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The Chemical Route to a Carbon Dioxide Neutral World

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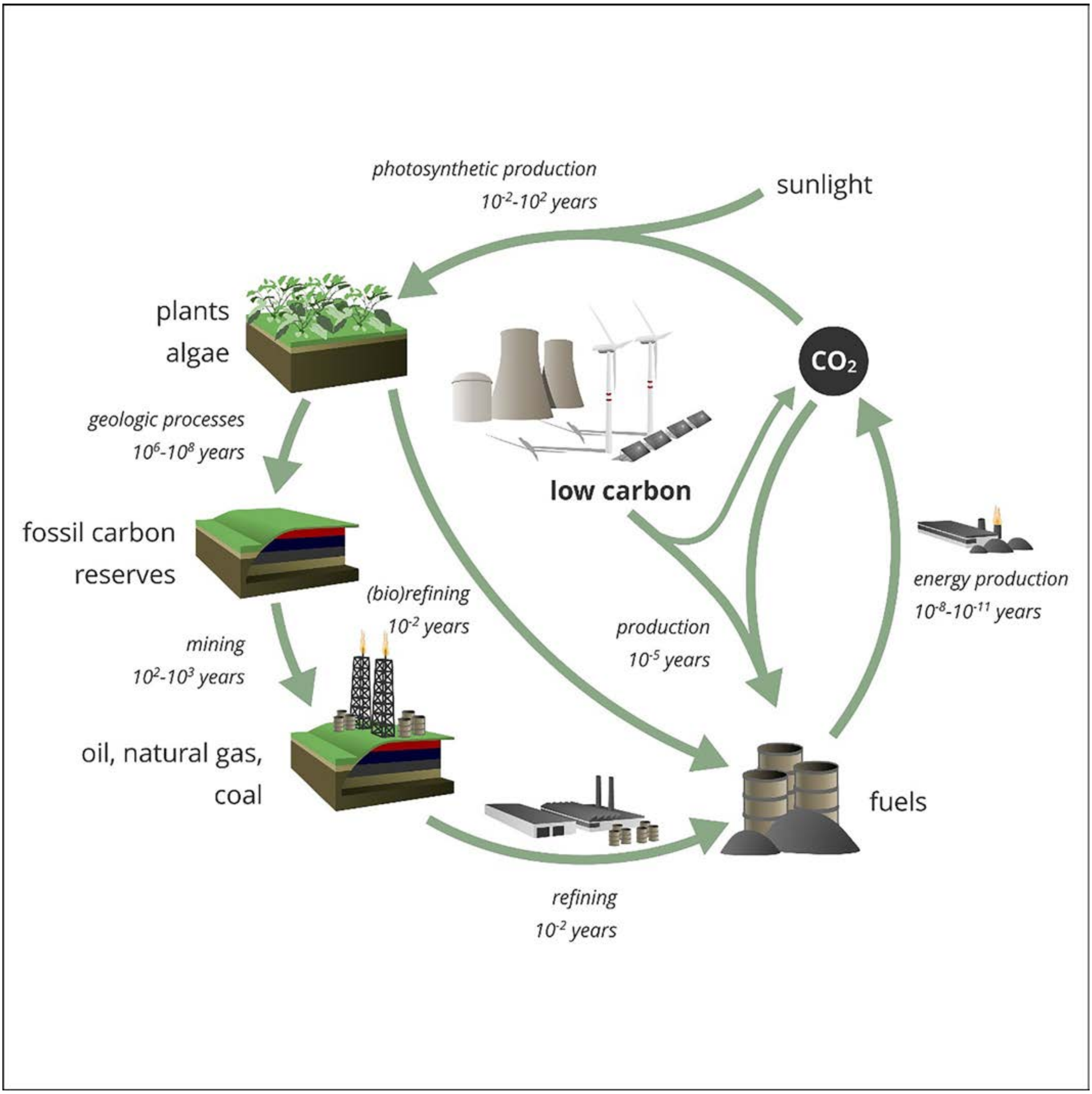

Excessive CO_2 emissions in the atmosphere from anthropogenic activity can be divided into point sources and diffuse sources. The capture of CO_2 from flue gases of large industrial installations and its conversion into fuels and chemicals with fast catalytic processes seems technically possible. Some 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 the conversion of CO_2 should come from low-carbon energy sources, such as tidal, geothermal, and 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, particularly for CO_2 emissions from road, water, and air transport, but steady progress in the development of 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 emissions 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, that is, 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^-), which thereby makes the oceans the second most important reservoir of carbonates.

Table 1. Estimation of the amounts of carbon in different compounds on earth.

Fully oxidized carbon	Content [Gt_{carbon}][a]	
in rocks (carbonates)	28 400 000	
dissolved bicarbonate in the oceans	38 000	
CO_2 in the atmosphere	830	
Partially oxidized carbon (biomass)		
soil	1500–2400	
permafrost	1700	
marine vegetation and dissolved organic matter	700	
land vegetation	350–550	
Reduced carbon	Reserves[b]	Resources[c]
petroleum	98–152	88–123
tar sands and shale oil	75–112	226–297
natural gas	76–108	110–136
shale gas	307–1026	614–1863
methane hydrates		500–2500
coal	446–542	7510–11 230

[a] 1 Gt = 10^9 t = 1 billion ton). [b] Reserves: recovery is possible with current technology and is economically viable. [c] Resources: not mineable or exploitation is currently not economically viable.

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 are converted into biomass by using light energy (mainly from the sun), and biomass is converted into chemical energy through catalysis by chlorophyll in green leaves; this 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 additional chemical reduction under the influence of elevated temperatures and pressures to form coal (carbon in its elemental form) and hydrocarbons $(CH_x)_n$, for example, petroleum, shale oil, tar sands, natural gas, shale gas, and methane hydrates. Oxygen atoms, produced by biological reduction of CO_2, accumulated

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as molecular oxygen (O_2) in the atmosphere. Thus, the original CO_2-rich earth atmosphere was gradually converted into 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.

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 decades, experts have warned of an impending oil shortage. On the basis of the current consumption and the known oil reserves, there is still plenty of oil for the next 50 years. For natural gas and coal, there are supplies 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 new reservoirs are regularly 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 in 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 by 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 owing 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.

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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 approximately one third to one sixth of the current reserve (estimated at 1000 to 2000 Gt) and only a small fraction of the total fossil carbon resources (estimated at 9000 to 16000 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 capture have been in 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 has been disturbed by the burning of fossil fuels, changes in land use, and the 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 concentration of CO_2 has exceeded the threshold of 400 ppm: a level that is, for 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 local air pollutants. The specificity of the CO_2 problem lies in 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, and it is generally assumed that a rise in its concentration contributes significantly to global warming. Greenhouse gases in the atmosphere absorb heat radiated from the earth's surface, and this heat is stored as 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 approximately $-18\,^{\circ}C$ on average and not the $14\,^{\circ}C$ 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 a rising CO_2 concentration in the atmosphere, it would be irresponsible not to 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 in that the total emission is limited by an emission ceiling ("cap"). In the period of 2013 to 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 either to reduce emissions or to purchase allowances. Businesses can get free allowances allocated to them by the government. In Europe, more than 11 000 installations have been covered by this directive. In total, approximately 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 the 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 of 2013 to 2016. In 2016, an expansion of the current cap was 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.).

Notably, 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, that is, 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 2015 contains the commitment to hold the increase in the global average temperature to well below 2 °C relative to preindustrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above preindustrial 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 1100 Gt so as to limit the temperature rise by 2 °C with 75% certainty (Table 2).[5,6] Estimates of greenhouse-gas emissions indicate that approximately 50 Gt CO_2 equivalents are emitted annually—this amount includes 70% CO_2, which is followed by methane and other greenhouse gases caused by human activity. If no decisive action is taken, the threshold of 1100 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, as a result of 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 1790 Gt, far beyond the stated amount of 1100 Gt CO_2.[2]

The allowable emissions of 1100 Gt CO_2 up to 2050 is equivalent to burning 300 Gt of fossil carbon. Until the year 2100, emissions may rise to 1907 Gt CO_2 or 520 Gt fossil carbon. The fossil carbon reserves are more than sufficient for this emission, even if fracking gases or other new sources are excluded (Table 1).[1] Experts warn of the 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 its release into the atmosphere is a more realistic goal.

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

	Emissions [Gt_{CO_2}]
total emissions since the industrial revolution	1340
still allowed amount to emit until 2050	1100
still allowed amount to emit until 2100	1900
current annual emissions—world	50
current annual emissions of CO_2—world	35

2. How Can CO_2 Accumulation in the Atmosphere Be Prevented?

To put a stop to the accumulation of CO_2 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, insulating buildings better 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 a low CO_2 energy supply will take decades. The development and implementation of technology is absolutely necessary for accelerating CO_2 absorption and avoiding 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), to prevent distribution into the atmosphere. Currently, industrial installations called carbon capture and storage (CCS) are used (Figure 1).

CCS can be implemented in situations for which 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 the one hand and other diffuse sources such as transport and climate control of buildings on the other hand. Globally, approximately half of the CO_2 emissions are from point sources (Table 3).[8] However, this share is slowly decreasing relative to the share of small diffuse sources. This decline is mainly due to the impact of controlling the climates of buildings and the transport sector. The

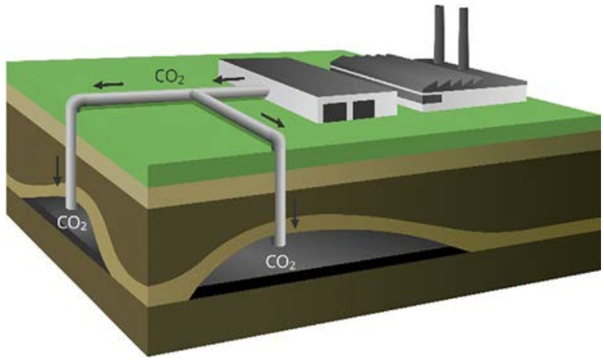

Figure 1. Carbon capture and storage (CCS) technologies typically involve the storage of CO_2 in underground layers (e.g., in mines or former oil extraction reservoirs). CO_2 is separated from flue gases and compressed before storage.

Table 3. Emission of greenhouse gases by sector and by share of point and diffuse sources.[8]

	Emissions [%]
energy	26
industry	19
forestry, land use, and agriculture	31
transport	13
buildings	8
waste and waste water	3
emission point sources—world	45
emission diffuse sources—world	55

IPCC indicates that there are more than 7500 "large point sources" worldwide with emissions of each over 100 000 t of CO_2 per year. Of this figure, 80 % are produced by power plants.

The energy and industrial sectors together account for approximately 50 % of the total amount of 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, approximately 40 million tons (0.04 Gt) of CO_2 was captured and stored underground.

Consequently, reducing the spread of CO_2 by applying CCS technologies for the energy and industrial sectors seems to be an obvious first step. The National Academy of Sciences in the USA in a recent study proposed CCS as a relatively realistic alternative in the short term.[10] Nonetheless, the idea has met 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 one (in addition to other measures). In the long run, captured CO_2 should be reused rather than stored in reservoirs.

Table 4. Life cycle analysis for emerging CCS technologies.[9]

Technology	$[g_{CO_2\ \text{equivalent}}\ kWh^{-1}]$ Minimum estimate	Median	Maximum estimate
coal	740	820	910
gas (combined cycle)	410	490	650
CCS coal: coal powder	190	220	250
CCS coal: integrated gasification combined cycle	170	200	230
CCS gas—combined cycle	94	170	340

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 monoethanolamine, wherein the amino groups selectively react with CO_2 to give a carbamate [Eq. (1)].[11]

$$2\,RNH_2 + CO_2 \rightleftharpoons RNH_3^{\ +} + RNHCOO^- \tag{1}$$

Captured CO_2 is released at higher temperatures by a reverse reaction. This technique is also used in coal power plants and 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 regeneration, and the need for a large reactor volume. Therefore, alternatives are sought for which 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 is 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 %). To store this CO_2 (i.e., CCS) or to use this CO_2 (i.e., carbon capture and utilization, CCU), separation between CO_2 and the other gases has to happen.

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 three to five times higher than the theoretical minimum. If combustion is combined with CO separation, three configurations (Figure 2 a) can be distinguished: one, CO_2 is separated after combustion (i.e., postcombustion); two, nitrogen (constituent of air) is separated before combustion (i.e., oxycombustion); three, combustion is divided into two stages with separation in the middle (i.e., precombustion).

For the different configurations and for different fuels, the energy penalty is estimated on the basis of practical and feasible energy separation (Figure 2 b). Separation of CO_2 after com-

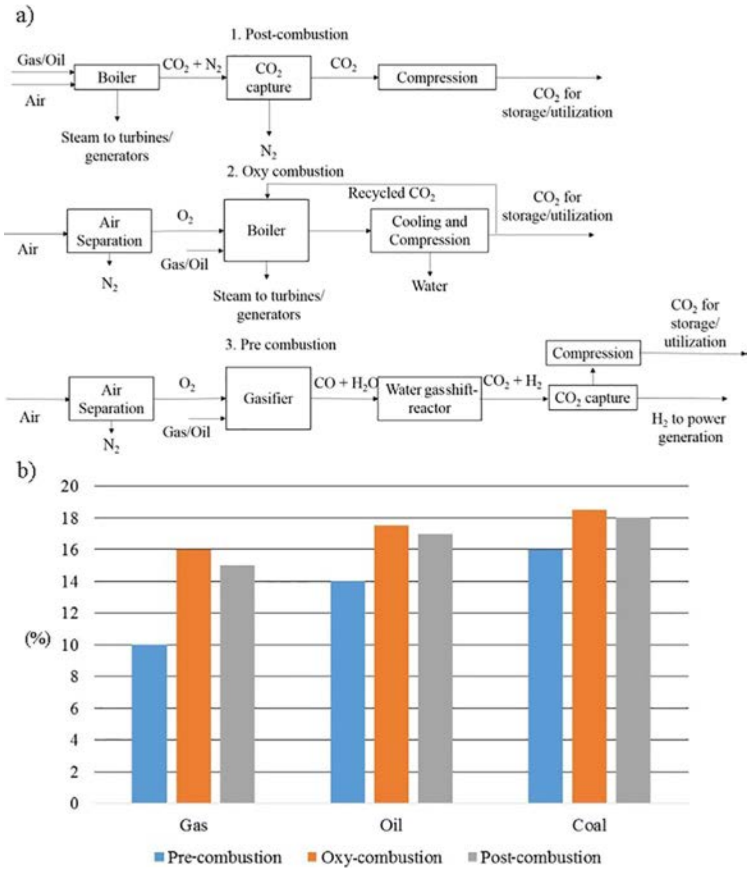

Figure 2. a) Technologies for the concentration of CO_2 streams. b) The energy penalties (%) for CO_2 separation.

bustion consumes approximately 15 to 20 % of the energy produced by the power plant. This postcombustion option is the easiest to implement in existing power plants. A much lower separation cost of approximately 10 % is found for a precombustion scheme such as that implemented in an integrated gasification combined cycle. Oxycombustion has the highest additional energy consumption (Figure 2 b). A very recent study shows that 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 owing to the cost of the "capture" part of the process.[13]

2.2. Mineralization

Mineralization of CO_2 is a process by which CO_2 reacts with minerals to form carbonates.[14] A typical example is illustrated by the following reaction [Eq. (2)]:

$$Mg_2SiO_4 + 2\,CO_2 \rightarrow 2\,MgCO_3 + SiO_2 \qquad (2)$$

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 reaction with byproducts from the metal industry. 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 today already neutralized by increased photosynthetic capacity. Sustainable forest management, which aims to increase carbon stocks in forests or at least retain them, has been 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 "geoengineering" options, that is, deliberate and large-scale intervention in the climate system. Several studies, however, advise against using this method given that the impact of such an intervention on a large scale is 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. To convert 90 % of the CO_2 produced by an 850 MW power plant, an algae farm of approximately 500 km^2 is needed or 2000 times the area of a power plant.

CO_2 capture from the atmosphere and its subsequent conversion into 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 into 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 if 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 timescale, 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 liquefied petroleum gas (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 into 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 on the same timescale 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 should come 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 into fuel is, however, a considerable scientific challenge.[18]

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: 1 h 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 1 s 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 (i.e., 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 the 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 into electrical energy with photovoltaic cells, wind turbines, and hydropower.

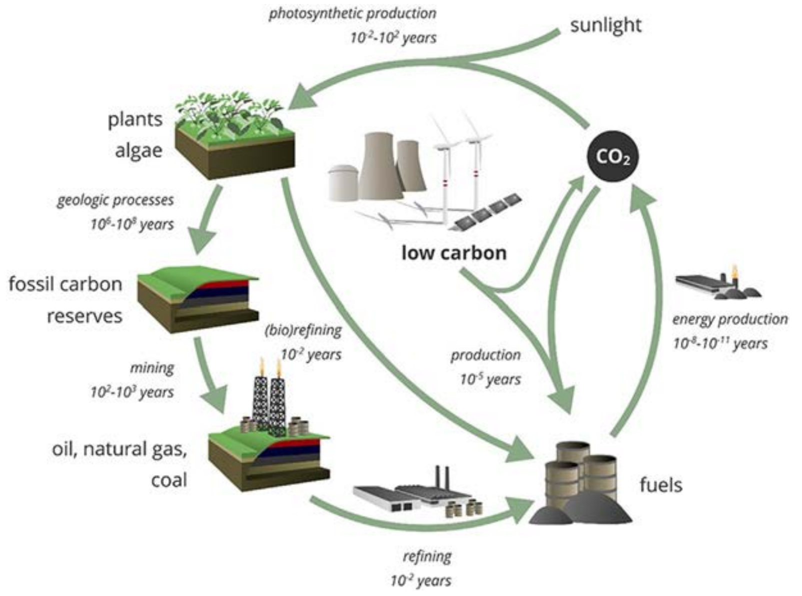

Figure 3. Timing in the carbon redox cycle.

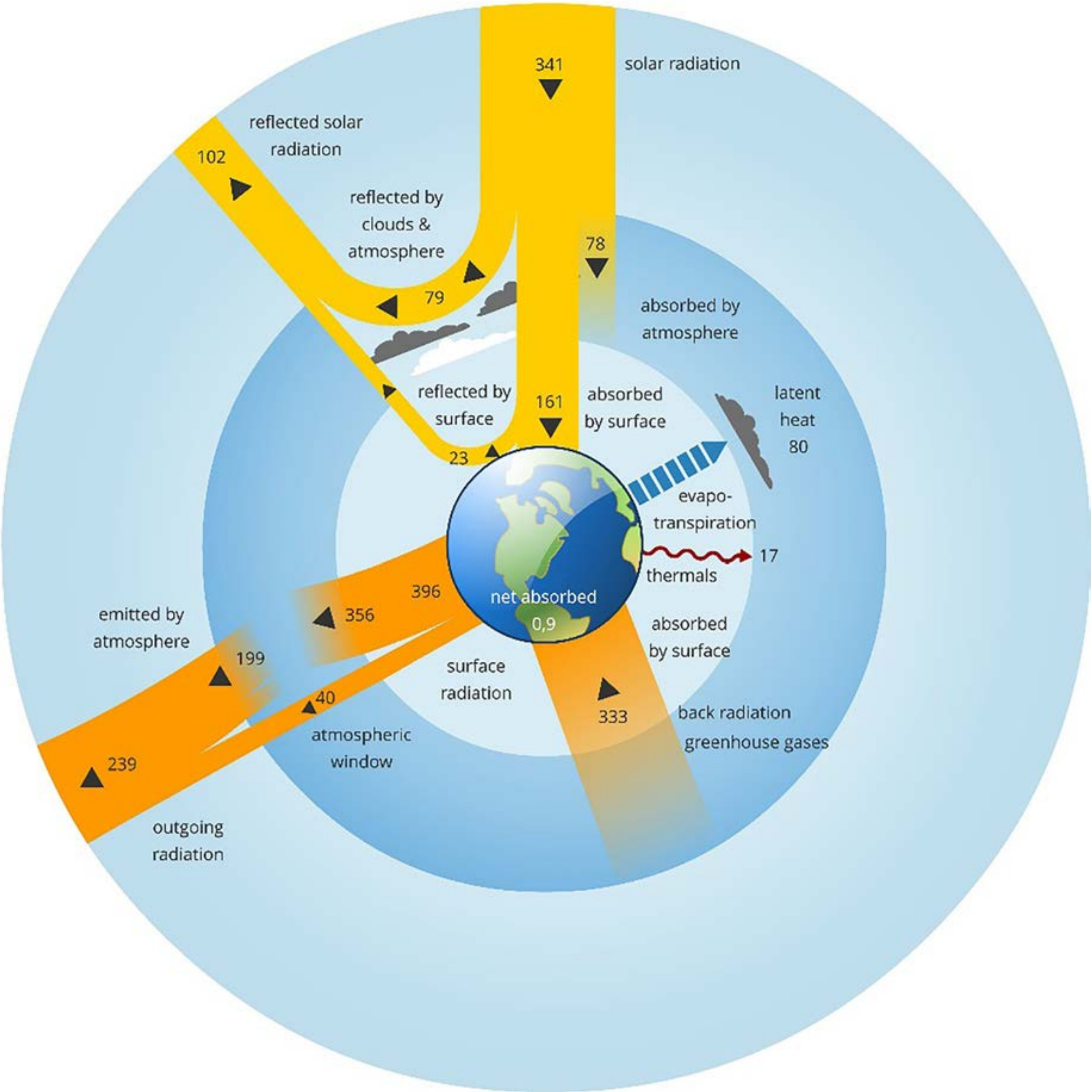

Figure 4. Global annual energy balance in W m^{-2} (measured March 2000 to May 2004). Adapted from ref. [19] More solar energy falls on earth per hour than what is annually consumed. Unfortunately, the vast majority of energy entering the earth almost immediately leaves the earth. Of the 173 000 TW (340 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 approximately 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 approximately 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 ($\approx$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 approximately 1 % of the energy that reaches the earth from the sun per year.

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 if there is a strong demand or low production. Large and efficient storage of solar energy will therefore be necessary to evolve to a nonfossil solar-energy-based economy.

Production of electricity by photovoltaic cells is quite efficient and is getting cheaper (0.12 € kWh^{-1} from solar energy across 0.04–0.06 € kWh^{-1} from coal). The problem with solar energy and electricity, in particular, is the lack of efficient methods for large-scale storage. Today, better batteries have an energy density (energy per kg) that is 10 to 100 times smaller than that of fossil fuels (Table 6).[20] Recently, it was estimated

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 the production of biomass, which is converted on a geological timescale 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 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

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

Fuel	Energy type	Specific energy [$MJ\,kg^{-1}$]
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	electrochemical	0.36–0.875
alkaline battery	electrochemical	0.67
nickel–metal hydride battery	electrochemical	0.288

that batteries should cost less than 135 € per kWh storage capacity to make electric vehicles competitive with conventional diesel vehicles, a goal that has not yet been achieved.[21] The energy content of 1 L of diesel is 40 $MJ\,L^{-1}$ and currently costs, for example, at the petrol station at many places on earth less than a 1 L bottle of sparkling water.[20] The impressive energy density of liquid fuels can be aptly illustrated. It only takes approximately 3 min to tank approximately 60 L of diesel fuel. From a simple equation it follows that the amount of energy output of 36 fueling diesel vehicles corresponds to the electrical power of a nuclear plant of approximately 430 MW. 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 h of sunlight is needed. Solar photons can be stored most compactly in the chemical bonds of fuel molecules.

“Green” electricity, among others, obtained by the (photovoltaic) conversion of sunlight or by wind energy, can split water into hydrogen (H_2) and oxygen (O_2) through electrolysis. In this way, solar energy is converted into chemical energy embedded in the hydrogen molecules. This production of solar fuel by electrocatalysis 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 electrocatalytic step into liquid fuels. Optimistic technoeconomic studies indicate that solar fuels, such as methanol, can in this way be produced from CO_2 and H_2 at a cost of 0.94–1.10 € per kilogram of diesel equivalent (equivalent energy content).[23] The conversion of hydrogen and CO_2 into carbon compounds requires 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 can 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. Notably, in addition to the massive volumes of hydrogen produced, equivalent volumes of pure oxygen are produced. This method could replace air as an oxidant in many stationary combustion processes, and as a direct result, this would increase the combustion efficiency. 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 [$kJ\,mol_C^{-1}$]	H_2 equivalents[b]	Stored fraction of the H_2 energy[c] [%]
hydrogen	−240[a]		100
methanol	−680	3	94[c]
dimethyl ether	−670	3	93
diesel fuel	−640	3	89
glucose	−450	2	94

[a] in $kJ\,mol_{H_2}^{-1}$. [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 $kJ\,mol^{-1}$, is 94 % that of the $3\,H_2$ molecules that are needed to reduce CO_2 to methanol [$=680/(240\times3)$].

By concentrating solar radiation with parabolic mirrors, temperatures of 1000 °C and higher can be reached. This approach has the potential to reach 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, that is, from cosmetics and food to clothing, 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 runs on a carbon economy. The production of materials and chemicals is responsible for 5 to 10% of the global fossil carbon consumption. Although the replacement of fossil carbon sources with biomass has already been implemented and leads to making the chemical industry more green, the production of chemicals is currently still mainly based on oil ($>$90%). The rest of the oil, and most of the natural gas and coal, are consumed as an energy source and, for this purpose, are combusted into CO_2. A question can be raised as to whether 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 is ultimately released as CO_2 but only after the life cycle of the product, that is, after a significantly longer period of time than that of the fuels. In addition, many of these materials contribute significantly to energy savings, for example, as insulating materials and plastics for making lighter cars. Life cycle analysis (LCA) indicates that for 1 t of CO_2 emitted by the chemical industry for such applications, 3 t of CO_2 is saved.

4.2. Life cycle analysis

Given the scale of the energy conversions, a detailed 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, and 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 approximately 50% of energy production is nuclear fueled—a nuclear phase out would increase CO_2 emissions by 60% if the share of renewable energy was increased to 57% by 2030. If the share of renewable energy by 2030 would remain limited to 28%, additional natural gas power plants would 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 kilowatt–hour should be used as a criterion (and set by policy).

Table 8. CO_2 emissions per energy technology; LCA emission[9]

	Emissions [CO_2 equiv. (g kWh^{-1})]		
	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

Owing 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 make the banning of fossil fuels in the next 20–30 years a utopian idea. For transportation purposes, liquid fuels are, to date, unmatchable because of 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 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 the Flemish road transport is responsible for 21% of greenhouse gas emissions. In 2013, petrol and diesel vehicles together consumed 186 PJ (PetaJoule $=10^{15}$ Joule). Thus, road transport alone consumed 19 times more energy than that 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, and even the water vapor produced may be collected and condensed for use. Water vapor is also a greenhouse gas, but the earth's atmosphere already contains so much water vapor (2.6% or 26000 ppm) that the added amount of water vapor from combustion processes barely makes a difference. The mass of the H atom is 12-fold lower than that of the C atom, and this 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 to collect more molecules in a given volume is the only option. H_2 is a particularly small molecule, and thus, leaks in tanks and pipelines pose a risk with pressurized hydrogen gas. It is not evident how an extensive network of pipelines can be built for hydrogen-gas distribution. For storage in vehicles, hydrogen is compressed at a pressure that is hundreds of times the atmospheric pressure, 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.

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

5.2. The H/C ratio of fuels

Current motor fuels show differences in H/C atomic ratios (Table 9).[27] The H/C atomic ratio of methane (=4), the main component of natural gas and compressed natural gas (CNG), reaches a maximum value for organic compounds here. Liquefied petroleum gas (LPG) is composed of light alkanes and has an average H/C ratio of 2.6. Gasoline and diesel with H/C ratios 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 H/C ratios that are slightly higher than 2. Coal, which consists of more than 90% (by weight percent) of carbon and approximately 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.

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
diesel (biodiesel)	2.0
coal	≤1

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 the lowest density (Table 10).[20,28] Among the liquid fuels, LPG, gasoline, and diesel have significantly different densities. Diesel is the densest and has the highest energy content per liter. The energy content of a liter of gasoline is only 89% that of a liter of diesel, and the energy content of a liter of LPG is only 72% that of a liter of diesel (Table 10). Because diesel has a higher carbon content than gasoline, the theoretical CO_2 performances of diesel and gasoline (defined as the weight of CO_2 produced at total combustion per MJ energy content) are similar (Table 10). The lower CO_2 emission per kilometer of vehicles powered with a diesel engine is merely due to the fact that this type of engine is more energy efficient than 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, namely, 58.5 g $CO_2\,MJ^{-1}$, and is the most environmentally friendly. The use of CNG and LPG instead of gasoline and diesel results in significant abatement of the CO_2 emissions per kilometer.[28]

High-grade diesel fuel consists mainly of long-chain alkanes having the formula $CH_3(CH_2)_nCH_3$ ($n=16$ 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 the chain from 20 carbon atoms to 10 carbon atoms, the H/C ratio increases from 2.1 to 2.2 or by approximately 5%, which reduces 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 in the short term one can make a contribution, albeit a modest one, to reducing the CO_2 emissions from road transport and certainly from heavier transportation, for which 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 kilowatt–hour than coal-powered power plants (Table 8).[9] A switch from coal to fossil fuels with higher H/C ratios and a switch to natural gas, in particular, also reduces CO_2 emissions. In this way, the USA has achieved the Kyoto emission

Table 10. CO_2 performance of current fuels.[20,28]

	Density [$g\,L^{-1}$]	C content [$g\,kg^{-1}$]	C content [$g\,L^{-1}$]	Energy content [$MJ\,kg^{-1}$]	Energy content [$MJ\,L^{-1}$]	CO_2 emission [$g_{CO_2}\,MJ^{-1}$]
diesel	835	862	720	43	36	74
gasoline	750	870	642	43	32	73
LPG	550	825	454	47	26	64
CNG (methane)[a]	–	750	–	47	–	58.5

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

target by substituting coal with shale gas, having a higher H/C ratio.

5.3. Captured CO_2 as a 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: one, the production of fuels; two, the production of chemicals and materials; three, the technological use of CO_2 without conversion. New fuels are the most suitable target for the conversion of large quantities of CO_2. In terms of tonnage, the fuels market is, after all, 12 to 14 times greater than the chemicals market. 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 into formic acid (e.g., food, feed, and leather industries), organic carbonates and polycarbonates (e.g., construction materials, automotive manufacturing, optical materials, and CDs), and (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 re-engineered 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 [Eq. (3)]:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

The WGS reaction is performed by using catalytic technology on a 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 most apparent 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 reaction). The energy requirements for catalytic CO_2 reduction are high, but part of the invested energy is recovered as high-temperature steam. Uncatalyzed 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.

The 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 is 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 the synthesis of methanol and dimethyl ether from CO_2 and H_2 occur as follows [Eqs (4) and (5)]:

$$2\,CO_2 + 6\,H_2 \rightleftharpoons 2\,CH_3OH + 2\,H_2O \tag{4}$$

$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{5}$$

In addition, methanol can be converted by zeolite catalysis into 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, it is much safer than natural gas, hydrogen, and gasoline. Methanol is an easily transportable liquid and has a high volumetric energy density that is twice that of liquid hydrogen. However, methanol has only approximately half 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 by pipelines is already present.

The use of formic acid, a highly corrosive liquid, is occasionally mentioned in the literature 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 [Eqs. (6)–(8)]:

$$CO_2 \xrightarrow{\text{reverse WGS}} CO \tag{6}$$

$$NaOH + CO \rightarrow NaOOCH \tag{7}$$

Formic acid is released from the sodium salt (up to 80% aqueous solution) with sulfuric acid (and equivalent amounts of Na_2SO_4 waste are formed).

$$CH_3OH + CO \xrightarrow{\text{carbonylation (iridium catalyst)}} HCOOCH_3 \text{ (methyl formate)} \xrightarrow{\text{hydrolysis } (H_2O)} HCOOH \text{ (formic acid)} + CH_3OH \tag{8}$$

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 [Eq. (9)]:

$$HCOOH \rightarrow H_2 + CO_2 \tag{9}$$

5.6. The carbon cycle of the CO_2-neutral world

Short cutting 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 into fuels, chemicals, and materials. The problem is twofold: it requires a solution to CO_2 conversion at CO_2 point sources and to diffuse CO_2 emissions, both of which are approximately the same size (Table 3). In a CO_2-neutral world economy, fossil carbon would no longer be used as a source of energy, and the carbon energy cycle (Figure 3) would be at its shortest. In this way, all CO_2 generated by human activity would immediately be 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 extremely slow natural conversion into fossil fuels, the chemical carbon cycle should be performed with fast chemical reduction reactions 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.

The direct use of solar photons in artificial photosynthesis is an option. With the help of solar photons, the conversion of CO_2 (and water) into synthesis gas, methanol, hydrocarbons, and formic acid can draw upon existing large-scale sustainable catalytic technology, whereas 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 thermal energy rather than electrical energy. The use of electricity to convert CO_2 directly into useful chemicals is, therefore, rather limited to, for example, the electrochemical conversion of CO_2 into methanol or formic acid.

Water splitting is suitable for delivering hydrogen gas as a sustainable primary energy source. The conversion of electric energy into 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 into 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 into 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 to 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 the 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 Strategic Nuclear Energy Technology Platform (SNETP) Initiative.

Electrolysis of water can be performed at both low and high temperatures, but it is more efficient at high temperatures. 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 the high-temperature electrolysis of water possible. The new generation of nuclear reactors (generation IV) is promising. The development of these reactors is a strategic part of the Strategic Energy Technology (SET) Plan 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

Given that approximately 50% of the global total CO_2 emissions happen at point sources (Table 3) and that it is energetically advantageous to work with concentrated CO_2 streams (Figure 2), it is logical first to capture CO_2 from point sources and then to convert it. The development of technology to capture CO_2 and to convert it into 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 in principle also be used, for example, chemical catalysis, electrocatalysis, photocatalysis, plasma technology, and biocatalysis. 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]

Table 11. Possible technologies for synthesis of fuels from captured CO_2 at point sources.

Technique	Maturity[a]	Time necessary until first commercialization [y]
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.

In the short term, CO_2 capture from point sources and its 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, and this has led to significant reductions in the energy costs to capture CO_2 from air. In recent studies, separation energies of approximately 100 $kJ\,mol^{-1}$ 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, for example, generated during electrolysis or in the hydrogenation of CO_2.[34]

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 the 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 into valuable synthesis gas, which can be further converted into fuels and chemicals. Synthesis gas can be produced by dry reforming, and, for instance, methanol can subsequently be synthesized.

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 [Eq. (10)]:[36]

$$CO_2 + CH_4 \rightarrow 2\,H_2 + 2\,CO \tag{10}$$

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

Dry and superdry 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

Owing to the high energy density of methanol, relative to that of 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 into 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. Owing to the less favorable equilibrium conversion and the greater effect of the pressure of the two reagents, processes at a very high pressure (50.0 MPa) 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 into 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. Owing to the cost, alternatives are being sought. Thus, silver catalysts are already being developed that with 92% selectivity can convert CO_2 into 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 electrocatalysts.[40] This technology has not yet been used on a large scale.

Currently, approximately 5 million liters of methanol is produced annually in Iceland by using geothermal energy. The geothermal energy is used to produce electricity, wherein H_2O and CO_2 are converted into synthesis gas by means of electrolysis and hydrogenation, and the synthesis gas 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 (as a result of their low mass) are accelerated. If 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 unfavorable 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), even though they classically would require much more severe reaction conditions. Plasma can be generated with electricity, and moreover, it can quickly be 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 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 (one to four carbon atoms) can be done directly from CO_2 with homoacetogen microorganisms such as *Clostridium ljundahlii* and *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 six to eight carbon atoms, precursors that are attractive for liquid fuels by Kolbe synthesis, reverse β-oxidation is stimulated in organisms such as *Clostridium kluyverii*, a process that has been known since World War II. 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 by using sunlight through 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 usually grow 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 culturing of the algae. However, there are also several challenges for this technique. Much energy is needed to dehydrate the algae and to 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 (i.e., artificial photosynthesis) to make fuels from CO_2 in this way and with target yields superior to those in nature. The reduction of CO_2 can lead to different products such as CO, methanol, and methane.

In artificial photocatalytic systems, the light falls on a semiconductor material. Thereby, electrons and holes are created that migrate to the surface, at which they provide the energy for oxidation and reduction reactions. In photoelectrochemical 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 into 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 timescale of hundreds of years on which the depletion problem will arise. A much more urgent problem is the ever-increasing CO_2 concentration in the atmosphere, which is causing climate change and threatening life on our planet in a much shorter timeframe. Not CO_2 production per se but the release of greenhouse gases in the atmosphere should be drastically reduced to achieve climate goals. Avoiding the production of greenhouse gases 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. Owing to the irreplaceable nature of carbon compounds in countless products, CO_2 production cannot be avoided.

Life cycle analysis and determining the CO_2 footprint are essential tools that can be used to evaluate correctly the environmental impact of energy-production systems. All energy sources, including the so-called renewable ones, have significant CO_2 emissions because of the materials used, transport, and maintenance. For transition from a fossil-carbon-based economy to an economy with alternative forms of energy, energy policy should use emissions of CO_2 per produced kilowatt–hour as a criterion.

The distinction between renewable and nonrenewable energy and products is counterproductive for developing solutions, as it leads to complex legislation, for example, 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 to convert it. This would, in the case of ethanol, avoid the need for a bioethanol label, which would directly benefit the party that captures CO_2 into ethanol to achieve net emission reduction. For CO_2 capture and conversion into 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, and geothermal and nuclear power). Integration of energy systems rather than gradual replacement of nonrenewable 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 be 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 to make the investment in CO_2 recovery and catalytic transformation into 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, for example, "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 new insights and stimulate efforts to reduce CO_2 emissions in a very direct manner.

Maximum efforts to reduce the CO_2 concentration in the atmosphere should be road mapped. In terms of controlling the climates of buildings (heating and air conditioning), the second largest contributor to 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 the amount of CO_2 discharged into the atmosphere, is a temporary but necessary interim measure on the road to a CO_2-neutral world. CCS should be recommended at a global level. Investment in research and development of technologies to capture CO_2 and to convert it into fuels, chemical building blocks, and materials deserves the highest priority. The world needs to evolve into a mixed carbon–hydrogen economy, but mature technology to achieve this goal is lacking. There are plenty of options and different approaches will contribute to solutions, but a major research and development effort is needed. Emerging technologies make use of chemical catalysis, electrocatalysis, photocatalysis, plasma technology, and biocatalysis. 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 carbon capture and utilization cycles.

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