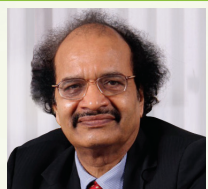


In Pursuit of The Net Zero Goal and Sustainability:

Hydrogen Economy, Carbon Dioxide Refineries, and Valorization of Biomass & Waste Plastic

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The overuse of fossil carbon including crude oil, coal, and natural gas during the past few decades is primarily responsible for the unprecedented emissions of carbon dioxide leading to climate change, global warming, floods and famines. The fossil carbon will all be exhausted in the foreseeable future bringing into picture the hunt for alternate sustainable resources for energy and materials. Global GHG emissions from fossil fuels and change in land use were

responsible for emissions of about 40 Gt CO₂-equivalent 2021. Since the industrial revolution, and particularly after the discovery of petroleum reserves, several billion tons of carbon dioxide have been released into the atmosphere and the concentration stands at 421 ppm (October 2022) with the USA being the topmost and China as the second largest emitters. India is at the third position according to the Global Carbon Project 2021. [1]. However, this scenario

will change in the near future as population rises and demand for energy and materials increases disproportionately and no superior technological advances are made. In its pledges - known as Nationally Determined Contributions (NDC) - India has assured that it will take steps to reduce the emissions intensity of its Gross Domestic Product (GDP) by 45% by 2030. The Paris Agreement of 2015 pledged that the nations of the world should restrict the global temperature rise



to less than 2°C and preferably below 1.5°C by adoption of new technologies, energy efficiency and alternate sources, and thus the plan for the net (carbon) zero emissions by 2050 was mooted [2]. In the COP26 held in Glasgow in November 2021, India committed to achieve the net zero goal by 2070 [3]. What is required is to promote carbon negative energy supply to attain the net zero goal at a faster pace.

It would be relevant to mention the Mission Innovation (MI), a global initiative of 23 countries, including the USA, China, Japan, the EU, and Saudi Arabia, which is meant to fast-track the global clean energy innovation to provide an opportunity for CO₂ utilization as Carbon Capture Utilization and Storage (CCUS). The annual rate of rise in atmospheric CO₂ concentration over the past 60 years is about 100 times greater than previous natural increases [4]. Modern societies are all accustomed to the fossil carbon-based economy- luxury, comfort,

longevity- which have revolutionized our lifestyle for more than a hundred and fifty years; however, alas, it has and will bring miseries too if we do not tackle the carbon dioxide emissions through technological interventions and innovations. The energy needs of the world are increasing day by day and the use of carbon-based fuels will continue to rise. To follow the requirements of international treaties, the use of renewable resources is advanced. The European Union revised its 2030 targets of reducing carbon dioxide emissions from 40% to 55% below 1990 level to achieve the net zero carbon goal by 2050. Whether the carbon is coming from fossil fuels, waste biomass, or biofuels, there is a dire need to convert carbon dioxide into fuels, chemicals, and materials to make a net-zero economy [5].

The world's economies are heavily dependent on carbon. It is predicted that by the middle of the 21st century, there may not be worthwhile petroleum reservoirs to be

exploited economically by using the current methods of production and hence alternate sources must be tapped for chemicals and materials, let alone energy. In the realms of renewable sources in 2050, 73% energy will come from renewables: solar, wind, geothermal, hydro, nuclear, and hydrogen. I believe in the carbon-negative scientific trinity: **Solar, Wind and Hydrogen** as green energy sources will be at the forefront, among which hydrogen will be the saviour of the environment and provide of sources chemicals and materials from waste carbon. Both blue and green H₂ will be part of the energy mix which will be about 25% by then [6]. Blue hydrogen is carbon neutral and not carbon negative. The green hydrogen and green ammonia policy declared by the Power Ministry of Govt. of India in February 2022, has envisioned that 50% of India's energy needs will be met by renewable sources by 2030. As regards carbon based chemicals and materials, CO₂ and (waste) biomass will be valuable sources if

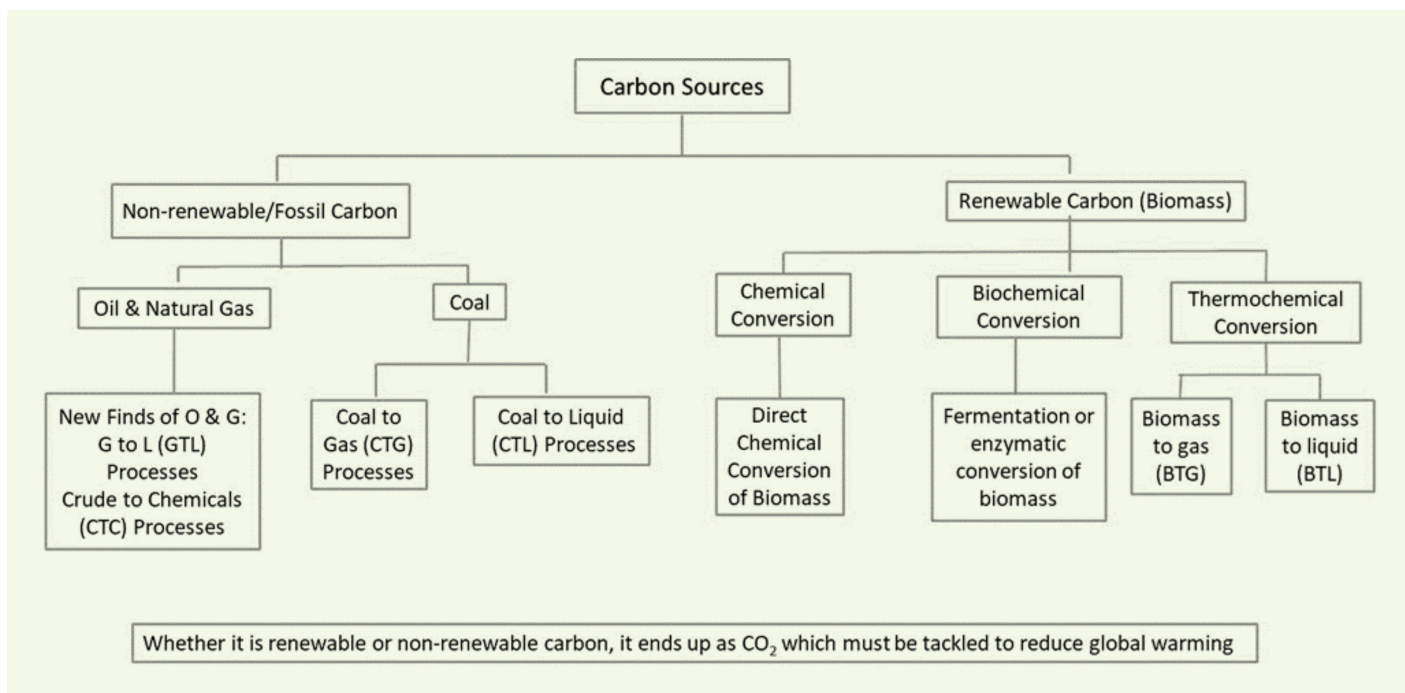


Figure 1. Carbon conversion processes to manufacture useful products. Carbon has been solely responsible for advancement in life style, comfort, luxury, transport, instant communication and longevity [5] (Open access, copy right with author of this article).

the hydrogen economy is adopted [7]. Not many realize that waste plastic is also an important source of energy, chemicals and materials and green technologies should be adopted and policies be in place to reduce the burden on the environment as well as to augment energy and material supply. Whether it is fossil fuel or renewable carbon source the fate of the carbon is ultimately carbon dioxide which must be dealt with to reduce global warming (Figure 1).

Hydrogen Production Technologies

Hydrogen can be employed as a fuel in many applications, including fuel cell power generation and fuel cell vehicles. It combusts cleanly, producing only water. The coal and oil-based economy for the manufacture of fuels, chemicals and materials is not sustainable and has done great harm to the environment. It is predicated that we will

run out of oil by the mid-2050s and new renewable sources of energy and materials are required. As stated earlier, the renewable energy share will rise to ~73% by 2050 in total of 49000 TWh [6]; however, coal will still play a role meaning thereby the need to hydrogenate CO₂. Thus, hydrogen share could grow from 2% of the global energy mix in 2018 to 13–24% by 2050, at ~ 8% CAGR at the mid-point. An investment of USD 150 billion by 2030 is predicted by the Hydrogen Council [8] and the European Union [9]. In the net-(carbon)-zero economy, green hydrogen will not only achieve the objective of converting CO₂ into fuels and chemicals, but also transforming (waste) biomass and waste plastics into fuels and chemicals. Thus, CO₂ and hydrogen are connected in more than one way for the protection of environment and provision of future stocks of chemicals and energy.

Hydrogen can be produced by water splitting or from any carbon source, fossil or renewable using steam reforming or pyrolysis. Steam reforming is accompanied by CO₂ emissions which will be different per ton of hydrogen depending on the source of carbon. (Figure 2).

Hydrogen production technologies are generally categorized into three types (sometimes five) such as grey hydrogen, blue hydrogen, and green hydrogen. Depending on the energy source and method, additional two categories are also mentioned in the literature such as Turquoise and brown hydrogen. The major difference among the grey, blue, and green hydrogen is that the hydrogen is produced using fossil fuels, non-renewable energy, and renewable energy, respectively. Electrolysis of water using clean electricity from wind, solar, hydro, or nuclear energy sources or thermochemical inorganic

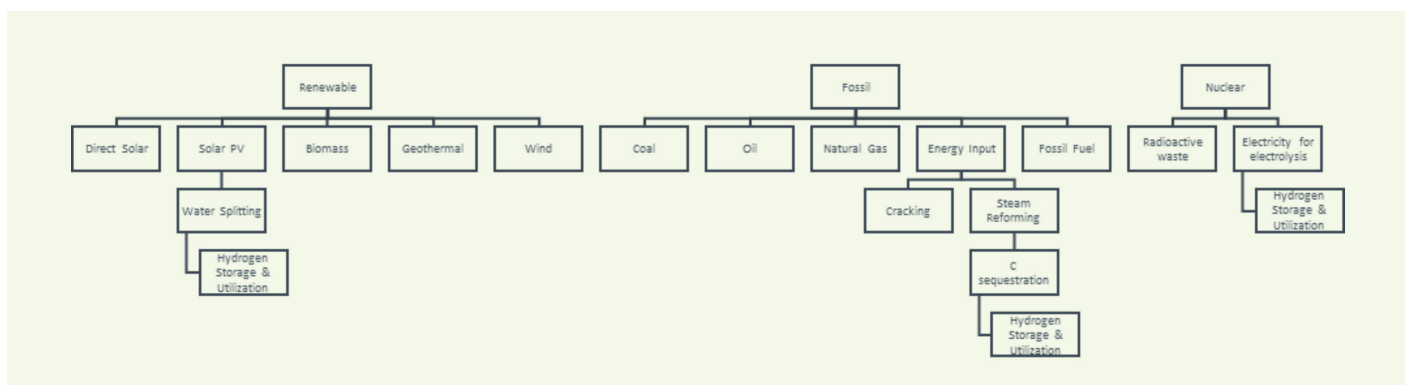


Figure 2. Hydrogen production methods from different sources

water splitting cycles such as copper-chlorine or sulfur-iodine will produce green hydrogen with zero carbon dioxide emissions. Steam reforming of virgin and waste biomass, biogas, bio-oil, or natural gas also gives hydrogen called blue hydrogen utilizing the other carbon portion in the feedstock as carbon dioxide which must be captured, stored and used (the so-called CCUS). It is estimated that blue hydrogen process captures up to 90% of the carbon having low to moderate carbon intensity as given in Table 1. The currently practised grey H₂ is the steam reforming of fossil coupled with co-generation of carbon dioxide; and this method is the most common technology which is increasingly unpalatable because of the emissions of carbon dioxide. In the Turquoise method methane pyrolysis is done to get hydrogen with the carbon being produced as carbon and not CO₂. Brown H₂ is produced from coal without CCUS.

Table 1 presents a comparison and approximate cost of production for 100 TPD of hydrogen production.

Type of Hydrogen	Brown	Grey	Torquise	Blue	Green	Green (ICT-OEC Process)
Source	Coal	Natural gas	Natural gas	Natural gas	Renewable electricity	Thermo-chemical
Process	Steam reforming	Steam reforming	Pyrolysis	Steam reforming	Electrolyzer Water splitting	Cu-Cl water splitting closed loop
Products	No carbon capture & storage	No carbon capture & storage	Hydrogen and carbon as co-products	Most carbon capture & storage	No GHG O ₂ as coproduct	No GHG O ₂ as coproduct
Ton of CO ₂ emitted per ton H ₂	19	11	0 (solid C as product)	0.2	0	0
Cost per kg H ₂ US\$	1.2-2.1	1-2.1	1	1.5-2.9	3-7.5	0.95 (credit of 0.9 for O ₂ not considered)

Table 1. Merits and demerits of different hydrogen production processes

The green hydrogen production by using electrolysis of water is currently not economical but hotly pursued by major players and governments. Based on the information provided by the Hydrogen Council [8], the International Energy Agency (IEA) [10], and Bloomberg New Energy Fund (BNEF) [11], the following statistics should give an idea of the hydrogen economy.

1. Electrolyser costs: 1100 US\$/kW (2020) to 550 USD/kW (2030), 220 USD/kW (2040).
2. The Institute of Chemical Technology (ICT)-ONGC Energy Centre (OEC) Cu-Cl thermochemical process is predicted to produce hydrogen at less than a dollar per kilo for 100 TPD capacity (author's own work on pilot scale).
3. Costs of CCS increases the costs of steam reforming of natural gas from 990 USD/kWh to 1850/kWh.
4. Low-carbon fossil-based hydrogen: Cost in 2030 from 2.5-3.0 USD in the EU,

5. Green hydrogen: USD 1.3-2.9/kg (Figure 3).
6. Target for solar electricity is to be cost competitive with the current fossil-fueled system.
7. If the cost of installed PV power can be reduced from the present cost of about USD 5/W installed to about USD 1/W installed, the cost of solar electricity is predicted to reach USD 0.10/kWh.

The ICT-OEC thermochemical Cu-Cl developed in this author's lab is a closed loop process with energy supply from solar energy stored in molten salts that promises to achieve '111' much before that [5, 7]. On the contrary, the steam reforming of fossil carbon likewise gives grey hydrogen coupled with co-generation of carbon dioxide; and this method is the most common technology used by many industries and it is cheap. However, it is gradually becoming unpalatable because of the CO₂ emissions. All refineries use grey hydrogen in eight of their conversion processes releasing huge quantities of CO₂. Hydrogen and ammonia (which on catalytic splitting gives green hydrogen and nitrogen) are envisioned as the future green fuels to substitute fossil fuels such as crude oil, coal and natural

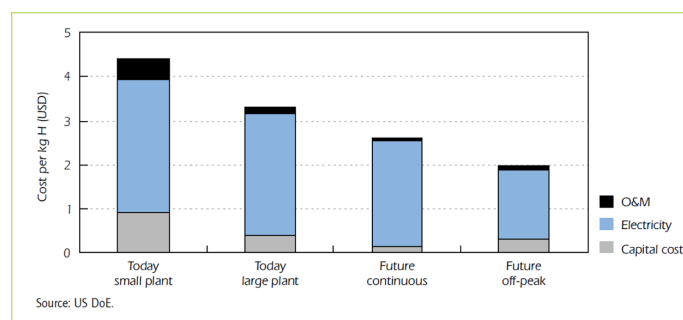


Figure 3. Hydrogen cost prediction of US Department of Energy [12]



Figure 4. Applications of green hydrogen in energy sector, CO₂ and biomass conversion

gas. Hydrogen economy will be a reality if the green hydrogen becomes as cheap as the grey hydrogen (Figure 3). Currently the clean hydrogen cost is in the range of ~\$2.50 – \$6.80/kg. The overall challenge to green hydrogen manufacture is its cost. US DOE's Hydrogen and Fuel Cell Technologies Office (HFCO) is working on developing technologies that will produce green H₂ at \$2/kg by 2025 and \$1/kg by 2030 via net-zero-carbon routes, in support of the Hydrogen Energy Earthshot goal of reducing the cost of green hydrogen by 80% to \$1 per 1 kg in 1 decade ("111") [12]. The various applications of green hydrogen are presented in Figure 4.

It is claimed by Haldor Topsoe that their high-temperature solid-oxide electrolysis cell (SOEC) permits to generate carbon-free hydrogen or carbon monoxide using renewable electricity [13].

Green Ammonia

While hydrogen has the benefit of high energy density on a mass basis, huge storage volumes needed for it, and limited existing infrastructure are viewed as a deterrent in the hydrogen economy. Therefore, ammonia is viewed to be a viable solution for transportation and storage of the fuel and crack it back to hydrogen at the user end.

Industrial production of ammonia is done usually by the so-called Haber-Bosch process, in which nitrogen from the atmosphere is catalytically coxed with hydrogen under high temperature and pressure. Currently, Ammonia manufacture across the world produces ~420 MMTA of CO₂, which together with hydrogen production, which accounts for 830 MMTA of CO₂; thus it is totally about 2% of GHG emissions per year. Green ammonia could make a substantial contribution to the decarbonization of agriculture through additional sustainable production of fertilizers. It can also assist in power generation or as a clean fuel for transportation, largely to power ships. Because of the much higher density of ammonia and its higher energy content, green ammonia lends itself to all applications of green hydrogen (Figure 5). The mass energy density of hydrogen is 120 MJ/kg vis-à-vis 18.6 MJ/kg for ammonia, hence its popularity as an alternative fuel. Although hydrogen is an energy carrier, the benefits of green ammonia might overwhelm those of hydrogen because ammonia is denser than hydrogen and needs to be compressed only to 10 atm or cooled to -33°C to store energy. On the contrary, hydrogen must be compressed to 350-700 atm or cryogenically cooled to -253°C as a liquid. Since NH₃ can be stored at lower temperatures, it is an ideal energy carrier. It is also suitable for storing and transporting energy from renewable energy

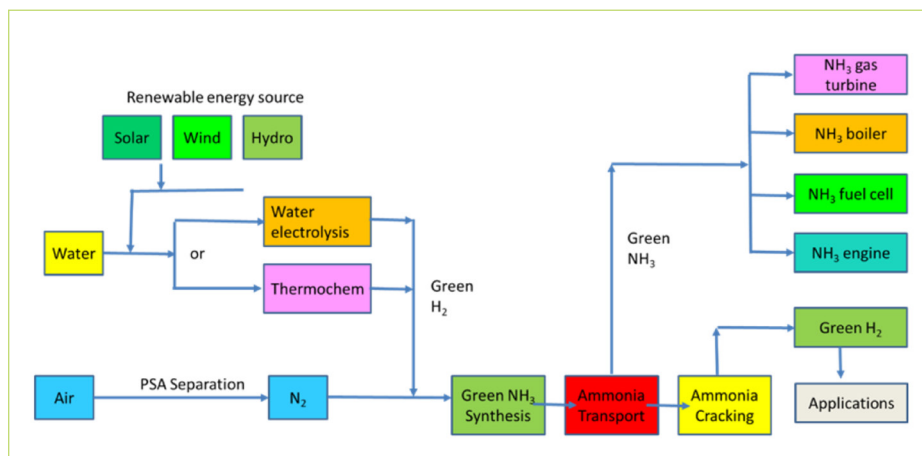


Figure 5. Synthesis and applications of green ammonia. Both water and air will be the feed stocks for green hydrogen and green ammonia.

sources [14]. Because ammonia is extensively used for fertilizers, there is already existing distribution network where ammonia is stored in large, refrigerated tanks and then transported by various means, such as pipelines and water which is also an advantage and could be used for green ammonia in the fertilizers sector, or if extended also in other ways (Figure 5).

Pitfalls of Fossil Carbon Based Energy Economy

Among all GHGs, carbon dioxide and methane are the principal constituents which contribute the most to the man-made GHG effect and climate change. Future processes or concepts that undertake this CO₂ reduction must consider the life cycle to assure that additional CO₂ is not released beyond what is already being removed from or going into the atmosphere. CO₂ sequestration is widely documented as an important choice to reduce increasing levels of its concentrations. CCUS technologies are viewed as a practical solution that involves recycling of CO₂ to various important industrial compounds, fuels and feedstock materials bringing to the core the synergism and innovations of catalytic chemistry, chemical engineering and technology, material science and biological sciences to alleviate climate change. However, CCUS technologies are criticized for permitting the continued use of fossil fuels.

In addition to the coal-based power plants, steel industry releases more than 3 billion metric tons of CO₂ each year, having the biggest climate impact. Currently China is the number one producer of steel and India is second; one ton of steel emits 2.3 tons of CO₂. To restrict the global warming, the steel industry must reduce its carbon footprint totally and make use of green hydrogen to produce green steel. The same argument holds for other metal industries. Much

attention has fixated on CO₂ but methane is a dominant and dangerous GHG. At the COP 26, over 100 countries signed up to the Global Methane Pledge to reduce global methane emissions by 30% by 2030. This includes six of the world's topmost 10 methane emitting nations like the USA, Brazil, EU, Indonesia, Pakistan, and Argentina and would account to a potential of 46% of global methane emissions and over 70% of global GDP, playing a critical role in keeping the goal of 1.5°C rise within scope [15]. Among all the anthropogenic GHG, CO₂ is largely responsible for global warming and climate change.

The sustainability of extravagant lifestyle of modern society requires gigantic quantities of energy which is primarily satisfied by the fossil resources. The concentration of carbon dioxide in the atmosphere increased from 280 ppm before the industrial revolution to 421 ppm in October 2022 [1]. The increased atmospheric CO₂ concentration is arguably one of the primary causes of accelerated climate change and global warming. This supply chain from fossil feedstock cannot sustain forever as all these energy sources will diminish within three centuries. From the economic point of view importing fossil fuel from foreign countries worth of billion dollars is a waste of foreign exchange for the marginal and developing economies having no oil reservoirs or coal deposits. For instance, a fast growing Indian economy imported 228.6 trillion tons of crude oil at US\$ 130 B in 2020 and the government wants to reduce import of oil by developing new technologies including renewable resources such as solar, wind, hydro, coal to fuels and chemicals, 2G ethanol, biodiesel, etc. India accounts for more than a quarter of the net global primary energy demand between 2017-2040 according to BP Energy [6]; 42% of this new energy demand is met through coal, meaning CO₂ emissions will roughly

double by 2040. The Paris Agreement 2015 is meant to reduce the risk and impact of global warming by adopting two long term temperature goals, i.e., to check the global average temperature rise well below 2 °C above pre-industrial level, and to take more deliberate actions to limit the rise in temperature to 1.5 °C above pre-industrial levels. To achieve this goal a 20/20/20 strategy was adopted, meaning thereby, 20% decrease in CO₂ emission, rise in renewable energy market share by 20%, and 20% increase in efficiency of current technology which calls for research and innovation. The share of the renewable energy will increase from current ~27% to ~51% by 2035 to ~73% by 2050 totaling 49000 TWh in which both green and blue hydrogen will have a substantial role [16].

Carbon Dioxide as the Future ‘New Oil’

Carbon dioxide is nontoxic, nonflammable and highly stable. Since it is produced by a number of power plants, refineries, fermenters, and other industrial processes, which are all contributors to the GHG related problems, CO₂ should not be treated as a liability but a great feedstock for preparing commodity chemicals, fuels, and materials by using innovative cost-effective catalytic processes. Since CO₂ is very stable, its activation is difficult requiring highly active catalysts. Carbon dioxide can be valorized while meeting the net zero goal and it will be the ‘new oil’. The future refiners will use carbon dioxide as a raw material for making fuels, chemicals, and polymers/materials, where green hydrogen will be the most important reactant.

As an economical, safe, and renewable carbon source, CO₂ turns out to be an attractive C1 chemical building block for making organic chemicals, materials, and carbohydrates (e.g., foods). The utilization of CO₂ as a feedstock for producing chemicals not only contributes to alleviating global climate changes caused by the increasing CO₂ emissions, but also provides a grand challenge in exploring new concepts and opportunities for catalytic and industrial development. Decreasing CO₂ concentration in the atmosphere while meeting the energy demands of an ever increasing population is a formidable task and requires long term planning and implementation of CO₂ mitigation strategies. Reduction of CO₂ production by shifting from fossil to renewable fuels, CO₂ capture and storage (CCS), and CO₂ capture, and utilization (CCU) are the possible areas for systematic control and reduction of atmospheric CO₂. Carbon Capture and Utilization and Storage (CCUS) is one of the key areas that can achieve CO₂

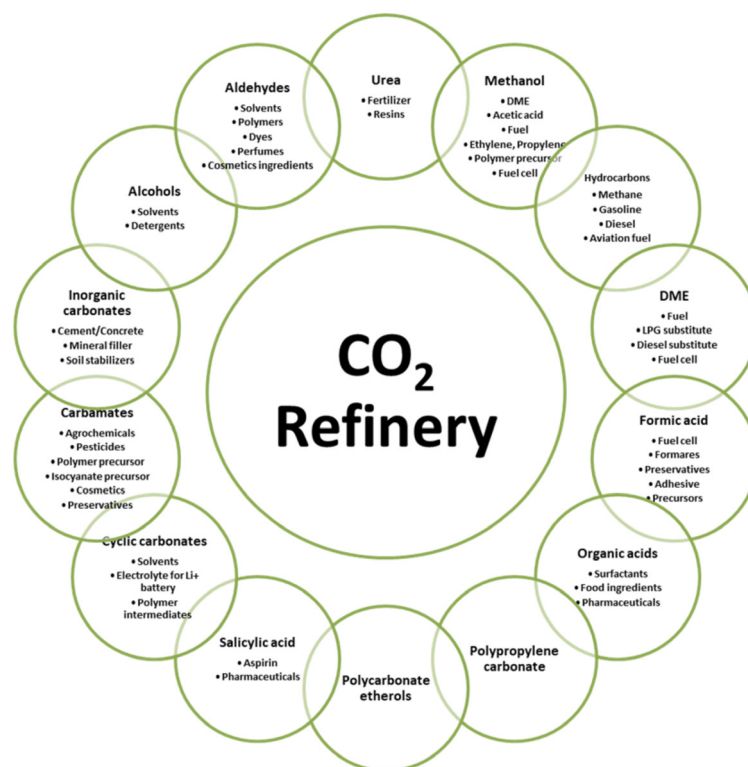


Figure 6. Carbon dioxide refinery: CO₂ as a feedstock for making a variety of products

emission targets while simultaneously contributing to the production of energy, fuels, and chemicals to sustain the increasing demands. In CCU concept, CO₂ is captured and separated from emission gases and then converted into valuable products. It is used to produce chemicals such as urea (75 million tons), salicylic acid, cyclic carbonates, and polycarbonates [17-20].

As of now, numerous CO₂ capture technologies related to physisorption, chemisorption, carbamation, amine absorption, amine dry scrubbing, membrane separation, and mineral carbonation have been practised. Therefore, CO₂ may turn out to be the future ‘new oil’ by catalytically converting it into synthetic fuels starting from the mixtures of carbon dioxide and hydrogen

with specific multiphase reactors. In that way CO₂ appears as one of the possibilities for high level energy storage, including the network regulation from renewable energy production. But, in each case, novel catalytic processes and plants are needed to develop this future industry. Flue gases from fossil fuel-based power plants are the main concentrated CO₂ sources. If CO₂ is to be separated, as much as 100 MW of a typical 500-MW coal-fired power plant would be necessary for today’s CCUS based on the alkanolamines absorption technologies [21,22]. Therefore, it would be highly desirable if the flue gas mixtures are used for vehicle CO₂ conversion but without its pre-separation. CO₂ conversion and utilization should be an integral part of CO₂ management, though the amount of

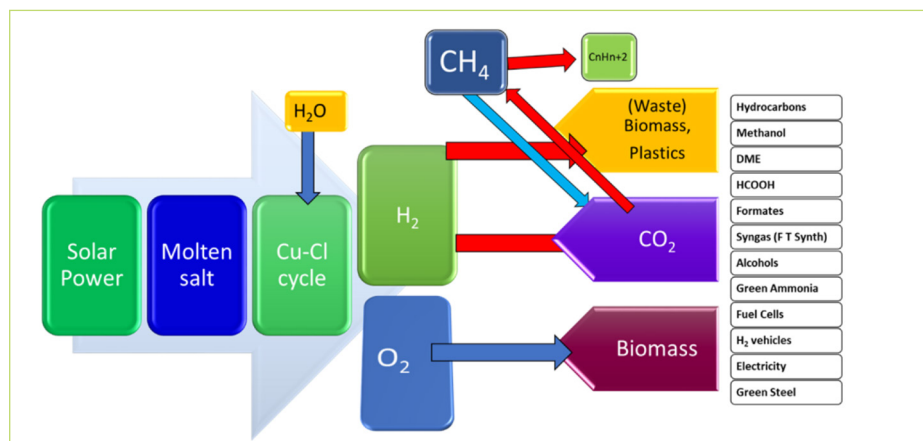


Figure 7. Carbon dioxide conversion to valuable commodity fuels and chemicals using green hydrogen developed in author’s lab by ICT-OEC technology [5,7].

CO₂ that can be utilized for making industrial chemicals is small vis-à-vis the amount of flue gas.

Bulk chemicals routinely manufactured from CO₂ include urea to make nitrogen fertilizers, salicylic acid as a pharmaceutical ingredient, and polycarbonate-based plastics (**Figure 6**).

However, carbon dioxide can be catalytically converted into methane and higher hydrocarbons, methanol, dimethyl ether (DME) and formic acid, and other formates as proved in the author's laboratory using hydrogen as also reported by other researchers (**Figure 7**). It forms a part of the hydrogen economy.

CO₂ also could be employed more widely as a solvent; for instance, the use of supercritical CO₂ provides benefits in terms of stereo-chemical control, product purification, and environmental factors for making fine chemicals and pharmaceuticals, for tertiary oil and gas recovery by CO₂ flooding, enhanced agricultural production, and ponds of genetically modified algae that can convert power-plant CO₂ into biodiesel [17,18, 23]. The extraction of CO₂ on gigantic scale including that from the atmosphere is a phenomenal task but it can be achieved by using novel catalytic technologies, process

intensification and multi-phase reactor design.

Flue Gas as Source of CO₂

On the basis of the economic and environmental viewpoints, there seems to be a unique benefit of using flue gases directly, rather than the pre-separated and purified CO₂. Typical flue gas composition from natural gas-fired power plants could be around: 8-10 CO₂, 18-20 water, 2-3 oxygen, and 67-72 nitrogen v/v %. Whereas a flue gas from coal-fired plants may contain 12-14 CO₂, 8-10 water, 3-5 oxygen and 72-77 nitrogen v/v %. The furnace outlet temperature of flue gases is normally ~1200 °C which will fall gradually along the pathway of heat transfer, while the temperature of the flue gases exiting to the stack is ~150 °C. Pollution control technologies can eliminate SO_x, NO_x, and particulate matter effectively, but CO₂ and water as well as oxygen remain largely unaffected [24]. Some important chemistries using CO₂ are given in **Figure 8**.

CO₂ conversion into gaseous or liquid hydrocarbon requires high temperature (523-723K) and pressure (20-40 atm), but the conversion is low due to problems in the activation of CO₂. Therefore, currently available technologies are not economically suitable for industrial application. Efficient heterogeneous catalysts can minimize the

energy needed for reactions by reducing the activation energy. A lot of literature exists on the utilization of pure CO₂ by different ways such as using plasma, photocatalytic system, electrochemical reduction, heterogeneous catalysis, etc. [26-30]. A few attempts have been made to develop continuous processes for converting carbon dioxide from flue gas to value-added products that are economical and have the potential to meet energy and material needs of the future. However, hydrogen plays an important part in CO₂ valorization and carbon sequestration.

The reduction of CO₂ emissions of ~40 Gt in 2021 to ~10 gigatons will contain the global temperature to within 1.5 °C by 2050 [6]. For hydrogen to contribute to mitigate climate change and climate neutrality, it must attain much larger scale of production, totally derived from water splitting using green technologies. The hydrogen economy must overcome many challenges including large-scale infrastructure for refilling stations of hydrogen, akin to those of petrol, diesel and natural gas, and the cost of hydrogen production, transport, and storage must be low. These challenges can be surmounted collectively by multiple partnerships among companies, nations, and research across institutions, and above all local government policies [8]. Green hydrogen must cost below 1.5-2 USD/kg to make the hydrogen economy a reality. As mentioned earlier, the cost of hydrogen production by Institute of Chemical Technology- ONGC Energy Centre (ICT-OEC) hydrogen production technology, developed by this author using water splitting in conjunction with solar energy is less than USD 1/kg [7].

One of the issues of using carbon-based technology, whether renewable or fossil, is the emission of CO₂ which can be valorized by using hydrogen into a few chemical products such as methane and higher hydrocarbons, methanol, dimethyl ether (DME), formic acid, formates, carbonates, ammonia, urea, etc. DME is the cleanest, colorless, non-toxic, non-corrosive, non-carcinogenic and environmentally friendly chemical replacing CFC. DME can be effectively used in diesel engines. Like methanol, it is a clean-burning fuel and produces no soot and black smoke. DME is the best substitute for LPG as a cooking fuel and the well-established LPG industry infrastructure can be used for DME [31-33]. Hydrogen can serve as a vector for renewable energy storage in conjunction with batteries, guaranteeing as a backup for season variation. To help limit global warming, the steel industry will need to shrink its carbon footprint significantly. Thus, hydrogen can substitute fossil fuels in some carbon intensive industrial processes,

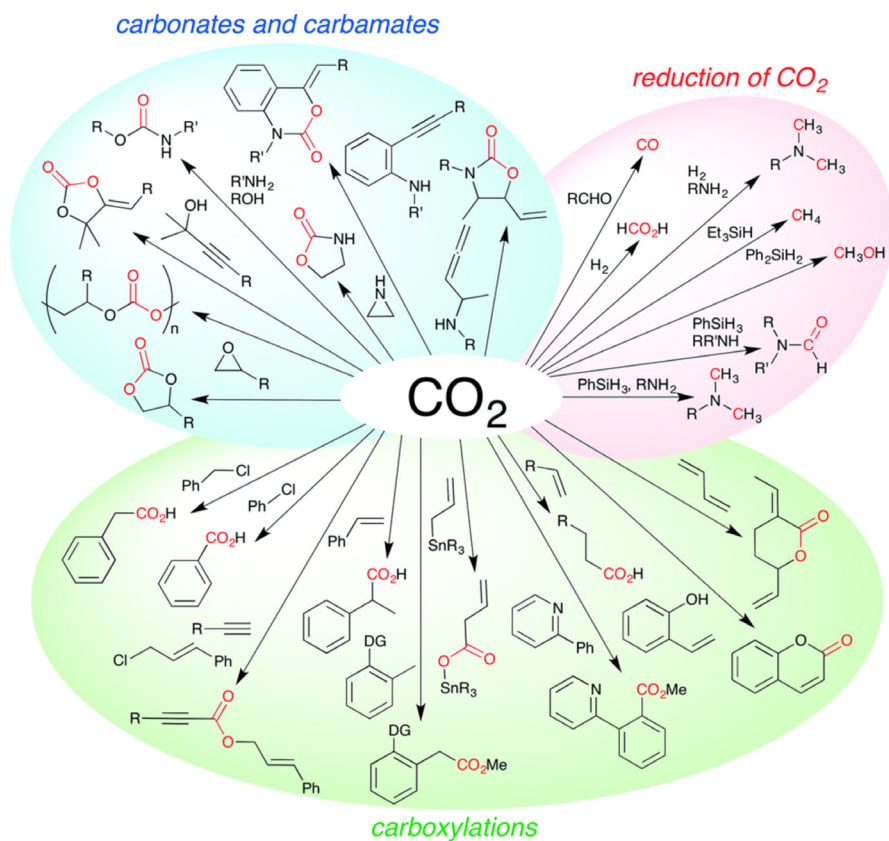


Figure 8. Schematic representation of possible usage of CO₂ for fuel and chemicals [17,18, 25]

such as steel, nickel, chemical and allied industries. It can present solutions for difficult to abate parts of the transport system, in addition to what can be accomplished through electrification and other renewable and low-carbon fuels.

Biogas as Source of CO₂

Biogas, typically containing 50-75% methane and 25-50% carbon dioxide is produced by anaerobic fermentation from almost all types of biomass, including wet biomass, (which is not usable for most other biofuels), vegetable and animal livestock waste, manure, harvest surplus, oil residues, municipal solid waste (MSW), etc. It is gaining significant industrial attention as a renewable source of carbon. Conventionally, after purification, biogas can be directly combusted for heat and electricity generation, yet the heat value of such combustion processes is low due to the high concentration of CO₂ in the feed gas. From an efficiency point of view, syngas production by biogas reforming with a H₂/CO ratio close to one is an appropriate option for the full utilization of both CH₄ and CO₂ in biogas for several industrial applications. Depending on the molar H₂:CO ratio in the reformed bio-syngas, it can be directly applied as a feedstock for the production of methanol, dimethyl ether (DME), long hydrocarbon chains via Fischer-Tropsch (FT) process, or NH₃ synthesis by the Haber route.

Another incentive for using gaseous biofuels for transport applications is the prospect to diversify feedstock sources. Biomethane, also called renewable natural gas (RNG), or sustainable natural gas (SNG), which is separated from biogas, is the most efficient and clean burning biofuel available today. Biomethane is upgraded to a quality like fossil natural gas, having a methane concentration of 90% or greater, by which it becomes possible to distribute the gas to customers via the existing gas grid within existing applications. Furthermore, it is very promising to use biogas containing carbon dioxide as the co-reactant for methane conversion in the so-called dry reforming process [34], since carbon dioxide can provide extra carbon atoms for methane conversion, while carbon dioxide also serves as a better oxidant, compared to oxygen or air. The co-feed of carbon dioxide will also increase the methane conversion and the yield of objective product. However, the introduction of carbon dioxide into the feed will lead to a complex product. In addition to syngas, gaseous hydrocarbons (C₂ to C₄), liquid hydrocarbons (C₅ to C₁₁₊) and oxygenates can be produced in methane conversion with the co-feed of carbon dioxide. The liquid hydrocarbons are highly branched, representing a high-octane number, while oxygenates mainly consist of a series of alcohols and

acids. The development of a production technology for direct conversion of methane and carbon dioxide to higher hydrocarbon and oxygenates using novel catalytic system will probably be more economically desired [35]. It is also important to note that carbon should not be used as a source of fuel but chemicals and materials and all non-carbon sources of energy such as solar, wind, geothermal, tidal, and nuclear and above all hydrogen from water splitting will meet the requirements of the Paris Agreement [5].

(Waste) Biomass as precursor for Chemicals and Materials

Biomass is a renewable energy source having sufficient energy value per unit mass, but which is lower than that of fossil fuels. Hence biomass must be valorized to produce biofuels (in solid, liquid, and gas forms such as methane and hydrogen) for sustainable development and green hydrogen from water splitting will play the most important role.

Worldwide attention is focusing on the use of lignocellulosic biomasses for the sustainable production of biofuels and bio-derived

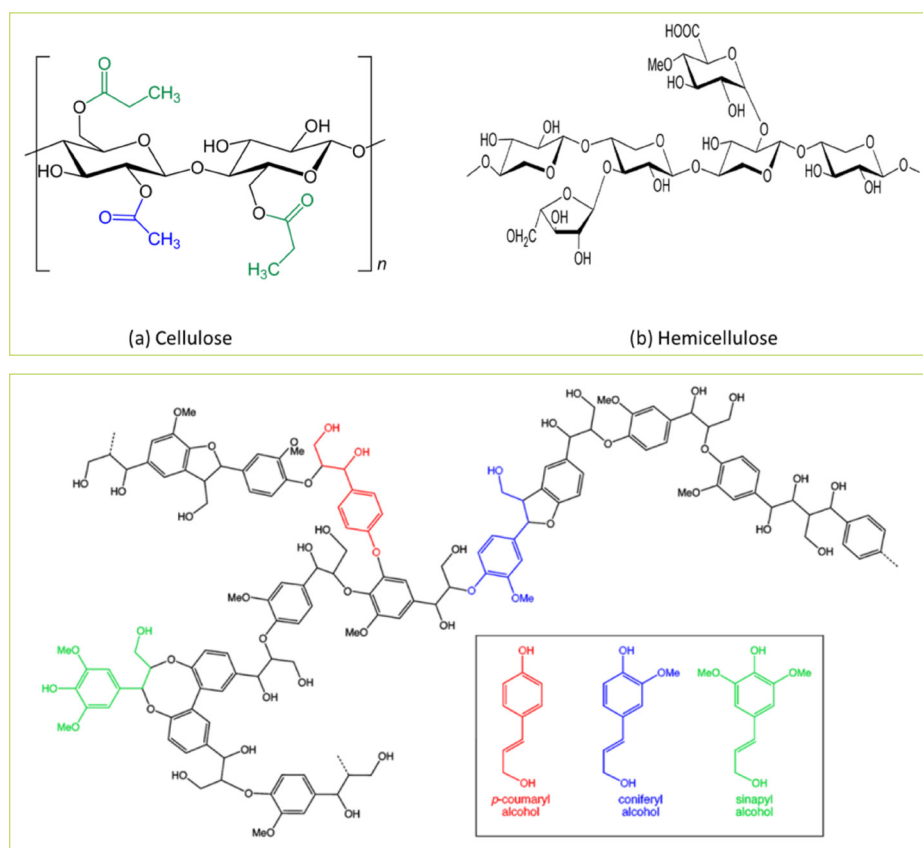


Figure 9. Basic structure of biomass as precursors of different chemicals which can be manipulated through catalytic processes such as hydrogenation/hydrogenolysis, dehydrogenation, oxidation, condensation, hydrolysis, hydration, isomerization, dehydration, esterification, alkylation, dealkylation, oligomerization and demethoxylation

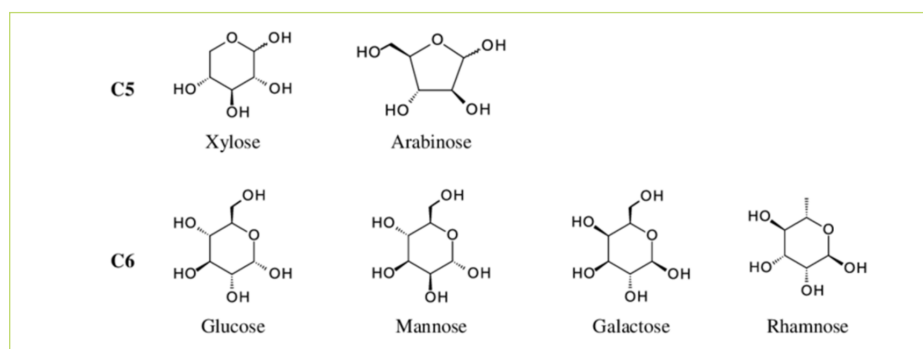


Figure 10. Common C5 and C6 sugars found in hemicellulose which are precursors to a number of chemicals

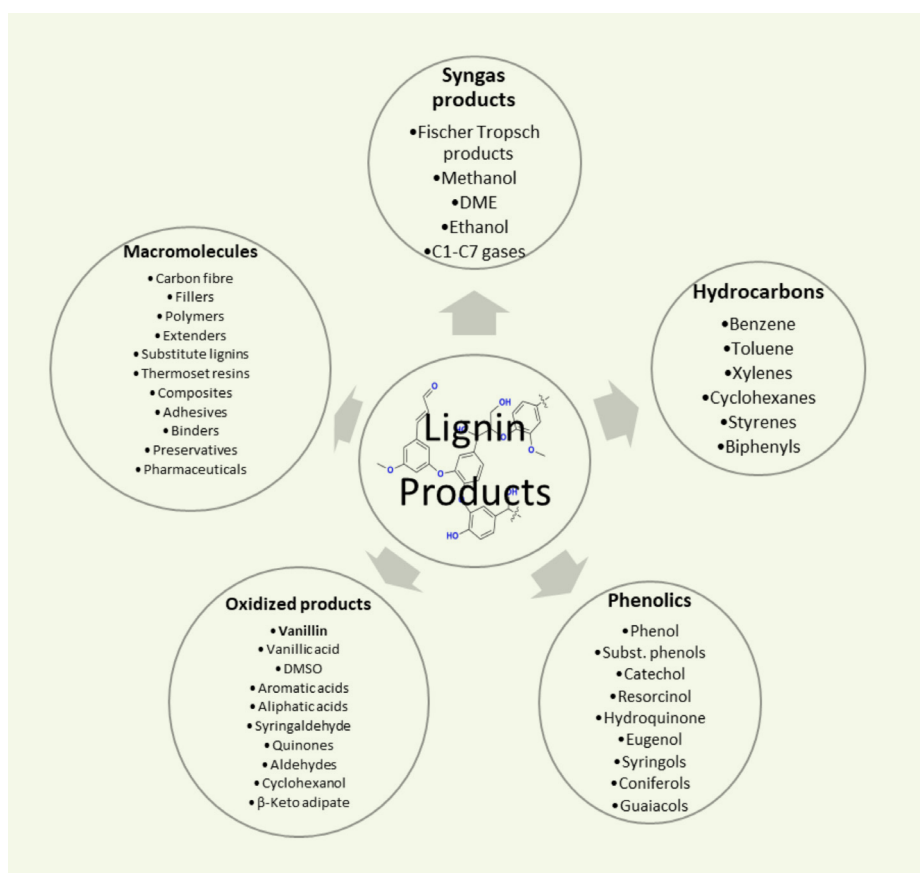


Figure 11. Lignin based valuable products

Table 2. Most important platform chemicals derived from biomass [5,38].

BPM	Structure	BPM	Structure
Fumaric acid		(<i>S,R,R</i>)-Xylitol	
Glycerol		3-Hydroxypropionic acid	
L-Glutamic acid		3-Hydroxybutyrolactone	
Itaconic acid		2,5-Furandicarboxylic acid	
Glucaric acid		Sorbitol	
L-Malic acid		Succinic acid	
Levulinic acid		L-Aspartic acid	

chemicals. The key components of biomasses (cellulose, hemicellulose and lignin) that have the potential for the sustainable production of several building block intermediates for modern bio-refineries. Cellulose and hemicellulose are mainly formed of C6- and C5-sugars, respectively, while lignin is mainly composed by phenolic units. Such a wealth of chemical functionalities represents, at present, the most promising alternative to petroleum resources.

A variety of chemicals can be derived from lignocellulosic biomass, whether waste or purposely grown, the structures of cellulose, hemicellulose and lignin suggest several catalytic processes can be used to depolymerize and make fuels and chemicals (Figures 9, 10 and 11). The importance of green hydrogen is clear since hydrogenation/hydrogenolysis, dehydrogenation and oxidation are needed to make bio-based highly valuable chemicals [5]. Other important chemicals can be derived through condensation, hydrolysis, hydration, isomerization, dehydration, esterification, alkylation, dealkylation, oligomerization and demethoxylation [36, 37]. The 14 top platform

chemicals derived from biomass are listed in Table 2.

Many agricultural waste are being produced in all countries that could be converted into biofuels using various treatment and production methods like thermochemical conversion (combustion, gasification, pyrolysis, hydrothermal liquefaction), biochemical conversion (anaerobic digestion, microbial fermentation, enzymatic hydrolysis), and chemical treatment (biodiesel production, transesterification).

Pyrolysis of biomass produces hydrocarbon gases, liquid bio-oils and porous biochar. Biochar could be employed in farms to hold nutrients and water. Biochar can also be used as a green binder to bind urea together to make a fertilizer. Steam reforming of bioethanol will give blue hydrogen. Other biomass derived chemicals like methanol, butanol, ethylene glycol and glycerol (from biodiesel) are important sources of blue hydrogen. Hydrogen production from biomass is a promising bio-energy with carbon capture and storage which is a blue hydrogen that could produce low-carbon hydrogen and generate the carbon dioxide removal envisioned to be required to offset hard-to-abate emissions.

Sustainable biomass feedstocks, namely, agricultural residues and waste will have negligible bearing on food security and biodiversity. The blue hydrogen manufacture from (waste) biomass or bio-derived alcohols represents a neglected near-term opportunity to generate CO₂ removal and low-carbon hydrogen. Hydrogen can aid to

decarbonize difficult-to-electrify areas, store energy from irregular renewable power, and be implemented as a chemical feedstock. However, the grey hydrogen is made from fossil natural gas (methane) through steam reforming which is responsible for about 2% of global GHG emissions. Hydrogen production from biomass generates a high purity stream of carbon dioxide well suited for CCUS. Bio-hydrogen is the only hydrogen production route that will lead to the net-negative CO₂ emissions when coupled with CCUS.

Biomass feedstocks for bioenergy are often cultivated in countries like Brazil, India and others in South East Asia in large-scale monoculture plantations like sugarcane that have numerous socio-environmental bearings, including compromising food security, harming biodiversity, increasing competition for natural and agricultural land, manipulating food prices, and aggravating water scarcity. With a rising demand for food production due to ever increasing population, and unprecedented biodiversity loss, biomass feedstocks for blue hydrogen manufacture should have minimal influences on food production, biodiversity, and the natural capital. Thus, purpose-grown bio-energy crops are becoming less appealing and crop residues, household food waste, and livestock manure are considered the most suitable for biogas production through anaerobic fermentation. These feedstocks do not necessitate purpose-grown bio-energy crops, their use does not compete with productive agricultural land and does not harm biodiversity through agricultural enlargement.

In our seminal paper [5] on comparison of crude oil versus bio-refinery, we proved that it makes more environmental and economic sense in using bioethanol as a feedstock than as biofuel. One kg of crude oil gives 32 MJ of energy and 0.2 kg of chemicals whereas 1 kg of biomass gives either 6 MJ energy or 0.8 kg of chemicals. So it is better to convert biomass into chemicals than to refine. Indeed biomass should never be used as a source of fuel but to make value added chemicals and materials; for instance, bioethanol (**Figure 12**).

Both green and blue hydrogen can be utilized in hard-to-electrify segments, namely, cement, steel, refining, ammonia, and glass industries. Biomass needs to be separated into cellulose, hemicellulose, and lignin fractions. Cellulose and hemicellulose are the sources for various platform chemicals like levulinic acid, 5-hydroxymethylfuran (HMF), and furfural. Lignin is a source of hydrocarbon compounds like olefins or aromatic derivatives, jet fuel and ethylene. The catalytic hydrogenation of (hemi)cellulose, hexose, furans, organic acid, lignin, and other bio-derivatives will contribute to the income of agriculturists. Hydrogenation is an efficient method for selective synthesis of combustible fuels and high value-added chemicals. Cellulose can be converted into combustible gases by hydrogenation, and methane is one such gas among them.

The sugars, hexoses and pentoses, can be dehydrogenated into furfural and HMF which are important chemical platform intermediates for tetrahydrofurfuryl alcohol, levulinic acid and its esters, furfuryl alcohol,

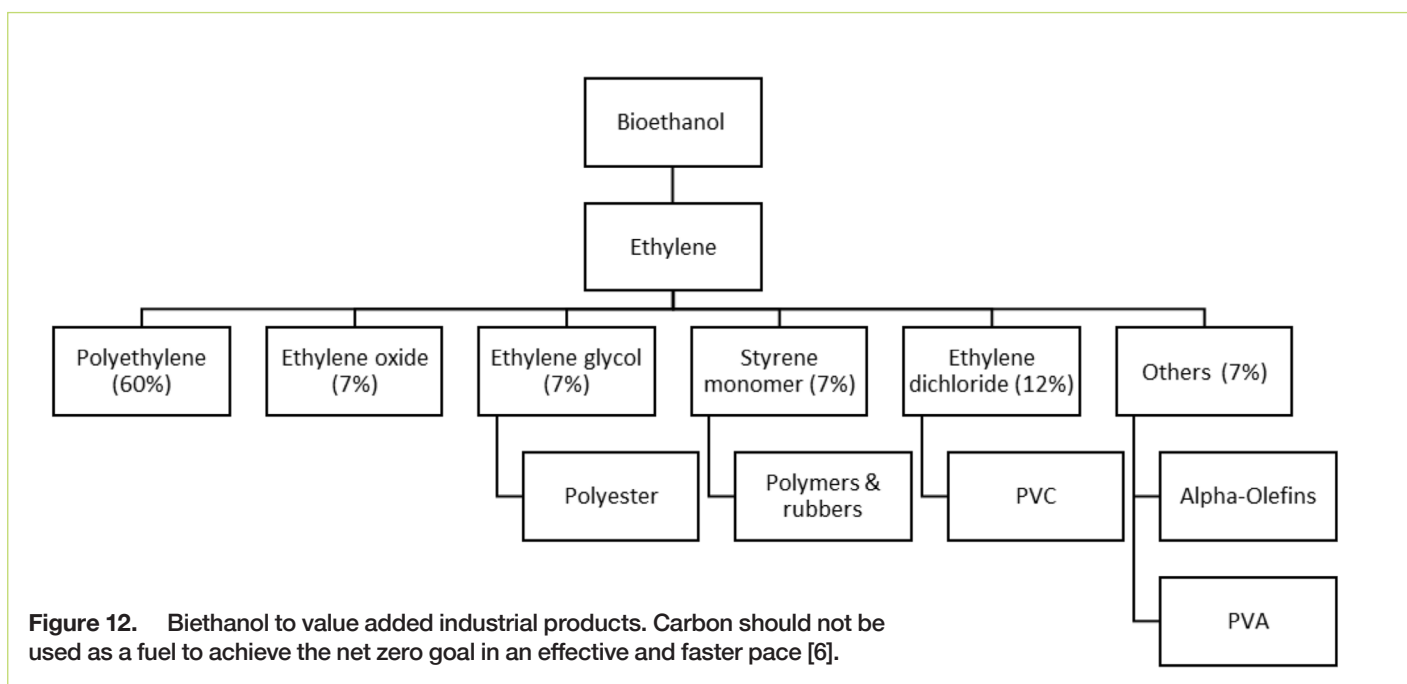


Figure 12. Biethanol to value added industrial products. Carbon should not be used as a fuel to achieve the net zero goal in an effective and faster pace [6].

HMF, γ -valerolactone, etc. The conversion of lignin to benzene, toluene, and xylene which are the major petrochemicals for chemical industry and produce 60% of all aromatic compounds is possible through hydrogenation/hydrogenolysis. Lignin depolymerization is required to produce platform chemicals, upgradation of bio-oils by hydrogenation and biochar. Polyols are definitely among the most appropriate substrates for the production of H_2 or syngas that can be further used as building blocks for the manufacture of methanol and other chemicals, including liquid hydrocarbons through the Fischer Tropsch synthesis.

After cellulose and hemicellulose are broken by acid or reductive catalyzed hydrolysis, glucose and xylose can be straightforwardly hydrogenated into the corresponding C6 and C5 polyols, sorbitol and xylitol, respectively. Thus, C6–C2 polyols, including 1,4-butanediol (1,4-BDO), 1,2- and 1,3-propylene glycol (1,2-PDO and 1,3-PDO) and ethylene glycol (EG), are extensively used as ingredient or additives in food, pharmaceutical and cosmetic industry as well as cheap monomers for the manufacturing of polymers, coatings, adhesives, etc. Xylitol is the most widely used sweetener characterized by a lower calorie-content and reduced glycemic index (GI) with respect to sucrose. Sorbitol has been successfully used for over the years for making polyurethanes. Ethylene glycol is an antifreeze agent which is a main component in the production of bio-PET while other bio-based diols, besides their direct uses, are now used as co-monomers in bio-elastomeric polymers. New catalytic technologies require a cost-effective reduction of the oxygen content in bio-polyols permitting the production of H_2 , fuels and other valuable chemicals. Glycerol is the co-product of bio-diesel, typically 10% by weight, that can be used to make more than two dozen chemicals. Unless glycerol is valorized, biodiesel production cannot compete with petro-diesel. Thus, farmers should recognize that there are marvelous opportunities to valorize agricultural waste using green and blue hydrogen to increase their income. Only the growth of grain or fruit production will not enhance their income but making sensible use of all parts of plants and waste thrown or burnt as waste will be part of a circular economy.

Plastic Refining: Chemical Recycling

Plastics refining is a GHG intensive process. Carbon dioxide emissions from ethylene production are projected to increase by ~ 34% over the period 2015-30. For instance, PVC is an extensively used thermoplastic due to its excellent properties such as stability, being cheap, and workability. It is

a multipurpose general plastic commonly used in construction, piping and many other consumer goods. PVC is highly polar and possesses a good insulation property, but it is inferior to other non-polar polymers like polypropylene (PP) and polyethylene (PE). PVC, PE and PP are usually used in piping, water supply, and medical industries, etc. whereas PP is extremely thermally resistant and it can withstand much higher temperatures than PVC. All these polymers including PET, nylon, and PU contribute to carbon footprint and global warming. PVC is demonstrated to have higher energy consumption and CO_2 gas emissions that show its high potential in global warming than other plastics. Likewise, the recycling of PVC has shown substantial contributions in lowering the effect on climate change [84].

About 40% of plastics are used in packaging globally. Typically, packaging is meant for a single use (SUP) and therefore so there is a reckless turnaround for disposal at all places. SUPs are used in many applications such as tires, fabrics, and coatings. Consumers need choices to avoid plastic waste such as legal means to encourage plastic collection through a refundable deposit scheme on SUPs, collection at regular intervals and avoiding plastic waste going as a mixture in municipal solid waste (MSW). The packaging can be dealt with in three different ways including landfill, incineration, or recycling. Waste incineration leads to the largest climate impact of these three options. According to the World Energy Council (WEC), based on the current trend in plastics production and incineration upsurge as anticipated, GHG will rise to 49 MMTA by 2030 and 91 MMTA by 2050. Landfilling has a much lesser impact on climate than incineration. But the landfill sites can be related with similar environmental issues. Recycling is a much better option. With regard to the little costs of virgin plastics, recycled plastics are high cost with low commercial value. It makes recycling lucrative only seldom, and so it calls for substantial subsidies by the government authorities. On the contrary the chemical recycling of polymers including depolymerization and hydrogenation are excellent choices.

Plastic products are an integral part of modern civilization and can be categorized broadly into the following types [39]:

Type 1: polyethylene terephthalate (PET) used in plastic beverage bottles

Type 2: high-density polyethylene (HDPE), used for milk pouches

Type 3: polyvinyl chloride (PVC), used pipes used in plumbing, vinyl tubing, and wire insulation

Type 4: low-density polyethylene (LDPE), used in plastic sheets or packaging

Type 5: polypropylene (PP), used in bottle caps, packaging, and plastic furniture

Type 6: polystyrene (PS), used in Styrofoam, beverage lids, and straws

Type 7: other non-recyclable plastics and all thermoset plastics (acrylics, nylons, polycarbonates, acrylonitrile butadiene styrene, ABS, and polylactic acid).

Type 8: Polyurethanes (PUs): extremely versatile elastomer used in countless such as furniture, bedding, and seating; thermal insulation; elastomers; footwear; straps; coatings

According to the survey by the Ellen MacArthur Foundation survey [40] only ~2% of plastics are recycled through chemical conversions into products with the similar functionality. Around 8% are “downcycled” to chemicals of lower quality whereas the remaining is landfilled, goes into the environment, or incinerated. Therefore, cutting down emissions associated with plastics would need the following approaches: reducing waste, retaining materials by restoring or remanufacturing, and recycling. Chemical recycling encompasses three mechanisms by which the polymer is purified from plastics without changing its molecular structure, is depolymerized into the monomer building blocks, which in turn can be repolymerized. It is converted into chemical building blocks that can thus be used to produce new polymers. Polymer upcycling such as SUP conversion into new products is all now worthy of practice. If government-established recycling targets are to be attained, the relationships between consumers, municipalities, and petrochemical production must be enhanced. After all, public opinion is moved by media images of an endangered planet and eco system. Only through the collaboration of people, municipalities, and industry - supported by improved technology along the recycled plastics supply chain, a solution for this global problem can be achieved.

The concept of circular economy for plastics will require many innovative ideas since plastics offer significant benefits to global sustainability, predominantly in transportation, and there are no substitutes readily available for immediate disposition at global scales. Therefore, plastics will be an integral part of in our activities for the foreseeable future. Design of plastic products

for circularity involves reuse, recycle, and remanufacturing principles. SUP must be the exemption rather than the rule.

The recycling of plastic is met with additional problems because different additives are used to enhance the performance, functionality, and aging properties of the base polymer. Additives are functional additives (plasticizers, lubricants, slip agents, stabilizers, antistatic agents, flame retardants, curing agents, nucleators, biocides, foaming agents, catalyst deactivators, etc.), colorants (pigments), fillers (calcium carbonate, barium sulfate, mica, talc, kaolin, clay,) and reinforcements (carbon fibres, glass fibres,). Identification, separation and disposal of additives are a big hindrance to recycling into the virgin resin [39].

Mixed plastics can be incinerated for energy recovery but it frequently creates carcinogenous pollutants. Therefore, only 12% of waste is incinerated in the U.S.A and incineration underestimates the potential that these polymers hold.

Plastic gasification, pyrolysis, and hydrothermal processing (HTP) are all thermolysis processes used to depolymerize plastics using heat). Pyrolysis of plastics into fuel oil is relatively mature technology. HTP takes place in an autoclave using water as a solvent, catalyst, or reactant requiring moderate temperatures (280–450°C) and pressures (70–300 bar). Supercritical water is used to liquefy polyolefins into oil or gas products (Figure 13) [42,43].

In solvolysis, xylene and toluene seem to be good solvents, whereas hexane and methanol work well as anti-solvents to recover the common polymers like HDPE, LDPE, and PS in high yields. On the contrary, methylene chloride (MDC) and benzyl alcohol are good solvents to dissolve PVC and PET. Chemolysis is meant to initiate a reverse reaction of the condensation reactions and uses chemicals to depolymerize polymers which only works for condensation polymers like PET and PU. Condensation polymers are equilibrium materials and hence addition of condensation product like ethylene glycol and heat reverses the polymerization. Thus, chemolysis cannot depolymerize additive polymers like polyethylene (PE) and PP. Chemolysis reactions include aminolysis, glycolysis, and methanolysis. Selective solvent extraction (SSE) and chemolysis are good for sorted plastics and condensation polymers, respectively, which cannot be used to treat mixed plastic [39].

Similar to pyrolysis, HTP favors polyolefins, but it can handle higher quantities of non-polyolefins plastics, including PVC and PET. HTP is used to convert PP into PET, PP, PS, and polycarbonate into fuels and naphtha [44,45], and wax [46].

Hydrogenation of plastic waste to valuable fuels, monomers and chemicals

Hydrocracking using metal catalysts over solid acid supports leads to cracking of heavy hydrocarbon molecules into lighter unsaturated hydrocarbons and the saturation of these newly formed hydrocarbons with hydrogen is a well established refinery

technology. It can be used for plastic waste. The advantages of hydrogenation over other methods including incinerations are conversion of waste plastic to high value products while simultaneously handling troublesome atoms (Cl, N, O, S) by hydrodechlorination (HDC), hydrodenitrogenation (HDN), hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) in the hydrotreating processes. The technologies for absorption of HCl, NH₃, H₂O and H₂S are already well established. Dioxin neither survives the hydrogenation process nor does produce super toxic products. The metal impurities remain in present state during the process due to hydrodemetallation (HDM).

A catalytic cascade process where hydro-pyrolysis can be coupled with downstream vapor-phase hydrotreatment to upcycle mixed plastic waste into fuels. This tandem vapor-phase hydrotreatment technology is feedstock-agnostic and therefore capable of upcycling different kinds of personal protective equipment (PPE) waste [47]. Thus, hydrotreating can be used as a favorable chemical upcycling technology for accomplishing a sustainable plastic circular economy.

Future direction

Many challenges exist in producing green hydrogen and to meet the so-called '111' objective as well as using or reusing carbon dioxide in an economical manner. A foremost challenge encompasses determining how best to tap energy sources, since converting carbon dioxide into fuels and chemicals would require large energy input. Another task is to find new reaction routes, including novel heterogeneous chemical and enzyme catalysts, and design and operation of multiphase reactors where process intensification is achieved economically.

Utilization of pure CO₂ by different ways such as using plasma, photocatalytic system, electrochemical reduction, heterogeneous catalysis, etc. has been reported in the literature, most of which is on lab scale. However, scarce attempts have been made to develop continuous processes for converting carbon dioxide from flue gas to value-added products that are economical and have the potential to meet energy and material needs of the future on commercial scale. Over the next two decades, capturing CO₂ from different sectors such as fossil-fuel based power plants, natural-gas processing plants, bioethanol plants, and cement plants could become an important method for mitigating climate change. Most of the captured CO₂ would probably be injected deep into depleted wells and stored, which is known as carbon capture and storage (CCS). One proposed means of reducing the cost of

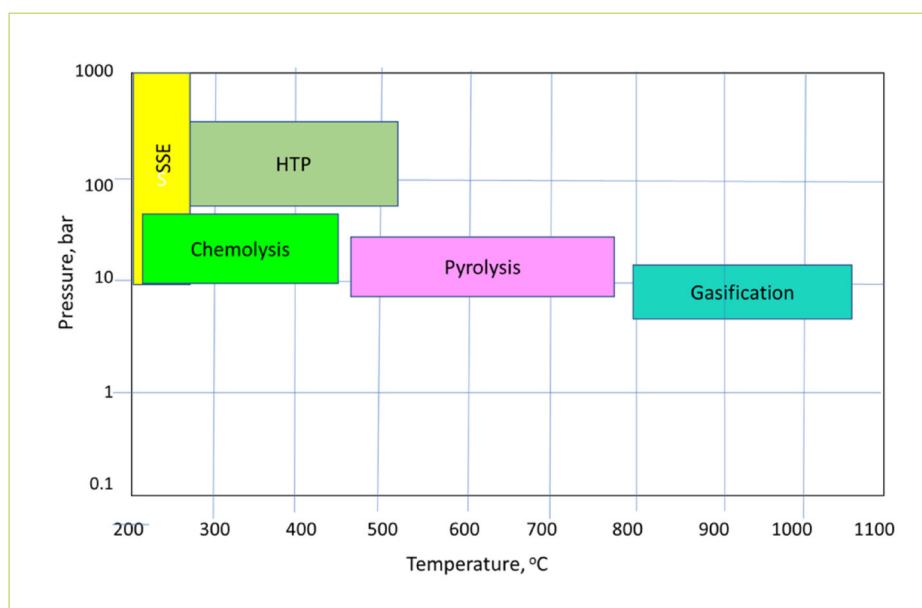


Figure 13. Opportunities abound for technological advancement in the field of chemical recycling; adopted from [39]

CCS is to trade some of the CO₂ for subsequent use. Thus, CO₂ is now considered not just a pollutant but a valuable commodity which can be used to produce fuels, chemicals and materials. In the chemical industry, the greatest use of CO₂ (~110–120 MMTA) is to produce urea. However, considering that global CO₂ emissions are around 10 billion MTA, converting it to useful chemicals is not expected to make a big difference in the GHG emissions problem. However, researchers are making progress in developing efficient methods for converting CO₂ into chemicals, so its potential use could be significant.

Decarbonization of the transportation industry is needed most urgently. The new setting trend of the mode of transportation is electric cars and hydrogen driven vehicles, but the question is unresolved as most of the power plants are still using coal and petroleum as the primary source of energy which releases a huge amount of CO_x, SO_x, and NO_x into the environment. However, the current refineries could use green hydrogen in their 8 different processes needing catalytic hydrogenation which will reduce CO₂ emissions from steam reforming of natural gas. It is predicted that by mid-2050s we may not have a viable means of extracting oil from the mother earth using current technologies. These problems along with GHG emissions, commitment to the Paris Agreement of 2015, aiming at net zero carbon by 2050, and containing global temperature rise to below 1.5 °C, have all propelled the development of a new clean energy alternative, which has to be renewable and can be utilized in the industry without any major modification of present infrastructure. For any alternate source, building new infrastructure in a short

period and that too economically, will be horrific. The three main characteristics of the energy supply chain which are essential for any type of energy infrastructure are the energy generation, storage, and distribution about utilization. There are a very few options available which can fulfill all the three criteria.

Conclusions

Net (carbon) Zero is a grand plan to restrict the global temperature rise to less than 1.5 °C whereby CO₂ emissions must be reduced from ~40 Gt today to less than 10 Gigatons by using non-carbon renewable energy sources. Green hydrogen will play a massive role in transforming CO₂ off gases like CO₂ into valuable chemicals and materials. By 2050, almost 49000 TWh of energy will be required among which about 73% will be from renewable resources in which solar energy, wind energy and hydrogen will contribute significantly along with hydro and nuclear. Both blue and green hydrogen will contribute about 24% in the renewables totaling to about 539 MMTA. Hydrogen production will be cheaper than the grey hydrogen cost during a foreseeable future.

The CO₂ conversion into gaseous or liquid hydrocarbons needs reaction conditions of high temperature (250–450 °C) and high pressure (20–40 bar), but the conversion is low due to difficulty in the activation of CO₂. Therefore, currently available technologies are not economically suitable for industrial implementation. Efficient heterogeneous catalysts can reduce the energy needed for reactions by reducing the activation energy. Various catalysts need to be actively investigated to enhance CO₂ conversion and to control selectivity toward the specific desired products. In fact, hydrogen will play

an important role in production of all these chemicals. Hydrogen is regarded as energy carrier, and it is only produced by using energy from other source.

Sustainable methanol economy refers to the combination of captured CO₂ from various waste sources and cheap hydrogen by using renewable energy to produce methanol. It is also referred to as “liquid sunshine” and has a great potential to resolve the energy crises and mitigate climate change. Throughout the last few decades, there is an advanced and viable development of technologies in catalytic hydrogenation of CO₂ for methanol synthesis, leading to a carbon-neutral energy sources by scavenging massive CO₂ released into the environment from various industries.

Most of the hydrogen is produced from hydrocarbon processing in the petrochemical industry, usually by gasification of coal or natural gas reform, which typically costs around at <2 USD/kg. The cost of hydrogen production mainly comes from the energy (heat and electricity) consumed during the process. Renewable energy is the cheapest option for hydrogen production, including geothermal, wind, hydropower, and solar energy. Therefore, the best approach to consider is to produce hydrogen by renewable energy, preferably solar or wind, and use that hydrogen for CO₂ hydrogenation to methanol, DME, and ammonia synthesis. For sustainable hydrogen production for ammonia synthesis, water electrolysis using wind and solar power is used, which provides a clue for methanol synthesis. In the future, thermochemical water splitting cycles such as Cu–Cl could compete for cheap production of green hydrogen if they are



coupled with solar energy as proved in the ICT-OEC (Institute of Chemical Technology-ONGC Energy Centre) hydrogen production technology.

DME is viewed as a '2G fuel/bio-fuel' and is a powerful, empowering fuel that can range from being ultra-low carbon to carbon-negative. It can significantly reduce the carbon footprint of the transportation sector and beyond (a) as an energy-dense, cost-effective means to move towards renewable hydrogen, (b) as a blending agent for propane, and (c) as a diesel replacement. DME can also be a clean fuel produced from emitted CO₂ captured from flue gases or directly from power plants.

Carbon dioxide refineries are not far away to be seen and to be believed. Thus, hydrogen can substitute fossil fuels in some carbon intensive industrial processes, such as steel, chemical and allied industries. It can present solutions for difficult to abate parts of the transport system, in addition to what can be accomplished through electrification and other renewable and low-carbon fuels. Net zero should happen much before 2050 during the lifetime of many readers. Biomass including waste and plastic waste will be major sources of chemicals and materials where hydrogenation/hydrogenolysis and oxidation will lead to protection of environment, provision of fuels, materials and energy.

Although bioethanol and other biomass derived chemicals can be used to make blue H₂, it should not be burnt as a fuel if we want to achieve the net zero goal before 2050.

Carbon should be used as a source of chemicals and materials. Bioethanol is more valuable as a feedstock for biorefinery than a fuel as our analysis showed [6]. It makes more economic sense in addition to the net zero target. Chemical recycling of waste plastics will have great benefit. Huge quantities of plastic waste can be converted into fuels and chemicals, and hydrogenation will play a significant role in treating all sorts of polymers and their mixtures. Circular economy must be made mandatory in all sectors and future societies should be taught that material recycling through physical, chemical and biological means and use of green energy will save us from climate change and GHG emissions. Hydrogen will be a true savior in these sectors.

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