An Economy Based on Carbon Dioxide and Water

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Potential of Large Scale Carbon Dioxide Utilization

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Preface

The Carbon Dioxide Problem

Surface (biomass) and sub-surface (fossil-C such as coal, oil, gas) C-based assets have been, and will be for long time yet, used as source of energy and goods by humans. The use of all such materials causes the formation of CO_2, which is emitted into the atmosphere. The intensity of the emission of CO_2 has continuously grown and parallels the growth of both the population and average standard of life. (Figs. 1 and 2).

This has caused the continuous accumulation of atmospheric CO_2 which has reached 408 ppm these days with respect to 275 ppm of the preindustrial era. The atmospheric level of CO_2 is the "warning light" for the "health" of our planet. A correlation exists between the consumption of energy—the CO_2 emission—the accumulation in the atmosphere and the increase of the planet temperature (Figs. 3 and 4) that may cause non-return catastrophic events. Whether CO_2 is the direct actor or is an "indicator" of the impact caused by human activities on the atmosphere, is in question. As a matter of fact, humans are using C-based resources in a "highly inefficient" way: the efficiency of conversion of chemical energy (fossils or biomass) into other forms of energy (electrical, thermal, mechanical, etc.) ranges around 27–35%. This means that 73–65% of the original chemical energy is released to the atmosphere in the form of heat, often at high temperature, causing its direct heating. As the emission of CO_2 is related to the amount of C-based fuels burned or goods used, it becomes an easy "witness" of the impact humans are causing on Earth (even if not the direct cause). However, there is a general fear that continuing to accumulate CO_2 into the atmosphere (or continuing with an inefficient use of natural resources) may increase the temperature of our planet. Although CO_2 is a greenhouse gas (GHG), its atmospheric concentration is much lower than that of other GHGs, e.g. water vapour. Is the atmospheric CO_2 that causes planet heating or the released heat or both? A question rises: Supposed that we capture all the produced CO_2, but continue to heat the atmosphere with inefficient conversion of chemical energy (C-based energy sources) into other forms of energy, shall we "cool down" our planet? The most effective solution would be to reduce the use of C-based fuels (that will imply the reduction of CO_2 emission) and the release of

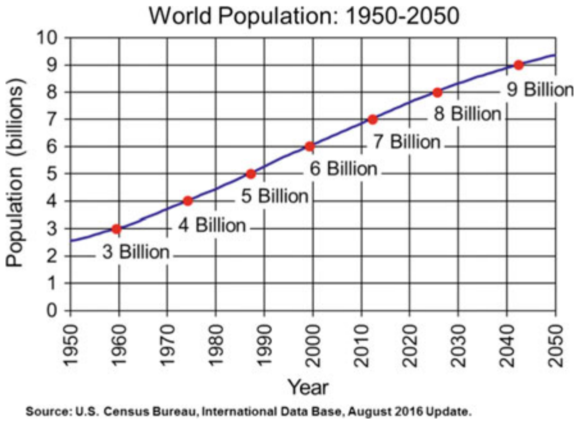

Fig. 1 Growth of world population

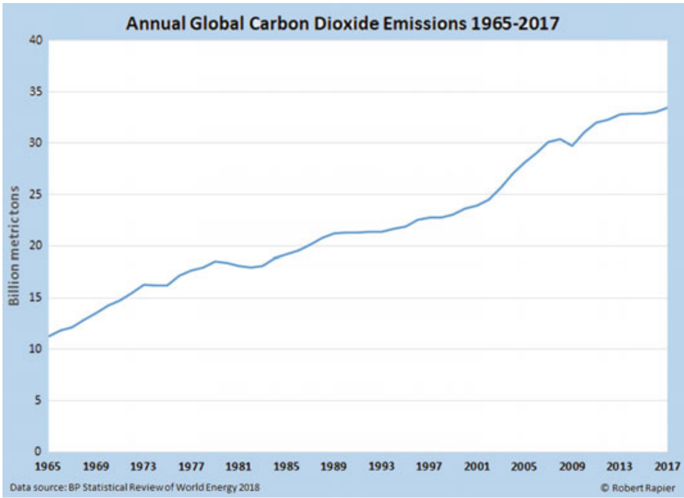

Fig. 2 CO_2 emission

heat to the atmosphere. This will require a great effort in terms of more efficient technologies in the use of primary C-based sources of energy, covering the entire chain of production of electric energy, heating systems, industrial plants and transport sector: our whole life! This will take long time and demand huge economic means. As for now, the policy is to reduce the emission of CO_2 into the atmosphere, will or will not such practice be the solution to the climate change (CC), shifting from fossil-C (that has produced a net increase of the atmospheric CO_2-level) to renewable-C and to perennial C-free energy sources.

How to avoid CO_2, thus?

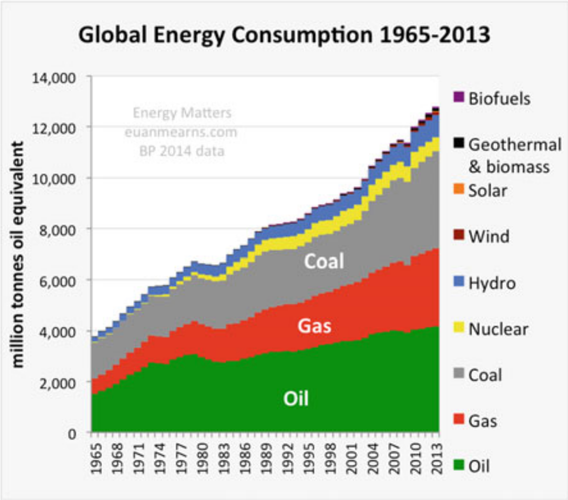

Fig. 3 Energy consumption

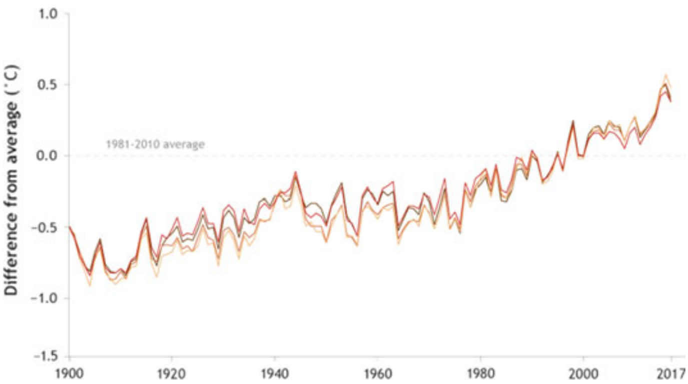

Fig. 4 Increase of average temperature

The agreed target (ONU 2018 and previous International Agreements) is to stay below 2° rise of the average temperature of our planet with respect to 1990. We are already 1.5° above; therefore, we must urgently slow down the use of fossil carbon in order to stay within the target. Defossilization of energy is the necessary action, and the proposal is to advance in such direction in next years. From now to 2050, fossil-C should slowly but steadily be replaced by *quasi*-zero-C emission energy sources. Alternatives are the use of solar, wind, geothermal, hydro-energy sources (SWGH, perennial energy sources). The question is whether or not such sources will provide energy with the requested density and intensity for powering industrial sites and other intensive energy users (megalopolis). (see P. Moriarty, D. Honnery, What is the global potential for renewable energy? Renewable and Sustainable Energy Review, 2012, 16, 244–252). On the other hand, the use of biomass will cover a minor part of the energy needs limited by the regeneration rate. The production rate of CO_2 is much higher (around 6–15 g_{CO2} m^{-2} s^{-1} from the combustion of several kinds of wood-see Tran, H.C.; White, R.H. *Fire and Materials*, **1992**, *16*, 197–206.) than the fixation of CO_2 by photosynthesis (the best values are observed in microalgae (see Adamczyk, M.; Lasek, J.; Skawinska, A. *Appl Biochem Biotechnol*, **2016**, *179*, 1248–1261), better fixing agents than terrestrial plants, that are in the range 0.1–1.7 g_{CO2} l^{-1} day^{-1} or 0.00057–0.0098 g_{CO2} m^{-2} s^{-1}). Therefore, the combustion rate is from 1000 to 10,000 times faster than the C-fixation by photosynthetic microorganisms and microalgae. Will nuclear come back? This is not excluded, if safe production of electricity will be developed. Our future looks quite problematic and to what extent energy-poor countries in Asia, America and Africa will rise their standard of life is an open question, as it is not easy to state whether Northern America, Europe, Japan will have all to restate their habitudes. Shall we necessarily go towards a global lower energy consumption? When this will occur? In the meanwhile, attention is devoted to reduce the CO_2 emission into the atmosphere.

Measures for the Reduction of the CO_2 Atmospheric Level

The technologies for reducing the use of fossil-C and the emission of CO_2 into the atmosphere can be categorized as reported below.

- *Higher efficiency in the conversion of chemical energy (fossil-C and biomass) into other forms of energy*: thermal, electrical, mechanical, etc. As said above, the average efficiency ranges today around 27–35%; therefore, 73–65% of the original chemical energy is released to the atmosphere in the form of heat, causing its direct heating. Improving the efficiency of the actual energy system is possible using both upstream and downstream technologies, but the economic cost is often quite high. In practice, power stations, industrial processes, transportation means should all be restyled and made adequate to the target of reducing the loss of energy in the form of heat. As a lower profile strategy, new power and industrial plants should all be built according to new efficiency criteria (e.g. all power plants should be built as IGCC), with much higher CAPEX. Heat could be recovered (when and where it makes sense) and used in a range of diverse low-temperature applications (in part this is already done, even if with rare-spot applications). The efficiency of primary energy conversion could be increased by 10–20 points, according to the different sectors. An improvement of the actual system is, thus, possible but it will take long time and demand a lot of economic resources.
- *Efficiency in the utilization of the different forms of energy, avoiding misuses*. This is the easiest route to C-saving and should be implemented by each single person. The implementation of virtuous practices can produce reduction of energy used, and thus produced, with reduction of conversion of fossil-C and CO_2 emission with a possible target of 5–10%.

- *Decarbonization of energy, by using perennial primary sources*, alternative to fossil fuels, such as SWHG. Such change is ongoing, and solar-, wind- and geo-power are being efficiently used, even if still at a moderate global intensity (5–8 % of global consumption) and leopard-spot distribution. It must be emphasized that perennial sources have a different availability on our planet and regional solutions must be implemented. Conversely, fossil-C (coal, oil, gas) is easily transportable and can reach any point on our planet: this is a plus in favour of existing fossil-C-based technologies. The moment being, anyway it is worth to emphasize that virtuous countries exist, which produce large amounts of their energy from SWHG (https://www.climatecouncil.org.au/11-countries-leading-the-charge-on-renewable-energy/) as reported in Table 1.
  It is worth to emphasize that if the energy sector can be decarbonized, the chemical, polymer, pharmaceutical, cosmetic, materials industry will not. Therefore, C-based goods will continue to exist and most likely the use of fossil-C will be continued for long time yet in the future. As a matter of fact, the international programme 205050 foresees 50% reduction of emissions with respect to 1990 (for USA with respect to 2005) for EU and G20 countries by 2050. Afterwards, the reduction should continue at a rate of 1.5% per year.
- *Use of renewable carbon, such as biomass*. Renewable carbon has a different abundance on Earth and can find a different utilization. Biomass (land and aquatic) already finds application in several fields: from energy to chemicals and materials production. Because of the relative abundance/scarcity, even biomass has an odd usability and its transport is not energetically and economically efficient. Even in this case, fossil-C is a winning option for its higher energy density.

Table 2 says that liquid fuels are the best options for energy storage and transportation. Therefore, the conversion of electricity produced *via* SWGH into liquid fuels by combining CO_2 reduction and water oxidation is a convenient way for storing and transporting energy.

Table 1 Use of energy sources alternative to fossil-C in some virtuous countries

Country	Actual use of SWHG for electricity generation	Perspective use of SWHG
Sweden		100% 2050
Costa Rica	99% (2015)	C-neutral 2021
Nicaragua	54%	90% 2021
Scotland	97% of household electricity	
Germany	36.1+ % average with some >85% spot	
Uruguay	95%	
Denmark	42%	100% (2050)
China	1000 coal mines closed in 2018	
Morocco		50% 2020
Kenya	51% (2015)	70% (2020)

Table 2 Energy density of a variety of energy carriers

Energy carrier	MJ/kg
Diesel	36
Gasoline	34
Coke	30
Brown coal	18
Methanol	17
Bio-oil from algae	13
H_2(liquid, 20 MPa)	9
H_2(compressed)	2
Battery (lead)	0.33
Battery (lithium)	2.8

Capture of produced CO_2 from point-continuous sources or from the atmosphere. Capture can be applied either to point-continuous-fixed sources (industries or power plants) or even everywhere if the source is the atmosphere. If practised at reasonable economic and energetic costs, capture will make available large amounts of CO_2 that can be either disposed (CCS) or converted into chemicals, materials and fuels (CCU). The separation of CO_2 from flue gases from power stations or industrial processes (Table 3) requires an amount of energy, which depends on the composition of the flue gas and the use one wishes to make of separated CO_2 that drives its purity. The separation is a process that requires energy, and in the actual energy system implies the use of fossil-C. It has been calculated by DoE-USA that recovering CO_2 and disposing it in land reservoirs 40 km away from the power station where it is generated (a particularly rare and favourable case) consumes 25% of the produced electric energy. Such amount increases with the distance of shipping and the nature of disposal site: it may reach 40%+. Consequently, the capture and housing of CO_2 expand the extraction of fossil-C because additional energy is necessary for such end-of-pipe operation. Modern power generation technologies (such as IGCC) proceed to the decarbonization of fossil fuels before combustion. This means that fossil fuels are converted into CO_2 and H_2 and the latter is used for clean energy generation, but not zero-C emission as CO_2 is anyway produced even if in the precombustion phase.

Table 3 CO_2 emission from industrial sectors

Industrial sector	Mt_{CO2}/y produced
Cement	>1000
Oil refineries	850–900
Iron and steel	ca. 900
Fermentation	>200
Ethene and other petrochemical processes	155–300
Ammonia	160
LNG sweetening	25–30
Ethene oxide	10–15

In the short term, it may make sense to recover CO_2 from industrial sources that may provide more pure CO_2 than flue gases from power stations. Table 3 shows that ca. 3 500 Mt/y of quite pure CO_2 is available, which covers ca. 10% of the total emission. The advantage of recovering–converting CO_2 on-site brings to a closed loop. Obviously, this approach is very proficient for sites where several industrial activities are present and an efficient recovery of CO_2 is possible: clustering process is a way to optimize the energy and waste system. And this can be an interesting option for the future of our industry and the energy sector.

Recovery from the atmosphere (medium–long term) has the advantage of not requiring an industrial site or a power station as source. Interestingly, the atmosphere can provide also water vapour: this means that co-processing atmosphere-sourced CO_2 and water vapour will make possible to produce Syngas and thereafter energy-rich products (fuels). Such practice is very suggestive of Nature and can be implemented everywhere on our planet, making possible a local production of necessary fuels and chemicals completely decoupled from the existence in situ of natural fossil resources or emitters, with great benefit for non-industrialized countries which are not even rich of fossil-C.

An Economy Based on CO_2 and Water: it is a *vision* today. Will science and technology be able to make it a reality? Yes, but the correct conditions for the use of perennial energies must be developed and investment in research is necessary at the correct level, with the integrated cooperation of academy, industry and governments.

It is an investment in the future of humankind and our planet.

This book makes the point on where we are and where we have to go for exploiting such option.

After presenting the potential and bottlenecks of large-scale CCU (Chap. 1), the capture (Chap. 2) and the technological applications (Chap. 3), various aspects of utilization are discussed in detail, namely carbonation of basic natural or industrial matrices (Chap. 4), conversion into energy-rich products (Chaps. 5 and 6), electrochemical and photo-electrochemical conversion (Chap. 7) and Plasma technologies (Chap. 8). Bio-based routes are discussed in Chaps. 9–11, highlighting the integration of biotechnologies and catalysis. Chapter 12 makes a techno-economic and energetic analysis of selected CO_2-based processes. At the end, the perspective use of CCU is presented.

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