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Review

Practicable Artificial Photosynthesis: Its Relevance, Fundamental Challenges and Opportunities

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Abstract: The single main resource for the survival of humankind on this planet is the sunlight and it is freely coming to every home like the life-supporting gas, oxygen, is coming to every individual. When society becomes master in harvesting such a precious, Omnipresent, carbon-neutral, clean, freely and abundantly available renewable energy resource sunlight in a suitable form of chemical energy such as, H_2, O_2, CO, methanol, gasoline (petrol), diesel, etc., with a minimum conversion efficiency of 10% by using carbon dioxide (CO_2) and water (H_2O) as energy storing materials, which is referred to as the "Practicable Artificial Photosynthesis (PAP)" process, it can be employed for commercial practice with economic viability to meet all the energy needs of the society without any back-up by electricity generated at thermal power plants by burning greenhouse gas CO_2 releasing fossil fuels. In fact, the PAP process is the only option available today for humankind to make energy, environment, economy, and life sustainable on our only habitable planet, Earth. In this article, (i) how the PAP process can change the global energy economy and energy dynamics of the world while solving all the humanities top 10 problems for the next 50 years, (ii) how the entire CO_2 gas generated as a waste across the globe at all the major outlets can be eventually converted into petrol (i.e., gasoline) given the fossil fuels cannot sustain our civilization's economic growth, (iii) the effectiveness of existing CO_2 sequestration vs. carbon capture and utilization (CCU) processes, (iv) nature's response to anthropogenic CO_2 gas rise in the atmosphere, (v) steps involved in the realization of a desirable PAP process, (vi) why silicon photovoltaic cell (SPVC) solar panels cannot solve the energy problems of our society considering the outcome of Germany's Energiewende program, etc., have been meticulously presented and described in this article.

Keywords: Practicable artificial photosynthesis; Solar energy harvesting; Semiconductor and liquid assisted photothermal effect; Electrochemical CO_2 reduction; Electrochemical water splitting

1. Humanities Top 10 Problems for Next 50 Years vs. the Practicable Artificial Photosynthesis (PAP) Process

According to *Prof. Richard E. Smalley* (June 6, 1943–October 28, 2005) at Rice University, USA (a nobel laureate in chemistry for the year 1996 for discovering *Buckminsterfullerene*, or *buckyball*, a new form of carbon), the humanity's top 10 problems for the next 50 years are (in order of preference) [1–15].

(i) Energy,
(ii) Water,
(iii) Food,

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(iv) Environment,
(v) Poverty,
(vi) Terrorism and war,
(vii) Disease,
(viii) Education,
(ix) Democracy,
(x) Population.

Ten threats formulated by the "*United Nations High Level Threat Panel*" in 2004 for the world population are also in corroboration with these ten-problems [16–28]. Out of these ten problems, energy, environment and poverty, which fall in top five list can be solved with a single solution [1]. When carbon-neutral and renewable sunlight is harvested in an economically viable process at a minimum conversion efficiency of 10% in a suitable form of chemical energy like the one present in fossil fuels that include crude oil, coal, natural gas, petrol (gasoline), diesel, liquid petroleum gas (LPG), compressed natural gas (CNG), etc., to meet all the energy needs of the society without the need of any back-up electricity generated at power plants by burning fossil fuels, like nature is harvesting (storing) solar energy in the form of food materials and bio-mass in a thin plant leaf in "*natural photosynthesis* (*NP*)" process to feed not only 800 crore people living on Earth today but also the entire life that is surviving to use them as and when required on a demand basis by using carbon dioxide (CO_2) and water (H_2O) as energy storing materials, all the problems related to energy, environment and poverty can be solved very easily [1]. Today, energy is nothing but money and vice versa given its value. The main energy resource of humankind, i.e., sunlight, comes to every home freely in abundance like oxygen (i.e., air) comes to every individual. Even wind energy also equally comes to every home with desired speed and throughout a day in certain days unlike sunlight, which comes only during the daytime. However, in comparison to wind energy, sunlight comes during majority of days in a given year with suitable power density to harvest it with the required efficiency. When electricity derived from sunlight is economically stored in the form of H_2 and O_2 gases by electrolysing water, these gases can be again used to generate electricity to use in the absence of sunlight (i.e., during nights, evenings, mornings and on cloudy days) as and when required on a demand basis by using fuel cells. This process is almost similar to the natural photosynthesis process [1]. When solar energy is stored outside of a plant leaf by human beings using man-made devices using CO_2 and H_2O or only H_2O as energy storing materials that process is termed as an "Artificial Photosynthesis (AP)" [1–4]. When this latter process is performed on a commercial scale with a minimum sunlight-to-chemical energy conversion efficiency of 10% so that it can be practiced at industry with economic viability to meet all the energy needs of the society without any back-up form of electricity generated at thermal power plants by burning fossil fuels, then this process can be referred to as the "Practicable Artificial Photosynthesis (PAP)" process [1]. Such a PAP process allows one to store solar energy at every home in the form of H_2 and O_2 gases, which can ensure everybody not to spend a single penny to buy electricity from outside to meet electricity needs at home. In fact, it converts every home a renewable energy producing unit. The electricity derived from sunlight can be used to charge the batteries used in electric vehicles (EVs) such as, cars, bikes, buses, etc., and to run every home appliance such as, cooker, refrigerator, television, air-conditioner/cooler, grinder, mixer, geyser, electric bulbs, etc., used in a home [1–4]. In this way a suitable PAP can avoid a major expenditure of the society. People just need food and clothes from outside to live. Thus, such a PAP process can i) completely eliminate the poverty from the society across the globe, ii) create several millions of new jobs across the globe, and iii) change the global energy economy and energy dynamics of the world [1].

If one looks at the energy consumption pattern by our society, the major amount of energy goes for domestic purposes, than for transportation, and then finally for the industry. So by using a suitable PAP process, energy can be generated at every home to meet domestic and transportation energy requirements. Today, each and every country spends a huge amount of money to buy energy to meet their primary energy requirement. Furthermore, self-sufficiency in energy production is a stated national goal for each and every country today across the globe [1−29]. In fact, most of the following strategies for achieving this goal are either environmentally unacceptable, or are not feasible except those depend on fossil fuel based resources such as, natural gas. The important resources of renewable energy are biomass, solar, wind, tides and hydro-based systems. For example, every year India spends several lakhs of crores of rupees to import fossil fuels to meet about 47% of its primary energy requirement, and it is predicted to increase to 53% in the coming few years [1,29]. This spending is one of the reasons for India still being a developing country even after 70 years of independence. Once a suitable PAP process is developed, India need not have to spend such a huge amount of money to important fossil fuels, and it can spend that money to completely eradicate the poverty from India. Today, in India, about 57% rural population is below the energy poverty line, and about 22% population is below economy poverty line [30]. In the case of urban areas, these figures are 28% and 20%, respectively. Energy poverty line is defined as the minimum quantity of physical energy needed to meet cooking and lighting purposes. To realize a fully developed India, at the outset, India needs to be self-sufficient in the production of an easily dispatchable form of energy from sunlight, which is also safe, clean, and abundant. In fact, the highest strength of India in comparison to many of the developed and developing countries such as, USA, China, United Kingdom, Germany, France, etc., is its annual solar insolation receiving capacity thanks to its geographical location (i.e., being a tropical country and relatively closer to the equator) [1]. When India becomes master in suitably harvesting solar energy, it can become a super-power eventually as it receives solar insolation continuously for more number of days in a given year with desired power density required for harvesting with the needed efficiency of minimum 10%.

In fact, the scarcity of wealth can be attributed to all the problems today world is facing such as, wars and conflicts occurring among different countries, riots and differences among various races and religions, disputes in a family, etc.. If there is a guaranteed way to receive sufficient and sustainable income of wealth and money for each and every individual like everybody receives oxygen in plenty without spending a penny, there will not be any conflicts among the people living in our society [1]. Today nobody is fighting for air (i.e., for life supporting oxygen gas), and if wealth is also available freely and abundantly like oxygen is available, nobody will ever fight for acquiring wealth and preserve it for their future generations like nobody is acquiring and preserving oxygen gas (i.e., air) for the future generations. Surprisingly and fortunately, wealth is also available abundantly and freely in the form of sunlight similar to oxygen (air). However, our society is yet to become a master in capturing sunlight reaching every home freely to meet all their energy requirements like they are using air. Once it is done, our society will not face any problems like those faced today [1].

In the past, the solar energy available in the form of food grains (rice, wheat, and different pulses) used to be used in place of currency during trades, and later on it has been slowly replaced by currency notes and coins. In fact, even today, the solar energy present in the form of fossil fuels is considered responsible for certain wars that are occurring among different nations particularly in central Asian region [1].

If economical poverty is considered in the society, it is not there with everybody and at every part of the world in equal levels. Some countries are very poor and some countries are very rich. There is a wide disparity among the people's wealth. Surprisingly, several prophets have come and gone, but the disparity among the people's wealth did not go. Not only that even the greatest inventions ever made by human beings such as, wheel[1], flywheel[2], steam-engine[3], and electricity with alternating current[4] also could not eliminate the economic inequality among the people. Even *Albert Einstein's* inventions (i) the famous energy matter equivalence equation ($E = MC^2$), (ii) photoelectric effect, (iii) the special theory of relativity, and (iv) the Brownian movement also could not wipe-out this economic disparity. *Albert Einstein's* photoelectric effect is the basis for today's *silicon photovoltaic cell* (*SPVC*) solar panels, for which he was awarded with Nobel Prize in 1915 [2]. Certain technologies facilitated the fast growth of industrialization and brought a lot of comforts to the human society but could not eradicate such an economic inequality [1]. Economic inequality and scarcity of the wealth are the two main reasons for all the unrest and chaos today our human society is seeing. A suitably developed PAP process can eliminate this economic disparity completely as sunlight reaches every home [1]. Wherever sunlight falls on the earth, there wealth can be created.

1. The wheel was invented in the 4th millennium BC in Lower Mesopotamia (Iraq), where the Sumerian people inserted rotating axles into solid discs of wood. In 2000 BC, discs were made hollowed to reduce the weight.
2. James Watt, an 18th-century Scottish engineer, tested successfully a flywheel in a steam engine to convert the up-and-down thrusts of steam-powered pistons into a continuous rotational motion. Even the internal combustion (IC) engines' working principle also based on the invention of flywheel.
3. Steam engine uses steam pressure to push a piston back and forth inside a cylinder, and to transform this motion by a connecting rod and crank, into rotational force to do a work with the help of a wheel or flywheel.
4. Michael Faraday discovered electricity with alternating current (AC), which periodically reverses direction and changes its magnitude continuously with time.

2. Energy Vectors Available Today to Meet the World's Primary Energy Requirement

Figure 1 shows the various fuels utilized during the past 50 years period through 1965 to 2015 to meet the world's primary energy requirement [1,2,31–41]. It can be concluded based on this information that our society could survive and all the industrialization growth took place just because of the ready-made availability of stored solar energy in the form of fossil fuels (crude oil, coal, and natural gas). Figure 2 depicts the percentage of each fuel contributed in the year 2018 to meet this world's primary energy requirement [1,36–41]. Table 1 summaries different types of energies utilized in the year 2018 in India to meet the primary energy requirement [1,36–41]. Table 2 lists the amounts of various fuels imported from foreign countries, which are accounted for about 46.13% [1,36–41]. These imports are expected to rise up to 53% by the end of the year 2030 [1,36–41]. This energy requirement was grown at the rate of 2.3% from 2019, and it is the third highest one in the world after China and USA with a global share of 5.8%. In the year 2017 in India, as far as electricity production is concerned, about 80% was generated by burning fossil fuels at thermal power plants [1,36–41]. Surprisingly, India is only next to China in terms of renewable energy production with 208.7 Mtoe (million tons of oil equivalence) in the year 2016 [1,2]. However, the carbon intensity in India is about 0.29 kg of CO_2 per kWhe in 2016, which is higher than those of USA, China, and EU. In India, for the financial year of 2020–2021, the per-capita energy consumption was about 0.6557 Mtoe, and the energy intensity of the economy was about 0.2233 Mega Joules per Indian rupee (INR) (53.4 kcal/INR) [1,36–41]. Today, India has one of the fastest-growing energy markets in the world, and it is expected to contribute about 18% in the global energy demand in the year 2035. Today's India's wind power market is the fourth largest in the world, and has the plans to establish about 100,000 MW capacity *silicon photovoltaic cell* (*SPVC*) solar panels by end of 2022 [2]. India has plans to raise its nuclear electricity from 4.2% to 9% in next 25 years period from now. In the year 2018, India's investment in energy sector is about 4.1% (US$ 75 billion) of US$ 1.85 trillion global investment [1,36–41].

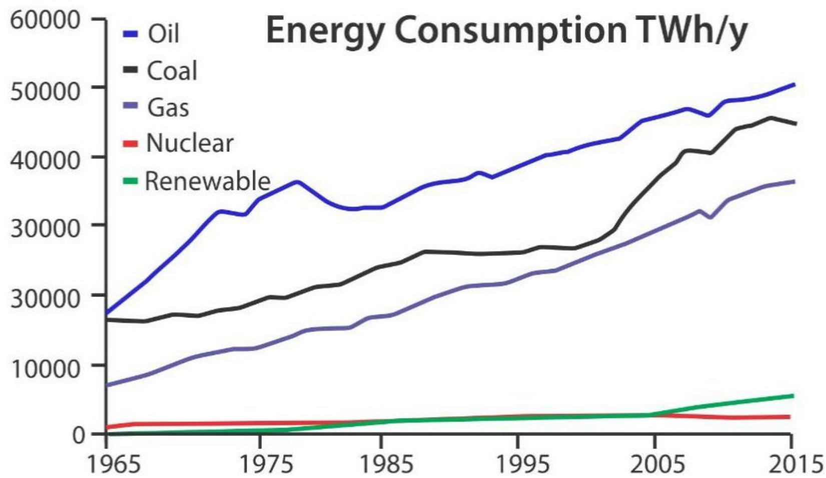

Figure 1. The world's energy consumption (2015 data). Each 10,000 TWh/y corresponds to an average value of about 1.14 TW [31–35].

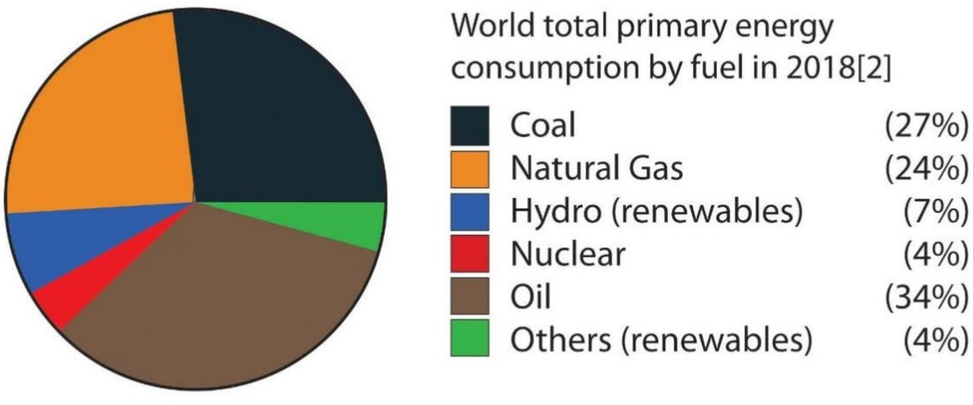

Figure 2. World primary energy consumption by fuel in 2018 [31–35].

Table 1. The share of various fuels utilized in the year 2018 to meet the primary energy requirement in India [1].

Fuel Type	Mtoe (Million Tons of Oil Equivalence)	Percentage (%)
Coal	452.2	45.88
Crude oil	239.1	29.55
Natural gas	49.9	6.17
Nuclear energy	8.8	1.09
Hydro electricity	31.6	3.91
Renewable power (wind and solar)	27.5	3.40
Traditional bio-mass	-	Balance

Table 2. The amounts of various fuels imported from foreign countries in the year 2018 to meet the primary energy requirement in India [1].

Fuel type	Mtoe
Coal	373.3
Crude oil	205.3
Liquefied natural gas (LNG)	141.7

In the year 2017, the global electricity derived from sunlight using SPVC solar panels is only about 1.73% [1,2,36–41]. In fact, the electricity derived from sunlight has never exceeded 0.5% in comparison to the total world's primary energy requirement [1,2,36–41]. This is the state-of-affairs even after 180 years of industrial revolution took place across the globe. It is surprising to note that even after 180 years of industrial revolution took place across the globe, the humankind is yet to become the master in harvesting the clean, safe, abundant, Omni present sunlight to meet the energy needs of the society without any back-up from fossil fuels [1,2]. Although, SPVC solar panels entered the market more than 40 years ago, they are yet to reach every home to generate electricity from sunlight to meet all the energy needs of a home. The reason for the underutilization of SPVC solar panels could be either they are not profitable enough or the unavailability of inexpensive methods to store the electricity derived from sunlight to use it in the absence of sunlight [1,2]. The time period consumed for mobile phones to reach each and every home across the globe was not even more than 10 years, whereas, for SPVC solar panels, even after 40 years period, they are yet to see such a feat. It is most unlikely that SPVC solar panels ever achieve such a feat. The tariff of electricity derived from sunlight using these SPVC solar panels was about ₹2.44 (3.2¢ US) per kWh in the year 2017 [1,36–41]. In 2020, the tariff in US$ was about 1.35 cents/kWh against the international tariff of about US$0.063/kWh. In fact, these tariff figures are lower than the electricity generated at thermal power plants by burning fossil fuels [1,36–41].

Table 3 shows the amount of coal burned year wise for a period of continuous nine years from 2004 to 2013 at thermal power plants to generate electricity in India [42]. There are about 118 thermal power plants, 220 cement industry, 650 steel plants (small and big) and several petrochemical gas refineries in India. These refineries also generate CO_2 that is equivalent to the total amount together generated at cement industry and thermal power plants. It is a known fact that every tonne carbon (molecular weight: 12 grams) generates about 4 tonnes of CO_2 (molecular weight: 44 grams) gas [1,2]. Several millions of tonnes of carbon is burned every day in India in the form of crude oil, coal, natural gas to generate electrical power at thermal power plants to meet energy demands, and the resultant CO_2 gas is released into the atmosphere [1,2].

Table 3. All India yearly coal consumption for power generation (utilities) [42].

Year	2004–2005	2005–2006	2006–2007	2007–2008	2008–2009	2009–2010	2010–2011	2011–2012	2012–2013
Coal (million tons)	278.00	281.00	302.00	330.00	355.00	367.00	387.00	417.56	454.60

3. Can fossil fuels sustain our civilization's economic growth?

Today, the majority of the world's primary energy is met from fossil fuels. Power plants use fossil fuels (coal, oil or natural gas) to produce electrical energy. Figure 3 shows the Hubbert's predictions for the period of 400 years from 1800 to 2200 [1]. As per today's consumption rate, the available coal reserves will last only for another 130 years, and oil for 42 years [1]. Fossil fuels cannot sustain our civilizations economic growth. Although, the Hubbert's curve is highly debatable, what is clear is that the crude-oil has a host of useful industrial applications, and if it is irreversibly burned, it will jeopardize the future. The vertical scale in this figure is in an arbitrary relative units, but to get an idea of scale, world production averaged at about 80 million barrels per day in 2008 [43]. Oil and natural gas are the starting materials for several important chemicals in our day-to-day life. It is important to realize reliable and alternative energy resources, before the oil resources are completely exhausted. Oil is the starting material for lubricants, dyes, plastics, and synthetic rubber, and natural gas supplies hydrogen for synthesizing ammonia, glass, and plastics. Similarly, coal produces creosote oil, benzene, toluene, ammonium nitrate, soap, aspirin, and solvents. Thus, we cannot afford to use such important as well as limited oil, natural gas and coal resources only to meet just the energy needs instead of several other important products of next several centuries to come [44–59]. Furthermore, these resources are not required for just next few decades but for several centuries to come. The current fossil fuel consumption rate, their particular geographic distribution, and the political control over them pose problems for the nations, which are fully dependant on them. The rapidly growing population and industrialization are also demanding the increased energy requirement. Out of today's total energy consumption, about 43% is provided by oil and derived liquid fuels, which include gasoline, diesel, jet fuels, gasoil, etc. [60].

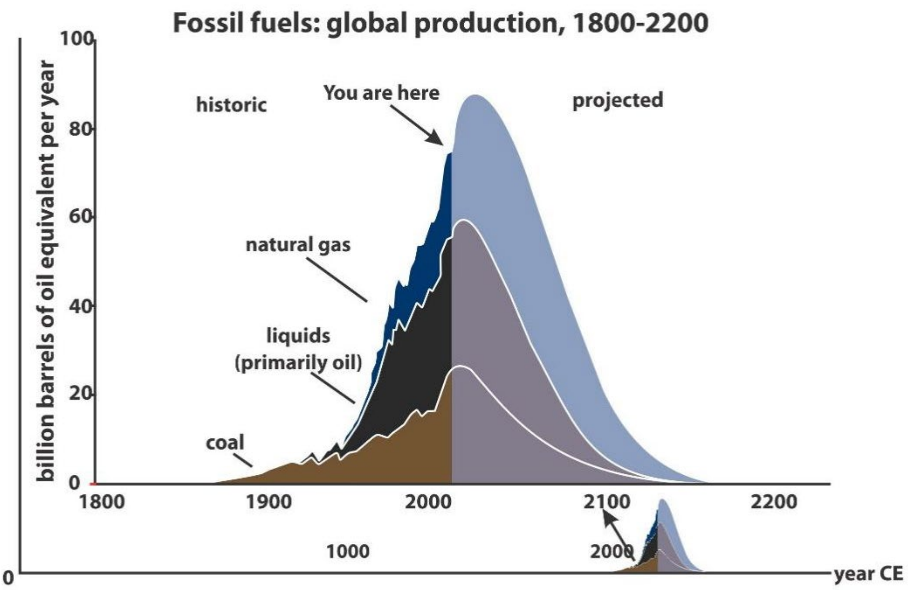

Figure 3. Hubbert's curve predictions indicating that world oil resources are on track to critically deplete within 40 years [1].

4. Renewable Energy Resources and Their Capabilities

Table 4 lists the seven different types of renewable energy resources available for humankind and the amount of each renewable energy that can be extracted in the year 2050 [61]. Figure 4 shows one of the Global energy inventory predictions for the year 2000 and for 2050 [1]. It can be seen from this figure that, in the year 2050, about 28 TW extra energy is needed in comparison to 12.8 TW that was needed in the year 2000 (1.4 TW = 10,000 TWh/y). This extra 28 TW energy must come from carbon-neutral renewable energy resources such as sunlight, wind, etc. In fact, as per the data in Table 4 only sunlight has the capability to provide the amount of energy needed by the society in the year 2050 [1]. Many of the renewable energy resources including wind and hydroelectricity are indirectly influenced by the sunlight. The amount of sunlight reaching the earth surface dictates the amount of rain to come in the corresponding season.

Table 4. Various renewable energy resources available for mankind [61].†

Resource Name	Energy Output	Expected Output in the Year 2050
Biomass	Chemical fuels	5–7 TW
Solar	Electricity	105 TW*
Wind	Electricity	2–4 TW
Tide	Electricity	2–3 TW
Hydro-based	Electricity	-
Nuclear	Electricity	-
Geo-thermal	Electricity	3–6 TW

* If the solar irradiance of 1% of the Earth's surface is converted into storable energy with 10% efficiency. † When it is electricity, it is either needs to be consumed immediately, or it needs a storage mechanism to use it effectively by the society.

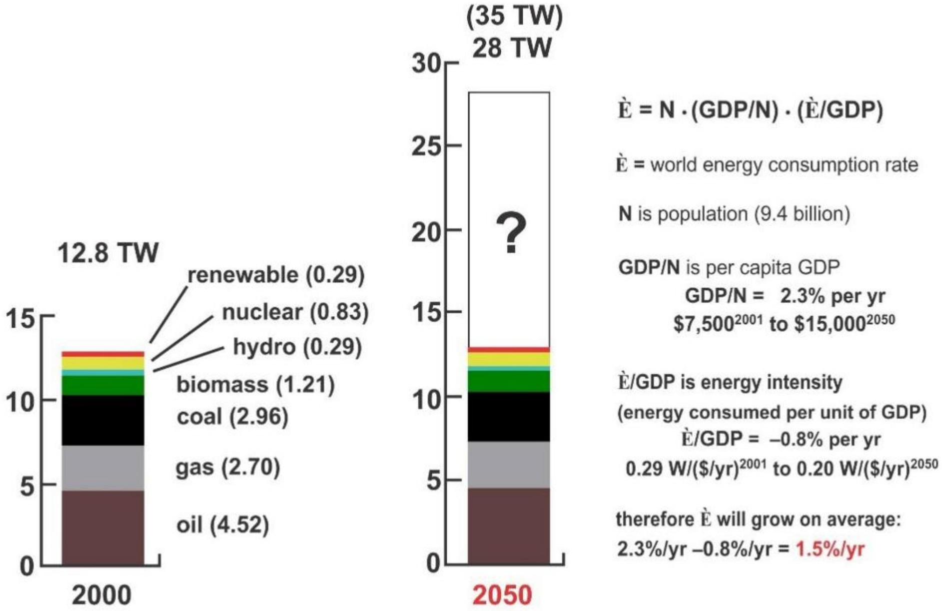

Figure 4. Global energy inventory [31–35].

The non-fossil energy alternatives such as nuclear and biomass cannot supply the today's energy requirement that is met from fossil fuels. Other than liquid fuels even if any other energy vector is produced from renewable energy sources like sunlight, that will disturb the present existing energy supply infrastructure leading to substantial consequences to the global economy. It was thought that, H_2 can replace the fossil fuels. But it could not because the today's main source of the most commercial H_2 is natural gas and for generating a unit of heat from H_2, more CO_2 is produced than directly burning that natural gas. The H_2 formed in electrolysis methods is expensive, and it cannot be compared with the cost of H_2 produced from natural gas via steam reforming of methane (SRM) process. At present, there is no method to produce H_2 from non-fossil fuel sources (e.g., water) using cost-effective renewable or nuclear energy sources. In fact, most of the strategies being followed for achieving this target are either environmentally unacceptable or are not feasible except those depend on fossil fuel based resources such as natural gas [55–59]. Since, the conventional nuclear power plants need uranium, which is limited and has always associated with the problem of radiation leakage that occurs sometimes due to natural calamities, hence, the solar energy is considered to be the only real non-fossil fuel renewable energy resource. It is estimated that in a fortnight, the surface of the earth receives the energy that is equal to the total energy that is present in the entire world's fossil fuel resources (10^{16} kW). The mean solar irradiance at normal incidence outside the atmosphere is 1360 W/m^2 and the total annual incidence of solar energy in India alone is about 10^7 kW and for the southern region, the daily average is about 0.4 kW/m^2 [56]. In every hour (Figure 5), earth receives solar energy that is equal to the entire world population requirement in a year [1]. Since, solar energy is clean, non-polluting, inexhaustible and carbon-free, there is no question of climatic problems.

In year 2004, the world's energy requirement was about 18 TW and it is expected that it will reach about 28 TW in the year 2030. The *Department of Energy (DoE),* USA, predicted that if the solar irradiance of 1% of the Earth's surface is converted into storable energy with 10% efficiency, it would provide a resource base of 105 TW that is equal to the several times of the estimated world energy requirement in the year 2050 [59]. According to Table 4, the amount of energy that could be extracted from wind, tides, biomass, and geothermal would be 2–4 TW, 2–3 TW, 5–7 TW, and 3–6 TW, respectively, in the same 2050 year [51,61]. Furthermore, society needs to be supplied with the energy continuously day and night. Although, the solar energy is enough, it is not available in the nights and on cloudy days. Hence, for continuous energy supply, it needs to be stored in a proper manner [60]. The most of the solar energy storage methods being practiced as on today are found to have low energy densities. The energy density by mass of compressed air (300 atm.), batteries, flywheels, super capacitors, H_2O pumped 100 m uphill are estimated to be ~0.5 MJ kg^{-1}, ~0.1–0.5 MJ kg^{-1}, ~0.5 MJ kg^{-1}, ~0.01 MJ kg^{-1}, and ~0.001 MJ kg^{-1}, respectively. The best suggested way for energy storage is converting electricity into liquid fuels [1].

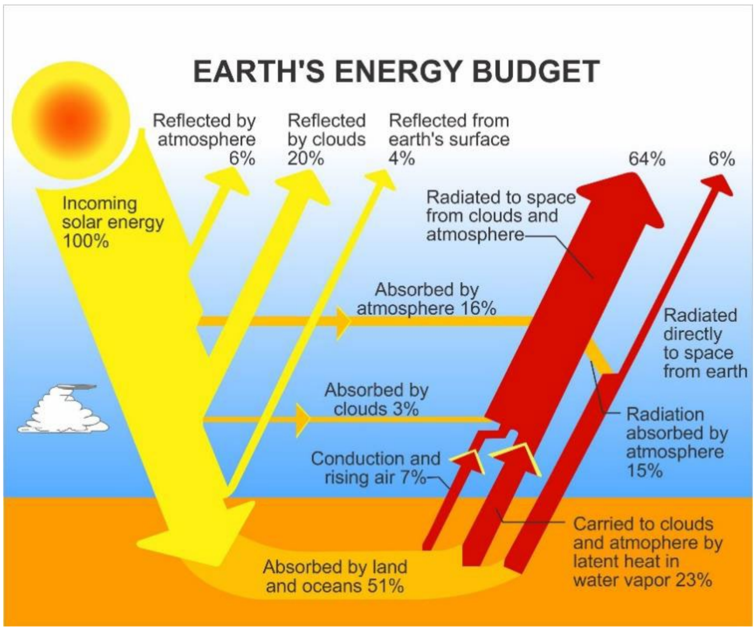

Figure 5. The amount of solar energy reaching the earth surface [1].

Among, various renewable energy resources such as, biomass, solar, wind, tides, hydro-based systems, etc., available today, except biomass all others produce electricity (Table 4) [1]. The production of liquid fuels from biomass has been identified to be quite laborious, and probably much research is still needed to find out a more economic and easier way [62–64]. Although recently, several technologies including silicon photovoltaic cell (SPVC) solar panels, solar thermal energy (Peltier/Seebeck modules), Fresnel lens based electricity generation, concentrated solar radiation, etc., have been developed for converting sunlight into electricity, there is a discontinuity between solar irradiation and power consumption during the year and in terms of geographical distribution. The same is true even for wind and tide based energy resources as well. Therefore, it is required to realize a suitable method to store and transport the solar energy in the form of a suitable chemical fuel. Using technologies available as on today, solar energy can be stored in the form of hydrogen by splitting water into H_2 and O_2 using electricity that is produced from sunlight (Eq. (1)) [65,66]. Although, certain methods such as, bio-chemical reactions (that use cyano-bacteria or green algae [67,68]), high temperature thermo-chemical reactions (that use concentrated solar radiation) [69–71], photoelectrochemical water splitting reaction and photo-electrolysis reactions [72–75], etc., produce H_2 at atmospheric pressure, eventually this H_2 needs to be compressed in a pressure cylinder that requires 40% of its energy for compression [1]. In view of these reasons, the reduction of CO_2 into CO or methanol could be more interesting for many of the prospective technologies in the renewable synthesis of carbon-containing fuels, as well as to address the problems associated with the CO_2 related global warming and energy storage. Recent research efforts have revealed that CO_2 could be converted in electrochemical cells using renewable electricity, hence, they can become efficient ways to the remediation of CO_2 associated global warming problem, and for alternative energy vectors production [4–7].

$$2H_2O + h\nu\ (\text{light}) + \text{semiconductor} \rightarrow 2H_2 + O_2 \qquad (1)$$

Furthermore, it is hard to depend only on electricity as the actual energy density of electricity storing batteries is too low for many energy-intensive applications as their capacity for storing energy per kilogram of weight or for the unit volume is only about 1% in comparison to gasoline's energy density [1]. Even if there is a breakthrough in the research of energy storing in batteries, the batteries energy storage do not meet many of the existing applications [52,59]. Besides these, batteries also have certain issues with respect to their cost, lifetime, recharge time, etc. Even if all the vehicles run with electricity in the future the demand for electricity would be increased by only <1% extra [53]. Of course, lithium ion batteries (LIBs) are indispensable today for portable device applications such as, mobile phones, laptops, etc., usage. Liquid fuels possess about 100 times higher energy density (~50 MJ kg^{-1}) in comparison to many of the available energy storage methods today [1]. Methods for carbon-neutral, sustainable and easy to scale-up fuel storage are being developed as alternatives to the fossil fuels. The International Energy Outlook 2010 reported that the world's total energy requirement will reach 739 quadrillion Btu in the year 2035 in comparison to 495 quadrillion Btu consumed in the year 2007 (i.e., 49% increase) [76]. Therefore, it is required to find out or to develop suitable methods to store and transport the solar energy in a properly usable manner [77–79]. Such energy storing methods are not only required for storing solar energy but also other renewable energies.

Based on today's available technology, solar energy can be stored in the form of H_2 and O_2 gases by splitting water using electricity that is derived from sunlight ($2H_2O$ + light = $2H_2 + O_2$; Eq. (1)) [65,66]. An advantage is that H_2 could be produced under pressure in modern electrolyzers, while other existing methods (bio-route using cyanobacteria or green algae [67,68], high temperature thermochemical one using concentrated solar energy [69–71], and photo(electro)chemical H_2O splitting or photoelectrolysis [72–75]) produce H_2 at atmospheric pressure, and they eventually require its compression for usage in any of its present applications. Recently, the different H_2 production routes and their advantages, perspectives, and limits have been reviewed in the literature [59,77,80], and discussed the general issues of renewable routes to produce H_2 [81–89]. Among all the methods available for producing H_2 from water, those depend on photovoltaic (PV) modules have been identified to be the best ones [59,79]. However, the energy density of H_2 gas is not suitable for several applications considering today's H_2 storage technology [82–90].

Figure 6 presents the energy densities of various materials such as, liquid fuels (from fossil or renewable sources), H_2 (gas, liquid, compressed or in storage materials), electrical energy (in conventional or new generation Li-batteries), etc. [59]. In fact, the practical applications require high energy densities per weight as well as per volume. In the case of light weight H_2 gas, energy density per volume is the main criterion. It can be clearly seen from Figure 6 that the energy densities of H_2 and electrical storage are far low in compared to those of liquid fuels based on fossil or renewable (biomass) sources [59]. Furthermore, H_2 gas usage requires large costs for a new energy infrastructure as it cannot be directly employed in the present existing energy infrastructure including in automobile vehicles (i.e., in internal combustion (IC) engines), thus not allowing a smooth transition from fossil fuel energy vectors to the non-fossil fuel energy vectors. Recently, several advantages and disadvantages associated with the existing H_2 production methods have been reviewed [59,77,80–89]. It has been estimated that about 40% value of the produced H_2 is needed to be spent for its compression into a pressure cylinder before it is used in any of its present existing applications. Among various methods developed so far for producing H_2 gas from water, the photovoltaic based technology has been identified to be more promising [59,79]. Furthermore, the energy density of H_2 gas is not suitable for most of the applications considering today's H_2 storage technology [82–90]. Thus, the production of liquid fuels (even if they are carbon-based) are preferable as they can be employed directly to replace the fossil fuels mainly diesel and petrol so that can be preserved for the future use, and global warming problem can be solved to some extent if CO_2 is used as a feedstock for forming these liquid fuels [87,91].

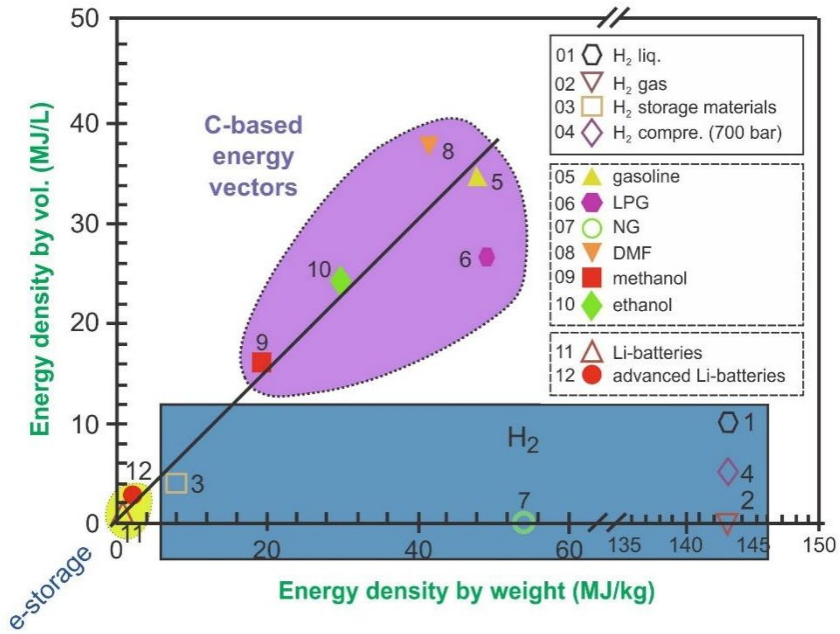

Figure 6. Energy density per weight vs. per volume in a series of liquid and gaseous fuels (from fossil sources, or renewable such as ethanol and DMF), H_2 (liquid, gas, compressed at 700 bar, and stored in advanced nano-material) and electrical energy (Li ion batteries, conventional and advanced). NG: natural gas; DMF: dimethyl furan; LPG: liquefied petroleum gas [59].

As direct H_2 storage, transportation and utilization have been associated with certain issues, it can be stored in the form of liquid chemicals such as, ammonia [59,91,92]. Ammonia selectively releases back H_2 gas over certain catalysts [59]. Ammonia can also be synthesized from H_2 produced from water hydrolysis using electricity generated from sunlight (using PV modules) by following well-established Haber-Bosch process. However, direct synthesis of ammonia from H_2 and N_2 gases using solar energy is yet to be mastered although the technology for this process has been very well developed by the nature. Nevertheless, ammonia is toxic and smells badly and it is potent greenhouse gas and causes severe constraints if it is leaked in the atmosphere. Further, there are certain risks related to BLEVE (Boiling Liquid Expanding Vapor Explosion) and UVCE (Unconfined Vapor Cloud Explosion). The current liquid fuels such as, gasoline, diesel, etc., fulfil all these requirements for suitable energy storage, except emission of greenhouse gases [1].

5. CO_2 Sequestration/Carbon Capture and Storage (CCS) or Carbon Capture and Utilization (CCU) Process, Which One is the Preferred One?

The *Intergovernmental Panel on Climate Change (IPCC), and United Nations Framework Convention on Climate Change (UNFCCC)* have declared that the burning of fossil fuels to meet the various energy needs of the society is responsible for the increased concentration of CO_2 gas in the atmosphere and for the resultant global warming and the social cost of carbon problems [1]. Several nations have signed and ratified both *Kyoto protocol 1997* and *Paris deal 2015* to cut short the CO_2 emissions into the atmosphere. To avoid further increase of CO_2 concentration into the atmosphere over the next few decades, improved actions than those of present should be taken to cut down the CO_2 emissions into the atmosphere. Today, the social cost of carbon has been estimated to be about 2000 US dollars per ton of CO_2 gas released into the atmosphere [93]. The atmospheric anthropogenic CO_2 concentrations have risen by 30% from pre-industrial (prior to 1750) levels of 280 ppm (parts per million) to 400 ppm today. The present CO_2 levels in atmosphere is higher than at any time during the last 6,50,000 years for which the reliable data was extracted from ice cores [94,95]. CO_2, a greenhouse gas, warms the planet's atmosphere and surface by absorbing and reemission of the infrared radiation of sunlight. The CO_2 associated greenhouse effect was first noted by Joseph Fourier in 1824 and was further substantiated quantitatively later on by Svante Arrhenius in 1896 [96]. The average global atmospheric temperature has been raised by 1.5 °C, and it has been attributed mainly to the raise of CO_2 concentration in the atmosphere. About 20% of ice has been melted away from the North Pole of our earth since 1979 in the arctic sea (Figure 7) [1].

Figure 7. The effect of anthropogenic CO_2 gas concentration in the atmosphere on earth climate change [1].

As of today, the readily available technology to tackle with the CO_2 associated global warming problem is the CO_2 sequestration process, which is also called as CO_2 capturing and storing (CCS) process. Figure 8 depicts a typical CCS (i.e., a man made sequestration) process, where the CO_2 captured at major out lets such as, thermal power plants, cement industry and gas refineries, is disposed-off in safe places such as, depleted coal seams, under deep sea water, etc. [1]. Most often, the CO_2 generating plants are far away from those sites normally used for *CO_2 sequestration* (*i.e., for CCS*) purposes. In certain places like those in Europe, transportation in pipelines to the storage sites is quite difficult and it will increase the cost of the process by at least 15–20%, which is considered to be unacceptable [1]. The *Department of Energy (DoE), USA,* suggests that the transportation of CO_2 in tankers on road is not acceptable if the distance is more than 100 km. In the total CCS process, about 35–40% is the transportation and storage costs. This cost would be between 35 and 50 €/ton for early commercial phase (after year 2020) and between 60 and 90 €/ton during demonstration phase, when transportation of CO_2 is made by pipelines for distances not over 200–300 km [1]. This cost would be further increased if the transportation is made by road (for example in certain European countries). Recently, Juerg Michael Matter et al. [97], from University of Southampton, England, reported a new process, which can also be considered as CO_2 sequestration process. In this latest process, when a mixture of water and CO_2 is pumped 540 meters deep into the Iceland rocks, this acidic solution causes the leaching of the magnesium (Mg) and calcium (Ca) metals out of the basalt rocks and converts them into $MgCO_3$ and $CaCO_3$ rocks. These latter rocks have been found to be stable for more than two-year period. The cost of this new CO_2 sequestration process has been estimated to be about 18 USD for disposing a ton CO_2 gas. In fact, CO_2 is a good source of C_1carbon, and it shall not be blocked under seawater in the form of solid CO_2 instead it shall be closed in natural carbon cycle. Nature does not store CO_2 in the form of solid CO_2 in seawater. Furthermore, it would be very expensive to sequester all the CO_2 generated across the globe at all the major outlets such as, thermal power plants, cement industry, steel plants and refineries (gas and oil), etc. as a waste, as there is no direct and immediate benefit to humankind upon implementing CO_2 sequestration (i.e., CCS) process to deal with CO_2 associated global warming problem. Given the exorbitant cost and labor intensiveness of today's CO_2 sequestration process, the other options such as, converting CO_2 back into value added industrial chemicals should be considered to protect the ecology from the dangers of anthropogenic CO_2 raise in the atmosphere [1,9,10,12–15,59,77,80,93,98–125].

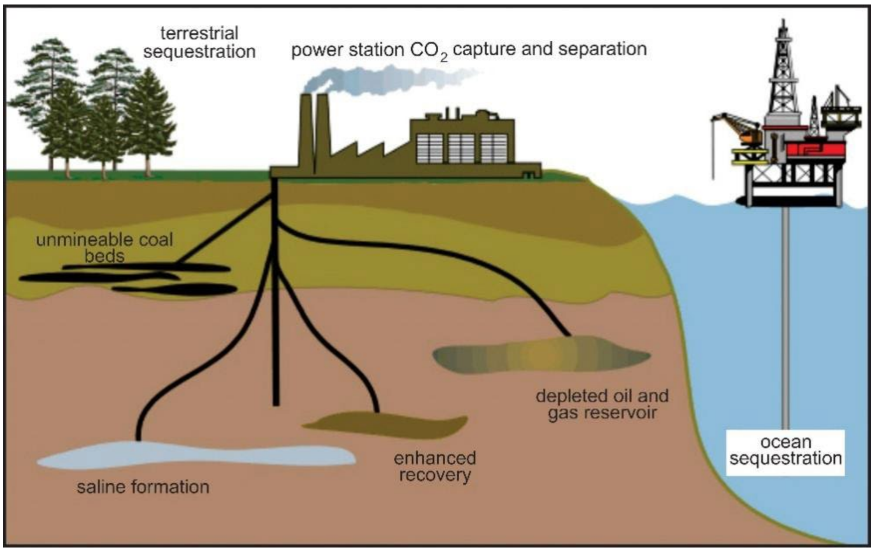

Figure 8. A schematic diagram showing the normally employed CO_2 sequestration processes [1].

According to IPCC as mentioned in above-paragraphs, fossil fuel burning and deforestation are responsible for increased CO_2 concentrations in the atmosphere. The civilization and industrialization have not only brought technology, modern life, and convenience to human life but also the pollution and emissions from factories, vehicles, and chemical plants. Several national governments have signed and ratified the *Kyoto Protocol* and *Paris Deal* of the *UNFCCC* aiming at reducing CO_2 gas emissions [94]. Recently, the *International Energy Agency* (*IEA*) in its latest *World Energy Outlook* (*WEO*) journal revealed that, based on policies being practiced at the moment, by 2030 CO_2 emissions will attain 63% from today's level, which is almost 90% higher than those of 1990 [94]. In the CO_2 sequestration process, CO_2 is reversibly adsorbed from a flue gas mixture into a 20 vol.% *aqueous monoethanolamine solution*, which releases back the CO_2 gas when heated at 80 °C. This process can be repeated using the same solution for about 1000 cycles with almost 80% efficiency [126,127]. At present, the CCS process is employed at almost more than 20 sites all over the world including USA and Europe [94]. The CO_2 captured at major outlets such as, thermal power plants, cement industry, etc., as a part of this

CCS process is transported and stored at safe places such as, depleted gas and oil reservoirs, coal seams, under deep sea levels, etc. [1]. As CCS process is expensive and laborious, and as it does not contribute to any of the beneficial activities of human life, there has been a quest for other alternative processes for scalable synthesis of carbon-containing fuels using renewable energy, H_2O, and CO_2. The reusing of the captured CO_2 as a renewable C_1 carbon resource can in fact contribute to a sustainable chemical industry, and as a consequence it reduces CO_2 emissions into the atmosphere [59,77,80]. CO_2 also has several direct applications in the industry such as a super critical fluid. In fact, the expenditure incurred for CCS process has been found to be sufficiently enough to convert the captured CO_2 into methanol following the thermo-chemical hydrogenation processes being practiced today at petrochemical industry [59,77,80]. This latter process can be considered as a part of *Carbon dioxide Capturing and Utilization* (*CCU*) process. The value of the product formed in CCU process could be considered as a bonus. Furthermore, if any of the renewable energy resources are integrated with these CCU processes effectively, it can indeed address the three major problems mentioned in the abstract simultaneously. Besides economic benefits, the socio-political benefits also come in terms of a positive image for companies adopting policies of utilizing CO_2 generated from fossil fuels [1].

The challenges for converting CO_2 into value added chemicals are great, but the potential rewards are also enormous [1]. Methanol, one of the products of CO_2 conversion processes, can be directly employed in place of gasoline and diesel smoothly in the present existing energy distribution infrastructure without any major changes, hence, there would not be any sever economic consequences while transforming from fossil fuel energy dependency to non-fossil fuel, renewable or solar energy dependency [1]. Methanol not only can be used as a direct fuel but also can be converted into products with high calorific value, such as, *dimethyl ether (DME)*, and other hydrocarbons (for e.g., synthetic petrol or gasoline). The additional advantages in producing methanol from CO_2 include (i) high energy density by volume and by weight; (ii) no need of high pressure to store methanol at room temperature like H_2 gas needs, (iii) safe to handle, and shows limited risks in its distribution (non-technical) use; (iv) no need to modify the internal combustion engines of the vehicles to use methanol; and (v) no impact on the environment during production as well as usage as methanol is a primary feedstock for many of the organic compounds synthesis, and is a vital intermediate for several bulk chemicals utilized in our day-to-day life such as, silicone, paint, formaldehyde, acetic acid, plastics, etc. [116,117,119]. Furthermore, methanol is a green fuel and has almost half of the energy density in comparison to mostly used gasoline fuel. At present, the most of the commercial methanol is produced from syngas that is a mixture of H_2, carbon monoxide (CO) and CO_2 on highly optimized $Cu/ZnO/Al_2O_3$ catalyst at temperatures up to 300 °C and pressured up to 100 bar, on large scale industrial plants in the order of several million tons per year [128]. The major drawback of the copper-based catalysts is sintering, which leads to severe deactivation. Besides this, the processes like, selective oxidation of methane, catalytic gas phase oxidation of methane, liquid phase oxidation of methane, mono-halogenation of methane, microbial and photochemical conversion of methane, etc., are also being employed to produce methanol [119]. All these processes can be replaced with CO_2 based process, if this latter process is suitably developed using any of the renewable energy resources as energy aid, and this process can save the natural fossil fuel resources. In this connection, methanol can be produced by hydrogenation of CO_2, according to Eq. (2) [1].

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \qquad (2)$$

Hydrogenation of CO_2 to methanol has been attracting worldwide research interest, recently, because of its positive environmental impact, and it is proposed as the basis of the so called *methanol economy*. However, a catalyst giving a high CH_3OH-to-CO ratio is required to make the process more feasible. Moreover, to achieve the *methanol economy*, methanol has to be produced in decentralized units, where a catalyst optimized for operating at low pressure is also required. Nevertheless, using water as a source of protons and electrons required to reduce CO_2 into value added chemicals including methanol could be a more promising route in comparison to the thermo-chemical hydrogenation of CO_2. Nature converts CO_2 into bio-energy *via natural photosynthesis* (*NP*) using exclusively solar energy and water as a source of protons and electrons. In NP process, somewhat less than 1% of the sunlight is converted into bio-energy in the form of plant materials, which when accumulated and transformed over geologic ages yielded fossil fuels [87,91]. In this connection, the *artificial photosynthesis (AP)* has a tremendous potential, and it is a scientific challenge, and upon successful development of it, the market would be gigantic [11–15,129]. Owing to CO_2's extremely stable nature, converting it back to a useful value added chemical in an endothermic reaction, on the same scale and with the same rate currently it is being produced is out of today's scientific and technological ability. However, a close study of the existing literature on this subject hints that the successful development of AP is no longer going to be an unrealistic dream [62,65,68,79]. Furthermore, this process could be developed quite efficiently in comparison to the NP [130–140]. For example, there are certain endothermic reactions which are being practiced at industry like production of syngas, H_2, methanol, etc., over certain metal oxide based catalysts in thermo-chemical routes in the petrochemical industry. A considerably great amount of efforts have been made to convert CO_2 into several industrially important chemicals following a great variety of methods in which different forms of energy has been utilized to drive this endothermic CO_2 reduction reaction to yield different kinds of value added chemicals, chemical intermediates and fuels [108,141–143]. On the other hand, the wide-scale implementation of solar and other renewable sources of electricity also requires improved means for energy storage [144–150].

Although, at present, the utilization of CO_2 volume is very meagre in the industrial sector, it is important to realize that several such small volumes can make a real considerable impact on the total CO_2 related global warming mitigation strategy [121,151–155]. CO_2 can be a feedstock to produce several useful chemicals. This in fact saves the money being spent for CCS process [156–159]. Furthermore, there are also several other considerable advantages if CO_2 is utilized as a chemical feedstock in some of the existing chemical processes. For example, (i) CO_2 is a renewable feedstock unlike oil or coal, (ii) CO_2 is an inexpensive and non-toxic gas, hence, it could be a substitute to replace several toxic chemicals such as, phosgene for isocyanates synthesis, (iii) production of chemicals from CO_2 can lead to all-new industrial productivity, and (iv) new routes to existing chemical intermediates and products could be economical than those of current methods [1]. Thus, the research on CO_2 conversion and utilization could be a proactive approach to the sustainable industrial and energy development. If the chemical activation of the inert CO_2 is achieved with only the required thermodynamic energy inputs without much of over-potentials requirement, there could be a boost for large scale industrial applications of CO_2 as a chemical feedstock. In the laboratory, a great variety of catalysts and methods have been employed so far to activate CO_2 to react with and form several value added chemicals. At present, the major chemicals being produced from CO_2 are *urea, salicylic acid, inorganic carbonates, ethylene/propylene carbonates, and polycarbonates* [160]. Furthermore, it is also used as an additive to CO in the production of methanol from syngas. Some of the major products produced from CO_2 industrially are shown in Figure 9 [160].

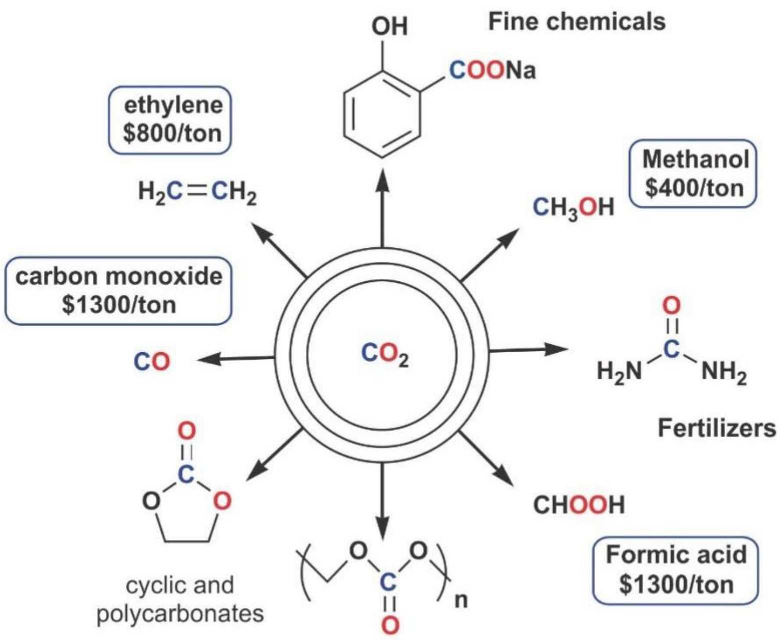

Figure 9. Carbon dioxide reduction to value added products [160].

The production of *sodium carbonate* (calcined soda) by the Solvay method consumes considerable volumes of CO_2. As on today, the annual production of *sodium carbonate* is about 30 million tons in entire industry. In the *salicylic acid* synthesis also, reasonably high amount of CO_2 is consumed. CO_2 is also employed in the carboxylation of phenol under pressure (*Kolbe-Schmitt* reaction). The co-oligomerization of unsaturated hydrocarbons and CO_2 results in the formation of various synthetic intermediates including *acids*, *esters*, *lactones and pyrones* [161]. The reaction of alkynes with CO_2 (to form 2-pyrones catalyzed by 3d metal complexes) is one of the few examples of a homogeneous catalytic reaction commercialized, which leads to the formation of C−C bond on CO_2 insertion. The variation of alkyne substituent could result into a wide variety of 2-pyrones [161]. However, the widespread use of CO_2, as a C_1 feedstock for the synthesis of methanol in the processes like electrochemical reduction of CO_2, needs a higher thermodynamic energy input (>1.5 V), hence, these processes will not be economical if fossil fuels are utilized as energy aid. This indicates the need of solar energy and judicious usage of catalysts for activating CO_2. Microalgae use solar energy to activate CO_2.

There are six types of reactions available for converting CO_2 into value added chemicals. The *stoichiometric reactions* [122,162–168], which are also called as redox, neutralization and spontaneous reactions, do not require any external energy aid as they utilize the internal energy (i.e., the chemical potentials) of the reactants to drive the reaction. Thus, the conversion of CO_2 in stoichiometric reactions cannot be considered as renewable energy production using CO_2 as a sustainable chemical feedstock. The *thermo-chemical* reactions [169–174], which consist both spontaneous as well as non-spontaneous reactions, utilize external energy in the form of heat to drive the reaction. As of now, these reactions are yet to be integrated with any of the renewable energy resources; hence, these reactions also cannot be considered as the development of renewable energy vectors using CO_2 feedstock. The *bio-chemical* reactions [107,175,176], which include algae production, mainly utilize sunlight, but the efficiency of this process has been found to be very less (<1%) not suitable for commercial practices without any government aid. Bio-ethanol is produced in this process. Unless, the efficiency of this process exceeds 10%, it cannot be practiced in a commercial plant economically. The photocatalytic reactions are associated with charge-separation problem [81,104,109,177–187]. Most often, the electrons generated upon irradiation of semi-conducting powder particles with light energy in the aqueous media normally attack the organic products formed in the reaction, instead of the reactant, CO_2; hence, the net efficiency of these process is always not encouraging. Although, the *photoelectrochemical (PEC)* reactions [157,188–194], yield highly reduced and selective CO_2 reduction products like methanol, ethanol, etc., at lower over-potentials, the instability of the involved semi-conducting electrodes has been found to be a major barrier for commercial practices as these electrodes often lose their semi-conducting property when they come into contact with aqueous solution due to severe photo-corrosion. The only option left with is the *electrochemical* reactions [110,160,193,195–204], which have been extensively studied, understood the underlying reaction mechanism to a great extent, and solved most of the associated drawbacks or bottle necks with this process. The recently investigated plasma-chemical conversion of CO_2 is also not found to be suitable for commercial practice based on today's state-of-the-art on it [205–209]. Very recently, nanoparticles have been employed as effective catalytic and cathodic systems in conjunction with *room temperature ionic liquids (RTILs)* in non-aqueous based electrolytes to electrochemically reduce CO_2 to CO with high faradaic efficiency (FE) and product selectivity at minimum overpotentials (<250 mV) [154,155,210–214]. It is a known fact that methanol ($CO + 2H_2 \rightarrow CH_3OH$) is produced industrially from syngas, and methanol is the starting material for producing gasoline. Today, syngas is produced from natural gas in a process called *steam-reforming of methane* ($CH_4 + H_2O \rightarrow CO + 3H_2$). The cost of CO is about 1300 USD/ton, which is highest in comparison to the cost of any of the CO_2 reduced products [160]. Furthermore, as CO is a gas, it does not need any extra efforts to separate it from the production mixture solution after completion of the reaction [1].

Among the above-mentioned reactions, the first two namely; (i) *stoichiometric* and (ii) *thermochemical* reactions are of exergonic in nature, spontaneous, and thermodynamically down-hill reactions owing to their negative ΔG ($\Delta G = \Delta H - T\Delta S$) values. These reactions meet their thermodynamic energy requirements to proceed from the internal energy available within the reactants in the form of chemical potentials (like acid-base neutralization reactions) as they are energy releasing (exothermic) reactions. However, these reactions need energy to cross the activation energy barrier while turning reactants into products according to the *Arrhenius'* equation; $k = Ae^{-Ea/(RT)}$; where, k is the rate constant, T is the absolute temperature (in Kelvin), A is the pre-exponential factor, a constant for each chemical reaction that defines the rate due to frequency of collisions in the correct orientation, E_a is the "activation energy" for the reaction (in Joules), and R is the universal gas constant [1]. Thus, these reactions can be considered for energy storage or renewable fuel synthesis purposes. Whereas, the remaining four reactions; namely, (i) *biochemical*, (ii) *photochemical*, (iii) *photoelectrochemical* and (iv) *electrochemical*, are not only considered for turning waste-stream green CO_2 gas into value added chemicals but also for storing electrical and (any) renewable energy in the form of chemical energy (as these reactions are energy consuming endothermic ones). Based on the available state-of-the-art today in the literature, among these four different types of reactions, only *electrochemical reduction of carbon dioxide (ERC)* can be considered for further development so that they can be taken to the industry for economically viable commercial practices [110,160,193,195–204].

6. Ocean Acidification and Nature's Response to Protect the Aquatic Life

A closer look at global climate change occurred over the past several decades indicates that the nature has its own way of dealing with the anthropogenic CO_2 gas being released into the atmosphere, and for protecting and safeguarding life in the ocean from the negative effects of increased CO_2 gas in the atmosphere [1]. The raise of CO_2 concentration in the atmosphere acidifies seawater (Figure 10) by releasing two-protons from water for every CO_2 molecule dissolved into the seawater when it comes into contact with water surface (3/4th surface of our planet is covered with seawater and only 1/3rd surface is covered with landmass, Figure 11) according to the reactions shown in Eqs. (3)–(9) [1].

$$CO_{2(aq)} + H_2O_{(aq)} \rightarrow H_2CO_{3(aq)}\ (K = 1.7 \times 10^{-3}) \quad (3)$$
$$H_2CO_3 \rightarrow H^+ + HCO_3^-(pK_{a1} = 6.363 \text{ at } 25\ °C\ \&\ I = 0) \quad (4)$$
$$HCO_3^- \rightarrow H^+ + CO_3^{2-}\ (pK_{a2} = 10.329 \text{ at } 25\ °C\ \&\ I = 0) \quad (5)$$
$$HCO_3^- + Na^+ \rightarrow NaHCO_3 \quad (6)$$
$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \quad (7)$$
$$CO_3^{2-} + 2Na^+ \rightarrow Na_2CO_3 \quad (8)$$
$$2HCO_3^- + Ca^{2+} \rightarrow Ca(HCO_3)_2 \quad (9)$$

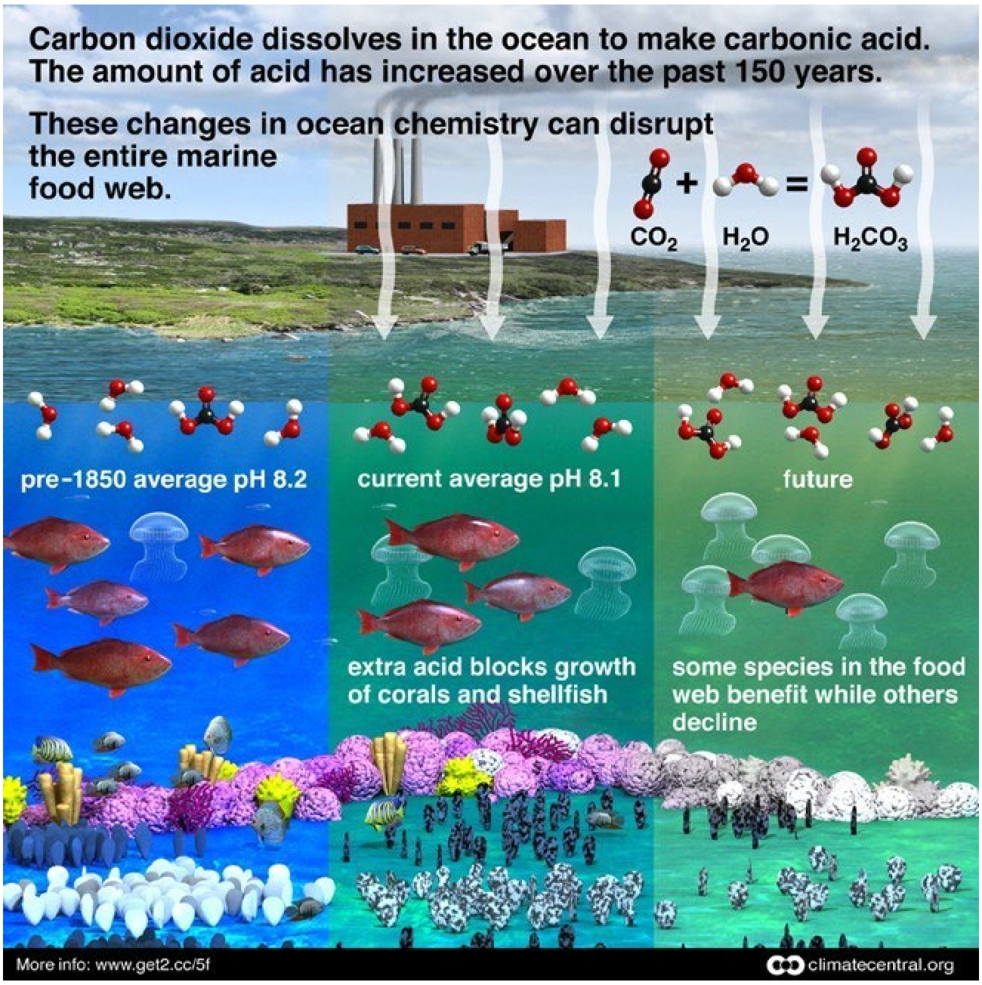

Figure 10. Ocean acidification [1].

Figure 11. An image of earth taken from Apollo 17 satellite [1].

However, at the same time, the increased concentration of CO_2 in the atmosphere causing melting of ice due to its greenhouse action and it is responsible for release of fresh water from ice melting into the sea; thereby, diluting or neutralizing acidity that occurs in seawater due to the dissolution of atmospheric CO_2 to some effect. Although, nature has its own ways of preserving certain life all the time on the earth from the dangers of human activities, it is the primary responsibility of human beings to stop further damage of ecology by stopping release of CO_2 into the atmosphere [1,93].

Today, the pH of the seawater is about 8.2. This pH is conducive for the dissociation of H_2CO_3 into bicarbonate (HCO_3^-) ion and proton (H^+) (Eq. (4)) as its acid dissociation constant (pK_{a1}) is only about 6.363 at 25 °C & ionic strength (I) of zero (0). According to *Henderson–Hasselbalch equation* (Eq. (10)), at a pH of 6.363 at 25 °C & ionic strength (I) of zero (0), the 50% of H_2CO_3 is dissociated into HCO_3^- and H^+ ions. Surprisingly, at a seawater pH of about 8.1, the dissociation of HCO_3^- into carbonate (CO_3^{2-}) ion also taking place (Eq. (5)), which requires a pH value of about 10.329 at 25 °C & ionic strength of zero. The proof for the occurrence of this HCO_3^- dissociation into CO_3^{2-} ion is the formation of coral reefs (Figure 12) [1]. It is a known fact that any solid object born out of a liquid must be spherical in shape due to the surface tension of that liquid. This is the reason most of the celestial bodies are spherical in shape indicating that when they were formed, they were in the state of liquid. The spherical primary particles of $CaCO_3$ coral reefs indicates that they are formed out of CO_3^{2-} and Ca_2^+ ions present in the seawater. This reaction can be considered as one of the unbelievable miracles of Mother Nature doing. The bio-catalysts (i.e., bacteria) present in the seawater performs the dissociation of HCO_3^- into CO_3^{2-} even at a pH of ~8.2, which will otherwise occur at a pH of 10.329 in the absence of a catalyst. However, if pH of the seawater further reduces to below 8.2, then the $CaCO_3$ shells undergo deformation (Figure 13) [1]. This dissolution of $CaCO_3$ shells present in seawater do not support the survival of certain aquatic life thereby disturb the complete food-chain of aquatic life in the seawater. This is the reason for the survival of life on this planet, the maintaining of the CO_2 concentration in the atmosphere in optimum levels is of utmost important [1]. The spherical structure of coral reefs primary particles confirm the *in situ* formation of $CaCO_3$ from dissolved ions, and it is a proof of dissolution of CO_2 into the sea water [1].

$$pH = pKa + \log_{10} ([A^-]/[HA]) \qquad (10)$$

Figure 12. Digital photographs of typical $CaCO_3$ coral reefs [1].

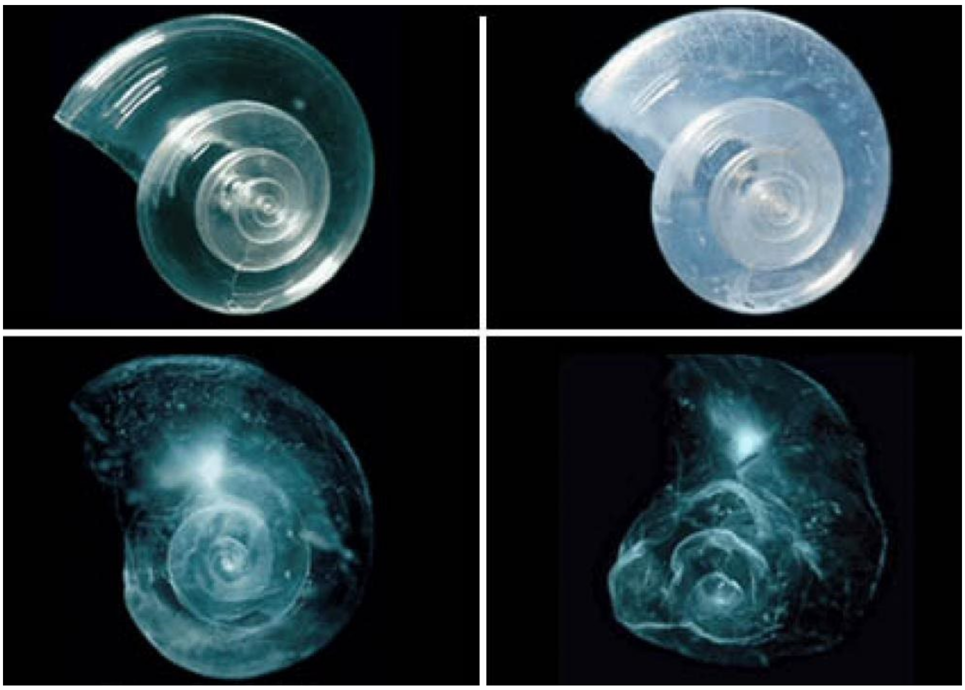

Figure 13. Ocean Acidification – the effect of acidification of sea water on marine life [1].

Over the last 250 years, ocean acidity has been increased by 30% as oceans absorbed around 530 billion tons of CO_2, which is equivalent to 500 years of CO_2 emissions occurred in the U.S. at current levels. The change in pH has troubled researchers in the recent years, as they predict ocean acidity will be more than double by 2100 if fossil fuels are burned at today's rate. The Polar Regions will be the first to undergo the most dramatic changes, as scientists forecast that the Southern ocean has the potential to become more corrosive with radically lowered pH levels by 2050. This change in ocean water pH causing harm to certain aquatic life [102].

7. Natural Way of CO_2 Sequestration in the Form of Natural Gas: An Assured and Sustainable Fossil Fuel

Higher the concentration of anthropogenic CO_2 in the atmosphere, higher will be rains as it causes evaporation of more amount of water from water bodies such as, ponds, rivers, sea, etc., by causing warming of the atmosphere as it traps infrared radiation. These more rains causes naturally increased amount of plants and crop growth by capturing CO_2 present in the atmosphere [1]. The bio-mass particularly the dried plant leaves are eventually transported by river water to seabed when floods occur, where these plant leaves are decomposed under anaerobic conditions to form natural gas below the high-pressures of huge water column of several tens of meters of height. Natural gas is nothing but methane clathrate ($CH_4{\cdot}5.75H_2O$ or $8CH_4{\cdot}46H_2O$), also called methane hydrate, hydromethane, methane ice, fire ice, natural gas hydrate, or gas hydrate, is a solid clathrate compound in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice [1]. Thus, the CO_2 present in the atmosphere is eventually stored at seabed in the form of natural gas but not as a solid CO_2. The man made CO_2 sequestration process can be a detrimental for certain aquatic life. There is a possibility that the solid CO_2 formed under deep inside seawater as a part of man-made sequestration process can get converted into CO_2 gas under certain unusual conditions, for example, during volcanos, etc., which can acidify the seawater [1]. Hence, it is not advisable to sequester CO_2 gas in the seawater. Instead it shall be converted into fuel chemicals using electricity derived from sunlight to drive this non-spontaneous energy consuming (i.e., energy storing) reaction in a process called carbon capture and usage (CCU) [1].

8. Can Dependency of Silicon Photovoltaic Cell (SPVC) Solar Panels Satisfy the IPCC and UNFCCC Impositions?

As a part of Germany's *Energiewende* program, the roof top silicon photovoltaic cell (SPVC) solar panels were deployed at every home by spending about 100 billion US dollars (i.e., Rs. 7,70,000 crores, when each USD is considered equal to Rs. 77/-) as a mission to stop using Nuclear energy to meet the energy needs of the society and to stop greenhouse CO_2 gas release into the atmosphere [215–220]. Since, none of these two targets were met, it is declared as a huge failure. According to *Energiewende* program website, "*until humans find a way to capture and store solar and wind energies to be used in a free standing facility without any back-up, renewable energy plans are just an expensive and faulty government experiments funded by public*" [221].

9. How the Practicable Artificial Photosynthesis (PAP) Process is the Only Option Available Today for Humankind to Solve the Problems Related Energy, Environment, and Economy Together?

The technology required to harvest the sunlight to meet all the energy needs of the society without any back-up from fossil fuels is yet to be developed. In fact, the energy present in fossil fuels is nothing but the solar energy stored by plant leaves in the form of food materials and bio-mass by using CO_2 and water as energy storing materials to feed human beings and animals living on our planet, Earth, in a *natural photosynthesis (NP)* process, which eventually got converted into fossil fuels over geologic ages [1]. When this solar energy storage is accomplished by human beings using manmade devices instead of plant leaves using the same CO_2 and water as energy storing materials, then this process is called as "*Artificial Photosynthesis (AP)*". However, performing such an *artificial photosynthesis* process using atmospheric CO_2 in thin devises like plant leaves with desired conversion efficiency is beyond today's human technological ability. In the NP process, the storage of solar energy in chemical bonds of food materials (i.e., carbohydrates) and bio-mass is carried out by plant leaves in three distinctly separate processes namely; (i) Conversion of sunlight into electricity, (ii) Splitting of water into protons (H^+), electrons (e^-) and molecular oxygen (O_2) (Photosystem-II) using electricity derived from sunlight by plant leaves, and iii) Reduction of CO_2 into carbohydrates and bio-mass using (H^+), electrons (e^-) derived from water (Photosystem-I), which occur simultaneously (bond-formation needs energy and bond-breaking releases energy). To drive the endothermic reactions of CO_2 reduction (*Photosystem-I*) and water oxidation (*Photosystem-II*) in NP process, the solar energy (i.e., sunlight) is utilized by the pigments present in plant leaves (Figure 14) [1]. Energy utilized to drive the thermodynamically up-hill reactions is nothing but energy storage, whereas, energy consumed to overcome the activation energy barriers is nothing but energy wastage. To avoid energy wastage in a particular reaction, the best catalysts, which drives the reactions in different pathways associated with lowest passible activation energy barriers, are normally employed. In fact, AP process can be performed with much more sunlight-to-chemical energy conversion efficiency by performing it in three separate experiments to carry out three processes of (i) converting sunlight into electricity initially, and (ii) reduction of CO_2 to value added and/or fuel chemicals, and (iii) splitting of water into H_2 and O_2 gases using electricity derived from sunlight to drive these two energy storing reactions separately. Plant leaves in NP process store solar energy at the rate of about 0.2% conversion efficiency. Even with such a low conversion efficiency, the nature is able to feed about 8 billion people and entire animals living on this planet. As already mentioned in previous paragraphs, the chemical energy present in the fossil fuels (i.e., in the form of crude oil, coal and natural gas) was also stored at the rate of 0.2% conversion efficiency only. When solar energy is stored at the rate of >10% conversion efficiency in the form of suitable chemical energy such as, H_2, O_2, CO, methanol, diesel, and gasoline using CO_2 and water as energy storing materials all the problems related to energy, environment and poverty can be solved vary easily. When all the energy needs of the society can be met by using solar fuels synthesized out of CO_2 and water using electricity derived from sunlight, then this process is referred to as the "*Practicable Artificial Photosynthesis (PAP)*" process [1]. In fact, people go to the farmland and fields to do cultivation (i.e., agriculture), which is nothing but storing of solar energy by following a natural process by using the zero energy containing CO_2 and H_2O as energy storing materials in the form of chemical energy (i.e., in chemical bonds of carbohydrates and bio-mass). This latter solar fuels can be preserved and used as and when required on a demand basis. Furthermore, every energy available on the earth surface is an indirect form of solar energy. Even wind blowing and raining are also caused by the actions of sunlight. The current state-of-the-art available in the society clearly indicates that the only practically feasible solution to solve the problems related to energy, environment and economy is to successful development of PAP process [1]. It is a known fact that, today, the development of a PAP process is considered as one of the top most research priorities across the globe as it can indeed solve the problems related to the (i) CO_2 associated global warming and the social cost of carbon, (ii) production of renewable carbon-neutral high-energy-density liquid fuels employable in place of petrol and diesel in the existing energy distribution infrastructure (i.e., in internal combustion (IC) engines) so that there would not be any severe economic consequences while transforming from fossil fuel energy dependency to non-fossil fuel, renewable and solar energy dependency, and (iii) depletion of fossil fuels mainly the important crude oil, which is resource of several commodity chemicals required for the future generations [1].

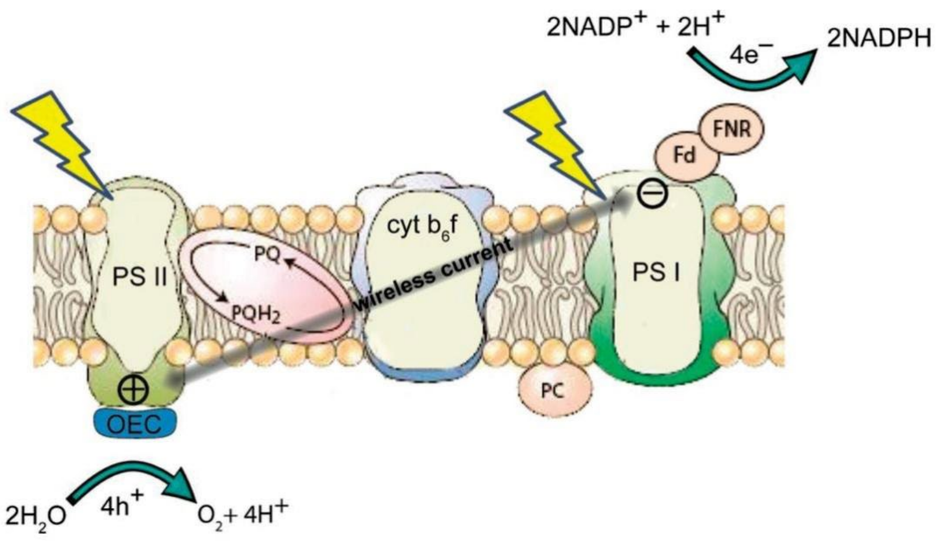

Figure 14. Photosystem-I (PS-I) and Photosystem-II (PS-II) reactions of *natural photosynthesis* [1].

10. Concluding Remarks

Today, the development of a simple, inexpensive and efficient process for producing electricity from sunlight, and use of that electricity to convert the waste-steam greenhouse CO_2 gas into energy rich fuel chemicals (i.e., solar-fuels), and to split water into H_2 and O_2 gases, has been considered as one of the top-most research priorities today across the nations as it can easily solve the problems related to (i) securing the self-sufficiency in energy production by each and every country, (ii) the CO_2 associated global warming, and the related social cost of carbon, (iii) the storing of renewable and surplus energy in an high-energy-density carbon-neutral liquid-fuels such as methanol so that they can be directly employed in place of diesel and petrol in the present existing energy distribution infrastructure (i.e., in the *internal combustion (IC)* engines) so that there would not be any severe economic consequences while transforming from fossil fuel energy dependency to non-fossil fuel, renewable and solar energy dependency, and (iv) depletion of fossil fuels mainly the crude oil, which is an important resource of several commodity chemicals required for the future generations [1,10,12–14]. Efficient sunlight-to-electricity conversion technology can eliminate up to 8–15% power transmission losses that are typically associated with the grid-connected electricity produced at remote places from the densely populated cities by burning fossil fuels (i.e., coal, natural gas and crude oil) at thermal power plants. In fact, as on today, the synthesis of liquid-fuels from CO_2, and, splitting of water into H_2 and O_2 gases using electricity derived from sunlight in electrochemical cells can be considered as one of the most effective, and economic way of storing energy to circumvent the daily and seasonal intermittency of solar energy as the energy stored in H_2 and O_2 gases can be taken back again as and when required on a demand basis using fuel cells [88,113,222–226]. Furthermore, today, the fossil fuels are the main resource to meet >85% of the primary energy requirement of all most all developed and developing countries except few countries including France, Island and Germany, and it was found to be responsible for raising concentrations of CO_2 in atmosphere and for the resultant global warming as well as for the social cost of carbon problems [59,77,80,146–149,227–230].

It is a well-known fact that nature stores solar energy to feed not only ~8 billion people living across the globe but also the entire life that lives on the earth surface by following the *natural photosynthesis (NP)* process [116,117,119,120,231–234]. The solar energy stored in the food grains can be preserved and used as and when required. They need not have to be used immediately like the electricity produced by using silicon photovoltaic cell (SPVC) solar panels, they can, in fact, be preserved. Furthermore, the amount of solar energy stored in a (sunny) day in the form of food material and bio-mass by plant leaves in the NP process cannot be stored in any of the existing energy storing devices including batteries and capacitors as it would be prohibitively expensive [59,80]. Nature clearly suggests that the CO_2 and water are the best energy storing materials, and by using them, any amount of (solar) energy can be stored safely to meet the energy requirements of the society while beneficially contributing to the environment, and this stored energy can be utilized on a requirement basis like fossil fuels are utilized today by properly and safely storing it [1]. It is also a well-known fact that the energy present in the fossil fuels is nothing but the solar energy that was stored by the plant leaves in the NP process long back. The energy present in fuel chemicals synthesized in *practicable artificial photosynthesis (PAP)* by using electricity derived from sunlight are exactly like those of fossil fuels. The major difference between the fossil fuels and solar fuels is that solar energy stored in the fossil fuels is long-time back, which causes global warming, whereas, the solar energy stored in solar fuels is now, that does not cause any global warming problem and this is the only difference [1]. Furthermore, harvesting of solar energy by following artificial processes can be performed with >10% efficiency (i.e., up to 5000 times higher when compared with the efficiency of natural photosynthesis process, which is only less than 0.2%). Hence, the entire energy distribution infrastructure available today (i.e., IC engines) to use fossil fuels can also be used for solar fuels formed in *PAP* process as well. Thus, the renewable solar liquid-fuel chemicals produced from CO_2 gas in *PAP* process can indeed replace the fossil fuels in all their current uses such as, powering of industrial processes, machinery and transportation, etc. [1]. In fact, the PAP process can establish a closed-loop CO_2 cycle that turns the conventional fuels into the "green energy vectors". Furthermore, the energy density of electricity storing batteries is far too low for most of the power-intensive applications (about 1–2%) in comparison to those can be stored in carbon-based fuels (50 MJ/kg with methane, methanol, diesel and gasoline) [59,80]. In fact, the e-batteries such as Li-ion batteries are best suitable, indispensable and opt for low-energy as well as low-energy density required portable devices such as, mobile phones, laptops, etc., but not for the transportation of heavy duty vehicles such as, buses, lorries, trucks, aero planes, etc., and to run a city having a demand for 500 MW with solar energy [1]. Furthermore, batteries also have certain limitations with respect to their cost, service life, recharging time, involvement of hazardous and polluting materials, etc..

Once a suitable and inexpensive method for converting sunlight into electricity is developed, and thus, obtained electricity is suitably utilized to convert the waste-stream greenhouse CO_2 gas into CO, and the water into H_2 and O_2 gases (Figure 15), all most all countries can generate solar energy in their own countries to meet their energy requirements without depending on foreign countries to import the fossil fuels while meeting all the deadlines imposed by *IPCC* and *UNFCCC* as far as environmental safety and release of CO_2 into the atmosphere are concerned [1,9–14]. Upon implementing such an PAP process worldwide, in about 10 to 15 years period, a lot of fossil fuels burned so far to meet the energy requirement of the society can be restored in the form of natural gas at all the sea shores across the globe as no CO_2 is freshly released into the atmosphere in large quantities, whereas, the already present CO_2 in the atmosphere is consumed by the plant leaves so that its concentration will come down to those levels (i.e., about 280 ppm) present in the atmosphere prior to the industrial revolution started during period of around 1750 to early 1800 century [1]. Once, this target is reached, the unseasonal and un-expected heavy rains and floods can be minimized, which disturb the functioning society for several days together in certain cities like those recently occurred in Chennai city in the year 2015, and Kerala in the year 2018 [1].

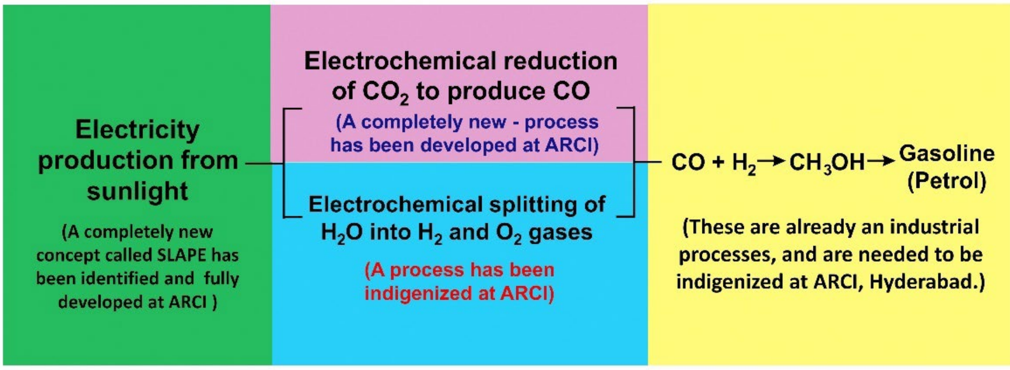

Figure 15. A schematic drawing showing the plausible route that can be used in an Artificial Photosynthesis (AP) process for producing solar fuels and/or carbon-neutral renewable energy vectors employable in the present existing energy distribution infrastructure using CO_2 and water as energy storing raw materials to mimic the natural photosynthesis (NP) process; SLAPE stands for semiconductor and liquid assisted photothermal effect [1].

In view of the above reasons, the development of a simple, easy to fabricate, and inexpensive method to produce electricity from sunlight, and using thus obtained electricity to drive the reactions of PAP is of utmost important to solve both the energy and environment related problems. For example, today, India alone has 118 thermal power plants, 220 cement industries, 650 steel plants (including those small scale industries), and 18 public sector refineries and five refineries in the private sector/or as a joint venture, the largest refineries being RIL Jamnagar (Gujarat), NEL Vadinar (Gujarat) and IOC Panipat (Haryana) [1]. All these industries together every day generate several million tons of CO_2 gas by burning fossil fuels such as, oil, coal, and natural gas to meet the energy requirements, and all thus generated CO_2 gas is released into the atmosphere. Once, an inexpensive and simple to fabricate device involving method to produce electricity from sunlight is developed to drive the reactions of PAP efficiently at lower processing cost, then by following that process all the generated CO_2 at major outlets across the globe can be converted into CO gas initially, and then into methanol, diesel and synthetic petrol [1,2,4]. The *IPCC* and *UNFCCC* are responsible for pledging 197 countries (as on December 2015) to take the responsibility to stabilize the greenhouse CO_2 gas concentration in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climatic system. Furthermore, for example, according to *IPCC* and *UNFCCC* by 2030, the *European Union (EU)* has to meet ≥27% of their primary energy requirement from the renewable energy resources, which ensures up to 40% reduction in *greenhouse gas (GHGs)* emissions in comparison to 1990 levels [235–239]. Today, EU gets about 50% of its primary energy from imported fossil fuels. In EU, the buildings are the leading consumers of energy (40%), ahead of transportation (32%), industry (27%) and agriculture (2%). Heating is at top of the consumption list accounting for 65% of domestic energy use [1]. As a result, 33% of the total CO_2 emissions in EU come from fossil fuels used for heating purposes only. Only ~17% of the total energy requirement is met by the electricity and out of which about 11.7% is met from hydroelectric power [1].

There are two ways to control the CO_2 associated global warming problem. One is to replace the fossil fuels usage with renewable energy vectors such as, solar energy, and the other one is to find out the solutions to solve the CO_2 associated global warming problem. Today, the readily available technology to solve the CO_2 associated global warming problem is the "*CO_2 sequestration*", which is also known as the "*carbon capture and storage (CCS)*" process. This latter process is not only expensive but also quite cumbersome. As a part of the CCS process, the CO_2 captured at various outlets such as, thermal power plants, cement industry, steel factories, gas refineries, etc., is transported and pumped mainly into the deep seawater below 3500 meters [240]. At 3500 meters deep in the sea, a pressure of >350 bar and a temperature of ~3 °C exist. When CO_2 is exposed to these conditions, it turns into CO_2 clathrate, which is a snow-like crystalline substance, composed of H_2O ice and CO_2. Nevertheless, its long term stability is still a debatable subject. It is also a known fact that the CO_2 capturing sites are most often far away from those sites normally used for CO_2 sequestration. The CO_2 sequestration processes are not only expensive and laborious, they also irreversibly blocks the important $\boldsymbol{C_1}$ carbon resource in the form of CO_2 cletherate in deep seawater, which cannot be used for any of the beneficial activities of the human beings [1]. In fact, the CO_2 shall be participated in the natural closed carbon cycle that is required for the sustainability of the life on earth [241,242].

Alternatively, CO_2 can be converted into several value added chemicals and fuels in a process called "*carbon capture and utilization (CCU)*" with the same expenditure that can be incurred for the CCS process [116]. Sometimes, the value of the product(s) formed in the CCU process can become a bonus as the cost of the products can offset the processing cost to some extent. It is also a known fact that CO_2 conversion into fuel chemicals needs thermodynamic energy input apart from those required for overcoming the activation energy barrier. In fact, the high thermodynamic stability of CO_2 is responsible for its ability to store the external energy in the form of fuel chemicals synthesized out of it [243]. Furthermore, the energy spent for overcoming the activation energy barrier is a loss; whereas, the energy spent for overcoming the thermodynamic energy barrier is energy storage. Thus, more amounts of thermodynamic energy requirement means more amount of energy storage in the form of products formed in a particular endothermic reaction. That is the reason why always researchers look for the best catalytic systems to perform a particular reaction to occur via a path that is associated with the least activation energy barrier. Lower the activation energy barrier means lower the amount of energy wastage while driving that particular thermodynamically favorable reaction. The high thermodynamic stability of water ($\Delta E° = -1.23$ V vs. NHE or 1.23 eV) is also responsible for its ability to store 1.23 eV energy in the form of H_2 and $½O_2$ gases formed out of it during an electrolysis of water. This same 1.23 eV equivalent electrical energy comes out again when these two gases are reacted in a fuel cell.

Even by replacing the usage of the *liquefied petroleum gas (LPG)* utilized for cooking with the electric stoves driven by electricity derived from sunlight, a significant amount of CO_2 gas generation can be avoided. Not only that now-a-days, even the cost of LPG gas has been increasing exorbitantly, and without the government aid or subsidy, it has become an unbearable cost for a common man living in India. In Telangana state of India, a 14.2 kg LPG gas cylinder costs about Rs. 1500/- without the Government subsidy, and with subsidy, it is about Rs. 950/- [1]. Even the petrol and diesel price is being increased now-a-days in India very exorbitantly. If all the CO_2 gas generated at all its major outlets in India alone is converted into synthetic petrol using electricity derived from sunlight, and used in place of petrol and diesel utilized today to meet the energy requirements, there would be a lot of reduction in the importing of fossil fuels from foreign countries [1]. This would ensure that during next few decades of time, a lot of fossil fuels burned so far to meet the energy requirements can also be slowly and but surely restored in the form of natural gas at all the sea shores. In fact, an inexpensive way of producing electricity from sunlight and using it for converting CO_2 gas produced at all its major outlets into fuel chemicals, and for splitting water into H_2 and O_2 gases can even change the global energy economy and energy dynamics of the world as well. In view of the above and to solve the CO_2 associated global warming problem, a simple, easy and highly economical method to produce electricity from sunlight, such as, the "*Semiconductor and Liquid Assisted Photothermal Effect (SLAPE) solar panels*" are highly essential [2,4]. Furthermore, to continuously supply the intermittently available solar energy to the society, it also required to be stored in a well usable form of energy. Fortunately, sunlight is abundant, clean, and free, and, all the world's population living areas also receive the required insolation levels (i.e., 150–300 watts/m^2 or 3.5–7.0 kWh/m^2 per day) [1]. With this insolation capacity, the required amount of electrical energy can be generated to meet all the energy needs of the society for buildings if a suitable PAP technology is developed.

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Conflict of interest

There is no conflict of interest for this study.

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