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# The Chemical Route to a Carbon Dioxide Neutral World. — Source link

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# The Chemical Route to a $CO_2$-neutral world

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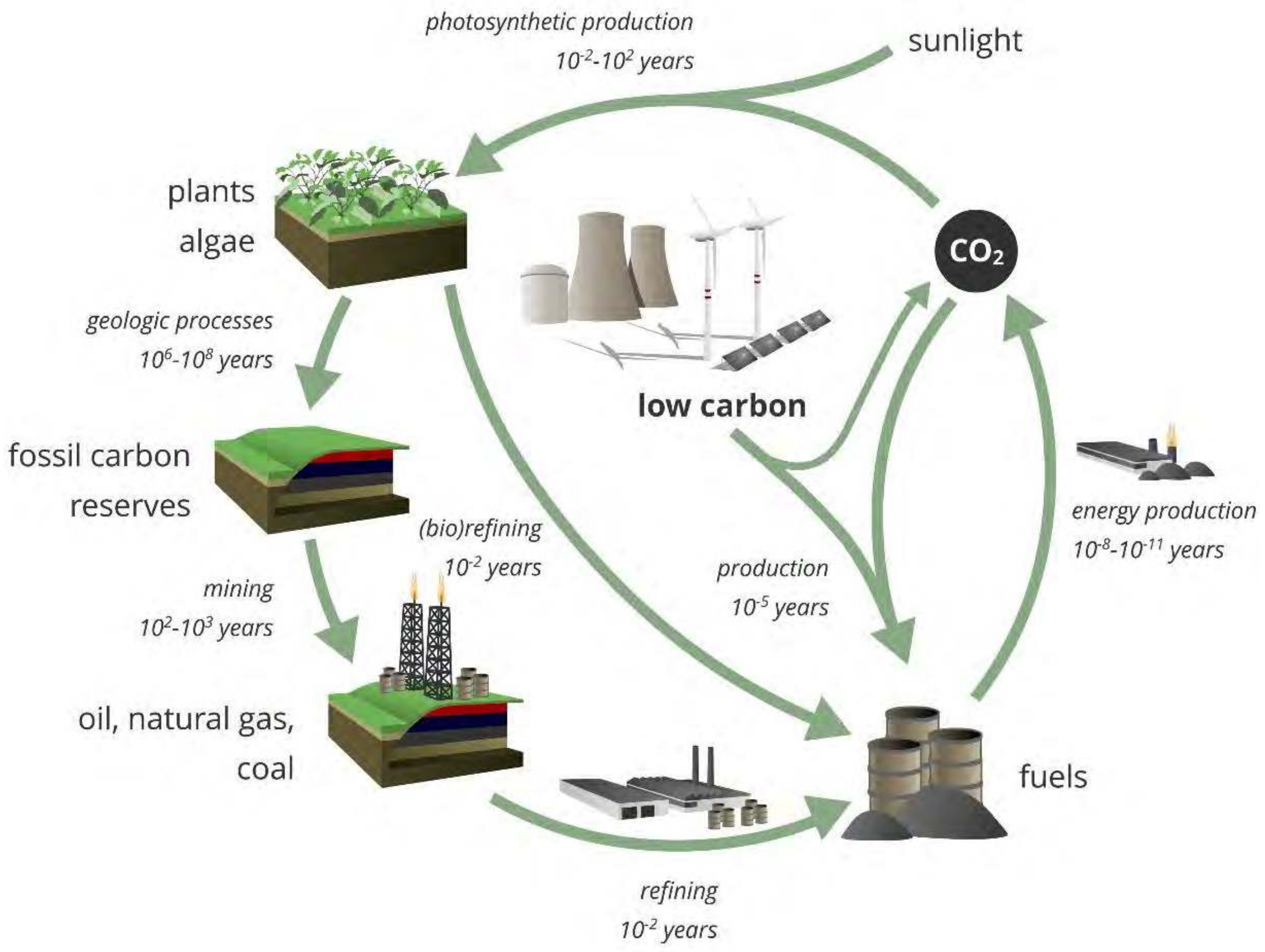

The excessive $CO_2$ emissions in the atmosphere from anthropogenic activity can be divided into point sources and diffuse sources. The capture of $CO_2$ from flue gases of large industrial installations and its conversion to fuels and chemicals with fast catalytic processes seems technically possible. Some emerging technologies are already being demonstrated on an industrial scale. Others are still being tested on a laboratory or pilot scale. These emerging chemical technologies can be implemented in a time-window ranging from 5 to 20 years. The massive amounts of energy needed for capturing processes and conversion of $CO_2$ should come from low-carbon energy sources, such as tidal, geothermal or nuclear energy but also, mainly, from the sun. Synthetic methane gas that can be formed from $CO_2$ and hydrogen gas, is an attractive renewable energy carrier with an existing distribution system. Methanol offers advantages as a liquid fuel and is also a building block for the chemical industry. $CO_2$ emissions from diffuse sources is a difficult problem to solve, and particularly for $CO_2$ emissions from road, water and air transport, but steady progress in developping technology for capturing $CO_2$ from air is being made. It is impossible to ban carbon from the entire energy supply of mankind with the current technological knowledge, but a transition to a mixed carbon-hydrogen economy can reduce net $CO_2$ emission and ultimately lead to a $CO_2$-neutral world.

## 1. The Problem: Rising $CO_2$ concentration in the atmosphere rather than the depletion of fossil fuel reserves

### 1.1. The immense reserves of fossil carbon

The chemical element carbon appears on earth in many different forms (Table 1).[1] The vast majority of carbon is oxidized, i.e. bound to oxygen atoms. Solid calcium carbonate ($CaCO_3$) is by far the most common form of carbon and is found mainly in limestone, marble, bluestone and skeletal remains of marine organisms. Carbonates are partially soluble in water as bicarbonate ($HCO_3^-$), thereby making the oceans the second most important reservoir of carbonates. Gaseous carbon dioxide ($CO_2$) represents a smaller amount of carbon in the atmosphere. $CO_2$ gas in the atmosphere partially dissolves in water as carbonic acid ($H_2CO_3$). Dissociation of carbon dioxide in slightly alkaline ocean water forms bicarbonate ($HCO_3^-$).

Life on earth manages to reduce oxidized carbon such as $CO_2$. Through the process of photosynthesis, $CO_2$ and water is converted into biomass by using light energy (mainly from the sun) and converting it into chemical energy that is catalysed by chlorophyll in green leaves, and which can be represented by the gross molecular formula of carbohydrates $(CH_2O)_n$. Fossil biomass that in the past 2 billion years has turned up in sediment, underwent a further chemical reduction, under the influence of elevated temperature and pressure, to coal (carbon in its elemental form) and hydrocarbons $(CH_x)_n$, e.g. petroleum, shale oil, and tar sands, natural gas, shale gas and methane hydrates. Oxygen atoms, produced by biological reduction of $CO_2$, accumulated as molecular oxygen ($O_2$) in the atmosphere. Thus, the original $CO_2$-rich earth atmosphere was gradually converted to levels that, at the beginning of the industrial revolution (second half of the 18th century), corresponded to 300 ppm $CO_2$ and 21% (= 210.000 ppm) $O_2$.

**Table 1:** Estimation of the amounts of carbon in different compounds on earth (in Gt C) (1 Gt = $10^9$ t = 1 billion ton)

| | | |
|---|---|---|
| **Fully oxidized carbon** | | |
| In rocks (carbonates) | 28,400,000 | |
| Dissolved bicarbonate in the oceans | 38,000 | |
| $CO_2$ in the atmosphere | 830 | |
| **Partially oxidized carbon (biomass)** | | |
| Soil | 1,500-2,400 | |
| Permafrost | 1,700 | |
| Marine vegetation and dissolved organic matter | 700 | |
| Land vegetation | 350-550 | |
| **Reduced carbon** | Reserves[a] | Resources[b] |
| Petroleum | 98-152 | 88-123 |
| Tar sands and shale oil | 75-112 | 226-297 |
| Natural gas | 76-108 | 110-136 |
| Shale gas | 307-1,026 | 614-1,863 |
| Methane hydrates | | 500-2,500 |
| Coal | 446-542 | 7,510-11,230 |

[a] Reserves: recovery is possible with current technology and is economically viable. [b] Resources: not mineable or exploitation is currently not economically viable.

Our current high-tech society owes its success to the presence and consumption of massive quantities of accessible and inexpensive energy sources such as fossil fuels. For many

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decades, experts have warned of an impending oil shortage. Based on current consumption and the known oil reserves, there is still plenty of oil for the next 50 years. For natural gas and coal, there is a supply for 55 and 110 years, respectively.[2] Although most of the known oil and natural gas fields are mined today, exploration still remains a main activity of oil and gas companies, and regularly new reservoirs are discovered. Thanks to technological innovation, oil fields that were previously inaccessible (e.g. deep sea and arctic fields) can now be exploited. Existing fields are operated more efficiently, which increases the available reserves over time.

It is important that new forms of fossil hydrocarbon resources are drawn upon. A striking example is the rapid rise of shale gas in the United States of America (USA). This kind of natural gas, which is located in source rock, is accessed by hydraulic fragmentation (i.e. hydraulic fracturing or fracking) of the rock using advanced drilling methods. In 2012, 40% of all the natural gas in the USA already came from shale.[3] The hydraulic fracturing production method is seen as the maker of the energy revolution in the USA. However, this approach is also controversial due to the negative impact it has on the environment.

Another example of untapped fossil fuel is methane hydrates, also known as methane ice.[4] In methane hydrates, methane molecules are individually encased in a mantle of water molecules. Huge methane (ice) reserves lie on the ocean floor, and in and under the permafrost in amounts greater than that present in all the current fields of natural gas and shale gas. Therefore, new production methods are intensively sought after.

The imminent depletion of fossil carbon sources is often cited as an argument for the use of alternative energy sources such as biomass, wind energy and photovoltaic solar panels. The relative size of the available reserves, however, weakens this argument. The combined consumption of fossil carbon by man since the beginning of the industrial revolution amounts to 365 Gt, which is according to the cited source only about one-third to one-sixth of the current reserve (estimated at 1,000 to 2,000 Gt), and only a small fraction of the total fossil carbon resources (estimated at 9,000 to 16,000 Gt).[1] The existence of an imminent fossil carbon shortage is a misconception.

### 1.2. Rising $CO_2$ concentration in the atmosphere

Nature has a natural capturing mechanism for $CO_2$: Green plants and small living organisms capture $CO_2$ from the air and convert it under the influence of sunlight in the process of photosynthesis. The oceans also absorb a considerable amount of $CO_2$ from the atmosphere. $CO_2$ is released back into the atmosphere by respiration of animal organisms and cell respiration of plants. Generation and capturing have been in a dynamic equilibrium for a long time. Increased human activity, however, has resulted in an imbalance between $CO_2$ emissions and the natural capturing mechanism. This dynamic equilibrium was disturbed by the burning of fossil fuels, changes in land use and decomposition of carbonates such as the production of calcium oxide from limestone in the cement industry. The atmosphere now contains 240 Gt more carbon than at the beginning of the industrial revolution, and the $CO_2$-concentration has exceeded the threshold of 400 ppm: a level that is the last 450 million years unprecedented. Increased $CO_2$ concentration in the atmosphere is a global phenomenon, whereas particulate matter and ozone are more of a local air pollutant. The specificity of the $CO_2$ problem lies in the widespread emissions and the inertia of the capturing mechanisms (i.e. dissolution in oceans and photosynthesis) whereby the worldwide turbulent mixed air mass exhibits an almost uniform $CO_2$ concentration.

### 1.3. $CO_2$ emissions trading system

$CO_2$ is a greenhouse gas in which it is generally assumed that a rise in concentration contributes significantly to global warming. Greenhouse gases in the atmosphere absorb heat radiated from the earth's surface and stores this heat like in a greenhouse. In addition to $CO_2$, various other gases (e.g. methane, nitrous oxide, fluorinated hydrocarbons and ozone) exhibit this property. Without the presence of greenhouse gases, the surface temperature of the earth would be about -18 °C on average and not the 14 °C it is now. Greenhouse gases are essential to life on earth, and their concentration is very critical.

Regardless of all the possible predictions about the effects of rising $CO_2$ concentration in the atmosphere, it would be irresponsible to not undertake anything against this increasing $CO_2$ concentration. Europe has already adopted various binding measures for companies to reduce $CO_2$ emissions. EU-ETS ("Emissions Trading System") is an emissions trading system between European companies. The scope is determined in Appendix 1 of Directive 2003/87/EG. It is a so-called "cap-and-trade" system: The total emission is limited by an emission ceiling ("cap"). In the period 2013-2020, this cap drops by 1.74% per year for industrial installations. The emission allowances themselves are traded on a market ("trade"). This trading gives companies the option to either reduce emissions or purchase allowances. Businesses can get free allowances allocated to them by the government. In Europe, more than 11,000 installations are covered by this Directive. In total, about 45% of the European $CO_2$-emissions fall under this system. The combustion of biomass is not included in the scope of this Directive. Since 2012, a ceiling has been set on the total $CO_2$ emissions for aviation within the EU-ETS system. The 'cap' is set at 95% of historical aviation emissions. Initially it was intended to apply the cap to all flights that departed or arrived within the EU, however, the cap was limited to flights within and between EU countries for the period 2013-2016. In 2016, an expansion of the current cap will be set for a period from 2017. Similarly, binding $CO_2$ emissions targets for member states will be set for the non-ETS sectors (i.e. buildings, transport, etc.).

It should be noted that not all $CO_2$ emissions are treated on an equal basis by legislators, for example $CO_2$ emissions from biomass combustion are not included in the regulations. $CO_2$-molecules are, however, not distinguished according to their origin, i.e. whether they stem from a fossil fuel or a newly formed biomass and both sources contribute to global warming.

### 1.4. $CO_2$-emission and climate change

The Paris agreement of end 2015 contains the commitment to hold the increase in the global average temperature to well below 2 °C compared to pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above pre-industrial levels. According to the Intergovernmental Panel on Climate Change (IPCC), the cumulative worldwide $CO_2$-emissions from 2000 to 2050 may not be more than 1,100 Gt in order limit the temperature rise by 2°C with a 75% certainty (Table 2).[5,6] Estimates of greenhouse gas emissions indicate that about 50 Gt $CO_2$ equivalents are emitted annually – this amount includes for 70 % $CO_2$, followed by methane and other greenhouse gases caused by human activity. If no decisive action is taken, the threshold of 1,100 Gt $CO_2$ will be exceeded even before 2050. The ever increasing demand for energy should similarly be taken into account. Predictions indicate that the energy need between 2010 and 2040 will increase by 56%[7], namely due to economic development outside the EU and USA. An estimate by BP shows that in the Business as Usual scenario the cumulative emission will amount to 1,790 Gt, far beyond the stated amount of 1,100 Gt $CO_2$.[2]

**Table 2:** Emission of greenhouse gases through human activity[6]

| | Gt $CO_2$ |
|---|---|
| Total emissions since the Industrial Revolution | 1,340 |
| Still allowed amount to emit until 2050 | 1,100 |
| Still allowed amount to emit until 2100 | 1,900 |
| Current annual emissions – World | 50 |
| Current annual emissions of $CO_2$ – World | 35 |

The allowable emissions of 1,100 Gt $CO_2$ up to 2050 is equivalent to burning 300 Gt of fossil carbon. Until the year 2100, emissions may rise to 1,907 Gt $CO_2$ or 520 Gt fossil carbon. The fossil carbon reserves are more than sufficient for this emission, even when fracking gases or other new sources are excluded (Table 1).[1] Experts warn for a danger of a “carbon bubble”. After all, the value of listed companies mining fossil fuels is partly based on their reserves. An exit scenario for the use of fossil carbon sources and the evolution to a carbon-free economy, would imply that a large share of the fossil carbon reserves would lose their economic value. However, a carbon-free economy is unrealistic given the high added value of carbon based fuels, chemicals and plastics. A $CO_2$-neutral economy, that does not prohibit the formation of $CO_2$ but rather avoids it being released into the atmosphere, is a more realistic goal.

## 2. How can $CO_2$-accumulation in de atmosphere be prevented?

In order to put a stop to the $CO_2$ accumulation in the atmosphere, there are two categories of possible measures: measures that aim to reduce $CO_2$ production and measures that aim to accelerate $CO_2$ absorption. Reduced power consumption leads directly to a reduction in $CO_2$ production. This reduction can be achieved by, for example, better insulating buildings in order to reduce HVAC costs (i.e. heating, ventilation and air-conditioning). In addition, alternative energy sources should increasingly be used to replace fossil carbon sources.

The transition to low $CO_2$ energy supply will take decades. The development and implementation of technology is absolutely necessary for accelerating $CO_2$ absorption and avoidance of $CO_2$ emission.

### 2.1. $CO_2$-sequestration

$CO_2$ sequestration involves capturing $CO_2$ immediately after it is formed and storing it, usually underground in geological reservoirs (storage) in order to prevent distribution into the atmosphere. Currently, industrial installations called "Carbon Capture and Storage” (CCS) are used (Figure 1).

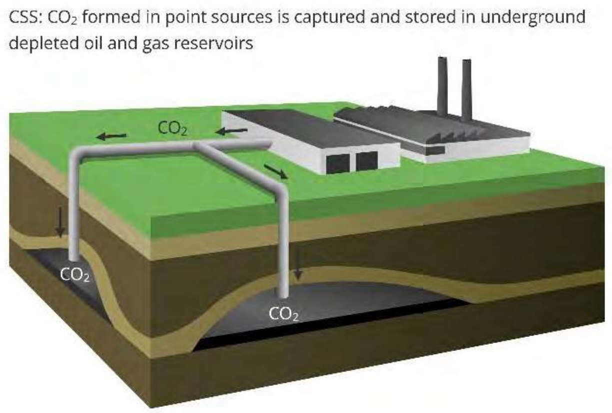

**Figure 1:** CCS technologies typically involve the storage of $CO_2$ in underground layers (e.g. in mines or former oil extraction reservoirs). $CO_2$ is separated from flue gases and compressed before storage.

CCS can be implemented where large and concentrated $CO_2$ emissions are present. $CO_2$ emissions can be divided into two parts. Large point sources such as power plants and industrial production sites on one hand and other diffuse sources such as transport and climate control of buildings on the other hand. Globally, about half of the $CO_2$-emissions are from point sources (Table 3).[8] However, this share slowly decreases relative to small diffuse sources. This decline is mainly due to the impact of climate control of buildings and the transport sector. The IPCC indicates that worldwide there are more than 7,500 "large point sources" with emissions of each over one hundred thousand tons of $CO_2$ per year. Out of this figure, 80% are produced by power plants.

The energy and industrial sectors together account for about 50% of total $CO_2$ emissions and, considering their constant emission, these sectors lend themselves best to the introduction of CCS technology. Thus, $CO_2$ emissions from power plants can be reduced by 75% (Table 4).[9] This technique has been commercialized on a limited scale but its use is on the rise. Globally in 2014, about 40 million tons (0.04 Gt) of $CO_2$ was captured and stored underground.

**Table 3:** Emission of greenhouse gases by sector and by share of point and diffuse sources (%)[8]

| | |
|---|---|
| *Energy* | 26 |
| *Industry* | 19 |
| *Forestry, land use & agriculture* | 31 |
| *Transport* | 13 |
| *Buildings* | 8 |
| *Waste and waste water* | 3 |
| | |
| Emission point sources – world | 45 |
| Emission diffuse sources – world | 55 |

**Table 4:** Life cycle analysis for emerging CCS technologies (g $CO_2$ equivalent / kWh).[9]

| Technology | Minimum estimate | Median | Maximum estimate |
|---|---|---|---|
| Coal | 740 | 820 | 910 |
| Gas (combined cycle) | 410 | 490 | 650 |
| CCS coal: coal powder | 190 | 220 | 250 |
| CCS coal: IGCC (integrated gasification combined cycle) | 170 | 200 | 230 |
| CCS Gas — combined Cycle | 94 | 170 | 340 |

Consequently, reducing the spread of $CO_2$ by applying CCS technologies for the energy and industrial sectors seems an obvious first step. "The National Academy of Sciences" in the USA has in a recent study proposed CCS as a relatively realistic alternative in the short term.[10] The idea meets a certain amount of resistance, given its analogy to "sweeping dirt under the rug" and the potential risks associated with this technique. Therefore, low social acceptance of CCS is a major obstacle to the required large-scale implementation of the technology. However, given the global increase in energy demand and the necessary reduction in $CO_2$ emissions, CCS seems an appropriate measure, albeit a temporary measure (in addition to other measures). In the long run captured $CO_2$ should be reused rather than stored in reservoirs.

Efficient storage of $CO_2$ from flue gases, however, requires that $CO_2$ be compressed before storage. Carbon dioxide can be collected in a liquid (absorption) or captured on a surface (adsorption). For more than 80 years now, absorption technology has been in commercial use for the removal of $CO_2$ from natural gas. For this purpose, the gas to be purified is sprayed with an amine solution such as mono-ethanolamine, wherein the amino groups selectively react with $CO_2$ to give a carbamate.[11]

$$2\ RNH_2 + CO_2 \rightleftarrows RNH_3^{\ +} + RNHCOO^-$$

Captured $CO_2$ is released at higher temperatures by a reverse reaction. This technique is also used in coal power plants, cement and steel factories, given the high concentration of $CO_2$ in the flue gases. This commercially applied technology has some disadvantages, such as equipment corrosion, energy consumption during the regeneration, and the need for a large reactor volume. Therefore, alternatives are sought where $CO_2$ is (selectively) captured in the pores of solid substances with a high internal surface area (e.g. silica, zeolites, and metal-organic frameworks (MOFs) with amino groups). However, the concentration of $CO_2$ represents a significant energy cost (Figure 2). $CO_2$ produced in point sources is not pure, but diluted with other gases. The flue gases of a power plant based on natural gas typically contain, for example, only 8% $CO_2$ in addition to water vapor, oxygen and inert nitrogen (73%). In order to store this $CO_2$ ("carbon capture and storage" - CCS) or use this $CO_2$ (" carbon capture and utilization " - CCU), a separation between $CO_2$ and the other gases has to happen.

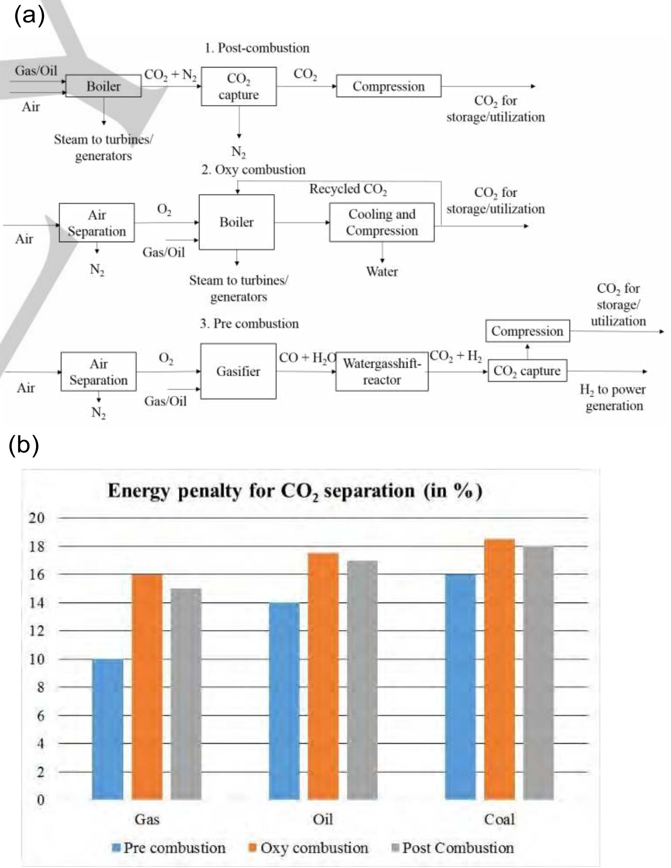

**Figure 2:** Technologies for concentration of $CO_2$-streams (a) and their energy penalty (b).

This separation requires energy, and is often expressed as a fraction of the energy produced by the power plant (i.e. the energy-penalty). The minimum separation energy is a precisely defined value, depending on the concentrations. Years of experience in separation processes indicates that the actual separation energy for a practical process is typically 3 to 5 times higher than the theoretical minimum. When combustion is combined with CO separation, three configurations (Figure 2a) can be distinguished. $CO_2$ is either separated after combustion ("post-combustion"), nitrogen (constituent of air) is separated before the combustion ("oxy-combustion"), or combustion is divided into two stages with a separation in the middle ("pre-combustion").

For the different configurations and for different fuels, the energy penalty was estimated based on practical and feasible energy separation (Figure 2b). Separation of $CO_2$ after combustion consumes about 15 to 20% of the energy produced by the power plant. This post combustion option is the easiest to implement in existing power plants. A much lower separation cost of ~ 10% is found for a pre-combustion scheme such as implemented in an Integrated Gasification Combined Cycle. Oxy-combustion has the highest additional energy consumption (Figure 2b). A very recent study showed that hereby electricity from coal becomes 64% more expensive.[12] In a recent study on applications in the cement industry in France, the feasibility of CCS is doubtful due to the cost of the "capture" part of the process.[13]

### 2.2. Mineralization

Mineralization of $CO_2$ is a process in which $CO_2$ reacts with minerals forming carbonates.[14] A typical example is illustrated by the following reaction:

$$Mg_2SiO_4 + 2\ CO_2 \rightarrow 2\ MgCO_3 + SiO_2$$

Mineralization is a very slow natural process. In available minerals such as olivine ($Mg_2SiO_4$), more $CO_2$ can be stored than the total historical $CO_2$ emission. This technique is currently not commercially in use. Extraction, crushing and transport of huge amounts of minerals is exceedingly energy-intensive.

$CO_2$ can also be captured by a reaction with by-products from the metal industry. The metal oxides, or so-called "slags", are separated from the molten metal and can be valorized for example by chemical reaction with $CO_2$ to carbonate-based building materials. Partial replacement of strong $CO_2$ polluting materials by less polluting materials has been successfully used in the cement industry. In the production of Portland cement, the main source of $CO_2$ is the thermal decomposition of limestone. Adding mineral additives that release no $CO_2$ can per ton of produced cement significantly reduce $CO_2$ emissions.[11]

### 2.3. Natural and artificial photosynthesis

It is evident that intensification of natural photosynthesis could capture a larger amount of $CO_2$ from the air. Part of anthropogenic $CO_2$ emissions are already today neutralized by increased photosynthetic capacity. Sustainable forest management, which aims to increase carbon stocks in forests or at least retain them, is put forward by the IPCC as an economically attractive option.[15] An active increase in biomass production, for example by feeding limited nutrients such as iron to sea algae, provides an additional option for increased carbon fixation and reduced atmospheric $CO_2$. This method belongs to the "geo-engineering" options, i.e. deliberate and large scale intervention in the climate system. Several studies, however, advise against using this method, given that the impact of such interventions on a large scale are difficult to estimate and the potential side effects are unknown. Moreover, the capture and conversion of $CO_2$ from natural photosynthesis requires large surface areas. In order to convert 90% of the $CO_2$ produced by an 850 MW power plant, an algae farm of about 500 $km^2$ is needed, or 2,000 times the area of a power plant.

$CO_2$ capture from the atmosphere and the subsequent conversion to carbohydrates with the help of sunlight and chlorophyll in plants has already been occurring in nature for millions of years. Therefore, artificial photosynthesis (i.e. catalytic conversion of $CO_2$ and water with sunlight to hydrocarbons, for example) seems to be an attractive concept. The feasibility of this concept has already been demonstrated by various research centers and companies,[16] and this concept will perhaps be, in the coming decades, economically viable for the conversion of $CO_2$ from point sources. An intrinsically insurmountable problem occurs when this concept is applied to undiluted $CO_2$: Capturing $CO_2$ from air with only 400 ppm $CO_2$ costs at least € 500 per ton of captured $CO_2$. This is a factor of 10 more expensive than capturing $CO_2$ from a concentrated source.[17]

## 3. The $CO_2$-problem is a timing problem

### 3.1. The energy cycle of carbon

The excessive emission of $CO_2$ is the net result of phenomena with very different time constants that are involved in the reduction of carbon for energy production, in which photosynthesis, fossilization and combustion form a cycle (Figure 3). By burning organic compounds (fuels), the released energy (heat) is immediately consumed or converted into other energy vectors such as electricity. Through photosynthesis, released $CO_2$ is converted back into biomass. On a geological time-scale, biomass underwent a fossilization process to form the fossil carbon reserves that are now being mined and refined into fuels. In this cycle, combustion is the fastest process whereas fossilization is the slowest process. A speed difference up to a factor of 10,000,000,000 can be noted. The imbalance between slow $CO_2$ reduction (photosynthesis and fossilization) and rapid combustion explains $CO_2$ accumulation in the atmosphere. Cars with diesel, petrol and LPG engines are driving on solar energy that was stored by photosynthesis in chemical bonds millions of years ago, and that are now converted in milliseconds to $CO_2$ in the engine. The slow fossilization step can be shortened by injecting fresh biomass immediately into the cycle and processing this mixture into fuel in a (bio-)refinery. However, the shortened cycle with chemical and/or biochemical refining of energy crops still shows a dramatic imbalance in the speed of the steps (Figure 3). $CO_2$ accumulation can be avoided only with processes that quickly and with high productivity convert $CO_2$ back into a fuel. Efficient and large-scale processes, in which $CO_2$ is chemically reduced to fuel in seconds, are needed for the steps replacing the slow photosynthesis. This type of cycle, in which $CO_2$ is formed in the same time-scale and converted back, is then a sustainable solution for achieving a $CO_2$-neutral world. The energy for rapid $CO_2$ reduction must be generated sustainably and comes indirectly from the sun. Another source with a minimal $CO_2$ footprint, such as nuclear power, may (temporarily) make a complementary contribution. The development of technology for the required rapid conversion of $CO_2$ to fuel is, however, a considerable scientific challenge.[18]

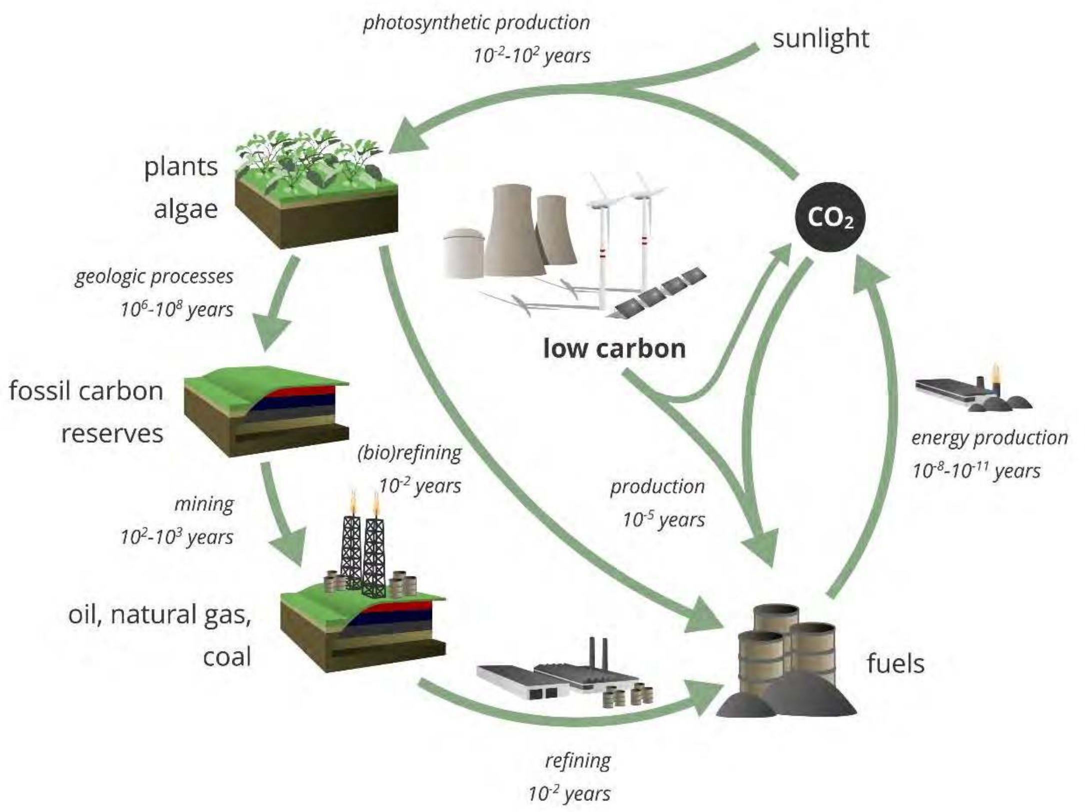

**Figure 3:** Timing in the carbon redox cycle.

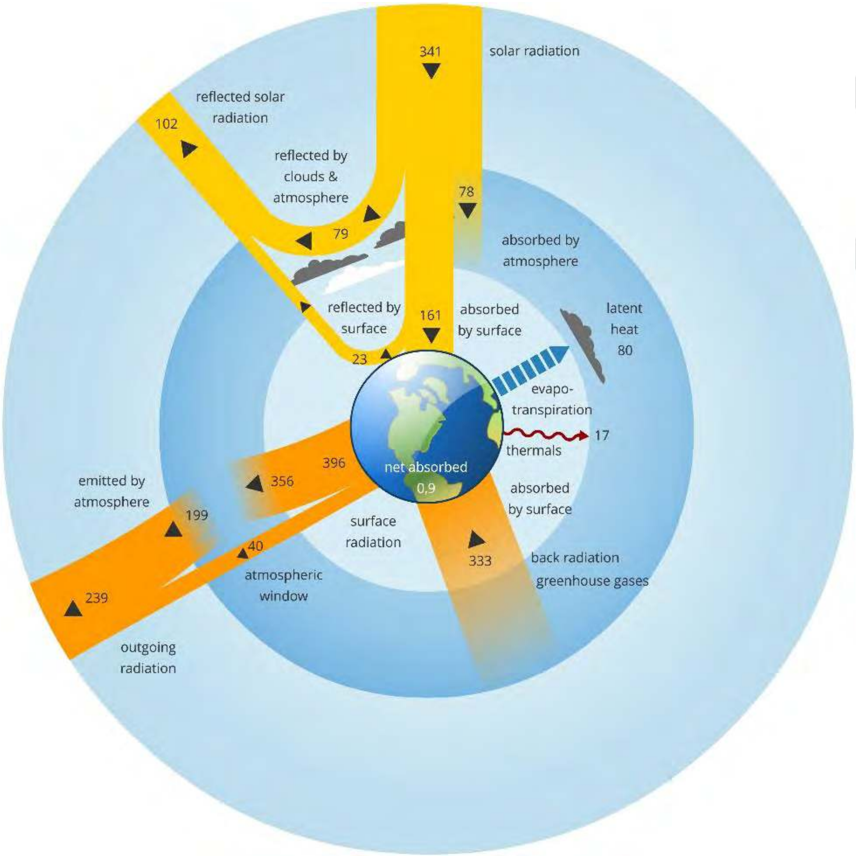

**Figure 4:** Global annual energy balance in $W/m^2$ (measured March 2000 to May 2004). Adapted from Trenberth *et al.*[19] More solar energy falls on earth per hour than what is annually consumed. Unfortunately, the vast majority of energy entering the Earth almost immediately leaves the earth. Of the 173,000 TW (340 $W/m^2$) entering the Earth, 18 TW (*1 TW = 1 terawatt =* $10^{15}$ *W)* is consumed by human activity. 29% is immediately reflected back by clouds, snow and ice. 23% is absorbed in the atmosphere, and about 50% reaches the earth's surface. Most of the absorbed solar energy, however, is sent back into space by the Earth on the same day in the form of heat (thermal infrared). Approximately 25% of absorbed solar energy is stored as latent heat by water evaporation. This huge amount of energy remains somewhat longer on earth and is released in the form of wind, rain, storms and hurricanes. Similarly, hydroelectric energy comes from this supply. Not more than about 1% of the solar energy is converted by photosynthesis into chemical energy in the form of biomass. Approximately 30% of this solar energy is captured by photosynthesis energy in blue-green algae. On an absolute scale, this energy is still enormous (about 520 TW) and it remains stored for several years on earth. The total amount of energy of the known reserves of fossil fuels is estimated to be 38 ZJ (zeta joule, *1 ZJ =* $10^{21}$ *J*). This amount is about 1% of the energy that reaches the Earth from the Sun per year.

### 3.2. Residence time of solar photons on earth

The timing issue can also be approached from the energy side in terms of the length of time the solar photons stay on earth. The energy that is radiated by the sun is enormous. One hour of sunshine on the whole earth is theoretically enough to supply mankind for a full year of energy (Figure 4). Unfortunately, most solar photons remain less than one second on Earth. Only a small fraction (1%) has a longer length of stay because their energy is utilized in converting $CO_2$ into biomass through photosynthesis. During combustion, heat is created and through radiation the photons are released again. Since the appearance of the "inventors" of photosynthesis (cyanobacteria) 3.5 billion years ago and that of land plants 470 million years ago, solar photons have been stored in fossil biomass. Consumption of stored fossil solar energy in a time span of a few generations of man has consequently led to excessive $CO_2$ emissions. The challenge is to hold the energy of more than 1% of solar photons on Earth longer and to use them to meet our energy needs. These captured solar photons can then be used to meet the need for rapid reduction of $CO_2$ in the carbon cycle (Figure 3).

### 3.3. Capture, storage and use of solar photons

There are several ways to capture and use solar photons. Solar photons are naturally captured by means of photosynthesis, wind power and hydropower (Table 5). Energy from the solar photons can be converted to electrical energy with photovoltaic cells, wind turbines and hydropower.

**Table 5:** Energy sources: Origin and development

| Energy Source | Origin | Explanation |
|---|---|---|
| Solar radiation | Sun | Nuclear fusion processes in the Sun |
| Fossil fuel | Sun | Indirectly from the Sun: Photons provide for photosynthesis processes and biomass production, which is converted on a geological time scale into fossil carbon |
| Biomass | Sun | Indirectly from the Sun: Photons provide for photosynthesis processes and biomass production, |
| Wind power | Sun | Indirectly from the Sun: heat from the sun provides for movement of air masses |
| Nuclear energy | Nuclear fission | Controlled fusion of $^{235}$U or $^{239}$Pu nuclear fuel |
| Geothermic energy | Earth | 30% wasted heat generated by the Earth<br>70% radioactive decay |
| Tidal energy | Gravity | Rotational system moon – Earth and seawater |
| Hydropower | Sun & gravity | Indirectly from the Sun: evaporation from the ocean and displacement in the form of rainfall at higher elevations |

However, solar radiation fluctuates greatly according to day-night and seasonal cycles as well as cloud cover. As such, energy usage (peaking early morning) and solar energy (peaking during the day) fluctuate according to different patterns. Nonetheless, large-scale energy-intensive processes, such as steel making, operate continuously. Imbalance in supply and demand can lead to surpluses during production peaks and form a threat to the continuity of the electricity supply when there is a strong demand or low production. Large and efficient storage of solar energy will therefore be necessary in order to evolve to a non-fossil solar energy-based economy.

Production of electricity by photovoltaic cells is quite efficient and is getting cheaper (€ 0.12 / kWh from solar energy across 0.04 to € 0.06 / kWh from coal). A problem with solar energy, and electricity in particular, has been a lack of efficient methods for large-scale storage. Today, the better batteries have an energy density (energy per kg) of ten to one hundred times smaller than those of fossil fuels (Table 6).[20] Recently, it was estimated that batteries should cost less than € 135 per kWh storage capacity in order to make electric vehicles competitive with conventional diesel vehicles, a goal that has not yet been achieved.[21] The energy content of one liter of diesel is 40 MJ/l and currently costs, for example, at the petrol station at many places on Earth less than a 1-liter bottle of sparkling water.[20] The impressive energy density of liquid fuels can be aptly illustrated. It only takes about 3 minutes to tank about 60 liters of diesel fuel. From a simple equation follows that the amount of energy output of 36 fueling diesel vehicles corresponds to the electrical power of a nuclear plant of ca. 430 MW. In order to produce the same amount of energy as in one full tank of diesel with solar cells on the roof of the car, no less than 800 hours of sunlight is needed. Solar photons can be stored most compactly in the chemical bonds of fuel molecules.

**Table 6:** Lower heating values for gaseous, liquid and solid fuels[20]

| Fuel | Energy type | Specific energy (MJ/kg)* |
|---|---|---|
| Uranium | Nuclear | 80,620,000 |
| Hydrogen | Chemical | 120 |
| Methane (natural gas) | Chemical | 47 |
| Diesel | Chemical | 43 |
| LPG | Chemical | 47 |
| Gasoline | Chemical | 43 |
| Coal | Chemical | 23 |

| | | |
|---|---|---|
| Methanol | Chemical | 20 |
| Lithium-ion battery | Electro-chemical | 0.36–0.875 |
| Alkaline battery | Electro-chemical | 0.67 |
| Nickle-metal hydride battery | Electro-chemical | 0.288 |

"Green" electricity, among others, obtained by (photovoltaic) conversion of sunlight or by wind energy, can by means of electrolysis split water into hydrogen ($H_2$) and oxygen ($O_2$). In this way, solar energy is converted into chemical energy embedded in the hydrogen molecules. This production of solar-fuel via electro-catalysis has a sunlight to chemical energy efficiency of more than 50%.[22] Thus, the storage of solar energy in molecular hydrogen is perfectly technically feasible and quite efficient. Several companies are active in this area. Green energy can be used in an analogous manner to convert $CO_2$ in a single electro-catalytic step to liquid fuels. Optimistic techno-economic studies indicate that in this way solar fuels, such as methanol, can be produced from $CO_2$ and $H_2$ at a cost between €0.94 and €1.10 per kilogram of diesel equivalent (equivalent energy content).[23] The conversion of hydrogen and $CO_2$ into carbon compounds requires relatively little extra energy with respect to the energy requirement for the production of hydrogen itself (Table 7). Simple molecules such as methanol, ethylene and propylene can be produced in this way from $CO_2$ and serve as building blocks for the chemical industry. This method requires at most minimal re-engineering of existing large-scale refining and/or petrochemical processes. It should be noted that in addition to the massive volumes of hydrogen produced, equivalent volumes of pure oxygen are produced. This method could replace in many stationary combustion processes air as an oxidant, thereby increasing combustion efficiency as a direct result. The (expensive) cryogenic air separation plants common to many industrial sites become superfluous in a hydrogen-based economy.

**Table 7:** Energy storage in chemical bonds

| **Molecule** | **Combustion heat kJ/mol C** | **$H_2$-equivalents[b]** | **Stored fraction (%) of the $H_2$-energy[c]** |
|---|---|---|---|
| Hydrogen | -240[a] | | 100 |
| Methanol | -680 | 3 | 94c |
| Dimethyl ether | -670 | 3 | 93 |
| Diesel fuel | -640 | 3 | 89 |
| Glucose | -450 | 2 | 94 |

[a] in kJ/mol $H_2$. [b] number of $H_2$-molecules needed to produce the corresponding molecule by hydrogenation of $CO_2$, e.g., $3 H_2 + CO_2 \rightarrow CH_3OH + H_2O$. [c] the combustion heat of methanol, 680 kJ/mol, is 94% of the combustion heat of the 3 $H_2$-molecules that are needed to reduce $CO_2$ to methanol (= 680/(240×3)).

By concentrating solar radiation with parabolic mirrors, temperatures to 1,000 °C and up can be reached. This approach has the potential to obtain an even higher efficiency than the photovoltaic approach (solar panels). The production of electricity occurs in a fairly conventional manner by producing steam and a generator is driven by a steam turbine. The possibility to store the heat temporarily (e.g. at night) in the form of molten salts, for example, makes this technology interesting because it offers the possibility to buffer energy at a central level with, as a result, a lower system integration cost.[24]

## 4. The current carbon economy

### 4.1. Irreplaceable carbon compounds

The entire fauna and flora on Earth consists largely of carbon compounds that are essential components in biochemical cycles. Carbon compounds are among the most commonly used substances, i.e. from cosmetics to food, clothing to materials, and fuels. Metallurgy uses coal, for example, to produce metals from ores. The presence of carbon atoms in materials and chemicals is usually essential. Therefore, our society is carbon based and is running on a carbon economy. The production of materials and chemicals is responsible for 5 to 10% of global fossil carbon consumption. Although the replacement of fossil carbon sources with biomass has already been implemented and leads to a greening of the chemical industry, the production of chemicals is currently still based mainly on oil (> 90%). The rest of the oil, and most of the natural gas and coal, are being consumed as an energy source and for this purpose are combusted into $CO_2$. The question can be raised as to if the burning of carbon compounds for energy purposes is a good thing, given the irreplaceable nature of these compounds in countless products. Carbon in materials and chemicals ultimately is released as $CO_2$, but only after the life cycle of the product, in other words after a significantly longer period of time than is the case for fuels. In addition, many of these materials contribute significantly to energy savings, e.g. as insulating materials and plastics for making lighter cars. LCA indicates that for every ton of $CO_2$ emitted by the chemical industry for such applications, three tons of $CO_2$ are saved.

### 4.2. Life cycle analysis

Given the scale of the energy conversions, a detailed life cycle analysis (LCA) of the various energy production processes is necessary for a grounded approach to the $CO_2$ emissions problem. Although there is a considerable spread in the estimated values, all energy production processes have, including renewable energy, a significant $CO_2$

footprint (Table 8).[9] The $CO_2$ footprint from electricity generation with photovoltaic cells, wind turbines, hydroelectric and nuclear power are due to the production processes of the materials, installations and transport; all of these footprints are based on carbon in the current carbon economy. This explains, for example, at first sight the contradictory conclusion from a recent study[25], that for the Flanders region of Belgium - for which ca. 50% of energy production is nuclear fueled - a nuclear phase-out would increase $CO_2$ emissions by 60% if the share of renewable energy will be increased by 2030 to 57%. If the share of renewable energy by 2030 would remain limited to 28%, additional natural gas power plants will be needed to generate the required electricity. Thus, the $CO_2$ emissions from these power plants would rise from the current 15 million tons to 37 million tons in 2030. Therefore, for quantification of the transition from a fossil carbon-based economy to an economy with alternative forms of energy, the $CO_2$ emissions per produced kWh should be used as a criterion (and set by policy).

**Table 8:** $CO_2$-emission per energy technology; LCA emission ($CO_2$-equiv (g/kWh))[9]

| | Minimum | Median | Maximum |
|---|---|---|---|
| Coal | 740 | 820 | 910 |
| Biomass co-incineration with coal | 620 | 740 | 890 |
| Gas (combined cycle) | 410 | 490 | 650 |
| Biomass | 130 | 230 | 420 |
| Photovoltaic | 18 | 48 | 180 |
| Geothermic | 6.0 | 38 | 79 |
| Concentrated solar power | 8.8 | 27 | 63 |
| Hydropower | 1.0 | 24 | 2200 |
| Wind offshore | 8.0 | 12 | 35 |
| Nuclear | 3.7 | 12 | 110 |
| Wind onshore | 7.0 | 11 | 56 |

### 4.3. Energy density of fuels

Due to the increasing energy needs of a growing world population and its prosperity, the tremendous energy benefits of fossil fuels and the absence of a readily available large-scale alternative makes the banning of fossil fuels in the next 20-30 years a utopian idea. For transportation purposes, liquid fuels are up to now unmatchable due to their high energy density (Table 6), especially for freight transport on the road, on water and in the air.[20] Even for passenger cars, the question remains as to whether a complete substitution of fossil fuels is possible in a few decades.

Solar energy alone cannot provide a global solution for all energy needs given the dispersed nature of the energy source and the large area required for capturing solar radiation. For example, the energy need of Flemish road transport is responsible for 21% of greenhouse gas emissions. In 2013, petrol and diesel vehicles consumed together 186 PJ (PetaJoule = $10^{15}$ Joule). Thus, road transport alone consumed 19 times more energy than was produced by wind power, hydropower and solar panels in that year.[26] This example illustrates how difficult it is for a densely populated region such as Flanders, in the short to medium term, to be supplied with solar photons of energy.

## 5. Towards a $CO_2$-neutral world with a mixed carbon-hydrogen economy

Given the $CO_2$ emissions problem, hydrogen atoms in fuels form a viable alternative to carbon atoms. Water as a reaction product is harmless, while even the water vapor produced may be collected and condensed for use. Water vapor is a greenhouse gas as well as $CO_2$, but the earth's atmosphere already contains so much water vapor (2.6%, or 26,000 ppm) that the added amount of water vapor from combustion processes barely makes a difference. The twelve-fold lower mass of the H-atom in comparison to the C-atom gives H-rich fuels a considerable advantage in fuel weight. Therefore, hydrogen gas ($H_2$) is the featherweight among the fuels (14 times lighter than air) and has only water as a combustion product. What then inhibits the transition from a carbon based economy to a hydrogen based economy?

### 5.1. Hydrogen as an energy carrier

The main problem with hydrogen is storage and transport. Hydrogen gas only becomes liquid at an extremely low temperature (-253 °C). Compression in order to collect more molecules in a given volume is the only option. $H_2$ is a particularly small molecule, which poses a risk of leaks in tanks and pipelines with hydrogen gas under pressure. It is not evident to build an extensive network of pipelines for hydrogen gas distribution. Compression at a pressure of hundreds of times the atmospheric pressure is applied to storage in vehicles, but even at that pressure the amount of hydrogen that can be stored in a tank remains limited. Cooling in combination with compression helps to increase the energy density but also incurs an energy cost.

**Table 9:** H/C ratio of fuels[27]

| Fuel | H/C ratio |
|---|---|
| CNG (natural gas) | 4 |
| LPG | 2.6 |
| Gasoline | 1.8 |
| Diesel | |

| | |
|---|---|
| - *Conventional* | 1.8 |
| - *Biodiesel* | 2.0 |
| Coal | ≤1 |

A lot of research has been invested in the search for materials that can reversibly bind large amounts of hydrogen. Storage of the $H_2$ molecules in narrow pores, or by chemical bonding through the formation of metal hydrides are options. The required capacity for practical application has not yet been achieved, despite intensive research and a breakthrough has become unlikely.

### 5.2. The H/C-ratio of fuels

Current motor fuels show differences in H-to-C atomic ratios (Table 9).[27] The H/C atomic ratio of methane (= 4), the main component of natural gas and CNG (*compressed natural gas*), reaches a maximum value for organic compounds here. LPG (*liquefied petroleum gas*) is composed of light alkanes and has an average H/C ratio of 2.6. Gasoline and diesel with a H/C ratio of 1.8 to 2.0 are comparable to each other. Long-chain alkanes and the alkyl chains of fatty acid esters (main component of first generation biodiesel) have a H/C ratio of slightly higher than 2. Coal, which consists of more than 90% (by weight percent) of carbon and about 4-5% weight percent of hydrogen, can have a H/C ratio less than or equal to 1 and contains the lowest number of H-atoms.

The volumetric mass density of a hydrocarbon fuel depends primarily on the aggregation state and the molecular mass of the molecules. CNG is gaseous and has lowest density (Table 10).[20,28] Among the liquid fuels, LPG, gasoline and diesel have significantly different density. Diesel is the densest and has the highest energy content per litre. The energy content of a litre of gasoline is only 89% of a litre of diesel, and for LPG it is only 72% (Table 10). Because of the higher carbon content of diesel compared to gasoline, the theoretical $CO_2$ performance of diesel and gasoline (defined as the weight of $CO_2$ produced at total combustion per MJ energy content) is similar (Table 10). The lower $CO_2$ emission per kilometre of vehicles powered with diesel engine is merely due to a better energy efficiency of this type of engine compared to a gasoline engine. LPG outperforms diesel in terms of theoretical $CO_2$ formation (Table 10). The theoretical $CO_2$ emission per MJ energy content of CNG is even lower, viz. 58.5 g $CO_2$ / MJ, and most environmentally friendly. The use of CNG and LPG instead of gasoline and diesel results in a significant abatement of the $CO_2$ emission per kilometre.[28]

**Table 10:** $CO_2$ performance of current fuels [20,28]

| | Diesel | Gasoline | LPG | CNG (Methane)[a] |
|---|---|---|---|---|
| Density (g/l) | 835 | 750 | 550 | - |
| C-content (g/kg) | 862 | 870 | 825 | 750 |
| C-content (g/l) | 720 | 642 | 454 | - |
| Energy content (MJ/kg) | 43 | 43 | 47 | 47 |
| Energy content (MJ/l) | 36 | 32 | 26 | - |
| $CO_2$-emission ($gCO_2$/MJ) | 74 | 73 | 64 | 58,5 |

[a] There are different types of CNG, which have different compositions; In this table only pure methane is shown.

High-grade diesel fuel consists mainly of long-chain alkanes having the formula $CH_3$-$(CH_2)_n$-$CH_3$ (n = 16 for cetane number 100). The H/C ratio is dependent on the number of methylene groups (-$CH_2$-) in the chains. For example, by shortening 20 carbon atoms to 10 carbon atoms per chain, the H/C ratio increases from 2.1 to 2.2, or with about 5%, reducing the $CO_2$ emissions also by 5%. Increasing the H/C ratio by adjusting the chain length of the alkanes is technically possible by adjusting the refining technique, and one can in the short-term make a contribution, albeit a modest one, to the reduction of $CO_2$ emissions from road transport and certainly from heavier transportation where electric alternatives do not offer an immediate solution.

The impact of the H/C ratio of fossil fuels is also reflected in the carbon footprint of the various types of power plants. Gas-fired power plants emit significantly less $CO_2$ per generated kWh compared to coal powered power plants (Table 8).[9] A switch from coal to fossil fuels with higher a H/C ratio, and a switch to natural gas in particular, also reduces $CO_2$ emission. In this way, the USA has achieved the Kyoto emission target by substituting coal with shale gas, having a higher H/C ratio.

### 5.3. Captured $CO_2$ as chemical building block

From $CO_2$, it is possible to synthesize a wide range of compounds for use in fuels, chemicals and materials.[29] The use of $CO_2$ can be classified into three categories, namely; (1) The production of fuels; (2) The production of chemicals and materials; and (3) The technological use of $CO_2$ without conversion. New fuels are the most suitable target for the conversion of large quantities of $CO_2$. The fuels market is in terms of tonnage, after all, 12 to 14 times greater than that of chemicals. Direct use of $CO_2$ gas without conversion (category 3) is quite limited.

The chemical industry has catalytic technology that produces an ever-increasing number of chemical compounds by introducing functional groups and by coupling functionalized building blocks. This increase can even emerge from a limited number of building blocks, in particular synthesis gas (mixture of carbon monoxide (CO) and $H_2$), light alkanes, aromatics, and alkanes. For example, $CO_2$ can be converted into inorganic carbonates (e.g. pulp and plastics), valuable chemicals (e.g. urea - fertilizer), and even finished pharmaceutical products (e.g. salicylic acid). $CO_2$ can be converted to formic acid (e.g. food, feed and leather industries), organic carbonates and polycarbonates (e.g. construction materials, automotive manufacturing, optical materials and CD's), (poly)carbamates and acrylates (e.g. plastics).[29] However, it should be emphasized that the diversity of end products from $CO_2$ can be further extended (through targeted research) and should be reengineered time and again to large scale sustainable chemical process technology.

### 5.4. $CO_2$ upgraded to fuel with the help of hydrogen

The water-gas shift (WGS) reaction establishes the chemical equilibrium between CO, $H_2O$, $CO_2$ and $H_2$:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The WGS reaction is performed using catalytic technology at large scale in petroleum refining and is an elegant way to produce $H_2$ on a large scale from CO. From natural gas (or LPG), a CO-rich mixture can be produced by "steam reforming" or (catalytic) pyrolysis.

The obvious way to convert $CO_2$ into a fuel is by deoxygenation to CO, which can be achieved by catalytic reduction with $H_2$ (reverse WGS). The energy requirements of catalytic $CO_2$-reduction are high, but part of the invested energy is recovered as high-temperature steam. Non-catalyzed thermal processes for performing a reverse WGS reaction are even more energy intensive. The CO that is formed can be used as an energy vector as such and combusted to $CO_2$.

Partial chemical-catalytic reduction of $CO_2$ yields methanol or higher alcohols, carboxylic acids, or even synthetic light methane. These yields are leading candidates for future large-scale fuel synthesis.

### 5.5. Methanol, dimethyl ether, synthetic methane or formic acid?

Methanol ($CH_3OH$) is, next to a bulk chemical, a suitable energy source with a high octane number and appropriate for use in gasoline engines. It is produced with large-scale catalytic technology (Cu / ZnO / alumina catalyst). Catalytic technology is available for producing short-carboxylic acids, formic acid and acetic acid. Dimethyl ether (DME) is obtained from methanol by acid-catalyzed dehydration. It is a suitable substitute for hydrocarbons in diesel, LPG and LNG. Chemical reduction of $CO_2$ to methanol requires three $H_2$ molecules per molecule of $CO_2$. The reactions for synthesis of methanol and dimethyl ether from $CO_2$ and $H_2$ occur as follows:

$$2\ CO_2 + 6\ H_2 \rightleftarrows 2\ CH_3OH + 2\ H_2O$$
$$2\ CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$$

In addition, methanol can be converted by zeolite catalysis to light olefins (ethylene and propylene), BTX (benzene Toluene Xylene) aromatics, and all kinds of hydrocarbons. Therefore, it is a technology that makes a bridge between methanol-ex-$CO_2$ and classic petrochemical technologies.[30] In the current context, methanol is for the time being a suitable source of energy, and because of the limited danger of explosion much safer than natural gas, hydrogen and gasoline. Methanol is an easily transportable liquid and has a high volumetric energy density, twice as much as liquid hydrogen. However, methanol has only about half of the volumetric energy density of gasoline and diesel. There are some safety hazards. Methanol vapors are very toxic and can cause blindness. Dimethyl ether vapors are extremely explosive.

Transforming $CO_2$ into hydrocarbons is an attractive option. Synthetic methane, (and other light hydrocarbons) obtained by the reaction of $CO_2$ with hydrogen gas, is equivalent to natural gas, for which the infrastructure for distribution via pipelines is already present.

Occasionally it is mentioned in literature about the use of formic acid (formic acid), a highly corrosive liquid, as an alternative fuel or as an energy vector. Some authors have spoken of a formic acid-based economy in this context. Through some, not always sustainable, chemical steps formic acid can be derived from $CO_2$:

- $CO_2$ → (reverse WGS) → CO; NaOH + CO → NaOOCH (sodium salt of formic acid); is released from salt (up to 80% aqueous solution) with sulfuric acid (and equivalent amounts of $Na_2SO_4$ waste are formed)
- $CH_3OH$ + CO → carbonylation (iridium catalyst) → $HCOOCH_3$ (methyl formate) → hydrolysis ($H_2O$) → HCOOH (formic acid) + $CH_3OH$.

On the condition that a sustainable formic acid synthesis is developed, this formic acid could be used as a chemical energy vector. By heating, hydrogen gas can be released suitably:

$$HCOOH \rightarrow H_2 + CO_2$$

### 5.6. The carbon cycle of the $CO_2$-neutral world

Short cutting of the carbon energy cycle (Figure 3) by catalytic reduction of $CO_2$ into fuels can provide a solution to the $CO_2$ emissions problem. The produced $CO_2$ should then be captured and converted to fuels, chemicals and materials. The problem is twofold: It requires a solution to the $CO_2$ conversion at $CO_2$ point sources and to the diffuse $CO_2$ emissions, both of which are about the same size (Table 3). In a $CO_2$-neutral world economy, fossil carbon will no longer be used as a source of energy and the carbon energy cycle (Figure 3) is at its shortest. In this way, all $CO_2$ generated by human activity is immediately converted back into fuels, chemicals and materials without releasing additional $CO_2$ into the atmosphere.

In contrast to the natural carbon cycle, based on photosynthesis with atmospheric $CO_2$ and an extremely slow natural conversion to fossil fuels, the chemical carbon cycle should be performed with fast chemical reduction reactions in order to generate a sustainable and safe carbon and hydrogen-based energy source. The energy used in current industrial chemical processes is usually derived from fossil fuels that will be excluded in the future as a source of energy for the conversion of $CO_2$ into fuels. Hence, the biggest challenge to achieving this goal is to find the extremely large amount of (sustainable!) energy needed to convert $CO_2$, the most oxidized end product of carbon compounds, back into fuels and chemical building blocks. This energy must be supplied in the form of photons, heat at high temperature, electrons from electricity or chemical compounds.

Hydrogen gas, which in the planned future energy scenario will play a key role, is currently mainly produced from coal or natural gas by "steam reforming" (reaction with steam) and the WGS reaction. Hydrogen gas should be produced in the future from energy sources with low $CO_2$ emissions. Energy strategies that are virtually carbon free should be developed.

Direct use of solar photons in artificial photosynthesis is an option. With the help of solar photons, the conversion of $CO_2$ (and water) to synthesis gas, methanol, hydrocarbons and formic acid can draw upon existing large-scale sustainable catalytic technology, while a number of steps that are already the subject of intense research can be developed further. Currently these steps are still in the 'proof-of-concept' stage.

In the chemical industry, most of the energy is used as a thermal energy rather than as electrical energy. The use of electricity to directly convert $CO_2$ into useful chemicals is, therefore, rather limited to, for example, the electrochemical conversion of $CO_2$ to methanol or formic acid.

Water splitting is suitable for delivering hydrogen gas as sustainable primary energy source. The conversion of electric energy to chemical energy in hydrogen gas ($H_2$) is performed in advanced electrolytic cells, with an efficiency of approximately 70%.[31] The electricity cost accounts for 80% of the cost to produce hydrogen gas in this way. This technology is the closest to large-scale commercialization. In Denmark, for example, a temporary surplus of wind energy is used for the electrolysis of water; the generated hydrogen is subsequently used in fuel cells for electricity or is further converted into methane.[32] Thus, the $CO_2$ captured at point sources can be catalytically converted to new fuels with the help of this environmentally friendly produced $H_2$ gas.

Carbon-free produced hydrogen gas is suitable to convert $CO_2$ from point sources back to fuel in a transition period toward a $CO_2$-neutral world. For diffuse sources, a chemical route to a solution seems momentarily less evident. It is recommended to electrify fleet vehicles and switch over to CNG for freight transport on the road. To replace kerosene as a fuel for aviation and heavy fuel for shipping, there is a need for new concepts. For climate control of buildings, the second major contributor to diffuse $CO_2$ emissions, the development of sustainable technologies is already in a very advanced stage and should be implemented without delay.

The bottleneck for conversion of $CO_2$ at point sources is the large need of energy for sources with low $CO_2$ emissions. Besides the Sun, there are not many alternatives to large-scale energy, except through nuclear, geothermal and tidal energy (Table 5). In addition to the low $CO_2$ emissions of these powers (see Life Cycle Analysis in Table 8), nuclear energy also offers opportunities to produce hydrogen gas. The potential of nuclear energy for electrolytic and thermochemical hydrogen production is being examined in the European SNETP Initiative (*Strategic Nuclear Energy Technology Platform*).

Electrolysis of water can be carried out at both low and high temperature, but is more efficient at high temperature. The current generation of nuclear reactors can handle low-temperature electrolysis, but this is not economically feasible. Only in the off-peak hours, when electricity demand is low, does this approach offer opportunities. Other types of reactors, such as the Fast Gas Reactor (GFR,) make it possible to carry out high-temperature electrolysis of water. The new generation of nuclear reactors (Generation IV) are promising. The development of these reactors is a strategic part of the SET Plan (Strategic Energy Technology) of the European Commission. Thermal chemical splitting of water to hydrogen and oxygen gas in "Very High Temperature Reactors" (temperatures higher than 800 °C) is proposed.

## 6. Technology for large scale $CO_2$ conversion at point sources

### 6.1. Need for technological development and scientific breakthrough

Since about 50% of the global total $CO_2$ emissions happen at point sources (Table 3) and it is energetically advantageous to work with concentrated $CO_2$ streams (Figure 2), it is logical to first capture $CO_2$ from point sources and then to convert it. The development of technology in order to capture $CO_2$ and to convert it to useful chemical compounds is a high priority. Large-scale catalytic technology for methanol production from $CO/CO_2$ and hydrogen gas is available in the petrochemical industry and can be applied, provided that certain process steps are eventually re-engineered.

For the conversion of $CO_2$, numerous techniques can also be used in principle, e.g. chemical catalysis, electrocatalysis, photocatalysis, plasma technology and bio-catalysis. Emerging technologies are discussed below and the current state of research and industrial development are explained. Table 11 provides an overview of the state of the art. Most of these technologies are not yet commercially available, and some are still being explored in the laboratory or on a pilot scale.[33]

In the short term, $CO_2$ capture from point sources and utilization has the potential to reduce $CO_2$ emissions by replacing the fossil carbon used to produce fuels and chemicals with carbon from $CO_2$. In the longer term, large point sources such as electricity plants should be replaced by renewable electricity plants, reducing the number of point sources, and $CO_2$ capture from air should be developed to recycle $CO_2$ emitted from diffuse sources. This research area is experiencing rapid growth, leading to significant reductions in the energy cost to capture $CO_2$ from air. In recent studies, separation energies of around 100 kJ/mol are reported for $CO_2$ capture from air, and this energy is mainly used to regenerate the sorbents. Often, low quality heat can be used, e.g., generated during electrolysis or $CO_2$ hydrogenation.[34]

**Table 11:** Possible technologies for synthesis of fuels from captured $CO_2$ at point sources

| Technique | Maturity[a] | Time necessary until first commercialization in years |
|---|---|---|
| Synthesis of polycarbonates and polyols | D | 5 |
| Methanol synthesis by direct hydrogenation of $CO_2$ | D | 5 |
| Methanol synthesis by indirect hydrogenation of $CO_2$ | L-P | 8-10 |
| Synthesis of fuels by indirect hydrogenation | L-P | 8-10 |
| Synthesis of inorganic carbonates by mineralization | D | >10 |
| Carbonation of concrete/cement | P-D | 5-10 |
| Dry reforming | P | <10 |
| Electrolytic synthesis of formic acid | L-P | >10 |
| Photocatalysis & photoelectron catalysis | L | >10 |
| Synthesis of syngas | P | <10 |
| Plasma technology | L | >10 |
| Biocatalysis | D | 5 |

[a] L = laboratory scale; P = pilot study; D = industrial demonstration.

### 6.2. Production of synthesis gas

Synthesis gas (CO and $H_2$) and short olefins together with aromatics are the most important building blocks in present day petrochemical industry. Synthesis gas is industrially made by gasification of coal or natural gas (steam reforming). With the help of catalysts and thermal energy, it can be attempted to convert $CO_2$ to valuable synthesis gas, which can be further converted into fuels and chemicals. Synthesis gas can be produced by dry reforming, and subsequently methanol is synthesized for instance.

### 6.3. Dry reforming

Dry reforming involves the reaction of $CO_2$ and methane to produce hydrogen and carbon monoxide. It can be directly applied to convert $CO_2$ from flue gases.[35] Two greenhouse gases are simultaneously converted (methane and $CO_2$) with a net reduction in greenhouse gas emissions if the necessary energy comes from energy sources that produce little $CO_2$:[36]

$$CO_2 + CH_4 \rightarrow 2\,H_2 + 2\,CO$$

The reaction is highly endothermic (i.e. it requires a lot of heat) and takes place at high temperatures (about 800 to 1000 °C). The investigated catalysts are often based on nickel.[37] A disadvantage of the technology is that both methane and the produced CO can be converted to solid carbon, which can deactivate the catalyst. Implementation of the latest catalyst design concepts today, such as stabilization of small metallic nickel particles with alkali metal oxides on the carrier, prevents deactivation by carbon deposits. However, this technology is not yet commercially available. Alternative processes such as Chemical Looping Reforming offer the possibility to convert three times more $CO_2$ per kg $CH_4$ ($CH_4 + 3\,CO_2 \rightarrow 4\,CO + 2\,H_2O$), and are being developed on a laboratory scale.

Dry and super-dry reforming[38] produce CO-rich syngas. CO-rich syngas can be used directly in carbonylation and hydroformylation, or can be mixed with renewable $H_2$ to increase the $H_2$/CO ratio.

### 6.4. Synthesis of methanol

Due to the high energy density of methanol, compared to other alternative energy carriers for powering transportation, such as batteries or hydrogen, it is a promising candidate as a future alternative fuel. Therefore, the synthesis of methanol from synthesis gas is a very attractive alternative, in part because it is already a commercial process. Methanol can also be synthesized in a two-stage process with the help of two successive reactors. In the first reactor, $CO_2$ is converted to CO by the reverse WGS reaction and after that water is separated. In a second reactor, methanol is produced from CO and $H_2$. In addition, the direct synthesis of methanol from $CO_2$ and $H_2$ is being developed. Due to the less favorable equilibrium conversion and the greater effect of the pressure of the two reagents, processes at a very high pressure (500 bar) are being considered.

### 6.5. Electro(cata)lysis

With the help of electricity and a catalyst, $CO_2$ can be converted into more reduced compounds such as CO, methane, methanol, formic acid and other chemicals. A typical electrochemical system consists of two electrodes: $CO_2$ and protons are converted at the cathode to the desired reaction products, and water is oxidized to $O_2$ at the anode. This process can be controlled by the applied electric potential and the reaction temperature. Often there is a high “overpotential” (i.e. difference between the theoretical minimum electric potential and actual voltage) required to drive the reaction quickly enough, and the electricity consumption is also high. If the electricity is derived from a $CO_2$-neutral energy form, this electrocatalytic technology offers opportunities to convert captured $CO_2$ at point sources into fuels.

Different types of electrocatalysts have already been tested for these electrochemical reactions. Gold-based catalysts are considered as a standard for this reaction. Due to the cost, alternatives are being sought. Thus, silver catalysts are already being developed that with 92% selectivity can convert $CO_2$ to CO.[39] The produced CO can then be used, for example, in the Fischer-Tropsch synthesis processes to produce hydrocarbons. Recently, it has also been discovered that much cheaper copper and cobalt catalysts can be used as an electrocatalyst.[40] This technology has not yet been used on a large scale.

Currently, about 5 million litres of methanol is produced annually in Iceland using geothermal energy: The geothermal energy is used to produce electricity, wherein $H_2O$ and $CO_2$ are converted to synthesis gas by means of electrolysis and hydrogenation, which is then converted into methanol.[16]

### 6.6. Plasma technology

Plasma, also called the fourth state of matter, is an ionized gas. Plasma is formed by introducing heat or electrical energy into a gas. As a result, the gas is split into ions and free electrons. An electric field is also created in which mainly the electrons (due to their low mass) are accelerated. When gas molecules and atoms collide, new particles are formed. Plasma is a "chemical cocktail" of atoms, molecules, free electrons and ions, as well as excited particles, radicals, and photons. Although plasmas have not been used commercially for $CO_2$ conversion, this technology looks promising. The gas itself can effectively remain at room temperature, but the reaction medium is "activated" by the highly reactive particles. Additionally, thermodynamically unfavourable reactions (such as $CO_2$ splitting into CO and $O_2$, production of syngas or the synthesis of methanol from $CO_2$ and $CH_4$) are possible under mild conditions (atmospheric pressure and room temperature) where they classically would require much more severe reaction conditions. Plasma can be generated with electricity, and moreover quickly switched on and off. Plasma technology can be built modularly and is also a promising technology for the temporary storage of solar photons and electricity, for example, during peak times in the production of renewable energy. The energy efficiency of plasma processes (electrical energy to chemical energy) is still relatively low and as a consequence the corresponding electricity consumption is high.

### 6.7. Biocatalysis

By use of biocatalysis, a wide variety of chemical compounds can be produced directly from $CO_2$, such as e.g. the microbial synthesis of ethanol or methane from $CO_2$ and $H_2$. The production of formic acid, acetic acid, propionic acid and butyric acid (1 to 4 C-atoms) can be done directly from $CO_2$ with homoacetogen microorganisms such as *Clostridium ljundahlii* or *Moorella thermoacetica*. This biocatalytic technique can also be driven directly by an electric current in a so-called microbial electrosynthesis, which still only exists on a laboratory scale.[41] To continue to 6 to 8 C-atoms, which are attractive precursors for liquid fuels by Kolbe synthesis, reverse beta-oxidation is stimulated in organisms such as *Clostridium kluyverii*, a process that has been known since the Second World War. Organisms such as *Cupriavidus necator* are currently being evaluated on a pilot scale for the production of polyhydroxybutyric acid, a biopolymer. This process runs on gases from the biorefinery.

### 6.8. Photocatalysis and artificial photosynthesis

Whereas in a classical combustion reaction fuel and oxygen react to $CO_2$ and $H_2O$, plants and algae do just the opposite. They make carbon compounds from $CO_2$ and $H_2O$ using sunlight via photosynthesis. Photosynthetic $CO_2$ conversion by algae and cyanobacteria is possible. Algae and cyanobacteria consume $CO_2$ and produce oil, which can be extracted and converted into fuels and chemicals. Algae grow usually in open areas or are cultivated in photobioreactors, and can use both sunlight and artificial light. Advantages are the high productivity per unit surface area and the fact that there is no additional energy needed for the culturing of the algae. However, there are also several challenges for this technique: There is a lot of energy needed to dehydrate the algae and extract the oil. In open spaces, there is a significant loss through evaporation, which requires a constant water flux. Energy efficiency (solar energy to chemical energy) and productivity (biomass $kg/m^3$ s) for photosynthetic processes are both lower than for (electro) chemical processes.

A lot of research is being devoted to mimicking natural photosynthetic systems ('artificial photosynthesis') in order to make fuels from $CO_2$ in this way and with target yields superior to those in the nature. The reduction of $CO_2$ can lead to different products such as CO, methanol or methane.

In artificial photocatalytic systems, the light falls on a semiconductor material. Hereby, electrons and holes are created that migrate to the surface, where they provide the energy for oxidation and reduction reactions. In the photo-electrochemical systems, the oxidation and reduction reactions are spatially separated. Only with very expensive photovoltaic elements and catalysts does the efficiency approach that of photovoltaic panels. With current materials, the yield from the conversion of sunlight to solar fuels is still far from competitive.[42]

## 7. Summary

The finite nature of fossil carbon reserves poses no imminent problem given the huge volume of reserves and the time scale of hundreds of years in which the depletion problem will arise. A much more urgent problem is the ever increasing $CO_2$ concentration in the atmosphere, causing climate change threatening life on our planet in a much shorter timeframe. Not the $CO_2$ production per se but the release of greenhouse gas in the atmosphere should be drastically reduced to achieve the climate goals. Avoiding production of greenhouse gas is, after all, not feasible. In the vital carbon economy, carbon-containing compounds will have a permanent place because of their exceptional energy density and chemical and material properties. Due to the irreplaceable nature of carbon compounds in countless products, $CO_2$ production cannot be avoided.

Life Cycle Analysis (LCA) and determining the $CO_2$ footprint are essential tools to correctly evaluate energy production systems on their environmental impact. All energy sources, including the so-called renewable ones, have significant $CO_2$ emissions because of the materials used, transport and maintenance. For a transition from a fossil carbon-based economy to an economy with alternative forms of energy, energy policy should use as criterion emissions of $CO_2$ per produced kWh.

The distinction between renewable and non-renewable energy and products is counterproductive for developing solutions, as it leads to complex legislation e.g. for the adoption of ethanol as bioethanol. All $CO_2$ emitted should therefore be considered equal, from a chemical perspective, with incentives focusing on efforts to decrease $CO_2$ emission or convert it. This would in the case of ethanol avoid the need for a bio-ethanol label, directly benefiting the party that captures $CO_2$ into ethanol and thus achieves net emission reduction. For $CO_2$ capture and conversion to renewable carbon-based fuels in large industrial plants, the carbon cycle should be shortened by using energy sources that produce low $CO_2$ emissions (e.g. solar power, wind power, tidal power, geothermal and nuclear power). Integration of energy systems, rather than gradual replacement of non-renewable by renewable, is the way to a $CO_2$ -neutral world.

## 8. Outlook

Given the huge task that lies ahead, it is particularly important that the economic aspects of all proposed technologies are analyzed thoroughly before decisions on a larger scale are made, this is of particular interest in achieving a global solution. General taxation of $CO_2$ emissions is necessary in order to make the investment in $CO_2$ recovery and catalytic transformation to renewed energy sources economically viable and not unnecessarily complex from a legislative and operational standpoint. For example, there is no scientific basis for distinguishing renewable carbon from biomass and fossil sources. Each carbon atom from biomass - fresh or fossil - is ultimately a $CO_2$ molecule in the atmosphere after completing the life cycle. All emitted $CO_2$, regardless of origin, should be treated on the same basis. General taxation is a simpler and more transparent model than selective subsidization, e.g. 'green certificates' leading to the aforementioned issues with ethanol and to volatility depending on governmental willingness to maintain such subsidies. Taxation should be constantly updated with the new insights and stimulate efforts reducing $CO_2$ emissions in a very direct manner.

Maximum efforts to reduce the $CO_2$ concentration in the atmosphere should be road mapped. For climate control of buildings (heating and air conditioning), the second largest contributor to the diffuse $CO_2$ production, the development of sustainable technologies is already very advanced. Implementation must be carried through immediately. The production of insulation materials from fossil fuels produces $CO_2$, but reduces energy consumption. The net impact is that for every molecule of $CO_2$ emitted in the production of insulation materials, there are already three or more savings in their application.

Carbon Capture and Storage '(CCS) at point sources, which are responsible for half of the $CO_2$ discharge into the atmosphere, is a temporary but necessary interim measure on the road to a $CO_2$-neutral world. CCS should be recommended at global level. Investment in research and development of technologies to capture $CO_2$ and to convert it to fuels, chemical building blocks and materials deserves highest priority. The world needs to evolve into a mixed carbon-hydrogen economy but mature technology for achieving this goal is lacking. There are plenty of options and different approaches will contribute solutions but a major research and development effort is needed. Emerging technologies make use of chemical catalysis, electrocatalysis, photocatalysis, plasma technology and bio-catalysis. Hydrogen, synthetic methane and methanol are likely the energy vectors of a $CO_2$-neutral world. The dense network of the chemical industry in some regions of our planet can play a leading role in the development and deployment of CCU (Carbon Capture and Utilization) cycles.

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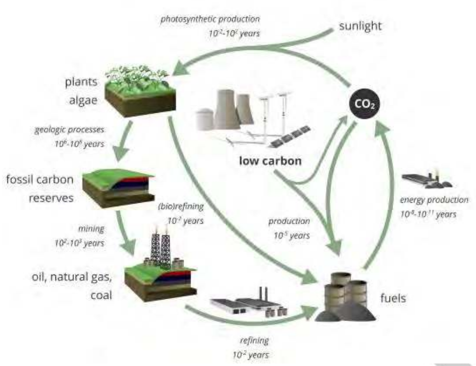
The $CO_2$ problem is a timing problem. Timing in the carbon cycle suggests large-scale chemical processes in which $CO_2$ is chemically reduced to fuel within seconds, needed to close the carbon cycle and avoid emission of greenhouse gas. This type of cycle, in which $CO_2$ is formed and converted back in the same time-scale, is a sustainable solution for achieving a $CO_2$-neutral world. The energy for rapid $CO_2$ reduction must be generated sustainably and come indirectly from the sun. The development of technology for the required rapid conversion of $CO_2$ to fuel is a considerable scientific challenge.



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