of compressed hydrogen, and costs of the fuel cell that converts
442 hydrogen to electricity. Currently, hydrogen powered transportation currently serves only
443 a limited niche market.

4.1.3 Prospectus. The use of renewable energy, and in particular biomass, wind, and

Figure 6: Electricity Generation from Renewables for various countries versus time. Data from the International Energy Agency.⁹

solar, has been increasing rapidly during the past 20 years in a number of countries (Fig. 6). Even in the U.S., which has historically been slow to adopt carbon treaties, renewables have seen tremendous growth (see Fig. 6 and Fig. 7), driven in part by policies such as the renewable energy credits at the state (rather than national) level. Specifically, in 2000, 86% of primary energy consumption in the U.S. came from fossil fuels, while renewables (excluding nuclear) provided just 6%.⁹ In 2014 (the most recent numbers available), the numbers are 81% and 10%, respectively, showing a decrease in the relative consumption of fossil fuels and an increase in the consumption of renewables. Worldwide, the energy production numbers are relatively static over the same time

period: fossil fuels at 80% in 2000 and 81% in 2014; and renewables at 13% in 2000 and 14% in 2014.⁹ During the same time period, the contribution of nuclear energy to the

Figure 7: Primary energy used in the U.S. Data from the U.S. Energy Information, from Cole et al., *Science of the Earth, Climate and Energy*,¹ and used with permission.

energy portfolio has decreased from 12% to 11% in the U.S., and 7% to 5% worldwide.

Lack of growth in nuclear energy is due largely to political controversy, rather than scientific or engineering challenges.

Despite this impressive rate of growth in renewables, Fig. 7 suggests that fossil fuels will dominate the U.S.'s energy portfolio for the foreseeable future. World trends are similar: despite increased use of renewables, fossil fuels continue to dominate total energy production and consumption. Continued use of fossil fuels in a carbon-constrained world means that we must explore means to utilize fossil fuels more sustainably, with decreased carbon emissions. This has come to be known as an “all of the above” energy approach.

4.2 Tier 1B. Reduce Carbon Emissions through Energy Efficiency

4.2.1 Reduced Consumption. A growing integration of modern conveniences into our daily lives is increasing our personal demand for electricity, while a growing consumption of consumer goods drives both commercial and industrial energy consumption, which comprise ~10% and 30%, respectively, of the world's demand for primary energy.⁹ Residential energy represents about ~20% of the world's total energy consumption,⁹ and residential and commercial climate control make up nearly half of residential energy consumption.^{†††}

Much of this consumption is driven by consumer choice, and efforts to decrease energy consumption include: (1) increasing the efficiency of automobiles, through Corporate Average Fuel Economy (CAFE) rules; (2) energy efficient certifications (e.g. *ENERGY STAR*) for home appliances to influence consumer choice; (3) design of energy efficient “green buildings” that incorporate passive heating and cooling, orientation to allow for natural lighting, a small external surface area to minimize heat loss to the environment, and energy-efficient insulation, windows and ventilation; and (4) substitution of energy-efficient compact fluorescent light bulbs for the traditional incandescent bulb. These initiatives are making progress, but there is much work to be done. For example, the American Council for an Energy-Efficient Economy ranked the U.S. 8th out of 23 industrial countries,^{†††} based on analyses of the energy efficiency within these societies, with an emphasis on policy.¹⁵ Increased energy efficiency in the face of increased

^{†††} In the United States, heating and cooling represented about 50% of the total energy budget, with the remainder directed towards water heaters (about 18%), various appliances (about 9%), lighting (about 5%) and electronics (about 4%) and “miscellaneous”. Data from the Energy Information Agency, October, 2015.

^{†††} The countries are (in the order they are ranked for energy efficiency): Germany, Japan, Italy, France, United Kingdom, China, Spain, South Korea, United States, Canada, Netherlands, Poland, Taiwan, India, Turkey, Australia, Indonesia, Mexico, Thailand, Russia, Brazil, South Africa, Saudi Arabia.

material consumption will depend on product design, labelling, education of the consumer, and likely, policy that drives consumer choice.

4.2.2 Low Carbon Manufacturing. The influence of scientists and engineers extends much farther than consumer choice and product design. Industrial activity accounts for ~30% of the world's energy consumption.⁹ Historically, the energy consumption of industrial facilities has taken low priority unless it played a primary role in the bottom line economics. Unlike those strategies discussed in the preceding paragraph, the strategies below are largely 'invisible' to the consumer. Implementation of many of these strategies may be dictated by centralized policy and regulations to limit carbon emissions, or economic initiatives if the price of energy rises substantially. Technological advances may also spur implementation of these technologies, but there tends to be a great deal of inertia due to large investments in capital equipment and current infrastructure.

There are a number of engineering textbooks that focus on clean manufacturing or green engineering, and it is beyond the scope of this paper to describe the premises found in these sources. Anastas and Warner¹⁶ have outlined the "12 Principles of Green Chemistry" that include many of the concepts outlined here (e.g. energy efficiency and use of renewable feedstocks) as well as prevention of waste and incorporation of inherently safer and more efficient atomistic designs into chemical synthesis. Subsequently, Anastas and Zimmerman¹⁷ outlined the "12 Principles of Green Engineering" and Abraham and Nguyan¹⁸ summarized the results of a conference in "The San Destin Declaration of 9 Principles of Green Engineering". A number of recent government funding opportunities are looking to increase energy efficiency through both

“advanced” and “smart” manufacturing (e.g. in the U.S., the National Network for Manufacturing Innovation, an initiative through the U.S. Department of Energy).

4.2.3 The Chemical Industry. Beyond the general engineering initiatives and guidelines outlined above, there is a growing impetus to scrutinize the high energy intensity of the chemical processing industry.¹⁹ Whereas industrial activity accounts for 30% of the world’s energy consumption, it is estimated that 10-15% of the worldwide energy consumption is devoted to separations of chemicals,²⁰ which ultimately go into making the materials we consume. This includes the necessary separation and purification of industrial feedstocks that go into consumer goods, such as plastics, and even further upstream, the distillation of petroleum that is the source of the feedstocks for the majority of consumer goods. In the U.S. alone, the chemical industry uses the equivalent of about 850,000 barrels of oil every day, roughly equal to the total quantity of oil used by Australia.¹⁹ Although the Principles of Green Chemistry tell us we should design chemical synthesis to avoid waste and energy-intensive separations through both better synthesis routes and the use of highly-selective catalysts, there is clearly a practical limit to the realization of this ideal.

In the U.S., it has been estimated that more efficient chemical separations technologies could save 100 million tons (0.1 GT) of carbon dioxide emissions,²⁰ a significant fraction (1-10%) of the targets for the CCS stream noted above, but importantly, are equivalent to a 100-fold increase in the rate at which CO₂ has been captured and sequestered in recent demonstration facilities; the potential carbon savings is through emission avoidance.

A 2005 study²¹ prepared for the U.S. DOE Energy Efficiency and Renewable Energy (EERE) Agency surveyed potential energy savings in the chemical industry, with a focus

on decreasing the significant energy consumption associated with chemical separations. The study focused on the existing practices of the four largest energy-consuming industries (chemicals, petroleum refining, forest products, and mining). It identified more than 240 TBTU/yr that could realistically be saved by developing new or advanced materials for low-energy intensity separation technologies. Many of the recommendations centred on replacing energy-intensive distillation with mass separating agents (membranes, adsorbents, solvents) that did not require a phase change. The basic premise of this strategy is that distillation requires a high energy phase change to drive separations, much of which exits the process as low-grade waste heat that is not recoverable. Successful energy efficient technologies will reduce energy consumption via strategies that approach the limiting thermodynamic efficiency of demixing^{§§§} through effective heat and mass process integration. For example, use of membranes for desalination is cited²² as the prototypical “success story” in decreasing energy consumption of a separation, as current process efficiencies approach the thermodynamic limit. The efficiency gains have come about via better membrane design, but also pressure recovery and integration strategies at the process engineering level. Other process (e.g. pre-combustion CCS) may have opportunities for heat integration, such that a ‘winning’ strategy cannot be easily identified without full consideration of the process flow diagram.

The energy input to distil petroleum is the most significant input of the separation energy in industry, with more energy lost in refining than is recovered in the final product sent to

^{§§§} The “thermodynamics of demixing” is the difference in Gibb’s free energy of a mixed solution versus that of the individual components. This includes a significant entropy component, as well as the heat of solution.

the consumer (27 MJ lost in refining vs. 20.5 MJ delivered to the consumer, Fig. 8). Notably, the EERE report did *not* identify replacement of petroleum distillation as a major opportunity, citing this as a mature technology with current products and performance being ‘cut-specific’, i.e. based on the fuel vaporization in an automobile. Of course, displacing petroleum provides a more direct strategy for minimizing these emissions. However, petroleum-based feedstocks are the primary source of raw materials in the chemical industry, used to make packaging, detergents, coatings, insulation, paint and even drugs. Thus in petroleum distillation, the report focused on the significant energy efficiency that can be gained in gas recovery, with opportunities to save 10 TBTU/year through use of membrane and absorptive separations. The chemical manufacturing industry provided a much larger energy savings opportunity, where it was proposed that substitution of distillation with mass separating agents could save up to 120 TBTU/year. The next largest opportunity (110 TBTU/year) identified was in the recovery of pulping chemicals in the paper industry, through possibly preparing better filters to

Figure 8: Energy loss associated with processing of petroleum from “well to wheel”. EROI stand for energy return on investment. The energy loss at each stage of processing is shown at bottom. From Ref. 42, and used with permission.

augment evaporation. Other large opportunities included oxygen enrichment, and hydrogen and organic recovery from flaring practices, with 5 and 3 TBTU/year, respectively.

Notably, many of the separations opportunities identified involve ‘classic’ separations problems involving separating components with similar boiling points (such as ethylene/ethane, propylene/propane, butadiene/butanes, styrene/ethylbenzene). Other separations with potential impact include the removal of organics from water, avoiding azeotropes, recovery of dilute organics from water, cryogenic separations, and polyol separations (i.e. ethylene glycol/diethylene glycol, ethylene glycol / propylene glycol). The success of membrane technology for approaching the thermodynamic limit for energy input illustrates the potential to make use of substantial material developments in the past decade to offset other significant energy inputs, and highlights the need for not only scientific advances, but also integration of scientific developments into process design. Although these are ‘classic’ separations, many emerging materials have been developed in the past decade. However, implementation of these emerging materials will require consideration of stability, cyclability, and chemical compatibility. The importance of process integration in full energy recovery suggests that material development cannot be considered in isolation. Whereas the design of a distillation tower is a rite of passage in every chemical engineering curriculum, few chemical engineering undergraduates are familiar with the design of membrane or adsorption processes. Attainment of these alternative separation technologies will likely require reenvisioning chemical engineering undergraduate education.

4.2.4 Biorenewable Feedstocks. Use of biorenewable feedstocks was one of the 12 key principles highlighted in the Green Chemistry and Green Engineering guidelines mentioned above. Notably, the carbon flows to the atmosphere through the natural processes of decomposition, respiration, and transfer are 10, 10, and 15-times, respectively, that of the human contribution to the FF stream (see Fig. 4). Compared to proposals to ‘upcycle’ CO₂ to hydrocarbon feedstocks via carbon reutilization, the carbon in these biological waste streams is already ‘upcycled’ (relative to CO₂), with energy input derived from the Sun’s radiation via the natural process of photosynthesis. Whereas the quantities of these carbon feedstocks are vast, use of renewable chemical feedstocks can introduce complexities into chemical processes. The conversion of agricultural land to dedicated sites for production of biorenewable feedstocks may introduce other complex environmental challenges⁸ along with ethical concerns about energy/feedstocks competing for land that might otherwise be used to drive down the cost of food for the masses. Additional considerations are how the use of biorenewable crops affects the net carbon balance, since the biomass acts as a carbon sink before it is harvested and crop age affects the natural rate of carbon uptake and crop management can be complex to achieve a net carbon sink.²³ Moreover, use of carbon waste streams as feedstocks introduces challenges to utilizing feedstocks with quite heterogeneous chemical structures.

4.3 Tier 2. More Efficient Use of Fossil Fuels.

4.3.1 Clean Natural Gas. Natural gas is often called “clean”, because methane, the principal component of natural gas, has the highest heat of combustion per unit carbon atom of any carbon-based fuel. Thus, combustion of methane leads to the greatest energy release per CO₂ emission. In addition, natural gas has the fewest toxic mineral impurities

of all fossil fuels and is much less prone to incomplete combustion, since it mixes readily with gaseous oxygen. Thus, natural gas is, indeed, the cleanest *burning* fossil fuel. Natural gas has particular regional applicability in the U.S. due to a “Shale Gas revolution” that has been occurring since ~2008, spurred by a significant increase in horizontal drilling techniques.

However, life cycle analyses of natural gas extraction, delivery, and storage suggest that the environmental impact of these stages may be significant,²⁴ although the comparison to other fossil fuels is highly dependent upon the assumptions in the model, in particular, practices in flaring, construction, transport and operation.²⁵ Fugitive emissions of methane can easily offset efficiency gains during combustion, due to the increased global warming potential (GWP) of methane relative to the CO₂ combustion efficiency gains. Quantification of methane fugitive emissions relies upon estimates, and a recent disaster in Southern California involving the largest natural gas leak in the history of the United States^{****} highlights our current limits for real time detection and response to methane leaks.

Sources of natural gas are abundant, and the domestic supply is increasing dramatically (as is the associated controversy concerning environmental ramifications). Importantly, natural gas may be produced via renewable sources, such as the anaerobic digestion of municipal waste, and there is an increasing impetus to use this renewable natural gas to fuel municipal fleets, with demonstration projects in California and Colorado.²⁶ Storing and transporting methane requires compression, which represents a parasitic energy loss

^{****} 97,100 metric tons of natural gas were released during a three month period before the leak was stopped, corresponding to 5 x 10⁹ cubic feet of gas, or 3% of the facility’s capacity. Nathaniel Rich, *The Invisible Catastrophe*, New York Times, Mar. 31, 2016.

and transporting a compressed gas safely requires expensive carbon fibre tanks. Often, methane produced in remote areas is mixed with other gases (e.g. nitrogen and/or carbon dioxide), which must be removed in order to compress and transport the gas economically.

4.3.2 Advanced Combustion Strategies. Advanced combustion strategies modify the combustion process in order to both increase fuel efficiency and concentrate carbon dioxide in the product to facilitate subsequent carbon capture. Advanced combustion encompasses the concepts of ‘clean coal’, oxycombustion, gasification, and chemical looping.

Although advanced combustion can generally be applied to any hydrocarbon, let us consider methane as a representative hydrocarbon to simplify the discussion and stoichiometry. First consider the “standard” combustion of methane, which is quite exothermic:

Generally, the combustion process is completed in air rather than oxygen. If the composition of air is approximated as a 4:1 ratio of N₂ to O₂, then the molar composition of CO₂ in the flue gas is 1/11th. This assumes complete combustion and ignores oxidation of trace N₂ to form nitrous oxides (NO_x). In practice, excess air is used to ensure complete combustion; excess air further dilutes the CO₂ concentration in the flue gas, to typical values of 3-13%.²⁷

Now consider the process of *gasification*, which replaces oxygen with water, leading to:

Gasification is endothermic, as shown. Gasification is the primary means to produce molecular hydrogen on an industrial scale. Gasification is also used in a number of power plants, generally replacing methane with more complex hydrocarbons such as those found in coal. Gasification is a means to break down a coal particle into smaller molecules (i.e. CO and H₂) that are more readily and efficiently combusted.

Coal gasification utilizes high temperatures (typically > 700 °C) and pressures to vaporize and break down complex hydrocarbons. These high temperatures and pressures are supplied by combining reaction [11] with reaction [10]. In other words, the exothermic combustion reaction is coupled with the endothermic gasification reaction. The combined reaction is known as *controlled partial gasification*. Adding reaction [10] with n reactions of [11] yields:

The value of n is dependent upon the temperatures and pressures desired, as well as the desired composition of the product stream. The product of partial gasification is synthetic gas (syngas), comprised of CO₂, CO, H₂, and H₂O. The desired composition of the syngas, in particular the CO:H₂ ratio, is dependent upon the desired application. Syngas may be converted to synthetic liquid fuels by a series of catalytic carbon addition reactions, known as the Fischer-Tropsch process. Alternatively, for power production, syngas should consist primarily of H₂ and CO₂. The CO:H₂ ratio of syngas is altered for the desired application via the water-gas shift reaction:

After [13], the syngas in a power plant consists primarily of H_2 and CO_2 (with some H_2O and N_2). As controlled partial gasification uses less oxygen than combustion, less N_2 is present in the product stream.

In a gasification facility, H_2 is separated from the other gases at high temperature and pressure, where the driving force and thermodynamics of separation are increased, and the H_2 -rich stream is sent to a combustion turbine. The resulting high-pressure, high-temperature CO_2 stream from a gasification facility is typically ~40-50% CO_2 ,²⁸ roughly a four to five-fold increase over a combustion process.

In order to further increase the CO_2 concentration (to better enable carbon capture and storage) N_2 may be removed from the combustion process altogether, via use of chemical looping or oxy-fuel combustion strategies. *Oxy-fuel combustion* utilizes purified oxygen rather than air in the combustion chamber, further minimizing the amount of nitrogen diluent, leading to a flue gas that is further enriched in CO_2 . Oxygen is purified from air at large scales via cryogenic distillation, which is energy intensive. The highly parasitic energy loss of cryogenic distillation makes this feasible only with the decreased oxygen input of gasification. The incentive to purify oxygen is that this has the potential to be less energy intensive than subsequent purification of CO_2 from the flue gas. Emerging separation technologies may change the economics of large-scale air purification²⁸ or carbon capture. An alternative to large-scale separation of air is chemical looping, which delivers oxygen via oxidation-reduction cycling of a metal oxide carrier; the metal oxide supplies oxygen for combustion and then is reduced by the fuel in the combustion chamber.

A significant drawback of these advanced combustion strategies is that it is not possible to retrofit existing power plants with these technologies. Both oxy-combustion and chemical looping require significantly higher temperatures, and thus require new structural materials for the reactor, especially since these reactions occur at very large scale at high pressure. Thus, advanced combustion strategies would require a major reinvestment in a new infrastructure.

4.3.3 Carbon Capture and Storage (CCS). Short of archiving carbon-based fuels, considerable reduction in carbon emissions is unlikely without capture of the CO₂ combustion product before it enters the ‘active carbon cycle’ in Fig. 4. Whether the CO₂ is to be utilized or sequestered, it must be purified, transported and stored; resulting streams are typically >90% CO₂ at pipeline pressures of 100-150 atm.²⁸⁻³⁰ Practically speaking, CCS is limited to point sources, such as those at centralized power and industrial facilities. These stacks are already heavily regulated, and provide point sources that are relatively concentrated in CO₂. The vast majority of today’s combustion facilities contain up to ~10% CO₂ in the flue gas (reaction [10], in N₂), which exits the stack at approximately atmospheric pressure. Thermodynamics dictates that concentration and pressurization requires a significant energy input, and thus CCS strategies represent significant parasitic energy losses that translate to additional fuel consumption and the corresponding environmental impacts of extraction.

Clean coal advocates suggest that end-of-pipe devices can be put in place to capture CO₂ emissions, with similar success that has been seen for other air pollutants through the use of end-of-pipe pollution control technologies such as baghouses and scrubbers (among others). Capturing CO₂ from these facilities is termed *post-combustion* CCS, as it

basically involves an end-of-pipe add on control technology, without modification of the process itself. CO₂ is scrubbed from the flue gas by injecting a basic amine-based solvent (such as monoethanolamine) that chemically absorbs the CO₂. This is currently the technology of choice, as it is amenable to large scale and the low pressures of flue gas. However, amine-based solvents are susceptible to thermal and oxidative degradation and require high energy input for regeneration.³⁰

4.3.4 Pre-combustion CCS strategies modify the combustion process to maximize the concentration of CO₂ in the flue gas, using the advanced combustion strategies outlined above. In addition to increasing fuel efficiency, the increased CO₂ concentration in the gasification minimizes the parasitic energy expenditure of the CCS process, as some of the work to concentrate the CO₂ has already been done. Moreover, the separation of CO₂ at high pressure leads to a greater driving force for separation, and minimizes the parasitic energy loss for compression and transport. The high-pressures and high-temperatures used in pre-combustion CCS open up new opportunities for solvents, adsorbents, membranes, or hybrid processes to capture the CO₂.

4.3.5 Prospectus. Capture and storage of CO₂ from power plants represents a significant engineering challenge and a tremendous expenditure of energy. Estimates of the process energy penalty for CCS include an 8-20% drop in net efficiency for post-combustion capture and a 12-20% drop for pre-combustion CCS.³¹ CCS will significantly increase the price of electricity; estimates are 25-40% for retrofitting new plants, to 80%³² for designing new plants. A DOE research target is to decrease this cost, such that 90% CO₂ capture can be achieved with an increase in cost of 20% for post-combustion and 10% for pre-combustion capture.³³ Despite apparent cost savings of the latter, it requires a major

reinvestment in infrastructure, money that is perhaps better spent investing in carbon-free energy sources. The next obvious question is what will be done with all the stored CO₂, an issue addressed in the next two sections.

4.4 Beneficial Reuse of Carbon Emissions

4.4.1 Carbon utilization suggests that the CO₂ captured from the combustion process will be put to beneficial reuse in developing or displacing other chemical feedstocks. Several strategies for carbon utilization have been reviewed elsewhere,³⁴ and include: (a) coupling endothermic CO₂ reforming of methane with other exothermic reactions, (b) use of CO₂ as a mild oxidant in industrial-scale reactions, (c) reaction of CO₂ with ammonia to produce a fertilizer, (d) substitution of CO₂ for other reactants in production of, for example, salicylic acid and dimethyl carbonate, (e) use of supercritical CO₂ as an industrial solvent, (f) use of a CO₂-rich gas in Fischer-Tropsch synthesis of synthetic liquids, or (g) hydrogenation of CO₂ to methanol using ‘renewable H₂’, with additional ‘upcycling’ to other hydrocarbons. Another emerging theme for carbon utilization is use of biochar, a byproduct of thermal pyrolysis of biomass, for soil amendment. As shown in Fig. 4, and discussed elsewhere,³⁵ the content of carbon in the soil exceeds that of the atmosphere by several-fold (estimates may vary from 5-15 times). The lifetime of soil organic matter can exceed thousands of years,³⁶ with impact on water quality and retention of nutrients in the soil for fertilizing plant growth.³⁶

There are several potential concerns related to the carbon utilization strategy. First, one must evaluate whether a proposed strategy represents a mere delay in returning the carbon to the much larger natural reservoirs, or sequestration over a much larger timescale (as may be the case for biochar if it is retained for thousands of years). Additional concerns

are how retention of carbon in various reservoirs may affect other ecological systems⁸. Second, there is a significant mismatch of scale between the FF mass flow rate and the scales of *all other anthropogenic flows* of carbon molecules. To put this issue in perspective, the carbon present in the *global* rate of worldwide plastic production is only 6% of the rate that CO₂ is emitted in the U.S.^{†††}

Third, many of these carbon utilization reactions are endothermic, and it has been proposed that they may be coupled to other exothermic reactions or powered by renewable energy; the proposal devalues other potential uses of this high value energy. Such a proposal to reduce CO₂ with ‘renewable’ H₂ or NH₃ generally involve high-pressure, high-temperature conditions, and precious metal catalysts, as well as the input of renewable energy to produce H₂ or NH₃, which are not naturally abundant. Even when/if the considerable energy input is acknowledged, one must analyse whether this energy may be more effectively used directly to offset the FF stream, for example, by producing electricity to power electrical vehicles. Another consideration is whether waste biological feedstocks represent a natural alternative to “upcycled CO₂”, with the energy input provide by photosynthesis to convert the CO₂ to a CH_xO_y molecule, thus alleviating the need for engineered methods to complete this conversion. For this reason, biological feedstocks was discussed as a “Tier 2” strategy, whereas upgrading CO₂ to CH_xO_y, in the authors’ opinion, is a lower priority.

4.4.2 Enhanced oil recovery (EOR) is a possible economic route for carbon utilization.

After hydraulic pressures are exhausted in an oil well, and physical stimulations methods

^{†††} According to the U.S. Energy Information Agency, 5,270 million metric tons of CO₂ were emitted to the atmosphere by the U.S. in 2012. The *global* worldwide plastics production in 2012 was about 300 million tons in 2013 (Gourmelon, Global Plastic Production Rises, Worldwatch Institute).

(such as water injection) have been used, more than 50% of the oil typically remains in the reservoir. *Enhanced oil recovery*, also known as tertiary recovery, uses a chemical means to recover oil from the subsurface by altering the properties of the oil. Examples of chemicals that are used include nitrogen gas, steam, surfactants, and CO₂, pertinent to the present discussion. CO₂ dissolves in the oil, altering its chemical properties, decreasing its viscosity and its binding to geological media. Tertiary oil recovery methods extend the lifetime of a reservoir, decrease the need for more exploratory or offshore drilling, and are partly responsible for the “Shale Gas revolution” in the U.S. since 2008. A life cycle analysis suggested that this is the only strategy that provides a net economic incentive for CCS.³⁷

4.4.3 Carbon Sequestration. Concentrated CO₂ may be removed from the active carbon cycle via *sequestration* in giant underground caverns, such as those found in depleted oil fields or in deep saline aquifers. Although creating *permanent* “carbon waste facilities” is considered inherently unsustainable by many, carbon sequestration may provide a short-term solution to make viable an “all of the above” energy approach in the face of climate change concerns. From the mass balance perspective illustrated in Fig. 4, this concept essentially involves recovering a resource, extracting its energy, and rerouting the waste products back to the original reservoir. However, capturing a sizable fraction of CO₂ from the stack of a power plant remains a considerable engineering challenge. Moreover, the assumption of carbon sequestration advocates is that major geological events will not compromise these facilities and that the injection of high-pressure waste fluids into the subsurface will not otherwise alter the environment. Yet, a similar assumption in the

injection of wastewater fracking fluids *has* been disproven, due to a number of environmental impacts associated with this practice.³⁸

Recent demonstration projects captured and sequestered CO₂ at a rate of approximately 1 million tons per year (in the U.S., with more worldwide), showing that sequestration in underground reservoirs is *technologically feasible*. However, the current scale relative to the demand is daunting: the 1 million tons per year captured in the U.S. is less than 0.06% of its total carbon emissions,^{****} suggesting that 1,500 such facilities would be required to sequester all CO₂ for this country alone. The demonstration projects are no longer in operation, as there was no financial or political incentive to continue injecting CO₂ in the ground once the demonstration ended. The CO₂ produced at these facilities is now used for enhanced oil recovery.

4.5 Tier 3: Clean-Up Carbon Emissions

4.5.1 Direct carbon dioxide removal (CDR) may refer to either engineered or natural systems that directly remove CO₂ from the atmosphere. In an engineered device, large quantities of atmospheric gas pass through a device that concentrates CO₂. Although there exist chemical technologies that retain CO₂ preferentially, the thermodynamics of “demixing” CO₂ from the atmosphere demonstrate the energy input for accomplishing this process will be significant, and moreover, as there is a small driving force for engineered mass transfer separations, the scale of this endeavour will be quite large. Given the large quantities of air that would need to be treated to have any appreciable impact on the atmospheric CO₂ concentration, engineered CDR technologies are likely to

^{****} According to the Energy Information Administration, the U.S. CO₂ emissions from coal-fired power plants in 2014 totalled 1,570 million tons. Total CO₂ emissions from all U. S. sources were 5,270 million metric tons in 2012.

be cost prohibitive. A recent National Academies study also concluded that CDR strategies, although potentially beneficial, are limited at present by cost and technological immaturity.³⁹

Natural CDR strategies include accelerating “carbonization” from the atmosphere. One will note in Fig. 4, that the FF stream is relatively small compared to other natural carbon flows to the atmosphere. Other strategies to remove carbon from the atmosphere include afforestation, soil modification, and a significant modification of agricultural processes. These strategies require tremendous land area and have other ecological concerns, including the potential to alter the Earth’s albedo⁸. The National Academies Study also considered “fertilizing” the ocean to accelerate algal photosynthesis and genetic modification of crops to increase the carbon uptake of plants. The study concludes that such concepts involve significant uncertainties and additional environmental concerns (i.e. putting chemicals into the ecosystem and genetically modified organisms), and are thus controversial. The ecological impacts of such strategies are also of concern, and the estimated effectiveness of these strategies has been revised downward.⁸

5. Conclusions

The purpose of this paper was to tie interdisciplinary concepts in energy and environment to basic scientific principles, using an energy and mass balance perspective. We have examined a basic one parameter, scalar description of the Earth’s energy balance to illustrate the relationship between Earth’s temperature and the atmospheric composition. The carbon cycle of the Earth is analyzed through a mass balance approach, and carbon remediation strategies are considered in a tiered framework based on the potential to affect the Earth’s carbon balance.

Although carbon-free energy sources, particularly renewables, should be pursued aggressively, the current rate of growth in renewable energy production suggests they will not displace fossil fuels in the foreseeable future. Thus, a more comprehensive strategy will be needed to affect the Earth's energy and carbon balance. Capturing carbon dioxide at the rates needed to offset recent climate trends is a tremendous engineering challenge. Utilizing the carbon dioxide for beneficial reuse will also be challenging at the scales needed, but increased use of biorenewable resources and enhanced oil recovery offer two promising scenarios. Of particular interest are processes that result in negative carbon emissions, such as use of biomass with carbon sequestration, drop-in biofuels, and conversion of waste into renewable methane, among others.

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