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CATALYTIC HYDROGENATION OF CO₂ TO OLEFINS

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ΚΑΤΑΛΥΤΙΚΗ ΥΔΡΟΓΟΝΩΣΗ CO₂ ΣΕ ΟΛΕΦΗΝΕΣ

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Περίληψη

Πλησιάζοντας στο πρώτο τέταρτο του 21^{ου} αιώνα, η επιστημονική κοινότητα έρχεται αντιμέτωπη με σοβαρά ενεργειακά και περιβαλλοντικά προβλήματα. Η εκτεταμένη χρήση των ορυκτών πόρων για κάλυψη των ολοένα και αυξανόμενων ενεργειακών και υλικών μας αναγκών έχει οδηγήσει σε μείωση των ενεργειακών αποθεμάτων σε συνδυασμό με μια άνευ προηγουμένου περιβαλλοντική υποβάθμιση. Οι επικείμενες συνέπειες, οδηγούν την ανθρωπότητα στην αναζήτηση νέων μεθόδων για να καλύψει τις ενεργειακές και υλικές της ανάγκες προς την κατεύθυνση της αειφόρου ανάπτυξης. Στην αναζήτηση αυτή, νέες τεχνολογίες παραγωγής ενέργειας κάνουν την εμφάνιση τους, βασιζόμενες κυρίως σε ανανεώσιμες μορφές ενέργειας καθώς και σε τεχνολογίες δέσμευσης και χρήσης του διοξειδίου του άνθρακα (CO₂). Ειδικότερα, η δέσμευση και μετέπειτα χρήση του διοξειδίου του άνθρακα, του αερίου με τη μεγαλύτερη συνεισφορά στο φαινόμενο του θερμοκηπίου, στοχεύει στην παραγωγή χρήσιμων χημικών προϊόντων, συνεισφέροντας παράλληλα στην προστασία του περιβάλλοντος, κλείνοντας τον 'κύκλο του άνθρακα'. Στην παρούσα διπλωματική εργασία, εξετάζονται οι διαφορετικές τεχνολογίες δέσμευσης και χρήσης διοξειδίου του άνθρακα ενώ δίνεται έμφαση στη χρήση του διοξειδίου του άνθρακα ως πρώτη ύλη για παραγωγή ολεφινών μέσω της μεθόδου της καταλυτικής υδρογόνωσης. Αναλύονται οι βασικές αρχές των αντιδράσεων/διεργασιών καταλυτικής υδρογόνωσης, ενώ παρουσιάζεται και η ανάλυση κύκλου ζωής του άνθρακα ως πρώτη ύλη της διεργασίας. Επίσης, παρουσιάζεται συγκριτική αξιολόγηση των καταλυτικών συστημάτων που χρησιμοποιούνται για την παραγωγή ολεφινών. Εξάγονται σημαντικά συμπεράσματα αναφορικά με τη σημασία της σύστασης του καταλύτη και των συνθηκών της αντίδρασης, προς την κατεύθυνση της ανάπτυξης αποτελεσματικών καταλυτών.

Abstract

It is a well known fact that over the last century, humanity has had to deal with the ever-increasing demands, both in energy and resources in order to support and upgrade the modern way of life. Since the start of the industrial revolution in the early 19th century, it was known that the resources like mineral raw materials for energy and value-added chemical production, seemingly vast, were limited. Now, the ever-increasing demand is forcing humanity to find new ways of producing energy and products from renewable resources. They need to be friendly to the environment and economically feasible to replace the well-established conventional production industry, in terms of energy and high value chemicals. One of the strategies towards generating renewable source of raw materials is the utilization of CO₂ emissions, which not only seems inexhaustible for the modern way of life (greenhouse emissions), but also has great potential to be used as chemical feedstock for chemicals like urea and olefins or even as fuel in the form of methanol and methane. This present thesis examines the capture and utilization technologies of CO₂, with the dual purpose of environmental mitigation and sustainable energy, under the influence of a Life-Cycle Assessment system. Furthermore, an extensive overview of catalytic hydrogenation of CO₂ into various value-added fuels/chemicals (especially olefins) was carried out. The state-of-the-art catalysts for the CO₂ hydrogenation to olefins were comparatively presented, providing valuable insights in relation to the impact of catalyst's composition and reaction conditions on activity and selectivity. Valued points were made on the efficiency and behaviour of the catalysts, as long as on the future aspects of catalytic hydrogenation of carbon dioxide-to olefins and value-added chemicals.

1 Acknowledgments

Having reached the end of my studies, I would like to take the opportunity to thank my supervising professor, Dr. Michalis Konsolakis, whose contribution, in terms of guidance and knowledge was immense towards the completion of my diploma thesis. My sincere thanks also go to Dr. Ioannis Nikolos and my friend, Dr. Stauros Leloudas who provided me with additional workspace for my research, which helped me significantly. Finally, I would like to thank my family for their invaluable support throughout my years of study, and my friend and co worker Alexandros Eskantar, who provided support during my struggle towards the end of my studies

2 Introduction to CO₂, Origin and Environmental Concerns.

2.1 Green House Gases

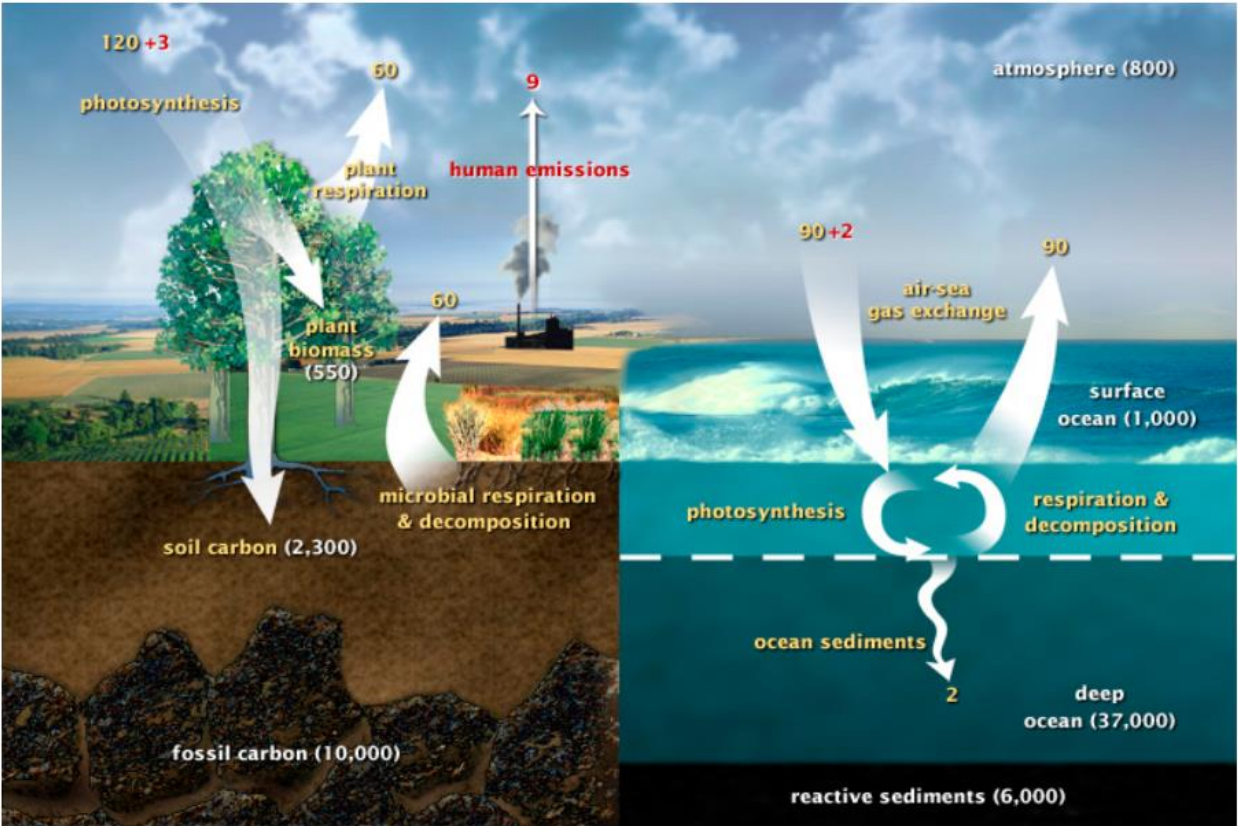
Greenhouse gases (GHG) are any gas that has the property of absorbing infrared radiation emitted from the Earth's surface, thus contributing to the greenhouse effect [1]. Naturally, GHG existed in the atmosphere a long time before anthropogenic activities started to contribute, keeping earth's climate in balance. Human activity over the past century has caused an increase of GHGs in the atmosphere and, due to the greenhouse effect, has triggered global warming. During this phenomenon, the global temperature rises due to trapped heat from the sun between the atmosphere and earth's outer layer. That heat is translated as a global temperature rise which contributes to the melting of the ice in the earth's poles and disturbance in earth's climate, affecting natural aspects in a way that we have yet to provision. Most of CO₂, the larger GHG emission on earth, gets absorbed by oceans. Ice has the largest reflect ratio of sunlight since it's the brightest natural surface on Earth, unlike open ocean water which is the darkest. Since water absorbs sunlight and therefore increases its temperature, a large portion of ice melts, exposing still more ocean surface, creating a positive feedback loop with the possibility of reaching a point of no return. With every year passing, larger quantities of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and flue gases are being pumped into the earth's atmosphere, increasing the phenomenon of global warming exponentially, with the CO₂ corresponding to 63% of total greenhouse emissions [2].

2.2 Carbon dioxide

Carbon dioxide or CO₂, is a linear molecule with a carbon atom at its centre and two pairs of double-bonds of oxygen atoms with a bond angle of 180° known to have great stability and low energy level ($\Delta_f G_{298K} = -396 \text{ kJ mol}^{-1}$) [3], (Table 1). It is also colourless and cannot be detected by the naked eye. It accounts as one of the three main major GHG, with the other two being Nitrous Oxide (N₂O) and Methane (CH₄). CO₂ is considered to be one of the main GHGs since accounts for more than 63% of total GHG emissions with N₂O and CH₄ stand for 24% and 3% of the total global emissions, respectively [4]. CO₂ is also used as metric for comparison with the effect of other GHGs on the atmosphere through the Global Warming Potential (GWP). This system allows a direct comparison between GHGs on scale of tones and the effects they have on the climate and Global Warming phenomenon [5]. CO₂ also represents one of the most important natural gases in the global atmosphere where, in concentrations of between 180 and 280 ppm, protects the climate from extreme low temperatures. Naturally follows a "Carbon Cycle" where a balance is maintained between emissions of carbon and storage keeping earth at relatively stable temperatures via respiration, absorption, photosynthesis and storage as shown in Picture 1. With anthropogenic activities though, CO₂ concentration was estimated around 407.4 ppm in 2018 in the atmosphere, more than twice the concentration produced by natural activities [6].

Table 1 : Properties of CO₂ at 25°C and Standard Pressure

Chemical Formula	CO ₂
Molecular shape	linear
Solubility in water	1.45 g/dm ³
Density (vapor)	1.7845 kg/m ³
Dipole moment	0 D
Standard enthalpy of formation	-393.5 kJ*mol ⁻¹
Standard molar entropy	214 J*mol ⁻¹ *K ⁻¹
Lifetime in atmosphere	2 to 200 years
Global Warming Potential (GWP-100 years)	1



Picture 1: Carbon Cycle. The numbers indicate quantity of carbon in gigatons of carbon per year. Yellow stands for natural contribution and Red for anthropogenic [7].

2.3 Nitrous Oxide

Nitrous Oxide is the third most potent Green House Gas emission of anthropogenic activities with agriculture being the largest source of N₂O, including 66% of total N₂O emissions. Under aerobic conditions, NH₄⁺ is converted into NH₂OH and then it is oxidized to NO₂⁻ by hydroxylamine oxidoreductase. Through nitrification (transformation of NO₂⁻ to NO₃⁻) and denitrification from synthesis of fertilizers, manure and biomass [4], approximately 6 Mt N₂O are deposited in the atmosphere every year which enhances significant the global warming effect since it has approximately 310 GWP higher than CO₂ (Table 2). Also, the long lifespan of Nitrous Oxide in the atmosphere, leads to the depletion concurrently of the ozone layer, in account for the fact that NO_x being a toxic gas [8]. In effort of stabilizing the earth climate, it is unparallel in controlling and decreasing Nitrous Oxide emissions to their source [9].

Table 2: Properties of N₂O at 25°C and Standard Pressure [9].

Chemical Formula	N ₂ O
Molecular shape	linear
Solubility in water	0.111 g/dm ³
Density (vapor)	1.8 g/dm ³
Dipole moment	0.166 D
Standard enthalpy of formation	82.05 kJ* mol ⁻¹
Standard molar entropy	219.96 J *K ⁻¹ * mol ⁻¹
Lifetime in atmosphere	114 years
Global Warming Potential (GWP-100 years)	310

2.4 Methane

Methane (CH₄) is considered to be the second most potent GHG in the atmosphere since a significant share of CH₄ emissions comes from leaks during transportation and other human activities. It is a colorless gas made by tetrahedral molecules with four equivalent Carbon and Hydrogen bonds making it the simplest alkane and a potent hydrocarbon considered to be an attractive fuel source although the capture and storage of CH₄ proves to be challenging and energy consuming due to methane gaseous state. The CH₄ production is separated into three stages that consist of hydrolysis and fermentation phase, hydrogen production acetogenesis phase, and methane production phase [10]. In the hydrolysis and fermentation stages, organic matter is decomposed into fatty acids and alcohols by the action of fermenting bacteria. In the second stage, hydrogen-producing acetogens convert propionic acid, butyric acid, and other fatty acids and ethanol into acetic acid, CO₂, and H₂ [4]. Afterward, acetic acid or CO₂ + H₂ convert into CH₄ through methanogens or, to some extent, hydrogenation of CO₂.

According to IEA [11], methane’s emissions in 2017 accounted for 80 Mt, the equivalent of which is 2.4 billion tons of CO₂ since methane has 25 times higher GWP than CO₂ [12]. Actions, according to reduction policy, have taken place but emissions are still considered to be high.

Table 3: Properties of CH₄ at 25°C and Standard Pressure

Chemical Formula	CH ₄
Molecular shape	Tetrahedral
Solubility in water	22.7 mg·dm ³
Density (vapor)	0,648 kg/m ³
Dipole moment	0 D
Standard enthalpy of formation	-74.48 kJ·mol ⁻¹
Standard molar entropy	186.2 J·K ⁻¹ ·mol ⁻¹
Lifetime in atmosphere	9.1 years
Global Warming Potential (GWP-100 years)	25

2.5 CO₂ Emissions

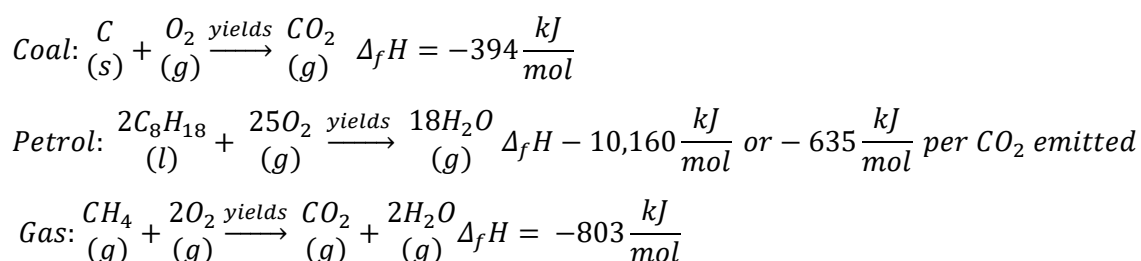
Nowadays, it is hard to imagine a world without the power to satisfy our daily energy needs or the abundance of products that fulfil our modern requirements for survival and pleasure. Before anthropogenic emissions of CO₂, nature kept the concentration of CO₂ in balance via the “Carbon Cycle” of photosynthesis and respiration by plants [13]. Since the Industrial Revolution though, from the early 19th century, concentrations of CO₂ in the atmosphere have been known to continuously increase ratios to this day, resulting to climate repercussions such as changing in rain ratios, melting of Ice in the poles, rise of the sea level, flooding and so forth [13]. The ever increasing power demands, that in 2018 has reached new heights in human history, is pushing humanity to find faster and more productive ways to cover them. The thriving of global economy, in comparison to the previous decade, is accompanied in some countries with needs of populace for heating, cooling and an overall power demand. To cover the exponential energy demand in all sectors, the consumption in fossil fuels has been increased, with natural gas acquiring the leading role. Even the use of renewable energy like solar and wind has seen considerable growth. Specifically, the electrical demand is responsible for more than half of the increased energy needs. Obviously, this kind of demand and energy consumption comes at a cost.

Our conventional methods of energy production through combustion, are responsible for the emissions of more than two thirds of the total Green House Gases (GHGs) emissions increase by all fossil fuels [6], resulting to Global Warming and other phenomenon of natural pollution. According to the International Energy Agency [6], the emissions of CO₂ have reached the all-time high of the 33,1 Gt in 2018 as is shown in Figure 1. If, for the sake of the argument, 33.1 billion tons of CO₂ were compressed in solid form, it would be the equivalent of the white cliffs of Dover in England. A prime example, just to visualize the amount of CO₂ emissions pumped into the atmosphere yearly (Picture 2). This kind of quantity of CO₂ is the results of consumption of natural recourses in order to cover the increasing energy demands in its various forms. As a result, Coal, Oil and Natural Gas are required in an increasing ratio (Table 4).

Although the coal demand is still increasing, there is a considerable decrease in the rate of demand for coal due to the recent predilection for natural gas. Nevertheless, coal is still the main source used for electricity production and primary energy.

Nuclear and RES have penetrated the global energy mix, notably within the last 10 years, with Renewables of Solar PV, Hydropower, Wind Power and Biomass representing 25% of the global energy output. Although energy efficiency is the main parameter which has the largest effect on the decrease of CO₂ emissions, 2018 was the third year in the row where improvement rates of energy efficiency slowed down. According to the Intergovernmental Panel on Climate Change or IPCC reports [14], we will have to nullified global CO₂ emissions until 2050, just to limit the global temperature rise to 1.5°C.

Combustion of the various fuels (Coal,Petrol,Gas) is a highly exothermic reaction, as shown in Scheme 1, which is conventional for power production. Although, the coal reserves are equipt with huge quantinties of carbon, combustion of natural gas produce more than twice amount of energy for every mol of the reaction. By that account, Natural gas has conquered an extensive portion of the market as the preferable fossil fuel. Nevertheless, Natural gas consumption will be an ephemeral solution since the global reserves of Natural gas are limited. In addition, the combustion of Natural Gas is still a source of carbon dioxide emissions [15].



Scheme 1: Combustion enthalpies of fossil fuels [15].



Picture 2 : White Cliffs of Dover [16].

Table 4 : Global energy demand and electricity generation by source by IEA [6].

Energy Demand (Mtoe)		Growth Rate (%)	Shares (%)	
	2018	2017-2018	2000	2018
Total Primary Energy Demand	14 301	2.3%	100%	100%
Coal	3 778	0.7%	23%	26%
Oil	4 488	1.3%	36%	31%
Gas	3 253	4.6%	21%	23%
Nuclear	710	3.3%	7%	5%
Hydro	364	3.1%	2%	3%
Biomass and waste	1 418	2.5%	10%	10%
Other renewables	289	14.0%	1%	2%

Electricity Generation (TWh)		Growth Rate (%)	Shares (%)	
	2018	2017-2018	2000	2018
Total Generation	26 672	4.0%	100%	100%
Coal	10 116	2.6%	39%	38%
Oil	903	-3.9%	8%	3%
Gas	6 091	4.0%	18%	23%
Nuclear	2 724	3.3%	17%	10%
Hydro	4 239	3.1%	17%	16%
Biomass and waste	669	7.4%	1%	3%
Wind	1 217	12.2%	0%	5%
Solar photovoltaics	570	31.2%	0%	2%
Other renewables	144	4.2%	0%	1%

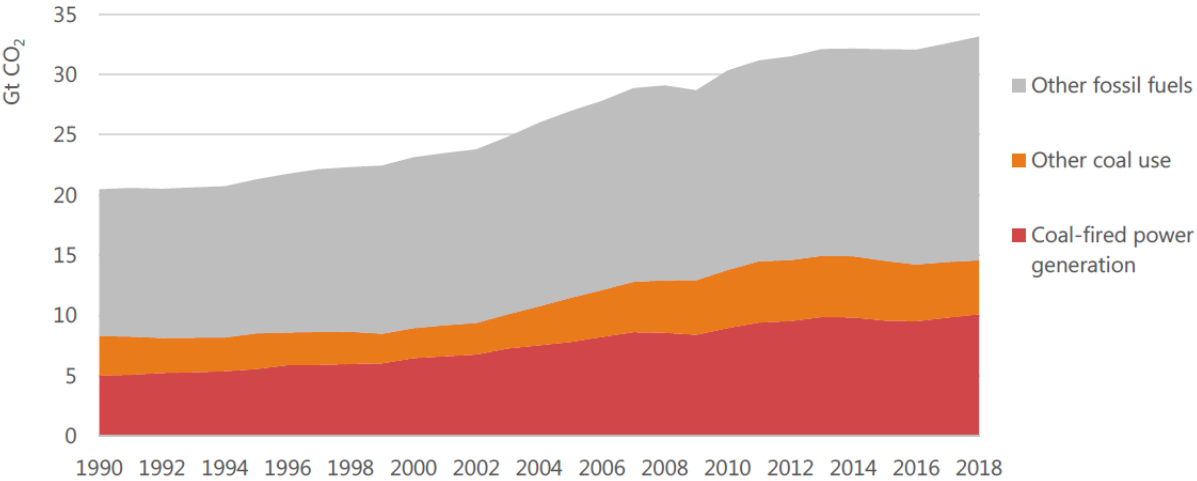


Figure 1: Global energy-related carbon dioxide emissions by source, IEA [6].

By putting under careful observation the CO₂ emissions on a global scale, it is notiable that during the period of time between 2014 and 2016, the CO₂ increasing ratio ceased. That would be the result of an increasing global economy and energy consumption due to advantages in new technological applications and improvements on energy efficiency. Still, the dynamic relationship between CO₂ emissions and energy efficiency changed in the following years with CO₂ emissions increasing 0.5% for every 1% increase in the global economy. Just Coal combustion was held responsible for 0.3 °C of 1°C increased annual global temperature, making Coal the largest source of Green House Emissions and a serious factor for the Global Warming phenomenon [6]. Fossil fuel combustion is producing up to 77% of total GWP.

Every year there has been approximately a +600 TWh increase in demand for electricity from 2000 to date, without decreasing the carbon emissions in every new generation. In addition, the relatively newly established role of Asia as a strong productive country, is based on coal-fired plans which, even with the decrease in green house gas emissions from most producers, render the world average on a stable increase. The role of industry is significant with 30 % of the global consumption of energy using coal and electricity with China and India tripling their consumption in the last two decades reaching 1 Gtoe and 0.2 Gtoe respectively. The worldwide steel industries, is responsible for around 2 of the 33.1 billion tons carbon dioxide emissions annually [17].

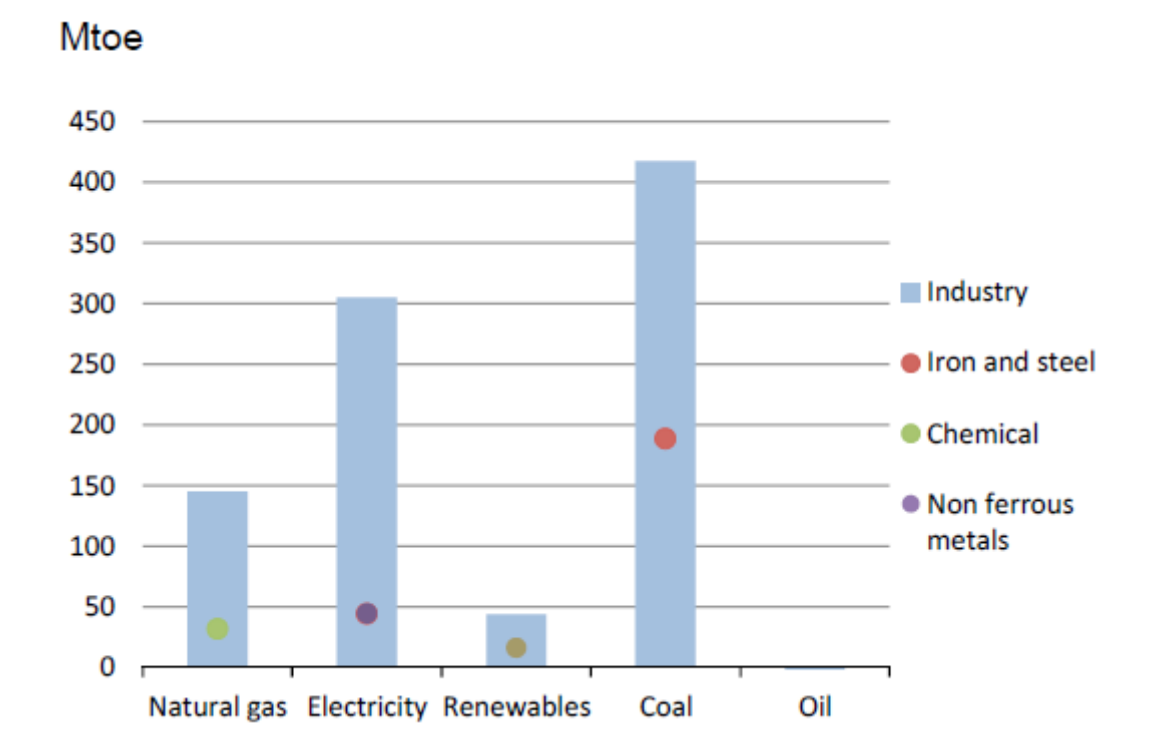


Figure 2: Industry energy consumption by source and sub-sector: 2000-2017 change [17].

Industrial, Land Use and Transportation sectors are also combined with activities which contribute to the total mix of CO₂ emissions. Industries that specialize in various chemical processes in order to produce there main products, like metals, cement, chemicals and petrochemical [4] represents, with energy industries included, almost half of the total CO₂ emissions, with building industry and transportation accounting for 25% each respectably [17]. Due to this fact, the United States, China and India have acquired the leading roles for producing GHG through their industrial sectors and therefore, in need for environmental and greener energy polices (

Table 5).

Table 5: Energy related CO2 emissions from fuel combustion by regions by IEA [6].

	Total CO ₂ emissions (Mt CO ₂)	Growth Rate (%)
	2018	2017-2018
United States	4 888	3.1%
China	9 481	2.5%
India	2 299	4.8%
Europe	3 956	-1.3%
Rest of world	11 249	1.1%
World	33 143	1.7%

The targets placed by the 21st United Nations Climate Change Conference in Paris, as COP21, set new benchmarks in order to halt global temperature rise to 2°C until 2030 and 2050. Until now it has been proven difficult to coordinate the efforts of European Union countries in order to achieve the goals set by the Committee, while the conventional armada of old Coal-fired Combustion are inflexible for satisfying lower emission levels and energy efficiency rendering them unable to contribute to overall environmental goals [18]. Market models still need to be investigated and applied in order to make economically feasible environmental targets, considering both producers (private or public) and customers since new projects for energy production are in need of investments. By applying policies like attractive taxation for customers and new opening sockets in the market towards renewable and low-carbon power technologies for investors, important steps can be made towards achieving the goals of COP21.

3 CO₂ Capture

3.1 Introduction to CCU

According to the data of carbon dioxide emissions presented in the previous chapter, there is still a long road ahead for realizing the goal of nullified global CO₂ emissions and stabilization of the exponential global warming phenomenon. The current energy grid relies heavily on the use of fossil fuel and the combustion of carbon. A complete renewable energy system will have to utilize a mixture of renewable energy sources and be compatible with different sectors such as heating, cooling, energy production and transportation. Since such a grid is far from realization due to technological boundaries and economical factors, Carbon Capture and Utilization technologies, or CCU, will play a major role in achieving a deeper decarbonisation level of the established energy systems as long as creating and enhancing the market of CO₂ as a feedstock for various products. Flexible and adaptive CCU can be the stepping-stone towards achieving the goal of deep global emission reduction, in cooperation with the use of renewable energy and Negative Emission Technologies such as Carbon Capture and Storage (CCS) and Direct air Capture (DAC). An integrated power system could combine the power produced by renewable and conventional energy, used for power and industrial plants with installed CCU. The captured carbon from the emissions can then be stored as electro fuel for further energy output, used as material for various products or stored. These technologies are deployed in alignment according to the concept of Circular Economy where the carbon emission can be used again to benefit both the environment and economy in chemical and energy markets (Figure 3). Such models are deployed in various departments of production industries, both in the European Union and China [19].

But in order to validate and avoid methodological pitfalls in the evaluation of CCU technologies, as a major wedge against the carbon dioxide emissions, a systematic framework of Life Cycle Assessment could take place where all aspects of CO₂ capture and usage are taken into account, since capturing and utilizing carbon dioxide is an energy demanding pathway [20], [21].

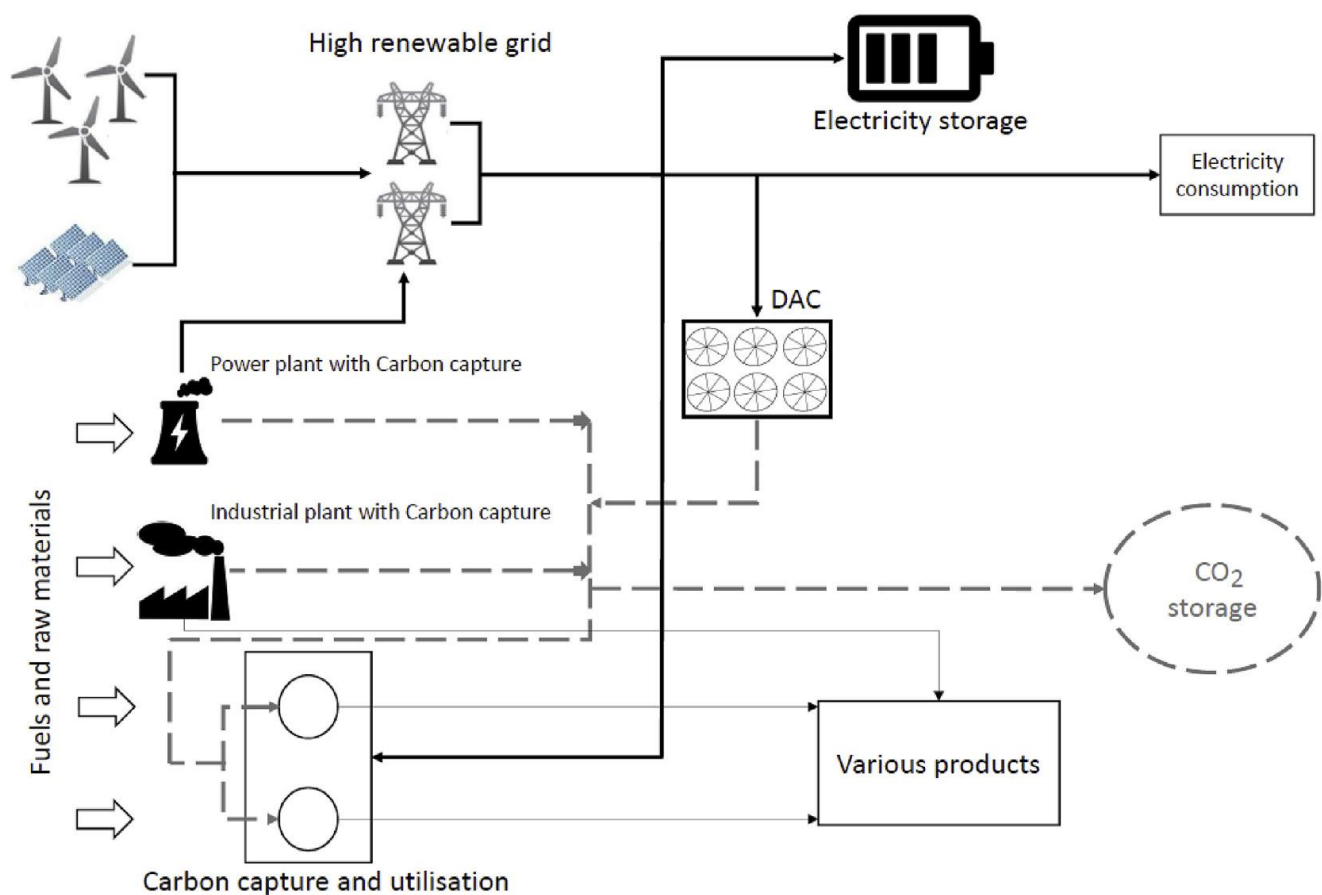


Figure 3: Power mixture grid with CCU applications [21].

3.2 Carbon Capture Technologies

Carbon Capture technologies could be summarized as follows [21]:

- Pre-combustion Capture
- Oxyfuel Combustion
- Chemical Looping Combustion or CLC
- Post-Combustion Capture
- Direct Air Capture (DAC)
- Amine Scrubbing
- Membrane CO₂ Capture
- Cryogenic CO₂ capture system

The above methods aim to capture CO₂ and produce a concentrated amount for Utilization. The capture of CO₂ with the purpose of sequestration will not be mentioned in this thesis, since storage of carbon dioxide without further utilization has very small impact on decreasing the carbon dioxide emissions, and hence the global warming effect [22]. According various researches ([23]–[25]) the technologies mentioned above have important applications in the current industry, but only a few have reached the level of commercialization. More specifically, according to Table 6, only Post-Combustion amines in power plants and Pre-Combustion Natural Gas processing have reached Commercialization levels and are in usage. The pathways have to be adaptable according to the compound which rests in the emissions, since their composition differ from industry to industry (Table 7).

Table 6: TRL of Carbon Capture Technologies [21], [25].

Technology readiness level (TRL)	Proposed technology
Concept. 1	
Formulation. 2	
Proof of concept. 3	<div>➤ Post-combustion Ionic liquids</div> <div>➤ Bio Energy with Carbon Capture and Storage power</div> <div>➤ Pre-combustion treatment</div> <div>➤ Membranes dense inorganic</div>
Lab prototype. 4	<div>➤ Oxy-combustion gas turbine</div>
Lab-scale plant. 5	
Pilot plant. 6	<div>➤ Membranes polymeric (power plants)</div> <div>➤ Post-combustion biphasic solvents</div> <div>➤ Chemical looping combustion</div> <div>➤ Calcium carbonate looping</div>
Demonstration. 7	<div>➤ Membranes polymeric (Natural Gas industry)</div> <div>➤ Pre-combustion Integrated Gasification Combined Cycle + Carbon Capture Storage</div> <div>➤ Oxy-combustion coal power plant</div> <div>➤ Post-combustion adsorption</div> <div>➤ Bio Energy with Carbon Capture and Storage industry</div> <div>➤ Direct Air Capture (DAC)</div>
Commercial refinement. 8	
Commercial. 9	<div>➤ Post-combustion amines (power plants)</div> <div>➤ Pre-combustion Natural Gas processing</div>

Table 7: Composition of emissions in different industries [26].

Emissions	Pre-combustion	Post-combustion	Iron blast furnace	Cement production
CO ₂	10–35 mol %	12–14 vol %	20 vol %	14–33 vol %
SO _x	–	1000–5000 ppm	–	0–150 ppm
NO _x	–	100–500 ppm	–	0–150 ppm
CO	300–4000 ppm	~ 10 ppm	22 vol %	0–130 ppm
H ₂ S	500–1000 ppm	–	0–5000 ppm	–
H ₂	~ 20 vol %	–	4 vol %	–
O ₂	0.03–0.6 vol %	4–6 vol %	–	–
Water	Saturated	Saturated	4 vol %	12.8 vol %

3.2.1 Pre-Combustion CO₂ Capture

An Integrated Gasification Combined Cycle (IGCC) is a different approach to power generation. The material used as feedstock, like coal and other carbon-based fuels, undergoes an oxidation procedure through enrichment with O₂ and steam in order to undergo the water-gas shift (WGS). With the help of water from the steam, the carbon monoxide produces carbon dioxide and hydrogen. This reaction can take place vice versa, as reverse water gas shift (RWGS) can occur. Through this procedure, Syngas is produced which consists of CO, H₂ and minor secondary components like CO₂, H₂O, H₂S and NH₃. Air Separation Unit (ASU), allow the separation of Syngas and CO₂. Later, Syngas will be purified from harmful dust particles and hydrogen sulphide in order to be used in a Combined Cycle Gas Turbine, while the separated CO₂ can be used or stored. The flexibility of IGCC plants allows production of chemicals and biofuel since a Fisher-Tropsch synthesis (FTS) can take place. That is highly conventional since FTS is the main pathway for the conversion of carbon monoxide to hydrocarbons. Although the usage of the Air Separation Unit is intensively energy demanding, recent studies illustrate that using air will decongest the energy demand of ASU while using a Heat Recovery Steam Generator, in combination with a steam generator, can use the heat produced by the procedure for additional electricity production. Although the results of Pre-Combustion Carbon capture are promising, the application of this method is limited to IGCC plants since, instalment of Gas Combine Cycle Turbines remains a costly endeavour [21], [27], [28].

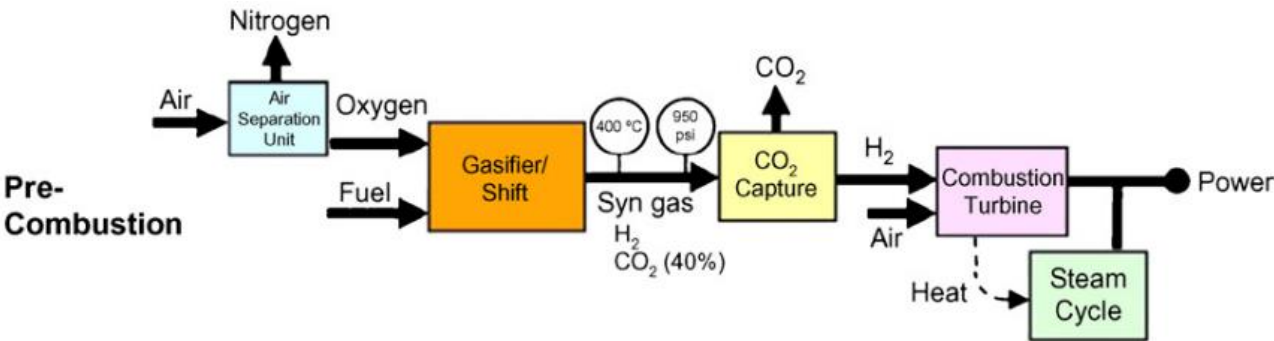


Figure 4 : Pre-Combustion Capture Schematic [29].

3.2.2 Post-Combustion CO₂ Capture

Post-Combustion CO₂ capture methods are the most common among industry and power-plants. CO₂ is removed from the flue combustion as an emission through various methods such as amine scrubbing, membrane capture and cryogenic capture. It is also a highly adaptable method of CO₂ capture since the variety of applications can be used for at least 2/3 of the existing fuel combustion systems. Amine solvents usage is the most common among the pathways for post-combustion capture, with demonstrations on full commercial scale since, on low particle pressure; the Amines have high selectivity towards desirable carbon dioxide over other gases in the emissions. Another example of commercially viable ways of post-combustion capture is by capturing high-quality CO₂ from bioethanol production. Since post-combustion systems have high adaptability, more than one method can be combined in order to have the required impact in the reduction of CO₂ emissions.

Other Post-Combustion technologies have reached the point of demonstration (TRL 7) and are on the verge of being used commercially, such as Polaris membrane and DAC installations. In the case of DAC, the first “commercialized” application took place in Hinwill, Switzerland on May 2017 with economical support from the Swiss Federal Office of Energy [30]. An annual supply of 900 tons of CO₂ captured from the plant, paves the way for further installation of DAC plants [15], [21], [25], [31].

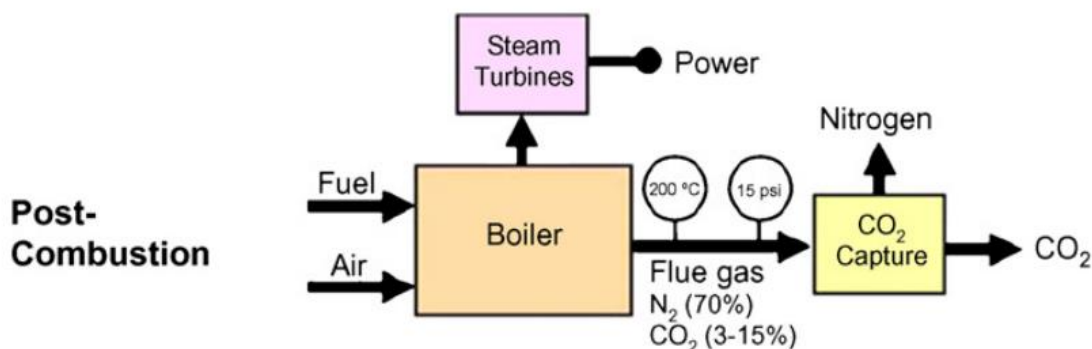


Figure 5: Post-Combustion capture schematic [29].

3.2.3 Amine Scrubbing

As mentioned before, Amine Scrubbing is the most common among the post-capture pathways for CO₂ capture, since carbon dioxide reacts with amines. As a chemical absorption method, it has been used for carbon dioxide capture for decades with a TRL of 9 (Table 6). One of the most commonly used amine solvents for the absorption of carbon dioxide is monoethanolamine, or MEA, dissolved in water and producing solutions up to 30% w/w of MEA. According to Figure 6, the absorption starts at 50 °C and needs elevated temperatures to drive the reaction of CO₂ with HO and NH₂. Nevertheless, higher temperatures represent loss, both economically and thermodynamically.

By forming chemical bonds with the reactance, further energy is required to reach the point of desorption. That is translated as large energy penalties reaching almost 30 % of the total power output of a power plant to drive the desorption process. In addition, the continuous usage of MEA, results to the deterioration of the material in time, and so decreases the efficiency of the desorption process. The replacing of MEA adds significant cost to the process. Furthermore, during the decomposition of MEA, new complex by-products are formed containing nitrogen, which is a far more harmful GHG than CO₂ and further scrubbing installation is required to be absorbed. Such are the problems of Amine solvents usage, and have to be considered thoroughly before installation and usage. One solution for economic feasible amine scrubbing, could be by flexible storage of degraded solvent when there is a rise in electricity cost and regeneration of the solvent when prices are low [32]. Still, the most serious problem in amine scrubbing is the regeneration of the solvent which requires high energy penalties. It should be noted that aqueous ammonia usage has a lower energy demand from regeneration making it cheaper than the use of various amines. Nevertheless, the disadvantages in the usage of ammonia are significant since there is grave danger of an ammonia leak and corrosion of the equipment through the formation of solid ammonia [33].

An alternative form of chemical absorption could be Ionic Liquids (ILs) which have a lower energy demand for desorption than amine solvents. Also, the use of solid ILs increases the performance further than liquid ILs with H₂O.

The disadvantages of ILs are only their high cost of production and high liquid viscosities. Nevertheless, recent studies indicate that they may be a viable economic solution in the recent years to come [14],[18].

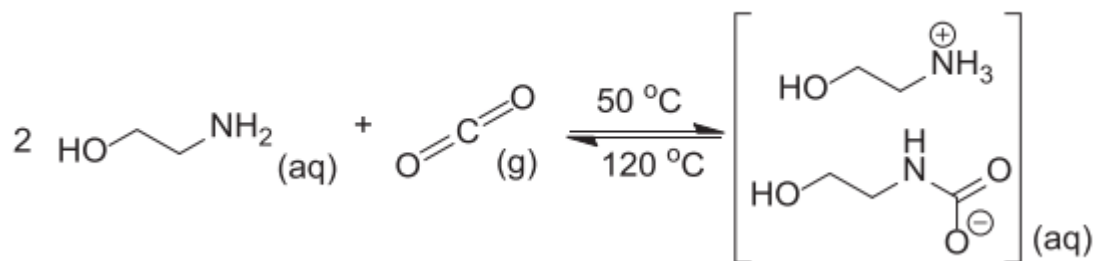


Figure 6: Carbon dioxide-absorption by MEA in aqueous solution [15].

3.2.4 Chemical Looping Combustion

A Chemical Looping Combustion ,or CLC, is usually achieved by a carrier of solid O₂ which is added to the reactants fuels in their gas form in order to achieve combustion. The carrier is usually made up of metal oxides with oxidative properties when combined with air in the reactor. The concentration of O₂ is then used for the combustion of fuel in the reactor, as the carrier reaches its original state. With the absence of nitrous and nitrous oxides, CLCs display low energy penalties. Still, the disadvantages lie in the need for replacement of the carrier, since its decline may harm the equipment through corrosion. Since the combustion takes place without contact, it produces mainly water vapour and high concentration of CO₂ which can be easily stored and used as a pool of chemical energy, since it is easy to remove the water vapour.

Such applications found their way to Biomass Direct Chemical Looping. According to Cormos *et.al* [34], a Biomass Direct chemical looping system could use wood for fuel with thermal efficiency of 42% with CO₂ captured reaching almost 99% of the total emissions. According to the mentioned data, Chemical Looping combustion in Biomass systems is far superior than pre- or post- combustion in Bio Energy with Carbon Capture and Storage power [21], [35].

3.2.5 Oxyfuel Combustion

Oxyfuel Combustion rests in the usage of high concentrated oxygen for the combustion of fuel in the absence of nitrogen, in order to avoid NO_x production. In order to use air with a high consternation of O₂, an ASU is required with the purpose of removing the undesirable nitrogen before combustion (Figure 7). Such units are usually based on cryogenic separation or pressure swing absorption, both of which have high energy consumption, driving to power penalties for the power-plant. In order to keep the balance of temperature and radiative profile of the flame used for optimal combustion, carbon dioxide is reused as a balancing agent [36].

Oxyfuel can also be applied to combust fuels with low calorific value such as biomass or municipal wastes, with flexible flue gas recycling to avoid incomplete combustion of the fuels [21], [37].

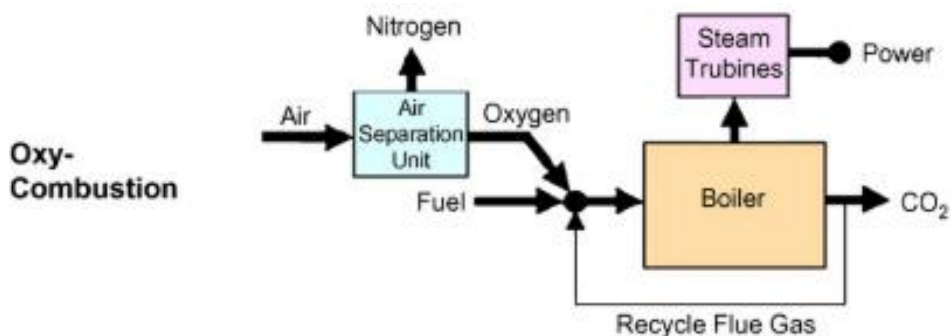


Figure 7: Oxy-Combustion schematic system [29].

3.2.6 The Membrane CO₂ Capture

The membrane CO₂ capture method is one of the most promising alternative routes for carbon dioxide separation and capture. Their synthesis varies since a variety of polymers can be used such as silica with inorganic nanocomposite for gas separation or different types of ceramics or metals. Despite the flexibility of the membrane production, especially polymeric, and the fact that it decreases the cost of production and simplifies the procedure of installation, certain limitation arises. For example, the polymeric membrane is prone to high pressures and temperatures. That contrasts with the fundamentals of the procedure since the flow rests in the difference of pressure between entrance and exit.

In high temperatures, the polymeric membrane poses a danger of plasticization, which lowers the selectivity and efficiency of the membrane. Also, a quantity of at least 20% of carbon dioxide of the total flue gas is required in order to have optimum concentration captured and therefore , economic feasible application [38].

Inorganic materials like ceramic or zeolite composed membranes may show higher resistance in swelling since they can function better in higher temperatures and pressure than polymeric membranes. Because of their high flexibility, membranes can be used in hybrid systems in cooperation with other methods like cryogenic capture for increase performance and liveability [21], [26], [38].

3.2.7 Cryogenic CO₂ Capture System

The cryogenic process of CO₂ capture can be a competitive pathway for the capture and storage of carbon dioxide. The procedure starts by first cooling the flue gas down to very cold temperatures, approximately -120°C where the carbon dioxide forms a solid product, dry ice made by carbon dioxide. Then the separation of solid CO₂ from the rest of the gases takes place.

A great advantage of the method is the easy capture of solid CO₂ and also the removal of the rest of the GHGs such as NO_x and SO_x, producing a pure stream of emissions from the harmful gases which are stored in solid form and can be used or recycled conventionally. Nevertheless, a high energy demand is needed in the absence of a free source of cooling energy, which doubles the energy penalties for the utilization of Cryogenic capture [39]. Furthermore, the giant thermodynamic leap between combustion temperatures to cryogenic is accompanied by energy loss.

In order to reach the cryogenic temperatures with lower energy penalties, high pressure could be applied at 100 bars. Such pressures were applied in the work of Li Yuen Fong *et al.* [40] where, in combination with high carbon dioxide concentration in the flue gas (70%), liquid CO₂ was produced with significant lower energy than compressing the gas in solid form. With the use of a Vacuum Swing Absorption and a multi-objective optimisation system, a minimum energy optimum was determined. The results showed that 1.40 GJ was consumed for every tonne of carbon dioxide produced, at an overall recovery rate of 88.9% for the total production work. This kind of energy demand outshines the conventional method of Cryogenic capture [25]. Also, hybrid systems of Cryogenic and membrane capture, have been deployed with a study showing the consumption of 1.7 GJ per tonne of carbon dioxide captured [21], [41].

3.2.8 Direct Air Capture

Direct Air Capture methods have been researched in the last fifty years. A relatively new technology of capturing and storing carbon dioxide directly from the atmosphere, appears to be a more direct way of dealing with the current global warming issues. The concept seems flexible and simple: installing DAC plants using capturing agents like sorbents, organic or metal carbonates, anywhere in the world, where capturing carbon dioxide in large quantities directly from the atmosphere, will bring the emission levels of the gas back to pre-industrial times. As might be expected, the use of DAC, even though it seems promising, is still far from reaching commercial level.

Technical and economic factors are still obstacles for launching economic feasible and efficient DAC systems. An important factor is the highly diluted concentration of carbon dioxide in the air which is around 400 ppm. The current capture technologies for CO₂ are designed for utilizing 100-300 times larger concentrations, with their installations being at the source of the emission like in gas, coal firing plants or Cement and Steel Industries. Furthermore, in order to realize a negative emission factor by capturing CO₂ from the air, a carbon cycle assessment should take place to validate the efficiency of DAC systems where, according to an article published by The Guardian [42], small scale plants have very limited effects on permanently reducing CO₂ emissions. As for the capturing agents, a fair amount of research has taken place in order to bring the TRL level of DAC systems one step closer to commercialization.

Organic carbon capture with the use of microorganisms through photosynthesis has distinct limits due to the fact that reduction takes place only one-time, making it an unattractive solution [43]. Alternately, fans for driving air current through towers loaded with scrubbing material, like sodium hydroxide solutions, could be used to deliberately concentrate larger quantities of carbon dioxide. Moreover, spray towers could prove useful. As mentioned before though, scrubbing materials are in need of regeneration in closed loop processes which pose a liability in the continuous usage of DAC plants [44]–[46].

A more practical approach took place in the work of Holms and Keith, [47], and in the work of Mazzotti *et al.* [48], with an air-liquid tower design for direct air capture and a conventional APS system used in entanglement with flue gas respectively. The carbon dioxide capture price procedure ranged, in both studies, between 300-600\$ per tonne captured, while the concentration of CO₂ quantities in the air played the most important role in the price range. Specifically, the more diluted the system is, the more demanding the separation process is, while unwanted materials deem the procedure even more cost demanding, estimating in some cases, 1000 \$ per tonne of CO₂ captured.

Whatever the case, DAC systems are still regarded by some as the last line of defence against the potential leakage of CO₂ from sequestrations planes or as a balancing agent for nullified carbon dioxide emissions from the transportation sector [49].

In terms of the research of Wilcox *et.al.* [50], a technical assessment of DAC systems took place, where the efficiency of the plan is associated with the absorption of carbon dioxide in flux, across on a gas-liquid interface. J_{CO_2} is measured by the following equation:

$$J_{CO_2} = c_i k_1 E$$

where J_{CO_2} is the flux of CO₂, c_i is the consternation of carbon dioxide across the gas-liquid interface, k_1 represents the physical mass-transfer coefficient and E is the enhancement factor from the chemical reaction which can take various forms in respect to the chemical reaction. In terms of c_i , the interfacial concentration, is determined by Henry's law where $P_{CO_2} = H C_{CO_2}$. The partial pressure of CO₂ equals the liquid phase of the gas-liquid film multiplied by the C_{CO_2} factor, the consternation of carbon dioxide in the solvent. By using the theoretical flex of CO₂ captured, various solvents can be determined as capturing agents for their efficiency in various pressures (atm) based upon Henry's law (H_L) of each material.

In addition, by extending the same principal, a direct comparison of the same solvents can take place, while installed in other post-combustion capture methods, other than DAC plans. Figure 8, shows that the interfacial concentrations c_i , while using the same materials, in DAC and Coal-NG plans, is 250 to 150 times more in respect to coal and natural gas plans. So, in order to achieve an absorption similar to coal fired or natural gas plans, from DAC systems, the enhancement factor E should be at least two orders of magnitude higher, for the gas-liquid interface k_1 is a parameter entangled only with the material of the solvent in usage (Figure 9). Choosing materials with fast kinetic capability though, like NaOH, results in the increasing demand of energy consumption for regeneration of the material [25], [50].

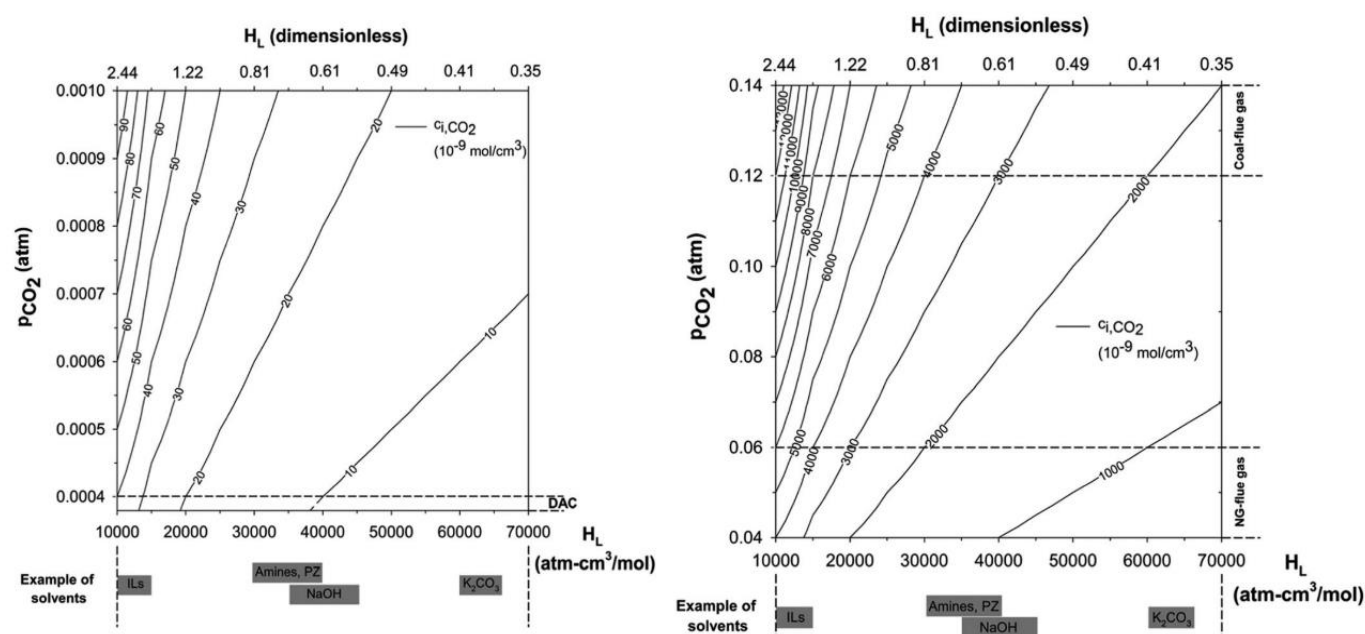


Figure 8: Interfacial concentration of CO₂, c_i , based upon Henry's law for DAC (left) and the flue gas of natural gas and coal (right) [49].

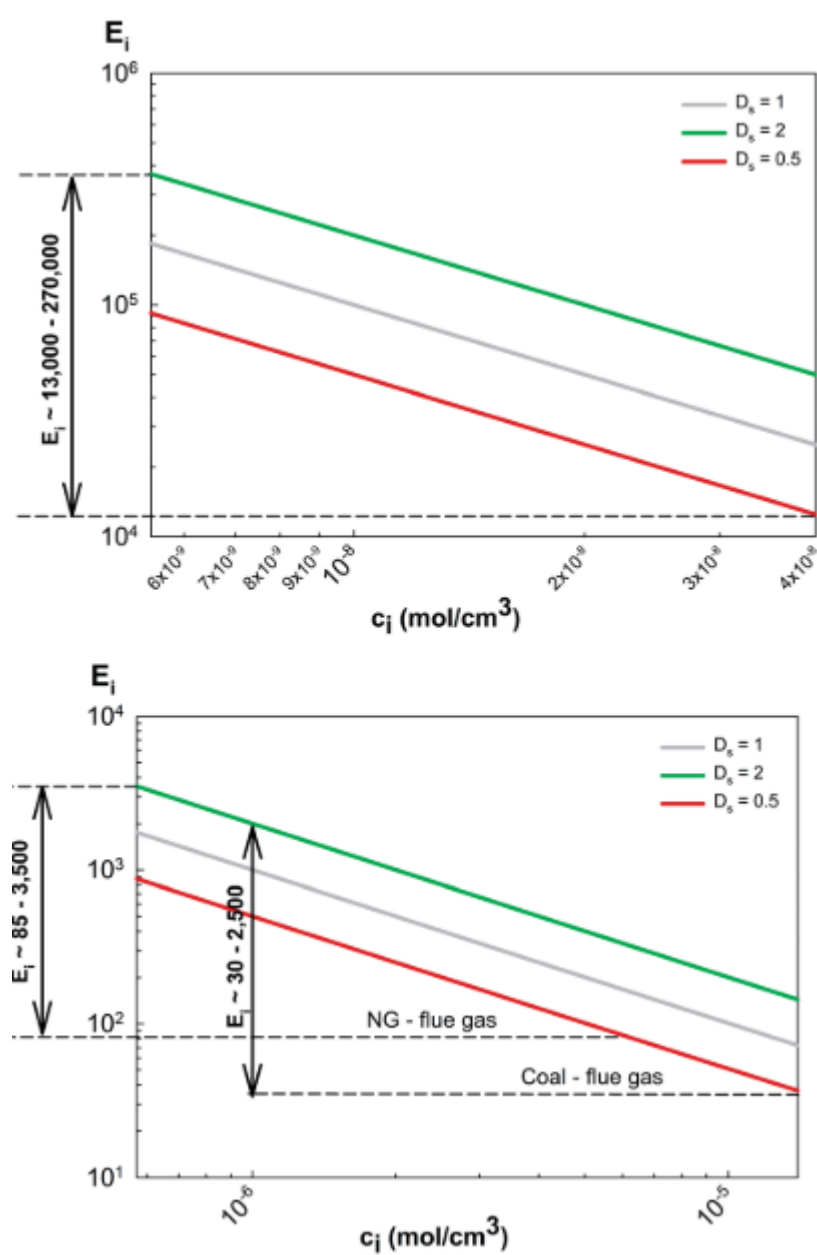


Figure 9: Instantaneous enhancement factor E as a function of interfacial CO₂ concentration for applications ranging from DAC (top) to flue gas from natural gas- or coal-fired power plant (bottom) [49].

In addition, a techno-economic assessment conducted by Bui *et.al* [25], shows the liveability of full-scale DAC systems is not yet feasible. Their studies show that in a hypothetical scenario of 400 ppm of carbon dioxide diluted in ambient air and with a 50% recovery rate, 2.11 million m³ of air will need to be processed in order to capture 830 kg of CO₂, which is approximately the amount of CO₂ produced for an MWh by supercritical coal-fired power-plant. In order to concentrate the quantities of carbon dioxide in the air, a pressure drop is required to 0.016 bars or 0.23 psi. To achieve the required pressure, at least 1 MWh has to be used which should come from carbon-free energy production. By that accord, for a DAC plant to be practical, pressure drop on the scale of 6.89×10^{-4} bar or 0.01 psi should be achieved which must be utilized by carbon-free sources in order to have a negative emission impact. One can understand that, by the present data, a use for carbon-free power source as a replacement for the fossil-fuel installations would have a much more useful impact, since the emissions of GHGs would be avoided in the first place.

3.2.9 Flexible CO₂ Capture Systems

To summarize, in order to effectively utilize most of the carbon capture systems, a great deal of research needs to be carried out on the energy consumption of the project and the techno-economic assessment. In order to stabilize the energy-demanding nature of carbon dioxide capture, flexible systems of CCS could be deployed in cooperation towards achieving larger absorption rates with lesser energy consumption. Such systems could use the energy surplus form of renewable energy power plans, in periods of low demand for electricity, to further decrease the cost for carbon dioxide capture. An example of common flexible capturing systems in pre-combustion capture, are bypassing or venting. In this case, the capture system is independent, with flue gas having the option to bypass it completely, and using it in times of low electricity prices, or renewable energy surplus for the energy-demanding process of regenerating the capturing agent. By some accounts, in a techno-economic analysis of a venting-based system, a price range of 20-70 US \$ per ton of CO₂ captured was deduced, indicating a profit increase of 10%, comparing with inflexible post-combustion CCS [51]. Other pilot-scaling plans of flexible systems were reported, where synthetic flue-gas in combination with 30% MEA was used for the capturing agent. By bypassing the capture plant entirely and stopping steam feed into the solvent recovery boiler, maximize of the efficiency of the capturing agent and regeneration process was achieved. The initial reuse of the steam, in times of energy availability, played a determining factor as far as efficiency of the solvent goes [52], [53]. Such cases could also be applied to post-combustion capturing systems, utilizing both cryogenic and membrane technologies.

Although, flexible CCS may seem a reliable compensation for utilizing the surplus energy in renewable energy grid, it poses a risk for CO₂ leakage since the energy production of renewable grids seems unstable and directly affected by weather change on a seasonal scale.

Still, flexible capture systems can be applied to post-, pre- and oxy-fuel combustion, with research showing promising results. For example, Ajiwobowo *et al.* [54] presented a concept with co-production of electricity and Hydrogen with methane as fuel.

Such concept was also applied to a CLC-CC plant in combination with electrolytic cell or SOEL, achieving maximum performance efficiency of up to 56%. In addition, by utilizing the product steam in a cryogenic carbon dioxide system, cold energy could be stored for further use in times of high demand.

Table 8, shows the limitations of flexible CCS but also their possible application and coefficient. In addition, for the various methods, buffer sequestration of carbon dioxide can play an important role since it is universally applicable, for storing carbon dioxide in geological formations.

Table 8: Flexibility enchantment techniques for CO₂ capture systems [54].

Technique of Capture	Pre-Combustion	Post-Combustion	Oxy-Fuel
Storage of CO ₂ capture solvent	Yes	No	No
Storage of liquid O ₂	Yes	No	Yes
Co-production and storage of H ₂	Yes	No	No
Switching off capture system	Yes	Yes	No
Buffer CO ₂ storage	Yes	Yes	Yes

4 CO₂ Utilization

4.1 Introduction to CO₂ Utilization pathways

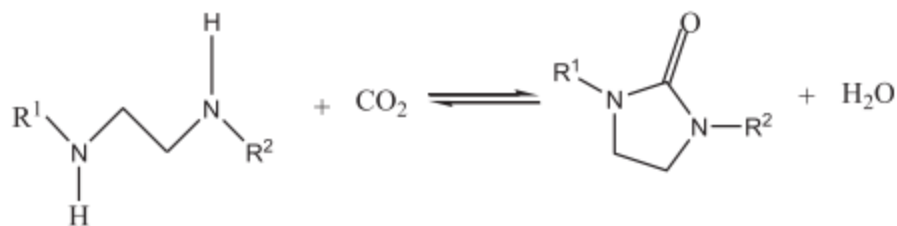
By capturing quantities of carbon dioxide, the scientific community comes face to face with an important decision: what to do with the gathered material. In order to realistically negate the effects of global warming emissions, several utilization pathways are required which will convey carbon dioxide as a feedstock, to products such as chemicals, fertilizers, solvents or polymers. Also, new applications arose in 2009, using CO₂ as an energy pool by converting it to electro fuels such as methanol, methane, biodiesel and petrol or as clean energy storage, a high-demand property in today’s energy industry. The climate benefit of mitigating carbon dioxide in storage has very little effect on the overview of the global warming impact, hence the past concept of CCS do not add up to a liveable solution. CCU is the final step towards closing the carbon cycle, since the emissions of carbon dioxide are just another source of high-energy product that is not used in a beneficial way. Different aspects of using carbon dioxide have been searched and studied. In the light of this thesis, basic kinetics and energetic aspects of CO₂ conversion are presented, highlighting the limitations and requirements for a profitable use of carbon dioxide. Certain pathways are mentioned and discussed in the concept of utilizing carbon dioxide as energy vector, polymeric products; oxygenate fuels and fertilizer for agriculture applications. All aspects of CCU should be naturally evaluated in the spirit of a Life-Cycle Assessment model to realize the true impact of utilizing procedures on the environment, spanning in a 100 years’ time lapse [15], [20], [21], [55], [56].



Picture 3: Sample of poly (methyl acrylate) containing 65% carbon dioxide by weight [15].

4.2 The Kinetics and energetics of CO₂ conversion

Combusting hydrocarbons, results in the release of energy with final products being water and CO₂ emissions, which are characterized by a thermodynamic stability. Relative to other molecules, carbon dioxide has the highest carbon strength which can lead easily to the presumption that conversion and use of CO₂ requires high energy input in order to break the strong double bonds of carbon and oxygen (Table 9). Undoubtedly, any oxidant reaction with CO₂ is in agreement with the previous statement. In other cases, the required energy is offered by the co-reactant, which enables the reaction to take place at ordinary temperatures. Such reactants, like hydroxides, amines and alkenes (or olefins) have the ability to contribute to the energy requirements of the reaction. A basic example of the use of co-reactant to drive the reaction would be the production of urea, by reacting CO₂ with NH₃. By following the chemical equilibrium of the reaction, a two-step reaction is observed. In the first step, the formation of ammonium carbamate is taking place (H₂N-COONH₄), which is the result of liquid ammonia in contact with gaseous carbon dioxide. Under high pressure (180-200 atm) and temperature (185-190 °C), the reaction becomes highly exothermic and fast. Following the second part of the reaction, ammonium carbamate decomposes into urea and H₂O, a slow and endothermic reaction. By using the energy of the first step, the final product is produced. Remnants of the reaction, unconverted carbon dioxide and ammonia, should be recovered and used, following the equilibrium of the reaction (Scheme 2). This endeavour though, proves to be a hard task. Selectivity towards undesirable products results in the formation of biuret carbamylurea (NH₂CONHCONH₂). By following similar patterns, roughly 130 Mt of carbon dioxide is used annually for urea, salicylic acid and carbonates, and polycarbonates, with urea consuming the largest portion of captured CO₂ [55], [57].



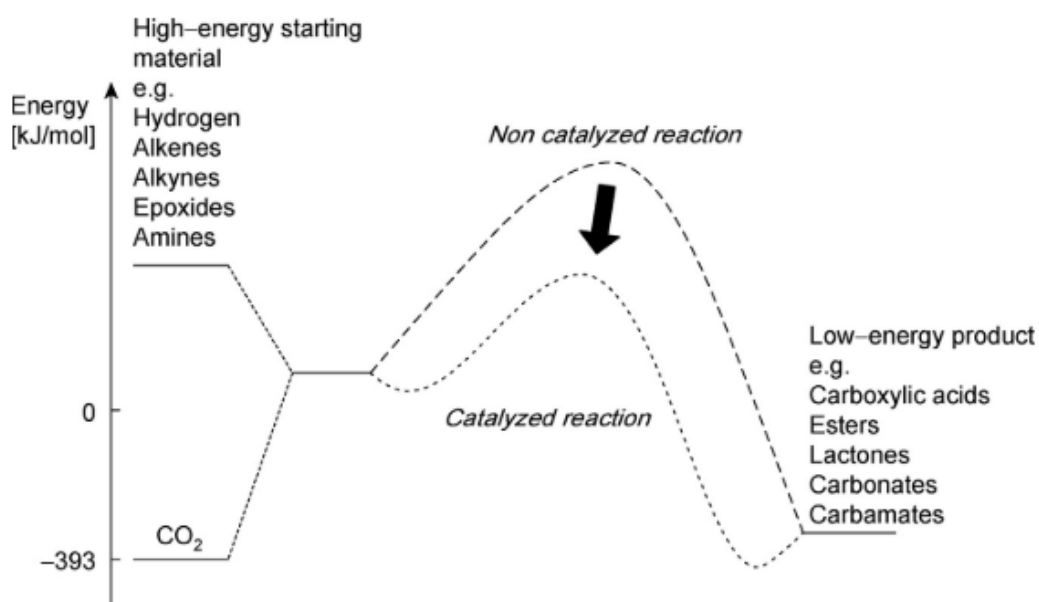
Scheme 2: Formation of urea and water from ammonia and carbon dioxide [55].

Table 9: Approximate chemical energy of some C1-chemicals and hydrogen relative to carbon dioxide [55].

C1-molecule	Relative Energy Level (Gibbs free energy)	Carbon bond strength	Characteristic	Heat of formation
Carbon dioxide (CO ₂)	-394 kJ/mol	Very high	Very stable and strong double bonds with oxygen.	-394 kJ/mol
Formic acid (CH ₂ O ₂)	-361 kJ/mol		Consists by hydrogen-bonded dimers.	-427 kJ/mol
Methanol (CH ₃ OH)	-166 kJ/mol		No stable double bond of carbon.	-239 kJ/mol
Carbon monoxide (CO)	-137 kJ/mol		Very high bond-dissociation energy and a triple bond with oxygen.	-110 kJ/mol
Formaldehyde (CH ₂ O)	-102 kJ/mol		Weaker carbon bonds with Hydrogen.	-109 kJ/mol
Methane (CH ₄)	-51 kJ/mol	Lowest	Only carbon-hydrogen bonds. Reacts more easily with other molecules.	-74 kJ/mol
Hydrogen (H ₂)	0 kJ/mol	N/A	No carbon-hydrogen bonds. Reacts easily with other molecules.	0 kJ/mol (arbitrary)

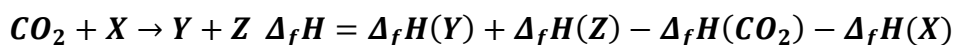
The chemical reaction with carbon dioxide is determined by two factors: the polarisation of carbon dioxide double bonds with oxygen and the nucleophiles which reacts with the central carbon atom. Elements which are rich in electrons will directly affect the nucleophiles and the carbon atom. Unavoidably, materials like metals have high coordination with CO₂, which leads to a change in both the electron distribution and molecular geometry of the carbon dioxide molecule. Hence, the main preference of the catalyst would be that of a metal base in utilization of carbon dioxide (Σφάλμα! Το

αρχείο προέλευσης της αναφοράς δεν βρέθηκε.). Nevertheless, the same ability of CO₂ leads to complications for driving reaction to desirable coordination of the metal factor with the reactant. 13 different coordination geometries are known in carbon dioxide-metal complexes which may take place either in oxygen or carbon atoms.



Scheme 3: Formation of urea and water from ammonia and carbon dioxide[55].

The reaction pathways for carbon dioxide, rest in the thermodynamic nature of the molecule. As mentioned before (Table 9), the highly endothermic heat of formation ($\Delta_f H^\circ$) of -394kJ/mol deems the stableness of CO₂. But it would be a mistake to assume that the heat of reaction would be thermodynamically uphill, since it is determined by the difference between heat of formation of products and reactants. By following the equilibrium of Scheme 4, it becomes clear that a reaction with carbon dioxide may also be exothermic, with respect to the reactants behaviour.



Scheme 4: General reaction of carbon dioxide and its enthalpy of reaction [55].

The reaction pathway though, as regards its position in the equilibrium, is determined by the free energy of reaction $\Delta_r G$ (Gibbs free energy) where $\Delta_r G = \Delta_r H - T\Delta_r S$. Reactions may have negative entropies if there is a change of state in their form, as carbon dioxide is converted from gas to liquid or even solid. In that case, the temperature of the reaction has certain limits, where if surpassed, the position of the reactant in the equilibrium will become unfavourable, based on the fact that if $\Delta_r S$ takes negative value, then $-T\Delta_r S$ will be positive and will increase as the temperature rises above the temperature ceiling. The driving force of the reaction is the free energy of formation $\Delta_r G$ and the activation energy E_a , with the latter limiting the reaction. In that case, suitable catalysts are used for lowering the required E_a and driving the reaction preference towards the desirable products (Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.,Figure 10).

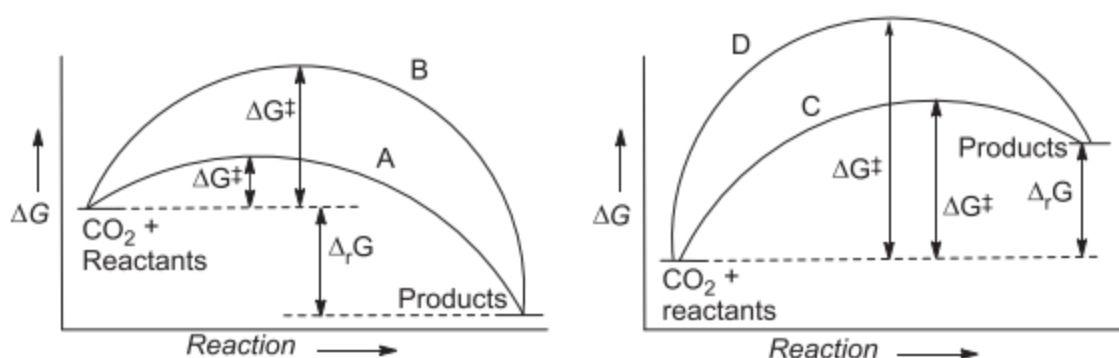


Figure 10: Reaction pathway energy diagrams for reactions of carbon dioxide [55].

In addition, the behaviour of carbon dioxide, presented in Figure 11, allows us to exploit the properties of CO₂ while in critical state (73.8 bars & 31°C). If carbon dioxide rises above the critical state, it will become a supercritical fluid with expanding properties, filling the container in which it rests. Reaching the supercritical state of carbon dioxide is relatively easy, in comparison with other common chemicals, which deems it ideal as a green solvent for chemical reactions, chromatography, extractions or even as a decaffeinated agent in the coffee bins [51],[54].

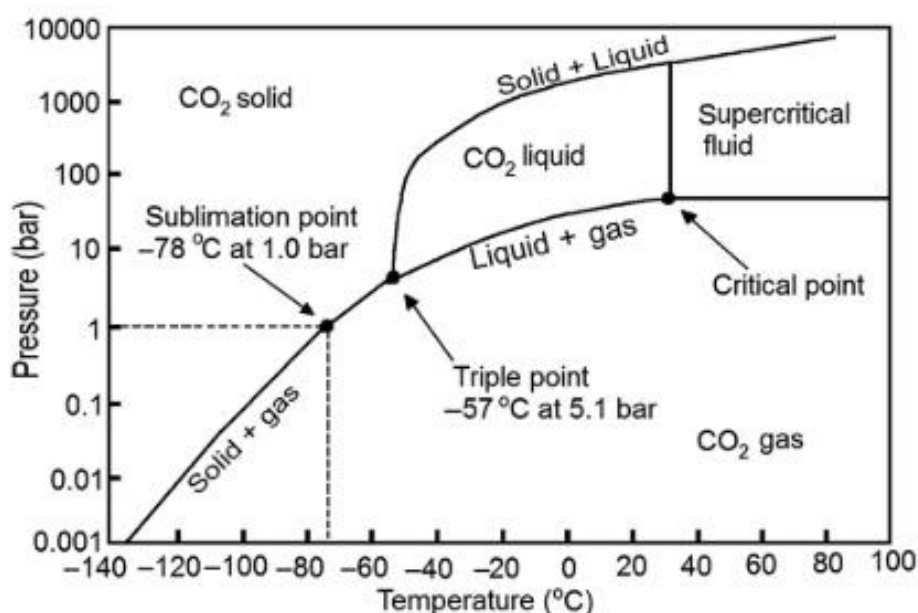


Figure 11: Carbon dioxide phase diagram [15].

4.3 CO₂ as an energy vector. Electofuels and chemical storage

Usually, the term ‘chemical storage’ is referred to the production of hydrogen mostly by utilizing renewable energy from RES plans. The application of electrolysis of water or processes like sulphur iodine cycle, are ideal for converting the desirable H₂. In our case, fuels which contain carbon from captured CO₂ in combination with H₂ can be produced and used as chemical storage of energy or as an energy vector. The source of CO₂ plays an important role in the yield of the synthetic fuel, since while in usage, may produce relevant carbon dioxide emissions. Nevertheless, the CCU of carbon dioxide with the aim of producing low carbon fuels is deemed to be the largest market opportunity, offering a realistic short term solution in utilizing CO₂. Interesting enough, if the required carbon dioxide is captured from DAC plans, then the use of the electro fuel produced by the procedure, is effectively closing the carbon cycle [21], [59], [60].

A large variety of products can be obtained by processes, as presented by Figure 12, with flexible applications on different sectors of industry and transportation. Yet the production of electro fuels is based on both technologies readiness level CCU and electrolysis, since hydrogen utilization constitutes the middle step of the procedure. The Polymer Electrolyte Membrane (PEM) and Solid Oxide Electrolysis cell (SOEC) have emerged as new and highly efficient technologies for isolating H₂ and may reach commercialization on a larger scale (TRL 9) in the following years. The addition of hydrogen in catalytic reactions of CO₂ is one of the main pathways for converting to the most commonly used fuels, such as methane and methanol as well as e-fuels like e-petrol and e-diesel by Fisher-Tropsch synthesis [21], [29], [61].

Ultimately, several studies have been conducted for evaluating the market and economic feasibility of electro fuels, with the potential of the commercialized and liveable replacement of conventional fuels. Brynolf *et.al* [62], published an overview of the production costs on electro fuels in 2030, between 160-210 €₂₀₁₅/MWh_{fuel} which seems promising enough for future applications. Other studies, where focused on the capability of electro fuels with current aircrafts engines [63], compartment of transportation fuels produced by green CO₂ and renewable H₂ on light duty vehicles [64], as far as a market model proving that the total cost of renewable energy systems with the production of electro fuels is similar with the conventional fossil fuel systems [65]. Most recent projects have reached the point of demonstration with the aim of expanding their productivity, focusing on producing methanol from carbon dioxide, like the FReSMe project which will utilize captured carbon dioxide from steel industry for methanol production via electrolytic hydrogenation [66].

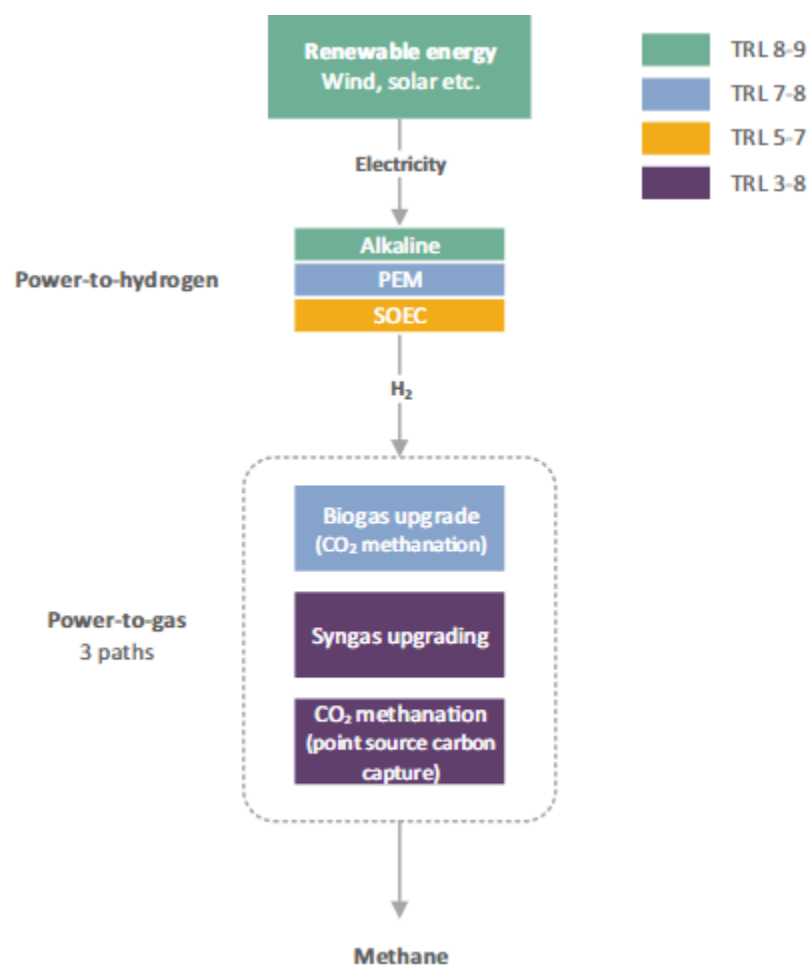


Figure 12: Electrofuel production concepts and technology readiness levels [67].

4.4 Polymers and chemical blocks from captured CO₂

Polymers are the backbone of everyday products. The application seems to be limitless, from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. By applying polymerization processes the conversion of a monomer or a mixture of monomers into a polymer becomes able, giving access to a vast usage of polymer as the basic material for the vast production of synthetic every-day products. Presently, the main feedstock, for chemical conversion and polymerization, is petroleum with roughly 6-7% of annual oil production being used for that purposes. Researchers are looking for ways to exclude, firstly at least partially and later completely, the use of petroleum as chemical feedstock. The utilization of carbon dioxide as a replacement of petroleum for the basic material in the chemical industry is one of the alternative and realistic scenarios with more than 200 Mt/year worldwide production [14],[51].

There are two main pathways for the chemical conversion of CO₂; carboxylation, where carboxylic acid groups are produced by treating a substrate with carbon dioxide, and reductions where one or both carbonyl bonds are broken to utilize the carbon and oxygen separately.

During carboxylation, CO₂ reactions take place without completely breaking the carbonyl bonds ($C=O$). By utilizing the carboxylic process, carbon-based chemicals and polymers can be produced, with some ecological advantages, since during the reaction; harmful reactants are excluded and enable safety long term carbon storage. The main chemical and final products produced by carboxylation in industry are presented on Table 10, with urea being the most common products of the utilization pathways of carbon dioxide [21].

During CO₂ reduction, the break of one or both carbonyl, enables the use of Fisher-Tropsch synthesis with various and useful products resulting from the reaction, including Methane (CH₄), Methanol (CH₃OH), Ethanol (C₂H₅OH), Carbon monoxide (CO), Synthetic gas, Formic acids (CH₂O₂) and Acetone (C₃H₆O). The energy required for the breaking of the bonds is immense and is usually provided by a high-energetic reactant such as heat, electricity, microwaves, sunlight or last but not least, hydrogen. The use of hydrogen produced by a renewable energy source, for catalysis, also known as catalytic hydrogenation of CO₂, is probably one of the most promising and interesting pathways for the utilization of carbon dioxide and will be elaborated on in chapter 5: [Catalytic Hydrogenation of CO₂ to Olefins](#) Catalytic Hydrogenation of CO₂ to Olefins [18],[20],[51],[68].

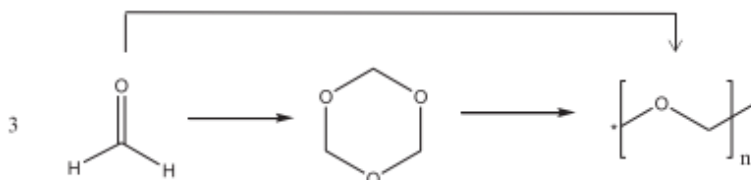
Table 10: Products obtained from carboxylation reaction of CO₂ [21].

<i>Products of CO₂</i>	<i>Application</i>
Urea	<ul style="list-style-type: none">• Fertilizer• Polymer synthesis (melamin and urea-formaldehyde resins).• DeNOx application for diesel-engine in transportation and power plants
Acrylates, Lactones and Carboxylic acids	<ul style="list-style-type: none">• Super absorbents in diapers acrylates)• Solvent, pharmaceuticals, surfactants, cosmetic
Monomeric Carbonate	<ul style="list-style-type: none">• Alternative to toxic phosgene
Isocyanate	<ul style="list-style-type: none">• Sealants and adhesive
Polymeric Material	<ul style="list-style-type: none">• Synthetic plastics etc.
Polycarbonate	<ul style="list-style-type: none">• Phosgene- free process to aromatic polycarbonates (APCs)• Ethylene carbonate
Polyolefin	<ul style="list-style-type: none">• Polypropylene and polyethylene carbonate
Polyhydroxyalkanoate	<ul style="list-style-type: none">• Biodegradable resins• Bioplastic
Polyether carbonate polyols	<ul style="list-style-type: none">• Polyurethane, elastomers, coatings, sealants and adhesives
Chlorinated polypropylene	<ul style="list-style-type: none">• Degradable CO₂ copolymer

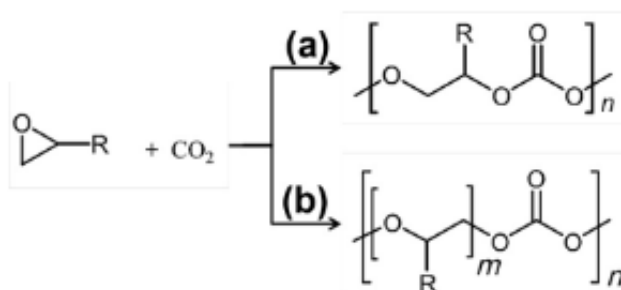
Polymers based on CO₂ rest on the property of carbon dioxide of organic and inorganic transformation. By directly utilizing the carbon dioxide as polymer building block or by combining it with other co-monomers, which may be obtained by other CO₂ reactions, polymers can be produced. CO₂ can directly be used in the catalytic copolymerization of epoxides, as a reactant for the strained oxygen which is subject to ring opening to create linear carbonate, depending on a suitable catalyst.

CO₂ will determine the yield of epoxide to alternating polycarbonates (Scheme 6a) or polyether carbonates (Scheme 6b), in combination with the proper catalyst. Vast research has been conducted in the previous decades for the direct catalytic application of carbon dioxide for polymer production, with the achievement of the selectivity of the catalytic reaction, in some cases, to reach over 99%.

The catalysts used in the reactions are usually well-defined metal complexes with discrete molecular structure, which allows the use of single site catalysts such as double metal cyanide complexes or DMC catalysts. Polyalkane carbonates are another example of a product resulting from the reaction of carbon dioxide and epoxides, which may be a realistic replacement for polyether in the polyurethane production. Similar properties can be found in polyoxymethylene or POM which is another polycondensation polymer produced by CO₂ and intermitted formic acid with 1,3,5-trioxane (Scheme 5). The applications the resulting chemical blocks are varied, including but not limited to thermoplastic polyurethanes or TPU, foams, elastomers, varnishes, impact-resistant modifiers, adhesives and sealants [15], [55], [69]–[71].



Scheme 5: POM produced via CO₂ and formic acid [55].



Scheme 6: Catalytic copolymerization of terminal epoxide and CO₂ to yield alternating polycarbonates (a) or polyether carbonates (b) [15].

With the indirect approach of polymer production via CO₂ as a chemical feedstock, the C1 undergoes transformation by contact with energy rich reactants. Intermediates resulting from the early reaction are then used for conversion in polymeric materials either by the homopolymerization or copolymerization with the carbon required for the final product being obtained by CO₂. Especially in the research of Peters *et.al* [72], an analytic overview is presented for the production of carbon based polymers via utilization of CO₂, with vast synthetic and structural possibilities. Still the atom economy in chemical synthesis and the remaining carbon footprint left in the polymer products produced by indirect step of synthesis, present economical and ecological limits.

This leads us to the conclusion that the direct approach of polymer conversion via CO₂ is a more attractive and sustainable way of utilizing the captured carbon dioxide [15].

4.5 Synthesis of oxygenate fuels

From the many products and materials produced by utilizing carbon dioxide, oxygenate fuels like methanol, dimethyl ether or DME, higher alcohols and ethers prove to be a very promising and interesting pathway, for absorbing the carbon footprint in fuels which are necessary for our everyday needs. Also, there is great potential for innovations which can open new market opportunities, adding to the value of CCU technologies for further applications.

The main reason for the interests shown in oxygenate fuels, is the high density and energy output during combustion as shown in [Figure 13](#). Take methanol for example: in comparison with methane, the volumetric combustion enthalpy energy density is several metric scales higher (17.93 MJ/L compare to 0.036 MJ/L). The physiology of methanol as a liquid fuel allows the concentration of potential release energy which is much denser than the energy stored in the gaseous form of methane, 5000 times more to be exact. Such energy density is ideal for fuel which can be used both for transportation and energy storage [\[15\]](#).

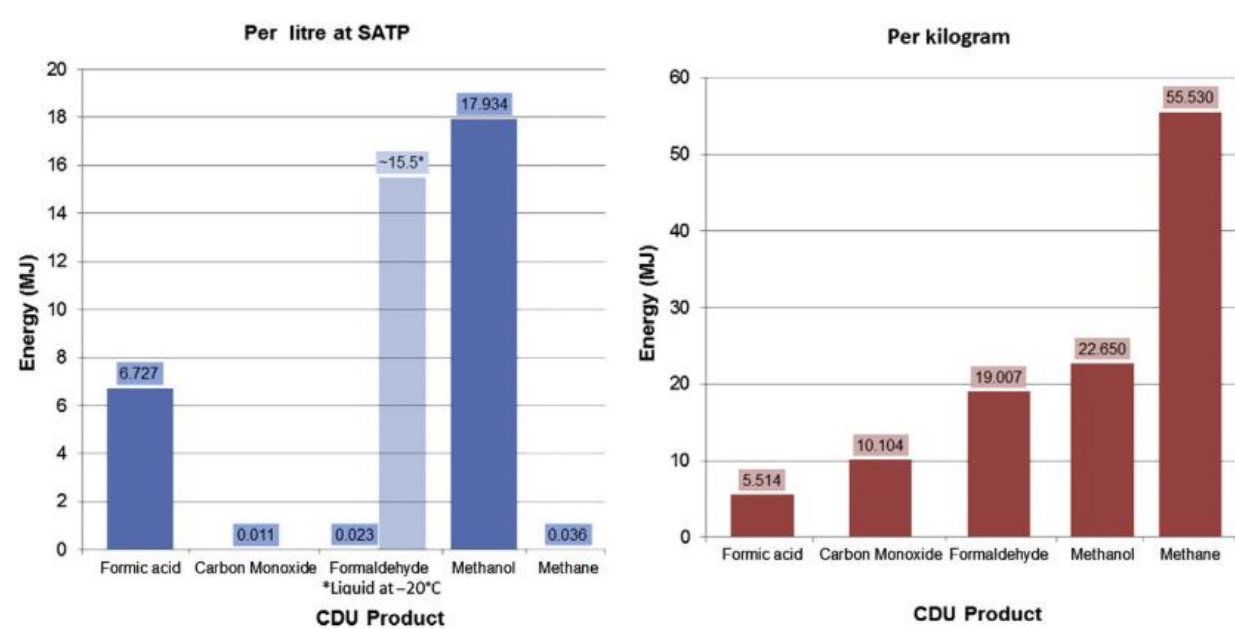


Figure 13: Comparison of volumetric and specific energy density of single-carbon CDU product [\[15\]](#), [\[73\]](#).

Oxygenate fuels have a useful property; they are prone to be in a liquefied state in room temperatures or can be easy liquefied with the application of easily accessible pressure. This ability rests in their chemical and structural form. The presence of at least one oxygen atom, which is highly electronegative, attracts a higher density of electrons, like in hydrogen bonds ([Figure 14](#)). The hydrogen captured in the structure of oxygenate fuels, keeps the form of fuel liquid at room temperature by elevating the boiling point significantly. In addition, the presence of oxygen lowers the energy requirement for utilizing the carbon dioxide, since at least one fewer carboxyls need to be broken. Still, at least one functional group of alcoholic OH or aldehyde C=O is retained in the form of methanol or other oxygenated fuels, keeping a certain amount of toxicity in the fuel. Environmental concerns should be present even for these fuels, such as capturing the toxic elements during combustion. Still, oxygenate fuels prove to be a useful intermediate for other reactions, resulting in other higher value products [\[15\]](#).

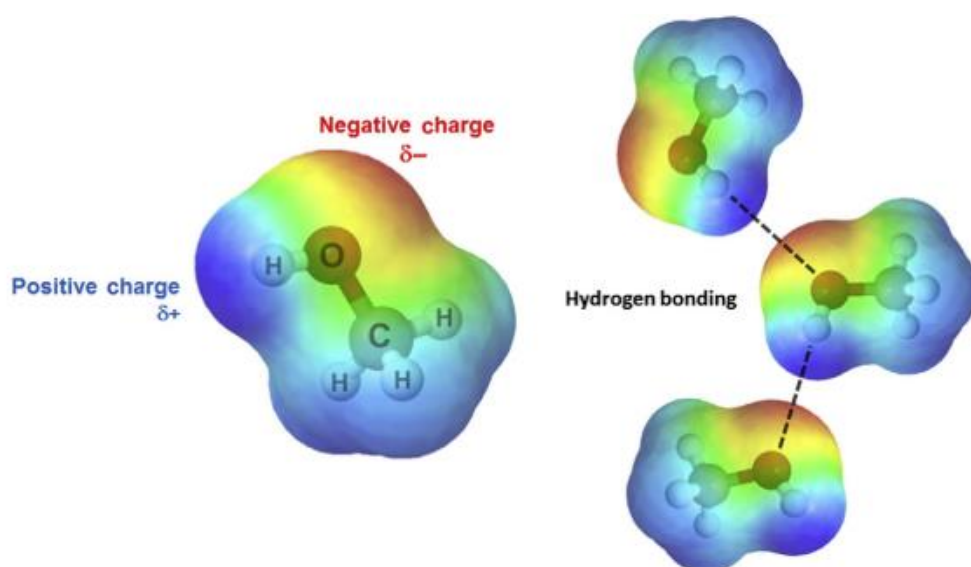


Figure 14: Electrostatic surface of methanol and illustration of hydrogen bonding between methanol molecules [74].

By including an alcoholic group in the synthesis, methanol, can be easily converted into hydrocarbons, olefins, carbonyls, carboxylic acid, amines and other groups (Figure 15). Amongst the various uses of methanol, it can also be used directly as a solvent, anti-freezer or wastewater treatment. Most of the reactions involving methanol take place with the use of appropriate catalyst, such as polymerizing methanol into long-chain hydrocarbons using a zeolite-supported catalyst and by applying modest pressure, between 10-20 atm, and elevated temperatures between 300-400 °C, imitating the Fisher-Tropch synthesis. Recent studies indicate the properties of ceria supported catalysts , with the aim of replacing noble metal bases with cheaper ones, like copper, and achieving higher conversion and selectivity towards desirable hydrocarbons [75]. The continuous use of the catalyst though, results in a build-up of carbon deposit (cocking) which has to be burnt-off or risk poisoning the catalyst [15].

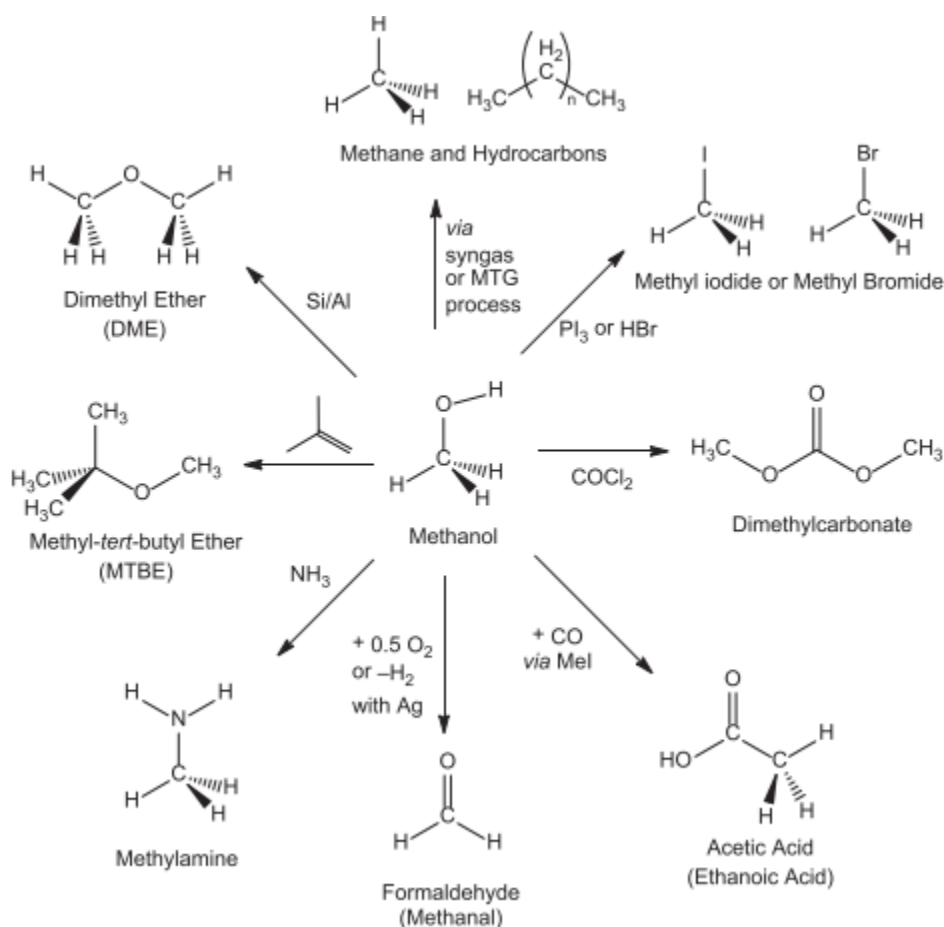


Figure 15: Synthetic uses for methanol and conversion to different products [15].

Dimethyl ether on the other hand is a major oxygenated fuel in gaseous form, produced by crude oil distillation, with a high boiling point, making it prone to liquefaction with an energy density suitable for heating, similar to the properties of liquefied petroleum gas or LPG. It can occur by thickening two methanol molecules while removing the H₂O, or alternatively directly from syngas, simpler and cheaper, in terms of energy than converting syngas to methanol. Under pressure, ignition can occur, making it also suitable for diesel engines [76].

Utilization of CO₂ for methanol production has attracted the most attention, with pilot and small scale plans already in usage ([66], [77], [78]) since it is by far the most efficient of the oxygenated fuels. Still, other oxygenates can be produced either by syngas or direct synthesis from carbon dioxide. Ethylene, ethanol, propanol, glycol and acetic acid are some of the products which have been studied extensively in these references [79]–[81].

4.6 Use of CO₂ in agriculture

Carbon dioxide, in gaseous form, can be used directly as a fertilizer. Fertilizer properties of CO₂ have been used for more than 30 years, with increasing crop yields, when applied, by 33.31%. Also, during photosynthesis, water absorption is increased by the carbon dioxide gas fertilizer, contributing to an increasing yield and decreasing the total water consumption. In one specific case, where research was conducted in the USA and Canada, wheat production increased by 10%, while water consumption decreased by 50%. In the absence of CO₂ fertilizer, at least 29% of the total yield was reduced due to a lack of sufficient water source [79]–[81].

In addition, carbon dioxide fertilizer, in comparison with other synthetic chemical fertilizers, is friendlier to the environment, since CO₂ can be captured in algal systems and utilized for algal-bio-fertilizer. Algal refinery is a carbon consuming process, with algal biomass consuming 1.8 tons of carbon dioxide to produce 1 ton of dry algal biomass. Usage of algal biomass though does not stop at fertilization, since it can also be used for bionenergy, carbohydrate, pharmaceuticals and protein extract. Other applications are in range, since carbon dioxide can be used and transformed by microorganisms that can break the bonds of carbonyls through consumption. *Escherichia coli*, for example, can use carbon dioxide indirectly, in combination with glucose from wheat or unrefined sugar, as a feedstock and produce succinic acid [21], [85].

4.7 Life-Cycle Assessment for CCU technologies

As mentioned in [Introduction to CCU](#), in order to fully realize the environmental impact of CCU and CCS technologies, a Life-Cycle assessment of carbon dioxide is mandatory. By following the cycle of carbon dioxide, from the point of capture, to storage, to utilization and rerelease into the environment, certain variables can be adapted that are used to describe the impact of carbon dioxide, in a realistic way, a way that is closer to reality. All life cycle stages of carbon dioxide interact with the environment and should be taken into account. An approach of CCU assessment without applying an LCA system, can lead to methodological pitfalls and false assumptions, with dire consequences to the environment, especially for pathways of utilizing CO₂ that are on the verge of commercialization. An ISO standard has been in place since 1993 for LCA systems and was updated in 2006 as ISO 14040 and 14044, which outlines the phases where an LCA system has to participate in order to be complete [86].

The first phase of LCA illustrates the definition of the goal, along with the conditions and assumptions, which in our case is the environmental impact of capturing and utilizing CO₂. Following on to the second phase, a list or an inventory is constructed (LCI analysis), including any input and output data of the whole life cycle assessment like energy flows and materials. During the third phase, the inventory is evaluated on the environmental impact of every procedure (LCIA), in our case, for product production based on captured carbon dioxide. With regards to the final phase, results of the evaluation are taken into account, concluding which stage of the life cycle has the most influential role [15], [20].

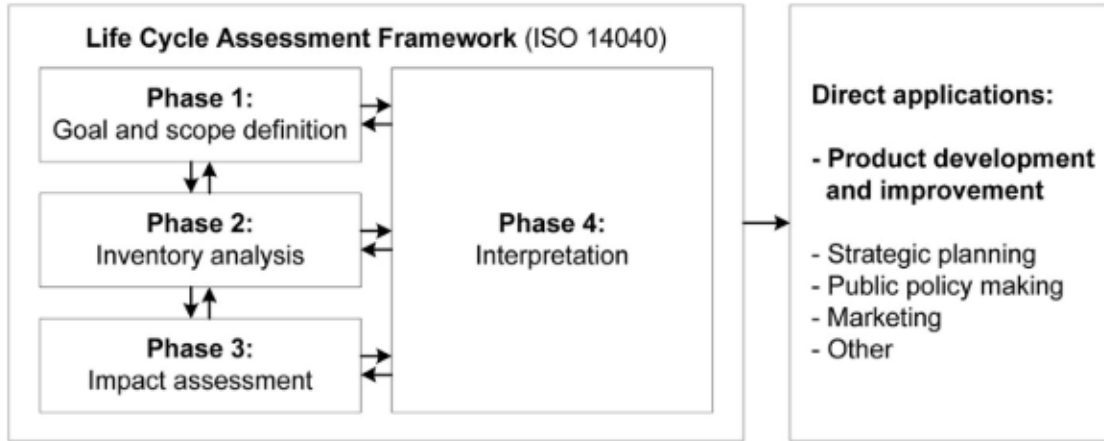


Figure 16: LCA structure according to ISO 14040 and ISO 14044 [15].

Pitfalls exist during every LCA phase, when applied to CCU technologies. An obvious example could be the global warming potential or *GWP* of green house gases or the fossil resource depletion. In the case of *GWP*, a different approach could be followed.

By using GWP_i , where i measure the relative global warming strength of the green house gas emission in comparison with CO₂, and adding the factor m_i , as the quantity of the green house gas emission, a total Global Warming variable can be expressed as follows:

$$GW = \sum_i m_i * GWP_i$$

By multiplying the quantity of the GHG with the factor of GWP_i and adding it to a total of GW, the actual global warming impact of a product's life cycle can be described. Alas by GWP_i the radiation absorption of a single GHG emission is assumed, isolated from the product's life cycle [87].

Another example is the so called negative emissions of GHG, which stands for the global warming impact of utilizing 1 kg of carbon dioxide or in GW terms:

$$GW = -GWP = -1kg CO_2 - \frac{eq}{kg} CO_2$$

In that case though, relative emissions produced by captured processes and energy consumption for CO₂ capture, are neglected and can lead to wrong assumptions [88]. In the case of LCA, input and output data are categorized in two distinct flows, namely elementary and economic.

Another impart factor, which has to be included in *GW* metric systems, in order to evaluate the global warming potential of products and emissions, is time. Along a time horizon *TH* between 50, 100 and 500 years, an absolute global warming potential could be calculated as:

$$AGWP_i(TH) = \int_{t=0}^{TH} a_i c_i(t) dt$$

$AGWP_i$ is considered as the total of the radiation efficiency α_i , as the strength of GHG to absorb radiation, multiplied by the decay function $c_i(t)$ of the GHG. GWP_i is then defined by the ratio of absolute global warming potential:

$$GWP_i(TH) = \frac{AGWP_i(TH)}{AGWP_{CO_2}(TH)}$$

By definition, GWP_{CO_2} equals 1, irrelevant to the time factor TH , while for any other GHG, the $GWP_i(TH)$ might change significantly, based on the decay function of $c_i(t)$. Alternate characterization factors, for calculating the global warming potential, have been studied ([22], [88]–[90]), but with all relying on the radiative force of GHGs as a metric system. The time horizon though, neglects the absorbed radiation of the GHG beyond the chosen time, making the choice of appropriate time horizon a difficult endeavour. Time of release of GHG emission is not included in the time horizon. By adding a corresponding characterization factor for $CO_2 - eq_{t=0}$, the release time of carbon dioxide t is considered 0. If t_s is the time delay of the pulse emission of GHG i then the time-corrected global warming potential t_cGWP_i is defined as ([20]):

$$t_cGWP_i(TH, t_s) = \frac{AGWP_i(TH - t_s)}{AGWP_{CO_2}(TH)}$$

Figure 17, illustrates the impact of the time delay on the time horizon. The curves of $t_cGWP_{CO_2}$ are non-linear since the decay fraction $c_i(t)$ change with respect to the time t .

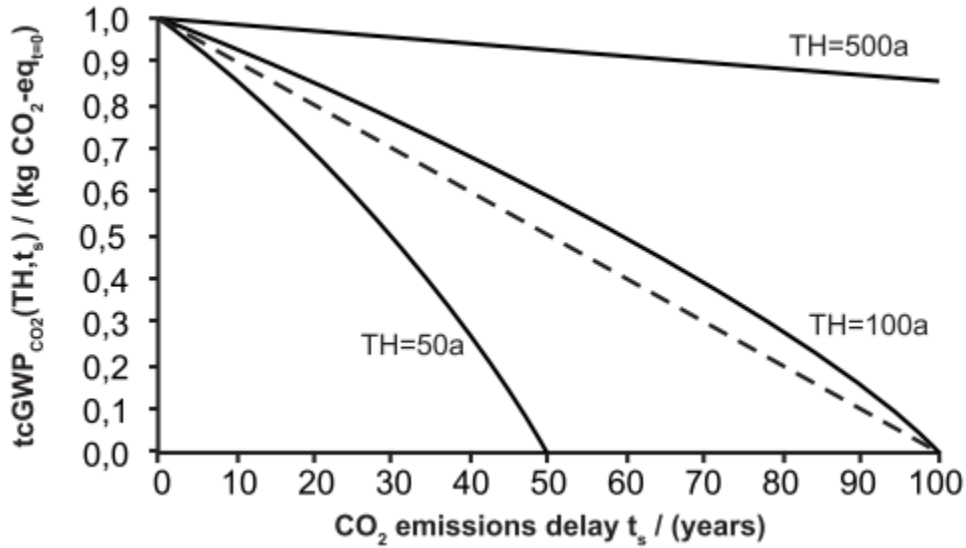


Figure 17 : Time-corrected characterization factors t_cGWP_i for delayed CO_2 pulse emissions using time horizons TH of 50, 100 and 500 years. The dashed-line represents a linear approximation to t_cGWP_i ($TH = 100a$) [20].

Finally, by adjusting the emission factor m_i to $m_i(t)$, a time corrected Global Warming score GW can be obtained totally as :

$$tcGW = \sum_i \sum_{t=0}^{TH} m_i(t) t_cGWP_i(TH, t).$$

The elementary flow is characterized as flow between techno sphere and environment without any human interaction as in transformation by anthropogenic factors. Additionally, a techno sphere is the total of the natural environment and the anthropogenic built installations, products and technologies.

In contrast with the elementary flow, economic flow embraces the processes which are taking place within the techno-sphere. Results of an economic flow, are the products and waste released into the techno sphere [20], [86].

In a CCU system, CO₂ is considered as a feedstock which is produced (captured) from different sources with different impacts on the environment. The point source of carbon dioxide captured can be categorized as illustrated in Figure 18:

- CO₂ captured from non-biogenic point-source
- CO₂ captured by biogenic point-source
- Direct air captured CO₂

Power plants and industrial processes belong to the first category, where CO₂ is a byproduct of the main product, that being electricity, chemicals etc. Systems are unable to capture 100% of the emitted CO₂, resulting in positive carbon dioxide emissions. In the second category, the captured CO₂ resting in biomass may be considered as negative emission, since carbon dioxide remains fixed. However, products produced from the biomass, carry the carbon footprint and may result again in positive carbon dioxide emissions. In the final category, DAC plants capturing CO₂ without any byproducts in the process may too be considered as a negative emission factor but with the prospect of future release of the captured CO₂ in a different form. Nevertheless, CCU systems can only be considered as economic flow, and not always as negative emissions of GHGs. In some cases, CCU installations may produce larger quantities of carbon dioxide, than an installation without the CCU.

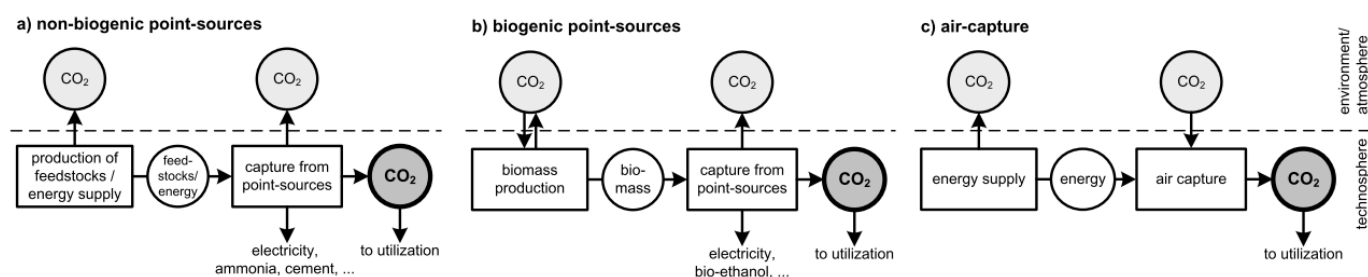


Figure 18: Classification of CO₂ capture systems according to carbon origin [20].

By following the example illustrated in the work of Niklas von der Assen *et al.*[88], it becomes clear that the beneficial environmental usage of CCUs installations “is not given by default”. In addition the use of time corrected global warming metric, as *tcGW*, produce different results in the evaluation of scenarios in terms of GWP for incorporating carbon dioxide as part of materials, like polymers. For the sake of argument, the same example will be presented in order to show the importance of a time corrected global warming metric for the purpose of realizing the environmental impact of CO₂ storage on materials.

The first scenario is a non-CCU plant which produces polymers by using petrochemical feedstock. The other three scenarios use captured CO₂, from a DAC installation as feedstock for producing polymers, with the same functionality as the ones from the non-CCU plant. The use of DAC plant in the CCU scenarios illustrates the capture process of CO₂ as a mono-functional system, since any other capturing method may produce GHG as byproducts of the capturing procedure or during restoration operations of the capturing agent. The scenarios are compared in terms of CO₂ production during *plant construction*, *polymer production* as well as the *use-phase of the polymer products* and *end-of-life treatment*.

The production capacity is the same for the four scenarios, as well as the operating years of the installation. The three CCU scenarios have by default, higher CO₂ emissions during installation of the DAC plant, while CO₂ emissions for the production of polymers are lower than the non-CCU scenario. The second CCU scenario has double the polymer lifetime than the first, while the third CCU scenario uses larger quantities of CO₂ as feedstock (-1 tCO₂-eq. per t polymer), but produces higher emissions during end-of-life treatment (+1 tCO₂-eq. per t polymer). The time profile of the emissions starts with the construction of the polymer production plant ($t = 0$), follows the years of operation of the plant ($1 \leq t \leq 40$), and ends with the end-of-life treatment, which for the non-CCU and first CCU scenario is $31 \leq t \leq 70$ and for the second and third CCU scenario is $61 \leq t \leq 100$ since they produce polymers with a longer lifespan.

Table 11: Parameters and cradle-to-grave GHG emissions for CCU and non-CCU polymer production. All values are purely fictitious to illustrate the effect of the time- corrected tcGWP metric [88].

Life-Cycle Stage	Unit	Non- CCU	CCU (i)	CCU(ii)	CCU(iii)
Plant Construction	t CO ₂ -eq. per t polymer	500 000	800 000	800 000	800 000
Production Capacity	t polymers/(year*plant)	15 000	15 000	15 000	15 000
Years of production	Year	40	40	40	40
Polymer Production	t CO ₂ -eq. per t polymer	4	3.5	3.5	2.5
Use Phase	t CO ₂ -eq. per t polymer	0	0	0	0
Polymer Lifetime	Year	30	30	60	60
End-of-life Treatment	t CO ₂ -eq. per t polymer	1.5	1.5	1.5	2.5

By adjusting the values from Table 11 to the GWP and tcGWP models, the authors conclude that, while a GW model produces the same results for every one of the four scenarios, a time corrected tcGW shows significant differences between the scenarios in terms of kg of CO₂ used for kg polymers produced, as shown in Figure 19.

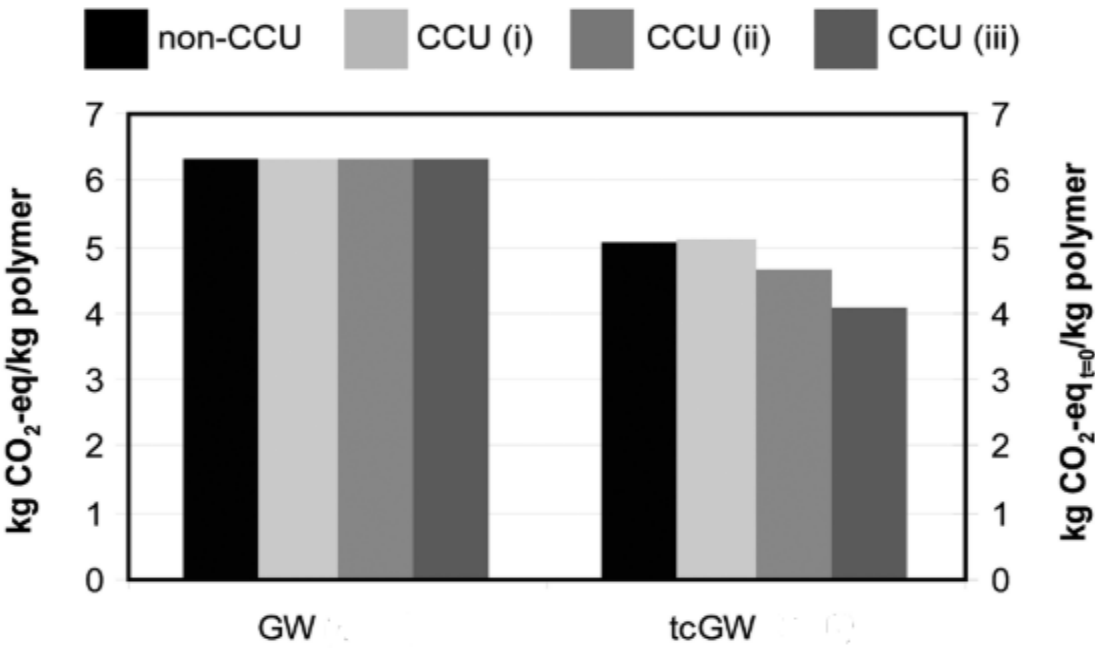


Figure 19: Evaluation of global warming impacts of polymer production by non-CCU and CCU technologies with variable polymer lifetimes and end-of-life CO₂ emissions using GW (left axis) and tcGW (right axis).

The tcGW comparison of the four scenarios shows that carbon dioxide storage alone does not offer any environmental benefits for the CCU system. Only by extending the polymer lifetime to a certain time scale, can lower GHG emissions be achieved. However, by extending the time of CO₂ storage in the form of polymers, it should lead to larger quantities of end-of-life treatment emissions. Also, in the comparison between the tcGW of the non-CCU and first CCU scenario, the non-CCU seems to have a smaller Global Warming impact than the CCU scenario. This example illustrates that even though CCU systems can have on many occasions, a significant impact in reducing GHG emissions; it should not be taken for granted, since without the application of Life-Cycle Assessment, the installation of CCU may result in worse environmental effects than the existing non-CCU.

The important challenge of CCU systems is to engage with low-GHG emissions as a feedstock, with a renewable energy source, in order to avoid further GHG emissions. Altogether, by following the presented framework for LCA of CCU, a sound environmental evaluation of CCU is obtained and can be used as a reliable basis for decisions on CCU implementations.

5 Catalytic Hydrogenation of CO₂ to Olefins

5.1 Introduction to Catalytic Hydrogenation

As mentioned in chapter 4.2, it is a well known fact that carbon dioxide is a very stable molecule, since the double bonds of oxygen and carbon are very strong, in comparison with others C1-chemicals. Therefore, one of the biggest obstacles in establishing CO₂ as a commercialized industrial feedstock is the high energy input needed to break the bonds between carbon and oxygen to produce useful products and materials. Thus the use of catalysts, to lower the required energy level of the reaction, and of high-energy material, like Hydrogen, for the final transformation of CO₂, is a well established method known as Catalytic Hydrogenation. With hydrogen being produced by renewable sources for the purposes of using it as an agent for the catalytic reaction, can contribute to the idea of circular economy. Through the use of renewable H₂, the energy of the element is stored in the form of fuels and chemicals. The main forms of hydrogen production, with either a renewable or non-renewable energy source, are electrolysis, thermolysis, photo-electrolysis and hybrid thermochemical cycles with new approaches currently under research. By using appropriate evaluation criteria, such as the time corrected global warming potential (*tcGWP*), social cost of carbon (*SCC*), acidification potential (*AP*), exergy and energy efficiencies, in combination with production cost, a realistically compare between the various methods of hydrogen production becomes able. In addition, the Life Cycle Assessment can contribute to the evaluation of the environmental impact of H₂ produced from non-renewable energy sources. Still, the price of production plays a crucial role for the industry, since in order for any environmental project to be commercialized it must be balanced in both economy and sustainability. For example, while photo-electrochemical projects of Hydrogen extraction from water dissociation looks promising, the cost of the method (\$10,36/kg H₂) in the R&D stage, is 13.8 times higher than the conventional method of producing hydrogen through fossil fuel reformation (\$0.75/kg H₂) or coal gasification (\$0.92/kg H₂) [3], [91], [92].

By achieving hydrogen production via renewable energy sources, new pathways can be opened for closing the carbon cycle, as in utilizing efficiently carbon dioxide.

Much attention has been paid to carbon dioxide hydrogenation in various products, as shown in Figure 20, where the pathways and reaction are illustrated. From the various products that are available for production via catalytic hydrogenation of CO₂, olefins (alkenes alternatively) are of particular interest to the researching community.

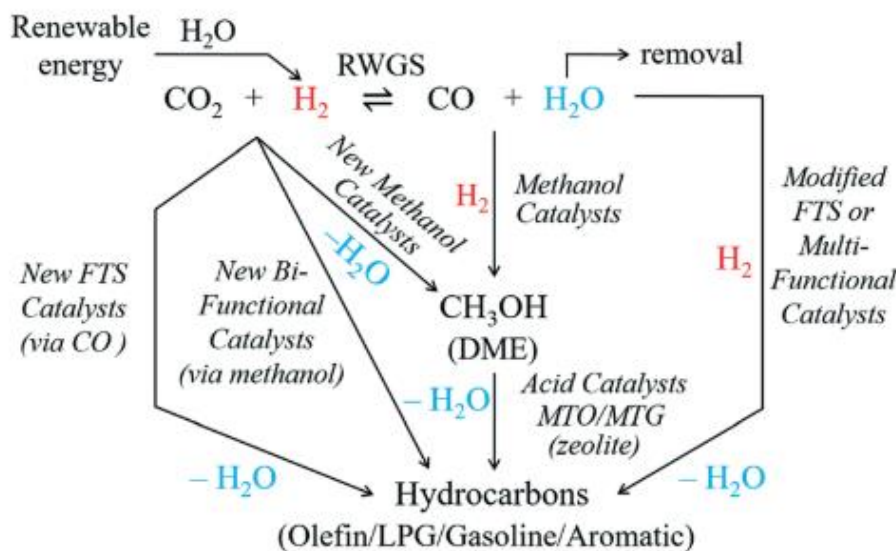


Figure 20: Details of the different possible routes to synthesize value-added hydrocarbons (olefin, LPG, gasoline, aromatics and so on) from CO₂ hydrogenation [93].

5.1.1 Methods & Products

As illustrated in Figure 20, the pathways for catalytic hydrogenation of CO₂ differ according to the desirable products. While adding H₂ to the reaction is the first step towards transforming CO₂ into various products, a catalytic reaction is required for the next step. Methods like photo-catalysis, electro-catalysis, heterogeneous catalysis and plasma catalysis are among the most common, with plasma catalysis being an interesting and emerging technology ([94], [95]). Also, the methods of catalytic hydrogenation can be categorized into direct and indirect pathways towards the desirable product. In the case of producing hydrocarbons, two parallel reactions usually take place in the same catalytic reaction: Reverse water-gas shift (RWGS-Scheme 7) and the synthesis of methanol (CH₃OH-Scheme 8). During the reverse water gas shift, CO and H₂O is produced which can be used by the Fisher-Tropsch synthesis (FTS-Scheme 9) to produce hydrocarbons directly, similar to the FTS of syngas (CO+H₂). Indirectly, hydrocarbons can be produced via an intermediate step; once the industrial methanol is produced from methanol synthesis, and through the use of the appropriate catalyst, a range of hydrocarbons becomes available such as methanol-to-hydrocarbon (MTH), methanol-to-olefin (MTO), methanol-to-propene (MTP) and methanol-to-gasoline (MTG). In addition, dimethyl ether (DME) can be utilized as an intermediate for achieving hydrocarbons. Indeed, promising reviews have been voiced and published on the transformation of carbon dioxide via catalytic hydrogenation methods ([91], [96]–[99]). Nevertheless, most of the reviews focused on producing C1 chemical blocks (like methane, methanol, carbon monoxide and formic acid) since the coupling barrier of double or triple bonds between C molecules are extremely high.

In fact, desirable products of two or more carbon molecules are the moving force of researching tandem and heterogeneous catalysis towards the goal of transforming CO₂ into liquefied petroleum gas (LPG, C₃⁰ – C₄⁰), lower olefins (ethylene, propylene and butylenes, C₂[–] – C₄[–]) and gasoline (C₅ – C₁₁).

RWGS: $CO_2 + H_2 \leftrightarrow CO + H_2O$ ($\Delta_r H_{298K} = 41.2 \text{ kJ mol}^{-1}$)

Scheme 7: Reaction pathways for the RWGS reaction [100].

Methanol Synthesis: $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ ($\Delta_r H_{298K} = -49.5 \text{ kJ mol}^{-1}$)

Scheme 8: Methanol synthesis in the hydrogenation process of carbon dioxide [93].

FTS: $CO + 2H_2 \leftrightarrow -(CH_2)_n + H_2O$ ($\Delta_r H_{573.15K} = -166 \text{ kJ mol}^{-1}$)

Scheme 9: Fischer-Tropsch synthesis utilizing CO to produce hydrocarbons [101].

Among the various products of carbon dioxide catalytic hydrogenation, such as CO, CH₄, CH₃OH, dimethyl ether [102], alcohol [103], isoparaffins [104] and aromatics [105], light olefins are one of the most promising routes of carbon dioxide utilization.

5.1.2 Olefins

Olefins, or Alkenes as they are commonly known, are acyclic hydrocarbons with one carbon-to-carbon double bond as $C = C$ and follow a general molecular formula of $C_n H_{2n}$. They do not occur naturally in crude oil, but they may be produced from refining processes, such as stream cracking (SC). In the petrochemical industry, they are referred to as olefins, originated from unsaturated aliphatics as shown in Figure 21. As a matter of fact, olefins comprise all aliphatic (both acyclic and cyclic) hydrocarbons having one or more carbon-to-carbon double bonds: alkenes, cycloalkenes, and polyenes (compounds exhibiting more than one double bond). While alkenes extend to higher hydrocarbons, the most commonly used olefins by the petrochemical industry are ethylene (C_2H_4), propene (C_3H_6) and butylene (C_4H_8), which exist in gaseous form in room temperatures [106], [107].

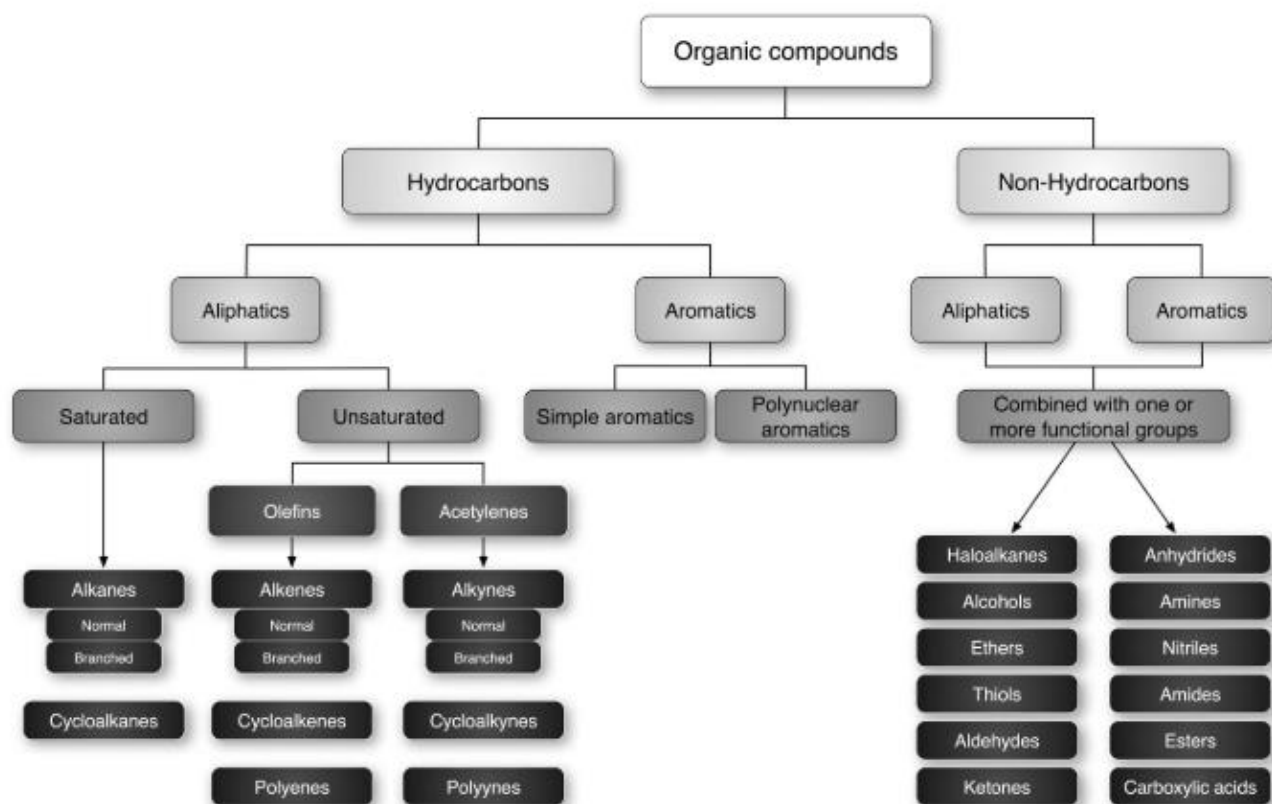


Figure 21: Classification of organic compounds [106].

Olefins, as compounds, are used for chemical feedstock in the petrochemical industry, with their uses being limited to industrial usage, since they are not directly available to customers or the public market.

Ethylene (C_2H_4), is the basic material for producing polyethylene and other polymers through polymerization. In fact, ethylene based polymers, have vast applications, with a huge variety of products manufactured, such as: fibers, bins, pails, crates, bottles, piping, food packaging films, trash liners, bags, wire, surface coatings for paper and cardboard *etc.* Their applications could also be extended to the construction sector, as ethylene polymers can be used in tile and flooring for buildings. As a chemical compound, ethylene can also be used as a refrigerant and as a ripening agent for commercial greenhouses. The annual global production of ethylene seems to be the largest of all the olefins, reaching 47.1 Mt in 2019. The continuous growth of the market, encouraged the annual global production to increase yearly, estimated to reach over 96.1 Mt by 2025. China alone produces approximately 13.3 Mt of the total global annual production, with an annual growth of 6.2%, while Japan follows at 5.4 Mt. The increasing demand in European markets will offer many opportunities for increased productivity for olefins, including ethylene [108], [109].

Propylene (C_3H_6), is the second most commonly known olefin which, in contrast to ethylene, can be found naturally in the environment. It occurs also as a combustion product from internal combustion exhausts. As a chemical product, it is deemed to be an essential chemical intermediate for other chemical manufacturing processes. Among other uses, the most important are the production of polypropylene, propylene oxide, acrylonitrile, oxo chemicals and acylic acid. While the global annual production of propylene reached 31.4 Mt in 2019, predictions indicate that the global needs will raise the production to 88.8 Mt by 2025, with China again leading the increase of production with 8.9 Million Metric Tons of the total global production, with Japan following at 5.2 Mt [108], [110].

Butylene (C₄H₈), usually rests in very small quantities in crude oil, and therefore is obtained by catalytic cracking or steam cracking. Usually, it is used as a monomer for polybutene, which is a polymer. The double carbon-to-carbon bond offers the high reactive properties of butane, deeming it more reactive than similar alkanes. It can be used to produce synthetic rubber used in tires, plastic gloves, wetsuits, rubber hoses etc. with vast applications including creating substance for other polymers. The annual global market worth of butene reached US\$1.9 billion with a potential growth over 7.3%, which may lead the market to reach up to US\$3.5 billion by the end of 2025 [111].

Olefins represent an important and growing chemical market with ethylene, propylene and butylene poised to be the backbone of petrochemical industry. With the annual global demand increasing significantly, appropriate methods have been used to keep the production of olefins at a steady and efficient pace. The current leading technology for olefins production is steam cracking. Thermal or steam cracking-based olefin production plants use several steps for achieving the final products such as cracking furnaces, quench sections, units for compression and chilling, and ,for the final step, separation columns with cold boxes, categorized in hot and cold sections (Figure 22).

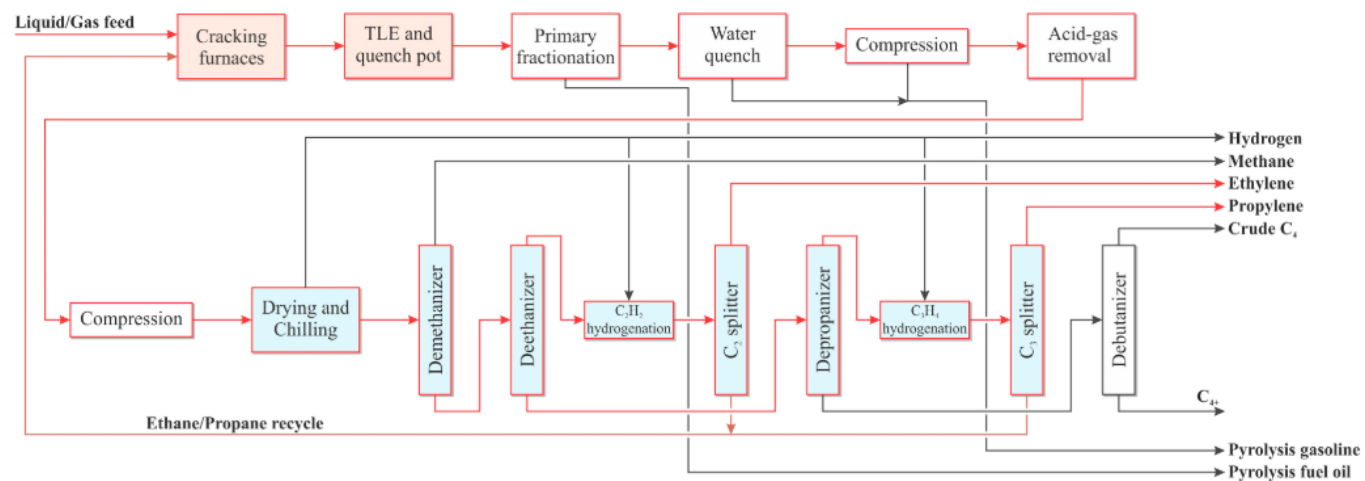
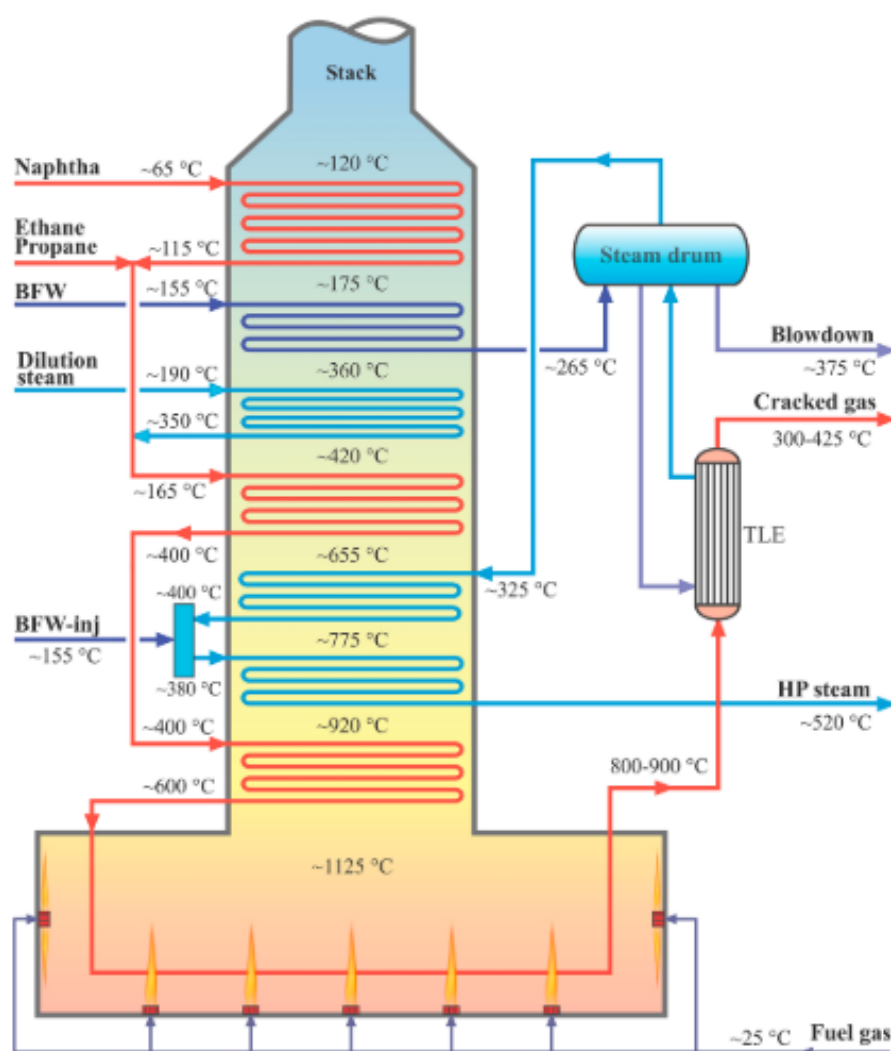


Figure 22: Conventional block flow diagram of naphtha cracking olefin plan, including cracking furnace, quench sections, compression and refrigeration systems and separation columns [112].

Firstly, the highly endothermic *cracking furnaces* are fed with liquid or gas feedstock which is heated at extreme temperatures, around 1125°C. The furnace itself is divided into three stages, with every stage decreasing in temperature as the steam rises in the furnace (Picture 4). The chemical reaction takes place in a fraction of a second (0.4-1s) and for the highly endothermic reaction to happen, several burners which consume fossil fuel, are located on the floor level of the furnace. In addition, the dilution stream (DS) is added to the mix to keep the temperatures high and lower the partial pressures of hydrocarbons. The flue gases, after several stages, exit the furnace at approximately 100°C, while the reaction forms coke as a byproduct. Coke formation will continue to deposit the byproduct on the reactor wall which lowers the heat transfer and the pressure inside the reactor. At some point, the furnace undergoes a decoking process.



Picture 4: Schematic diagram of a typical furnace and Transfer Line Exchanger (TLE) in olefin plants [112].

After the heating of the feedstock, the cracked gas will exit the furnace and continue onto the *quench section*, where it must be cooled very quickly to obtain the optimum yield towards desirable products. First, an indirect quenching system takes place by utilizing a special multi-tube heat exchanger called a Transfer Line Exchanger (TLE, [Picture 4](#)) where the cracked gas is cooled from 800-900°C to 300-425°C. Usually up to 3 TLEs systems are used for each cracking furnace. Then the cooled cracked gas travel along to direct quenching systems where the temperature will decrease further. The direct quench system is adapted according to the desirable products, reaching ambient temperatures. For example, for ethane crackers, the water quench tower is applied, while for naphtha crackers a quench fitting valve and primary fractionators is required before the processed gas reaches the water quench tower, since naphtha crackers produce primarily massive quantities of fuel oil. After direct quenching, sprayed water will come in contact with the gases, further decreasing the temperature, with the process gas exiting the final quenching water tower at temperatures around 15°C [112], [113].

The cooled processed gases will then continue along to be dried and compressed in the *compression and refrigeration systems*. The pressure of the gas, after drying, must be elevated from 1-2 bars to 40-50 bars via high pressure steam turbines. The steam required for the elevation of the pressure is provided by the TLE of the furnace. Then the gas must be again cooled and separated, since the gas is mixed with liquid hydrocarbons and water. During the separation process, H₂S and CO₂ must be captured and removed since they act as a poison for polymerization processes [112].

Finally, the gas reaches the *separation columns*, where various methods, as illustrated in Figure 22, such as front-end demethanizer, front-end deethanizer and front-end depropanizer, are used to separate the required olefins. It is proven that among methods of separation techniques like membrane or absorption, the cryogenic method of separation is the only feasible one for producing satisfactory results [112].

While steam crackers are used extensively to produce the required quantities of ethylene, propylene and butylene, this method depends heavily on the consumption of crude oil as a feedstock and as a heating contributor for the cracking of fuel gas to hydrocarbons. The steam cracking method contributes further to the CO₂ emissions (Figure 23). While as a method, it may seem the most efficient and low-emission method in comparison with others, tons of CO₂ per ton of high-value chemicals (HVC) produced are still significant for coal consumption. Still, in the case of steam cracking furnaces, oxyfuel-combustion and post-combustion process, may be utilized to decrease carbon dioxide emissions since they are intertwined with high temperatures, which can be found in the firing duty of the furnace [107].

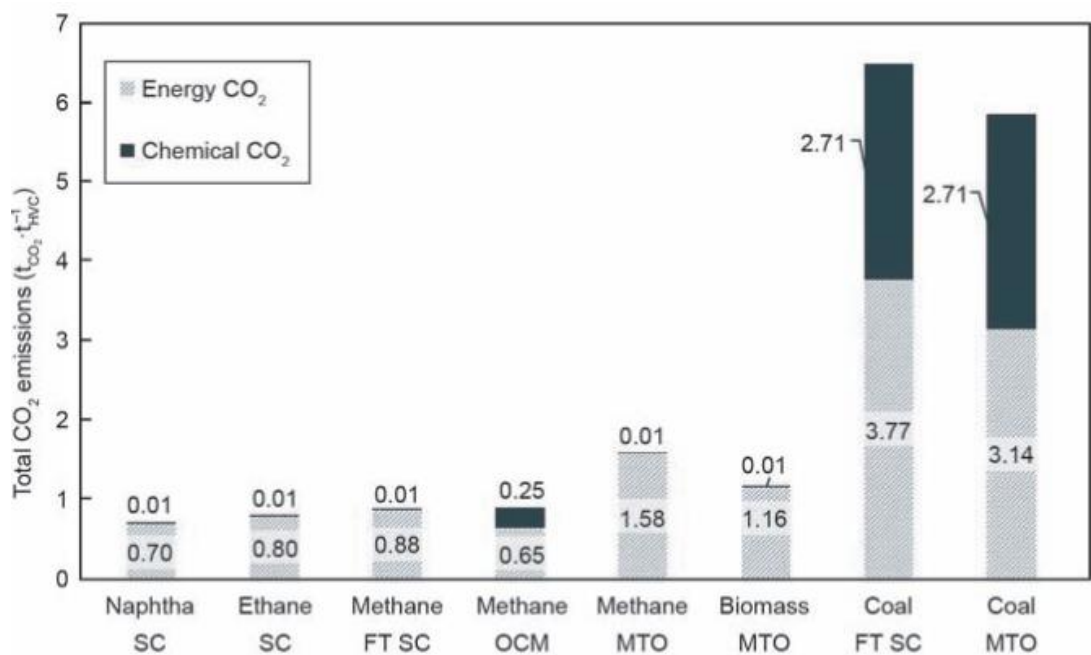


Figure 23: Total CO₂ emissions per ton of high-value chemicals ($\frac{t_{CO_2}}{t_{HVC}}$) for different technologies [114].

Environmental awareness seems to have had very little effect on the petrochemical industry, since the lack of economic viable solutions discourage large scale investments towards solutions which use sustainable or renewable sources of energy for the cracking processes. Nevertheless, the aim of this project is not to replace the strongly established mass production methods of olefins, but to close the carbon cycle, using carbon dioxide as a feedstock to produce useful products. By deploying the method of catalytic hydrogenation of CO₂, an important addition to the productivity of required olefins can be made, while at the same time, utilizing harmful emissions.

5.2 Catalytic Mechanism and Kinetics

As mentioned before, there are two pathways for yielding olefins during the catalytic hydrogenation of carbon dioxide: a direct and indirect way. Directly olefins can be obtained via RWGS (Scheme 7) where the addition of hydrogen in the CO₂ mix, produce carbon monoxide which then reacts with the Fisher-Tropsch mechanisms to synthesize hydrocarbons. Indirectly, via the methanol-mediated reaction, hydrogen is used with the appropriate catalyst to produce methanol (Scheme 8) with DME produced as a main product, which is later combined with the catalyst, usually zeolite-based, in order to produce light olefins. Using the direct approach for producing light olefins, via the combination of RWGS and FTS, may be more significant than methanol synthesis from carbon dioxide hydrogenation, since methanol is used extensively in the petrochemical industry for olefin production (MTO) by applying zeolite-based catalysts, like SAPO [92], [93].

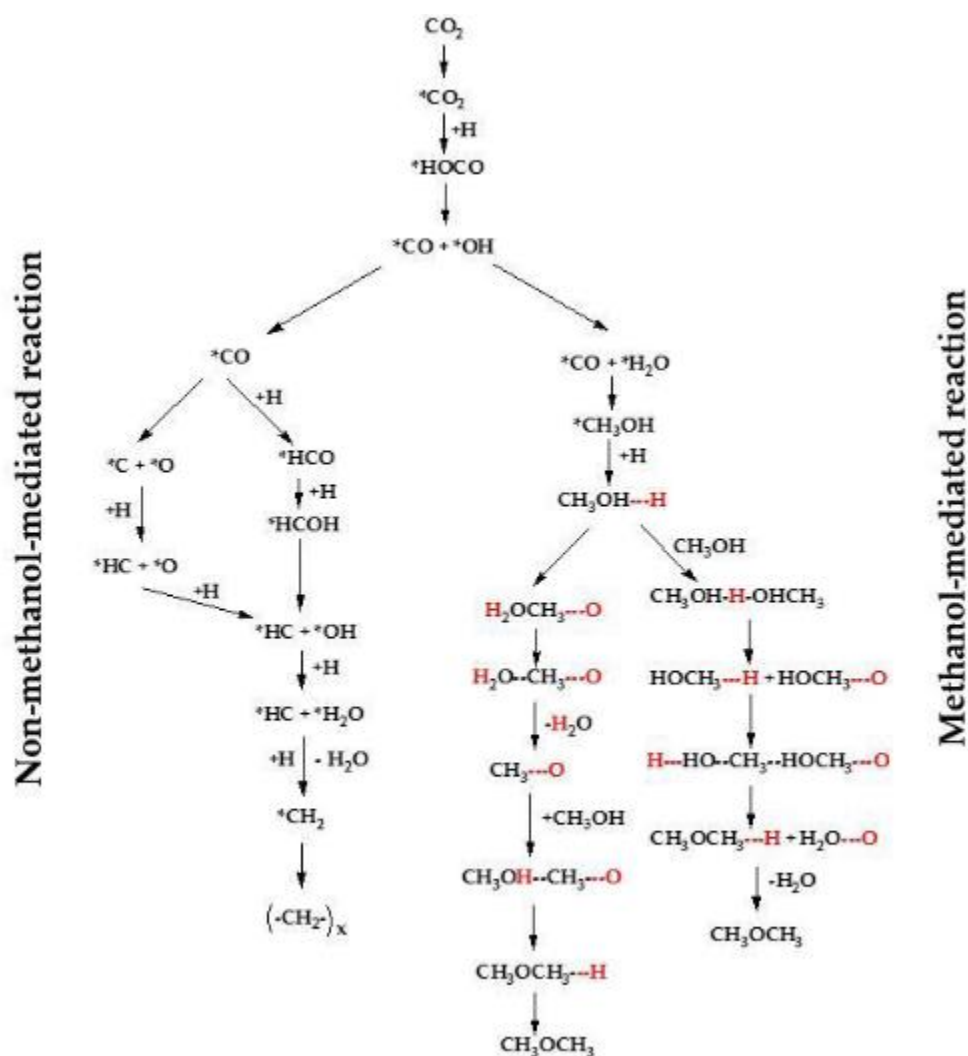


Figure 24: Possible reaction pathways for CO₂ hydrogenation to DME and light olefin, by using an H-ZSM5 zeolite catalyst [92].

According to the literature ([115]–[118]), during the water gas shift (WGS), kinetic parameters, the reaction order, rate constant and activation energy are used to describe the time-lapse of the reaction. The rate of the CO shift reaction r_{SH1} is described in Scheme 10:

$$r_{SH1} = k_{SH1} \frac{P_{CO}P_{H_2O} - P_{CO_2}P_{H_2}/K_{eq}}{P_{CO} + a_{SH1,H_2O}P_{H_2O}}$$

Scheme 10: Kinetic rate equation of WGS [99].

Where k_{SH1} stands for the temperature dependence of rate constant; P_i is the partial pressure of each element; a_{SH1} is the reaction order where a starts first, b second etc.; and K_{eq} is the equilibrium constant which maintains thermodynamic tency as illustrated in Scheme 11.

$$K_{eq} = \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right)_{eq} = 10^{(0.0003855T + \frac{2180.6}{T} - 2.4198)}$$

Scheme 11: Equation of the equilibrium constant K_{eq} [101].

Similar to the WGS reaction kinetic mechanism, there are reports of RWGS, FTS and Direct hydrogenation, adopted by the research of Saeidi *et.al* and Riede *et.al* respectively [101], [119], which simulate the final kinetic rate equations. Unfortunately, there is still a lack of a general micro-kinetic model mechanism for RWGS and FTS, which would be able to indicate, step by step the reaction mechanism and the various transformations that take place. The close observation of the elementary reactions taking place on the surface of the catalyst may prove useful to further contribute to the study of the kinetic mechanism for both reactions.

$$RWGS: r_{SH2} = k_{SH2} \frac{P_{CO_2} P_{H_2} - P_{CO_2} P_{H_2} / K_{eq}}{P_{CO} + a_{SH2,H_2O} P_{H_2O} + b_{SH2,CO_2} P_{CO_2}}$$

$$WGS: r_{SH1} = k_{SH1} \frac{P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} / K_{eq}}{P_{CO} + a_{SH1,H_2O} P_{H_2O}}$$

$$FTS: r_{FT} = k_{FT} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FT,H_2O} P_{H_2O} + b_{FT,CO_2} P_{CO_2}}$$

$$Direct\ hydrogenation: r_{DH} = k_{DH} \frac{P_{CO_2} P_{H_2}}{P_{CO} + a_{DH,H_2O} P_{H_2O} + b_{DH,CO_2} P_{CO_2}}$$

5.2.1 WGS & RWGS

During the initial step of the WGS reaction, with the aim of producing CO from the catalytic hydrogenation of CO₂, several catalysts have been researched in order to efficiently produce results. In order for the equilibrium constant K_{eq} to reach 1, high temperatures are required, reaching 800°C, while at 400°C the constant exceeds 10. Metal based catalysts were used in order to achieve CO transformation and continue to work under these elevated temperatures. The same stand for the RWGS, which starts the reaction with low equilibrium constant. For the equilibrium to increase in favor of CO formation, some aspects of the reactions can be adjusted accordingly:

- By increasing the concentration of CO₂ in order to completely utilize the H₂, while recycling the unused carbon dioxide [120].
- By increasing H₂ concentration to completely utilize the CO₂, while recycling the unused hydrogen for further use by capturing it via Pd-Ag membrane [101]

- By reducing water vapor during the reaction by using for example a membrane similar to the membrane used in FTS reactors where hydroxysodalite (H-SOD) or zeolitic form a perm-selective membrane [121].

In addition, some useful points were raised by Saeidi *et.al* [101], on the nature of the catalysts used for RWGS and WGS:

- Copper-based catalysts, like CuO/ZnO oxides modified by TiO₂, ZrO₂, Al₂O₃ or SiO₂. The CuO/ZnO based catalysts are usually made by 30% CuO and 33-60% ZnO, and are pyrophoric which means that they are sensitive to high temperatures, susceptible to copper poison and sintering [122].
- Iron-based catalysts have a high temperature activation point which makes them ideal to operate above 400°C. The nature of the catalyst makes it resilient to poisoning and sintering [101].
- Ceria-based catalysts, like CuO/CeO₂ can be effectively employed for the aforementioned reactions. The fine-tuning of both copper and ceria oxides morphological characteristics (mainly morphology and particle size) can notably affect the metal-support interactions and in turn the catalytic performance. Through this route, the usage of precious metals can be avoided, reducing the cost of the catalyst while keeping efficient levels high [75].

RWGS increase the yield of CO with rising temperatures. Instability of copper nanoparticles may occur at high temperatures. Nevertheless, copper based catalysts are cheaper than iron based, and their performance may be improved with the installation of a thermal stabilizer during the reaction. By, for example, adding a small amount of Fe as promoter in Cu/SiO₂, the catalyst works efficiently with keeping the stability, up to 120h at 600°C, while the Cu/SiO₂ without Fe lost 10 wt% of its activity very quickly [123].

Ceria had catalytic effects on both WGS and RWGS, where a catalyst Ni/CeO₂ posed high stability, selectivity and conversion of carbon dioxide. The yield took place at 600°C with 35% selectivity in 9 h, with prolific nickel scattered, playing a major role in the stability and selectivity of the catalyst. Also, using bulk nickel instead of scattering it in the catalyst, favoured the formation of methane instead [124]. The deactivation of ceria based catalyst occurs under many conditions of temperature, pressure and yield. Nevertheless, during the research of Konsolakis [75], the geometry of nanoparticles of a copper-ceria based catalyst, was made clear that play a crucial role in the efficiency and stability of the catalyst, with increasing selectivity while using for instance nano-rods instead of nano-polygons.

Noble metals like rhodium, platinum and ruthenium prove to have high activity for carbon dioxide hydrogenation. In addition, Li increase the activation sites of the catalyst, but on the other hand shifts the reaction towards producing CH₄. By adding Li in Rh ion-exchange zeolite, at an atomic ratio 10:1 in favor of the Rh, the selectivity towards CO reaches approximately 84% [125].

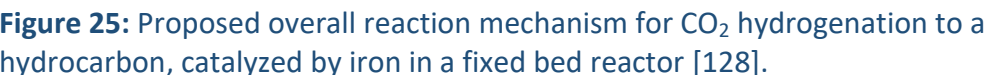
While noble metals exhibit adequate activity for catalytic hydrogenation of carbon dioxide, the scarcity and required quantities for catalytic applications, have skyrocket the prices of noble metals through the roof. The role that mass-usage and the fine-tuning of non-precious metal oxides will play is crucial towards replacing the noble metals catalysts with cheaper materials like copper.

5.2.2 MFTS & FTS

In order to reach the desirable products of olefins, carbon dioxide has to be catalytically hydrogenated either, or indirectly via a methanol intermediate step modified Fisher-Tropsch synthesis. In the indirect route, a multi-stage approach is required where separate reactors are used for the different steps of hydrogenation. In addition a hybrid catalyst can be used in order to perform the several steps of the transformation [126]. However, a methanation intermediate step proves to have several disadvantages concerning hydrogen consumption and less energy per volume and storage. Cobalt based catalysts seem to favour yields towards CH_4 production and may not be appropriate for producing hydrocarbons. On the contrary, Fe-based catalysts like a Fe-Zn-K catalyst used in the research of You *et.al* [127], indicated excellent results of 51.03% CO_2 conversion and 53.58% C_2^- - C_4^- olefins selectivity at 593 K and 0.5 MPa. In many iron based catalysts the selectivity and conversion remained unchanged during different CO/H_2 ratios, but were affected while changing the CO_2/H_2 [101]. This indicates that transforming carbon dioxide in carbon monoxide via the RWGS is an important step for increasing the efficiency of the FTS.

A reaction mechanism was proposed for MFTS, by Lee *et.al* [128], where CO_2 hydrogenates into hydrocarbon via Fe (II) reduction. During the reduction of carbon dioxide by Fe, H is absorbed on the catalyst surface. Secondly, the remained H reacts with C and creates OH, HCOOH and carbon monoxide. In a similar way, Fe- CH_2 is as a main product, following the main route of the reaction, in addition to the higher hydrocarbons. Having finished the reaction pathway, it becomes noticeable that there no excess of hydrogen in the reaction system, concluding that H_2 ratio contribution to the reaction is critical for the selectivity of the products (

Figure 25).



FTS plays a vital role of transforming carbon dioxide into hydrocarbons. During the reaction, FTS converts the feedstock with a step wise chain growth polymerization reaction into monomers to form hydrocarbons. The initial monomer transformation plays an important role in the synthesis, since according to the monomer certain pathway will be followed towards the final product (Table 12) [129]. FTS could be described by three stages, according to Davis *et.al* [130]; gas absorption, chain initiation step and chain growth step. Ni, Ru, Rh, Co and Fe have been studied and proven to be compatible with the FTS, resulting in methane, higher hydrocarbons and lower olefins [90].

Table 12: Fischer-Tropsch reaction pathways and products [129].

Fisher-Tropsch Synthesis	Reaction Pathway
Methane	$CO + 3H_2 \rightarrow CH_4 + H_2O$
Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
WGS (side reaction)	$CO + H_2O \rightarrow CO_2 + H_2$
Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+1}O + nH_2O$
Boudboudard reaction (catalyst modifications)	$2CO \rightarrow C + CO_2$
Catalyst oxidation/reduction	$M_xO_y + yH_2 \rightarrow yH_2O + xM$ $M_xO_y + yCO \rightarrow yCO_2 + xM$
Bulk cabide formation	$yC + xM \rightarrow M_xC_y$

During the *absorption step* (Scheme 12), CO is molecularly adsorbed on the catalyst’s surface, while H₂ is dissociated to H species. CO can intertwine with one or two active sites and form a weak absorbed planar structure. According to the element of the catalyst, the conditions differ. For example, on Ni-based catalysts, both structures are identified under FTS conditions, while on Fe-based catalysts, the linear structure is observed. In that case, the single-site absorbed CO is the feedstock for the chain growth monomer in the FTS.



Scheme 12: Two types of CO absorption; (a) single-site absorption and (b) double-site absorption [130].

Still, two carbon pools exist simultaneously on the surface of the catalyst; a CH_x element and absorbed CO. If the absorbed CO undergoes hydrogenation, it will yield CH_x elements. In addition, the bonds of planar CO can be broken to separate C from O and form carbide. The presence of hydrogen though may prevent the carbide formation, and lead the C to yield CH₂, as shown in the initial steps on

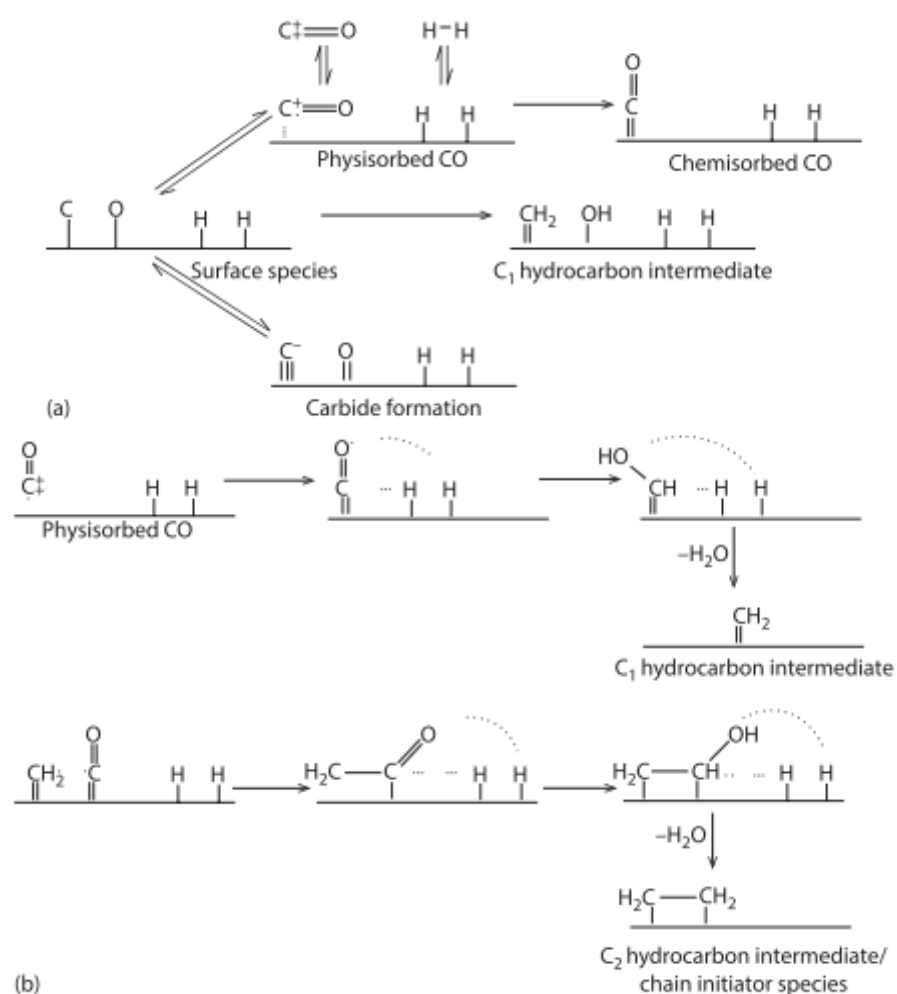
Scheme 13 [130].

In the *chain initiation step*, CO may undergo a step-by-step hydrogenation to form C_1 oxygenate complex. The C_1 can follow two different paths; either desorbed as an alcohol, utilizing hydrogen to break carbon-oxygen bond and form methylene, or completely transformed into CH_4 , due to hydrogenation.

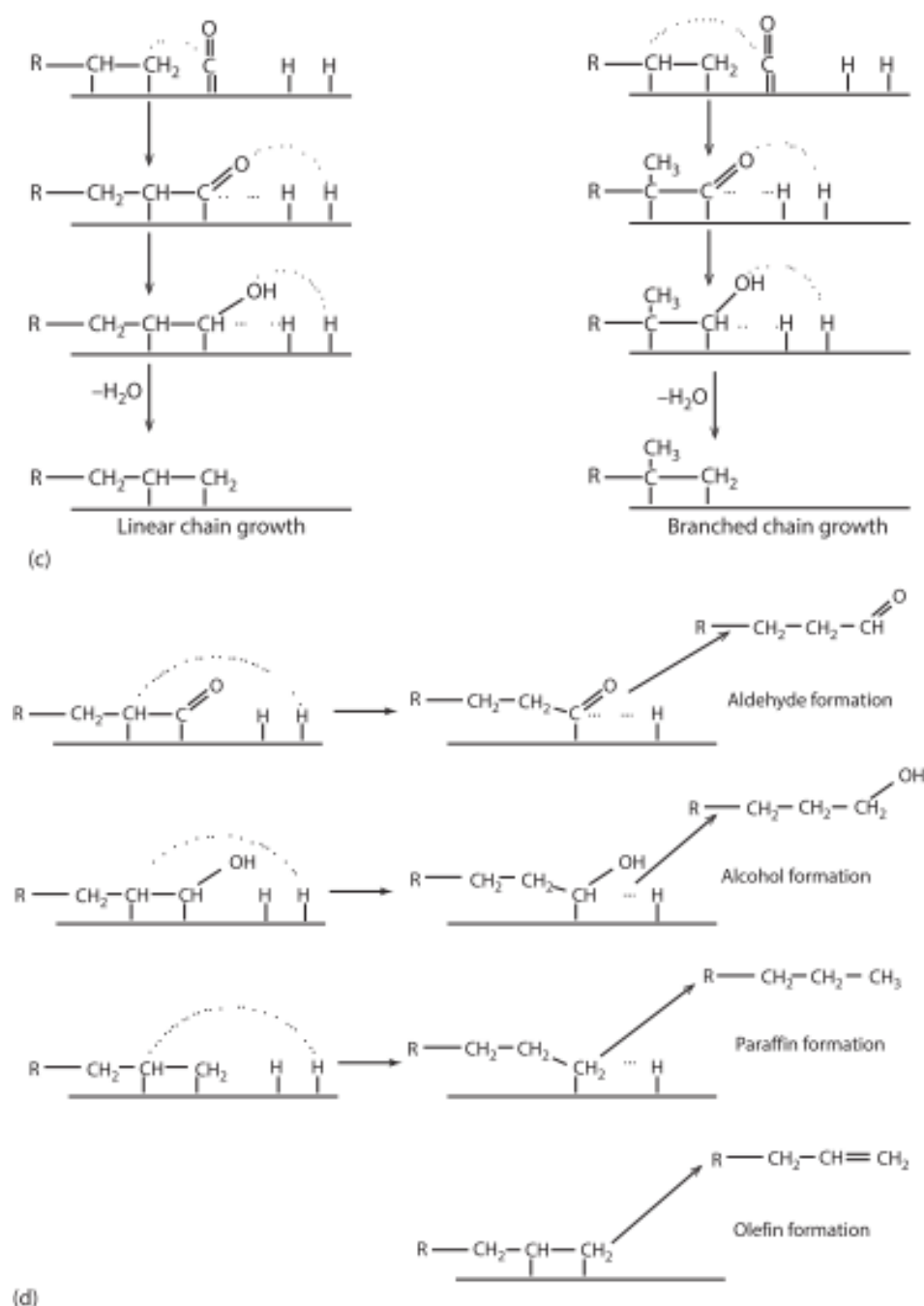
In the case of the second pathway, methane can be used independently to create chain growth by using further hydrogen. The surface carbide with low quantities of carbon dioxide can be used as the initial step for chain growth. Although that can be the case for the carbides, it cannot be sure that they will be used as a chain growth intermediate. For the intermediate step of the chain growth during FTS, methylene elements must be combined with CO to form C_2 oxygenate complex. The C_2 becomes the feedstock for the FTS to form higher chains. By adding hydrogen to the complex, C-O bonds can break further and create C_2 intermediates which will be the backbone for forming hydrocarbons (

Scheme 13(b) [130]). For olefin transformation to be achieved, the C_1 product, which will eventually form CO and/or CH_4 , must be suppressed, while the selectivity on C_2 is enhanced.

Finally, in the *chain growth step*, the final products are produced. Here, the final chain growth is affected by the type of the catalyst, where by adding CO, chain growth takes place towards carbons atoms at the terminal (C_α) and adjacent-to-terminal (C_β). If CO is attached to a C_β , then a hydrogen shift will form the $C_\beta-C_\alpha$, while the hydrogenation of C_α will create a branched methyl group which will result in branched hydrocarbon intermediate. Nevertheless, the high presence of linear hydrocarbons in the product indicates that it is harder to select the C_β than the C_α during the FTS. When the intermediate takes form, the presence of unpaired electrons in the intermediate or a charge on a tertiary carbon leads to desorption of the process, resulting in large quantities of 2-methyl branch. Methyl group will continue to affect the evolution of the chain growth. C_β requires methyl migration to act as a position for the chain growth, while C_α requires hydrogen migration. In addition, the mechanisms prevents desorption of the carbon molecule, which will act as the base of the base of the chain growth. The final products are formed in the final step of chain growth, as shown in **Scheme 14** [130].



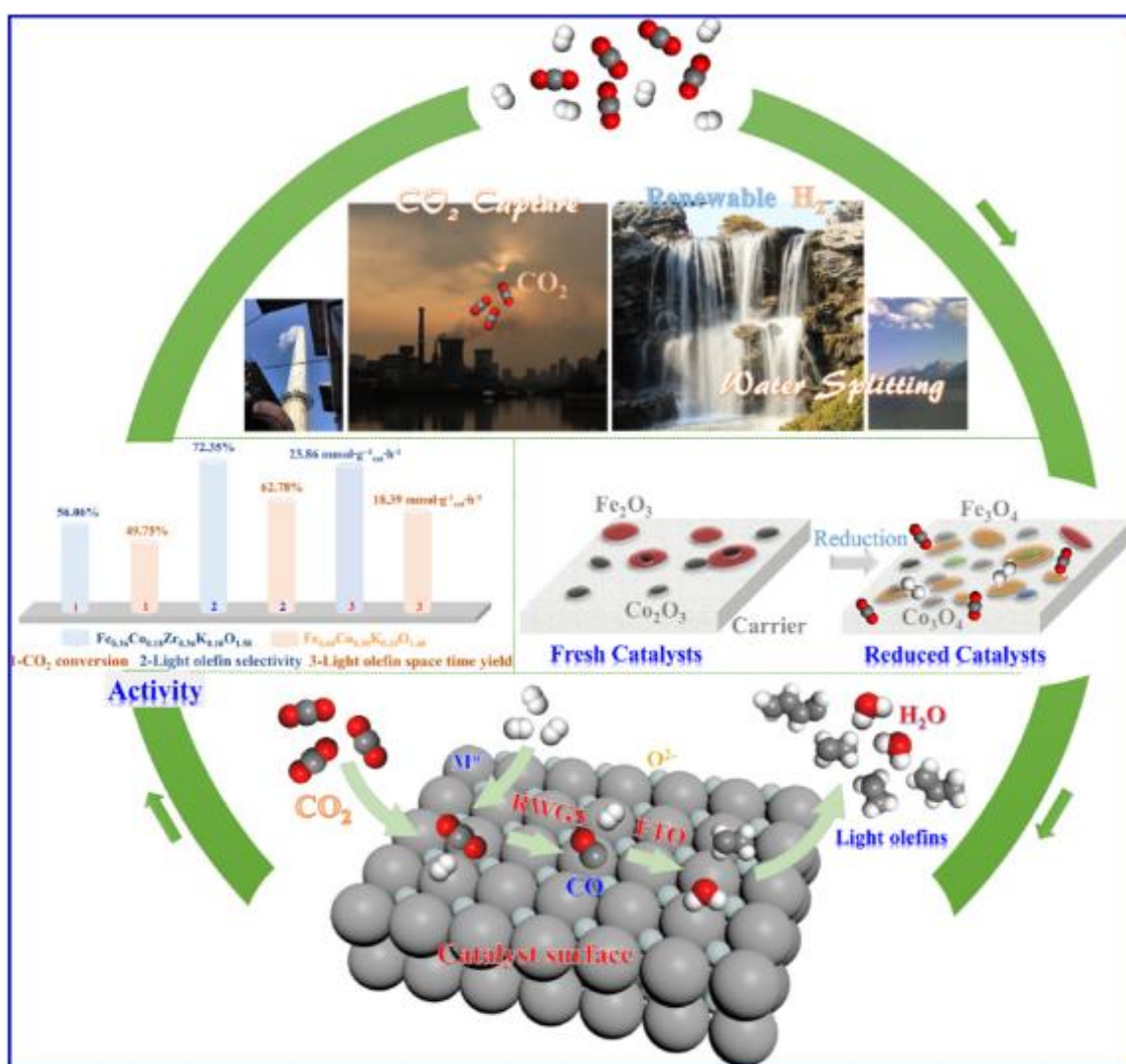
Scheme 13: (a) CO adsorption on Fischer-Tropsch synthesis reaction site. (b) Chain initiation step on FTS reaction site [130].



Scheme 14: Continued from

Scheme 13, (c) Chain growth step on FTS reaction site. (d) Chain termination steps on FTS reaction site [130].

5.3 Catalytic evaluation studies and conclusions



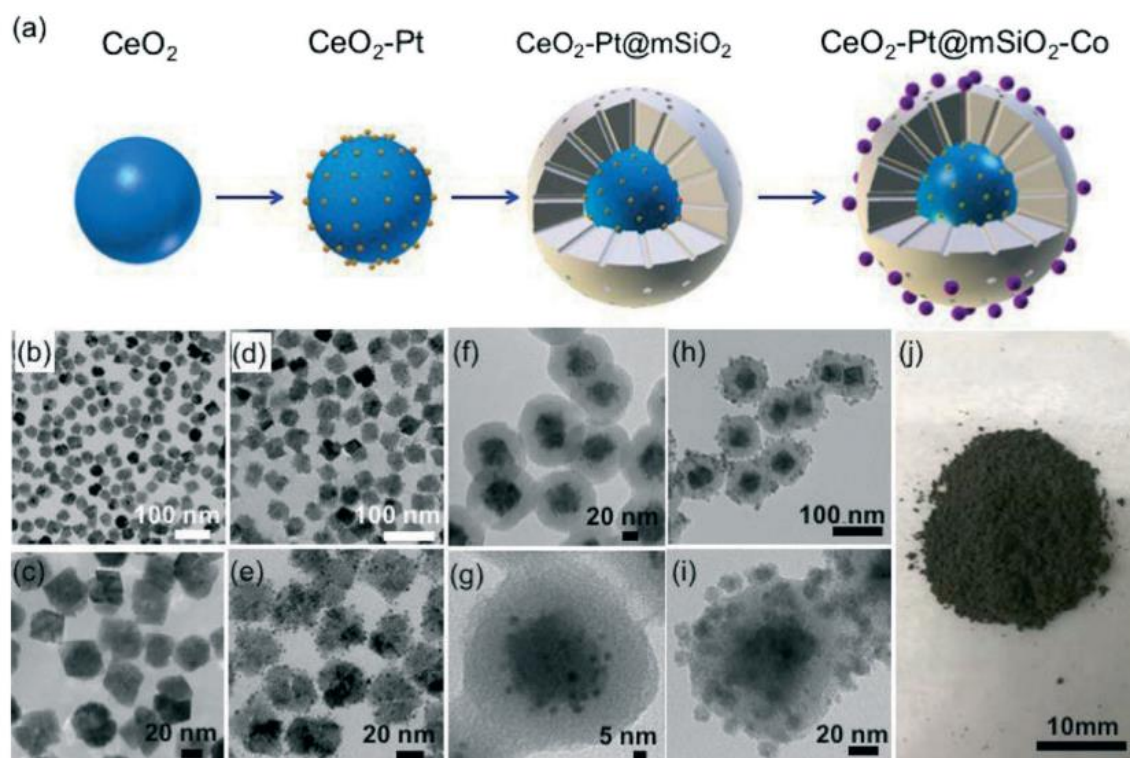
Picture 5: Concept of catalytic hydrogenation of CO₂ to olefins and the close of the carbon cycle [131].

In the framework of the present thesis, the latest advances on the catalytic hydrogenation of carbon dioxide to olefins are presented and discussed. An abundance of experimental catalysts and data were found and examined. All of them are still at an experimental level, since there is still no attempt for mass production of olefins via catalytic hydrogenation of carbon dioxide. It seems that the lack of detailed analysis of the micro kinetics of the reactions (RWGS and FTS) is still an important benchmark that needs to be crossed in order to realize and anticipate the activity/selectivity of the various catalysts. In addition, there still needs to be a techno economic assessment for a scale-up of catalytic hydrogenation for industrial applications. Cost analysis of high selective but expensive catalyst in comparison with low selective but cheap ones will have to be conducted in order to find the most efficient solution, which may lead to the commercialization of the method.

Still, the articles and reviews on the catalysts for hydrogenation of carbon dioxide to olefins were numerous. Most of them are recent works and are enriched with interesting experimental details like procedures for the catalyst's synthesis, information on experimental conditions like temperature, pressure, CO₂/H₂ ratio, weight hourly space velocity (WHSV), etc. and final yields and selectivity towards products.

The research work, included on the present thesis, was categorized according to the type of catalysts used. Important work has been conducted on Iron-based catalysts with various supports and promoters, especially zeolites like SAPO-34 and K ([90], [91], [101], [129]–[135], [136]–[139]), Zinc-based catalysts ([90], [91], [130], [140]–[142]) and bifunctional catalysts ([143], [144]), while catalysts with Cu, Na or In were mentioned and compared in these studies.

During the experiments, the catalysts were characterized by various methods of capturing the image of surface and pore-diameter with transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTM) images. High-angle annular dark-field (HAADF), which is a scanning transmission electron microscope method (STEM), was used in many cases for capturing images of the element distribution of the catalysts. X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used systematically to characterize the elemental structure of the catalysts before, during and after the experiments. The images and charts, produced by the characterization methods offered insight into the structure and surface features of the catalysts. In [Picture 6](#) for example, there is a step-by-step analyses of the construction of a $\text{CeO}_2\text{-Pt@mSiO}_2$ tandem catalyst, with scale-up images of the catalyst, starting with TEM images at 100nm and reaching 10 mm, visible to the naked eye.



Picture 6: Synthesis and characterization of the $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ tandem catalyst. (a) Schematic of the synthetic process followed by TEM images of each step: (b and c) CeO_2 nanoparticles, (d and e) overgrowth of Pt nanoparticles on CeO_2 , (f and g) silica shell coating on $\text{CeO}_2\text{-Pt}$ composite nanoparticles, (h and i) deposition of Co nanoparticles on $\text{CeO}_2\text{-Pt@mSiO}_2$, and (j) scaled up preparation of $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ nanoparticles. One-pot synthesis can yield 300 mg of catalyst [3].

Fisher-Tropsch catalysts with high selectivity to olefins (FTO) and CO_2 conversion are still in an early stage of research. The recent exploits of natural gas consumption, though, leads the scientific community to further study FTO synthesis, which could provide information on the hydrogenation of carbon dioxide to olefins.

While unprompted iron-based catalysts do not seem to lead to desirable olefin products, Fe promoted with K supported on reduced graphene oxide exhibits promising selectivity to lower olefins, but with low CO₂ conversion [137].

In the search for FTS catalysts promoters, Mn has been widely studied, exhibiting interesting results with a Co₂C catalyst. During the experiment conducted in the research of Zhong *et.al* [147], the Mn promoted catalyst shows a 31.8% CO conversion with olefins selectivity of up to 60.8% and with low CH₄ production. The authors noticed that by adding Mn as a promoter, the nanoparticle geometry of the catalyst changed to nanoprism with exposed (101) and (020) facets, favouring olefins selectivity.

Moreover, alkali metal promoters tend to increase the binding energy of carbon dioxide while at the same time decrease the binding energy of hydrogen, which leads to less selectivity towards CH₄. For instance, it was reported that by adding potassium as a promoter to Fe-Co-Zr polymetallic fibber catalyst, the olefin selectivity changed from <5% to 27.5% [148]. Respectively, K promoter acts as an electron donor to the catalyst, which works in favour of olefin yielding. In a similar manner, G, Muthu Kumaran *et.al* [149], investigated the effect of different alkali metals like Li, Na, K, Rb and Cs on iron oxalates. They concluded that the promoter with the largest yield towards olefins was Rb, followed by K, Cs, Na, and Li. Also the basicity of alkali metal promoters appears to have a direct impact on the stability of the iron-base catalyst.

While, single-material based catalysts show moderate efficiency, new studies on tandem catalysts took place in order to create multi-stage catalysts with application to both RWGS and FTO synthesis, since the Fisher-Tropsch mechanism works better with CO consumption. During a study conducted by Jiao, Feng *et.al* [150], a ZnCrO_x catalyst combined with a mesoporous SAPO zeolite (MASAPO) was used for the hydrogenation of CO to light olefins. The zeolite pores of MASAPO played an important role in increasing the selectivity of the catalyst towards the desirable product, controlling the intermediate step of C-C coupling. The authors explored the effect of the zeolite by comparing the efficiency of ZnCrO_x with that of ZnCrO_x/MASAPO, with a CO feedstock (Figure 26). Upon adding MASAPO zeolite, the selectivity of CH₄, dropped from 50% to lower than 10% while the selectivity towards olefins was increased.

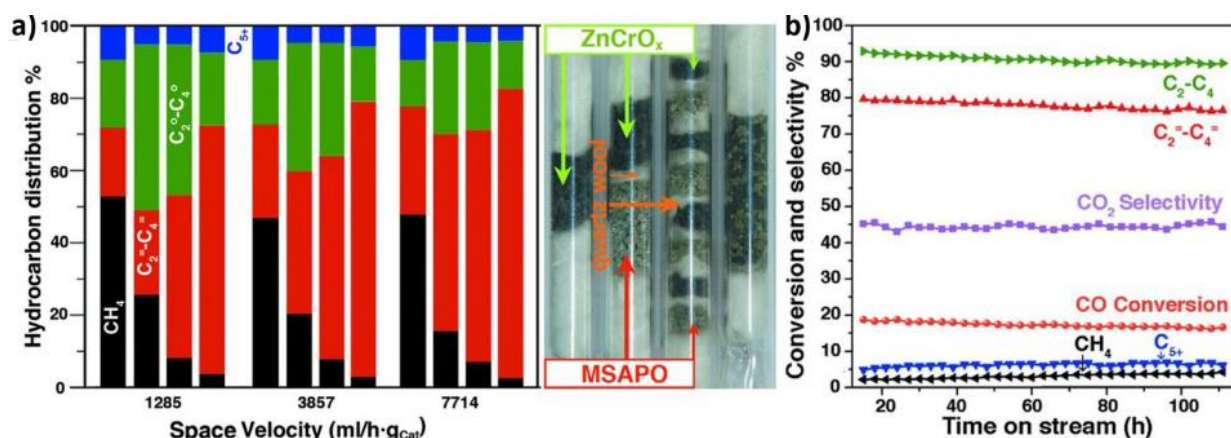


Figure 26: Catalytic performance of ZnCrO_x/MASAPO for syngas to light olefins. a) Reaction performance over the catalysts packed in different modes as a function of space velocity. Mode 1: ZnCrO_x only; Mode 2: MASAPO packed below ZnCrO_x; Mode 3: MASAPO and ZnCrO_x packed in an alternating layers; Mode 4: MASAPO and ZnCrO_x well-mixed. b) Stability test of a composite catalyst with ZnCrO_x:MASAPO ratio = 0.9. Reaction conditions: T = 400 °C, P = 2.5 MPa, WHSV = 6.8 L h⁻¹ g⁻¹, H₂:CO₂ ratio = 2.5 [150].

It seems that, zeolite materials are essential in sifting the selectivity of the catalyst towards larger quantities of light olefins by controlling the C-C coupling and cracking larger hydrocarbons fragments into olefins. Catalysts based on metal oxides (Fe_3O_4 , In_2O_3), bimetallic (Co-Fe, Co-Fe-Zr) and noble metals (Pt, Pt-Co) combined with zeolites are able to keep the stability of the catalyst longer and under high temperatures, while shifting the reaction towards producing olefins [143].

The local structure of each active component directly affects the interface between the catalyst and the consumption of feedstock. Xie *et.al* [140] used an interesting approach to characterize the activation sites of a $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ catalyst with a well-defined nanostructure (Picture 6). Through the interface analysis, the authors reached the conclusion that the CeO_2/Pt reacts at first with carbon dioxide and hydrogen producing CO via the RWGS reaction, followed by CO hydrogenation by the Co/ mSiO_2 to light olefins $\text{C}_2^- \text{-C}_4^-$ via the FTS, with selectivity of 60%. Yet the selectivity of the hydrocarbons over the $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ did not reach the levels of $\text{Fe}_3\text{O}_4/\text{H-ZSM-5}$ catalyst, conducted by Wei *et.al* [151], which achieved selectivity of up to 78% for lower olefins without a CO intermediate step. In addition, the use of noble metals like Pt, seems unattractive for industrial applications due to the high prices of noble metals.

Designing tandem and novel catalysts, which preserve high selectivity and stability under suitable industrial conditions, require a systematic approach on the condensation of microkinetics of the reaction. By applying the density functional theory (DFT) calculations (Figure 27), the various catalytic pathways become clear. During DFT calculations, reactions are proposed according to the energy level of the catalyst in a time-lapse. Other measurements, like kinetic Monte Carlo (KMC) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), could also be applied *in situ* in order to provide a better insight into the kinetic mechanism of the reaction.

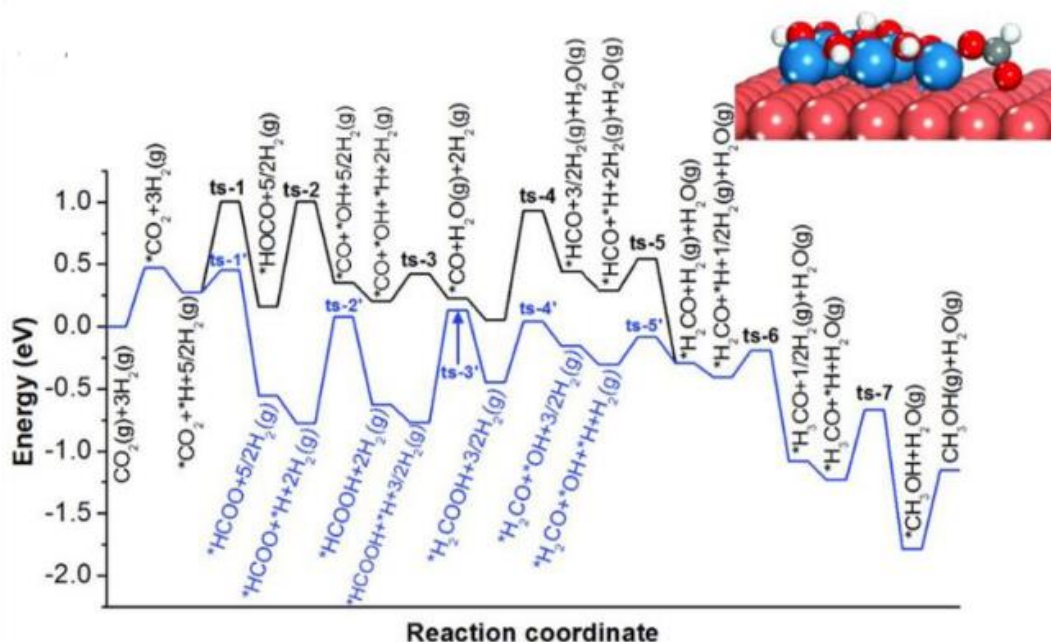


Figure 27: Proposed reaction mechanism of CO_2 hydrogenation to methanol over Zn-Cu bimetallic surfaces by DFT calculations [143].

Unfortunately, the insight of theoretical DFT calculations on reactions is limited, since the reactions usually take place in laboratory conditions, in ultra-high vacuum or on well-defined, single crystal surface. The ideal conditions cannot always apply to applications outside the sterile environment of laboratory, or even to small scale pilot reactors.

Nevertheless, as the computing power increases exponentially, machine learning could be applied on DFT calculations which will allow a deeper understanding of the complex catalytic network, involved in the catalytic hydrogenation of carbon dioxide towards olefins. For example, there is still uncertainty on the pathway that leads to the CH₄ formation during the RWGS. Successful DFT calculations could indicate if the formation of methane during RWGS is an intermediate step of the reaction or if it is formed separately. In the case of the latter, the use of appropriate catalyst could avoid the formation of methane altogether. In similar way, DFT calculations could clarify the paths of RWGS, which will lead to the desirable product. The data collection for a successful DFT model must be gathered *in situ* of the reaction in order to validate the result of the calculation method [143], [152].

While zeolite seem to be extremely beneficial in increasing the selectivity of metal-based and tandem catalysts towards olefins, catalytic deactivation may occur due to carbonaceous deposits on the active site which block the pores of the zeolite. Moreover, during the time-laps of the catalysis, a phase transformation may occur, which decrease the efficiency and selectivity of the catalyst. Furthermore, during RWGS, FTS and MTO reactions, large quantities of H₂O are produced which can work in either a positive or negative way. For example, if water is added to a Co-based catalyst during FTS, the selectivity towards olefins may increase since less hydrogen gets absorbed by the surface of the catalyst. Instead, if water is added to zeolites during FTS, the high temperature which usually exists during the reaction will cause structural changes, at the expense of the crystal geometry of the zeolite, which will cause deactivation of the catalyst. In order to avoid side effects caused by water, some methods of water concentration or evaporation could be applied.

Another potential method to increase the “life expectancy” of zeolites is to synthesize nanocrystals appropriate to the catalyst. SAPO-34 for example, has been recrystallized during the research of Yang *et.al* [153], which resulted in increasing the catalytic performance and decreasing the acidity [143].

Having pinpointed some useful information on the effectiveness and evaluation of the various catalysts, a state of the art table of 25 catalysts was constructed from various references in order to confirm the facts made by the references so far, and to allow for the contribution of additional ones. In order to compare the various catalysts, several calculations were made on the factors of every catalytic experiment, in order to have the same magnitude and be comparable.

Table 13: Concentrated table of 25 catalysts adopted from Ref.

Catalysts	H ₂ :CO ₂ ratio	WHSV/GHSV	Temperature (°C)	Pressure (Mpa)	CO ₂ conversion (%)	Olefin selectivity (%)	Main byproduct (%)	Ref.
Fe-Zn-K	3.0	1000/h	320	0.5	51.0	53.5	CH ₄ (34.8)	[136]
Fe/Alumina	3.0	3400/h	400	2.0	48.9	44.2	CH ₄ (48.4)	[154]
R-FCKZr	4.0	3500/h	310	2.0	64.0	63.4	C ₂ ⁰ -C ₄ ⁰ (32.0)	[131]
K-Fe	3.0	1200ml /(g _{cat} *h)	340	2.0	38.0	34.0	CH ₄ (21.0)	[155]
K/Fe	3.0	2700ml /(g _{cat} *h)	340	2.0	38.0	34.0	C ₅₊ (30.0)	[156]
Fe-K/HPCMs-1	3.0	3600ml /(g _{cat} *h)	400	3.0	33.4	47.6	CO (38.9)	[103]
K-Fe/ZrO ₂	3.0	1200ml /(g _{cat} *h)	340	2.0	43.0	44.0	C ₅₊ (27.8)	[157]
Fe-Ce/KY	3.0	1900ml /(g _{cat} *h)	300	1.0	20.1	36.7	C ₅₊ (49.6)	[158]
K-Fe/Graphene Oxide	1.0	4970ml /(g _{cat} *h)	340	2.0	58.0-64.0	68.0	CH ₄ (20)	[159]
K-Fe- Co/Al ₂ O ₃	3.0	650ml /(g _{cat} *h)	300	1.1	31.0	57.8	CO (18)	[160]
K-FeCu/Zeolite Beta1	2.0	360ml /(g _{cat} *h)	300	1.0	63.9	29.2	C ₁ (31.5)	[161]
K-FeCu/ZSM- 5	2.0	320ml /(g _{cat} *h)	300	1.0	81.1	30.3	C ₅₊ (37.8)	[161]
92.6Fe7.4K	3.0	1120ml /(g _{cat} *h)	300	2.5	41.7	23.0	C ₅₊ (56.0)	[162]
Mn/Na/Fe	3.0	250ml /(g _{cat} *h)	320	3.0	38.6	30.2	C ₅₊ (42.1)	[156]
CuFeO ₂ -12	3.0	1800ml /(g _{cat} *h)	300	1.0	18.1	31.3	C ₅₊ (60.3)	[163]
Cu-Zn- Al/HBeta zeolite	3.0	180ml /(g _{cat} *h)	300	1.0	27.6	43.2	CO (53.4)	[164]
Zn-Ga-O/SAPO-34	3.0	4030ml /(g _{cat} *h)	370	3.0	13.0	86.0	C ₂ ⁰ -C ₄ ⁰ (10.0)	[165]
ZnZrO/SAPO	3.0	3600ml /(g _{cat} *h)	380	2.0	12.6	80.0	C ₂ ⁰ -C ₄ ⁰ (12.0)	[144]
Zn-Na- Fe ₅ C ₂	2.0	1600ml /(g _{cat} *h)	340	2.0	77.2	25.9	C ₅₊ (40.6)	[166]
Zn-CrO _x /MSAPO	2.5	500ml /(g _{cat} *h)	400	2.5	17.0	80.0	C ₂ ⁰ -C ₄ ⁰ (13.5)	[167]
Zr-In ₂ O ₃ /SAPO- 34	3.0	470ml /(g _{cat} *h)	400	3.0	35.0	80.0	C ₂ ⁰ -C ₄ ⁰ (12.0)	[146]
In-Zr/SAPO-34	3.0	9000ml /(g _{cat} *h)	400	3.0	35.5	76.4	C ₂ ⁰ -C ₄ ⁰ (13.0)	[168]
In ₂ O ₃ -ZrO ₂ /SAPO- 34	3.0	220-259 ml /(g _{cat} *h)	400	1.5	20.0	80.0-90.0	CO(13.0)	[169]
CeO ₂ -Pt@mSiO ₂ - Co	3.0	1300ml /(g _{cat} *h)	250	0.6	26.0	59.0	CH ₄ (41)	[140]

WHSV: weight hourly space velocity [=] $ml\ g_{cat}^{-1}h^{-1}$

GHSV: gas hourly space velocity [=] h^{-1}

All the reactions use as a feedstock CO₂ or CO which results from a WGS or RWGS.

All the reactions produce CO and hydrocarbons; CH₄, C₁, C₂⁰-C₄⁰ paraffins, C₂⁼-C₄⁼ olefins, C₅₊

At first glance at Table 13, it becomes clear that the use of metal-based catalysts (Fe, In, Zr, Zn, Cu, Mn and Ce) dominate the catalytic hydrogenation of carbon dioxide to olefins. All the reactions took place at a temperature range of between 300-400°C and high pressure, from 0.5 to 3.0 Mpa. Hence, the use of metal-based catalysts may contribute to strengthen the stability and efficiency of the catalytic for long periods of time (100-250h).

Nevertheless, the use of a metal-based catalyst, like iron, without promoters exhibits a very low yield towards light olefins while it seems to favour yields towards methane. The use of appropriate promoters is mandatory in order to shift the yield of the reaction towards the desirable product. Noble metals, like Pt, showed promising results with 26% of the total CO₂ converted and selectivity towards light olefins close to 60%. On the other hand, the basic by-product of the reaction is methane at 40% yield, which may be problematic, since it will need to be processed further. In addition, the use of noble metal materials is discouraged due to the high prices and the scarcity of noble metals.

Adding potassium promoter to metal-based catalysts seemed to do the trick, since it significantly raise the selectivity of the catalyst towards light olefins, with the most interesting application on a Fe-based catalyst supported on Graphene Oxide and promoted by K (K-Fe/Graphene Oxide). The addition of K shifted the selectivity from methane towards light olefins, with a 54-68% conversion of the total CO₂ and an excellent selectivity of 68% towards light olefins. Still, methane remained the main byproduct of the reaction, with an approximate yield of 20%. In addition, other K-promoted catalysts showed promising results on CO₂ conversion and light olefins selectivity, in comparison with Cu or Mn promoters.

The most promising results for future industrial applications were exhibited from the various zeolites used as support of the catalyst. Zn-CrO_x /MSAPO showed very high selectivity towards olefins with a selectivity of 80%, whereas the main by-product consisted of paraffins, a useful compound for the petrochemical industry. Similar results were presented by Zr-In₂O₃/SAPO-34, ZnZrO/SAPO, In₂O₃-ZrO₂/SAPO-34 and Zn-Ga-O/SAPO-34 with selectivity towards light olefins ranging between 80 to 90%.

Interestingly enough during the catalytic test of the bifunctional Zr-In₂O₃/SAPO-34, the highest selectivity, to date, was recorded. Among the other SAPO and SAPO-34 based catalysts, the Zr-In₂O₃ based on a SAPO-34 supported achieved the highest selectivity, reaching 90%. The bifunctional role of the catalyst rest on the fact that the Zr-In₂O₃ conveyed the captured CO₂ in methanol, while SAPO-34 used the produced methanol as an intermediate to achieve the high yields of light olefins. The pores of the zeolite directly contributed to the high olefin yields, since they worked as efficient activation sites.

Still, with the contribution of Table 13, assumptions can be made as regards the most effective state of the art catalysts that exist up to date. In terms of the conversion of the total CO₂ feedstock, K-FeCu/ZSM-5 reached the peak of 81.1%, with preferable selectivity towards longer hydrocarbons C₅₊ at 37.8%. As regards the highest selectivity yield towards light olefins, bifunctional In₂O₃-ZrO₂/SAPO-34 reached a 90% yield of the 20% converted carbon dioxide, with In₂O₃-ZrO₂ converting the CO₂ feedstock to methanol, while SAPO-34 converted the produced methanol to light olefins with high selectivity. Nevertheless, it must be noted that SAPO-34 is an expensive material which is deemed difficult for extensive industrial applications.

Table 13 offers a unique perspective into finding the catalyst that balances high conversion with high selectivity towards the desirable product. R-FCKZr or R- $\text{Fe}_{0.30}\text{Co}_{0.15}\text{Zr}_{0.45}\text{K}_{0.10}\text{O}_{1.63}$ shows a promising efficiency with significant carbon dioxide conversion and olefin selectivity. During the catalytic test, which lasted for 250h, the catalyst managed to convert 64% of the total carbon dioxide, while in the meantime yielded 63.4% light olefins, with the rest of the byproducts consisting of paraffins. The research of Gu *et al.* [131] could be a promising steppingstone towards producing systematically cheap catalysts with high conversion and selectivity, which could lead to pilot plans and industrial applications. In addition, the contribution of zeolite promoters supports is obvious and should be studied accordingly, with DFT calculations and experimental data of high-selective catalysts, like the ones that were mentioned in this thesis.

6 Outlook and final verdict

To summarize, the 21st century is being afflicted by environmental catastrophes. It is unavoidable, that the consequences of extensive fossil fuel consumption, will seriously impact the environment and by extension, societies in the near future. Still, simple and easy answers do not exist for complicated problems, and the attempts to reduce dependence on fossil fuels, is without doubt one of the most challenging endeavours the scientific community has undertaken.

Carbon dioxide emissions continue to rise and contribute to the green house effect. Nevertheless, emissions of carbon dioxide are basically carbon that is not utilized effectively. In the spirit of closing the carbon cycle by capturing and utilizing the unused carbon, new pathways are being investigated, towards a sustainable and prosperous future.

The method of capturing emissions varies, and the utilization pathways are numerous, with carbon dioxide being used from fertilizer for crops to basic chemical components and intermediates for electro-fuels. Although the abundance of methods and pathways may fill us with hope for the future, the applications of these methods are proving to be challenging. Any attempt at effectively applying carbon capture and utilization methods has drawbacks, which have to be taken into careful consideration, with the present and use of renewable sources of energy, in order to serve as realistic solutions. A systematic approach like the Life Cycle Assessment is mandatory, before any attempt at applying CCU systems to the industry can be achieved.

The petrochemical industry seems unmoved by the environmental impact of the increased consumption of fossil fuels. Still, improvements can be made that will have a significant impact on the total global carbon dioxide emissions, like, for example, the preference of naphtha steam crackers instead of the ones that use coal as a feedstock for the steam cracking of syngas into various hydrocarbons.

Nevertheless, the utilization of carbon dioxide via catalytic hydrogenation seems to be one of the most promising routes towards closing the carbon cycle. Hydrogen, produced by renewable sources of energy, can be utilized effectively, in synergy with the appropriate catalyst, for using carbon dioxide as a feedstock for various reactions which will result in value added products. Olefins hydrocarbons are important compounds used as a basic material for an abundance of everyday products.

By utilizing catalytic hydrogenation towards yielding carbon dioxide into light olefins, a new path towards a sustainable future is added. While the subject is still under careful examination, the catalytic experiments that have been conducted so far seem to be promising. Still, the absence of micro-kinetic models is an important gap that has to be filled in order to create industrial-efficient catalysts. Density functional theory calculations, in combination with *in situ* experimental data and machine learning, could be the key to unlocking future perspectives, for realistic micro-kinetics simulations of the reactions pathways.

That said, there is a lot of conducted research with valid points which can be used effectively for future researchers. The latest articles, reviews and papers on the subject of the catalytic hydrogenation of carbon dioxide to olefins were used as a knowledge-well for the completion of the thesis project. Even though there is still a need for mandatory research into the kinetics of the reactions and techno-economic assessment for industrial applications, the catalytic hydrogenation of carbon dioxide towards olefins is and will be an important field of research in the years to come.

7 References

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