Review

Carbon Capture Utilisation and Storage in Extractive Industries for Methanol Production

Antonis Peppas *[ID], Sotiris Kottaridis [ID], Chrysa Politi [ID] and Panagiotis M. Angelopoulos [ID]

School of Mining and Metallurgical Engineering, National Technical University of Athens (NTUA), 15780 Athens, Greece
* Correspondence: peppas@metal.ntua.gr

Abstract: The elevated increase of CO_2 emissions related to activities of the extractive industry is becoming a challenging issue gradually affecting climate change and global warming. In this frame, the effective utilisation of CO_2 through the techniques of Carbon Capture and Storage (CCS) as well as Carbon Capture and Utilisation (CCU) can alleviate the greenhouse effect. Converting CO_2 into a value-added chemical or liquid fuel (e.g., methanol, hydrocarbons, propylene, dimethyl ether, ethylene, etc.) is a promising approach in this regard. Methanol (MeOH) synthesis offers a key feedstock for industries, being both an industrial commodity for several chemical products and an efficient transportation fuel. This article presents a review of the CCS and CCU technologies for the production of MeOH in extractive industries. The CCS technologies investigated in this framework are the amine-based absorption and the WGS-enhanced CCS. The CCU technologies are CO_2 hydrogenation and enhanced CO_2 transformation by the Fischer-Tropsch reaction. Incorporating these systems for the processing of the flue-gases of the extractive industries significantly reduces the CO_2 emissions, while creating new revenues by the production of valuable MeOH.

1. Introduction

In recent decades, the increasing research interest in carbon dioxide (CO_2) was driven by its immensely high effect on the global warming challenge. In 2019, extraction and primary processing of metals and minerals were responsible for 26% of Global Greenhouse Gas (GHG) emissions, as well as 20% of all health impacts [1,2]. In 2021, the metals and mining sector accounted for approximately 4.5 Gt of CO_2 equivalent [3]. Many studies and research projects have focused on the mitigation of GHG emissions, especially CO_2, which accounts for more than 80% of these emissions [4].

Over the years, various technologies have been investigated, focusing mostly on energy efficiency, fuel switching and innovative use of existing knowledge. However, in steel industry, they can only account for a 15% reduction in CO_2 emissions [5].

The concept of Carbon Capture Utilisation and Storage (CCUS) has received significant attention in recent years, as the means to further decarbonize the extractive industries. CCUS comprised methods and technologies to collect CO_2 from the flue-gas and from the atmosphere and provide safe and permanent storage options, i.e., Carbon Capture and Storage (CCS), followed by recycling the CO_2 for the production of valuable products, such as methanol (MeOH), i.e., Carbon Capture and Utilisation (CCU) [4].

CCS technologies can be classified into three different categories, depending on the suitability of each approach to industrial processes. These categories include pre-combustion, post-combustion and oxy-combustion technologies. Pre-combustion capture refers to the removal of CO_2 from fossil fuels before the combustion's completion [6]. In these applications,

a feedstock, such as coal, is partially oxidized in steam and oxygen/air at high temperature and pressure by a gasification process to produce synthesis gas, also known as syngas. The syngas, containing mostly carbon monoxide (CO), CO_2 and hydrogen (H_2), typically undergoes the water gas shift (WGS) reaction, for the conversion of unexploitable CO to CO_2, which can be captured and later stored or transported. Post-combustion capture refers to the capturing of CO_2 contained in flue-gas streams. These technologies typically operate at low pressures, and are most suitable for the processing of gases with low CO_2 concentrations, 5–15%. Post-combustion capture is an already mature technology, finding application in various fields such as oil refineries, petrochemical plants and other industries [7]. Of all the available techniques, absorption-based capture is widely researched and utilised, with proven high efficiencies from laboratory to commercial scale. Specifically, amine-based CO_2 capture is the most commonly used approach, reaching capture efficiencies up to 95% and CO_2 purities higher than 99%. Oxy-combustion capture refers to the capturing of CO_2 deriving from the combustion of fuels with pure or nearly pure oxygen instead of air. In oxy-combustion, nitrogen is separated from the air, resulting in almost zero nitrogen oxides (NO_x) formation. As a result, the flue-gases of the combustion have CO_2 content as much as 90% [8]. These high contents enable larger amounts of CO_2 to be captured and utilised in carbon transformation units.

In 2021, 27 CCS units were already operating globally, with 4 more being under construction [9]. On the global scale, these facilities account for a 36.6 Mtpa CO_2 captured and stored. The field of activity and capture capacities of these units are summarized in Table 1. Concerning extractive industries, the Ultra-Low CO_2 Steelmaking (ULCOS) research project proposed various novel CCS routes aiming for the reduction of CO_2 emissions by 50% in the steelmaking industry [10]. It was estimated that, while process modifications, such as the utilisation of top gas recycle blast furnaces (TGR-BF) for replacing hot blast with pure oxygen, allow for 20–25% reduction, only CCS technologies are capable of 55–60% overall reduction.

Table 1. Main characteristics of operating CCS plants globally in 2021 [9].

CCS Plant	Location	Starting Date	Main Processes	Capacity (Mtpa CO_2)
Terrell NG Processing Plant	United States	1972	NG Processing	0.50
Enid Fertilizer	United States	1982	Fertilizer Production	0.20
Shute Creek Gas Processing Plant	United States	1986	NG Processing	7.00
MOL Szank field CO_2 EOR	Hungary	1992	NG Processing	0.16
Sleipner CO_2 Storage	Norway	1996	NG Processing	1.00
Great Plains Synfuels Plant & Weyburn-Midale	United States	2000	Synthetic NG	3.00
Core Energy CO_2-EOR	United States	2003	NG Processing	0.35
Sinopec Zhongyuan CCUS	China	2006	Chemical Production	0.12
Snøhvit CO_2 Storage	Norway	2008	NG Processing	0.70
Arkalon CO_2 Compression Facility	United States	2009	Ethanol Production	0.29
Century Plant	United States	2010	NG Processing	5.00
Petrobras Santos Basin Pre-Salt Oil Field CCS	Brazil	2011	NG Processing	4.60
Bonanza BioEnergy CCUS EOR	United States	2012	Ethanol Production	0.10
Coffeyville Gasification Plant	United States	2013	Fertilizer Production	0.90
Air Products Steam Methane Reformer	United States	2013	Hydrogen Production	1.00
PCS Nitrogen	United States	2013	Fertilizer Production	0.30
Boundary Dam 3 CCUS Facility	Canada	2014	Power Generation	1.00
Quest	Canada	2015	Hydrogen Production	1.20
Uthmaniyah CO_2-EOR Demonstration	Saudi Arabia	2015	NG Processing	0.80
Karamay Dunhua Oil Technology CCUS EOR	China	2015	Methanol Production	0.10
Abu Dhabi CCS	United Arab Emirates	2016	Iron And Steel Production	0.80
Illinois Industrial CCS	United States	2017	Ethanol Production	1.00
CNPC Jilin Oil Field CO_2 EOR	China	2018	NG Processing	0.60
Gorgon Carbon Dioxide Injection	Australia	2019	NG Processing	4.00
Qatar LNG CCS	Qatar	2019	NG Processing	2.20
Alberta Carbon Trunk Line—North West Redwater Sturgeon Refinery CO_2 Stream	Canada	2020	Hydrogen Production	1.60
Alberta Carbon Trunk Line with Nutrien CO_2 Stream	Canada	2020	Fertilizer Production	0.30

CCU technologies refer to the utilisation of CO_2 for the production of valuable products including urea, MeOH, formaldehyde, formic acid, carbamates, polymer-building blocks and fine chemicals. CCU can be divided into five main utilisation pathways including CO_2 through chemical conversion, mineral carbonation, enhanced oil recovery, biological conversion and direct utilisation [11]. Among them, the leading category in the sector is chemical conversion which refers to the conversion of carbon into urea, formic acid, organic carbonates, and fine chemicals such as biotin, etc. In addition, CO_2 can be converted to fuels such as methane, MeOH, and syngas through CO_2 hydrogenation and the Fischer–Tropsch reaction. The CO_2 to fuels and chemicals pathway offers several advantages for the extractive industry, contributing to the decarbonisation goals as well as the additional sustainable production of fuels and chemicals, and the reduction of fossil-fuel consumption.

Among CO_2 by-products, urea and MeOH are the leading consumers of CO_2 in industry with an annual consumption of CO_2 of more than 110 Mt/year [12]. Respectively, in 2021, global MeOH demand reached more than 164 million tonnes, seeing constant rise [13]. MeOH sees use in multiple sectors, from fuel for the automotive and marine sectors, to feedstock for plastics manufacturing, to pharmaceutical applications. For the automotive and marine sector specifically, production of MeOH-based fuels accounted for 31% of the global MeOH consumption, with 11.7 million tonnes being used for gasoline blending and combustion in 2021 [14,15]. The growing popularity of renewable MeOH as a fuel is due to its many environmental benefits, accounting for reductions of up to 95% CO_2, 80% NO_x and almost 100% in sulphur oxides and particulate matter [16].

This study focuses on CCUS technologies oriented to the production of MeOH on industrial scale. The benefits for extractive industries comprise the significant reduction of the GHG emissions that end up in the atmosphere and increased economic viability, not only by reducing emissions related costs (i.e., carbon taxation), but also creating revenues from the production of valuable products. The study is divided in two sections analysing the CCS technologies and the CCU.

2. Carbon Capture and Storage Technologies for Extractive Industries

The suitability of the CCS technologies for the different industrial applications is highly associated with the related composition of the flue-gases. Considering that typical flue-gases produced by extractive industry activities have low CO_2 content, amine-based absorption is considered the most suitable for CO_2 capture. Despite this, the flue-gases of extractive industries typically have high concentrations of CO, which cannot be captured and is more toxic than CO_2. For this reason, many applications utilise the WGS-enhanced CCS technologies, where CO is transformed to CO_2 by the WGS reaction, to increase the overall carbon capture efficiency of the CCS. In this line, the CCS technologies presented in this section are the amine-based absorption for post-combustion capture and storage and the WGS-enhanced CCS, focusing on relative applications in the extractive industry.

2.1. Amine-Based Absorption for Post-Combustion Capture and Storage

Amine-based absorption for post-combustion capture and storage is one of the most commonly utilised technologies for CO_2 capture from flue-gases of energy intensive industries, such as extractive industries. These technologies typically comprise of the following main parts: (1) a cooling system for lowering the temperature of flue-gases, (2) an absorption column, where CO_2 is captured by the use of amines, (3) a regeneration column, for the removal of CO_2 from the amine stream and (4) a multistage compression system, raising the pressure of CO_2 to be stored or transported [1]. A conventional amine-based CCS system is shown in Figure 1.
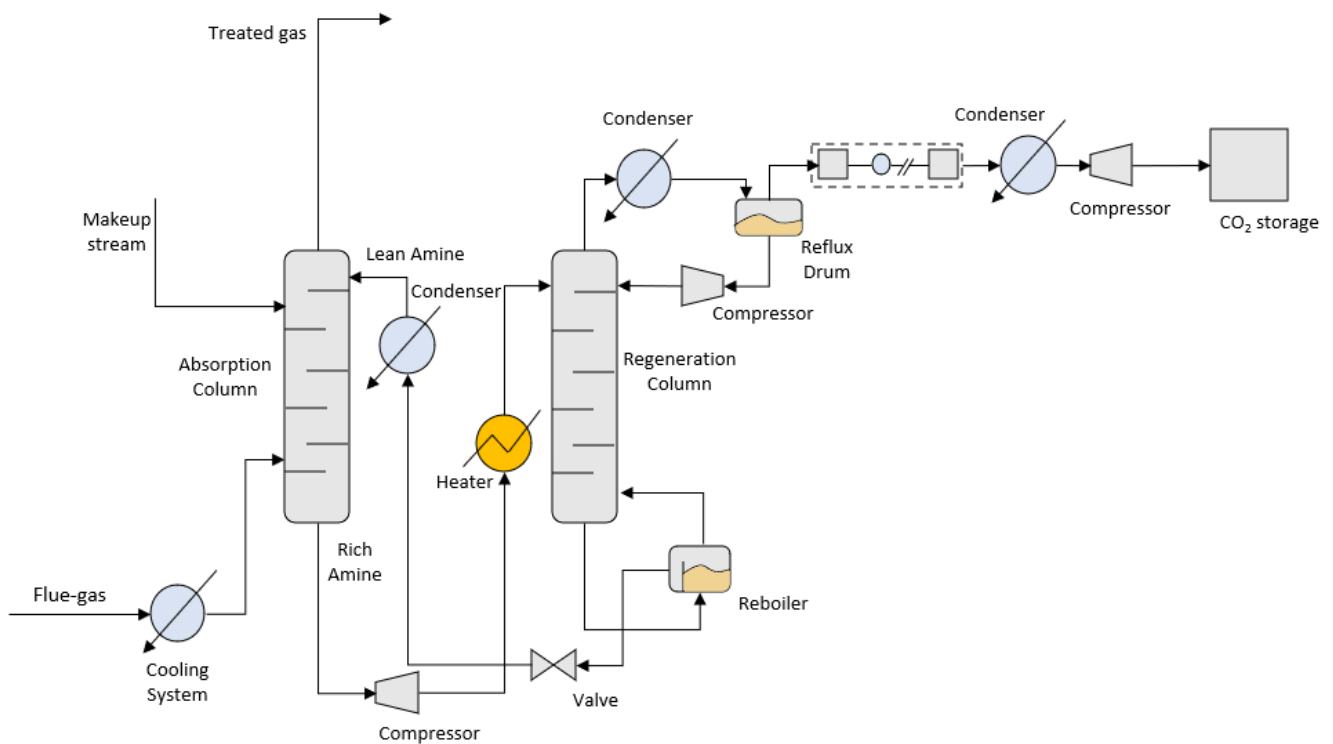
Figure 1. Schematics of a conventional amine-based CCS system.

Flue-gases are introduced to the cooling system where the temperature is decreased to the absorption column operating conditions. The cooled gases are then fed to the absorption column's bottom where, moving upwards, make contact with a liquid amine stream moving downwards from the column's top. CO_2 absorption by the amine takes place on the column's trays, designed to increase the contact area.

Liquid amine containing the absorbed CO_2 (rich amine) is then compressed, preheated and fed to the regeneration column, where separation of CO_2 from the amine occurs. The amine stream enters the regeneration column and concentrates at its bottom. The bottom is continuously heated for the volatile CO_2 to be vaporized and exit the column from the top. After initial separation, the liquid amine in the column's bottom is fed to a reboiler, for further CO_2 vaporization and separation. The low CO_2 containing amine stream (lean amine) is then cooled and fed to the top of the absorption column, closing the amine loop.
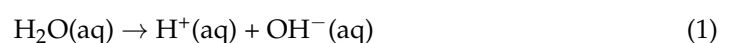
The CO_2 stream exiting from the regeneration column's top is condensed and fed to a flash separator where impurities such as amine and water are removed and sent back to the column. The purified CO_2 stream then passes through a multistage compression system and is afterwards condensed and repressurized to be stored in tanks.
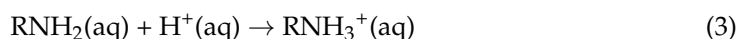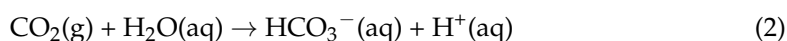
2.2. Amine-Based Absorbents

2.2.1. Primary Amines

Monoethanolamine (MEA) is one of the most widely used primary amines in amine-based CCS technologies, achieving removal capacities from 87.1 to 100% and producing CO_2 of more than 99% purity [17]. Other primary amines used are 2-(2-aminoethoxy) ethanol (DGA), 1-amino-2-propanol (1A2P) and 2-amino-1-butanol (2A1B). Primary amines are very commonly used due to their fast kinetics, high water solubility, as well as their low price. They are typically used in aqueous form rather than in their pure state.

CO_2 capture by amines is a four-step reaction process, including the ionization of water, the CO_2 hydrolysis and ionization, the protonation of alkanolamine and lastly the formation of carbamate [17]. The reactions taking place are shown below:

$$H_2O(aq) \rightarrow H^+(aq) + OH^-(aq) \tag{1}$$

$$CO_2(g) + H_2O(aq) \rightarrow HCO_3^-(aq) + H^+(aq) \tag{2}$$

$$RNH_2(aq) + H^+(aq) \rightarrow RNH_3^+(aq) \tag{3}$$

$$RNH_2(aq) + CO_2(aq) \rightarrow RNHCOO^-(aq) + H^+(aq) \tag{4}$$

Due to its commercial popularity, MEA has drawn the most attention. In 2021, Akram et al. used a typical 30 wt%. MEA system as a benchmark for comparing with a 40 wt% MEA [18]. The study considered a 6.6 vol% CO_2 gas stream. It was demonstrated that the second system was able to achieve CO_2 capture efficiency of 89.6%, practically equal to the 90% of the benchmark, with the main advantage being the 25.1% reduction in regeneration energy consumption. In addition, it was concluded that increasing the regeneration temperature from 125.7 to 126.8 °C increased the capture efficiency and capacity to 91% and 74.6 g CO_2/kg MEA, respectively. On the other hand, increase in the regeneration temperature accounted for a 12.3% increase in overall energy consumption, as well as faster thermal degradation of the solvent.

An amine-based CCS system using the conventional 30 wt% MEA was also studied in the pilot plant of Niederaussem, from 2017 to 2019 [19]. The flue-gas of the plant had a CO_2 content of 14.2%. The system achieved carbon capture efficiency of 90%, with a capacity of 0.25 tonnes CO_2 daily. The focus of the particular study was the degradation of MEA, defined by the formation of oxidative degradation products, such as acetate, formate and oxalate, as well as the increase in trace elements, such as chloride, sulphur, sulphate, nitrate and iron. The results showed a 0.47 wt% degradation after 100 h, accounting for MEA consumption of 0.21–0.35 kg/t CO_2.

Pellegrini et al. investigated the absorption capacity of DGA as an alternative to the conventional MEA [20]. In this study, the efficiency of a 13–27 wt%. MEA system was compared to an 8–27 wt% DGA., on a flue-gas of 7 wt% CO_2. The results showed that the MEA system achieved 95% capture efficiency in comparison with the 88% of the DGA system, both operating at 20 °C. Despite this, it was concluded that the temperature in which the DGA system achieved efficiency of 90% was lower than what the MEA system required to achieve the same results, 63 °C compared to 67.5 °C. In addition, the reported regeneration efficiency of DGA was higher. For a reboiler operating at 110 °C, DGA regeneration efficiency was 90%, in comparison with the 66% of MEA. The studies conducted for MEA and DGA systems prove there are advantages to both approaches, depending on the application. The carbon efficiencies of various primary amine solvents in CCS systems are summarized in Table 2.

Table 2. Capture efficiencies of various primary amine solvents in CCS systems.

Solvent	CO₂ Content (%)	Capture Efficiency (%)	Reference
30 wt% MEA	6.6 vol	90.0	[18]
40 wt% MEA		86.9	
30 wt% MEA	14.2	90.0	[19]
13–27 wt% MEA	7 wt	95.0	[20]
8–27 wt% DGA		88.0	

2.2.2. Non-Primary Amines

In addition to primary amines, various secondary and tertiary amines also see use in numerous applications across the industry. Typical secondary amines for CCS systems include 2-(methylamino) ethanol (MMEA), N-ethylmonoethanolamine (EMEA) and the most commonly used diethanolamine (DEA) [6,7,21,22]. These amines display similar behaviour with primary amines, presenting high capture efficiencies of up to 90% as well as high regeneration energy demand, due to carbamate formation. Typical regeneration temperature for such amines is 70–200 °C [6,23]. The reaction mechanisms are also similar and can be expressed simply by substituting primary amines (RNH_2) with secondary amines (R_2NH) [24].

Barzagli et al. compared the performance of MMEA and EMEA and other amines, such as MEA, for a gas mixture of 15% CO_2 [25]. All experiments used 0.12 mol of amine. MMEA achieved capture efficiency of 92%, at 21 °C and 1.0145 bar. EMEA achieved 92.4%, at 24 °C and 1.0013 bar. In comparison, the 30% MEA solvent achieved 82.2% capture efficiency despite operating at slightly higher temperature and pressure than EMEA, 25 °C and 1.0067 bar.

Wang et al. conducted a study in 2021 over a lab-scale CO_2 capture system including DEA [26]. The study proposed an integrated absorption and mineralization process where, after the absorption, CO_2-rich solvents are regenerated by mineralization with semidry desulphurization slag. The experiment utilised a 15 vol% CO_2 and 85 vol% N_2 gas. After absorption, the CO_2-rich solvent was mixed with Ca-rich compound for the formation of calcium carbonate and the regeneration of the solvent. The results showed CO_2 loading of 0.73 and 0.18 mol CO_2/mol DEA for the rich and lean DEA, respectively. The desorption process achieved efficiency up to 85%. The main advantage of this approach was the lack of need for a compressor and reboiler in the regeneration system, thus reducing the energy consumption by as much as 93.7% in relation to conventional systems.

Tertiary amines for CCS systems include 2-(dimethylamino) ethanol (DMAE), N-methyldiethanolamine (MDEA) and 2-diethylaminoethanol (DEAE). In recent years, such amines have drawn much attention due to their high CO_2 absorption capabilities of 1 mol CO_2/mol solvent, almost two times higher than primary and secondary amines [26]. In addition, the inability of these amines to react with CO_2 accounts for no carbamate's formation [24]. Instead, bicarbonate ions are formatted, which require far less regeneration energy, approximately 58.5 kJ/mol compared to 86.9 and 68.9 kJ/mol for primary and secondary amines, respectively [6,23,27].

The main disadvantage of tertiary amines is the low CO_2 absorption rate of approximately 2.13 mol CO_2/hr [26]. To counter this issue, these amines are usually mixed with promoters such as piperazine (PZ) or carbonic anhydrase (CA) to increase absorption [22,28]. The reaction taking place is the following [23]:

$$R_3N(aq) + CO_2(g) + H_2O(aq) \leftrightarrow R_3NH^+(aq) + HCO_3\text{-}(aq) \qquad (5)$$

Antonini et al. examine the use of an MDEA carbon capture system for producing low-carbon H_2 [29]. The system utilised a high-pressure and a low-pressure flash separator for the recycling of CO_2 not absorbed and semi-lean amine solvent that can further contribute to absorption in the absorption column. The gas considered in this study contained 16.27 mol% CO_2. The solvent was a conventional 40 wt% MDEA. The results of the study showed that utilising these recycling streams in the system accounted for a 54.5% reduction in regeneration energy demand, and capture efficiency of 90%.

Zhao et al. also examined post-combustion CCS using an MDEA+PZ solvent for a 650 MW power plant [30]. The flue-gases treated had a CO_2 content of 12%. The study examined the effect of the MDEA/PZ ratio as well as the targeted carbon capture capacity on the overall performance of the system and energy demand. The results showed that 30% and 20% of MDEA and PZ, respectively, allowed for high carbon capture efficiencies of 90%, without significantly increasing the reboiler heat duty for the amine regeneration.

Another study of a MDEA CCS system was conducted by Jaffary et al. in 2021 [31]. In this study, polyamines were used as activators for the absorption of 100% CO_2 gas. The polyamines examined were polyethylenimine (PEI-B), tetraethylenepentamine (TEPA) and PZ. The results of the study showed that MDEA enhanced with PEI-B had an increased CO_2 loading and specific desorption rate of 1.08 mol CO_2/mol solvent and 0.0385 mol CO_2/mol amine/min, respectively. Despite these benefits, incorporating PEI-B in the solvent accounted for increased viscosity, which results in decreased CO_2 absorption rates. PZ on the other hand accounted for a moderate increase in both the CO_2 loading and desorption rate, 0.67 mol CO_2/solvent and 0.0352 mol CO_2/mol amine/min, respectively, without increasing viscosity. The performance of various secondary and tertiary amine solvents is summarized in Table 3.

Table 3. Capture efficiencies of various secondary and tertiary amine solvents in CCS systems.

Solvent	CO_2 Content (%)	Capture Efficiency (%)	Reference
DEA	15 vol	85.0	[26]
MMEA	15	92.0	[25]
EMEA		92.4	
MDEA	16.27	90.0	[29]
MDEA/PZ	12 vol	90.0	[30]

CCS systems in extractive industries aim for the exploitation of CO_2 after the separation from the amine solvents, therefore, the most efficient amines are those having high capture efficiencies but also low regeneration energy, to allow for higher separation and reduced energy consumption.

Primary amines offer high capture efficiencies, up to 95% for the commercial MEA. Other primary amines, such as DGA, require significantly less regeneration energy while also having high capture efficiencies and thus can be considered another viable option. Secondary amines exhibit similar capture efficiencies to primary amines. Studies comparing MEA with EMEA specifically, have shown that EMEA can achieve carbon efficiency as high as 92.4% in comparison to MEA's 82.2%, with a slight increase in temperature and pressure. Tertiary amines, however, specifically MDEA, provide similarly high carbon capture efficiencies, while also requiring significantly less regeneration energy, 1.34 MJ/kg CO_2, than other amines [32]. For these reasons, MDEA is considered one of the most efficient options, used in various applications in CCS systems in the industry. While these amines have lower absorption rates on their own, these disadvantages are easily dealt with when mixed with promoters, especially PZ. In that sense, the use of MDEA+PZ solvents in novel systems utilizing recycle streams can be considered one of the most optimal approaches for CCS systems.

2.3. Innovative Amino Acids

Amino acids have seen significant research over the years as an energy-efficient replacement of conventional amines. The use of these solvents allows for the mitigation of CO_2 emissions in plants while also reducing the economic impact of these technologies.

In 2019, Moioli et al. examined a CCS system capturing CO_2 by precipitating potassium taurate solvent [33]. The unit's layout is nearly identical to the conventional amine-based, with the main differences lying in the optional components related to the processing of formed solids. Specifically, the reactions taking place result in the formation of solid taurine. Precipitation of taurine shifts the equilibrium toward the formation of more products, resulting in increased CO_2 capture. The production of solid taurine results in a slurry, comprising of solid taurine and a mixture of ionic species and water, obtained at the absorption's column bottom, which can optionally be fed to a solid-liquid separator, where supernatant liquid is returned to the absorption column, while the solids are led to the regeneration column, after being dissolved.

The advantage of this approach lies in the lower regeneration energy required. Specifically, the amino acid rich slurry stream entering the regeneration column has a lower pH which favours the desorption of CO_2. The case studies examined both the inclusion and not inclusion of a solid-liquid separator in the CCS unit for a 500 MW output power plant. The CO_2 removal efficiency was fixed at 90%. The analysis highlighted the benefits of incorporating the optional solid-liquid separator to allow for a fraction of liquid to be recycled to the absorption column without the need of regeneration, thus reducing energy requirements. For a recycle split fraction (liquid recycled/total liquid fed to the separator) of 0.2, corresponding to 0.255 lean loading, the reboiler duty was at its minimum, lower than 2.9 MJ/kg CO_2. For comparison, conventional amines such as MEA, have shown reboiler duties as high as 3.8 MJ/kg CO_2 for 0.23 lean loading.

Garrabrant et al. also examined the use of amino acid salts for energy-efficient CCS systems [34]. Specifically, the study examined CO_2 absorption by a hybrid potassium glycinate and sarcosinate followed by the amino acid regeneration and bicarbonate removal crystallization with a simple bis-iminoguanidine base (GBIG), and examined the regeneration energy with that of industrial benchmarks such as 30% aqueous MEA and 30% aqueous sodium glycinate (SG). The results showed that, while the required regeneration energy for SG was higher than MEA, approximately 5.7 MJ/kg CO_2 in comparison to 4.5 MJ/kg CO_2, the required regeneration energy for the potassium glycinate/sarcosinate + GBIG case was 3.4 kJ/kg CO_2, a reduction of 24% in comparison with MEA. This reduction in the regeneration energy lies in the ability of the GBIG process to regenerate the solvent in ambient temperatures.

In 2021, Xu et al. also examined the use of amino acid salts for CO_2 capture from a flue-gas containing 15% CO_2, proposing the encapsulation of amino acid salts into solid particle matrices for the production of liquid amino acid salts hydrogel (LAHP) [35]. The proposed approach allowed for bigger contact areas and more intense interactions with CO_2 uptakes increased as much as 40%, compared to stirred aqueous amino acid salts solutions. The study concluded that the heat of absorption for potassium sarcosinate LAHP was 35% lower than MEA's, 53.3 kJ/mol CO_2 in comparison to 81,77 kJ/mol CO_2, suggesting lower regeneration energy requirements. In addition, the study proposed the replacement of water with solvents of higher boiling points, i.e., ethylene glycol, to further reduce the required energy. With a boiling point of 60 °C, ethylene glycol opens up the approach of using waste industrial steam to further reduce operational costs. The regeneration energy for the different solvents is shown in Table 4.

Table 4. Regeneration energy for innovative solvents.

Solvent	CO_2 Content (%)	Capture Efficiency (%)	Regeneration Energy (MJ/kg CO_2)	Reference
MEA	-	90	3.8	[33]
Potassium taurate		90	2.9	
30% MEA	12.8	-	4.5	[34]
30% SG			5.7	
Potassium Glycinate/Sarcosinate + GBIG			3.4	

2.4. WGS-Enhanced Carbon Capture and Storage

Many industries, including extractive industries, produce flue-gases of very small CO_2 concentrations and high concentrations of CO, which is far more toxic and cannot be captured. To tackle this issue, many CCS technologies utilise the WGS-enhanced CCS, which is the incorporation of a CO to CO_2 transformation system before capture, in the form of a WGS reactor. Water reacts with CO for the production of CO_2 and H_2. The produced H_2 is separated and can be used in the carbon transformation technologies. The reaction taking place is the following [36]:

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g), \Delta H = -41 \text{ kJ/mol} \tag{6}$$
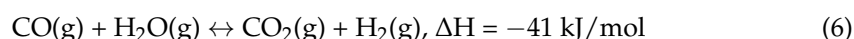
CO conversion to CO_2 is highly exothermic and thus is favoured in low temperatures. Specifically, studies have shown than a reduction of the reaction temperature from 800 to 200 °C can increase the equilibrium constant up to 80 times [37]. In addition, the reaction's equilibrium is proven to be unaffected by pressure increase, but CO conversion is favoured due to higher reaction rates.

WGS reaction commercially takes place in two adiabatic catalytic reactors arranged in series for maximum CO transformation [38]. The first reactor is a high-temperature WGS (HT-WGS) operating with a Fe-based catalyst at 350–500 °C and 10–60 bar, while the second reactor is a low-temperature WGS (LT-WGS) operating with a Cu-based catalyst at approximately 200 °C and 10–40 bar [39]. HT-WGS are characterized by fast kinetics, but equilibrium-limited conversion. On the other hand, LT-WGS have slower kinetics, but are much less limited by the thermodynamic equilibrium, allowing for higher CO conversion. The combination of the two allows for fewer thermodynamic limitations and the ability to adjust the H_2:CO ratio in the final gas product.

Despite this, most CCS units using WGS reactors for enhanced decarbonization incorporate a single HT-WGS reactor. The Fe-based catalysts used in such reactors can tolerate small quantities of particles commonly found in the flue-gases of extractive industry's processes, such as sulphur-based compounds, in contrast with Cu-based catalysts used in LT-WGS reactors [40]. In addition, any traces of hydrogen sulphides (H_2S) in the flue-gas can be separated along with CO_2 in the absorption process. For these reasons, WGS-enhanced CCS is considered one of the most efficient approaches for CCS in extractive industries. A conventional WGS-enhanced CCS system is shown in Figure 2.
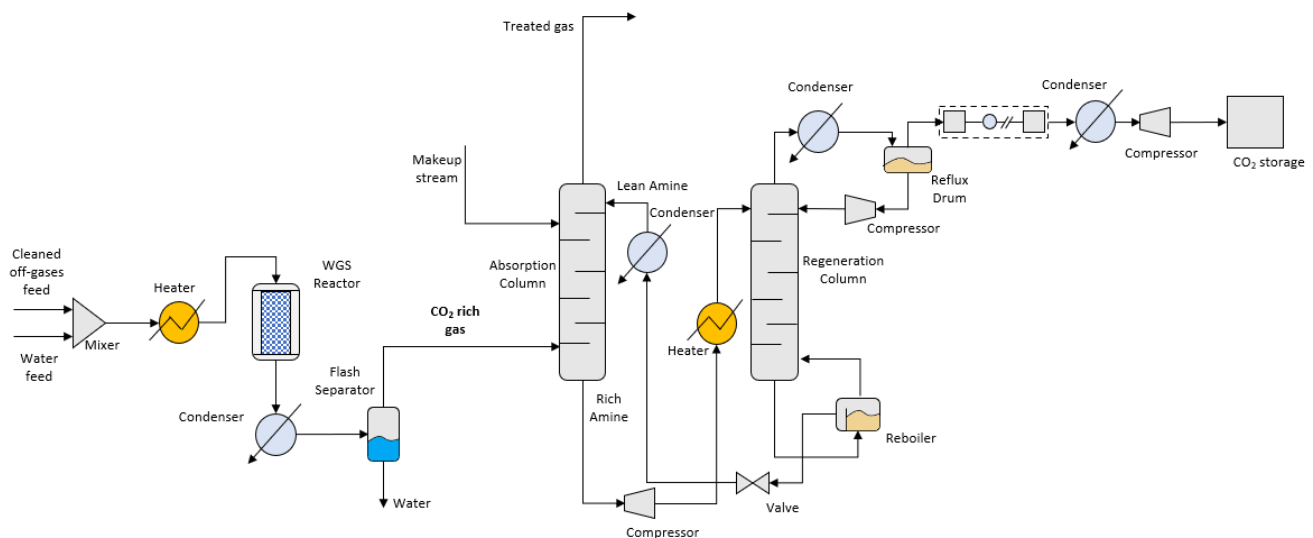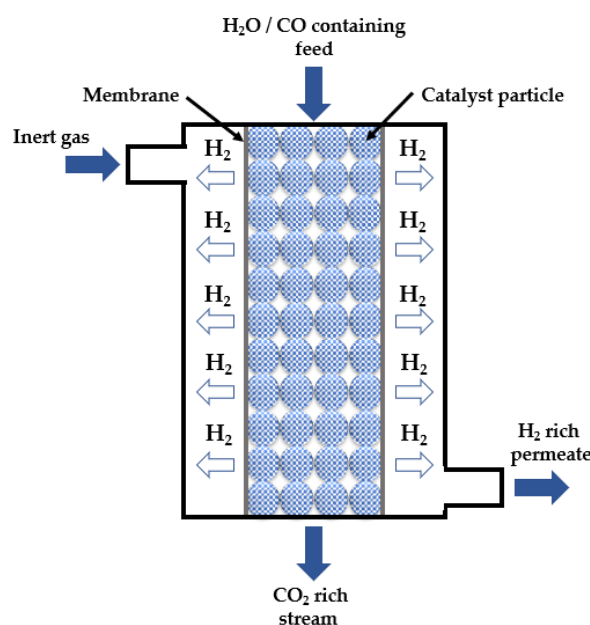

Figure 2. Schematics of a conventional WGS-enhanced CCS system.

Catalytic Membrane Reactors for WGS Reaction

Commonly used reactors for WGS reaction are catalytic membrane reactors (CMR). Such technologies allow for the immediate separation of either CO_2 or H_2 from the product stream. This continuous separation allows for higher CO conversion than a conventional reactor limited by equilibrium. Numerous studies have been conducted for high-grade H_2 recovery using dense Pd-based, composite Pd-based or silica and zeolite membranes. A conventional CMR for WGS reaction is shown in Figure 3.

For Pd-based CMR, several studies indicate CO conversion up to 98% and H_2 recovery up to 94%, but for small-scale reactors [41]. In large-scale applications, multi-tubular systems with membranes of 50–60 μm thickness or composite planar membranes based on foils of 20–25 μm are the most commonly used. Of the two approaches, composite Pd membranes generally achieve higher H_2 production rates, due to higher permeances of the thinner membrane.

Figure 3. Schematics of a conventional CMR reactor for WGS reaction.

Catalano et al. investigated the performance of <10 μm Pd membranes over a porous (316 L) stainless steel (PSS) tubular support [41]. The tube-and-shell reactor used was filled with a commercial Fe/Cr catalyst for high temperature WGS reaction. The gas used was decided to simulate actual gasifier syngas, with a composition of 40% H_2, 42.2% CO and 17.8% CO_2. The H_2O:CO ratio ranged from 2.5 to 3.5 and the total feed flow was up to 1.5 Nm^3h^{-1}. The temperature raged from 420–440 °C and the pressure was up to 20 bar. The study concluded that for an 8.3 μm Pd membrane and operating temperature and pressure of 440 °C and 20 bar, respectively, CO conversion reached 84.9%, H_2 recovery 42.8% and H_2 purity 99.5%.

Augustine et al. also investigated the performance of a CMR using Pd-membranes, over different H_2O:CO ratios, temperatures, gas compositions, and gas hourly space velocity (GHSV), at a fixed 14.4 bar pressure [42]. The reactor was using an iron-chrome oxide catalyst. The experiments conducted examined both the use of a CO feed as well as a syngas feed with a composition of 22.7% CO, 45.4% H_2O, 22.0% H_2 and 9.9% CO_2, a H_2O:CO ratio of 2. For the syngas, results showed that a H_2O:CO ratio of 1.3:1 was the optimal, reaching CO conversion and H_2 recovery of more than 95% and 85%, respectively, at 450 °C. Increase of the ratio beyond this point had a minor effect on CO conversion, but a negative effect on H_2 recovery. Indicatively, at a H_2O:CO ratio of 2.5:1, CO conversion and H_2 recovery were 94% and 78%, respectively.

Nishida et al. investigated the performance of a silica membrane developed with the counter-diffusion chemical vapor deposition (CVD) method [43]. The silica membrane had a H_2 permeance of 1.29×10^{-6} mol $m^{-2}s^{-1}Pa^{-1}$. The reactor tube was filled with 1.05 g of a commercial $Cu/ZnO/Al_2O_3$ catalyst. The test was conducted with a blast furnace gas (BFG) feed with a composition of 52% N_2, 22% CO, 22% CO_2 and 4% H_2, at 300 °C and 3.05 bar. The study showed that operating the reactor with a space velocity of 7000 h^{-1} accounted for a CO conversion of 95–97%, H_2 recovery of approximately 60% and an H_2 purity around 94%. The study also examined the effect of space velocity in the reaction, in the range of 3500 to 10,500 h^{-1} and concluded that the increase in space velocity resulted in decreased CO conversion and H_2 recovery but increased H_2 purity.

Battersby et al. also examined the effect of H_2O:CO molar ratio in a silica membrane reactor using $Cu/ZnO/A_2O_3$ catalyst, prepared by $NaCO_3$ co-precipitation of precursor salts and followed by consequent aging, filtration, washing drying and calcination [44]. The tests were conducted with a fixed reactants' flow rate of 80 mL/min and varying H_2O:CO ratios. It was concluded, that increasing the H_2O:CO molar ratio from 1 to 4 increased

the CO conversion from 20% to 29%, at 250 °C. The study also examined the effect of temperature on CO conversion for a $H_2O:CO$ molar ratio of 1. The results showed that increasing the temperature resulted in increased CO conversion, reaching almost 80% at 300 °C. The performances of the various CMR reactors are summarized in Table 5.

Table 5. Performance of CMR reactors for WGS reaction.

Membrane	$H_2O:CO$ Ratio	Temp. (°C)	Pressure (bar)	CO Conversion (%)	H_2 Recovery (%)	H_2 Purity (%)	Reference
Pd-based	2.5:1	440	20	84.9	42.8	99.5	[41]
Pd-based	1.3:1 2:1	450	14.4	96.0 94.0	85.0 78.0	-	[42]
Silica	-	300	3.05	95–97.0	60.0	94	[43]
Silica	1:1 4:1	300 250	-	80.0 29.0	-	-	[44]

The studies conducted over the CMR reactors using Pd-based membranes show the highest CO conversion and H_2 recovery at a temperature of approximately 450 °C. In terms of the $H_2O:CO$ ratio, near stoichiometric conditions are generally preferred, as higher ratios negatively affect both the CO conversion and H_2 recovery. Considering the operating pressure, the reaction is generally unaffected.

On the other hand, CMR reactors using silica membranes exhibit high CO conversion at relatively moderate temperatures of 300 °C, as well as significantly lower operating pressures. For these reasons, CMR reactors with silica-based membranes can be considered one of the most efficient options. Incorporating such reactors before amine-based CCS allows for increased CO_2 content in the stream and thus maximum carbon capture.

2.5. CCS Applications in Extractive Industries

The transformation of an energy-intensive industrial sector towards the transition to a low carbon economy, without reducing the production volume, requires joint, collaborative efforts to develop and invest in novel process designs and solutions. In this context, CCS applications in extractive industries are highlighted with main focus on the capture, transport and storage of CO_2 that would otherwise have been emitted to the atmosphere.

The ULCOS project investigated various CCS technologies for implementation in extractive industries. These technologies were pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), VPSA and cryogenic separation and compression, amine-based capture and compression and PSA and cryogenic distillation and compression [10]. The process gas composition was almost identical for all technologies, with compositions of 2.7–3 vol% CO_2, 67.8–71.4 vol% CO, 12.1–13 vol% H_2, 13.5–15.7 vol% N_2 and 0–2.1 vol% H_2O. The results showed that of all the aforementioned technologies, amine-based capture and compression and PSA and Cryogenic distillation are the most efficient approaches accounting for almost 100% CO yield in the recycled gas and 100% captured CO_2 purity. For comparison, PSA accounted for 88% CO yield and 79.7% captured CO_2 purity. In addition, these technologies were concluded to be the only two 100% suitable for CO_2 transport and storage.

WGS-enhanced CCS has received significant attention for utilisation in extractive industries over the last years. European project C4U, started in 2020, examined the utilisation of a WGS-enhanced CCS system in iron and steel industries [5]. The performance of the system was compared with a base case scenario of a conventional amine-based CCS without a WGS reactor. The flue-gas examined was a BFG with a composition of 21.2 mol_{dry}% CO_2, 22.7 mol_{dry}% CO, 0.2 mol_{dry}% C_2H_4, 2.4 mol_{dry}% H_2, 53.5 mol_{dry}% N_2 and a total flow rate of 125 kg/s. The amine-based CCS systems utilised a 25 wt% MDEA solvent. In the base case, the CCS system delivered 36.8 kg/s of 98.2% pure CO_2. The system also accounted for approximately 0.92 kmol/s of CO and 0.03 kmol/s of uncaptured CO_2. The WGS-enhanced

CCS system delivered 66.3 kg/s of 98.1% pure CO_2, an increase of approximately 80%. The system also accounted for approximately 0.01 kmol/s CO and 0.0036 kmol/s uncaptured CO_2, a decrease of almost 99% and 88%, respectively. The results of this examination clearly displayed the advantages of the WGS-enhanced CCS technologies over the conventional amine-based.

The STEPWISE project executed within the European H2020 LCE program also aimed for the demonstration of an advanced pre-combustion CO_2 removal technology for iron and steel industries [45]. The technology was based on sorption enhanced water gas shift (SEWGS) using regenerative solid adsorbents at elevated temperatures. The solid adsorbent was regenerated by pressure swing, resulting in CO_2-rich streams suitable for storage and transport. The H_2 produced by the WGS reaction was considered suitable for power generation. In the project, the process was demonstrated at a scale of 14 t/day CO_2 removal. For simple integration of the technology, carbon intensity was reduced to 1.26 t CO_2/t steel, with an energy consumption of 1.95 MJ/kgCO_2 and CO_2 avoidance costs of 32 €/t CO_2. For intensified implementation, focusing on internal uses and electricity production, carbon intensity was reduced to 0.60 t CO_2/t steel.

The technology developed utilised a WGS active sorbent, allowing for the in-situ removal of CO_2, to account for limitations set by equilibrium. Thus, there is no need of two or more WGS reactors [46]. The dry gas considered had a conventional composition of 19% CO, 25% CO_2, 3% H_2, 15–20 ppm H_2S + carbonyl sulphide (COS) and 53% N_2. Implementation of the WGS reactor allowed for the reduction of CO content to 5%. The SEWGS unit utilised a catalytically active potassium-promoted hydrotalcite-based sorbent for both CO conversion completion and separation of CO_2 from H_2.

In 2020, Manzolini et al. performed a techno-economic assessment of SEWGS technology for integration in a steel-plant, as a follow-up study of the STEPWISE project [47]. The study compared the performance of a conventional amine wet scrubbing technology and the solid adsorption technology of the STEPWISE project. Simulation results showed that the SEWGS using solid absorbents accounted for a specific energy consumption for CO_2 avoided (SPECCA) of around 2.5 MJ/kg CO_2, in comparison to the 4.8 MJ/kg CO_2 of the conventional amine scrubbing.

3. Carbon Capture and Utilisation Technologies for Extractive Industries

CCU solutions typically opt for the transformation of CO_2 to valuable products, such as MeOH, using an external H_2 feed. Commonly used approaches comprise the CO_2 hydrogenation, for the immediate utilisation of the captured CO_2, and the enhanced CO_2 transformation by the Fischer-Tropsch reaction, where CO_2 is transformed into CO by the reverse water gas shift (RWGS) reaction to allow for higher carbon conversions and MeOH production. In this frame, CO_2 hydrogenation and the Fischer–Tropsch reaction process will be reviewed, as the one of the most commonly used and promising approaches for MeOH production in extractive industries.
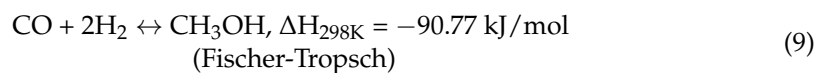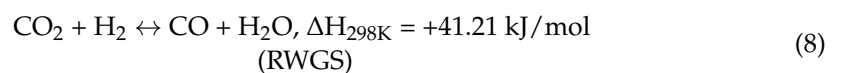
3.1. CO₂ Hydrogenation

CO_2 hydrogenation utilises reactors where CO_2 reacts with H_2 for the production of methane or MeOH. A typical CO_2 hydrogenation system is comprised of the following main components: (1) a CO_2 hydrogenation reactor and (2) a distillation column for the separation and collection of produced MeOH. A conventional system using CO_2 hydrogenation for MeOH production is shown in Figure 4.
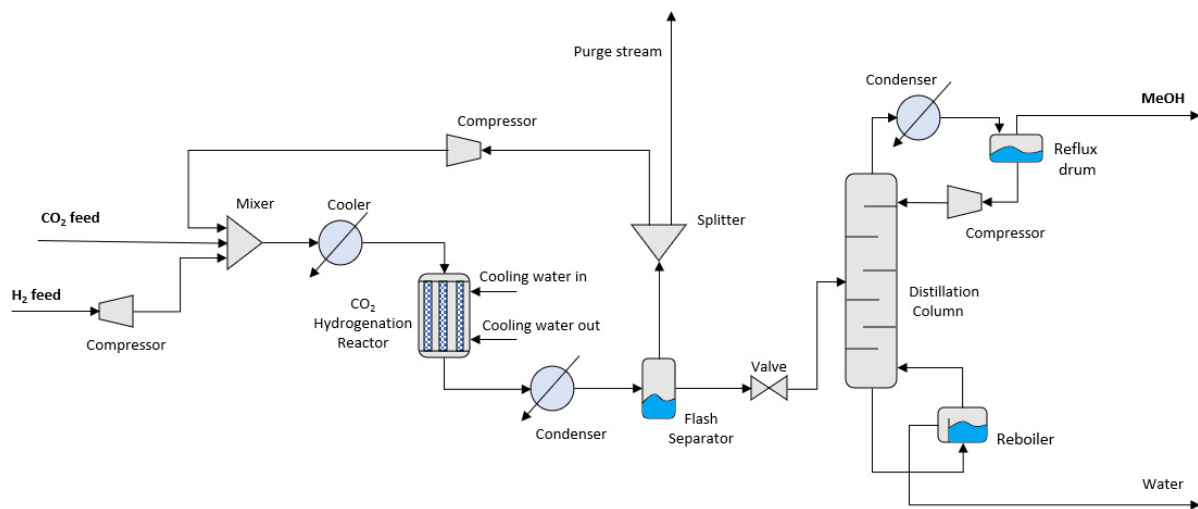
Figure 4. Schematics of a conventional CO_2 hydrogenation system for MeOH production.

CO_2 feed is mixed with an H_2 stream and preheated before entering the reactor. Inside the reactor, the CO_2 hydrogenation occurs, and MeOH is produced, as well as by-product water and CO. CO specifically results from the RWGS reaction, naturally occurring in the reactor. CO produced reacts with the H_2 in the Fischer-Tropsch reaction for enhanced production of MeOH. The reactions taking place in the reactor are the following [48]:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \Delta H_{298K} = -49.16 \text{ kJ/mol}$$
$$\text{(CO}_2 \text{ hydrogenation)}$$
(7)

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \Delta H_{298K} = +41.21 \text{ kJ/mol}$$
$$\text{(RWGS)}$$
(8)

$$CO + 2H_2 \leftrightarrow CH_3OH, \Delta H_{298K} = -90.77 \text{ kJ/mol}$$
$$\text{(Fischer-Tropsch)}$$
(9)
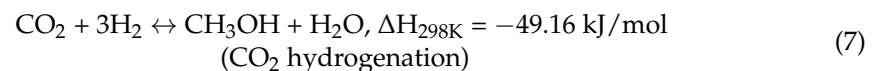
The stream exiting the reactor consists of MeOH, water and unreacted CO_2, CO and H_2, and therefore, requires separation. The stream is condensed and passes through a flash separator where the unreacted gas is separated from liquid MeOH and water. A significant part of this unreacted gas is repressurized and recycled back to the reactor to enhance the final CO_2 conversion.

The liquid MeOH and water are separated in the distillation column of the system. The stream introduced at the middle trays concentrates at the bottom of the column, which is constantly heated for the vaporization of volatile MeOH and separation from water. After initial vaporization, the liquid in the bottom of the column is fed to a reboiler which facilitates further separation. The gaseous MeOH exits the distillation column from the top, and the stream is condensed and passes through a flash separator for the separation of any water vaporized along, and the production of the final MeOH product.
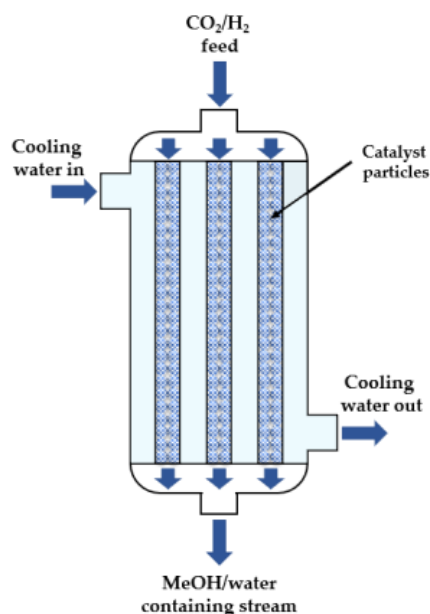
3.1.1. CO_2 Hydrogenation Reactors

The main concern when developing a CO_2 hydrogenation reactor is the efficient removal of the heat produced by the highly exothermic reaction. Efficient heat removal facilitates avoiding the formation of by-products, achieving high CO_2 conversion by low outlet temperatures and good energy efficiency by internal heat recovery [49]. Current designs have shifted from the previously used quench reactors to the quasi-isothermal steam-raising fixed bed reactors, or steam-raising converters (SRC), which allow for more efficient heat recovery and temperature control [49].

One of the most commonly used SRC reactors is the multi-tubular packed bed catalytic reactor, also known as the Lurgi reactor. Lurgi reactor comprises multiple tubes filled

with catalyst particles to enhance the reaction rate and overall CO_2 conversion. Such designs incorporate an inner cooling system, in the form of a coolant, typically water, flowing between the space of the tubes. The feed gas feed flows through the tubes in an axial direction. Approximately 80% of the reaction heat is converted to medium pressure steam [50]. A conventional Lurgi reactor for CO_2 hydrogenation is shown in Figure 5.

Figure 5. Schematics of a conventional Lurgi reactor for CO_2 hydrogenation.

3.1.2. CO_2 Hydrogenation Catalysts

Currently, the majority of commercial low-pressure catalysts are CuO and ZnO based. In most cases, Al_2O_3 carriers are utilised, along with various stabilizing additives and promoters such as Zr, Cr, Mg and rare earth metals [49]. Several studies showed space time yields (STY) for CO gases being 0.7–2.3 kg of MeOH per litre of catalyst. For CO_2 gases the STY was significantly lower, 0.4–0.8 $kgl_{cat}^{-1}h^{-1}$. The studies considered operational pressures 40–100 bar and GHSV about 10 000 h^{-1} [45,50,51]. Modern copper catalysts achieve selectivity of more than 99% for conventional gases [52]. Impurities in the gas feed, high pressure and temperature, high $CO:H_2$ and $CO:CO_2$ ratios and low space velocities are some of the factors reducing MeOH selectivity.

The typical lifetime of industrial catalysts is 4–6 years [49]. Deactivation as a result of poisoning or thermal sintering is the main limitation of the catalysts' lifetime. For copper-based catalysts, sulphur compounds and chlorides are the major causes of poisoning, resulting in blocking of active sites and acceleration of sintering, respectively. Arsenic and carbonyls are other poisons reported, promoting the Fischer-Tropsch reaction and thus decreasing selectivity [53]. To prevent such issues, a prior gas cleaning step is usually implemented, as well as guard beds, such as ZnO targeting sulphur, for the catalyst's protection [52]. For commercial Cu/ZnO catalysts, typical gas requirements are: 0.05–0.5 ppm H_2S, 1 ppb HCl, few ppb metal carbonyl, less than 0.1 mg N m^{-3} particles, less than 1 mg N m^{-3} tar and less than 0.25 mg N m^{-3} alkalis [49].

Liao et al. examined the effect of the $H_2:CO_2$ ratio and temperature of the reaction over a Cu/rod ZnO/Al_2O_3 and Cu/plate ZnO/Al2O3 catalyst at 45 bar [54]. Results showed that increasing the $H_2:CO_2$ ratio from 2.2:1 to 2.5:1 had a positive effect on the CO_2 conversion, but decreased MeOH selectivity for both catalysts at 270 °C, as well as 280 °C. Increase in temperature also resulted in increased CO_2 conversion but decreased MeOH selectivity for both catalysts and the different $H_2:CO_2$ ratios. The results also suggested that the Cu/rod ZnO/Al_2O_3 catalysts exhibited slightly higher CO_2 conversion but significantly lower MeOH selectivity.

Sahki et al. examined the effect of pressure in the reaction over a $CuO/ZnO/Al_2O_3$ catalyst [55]. The reaction took place at 230 °C at varying pressures of 1–75 bar, with a flow rate of 2 L h^{-1} and a stoichiometric H_2:CO_2 ration of 3:1. The results showed that increasing pressure from 1 to 75 bar increased the CO_2 conversion from 3.1 to 11.9%, and MeOH selectivity from 5.3 to 47.1%. CO selectivity decreased from 94.66 to 52.9%.

To highlight the effect of the H_2:CO_2 ratio and pressure in the reaction, Bansode et al. examined the performance of a $Cu/ZnO/Al_2O_3$ catalyst for a 10:1 ratio and a high pressure of 360 bar [56]. The results showed a CO_2 conversion of 65.8% on a single pass, almost six times higher than other applications opting for near stoichiometric ratios and moderate pressures. The MeOH selectivity was 77.3%.

Table 6 summarizes the performance of the various Cu-based catalysts for CO_2 hydrogenation found in literature.

**Table 6.** Performance of Cu-based catalysts for CO_2 hydrogenation.

Catalysts	H$_2$:CO$_2$ Ratio	Temperature (°C)	Pressure (bar)	CO$_2$ Conversion (%)	MeOH Selectivity (%)	Catalyst Cost (€/kg cat.)	Reference
Cu/plate ZnO/Al$_2$O$_3$	2.2:1	270	45	10.9	72.7	~18.1	[54]
		280		12.0	71.6		
	2.5:1	270		15.5	64.5		
		280		14.7	63.3		
CuO/ZnO/Al$_2$O$_3$	3:1	230	1	3.1	5.3		[55]
			75	11.9	47.1		
Cu/ZnO/Al$_2$O$_3$	10:1	260	360	65.8	77.3		[56,57]

The studies on the performance of these catalysts show the importance of the operational parameters in the CO_2 hydrogenation reaction. In terms of H_2 supply, high H_2:CO_2 ratios tend to benefit the overall CO_2 conversion. Despite this, raising the H_2:CO_2 ratios results in decreased MeOH selectivity, as well as increased energy demand and cost for the production of H_2. For these reasons, the majority of applications opt for a stoichiometric H_2:CO_2 ratio of 3:1.

Operational temperature also significantly affects the reaction. Higher temperatures result in increased overall CO_2 conversion but decreased MeOH selectivity. The most influential parameter is pressure. While an increase in pressure results in significantly higher conversion, applications need to account for the safety of the systems. Thus, reactors typically operate at pressures up to 100 bar.

3.2. Enhanced CO$_2$ Transformation by Fischer-Tropsch Reaction

CCU commonly utilise RWGS reactors for the conversion of CO to CO_2 to increase carbon conversion efficiency. This approach aims for optimising the CO_2 hydrogenation reaction with the Fischer-Tropsch reaction. As the Fischer-Tropsch reaction for MeOH production is almost twice as much exothermic, $\Delta H_{298K} = -90.77$ kJ/mol compared to $\Delta H_{298K} = -49.16$ kJ/mol, the required activation energy is lower, resulting in increased reaction rate and conversion to account for the decreased selectivity. A conventional system for MeOH production from CO_2 utilising a RWGS reactor is shown in Figure 6.
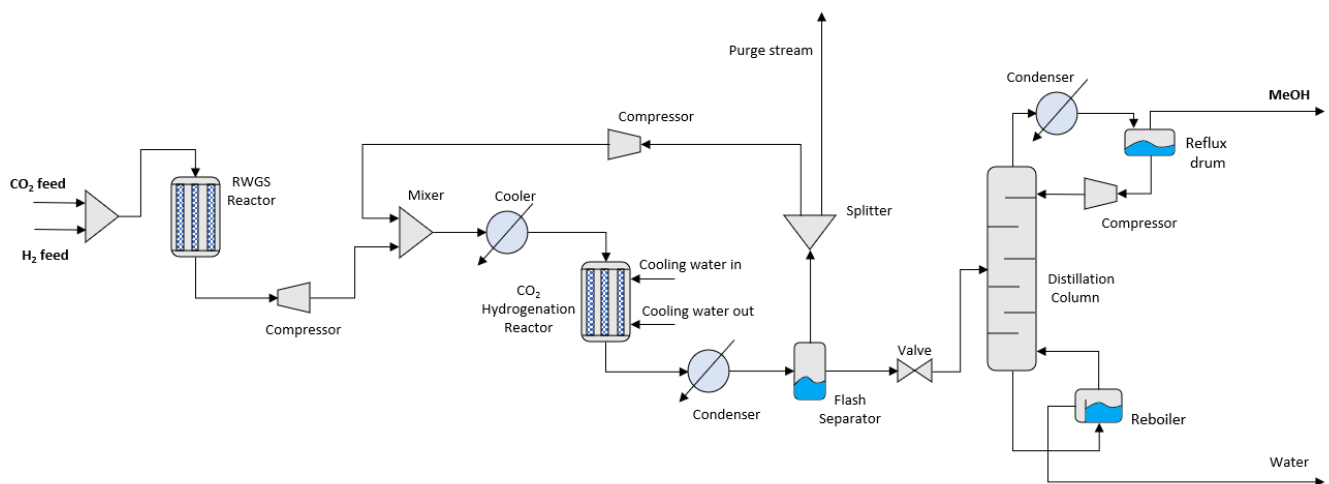
Figure 6. Schematics of a conventional CO_2 to MeOH production system utilizing a RWGS reactor.

The RWGS reaction is endothermic, thus high reaction temperatures are required, increasing the energy consumption of such systems. Specifically, CO becomes the main product of the reaction at temperatures above 700 °C [58]. The H_2:CO_2 ratio for the RWGS reaction ranges from 1:1 to 4:1. In general, the chemical equilibrium of the reaction is pressure independent.

For the RWGS reaction, numerous reactor designs have been studied such as the packed-bed, the fluidized-bed and the moving-bed reactors. A number of catalysts have been investigated for the RWGS reaction, with precious metals such as Pt, Pd, Ru and Au finding successful application as the active sites of the catalysts [59]. Recent studies have also focused on Cu, Ni and Fe catalysts, as the high prices of noble metals such as Pt limit their availability. The results show that, while Pt catalysts exhibit the highest CO_2 conversions, Cu and Fe display the highest CO selectivity [60].

Zhuang et al. specifically examined the performance of a 0.5 wt% Ru-promoted $Cu/ZnO/Al_2O_3$ catalyst compared to a conventional $Cu/ZnO/Al_2O_3$ catalyst, under identical operational parameters. The results showed that under 500 °C, CO_2 conversion of the Ru-promoted catalyst was 46%, in comparison to 17%. Metal catalysts are typically coupled with reductive oxides such as CeO_2, MN_2O_3, CrO_2, FeO_X or TiO_2 [61]. In addition, many catalysts incorporate transitional metals or rare earths such as Zr, Fe, La and Y into the reducible oxide lattice [62].

To demonstrate the efficiency of high temperatures in the reaction, various studies examined the performance of catalyst under different reaction temperatures. Zhuang et al. also examined a similar Pt/TiO_2 at a slightly higher H_2:CO_2 ratio, 3:1, and higher temperature, 600 °C. The study showed that when operating under these conditions, CO_2 conversion reached 56% [63]. Kim et al. in their study examined the performance of a Pt/Al_2O_3 and a Pt/TiO_2 catalyst under different temperatures, keeping other operational parameters such as H_2:CO_2 (3:2.1) ratio and space velocity the same [64]. The results showed that, at 500 °C, CO_2 conversion was approximately 34% and 39%, while at 300 °C it was only 6% and 15%, for the Pt/Al_2O_3 and Pt/TiO_2 catalyst, respectively.

For even higher temperatures, Zonetti et al. examined the performance of a $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst at 700 °C, at a H_2:CO_2 ratio of 3:1. The study showed that when operating at these conditions, CO_2 conversion reached 62.5%. The performance of the various catalysts is summarized in Table 7.

Table 7. Performance of catalysts for RWGS reaction.

Catalyst	H_2:CO_2 Ratio	Temperature (°C)	CO_2 Conversion (%)	CO Selectivity (%)	Catalyst Cost (€/kg cat.)	Reference
$Cu/ZnO/Al_2O_3$ Ru-$Cu/ZnO/Al_2O_3$	4:1	500	17.0 46.0	100	~18.1	[57,63]
Pt/Al_2O_3	3:2.1	500 300	34.0 6.0	100	6520	[64,65]
Pt/TiO_2		500 300	39.0 15.0		-	
Pt/TiO_2	3:1	600	56.0	100	-	[66]
$Ni/Ce_{0.75}Zr_{0.25}O_2$	3:1	700	62.5	99.5	-	[67]

Studies conducted on the effect of CO_2:CO ratio in MeOH production have shown that the MeOH yield for CO_2-based gases is 18–58% at 200–250 °C and 50–100 bar, significantly lower than for CO-based gases, which accounted for 55–89% [49].

Klier et al. examined the effect of CO_2:CO ratio in the production of MeOH over a Cu/ZnO-based catalyst [68]. The results showed that the complete absence of CO_2 from the syngas accounted for reduced carbon conversion, as a small amount is required as a promoter of the reaction. Despite this, at higher concentrations, carbon conversion was significantly hindered. At 250 °C, carbon conversion to MeOH for a CO_2:H_2 gas of zero CO content was only 9.7%. For a syngas of 2:28 CO_2:CO ratio, at the same temperature and H_2 supply, carbon conversion was up to 69.7%.

Ng et al. also examined the influence of the CO_2:CO ratio in the feed composition for the production of MeOH and dimethyl ether (DME) over the commercial $CuO/ZnO/Al_2O_3$ catalyst [69]. At 250 °C, 50 bar and a GHSV of 27,500 h^{-1}, the MeOH yield was the highest, more than 50% at less than 10% CO_2:(CO_2+CO) ratio. In the absence of CO from the gas, MeOH yield was lower than 20%. The effect of the CO_2:CO ratio in the production of MeOH for the various catalysts is summarized in Table 8.

Table 8. Effect of CO_2:CO ratio in the production of MeOH for various catalysts.

Catalyst	CO_2:CO Ratio	Temperature (°C)	Carbon Conversion to MeOH (%)	Catalyst Cost (€/kg cat.)	Reference
Cu/ZnO-based	2:28	250	69.7	-	[68]
	No CO		9.7	-	
$CuO/ZnO/Al_2O_3$	1:9	250	>50	18.1	[57,69]
	No CO		<20		

Enhanced CO_2 transformation by the Fischer-Tropsch reaction is a widely used approach for the production of MeOH. For the transformation of CO to CO_2, the commercial $Cu/ZnO/Al_2O_3$ catalyst is used, mixed with precious metals such as Ru to enhance the conversion. As the RWGS reaction is highly endothermic, high temperatures of 500 °C are generally preferable. In terms of H_2:CO_2 ratio, near stoichiometric ratios are generally preferred.

Incorporating a RWGS reactor prior to the CO_2 transformation process significantly increases the overall carbon conversion and MeOH production. Studies have shown that the production of MeOH from CO gases can be up to 6–7 times higher than from CO_2 gases. Despite this, such systems account for higher energy consumption, thus incorporating them or not depends on the techno-economical specifications and the desired MeOH production capacity of each system.

3.3. Applications of CO$_2$ Transformation to MeOH in Extractive Industries

MeOH production from the flue-gases of extractive industries, such as steel mills, is an already commercial technology. For instance, in 2011, 11% of the total MeOH production of China, which is currently the largest market, derived from such processes [70]. However, most of these processes were not focused on exploiting renewable electricity for the production of the H$_2$ required for the MeOH synthesis, often increasing the total CO$_2$ emissions [71]. To tackle such issues, numerous studies and projects have focused on modernizing the process to achieve the industries' decarbonization.

Carbon2Chem is one of the projects focusing on the power to MeOH concept, promoting numerous studies on the subject [72]. Bender et al. examined the coupling of steel and chemical production, proposing different scenarios, one of them being the direct reduced iron (DRI) process coupled with MeOH production by green H$_2$, using the flue-gases of a steel mill [73]. The study was conducted for the implementation of the scenario in the Duisburg site, with a nominal production rate of 12 MMTA of iron products. The flue-gases derived by a blast furnace by 85.5%, a coke-oven by 9.45% and a basic oxygen furnace by 5.05%, and comprised mostly of CO, CO$_2$, N$_2$ and H$_2$. The results of the study suggested that the proposed scenario can reduce the total CO$_2$ emissions from 21.9 to 0.5 MMTA, a reduction of almost 98%, and is dimed the most efficient approach for the decarbonization of the site's activities.

Schlüter et al. developed a model for the catalytic conversion of steel mill gases for MeOH synthesis [70]. Three different cases were examined, with different rates of coke oven gas (COG), BFG and basic oxygen furnace gas (BOFG) in the flue-gas. The study examined the commercial Cu/ZnO/Al$_2$O$_3$ catalyst with a bed porosity of 0.38. The reactor was 7.5 m in length, with tubes of 44 mm diameter. The number of tubes varied for every examined case. The reaction took place at 240 °C and 85 bar. The steel mill had a production capacity of 16.4 kt$_{steel}$/day, with a CO$_2$ production of 2.74 kt/day (0.34 ktCO$_2$/day by COG, 1.38 ktCO$_2$/day in BFG and 1.02 ktCO$_2$/day in BOFG). Case 1 examined the MeOH production without additional H$_2$ demand, by limiting the BOFG content in the flue-gas. Case 2 examined the use of additional H$_2$ for maximum utilisation of BOFG. Both these cases excluded BFG, accounting for MeOH productions of 155.81 and 370.32 kt/a, respectively. Case 3 examined the utilisation of the BFG gases, accounting for a MeOH production of 669.05 kt/a. The carbon efficiency of cases 1,2 and 3 were 90.6%, 92.8% and 82.5%, respectively.

The FReSMe project, which concluded in 2021, also aimed for the production of MeOH from CO$_2$ deriving from the residual steel gases recovered from an industrial blast furnace [74]. The produced MeOH was to be used as fuel in ship transportation. The pilot plant was designed for a nominal production rate of 50 kg/hr with an input of 800 m^3/hr CO$_2$. The pilot plant constructed utilised a SEWGS CCS system for the production of a CO$_2$ rich stream and a H$_2$/N$_2$ stream from the BFG [75]. The CO$_2$ rich stream was cooled, buffered and compressed before entering the desulphurization step. After desulphurization, the pure CO$_2$ stream was introduced to the reactor system for the production of MeOH to be stored in tanks. The H$_2$/N$_2$ stream passed through a membrane skid for the separation of H$_2$ and N$_2$. The produced H$_2$ was used as a feed for the CO$_2$ hydrogenation reaction, along with the feed produced by an electrolyser. The FReSMe project is the integration of the CCS technology developed in the aforementioned STEPWISE project and the improved technology for MeOH production by CO$_2$ developed in the MefCO$_2$ project [74,76].

MefCO$_2$ project designed a Lurgi reactor utilising a commercial CuO/ZnO/Al$_2$O$_3$ catalyst for CO$_2$ hydrogenation [77]. The experiments showed that at 20 bar, 280 °C and 12,030 h^{-1} GHSV, CO$_2$ conversion reached 25% in a single pass, with MeOH selectivity being 10%. At 200 °C, keeping the other operational parameters constant, CO$_2$ conversion was less than 5%, while MeOH selectivity reached as high as 80%. The results proved that higher temperatures result in higher conversion while lower temperatures result in higher selectivity, thus moderate temperatures are considered optimal. The project's pilot plant at Niederaussem was designed for 1 tonne of pure MeOH production daily. The

reactor developed was a 7.022 m Lurgi reactor of 2962 tubes of 0.053 m diameter each. The catalyst used was a conventional $Cu/ZnO/Al_2O_3$ with a bed porosity of 0.39. The reactor operated at 80 bar, with a feed of 10.2 kg/hr of H_2 and 66.1 kg/hr of CO_2, a conventional H_2:CO_2 molar ratio of 3:1 [77]. The system also incorporated a recycling stream, with a CO_2 recycle ratio (fresh CO_2 feed/CO_2 feed of reactor) of 0.25, thus the system accounted for 4.89 kmol/h and 1.63 kmol/h of fresh H_2 and CO_2, respectively, and a MeOH production of 1.2 ton/day.

4. Sustainability Analysis of MeOH Production from CO_2

MeOH production through CO_2 is an approach seen constant rise in popularity and application. Various studies over the recent years have focused on the environmental impact and the sustainability of these systems. Key points comprise the comparison of MeOH production from CO_2 with the conventional processes, and the energy efficiency of the process.

In 2021, Ryoo et al. conducted a Life Cycle Assessment (LCA) for the CO_2 to MeOH conversion process and its energy optimization [78]. The study examined three different scenarios, MeOH production from the CO_2 deriving from coal gasification, coal coking and production by photocatalytic conversion. All systems utilised an amine-based CCS system using MEA. For CO_2 hydrogenation, a $La/Cu/ZrO_2$ catalyst was examined. The study considered various energy sources for the supply of the required heat and electricity in the system. Solar thermal, natural gas (NG), oil, coke (coal) and steam were examined as heat sources. Nuclear, wind, photovoltaic, hydro and grid electricity were examined for electricity. The results showed that, when using grid electricity and steam, the photocatalytic conversion had the least GHG emissions, 2.28 kg CO_2 eq/kg MeOH, followed by the coke coking conversion process, with 2.9 kg CO_2 eq/kg MeOH. Coal gasification conversion on the other hand was concluded to have the greatest environmental impact, with 17.7 kg CO_2 eq/kg MeOH. CO_2 hydrogenation accounted for 10.7 kg CO_2 eq/kg MeOH. The results also highlighted the importance of energy optimization in the processes, especially for CO_2 hydrogenation. With the use of nuclear and solar thermal energy, the process accounted for 1.67 kg CO_2 eq/kg MeOH, a reduction of more than 84%.

Rosental et al. conducted an LCA on CCU for the production of large-volume organic chemicals [79]. The study examined various CO_2 sources, and the corresponding carbon capture technologies. One of these was the amine-base carbon capture from flue-gases. The amine used by the system was MEA. The MeOH production took place over a $CuO/ZnO/MgO/Al_2O_3$ catalyst. The thermal energy for the carbon capture was supplied by the excess heat of the chemical reactions with a 100% efficiency. The required electricity was provided by offshore wind turbines. The results showed that MeOH produced by CCU had significantly less impact on GHG, approximately 1.5 kg CO_2 eq/kg MeOH, in comparison to the production from syngas, which accounts for 2.002 kg CO_2 eq/kg MeOH.

Hoppe et al. also performed an LCA for the production of MeOH from CO_2 [80]. The study compared the production of MeOH from CO_2, captured by various gases, and H_2, produced by electrolysis from wind power electricity, with the conventional production method from Natural Gas (NG). The results showed that production of MeOH from CO_2 captured besides from air (direct air capture), resulted in <0 kg CO_2 eq/kg MeOH, as a result of utilizing the CO_2 otherwise released into the atmosphere. On the other hand, production from NG and CO_2 from direct air capture accounts for approximately 0.9 kg CO_2 eq/kg MeOH and 0.5 kg CO_2 eq/kg MeOH, respectively.

The environmental benefits of MeOH production from CCUS lie in both the CO_2 emissions reduction from the process, as well the use of the eco-friendlier MeOH, compared to conventional fuels. Rigamonti et al. performed an LCA for MeOH production from the CO_2 of steel mill gases, to be used in ship transportation [81]. The gases examined were a mix of BOFG and COG. The system was a conventional CCU, utilizing the SEWGS CCS technology and CO_2 hydrogenation technology. The CO_2 hydrogenation reactor utilised the commercial $Cu/ZnO/Al_2O_3$ catalyst. The required electricity was provided from a

power plant utilizing the remaining flue-gases of the steel mill, to allow for their maximum exploitation. In this frame, Table 9 depicts the environmental impact of CO_2 to MeOH conversion processes in relation to the Global warming potential indicator.

Table 9. Global warming potential of CO_2 to MeOH conversion processes.

CO_2 to MeOH Conversion Processes	Global Warming Potential [kg CO_2 eq/kg MeOH]	Life Cycle Identification	Reference
Coal gasification conversion	17.7		
CO_2 hydrogenation	10.7		
Coke coking conversion	2.90	1 kg MeOH production ReCiPe midpoint impact assessment	[78]
Photocatalytic conversion	2.28		
CO_2 hydrogenation (nuclear and solar thermal energy)	1.67		
Amine-based CCS + CO_2 hydrogenation	1.05	1000 kg CCU products IPCC, 2013	[79]
Production from syngas	2.002		
Production from NG	~0.9		
Direct air capture + CO_2 hydrogenation	~0.5	1 kg MeOH production ecoinvent 3.1	[80]
No direct air capture + CO_2 hydrogenation	<0		

The studies conducted on the sustainability of MeOH production from CO_2 show the environmental benefits of this approach, in comparison with conventional production methods. The studies indicate that CO_2 hydrogenation is significantly less GHG emissive than other conventional MeOH production methods. While other processes, such as photocatalytic conversion also allow for a very high reduction in GHG emissions, CO_2 hydrogenation, as a mature and relatively simple approach, can have even greater mitigation capabilities when coupled with renewable energy sources. Compared to coal gasification, CO_2 hydrogenation using green energy produces approximately 10 times less kg CO_2 eq/kg MeOH. Amine-based CCS coupled with CO_2 hydrogenation processes accounts for as much as 47% reduction in the overall CO_2 emissions of MeOH production, compared to the production from NG. In addition, non-direct air capture, such as amine-based capture, can account for almost 100% reduction in GHG emissions, compared to direct air capture. The use of CCUS allows for significant mitigation of GHG emissions thanks to the avoidance of MeOH production by highly emissive conventional processes.

5. Cost Comparison of CCUS for MeOH Production

A short literature review of studies focused on the techno-economic analysis of the CCS and CCU systems for MeOH production is presented. The evaluation of the economic sustainability and the cost comparison of the different practises is key for the optimisation and consequently the large-scale commercialisation of the different solutions.

Roussanaly et al. performed a techno-economic analysis over a CCS system using MEA for the CO_2 capture from a flue-gas of approximately 20 vol% CO_2 [82]. The study concluded that, with a capture efficiency of 90%, the cost of CO_2 capture was 63.2 €/ton CO_2. The study also concluded that the CO_2 avoided cost was 83.2 €/ton CO_2, highlighting the economic benefits of incorporating a CCS unit. Panja et.al also performed a techno-economic analysis for an amine-based CCS unit, using the PacifiCorp's Hunter Plant as the case study [83]. The study examined the use of MEA for different capture capacities. For a 65% capture efficiency, the estimated carbon capture cost was approximately 52 €/ton CO_2 [84]. Increasing capture efficiency to a conventional 90% resulted in decreased costs, to approximately 43 €/ton CO_2.

Moioli et al. performed a cost comparison of the conventionally used MEA scrubbing to potassium taurate absorption [85]. The study examined a potassium taurate system with an almost identical layout to the amine-based systems, without the use of the optional solid-liquid separator for separating solid taurine. The study assessed the costs for the two practices, in terms of total capital and operating costs and the capital costs of the

absorption and regeneration processes. For MEA, the analysis concluded capital and operational costs of approximately 180 million €/year and 43 million €/year, respectively. For potassium taurate the corresponding costs were approximately 150 million €/year and 38 million €/year. In terms of the absorption and regeneration processes, the capital costs for MEA were approximately 17 million €/year and 26.4 million €/year, respectively. For potassium taurate, these costs were 13.6 million €/year and 6.4 million €/year. The aforementioned costs were estimated for a 90% capture efficiency, for a flue-gas of 13 mol% CO_2 content, a flowrate of 19.6 kmol/s, and an operating load of 8000 h/year. Thus, the capital and operational costs for MEA can be expressed as 62 €/ton CO_2 and 14.7 €/ton CO_2, respectively. For potassium taurate, the corresponding figures were 51.6 €/ton CO_2 and 13.1 €/ton CO_2, highlighting the potential of using energy-efficient solvents such as amino acids.

Khallaghi et al. performed a techno-economic analysis comparing a base case of a conventional amine-based system to a WGS-enhanced system, used for carbon capture from the BFG of a steel mill [40]. The results of the study showed that the base case accounted for a total CO_2 capture cost of 39.84 €/ton CO_2, in comparison to 44.35 €/ton CO_2 for the WGS enhanced case. It is evident that while the WGS-enhanced approach significantly improves the overall capture capacity of CCS systems, the extra components required, as well as the increased energy consumption, accounted for increased operational costs.

Considering the economic sustainability of CCUS, the benefits of this approach lie in the mitigation of emissions related costs (i.e., carbon taxation) and the creation of revenues from the production of MeOH. In 2020, Centi et al. performed a techno-economic analysis for the production of MeOH by CO_2 hydrogenation [86]. The study compared the cost of MeOH production in relation to an average value of 400 €/ton MeOH in Europe. In addition, the study examined the MeOH production cost considering the case study of renewable energy production from remote areas, as proposed by Barbato et al. [87]. Both infrastructure and operation for CO_2 capture and hydrogenation were considered and a 20 €/ton CO_2 benefit of avoided emissions was estimated. The study concluded a net MeOH production cost of 294 €/ton MeOH. The costs of the different CCUS technologies are summarized in Table 10.

Table 10. Cost of different CCUS technologies.

CCUS Components	Solvent	Carbon Capture Efficiency (%)	Cost for CCS (€/ton CO_2)	Cost for CCU (€/ton MeOH)	Reference
CCS	MEA	90	63.2	-	[82]
CCS	MEA	90	43	-	[83]
CCS	MEA	90	76.7	-	[84]
CCS	Potassium taurate	90	64.7	-	[84]
CCS	MDEA	46.5	39.84	-	[40]
CCS (WGS-enhanced)	MDEA	83.8	44.35	-	[40]
CCU	-	-	-	294	[86]

6. Summary and Future Perspectives

CCUS technologies are considered an efficient and promising approach to increase the environmental sustainability of energy-intensive industries such as extractive industries. With an average CO_2 capture efficiency of approximately 90%, CCS technologies have the potential to significantly reduce CO_2 emissions. CCU technologies for the production of MeOH facilitate the circular economy of the industrial sector, creating revenues from green fuel production.

The cost to capture and store post combustion emissions is very high, even though the technology has been around for a long time. The capital and high operational costs of

such systems pose a major challenge towards their commercialisation. The development of CCUS faces a number of barriers lying mostly on the economic feasibility. The high energy requirement of the conventional CCS units, mostly due to the required regeneration energy for the solvents, significantly affects economic sustainability. In addition, incorporating CCS systems in industrial plants results in decreased plant efficiencies and increased water use, adding to the operational costs [88]. Transportation of the captured CO_2 requires significant amounts of energy for the compression, as well as maintaining the high pressure in the pipelines. The pipelines themselves must be specially designed, as existing oil and gas pipelines are not suitable. Impurities in CO_2, such as water, can damage pipelines, leading to leaks or even explosions due to the rapid expansion of the compressed fluid.

According to the literature, CCS solutions and suppliers have increased steadily, which means that the general technical availability is no longer a hurdle in itself for industrial applications. Nevertheless, further investigation can be performed, focusing on reducing the costs of CO_2 capture for investors as well as boosting technological progress. In this regard, it is clear that the next developments of CCS will have a focus on increasing their capture rates and the overall efficiency.

Captured CO_2 can also be used as a feedstock for a variety of industrial purposes (e.g., methanol). CO_2 hydrogenation for MeOH production is one of the most common practices. Current operational conditions significantly rise the energy demand for the compression and heating of the reactants, while achieving CO_2 conversions of less than 16% in a single pass, except in cases of extremely high pressures, which are mostly limited in lab-scale studies due to safety reasons. To tackle these issues, incorporation of recycling streams is necessary to achieve conversion efficiencies high enough to justify the high energy consumption. In addition to recycling, the use of RWGS reactors prior to CO_2 hydrogenation can significantly increase the overall CO_2 conversion of CCU, by converting CO_2 to CO. A key factor towards achieving the optimal and sustainable use of these technologies is the development of efficient CO_2 reactors. CCU comprises technologies at different levels of maturity and process complexity. In this respect, the development of highly selective, low cost and long-term recyclable catalysts for the production of MeOH with CO_2 in absence of CO is also investigated.

The production of the necessary H_2 for the CO_2 hydrogenation is another aspect requiring considerable research. Most commonly used H_2 production methods rely on the reforming of hydrocarbons. While production by water electrolysis has seen a constant rise over the years, the high energy costs result in scaling-up difficulties. Energy optimisation and scaling up of water electrolysis technologies are key to increase the sustainability of CCUS and promote the development of CO_2 hydrogenation technologies. A promising solution finding ground is the production of H_2 through photochemical water splitting with CO_2 reduction. Complimenting CO_2 hydrogenation systems with energy-efficient H_2 production solutions is a major challenge towards increasing the technologies' sustainability and promoting its future development.

In general, limited awareness is reported regarding CCS and CCU technology advantages. It is necessary to communicate how CCUS affect the everyday life of EU citizens and consumers' choices. To this end, the coaction of policymakers at national and European level with companies and other societal actors, such as trade unions, will facilitate the further deployment of CCUS projects and raise awareness about their climate and economic benefits.

To sum up, existing barriers to the industrial scale deployment and development of CCS and CCU have to be addressed. The European climate targets provide better prospects to overcome economic barriers in order to enable the take-off of CCS and CCU projects and to introduce incentives for the technologies. At the same time, technical constraints are also essential for creating new CCU decarbonisation pathways (e.g., ensuring symbiotic infrastructure among CO_2 emitters and CO_2 converters in clusters of concentrated industrial activity).

7. Conclusions

The CCUS technologies provide a path towards a carbon neutral society through mitigating CO_2 emissions from fossil fuels by capturing and converting them into fuels and chemicals. Among the CCS, chemical absorption using amine-based solvent is one of the most commercially used, being suitable for the low CO_2 containing flue-gases deriving from the processes of extractive industries. Evidence suggests that tertiary amines in particular, such as MDEA, account for carbon capture efficiencies of up to 90% while having significantly lower regeneration energy demands than other amines. When mixed with promoters such as PZ, such systems are able to achieve absorption capacities as high as 0.99 mol CO_2/kg solvent.

To achieve even higher CO_2 capture, amine-based CCS processing flue-gases of high CO content, such as the flue-gases of steel mills, often utilise WGS reactors for the transformation of CO to CO_2, in the WGS-enhanced CCS. WGS-enhanced CCS has received great attention with several projects focusing on the development of such systems to be used in extractive industries. C4U project examined the CO_2 capture from BFG gases in the steel industry. Compared to conventional amine-based systems, the WGS-enhanced CCS accounted for an increase of approximately 80% in CO_2 production.

CCU for carbon transformation to MeOH is widely applied with MeOH finding commercial applications in various sectors. CO_2 hydrogenation for MeOH production takes place in catalytic reactors, typically Lurgi reactors. The most commonly used catalysts are $Cu/ZnO/Al_2O_3$ and $CuO/ZnO/Al_2O_3$ catalysts, being able to achieve CO_2 conversion and MeOH selectivity up to 65.8% and 77.3%, respectively, when operating at high H_2:CO_2 ratios and pressures. In addition to CO_2 hydrogenation, production of MeOH from CO is also applied. Such systems utilise RWGS reactors for the conversion of CO_2 to CO for the Fischer-Tropsch reaction. This approach allows for higher CO_2 conversion, but lower MeOH selectivity.

Overall, CCUS has already seen several applications in the extractive industry, with CCS especially already being considered a commercial technology. Utilisation of these technologies is key for the decarbonization, with new projects and plants constantly arising. For these reasons, further investigation for maximizing the CCUS capture and transformation efficiency is required. The optimization of these technologies is a major factor towards the mitigation of GHG emissions, for the extractive industries to play their part in the net zero emissions milestone of 2050.

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Abbreviations

1A2P	1-amino-2-propanol	La	Lanthanum
2A1B	2-amino-1-butanol	LAHP	liquid amino acid salts hydrogel
ACTL	Alberta Carbon Trunk Line	LCA	Life cycle assessment
Al_2O_3	Alumina	LNG	Liquified Natural Gas
Au	Gold	LT-WGS	Low-temperature water gas shift
aq	Aqueous	MDEA	N-methyldiethanolamine
BFG	Blast Furnace Gas	MEA	Monoethanolamine
BOFG	Basic oxygen furnace gas	MeOH	Methanol
CA	Carbonic anhydrase	Mg	Magnesium
CeO_2	Cerium Oxide	MgO	Magnesium Oxide
CCS	Carbon Capture and Storage	MMEA	2-(methylamino) ethanol
CCU	Carbon Capture and Utilisation	MMTA	Million metric tons per annum
CCUS	Carbon Capture Utilization and Storage	MN_2O_3	Manganese Oxide
CMR	Catalytic Membrane Reactor	N_2	Nitrogen
CO	Carbon Monoxide	$NaCO_3$	Sodium Carbonate
CO_2	Carbon Dioxide	NG	Natural Gas
COG	Coke oven gas	Ni	Nickel
COS	Carbonyl Sulphide	NO_x	Nitrogen Oxide
Cr	Chromium	Pd	Palladium
CrO_2	Chromium Oxide	PEI-B	Polyethylenimine
Cu	Copper	PSA	Pressure swing adsorption
CuO	Copper Oxide	PSS	Porous Stainless Steel
CVD	Chemical vapor deposition	Pt	Platinum
DEA	Diethanolamine	PZ	Piperazine
DEAE	2-diethylaminoethanol	Ru	Ruthenium
DGA	2-(2-aminoethoxy) ethanol	RWGS	Reverse water gas shift
DMAE	2-(dimethylamino) ethanol	SEWGS	Sorption enhanced water gas shift
DME	Dimethyl ether	SG	Sodium glycinate
DRI	Direct reduced iron	SPECCA	Specific primary energy consumption per unit of CO_2 avoided
EMEA	N-ethylmonoethanolamine	SRC	Steam raising converter
EOR	Enhanced oil recovery	STY	Space time yield
Fe	Iron	TEPA	Tetraethylenepentamine
FeO_x	Iron Oxide	TGR-BF	Top gas recycle blast furnaces
g	Gaseous	TiO_2	Titanium Oxide
GBIG	Glyoxal-bis-iminoguanidine	ULCOS	Ultra-Low CO_2 Steelmaking
GHG	Greenhouse Gas	VPSA	Vacuum pressure swing adsorption
GHSV	Gas Hourly Space Velocity	WGS	Water Gas Shift
H_2	Hydrogen	Y	Yttrium
H_2O	Water	ZnO	Zinc Oxide
H_2S	Hydrogen Sulphide	Zr	zirconium
HCl	Hydrochloric acid	ZrO_2	Zirconium Oxide
HT-WGS	High-temperature water gas shift		

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