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Feature Article

The increased anthropogenic gas emissions in the atmosphere and the rising of the Earth's temperature: are there actions to mitigate the global warming?

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Abstract. Some frozen bodies have been recently discovered in the Alp glaciers because the global warming is forcing the ice to retreat. Many years have passed since the first perception of a strong link between the temperature of the Earth and the amount of some gases in the atmosphere, the so called greenhouse gases. Today there is a general consensus among the governments, the scientists and industrial organizations of most countries in recognizing the relationship between the increase of the atmospheric CO_2 concentration resulting from over a century of combustion of fossil fuels and the observed global warming. The development of technologies to reduce the anthropogenic emissions should not be further delayed, in accordance with the Paris Agreement that recommended keeping the global mean temperature well below 2 °C above pre-industrial levels to reduce the risks and impacts of climate change.

This paper gives an overview of the different greenhouse gases, their emissions by economic sectors and the international treaties that require the most developed countries to pursue the objective of reducing their greenhouse gas emissions. Amongst the different actions directed towards a low-carbon economy, the chemical capture of CO_2 from large stationary emission points is the most efficient and widespread option. Additionally, new technologies are currently exploited to capture CO_2 directly from air and to convert CO_2 into fuels and valuable chemicals.

Keywords. Global warming, climate changes, greenhouse gas emissions, CO_2 capture, CO_2 utilization.

THE GLOBAL WARMING AND THE POLICIES FOR ITS MITIGATION

It is very likely the relationship between the Earth's temperature, climate and the concentration of some gases, the so called greenhouse gases (GHGs), in the atmosphere. As a matter of fact, the greenhouse effect made our planet habitable with an average temperature of 18 °C, otherwise it would be – 19 °C.

If we look back to hundreds of thousands years ago, cooler glacial and warmer interglacial cycles occurred with periods of about 100,000 years (Figure 1). They are related to the variation of the amount of solar radiation with time, caused by the precession of the equinoxes (the rotation of the Earth's direction axis), the variation of the obliquity of the Earth's axis with respect to the perpendicular to the plane of the orbit around the sun, and the variation of the eccentricity of the orbit that varies the Earth-Sun distance. It must be noted that the variation of CO_2 concentration over time was a *consequence* of the variation of the temperature: the increasing temperature released more dissolved CO_2 from the oceans and permafrost, thus increasing the greenhouse effect that accelerated the global warming. The opposite effect occurred when the temperature decreased.

The last glacial period ended about 21,000 years ago, and currently we are in an interglacial period of very low increasing Earth's temperature that has been accelerated in the last century, most likely by the increasing GHG emissions from human activities. The anthropogenic GHG emissions, predominantly carbon dioxide, add to the "natural" greenhouse effect and could result in Earth's temperature rising and subsequent climate change.

The "greenhouse effect" and the global warming have a long history, that started two centuries ago. The famous French mathematician and natural philosopher Jean-Baptiste Fourier (Auxerre, 1768 – Paris, 1830), suggested in the late 1820 that the atmosphere limits the heat loss from the Earth's surface, that is warmer than it would be in the absence of this effect. In 1860 John Tyndall (Leighlinbridge, 1820 – Haslemere (UK), 1893), an Irish scientist, measured the absorptive power of some gases and discovered that water vapour and "carbonic acid" (carbon dioxide) absorb the re-emitted heat from the Earth's surface that cools overnight. He realised that climate changes could be related to the concentration of these gases. Svante Arrhenius (Vik, 1859 – Stockholm, 1927), a Swedish physicist and chemist, Nobel laureate for Chemistry in 1903, in 1896 calculated that 50% increase of CO_2 concentration in the atmosphere would take thousands of years and would increase the Earth's temperature of 2.5-3 °C. Arrhenius concluded that the world population would benefit in the future from a warmer climate that would prevent new glacial ages, thus affording more land for harvesting. Contrary to the Arrhenius' belief, the 50% of CO_2 concentration has increased in the last two centuries, because of the fossil fuel combustion to sustain the continuously increasing demand of energy of the industrial revolution and the economic growth of the population that, additionally, rose from about 1 billion in 1800 to today 7.6 billion.

Now, there is a general consensus among the governments, the scientists, and industrial organisations of most countries about the correlation (95-100% probability) between the GHG emissions in the atmosphere originating from the human activities, the rise of the Earth's temperature and the climate change (Figure 2).[3-5] It has become a worldwide priority to reduce the anthropogenic GHG emissions, particularly those of CO_2, the main component of GHGs, together with the techniques for the adaptation to climate change.

Afterwards the first stations at South Pole and Mauna Loa, Hawaii, in 1950 began measuring the CO_2 concentration in the atmosphere, accurate data were available. In 1988 the *Intergovernmental Panel on Climate Change* (IPCC) was established by the *World Meteorological Organization* (WMO) and the *United Nations Environmental Programme* (UNEP) to provide "*policy-*

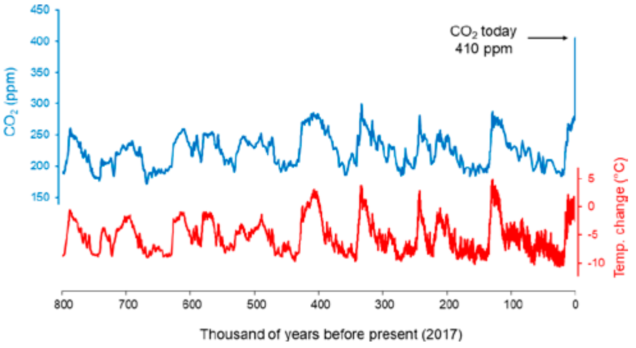


Figure 1. Correlation between CO_2 concentration[1] in the atmosphere and Earth's temperature[2] over the last 800,000 years. Temperature change is the difference from the average of the last 1000 years.

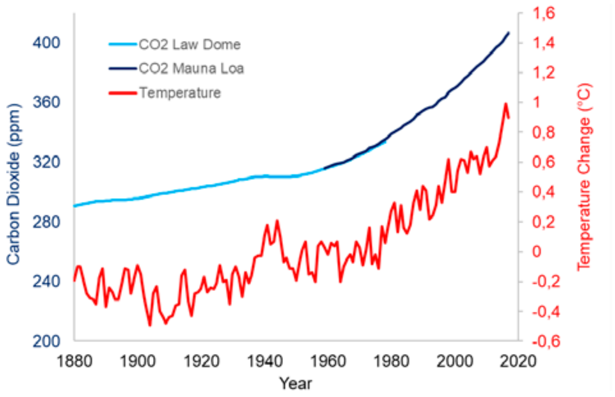


Figure 2. Correlation between the change in the mean annual temperature records and the CO_2 concentration. Temperature data from NASA/GISS;[3] CO_2 concentration data from Mauna Loa, Hawaii,[4] and from ice cores from Law Dome, Antarctica.[5]

makers with regular assessments of the scientific basis of climate change, its impacts and future risks, and options for adaptation and mitigation".

Until now IPCC has released five *Assessment Reports*,[6,7] and the sixth will be completed in 2021. The fifth Assessment Report (IPCC AR5)[8] is referred to 2014 and is based on the work of 831 worldwide experts on physics, engineering, chemistry, meteorology, oceanography, ecology, economics. The scenarios provided on the GHG emissions by human activities and global warming are indisputable.

The CO_2 concentration in the atmosphere, largely the main component of GHGs, increased from 280 ppm (0,028 % v/v) of the pre-industrial level (the beginning of the industrial society is conventionally fixed to 1750) to today 410 ppm (0,041%; April 2017). In the same time the Earth's temperature increased approximately of 1.0÷1.2 °C, most of which in the last century. Before 1750 the mean temperature, even if with ± 0.3 °C variations, and GHG concentration remained roughly constant for hundreds of years.

Carbon dioxide emissions from fossil fuel combustion and industrial processes account for about 76% of the current total GHG emissions. The percentage of the other GHGs is reported in Table 1 as CO_2-equivalent (CO_2eq), that takes into account for the relative amount of emissions and for the global warming potential (GWP) relative to CO_2.[9] GWP_{100} measures the warming effect of a mass of a GHG relative to that of the same mass of CO_2, over a period of 100 years. The lifetime of each GHG in the atmosphere, and consequently its GWP, is different to each other, because of the different reactivity with the other components of the atmosphere and with solar radiation.

About 75% of overall anthropogenic CO_2 emissions between 1750 and 2010 occurred in the last 60 years, because of the unrestrainable growth of the population (from 2.5 billion in 1950 to 7.6 billion in 2018), the energy intensive lifestyle of the population and the economic activities of the developed countries, and the socio-economic growth of rapidly developing countries (currently, China, India, Brazil), that require more and more energy production. Total anthropogenic GHG emissions increased over 1970 to 2012 of 91% from 24 to 47 Gtonne CO_2eq/y, the highest in human history. Also the rate of warming of the atmosphere and ocean since 1950 is the greatest ever recorded.[10]

Table 1. Contribution of each gas to global GHG emissions, relative to CO_2, based on the amount of gas emitted and on the relative global warming potential (GWP_{100}).

	GWP_{100}	emissions (CO_2eq)
CO_2	1	76%
CH_4	21	16%
N_2O	310	6%
HFC/PFC[a]	650 ÷ 11,700	2%[b]
SF_6	23,900	

[a] hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs); [b] summed fluorides.

The Kyoto Protocol (December 1997) is an international treaty that commits the 39 most industrialised countries to tackle the global warming by reducing their GHG emissions in the atmosphere to a level that "*would prevent dangerous anthropogenic interference with the climate system*". The six greenhouse gases taken into consideration by the Kyoto Protocol were carbon dioxide (CO_2), methane (CH_4), dinitrogen oxide (N_2O), sulfur hexafluoride (SF_6), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) (Table 1). The treaty was signed and ratified by 187 countries and entered into effect on 2005, after being ratified by at least 55 of the most industrialised countries which accounted in total for at least 55% of the total CO_2 emissions for 1990 ("55%" clause). USA and Australia did not ratify the treaty; China, India and Brazil had no targets of reduction. By 2012 the signatory countries should have fulfilled the cut of GHG emissions of 5.2% below the 1990 level (–8% for European Union); the reduction target 2013-2020 should be –18%. European Union met the objective of Kyoto Protocol by 2011.

In the 21st Paris Climate Conference (COP21, 2015), an agreement was signed by 195 countries and entered in force in 2016. For the first time the countries signatories agree to carry out actions to limit the increase of the Earth's temperature in the range 1.5 - 2 °C above pre-industrial levels; the increase of temperature from today should be comprised between 0.65 °C and 1.15 °C. Each country is committed to provides the GHG inventories every five years, starting from 2023. However, it must be pointed out that the Paris Protocol is not a legally binding treaty, and, additionally, a country that did not accomplish its reduction target may purchase carbon credits (GHG certificates) from other countries that have no reduction obligation or are below their reduction target. In 2017 Donald Trump declared he is going to withdraw US from the Paris Agreement, which was previously signed by the former US President Barack Obama.

To keep the temperature increase below 2 °C relative to pre-industrial level, the CO_2 concentration in the atmosphere by 2100 should be about 450 ppm, compared to current 410 ppm. The fulfilment of that objective relies on some strategies, namely reducing fossil fuel combustion increasingly substituted by renewable energy sources, improving the efficiency of energy production and use, enhancing the CO_2 capture from large-point sources, the so called Carbon Capture and Sequestration (CCS) technology. Without mitigation scenarios, by 2100 the CO_2 concentration in the atmosphere is expected to increase up to 750 ppm and the Earth's surface temperature between 3.7 to 4.8 °C. Obviously, the mitigation objectives cannot be an obstacle to the increasing food production and to the socio-economic development of the world population that is expected to grow to at least 9 billion over the next 35 years.

From the data reported in Table 1 it is clear that the greatest contribution to the overall GHG effect comes from CO_2 emissions, mainly originating from fossil fuel combustion in power plants, transportation and building heating. Livestock farming, agricultural and other land use, waste management, account for most of non-CO_2 (CH_4 and N_2O) GHG emissions. Due to their sparse point sources, most of the non-CO_2 emissions cannot be abated. Consequently, the strategies aimed at reducing the overall GHG emissions should be focused on the abatement and capture of CO_2 emissions from the energy sectors (fossil fuel power generation without CCS technology should phase out by 2100),[8] industry and transport. In summary, most of the sectors of the human activities must be redirected towards a sustainable low–carbon economy. Replacing coal and oil by less carbon containing fuels in all of the sectors of energy production, are feasible objectives. For instance, an immediate great contribution to the CO_2 emission abatement from combustion (between 11% and 25%) should be gained by replacing carbon rich fossil fuels with natural gas (CH_4).

The global GHG emissions by economic sector are reported in Table 2.

Low carbon electricity must play a crucial role in accelerating the global transformation to a low-carbon society, by substantially increasing the use of renewable technologies: photovoltaic cells, wind farm, solar energy, will continue to grow and to become cheaper and more competitive compared to fossil fuel combustion. However, it must be pointed out that wind and solar are intermittent energy sources, and their transformation and storage in the form of chemical energy would be a feasible solution. Nuclear energy also cannot be omitted, even though in Europe its contribution is decreasing; however, contrary to popular belief and mass media information, 59 new nuclear reactors are under construction around the world.

Table 2. The global GHG emissions percentage by economic sector.[a]

Power plants	38%
Agriculture and forestry	22%
Transport	20%
Buildings	10%[b]
Industry	10%[b]

[a] there is poor agreement amongst different sources on the share of individual sector: the data are adapted from references 8 and 11; [b] doesn't comprise the consumption of electricity.

In Europe, the production of electricity by renewable sources (wind, solar, biomass) should increase from the current 32% to 80% by 2050. Afforestation, reduced deforestation and bioenergy production are natural sinks of CO_2. To date, the decarbonisation of energy generation occurs at a greater rate than in industry, building and transport sectors. As worldwide transportation sector accounts for about 20% of CO_2 emissions from fossil fuel combustion, it is expected a substantially reduction of the CO_2 emissions attained from technological innovations that include more efficient thermal engines, cleaner fuels (natural gas, biofuels produced by biomass and regenerated fuels), light materials and electric propulsion systems. Hybrid, plug-in-hybrid and full electric vehicles (powered by improved batteries or fuel cells) should eventually replace those equipped with thermal engines. By 2025, it is expected that the electric cars equipped with more efficient batteries will have cruising range over 600 km and substantial reduction of charge time. Sustainable biofuels should replace kerosene in aviation and diesel fuel in heavy duty trucks.

The building conditioning should reduce their CO_2 emissions by about 90% by 2050: this objective can be achieved by the new zero-energy buildings, and by refurbishing as much as possible the yet existing buildings, in particular the commercial and tertiary ones.

The industrial sector, especially the cement and steel production, could reduce their GHG emissions (mostly CO_2) by about 80% with more energy efficient processes and increased recycling of the wastes and by-products. Also, CCS technology should be applied to reduce CO_2 emissions of the industrial sector.

The agricultural sector is expected to have a less impact in the GHG reduction with a non-CO_2 GHG emission (CH_4 and N_2O) reduced by 45-50%, thanks to an improved land and fertiliser use, improved livestock farming, and bio-gas recovery from organic manure. Moreover, improved agricultural and forestry activities can increase CO_2 sink and can provide feedstock for energy and industry. It must be considered that the biosphere (land and oceans) takes part to the global cycle of CO_2 through photosynthesis of green plants and phytoplankton, that represent a natural 50% sink of the global anthropogenic emissions of CO_2.

It is hard to believe that hydrogen could be a substitute of fossil fuels in a short-term (hydrogen economy), even if it could have a crucial role in the conversion of CO_2 into liquid fuels. Hydrogen is currently produced by fossil fuels (mostly from methane), because its production from water electrolysis is not cost-effective.

Finally, an appreciable contribution to the mitigation scenarios could be given by a less energy consuming lifestyle of the population of the most developed countries, for instance less mobility demand, less energy use in households, choice of longer-lasting products, less disposable items, reduction in food wastes; moreover, it would be highly beneficial recycling wastes into industrial new products (Italy is a European leader in this field).

Noticeable, thanks to the policies of low-carbon technologies, yet worldwide adopted mostly for energy production, the global emissions of CO_2 remained stable to 35.8 Gton CO_2/year in the last three years (2014-2016). On the contrary, the GHG emissions increased in 2017 because of the growing industrial emissions that weren't compensated by the increased energy production by renewables and by the reduction of coal use.

Benefiting from low-carbon energy sources and energetic efficiency, European Union has set up the ambitious objective of the following reductions compared to 1990, to be completed before 2020 (before 2030 in parenthesis):[11]

1) 20% (40%) reduction of GHG emissions;
2) 20% (27%) of the overall energy from renewable sources;
3) 20% (27%) of the increase of energetic efficiency.

Currently the 26% reduction of CO_2 emissions has been attained in Italy. By 2050 the reductions of GHGs in the 28 countries of the European Union should be: CO_2 – 63%; CH_4 – 60%; N_2O – 26%. Nevertheless, it must be pointed out that Europe accounts for only 9.6% of the worldwide CO_2 emissions (compared to 14.0% of US and 29.2% of China; 2016 data),[10] and once these objectives were reached, they would not sufficient for the 2 °C target.

Last but not least scenarios are the technologies of CO_2 capture from large point sources (the CO_2 concentration in the exhaust gases may be comprised between 5% and 40% v/v), such as fossil fuelled power plants and some industrial processes, and the safe CO_2 storage underground (CCS technology). Notwithstanding its low concentration (0,04% v/v), CO_2 can be also captured directly from air (DAC technology). Contrary to the CO_2 storage, in the carbon capture and utilization option (CCU technology), pure CO_2 could be used as a feedstock for producing chemicals and fuels.

TECHNOLOGIES OF CO_2 SEPARATION FROM GAS MIXTURES

The CO_2 separation from gas mixtures is a technology applied at industrial scale in hydrogen and ammonia production, natural gas processing and sweetening. These methodologies can be also applied to large fixed-point sources, such as cement and steel production, and to post combustion gases from fossil fuelled power plants, the main sources of GHG emissions (Table 2). Chemical capture of CO_2 by a liquid alkaline solution (the absorbent) is recognized as the most efficient technology for dilute CO_2 (low partial pressure) removal from a gas mixture.

Different technologies for CO_2 capture have been also proposed, based on physical methods, cryogenic and membrane separation processes, biological fixation, but none of them went into application to large scale separation of CO_2 from exhaust gases because of the low efficiency or high costs.

In this section, an overview of the chemical capture of CO_2 with possible application to power plants is presented.[12,13]

Combustion of fossil fuels with air produces exhaust gases containing 4-15% (v/v) CO_2, N_2 (from air), with residual O_2, water vapour, and variable amount of sulfur and nitrogen oxides as well as particulate matter. The CO_2 percentage depends on the carbon content of the fossil fuel and the technology employed: the lowest value refers to a gas turbine combined cycle, where the combustion is accomplished with a large excess of air.

A typical coal-fired power plant of 1000 MW can emit about $3{\cdot}10^6$ m^3/h of exhaust gases containing 15% (v/v) of CO_2.[14] The storage underground of that huge amount of combustion gases is not a feasible option, because of the high compression costs and of the very large geologic reservoirs where the gas mixture should be stored. On the other hand, the storage in the deep sea is not safe, and would increase the water acidity which is harmful for sea life. Therefore, it is firstly necessary to remove CO_2 from the gas mixture, afterwards the nearly pure CO_2 is compressed and injected underground (carbon capture and storage, CCS technology). An accurate geological investigation must be performed to select the site of CO_2 storage, that should reduce as most as possible leakage in time of sequestered CO_2 from the reservoirs.[15]

The employed technologies for the chemical capture of CO_2 are substantially similar to each other and differ, at most, in the liquid absorbents. To be a cost-effective process and to avoid millions of tons of wastes per year (the carbonated absorbent), the CO_2-loaded absorbent

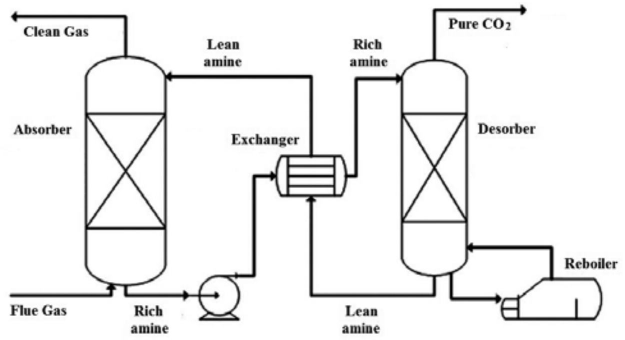


Figure 3. A simplified flow sheet for the CO_2 removal process

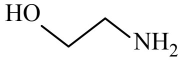
must be regenerated and recycled: the reactions of CO_2 with the absorbent must be reversible.

The equipment for CO_2 capture comprises the stainless-steel absorber (the scrubber) and desorber (the stripper) units connected to each other through a heat exchanger (Figure 3). The absorber and the desorber are packed columns that maximize the gas-liquid exchange surface, thereby enhancing the reaction rate. The absorbent circulates continuously between the two devices in a continuous cyclic process. The gas stream (12-15 % CO_2 v/v) is injected to the absorber (kept at about 40-50 °C) and the carbonated solution exiting from the absorber is preheated by the cross-heat exchanger and sent to the desorber where it is heated to 110-130 °C (at pressure of 1-2 bar) by steam. The regenerated solution is cooled and then it is circulated back to the absorber and reused for further CO_2 capture. Finally, the nearly pure CO_2 released from the top of the stripper can be compressed at 100-200 bar and transported to the storage site by a pipeline.

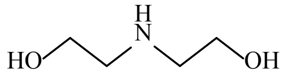
The size of the equipment to be fitted in a power plant is proportional to the flow rate of the exhaust gas *i.e.* to the amount of CO_2 to be captured. The height/diameter of the packed columns may be 15 m/7 m for the absorber and 10 m/4.5 m for the desorber; the plants have a capacity of CO_2 capture in the range of $3\text{-}4{\cdot}10^6$ tonne/year.

Most of the absorbents for CO_2 removal from gas mixtures are based on aqueous solutions of primary and secondary alkanolamines;[12-17] a few examples are:

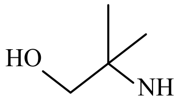
MEA (monoethanolamine) 2-aminoethanol



DEA (diethanolamine) 2,2'-iminodiethanol



AMP (aminomethylpropanol) 2-amino-2-methyl-1-propanol



The hydroxyl functionality of the amines provides their sufficient solubility in water and substantially lowers their vapour pressure, to reduce as much as possible the amine loss by evaporation. In the continuous search of more efficient absorbents, blends of amines and non-aqueous absorbents have been also investigated.[18-21] The concentration of the aqueous absorbents is usually limited to 30% (wt/wt), to reduce corrosion of the equipment and amine loss by heating, yet pursuing the target of 90% (v/v) of CO_2 removal from the gas stream.

The main reactions of CO_2 with aqueous primary and secondary alkanolamines are:

$$AmH + CO_2 + H_2O \rightleftarrows HCO_3^- + AmH_2^+ \qquad (1)$$

$$2AmH + CO_2 \rightleftarrows AmCO_2^- + AmH_2^+ \qquad (2)$$

where AmH denotes the free amine; $AmCO_2^-$ and AmH_2^+ indicate, respectively, the amine carbamate and the protonated amine. Equation (2) doesn't apply to tertiary amines that are unable to form carbamate, as well as to amines featuring steric hindrance around the amine functionality (AMP) because the carbamate is less stable than bicarbonate in aqueous solution.

The forward reactions (1) and (2) are exothermic and the reverse endothermic reactions account for CO_2 release and amine regeneration in the desorber.

Whatever the technology and absorbent may be used, the overall process of CO_2 separation from gas mixtures is energy intensive, therefore the CO_2 capture from a fossil fuelled power plants reduces the output electric power by 20% up to 40%, depending on the process configuration and fuel used; the cost of CO_2 capture from a power plant can be as high as 50-60 \$/tonne CO_2. As a result, more fuel is consumed (additional 15-45%), more CO_2 is emitted that must be captured, for a given output of electric power.[22-26] The main operating cost of any process of CO_2 removal is the heat for absorbent regeneration, namely to reverse the exothermic absorption reactions (1) and (2). Additional energy is required to pump the absorbent within the entire apparatus and for final CO_2 compression. Moreover, the thermal and oxidative degradation of the alkanolamines may be another serious concern in the CCS technology.[27]

Compared to organic absorbents, very few inorganic solvents have been investigated, mainly aqueous Na_2CO_3, K_2CO_3 and NH_3.

Aqueous alkali carbonates do not suffer of thermal degradation and loss of the absorbent, have low regeneration energy and high absorption capacity (mass CO_2/mass absorbent), but have low rate of reaction with CO_2.[28]

$$CO_3^{2-} + CO_2 + H_2O \rightleftarrows 2HCO_3^- \tag{3}$$

Absorbents based on aqueous NH_3 display fast absorption rate, significantly lower regeneration energy and thermal and oxidative stability compared to alkanolamines, but entail a major concern related to its high volatility.[29-31]

The reactions of aqueous ammonia with CO_2 are:

$$NH_3 + CO_2 + H_2O \rightleftarrows HCO_3^- + NH_4^+ \tag{4}$$

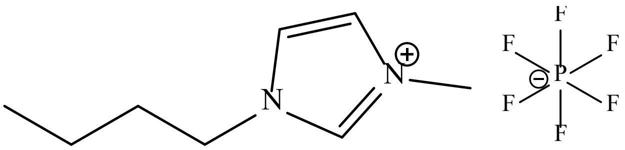
$$NH_3 + HCO_3^- \rightleftarrows CO_3^{2-} + NH_4^+ \tag{5}$$

In the absence of water, ammonium carbamate is the sole reaction product

$$2NH_3 + CO_2 \rightleftarrows NH_2CO_2^- + NH_4^+ \tag{6}$$

With the purpose of substantially reducing the energy penalty of absorbent regeneration, new absorbents based on "ionic liquids" and "demixing solvents" have been recently developed. Both methodologies avoid the heat wasted to bring the diluent to the desorption temperature (sensible heat), a significant share of the overall desorption energy; it must be pointed out that water account for 70 wt% of the aqueous absorbents. Additional cost saving and advantages come from the reduced size of the equipment and from the negligibly vapour pressure and high thermal stability of ionic liquids.

Ionic liquids are organic salts in the liquid phase at room temperature (RTILs): as an example of a common ionic liquid, the chemical structure of 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$), a common ionic liquid is reported.



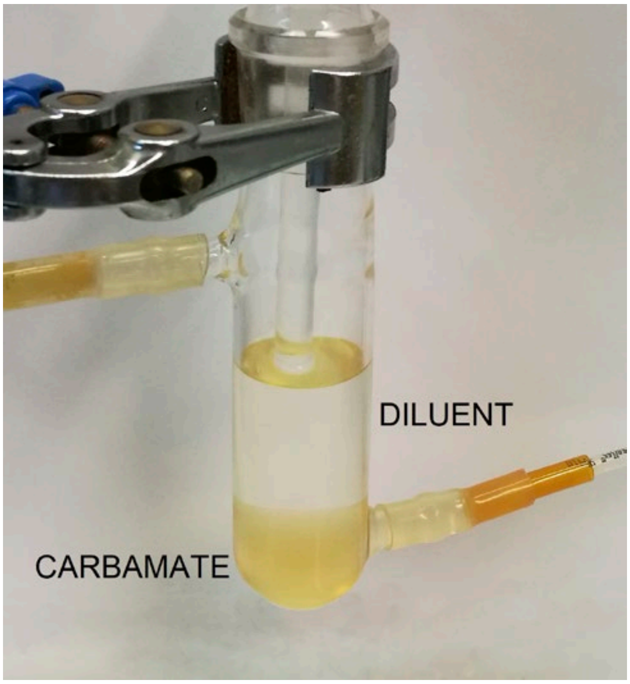


Figure 4. Two liquid phase recovered from CO_2 capture: the lower phase is the carbonated absorbent and the upper phase is predominantly the diluent with a small amount of the amine carbamate.

One-component RTILs containing an amine functionality or mixtures of RTILs and alkanolamines have been exploited for the CO_2 capture.[32-34] Because those absorbents are liquid before and after the CO_2 capture, no added diluent is necessary. To overcome the intractable viscosity of most of the carbonated absorbents based on RTILs, commercially available and inexpensive secondary amines (2-(butylamino)ethanol, for example) have been recently formulated[35,36] that reversibly react with CO_2 at room temperature and pressure to form liquid carbonated species without any aqueous or organic diluent.

Demixing solvents are based on two liquid-liquid phase separation. Upon CO_2 capture, some aqueous or non-aqueous amines split into two separate, immiscible, liquid phases (Figure 4) which separate by virtue of their different density.[37,38] Only the lower phase that contains the carbamate and the protonated amine must be thermally regenerated, thus avoiding to heat the diluent in the upper phase.

DIRECT CO_2 CAPTURE FROM THE ATMOSPHERE

The objective of zero-emission energy should be fulfilled by 2100 in most of the developed countries. Meanwhile, the lifetime of CO_2 in the atmosphere and the inertia of the climate change, strongly suggest to reduce

Figure 5. Proposed design to capture 1 million tonnes of CO_2 per year. Photo-illustration: courtesy of Carbon Engineering Ltd.

the CO_2 concentration in the atmosphere. Moreover, the direct CO_2 capture from air (DAC technology) is the only method to contrast the dispersed emissions from transport, heating systems of buildings and biomass burning, that cannot be captured at their sparse sources. A comprehensive overview of DAC is provided by the American Physical Society report (June 2011).[39]

The DAC method is at the early stage of investigation and no proposed process is today suitable for large scale application because of the low efficiency and high costs. Because of the very low concentration of CO_2 in the air (0,04% v/v), large air-absorbent contactors are necessary equipped with many fans to blow air to the absorber (Figure 5).

The absorbents so far used are concentrated aqueous solutions of NaOH or KOH (2–3 mol dm^{-3}) which capture CO_2 as soluble Na_2CO_3 or K_2CO_3; the efficiency of CO_2 capture is usually no more than 50%.[40] To be a feasible process, the hydroxide regeneration is accomplished with lime

$$2Na^+ + CO_3^{2-} + Ca(OH)_2 \rightarrow CaCO_3 + 2Na^+ + 2OH^- \qquad (7)$$

Once separated from the solution, calcium carbonate is calcinated at 900-1000 °C to restore quicklime (CaO) and to release CO_2

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (8)$$

The entire energy requirement of the process has been estimated 17 GJ/tonne CO_2 captured ($4.7{\cdot}10^6$ kWh/tonne CO_2 captured) and about half is due to the calcium carbonate calcination.[41] The production of the same amount of energy (thermal and electric) from coal combustion, releases in the atmosphere 1.89 ton of CO_2: more CO_2 is emitted than captured! The CH_4 combustion produces less CO_2 but it doesn't compensate the investment, maintenance and overall operational costs. To make the DAC technology attractive, it is mandatory to produce the energy to run the process (thermal and electrical) with photovoltaic cells and solar heat concentration. Benefiting of the advantage of the DAC technology that can be placed everywhere, areas with higher solar radiation should be preferred. Moreover, the aqueous NaOH or KOH solutions must be replaced by new absorbents that require less regeneration energy, yet maintaining sustainable efficiency. If that method will be successfully implemented at a pilot-scale, CO_2 will be captured from air by using the solar radiation, as green plants are used to do.

FROM CO_2 TO VALUABLE PRODUCTS

At present, the carbon capture and utilisation (CCU) technologies are non-profit options, because of their high costs. Notwithstanding, the CCU technology is more and more studied, because it has the potential of converting CO_2 into value-added chemicals and synthetic fuels, combined with the mitigation of CO_2 emissions, yet at a low extent.[42-48] In other words, the energy depleted CO_2 is captured and converted into reusable chemical energy, contrary to the CO_2 storage underground of CCS technology. It must be pointed out that CCS technology can store underground billions of tonnes CO_2 per year (about six million per year from a single 1000 MW power plant), whereas CCU relies on different products that overall could capture millions of tonnes of CO_2 per year.

The very high stability of CO_2 ($\Delta G° = -395$ kJ mol^{-1}) is a great advantage in the energy production from the combustion of carbon containing fuels [equation (9), for example], but has an adverse effect on its reactivity. For instance, the reverse of reaction (9) is thermodynamically disfavoured, whereas the reduction of CO_2 with hydrogen, [reaction (10)], features a severe kinetic obstacle; much energy together with catalysts therefore are necessary to convert CO_2 into useful chemicals.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g) \quad (9) \quad \Delta H° = -803 \text{ kJ mol}^{-1} \quad \Delta G° = -801 \text{ kJ mol}^{-1}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (10) \quad \Delta H° = -131 \text{ kJ mol}^{-1} \quad \Delta G° = -9 \text{ kJ mol}^{-1}$$

Europe is leader in the study of the CCU technology, in particular Germany, thanks to its long-lasting traditional leadership in the chemical industry. The first company that has demonstrated (2015) the feasibility of the production of a liquid fuel from CO_2, H_2O and renewable energy is based in Dresden.

Without any doubt, the most challenging option of CCU is the conversion of CO_2 into liquid fuels (power to liquid technology, PtL), to reduce the dependence from the fossil fuels and to address the progressive decarbonisation of the fuels for the transportation sector (an example of the so called circular economy). The most promising PtL technology is the methanol production,[49] obtained by reacting CO_2 with hydrogen [equation (10)]. To increase its rate, the reaction is accomplished at 200 °C with copper-based catalysts; notwithstanding, the yield of reaction is no more than 40%, based on today technologies. The cost, mainly due to the cost of electricity, is estimated to be about 600-700 euro/tonne CH_3OH, which is not competitive with the standard production of methanol from methane, and with the methane itself as a fuel. To be sustainable, the reaction (10) must be accomplished with solar and wind energy, so that intermittent and fluctuating energy is stored as disposable chemical energy of methanol. Methanol, directly or in blends, can be used as fuel for thermal engines in transportation, or converted into gasoline (methanol to gasoline, MtG, process) or into dimethyl ether, a possible substitute of propane, a liquefied petroleum gas (LPG). Liquified DME has been also proposed as an alternative fuel to diesel for compression ignition engines. Combustion of DME eliminates particulate and greatly reduces nitrogen oxides from exhaust emissions, compared to conventional diesel fuel, but at the expense of about half energy density.[50]

Biofuels as alternative to the fossil fuels are currently produced at industrial scale (millions of tonnes every year), mainly in Brazil and USA. Gasoline blended with 25% up to 85% of ethanol is delivered in USA, and ten million of vehicles in Brazil are fuelled by 100% ethanol.[51]

All the efforts to imitate the photosynthesis of the green plants that converts sunlight into chemical energy are failed because the energy costs to produce useful chemicals from artificial photosynthesis by far overcome the energy output of the combustion of those artificial fuels. Consequently, it is much more advantageous to allow the nature make most of the work. Based on that strategy, ethanol is produced in Brazil from sugarcane, whereas corn is the main feedstock in USA. Biodiesel as alternative fuel for diesel engines is produced with the alkaly-catalyzed transesterification process which converts vegetal oils into methyl or ethyl esters, featuring a reduced viscosity compared to the natural sources.[52]

The production of biofuels points out some problems.[51] The cost of the raw material (planting, irrigation, fertilization, harvesting and transportation) accounts for 60% to 75% of the cost of biodiesel producing. If the life cycle assessment of the process is taken into account, the biofuels are still not a viable alternative to fossil fuels, in the absence of the government support. As a final consideration, it should be a better option to use farmland for food production instead of crop-based biofuels.

In the search of nonedible sources of biofuels, any form of biomass can be converted into a liquid fuel by means of a thermochemical process, but at unsustainable costs. In that contest, algae-based biodiesel has emerged as a promising option, because it doesn't entail a reduction of food production and features a substantially higher photosynthetic efficiency compared to land crops.[53,54]

Using CO_2 for the manufacture of plastics and speciality chemicals is a further option to store and re-use CO_2. However, the estimated worldwide production of such products is about 180 million tonnes every year, that corresponds to less than 1% of the anthropogenic CO_2 emissions. Compared to the production of fuels, the production of chemicals doesn't have an appreciable impact on the reduction of CO_2 emissions.

Taking the advantage of the thermodynamically favoured and fast acid-base reactions between CO_2 and NH_3, it has been recently developed an innovative process that integrates the CO_2 capture with the production of urea, the most worldwide used nitrogen fertilizer, more than 10^8 tonne/year. The CO_2 capture (15% v/v in air) in water-ethanol produces solid mixtures of ammonium bicarbonate and carbamate [reactions (4), (6)]. By heating the solid mixtures at 165 °C in a closed vessel without any external pressure, both ammonium carbamate, and bicarbonate are converted into urea.[55,56]

$$NH_2CO_2NH_4 \rightleftarrows NH_2CONH_2 + H_2O \qquad (11)$$

$$2NH_4HCO_3 \rightleftarrows NH_2CONH_2 + CO_2 + 3H_2O \qquad (12)$$

The industrial production of urea is carried out with NH_3 and purified CO_2 in the gas phase at high temperature (180 –230 °C) and pressure (150 – 250 bar). Pure CO_2 is obtained by the conventional aqueous amine scrubbing and thermal stripping. The advantage of process based on the solid ammonium salts compared to the industrial process, is the potential energy saving because both the CO_2 purification step with aqueous amine scrubbing and the high pressure working are avoided, yet with efficiency (about 47% with respect to NH_3) and reaction time (60 min at most) comparable with the industrial process.

As a final consideration, 60 million tonnes of CO_2 are employed in different commercial sectors every year, and are currently extracted from natural sources underground. A cheap capture technology from exhaust gases yet recovering high purity CO_2, could replace the current CO_2 production that is re-emitted in the atmosphere and the end of its utilization cycle.

CONCLUSIONS

The increased greenhouse effect originating from human activities is most likely responsible of the increase of Earth's temperature in the last century, and possibly of the climate change. The climate change has, and will have to a greater extent in the future, adverse impacts on the society development and world economy, because of the increasing extreme weather events such as storms, floods, drought and heat waves. The frequency of snowfall and rain is reduced in the recent years, but they are heavier. The objective of mitigation of climate change cannot be further delayed, and many possible actions have been proposed to reduce the GHG anthropogenic emissions. As most of the GHG emissions is due to combustion of fossil fuels, the reduction of dependence from fossil fuels would provide further benefits to the economy of most countries, whereas the improved air quality will have noticeable beneficial effects on human health.

The world economy will be more and more dependent from solar and wind energy; this form of energy is intermittent, and its storage as chemical energy (renewable fuels) and chemicals (fertilizer, plastic) by using the CCU and DAC technologies should be possible options.

Innovative solutions in all of the sectors of the human activities that include both the reduction of combustion of fossil fuel and the CCS, CCU and DAC technologies can contribute to the objective of a progressive decarbonisation of the world economy in the sectors of energy generation, transport and industry. However, that objective appears doubtful in the absence of governmental obligations and of the carbon tax. Meanwhile, adaptation strategies to the foreseen extreme events of the climate change should be adopted.

REFERENCES

1. D. Luthi, M. Le Floch, B. Bereiter, T. Blunier, J.-M. Barnola, U. Siegenthaler, D. Raynaud, J. Jouzel, H. Fischer, K. Kawamura, T.F. Stocker, *Nature* **2008**, *453*, 379.
2. J. Jouzel, V. Masson-Delmotte, O. Cattani, G. Dreyfus, S. Falourd, G. Hoffmann, B. Minster, J. Nouet, J.M. Barnola, J. Chappellaz, H. Fischer, J.C. Gallet, S. Johnsen, M. Leuenberger, L. Loulergue, D. Luethi, H. Oerter, F. Parrenin, G. Raisbeck, D. Raynaud, A. Schilt, J. Schwander, E. Selmo, R. Souchez, R. Spahni, B. Stauffer, J.P. Steffensen, B. Stenni, T.F. Stocker, J.L. Tison, M. Werner, E.W. Wolff, *Science* **2007**, *317*, 793.
3. Data from NASA's Goddard Institute for Space Studies (GISS)
4. Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu/).
5. D.M. Etheridge, L.P. Steele, R.L. Langenfelds, R.J. Francey, J.-M. Barnola and V.I. Morgan. *Carbon Dioxide Information Analysis Center*, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A, **1998**.
6. IPCC, 2001: *Climate Change 2001, Synthesis Report. Contribution to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK, 398 pp.
7. IPCC, 2007: *Climate Change 2007, Synthesis Report. Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK, 939 pp.
8. IPCC, 2014: *Climate Change 2014, Fifth Assessment Report*; www.jrc.nl.
9. *US Environmental Protection Agency*. www.epa.gov
10. *Fossil CO_2 and GHG emissions of all world countries*; EUR 28766, Publication Office of the European Union, Luxemburg, **2017**.
11. *European Environmental Agency*, www.eea.europa.eu/clima/policies /strategies /2020.
12. *IPCC Special Report on CO_2 Capture and Storage* (2005); B. Metz, O Davidson, H. de Coninck, M. Loos, and L Meyer , *Cambridge University Press*, Cambridge UK, **2005**, p.442. See :http//www.ipcc.ch/ipccreports/srccs.htm
13. *CO_2 capture from Existing Coal-fired Power Plants*; DOE/NETL-401/110907
14. H.H. Rao, R.B.H. Tan, *Energy Fuels*, **2006**, *20*, 1914
15. F.M. Orr Jr, *Energy Environ. Sci.*, **2009**, *2*, 449
16. G. Astarita, D.W. Savage, A. Bisio, *Gas Treating with Chemical Solvents*, Wiley, New York, **1994**.
17. G.T. Rochelle, *Science* **2009**, *325*, 1652.
18. F. Barzagli, F. Mani, M. Peruzzini, *Energy Environ. Sci.*, **2010**, *3*, 772.
19. F. Barzagli, M. Di Vaira, F. Mani, M. Peruzzini, *ChemSusChem*, **2012**, *5*, 1724.
20. D. Bonenfant, M. Mimeault, R. Hausler, *Ind. Eng. Chem. Res.*, **2005**, *44*, 3720.
21. W.J. Choi, K.C. Cho, S.S. Lee, J.G Shim, H.R. Hwang, S.W. Park, K.J. Oh, *Green Chem.* **2007**, *9*, 594.
22. K.Z. House, C.F. Harvey, M.J. Aziz, D.P. Schray, *Energy Environ. Sci.*, **2009**, *2*, 193.

23. A.B. Rao, E.S. Rubin, *Ind. Eng. Chem. Res.* **2006**, *45*, 2421.
24. J. Oexmann, A. Kather, *Int. J. Greenhouse Gas Control* **2010**, *4*, 36.
25. E.J. Stone, J.A. Lowe, K.P. Shine, *Energy Environ. Sci.* **2009**, *2*, 81.
26. J. Davison, *Energy* **2007**, *32*,1163.
27. A.J. Reynolds, T.V. Verheyen, S.B. Adeloju, E. Meuleman, P. Feron, *Environ. Sci. Technol.* **2012**, *46*, 3643.
28. B. A. Oyenekan, G.T. Rochelle, *Int. J. Greenhouse Gas Contr.* **2009**, *3*, 121.
29. V. Darde, K. Thomsen, W.J.M. van Well, E.H. Stenby, *Int. J. Greenhouse Gas Control* **2010**, *2*, 131.
30. H. Huang, S-G. Chang, T. Dorchak, *Energy Fuels* **2002**, *16*, 904.
31. A. Pérez-Salado Kamps, R. Sing, B. Rumpf, G. Maurer, *J. Chem. Eng. Data* **2000**, *45*, 769.
32. D. Camper, J.E. Bara, D.L. Gin, R.D. Noble, *Ind. Eng. Chem. Res.* **2008**, *47*, 8496.
33. C. Wang, X. Luo, H. Luo, D. Jiang, H. Li, S. Dai, *Angew. Chem., Int. Ed.* **2011**, *50*, 4918.
34. D.J. Heldebrant, C.R. Jonker, P.G. Jessop, L. Phan, *Energy Environ. Sci.* 2**008**, *1*, 487.
35. F. Barzagli, S. Lai, F. Mani, *ChemSusChem* **2015**, *8,* 184.
36. F. Barzagli, F. Mani, M. Peruzzini, *Environ. Sci. Technol.* **2016**, *50*, 7239.
37. Q. Zhuang, B. Clements, J. Dai, L. Carrigan, *Int. J. Greenhouse Gas Control* **2016**, *52*, 449.
38. F. Barzagli, F. Mani and M. Peruzzini, *Int. J. Greenhouse Gas Control* **2017**, *60*, 100.
39. R. Socolow, M. Desmond, R. Aines, J. Blackstock, O. Bolland, T. Kaarsberg, N. Lewis, M. Mazzotti, A. Pfeffer, K. Sawyer, J. Siirola, B. Smit, J. Wilcox, *Direct Air Capture of CO_2 with Chemicals: A Technology Assessment for the APS Panel on Public Affairs*, American Physical Society, **2011**.
40. M. Mahmoudkhani, K.R. Heidel, J.C. Ferreira, D.W. Keith, R.S. Cherry, *Energy Procedia* **2009**, *1*, 1535.
41. R. Baciocchi, G. Storti, M. Mazzotti, *Chem. Eng. Process.* **2006**, *45*, 1047.
42. X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27.
43. A.S. Bhown, B.C. Freeman, *Environ. Sci. Technol.* **2011**, *45*, 8624.
44. P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Lissen, P. Zapp, R. Bongartz, A. Schreiber, T.E. Müller, *Energy Environ. Sci.* **2012**, *5*, 7281.
45. M. Aresta, A. Dibenedetto, A. Angelini, *J. CO_2 Utilization* **2013**, *3-4*, 65.
46. G. Centi, E.A. Quadrelli, S. Perathoner, *Energy Environ. Sci.* **2013**, *6*, 1711.
47. V. Barbarossa, G. Vanga, R. Viscardi, D.M. Gattia, *Energy Procedia* **2014**, *45*, 1325.
48. A. Goeppert, M. Czaun, J.P. Jones, G.K.S. Prakash, G.A. Olah, *Chem. Soc. Rev.* **2014**, *43*, 7995.
49. G. A. Olah, A. Goeppert, G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy, Second updated and enlarged edition*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, **2009**.
50. A.M. Namasivayam, T. Kovakianitis, R.J. Crookes, K.D.H. Bob-Manuel, J. Olsen, *Applied Energy* **2010**, *87*, 769.
51. J. Hill, E.Nelson, D. Tilman, S. Polaski, D. Tiffant, *Proc. Natl. Academy Sci. USA* **2006**, *103(30)*, 11206.
52. L.C. Meher, D. Vidya Sagar, N.S. Naik, *Renewable and Sustainable Energy Reviews* **2006**, *10*, 248.
53. G. Huang, F.Chen, D. Wie, X.W. Zhang, G. Chen, *Applied Energy* **2010**, *87*, 38.
54. P.T. Vasudevan, M. Briggs, *J. Ind. Microb. Biotech.* **2008**, *35*, 421.
55. F. Barzagli, F. Mani, M. Peruzzini, *Green Chem.* **2011**, *13*, 1267.
56. F. Barzagli, F. Mani, M. Peruzzini, *J. CO_2 Utilization* **2016**, *13*, 81.