Petroleum Technologies and Sustainability in the Era of Climate Change

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1 Introduction

The climate change is the biggest challenge that the human kind have ever had to deal with. Despite a residual skepticism on the topic, "climate change is real"[1] and it is already influencing and it will influence the life on Earth.
The cause of climate change is attributed to the significant increase of greenhouse gases (mainly CO_2) in the atmosphere, able to trap heat radiating from Earth toward space. By means of the analysis of ice cores[2] it has been discovered that, for millennia, the concentration of carbon dioxide in atmosphere has been below 300 ppm. As it is shown in the Figure 1, such threshold was broken in 1950 and, since then, the concentration of CO_2 has never stop growing reaching in 2019 the value of 410 ppm[3].

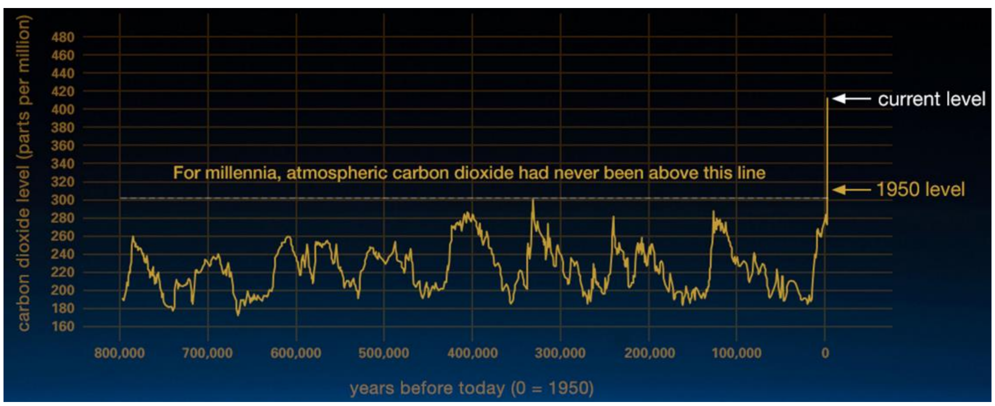

Figure 1 Variation of carbon dioxide concentration during millennia estimated from atmospheric samples collected from ice cores[3].

According on the considerations mentioned above, the 21th century is indeed recognized as the "*era of climate change*" mainly characterized by the increase of the land-ocean mean surface temperature (GMST) and, as a consequence, by other environmental phenomena such as the increase of the average sea level and the retreat of glaciers.

The reason why the amount of GHGs in the atmosphere is increasing so rapidly is strictly connected to the growth of the world population driven by the development of the industrial sector. Since the mid-20th century the anthropogenic CO_2 emissions have raised exponentially (see Figure

[1] https://sites.nationalacademies.org/cs/groups/internationalsite/documents/webpage/international_080877.pdf
[2] To find more: https://icecores.org/about-ice-cores
[3] https://climate.nasa.gov/

2) in line with the trend detected of the carbon dioxide concentration in atmosphere. On top of this, the human action is identified as the main cause of the global warming.

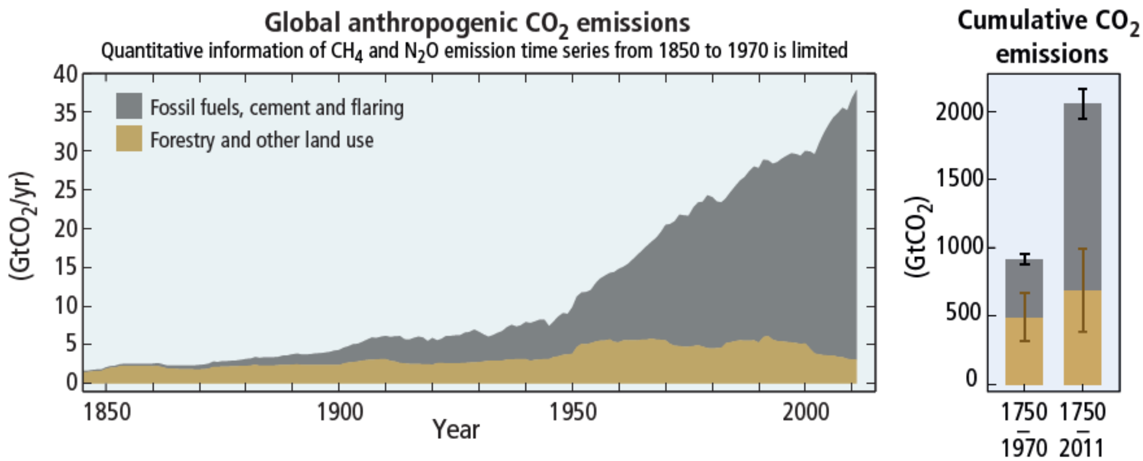

Figure 2 Global anthropogenic CO2 emissions[4].

The sign of the Paris Agreement (Paris climate conference - COP21, December 2015), the first-ever universal, legally binding global climate change agreement, represents an important act to the fight against the climate changes. Major players of the Oil & Gas and Energy sector are financing the development of sustainable technologies in order to diminish their significant carbon footprint. The actions of mitigation of the emissions of carbon dioxide are mainly directed to the main sources of CO_2 which, as shown in the Figure 3, comes from the combustion of *coal, oil and gas*, and from the operations of *flaring* and *cement production*[5].

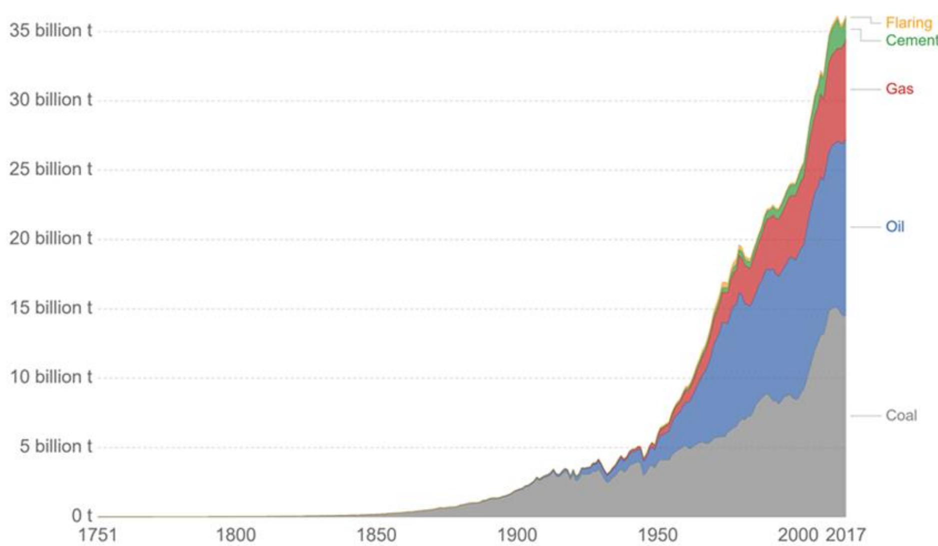

Figure 3 CO2 emissions by fuel type, 5.

[4] "Climate Change 2014 Synthesis Report Summary Chapter for Policymakers," 2014.
[5] https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

2 Carbon capture, utilization and storage (CCU&S)

The reduction of CO_2 emissions derived from combustion is performed by means of *carbon capture* techniques. As it is known, the combustion reaction of a fuel in presence of air generates gas rich in N_2 (~70 % mol), H_2O (~10% mol), CO_2 (4 ÷ 13 % mol depending on the carbon source) and other components (i.e. O_2 not reacted). Since it would be very expensive to storage all the gas produced, carbon dioxide must be separated from the other components in order to be captured.
Three different carbon capture configurations exist depending on the conditions of combustion or whether the capture step is performed before or after the combustion:

- **Oxy-fuel combustion.** In this typology, pure oxygen is introduced in the combustion chamber avoiding the presence of nitrogen and consequently assuring the formation of fumes already rich in CO_2. The separation process is, therefore, easier and mainly consists of a condensation step, for the removal of moist, and of a flue gases desulfurization (FGD) step, for the removal of SO_2. The main drawback of this carbon capture method lays in the cost expensive process for the production of pure oxygen (i.e. air distillation).
- **Post-combustion capture.** In this case, the combustion occurs with an excess of air (an amount of exceeding air respect to the stoichiometric one needed to burn all the fuel) and the capture unit is located after the combustion chamber. As it is shown in the Figure 4a which represents combined power production cycle, the flue gases exiting the combustion chamber are firstly expanded and cooled (for power production purposes) and secondly treated in a carbon capture system
- **Pre-combustion capture.** This technique consists on the removal of carbon from the fuel in order to obtain almost pure hydrogen which combustion doesn't produce additional CO_2. In other words, the fuel treatment has as output a mixture composed mainly of CO_2 and H_2 which separation takes place before the combustion. As it is shown in Figure 4b coal is fed to the plant cut, after the gasification process, and a carbon capture unit, an hydrogen stream enters into the combustion chamber.

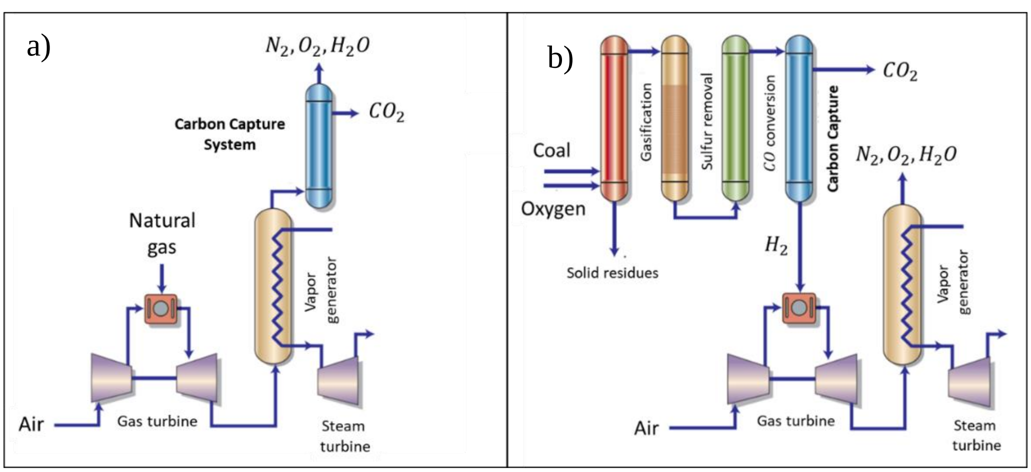

Figure 4 a) Example of a post-combustion configuration; b) Example of a pre-combustion configuration.

In addition, the carbon capture unit may be divided in the following categories:

- *Physical separation*, such as the absorption technique which is performed with the aim of a chemical solvent (Mono-Di- Ethanol-Amine (MDEA), Mono-Ethanol-Amine (MEA)).

- *Chemical separation*, such as the adsorption technique based on the capacity of a porous media (activated carbon, zeolites) to selectively capture/release CO_2 by modifying the pressure (Pressure Swing Adsorption-PSA) or the temperature (Temperature Swing Adsorption-TSA).

Once the carbon dioxide has been captured it should be transported and then used or stored. The most effectively method of storing CO_2 is to inject it in the underground. The most suitable sites for such type of storage are: former gas and oil fields, deep saline formations, depleting oil fields. In the latter CO_2 promotes the extraction of fossil fuels constituting a clear example of CO_2 utilization. All the possible methods for carbon dioxide utilization are illustrated in the Figure 5 below.

Figure 5 Overview of all the possible strategies for carbon dioxide utilization.

2.1 Carbon Capture and Hydrogen

Hydrogen is considered one of the most promising fuel for the achieving the global decarbonisation targets by 2050 since it does not contain carbon atoms and its use does not generate emissions of climate-changing gases. It is possible to distinguish three types of hydrogen depending on the emissions related to their production process:

1. *Grey hydrogen.* This name is used to indicate the hydrogen obtained from fossil fuel sources. The production of grey hydrogen is then related to emissions of CO_2 in the atmosphere. The most used processes are the steam methane reforming (SMR) or the coal gasification.
2. *Blue hydrogen.* In this case hydrogen is still produced using fossil fuels as raw materials, but the production plant is connected to a Carbon Capture and storage unit which avoids any CO_2 emissions: this a clear example of *Pre-combustion capture*. In Figure 6 is reported a SMR scheme for H_2 production in which a CCS unit has been inserted to capture the carbon dioxide outcoming from the burner. In this case the Pressure swing adsorption unit is used to separate hydrogen from the remaining gas which, since contains non reacted CH_4, is recycled into the burner. Today around 95% of all hydrogen is generated from natural gas and coal[6].
3. *Green hydrogen.* The expression "green hydrogen" it is referred to H_2 produced from renewable sources such as solar or wind. The most common method to produce green hydrogen is electrolysis. In the near future this could be a strategy to storage the surplus of electrical energy.

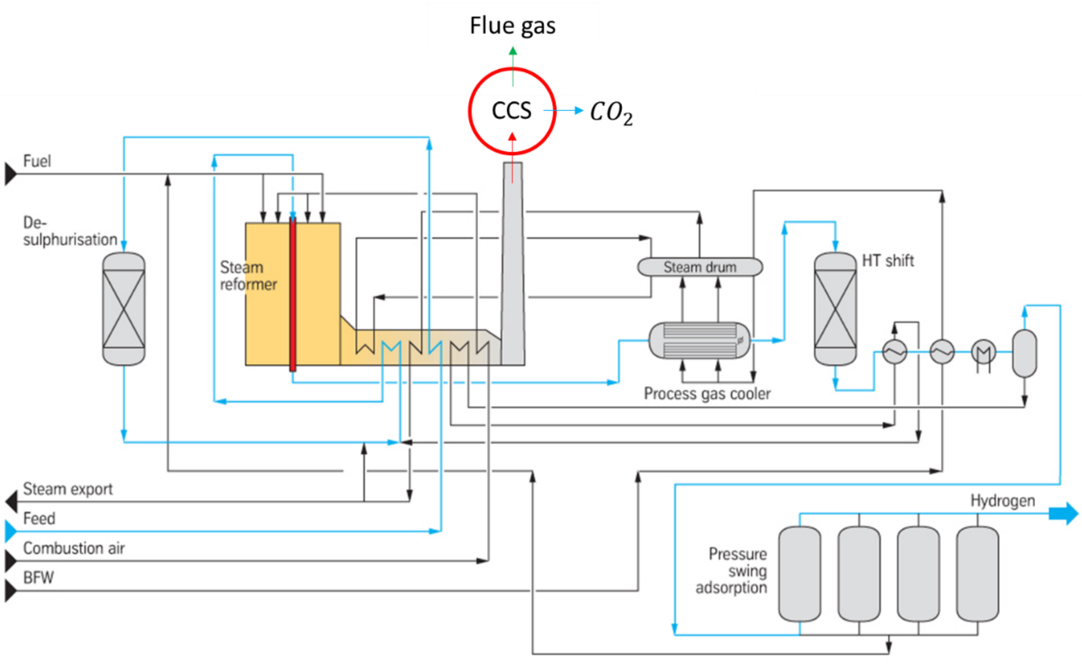

Figure 6 Stem methane reforming (SMR) scheme coupled with a Carbon Capture unit.

[6] I. Renewable and E. Agency, HYDROGEN: A RENEWABLE, no. September. 2019.

3 Natural gas transition

Natural gas is a fossil gas mixture consisting mainly of methane (C1). The remainder is heavier hydrocarbons: ethane (C2), propane (C3), isobutane (iC4), n-butane (nC4), and small amounts of heavier components down to C7s. Among all the fossil primary energy sources, natural gas presents the highest hydrogen to carbon ration. According to this property, the substitution of all the others fossil fuels with natural gas during combustion processes will generate less CO_2 emissions per energy produced (kWh). In this sense the "natural gas transition phase" is taking place for the reduction of greenhouse gases emissions.

Several technologies have been developed in order to facilitate the transportation and storage of natural gas such as:

- **Liquefied Natural Gas (LNG)** which consist in bringing the natural gas, after been previously treated for the elimination of solid particles, water and acid gases, to a temperature of around -160°C in order to condensate all the methane. In this way the density of natural gas is increased of 600 times allowing an easier storage and sea transportation by means of special vessels.
- **Floating Liquefied Natural Gas (FLNG)** is a technique that is used for the production of LNG on a floating vessel (see Figure 7) on top of the off-shore extraction well.
- **Compressed Natural Gas (CNG**) is made by compressing natural gas to less than 1% of the volume it occupies at standard pressure. It is stored and distributed in hard containers at a pressure ranging from 20 - 25 MPa, usually in cylindrical or spherical shapes.

Figure 7 FLNG vessel called "Prelude" of the Royal Dutch Shell[7].

[7] https://marinecue.it/progetto-italiano-flng-prelude/9326/

3.1 Natural gas and Flaring

Flaring is the action of burning the natural gas lifted together with crude oil during extraction operations. When transportation or treatment of this type of natural gas, due of lack of pre-existing pipelines, is economically inconvenient, in order to avoid the direct emission of natural gas into the atmosphere (gas warming potential of methane (GWP) is around 25 times of the one of CO_2 over a period of time of 100 years), the latter is simply burned. Since it is an active source of CO_2, as already highlighted in Figure 3, Flaring is a major concern in petroleum producing areas. Several are the solutions to avoid the flaring operations such as:

- **Reinjection for Secondary Oil Recovery.** In this case the natural gas is injected into the oil reservoir in order to increase its pressure favoring the extraction of the oil itself.
- **Gas Hydrate** is characterized of an atom of gas trapped (the interactions between the molecule of gas and the ones of water are only constituted by Van der Waals forces) into the ice crystal lattice (see Figure 8). Several investigations are in progress to understand better how to reproduce the phenomenon. The production of gas hydrate is considered a promising way to store natural gas as hydrate instead of flaring it[8].

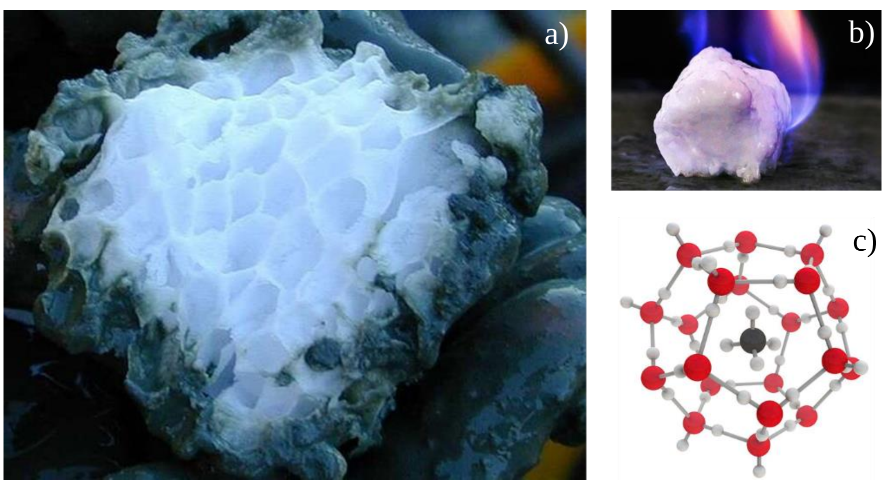

Figure 8 How does a gas hydrate looks like a); The combustion of the methane trapped into the ice may lead to unexpected phenomena such as the burning of a piece of ice b);3D molecular representation of a gas hydrate, in particular a methane hydrate c).

4 Biofuels

The exploitation of biomass as raw material for the production of fuels, so called *biofuels*, is an example of a sustainable utilization of natural resources. Biomass derives, in fact, from the fixation of CO_2, taken from the atmosphere, in organic matter by means of the chlorophyll photosynthesis. Bearing in mind this, all the carbon dioxide emitted by the combustion of biofuels simply closes

[8] A. G. Aregbe, "Natural Gas Flaring — Alternative Solutions," no. February 2017, 2018.

the CO_2 cycle resulting in zero net emissions (see Figure 9). Despite such positive presupposition it is hardly possible that biofuels alone could satisfy the global energy demand.
Biofuels are divided in three categories depending of which kind of biomass they had as raw material:

- **First-generation Biofuels** are produced using raw materials belonging from the food industry such as sugar cane and corn.
- **Second-generation Biofuels** are produced using organic waste as raw materials (municipal solid waste, agriculture residues, wood residues).
- **Third-generation Biofuels** are derived from algae which are cultivated in particular biological reactors (Photobioreactors) or in open ponds.

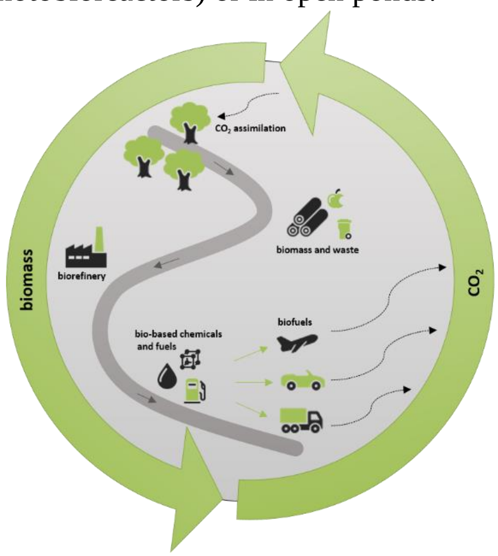

Figure 9 Carbon cycle regarding the production and utilization of biofuels[9].

5 Conclusion

In this paper different technological and process improvements which have already been adopted to face the global warming were illustrated. All the companies of the world and especially the Oil & Gas ones are investing in sustainable technologies in order to meet the environmental goals fixed by the international agreement between countries.
Just to give an example, ExxonMobil has invested more than $300 million on biofuels research in the past decade and it is developing new *advanced biofuels* to enhance the yield lipid production of algae. Regarding the CC&S sector, ExxonMobil is developing new *carbonate fuel cells* with the aim of capture up to 90% of CO_2 from large industrial sites[10].

[9] https://www.oxfa.eu/en/markets/#markets-lse
[10] https://www.exxonmobil.ru/-/media/Russia/Files/Research-and-innovation/Research-and-innovation-highlights/Innovating-Energy-Solutions-R-and-D-brochure.PDF