# 5 Climate change mitigation: global sustainable chemistry

We can state that humans became a global force in the chemical evolution with respect to climate change by interrupting naturally evolved biogeochemical cycles. But humans also do have all the facilities to turn the "chemical revolution" into a sustainable chemical evolution. That does not mean "back to nature". At the beginning of Chapter 4, we defined a sustainable society as being able to balance the environment, other life forms, and human interactions over an indefinite time period. "The Great Acceleration is reaching criticality. Whatever unfolds, the next few decades will surely be a tipping point in the evolution of the Anthropocene" write Steffen et al. (2007).

A global sustainable chemistry first needs a paradigm change, namely, the awareness that growth drives each system toward a catastrophe (Möller 2015). Sustainable chemistry, also known as green chemistry, is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances. Anastas and Warner (1998) developed 12 principles of green chemistry:

1. *Prevention*: It is better to prevent waste than to treat or clean up waste after it has been created.
2. *Atom economy*: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. *Less hazardous chemical syntheses*: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. *Designing safer chemicals*: chemical products should be designed to affect their desired function while minimizing their toxicity.
5. *Safer solvents and auxiliaries*: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. *Design for energy efficiency*: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. *Use of renewable feedstocks*: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. *Reduce derivatives*: Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because these steps require additional reagents and can generate waste.

https://doi.org/10.1515/9783110561340-005

9. *Catalysis*: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. *Design for degradation*: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. *Real-time analysis for pollution prevention*: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring, and control prior to the formation of hazardous substances.
12. *Inherently safer chemistry for accident prevention*: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

With respect to the climate system, principles 1, 2, 7, and 11 are most important. The basic principle of global sustainable chemistry, however, is to transfer matter for energetic and material use only within global cycles without changing reservoir concentrations above a critical level, which is "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt 1988).

To keep the 2 °C climate warming goal, the cumulative $CO_2$ emission must be limited to about 1,000 Gt carbon (at present we are approaching 650 Gt). Hence, the atmospheric $CO_2$ increase must be stopped in next few decades and the "energiewende" (energy transition, energy turnaround, energy revolution or energy u-turn) must be completed by the end of this century. There are several ways as a consequence of the nearly irreversible accumulation of anthropogenic $CO_2$ in air and the cognition that carbon from fossil fuels is limited, but the findings that carbon compounds are optimal carriers for energy conversion and materials:

- to reduce fossil fuel combustion (replacement by solar energy);
- to capture $CO_2$ from exhaust gases and storage (carbon capture and storage (CCS) technology);
- to capture $CO_2$ from ambient air (DAC) air (and/or other reservoirs such as seawater[603]); and
- to recycle $CO_2$ into utilizable carbon compounds (or sequestration achieving a negative flux).

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[603] The desorption of dissolved $CO_2$ from seawater (being 90% $HCO_3^-$ with a mean total DIC concentration of ~28 mg C $L^{-1}$ – by a factor of 1,000 larger than atmospheric carbon) could be another approach for closing the carbon cycle (we currently call it *seawater capture*). Hence, in the case of a technology with 60% desorption efficiency, "only" 150 $km^3$ seawater must be globally processed daily to attain the production mentioned above (1 Gt $yr^{-1}$). In our laboratory, an ultrasonic-based $CO_2$ desorption technique has been developed as an alternative to the thermal stripping in the CCS process, and it is not difficult to believe that this technology could be applied to seawater decarbonization.

CCS is an essential element of any low-carbon energy future and industrial future, but policy is the main issue, not technology. The world's first large-scale application of $CO_2$ capture technology in the power sector commenced operation in October 2014 at the Boundary Dam Power Station in Saskatchewan, Canada. There are 22 large-scale CCS projects currently in operation or under construction around the world, with the capacity to capture up to 40 million tonnes of $CO_2$ per year (World Energy Resources 2016).

From the long-term perspective, the transmission to renewable energies will solve the problem of the depletion of fossil fuels but is surely too late to minimize climate change. Although future oil consumption might stagnate or even decrease, coal consumption remains important for long time. CCS technology is considered the only practical solution for early $CO_2$ control. $CO_2$ storage (and sequestration) is not only the ultimate technology for "neutralizing" the $CO_2$ budget through the combustion of fossil fuels but also the only way to make the biosphere-atmosphere $CO_2$ budget "negative", that is, reducing atmospheric $CO_2$ loading. CCS technology is now widely accepted as a solution for meeting the climate protection targets ($CO_2$ emission reduction) worldwide and a precondition for further use of coal-fired power plants beyond 2020 in Europe. However, the reduction in energy efficiency by about 25% because of carbon capture (based on $CO_2$ washing by monoethanolamine and subsequent thermal $CO_2$ stripping) needs an equivalent increase in coal combustion to maintain the energy budget. Moreover, $CO_2$ storage is accompanied by several problems that have not yet been fully solved. The main objection, however, lies in the one-way function: the one time use of fossil fuels by transforming them into carbon dioxide, which is at best deposited for a million or more years in geological stocks.

The "safety" of $CO_2$ storage is realized by a small diffusive loss rate compared with the capture rate (catastrophic events of $CO_2$ eruptions from geological stocks are postulated not to occur). Hence, a $CO_2$ residence time of only a few hundred years in geological stocks is sufficient to compensate effectively climate impacts from $CO_2$. Moreover, $CO_2$ storage is a resource for future carbon use. But even if CCS technology is deployed at all large industrial facilities, more than half of global $CO_2$ emissions would remain.

Instead of storing $CO_2$, it is suggested that it should be recycled by transformation into different reduced carbon species ($CH_4$, CO, C, and many hydrocarbons), now termed *solar fuels* (see Section 5.3.2). The ultimate solution of the $CO_2$ problem in terms of atmospheric recovery and providing a carbon feedstock is direct air capture (DAC); see Section 5.2.3.

## 5.1 Growth and steady-state economy

In nature, many processes follow this simple law (5.1), which expresses that the change of a quantity $N$ (for example population, mass, energy) is proportional to the quantity itself. In other words, exponential growth occurs when some quantity regularly increases by a fixed percentage. The proportionality coefficient $\lambda$ characterizes the process (biology, chemistry, physics, economy, etc.) as follows:

$$\frac{dN}{dt} = \lambda \cdot N = F \text{ and } N(t) = N_0 \exp(\lambda t) \qquad (5.1)$$

We see that $dN/dt$ denotes a flux $F$; according to the sign, it could result in a growth (positive sign) or decline (negative sign). It is clearly seen that a negative flux will end with $N(t) = 0$ with $t \to \infty$ when there is no permanent source (positive flux) of $N$ to maintain a pool of this quantity.

Growth (positive sign), however, is first a mathematical problem but bacterial growth is the best example. Crichton (1969) wrote (fortunately, mathematics describes natural processes but does not control them):

> The mathematics of uncontrolled growth is frightening. A single cell of the bacterium *E. coli* would, under ideal circumstances, divide every twenty minutes. That is not particularly disturbing until you think about it, but the fact is that bacteria multiply geometrically: one becomes two, two become four, four become eight, and so on. In this way it can be shown that in a single day, one cell of *E. coli* could produce a super-colony equal in size and weight to the entire planet Earth.

The growth of a population is only possible if nutrients or food are available to allow the increase in *N*. As discussed, this concerns the super-exponential growth of the human population from the eighteenth century onward. Any (exponential) growth of nonhuman population will soon be limited through nutrition, water, and the subsequent limits of the habitat. As a consequence of the increasing population and the limits in its sustainability, a decline (negative growth) starts, in other words, the death of individuals. Basically, this is also valid for humans without solving the supply problems concerning energy, food, and materials. Scientific and technical innovation, however, has (so far) overcome the limits. But there is a fundamental difference to nonhuman populations; in nature (without humans) producers and consumers are balanced – the mass budget is zero.[604] Moreover, any growth is limited through the flux of renewable (solar) energy to provide process energy.

Humans exceeded these natural limitations by exploiting raw materials from the lithosphere (fossil fuels and minerals) and biosphere (wood), disregarding (or shifting it into future) that the extraction fluxes are larger than the recovery fluxes. For abiogenic matter (natural deposits recovery), the latter one is zero over human time scales. Hence, the limits are well defined and replacement strategies were developed or designed. The problem of why they are not yet or only hesitantly introduced is simply the economy, or more correctly the price. For so long traditional technologies (especially mining, transportation and the combustion of fossil fuels)

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[604] That is not fully true. Permanent climate change occurs but over long time scales allowing adaption through evolution.

have produced more profit, with solar energy (which first needs a new infrastructure) secondary. Hence, the economic paradigm has to be changed: the costs of energy must include the costs of sustaining the climate and/or the cost of climate change on long-term basis. This done, only solar energy (direct or indirect) is much cheaper.

Another much more serious problem than resource limitation is the waste accumulation in the climate system. The challenge is clear: to adopt the natural model of cycling matter. Each produced good (from nature-extracted matter) must be recycled to the chemical status of the primary compound or (compromising) transferred to a pool without climate impact.

Another message to traditional economists and politicians[605] is that exponential growth is far away from any idea of a sustainable society. Growth leads to crisis: financial, pollution, and supply. A sustainable society is characterized by equilibrium:

$$\left(\frac{\mathrm{d}N}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_{\text{product}} - \left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_{\text{waste}} = 0 \tag{5.2}$$

This does not exclude growth but growth (production ≈ consumption assumed[606]) must be compensated by removal. Self-limitation of this system is naturally given if waste cannot be turned back into products.

The observation that economic growth has limits led to the development of "steady state economics" (sometimes also termed ecological economics or full-world economics). Ecological economists also observe that an economy is structured such as an ecosystem. Permanent growth – as stated by politicians – will not solve life problems such as employment; this is a question of reorganizing society. After productivity (expressed as constant annual turnover) satisfies social consumption needs, stationary conditions are then achievable, that is, $\lambda$ becomes zero in eq. (5.1). Before 1800, global growth was less than 0.1% $\text{yr}^{-1}$ and increases to more than 3% $\text{yr}^{-1}$ in the second half of the twentieth century. Naturally, the human population will (and must) tend to a constant number. This limitation process is likely to go on over the next 200 years. Another limitation must be set through per capita consumption to provide social and cultural standards. The growth, however, is going on this century. Without revolutionary technological changes, the climate becomes out of control.

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[605] It is a traditional believe that annual growth of GNP (gross national product) leads to more prosperity. The GNP is obviously not a measure of progress; it is a measure of monetary flow, effort, and expense. A nation with a constant population can obtain a maximum of annual consumption, dependent from many factors, and even reduce the consumption to a level, defined by sustainability. So, why further growth of GNP? Economy needs simple reproduction (after getting a social defined level) and no more advanced reproduction,

[606] In reality, production > consumption because of losses. It is a challenge to achieve production ≈ consumption both from resource management and climate control.

The steady-state economy is an entirely physical concept. Any nonphysical components of an economy (e.g., knowledge) can grow indefinitely. But the physical components (e.g., supplies of natural resources, human populations, and stocks of human-built capital) are constrained and endogenously given. An economy could reach a steady state after a period of growth or after a period of downsizing or degrowth.

However, the technical man also uses materials (nonorganic such as minerals and elements) with life-cycles being extremely small comparing to its geochemical recycling. Even in a steady-state economy, simple reproduction consumes materials not being in time scale of natural reproduction. Hence, sustainable economy also leads on long-term scale (thousands of years) to an irreversible degradation. The technical society remains therefore always a factor in global chemical weathering and dissipation. The challenge of sustainable chemistry is looking for replacement of inorganic through organic (hence reproducible) materials and substances; the carbon-based economy is later described in Section 5.3.1.

## 5.2 The carbon problem: out of balance

From the analysis of the history of anthropogenic trace compounds in the atmosphere, its impacts on the climate system – so far we understand the processes of climate change – and recognizing the introduced abatement, few atmospheric environmental problems remain that are connected with the compounds $N_2O$, $CH_4$, and $CO_2$. The carbon dioxide problem is by far the most serious. There is no or only very little hope that global $CO_2$ emissions will significantly decrease in the next two or three decades. In contrast to $N_2O$ and $CH_4$, the atmospheric residence time of "anthropogenic" $CO_2$ is orders of magnitudes larger (Section 5.2.2); in other words, even when there would be a zero $CO_2$ emission world soon, the subsequent "greenhouse" effect will still last several hundreds of years. However, there are ways to solve the problem (Section 5.3.1). That part of $N_2O$ and $CH_4$ linked with fossil fuels will "automatically" be solved together with the $CO_2$ problem. Hence, because the remaining sources of $N_2O$ and $CH_4$ are linked with agriculture and food production (Section 4.2.3), they are likely to become the dominant residual problem in 100 years, but with a far lower impact factor than today. In the following two subsections, the "carbon problem" is characterized in terms of the budget, residence time, and global equilibrium.

Climate scientists have warned that to have a 50-to-50 chance of limiting global warming to not more than 2 °C above the average global temperature of preindustrial times throughout the twenty-first century cumulative carbon emissions between 2011 and 2050 need to be limited 300 Gt C (Allen et al. 2009, Meinshausen et al. 2009). Recent calculations suggest that this necessitates one-third of oil reserves, half of gas reserves, and over four-fifths of coal reserves to remain untapped from 2010 to 2050

(McGlade and Ekins 2015). With business as usual, global warming leads to unacceptable degrees of peak global warming, around 5 °C. This highlights the urgency and scale of the climate policy challenge. Van der Ploeg and Rezai (2017) estimate of the optimal time paths for the carbon tax significantly curb cumulative fossil fuel use to 670 Gt C. As a consequence, peak temperature reduces to 2.2 °C in their baseline scenario but ranges between 1.2 °C and 3 °C across scenarios with cumulative emissions ranging from 30 to 1430 Gt C. These results illustrate how previous estimates of the carbon budget for 2 °C (usually cited at around 300 Gt C) have been too pessimistic.

### 5.2.1 The carbon budget

Since the beginning of the Industrial Revolution, humans have emitted about $(365 \pm 30) \cdot 10^{15}$ g $CO_2$–C from the combustion of fossil fuels and cement production, and about $(180 \pm 80) \cdot 10^{15}$ g $CO_2$–C from land-use change, mainly deforestation (period 1750–2011, IPCC 2013). Vegetation biomass and soils not affected by land use change, stored 150 ± 90 Pg C (IPCC 2013). Hence, the net effect was an emission of 355 Pg C into the atmosphere for the 1700–2011 period (350 Pg C for the period 1750–2000 after Minnen et al. 2009). The atmospheric increase amounts $(240 \pm 10) \cdot 10^{15}$ g $CO_2$–C and the oceans take up $(155 \pm 30) \cdot 10^{15}$ g $CO_2$–C and the residual terrestrial uptake amounts $(150 \pm 90) \cdot 10^{15}$ g $CO_2$–C. The world carbon stocks for about 1990 are (Scurlock and Hall 1991), in $10^{15}$ g C:

- in plant biomass (80% in trees) 560,
- in ocean 75 m surface layer 725,
- soil carbon content 1,515,
- deep ocean carbon 38,000, and
- fossil fuel resources (92% as coal) 5,900.

In 1750, the atmospheric $CO_2$ level was 278 ± 5 ppm, which increased to 390.5 ± 0.1 ppm in 2011 (Ballantyne et al. 2012). Since 1950 these sources have amounted to about $400 \cdot 10^{15}$ g $CO_2$–C, that is, 70% of the total carbon release. Measurements and constructions of carbon balances, however, reveal that less than half of these emissions remain in the atmosphere (Prentice et al. 2001). The anthropogenic $CO_2$ that did not accumulate in the atmosphere must were taken up by the ocean, by the land biosphere, or by a combination of both. The fraction of $CO_2$ remaining to the atmosphere from fossil fuel combustion was 59% (Thoning et al. 1989). Hence, with constant increases expected the atmospheric $CO_2$ mixing ratio is predicted to grow to 500 ppm in 2050 and to 700 ppm in 2100. There is no doubt that $CO_2$ was increasing since the Industrial Revolution and has reached a concentration unprecedented for over more than 400,000 years.

It is easy to calculate the amount of $CO_2$ accumulated in the atmosphere. Between mass and atmospheric mixing ratio $x$, the following relationship is valid. The changing air concentrations of trace compounds do not influence the value of the total mass of the atmosphere in any detectable way.

$$\text{mass of } CO_2 = x(\text{in ppm})10^{-6}\frac{\text{mol mass of } CO_2}{\text{mol mass of air}}\text{mass of the atmosphere} \quad (5.3)$$

The mass of human cumulated $CO_2$ in the atmosphere at a given year $i$ is

$$m = (1-\alpha)\sum_{i=1}^{t} Q_i \quad (5.4)$$

where $Q$ emission for year $i = 1$ until $i = t$ and $\alpha$ fraction (0 . . . 1) of up taken anthropogenic $CO_2$. It follows for the atmospheric $CO_2$ concentration (taking into account the values for the parameters in eq. (5.3); $Q$ in Pg $CO_2$-C (Gt):

$$x(t) = x(0) + \frac{1-\alpha}{2.15}\sum_{i=1}^{t} Q_i \quad (5.5)$$

This is equivalent to the regression shown in Figure 5.1. The point of intersection for zero emission amounts $x(0) = 286$ ppm in sense of a “pre-industrial level” (see Section 4.4.3.1). The slope $(1-\alpha)/2.15 \approx 0.20$ represents the atmospheric $CO_2$ increment (in ppm) per Pg ($10^{15}$ g) of total emitted $CO_2$. It follows from eq. (5.5) $\alpha = 0.57$, that is, 57% of emitted anthropogenic $CO_2$ is removed by the biosphere; $(1-\alpha)$ represents the airborne fraction (0.43). As seen from Figure 5.1, the slope (which corresponds to the airborne fraction) varies over the whole period 1850–2010, giving $(1-\alpha)$ between 40% and 60%. On average, 50% of the cumulative emissions were absorbed by the environment assuming, of course, that the carbon source is entirely

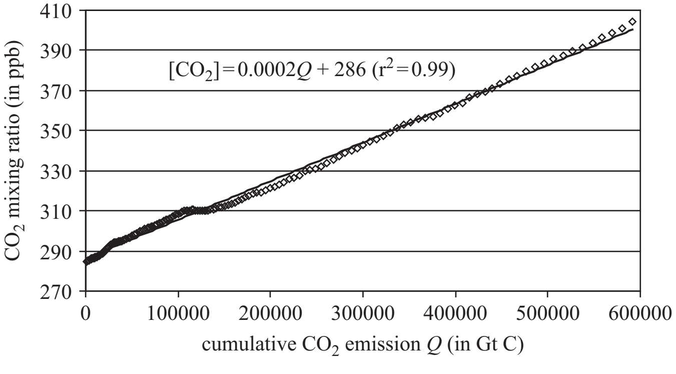

**Fig. 5.1:** Relationship between cumulative total anthropogenic $CO_2$ (from fossil fuel use and land-use change) and atmospheric $CO_2$ mixing ratio (data source see Figs. 4.45 and 4.49).

human (there is no doubt). This means that the emitted carbon dioxide is directly "partitioned among reservoirs".

By 2016, $CO_2$ mixing ratio (404 ppm) corresponds to $869 \cdot 10^{15}$ g $CO_2$–C: taking into account the total mass of the atmosphere ($5.2 \cdot 10^{21}$ g; Table 1.2 in Vol. 1) it follows that[607]

$$\text{atmospheric } CO_2 - C \text{ mass} = 0.0404 \ [\text{vol\%}] \cdot 10^{-2} \cdot \frac{12}{29} \cdot 5.2 \cdot 10^{21} = 869 \cdot 10^{15} \text{g}$$

where 12 is the molar mass of carbon and 29 the molar mass of air. Hence, the "reference" level of 285 ppb (related to about 1850) is equivalent to $613 \cdot 10^{15}$ g $CO_2$–C; the total added $CO_2$ mass since 1850 is, therefore, $256 \cdot 10^{15}$ g $CO_2$–C, less than half (43%) of the total emitted carbon ($591 \cdot 10^{15}$ g: 422 from fossil fuels and 169 from land-use change 1850–2016). In other words, the airborne fraction amounts as mean over the period 1850–2016 about 0.57. Without ocean and land uptake, the atmospheric $CO_2$ concentration would have increased to 566 ppm, if it had all stayed there.

Bolin et al. (1981) estimated a "pre-industrial" atmospheric $CO_2$ content of 614 Pg (290 ppm) assuming a constant airborne fraction of 0.54. The airborne fraction will increase if emissions are too fast for the uptake of $CO_2$ by the carbon sinks (Raupach 2013). It is thus controlled by changes in emissions rates, and by changes in carbon sinks driven by rising $CO_2$, changes in climate, and all other biogeochemical changes. However, the percentage of $CO_2$ injected into the atmosphere from human activities that remains in the atmosphere has remained pretty much constant for the last 50 years (Ballantyne et al. 2012). Knorr (2009) extended his analysis back 150 years, and concluded that the airborne fraction of carbon dioxide had remained constant over that longer period as well. Thus, identifying the mechanisms and locations responsible for increasing global carbon uptake remains a critical challenge in constraining the modern global carbon budget and predicting future carbon–climate interactions.

From eq. (5.5) we can simply calculate the future $CO_2$ concentration assuming different $CO_2$ emission scenarios based on the slope[608] given by Figure 5.1 and assuming (which is not self-evident) that the airborne fraction (~50%) also remains constant in future. In Figure 5.2, two different emission scenarios are presented:

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**607** Expressed in other terms, it follows that per ppm $CO_2$ the atmospheric increase amounts 2.150 Gt $CO_2$–C; Prater et al. (2012) use a "conversion factor" to be 2.120 Pg per ppm.

**608** It is remarkable that the linear fit ($r^2 = 0.996$) only begins at 1850. The period before (Fig. 4.50) is characterized by several distinguished positive and negative trends in $CO_2$. Between 1600 and 1800 there is a $CO_2$ minimum plateau (~270 ppm). This period is called the little ice age (LIA). It is generally agreed that there were three minima, beginning about 1650, 1770, and 1850, each separated by intervals of slight warming. Beginning around 1850, the climate began warming and the LIA ended. We may assume that natural $CO_2$ exchange was dominant and that the anthropogenic signal masked before 1850.

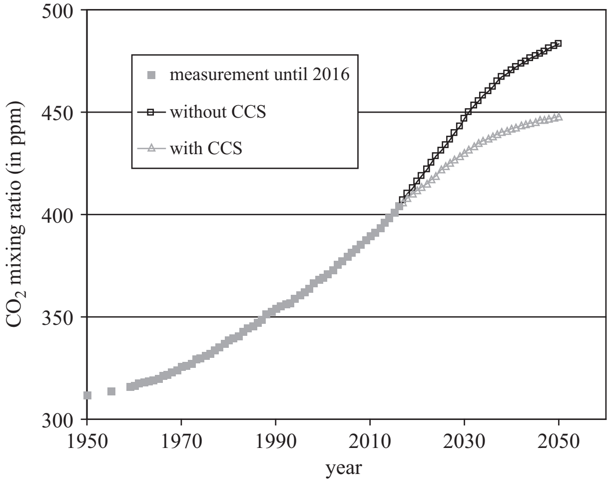

**Fig. 5.2:** Two scenarios of future atmospheric $CO_2$ development (see text for assumptions).

a) a further but slowing down increase of $CO_2$ emission (3% until 2020, then 2% until 2030 and further 1% growth); land use change and biomass burning 3 Gt $CO_2$–C $yr^{-1}$ constant until 2040 and further 2 Gt $CO_2$–C $yr^{-1}$, no carbon capture; and
b) the continuous increase of $CO_2$ emission, but with a faster slow down (3% until 2010, then 2% until 2015 and 1% until 2020), from 2020 carbon capture (1% $yr^{-1}$ increase until 2015 and then 5% $yr^{-1}$ until 2050).

Scenario (b) seems to be very optimistic – it results in a constant $CO_2$ mixing ratio of 450 ppm after 2050. It is more likely that carbon capture and sequestration/storage (CCS) technology (Section 5.2.3) becomes important only after 2030 and will capture a maximum of 50% of the fossil fuel-released $CO_2$. It is also unlikely that the yearly consumption of fossil fuels will be more reduced before 2050 because of the increasing alternative energy source percentage of the total energy consumption. Hence, in 2050 a value between 450 and 500 ppm $CO_2$ seems to be more likely.

The most important reservoir is the backmixed surface layer of the ocean (Table 5.1). The anthropogenic emissions are added to the atmosphere, continuously increasing the equilibrium carbon content of the surface layer as a result of the increasing partial pressure of the carbon dioxide in the gas phase (see Section 4.4.1.6 in Volume 1). The further transport of anthropogenic carbon from the surface to the ocean bulk (deep sea) is believed to be extremely slow (thousands of years) and hence the limiting step. A first quantification of the oceanic sink for anthropogenic $CO_2$ is based on a huge amount of measured data from two international ocean research programs; the cumulative oceanic anthropogenic $CO_2$ sink for 1994 was estimated to be $(118 \pm 19) \cdot 10^{15}$ g $CO_2$–C (Sabine et al. 2004). The cumulative uptake for the 1750–2011 period is ~ $(155 \pm 30) \cdot 10^{15}$ g $CO_2$–C from data-based studies (IPCC 2013), about 30% of the total cumulative anthropogenic $CO_2$ emission. Similar results were obtained by DeVries (2014) using a global steady-state ocean circulation inverse model, estimating the oceanic anthropogenic carbon storage to be 160–166 Pg C in 2012, and the oceanic anthropogenic carbon uptake rate averaged over the period 2000–2010 is 2.6 Pg C $yr^{-1}$ or about 30% of current anthropogenic $CO_2$ emissions. This result implies a residual (primarily terrestrial) anthropogenic carbon sink of about 1.6 Pg C $yr^{-1}$ for the same period. Ballentyne et al. (2012) estimated the uptake by a combination of land and ocean carbon reservoirs to be 2.4 ± 0.8 Pg C $yr^{-1}$ in the 1960s and 5.0 ± 0.9 Pg C $yr^{-1}$ in the 2000s.

**Tab. 5.1:** Global carbon budgets (in $10^{15}$ g C $yr^{-1}$) .

| | **(Denman et al. 2007)** | | **(Sabine et al. 2004)** | | |
|---|---|---|---|---|---|
| **process** | **1990s** | **2000–2005** | **1800–1994** | **1980–1999** | **total cumulative** |
| industrial $CO_2$ emission[a] | 6.4 ± 0.4 | 7.2 ± 0.3 | 244 ± 20 | 117 ± 5 | 329[d] |
| land-use change | 1.6[b] | 1.6[b] | 100–180 | 24 ± 12 | 156[e] |
| sum | 8.0 | 8.9 | 344–424 | 141 | 485 |
| atmospheric increase | 3.2 ± 0.1 | 4.1 ± 0.1 | 165 ± 4 | 65 ± 1 | 225[f] |
| difference (biospheric uptake) | 4.8 | 4.8 | 179–259 | 76 | 260 |
| ocean uptake | 2.2 ± 0.4 | 2.2 ± 0.5 | 118 ± 19 | 37 ± 8 | 165[g] |
| terrestrial uptake | 2.6[c] | 2.6[c,e] | 61–141 | 39 ± 18 | 95 |

[a] From fossil fuel use and cement production.
[b] Range 0.5–2.7.
[c] Range 0.9–4.3.
[d] 1751–2005 (Boden et al. 2015).
[e] 1850–2005 (Houghton 2008).
[f] Calculated from the difference 384 to 280 ppm $CO_2$.
[g] To be assumed 50% of cumulative industrial $CO_2$ emission.
[e] Forest sequestration for the period 1993–2003 has been estimated to be $0.3 \cdot 10^{15}$ g C $yr^{-1}$ (IPCC 2007).

The total oceanic dissolved carbonate carbon (Table 3.9 on p. 327) corresponds to 0.028 g $L^{-1}$ as carbon in seawater taking into account the volume of the world's oceans (Table 3.2 on p. 303). The experimentally estimated seawater standard carbonate carbon is 0.0244 g $L^{-1}$ seawater (Dickson et al. 2007). In the first 200 m of the ocean, the total deposited anthropogenic $CO_2$ (Table 5.1 and assuming that 30% is within this layer) only contributes to 3% to dissolved inorganic carbon (DIC). Hence, it is very difficult to measure trends in the DIC because of man-made changes (see Fig. 4.10 in Volume 1).

The kinetic processes of exchange and transport have a characteristic time of a few years for the system atmosphere – the mixed surface layer of the ocean – whereas the exchange time with the deep sea is between 500 and 2,000 years (Wagener 1979). Variations in surface concentration are related to the length of time that the waters were exposed to the atmosphere and the buffer capacity for seawater, as expressed by the *Revelle* factor. This factor represents the ratio of the instantaneous fractional change in the partial pressure of $CO_2$ ($\Delta p/p_0$) exerted by seawater to the fractional change in total $CO_2$ dissolved in the ocean waters ($\Delta\Sigma CO_2/(CO_2)_0$), where the subscript 0 denotes the reference status and $\Sigma CO_2$ denotes all forms of DIC (see Section 4.4.1.6 in Volume 1). Changes between ocean sediment and deep water play no role on a time scale of a few hundred years of anthropogenic perturbation of the surface layer $CO_2$. But over thousands of years nearly all anthropogenic $CO_2$ will be captured by the ocean.

The impact of global climate change on future carbon stocks is particularly complex. These changes might result in both positive and negative feedbacks on carbon stocks. For example, increases in atmospheric $CO_2$ are known to stimulate plant yields, either directly or via enhanced water use efficiency, and thereby enhance the amount of carbon added to soils. Higher $CO_2$ concentrations can also suppress the decomposition of stored carbon because C/N ratios in residues might increase and because more carbon might be allocated below ground. Predicting the long-term influence of elevated $CO_2$ concentrations on the carbon stocks of forest ecosystems remains a research challenge (Prentice et al. 2001). The severity of damaging human-induced climate change depends not only on the magnitude of the change but also on the potential for irreversibility. Solomon et al. (2009) show that climate change that takes place because of increases in carbon dioxide concentration is largely irreversible for 1,000 years after emissions stop. The question of how large the residence time of anthropogenic $CO_2$ in the atmosphere is will be discussed in next Section 5.2.2. There are strong arguments that the anthropogenic-caused $CO_2$ increase is largely irreversible; hence, stopping emissions will not solve (though might smooth) climate change problems. As a consequence, $CO_2$ capture from the atmosphere remains the challenge for climate sustainability (Section 5.2.3). The oceans have certainly been identified as the final sink of anthropogenic $CO_2$ but after thousands of years; moreover, the seawater uptake capacity will decrease and oceanic acidification will result in serious ecological consequences.

### 5.2.2 Atmospheric $CO_2$ residence time

As mentioned already, the $CO_2$ cycle has one major problem in the atmosphere – there is no direct chemical sink. In nature, $CO_2$ can only be assimilated by plants (biological sink) through conversion into hydrocarbons (Section 3.2.2.3) and stored in calcareous organisms, partly buried in sediments but almost completely turned back into $CO_2$ by respiration; hence, $CO_2$ partitionates between the biosphere and atmosphere. The only definitively carbon sink is the transport of DIC to deep ocean – when the ocean–atmosphere system is not in equilibrium, that is, in the case of increasing atmospheric $CO_2$ levels (due to anthropogenic and volcanic activities). The $CO_2$ source term by volcanic exhalations is very uncertain but is likely to be a value much less than $0.1 \cdot 10^{15}$ g $yr^{-1}$ carbon (see Section 6.3.3.3 in Volume 1). Hence, with respect to time periods being of interest for humankind (from decades to hundreds of years), this natural biogeochemical recycling can be regarded to be closed or, in other words, the net flux is zero. Consequently, all concentrations (pools) in the biosphere and atmosphere remain constant (we should not consider short-term variations because of seasonal and interannual fluctuations).

The only driving forces behind removing $CO_2$ from the atmosphere are dry deposition (including plant uptake) and wet deposition ($CO_2$ scavenging). As discussed, the marine and terrestrial earth surface can be assumed to be carbonate saturated. This equilibrium is only disturbed by the yearly increase of the $CO_2$ level due to anthropogenic emissions. Hence, the physical (not the biological) surface resistance is very large and no physical dry deposition flux results (Section 2.6.1 in Volume 1 for details). Therefore, the only abiogenic removal pathway from the atmosphere is $CO_2$ scavenging by clouds and finally precipitation. We can easily calculate the DIC in precipitation (assuming equilibrium; see eq. (4.87b) in Volume 1). Thus, we get 0.21 and 0.28 mg $L^{-1}$ carbon for 280 and 383 ppm $CO_2$, respectively (pH = 5.6 and at 10 °C). By using the global precipitation (Table 6.1 in Volume 1) it results in a very small total of wet removal fluxes (in $10^{15}$ g $yr^{-1}$ carbon):

- 280 ppm $CO_2$ (preindustrial): 0.08 and 0.02 for marine and terrestrial precipitation, respectively and
- 400 ppm $CO_2$ (today): 0.10 and 0.03 for marine and terrestrial precipitation, respectively.

The river run-off (Tables 6.3 and 6.4 in Volume 1) is about $0.46 \cdot 10^{15}$ g $yr^{-1}$ carbon and is much larger than the total wet-deposited carbonate ($0.13 \cdot 10^{15}$ g $yr^{-1}$ carbon). The global volcanic $CO_2$ emission is uncertain and there is given a value (Table 6.29 in Volume 1) of $0.02 \cdot 10^{15}$ g $yr^{-1}$ carbon. We state that the global carbon wet removal is significantly larger (by about a factor of 6 – 7) than the annual volcanic $CO_2$ release. Hence, it is likely that biogenic $CO_2$ is precipitated, but this amount is extremely small compared with the assimilation flux (about $0.1 \cdot 10^{15}$ g $yr^{-1}$ carbon). Moreover, the river run-off is much larger than the total continental wet removal flux (by a factor of ~15). It is likely that it comprises biospheric carbonate from soils but we cannot exclude anthropogenic $CO_2$. We can summarize that the maximal physical removal fluxes are $0.13 \cdot 10^{15}$ g $yr^{-1}$ carbon wet deposition and $0.46 \cdot 10^{15}$ g $yr^{-1}$ carbon river run-off.

The residence time $\tau$ in sense of a turnover from one reservoir (atmosphere) to another (biosphere) is generally described by (cf. Section 2.7 in Volume 1):

$$\tau = \frac{m}{F_{\text{sink}}} \tag{5.6}$$

where $m$ mass of the compound in the reservoir. The $CO_2$ mass in the preindustrial atmosphere amounts to about $600 \cdot 10^{15}$ g yr$^{-1}$ carbon with a global assimilation rate (Fig. 3.8) of about $200 \cdot 10^{15}$ g yr$^{-1}$ carbon, meaning the turnover time (a "pseudo-residence time") of natural $CO_2$ amounts to about three years. Some climate skeptics (Segalstad 2009) use this time quantity (enlarged because of rising atmospheric $CO_2$ mass to about four years) to explain that after the cessation of anthropogenic $CO_2$ emissions the recovery of the atmospheric $CO_2$ concentration will soon be expected (within less than 10 years). However, this is misinterpreting the conception of budgets and fluxes (Prather 2007). As discussed above, it follows that the natural removal is balanced with the new yearly input by respiration. In Section 2.7 in Volume 1 we define the residence time mathematically and see that eq. (5.6) is valid only for removal processes, which can be described by a first-order rate equation (cf. eq. 5.7):

$$F_{\text{sink}} = \frac{\mathrm{d}m}{\mathrm{d}t} = k \cdot m \tag{5.7}$$

Because almost all chemical reactions can be described as pseudo-first order (see Section 4.2.3 in Volume 1) and dry deposition (so far it is driven by physicochemical sorption) as well wet deposition can also described mathematically as first-order rate, removal of most atmospheric trace constituents can be described by eq. (5.6). However, $CO_2$ assimilation must be considered as a zero-order process, that is, the removal rate is constant and (largely) independent from the atmospheric $CO_2$ concentration. This becomes reliable when considering the global biosphere as heterogeneous uptake process, only depending on the plant amount. This consideration should not be fully valid but explains that application of eq. (5.6) is invalid. The above estimated "pseudo-residence time" of $CO_2$ is the time when all atmospheric $CO_2$ (assuming no $CO_2$ source via respiration) is completely consumed and the "reaction" (photosynthesis) abruptly stops. However, because respiration brings about at the same rate $CO_2$ back to the atmosphere, the "pseudo-residence time" of $CO_2$ becomes infinite. Only burial of organic matter (lignin-derived organic matter, relatively nonbiodegradable) in sediments, representing a small excess of photosynthesis over respiration, is important over million of years for control of $CO_2$ and $O_2$ (Berner 2005, Beerling and Berner 2005).

The $CO_2$ measurement clearly shows that the accumulative $CO_2$ increase is due to anthropogenic emission without fully balancing it by a sink. We have discussed in Section 5.2.1 that only about 50% of annual anthropogenic $CO_2$ is taken up by the biosphere and ocean. The remaining 50% builds up the carbon stock in the atmosphere ("airborne fraction") and can only be removed physically.

Taking the present anthropogenic $CO_2$ mass in the atmosphere (Table 5.1) of about $225 \cdot 10^{15}$ g carbon, and assuming that the river run-off represents the maximum physical removal rate, it follows from eq. (5.6) that there is a residence time of about 500 years. Taking into account only the atmospheric wet removal flux ($0.13 \cdot 10^{15}$ g $yr^{-1}$ carbon), the residence time is 1,700 years. Moreover, the residence will increase with increasing airborne $CO_2$. Having a mixing ratio of 500 ppm (corresponding to about $300 \cdot 10^{15}$ g carbon) by 2050, the residence time increases to 650 and 2,300 years, respectively. It is, therefore, likely that the removal capacity of our climate system for the recovery of anthropogenic atmospheric $CO_2$ is in the order of 1,000 years. Then, the removal flux amounts to $0.2 \cdot 10^{15}$ g $yr^{-1}$ carbon, only 2% of the present man-made emission flux.

### 5.2.3 Direct air capture (DAC)

The idea of DAC ($CO_2$ extraction from air) as climate control strategy is now accepted and seriously considered in global ecological (e.g., Cao and Caldeira 2010) and economic models (e.g., Edenhofer et al. 2006). Keith (2009) writes:

> Air capture is an industrial process for capturing $CO_2$ from ambient air; it is one of an emerging set of technologies for $CO_2$ removal that includes geological storage of biotic carbon and the acceleration of geochemical weathering. Although air capture will cost more than capture from power plants when both are operated under the same economic conditions, air capture allows one to apply industrial economies of scale to small and mobile emission sources and enables a partial decoupling of carbon capture from the energy infrastructure, advantages that may compensate for the intrinsic difficulty of capturing carbon from the air.

A complete air capture system requires both a contactor and a system for regenerating the absorbing solution. However, with the exception of CCS, which is presently transferred to larger technical equipment being tested in pilot plants, DAC and CCU (carbon capture and utilization) still only exist in laboratory or only on conceptual levels, characterized by different approaches.[609] Recently, the world's first commercial DAC plant for supply and sale of $CO_2$ opened on May 31, 2017 near Zurich in Switzerland. The commercial-scale DAC plant uses technology patented by Swiss company Climeworks that filters and captures pure carbon dioxide. The filter material is made of porous granulates modified with amines, which bind the $CO_2$ in conjunction with the moisture in the air. This bond is dissolved at temperatures of 100 °C.

The idea of $CO_2$ capture from ambient air using alkaline solution is not new (Tepe and Dodge 1943, Spector and Dodge 1946, Greenwood and Pearce 1953) and

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[609] A critic of the American DAC Report also comes from the Climeworks Company, which is doing solar-thermal $CO_2$ capture and conversion in cooperation with the Professorship of Renewable Energy Carriers, Institute of Energy Technology at ETH Zurich (Switzerland).

was used as a pretreatment before cryogenic air separation. In general, air capture includes all processes of $CO_2$ fixing and sequestration. In the past it focused on biomass (Marchetti 1977, Keith 2000, Metzger and Benford 2001), but it remains an option today and for the future too. Bio-energy with carbon storage is the term referring to a number of biofuel technologies, which are followed by carbon sequestration and yielding "negative emission energy" (Read and Lermit 2005). However, the key factor in $CO_2$ removal from the atmosphere is the specific carbon flux per time and square. Plant assimilation needs time and a large area, whereas bringing biomass (almost always wood) to biofuel power plants also needs energy. However, it is important to study all practical measures to slow down climate change and ensuring the safety of risky geo-engineering (Lenton and Vaughan 2009).

The large-scale scrubbing of $CO_2$ from ambient air was first suggested by Lackner et al. (1999). Zeman and Lackner (2004) write:

> It is not economically possible to perform significant amount of work in air, which means one cannot heat or cool it, compress it or expand it. It would be possible to move the air mechanically but only at speeds that are easily achieved by natural flows as well. Thus, one is virtually forced into considering physical or chemical adsorption from natural airflow passing over some recyclable sorbent.

The basic principles of $CO_2$ capture from ambient air with respect to a climate strategy were described in Elliott et al. (2001), Dubey et al. (2002), Keith et al. (2005), and Keith (2009). Almost all these authors suggested techniques based on sodium hydroxide, whereas sodium carbonate is converted back into NaOH by "causticization", one of the oldest processes in the chemical industry. Different absorbers were proposed such as large convective towers (Lackner et al. 1999), packed scrubbing towers (Zeman 2007), and a fine spray of the absorbing solution in open towers (Stolaroff et al. 2008). $CaO–CaCO_3$ cycles have also been proposed using solar reactors (Nikulshina et al. 2009).

Holmes and Keith (2012) adapt technology used in large-scale cooling towers and waste treatment facilities, which are designed to efficiently bring very large quantities of ambient air into contact with fluids. The design they present assumes that absorber fluid is an aqueous solution that absorbs $CO_2$ from ambient air (typically of a 1–2 M NaOH solution) with flux across the surface of the liquid film of order 1 mg $m^{-2}$ $s^{-1}$, and that, under typical operating conditions, each kilogram of solution absorbs about 20 g of $CO_2$ before it is returned for regeneration. A new generation of polymeric resins, containing specific primary amine functionalized based sorbents, have been developed (Buijs and Flart 2017 and literature therein). They are completely regenerated at temperatures in the order of 100 °C and show a low $H_2O$ adsorption of 1.5 mol $kg^{-1}$.

Generally, it is a huge challenge to believe that direct $CO_2$ extraction from air can be achieved in quantities approaching an order of several Gt C $yr^{-1}$. Note that about 50% (about 4 Gt C $yr^{-1}$) of technically emitted $CO_2$ comes from small and mobile units, a percentage likely to increase further in the future. Additionally, about 1–2 Gt C $yr^{-1}$ comes from land use change and wood fuel use, which are categories that should diminish in the future. Some 4 Gt C $yr^{-1}$ is absorbed by the biosphere (ocean and forest) but with an anticipated decreasing capacity. This “uptake capacity” is not constant but at a certain percentage (likely non-linearly) of the total $CO_2$ release into the air. Hence (assuming full $CO_2$ capture from stationery large sources), there is a requirement of at least 2 Gt C $yr^{-1}$ air capture. A compensation of atmospheric $CO_2$ buildup through engineered chemical sinkage was proposed by Elliott et al. (2001). They calculated the $CO_2$ removal from air by asking for the area needed if this was a perfect, flat sink with a dry deposition velocity of 1 cm $s^{-1}$. It is a hundred thousand square kilometer value, which constitutes an upper limit for absorbing the annual anthropogenic $CO_2$ input. Roughness elements and vertical fences could increase the transfer velocity (by reducing the atmospheric residence) and increase the specific absorbing area per horizontal air column surface. A total square reduced by a factor of 10 might be able to be reached.

Technically, $CO_2$ is extractable from air by cryogenic techniques. However, based on 400 ppm $CO_2$, an air volume of about 10 $km^3$ must be processed daily to get 0.1 Mt C $d^{-1}$ (this rate corresponds to about 30 “capture units” globally to achieve a yearly capture of 1 Gt C). Today’s high-performance cryogenic air separation plants have an air capacity of about 0.02 $km^3$ $d^{-1}$. In other words, more than 10,000 these plants would have to be in use to provide $CO_2$ capture of 1 Gt C $yr^{-1}$ from air. The nonuse of other gases from air separation would also not to be conform to a sustainable approach. However, new air separation techniques will eventually make it possible to generate only carbon dioxide and water from air and to increase the daily capacity by a factor of 10. In that case, “only” 1,000 of these plants will be needed for the extraction of 1 Gt C $yr^{-1}$ from air, less than the global number of coal-fired power stations.

Carbon dioxide capture can be applied both in closed technical plant systems as well as in an open-field technology (geo-engineering). The processed air volume is large ($10^7$ $km^3$ because of about 40 t $CO_2$–C $km^{-3}$), but corresponds to the air volume passing through about 100 cooling towers of large power plants.

Assuming $CO_2$ solvents having a surface resistance being zero, the atmospheric (dry deposition) flux is determined only by the quasi-laminar and atmospheric resistance (see Section 2.6.1 in Volume 1), and a value between 0.4 and 1.2 kg $CO_2$-C $m^{-2}$ $d^{-1}$ can be estimated. This corresponds to an uptake rate of about 2,000 t C $ha^{-1}$ $yr^{-1}$; at least 50 times more than most manipulated algal aquacultures will yield.[610]

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[610] Algal productivity rates between 5 and 10 g C $m^{-2}$ $d^{-1}$ have normally been cited (Drapcho and Brune 2000), but were reported to be up to 15 C $m^{-2}$ $d^{-1}$ in highly modern farming systems (Shelef et al. 1978). Again, to achieve 0.1 Mt C $d^{-1}$, a farming area of about 7,000 $km^2$ is needed or 210,000 $km^2$ globally, which corresponds to an area roughly 50% of the size of Germany. Surely there is a research needed to optimize (and maximize) $CO_2$ capture by industrial biofarming in sun-belt

To “capture” 1–2 Gt $CO_2$–C yearly, a square (assuming 50% scrubbing efficiency) of $10^4$ $km^2$, smaller than the State Brandenburg, is (“only”) needed. However, in contrast to CCS in this approach it is not the aim, to extract $CO_2$ in short time from a given volume of gas (air) but to reach a saturation of the $CO_2$ solvent for further desorption and solvent cycling.

Design and synthesis of new $CO_2$ absorbing materials is the key for applications of DAC. The argument of large costs will limit the technology can be overcome when the costs for climate change is included into energy price. It is self-evident that only solar energy is used for DAC. In the Section 5.3.1 we will see that DAC is a basic technology for the carbon economy similar to biogenic assimilation. From today’s perspective, it seems that as a result of the extremely low concentration of $CO_2$ in the air, the technical and economic solution of direct atmospheric $CO_2$ reuse is not very likely (DAC 2011). However, any technical solution in our concept is based on the paradigm change to establish a zero-carbon budget (not zero emissions!), and to no longer measure the effect on energy efficiency (solar energy is in “excess”) but on budget, with respect to climate sustainability. The “price” of $CO_2$ emitted from fossil fuels (and hence fossil fuel costs) must include climate change affects; this would encourage energy transition and also DAC technologies.

## 5.3 The energy problem: the last industrial revolution

The first Industrial Revolution (nineteenth century) is now characterized as the period of mechanization using water and steam power, followed by the second Industrial Revolution (first half of the twentieth century) using electricity for mass production via assembly that transferred to the end of the twentieth century to the third Industrial Revolution using computers and automatization (digitalization). This phase surely is going on with cyber physical systems (also called fourth Industrial Revolution). However, since the second Industrial Revolution, electricity is based up to present on fossil fuel burning. In my opinion, we expect a fifth Industrial Revolution by providing electricity solely based on solar radiation (second half of twenty-first century). Together with that a sixth Industrial Revolution is inevitable, the use of carbon as material and energy carrier from the atmosphere, the $CO_2$ cycling. This could be the last industrial revolution reaching global steady states and gaining sustainable societies.

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countries. For example, nutrients for biofarming could be taken from municipal wastewater of nearby “solar cities” and/or recycled from the biomass conversion process into $CO_2$ (note that fixed $CO_2$ is the aim rather than biofuel).

### 5.3.1 The carbon economy: $CO_2$ cycling

Mining and combustion of fossils fuels now results in geological reservoir redistribution of carbon close to (or even passing?) the “tipping point”. In the last two decades, we observed an acceleration of $CO_2$ release due to economic growth, which presently seems to go further on a constant level. The large $CO_2$ residence times in air and seawater avoid reaching a steady-state (global cycle in-time) and a recovery (climate restoration) also after full stop of fossil fuel use.

Therefore, much more forced by climate change than by fossil resource limits, we need the transfer into the “solar era” as soon as possible. Nuclear power may concern as “bridging technology”, but risks may not be longer accepted by society. Secondary “renewable” energy, for long time already in use (and we should not forget, it was the only significant source of energy before first Industrial Revolution), such as water and wind, will probably never contribute on global scale to fit the energy demand (this not excludes national and regional solutions, at presently proposed for Germany). Hence, only direct use of solar energy as it is proposed, for example, by the *Desertec* conception, can realistically solve the global energy problem and fully replace fossil fuels. Without any doubt, electricity is the unique form of energy in future and its direct application (also for mobility and heating) will increase – and can replace to a large percentage traditional fuels based on fossil resources. The *Desertec* consortium was a splash with its ambitious plans to harvest huge amounts of solar energy from the Sahara Desert, but the dream did not die – such technology is not unlikely to apply in next few decades to replace fossil fuels remarkable – if political (and thus financial) willingness is given. However, there are some open questions that have to be answered and transferred into technical solutions to establish the solar era.

- Electricity will be produced not constant over time and not correlated with the demand of energy; hence, it must be stored, likely best by transfer into “chemical energy”, to manage energy supply.
- Due to safety reasons, excess energy must be stored (e.g., in water reservoirs, but this way is limited), again best way seems to transfer electricity into “chemical energy”,
- There are technological processes (e.g., air traffic, long-distance street traffic, ship traffic, metallurgy) where electricity cannot be taken directly from nets or storage units and will be neither ecological neither economic.
- Humans always need synthetic organic materials (polymers, drugs, chemicals, etc.). These can be produced not only from remaining fossil resources but also from biomass – and from $CO_2$.

Möller (2012) put forward an option to create a global closed anthropogenic carbon cycle by using only solar energy to (a) stop further increase of $CO_2$ emission and to get a global zero-carbon budget, (b) to solve the problem of electricity storage based on $CO_2$ utilization, (c) to provide carbon-based materials only form $CO_2$ utilization, and (d) to use further the infrastructure developed for the fossil fuel era, termed SONNE[611] conception ("Sonne" is the German word for sun). The SONNE conception (Möller 2016) will interlink solar electricity conceptions such as *Desertec* with $CO_2$ utilization to overcome the above-mentioned open problems after the fossil fuel era. In other words, SONNE build a man-made carbon ($CO_2$) cycle in analogy to the natural assimilation-respiration carbon cycle (Figure 5.3). $CO_2$ is recycled within hybrid power plants (see Figure 5.4) and captured from ambient air. It is replaced from waste (emission) to resource; process energy is taken from solar energy.

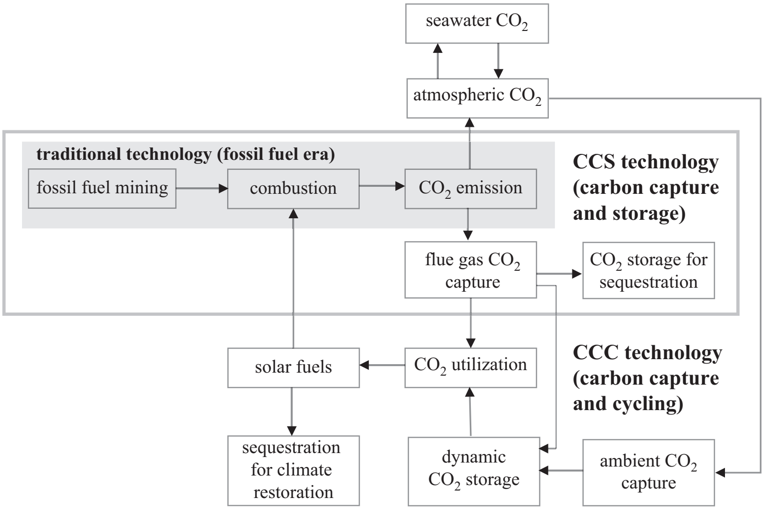

**Fig. 5.3:** Scheme of energy transition from fossil to solar era including a $CO_2$ economy (SONNE conception). Three overlapping systems: fossil fuel burning without (grey box) and with carbon capture (dotted box) as well solar fuel production/use and global carbon cycling. The driving force is exclusively solar radiation; hence, the $CO_2$ economy is interdependent with solar electricity conceptions such as DESERTEC. Elements of this concept can be introduced parallel with further use of fossil fuels aimed by its stepwise replacement.

The specific approaches put together in this "$CO_2$ economy" are already known and/or proposed, but to my knowledge, the creation of a man-made carbon cycle in such an integrative approach and with these rigorousness in linking energy with material economy adopting the principle of natural cycling but not copying natural

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[611] SOlar-based maN-made carboN cyclE.

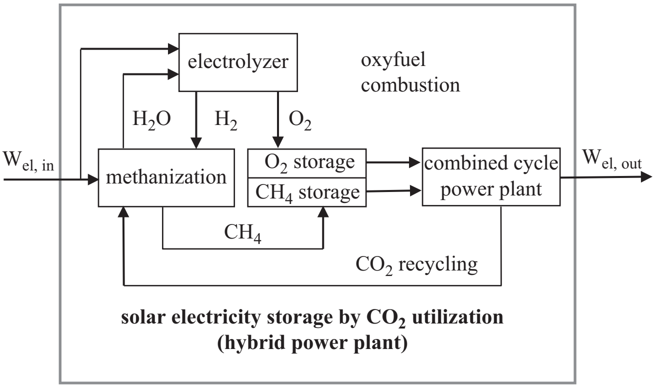

**Fig. 5.4:** Schema of a "hybrid power plant": chemical storage of "renewable" energy (preferably solar electricity) by $CO_2$ utilization (likely best by methanization) and internal $CO_2$ recycling (likely best by oxyfuel combustion); $W_{el, in}$ – direct solar electricity, $W_{el, out}$ – indirect energy solar energy (electricity/heat) "on demand". The energy efficiency is negative (e.g., in the case of $CH_4$ production from $CO_2$, only 30% of electricity input can be reused).

processes,[612] as suggested here, is world-wide unique and new (even much more complex than the "methanol economy"). $CO_2$ is unique,[613]

- as final oxidation product of all organic matter and materials,
- because of its globally cycling and homogeneous distribution in the atmosphere,
- as resource for organic materials concerns carriers of energy and functional materials,
- carbon is the only element forming complex molecules and substances and being within a global dynamic[614] cycle and gaseous compounds on lowest ($CH_4$) and highest oxidation state ($CO_2$),
- the only environmental problem of $CO_2$ is its rise in atmosphere (and seawater) with climatic implications; hence controlling its level on acceptable values will overcome the environmental problem.

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[612] For illustration, some scientists' dream from the artificial leaves to transform $CO_2$ into (solar) fuels. Our approach consists in "secondary" use of solar energy in terms of electricity and heat in large industrial operational units, which principally already are known.

[613] In a certain sense, hydrogen ($H_2$) can also play this role when we adopt the natural water splitting process, which was already proposed as "hydrogen technology" in the early 1980s. But there are several problems, (a) safety in storage and transport, (b) leakage and atmospheric implications, and (c) missing material supply. Water electrolysis will play an important role in SONNE for oxyfuel combustion ($O_2$ supply) and $CO_2$ reduction ($H_2$ supply).

[614] In (biogeochemical) cycles move all elements and its compounds – but often on geological time scale (beside carbon only sulfur and nitrogen are in similar dynamic cycles).

It is evident that through the realization of these principles a $CO_2$ "zero-budget world" rather than a "$CO_2$ free world" can be reached because there is a closed anthropogenic carbon cycle (we call it $CO_2$ economy). All $CO_2$ still emitted – and also cannot be technically captured in future from mobile and small equipment's – will be captured from air and cycled for reuse; I call it "Carbon Capture and Cycling" (CCC) technology. With this in mind, CCS technology (CCS/sequestration) makes (more) sense – despite of the controversially discussed $CO_2$ storage problems – and provides considerable incentive because $CO_2$ storage is now only temporary (we call it dynamically) until it is recycled from waste to feedstock. The proposed CCC technology allows a stepwise replacement of coal and other fossil fuels by solar fuels but keeping the carbon-based infrastructure such as pipelines, tankers, storage facilities, engines, and allows the continuous use of other available technical applications developed in last hundred and more years, but within a $CO_2$ neutral closed loop.

A closure of the carbon cycle, however, is only possible when $CO_2$ will be extracted from natural reservoirs such as the atmosphere and seawater (DAC, see previous Section 5.2.3) because a complete "industrial" $CO_2$ capture will be impossible with regard to many small and mobile sources.

Principally, the SONNE conception is not aimed for the very near future but for the solar era with "unlimited" access to useable solar energy, likely after 2050. However, because CCS will be an essential technology in "internal cycle" of hybrid-type power plants (Figure 5.4), CCC could be introduced to some extent parallel with further use of fossil fuels and stepwise replacing them until full establishing the SONNE cycle. The principal scheme of $CO_2$ use in solar electricity storage (valid also for other "renewable" energy such as wind) could be soon realized. The so-called oxy-fuel combustion would provide high purity $CO_2$ as exhaust gas, which can be recycled without energy-intensive capture (Figure 5.4). We can set 10 mission statements or principles:

1. further use of fossil fuel combustion in large stationary units but only with $CO_2$ capture (CCS technology) until the full transfer into the solar fuel world: capture $CO_2$ from combustion units as much as possible;
2. replacement of fossil fuel use in small stationary and mobile units as far as possible (electricity-based and hybrid techniques): reduce carbon carriers as fuels as much as possible;
3. sequestration of carbon (not $CO_2$) on medium- and long-term scale for buffering the further $CO_2$ emission increase in next decades and climate sanitation in far future;
4. developing technologies for $CO_2$ extraction from natural reservoirs (ambient air, seawater) to achieve a global man-made carbon cycle while allowing $CO_2$ emissions into the atmosphere from mobile and small sources: atmospheric $CO_2$ is considered as the only carbon reservoir for chemical $CO_2$ utilization (CCU);
5. developing technologies for $CO_2$ reduction but applications only with renewable energy, namely, solar radiation (solar fuel production);

6. introduction of large solar thermal power plant units for electricity generation;
7. developing technologies for electricity conversion into chemical energy carriers (solar fuels used in hybrid power plants);
8. build-up a solar fuel infrastructure (widely on the basis of the existing fossil fuel infrastructure);
9. developing technologies for electricity conversion into large central heat storage units (based on molten minerals); and
10. economic paradigm change: solar energy is "in excess" (comparing with the global human demand) and is naturally dissipated in the atmosphere; hence, large energy consuming conversion processes and DAC can be carried out for resource generation and climate sustainability: a new economy-thinking based on sustainability (or closed carbon cycle) is needed. In other terms, not energy but material efficiency becomes the key factor.

Human's evolutionary responsibility should also consider the retransfer of emitted $CO_2$ into geological stocks, for example, as elemental carbon for safe sequestration and stepwise but long-lasting climate recovery.

All $CO_2$ still emitted will be captured and cycled for reuse. Naturally, the energy needed for $CO_2$ reduction comes from renewable sources. The proposed CCC technology allows a stepwise replacement of coal and other fossil fuels by solar fuels. Finally, there is a closed carbon cycle similar to the natural photosynthesis, a respiration cycle (Figure 5.3). Carbon-based solar fuels solve the problem of energy storage and allow the continuous use of available technical applications to provide products for materials, and are within a $CO_2$ neutral closed loop.

Olah (2005) proposed the "methanol economy", but in the SONNE concept, $CH_3OH$ is only one possible product among $C_1$ chemicals; the *Fischer-Tropsch* synthesis (from $CO + H_2$) basically offers a wide range of organic compounds including liquid fuels. Our "$CO_2$ economy" includes the "$CH_3OH$ economy". Recently it was provided that the energetic efficiency of the overall energy conversion-storage system (see Figure 5.4) including $CH_3OH$ as a storage medium is only 17.6% in contrast to 29.7% for $CH_4$ (Rihko-Struckmann et al. 2010). However, taking into account ambient $CO_2$ capture, the overall energetic efficiency will drastically lower. Such as in nature (the photosynthesis efficiency concerning solar light is only 2–3%), we realize a closed carbon loop only with large energy input (in other words low energetic efficiency), but based on incoming solar radiation, 1,000 times higher than present global human energy demand. Still unanswered is the question, however, what are the limits of solar use without getting other climate implications.

It is remarkable that establishing the SONNE conception ($CO_2$ economy), we first see that sun-belt countries, many of them are privileged by natural oil and gas reservoirs, will provide "solar sites" for electricity generation and likely $CO_2$ processing (Figure 5.5). On the other hand, future use of fossil fuels is mainly in the non-sun countries in the Northern Hemisphere, which should become responsible for ambient $CO_2$ capture (there are good reasons, to establish DAC units more in the north because $CO_2$ absorption processes needs low temperature and DIC in seawater is significantly higher in cold areas). For example, Northern Europe will capture ambient $CO_2$ and transport them to Northern Africa as "fuel feedstock" for solar processing (Figure 5.5). Thus, a social win–win situation with many positive political and educational effects may be created.

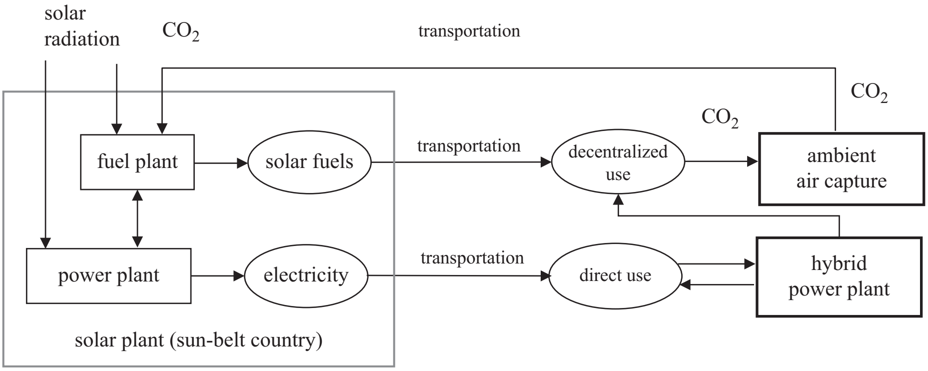

**Fig. 5.5:** Solar plant complex (solar-to-electricity and $CO_2$-to-fuel conversion in sun-belt countries), interlinked with transportation of fuels, chemicals and materials, and electricity to Northern Hemispheric countries (to be used there) and back transport of $CO_2$ captured from ambient air to solar plants (getting a geo-economics equilibrium and political interdependence as win–win situation). Note that the whole system dissipates solar energy as it happens in the climate system by natural processes. Therefore, the energy efficiency plays a minor role (but should be maximized in singular technical process); the key for a sustainable economy (socioecological system) is the closed cycling of matter (here carbon, but this is true for all element to be used).

At this point, it is important to state that SONNE is based on ideas already known and further investigated (e.g., CCS, CCR,[615] CCU, DAC) at many scientific institutions worldwide. As mentioned, a key idea of CCC technology is the capture of $CO_2$ from the atmosphere (and its dynamic storage) to close the man-made global carbon cycle analogously to the biosphere. The $CO_2$–carbon economy is the adaption of the biospheres' assimilation–respiration cycle by humans, the only long-term sustainable way of human's surviving.

From today's perspective it seems that due to the extremely low concentration of $CO_2$ in air, the technical and economic solution of direct atmospheric $CO_2$ reuse is not very likely (DAC 2011). However, any technical solution in our conception is based on

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[615] R stands for recycling.

the paradigm change to establish a zero carbon budget (not zero emission!) and measuring the effect not longer on the energy efficiency (solar energy is in “excess”) but on the matter budget with respect to climate sustainability. The “price” of $CO_2$ emitted from fossil fuels (and hence fossil fuel costs) must include climate change affects; this would force the energy transition and also DAC technologies.

### 5.3.2 Solar fuels: carbon as a material and energy carrier

The idea of using $CO_2$ as a chemical raw material is not new (Aresta and Forti 1987, Edwards 1995, Aresta and Aresta 2003, Park et al. 2004, Olah 2005, Wu 2009, Aresta 2010). However, when using $CO_2$ from fossil-fuel gases, it is only climate sustainable if the products are “sequestrated”, for example, by long-term use in carbon materials such as polyurethanes. $CO_2$ captured from fossil-fired power plants and “utilized” for storage of excess electricity (e.g., from wind power) may help to improve the energy efficiency (because the excess electricity cannot be used on demand) but not solve the climate problem. Zeman and Keith (2008) also suggested synthesizing carbon neutral hydrocarbons from air-captured $CO_2$. This term (in fact $CO_2$ neutral) is inconsistent, and in its place we will use “solar fuels” to express that the supply of process energy for the chemical reduction of captured $CO_2$ must be based on *solar* energy processing instead of fossil (geothermal heat is another option).

In last years considerable progress was achieved in the catalytic hydrogenation of $CO_2$ (methanization). The possible synthesis of $C_1$-chemicals (CO, C, $CH_4$, $CH_3OH$, and HCHO) from $CO_2$ and directly further to $C_3$ in analogy to the assimilation process (see also Fig. 6.13 in Volume 1) leads to a variety of important basic chemicals being available for either direct combustion or material use (industrial synthesis in organic chemistry); we now call them *solar fuels*. The possible synthesis of methanol and formic acid from $CO_2$ leads to important basic chemicals for industrial synthesis in organic chemistry. However, a global $CO_2$ economy must not only provide chemicals in the order of hundred million tons but also an amounts of 1–2 orders of magnitude more gaseous and liquid fuels. By using high-temperature chemical processes (which were known for many years but due to the high energy consumption have hardly been mentioned before) based on solar thermal energy it is also possible to remake “coal chemistry” (gasification and liquefaction) via $CO_2$ reduction. Namely, carbon monoxide (CO) and elemental carbon may be produced and inversely transformed. For example, elemental carbon could be stored better than carbon dioxide (for sequestration aiming climate abatement) but could also be reused directly in an early stage of the CCC technology. It is known that in high-temperature processes of conversion of carbon compounds to elemental carbon the yield of polymeric carbon structure (fullerenes) are large and unforeseen changes in creating new carbon materials are made possible. It is self-evident that all energy for processing is solar based. It is out of the focus of this book to review the chemical processes of $CO_2$ utilization – this section will present only the basic ideas of chemical conversion in sense of the chemical evolution sustained by humans – and the reader is referred to (as examples) Aresta and Aresta (2003), Park et al. 2004, Grimes et al. (2007), Rajeshwar et al. (2008), and Varghese et al. (2009).

There are several modular technical systems for realizing the CCC conception (Figure 5.5) where the solar (desert) site in sun-belt countries (module A) plays a key function by providing solar-based electricity (and heat for on-site chemical processing). Principally, it is possible to combine the solar site with other modules (B – air capture and $CO_2$ supply and C – $CO_2$ processing), but there are arguments to localize air capture close to $CO_2$ storage (module E) to avoid transportation to sites where climatic conditions support large $CO_2$ absorption (see above) and/or to sites of $CO_2$ processing. Solar power plants are decentralized close to urban and industrial areas (module D). Solar fuel (in contrast to $CO_2$) can be easily transported and stored using traditional infrastructure for liquids and gases. Processing sites (module C) must have access to solar (or non-fossil) energy. Then, by using high-voltage direct current transmission lines (*Desertec* conception), they can be sited several thousands of kilometers from the solar thermal power plants. An interesting site would be Iceland, which might be able to provide power from geothermal heat and cold carbon-rich seawater for $CO_2$ extraction as well as air capture because of the large temperature differences in rich and lean $CO_2$ loading. Captured $CO_2$ could be reduced on site to solar fuels that are transported by tank ships to Central Europe.

There is no need for long-range transportation of hydrogen (which is one feedstock for $CO_2$ reduction) because electricity (according to the *Desertec* conception) can be transported advantageously in comparison to $H_2$. Hydrogen can also be produced at any site by water electrolysis (also using renewable sources other than direct solar electricity). There are clear advantages to $CO_2$ reduction close to the solar fuel consumers including the avoidance of the expensive transportation of $CO_2$ back to the sun-belt countries and the possibility of mixing solar fuels directly with oxygen from the water electrolysis to create “oxyfuels”. Oxyfuels can be burned in stationary power plants with the result that the flue gas is almost all pure $CO_2$. However, there is an interesting aspect for back transportation of $CO_2$ from industrial to sun-belt countries. The solar site depends on the delivery of feedstock $CO_2$. Thus, a geopolitical equilibrium can be reached in sense of a win–win situation.

As mentioned, the world’s infrastructure is based on fossil fuels and products derived from coal and petrochemistry. The following groups of substances are delivered from fossils fuels and can be also produced from $CO_2$ using solar-based processes:

- gaseous hydrocarbons ($C_nH_{2n+2}$ with $n < 6$); methane as a key substance; all substances with $n > 2$ are easily liquefiable;
- liquid hydrocarbons ($C_nH_{2n+2}$ with $n > 5$) such as alkanes but also oxygenated liquid compounds from $C_1$ upward (e.g., methanol);

- gaseous CO (the typical town gas in the past); and
- elemental carbon (C in different modifications).

Energy use is simply combustion in different burners and engines with, ideally, transformation back into $CO_2$. Reaction enthalpies are different and thereby provide possible usable energy.

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + 802\ \text{kJ mol}^{-1} \tag{5.8}$$

$$C_nH_{2n+2} + (3n+1)/2\ O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O + \left(2,214\ \text{kJ mol}^{-1}\ \text{for}\ n = 3\right) \tag{5.9}$$

$$CH_3OH + 1.5\ O_2 \rightarrow CO_2 + 2\ H_2O + 727\ \text{kJ mol}^{-1} \tag{5.10}$$

$$CO + 0.5\ O_2 \rightarrow CO_2 + 283\ \text{kJ mol}^{-1} \tag{5.11}$$

$$C + O_2 \rightarrow CO_2 + 393\ \text{kJ mol}^{-1} \tag{5.12a}$$

$$C + 0.5\ O_2 \rightarrow CO + 110\ \text{kJ mol}^{-1} \tag{5.12b}$$

Despite the lower energy yield, it is evident that hydrogen-free carbon carriers such as CO and C have the large advantage of consuming much less oxygen and producing only $CO_2$, when considering oxyfuel technology in the future. That could be an important feature in establishing the carbon cycle and turning $CO_2$ back into the feedstock for solar fuels. In the production of group one and group two compounds in the list above, some progress has already been made toward $CO_2$ hydrogenation (reactions 5.13 and 5.14). Catalytic $CO_2$ methanization is carried out at 160 °C and below 100 °C at pressures of 80 kPa (Abe et al. 2009). Reaction (5.13) has already been discovered by *Paul Sabatier* in the nineteenth century.

$$CO_2 + 4\ H_2 + 618\ \text{kJ mol}^{-1} \rightarrow CH_4 + 2\ H_2O \tag{5.13}$$

$$CO_2 + 3\ H_2 + 523\ \text{kJ mol}^{-1} \rightarrow CH_3OH + H_2O \tag{5.14a}$$

$$CO + 2\ H_2 + 308\ \text{kJ mol}^{-1} \rightarrow CH_3OH \tag{5.14b}$$

What must be considered in carrying out reactions (5.13) and (5.14) is the source of $H_2$. It is clear that “traditional” reactions (water–gas shift and $CH_4$ reforming) cannot be used and that $H_2$ must be generated via water electrolysis using renewable energy sources such as solar radiation. Thus, the argument that it is preferable to use $H_2$ directly as a fuel is inconsistent with our aim of carbon cycling. Moreover, carbon carriers provide a range of products that are better suited to the available infrastructure than $H_2$. Overall, the photosynthesis-like reactions (5.15) and (5.16) are carried out.

$$CO_2 + 2\ H_2O + \text{solar energy} \rightarrow CH_3OH + 1.5\ O_2 \tag{5.15}$$

$$n\ CO_2 + n\ H_2O + \text{solar energy} \rightarrow (CH_2O)_n + n\ O_2 \tag{5.16}$$

The formation of methanol from $CO_2$ hydrogenation is known as the *CAMERE* process (Melián-Cabrera et al. 1998, Joo et al. 1999). In the past, a thermochemical heat pipe application was proposed (Edwards 1995), which is based on reaction (5.17a), where $CO_2/CH_4$ reforming (using solar energy) gives $CO/H_2$ gas, which can be converted back (5.17b) in an exothermic reactor with an equivalent energy output. However, this technology needs an entirely new infrastructure.

$$CH_4 + CO_2 + \text{energy} \rightleftarrows 2\,CO + 2\ H_2 \tag{5.17a, b}$$

The $CO/H_2$ gas (also termed *water–gas*) – depending on the $CO{:}H_2$ ratio – can also be converted (using the *Fischer-Tropsch* synthesis) to alkanes, alkenes, and alcohols. Preferably, substances should be generated for applications in known technical systems such as liquefied petroleum gas or low-pressure gas and gasoline as well as natural gas. The production of solar substitutes for diesels and oils ($C > 8$), that is, petrol products from the fractional distillation of crude oil between 200 °C and 350 °C, is also possible, but offers no advantages in the solar fuel cycle and its stepwise replacement by gases and gasoline should be foreseen.

An interesting way of generating solar fuels can be seen in two "classical" inorganic carbon carriers: CO and carbon itself. The gasification of carbon (5.18a) produces CO (generator gas) in the so-called *Boudouard* equilibrium:

$$C + CO_2 + 172\ \text{kJ mol}^{-1} \rightleftarrows 2\,CO. \tag{5.18a, b}$$

The inverse reaction (5.18b) opens the way to finally convert $CO_2$ to elemental carbon via reactions (5.13) and (5.17a). Alternatively, CO can be produced by the high-temperature electrolysis of $CO_2$:

$$CO_2 + \text{energy} \rightarrow CO + 0.5\ O_2. \tag{5.19}$$

where the overall reaction represents the inverse reaction (5.12a). High-temperature electrolysis using solid oxide electrolytic cells offers absolute new synthesis pathways. In contrast to reaction (5.19), the electrolysis of $CO_2/H_2O$ leads to CO and $CH_4$:

$$CO_2 + H_2O + \text{energy} \rightarrow CO + H_2 + 1.5\ O_2, \tag{5.20}$$

$$CO_2 + 2\ H_2O + \text{energy} \rightarrow CH_4 + 2\ O_2. \tag{5.21}$$

For long-term space missions, these reactions were considered to provide a closed cycle of production of oxygen and consumption of respiratory $CO_2$. A final pyrolysis reaction (5.22) recycles hydrogen, but more interesting for earth applications is the formation of elemental carbon according to the gross conversion process shown in eq. (5.23).

$$CH_4 + \text{energy} \rightarrow C + 2\ H_2 \tag{5.22}$$

Reactions (5.19) and (5.21) provide the following overall reaction:

$$CO_2 + H_2O + \text{energy} \rightarrow C + 2\ H_2 + 2\ O_2. \tag{5.23}$$

This set of reactions based on solid high-temperature electrolytic $CO_2$ reduction shows that more advantages are likely at desert solar sites than the conversion processes in detail decisions will be ever made. The general budget is described by

$$CO_2 + H_2O + \text{solar energy} \rightarrow \text{solar fuels}\,(C, CO, CH_4, H_2, O_2, \text{etc.}), \tag{5.24}$$

independent of the detailed conversion processes. In inverse reaction (5.24), solar fuels reconvert into $CO_2$ and $H_2O$ via the combustion or electricity in fuel cells and set the energy free, primarily as heat, for energetic use.