Carbon capture and utilization

HIGHLIGHTS

Processes and technology status – Carbon dioxide (CO_2) capture, storage, and utilization (CCS and CCU) are effective technologies for CO_2 fixation [1], [2]. CCU is about the reusing of the captured CO_2 by utilizing it directly or as a feedstock for the production of valuable products [3].

Cost - The cost of CCS/CCU depends mainly on the CO_2 source and purity. The scale of CO_2, the implemented capturing technology, and CO_2 taxes are significant factors in the calculation of CCS/CCU costs [4], [5]. High purity CO_2 sources represent relatively low-cost CCS project opportunities because of the avoided costly step of separating and capturing CO_2 from the flue gas stream [6]. The impurities in the CO_2 stream reduce the efficiency of carbon capture [4]. The specific capital costs per ton of captured CO_2 by 2025 are estimated to be 20-40 €$_{2013}$ [7].

Potential and barriers – CCS/CCU technologies are at a good advanced status concerning its design and optimization at a significant rate over the past years and are a potential solution to the problems of greenhouse-gas emissions [4]. The most threatening risks are the high costs and a lack of supporting regulation [8].

1- Carbon capture and utilization – Carbon capture, storage, and utilization or separation (CCS/U) aim to reduce global anthropogenic CO_2 emissions to tackle climate change by capturing carbon at the emission source and preventing its entry into the atmosphere. In parallel, some studies deal with the capturing of CO_2 from the ambient air. The captured carbon is then either utilized in industries or sequestered geologically [4].

For both utilization and storage, CO_2 capture is a key process. The current progress of carbon capture development routes and CO_2 utilization pathways is considerable. The main challenges of the successful industrial CCS/U development are high costs of CO_2 separate from flue gas or ambient air and the high costs of CO_2 conversion in various utilization pathways [9]. Possible carbon utilization pathways include the usage of CO_2 in oil and gas recovery enhancement, polymer

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processing, the manufacturing of fertilizers [10], [11], [12], urea [13], [14], [15], methanol synthetic methane, synthetic crude, electrochemical conversion to certain chemicals, and water desalination projects [4], [16], [17], [18].

Heavy industries including cement, iron and steel, oil refining, and petrochemicals are collectively responsible for about 22% of global CO_2 emissions. Among these industries, oil refineries account for 4-6%, of which typically 25-35% arise from the regenerators in Fluid Catalytic Cracking (FCC) units [5].

2- Process overview – CO_2 capture is accomplished by employing several methods like the use of membranes, chemical looping, cryogenic distillation, etc. [4]. The collected CO_2 can be stored in geological sites or can be utilized for enhanced oil recovery or in chemical industries. The CO_2 utilization techniques are young and significant research is needed to make these processes economically viable [19]. Various carbon capture and utilization technologies are discussed in the following.

3- Carbon capture technologies and methods – Different capture and separation technologies via several methodologies exist, and their costs depend on the CO_2 amount, CO_2 concentration, partial pressure, and the concentrations of contaminations such as N_2 [8], [20].

Capture technologies are typically categorized as pre-combustion, oxy-fuel combustion, and post-combustion processes [19], [8]. The post-, pre- and oxy-fuel combustion carbon capture technologies make use of various materials and separation methods depending on the need and demand [4]. Figure 1 depicts a schematic overview of the different CO_2 capture categories [8], and figure 2 presents the schematics of three different types of pre-, post-, and oxy-combustion carbon capture technologies.

Pre-combustion capture (PCC) is used in gasification, where carbonaceous materials such as coal and biomass are reacted at high temperatures to produce CO and H_2, which form the synthetic gas. Water-gas shift (WGS) reformer or auto-thermal-steam reformer releases CO_2 and H_2 by taking CO and steam as feed [4]. However, the main issue of pre-combustion route is H_2 combustion. H_2 cannot replace conventional fuels such as methane due to the physics of H_2 combustion. Pre-combustion implies, in many cases, to replace existing kilns or boilers with new kilns and boilers, however, the technology readiness times and its costs are not available yet. Lastly, H_2 combustion with

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air produces not only water but also NO_x which are environmentally harmful [21], [22], [23].

Oxy-fuel combustion is almost an alternative to the post-combustion CC technique [20]. Oxy-fuel combustion technology burns fuel in a mixture of oxygen and recycled flue gases (RFG) rather than air which is the case in post-combustion. Hence, the end-stage mixture consists mainly of CO_2 and condensable water vapor. Consequently, separation of the water vapor is possible during the compression process [4], [20].

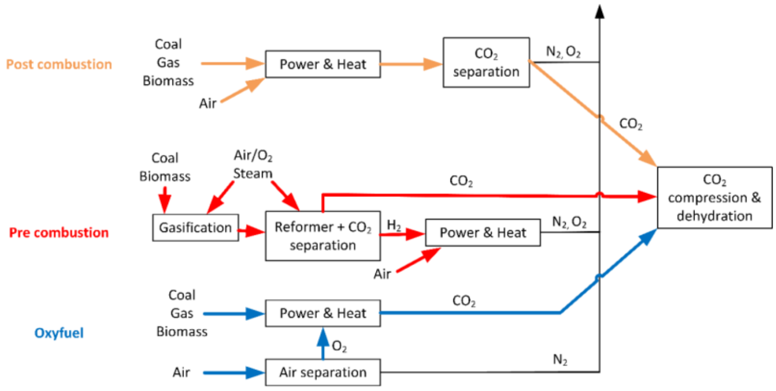
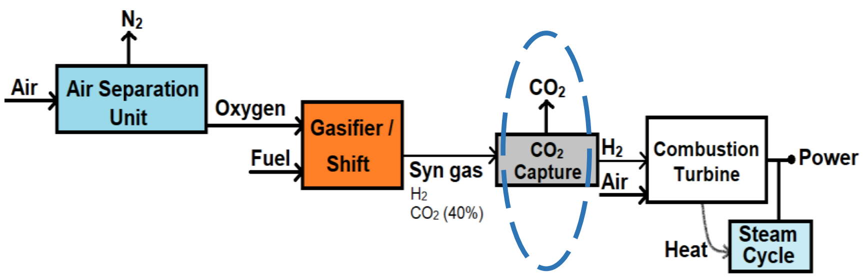


Figure 1. Overview of CO_2 capture technologies [8].



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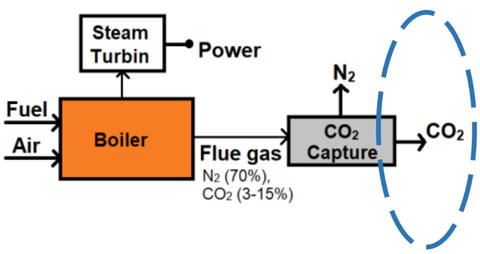

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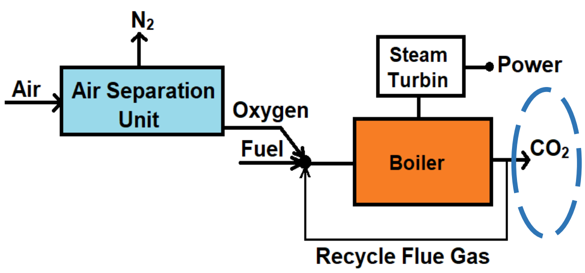

(c)

Figure 2. a) Pre- combustion, b) post- combustion, and c) oxy-combustion carbon capture schematics

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In oxy-fuel combustion, O_2 is used instead of air to reduce the amount of nitrogen in the exhaust gas. The other source for high purity O_2 production is green H_2 production via electrolysis of water. So, the H_2 economy will probably have a huge impact on O_2 production costs. The oxy-fuel combustion process is interesting because it produces a gas mainly composed of CO_2, H_2O, particulates, and SO_2. Then, H_2O can be removed by condensation and the particulates, while SO_2 can be eliminated by electrostatic precipitation and desulphurization. These refines will result in a pure CO_2 stream suitable for compression, transport, and storage. This process is combusting fuel in a mixture of pure O_2 (with purity above 95%) and CO_2 (80-98%). The major challenge is the energy-intensive air separation unit [8]. Figure 3 depicts a schematic of the oxy-fuel combustion technology.

Among CCS technologies, post-combustion is the most mature alternative to capture CO_2 and finds use to retrofit existing carbon emissions [24]. Post- and pre-combustion captures rely on methodologies that can separate CO_2 from the mixed stream, via 1) Solvent scrubbing, 2) Adsorbent, 3) Membrane, 4) Cryogenic distillation [4]. Figure 4 shows different separation methodologies.

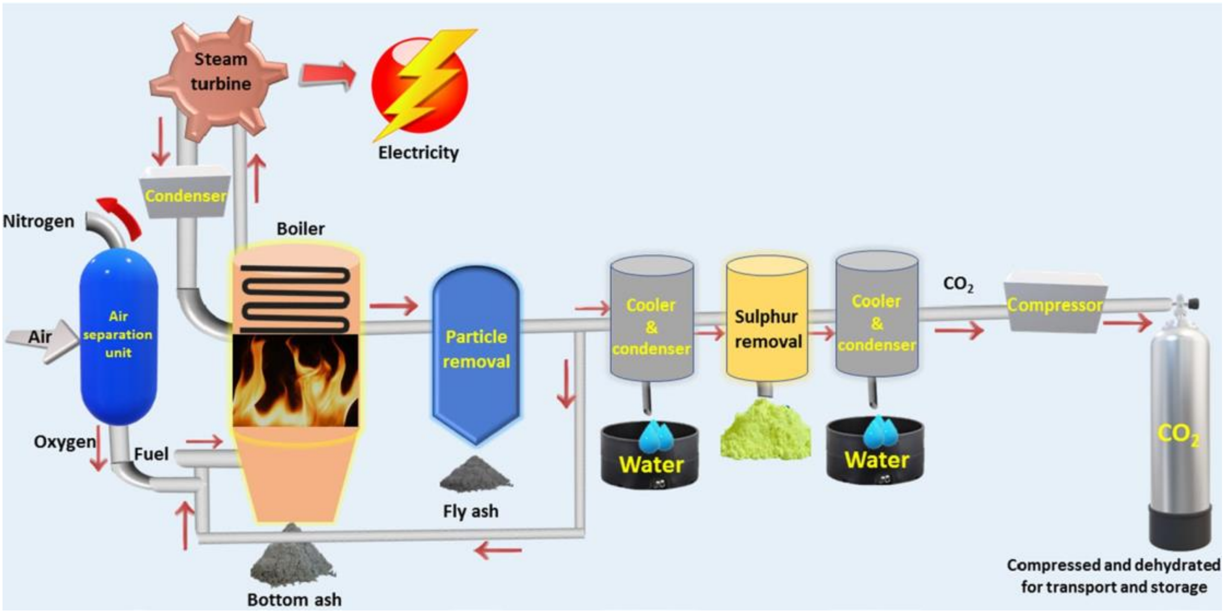

Figure 3. Oxy-fuel combustion technology [25]

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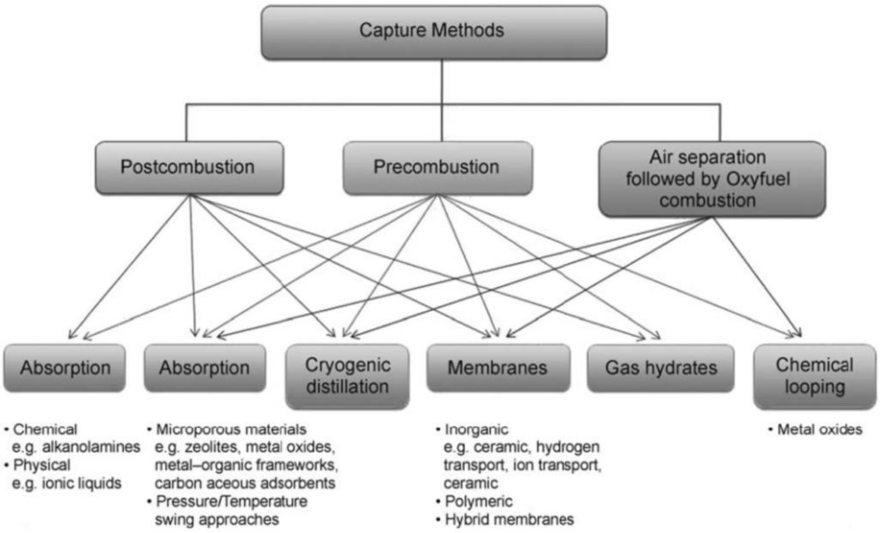

Figure 4. Separation methodologies [4]

The main methodologies of carbon fixation are chemical looping combustion, biological CO_2 fixation and fuel cells for CCS, fuel cells for CO_2 capturing, and CO_2 electrolyzer.

3-1- Carbon separation techniques

3-1-1- Solvent scrubbing - Solvents for CO_2 capture can be physical solvents such as methanol that absorb CO_2 based on Henry's law or chemical solvents that absorb CO_2 through chemical reactions [2]. Physical solvents are suitable for the separation of CO_2 with high pressure.

Generally, a CO_2 capture process consists of two steps: (i) separation of CO_2 from a gas mixture through a selective reaction and (ii) regeneration of the material used for CO_2 separation by a reverse reaction. Capturing of CO_2 can continue by reusing the utilized material and sequentially repeating these two steps. To capture CO_2 efficiently, one practical requirement is "reversibility." Between variable CO_2 capture materials such as chemical solvents, porous sorbents, gels, and membranes, amines are the most widely utilized chemicals [2], [26]. Amine scrubbing is the most mature CO_2 capture technology by year 2022 [27]. The main reason is that the moderate interaction allows for the effective separation of amine and CO_2 via a reversible reaction. Due to high variations in amine molecular structure, the CO_2 capture material within the range of moderate reactivity can be further adjusted based on the amine structure and/or blending amines. Such adjusting has been one of the central themes in the development of CO_2 capture technologies [2].

Amines are consisting of three types based on the number of hydrogen atoms attached

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to the nitrogen atom. Primary, secondary, and tertiary amines contain nitrogen atoms that are covalently attached to two hydrogen atoms, one hydrogen atom, and only non-hydrogen atoms, respectively (primary (−NH_2) > secondary (>NH) > tertiary (>N−)) [2]. Primary and secondary amines react with CO_2 to form the carbamate anion and protonated amine as the following reaction [2]:

$$R^1R^2NH + CO_2 + B \rightleftarrows R^1R^2NCOO^- + BH^+$$

Where Rn represents the substituent, such as an alkyl group, and B is the Brønsted base, such as another amine in the system. Carbamic acid may be produced as an intermediate or byproduct of the amine-CO_2 reaction depending on the substituents and reaction field [2].

$$R^1R^2NH + CO_2 \rightleftarrows R^1R^2NCOOH$$

3-1-2- Adsorption - Post-combustion CO_2 capture by adsorption using solid materials is considered an attractive technology for carbon emission reduction [28]. Generally, adsorption technology is widely considered for gas purification due to its flexibility and efficiency [29]. CO_2 adsorption using solid materials is considered a promising technology to overcome the challenges related to amine-based absorption [28]. They can massively capture CO_2 in industries due to their outstanding properties such as strong stability at high temperatures and high adsorption amounts in different modified forms [30]. The CO_2 adsorption materials are porous solids such as activated carbon zeolites, porous silicates, microporous organic polymers (MOPs), metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), covalent organic frameworks (COFs), amine functionalized adsorbents, metal oxides, hydrotalcite-like compounds, alkali metal carbonates, ceramics, and porous carbon adsorbents [28], [29], [31]. As a case in point, the reversible CO_2 adsorption/desorption by Li_4SiO_4-based sorbents under high temperature has attracted much attention in recent years due to its potential to capture CO_2 with a high capacity and excellent cyclic stability [32].

3-1-3- Membrane separation - Membranes are more effective and economical alternatives to the existing options [4]. However, they are one of the least matured technology because there is no practical demonstration of their theoretical energy advantages [4]. CO_2 diffuses through the membrane as a permeate proportional to its partial pressure separating itself from the mixed stream across the membrane [4]. Various studies have made use of polymeric membranes (polyacetylenes, polyaniline, poly(arylene ether)s, etc.), porous inorganic membranes (Al_2O_3, C, SiC, TiO_2, $M_{2/n}OAl_2O_3{\cdot}xSiO_2{\cdot}yH_2O$, ZrO_2), dense inorganic membranes (thin layers of metal like Pd and its alloys, or solid electrolytes like ZrO_2), alumina membranes, silica membranes, zeolite membranes (ZSM-5, Y type, silicalite, A-type, P-type, modernite), mixed matrix membranes (polydimethylsiloxane-silicalite, polyimide-carbon molecular sieve, polyimide-silica, Nation-zirconium oxide), hybrid membranes (polyether-silica, trichlorosilane- γ-alumina) and facilitated transport membranes for CO_2 separation [4].

The membrane-assisted liquefaction is the most cost-efficient capture technology if steam must be supplied through an electric boiler [33]. Membranes with high selectivity need large areas as they have lower permeability and high energy requirements are involved in feed compression to maintain pressure driving force across the membrane making the process costly [4].

3-1-4- Cryogenic separation - Cryogenic separation is done at a sub-ambient temperature under high pressure by employing a series of cooling and compressing operations to produce high purity liquid CO_2. It operates at extremely high pressure, is energy-intensive, and generally is not used to capture CO_2 from the flue gases [4]. Among these methods, cryogenic distillation seems to be unsuitable for large-scale CCS. This is because distillation is an energy-intensive process with the power requirement estimated to be 600–660 kWh/t-CO_2 due to the extremely low temperature and high pressure of the process [2].

Overall, advancements in material science and process engineering will lead to the creation of in situ capture-conversion technologies. These technologies will improve the cost and efficiency of CCS/CCU integration systems, hybrid adsorbent/catalyst, high-performance dual-function materials, etc., to create high cost-effective technology [4]. The prospect primarily lies in the direction of hybrid processes and simultaneous capture-utilization processes due to their energy efficacy and cost-effectiveness [4]. After the CO_2 capturing, the next process is the transportation of liquefied CO_2 through pipelines or tankers followed by sequestration or storage deep inside the earth or simply its utilization [4]. There exist several demonstration plants for deep storing of CO_2 worldwide, such as the Lacq pilot in south France, Norwegian CLIMIT project, STEMM-CCS, lake Charles Methanol, CarboNet, Quest project in Canada, In Salah CO_2 storage project in

Algeria, Shenhua CCS demonstration project in China, Gorgon storage project in Australia, etc [34], [35], [36], [37], [38], [39].

3-2- Carbon fixation

3-2-1- Chemical looping combustion - Chemical looping combustion (CLC) is an advanced oxy-fuel technology using a metal oxide to transport oxygen from air to the fuel, thus avoiding direct contact between fuel and air [5], [40]. The separation of CO_2 is inherent in the process so that the CLC process imposes a very low energy penalty in the order of 4% points (incl. compression) [5]. In CLC, the oxygen carriers which bring oxygen from the air to fuel are generally smaller particles of metal oxides such as Fe_2O_3, NiO, CuO, or Mn_2O_3. Oxygen carriers circulate between the air reactor (where it gets oxidized) and the fuel reactor (where it gets reduced by fuel) in CLC. CLC avoids energy penalties observed in the traditional amine scrubbing process [4]. In recent years, CLC was investigated as an option for CCS in various test rigs for gaseous fuels and solid fuels [5].

3-2-2- Biological CO_2 fixation and fuel cells for CCS - There is no single solution for damping the repercussions of climate change [20]. During the last decade, biological technologies have been proved as valid alternatives to physical/chemical carbon capture technologies thanks to lower environmental impact, less operating costs, and higher robustness. Bio-fixation of CO_2 by photosynthetic microorganisms (such as microalgae) has drawn attention because it allows removing CO_2 from waste gas along with the advantage of converting inorganic carbon into valuable algae biomass that can be used for many industrial applications [41].

As reported in the scientific literature, microalgae can grow either in open or closed photo-bioreactors. Open photobioreactors (e.g. high rate algal pond) exhibited lower biomass productivity and can be easily affected by external contamination. In contrast, closed PBRs (e.g. tubular, flat panel, bags, etc.) demonstrated several advantages such as higher biomass productivity and better control of the operating parameters in optimal ranges [41]. The maximization of CO_2 bio-fixation requires the optimization of microalgae growth rate and biomass productivity [41].

3-2-3- Fuel cells for CO_2 capturing - Recently varying kinds of fuel cells are considered as an effective method for CO_2 capturing and/or conversion. Fuel cells (FCs) are efficient energy converting devices that produce energy via an electrochemical process [20]. Fuel cells (FCs) have high efficiency, silent operational

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characteristics, compact size, and low or no environmental impacts, especially when fueled with hydrogen obtained from renewable energy sources [20]. Among the different types of fuel cells, solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), and microbial fuel cells (MFCs) demonstrated promising results in this regard. High-temperature fuel cells such as SOFCs and MCFCs are effectively used for CO_2 capturing through their electrolyte and have shown promising results in combination with power plants or industrial effluents. An algae-based microbial fuel cell is an electrochemical device used to capture and convert carbon dioxide through the photosynthesis process using algae strains to organic matters and simultaneously power generation [20].

Direct CO_2 electro-reduction suffers from carbonate formation. In a low-temperature CO_2 electrolyzer, electrons reduce CO_2 to the products and OH^-. Carbonate formation brings a dramatic rise in the energy consumption of CO_2 electro-reduction. A direct CO_2-to-C_2H_4 process, including electrolysis, separation, and carbonate regeneration, revealed that carbonate formation might cause energy penalties up to 278 GJ for producing 1 ton ethylene, accounting for 60%–70% of the total energy cost. Using CO_2–CO–C_{2+} tandems are a promising strategy to avoid the energy penalty caused by carbonate formation, because CO does not react with OH^-. Carbon-free CO_2 tandem electrolysis requires an OH^--free CO_2-to-CO process. Some study has introduced CO_2–CO–C_{2+} tandems to avoid carbonate formation. The suggested prototype includes a CO_2–CO–C_{2+} tandem consisting of a solid oxide electrochemical cell and a membrane electrode assembly as depicted in figure 5 The entire process is carbonate-free and rewires 138 GJ per ton ethylene [42].

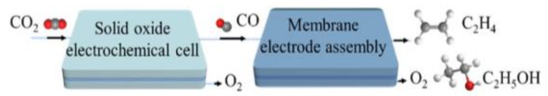

Figure 5. The schematic illustration of a carbon-free CO_2–CO–C_{2+} tandem [42].

3-2-4- CO_2 electrolyzer – The electrochemical enhancement of CO_2 to fuels has a two-fold benefit. First, this process reduces CO_2 to value-added molecules. Second, it stores excess renewable at the peak production period into energy at chemical molecules [43]. The existing designs of CO_2 electrolyzers range from microfluidic flow cells (figure 6a) to polymer-membrane based reactors (figure 6b) [43], [44], [45].

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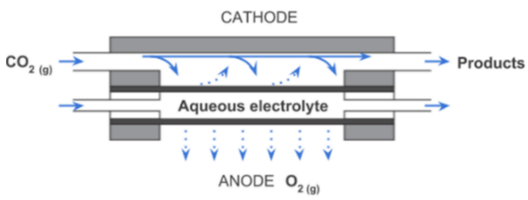

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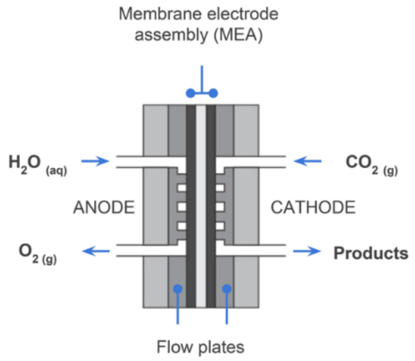

(b)

Figure 6. a) Microfluidic reactor consisting a liquid electrolyte flow channel between the anode and cathode gas diffusion electrodes (GDE) materials. b) Membrane-based reactor containing a membrane electrode assembly (MEA) consisting of the anode and GDEs on either side of a polymer electrolyte membrane (PEM) [46].

An electrolyzer that uses green power, carbon dioxide (CO_2), and water to produce a synthesis gas consisting of carbon monoxide (CO) and hydrogen. An eight-meter high steel cylinder in an adjacent hall. In the cylinder, bacteria convert the gas into chemical substances such as hexanol and butanol. Siemens Energy and Evonik have demonstrated this CO_2 electrolyzer through the Rheticus project in Marl, Germany [47].

The membrane electrode assembly (MEA) electrolyzer is the state-of-the-art reaction platform for CO_2 reduction reaction (CO_2RR) at industrially relevant scales. With the cathode, membrane, and anode connected in a zero-gap fashion, this electrolyzer provides lower resistance and greater stability than the liquid flow cell electrolyzer. The absence of the electrolyte on the cathode side also provides the opportunity to collect concentrated liquid products from the cathode. Recent progress in CO_2RR catalysts has enabled selective and high-rate electro-synthesis of ethanol in the MEA electrolyzer [48], [45].

A zero gap electrolyzer cell continuously converts gas phase CO_2 to products without using any liquid catholyte. In this electrolyzer, two electrodes are pressed to each other with an ion-exchange membrane in between. This configuration could significantly decrease mass transfer and electron transfer resistance and thus improve energy efficiency, making it more feasible in practical applications [49], [50]. In zero gap membrane electrolyzers, CO_2 gas is directly fed to the cathode. These cells offer a simple technological solution, in which (i) the cell resistance can be very low (which translates to high energy efficiency), (ii) the inlet can be pressurized relatively easily, (iii) no catholyte is used

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and, hence, no liquid catholyte circulation loop is required, and finally, (iv) the losses due to CO_2 dissolution in the catholyte are minimal. The knowledge gathered with fuel cells and PEM water electrolyzers might contribute to future scale-up of this technology, as these are mature electrochemical technologies with cells of similar structure [49].

Microfluidic electrolytic cells (MECs) are a kind of highly attractive electrolyzer configuration developed by Kenis and coworkers (39, 114). In this device, the membrane is replaced by a thin space (<1 mm in thickness) filled with flowing electrolyte stream to separate the anode and cathode [50].

H-type electrolyzers are capable of screening a number of catalysts in a short span of time, making it easy to operate and cost-effective. Despite their low CO_2 solubility and poor mass transport, H-type electrolyzers are commercialized due to their screening of a vast number of catalysts. In contrast, membrane-based gas and liquid phase flow reactors break the barriers faced by H-types through the incorporation of gas diffusion electrodes (GDEs) and the membrane electrode assembly (MEA) [51], [52]. As the GDE forms the gas–liquid–solid interface, it allows the electrolyzers to generate current densities at the industrial level (200 mA/cm^2). a continuous liquid fed intermittent flow electrolyzer can control the electrolyte flow at a desired frequency and allow sufficient time for CO_2 gas molecules to effectively reduce into HCOOH. Recent studies show that recirculation of by-products to the liquid phase MEA flow reactors substantially improves $HCOO^-$ selectivity, lowers material costs, and promotes CO_2 mass transfer. The zero-gap electrolyzer has newly emerged and leads to a straight-forward implementation of industrial systems for CO_2 reduction to value-added products in the future [51], [50].

CO_2 electrolyzers using molecular catalysts can improve efficiency of CO_2 reduction reaction (CO_2RR) in CO_2 electrolyzers [53].

The focus of main studies on CO_2RR is the formation of C─O and C─H bonds, such as ethanol, acetic acid, and ethylene, in ECR technology. Exploration of other types of products is also important for CO_2RR and shows economical interest. For example, in situ formation of C─Br bond transforms open the routes towards 2-bromoethnol production, which is an important building block in chemical and pharmaceutical synthesis [50].

4- Carbon utilization pathways -

CO_2 utilization is the process of using

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emitted carbon dioxide (CO_2) as a raw material or as a catalyst for new products [4].

Conversion of CO_2 to synthetic fuels was identified as a promising pathway to scaling up the carbon capture technologies, as the valuable products would offset the carbon capture and conversion costs [9]. Other ways of reducing carbon emissions include negative emission techniques, renewable resources, and direct air capture techniques [4]. CO_2 utilization is possible via both direct and indirect pathways available in table 1. In direct utilization, CO_2 of high purity is directly used in many food and beverage industries. Microalgae production can be used as a major CO_2 sink [4]. Moreover, as the cost of fossil-based energy continues to climb, the interest in the utilization of CO_2 will intensify [9].

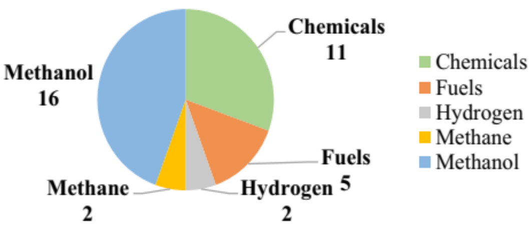

Figure 7. CO_2-derived product categories addressed in the literature set [3]

5- CCS and CCU in Belgium –

ArcelorMittal Belgium has started the construction of two new groundbreaking facilities at the Ghent site to reduce carbon emissions. The two installations represent a total investment of 160 million euros and will avoid approximately 400,000 tons of CO_2 emissions per year in the first phase [54].

Moreover, The Power to Methanol project in Antwerp will produce methanol from captured CO_2 combined with hydrogen that has been sustainably generated from renewable electricity [55].

6- Investment and production costs

6-1- Capture costs - CO_2 is not available cost-free and requires financial investments for capturing, purification, and transportation depending on the site location. Some studies state that the capture cost amounts to 70-80% of the total cost of a full CCS system [8].

Carbon capture routes and CO_2 utilization pathways (CCS/U) have considerable progress at lab and pilot scales. However, the industrial development of carbon capture is still facing main challenges. For example, high costs of CO_2 separation from flue gas or ambient air into a usable stream and the high costs of CO_2 conversion in various utilization pathways are the essential obstacles ahead of CCS/U [9].

The most important drivers of CCS cost are the economics of scale, partial pressure of CO_2, energy costs, and technology innovation. By increasing the storage size

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Table 1. Classification of CCU pathways [3]

Pathways	Applications	Examples
Direct use	Yield boosting	Greenhouses, algae, fertilizer/urea
	Solvent	EOR
	Heat transfer fluid	Refrigeration
	Other	Food and beverages, medical uses, welding
Indirect use	Fuels	Methane, methanol, gasoline/diesel
	Chemicals	Chemical intermediates, polymers
	Building materials	Cement, concrete

and the CO_2 patricidal pressure, CCS costs decrease [56].

The costs of CCS are higher in the case of purifying CO_2 and removing toxic or hazardous chemicals [8]. However, innovations in carbon capture address many of the traditional operational concerns. Prefabricated, modular carbon capture technology can reduce capital and operational costs by up to 75% and 50%, respectively [57]. For example, the CO_2 concentration in the flue gases of steam crackers is 5% vol., and the proper capturing technology is post-combustion. Integration of this technology to steam crackers requires retrofitting of the conventional plant, which imposes extra capital. Moreover, this technology demands stable solvents that stand for operational costs. Costs of the application of CCS in a steam cracker are available in table 2. The CAPEX value refers to the equipment costs for the capture system (absorption, desorption, and compression) and the piping for interconnecting with the steam cracking stacks. The fixed OPEX is 4% of the CAPEX, and it does not include energy costs [58]. Overall, high purity sources include ethylene oxide (EO) and ammonia plants. For example, the potential of CCS in the EO plants in the Dutch industry is abating ~0.1 Mt_{CO2} at an abatement cost of ~25 $€_{2013}/t_{CO2}$ [7].

Table 2. Investment costs for retrofit post-combustion CCS in steam cracker furnace with 5%vol. CO_2 concentration in the flue gas - Post-combustion using mono-ethanolamine (MEA) solvents [58]

	Value	Unit
Capacity	428	kt CO_2 captured/yr
CAPEX	156	$€_{2010}$/t CO_2 captured/yr
Fixed OPEX	6.8	$€_{2010}$/t CO_2 captured

In general, CCS costs may vary widely on a case-by-case basis [33]. For example, a general study on the ethylene oxide production plant in the year 2017 has predicted the following technology

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availability time and the investment costs [59]:

- Process CO_2 reduction [1]
- Year of availability = 2030[2]
- Reference capacity (kt/y) = 260
- Cost ($€_{2013}/t_{CO2}$) = 39
- Investment cost ($€_{2013}$) = 500000

Some research has proposed the following method for calculation of investment costs for ethylene oxide production:

Investment cost = GHG Reduction × Process emission factor × CCS cost × Reference capacity [59]

Costs in natural gas processing, fertilizer, and bio-ethanol have a relatively narrow band of variance across all countries, with a range of 17.7 – 23.9 $€_{2017}$[3] per ton of avoided CO_2. Avoided CO_2 costs in cement have a much larger range, from 92 – 171.7 $€_{2017}$ [4]/t_{CO2}, while iron and steel costs vary from 62.8 to 105.3 $€_{2017}$[5]/t [60]. Conversely, the higher proportion of capital costs for coal-fired plants makes them more sensitive to nonfuel input costs. For example, increasing labor costs by 100% increases the installed capital cost of the PC coal plant by 29%, and the levelized cost of energy (LCOE)[6] increases by 14% [60]. CO_2 capture costs via CLC technology are potentially as low as 10 $€_{2009}$/t of CO_2 captured [5].

CCS heat-integrated to power plants is an important option to mitigate carbon emissions and postpone replacing fossil-carbon-fired power plants. However, the high cost of retrofitting may create a technology lock-in [24]. For coal-fired power plants, the avoided cost is estimated between 34 and 68 $€_{2018}$//t_{CO2}. The captures costs are closer to 20 to 40 $€_{2018}$ per ton CO_2 [8].

Atmospheric CO_2 concentrations are globally around 400 ppm (monthly average). Many of the technologies to capture CO_2 from the atmosphere are still in development. The technologies for 'Direct Air Capture' (DAC) are more expensive than the technologies for capture from point

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[1] Due to lack of data, a conservative value of 50% has been assumed (in reference 18) [59]

[2] Lack of information. (According to (Carbon Counts, 2010) this industry shows low interest to implement CCS.). Hence 2030 can be acceptable

[3] 20 $\$_{2017}$ to 27 $\$_{2017}$, 1 $€_{2017}$ = 1.13 $\$_{2017}$ [74]

[4] 104 $\$_{2017}$ to $\$194$ $\$_{2017}$/ton

[5] 71 $\$_{2017}$ to 119 $\$_{2017}$/ton

[6] The levelized cost of energy (LCOE), or levelized cost of electricity, is a measure of the average net present cost of electricity generation for a generating plant over its lifetime. It is used for investment planning and to compare different methods of electricity generation on a consistent basis. LCOE is calculated as the ratio between all the discounted costs over the lifetime of an electricity generating plant divided by a discounted sum of the actual energy amounts delivered.

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sources and on top, they require large amounts of energy. Energy is used for air transportation and sorbent regeneration. The minimal theoretically needed energy is about 3.4 times higher compared to point sources with a 10% CO_2 concentration. However, DAC can become interesting in the future if other CO_2 sources start to decrease due to the use of low carbon technologies [8].

A study by David W. Keith et. al. describes a DAC process with a levelized cost of ca. 75 to 195 €$_{2018}$ per ton CO_2. The process requires 5.25 GJ of gas and 366 kWh of electricity per ton CO_2 captured in case the CO_2 is delivered at 150 bar [8].

DAC is an energy-intensive process, which directly reflects on the higher costs of capture from this application ~ 24 - 901 €$_{2015}$[7]/t$_{CO2}$ as compared to carbon capture from large CO_2 exhaust sources ~18 - 90 €$_{2015}$[8]/t$_{CO2}$, and to high purity sources such as ethanol processes with cost estimates for carbon capture of ~ 5.4 – 10.8 €$_{2015}$[9]/t$_{CO2}$ [61]. The other cost estimate shows the cost of 200 to 1000 €$_{2018}$/t$_{CO2}$ for capturing CO_2 from ambient air [8]. House et al. estimate the cost for air capture in the order of 700 €$_{2011}$/t$_{CO2}$ [8].

Although pre-combustion technology offers higher efficiency than post-combustion technology, it is more expensive. Currently, post-combustion technology is the most mature and widely used route among the three main routes of carbon capture and storage. However, partial pressure of CO_2 is low in flue gases, which is due to the presence of N_2 molecules in the air. A low concentration of CO_2 increases the cost of capturing. Consequently, the electricity generation cost increases by approximately 60–70% for the new infrastructure or 220–250% for the retrofitting [25].

Table 3 presents the cost and CO_2 emissions intensities based on the heat supply evaluation performed in the cement industry [33]. As seen in table 3, extracting steam from a low-pressure turbine or steam originating from waste heat recovery in core industrial processes are cheaper options and have lower CO_2 emissions intensity. Thus, integrating excess heat available in the industrial plant or another facility near the CO_2 capture unit is expected to be a cost-effective solution [33].

[7] 27 - 1000 \$$_{2015}$
[8] 20 – 100\$$_{2015}$
[9] 6 – 12\$$_{2015}$

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Table 3 - Cost and CO_2 emission intensity of different stream supply options [33].

Source	Emission intensity [$kgCO_2/GJ$]	Steam cost [$€_{2015}/GJ$]
Electric boiler	87	18
Natural gas boiler	57	7.2
Natural gas-CHP plant	57	6.4
Coal CHP plant	127	6.1
Steam extraction from an LP Turbine	49	3.7
Excess heat from industrial core process	0	1.9

6-2- CCU costs - Electricity is an important cost factor for CCU processes [8]. The price of green hydrogen should be in the range of 2 to 4 €/kg to be competitive for the chemical industry. By the year 2018, hydrogen from electrolysis cost was between 2.6 and 3.8 $€_{2018}/kg_{H2}$ [8].

Other techno-economic studies on the production of low-carbon fuels also provide significant insights. For example, in the production of light olefins (C_2-C_4) from coal-based CO_2 catalytic hydrogenation, the renewable energy sources (RES) hydrogen (RES-H_2) production costs dominate the process economics; a break-even price of 2500-3300 $€_{2020}$/ton for the produced petrochemicals was estimated [62].

The estimated cost of unit production for the C_2-C_4 hydrocarbons from captured CO_2 and renewable hydrogen (H_2)[10] is 2.52 $€_{2020}$[11]/kg, and the CO_2 emission was estimated to be negative (−1.85 kg CO_2 per kg C_2-C_4 hydrocarbon) [63]. The results of this study showed that the price of renewable-based H_2 was the dominant and most sensitive factor [63].

6-3- Storage and transport costs - Both capture and transport of CO_2 are in general only interesting if large volumes can be processed [8]. Plant operators may decide to capture only a share of the plant's CO_2 emissions, either because it is physically impossible to capture all CO_2 emissions due to spatial constraints or because of economic reasons. Many literature studies assume a fixed cost for CO_2 transport and storage (often 10 $€_{2017}/t_{CO2}$) regardless of their considered CO_2 flow rate [33]. Pooling demand for transport and storage capacity by sharing pipeline and storage

[10] The process consists of two main stages: i) A reaction stage in which CO_2 is converted into alkene-range hydrocarbons over a K-promoted Fe catalyst, and ii) a separation stage in which multiple technologies are integrated for the recycling of CO_2, carbon monoxide (CO), and H_2 and the purification of the main C_2-C_4 hydrocarbon products (e.g., light olefins) and byproduct (C_{5+}).

[11] 3.58 USD_{2020}; 1 $€_{2020}$ = 1.42 $\$_{2020}$

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infrastructures can significantly reduce the average unitary cost, which might be particularly beneficial for small emitters. For example, for a transport distance of 250 km via onshore pipeline, increasing the annual transport flow rate from 0.5 to 5 Mt_{CO2}/y would reduce average transport cost more than three times, from over 20 $€_{2017}/t_{CO2}$ to around 6 $€_{2017}/t_{CO2}$ [33].

The cost of CO_2 storage contributes relatively small amounts to overall project costs. For onshore storage, the combined cost of transport and storage is estimated to be between 6.2 and 10.6 $€_{2017}$ [12]$/t_{CO2}$. Offshore transport and storage costs are estimated to be between 14.2 and 32.7 $€_{2017}$[13]$/t_{CO2}$ [60].

For transport by truck, the CO_2 is liquefied, typically at 17 bar and -30°C. The cost is estimated at 0.22 euro per ton per km. CO_2 storage costs in liquid form are between 4.46 to 13.86 $€_{2018}/t_{CO2}$ [8].

Ship-based transport of CO_2 can be an attractive option for industrial emitters in some cases due to its cost efficiency for small CO_2 volumes and transport over long distances [33]. Furthermore, shipping typically involves lower upfront investments, shorter construction time, offers more flexibility, could be easier in terms of environmental permitting, and may present opportunities for co-utilization of infrastructures. Shipping transport can be the preferred means of transport for a wide range of transport distances, especially for small annual flow rates. For example, shipping between harbors would be the cost-optimal option for distances above 250 km when transporting an annual flowrate of 1 Mt_{CO2}/y, while for higher annual flow rates pipeline transport is more cost-efficient for a wider range of transport distances [33].

7- Energy requirements – Compared to the chemical absorption processes, the physical solvent-based-processes have lower energy requirements. Energy demands range between 160 and 180 kWh per ton CO_2 recovered. The biggest difference is that physical-solvent based processes use weak physical bonds and, therefore, use pressure swing adsorption (PSA) or temperature swing adsorption (TSA) to release the CO_2. These processes are preferred for gas streams with high partial pressures over 3.5 bar or high overall pressures. PSA is often used for power plants and has a typical efficiency of over 85%. TSA results in a CO_2 purity of 95% [8].

[12] 7 USD$\$_{2017}$ and 12 $\$_{2017}$; 1 $€_{2017}$ = 1.13 $\$_{2017}$

[13] 16 $\$_{2017}$ and 37 $\$_{2017}$

For the production of chemicals, the CO_2 reacts with organic compounds to form carbonates/carbamates via the carboxylation process. Although the conventional processes are broadly used the CO_2 reaction with organic substances gives better fixation with fewer energy requirements [19].

The reforming of methane with CO_2 exhibits two main advantages: (i) both are greenhouse gases and this process can reduce overall carbon emissions, and (ii) more economical as gas separation process is not required. However, the process is more endothermic than steam reforming, which makes it an energy-intensive process. In addition, stable catalysts need to be developed to make this process viable [19].

8- Electricity and Hydrogen market - Using renewable energy for the electricity provision of CCU processes is not only necessary from an environmental point of view, but provides also advantages for grid stabilization and long-term, largescale, seasonal storage. Also, the use of green hydrogen is a prerequisite for CCU processes to have an environmental advantage over conventional production routes [8]. Moreover, reducing CO_2 emissions through CO_2 utilization is only possible if the electricity is from renewable sources [8].

In 2030 the technical potential of hydrogen in Flanders is estimated at 61 kiloton H_2 which requires 1.9 GW of renewable energy. This potential is estimated to increase to 481 kiloton H_2 by 2050, requiring 14.5 GW of renewable energy [8].

For green H_2 production also the electricity cost is important and is too high at the moment, especially if the distribution costs and taxes need to be paid [8].

**9- Challenges and future prospects - ** Among the various technologies mentioned for carbon capture, each one comes with its own set of challenges and engineering problems. In large-scale power plants (> 500 MW) that emit CO_2 at a daily average of 8000 tons, the existing capture equipment requires unique design and various adjustments to allow for enhanced advances in processes such as oxy-combustion and chemical looping, thus easing the processes of O_2 purification and dual fluidized beds. The impurities in CO_2 reduce the efficiency of carbon capture, and large costs are spent in attaining high purity of CO_2, which demands the development of new technologies for cheap and efficient removal of SO_x and NO_x. Ardent research is required for the novel production of

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Table 4: Electricity prices for non-household consumers in €$_{2017}$/kWh; Eurostat: nrg_pc_205 [8]

Consumption (MWh)	Price component	Belgium	The Netherlands
<20	Incl. all taxes and levies	0.259	0.195
	Energy and supply	0.067	0.060
	Network costs	0.093	0.053
	Taxes, fees, levies and charges	0.097	0.071
20-500	Incl. all taxes and levies	0.188	0.139
	Energy and supply	0.054	0.049
	Network costs	0.056	0.025
	Taxes, fees, levies and charges	0.077	0.066
500-2000	Incl. all taxes and levies	0.134	0.096
	Energy and supply	0.047	0.042
	Network costs	0.025	0.019
	Taxes, fees, levies and charges	0.059	0.035
2000-20,000	Incl. all taxes and levies	0.111	0.093
	Energy and supply	0.045	0.040
	Network costs	0.018	0.020
	Taxes, fees, levies and charges	0.047	0.033
20,000-70,000	Incl. all taxes and levies	0.086	0.069
	Energy and supply	0.042	0.039
	Network costs	0.010	0.013
	Taxes, fees, levies and charges	0.034	0.017
70,000-150,000	Incl. all taxes and levies	0.072	0.064
	Energy and supply	0.041	0.038
	Network costs	0.005	0.012
	Taxes, fees, levies and charges	0.024	0.014
>150,000	Incl. all taxes and levies	0.070	0.066
	Energy and supply	0.041	0.039
	Network costs	0.000	0.014
	Taxes, fees, levies and charges	0.013	0.013

value-added products from CO_2 emissions from plants on a daily basis [4].

The deployment of CO_2 management technologies faces the challenge of high investments, the returns on which are in a distant and uncertain future. Uncertainty results from policy outcomes, technology disruptions, and capital intensity. Additionally, nations hold different social and political perceptions and foresee opportunities to overtake the economic and political scene [24].

10- Potential for CCS deployment

– World-wide the highest potential and market size for CO_2 utilization are in the chemical and oil industry, with the Enhanced Oil/Gas Recovery (EOR/EGR) and to have the greatest potential for non-captive demand, the urea production, the polymer processing as well as in fuel and chemical synthesis such as renewable methanol, formic acid. It is also important that the cement sector has a great uptake potential whereas in the food sector, also a medium potential exists (e.g. carbonation,

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packaging, and horticulture) [64]. A high deployment scenario for global capture from high purity CO_2 sources by 2050 is available in figure 8 [65]. There exist gaps and barriers to CCS demonstration and deployment in high purity CO_2 sectors[14].

1. Data gaps – where missing information inhibits understanding of the sector potential to apply CCS;

2. Information gaps – where additional analysis of the sector characteristics may be warranted to better understand the scope for CCS application in the sector;

3. Knowledge gaps – where additional experience and knowledge-sharing, including potential pilot and demonstration projects, is required to enhance understanding;

4. Policy gaps – where additional awareness, policy, and regulatory developments by governments may improve the prospects for deployment of CCS in high purity CO_2 sectors.

Since 1972, CCS has been applied to capture CO_2 from an extensive range of sectors and industries. Typically, the progress of technology development

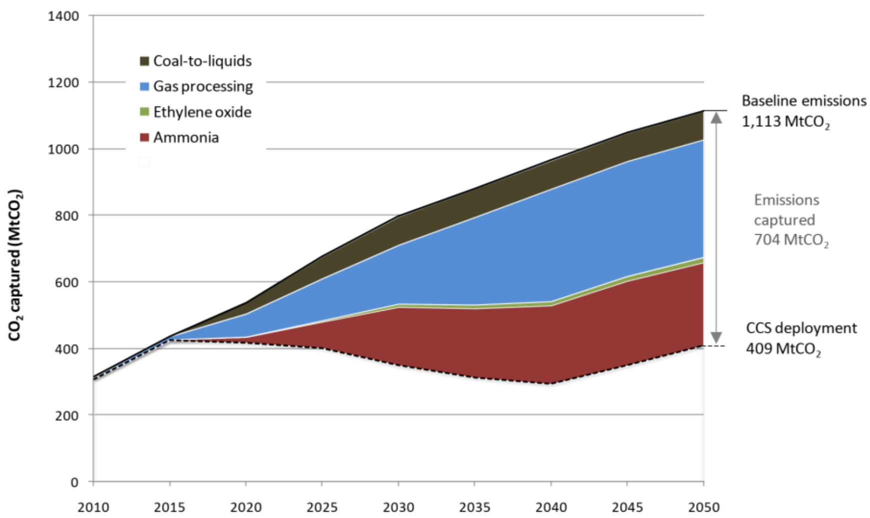

Figure 8. Global deployment of CCS from high purity CO_2 sources 2010-2050 [65]

[14] Some of these gaps are cross-cutting factors which are not specific to high purity CO_2 sources.

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contains a series of scale-up steps: first, laboratory-scale or bench; second, pilot-scale; third, demonstration-scale; fourth, commercial scale. Currently, there are eighteen large-scale facilities in operation in the world, five under construction, and twenty in various stages of development. Table 5 shows a summary of developed progress technologies by 2021 in terms of technology readiness level (TRL): carbon capture (C); transport (T); storage (S); and utilization (U) [66].

Table 5. Development progress of technologies in terms of technology readiness level (TRL) [66]

Technology Readiness Level	Current Development
TRL1	Concept
TRL2	Formulation
S	Ocean Storage
TRL3	Proof of concept (lab tests)
C	Ionic Liquids-Post-combustion
C	BECCS Power
C	Low T separation-Pre-combustion
C	Membranes dense inorganic (CO_2 separation)
S	Mineral storage
TRL4	Lab prototype
C	Oxy-combustion gas turbine (water cycle)
TRL5	Lab-scale plant
C	Membranes dense inorganic (H_2 separation for reformer)
TRL6	Pilot plant
C	Membranes polymeric (power plants)
C	Biphasic solvents-Post-combustion
C	Chemical looping combustion (CLC)
C	Calcium carbonate looping (CaL)
U	CO_2 utilization (non-EOR)
TRL7	Demonstration
C	Membranes polymeric (NG industry)
C	Pre-combustion IGCC + CCS
C	Oxy-combustion coal power plant
C	Adsorption-Post-combustion
C	BECCS industry
C	DAC
S	Depleted oil & gas fields
S	CO_2-EGR

Notes for table 5 are as following. BECCS: Bioenergy with Carbon Capture and Storage; DAC: Direct Air Capture; IGCC: Integrated Gasification Combined Cycle; NG: Natural Gas; EGR: Enhanced Gas Recovery [66]

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11- CCS characteristics and related costs [59] **-** CCS cost and technology availability differs for each production line. The complexity of EII processes, especially in the case of petro-/chemical sectors, and confidentiality of data are the main obstacles ahead of CCS deployment. Hence, for each production line, specific studies are required to determine investment costs.

As far as ethylene oxide production is concerned, CCS is a possible technology for this subsector and is installed in facilities after 2030. By 2050, 70% of the facilities practice CCS, which leads to emission savings as illustrated in figure 9 [59]. The specific energy consumptions for ethylene oxide is 25.3 TJ/kt_{EO} in 2050.

Overall, the cost of CCS is case-dependent. Hence, detailed studies for each plant are required to determine the emission points at processes, their quality, and their quantities. Having these data in combination with novel production routes and innovative carbon capture technologies is necessary for defining the pathways for industrial decarbonization. A research study on the narrative-driven alternative roads to achieve mid-century CO_2 net neutrality in Europe has illustrated that the electrification of end-use sectors combined with the large-scale expansion of renewable energy is a no-regret decision for all strategies. Moreover, hydrogen and synthetic fuels can be a relevant mitigation option for mid-century mitigation in hard-to-abate sectors. Authors of this study, also, have claimed that high carbon prices (300-900 €/t_{CO2}) are needed under all strategies to achieve carbon net neutrality in 2050 [67]. However, these cost data can differ by implementing disruptive technologies. For example, one of the newly emerged technologies, the CycloneCC [68] will reduce the carbon-capturing costs. Details of this technology are explained in the next section.

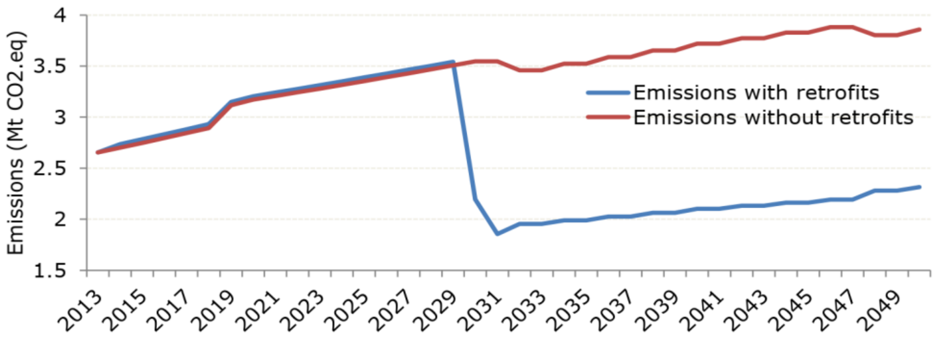

Figure 9. Trends of total GHG emissions in ethylene oxide production, according to the baseline scenario [59]

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12- Recent innovations on CCS/CCU - The recent innovation on carbon capture is the modular CycloneCC which works with patented APBS solvents[15] to achieve a 50% operating cost reduction [68]. CycloneCC is based on a novel process technology called rotating packed beds (RPBs) as depicted in figure 10. RPBs are a process intensification technology that improves the absorption of CO_2 into the solvent. At its heart, an RPB contains a disk of packing material that rotates about its axis. This generates a centrifugal force within the packing which enhances the CO_2 absorption process. The solvent is introducing into the RPB at its center where it is sprayed on to the packing via a liquid distributor. When the solvent contacts the packing the centrifugal force applied to the solvent from the rotational motion forces the solvent to travel radially towards the outer edge of the packing where it drains down to a sump before being pumped to the next stage of the process. The flue gas is introduced to the RPB from the outer edge of the packing and exits at the inner edge where the solvent enters. Therefore, the gas and the liquid contact each other in a counter-current fashion. The flue gas is absorbed by the solvent and the CO_2 present selectively reacts with the active components in the solvent thereby temporarily locking the CO_2 within the solvent [68]. The mission of CycloneCC is to achieve 25.8 €$_{2021}$ [16] cost of carbon capture especially for the hard-to-abate industries [68]. Moreover, CycloneCC technology offers a smaller size which is 10 times smaller than the conventional CO_2 capturing unit as depicted in figure 11. When commercialized, industrial companies and customers will be able to install these units in less than 8 weeks highly improving their operational profile and any downtime our customers may face [68].

Figure 10. CycloneCC unit structure

[15] APBS-CDRMax® is a commercially-available CO_2 capture solvent used for industrial flue gases or off-gases with CO_2 concentrations ranging from 3-25% by volume.

[16] 30 \$$_{2021}$; 1 \$$_{2021,\ Oct.}$= 0.86 EUR$_{2021,\ Oct.}$ (average) [75]

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Figure 11. Reduced size of CycloneCC in comparison to the conventional capturing unit

13- CCUS and required policies

Climate targets can only be achieved with a shift to new technologies and practices for the production and use of basic materials, as this accounts for around 16% of European greenhouse gas emissions [69]. Integration of captured CO_2 from carbon-intensive industries with green energy sources provides solutions for the storage and transport of renewable energy [70]. The long-term vision is to integrate the direct and indirect (via carriers such as H_2) use of renewable energy sources, together with the use of alternative carbon sources and technologies to close the carbon cycle and progressively phase out the use of fossils [70]. Carbon capture utilization and storage (CCUS) certainly feels like a strong solution to reduce carbon emissions, but many questions remain around rollout, costs, and business models [57].

Energy-intensive industries (EIIs) are responsible for about 70% of the total CO_2 emissions in the EU ETS - Emissions Trading System. Closing the carbon cycle in EIIs requires a regime transition, where hydrogen can play an important role [70].

Innovative technologies for emission reduction in the industrial sector are often not only characterized by higher investment costs, but also by higher operating costs. In the case of funding schemes that only provide investment grants, there is a risk that, at low CO_2 prices, the operation of an already constructed plant will not be worthwhile and the plant will become an investment ruin [69]. Hence, the project-based Carbon Contracts for Differences (CCfDs) are introduced as an important element in the policy mix to trigger emission reductions in industry [69]. CCfDs[17] can serve as a tool to make long-term political goals and political ambition visible and represent a credible voluntary commitment of climate policy [69].

[17] As governments incur higher costs for CCfDs if CO_2 prices remain low or even fall over the long term, these agreements are also an incentive for policymakers to contribute to a strong European emissions trading framework. On the other hand, rising CO_2 prices would allow governments to recuperate costs of CCfDs over time [69].

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Based on the CCfD, governments pay out the difference between the price of emissions allowances (EUAs) on the carbon market and a pre-agreed CO_2 contract price, thereby ensuring a guaranteed carbon price for clean energy projects[18]. For instance, companies that invest in green steel production will also be offered free allocations under the ETS to encourage them to invest. So the sector can get a lot of cash from the ETS [71]. One major advantage of CCfD is stabilizing the revenue streams from the normally highly volatile CO_2 prices. Accordingly, investors can rely on secure loans and reduction of financing costs [69]. Carbon contracts for differences started the design stage by 2020 in several countries such as Germany and the Netherlands, as a policy proposal for the decarbonization of heavy industries [72].

The other fact to boost carbon mitigation is that the deployment of new decarbonization technologies and associated policies consider wider environmental outcomes, such as air quality and water conservation [73].

Table 6. Summary table of CCS costs

Plant	Cost *
EO	25 $€_{2013}/t_{CO2}$
Natural gas and bio-ethanol processing,	17.7 – 23.9 $€_{2017}/t_{CO2}$
Cement	92 – 171.7 $€_{2017}//t_{CO2}$
Iron and steel	62.8 - 105.3 $€_{2017}/t_{CO2}$
Coal-fired power plants	34 - 68 $€_{2018}/t_{CO2}$
Direct Air Capture	200 - 1000 $€_{2018}/t_{CO2}$[19]
Large CO_2 exhaust sources	18 - 90 $€_{2015}/t_{CO2}$
High purity CO_2 sources	5.4 – 10.8 $€_{2015}/t_{CO2}$
Price of green hydrogen	2.6 - 3.8 $€_{2018}/kg_{H2}$
Coal-based CO_2 catalytic hydrogenation	2500-3300 $€_{2020}/t_{\text{Produced petrochemicals}}$
CO_2 transport and storage	10 $€_{2017}/t_{CO2}$**
Offshore transport and storage	14.2 - 32.7 $€_{2017}/t_{CO2}$
CO_2 storage costs in liquid form	4.46 - 13.86 $€_{2018}/t_{CO2}$
Truck transportation of the CO_2[20]	0.22 $€_{2018}/t_{CO2}$ per km

* Costs depend on the type of capturing. For example, the pre-combustion route could offer a cheaper cost than that of post-combustion and oxy-fuel combustion routes by 38–45 and 21–24%, respectively (in theory).

[18] The CCfD pays out the difference between the yearly average auction price of emissions allowances (EUAs) and the contract price, thus effectively ensuring a guaranteed carbon price for the project. In exchange for this insurance, investors are liable for payment if the carbon price exceeds the contract's strike price [69].

[19] And the levelized cost of 75 to 195 $€_{2018}/t_{CO2}$ by David W. Keith et. al. [8]; and it is 700 $€_{2011}/t_{CO2}$ as estimated by House et al.

[20] Typically, at 17 bar and -30°C

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** Increasing the annual transport flow rate from 0.5 to 5 Mt_{CO2}/y would reduce average transport cost more than three times, from over 20 $€_{2017}/t_{CO2}$ to around 6 $€_{2017}/t_{CO2}$ [33]. Moreover, the cost of CO_2 storage contributes relatively small amounts to overall project costs [60].

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