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CCUS: Green Chemistry Based Technological Solutions and Research Paths

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ABSTRACT

Carbon Capture, Utilization, and Storage (CCUS) is among the largest challenges on the horizon. CCU is considered an important CO_2 mitigation strategy to support CCS objective for the abatement and sequestration of captured CO_2, captured from different sources. While many CCU applications can be considered technically feasible, main barriers to their industrial implementation are: Energy penalty in general, higher costs compared with conventional production paths and hydrogen from renewable resources. The applications of principles of Green Chemistry (GC) and engineering have enabled solutions to these barriers.

Since 2000 onward, the chemical industry has moved into new realm of processes which are less energy intensive, of higher efficiency and environmentally more acceptable. Examples include green solvents such as ionic liquids and supercritical CO_2, cryogenic carbon capture, co-production of hydrogen electrochemical CO_2 capture and chemical looping combustion systems. Conversion of captured CO_2 into value added products is being achieved through novel technological approaches such as plasma chemical, co-reactant and green hydrogen based CO_2 conversion, and "solar fuel" conversion paths.

Keywords: Green chemistry; Carbon capture; CO_2 conversion; Ionic liquids; Plasma chemicals; Solar fuels

INTRODUCTION

There is growing scientific consensus that Carbon Capture, Utilization, and Storage (CCUS) and Carbon Dioxide Removal (CDR) together play a critical role in decarbonization efforts and by accelerating CCUS deployment globally along with focused R and D, can drive down technology costs. This is particularly true in the industrial sector, where high temperatures are required to drive industrial activity and where process emissions from chemical reactions are more difficult to address. There is a wide array of carbon utilization options. Each technical approach for carbon utilization (pathway) has specific characteristics in terms of technical maturity, market potential, economics, CO_2 reduction potential, and may have different societal and environmental impacts as well.

Carbon Capture and Storage (CCS) represents a primary, probably essential component of any successful climate change mitigation policy. This mitigation approach will require reducing CO_2 emissions from transportation, commercial and

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residential, industrial, and utility sources. Transportation CO_2 emissions are mobile, intermittent and small scale. Commercial and residential CO_2 emissions are stationary, intermittent and also small scale. Mitigation of both types probably requires foundational technical changes such as conversion to electricity or hydrogen as the energy source. Industrial and utility sources are stationary, continuous, and large scale and represent some of the lowest cost and most effective opportunities for CO_2 emissions. Renewable energy sources can provide some of this energy, but a candid examination of recent regional and local CO_2 emission trends and realistic options indicates that CO_2 emissions from these sources will likely to continue for many scores of years and that CCS technology will play a major role in their mitigation [1].

Julien and David in their publication, state "CCUS is among the largest challenges on the horizon" and we call upon chemists, engineers, scientists for their help to focus on identifying the critical research needs/paths to make CCUS a reality, with an emphasis on how the principles of Green Chemistry (GC) and green engineering can be used to help address this challenge.

From the beginning of the 1990s, the idea of green chemistry started to have a more international outlook. In 1998 the Organization for Economic Cooperation and Development (OECD) through programs such as risk management promoted new and innovative activities under the broader umbrella of sustainable chemistry meaning-a more systems based life cycle informed and interdisciplinary practice of chemistry. The purpose was to initiate alternative practices in the chemical industry and processes more benign to the environment with the basic areas of research and development for green chemistry applications.

Green and sustainable chemistry innovations have the potential to drive sustainability in important sectors of the economy. This primarily includes sectors like energy, transport, agriculture, textile and others. Energy being one of the key sector addressing climate change, necessarily it is briefly touched to illustrate how green and sustainable chemistry is relevant for and how it can make a difference in shaping a sustainable transformation at the sectoral level.

LITERATURE REVIEW

Green Chemistry-Birth and Growth

Before discussing the CCUS technologies, based on green chemistry principles and work towards: A call to green arms, it is almost essential to briefly mention about the birth, growth and principles of green chemistry. The Office of Pollution Prevention and Toxics (OPPT) in USA, explored the idea of developing new or improving existing chemical products and processes to make them less hazardous to human health and the environment. In 1991, OPPT launched a model research grants program called alternative synthetic pathways for pollution prevention. This program was provided with unprecedented grants for research projects that included pollution prevention in the design and synthesis of chemicals. Paul Anastas, who was responsible for these programs and coined the term green chemistry worked very hard for many years to promote the principles of green chemistry and rightly is considered as the father of green chemistry. In 1993, the program was expanded to include other topics, such as greener solvents and safer chemicals, and was rechristened as green chemistry. Since then, the green chemistry program has built many collaborations with academia, industry, other government agencies, and non-governmental organizations to promote the use of chemistry for pollution prevention through completely voluntary, non-regulatory partnerships [2].

Anastas and Warner developed the twelve principles of green chemistry in 1991. These principles can be grouped into reducing risk and minimizing the environmental footprint. Risk has been a legacy of some chemical industries in the past. The environmental footprint is more to do with energy consumption, the climate crisis and depleting natural resources. Green chemistry aims to reduce risk in the laboratory, use safer chemicals, design less hazardous synthesis methods, use safer solvents and reaction conditions and accident prevention. Further it minimizes the environmental footprint: Waste minimization and prevention-use of catalysts instead of stoichiometric quantities, reduce the use of chemical derivatives and synthetic efficiency. Taking advantage of chemicals designed for degradation, establishment of process controls for pollution prevention-use of renewable feedstocks and encourage energy efficiency. Recognizing the importance of subject MaltiGoel, et al. have published a book in 2021 under the title: Climate change and green chemistry of CO_2 sequestration, highlighting-in-depth information on topics relating to recent advances in carbon capture technology and its reuse in value added products.

Much of the progress to date in advancing green chemistry can be attributed to two main drivers: Government regulation and consumer awareness. Green chemistry with its many advantages has a vast scope for waste elimination through the conversion of captured CO_2. However, future efforts need to better address the slow adoption of green chemistry.

CCUS Processes

CCUS is the combined term covering two alternatives, both of which start with the process of capturing the CO_2: In CCU-the captured CO_2 is recycled for further use, whereas with CCS the captured CO_2 is compressed as pressurized gas for long-term storage at geological sites. Both CCU and CCS offer potential technological solutions to mitigate the deleterious impact of climate change caused by excessive burning of fossil fuels and the resultant Green House Gas (GHG) effect of high levels of CO_2. In addition, the captured CO_2 can also be used for a variety of industrial purposes such as the production of synthetic fuels or in the food and beverage industry.

Several CO_2 capture approaches, in the last decade, have been developed, such as absorption, adsorption, and membrane, cryogenic, hydrate formation, mineralization and chemical looping combustion etc. However, the energy penalty is a general challenge for each technology. To

overcome the disadvantages of standalone technology, the combination of two or more approaches (namely hybrid CO_2 capture processes) has been considered as a potential option. As per Song, et al. hybrid processes show the superiority not only in CO_2 recovery and energy penalty, but also in the installation investment. Therefore, hybrid processes can be a promising alternative to conventional CO2 capture technologies in future [3].

Enhancing Energy E iciency through Innovations

The 6th principle of green chemistry states that energy requirements should be recognized for their environmental and economic impacts and be minimized. Synthetic methods should, if possible, be conducted at ambient temperature and pressure. While significant steps have been taken by the chemical industry to save energy in producing chemicals, it is challenging to make further significant gains through process efficiency measures, pointing to the need for technology disruption, based on green chemistry reactions which are less energy intensive. Disruptive concepts such as electrochemical synthesis and other innovative catalysis techniques are being researched to replace thermo chemical methods with milder, less energetically demanding processes. Passive separation techniques using membranes have already begun to outpace demanding traditional separations.

CO_2 Capture Options-Classical and Low Energy Based Processes

The main CO_2 capture options are post- and pre-conversion capture and oxy-fuel combustion. Figure 1 presents the methods and techniques for CO_2 capture. As indicated, post-conversion capture methods (also referred to as post combustion) include absorption in solvents, adsorption by solid sorbents, including porous organic frameworks, membranes and cryogenic separation as well as pressure and vacuum swing adsorption. Among these, absorption by Mono Ethanolamine (MEA) is most commonly used. However, this method is not economically viable for all industries as MEA regeneration has high heat consumption, so that the development of more environmentally sustainable sorbents is one of the challenges for both CCS and CCU.

Pre-conversion combustion (also referred to as pre combustion) refers to capturing CO_2 generated as an undesired co-product of an intermediate reaction of a conversion process. Some examples include the production of ammonia and coal gasification in power plants. In ammonia production, CO_2 that is co-produced with hydrogen during steam reforming must be removed before the ammonia synthesis can take place absorption in MEA is commonly used for these purposes. Similarly, in an Integrated Gasification Combined Cycle (IGCC) power plant, CO_2 must be separated from hydrogen. This is typically achieved using physical solvents such as selexol and rectisol. Porous organic framework membranes can also be used for CO_2 capture owing to their high CO_2 selectivity and uptake; however, no applications have been reported to date. Like post-conversion, pre-conversion capture also incurs energy penalties for regeneration of chemical solvents; these are lower for the physical solvents as they are regenerated by reducing pressure rather than by heat. Physical solvents are, therefore, more suitable for applications with high operating pressure; they are also more efficient for concentrated CO_2 streams as well. Oxy-fuel combustion capture, as the name would suggest, can only be applied to processes involving combustion, such as power generation in fossil fuelled plants, cement production and the iron and steel industry. Here, fuel is burned with pure oxygen to produce flue gas with high CO_2 concentrations and free from nitrogen and its compounds such as NO and NO_2. While this avoids the need for chemicals or other means of CO_2 separation from the flue gas, a disadvantage is that oxygen is expensive and the environmental impacts, including CO_2 emissions, associated with its production are high because of the energy intensive air separation processes. The alternatives to the oxy-fuel process are Chemical Looping Combustion (CLC) and Chemical Looping Reforming (CLR). Both use a metal oxide to transfer oxygen selectively from an air reactor to a fuel combustor. However neither of the oxy-fuel technologies is expected to be fully deployed before 2030 [4].

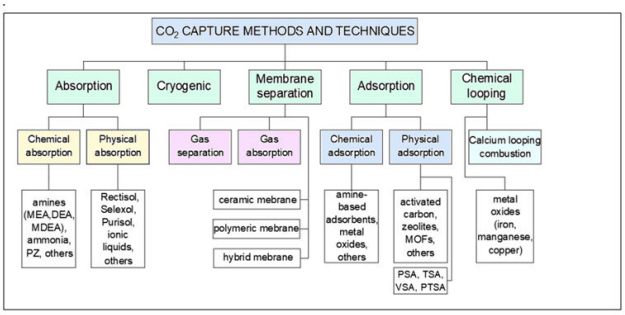

Figure 1: Methods and techniques of CO_2 capture.

CO_2 Capture *via* Green Chemistry

Since 2000 onward the chemical industry has taken steps to develop new processes which are less energy intensive, have higher efficiency and environmentally acceptable. New methods and techniques applicable to carbon dioxide capture, its utilization and storage have equally being developed or exiting one being modified. Accordingly description below attempts to present some green chemistry based new/ emerging methods and technologies as applicable largely to carbon dioxide capture, utilization and storage.

Applications of green solvents: A solvent can be the key to a good chemical process, as it determines the solubility, meaning the concentration at which reactants can be processed, determines the stability of excited states, and thus guides the potential energy curves of activation. In the last two decades, the green chemistry has come out, by expanding the capabilities of conventional solvents, with a new class of so called master solvents, which have also been termed green or designer solvents. By definition an ideal fully sustainable green solvent would not have an ecological impact at any stage, and it would ease process conditions and at the same time make them milder and more sustainable.

Such solvents also rule over productivity a nd economic/ environmental benefits.

The green solvents considered under this head are: Ionic liquids and super critical CO_2 as well as deep eutectic, themomorphic andfluorous solvents. Water is considered to be the nature's green solvent for its bio-catalytic processes. Some of the green solvents are widely used even on a production level such as ionic liquids, while some others are more specifically used such as flouros and supercritical carbon dioxide as green solvents. Keeping with the theme of present article Figure 2 present green solvents proposed for CO_2 sorption and the pursued technologies to make CCUS a reality.

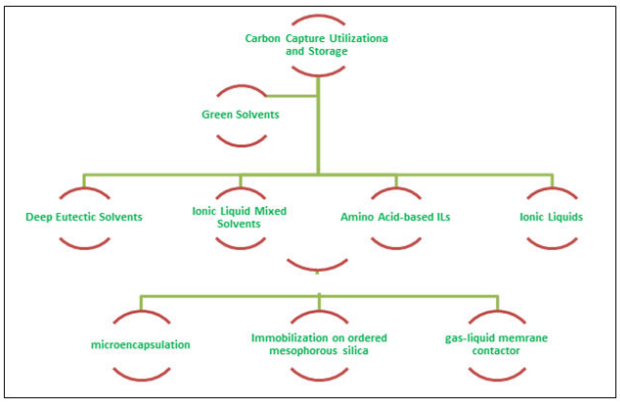

Figure 2: Schematic representation of the carbon capture.

Ionic liquids as green solvents: Ionic Liquids (ILs) are defined as a large category of salts that, due to differences in their cation and anion sizes, are normally liquid at a temperature less than 100°C. Due to the low stability, high volatility and corrosivity of materials used in conventional CO_2 capturing processes, such as amine based absorption, water and organic liquid scrubbing and hollow fiber membranes, they potentially infract green chemistry principles. Therefore, ILs have gained specific interest due to their advantages of good dissolution properties, low volatility, high decomposition temperature, energy, and cost efficient separation of CO_2 from post-combustion flue gas. These solvents can be readily removed and recycled and their properties enable Room Temperature Ionic Liquids (RTIL) to give a wider acceptance as possible green solvents, which substitute classical volatile organic solvents in a variety of processes, including industrially essential chemical process. Ionic liquids, in the past decade, were extensively studied as scrubbers of greenhouse gases. A large number of papers studied imidazolium based ILs for CO_2 capture [5].

Of these, the representative cation class consists of imidazolium, pyridinium, etc and amines. The anion class consist of organic/inorganic (carboxylate, azolate, phenoxideetc. The basicity of the anion was noted to influence more the CO_2 uptake as compared to cation in ILs. Process simulations showed that use of ILs in place of well known MDEA can bring down the total electrical and thermal energy by 42.8% and 66.04%, respectively. The regeneration energy demand also decreased by 15% when IL (1-butylpyridinium tetrafluoroborate) was used in place of MEA.

Deep eutectic solvents and supercritical CO_2: The concept of Deep Eutectic Solvents (DESs), a mixture of a Hydrogen Bond Acceptor (HBA) and a Hydrogen Bond Donor (HBD), has surfaced recently as a new class of solvents with high potential for acid gas separation. The advantage of these eutectic solvents on many applications stands indisputable. DESs have been proposed for CO_2 capture by Li, et al. using eutectic mixtures composed of choline chloride and urea. Since then, many more workers have evaluated other HBDs and HBAs, such as glycerol, ethylene glycol, ammonium based, phosphonium based and amine based, aiming at enhancing the CO_2 solubility. Although, DESs have shown high potential for CO_2 capture, the number of experimental studies on gas solubility is remarkably limited.

Supercritical Carbon dioxide (CO_2) is well established for use as a processing solvent in polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization. Another promising areas where supercritical carbon dioxide, can be used is the oil industry for supercritical extraction in the course of oil refining, increasing oil recovery in the production of heavy oil, hydraulic fracturing, as well as processing and disposal of oil sludge and asphaltenes.

Cryogenic carbon capture: Cryogenic Carbon Capture (CCC) represents a rapidly developing and highly competitive CCS option. A recent review stated of all the carbon capture processes, I regard the CCC process to have the greatest potential. Low temperature CO_2 capture technologies, separates CO_2 from light gases in essentially any continuous process. The process relies on phase change, thus separating the CO_2 from the gas in the form of a liquid or solid. The method offers various benefits such a high purity product, avoids the need for toxic chemicals and can be applied to a range of CO_2 concentrations. The process also recovers all gas moisture and most gas impurities, less volatile than CO_2 (NO_x, SO_x, Hg, PM, etc.) in separable streams [6].

CCC involves a physical separation process based on the differences between the boiling points and the de-sublimation properties of the components in the gas mixture. Therefore, phase equilibria data are indispensable to define the pressure-the temperature conditions in which the CO_2 in a mixture remains as a liquid, gas or solid. The two phases provide two different types of cryogenic methods: Liquid-vapour separation, or conventional cryogenic methods (cryogenic distillation above 193°K), and solid-vapour separation, or nonconventional methods (cryogenic liquid heat exchangers) and packed bed. Since cryogenic separation offers high CO_2 recovery rates and purity levels of around 99+ % this technology is gaining considerable attention and exist in the form of hybrid technologies as well.

Song, et al. have reviewed and summarized major strategies and technologies for CO_2 capture from fossil fuel combustion and simultaneously the characteristics of cryogenic technologies for CO_2 capture. The existing challenges that need to be overcome in cryogenic technology include cold energy sources, capture costs, and impurities. The results of

this investigation indicated that cryogenic CO_2 capture processes can be easily retrofitted to the existing industrial emission facilities and avoid the challenges associated with chemical solvents or physical sorbents, with the remark that opportunities exist for the future development of cryogenic based technologies.

Sustainable Energy Solutions (SES) has scaled this technology, called the skid system through several levels, the largest of which captures nominally 1 ton of CO_2/day. Skid system field tests include utility scale power plants, cement plants, heating plants, and other industrial sites that burn natural gas, biomass, coal, shredded tires, municipal waste, and combinations of these fuels. These field tests produced 95%-99% CO_2 capture with purities of 99+%, from captured CO2 gas having an initial CO_2 contents that vary from 4% to 28%. SES currently working to upscale the system to commercial scale (10 tons-80 tons of CO_2 per day). SES through this approach has demonstrated the potential for CCC to contribute to energy storage and direct air capture in innovative and cost-effective way.

Co-production of hydrogen and CO_2 capture: The key pillars of de-carbonizing the global energy system are: CCUS, energy efficiency, electrification, renewables, hydrogen, hydrogen based fuels, and behavioural change. The importance of hydrogen in the net zero emissions scenario is evident from its increasing share in cumulative emission reductions. Intensive hydrogen growth demand and adoption of cleaner technologies for its production may enable hydrogen and hydrogen based fuels to reduce up to 60 Gt CO_2 emissions in 2021-2050, representing 6% of total cumulative emissions reductions in the net zero emissions scenario.

Foster Wheeler Italiana, on behalf of IEA conducted an important study “greenhouse gas R and D programme” on electricity and hydrogen production with CO_2 capture. The plant marked for study shell dry feed entrained flow coal gasification process with CO_2 capture uses a sulphur tolerant shift conversion process and a selexol acid gas removal process. Two main products of the plants are: Electricity and hydrogen. By-products includes sulphur (liquid or solid), carbon dioxide and solid by-products (slag, fly ash and filter cake, depending on the gasification technology). The IGCC is designed to remove from the syngas 85% of the CO_2 generated. The other emissions produced includes NO_x, SO_x, particulate and CO, much lower than those defined by the applicable european directive, without significantly penalizing the plant efficiency and investment cost. The cost of producing hydrogen by coal gasification with CO_2 capture in a base load plant is estimated to be € 15.8/GJ. Flexible co-production plants with CO_2 capture and hydrogen storage may help to facilitate greater use of variable renewable energy sources in future by providing back-up energy supplies and the ability to satisfy peaks in energy demand, while having low emissions of CO_2.

Regarding using fossil fuels with CCUS for hydrogen production, shell was the first big mover, in the Netherlands, with its 2005 project at pernis refinery to capture CO_2 from heavy residue gasification units. Others have followed since, and there are already six facilities producing hydrogen from fossil fuels coupled with CCUS, the last one entering into operation in 2020 at the North West sturgeon refinery (Canada). These facilities have a production capacity of 320 kt of low carbon hydrogen (25% higher than in 2019), but production could rise to 380 kt in 2021, if two projects currently under development in China become operational.

Electrochemical CO_2 capture: Electrochemical CO_2 capture methods are experiencing a renaissance as their applications expand due to their positive features like, higher energy efficiency, flexibility and sustainability as compared to the conventional approaches. Electrochemical CO_2 capturing methods can be classified into four types:

- Methods that use a pH-swing to capture and recover CO_2
- Methods that rely on the binding affinity of CO_2 molecules to redox active species
- Molten carbonate cells
- Hybrid electrochemical processes that combine CO_2 capture and e.g., direct conversion

Chemical Looping Combustion (CLC) systems for CO_2 capture: Chemical Looping Combustion (CLC)-A novel technique of energy conversion enables burning of hydrocarbon fuels with dramatically reduced CO_2 emission into the atmosphere. It represents recent advances in CO_2 capturing technologies, appears to be most promising to achieve this goal. The inherent separation that takes place in the CLC reactors results in a highly reduced internal load of the plant, and hence the CLC technology can compete with other pro-CCS technologies [7].

CLC which is either classified as a pre-combustion method or as the fourth capturing method is a two-step cyclic process. The process is usually conducted in a system of two reactors (Figure 3), which consists of a Fuel Reactor (FR), where combustion takes place, and the Air Reactor (AR), where Oxygen Carriers (OC) are regenerated. These interconnected reactors facilitate alternate oxidation and reduction of the oxygen carrier, as shown in equations 1 and 2. Oxygen carriers demands a higher particle residence time for the reduction reaction than for the oxidation while they circulate throughout the combined CLC unit. There are two crucial benefits of OCs applications in a power generation system namely: The elimination of conventional energy consuming air separation units and the inherent separation of forming flue gases (mainly CO_2 and H_2O) from the air supplied to the combustion process. As a result, the flue gas that leaves the fuel reactor is free of atmospheric nitrogen and thus it becomes almost ready for geological sequestration-CCS and/or commercial utilization-CCU. Consequently, the exhaust gas from the air reactor consists essentially of nitrogen and the remaining oxygen, which are both environmentally friendly gases.

Air Reactor: $M_xO_{y-1}+0.5O_2 \rightarrow MyO_x$ (1)

Fuel Reactor: $(2n+m)M_yO_x + CnH_2m \rightarrow (2n+m)M_yO_{x-1}+mH_2O+nCO_2$ (2)

The net reaction of the CLC: $CnHm + ½ (2n+m) O_2 \rightarrow n CO_2 + mH_2O + heat$ (3)

The CLC has been mostly operated employing gaseous fuels using metal oxide carriers based on Cu, Mn, Co, Ni and Fe. This technology needs to be greatly extended to solid fuels like coal that would require higher combustion efficiencies and more effective metal oxides as the fossil fuels are more abundant and underutilized than gaseous fuels and would continue to be the main source of power generation in near future. Several different systems based on chemical looping principles are developed concurrently in order to burn fossil and other fuels in a clean and efficient manner. Basically they can be distinguished into two groups namely: Systems with oxygen carriers and so called carbonate looping systems with CO_2 carriers. As per TRL considerations the CLC technology is still not mature enough for commercial implementation.

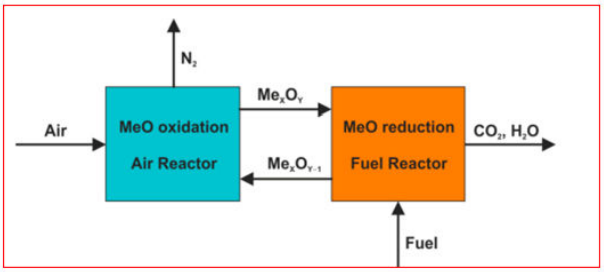

Figure 3: Block diagram of chemical-looping combustion process.

DISCUSSION

Conversion of CO_2 to High Value Products: Chemicals and Synthetic Fuels

Conversion of pure CO_2: Captured CO_2 from the combustion of fossil fuels can be treated as an asset by employing appropriate technologies to convert it into value added products like; solar fuels, chemicals and others. Such recycling of CO_2 can be an expedient accomplishment for the solution of problems namely: Emission of large concentrations of CO_2 resulting in global warming and alarming utilization of energy assets.

The CO_2 conversion reactions can be categorized into fuel production and chemical production. The fuel production is considered to be a highly suitable objective for the transformation of large amounts of CO_2 because it controls large market size as compared to chemicals. Methanol is an interesting chemical and is in the middle of these two options because it finds application as fuel and chemical in fuel cells and engines. The direct and indirect oxidative routes are the approaches that can be utilized to accomplish this. The former approach is used to produce short chain olefins (C_2H_4, C_3H_6), oxygenated products (CH_3 OH, CH_2O, HCOOH) and hydrocarbons. The latter approach yields syngas which H can be further processed into almost any kind of fuel or chemical, while keeping the H_2/CO ratio under control because it plays an important role in the production of desired products [8].

CO_2 conversion into useful products was initially practiced through the conventional thermal approaches before the utilization of modern technologies. The main difference between two routes being the use of 'fossil fuels' by the conventional practices to provide the necessary thermal energy in order to carry out their processes. Commercial scale conventional thermal routes may be divided into: Pure CO_2 splitting and conversion of CO_2 along with a co-reactant H_2, CH_4 and H_2O.

Pure CO_2 splitting: CO_2 is a highly stable molecule with Gibbs free energy of formation for C-O bond being -394 kJ/mol, thus, requires substantial thermal energy along with a highly active catalyst and optimal conditions for the occurrence of the chemical reaction. In addition thermo dynamically, both enthalpy and entropy are also unfavorable for the conversion as well. As such pure splitting of CO_2 is mainly ineffective.

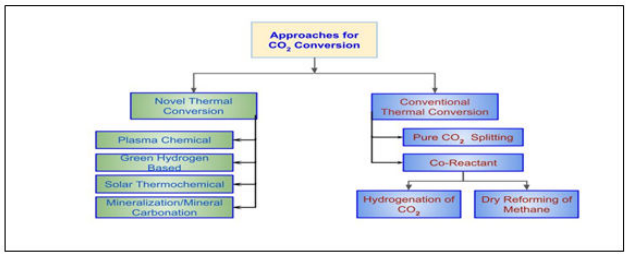

Figure 4: Approaches for CO_2 conversion, conventional and novel.

The splitting reaction of CO_2 can be written as:

$$CO_2(g) \rightarrow CO\,(g) + 12O_2\,(g) \quad H^{\circ} = -293\ \text{kJ/mol} \quad (1)$$

Despite all the barriers such as high thermal energy needs to proceed for this splitting, there are many industrial applications which involve endothermic reactions and can support this conversion e.g., steam reforming of methane which is highly endothermic reaction and has worldwide applications.

$$CH_4\,(g) + H_2O\,(g) \rightarrow CO\,(g) + 3H_2\,(g) \quad H^{\circ} = +206.3\ \text{kJ/mol} \quad (2)$$

Some researchers, in the past have attempted splitting and separation of CO_2 into various chemicals -CO and O_2 using different kinds of membranes and semi permeable membranes. The net results from these studies was that not only these researches required high temperature but they showed very small conversion rates and hence not successful and efficient, therefore not transferable able to commercial scale.

Co-reactant based CO_2 conversion: Co-reactant based CO_2 conversions involves coupling with reactants having higher values of Gibbs free energy, e.g., CH_4 and H_2. In such reactions, the inherent chemical energy of hydrogen carriers will be utilized to support the CO_2 conversion. There are other hydrogen donors which may be considered in place of CH_4, H_2, and H_2O e.g., Glycerol. Of these donors the combined reaction of water with carbon dioxide is of interest.

Dry Reforming of Methane (DRM) is the process of converting CO_2 in the presence of methane while, in steam reforming of

methane, CH_4 reacts with water instead of CO_2. The DRM is a complex process and requires high temperature of the order of 900 K to 1200 K and appropriate catalyst to overcome the high stability of CO_2 molecule and inert nature of CH_4. Steam reforming of methane on the other hand is a straight forward process due to the presence of water. DRM, to date, is not widely utilized on the commercial scale, as a major drawback of this process is the formation and deposition of soot which results in the early deactivation of the catalyst.

Production of methanol *via* selective hydrogenation of carbon dioxide is a widely practiced path on the industrial scale across the globe. The overall chemical reaction for methanol production is as below:

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O \quad \Delta H^\circ = -49.9\ kJ/mol \quad (3)$$

The production of by-product H_2O in the methanol synthesis is the main limitation of this process. Despite the problems associated with the formation of methanol through the reaction of CO_2 and H_2, it is the most effective industrial scale route for the conversion of CO_2 into value added chemicals.

Recently, the hydrogenation of CO_2 to yield C_{2+} chemicals has acquired a growing interest. The path however faces major hindrance in the hydrogenation of CO_2 to produce C_{2+} chemicals, is the high coupling of C-C and C_{2+} product selectivity and time yields has not sufficiently been achieved. More research is still in progress.

Methanation of CO_2, also known by the name of Sabatier reaction is an another important catalytic process whereby methane is produced by reacting H_2 with CO_2 (equation 4) in the presence of catalyst and commercially it is an interesting process. Many investigations about the catalytic conversion of CO_2 with H_2 have been carried out.

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O \quad \Delta H^\circ = -252.9\ kJ/mol \quad (4)$$

Syngas and compressed natural gas are one of those many applications which are formed by the methanation of carbon dioxide. Thermodynamically, this is quite a favorable reaction; however, this reaction has considerable kinetic limitations. There are some other such as ethylene, formaldehyde, and ethanol can also be produced through conventional thermal conversion of CO_2.

It stands without doubt that the efficient conversion of CO_2 to useful molecules presents an important challenge as the process efficiency for these products is not notable and it offers a great opportunity for chemists today.

Due to the inability of the traditional thermal approaches to address the worldwide CO_2 conversion challenges, several under development promising novel CO_2 conversion technologies such as plasma chemical, green hydrogen based, solar thermo chemical and mineralization are now subject of discussion in scientific publications.

Plasma chemical conversion of CO_2: Plasma, also called the "fourth state of matter," is an ionized gas consisting of electrons, ions of various types, radicals, excited atoms, and molecules, besides neutral ground state molecules represents a highly reactive environment which finds many applications. Plasma is created by applying electricity to a gas. The applied electric field activate and heat up the light electrons which activate the gas molecules by excitation, ionization, and dissociation, creating the above mentioned reactive species and allowing chemical reactions to occur at mild conditions. This makes plasma of particular interest for CO_2 conversion into new products because the electrons can activate even the chemically stable CO_2 molecules [9].

There are two main options for converting CO_2 to chemicals/ fuels by using Renewable Energy Sources (RES). The first is the production of H_2 by electrolyzers followed by the catalytic conversion of CO_2 to different products, from methane to methanol or synfuels. The second is the direct CO_2 conversion in electrocatalytic reactors using RES or in Photo Electrocatalytic (PEC) reactors, where the solar cell is integrated into the electrocatalytic cell for CO_2 reduction. Although the latter is still the more challenging, it offers two main benefits:

- It greatly reduces several of the energy losses due to coupling different components, and
- It avoids energy losses related to the over potential in forming H and in using H_2.

Green hydrogen based CO_2 conversions: This approach is being mostly attempted and practices by major oil company with the support of academia, due to the significant role of hydrogen in crude oil refining operations. Three recent efforts on this subject are:

John Matthey's approach: The global aviation industry is responsible for 12% of transport related CO_2 emissions, therefore substantial production of low carbon intensity Sustainable Aviation Fuel (SAF) is essential to mitigate emissions. John Matthey recently announced (JM May 2022) the launch of an innovative HyCOgen™, a reverse water gas shift technology designed to help enable the conversion of captured CO_2 and green hydrogen into sustainable aviation fuel-SAF.

HyCOgen is a catalyzed process to convert green hydrogen and CO_2 into carbon monoxide, which is combined with additional hydrogen to form synthesis gas (syngas), a crucial building block in the manufacture of fuels and chemicals. The integration with the FT CANS technology (developed in collaboration with BP) provides end to end, optimized and highly scalable process that turns over 95% of the CO_2 into high quality synthetic crude oil. This synthetic crude oil can be further upgraded into sustainable drop in fuel products including aviation fuels, renewable diesel and naphtha.

The scalability of the integrated HyCOgen/FT CANS solution enables cost effective deployment across a wide range of project sizes-from small scale, fed by hydrogen from a single electrolyzer through to world scale with multiple large electrolyzer modules. Both the European Union (EU) and United States (US) are setting bold targets for its scale up and blending, and this is expected to increase SAF demand significantly. Johnson Matthey's integrated technology, can

help increase the supply of SAF through its efficient production at scale.

Ruxing Gao, et al. approach-China: Ruxing Gao, et al. have announced Power-to-Liquids (P2L) and Power-to-Gas (P2G) processes which utilize renewable power to convert carbon dioxide and water into value added syncrude and synthetic natural gas, as an efficient way for CO_2 mitigation. CO_2 is converted *via* reverse water gas shift, Fischer-Tropsch synthesis and CO_2 methanation. Based on their past work experience, the team reports the development of the indirect P2L and P2L/P2G hybrid processes combined with the reverse water gas shift unit, which produce solely syncrude and the combination of syncrude and synthetic natural gas, respectively. A comparative study of the indirect and direct P2L and P2L/P2G hybrid processes *via* the process modelling and techno economic analysis was applied to quantitatively evaluate their process performance differences. It was observed that:

- The indirect CO_2 hydrogenation processes have higher syncrude production than the direct ones.
- The direct CO_2 hydrogenation processes are more energy-efficient than the indirect ones.

The study indicated that the indirect P2L and P2L/P2G hybrid processes were also able to be considered as suitable technologies for the transformation of CO_2 into high value hydrocarbons.

Repsol integrated approach: The spanish oil major Repsol is investing € 2.549 billion in a project to build one of the world's largest facilities to manufacture net zero emissions fuels using CO_2 captured from the Petronor refinery and green hydrogen generated with renewable energy, as well as pyrolysis of urban waste from the city of Bilbao. A schematic plan of the world's largest net zero emissions synthetic fuel production plant based on green hydrogen being built is shown in Figure 5. The plant will be commissioned in 2024 with a starting capacity of more than 2,100 tons of synthetic fuel per year. It will use cutting edge technology to combine green hydrogen that will position Repsol on the leading edge of the development of net zero emissions fuels.

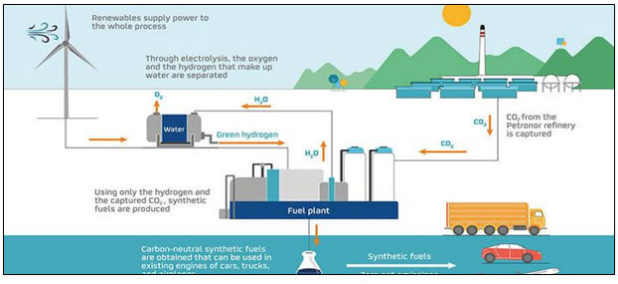

Figure 5: Repsol unveils green hydrogen project-source repsol.

Renewable energy is one of Repsol's strategic pillars to achieve net zero emissions by 2050, that plans to install 1.9 GW of green hydrogen capacity. The company will use different technologies to reach its renewable hydrogen production targets, including electrolysis, biogas production, and photo electro catalysis. The main advantage of photoelectro catalysis technology over current solutions is that only water and sunlight are needed as raw materials to produce 100% renewable hydrogen.

Currently, 90% of all hydrogen produced is used in the industrial sector as a raw material in refining, ammonia production, and others. For this reason, the EU envisages the deployment of renewable hydrogen to decarbonise industrial sectors where electrification is not an alternative in the short to medium term. Hydrogen is also essential in the production of liquid fuels with a low carbon footprint, such as bio-fuels and synthetic fuels. The advantage of these products over other options is that their performance is similar to traditional fuels.

On the other hand, the production of liquid fuels with a low carbon footprint, especially synthetic fuels, is also a way to store energy for later use or transport in a simple and efficient way. This conversion takes full advantage of renewable energy production to store the surplus that is produced when supply exceeds demand. It is also an efficient way to export energy to new markets and boost a new hydrogen economy, promoting industry, and generating quality employment, investments, and wealth.

As per Repsol's recent announcement 20th Jan 2022, the Spanish Hydrogen Network (SHyNe) project aims to install the renewable hydrogen capacity through projects across 10 autonomous communities. The projects will require a total investment of € 3.23 bn that will serve to develop more competitive technologies and evolve both the spanish industry and its infrastructure towards decarbonization, generating more than 13 K jobs, Repsol will further install 500 MW of renewable hydrogen capacity by 2025 GW and 1 GW by 2030.

In addition, projects will be promoted throughout the value chain, including installing renewable generation and stimulating the different industrial uses of hydrogen through a strong sectoral integration. It will also promote the use of hydrogen in all transportation segments, through the production of synthetic fuels and the creation of an infrastructure with at least 12 hydrogen filling stations by 2025.

Solar fuels "arti icial photosynthesis" based CO_2 conversion processes: Department of Energy (DOE) defines solar fuels, as fuels made from common materials like water and carbon dioxide using the energy of sunlight. There is vast energy in sunlight striking the earth surface in one hour about 170 petawatt hours of energy which is enough to support the world's energy consumption for an entire year, about 160 petawatt hours of energy. However because of its time varying and dispersed nature, it is challenging to harness sunlight for practical use. Technologists have successfully resourced solar energy to make electricity but aren't yet able to efficiently make liquid fuels from it. "Artificial photosynthesis" developed and designed on principles similar to natural photosynthesis, is one possible route to producing solar fuels using only water, carbon dioxide, and sunlight to generate fuel/energy rich chemicals. Melvin Calvin received

the 1961 nobel prize in chemistry for uncovering the mechanism nature uses during natural photosynthesis.

Three possible options for solar fuels include:

- Making hydrogen as a fuel by using solar energy to split water.
- Producing alcohols such as ethanol and methanol by using solar energy to reduce CO_2 with hydrogen.
- Creating less conventional fuels such as ammonia and hydrazine by using solar energy to reduce nitrogen with hydrogen.

Such solar fuels would diversify the fuel supply and increase the sustainability of overall energy system, by using the existing fuel infrastructure: Storage and transportation for a huge range of applications.

The National Renewable Energy Laboratory (NREL) researchers are working to make these processes more cost effective and commercially viable. Lewis research group that specializes in semiconductor materials, photo-electrochemistry and energy systems is equally active in this new innovative research.

A number of conversion technologies are currently being developed to obtain a range of solar fuels and chemicals. A schematic overview of solar fuels conversion pathways is presented in Figure 6, with sunlight, CO_2, water, and air as feed stocks.

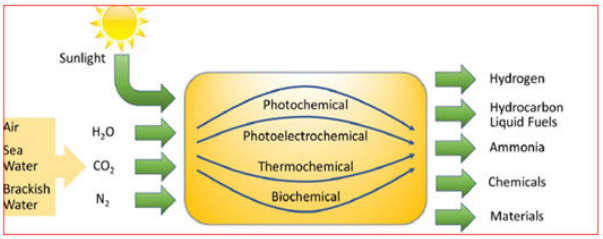

Figure 6: A schematic overview of the direct solar fuels conversion technologies.

Mineralization/Mineral Carbonation

Nature's way to sequester CO_2 is through a slow process called mineralization. The hydrolysis of CO_2 in moist air or water is a major driver of rock chemical weathering. It is one of the most efficient, thermodynamically favorable methodologies. Mineral carbonation is based on the reaction of CO_2 with metal oxide bearing materials to form insoluble carbonates, with calcium and magnesium being the most preferable metals. Such reactions are called silicate weathering and takes place in nature on a geological time scale. The reaction involves naturally occurring silicates as the source of alkaline and alkaline earth metals and consumes atmospheric CO_2, thereby leading to its fixation. The chemical reactions between these materials and CO_2 produces compounds such as magnesium carbonate and calcium carbonate that are stable over long time scales and can therefore be disposed of in areas such as silicate mines, or re-used for construction purposes. As a consequence, there would be little need to monitor the disposal sites and the associated risks would be very low [10].

Carbon mineralization can be achieved by various methods:

- *Ex-situ*, where the alkalinity source is transported to a site of CO_2 capture, ground to a small particles, and combined with CO_2 in a high temperature and pressure reaction vessel,
- Surficial, where dilute or concentrated CO_2 is reacted with the alkalinity source on-site at the surface (e.g., mine tailings, smelter slag), and
- *In-situ*, where CO_2 bearing fluids circulate through subsurface porosity in geological formations.

Carbon Dioxide Sequestration/Storage

The mother earth has a natural process of CO_2 sequestration in its oceans, forests, and grasslands, but these resources are fast depleting for carbon absorption. The nations world over are relying on technological innovations for carbon sequestration methods/solutions to help remove the massive amounts of carbon pollutants that have built up in the atmosphere over the last 150 years. The results suggest, so far, solutions are expensive on a cost per tonne basis ($70 or more) and not necessarily ready to deploy at scale. Companies and governments are working towards increasing the pace of solutions, while researchers and scientists improve techniques to stabilize and store carbon in either solid or dissolved states to inhibit it from heating the planet's surface.

CONCLUSION

CCUS, using CO_2 separation/capture, storage, utilization, and sequestration processes, is currently considered as the most proactive method to prevent the emission of CO_2 to the atmosphere and mitigate climate change and global warming. In order to employ this technology as a cost-effective technology for the reduction of CO_2 emissions from the use of fossil fuels, research and development in its related processes and materials are vital. With this perspective in view, this article has made an attempt to assess the status of existing CCUS technologies and new technological developments against the principles of green chemistry such as: Improve the energy or atom efficiency of processes or reduce the environmental impact and potential paths forward to minimize the environmental impacts of chemicals and processes.

CO_2 capture is an integral part of several industrial processes and accordingly, technologies to separate or capture CO_2 from flue gas streams have been commercially available for many decades. The most advanced and widely adopted new capture technologies are chemical absorption and physical separation; other technologies include membranes and looping cycles such as chemical looping or calcium looping.

CO_2 can be used as an input to a range of products and services. The potential applications for CO_2 use include direct

use, where the CO_2 is not chemically altered (non-conversion), and the transformation of CO_2 to a useful product through chemical and other conversion processes. New CO_2 use pathways include: Carbon-neutral fuels for jets, carbon fibre and more, chemicals and building materials such as cementing in CO_2 for the ages.

Storing CO_2 involves the injection of captured CO_2 into a deep underground geological reservoir of porous rock overlaid by an impermeable layer of rocks, which seals the reservoir and prevents the upward migration or leakage of CO_2 to the atmosphere. The gas is usually compressed first to increase its density and the reservoir typically must be at depths greater than 800 meters to retain the CO_2 in a dense liquid like state. The CO_2 is permanently trapped in the reservoir through several mechanisms. Scientists are now working on technological sequestration of CO_2 as well.

The projected growth in CO_2 capture over the next decade in the sustainable development scenario is characterized by three important trends:

- Retrofitting of large numbers of existing power and industrial facilities that significantly reduces lock-in of emissions.
- The scale-up of low-carbon hydrogen production with CCUS.
- The rapid adoption of CCUS technologies and applications that are currently in the prototype or demonstration phase.

Advanced technologies will be critical to stopping climate change. Mc Kinsey's analysis of the net zero pathways for Europe dated 5th November 2021, indicates that some 40 percent of the necessary emissions abatement could come from technologies that are either still in R and D or demonstrated but not yet mature. The remaining 60 percent could be achieved by widely deploying proven, mature technologies. H. Singh has published an update on CCUS R and D that could significantly reduce the net CO_2 emissions by way of identifying research gaps, opportunities in CCUS.

Despite being an undeniable strategy to contribute to GHG mitigation, CCUS is deployed slowly due to the prohibitive cost of capture, which censors many possible pathways of subsequent CO_2 utilization and transformation into chemicals, fuels and materials. Integrative capture and utilization appears as a promising route toward economically viable chains of values.

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