

# Trends in renewable energy: an overview

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## Abstract

This essay deals with the prospects of supplying humanity with energy in the twenty-first century. The gradual replacement of fossil fuels by green electricity, hydrogen and biofuels is examined in the context of deteriorating climate change and the ongoing depletion of fossil fuels. The production of large amounts of green electricity through the spreading of wind-energy, photovoltaic, concentrated solar power, hydroelectric power and high temperature geothermal plants and its storage through the global interconnection of electricity grids, the spreading of pumped hydro energy storage and melting salts plants and the lithium batteries leads certainly to a future world largely but not exclusively electrical. Hydrogen will be a very important energy carrier. The production of blue and green hydrogen, their transport and usage in cars, industry and trains in the near future as well as in ships and airplanes in the distant future is outlined. Biofuels must be inevitably added to the future energy profile of mankind besides green electricity and hydrogen. The modern trend of producing biofuels from residual fatty raw materials, microalgae and agricultural / forest residual raw materials to overcome the competition with foods production for land and water as well as the residual biomass utility for the production of aircraft fuels and bio-chemicals in the near future is also illustrated. Finally, the increasing contribution of biogas / biomethane to the future energy profile has been presented.

## 1. From fossil fuels to renewable energy

In this essay we are concerned with the prospects of supplying humanity with energy in the twenty-first century in the context of deteriorating climate change [1-16] and the ongoing depletion of fossil fuels [1,17,18]. The technological and economic development of humanity was largely due to fossil fuels, namely coal (C), petrol oil (hydrocarbons,  $C_x H_y$ ) and natural gas (essentially methane,  $CH_4$ ) [19,20]. The worldwide proven oil, natural gas and coal reserves are respectively equal to 1688Bb (billion barrels), 6558TCF (trillion cubic feet) and 891Bt (billion tons). These reserves are increasing, respectively, at the rate of 0.6 Bb, 0.4 (TCF) and 19.2 Giga tons of oil equivalents (GTOE) per year. On the other hand, the rate of consumption of these fossil fuels is respectively equal to 0.092 Bb, 0.329 TCF and 7.89 Bt per day, respectively, whereas the rate of annual increase in consumption of oil, natural gas and coal is respectively equal to 0.0014Bb, 0.0045TCF and 0.0031Bt [20]. A portion, of fossil fuels,

mainly petrol oil, were extensively used for the production of simple - platform molecules (petrochemicals) which in turn were widely used by the chemical industry to produce many very useful products, ranging from polymers to pharmaceuticals. Typical examples are ethylene, butenes and butadiene as well as aromatic hydrocarbons (benzene, toluene and xylenes) [21, 22]. According to the U.S Energy Information Administration, roughly 80% of every barrel of oil refined in the US today is used to produce gasoline, diesel and jet fuel, with the rest going into petrochemical products [21,22]. From the data presented before concerning the reserves and the consumption of fossil fuels it is clear that the fossil fuels are depleted whereas energy demand and the need for chemicals are increasing along with the increase of the world population and the industrialization in large areas of the planet. It is therefore almost certain that towards the end of this century humanity will be faced with the depletion of fossil fuels, at least of petrol oil [1, 17, and 18]. Moreover, burning fossil fuels causes the emission of huge amounts of carbon dioxide ( $\text{CO}_2$ ), which is responsible for global warming and therefore for climate change and its consequences. More specifically, the now day global annual energy demand of over 12 billion tons of oil equivalent (BTOE) is causing the emission of 39.5 Giga tons of carbon dioxide. It is expected that the annual future energy demand will reach the 24–25 BTOE bring about an increase in the annual emission of carbon dioxide up to 75 Giga tons [20]. It is therefore very likely that we will be forced to stop using fossil fuels before they are even depleted [e.g. 1].

This has already begun to happen for coal with the gradual closure of lignite plants because coal combustion ( $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ) emits the most carbon dioxide per unit of energy produced compared with oil and natural gas. In fact, while in the first case only carbon dioxide is produced, in the last two cases the hydrogen contained is also burned resulting to water ( $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ ) and extra energy. Obviously, the combustion of natural gas emits less carbon dioxide per unit of energy produced than petrol oil as it contains four hydrogen atoms per carbon atom ( $\text{CH}_4$ ) whereas the hydrocarbons of petrol oil two hydrogen atoms per carbon atom. Therefore, natural gas is going to be the fuel for the transition to renewable energy, because its combustion causes less, but not zero, accumulation of carbon dioxide in the atmosphere. It is worth noting that the accelerating delignification combined with the rapid decline of petroleum fuels supply [1, 17, 18, 23] and the increasing use of natural gas, as a transitional fuel, will probably make natural gas the most important source of carbon dioxide emissions on the planet in the period 2030 - 2050, unless the conversion of natural gas to blue hydrogen begins as quickly as possible, as we shall see in the next section.

The effort to tackle the energy problem in the context of ever-increasing global warming follows two paths. The first, which does not concern us here, although it is very important, is related to the bioclimatic design and energy upgrade of buildings, mainly through passive energy saving systems, and the bioclimatic design of residential and industrial complexes [1, 24,25,26]. In this context, the development of smart shading / cooling and heating / cooling systems will be critical, while it is expected the extension of geothermal based hybrid energy systems such as the combined 'solar accumulators / shallow geothermal' devices [e.g. 27]. Actions under this framework are indeed extremely necessary, as 30% of the total energy produced worldwide is consumed for buildings.

The second way, which is the subject of this essay, is related to the gradual replacement of fossil fuels by renewable energy, namely electricity that will be produced mainly by wind – energy and photovoltaic parks and hydropower plants, as well as energy from hydrogen and biofuels [e.g. 1, 28, 29]. The energy used in activities relevant to the goods production (Industry, Agriculture etc) consumes 53% of the energy whereas the transports 17%. The latter is distributed between maritime transport, air travel and land transport by trains or large vehicles that consume 11% and urban passenger cars consuming 6%. The effort replacing fossil fuels by renewable energy follows different intersecting paths, each of which is determined by the kind but also by the source of renewable energy.

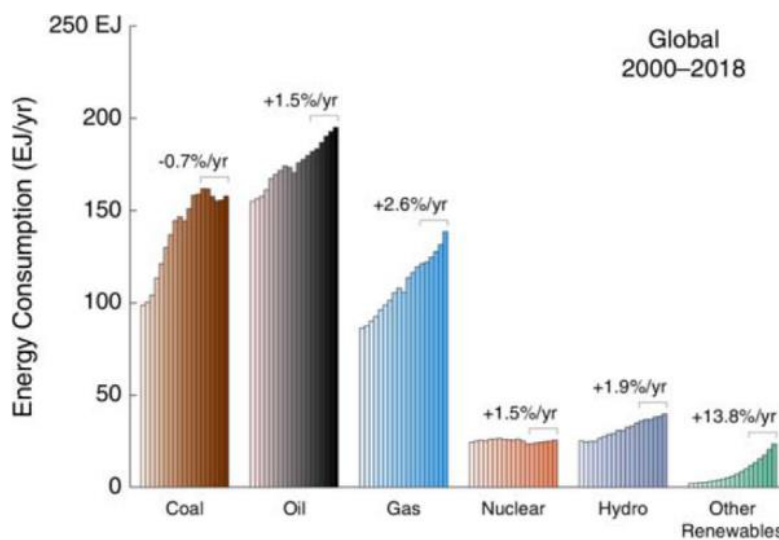
The key question in this point, however, is how much time do we have to make the transition from fossil fuels to renewable energy? How fast should this transition be done to avoid the unpleasant consequences of global warming? The news concerning the continuing rise in temperature is rather disappointing. The previous year 2020 as well as 2016 were the warmest years ever, ending with a rise of 1.25°C with respect to the pre-industrial period [e.g.30]. Therefore, we are already four-fifths of the way towards the 1.5°C considered as “safe” level [1-16]. According to the UN Secretary General, this could lead to a catastrophic rise in temperature from 3 to 5°C during the 21st century.

Global warming is directly reflected to the increasing rate of ice melting. For example, the European Space Agency recently announced that the 4320-square-kilometer A-76 iceberg, the largest on the planet, was cut off from the Ronne Glacier in the coast of West Antarctica and is sailing in the Weddell Sea (Figure 1). The increasing rate of ice melting brings about the continuing increase of the sea level determined by altimetry satellites [31–33]. In fact, satellite altimetry has shown that global mean sea level has been rising at a rate of ~3mm per year since 1993 with an acceleration of 0.084 mm. In the very optimistic scenario that the sea level continues to change at this rate and acceleration, it is expected that sea-level rise by 2100 will reach 65 cm [31].



**Figure 1.** The A-76 iceberg in recent satellite image taken by the Copernicus Sentinel-1 mission [34].

Meanwhile, coal, oil and natural gas remain by far the main global energy sources, as shown by the chart illustrating the share of different sources in global energy consumption per year from 2000 to 2019 (Figure 3a, ref 35). In 2018, the share of coal, oil and gas was 27.0, 33.1 and 24.2%, respectively, while the share of nuclear power was equal to 4.3% [35, 36]. Unfortunately, the coal energy consumption has decreased very slightly (-0.3% / year) from 2014 to 2019, due to delignification. This clearly indicates that the rate of delignification must be drastically accelerated as soon as possible. On the other hand, the share of hydroelectric energy has increased by 1.9% / year reaching 6.4% in 2018, thus surpassing nuclear power. More important is the increase of energy by 13.8% / year from photovoltaic, wind and biofuels that reaching 5% in 2018 exceeding, for the first time, nuclear energy. However, the difference between energy from fossil fuels and energy from green renewable energy sources remains huge and there is no doubt that the development of the latter needs to be done at an extremely fast rate in the coming years in order to curb global warming.



**Figure 2.** Global energy consumption during the period 2000-2018 [35]

## 2. Green Electricity

The production of electricity through the development of wind-energy [37, 38] and photovoltaic [39, 40] parks and concentrated solar power plants [41, 42] as well as hydroelectric power plants [43, 44] and typical high temperature geothermal units [45 - 47] seems to be the strongest arm of the effort to switch from fossil fuels to renewable energy [e.g. 1, 48] (figure 3). It is worth noting that concentrated solar power plants utilize mirrors for concentrating the sun's energy as heat. This in turn is used to drive traditional steam turbines or engines that create electricity.

As already mentioned among the above mentioned energy sources photovoltaics and wind generators are dynamically increasing in the last decade in various countries. Concerning photovoltaic and concentrated solar power energy this is shown in table 1 which illustrates fourteen countries with the largest solar photovoltaic capacities, fourteen countries with the largest solar photovoltaic capacities per capita and twelve countries with the largest concentrated solar power capacities. It is important to note that the worldwide cumulative

solar photovoltaic capacity was reached 850 GW up to 2021 with the prospect to reach 1TW very shortly. It is, moreover, seen that although China is the leading country, followed by the European Union and the United States, concerning the cumulative solar capacity, the contribution of many European countries as well as Australia, Japan, South Korea and Taiwan is more important taking into account the population of these countries (Solar PV, W per capita). Finally, it may be seen that the worldwide cumulative CSP capacity up to 2018 (5465 MW) is very small compared to the corresponding solar PV capacity. Spain is the leading country in this domain followed by the United States. It should be noted that China and Saudi Arabia have inserted dynamically in the domain by adding respectively 200 and 50 MW between 2016 and 2018.

**Table 1** Illustrates fourteen countries with the largest solar photovoltaic capacities, fourteen countries with the largest solar photovoltaic capacities per capita and twelve countries with the largest concentrated solar power capacities

Country	Solar PV capacity/MW <sup>1</sup>	Country	Solar PV, W per capita	Country	CSP capacities /MW <sup>2</sup>
China	306973	The Netherlands	817	Spain	2300
European Union	178700	Australia	742	United States	1738
United States	95209	Germany	702	South Africa	400
Japan	74191	Japan	590	Morocco	380
Germany	58461	Belgium	569	India	225
India	49684	European Union	400	China	210
Italy	22698	Switzerland	399	United Arab Emirates	100
Australia	19.076	Italy	381	Saudi Arabia	50
South Korea	18161	Malta	373	Algeria	25
Vietnam	16660	South Korea	350	Egypt	20
Spain	15952	Luxembourg	330	Australia	12
France	14718	Greece	329	Thailand	5
The Netherlands	14249	Taiwan	327	<b>Worldwide</b>	<b>5465</b>
United Kingdom	13689	Estonia	311		
<b>Worldwide</b>	<b>About 849473</b>				

1. Cumulative values up to the year 2021, Sources: (a). "Snapshot 2022". IEA-PVPS. International Energy Agency, (b) Renewable Capacity statistics 2022 (International renewable energy agency), 2. Cumulative values up to the year 2018, Source: Renewables global Status report REN21, 2017 and 2018.

Recent data concerning the wind power parks are presented in table 2. As in the case of photovoltaics the leading country is China. This is also followed by the European Union and the United States. It is worth noting that Japan is not involved between the countries with largest installed wind power capacities. An interesting observation is that the worldwide wind power capacity (824874 MW) is very close to that of the photovoltaics though its distribution in the various countries is different. Concerning the installed wind power capacity per capita

we are observing that the European countries, mainly those of Scandinavia, have the largest share.

Table2. Illustrates twelve countries with the largest installed wind power capacities and twelve countries with the largest installed wind power capacities per capita

Country	installed wind power capacity(MW) <sup>1</sup>	Country	installed wind power capacity (W per capita) <sup>2</sup>
China	328973	Denmark	1068
European Union	187497	Sweden	933
United states	132738	Ireland	864
Germany	63760	Germany	747
India	40067	Norway	738
Spain	27497	Spain	572
United Kingdom	27130	Portugal	509
Brazil	21161	Finland	449
France	1866	Uruguay	426
Canada	14304	Belgium	406
Sweden	12080	Greece	384
Italy	11276	Netherlands	375
<b>Worldwide</b>	<b>824874</b>	<b>Mean worldwide capacity</b>	<b>93</b>

1. Cumulative values up to the year 2021, Sources: "Renewable Energy Capacity Statistics 2022" (PDF),
2. Refer to the installed wind power capacity of 2020 divided by the corresponding country population.

Going to hydroelectric power energy it should be noted that the total global hydropower installed capacity reached 1308000 (MW) in 2019. The increase in the aforementioned capacity was equal 1.2% in the last year which was smaller compared to the last five years annual average (2.1%). This is also below 2.0% annual growth necessary to fulfill the Paris Agreement targets. Table 3 illustrates the twenty top hydro producing countries in the world for 2020.

Table 3. The twenty top hydro producing countries in the world (2020)<sup>1</sup>

Country	installed hydro power capacity( MV)	Country	installed hydro power capacity( MV)
China	356400	Italy	22600
Brazil	109100	Spain	20400
United States	102800	Switzerland	16900
Canada	81400	Vietnam	16800
India	50100	Sweden	16500
Japan	49900	Venezuela	15400
Russia	49900	Austria	14500
Norway	32700	Iran	12200
Turkey	28500	Mexico	12100
France	25600	Colombia	11900

1. References: 43, 44.

Again China is the leading country followed by Brazil and the United states. However, it is clear that Norway, Sweden and Austria are actually very important hydro producing countries taking into account their population. During 2019 fifty countries have added hydropower

capacity. The most important additions were obtained by Brazil (4920MV), which utilizes the Amazon River, followed by China (4170MV) and Laos (1890MV). Hydropower is expected to be a very important source of renewable power in 2024, with over 9% (about 121000 MW) capacity growth over the period 2019 -2024. China, India and Brazil are expected to be the leading countries. It is estimated that 25% of this growth will be achieved on the base of two projects in China of 26000MV and one project in Ethiopia of 620 MV.

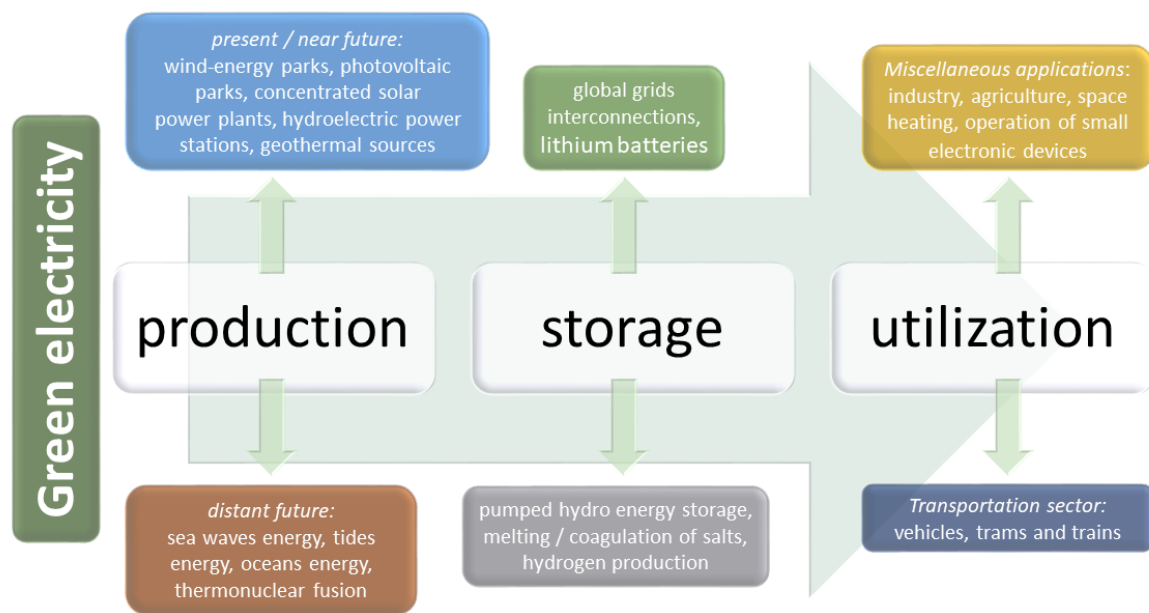
Compared to wind, solar- photovoltaic and hydropower capacities of installed units world widely those of geothermal units for electricity production are quite small. Table 4 illustrates the top ten countries with the highest installed geothermal electric capacity determined for the 2021.

Table 4. The ten top countries with the highest installed geothermal electric capacity (2021)<sup>1</sup>

Country	Capacity (MV)
United states	3722
Indonesia	2276
Philippines	1918
Turkey	1710
New Zealand	1037
Mexico	963
Italy	944
Kenya	861
Iceland	754
Japan	603
Others	1067
World wide	15854

References:<https://www.thinkgeoenergy.com/thinkgeoenergys-top-10-geothermal-countries-2021-installed-power-generation-capacity-mwe/>

Taken into account the above many scientists imagine the future world to be completely electric with electricity generated from the above sources. The most imaginative of them add to the above sources the energy from the sea waves, tides and oceans [49, 50] and the nuclear- breeder reactors [17, 51, 52], which will dramatically increase the stocks of nuclear fuel but also the dangers associated with the spread of nuclear weapons. Nevertheless, some ones believe that ‘the world must make a concerted effort today to develop nuclear breeder reactors to keep the world electric grid functioning in 2100’ [17]. The more ambitious scenarios of using the controlled thermonuclear fusion (Tokamak reactors) for generating electricity have been also formulated [53, 54].



**Figure 3.** Schematic representation of green electricity, production, storage and utilizations.

It is of course very encouraging that the cost of producing electricity from solar / wind energy has dropped dramatically over the last decade. In fact, the electricity prices from photovoltaic or wind farms have dropped to around 2 cents of euro per kilowatt-hour [55]. It is expected that these prices will continue to decrease in the future. A rather realistic estimate is that they can even reach 1.3 cents of euro per kilowatt-hour [55]. From the beginning to the mid-1930s, a drastic increase in wind energy is expected with the spread of mainly offshore wind farms in northwestern European countries as well as a drastic increase in photovoltaic parks in areas with high sunshine, such as Middle East, North Africa and Mediterranean European countries. It is clear the drastic expansion and improvement of the efficiency of wind, photovoltaic and solar concentrated power plants as well as of hydroelectric units will be intensively attempted in the coming years.

There is no doubt that electricity is a very high quality form of energy with the most important advantage being its lightning transfer over long distances. Electricity, however, presents huge storage problems. Using fossil fuels or hydroelectric power plants this problem is much smaller, as we can generate electricity when we need it. Obviously, this is not possible with the electricity generated in wind or photovoltaic parks. Thus, a considerable amount of electricity generated from these sources is lost as it cannot feed the grid without destabilizing it.

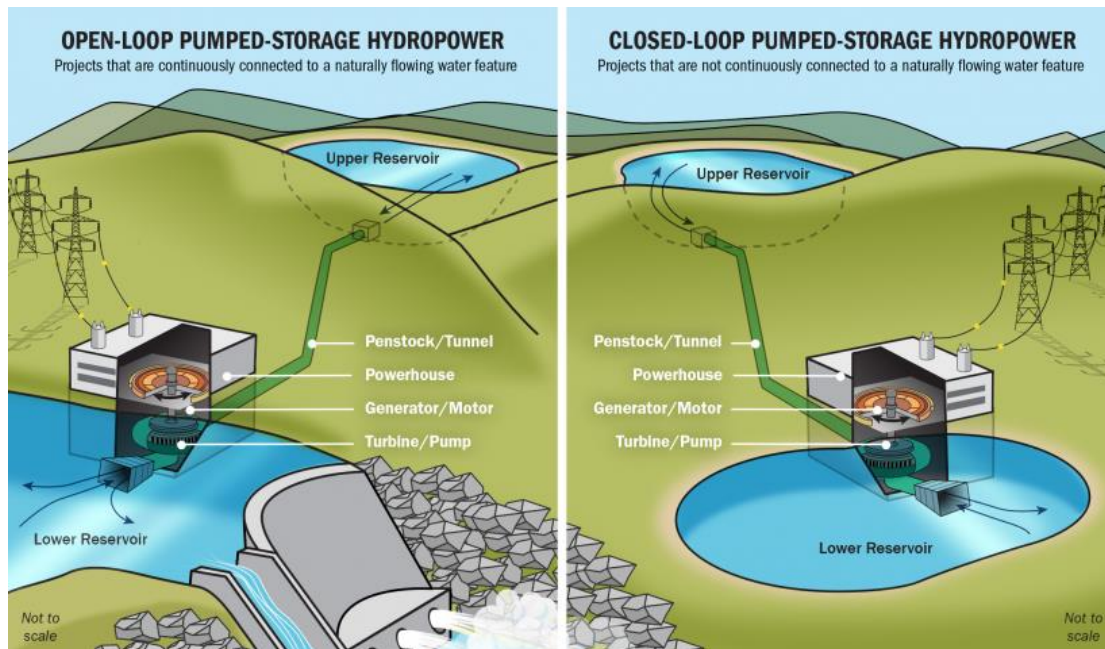
The interconnection of electricity grids for the transmission of electricity over long distances, even with submarine pipelines at very great depths, from areas with surplus electricity to areas that they need it is intensively being sought today in order to face this destabilization of the grids [56 - 66] (figure 3). Unfortunately, the most suitable locations for the generation of green electricity are not uniformly distributed. Significant renewable energy resources are



located in sites far from the power grid or where grid transfer capacity is low. Thus, grids should be strengthened allowing green electricity to be transported to the main demand / storage areas. A flexible though strong green-electricity transmission grid may help interlinking distant sources and electricity markets on the base of temporal and spatial complementarities. The development of transcontinental higher transfer capacity grids transferring large amounts green electricity over long distances is very probable in the near future. In this context the application of High Voltage Direct Current technologies is actually attractive due to their lower energy losses and weaker effects on environment.

Moreover, the development of electricity storage technologies is also sought. Luo *et al* have proposed that the storage technologies can be classified into 'mechanical (pumped hydroelectric storage, compressed air energy storage and flywheels), electrochemical (conventional rechargeable batteries and flow batteries), electrical (capacitors, supercapacitors and superconducting magnetic energy storage), thermo chemical (solar fuels), chemical (hydrogen storage with fuel cells) and thermal energy storage (sensible heat storage and latent heat storage)' [67]. Moreover, Amirante *et al* [68] provided an overview of mechanical, electrochemical and hydrogen technologies and presented a comparison among the potential utilizations of energy storage systems. Among the above storage technologies the most important are the pumped hydro energy storage, the energy storage based on melting salts, the storage by means of electrical batteries and the storage through the green hydrogen production (figure 3).

The development of pumping stations-reservoirs (pumped hydro energy storage) to raise water using the excess electricity and its recovery when we need it by falling water is very important in the context of electricity storage technologies. Pumped hydro energy storage covers about 96% of global storage power capacity [69]. Many pumped hydro energy storage systems have been already developed in conjunction with typical hydroelectric stations based on river – flows [69]. In this context two reservoirs are created, close to each other, at different altitudes. In most of the cases the lower reservoir is large and located near to the main river, whereas the upper reservoir is smaller, and located higher up on the river or in a high tributary valley (figure 4 left). In these combined units the most amount of water passes through the system generating electricity. Moreover, a certain amount of water is cycled between the two reservoirs in order energy storage to be obtained. The pumped hydro energy storage technology is expected to be rapidly extended to closed loop off-river pumped hydro storage units (figure 4 right). There, the water will be cycled repeatedly between two closely spaced small reservoirs located away from a river. A suitable place for developing this kind of units should allow the construction of reservoirs using relatively small amounts rock and other material compared to the amount of the stored water. Moreover, it is important finding closely spaced pairs of sites (e.g. several kilometers apart) with large differences in altitude, because the increase of difference in altitudes brings about an increase of the stored energy capacity. In the last years intensive investigation takes place worldwide for finding out areas suitable for developing pumped hydro energy storage units. In this respect the use of efficient computer algorithms is very important [70]. Compared to batteries pumped hydro energy storage is more suitable and considerably cheaper for large-scale energy storage, namely for several hours to weeks.



**Figure 4.** Schematic representations of pumped - storage hydropower plants: (left) open-loop, right (b) closed – loop. <https://www.energy.gov/eere/water/pumped-storage-hydropower>, retrieved 25/10/2021.

In this point it is useful to mention the installed capacities of pumped hydro energy storage in various countries. Table 5 illustrates eleven countries with the highest installed capacities of pumped hydro energy storage in 2021. China is the leading country followed by United States and Japan. The installed capacities in the remaining countries are considerably lower. As already mentioned a considerable amount of electricity generated in wind or photovoltaic parks is lost as it cannot feed the grid without destabilizing it. It is therefore interest to calculate the installed capacities in different countries of pumped hydro energy storage as percentage of the corresponding sum of the solar photovoltaic and wind power capacities. These percentages can be calculated from the data of Tables 1,2and 5. Some indicative values so calculated for China, United States and Germany and India are respectively equal to 0.6% , 9.6%,4.3% and 5.3%.

Table 5. Illustrates eleven countries with the highest installed capacities of pumped hydro energy storage in 2021

Country	Capacity of pumped hydro energy storage (MV)
China	36390
United States	21912
Japan	21894
Germany	5212
India	4786
South Korea	4700
Italy	3940
Spain	3331

South Africa	2732
Taiwan	2602
United Kingdom	2600

References: <https://www.statista.com/statistics/689667/pumped-storage-hydropower-capacity-worldwide-by-country/#statisticContainer>

The energy storage by melting suitable salts and its recovery by coagulation of these salts is used in the concentrated solar power plants and therefore its spread is strongly related with the wide spread of these plants. This technology allows generating electricity during cloudy periods or for hours after sunset or before sunrise [41, 42].

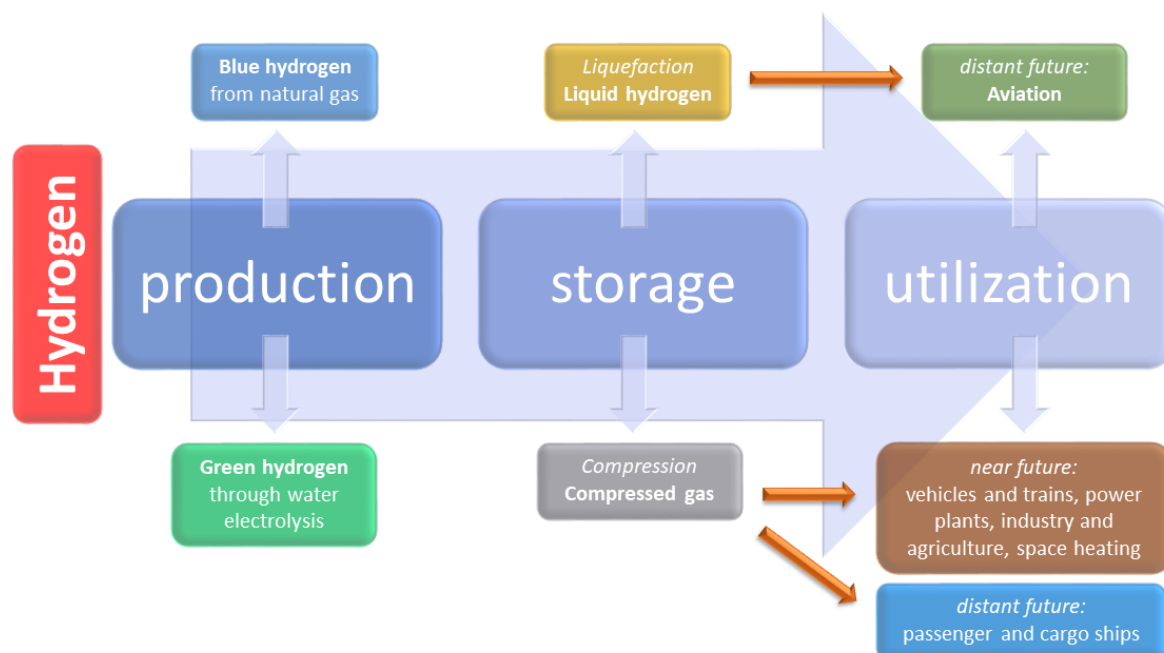
The development / production of electric batteries, currently of lithium, which increases markedly in recent years for passenger cars, must also be included in the context of electricity storage. Batteries occupy most of the electricity storage market concerning home and electric vehicle batteries. The price of batteries is rapidly falling. They are very attractive for short-term storage, namely for minutes to hours. The introduction of electric cars on a global scale will have to deal with the rather limited lithium reserves, a problem that could be addressed by improving the efficiency of lithium batteries as well as by developing batteries based on other elements found in greater abundance in nature. A future world of electricity should certainly be linked to the impressive development of electric railways, trams and subways, not associated with high storage requirements like the electric cars.

The issue of storing electricity generated from the renewable sources will remain critical and the problem will be even more difficult in the days when extreme weather events, due to climate change, will occur more and more often and shall threaten not only the electrical grids but also the wind and photovoltaic parks themselves. In addition, it is difficult to imagine airplanes or ships, which require vast amounts of energy to travel, to be powered by electricity stored in batteries alone.

### 3. Hydrogen

Most scientists, therefore, argue that the future world cannot be exclusively, but only partly, electric. Indeed the world will be more complex from the view point of energy supply; with more than one energy carriers, with more than one fuel. The most popular of these future fuels will certainly be hydrogen [e.g. 71 -75]. A schematic representation of hydrogen production, storage and usage in the near and distant future is illustrated in figure 5. It is very likely that hydrogen will dominate in the energy supply. But what justifies this prospect? Where this perspective is based? The hydrogen molecule consists of two hydrogen atoms ( $H_2$ ). When it is burned with the atmospheric oxygen produces clean water and heat ( $H_2 + 1/2O_2 \rightarrow H_2O + \text{heat}$ ). Therefore, it can be used as fuel in combustion engines of industrial units and vehicles, like natural gas or liquefied petroleum gas (LPG) mainly consisting of propane. The main difference is that now the product of combustion is not carbon dioxide and water but clean water. Consequently, the prospect of using hydrogen instead of fossil fuels seems very attractive. In addition, hydrogen can be "burned" in the most efficient "fuel cells" where electricity is produced ( $H_2 + 1/2O_2 \rightarrow H_2O + \text{electricity}$  [e.g. 76]. Therefore, hydrogen could be used as fuel in both electric and conventional vehicles. It is noteworthy that hydrogen contains

more energy per unit weight than other fuels. For example, the energy contained in one kilogram of hydrogen (119,972 kJ) is contained in 2.1 kilograms of natural gas and 2.8 kilograms of gasoline.



**Figure 5.** Schematic representation of hydrogen production, storage and usage in the near and distant future.

What hinders the widespread production and use of hydrogen today? The most important problem is that unlike fossil fuels, hydrogen gas ( $H_2$ ) is free in very small quantities. Therefore, we have to produce hydrogen at the lowest possible cost from the water ( $H_2O$ ) that abounds on the planet. This is done today, on a small scale, with the supply of electricity that brings about the electrolytic dissociation of water into hydrogen and oxygen ( $H_2O + \text{electric current} \rightarrow H_2 + \frac{1}{2} O_2$ ) using the so-called electrolytic devices or electrolyzers [e.g.77, 78], mainly in countries with cheap electrical energy. Unfortunately, significant energy loss takes place upon the conversion of electricity into chemical energy enclosed in the hydrogen molecule and thus intensive research is currently being conducted to improve the efficiency of electrolyzers. In effect, progress is demanded in the near future for reducing cost by improving efficiency and durability of electrolyzers. In any case the production of hydrogen through the water electrolysis seems to be a one-way street as the photocatalytic dissociation of water or its decomposition via thermo chemical cycles by heating it to very high temperatures (which will be achieved by concentrated solar power plants or waste heat of nuclear power reactions) seems to be less promising for the moment. However, one cannot exclude that the intensive research taking place currently associated to the development of these methods [e.g.79-81] may render these methodologies practically applicable in the future.

The hydrogen produced through water electrolysis does not obviously relate to serious carbon dioxide emissions. For this reason it is called 'green hydrogen'. The price of green hydrogen,

however, is currently extremely high, around 4 euros per kilogram. It is expected that the increase in efficiency and size of electrolyzers in combination with the ongoing reduction in the cost of electricity produced by photovoltaic and wind-energy farms will drastically reduce this price even to 1.0 - 2.5 euro per kilogram by 2030 accompanying the aforementioned decrease in the price of the green electricity. The rate of increase in the amount of excess green electricity is expected to allow the production of actually large amounts of green hydrogen but not before 10-15 years ago, starting from countries having large wind or photovoltaic farms.

On the other hand, the faster reduction of carbon dioxide emissions to confront global warming requires not only rapid delignification but, in addition, early transition from natural gas to hydrogen. The conversion of natural gas to hydrogen is obtained through two simple catalytic reactions. In the first, called steam-methane reforming (SMR), methane reacts with water to produce carbon monoxide and hydrogen ( $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ ) [82,83]. It occurs at a very high temperature (around 700 - 1000°C) and therefore needs a fairly large amount of heat that we get from the combustion of a part of natural gas. In the second step, called water-gas shift reaction (WGS), taking place at moderate temperatures, the carbon monoxide produced in the first reaction reacts with an additional water molecule producing carbon dioxide and an additional molecule of hydrogen ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) [84,85]. In a final step of the process, called pressure-swing adsorption (PSA) [86, 87], carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Thus, four molecules of hydrogen are produced from one molecule of methane whereas one molecule of carbon dioxide is emitted together with a small amount of carbon dioxide released from the combustion of a portion of methane necessary to increase the temperature upon SMR. It is worth noting that two of the four hydrogen molecules come from water. Therefore, through these reactions, we also exploit the hydrogen of the water, without spending electricity for electrolysis. This is why hydrogen produced in this way is much cheaper than green hydrogen. The ¾ of the hydrogen produced worldwide nowadays is due to the aforementioned reactions. Since we do not avoid carbon dioxide emissions the hydrogen produced by this way is called 'gray hydrogen'. Gray hydrogen may be also produced from natural gas through methane partial oxidation (MPO). In this case methane reacts with a limited amount of air resulting, mainly, to hydrogen and carbon monoxide  $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$  [88 - 91]. As in the case of SMR, MPO is followed by WGS and PSA. MPO is exothermic releasing also heat and much faster than SMR requiring smaller reactors. On the other hand, in the MPO step are produced two hydrogen molecules from one molecule of methane instead of three produced in the step of SMR.

In order to prevent carbon dioxide emissions in the SMR/ WGS or MPO/ WGS industrial units this could be collected and then transferred and entrapped in underground cavities such as depleted oil or natural gas sources, depleted mines, etc. It is estimated that in this way we can trap 90% of the emitted carbon dioxide. Therefore, the hydrogen that will be produced in this way, called 'blue hydrogen', will be very close to green hydrogen. It is expected to replace gradually the natural gas as a transitional fuel during the period 2030 - 2050. After this period the goal of zero emissions will be achieved using green electricity and green hydrogen as well as biofuels as we will see in the next section. In the meantime, the amount of green electricity, blue hydrogen and later on of green hydrogen will increase continuously. According to very

optimistic recent forecasts of NDV GL, even 80% of the natural gas consumed in Europe could be converted into blue hydrogen towards 2050, provided that the development of carbon dioxide storage facilities will be significantly accelerated. It is the relative cost of the green and blue hydrogen which will determine which one of them will prevail in the energy market. Green hydrogen will be produced in areas with high wind potential or high sunshine, while the blue one in areas closer to natural gas sources.

In contrast to the above optimistic perspectives concerning the utility of transforming natural gas to blue hydrogen a recent publication, examining the lifecycle greenhouse gas emissions upon this transformation, showed that the greenhouse gas emissions from the production of blue hydrogen are quite high because fugitive methane emissions for the production of blue hydrogen are higher than for the production of gray hydrogen due to the increased use of natural gas to obtain additional energy required for the carbon dioxide capture[92]. There is no doubt that if the findings of this study will be confirmed by other researchers, the prospect of producing blue hydrogen from natural gas will be questioned. In this case, the production of green hydrogen should certainly be accelerated.

An issue related to the widespread use of hydrogen as an alternative fuel is its storage difficulties, though it is much easier to store hydrogen than electricity. It is therefore understandable why intensive investigation currently occurs for improving the hydrogen storage technologies (compression, liquefaction, physisorption, development of metallic hydrides and complex hydrides etc.) among which mechanical compression is very important [93- 96]. Hydrogen is a very light gas with a very low mass (and thus energy) density with respect to liquid fuels. In order to increase the energy density we have to compress hydrogen too much to bring the hydrogen molecules as close as possible and concentrate the large mass and thus energy in small volume. The achievement of high pressures, for example over 2000 atmospheres, requires the development of cylindrical containers made from very durable / light materials in order to avoid increasing the vehicles weight too much. The great progress in the field of materials in combination with the development of more smart storage methods allow, even today, the use of hydrogen in both vehicles and urban / industrial applications provided that its production cost will markedly decrease.

Therefore, one can imagine the future energy profile to be composed of electricity and hydrogen, which means electric trains, trams and cars as well as hydrogen-powered cars. One can also imagine many industries choosing hydrogen as a fuel instead of natural gas. Finally, it can be predicted that today's natural gas-fired power plants will be converted to hydrogen-powered plants. Hydrogen can be transported as a gas in high-pressure containers or as a liquid in thermo-insulated containers. More important is that hydrogen in gaseous form can be transported through pipelines like natural gas. Transporting hydrogen gas through existing pipelines is a low cost option for delivering large volumes of hydrogen. In any case, one could reasonably predict the development of extensive pipelines in the future to transport hydrogen from its production sites to areas where it is consumed.

Focusing on cars, we are noting that power is generated by converting the chemical energy of hydrogen into mechanical energy. This is achieved either by reacting compressed hydrogen with oxygen in a fuel cell to produce electricity which power electric motors or, less

commonly, by burning hydrogen in an internal combustion engine. A fuel cell electric vehicle (FCEV) uses a fuel cell, sometimes in combination with a small battery or a super capacitor. The first FCEV was introduced by Hyundai (2013) followed by Toyota (2015) and then Honda (2016). Up to December 2020, 31,225 passenger FCEVs have been sold worldwide [97]. Meanwhile fuel cells are being developed and tested in trucks, buses, boats, motorcycles and bicycles. However, it is questionable whether the passenger FCEVs will cost-effective for automobiles as compared with other zero emission technologies [98]. In the near future, one should not rule out the development of three types of electric cars: those using lithium batteries to store electricity, those generating electricity through fuel cells installed inside the vehicles from stored hydrogen and hybrids that will also work with both ways.

With regard to trains, very serious efforts have already begun in Germany and other countries for developing hydrogen-powered trains for areas where the construction of electrical infrastructure for electric trains will be considered less profitable [99]. Specifically, the first worldwide hydrogen powered train (Coradia iLint) was presented by Alstom at Inno Trans 2016 in Berlin. This was specifically designed for operation on non-electrified lines. Two years later this train was entered into commercial service in Germany. It uses principally the fuel cell technology in combination with batteries to produce electrical power for traction. The fuel cell generates electricity by combining the hydrogen stored on the train's roof with oxygen in the air. The Coradia iLint can carry up to 150 seated passengers and 150 standing passengers. It can reach a range of up to 1,000km with a maximum speed of 140km/h. Due to the successful operations of hydrogen-powered trains in Germany, the aforementioned company has received several orders for its hydrogen-powered trains from Italy, France and Austria. The UK's first hydrogen-powered train, HydroFLEX, was developed from Class 319 conventional trains. The train is fitted with hydrogen fuel tanks, a fuel cell and battery packs. The fuel cell converts the mixture of hydrogen and oxygen to electricity of up to 100kW whereas two lithium-ion battery packs allow the electrical energy to be stored. Thus this is the world's first example of bi-mode electric -hydrogen train. This train carried out its first successful mainline test at the end of 2020.

Concerning the maritime transport, the direct use of electricity through batteries is rather unlikely at least for passenger or cargo ships. Could hydrogen be used as fuel? Before dealing with this issue it is convenient to briefly deal with the previous transition from fossil fuels to natural gas. As already mentioned, in the interval between the transitions from fossil fuels to renewable energy the natural gas will predominate. Natural gas is cooled to  $-162^{\circ}\text{C}$  and turns into liquid (LNG). The liquefaction reduces the volume to 1/600 of that of gas allowing its transportation in large quantities by sea. The volume of LNG trade is expected to increase by 21% in 2025 compared to 2019 and the demand for maritime transport is expected to continue to grow [100]. On the other hand, due to the tightening of international legislation concerning sulfur oxides, introduced in January 2020, most ocean-going vessels now use low-sulfur heavy oil. Nevertheless, the use of this fuel does not affect the carbon dioxide emissions. Therefore, using this fuel the IMO (International Maritime Organization) goal of reducing carbon dioxide emissions by more than 40% in 2030 compared to 2008 cannot be fulfilled. This is the reason for which LNG has recently been introduced as marine fuel instead of heavy oil. In fact, the combustion LNG does not practically emit sulfur oxides or particulate matter whereas it emits less nitrogen oxides and carbon dioxide (25% reduction in carbon

dioxide emissions) compared to petroleum oils. Most importantly, the proven reserves of natural gas getting over those of oil allowing a stable long-term supply of ships for more than 50 years [100]. Moreover, natural gas is lighter than air and can be easily diffused. Consequently there is less risk for explosion. Finally, the price of LNG is lower than that of low sulfur heavy oil. Therefore, there is no doubt that more and more ships will run using LNG, starting with LNG transport ships and coastline ships utilizing near LNG units. In fact, the use of LNG as a ship fuel is rapidly advancing in the ocean shipping industry. Globally, the number of LNG-fueled vessels has increased from 18 in 2010 to 198, with more than 277 on order in 2020. Most of these vessels concern Europe. An increasing development of LNG bunkering infrastructure worldwide is observed in the most important ports [100]. This is obviously essential for the widespread use of LNG-fueled ships. There is no doubt that the transition from ship oil to natural gas will be completed inside the period 2030-2050 though the exact time cannot be predicted.

It cannot be excluded that the transition from natural gas to blue hydrogen and then to green hydrogen to start before this time. The most optimists imagine that this would be feasible despite that hydrogen is more difficult to be liquefied and it is maintained in the liquid state at a higher cost than natural gas. The use of hydrogen as passenger or cargo ship fuel is in principle feasible. However, much work is needed before this goal will be achieved by overcoming serious technical problems. Many in shipping recognize hydrogen's future potential, but the barriers to implement the required technology are actually substantial.

Efforts to this direction have been already begun. In the first two decades of the 21st century the development of small size ships fueled by hydrogen has been already started. (e.g. 22-person Hydra ship, Duffy-Herreshoff water taxi, Yacht No.1, Hydroxy3000, AUV DeepC, Yacht XV 1, 12-person Xperiance, Zebotec, 8-person Tuckerboot, Canal boat Ross Barlow, 100-passenger Zemships, Nemo H<sub>2</sub>, Frauscher 600 Riviera HP, Hydrogenesis Passenger Ferry, car ferry MF Hydra e.t.c. [101]). In 2005 the first example of the Type 212 submarine, which is powered underwater by fuel cells, went into service with the German navy. Fuel cells are operated in almost all cases for producing the necessary electricity. For example the car ferry MF Hydra uses liquid hydrogen, two 200 kW fuel cells, a 1.36 MWh battery and two 440 kW diesel generators. The hydrogen tanks and the fuel cell are located on top of the ferry [101]. Important studies, therefore, deal with the fuel cell systems with regard to maritime power generation requirements. A review of these studies regarding the efficiency, gravimetric and volumetric density, dynamic behavior, environmental impact, safety and economics showed that the most suitable fuel cell system/fuel depends on the operational requirements of the vessel. Regarding hydrogen the low temperature fuel cells (LT-PEMFC systems) using liquefied hydrogen are quite suitable for ships with a refueling interval up to tens of hours. However, for sailing times over 100 h the limited hydrogen storage density is expected to result in 1.5–5 times larger total system volumes compared to alternative systems with more energy dense logistic fuels [102]. Due to the low volumetric energy density of hydrogen under standard conditions, the need for efficient storage of this fuel is high. Therefore, the development of hydrogen storage technology is a key factor. In this context, a recent review deals with the storage of hydrogen at high pressure, in liquefied form at cryogenic temperatures and via various carriers like ammonia, methanol, formic acid, aromatic liquid organic compounds (toluene, n-ethyl



carbazole, dibenzyltoluene) and solid-state carriers (metal hydrides, boron compounds- $\text{NaBH}_4$  and  $\text{NH}_3\text{BH}_3$ ) in relation to its use in the ships [103]. It seems that there is no a unique storage method combining high energy density, low energy input, readily available resources, non-toxicity and easily handle and storing. Therefore, we will have to make strategic choices on the methods of hydrogen storage for shipping. Moreover, major challenges will be the development of a new bunkering infrastructure and suitable monitoring to ensure safe operation of the hydrogen carriers on board the ship. Twenty six partners and observers have come together in the *MarHySafe* joint development project to address the challenges concerning the prospect of using green hydrogen or hydrogen carriers in shipping using fuel cells [104]. The goal of this project is the establishment of a roadmap concerning the safe hydrogen operations. Having accomplished the phase 1 of the project, the consortium published the *Handbook for Hydrogen-fueled Vessels* which will be updated continually following the progresses of the project. The following conclusions can be drawn from the study reported so far [104]. (i) More testing is needful on the safety aspects of handling, storage and bunkering hydrogen. (ii) Although the experience of working with natural gas can be proved very useful for studying hydrogen operations in shipping there are considerable differences between these different fuels. For example hydrogen is the lightest of all atoms making it harder to be stored whereas it ignites more easily than natural gas and has a wider flammability range. (iii) The most suitable way of generating power from hydrogen is using pure hydrogen fuel cells whenever it is feasible. This is important within coastal and short-sea shipping in the cases where battery electric solutions are not feasible mainly due to a lack of local grid. On the other hand, the direct transformation of hydrogen to electricity may reduce the energy losses happen using combustion engines. Nevertheless, the use of hydrogen, hydrogen mixtures with other fuels or hydrogen stored in a liquid organic solution or as ammonia using combustion engines cannot be excluded especially for big vessels and high sailing times. (iv) Using hydrogen requires the development of a new technology in a new environment. Consequently, a risk-based design process is needed for novel ship designs that cannot be approved with the current regulations and need safety optimization. Indeed an alternative design process is currently required. In this context the aforementioned Handbook for Hydrogen-fuelled Vessels examines alternative designs. (v) The scale up of hydrogen operations in a ship and transition from land-based applications to maritime ones is a difficult task and it will be a real challenge for the future.

The prospect of using hydrogen in airplanes in the future is much more difficult. A recent article examines in details this issue [105]. Airplanes need fuels with very high energy densities which are now provided by aircraft fossil fuels. In fact, the energy density advantage of fossil fuels is very difficult to overcome. The biggest problem is the extra weight required to store hydrogen either in gaseous or liquid form. For liquid hydrogen, the challenge will be to build lightweight vacuum insulated tanks that keep the fuel below the boiling point of 20 K. The storage of compressed hydrogen further increases the weight of the aircraft as the tanks must be constructed to withstand high pressures 250-350 bar. This requires a much more robust tank and would take up about twice as much space as liquid hydrogen-containing tanks. From this viewpoint the liquid hydrogen seems more attractive [105]. Despite the above ominous prospects the world's major airliner manufacturers are looking at hydrogen as one eventual option for reducing carbon dioxide emissions but in the distant future. As we shall see in the

next section, the first urgent choice is the use of biofuels. Thus, Airbus will decide by 2025 whether the market can support hydrogen-powered aircrafts. In the positive case, its first hydrogen airplane will be put into service in 2035. Similarly, Boeing estimates that it will take more than two decades for hydrogen to be introduced into its airplanes. Nevertheless, several companies have already started the development of relatively small aircrafts fueled by hydrogen. In 2008 Boeing built the first single-person plane flying solely by hydrogen power. The fuel cells were supplemented with power from lithium ion batteries during takeoff and ascent. In 2012 this company developed a liquid-hydrogen-powered unmanned aerial vehicle (UAV) for reconnaissance missions of up to four days at an altitude of 20 000 meters. The Zero Avia, a small company, pursues the manufacture by 2023 of a 10- to 20-passenger aircraft which will be powered by hydrogen fuel cells whereas this company expects to debut 50- to 100-passenger fuel-cell aircraft powered by liquid hydrogen by the end of the decade [105]. An important issue to be addressed regarding the use of hydrogen in aviation is whether we should burn hydrogen instead of fossil fuels using conventional airplane turbines. This is easier but in this case we will not avoid the formation of nitrogen oxides due to the reaction of nitrogen with oxygen at high combustion temperatures. On the other hand, the use of fuel cells is for the moment less efficient than gas turbines and requires much larger changes in the design of the aircrafts. This solution is perhaps more likely for relatively small aircraft and flight times [105]. In the context of using fuel cells, several companies have started to promote R / D programs for developing light and efficient fuel cells suitable for aviation. The effort concerns both the PEM fuel cells rely on a liquid electrolyte to shuttle protons between electrodes and the solid oxide fuel cells (SOFCs) which use an oxidic material, usually yttria-stabilized zirconia, as the electrolyte to produce electricity by oxidizing the fuel. The development of hydrogen aircraft supply infrastructure is certainly necessary for its widespread use in aviation. On-site hydrogen production by electrolysis of water at airports and its storage seems attractive in order to avoid the transport of hydrogen over long distances. ZeroAvia for example plans to use nearby green electricity sources. It is estimated that only an airport junction could serve multiple return routes of his aircraft, since the flights are up to 460 km. In conclusions, the above show that we are very far from the extensive use of hydrogen in aviation. As already mentioned this does not a top priority of the airline companies to directly address the carbon dioxide emissions.

#### 4. Biofuels

In view of the above and regarding the future energy profile of mankind we must add a third component to green electricity and hydrogen: that of biofuels. An overview of the present and future biofuels is illustrated in. Table 6 Biofuels are produced from biomass, which is synthesized daily all over the planet in huge quantities from carbon dioxide and atmospheric water in the presence of sunlight through a relatively slow photosynthetic-enzymatic reaction ( $\text{CO}_2 + \text{H}_2\text{O} + \text{solar light} \rightarrow \text{biomass}$ ) responsible for plant growth [106 - 109]. The biomass molecules mainly contain carbon and hydrogen atoms derived from water and atmospheric carbon dioxide. Therefore, the combustion of biomass, more precisely of its bio-molecules, produces carbon dioxide, water and energy in the form of heat, just like the combustion of fossil fuels. But there is a fundamental difference: the carbon dioxide emitted by the combustion of biomass is equal to that which had been absorbed by the plants to create the biomass during photosynthesis. Consequently, the carbon dioxide emissions during the

combustion of biomass do not disturb the carbon dioxide balance in the atmosphere [1]. This is why burning of plant biomass, which was the main energy resource from prehistoric man to the discovery of fossil fuels three centuries ago, does not cause carbon dioxide accumulation in the atmosphere. The same of course is valid for biofuels which are already produced and used today as well as those that will be produced in the future.

**Table 6** An overview of the present and future biofuels

Kind of Biomass	Preparation Process	Biofuel type	Biofuel utilization
<b>Triglyceride biomass</b>			
Vegetable oils	Transesterification	Biodiesel	Vehicles ( <i>present</i> )
Waste cooking oils	Deoxygenation	Green diesel	Vehicles ( <i>near future</i> )
Discarded animal fat	Deoxygenation	Green Kerosene	Sustainable aircraft fuels ( <i>near future</i> )
Coffee beans oils			
Residual Fatty acids			
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Algae oils	Deoxygenation	Green Kerosene	Sustainable aircraft fuels ( <i>distant future</i> )
<b>Carbohydrate biomass</b>			
Cane	Chemical - enzymatic processes	Bioethanol	Vehicles ( <i>present</i> )
Sweet sorghum			
Sugar beets			
Corn grains			
<b>Organic waste with a sticky-liquid texture</b>	Anaerobic digestion	Bio-gas ↓ Bio-methane	Heating / electricity generation ( <i>present</i> )  Vehicles ( <i>present-near future</i> )
<b>Lignocellulosic biomass (agricultural and forest residues)</b>	Enzymatic processes	Bioethanol	Vehicles ( <i>near future</i> )
	Fast pyrolysis	Bio-oil ↓ Hydrocarbons	Vehicles ( <i>near future</i> )
	Integration of bio-oil		
	Gasification / F-T process	<i>Synthetic biofuels:</i> ↓ Gasoline Diesel Kerosene	Vehicles ( <i>near future</i> ) Vehicles ( <i>near future</i> ) Sustainable aircraft fuels( <i>near future</i> )

Three well-known biofuels are currently produced: biodiesel-green diesel, bioethanol and biogas (table 6). In the period 2000-2019 both the production and consumption of liquid biofuels (biodiesel - green diesel and bioethanol ) have increased from about 20,000,000(2000) to more than 163,000,000(2019)m<sup>3</sup>. In 2020 they decreased, due to the restrictions on mobility and the decrease of the world economy, to 151,000,000m<sup>3</sup>. However, data obtained in 2021 indicate recovering in the production and the consumption of the above mentioned liquid biofuels. In each year inside this period the amount of the liquid biofuels consumed is almost identical to corresponding one produced. United States (41 %), Brazil (26%), Indonesia (35%), China (3%) and Germany (3%) are the leading countries in the production of liquid biofuels. The production in Thailand, France, India, Canada and Argentina is also quite significant. [The statistical data presented in this subsection concerning biodiesel - green diesel and bioethanol were drawn from a recent text of Agustin Torroba: "Liquid biofuels atlas 2020-2021" presented in

<https://repositorio.iica.int/bitstream/handle/11324/18661/BVE21097939i.pdf?sequence=5&isAllowed=y>

Biodiesel is produced from vegetable oils and animal fats rich in triglycerides (e.g. rapeseed, soybean, palm, sunflower and jatropha oil) [110, 111]. These are converted to mixtures of fatty acid esters with methanol (FAME or biodiesel) through a relatively easy and inexpensive chemical process (transesterification) realized in small industrial plants [112, 113]. Biodiesel production has increased by 78% over the period 2011-2020 reaching 43,000,000 m<sup>3</sup> in 2020. United States (18 %), Indonesia (17%), Brazil (13%), Germany (8%) and Thailand (4%) are the leading countries in the production of biodiesel. The production of biodiesel in France, China, Spain Malaysia and Argentina is also quite significant. The molecules of these esters, though similar, are not identical to the molecules of petroleum hydrocarbons and this creates problems in both the storage and usage of biodiesel. For this reason, the share of biodiesel in its mixture with petrol diesel which can be burned in car engines is limited to around 5-10%. It is anticipated that biodiesel will gradually be replaced by green or renewable diesel in the near future [114 - 117] (table 6). The latter is also produced from the triglycerides of vegetable oils and animal fats, which are converted to hydrocarbons in the diesel range (12-18 carbon atoms) by reacting with hydrogen. This reaction is causing the removal of oxygen atoms contained in the triglycerides. Therefore, green diesel can be used for vehicles instead of petrol diesel and not just in a mixture with it as is the case of biodiesel. The technological problems for the production of green diesel have already been solved with the development of very active catalysts [114 - 117]. The green diesel production has increased by 459% over the last decade reaching 7,000,000m<sup>3</sup> in 2020. However, that will block the production of the huge quantities of green diesel required is that the plants providing vegetable oils will more and more compete for soil and water the crops for the food and animal feed production. This is why modern research focuses on the use of plants that will be grown in degraded or brackish soils, unsuitable for food production [118]. It also focuses on the cultivation of microorganisms – algae, rich in non-edible oils, which do not necessarily require soil, as they can multiply by photosynthesis even in closed tanks or artificial ponds, absorbing large amounts of carbon dioxide [e.g. 119, 120] (table 1). Although the use of algae seems attractive, more research is

needed, at least for two decades, before it becomes practically feasible. In this context it is pursued the increase of algae density in the aquatic environment where they grow in order to be decreased the too high harvesting costs. Awaiting these developments the research effort is also directed towards the utilization of other raw materials rich in triglycerides such as wasted cooking oils [121- 124 ], discarded animal fat [125, 126] and oils from coffee beans after the extraction of its juice [127-131]. It also focuses on the utilization of released fatty acids from edible oil refining units [132-135]. There is no doubt that the amount of the natural triglycerides and free fatty acids used for hydrocarbon productions will be increased drastically in the future utilizing the aforementioned vegetable oil/animal fat sources.

However, it is highly probable that the whole amount of triglycerides and fatty acids will be directed to the production of aircraft fuels where there will be the greatest need and not to green diesel for vehicles which much probably will use green electricity/green hydrogen, biomethane and presumably bioethanol (see below). The aircraft fuels are also paraffinic hydrocarbons (with 10-15 carbon atoms, Kerosene). It should be noted that air travel accounts for about 2% of carbon dioxide emissions [136]. Intensive research/development is currently being carried out to convert triglycerides into sustainable aircraft fuels (SAF). This will be very valuable because as already mentioned we are very far from the extensive use of hydrogen in aviation. It is estimated that using SAF the carbon dioxide emissions can be decreased from 80 to 90%. The first test flight was taken place in 2008 using biofuels blended with fossil fuel whereas blended fossil fuels with 50% biofuels were allowed in commercial flights from 2011 [136, 137]. Two similar technologies are emerging for production of sustainable aircraft fuels using natural triglycerides. The first and more mature technology called "Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK)" has been already developed [136, 138 - 140]. According to this technology the fuel is produced by the deoxygenation and hydroprocessing of, mainly, jatropha and camelina oil. The second technology is under development and will utilize oils and fat extracted from Jatropha, tallow, waste oils, Babassu and Camelina [141]. The production of the so called "bio derived synthetic paraffinic kerosene (bio-SPK)" will be obtained by cracking and hydroprocessing [141]. Several companies, research groups and airlines are now cooperated on algae sustainable aircraft fuels. Moreover, Air France, KLM and SkyNRG are building an industrial unit for producing 100.000 ton/year of sustainable aircraft fuels using waste / discarded vegetable oils / animal fats.

Bioethanol is a very important biofuel used as cars fuel in many countries, most notably Brazil [142-144] (table 1). It contains carbon, hydrogen and oxygen ( $C_2H_6O$ ). The first two are burned producing carbon dioxide and water, respectively, and providing the required energy. Bioethanol can be mixed at 5% gasoline without modifying the engine. By modifying the engine we can use mixtures with a higher percentage of bioethanol up to 95%. A typical gasoline-bioethanol mixture contains 25% bioethanol [1]. It is produced in many countries, through enzymatic processes in large and ever-increasing quantities, greater than biodiesel, from sugars obtained from cane, sweet sorghum and sugar beets and from starch, mainly from corn grains [1]. The amount of bioethanol produced in the last decade (2011- 2020) was increased by 18% reaching 101,000,000 m<sup>3</sup> at 2020. As in the case of green diesel, the production of bioethanol from the above plants will increasingly compete with the production of food and animal feed for soil and water. This is the reason for which the research /

development effort is directed to the second generation bioethanol which will be prepared using non-edible feedstock sourced from agriculture and forestry wastes. Lignocellulosic and starchy materials in them are convertible to fermentable sugars that are able to be further processed, leading to bioethanol [145, 146]. Another issue is that the cars which will use bioethanol will have to compete the electric, hydrogen-powered and presumably biomethane-powered cars. Thus, the research is directed to the production of airplane fuels based on bioethanol. In this context the transformation of bioethanol to sustainable aircraft fuels (Synthetic Paraffinic Kerosene) is systematically investigated as it is indicated by recent efforts [147-149].

Biogas is a gaseous mixture of methane ( $\text{CH}_4$ , 40–80%) and carbon dioxide ( $\text{CO}_2$ , 20–60%). It is produced in the absence of oxygen, through a rather slow biochemical process (anaerobic digestion) from any organic waste with a sticky-liquid texture (table 1). A recent review deals with the biogas production and usage and the legislations framework across the globe [150]. Agricultural or livestock waste or even municipal wastewater can be used [151-155]. The biogas production is usually realized in small units installed everywhere, in contact with the places of accumulation of the raw material [1, 156]. The anaerobic digestion is catalyzed from various types of bacteria [151-155]. It is remarkable that the production of biogas does not compete the food or animal feed production. The amount of the biogas produced in the five continents at 2019 is illustrated in table 7.

Table 7. Biogas produced in the five continents at 2019\*

Continent	Amount of the produced biogas ( billion cubic meters )
Europe	31.2
Asia	21.8
America	8.44
Oceania	0.85
Africa	0.01

\*Source: <https://www.statista.com/statistics/481828/biogas-production-worldwide-by-region/>

Biogas can be used for heating or electricity generation [157, 158]. More importantly, 'biomethane' can be produced by removing carbon dioxide from biogas [159.] This contains only 2 % carbon dioxide and can be utilized as vehicles fuel. It is clear that although biomethane has exactly the same composition with natural gas, as both are practically composed of methane, the carbon dioxide emitted from the combustion of biomethane does not disturb the carbon dioxide balance in the atmosphere. Thus, in terms of climate change biomethane is comparable to green hydrogen. It cannot be excluded that approaching 2050, a significant number of vehicles will use biomethane in addition to those that will use green electricity and/or hydrogen. This is probable because the prospects for the rapid development of biogas - biomethane plants worldwide are indeed extremely optimistic. For instance, 10000 biogas plants operate today in Germany while the growth rate of biogas plants is really high in many countries. An increase of ~90% in the biogas industry was pointed out in the last

decade worldwide (120 GW in 2019 compared to 65 GW in 2010) [150]. The biomethane that could be potentially produced annually using all of the animal manure would be about one-fifth of the natural gas consumed [1]. The collection of biogas and the combustion of the biomethane in the transport sector will be extremely beneficial for the climate from another point of view as well. In effect, the release of biomethane into the environment upon the uncontrolled decay of organic matter has a much more negative effect than the carbon dioxide released from the burning of fossil fuels. We are noting that solving problems related to the disposal and agricultural utilization of the biogas production residues will reduce its production cost and accelerate the development of new plants [150]. The above considerations imply that future vehicles will utilize biofuels in internal combustion engines in parallel to those will use lithium batteries or fuel cells for transforming green hydrogen into electricity. However, if this does not happen and a large part of future vehicles will use green hydrogen, it is very likely that the biomethane produced from the biogas will be converted to green hydrogen through the so called dry reforming ( $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ ) followed by the water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) mentioned previously. Several recent works are devoted to the study of this process [160].

While the prospect of biomethane concerning the energy profile of the 21<sup>st</sup> century is anticipated to be significant, the perspective of the liquid biofuels (bioethanol, green diesel, and green jet oil) will be less important mainly due to the competition of the large-scale energy crops with food and animal feed crops. It is estimated that replacing 5% of gasoline and diesel by liquid biofuels in Europe and the United States, requires the 20% of the cultivated land, which is unlikely to happen. For this reason the effort now focuses, in addition, on the utilization of both agricultural and forest residues, for example straw, grass and useless woods [108, 109] (table 1). These raw materials are indeed abundant on the planet. The biomass of these raw materials is composed mainly of two polysaccharides cellulose (40-50%) and hemi-cellulose (25-30%), as well as lignin (15-20%) [1, 146]. These form a complex-stable lignocellulosic structure [161], which consists of mainly carbon and hydrogen atoms and less oxygen atoms. This kind of biomass is called 'lignocellulosic biomass'. Cellulose, the most important component of lignocellulosic biomass, contains about half the amount of carbon in the entire biosphere. The research efforts follow three general directions in the context of exploiting lignocellulosic biomass. The first seeks to produce bioethanol from cellulose and hemi-cellulose through enzymatic processes, after the removal of lignin [162-164]. This approach is currently cost unprofitable but it is expected to be improved significantly in the near future. The second, more mature approach, seeks to convert biomass into 'bio-oil', mainly by fast pyrolysis (heating at high temperature in the absence or in the presence of very low amount of air) [165-168]. This is anticipated to take place using a reactor mounted on a large vehicle – tank very near to the place where the biomass is collected [1]. Upon fast pyrolysis the aforementioned high molecular weight compounds are decomposed to smaller molecules whereas lot oxygen contained in the biomass is released to the atmosphere. Beside fast pyrolysis several other methodologies have been tested to produce bio-oil by lignocellulosic biomass. Among these methodologies biomass liquefaction [169] seems to be promising. The bio-oil produced will be transported and upgraded in the refineries resulting to liquid biofuels for vehicles [170-172]. The third approach (biomass to liquid, BtL process) starts with the gasification of biomass into a mixture of carbon monoxide and hydrogen

(CO+H<sub>2</sub>) called 'synthesis gas' [173-177]. The so called 'synthetic biofuels', namely hydrocarbons in the gasoline, aircraft and diesel range can be produced from synthesis gas through a well-known catalytic process [Fischer–Tropsch (FT) process] [178-181]. The prospect producing sustainable aircraft fuels by exploiting the abundant lignocellulosic biomass could render the third approach more popular in the coming years provided that significant technological problems related to the gasification stage will overcome. Recently, it has been proposed this route in the context of producing "Fischer–Tropsch Synthetic Paraffinic Kerosene" (FT-SPK) [141]. The synthesis gas obtained by the gasification of biomass could be alternatively used for the synthesis of methanol [ $\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$ ] which could be used alone or in hydrocarbons blends as a car fuel as well as for the production of hydrocarbon fuels or hydrogen [182-184].

However, even if the technological problems related to the gasification stage will be solved, only a part of the residual biomass is expected to be used for the production of jet oil. The rest will very likely be directed to the production of platform molecules for chemical products whose the production was based up to now on petrol oil. The transformation of lignocellulosic biomass into platform molecules [185] and chemical products will be achieved through rather mild chemical and biochemical processes in combination with the production of jet oil in the context of the operation of a bio-refinery since cellulose, hemicellulose and lignin will be separated first [186]. For example, phenols, aromatic compounds, dibasic acids and olefins can be produced from lignin. From the hemicellulose can be produced xylose and then γ-valerolactone, tetrahydrofurfural pentanoic acid and pentanol -1. Finally, glucose can be produced from cellulose and from there formic acid, ethanol, acetic acid, lactic acid, glyceraldehyde, hydroxyacetone, maleic acid, erythrose, levulinic acid, sorbitol, fructose, mannitol, furfural etc. These can be further used for the production of a variety of important chemicals on an industrial scale [187, 188]. The future demands will determine the percentage of residual biomass will be used for chemical or sustainable aircrafts fuels.

Recently, it is widely argued that instead using biomasses carbon and hydrogen for producing hydrocarbon biofuels, methanol and chemicals we could alternatively use green hydrogen and the 'waste carbon dioxide' in the context of 'carbon dioxide capture and utilization' (CCU) methodology [189]. For example green ammonia can be prepared by atmospheric nitrogen and green hydrogen [ $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ ] [190, 191]. This can be then transformed to urea, which is the basis of fertilizers, using the waste carbon dioxide [ $\text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$ ]. Thus, according to this idea the recycling of carbon dioxide will be in the future a useful source of carbon for both the production of biofuels and the manufacture of chemicals. However, the collection of carbon dioxide from the atmosphere is extremely difficult and currently economically prohibitive, considering that only about 400 molecules of carbon dioxide can be collected from a volume of atmospheric air containing around one million molecules of nitrogen and oxygen [1]. Thus, the interest is directed to point sources of carbon dioxide such as coal gasification and steel cement plants. In this context ~~and~~ several liquid and solid systems have been developed [192]. However, with the prospect of phasing out all fossil fuel combustion plants, the only significant point source of carbon dioxide emissions will be the conversion of natural gas to blue hydrogen. Utilizing carbon dioxide from this point source and green hydrogen to produce chemicals is indeed a realistic and very useful prospect. In contrast, the production of fuels by recycling carbon dioxide will not offer a significant benefit



to the climate, as the carbon dioxide incorporated into the fuel will be reproduced as it burns in vehicles or aircrafts and will diffuse back into the atmosphere. Therefore, the benefit for the climate will be only one additional use of mineral coal.

## **5. Concluding remarks**

In this essay we outlined the prospects for supplying humanity with energy during the 21st century in the context of deteriorating climate change and the ongoing depletion of fossil fuels. The transition from fossil fuels to renewable energy needs to be significantly accelerated in order to avoid the widespread of nuclear- breeder reactors which will dramatically increase the stocks of nuclear fuel but also the dangers associated with the spread of nuclear weapons.

The transition from fossil fuels to electric energy will be mainly achieved by drastically accelerating the development of wind-energy, photovoltaic and concentrated solar power plants as well as hydroelectric power plants and typical high temperature geothermal units. It is very encouraging that the cost of producing green electricity from solar/ wind energy has dropped dramatically over the last decade. This is expected to be decreased further from the beginning to the mid-1930s, due to the drastic expansion and improvement of the efficiency of wind, photovoltaic and solar concentrated power plants as well as of hydroelectric units. The future world is expected to be largely electrical provided that the inherent problem of electricity storage will be overcome through the global interconnection of electricity grids for the transmission of electricity over long distances, the spreading of pumped hydro energy storage and melting salts plants and the lithium batteries. Nevertheless, it is difficult to imagine airplanes or passenger/cargo ships, which require vast amounts of energy to travel, to be powered by electricity stored in batteries alone. Therefore, the future world cannot be exclusively, but only partly, electric, with more than one energy carriers.

Among these carriers hydrogen will be certainly the most important. The price of 'green hydrogen', produced through water electrolysis is expected to be reduced drastically by 2030 accompanying the decrease in the price of green electricity. Thus, large amounts of green hydrogen will be produced, but not before 10-15 years ago. The required faster decarbonization imposes early transition from natural gas to 'blue' hydrogen. This can be obtained by transformation of natural gas to blue hydrogen through steam-methane reforming reaction accompanied by the water-gas shift reaction and pressure-swing adsorption. In order to prevent carbon dioxide emissions upon these reactions, CO<sub>2</sub> must be collected and then transferred and entrapped in underground cavities. It is estimated that in this way we can trap 90% of the emitted carbon dioxide. Green hydrogen will be produced in areas with high wind potential or high sunshine, while the blue one in areas closer to natural gas sources. The relative cost of the green and blue hydrogen will determine which one of them will prevail in the energy market. It can be predicted that future industries and power plants will use largely hydrogen instead of natural gas. It can reasonably be predicted the development of extensive pipelines in the future to transport hydrogen from its production sites to areas where it will be consumed. The operation of three types of electrical cars will be very probable: those using lithium batteries alone, those generating electricity through fuel cells installed inside the vehicles from stored hydrogen, and hybrids that will also work with both ways. Moreover, it is very likely the widespread of hydrogen-powered trains for areas

where the construction of electrical infrastructure for electric trains will be considered less profitable. Concerning the maritime transport, the natural gas will predominate in the interval between the transitions from fossil fuels to renewable energy. The transition from ship oil to natural gas will be completed inside the period 2030-2050 though the exact time cannot be predicted. The transition from natural gas to hydrogen before this time is probable, because the use of hydrogen as ship fuel is in principle feasible. However, much work is needed for overcoming serious technical problems. The prospect of using hydrogen in airplanes is much more difficult. Airplanes need fuels with very high energy densities provided by aircraft fossil fuels. The biggest problem is the extra weight required to store hydrogen either in gaseous or liquid form. Nevertheless, the world's major airliner manufacturers are looking at hydrogen as one eventual option for reducing carbon dioxide emissions but in the distant future. Their first urgent choice is the use of biofuels.

Therefore, biofuels must be inevitably added to the future energy profile of mankind besides green electricity and hydrogen. Liquid biofuels currently used in cars (biodiesel, bio-ethanol), which are mainly produced from energy plants, will face more intense competition in the future with the production of food for agricultural land and water. That is why the effort is focused on the production of biofuels either from residual fatty raw materials and microalgae (green diesel for cars, green kerosene for aircrafts) or agricultural and forest residual raw materials (bioethanol, hydrocarbons from the integration of bio-oil and hydrocarbons from the synthesis - gas resulting from the gasification of the biomass). Moreover, the aforementioned liquid biofuels will face the competition of green electricity and hydrogen concerning the vehicles. Therefore, it is anticipated that a considerable portion of biofuels will be directed to the aviation. Concerning the lignocellulosic biomass (agricultural and forest residual raw materials) it will very likely to be directed to the production of platform molecules for chemical products whose the production was based up to now on petrol oil. Platform molecules and bio-chemical products will be also produced by utilizing green hydrogen and carbon dioxide released upon the transformation natural gas to blue hydrogen. Biomethane, readily produced from biogas, is expected to be increasingly involved in the energy profile either itself or converted to pure hydrogen.

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