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"CARBON DIOXIDE (CO$_2$) CAPTURE AND UTILIZATION TECHNOLOGIES"

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«ΤΕΧΝΟΛΟΓΙΕΣ ΔΕΣΜΕΥΣΗΣ ΚΑΙ ΜΕΤΑΤΡΟΠΗΣ ΔΙΟΞΕΙΔΙΟΥ ΤΟΥ ΑΝΘΡΑΚΑ (CO$_2$)»

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SCHOOL OF PRODUCTION ENGINEERING & MANAGEMENT

DIPLOMA THESIS

"CARBON DIOXIDE (CO$_2$) CAPTURE AND UTILIZATION TECHNOLOGIES"

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Περίληψη

Η επικείμενη εξάντληση των ορυκτών πόρων σε συνδυασμό με τις ορατές πλέον περιβαλλοντικές τους συνέπειες, έχει οδηγήσει την ανθρωπότητα στην αναζήτηση νέων μεθόδων για να καλύψει τις ενεργειακές της ανάγκες προς την κατεύθυνση της αειφόρου ανάπτυξης. Το τελευταίο συνεπάγεται την ανάπτυξη προηγμένων τεχνολογιών παραγωγής/αποθήκευσης ενέργειας, οι οποίες θα βασίζονται σε ανεξάντλητους πόρους και παράλληλα θα είναι οικονομικές και φιλικές προς το περιβάλλον. Προς την κατεύθυνση αυτή, η δέσμευση και μετατροπή εκπομπών CO_2 (το κατεξοχήν αέριο του θερμοκηπίου) σε αλκοόλες (μεθανόλη και αιθανόλη) δύναται να συμβάλλει τα μέγιστα στην κάλυψη των ενεργειακών αναγκών και στην προστασία του περιβάλλοντος.

Η παρούσα εργασία εξετάζει τις υπάρχουσες τεχνολογίες για την δέσμευση και μετατροπή CO_2. Παρουσιάζονται οι τρόποι παραγωγής και εκμετάλλευσής του παράγωγου καυσίμου. Ιδιαίτερη έμφαση δίνεται στη δέσμευση, αποθήκευση και χημική μετατροπή του διοξειδίου του άνθρακα σε μεθανόλη (CH_3OH).

Abstract

The impending depletion of fossil resources combined with their most visible environmental consequences has led mankind to seek new methods to meet its energy needs in the direction of sustainable development. The latter implies the development of advanced energy production and storage technologies, which will be based on inexhaustible resources while being economical and environmentally friendly. In this direction, capturing and converting CO_2 emissions (the most important of greenhouse gases) into alcohols (methanol and ethanol) can make the greatest contribution to meeting energy needs and protecting the environment.

The present thesis examines the existing technologies for CO_2 capture and conversion. The ways of producing and exploiting the derived fuels are presented. Particular emphasis is placed on the capture, storage and chemical conversion of carbon dioxide into methanol (CH_3OH).

Thanks

Coming to the end of my studies, I would like to thank my supervising professor, Dr. Michalis Konsolakis, for his valuable help and for the time and effort he has devoted to the preparation of the present thesis. I would also like to thank my family for their valuable support during all these years of study, because with their own hard work my dream of becoming an engineer came true.

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1.   Introduction

This chapter gives an introduction and overview of the thesis. Since the appearance of man on Earth, there has been a constant need for energy. In the beginning, energy took the form of fire; man used thermal energy for warmth, food preparation and illumination. Later man began to harvest wind to travel through the seas. Coal mining made its' first appearance in the 17th century and not long after the first steam engine was constructed. Over the years there has been an exponential increase in human energy needs, which goes hand in hand with the development of technology.

The Industrial Revolution was a historical milestone, which consolidated the use of fossil fuels in energy production. To this day, fossil fuels are the main and most common source of energy. However, few countries have the privilege of having deposits, which results in numerous political and economic tensions [1–4]. These tensions have led to fluctuations in fossil fuel prices.

A positive development in the rise in prices was the emergence of renewable energy sources (RES). The cost and the small life expectancy of fossil fuel deposits, as well as the severe environmental issues due to massive CO_2 quantities emitted by coal burning, led to the consideration of RES as alternative, inexhaustible and environmentally friendly forms of energy. RES present an ideal solution for countries that do not have fossil fuel deposits, as they could thus be energy-independent from other nations. Extensive use of RES could also help avoid the use of nuclear energy and its hazards (harmful accidents, non disposable nuclear waste etc). The concept of 'sustainable development' gains more and more popularity, so that many governments adopt 'green energy' policies. The present work also aims to contribute to the direction of sustainable development.

CO_2 is a gas abundant on Earth; one could support that it is endless. Its anthropogenic origin focuses on the burning of fossil fuels to generate electricity, power factories and power the means of transportation. Due to increased human energy needs, its concentration in the atmosphere has risen dramatically, so we are already at the point of climate change and global warming discussions. The development and large scale implementation of CO_2 emission reduction technologies is now, more than ever, crucial. This thesis examines the existing technologies for CO_2 capture and conversion as well as converting CO_2 emissions into alcohols, particularly methanol.

In Chapter 2 and 3 the sources of CO_2 emissions are examined. The concentration of CO_2 in the atmosphere rises year by year and is expected to rapidly reach even higher levels. CO_2 is a strong greenhouse gas, thus considered to add greatly to climate change and global warming. Various means of carbon sequestration are discussed, like oceanic carbon sequestration or geological or biological carbon sequestration.

In Chapter 4 a general summary of the various CO_2 capture and storage processes is given, focusing on post-combustion capture as well as on CO_2 capture methods in the transportation sector, the cement and steel industry and the naval sector. It is observed that the technological advancements require time regardless well-tested procedures such as oxyfuel combustion, chemical looping combustion (CLC) and calcium looping (CaL). The most commonly known post-combustion carbon capture and storage (CCS) method is

amine scrubbing. There have been examples of its application at commercial scale for the management of flue gases from coal firing.

In Chapter 5 details on oxyfuel combustion are presented, primarily by means of fluidized bed process. In oxyfuel combustion, oxygen replaces air in the combustion, which involves an air separation unit (ASU). To sustain temperature at optimum operating level and to provide a heat carrier, flue gas recirculation (FGR) is necessary. Oxyfuel combustion is particularly beneficial because the technology is unchallenging in its technical aspects and the resultant flue gas contains, apart from trace pollutants, mostly CO_2 and water vapour. Those can be effortlessly separated, rendering CO_2 available for additional utilization. Additionally, formation and reduction of pollutants like CO, NOx and SO_2 throughout oxyfuel combustion are described.

Finally, in Chapter 6, CO_2 to Methanol synthesis route is shown and discussed, by CO_2 hydrogenation. Methanol is a small but significant group in the chemical industry and a base matter for additional production of larger molecules. Methanol can also be utilized as an energy carrier and straight as a first-rate fuel, e.g. for internal combustion engines and direct methanol fuel cells.

2.   Carbon Dioxide

2.1.   Basic Information

Carbon Dioxide (CO_2) is a colourless gas. It consists of a carbon atom covalently double bonded to two oxygen atoms. It is one of the natural gases in the Earth's atmosphere and the current concentration of CO_2 is around 0.04% (410 ppm) by volume, a significant increase since before the Industrial Revolution the concentration of CO_2 in the atmosphere was 280 ppm [5]. Carbon dioxide in the atmosphere is of considerable importance for life on Earth. The pre-industrial concentration of CO_2 has been regulated by photosynthetic organisms and geological phenomena. CO_2 is also returned to water and air via the breathing mechanisms of fish and land animals. CO_2 is also produced by combustion of wood and fossil fuels.

2.2.   Carbon Cycle

The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere and atmosphere of the Earth. Such cycles, carbon along with the nitrogen cycle and the water cycle, are crucial for sustaining life on Earth. The carbon cycle basically maintains a balance that stops all of the Earth's carbon from entering the atmosphere as well as being stored entirely in rocks. This process works as a thermostat that helps keep Earth's temperature relatively stable [6].

2.3.   Greenhouse gases

Greenhouse gas (GHG) is any gas that has the property of absorbing infrared radiation emitted from Earth's surface, thus contributing to the greenhouse effect [7]. Human activity in the past century has caused an increase of GHG in the atmosphere and due to the greenhouse effect has caused global warming. Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and flue gases are the most important GHGs and CO_2 corresponds to 63% [8].

2.3.1. Carbon Dioxide

Carbon dioxide is generated from the oxidation of organic fuels, as well as food oxidation, decomposition of organic matter and industrial processes such as cement or steel production, power generation etc. Prior to the Industrial Revolution the CO_2 in the atmosphere was around 280 ppm in practically stable concentration. Since then, the extended use of fossil fuels has caused CO_2 concentration in the atmosphere to increase over 360 ppm. CO_2 production from fossil fuel varies depending on the quantity and type of fuel. For every ton of coal combustion, 2.5 – 36 tons of CO_2 are emitted (depending on carbon quality). Every ton of crude oil produces around 3 tons of CO_2 and every ton of natural gas emits 2.7 tons of CO_2. Having in mind that these fuels have different calorific value per weight unit, emissions are commonly compared based on combustion produced heat (kg CO_2 /toe released heat) [9].

Table 1.1 Emission Factors of known fuels [9]

Fuel	Emission Factor
Coal	≈5250
Brown Coal	5500-6500
Diesel	3000-3100
Mazut	3200-3300
Gasoline	2850-3000
Natural Gas	2250-2350

2.3.2. Methane

Methane (CH_4) is the main component of natural gas and coexists with other hydrocarbons in crude oil deposits. Its current concentration in the atmosphere is around 2 ppm and increases annually. A significant share of CH_4 emissions comes from leaks during transportation and other human activities [9]. CH_4 is a long-lasting GHG, which can increase the long-wave radiation and then consequence the rise of temperature [10]. Mentioned in the same study and as explained in [11], the CH_4 production is separated into three stages that consist of hydrolysis and fermentation phase, hydrogen production acetogenesis phase, and methane production phase. 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, CO_2, and H_2. Afterward, acetic acid or $CO_2 + H_2$ convert into CH_4 through methanogens. It is generally believed that during anaerobic biological treatment, about 70% of CH_4 in anaerobic biological treatment is derived from the decomposition of acetic acid, and the remaining CH_4 is produced from CO_2 and H_2 [12]. The CH_4 emission primarily strikes in the thermophilic phase due to the fast degradation of organic matter, which consumed oxygen to result in part-anaerobic condition to produce CH_4.

2.3.3. Nitrous Oxide

In relation to the biochemical cycle, nitrification and denitrification are two main processes to produce N_2O [13]. Under aerobic conditions, NH_4^+ is converted into NH_2OH with the aid of bacteria and archaea. Then, NH_2OH is oxidized to NO_2^- by the action of hydroxylamine oxidoreductase. Afterward, the NO_2^- is transformed to NO_3^- through nitrite oxidoreductase [14]. The transformation of NH_4^+ to NO_3^- is known as nitrification. However, N_2O is a product of denitrification and nitrification is one of the principal ways of nitrogen conversion in the composting procedure [11].

2.4. Sources of CO_2 Emission

A CO_2 emission source is a large, stationary source that emits more than 0.1Mt CO_2 annually from fossil fuel or biomass combustion. CO_2 emissions, in their majority, are product of carbon oxidation during fossil fuel combustion in power plants, oil refineries and large scale industrial facilities. Other than combustion CO_2 is also emitted from chemical, physical and biological transformation processes of materials. Such processes are the use of fuel as a raw material in petrochemical processes, the use of coal as a reducing agent in the commercial production of metals from minerals, the thermal decomposition of limestone and dolomite in the production of cement and lime, as well as biomass fermentation (such as sugar conversion to alcohol). The table below shows the top CO_2 emitters (Mt CO_2) by country as of 2017. It is noted that the World Total emissions of CO_2 in 1960 was 9411Mt [15].

Table 1.2 Top 6 & World Total Territorial CO_2 Emissions (MtCO$_2$) [15]

Countries	CO_2 Emissions (Mt CO_2)
China	9.839
USA	5.270
India	2.467
Russian Federation	1.693
Japan	1.205
Germany	799
World Total	36.153

3.   Carbon Sequestration

3.1. What is Carbon Sequestration?

Sequestration of carbon is a method in which atmospheric CO_2 is sidetracked or removed from an emission source. It is the technology of extended storage of CO_2 to lessen global warming and climate change. One of the options to achieve that is sequestering carbon (CO_2) in various carbon sinks. Carbon sequestration is a process through which CO_2 is captured and stored in a reservoir referred to as carbon sink. Such sinks can be subterranean saline aquifers, ocean water or aging oil fields. In depths bellow 800m, CO_2 has a liquid-like density that provides the potential for efficient underground storage [16]. The technologies that have been developed for and applied by the oil and gas industry, such as drilling wells, injection and monitoring methods can be adapted to storing CO_2 in deep geological formations.

3.2. Geological Sequestration

Geological sequestration of CO_2 is a method through which CO_2 is stored in deep geological formations in order to moderate high CO_2 concentrations in the atmosphere and avoid climate change [17]. Geological carbon storage reduces CO_2 emissions in the atmosphere if it is applied to the main stationary sources (power plants, steelmakers, cement plants, etc.), where CO_2 is captured, transported by pipeline and introduced into porous rocks below the surface [16]. This CO_2 once mixed with water will flow into the ground water and will remain CO_2 while some part will remain trapped as carbonate [17]. There are various rock formations that can store CO_2, as is for example tanks depleted petroleum gas, deep saline formations and radioactive seams [16]. The high financial risk and environmental hazards such as seismic disturbances, contamination of drinking water and adverse impacts on ecosystems are the main drawbacks of the storage method [18].

3.3. Biological Carbon Sequestration

Biological carbon sequestration involves the removal and storage of carbon from the atmosphere using biological storage areas such as soil, vegetation, wood products and wetlands. Biological carbon sequestration or as it is also known, terrestrial carbon sequestration, can be effectively used to address the challenges of climate change [19], while it is a natural way to make it cost-effective to limit the CO_2 concentration in the atmosphere. Biological sequestration is primarily accomplished by the environment. Nonetheless, technologies are also developed for the same purpose [20]. The types of biological sequestration include soil carbon sequestration and phytosequestration.

3.3.1. Soil carbon sequestration

Through photosynthesis, atmospheric CO_2 is captured by plants and converted to organic material, while a small percentage is transported through the roots of the plant to the ground where it is stored in organic and inorganic forms. Soil carbon sequestration and phytosequestration are more or less relevant terms. The efficiency of carbon sequestration in soil depends primarily on the climate, temperature, rainfall, the aluminium content, mineralogy, moisture content and texture of the soil [6, 7]. In order to enhance carbon capture, it is necessary to manage ecosystems properly using various advanced management practices such as restoration of degraded soils to increase biomass production. Some of the ways to increase organic carbon in the soil are: no-till farming, biochar, bioenergy crop, wood burial and various plant products.

No-till farming

Farmers usually prefer cultivation methods include physical disturbances in the soil to enhance soil respiration. These practices increase the soil aggregate turnover and result in a decrease in soil carbon content [22]. For sequestering and retaining atmospheric carbon into the soil, farming without tillage practices can be used to grow crops annually without any disturbance in the soil. Methods of no-till farming can enhance carbon content capacity of soil, and in that way, preservation of earlier crop increases carbon content in soil. This technology also helps to reduce soil erosion and improves infiltration as well as water preservation capacity of the soil [22]. Therefore, no-till practices add to soil carbon sequestration.

Biochar

Biochar, also called black carbon, is a very poor substrate for microorganisms and is therefore more resistant to microbial decomposition. Black carbon is generally chemically inert and extremely resistant to degradation [23]. Biochar has a look similar to charcoal. The difference between the two is that the first is derived from incomplete combustion process of wood and other organic materials in a limited oxygen condition and the second is the product of a complete combustion process [24]. Production of biochar, in combination with its storage in soils, is one of the strategies to remove CO_2 from the atmosphere. Biochar is resistant towards microbial decomposition so the long-term storage of carbon is possible. It is a product of biomass pyrolysis and can be in the soil from centuries to millennia [22].

Bioenergy crop

A plant species that can be used as a renewable energy source for future prospects is called bioenergy crop. These crops can be designed to enhance biomass and its energy potential so that the bioenergy production increases [25]. Conversion of the cultivation unit to bioenergy crop acts as a renewable energy source, thus reducing carbon emissions from fossil fuels as well as improving carbon sequestration in soil organic matter. All of this eventually helps to reduce the concentration of atmospheric CO_2 [10, 13]. It is reported that bioenergy crops have the potential to seize 317.5Gt CO_2 per year [19]. Bioenergy crops can be used as an alternative source of energy without increasing net CO_2 emissions, while increasing biomass yields traps atmospheric CO_2 and therefore helps to regulate atmospheric carbon dioxide. The bioenergy capacity and CO_2 capture varies with the kinds of crops [25].

Wood burial

For the process of wood burial, dead or live trees are harvested and buried in areas above ground, under conditions generally anaerobic. This does not allow the decomposition process to take place, but CO_2 will remain isolated [20]. It has been reported that wood burial has the potential for long-term carbon sequestration, which is 10±5 Gt of carbon per year. Today we have about 65 Gt of carbon in the world's forests in the form of crude wood fragments suitable for burial [26].

Various plant products

Different types of plant products such as wood used as raw material for construction of buildings and houses, could store carbon for long time. *Phytoliths* (plant derivatives released after burning, digesting and decaying a plant [27]) serve as a soil carbon pool. The global potential of *phytoliths* as carbon storage represents 1,5Gt of carbon annually [8].

3.3.2. Phytosequestration

Photosynthesis is a process by which plants convert inorganic carbon into organic carbon, CO_2 in carbohydrates thanks to solar energy. In this way the atmospheric carbon is distributed over the different parts of the plant. Carbon stabilization processes, therefore, improve the isolation of global atmospheric carbon. It has been said that enhancing photosynthetic efficacy, either using natural or mechanical approaches, will lead to the concentration and storage of carbon to increase [27]. Various photosynthetic organisms such as C_3 plants, C_4 plants, crassulacean acid metabolism plants (CAM), cyanobacteria, microalgae and others have different types of carbon binding pathways. In addition to the C_3 plants, all the others mentioned above contain some form or another of carbon concentration mechanisms (CCM) [20].

C_3, C_4 and CAM photosynthesis[1]

In C_3 plants, CO_2 enters the plant cell from the stomata in the intracellular spaces of air reaching the chloroplast. The CO_2 in chloroplast is stabilized by the RuBisCO enzyme and converted to three organic carbon compounds (phosphoglyceric acid), resulting in the name C_3 photosynthesis [28]. The RuBisCO is a bifunctional enzyme that acts as a carboxylase and oxygenase (low CO_2 environment). The high concentration of O_2 decreases the specificity of the enzyme towards CO_2 [20]. The enzyme activity to act as carboxylase or oxygenase depends on the ratio of carbon dioxide and oxygen molecules. C_4 photosynthesis

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[1] The key difference between C3, C4 and CAM photosynthesis is the way plants extract carbon dioxide from sunlight, which depends largely on the plant's habitat. C3 photosynthesis produces a three-carbon compound via the Calvin cycle while C4 photosynthesis makes an intermediate four-carbon compound that splits into a three-carbon compound for the Calvin cycle. Plants that use CAM photosynthesis gather sunlight during the day and fix carbon dioxide molecules at night [164].

represents a modification of the C_3 plant to enhance the enzyme-carboxylase activity [29].

It has a specific tissue layout called Kranz anatomy, which facilitates the reaction of RuBisCO and CO_2 to stabilize the carbon. In the photosynthetic pathway C_4, CO_2 is absorbed by the phosphoenylpyruvate (PEP) enzyme, which forms the first product of four-carbon compound oxaloacetate (OAA).

They are therefore called C_4 plants [30]. In addition to C_3 and C_4, there is another way of photosynthesis found in the CAM to cope with the warm and dry environment. During the night, the CO_2 absorbed by the PEP enzyme present in the cytosol, forming malate and stored in vacuoles which transport it to the chloroplast during days where there occurs the capture of CO_2 from RuBP enzyme. Thus, the CAM units are able to operate efficiently in harsh conditions for water and CO_2 [31].

Cyanobacterial carboxysomes

Cyanobacteria have a unique type of CO_2 concentration mechanism to improve the effectiveness of the RuBisCO enzyme in photosynthesis. In cyanobacteria carboxysome, there are structures and various inorganic carbon carriers for the concentration of CO_2 near the enzyme. Carboxysomes are protein polyhedral bodies with an outer shell of protein. Most of RuBisCO content of the cell is present in carboxysome [11, 23]. There are transporters within the cell that undertake the accumulation of bicarbonates (HCO_3^-) and carbon dioxide (CO_2). An enzyme in the carboxysome converts an accumulated cytosolic pool of HCO_3^- into CO_2. Concentrated CO_2 is used by the RuBisCO enzyme in the carboxysome [32]. Therefore, in the cyanobacterial carboxysomes there are areas where the level of CO_2 remains high for capture with RuBisCO to stabilize CO_2 [8].

Algal pyrenoids

Greater variety in CO2 concentration mechanisms is found in algae than in cyanobacteria. The binding of carbon to the algae is carried out with the help of a structure known as pyrenoids. Pyrenoids are akin to cyanobacterial carboxysomes, although they are in a chloroplast layer and contain the RuBisCO enzyme [33]. Pyrenoids help concentrate CO_2 near RuBisCO and stop the photoabsorption process [11, 25].

3.4. Oceanic Carbon Sequestration

Another viable strategy for mitigating the concentration of carbon dioxide in the atmosphere is oceanic carbon sequestration, which includes capture of carbon dioxide from large sources and injecting it into deep ocean. Ocean works as a large long term sink for CO_2 emissions and it takes around 2 gigaton of global net of carbon annually [18]. Due to pressure difference between ocean and atmosphere, carbon dioxide is absorbed by the ocean. Practically, there is no storage limit of CO_2 in deep ocean, as the ocean covers 70% of the surface of the earth with average depth 3800m. However, carbon dioxide is an acidic gas and seawater has a mild alkaline condition due to dissolved minerals. The method of storing carbon dioxide in the ocean has the harmful potential of turning seawater acidic and can lead to ocean acidification.

4.   Post-Combustion CO₂ Capture and Storage in Industry

4.1.   Introduction

Post-Combustion carbon dioxide capture and storage (CCS) is one of the most promising technologies to cut down CO_2 emissions from conversion of fossil fuels. It is commercially available today, in the form of amine scrubbing. Other methods of CCS also exist in the commercial or semi-commercial scale, such as pre-combustion capture and oxyfuel combustion. There are many industrial scale opportunities for CCS technology implementation, in order to mitigate carbon dioxide emissions, which include cement and steel industries as well as sectors like fossil fuel power stations[16].
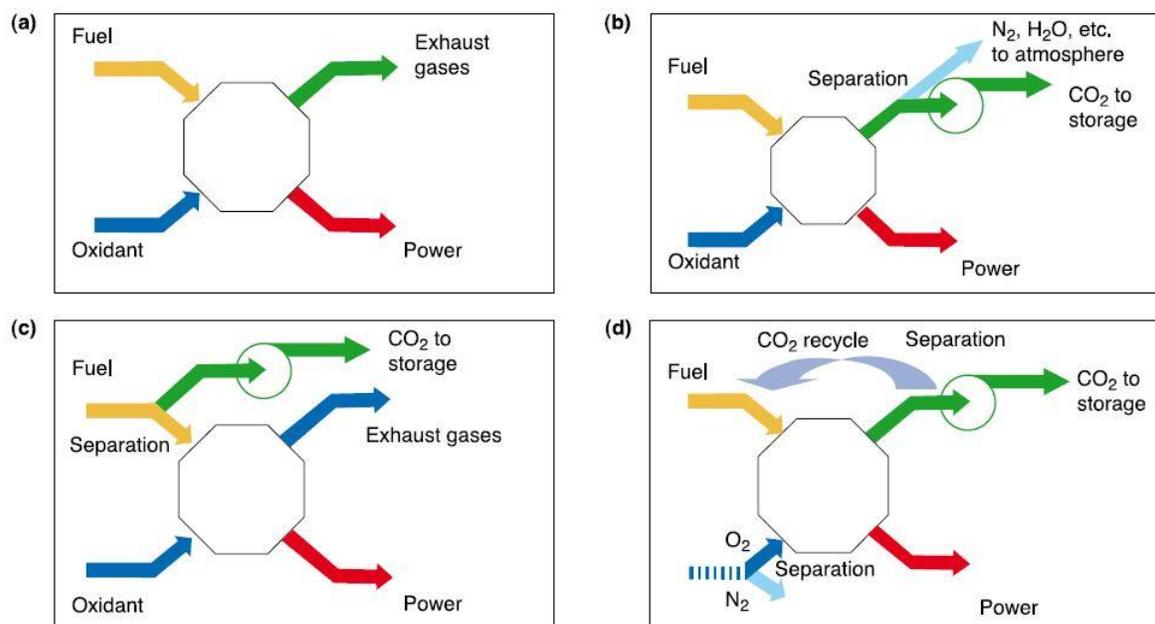

Figure 4.1 a) Schematic diagram of fossil-fuel-based power generation; b) Schematic diagram of post-combustion capture; c) Schematic diagram of pre-combustion capture; d) Schematic diagram of oxyfuel combustion [16]

Currently, the most commonly used CCS technology is amine scrubbing, which has been established in commercial scale for carbon combustion exhaust gases. Significant projects that represent CCS demonstration are the 115MW SaskPower Project at Boundary Dam, Saskatchewan [35], the 240MW Petra Nova facility in Houston, Texas [36]. Both can capture up to 90% of the CO_2 produced. Each and every technology presents its problems. As for amine scrubbing, we have to deal with high economic costs, volatized amine loss and significant efficiency penalty associated with the amine sorbent regeneration process using steam. However, there isn't an important implementing issue, aside the cost and efficiency regarding penalties. For pre-combustion processes (or else gasification), economic costs are again an issue, especially if the exhaust gas needs to be shifted to produce H_2; pre-combustion capture has proved not to function properly in large-scale industrial plants, when the fuel to be gasified is coal. A recent big-scale failure in pre-combustion technology is the 582MW Kemper County project in Mississippi, whose price was around $7.1 billion [37]. Regarding oxyfuel combustion, the main drawback is the absence of full-scale demonstration plants.

It is considered more likely that many economies turn to natural gas over coal due to low prices of natural gas and the public pressure for air quality improvement. It is notable that SaskPower decided to construct a natural gas powered plant in the future, as well as expanding solar and wind power, rather than going after more CCS technology with amine scrubbing. However, if CCS technologies are not included, the anthropogenic CO_2 emissions will continue to rise to exceed 450 ppm CO_2 and towards 500-600 ppm before the turn of the century. Thus, both for coal-powered, as well as gas-powered plants the use of CCS technologies is crucial for preventing CO_2 concentrations to reach 500-600ppm. The most promising option would be to ascertain the principle that for every tone of CO_2 produced the same amount is stored, sequestered or used (on condition that use does not make up a short term route for reintroducing the CO_2 back into the atmosphere).

4.2.   Industrial CCS

Another subject worth mentioning is whether there are more sectors in which regulating CO_2 emissions is cost-effectively beneficial and amine scrubbing might not be the obvious technical solution. Obviously, there are a lot of major candidates, such as transportation, steel industry, cement industry and oceanic transportations. Despite the fact that these areas are accountable for about 20% of world CO_2 production [38], it is improbable that the post-combustion CO_2 capture methods used for the power generating sector would be appropriate due to flue gas quality. Thus, rises an opportunity for new post-combustion CCS technologies to develop, especially if CO_2 mitigation is tied with profit.

4.3.   Transportation

Regarding CCS applications in transportation, it is unlikely that it is cost-effective due to simple weight considerations. Instead, uses of advanced batteries or hybrid technology prove to be more viable options. Perhaps the only problematic area is aviation, where use of hydrogen and batteries are likely to be excluded for safety and weight reasons. On the contrary, these issues might be solved by capturing CO_2 from the atmosphere, following an air capture route [39]. However, it needs to be said that there is scepticism regarding the ability of negative emissions technology to really affect anthropogenic production of CO_2 and the opinion that "negative emissions technology is not an insurance policy but rather an unjust and high-stakes gamble" has been stated by Howard J. Herzog [40]. Even so, regarding aviation, the idea that negative emissions could displace fossil fuels seems more modest and feasible.

Alternative technologies may come to light, though it is clear that most alternatives are relatively new and cannot be depended on to present effective solutions without extensively more research and potentially substantial investment. Thus CCS is unlikely to be precluded.

4.4. Cement Production

Global CO_2 emissions from cement production were estimated as 1.45 ± 0.2 Gt CO_2 in 2018 [41]. As such, the cement industry is attracting more and more attention as a plausible CCS implementation sector. Which kind of CCS technology is used can depend on various aspects, like size and location of the factory but it is clear that amine scrubbing is effectively used in this area to cut down emissions, with estimated cost in the proximity of 90-100 Euro/ton of avoided CO_2 [42].

Calcium looping (CaL) is the constant temperature swing cycling of a Ca-based CO_2 sorbent between two reactors, a calciner and carbonator, where CO_2 is released and absorbed, respectively. The basics of the cycle is that CO_2 passes through a CaO based sorbent, usually from limestone, and reacts with the reversible reaction in Eq. 1. The forward step is known as calcination and is an endothermic process and the backwards step is known as carbonation [43].

$$CaCO_{3(g)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \quad \Delta H^o = +178 \text{ kJ/mol} \tag{1}$$

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \quad \Delta H^o = -41 \text{ kJ/mol} \tag{2}$$
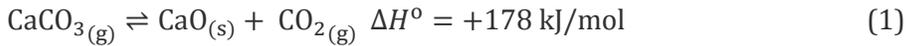
The equilibrium vapour pressure of CO_2 over CaO according to Eq. 1 can be calculated as a function of temperature. At a given temperature, partial pressures of CO_2 higher to the partial pressure of the equilibrium will favour carbonation, while those lower than the equilibrium will result in calcination.
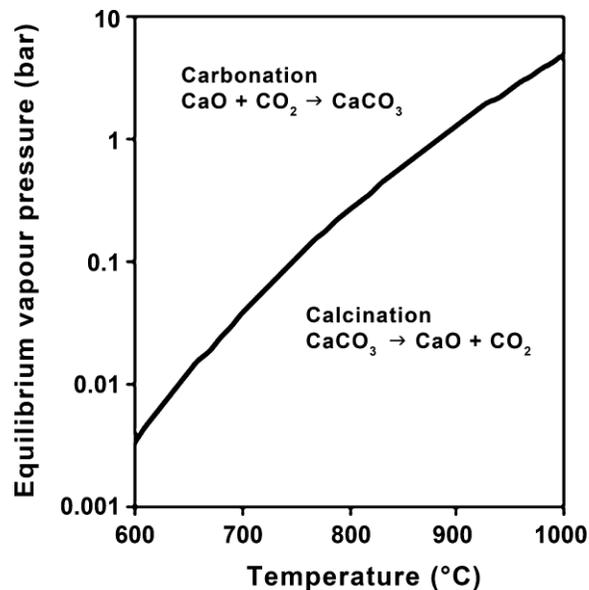
Figure 4.2 Equilibrium vapor pressure of CO_2 over CaO as a function of temperature [43]

Like all other CCS technologies, one of the most important issues for CaL is its cost and possible energy penalty imposed by the technology. What can be said for CaL regarding cost is that it is competitive to amine scrubbing and presents lower energy penalty than amine scrubbing [8]. A typical scheme of how CaL works in a cement factory is shown in Figure 4.3 [44] and the authors of this particular scheme estimate an avoided cost of 23\$/ton CO_2 with 99% capture of CO_2 emissions.
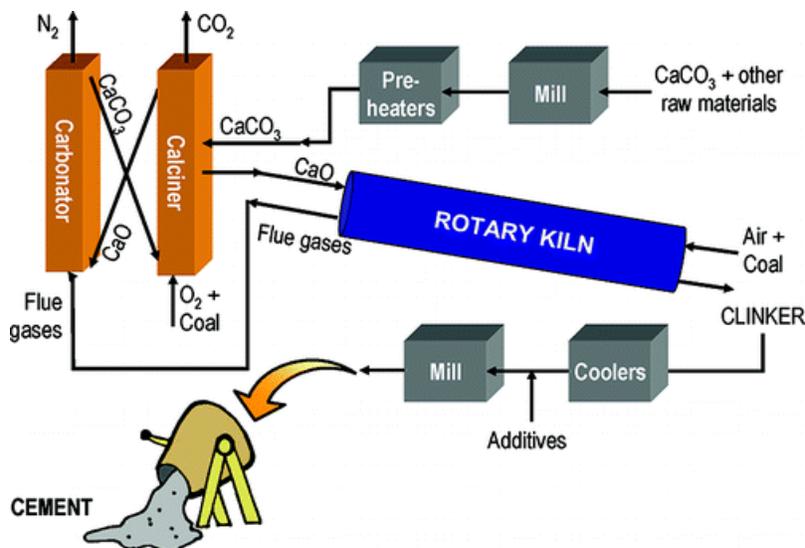

Figure 4.3 How Calcium Looping works in a cement factory [44]

Under UNIDO (United Nations Industrial Development Organization) and IEA (International Energy Agency) planning, about 495 CCS projects are expected in the cement industry by 2050 [45]. Regardless if calcium looping is directly applicable in a cement industry, the ability to use spent lime as a marketable industrial product presents a significant possibility of making the technology exceptionally attractive, nonetheless there is still the need to validate the technology in bigger scale. Additionally, the European Commission has granted in 2016 €12 million to a €21 million pilot plant project for the design, manufacture and testing of a new calciner that is indirectly heated, called the LEILAC (Low Emissions Intensity Lime And Cement) project, where the pilot plan is hosted at Heidelberg Cement's Lixhe plant in Belgium [37, 38].
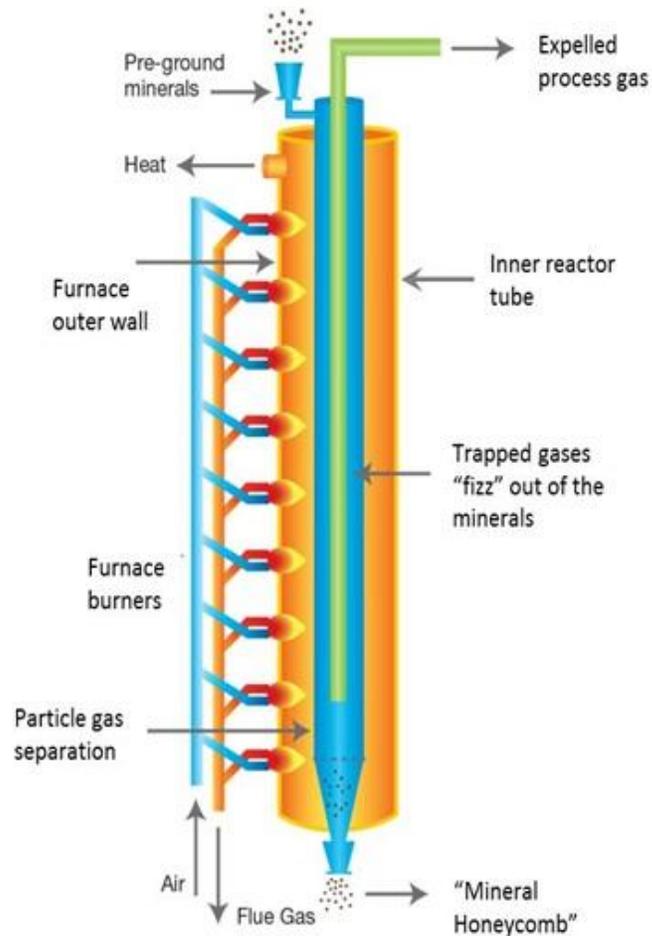

Figure 4.4 CO_2 Capture from Cement Plants Using Calcium Looping Technology [44]

4.5. Steel Industry

Ordinarily, a modern steel production plant can produce more than 1 ton of CO_2/steel ton, though recent findings suggest that this number can reach 1.8 t CO_2/t of steel [48]. Decarbonization of the steel industry has significant part in reaching the Paris agreement goals and other national aspirations. The majority of CO_2 emissions in a steel plant come from blast furnaces [49]; therefore, they are the priority target for CCS implementations. One choice would be to apply post-combustion CCS calcium looping as shown in Figure 4.5.
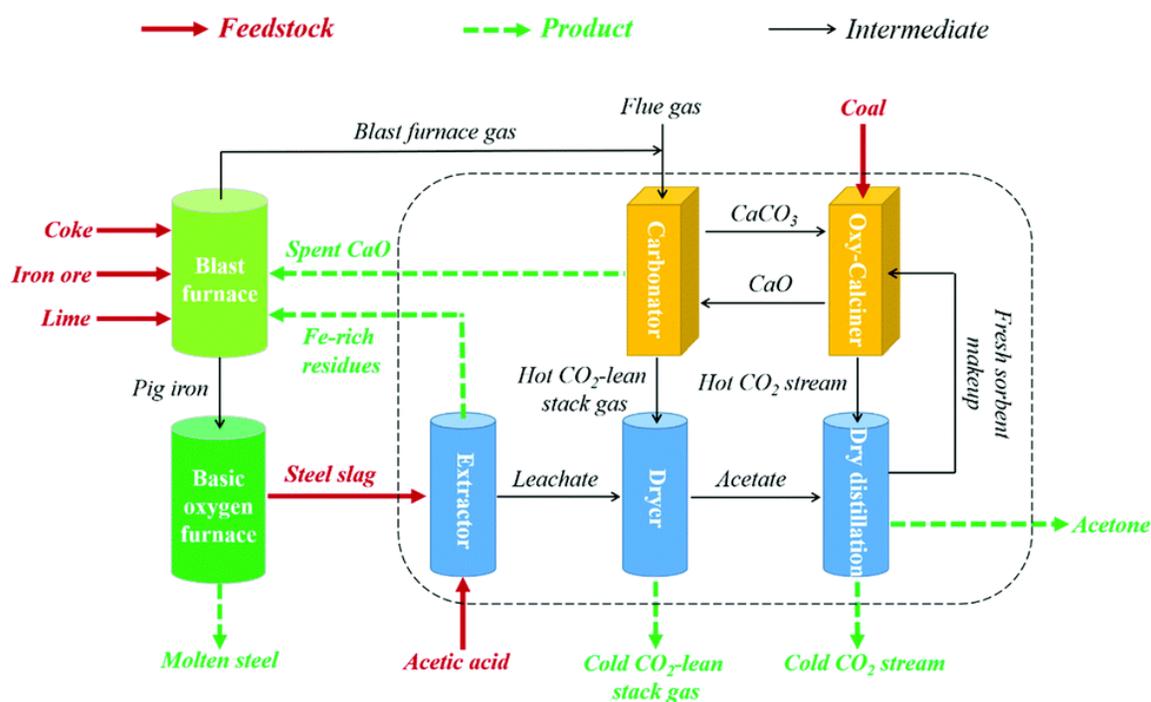
Figure 4.5 Post-combustion Carbon Capture and Storage Calcium Looping [50]

The opinion that the cheapest approaches are those with membrane technology in comparison to traditional amine has been stated [51], and that a base cost is roughly $85 per ton of CO_2 avoided. The fact that amine capture from the lime furnace was found to cost $110/ton is interesting, as it shows promising for savings and simple application of calcium looping technology. A blast furnace with CCS is depicted in Figure 4.6.
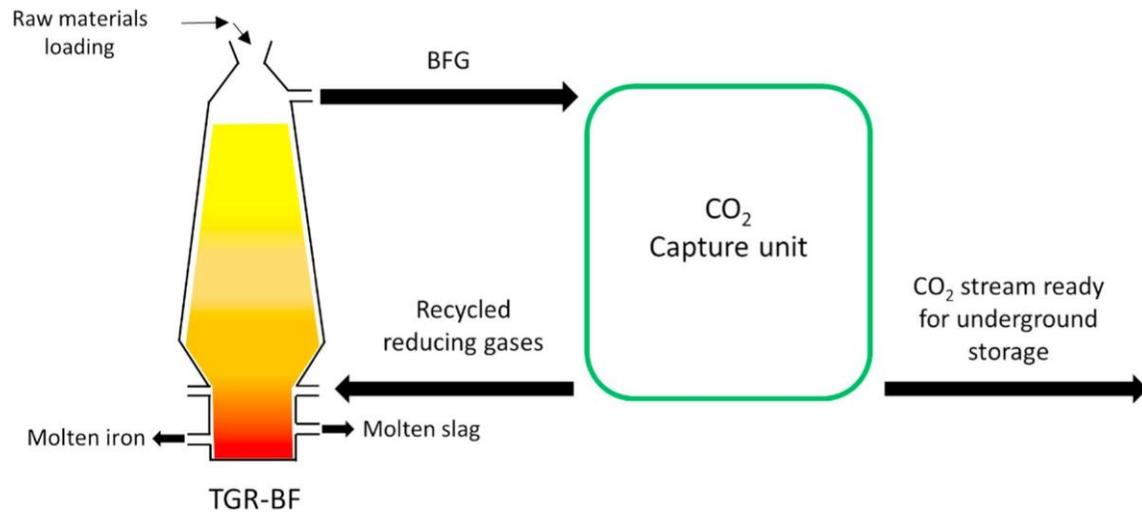
Figure 4.6 Blast furnaces with Carbon Capture and Storage [48]

Other than calcium looping technology, there are other methods being explored on the subject of CCS in the iron and steel industry. One of those developments is a chemical looping process of calcium and copper for the production of hydrogen enriched fuel gas via the sorption enhanced water gas shift of blast furnace gas in steel mills. Carbon dioxide is at the same time separated from the gas with a CaO-based sorbent [52].

4.6. Marine Technology

The International Maritime Organization (IMO) has set a target of 30% CO_2 shipping produced emissions reduction by 2020 [53]. A big difference between naval and dry-land technologies is evidently the size and limited space that large vessels offer. Since large amount of cryogenic products such as liquefied natural gas are presently shipped, it looks as if there is no fundamental trouble in capturing and storing CO_2 on board, to be cleared at port, or to a dedicated pipeline network. A matter to bear in mind is that the contemporary principal conventional naval fuel, heavy fuel oil, is rich in sulphur and therefore any technology used must take into account the high levels of SO_2 in the flue gas, if on-board capture is considered.

An additional maritime option to increase the flexibility of CCS technology is to actually construct marine transportation to ship CO_2 in carriers. At this point, a recent study has proposed that liquefied natural gas (LNG) could be used as a naval fuel for CO_2 carriers as compared to marine gas oil [54].

5.   CO₂ Capture by Oxy-fuel Combustion

5.1.   Introduction

Oxyfuel combustion is one of the primary technologies examined for CO_2 capture in power plants with CCS. The technology engages fuel combustion in pure oxygen instead of air and so as to regulate the flame temperature, part of the flue gas recycles back into the boiler. In oxyfuel combustion, the oxygen concentration needs to be at least 21%, which is the oxygen concentration in the air. Oxygen in concentration 21-100% can be used for the combustion, though in real cases, we can hardly reach truly 100% oxygen concentration in the combustion oxidizer, for the reason that to produce and use high purity oxygen for the industrial scale it would present an economically impracticable technique. Consequently, nitrogen and argon molecules are present due to air separation [46, 47].

The theory of oxyfuel combustion was originally implemented in various industrial applications, such as cement or glass production. In the interest of enhanced crude oil recovery (EOR), oxyfuel combustion has already been present since the 1980s, in order to provide flue gas rich in CO_2. The advantage of using high oxygen concentration in a combustion process eradicates nitrogen as the core flue gas component in an air-fired mode. As a result, the flue gas is then composed mainly of CO_2, water vapour and residual oxygen, making CCS easier to realize.
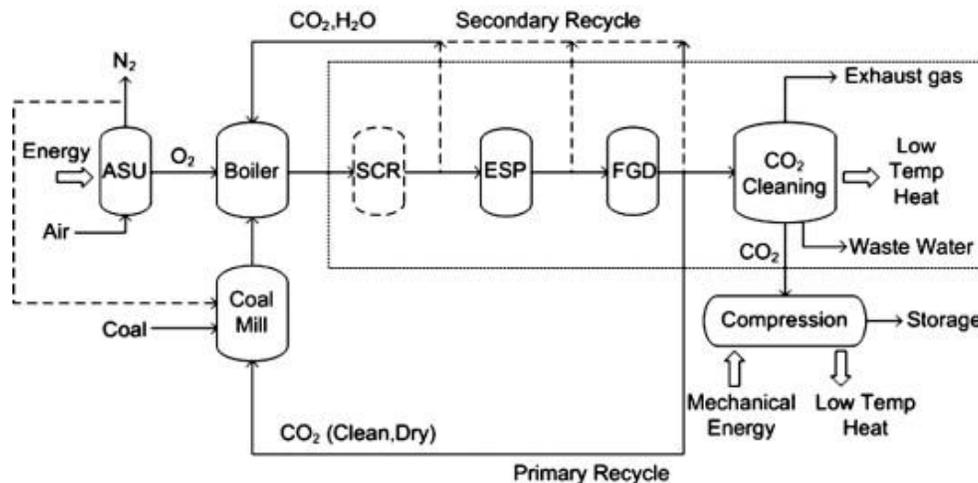

Figure 5.1 Possible configuration of an oxy-fuel power plant. ASU: *Air Separation Unit*, SCR: *Selective Catalytic Reduction reactor (deNOx)*, ESP: *Electrostatic Precipitator*, FGD: *Flue Gas Desulphurization*. Energy inputs and low-temperature-heat outputs new to the plant in case of a retrofit are indicated [57]

5.2. Principles of Oxyfuel Combustion

Compared to the conventional air combustion, oxyfuel combustion differs in the following aspects; the use of an air separation unit (ASU), use of extensive flue gas recirculation (FGR) and use of a gas processing unit.

5.2.1. Air separation unit (ASU) and oxygen supply into the combustor

The air separation unit feeds oxygen into the combustor and it requires the most energy in the oxyfuel technology; it costs the net power plant efficiency by 7–9%. Today, the best option of the oxygen feed for the industrial oxyfuel combustor is a cryogenic distillation unit. Few other technologies that size can produce enough oxygen for common industrial consumptions. The oxygen input point is important for the design of the combustor, mainly for safety reasons.

Oxygen must not be used likewise as combustion air is utilized in air-fired boilers to bear solid fuel transport to the boiler. It cannot be even supplied to the flue gas recirculation (FGR) stream before coal mill for the case of pulverized coal (PC) combustion[2], or before grinders in the case of fluidized bed (FB) combustion[3]. Though CO_2 has an explosive inhibitory effect and could increase the O_2 level in the fusion by over 21%, probable damage to control valves, recycling fans and other equipment is considered a safety risk. Regarding pulverized coal-fired boilers, the manner of oxygen injection and mixing is done in mind of optimal burner design, having regard to suitable ignition, flame stabilization or NOx formation optimization. In the case of fluidized bed-fired boilers oxygen is supplied always in the main fluid stream, which mainly consists of recycled exhaust gases.

5.2.2. Flue Gas Recirculation (FGR)

Flue gas recirculation (FGR) is compulsory for temperature drop and sufficient heat carrier amount in order to take away the heat produced by oxyfuel combustion, since the fuel amount is 80% lower compared to conventional air combustion. There can be either wet or dry FGR. Wet flue gas recirculation refers to maintaining the exhaust gas

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[2] The basic outline is a system that uses pulverized fuel in order to utilize the whole volume of the solid fuel burning boiler. Coal is ground to a fine grain size, mixed with air and burned in the flue gas flow.

[3] In fluidized-bed combustion, fuel is fed in a solid bed, which has been fluidized by an upward air movement. Such systems offer various advantages, such as high combustion efficiency in significantly low temperatures (750–950°C) compared to other coal utilization technologies [165]

temperature above its dew point, to keep water vapour in gas state [58].

The wet FGR line is thermally insulated to avoid unwanted condensation, particularly under partial loads of the boiler. Dry FGR regards to flue gases being cooled down bellow dew point and the water vapour is condensed. Applying dry FGR is usually necessary in the case of pneumatic transport of the fuel. In this case, the volumetric flow of the FGR drops accordingly to its actual temperature, determined by the water vapour saturation pressure [58].

5.2.3. CO_2 Processing

Oxyfuel combustion system utilizes all usual measures for pollutant concentration decrease (sulphur and nitrogen oxides). In the ideal scenario, final CO_2 consists only of water vapour and left over oxygen. The next step is to compress and dehydrate CO_2 flow, which as a process is energy consuming and drops electrical efficiency by 2-3% [59]. A possible process for CO_2 processing and purification steps in an oxy-fuel plant is shown in Figure 5.2. It is possible that an initial dehydration of the flue gas is performed in combination with the flue gas cleaning step before the initial compression in order to reduce the total flue gas volume and thus costs and equipment size [56].
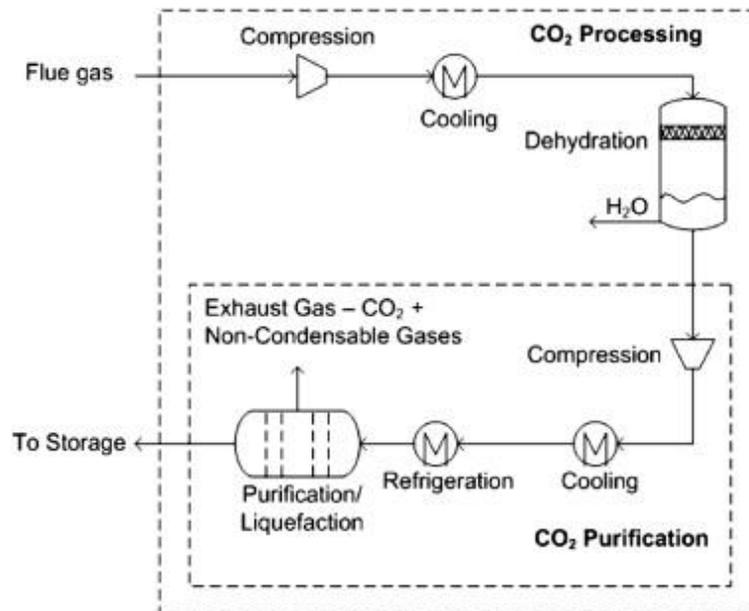

Figure 5.2 Possible configuration of an oxy-fuel power plant [60]

5.3. Formation Principles and Reduction Possibilities of Gaseous Pollutants

This part of the chapter deals with the formation of three basic gaseous pollutants that are always in focus and are unwanted in the output CO_2 from the oxyfuel combustion. These are carbon monoxide (CO), sulphur dioxide/trioxide (SO_2, SO_3) and nitrogen oxides (NO_x).

5.3.1. Carbon Monoxide

Carbon monoxide is a product of incomplete oxidation of hydrocarbons in fuels. Still, in high CO_2 gas state concentrations (characteristic in oxyfuel combustion) CO can also be produced by CO_2 separation:

$$2CO_2 \rightleftharpoons 2CO + O_2$$
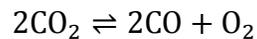
The above reaction is strongly endothermic and as a result it can take place in the flame zone or in the nearly stoichiometric conditions. Commonly, in a pulverized combustion, it is in the main mixture zone. In fluidized bed combustion, it is in the dense part of the fluidized bed. An additional significant way leading to the increase of CO concentration in the flame zone of oxyfuel flames is the reaction between CO_2 and H radical:

$$CO_2 + H \rightleftharpoons CO + OH$$
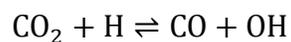
The last chief source of CO in oxyfuel combustion is the Boudouard reaction:

$$C + CO_2 \rightleftharpoons 2CO$$
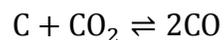
The Boudouard reaction is also an endothermic reaction. All of the above reactions are initiated by high CO_2 concentration and high temperatures [56]. The Boudouard reaction, initially known from gasification, is further supported by the large concentration of unburned carbon particles in the mix.

The combustion of CO is affected by temperature and oxygen availability [61]. In Figure 5.3 and Figure 5.4 bellow, the affiliation of CO emission factors in air and oxyfuel combustion is shown, in 30 and 500kW bubbling fluidized bed (BFB) combustion boilers. From these figures it is apparent that the same oxygen content in the exhaust gases differs from oxygen surplus ratio (calculated as specific volume of total oxygen used/stoichiometric volume of oxygen) among air and oxyfuel approaches. Figure 5.4 shows that at low stoichiometry, CO levels are higher in oxyfuel method and rapidly decrease provided that there is enough oxygen to burn out the solid carbon excess, which supports the Boudouard reaction. At oxygen surplus ratio 1.20 the CO emission factors are significantly lower, compared to air-fired mode, by about a factor of two. From this point of view, 20% oxygen excess is fully satisfactory for the oxyfuel combustion to keep the CO levels at acceptable low values. For the same case in air mode, the CO levels are 3–4 times higher and drop to the factor of two at oxygen excess ratio of about 1.80 [62].
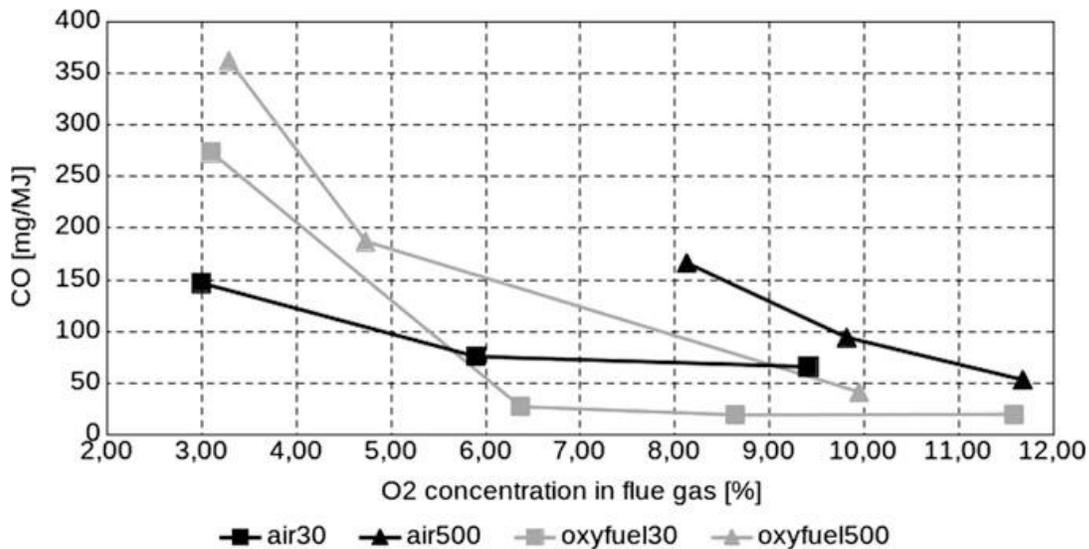
Figure 5.3 Affiliation of CO emission factors in air and oxyfuel combustion, in 30kW and 500kW bubbling fluidized bed (BFB) combustion boilers [63]
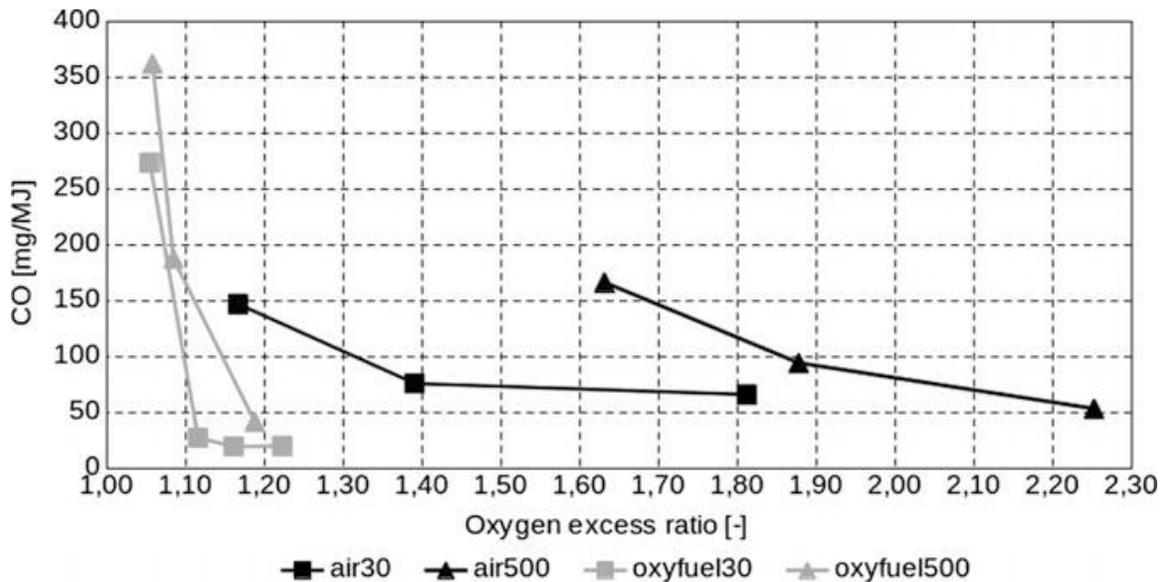
Figure 5.4 Affiliation of CO emission factors in air and oxyfuel combustion, in 30kW and 500kW bubbling fluidized bed (BFB) combustion boilers [63]

5.3.2. Nitrogen Oxides

There are three widely known paths of NOx formation. Thermal (Zeldovich), prompt (Fenimore) and fuel N-oxidation. The importance of these pathways varies depending on the fuel combustion method. In air-fired pulverized coal combustion, about 20% of NOx produced comes from thermal mechanism and the rest is formed by fuel nitrogen (nitrogen-containing organic compounds present in liquid or solid fossil fuel [64]). In air-fired fluidized bed combustion, almost 100% of NOx emission is formed by fuel nitrogen and all other mechanisms have little importance because of generally low combustion temperature.

As a general rule absence of nitrogen in oxyfuel combustion interferes negatively with thermal and prompt formations of NOx, as they are both closely connected with N_2 reactions from the air. Moreover, the reaction equilibrium in thermal NOx formation can be negatively affected by superfluous NO compared to N_2 concentration. In oxyfuel, there is almost no nitrogen as an input molecule to the Zeldovich reaction, but there is considerably higher relative concentration of NO compared to air-fired combustion. Thus, the Zeldovich reaction supposedly reverses to mitigate NO to N_2. In Figure 5.5 is shown that the nitrogen in volatile matter is moving the equilibrium nitrogen monoxide toward nitrogen.
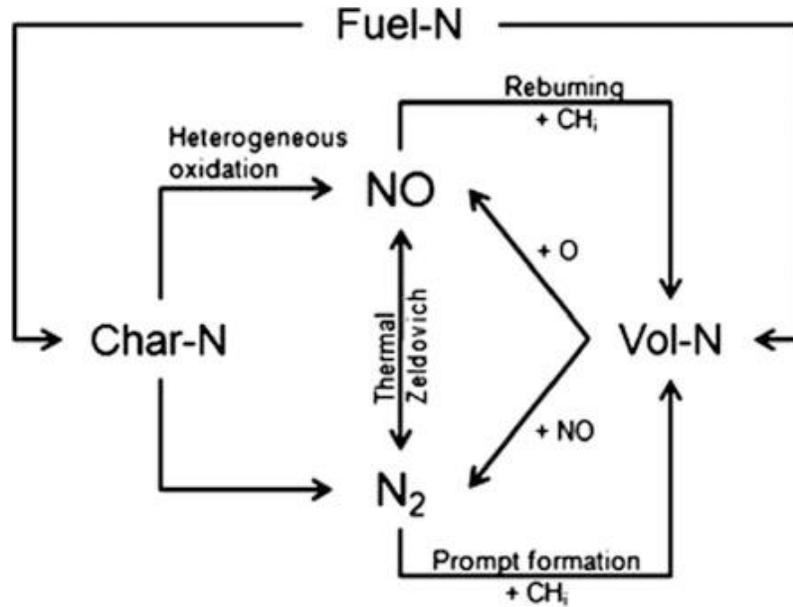
Figure 5.5 NO formation and reduction. Vol-N is an intermediate gaseous compound, e.g. HCN or NH_3 [63]

To gain from this reduction, it is vital to keep nearly stoichiometric conditions in the main combustion zone, and entrance of air must be prevented. An important additional reduction factor for the NOx emissions is the flue gas recirculation that causes the NOx to pass through the fuel rich regions and undergo reduction reactions to N_2 [47, 53, 54]. Nitrogen oxides formation in oxyfuel combustion therefore depends on oxygen availability for fuel nitrogen oxidation. In Figure 5.6 and Figure 5.7 the correlation of NOx and oxygen concentration is shown in off-gas and oxygen excess ratio for air and oxyfuel combustion methods. The data derives from experiments carried out in the 30 and 500 kW combustors [62].
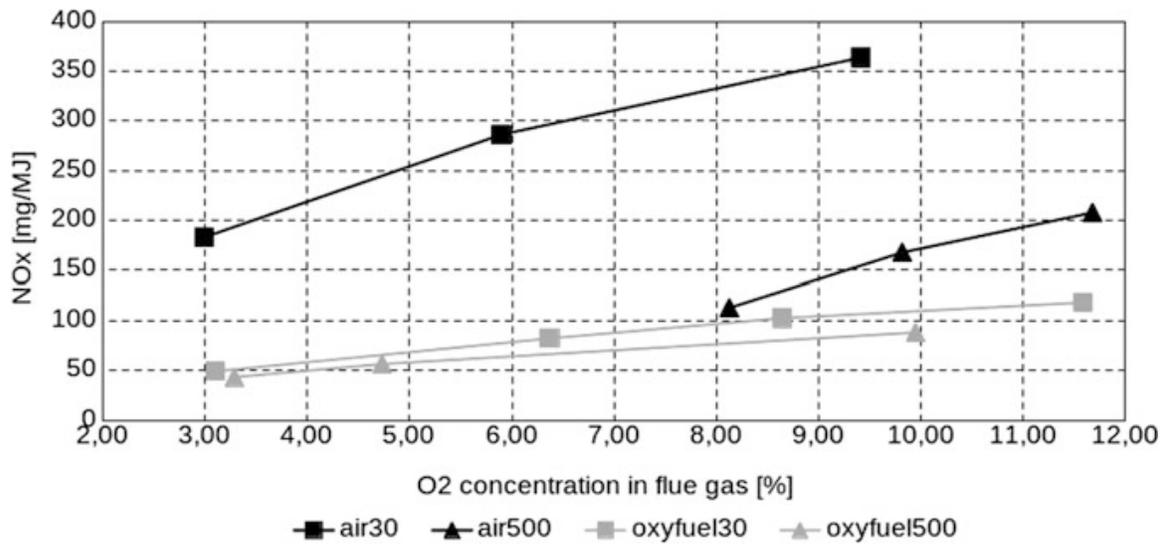
Figure 5.6 NOx emissions in air and oxy-fuel in 30 and 500 kW combustors [62]
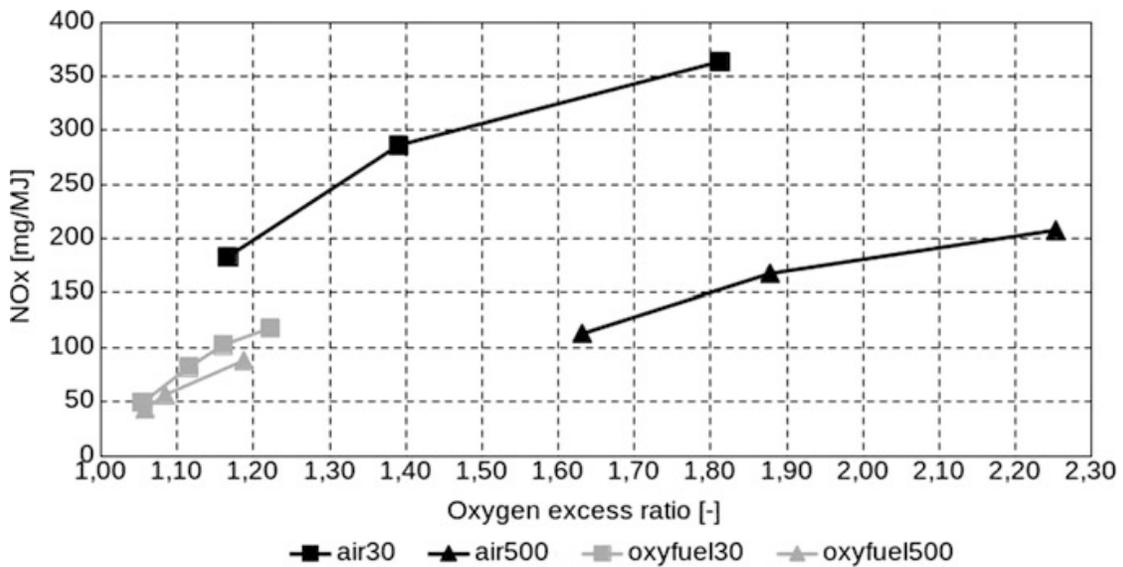
Figure 5.7 NOx emissions in correlation of oxygen stoichiometry [62]

From Figure 5.6 the conclusion could be derived that, real NOx emissions are significantly lower in oxyfuel compared air-fired combustors. This is generally true, for combustion systems where nitrogen oxides come from atmospheric nitrogen formed from immediate thermal mechanism. In the case of fluidized bed though, the only mechanism in relation is fuel nitrogen oxidation. The chart in Figure 5.7 shows that it is only about the correlation of oxygen stoichiometry and correct plotting of the correlation curves, since fuel-N oxidation depends practically only on oxygen availability. This figure shows that regardless of the principle of combustion (air/oxyfuel) the correlation is very similar and the real benefit of the oxyfuel mode is that the oxygen stoichiometry is much closer to one compared to air mode. However, since combustors in oxyfuel mode can operate suitably at lower oxygen stoichiometry for CO burnout, the NOx production can be actually inferior in oxyfuel, as oppose to air combustion.
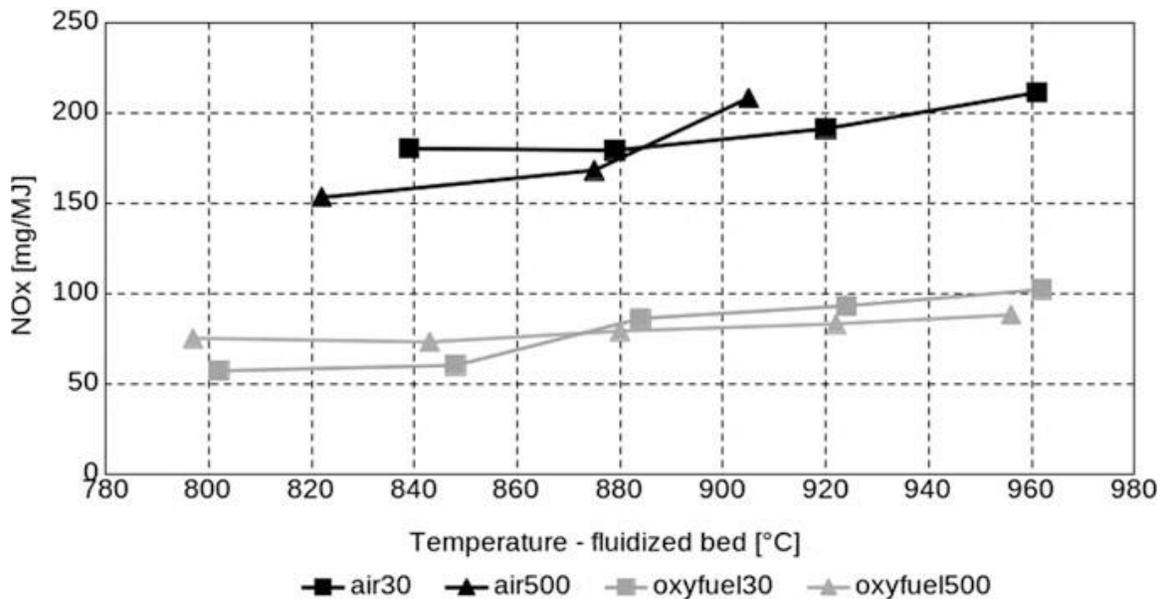
Figure 5.8 NOx emissions/temperature relations in fluidized bed combustion [62]

In Figure 5.8 there is the relationship of NOx emissions with temperature. The temperature range in this figure is limited between 800-960°C, which is the temperature in fluidized bed boilers. The data shown are all for 6% oxygen concentration in the off-gas, which responds to oxygen excess ratio of about 1.40 and 1.12 for air and oxyfuel combustion respectively. This is why the emission factors of NOx are higher for the air rather than oxyfuel mode [62].

5.3.3. Sulphur Dioxide

In fuels sulphur exists in forms of pyrite, sulphates, organic bonds and elemental sulphur (S). Share and quantity of sulphur in fuels depends on fuel type and sum of sulphur that is oxidized and converted in SO_2 or SO_3. In classic air combustion, chief sulphur product is SO_2. In oxyfuel combustion there is increased SO_3 production compared to air-fired mode which is particularly important because of its reaction with water vapours which produces sulphuric acid [53, 55]. This reaction starts around 400°C and is almost completed at 200°C, which implies risk of corrosion in the oxyfuel combustion, typically at locally cold surfaces, for example water or air preheaters [67].

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Technologies developed to cut down SO_2 and SO_3 concentrations in the off-gas are either based on post combustion methods or direct SO_2 capture in the combustion process. Amongst post combustion technologies is the flue gas desulphurization (FGD) technology, which involves a flue gas scrubbing process. As to the recent knowledge, converting the combustion mode from air to oxyfuel does not affect negatively either SO_2 capture ratio or quality of the final product by the elevated CO_2 partial pressure [68].

Direct capture of sulphur oxides has the advantages of technological simplicity and relatively low investment and operation costs. In theory, an additive, usually calcium or magnesium carbonate, is either directly fed into the combustion or it can be added in fuel pre-combustion. Yet, its efficiency is strongly affected by a number of process factors, like heat and mass transfer rates, temperature or composition of gas phase and by material properties of the additive, such as porosity, reactivity and particle size. These conditions limit its implementation to fluidized bed combustion methods, where the conditions can be satisfied successfully. The reaction mechanism is calcination of the sorbent based on carbon (usually limestone $CaCO_3$) and consequent reaction with SO_2 (or SO_3), or direct sulfation.

The final product is in both cases calcium sulphate, yet the reactions deviate on reaction rate and conversion degree. In general, the calcination mechanism is preferred (higher SO_2 capture ratio), but performance of this method is limited by partial pressure of CO_2 in the gas phase [50, 58, 59]. In the oxyfuel approach, CO_2 partial pressure is notably higher than in air-fired combustion. In Figure 5.9 the calcination equilibrium curve is depicted, derived from [71].
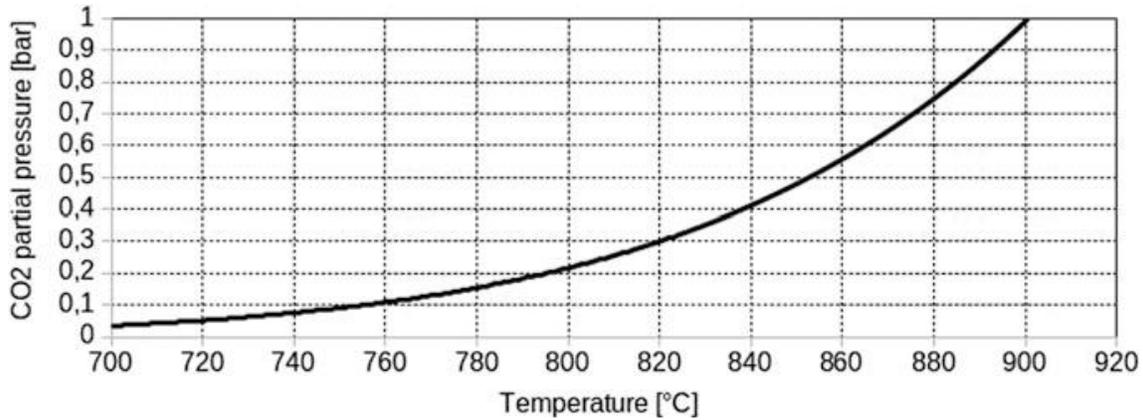
Figure 5.9 Calcination equilibrium curve [62]

Figure 5.9 shows the typical operating ranges of air-fired and oxyfuel combustion for CO_2 partial pressure (or in case of ideal gas behaviour, concentration) and temperature. The left part of the equilibrium curve shows that direct binding of SO_2 leads to immediate sulfation. Therefore, a lower capture ratio and a lower reaction rate may occur. In practice, this indicates a higher consumption of absorbent material to achieve the required high trapping ratio. Referring to Figure 5.9, the reaction mechanism is always calcination in air-fired combustion. In the oxyfuel mode, the CO_2 partial pressure reaches about 0.5 bar, also shown in Table 5.1. At this level, the turning point is around 855°C, which must be overcome if calcination is required. For fluidized bed burners, this is a major operating issue, as fluidized bed burners typically run in a temperature range of 800 to 900°C [50, 61].

Table 5.1Flue gas from air and oxyfuel combustion, 20% oxygen excess, and lignite coal [62]

	Air mode	Oxyfuel mode	Unit
O_2 in flue gas	3.6	18.2	vol%
Specific volumes			
O_{2min}	1.032	1.032	Nm³/kg
Oxidizer dry, min	4.916	1.032	Nm³/kg
Oxidizer wet, min	4.995	-	Nm³/kg
Oxidizer total, dry	5.90	1.239	Nm³/kg
Flue gas dry	5.793	1.133	Nm³/kg
Flue gas wet	6.55	1.596	Nm³/kg
Concentrations of flue gas components, wet/dry, normal conditions			
CO_2	14.0/15.9	50.9/80.9	vol%
H_2O	11.6/0.0	37.1/0.0	vol%
N_2	70.3/79.6	0.3/0.4	vol%
SO_2	0.08/0.09	0.3/0.4	vol%
O_2	3.1/3.6	11.5/18.2	vol%
Noble gases	0.8/0.9	0.0/0.0	vol%

5.4. Summary

The goal of this chapter was to demonstrate the most important aspects of oxyfuel combustion compared to conventional air combustion. The differences in these aspects are mainly determined by alteration of oxidizer from air to oxygen of technical purity. As a result, the off-gas volume is about 80% lower and consists mainly of CO_2 and water vapours. The different composition is due to the different material properties such as density, viscosity or specific heat capacity and in the different formation chemistry and reduction of undesirable pollutants. The lower volume of specific exhaust gas is reflected in the requirement for a high exhaust gas degree of recirculation, which is needed to provide the heat transfer medium to reduce adiabatic flame temperature back to typical air combustion levels. Furthermore, for the fluidized-bed combustion, a change in the oxygen combustion mode is associated with a parallel need to maintain adequate fluidization conditions.

Consequently, it is not possible to achieve flow and heat conditions at the same time

as in the way of combustion of air. The concentrations of species in the flue gases in the operation of the oxyfuel are completely different from the air and an emission factor must be used for quantity comparison. The different specific volume of exhaust gas used as concentration reference makes the use such a comparison factor necessity. The carbon dioxide, which is the required product of the oxyfuel combustion, has, in an ideal practical case, usually a share not exceeding 50% in wet exhaust gas. However, this level is specifically depended on water consistency in fuel and on FGR type (wet or dry). Other common species in flue gases are water vapours and residual oxygen.

Comparing the stoichiometric conditions of the combustion processes by oxygen concentrations, the oxyfuel mode runs in far lower stoichiometry (excess of oxygen) than the air-fired process. The actual oxyfuel combustion operating conditions suggest that, less CO_2 is emitted because it is diluted by air that comes from leakages and unsealed components in the combustor. True CO_2 concentrations do not exceed 80-85vol% dry gas. The CO_2 must be free of any condensable or acid-forming substances before further condensation, compression and transfer. In oxyfuel combustion technology, this means that all major gas contaminants need to be removed.

This chapter focused on three of the most important: carbon monoxide, nitrogen oxides and sulphur oxides. Different process conditions affect the formation and removal processes. Carbon monoxide formation is enhanced by reactions that are not significant in air-fired combustion, such as char gasification. In NOx chemistry, thermal and prompt ways of formation are practically impossible to occur in oxyfuel since atmospheric nitrogen is non excitant in the combustion process. This is not applicable for fluidized bed oxyfuel combustion, where NOx are formed by fuel nitrogen oxidation. In general, NOx emission factors are lower compared to air mode, but though be it at different oxygen stoichiometry. Removal of sulphur oxides is necessary and technologies similar to conventional air combustion can be used for this purpose. Post-combustion methods, such as liquid FGD, are not primarily affected and can maintain the high degree of capture and the quality of their by-products. The yield of the direct method used for the fluidized-bed technology is enhanced as compared with the air combustion, even if the optimum operating conditions are slightly different.

Oxyfuel combustion undoubtedly belongs to the newly developed CCS and CCU technology sector, which is confirmed by the number of pilot scale and demonstration facilities at various scales worldwide. It benefits primarily by the relative strength and technological simplicity and maturity of the basic components of a hundred-year old combustion technology development, but suffers mainly from the energy penalty and the low flexibility of oxygen production. In order to introduce combustion technology in industrial and commercial practice in the future, there are several aspects that we need to focus on. Initially, oxygen production must be flexible and require less energy. Then the fuel in Europe - there is a significant fall in the burning of fossil fuels, such as coal, and it is not to be expected that large coal-fired boilers will be built in the future. Apart from the modernization of the recent burners, the technology should be transformed efficiently to be implemented at provincial level and to operate on a multi-fuel scale by combining locally available fuels for biomass, alternative fuels or discarded fuels [62].

6.   Methanol Synthesis from CO_2 Hydrogenation

6.1.   Introduction

The increased level of CO_2 emissions on earth has forced research to focus on reducing carbon dioxide emissions to the atmosphere, since its concentration has reached extremely high levels due to the continuous fossil fuel burning and stripping of forests, which is emphasized by the Intergovernmental Panel on Climate Change (IPCC) [73]. Solar radiation heats the surface of the earth and the lower energy infrared radiation is absorbed by surplus carbon dioxide. This leads to global warming. Environmental pollution and carbon dioxide emissions originate from the industrial revolution and culture, and offer a comfort zone in human life, as they provide new technologies to be exploited. This is why the conversion of CO_2 into a valuable product is considered necessary to prevent global warming and to switch off the burning of fossil fuels. As is known, methanol is not only a cleaner energy fuel but also a reagent for the production of olefin and other chemicals, equally significant [74].

Thus the conversion of CO_2 to methanol is an effective way to use CO_2 having in mind the inflated environmental problems. However, activation of CO_2 and its hydrogenation in hydrocarbons or alcohols are a challenge because CO_2 is a thermodynamically stable, fully oxidized and chemically inert molecule. Another challenge comes up with the low carbon/hydrogen ratio achieved during CO_2 hydrogenation, as a result of the relatively low heat of CO_2 adsorption on catalyst surface. This leads to the fast hydrogenation of intermediates adsorbed in the surface, leading to the formation of methane (CH_4) and a decrease in chain growth [75]. On an industrial scale, methanol is produced from syngas (synthesis gas or met gas is a mixture of CO, CO_2 and H_2) using a variety of catalysts based on copper, zinc oxide and alumina (Cu, ZnO, Al_2O_3) [76].

6.2. CO₂ and H₂ for Methanol Production

The use of CO_2 for methanol is made in conjunction with hydrogen, which is produced with the help of renewable energy sources. In special cases, the use of the hydrogen residue or by-product may be advantageous.

Hydrogen

Surplus hydrogen sources include crude oil refineries that make use of thermal or catalytic crackers and catalytic converters. The hydrogen excess is the amount that is not needed in the capture processes, such as hydroelectric processing and energy production. Depending on the structure of the refinery, it may be a net hydrogen generator or in need additional hydrogen, which is often produced by steam reforming.

A major source of hydrogen is the electrolytic production of chlorine:

$$NaCl + H_2O \rightarrow \frac{1}{2}Cl_2 + NaOH + \frac{1}{2}H_2$$
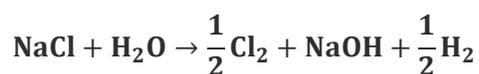
Hydrogen can be also produced by various other sources such as the production of lower olefins by steam cracking, the production of acetylene by partial oxidation (POX) of methane and the dehydrogenation of ethylbenzene to styrene monomer [77].

Carbon Dioxide

Interest in the use of CO_2 in chemical processes has increased due to rising fuel costs, worrying about scarce resources and discussions on climate change. Multiple efforts are aimed at using CO_2 as a carbon building block for fuels. The high thermodynamic stability of CO_2, along with a free enthalpy of -393kJ/mol, demands a high energy supply to reverse the formation of CO_2 as the final product of any combustion process. Chemical processes using CO_2 as a building block are known and have been applied on a large scale. Such processes come across in the production of urea from ammonia and CO_2, the manufacture of certain polycarbonate polymers and the production of salicylic acid by phenol. Other pathways for the use of CO_2 as a chemical structural element require especially reactive reducing components, such as hydrogen, or require electricity input in conjunction with catalysts to convert the very stable $C = O$ bond [77].

Cases in point of chemical CO_2 activation with hydrogen or methane as reducing agents are:

Dry CO_2 reforming of methane:	$CO_2 + CH_4 \rightarrow 2CO + 2H_2O$
Methane production with hydrogen:	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
Reverse Water Gas Shift:	$CO_2 + H_2 \rightarrow CO + H_2O$
Hydrogenation to formic acid:	$CO_2 + H_2 \rightarrow HCOOH$
Hydrogenation to oxalic acid:	$2CO_2 + H_2 \rightarrow (COOH)_2$

A blend of dry and wet reforming to produce a synthesis gas with methanol has been proposed by researchers in the past [78]. Both reactions can happen in two separate steps to compose the synthesis gas or they can occur in one step with a nickel catalyst at 800–1000°C and 5–40 bar of pressure:

$$3CH_4 + CO_2 + H_2O \longrightarrow 4CO + 8H_2 \longrightarrow 4CH_4OH$$

The process, called "bi-reforming", has been proposed for all natural and/or shale gas. Often CO_2 already exists in these gases and only an additional adjustment is required for the methane/CO_2 percentage, normally done by adding CO_2 from other outside sources [79]. Methanol can also be produced by direct hydrogenation of CO_2 over copper and zinc catalysts under condition that they have been adapted to handle high CO_2 percentage in the feed gas. It is understood that hydrogenation can occur if hydrogen is available from excess hydrogen by-product and from other sources not derived from fossil fuels, such as electrolysis.

6.2.1. Hydrogen Generation

Hydrogen is known to be the lightest atom and is found in abundance in the universe. On our planet, it is commonly compounded with other elements. It is found as hydrogen gas, H_2, as an isolated element. Information such as its formation, reactions and use can be found in any chemistry textbook [80]. Hydrogen can be in various formal oxidation states: hydron as H+, neutral as an H_2 molecule and H- as hydride. The thermodynamic stability of the hydrogen ion depends on where the ion is found. In Earth's biosphere in all compounds with oxygen, hydrogen is found in an H^+ state. For that reason, it always needs energy intake to create molecular hydrogen H_2 or a hydride H- in an environment such as our planet. However, this need of energy input is often neglected in public debates on future energy concepts that affirm water is a rich source of hydrogen on earth and do not keep in mind the atom availability or the energy needed to convert it.

For hydrogen generation out of liquid water, a formation enthalpy of 285.9kJ/mol (15.87 MJ/kg H_2O; 12.76 MJ/m^3 standard temperature and pressure [STP] H_2) is needed, equal to 3.55kWh/m^3 STP H_2. For comparison, industrial water electrolysis usually needs electrical energy of approximately 4.5–5.0kWh/m^3 standard temperature and pressure H_2 due to overvoltage and resistance losses. Even so, hydrogen is energy carrier thanks to its strong energy content. The following table presents a set of reactions that are commonly used in industrial processes for hydrogen generation purposes. The hydrogen-containing compound itself can be utilized as a primary energy source (partial oxidation of methane) and in other cases the energy sources can be the energy carrier (carbon/coal gasification), a reduced metal that is oxidized (Kipp gas generator; zinc/steam high temperature reaction), or an external source (heat, radiation, electric arc) [77].

Table 6.1 Known production methods for H_2 generation [81]

Process/reaction	Hydrogen source	Redox partner	Energy source
Hydrocarbon Steam Reforming $CH_4 + H_2O \rightarrow CO + 3H_2$	C_xH_y/H_2O	C_xH_y	C_xH_y/heat
Partial Oxidation $CH_4 + O_2 \rightarrow CO_2 + 2H_2$	CH_4	O_2	CH_4/heat
Gasification of carbon feedstock $C + 0.5O_2 + H_2O \rightarrow CO_2 + H_2$	H_2O	C/O_2	$C^{(0)}$
Kvaerner process $CH_4 \rightarrow C + 2H_2$	CH_4	CH_4	Electric arc
Electrolysis $H_2O \rightarrow H_2 + 0.5O_2$	H_2O	H_2O	Electric potential
Historic *Kipp* gas generator $Zn + 2HCl\ (aq) \rightarrow H_2 + 2ZnCl_2\ (aq)$	HCl acid	Zn	$Zn^{(0)}$
Metal water reaction (solar concept) $Fe + H_2O\ (g) \rightarrow H_2 + FeO$	$H_2O\ (g)$	Fe	$Fe^{(0)}$/heat
Metal water reaction (solar concept) $Zn + H_2O\ (g) \rightarrow H_2 + ZnO$	$H_2O\ (g)$	Zn	$Zn^{(0)}$/heat
Metal water reaction (e.g. nuclear accident) $Zr + H_2O\ (g) \rightarrow H_2 + ZrO$	H_2O	Zr	$Zr^{(0)}$/heat
Photolysis $H_2O \rightarrow H_2 + 0.5O_2$	H_2O	H_2O	X-ray, visible ultraviolet light
Thermolysis $H_2O \rightarrow H_2 + 0.5O_2$	H_2O	H_2O	Heat > 2000K

6.2.2. Hydrogen Production: Water Splitting Technologies with Renewable Energy

Besides carbon dioxide, the main resource for methanol production in carbon capture and utilization technologies is hydrogen and therefore, its production needs to be cost effective. Nowadays, hydrogen is majorly collected by fossil dehydration or syngas production from fossils.

The simplest available source of hydrogen is water, which can be separated in hydrogen and oxygen, as shown bellow.

$$2H_2O \rightarrow 2H_2 + O_2 \quad \Delta_R H = 572 kJ/mol$$

Several water separation processes can be applied with renewable energy input or hybrid technologies, for instance high temperature electrolysis.

Table 6.2 Water-splitting technologies with renewable energy [77]

Technology	Geothermal	Solar	Water power	Wind power
Electrochemical	X	X	X	X
Photochemical	-	X	-	-
Photoelectrochemical	-	X	-	-
Piezoelectrochemical	X	X	X	X
Pyroelectrochemical	X	X	-	-
Thermochemical	X	X	-	-

Electrochemical

The process of water splitting via electrolysis is one of the most common hydrogen production technologies and one of the few that can be applied in industrial scale. In 2018, nearly 4% of all hydrogen was derived from electrolysis [82]. By means of electricity, water is separated in hydrogen and oxygen compounds which are deposited at cathode and anode, correspondingly:

$$\text{Cathode:} \qquad \mathbf{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$$

$$\text{Anode:} \qquad \mathbf{2H_2O \rightarrow O_2 + 4H^+ + 4e^-}$$
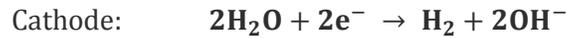
In electrolysis, water can be in either liquid or gas state, depending on the technology applied. Between various electrolysis technologies, a distinction is made for high temperature electrolysis (HTEL) and low temperature electrolysis (LTEL). Low temperature electrolysis is most common and subcategorized in alkaline electrolysis (AEL) and proton exchange membrane electrolysis (PEMEL).

Alkaline Electrolysis

Alkaline electrolysis (AEL) is a well-known electrolysis process and it is commonly held in water solution with 30% KOH (potassium hydroxide) in 80-90°C. The way the method works, is that the hydroxide ions migrate through the diaphragm from the cathode to the anode:

$$\text{Cathode:} \qquad \mathbf{2H_2O\ (I) + 2e^- \rightarrow H_2 + 2OH^-}$$

$$\text{Anode:} \qquad \mathbf{2OH^- \rightarrow O_2 + 2H_2O + 4e^-}$$
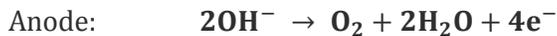
Electrodes are mainly made out of nickel, because of its durability from corrosion in such an environment. For the same reason, expensive alloys and noble metals are to be avoided. The electrolysis cell is also made from low cost materials and has long life expectancy. Difficulties come up from liquid electrolyte, which is especially corrosive to the rest of the setup and affects negatively the gas formation reaction kinetics. Additionally, the electrolyte's concentration must be checked and regulated on a standard basis, thus making it a more complex system. The major downsides with the electrolyte's application with variable renewable energy (e.g. wind energy) are the poor partial load properties and the

delay time for start-up and shutdown of the electrolysis plant [56, 61].

Proton-exchange Membrane Electrolysis

Electrolysis in acidic conditions involves a proton exchange membrane that allows the protons to shift from the anode to the cathode.

Cathode: $\mathbf{2H^+ + 2e^- \rightarrow H_2}$

Anode: $\mathbf{H_2O(l) \rightarrow {}^1\!/_2\,O_2 + 2H^+ + 2e^-}$
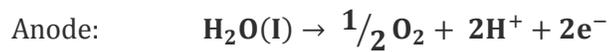
The proton-exchange membrane electrolysis process has a more compact setup and higher power efficiency and density than the alkaline electrolysis process. Consequently, it shows faster production rate for hydrogen per cell and the partial load properties are better, which makes the process appropriate for fluctuating power (common in renewable energy sources). The main issue is that the applied membranes for this technology are expensive and therefore present high investment costs and restricted long-term stability [72, 73].
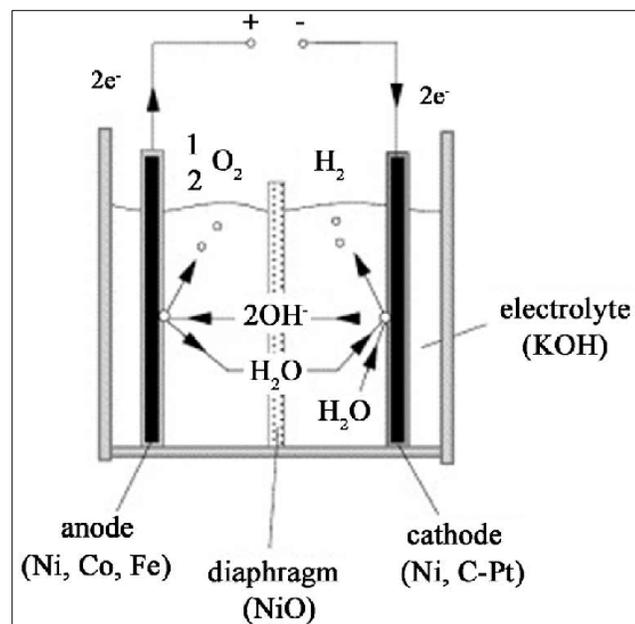
Figure 6.1 General setup of alkaline electrolysis [86]
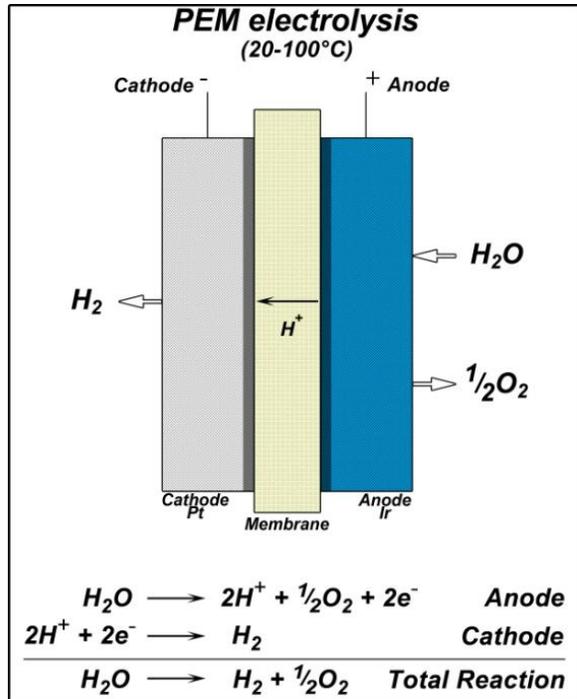
Figure 6.2. Schematic of the basic operating principle of a polymer electrolyte membrane electrolysis cell [86]

High-temperature Electrolysis

In high temperatures, water decomposes with lower voltage and overvoltage at the electrodes decreases at the same time as ion conductivity increases. This makes high temperature electrolysis very attractive to researches [86]. The process operates under temperatures higher than 800°C in solid oxide electrolysis cells, where oxide ions shift from cathode to anode [77].

Cathode: $\quad 2H_2O(g) + 4e^- \rightarrow 2H_2 + 2O^{2-}$

Anode: $\quad 2O^{2-} \rightarrow O_2 + 4e^-$
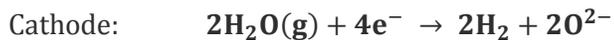
In order to achieve clean oxygen, it is fundamental for it to be separated from steam. This could be avoided in the case of proton conductors' use, though it has been proven that such conductors also work on oxide ions in unregulated high temperatures [87]. Concentrated sunlight can be utilized for heat and electricity production via solid oxide

electrolysis cells. For this process, reflectors are used to concentrate and direct sunlight through a ray separator, which then reflects heat radiation and lets visible light pass through. Heat radiation is then concentrated in a steam generator for a solid oxide electrolyser cell, while photovoltaic (PV) cells located behind the separator convert the visible light and provide the electricity needed [88].

Photochemical

An alternative to electrochemical electrolysis processes, is to separate water by sole use of sunlight. In this way, sunlight is directly utilized without the use of electrolysis. However, supporting reagents are necessary to supply the photon generated electrons to reduce H^+ on top of absorbing electrons from O_2 oxidation. Parts of a photochemical system are a sensitizer to absorb photons and two catalysts for the redox reaction. Yet, hydrogen and oxygen are not produced separately and conversion rates vary less than 1%.
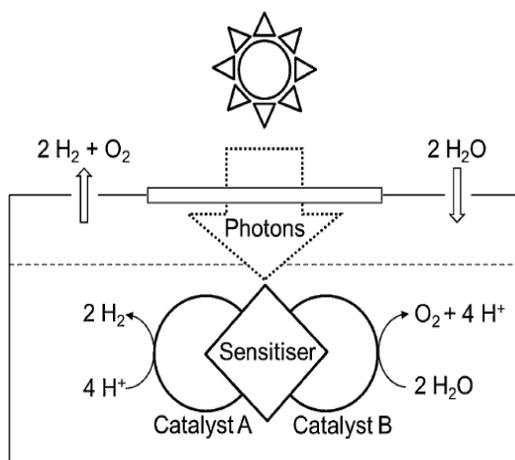
Figure 6.3 Photochemical production of hydrogen: Sensitizer activates electrons with photons; Catalyst A donates electrons for proton reduction; Catalyst B collects electrons for water oxidation [77]

Thermochemical

Thermal breakdown of water in its core elements can be achieved either by geothermal heat (reaching 600°C) and solar generated heat (reaching 3000°C) with various technologies. It is not feasible for the process to directly split water, as the needed temperature reaches above 2500°C and the coincident production of hydrogen and oxygen.

As a result, many thermal and thermal-thermochemical hybrid methods have been developed to this day. The most promising is the hybrid Cu-Cl cycle for geothermal plants, the S-I cycle process and the hybrid sulphur cycle (HyS) for solar thermal plants. The latter, involves electrolysis of a water solution of sulphur dioxide (SO_2) to produce hydrogen. The produced sulphuric acid decomposes at 800-1000°C and generates SO_2, thus closing the loop [88], 77]. Some of the most promising technologies in thermochemical water splitting are the Hysrosol-3D plant and the HycycleS plant [78, 79].

Biological

There are three main models for generating hydrogen with biological and biochemical means:

Biological water-gas shift reaction via purple bacteria

Fermentation with bacteria like Enterobacter aerogenses

Photosynthesis by means of cyanobacteria or green algae

An issue met with the technology based on bacteria is the substrate required for consumption, which antagonizes the direct gasification of biomass to methanol. In addition, there is the potential to use bacteria that directly produce methanol.

Water-Gas Shift Reaction

In anaerobic conditions, purple bacteria are known to produce hydrogen. Since the 1970s, researchers have developed bacteria (e.g. Rodopseudomonas sp.) that produce H_2 and CO_2 from carbon monoxide and water in the dark [92]. It was later discovered that some bacteria require simpler media for the production of hydrogen and can be implemented in hollow fibber batch reactors. In this way, the generated hydrogen was free

of CO and could be directly utilized in fuel cells [93]. Carbon monoxide for this reaction can be produced by methanogenic bacteria, which oxidize methane to CO by photocatalysis [94]. In this process though, methane is either directly utilized or headed for methanol synthesis (via steam reforming), therefore the process is used only in carbon monoxide as an exhaust gas specific applications.

Fermentation

Certain kinds of bacteria generate hydrogen via an organic substrate in an anaerobic environment with the following process:

$$[CH_2O]_n \rightarrow \text{ ferredoxin } \rightarrow \text{ hydrogenase } \rightarrow H_2$$
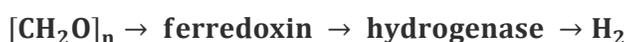
This is a familiar process by which the fermentative conversion of organic substrates to H_2 can also be implemented on existing facilities. Compared to purple bacteria, the hydrogen comes from the organic substrate, which opposes the direct methanol fermentation [77].

Photosynthesis

Hydrogen production by cyanobacteria or green algae is a method that captures the interest of researchers because it represents the biological variation of the photochemical route. For different microorganisms, the reactions are divided into two formats [77]:

Cyanobacteria

$$H_2O \xrightarrow{-O_2} \text{Photosystem I} \rightarrow \text{Photosystem II} \rightarrow \text{Ferroxidin} \rightarrow [CH_2O]_n$$

$$[CH_2O]_n \rightarrow \text{Photosystem I} \rightarrow \text{Ferroxidin} \rightarrow \text{Nitrogenase} \rightarrow H_2$$

Green Algae

$$H_2O \xrightarrow{-O_2} \text{Photosystem II} \rightarrow \text{Photosystem I} \rightarrow \text{Ferroxidin} \rightarrow \text{Hydrogenase} \rightarrow H_2$$

Due to the high need of energy for cyanobacteria to regulate nitrogen at the point where hydrogen is produced as a by-product, it is necessary to keep the nitrogen concentration low. Green algae can produce only hydrogen for a short time in an anaerobic environment for the reason that their hydrogenase is highly oxygen-sensitive [93].

Table 6.3 Summary of technologies for water splitting by renewable energy [77]

Technology	Pros	Cons
Alkaline electrolysis	High conversion efficiency, long lifetime, easy setup, universally usable, available for large plants	Insufficient partial load behaviour
Proton-exchange Membrane electrolysis	High conversion efficiency, good partial load behaviour, universally usable	High investment costs, only available for small plants, low lifetime
High-temperature electrolysis	Decrease of electricity with usage of heat	High requirements for materials, still under research
Photochemical	Easy setup	Separation of hydrogen and oxygen needed, low conversion efficiency (<1%) and lifetime [88], still under research
Thermochemical	Usable as a hybrid technology with electrolysis, high conversion efficiency of sunlight	Still under research
Biological	Easy setup	Low production rates, high need for research, concurrence with biomass gasification and methanol fermentation

6.2.3. Advantages of converting CO_2 to Methanol

Many possible ways to utilize the CO_2 to CH_3OH conversion have been discussed in the past [67, 83, 84]. If we are able to successfully convert collected CO_2 into pure liquid fuel methanol with the use of molecular hydrogen generated from a renewable energy source, there will be no other need for an alternative energy source [94–96]. Methanol, aside the fact that it can be stored and used fairly easily, it also has higher energy density compared to today's common liquid fuels (diesel and gasoline) that have high greenhouse-gases emissions. Methanol is highly volatile and can be effectively blended with gasoline, thanks to its high octane rating in internal combustion engines [100]. There have been also reports on effective methanol use in specially modified diesel engines [101]. Vehicles powered by methanol fuel have clean combustion without harmful emissions, making the environment cleaner, with many lower gaseous pollutants percentages leading to health problems decrease. It is also important to point out that through the process of CO_2 hydrogenation to CH_3OH, the percentage of the CO_2 greenhouse-gas in the atmosphere drops, thus helping towards arrest of global warming.

6.2.4. Thermodynamic Analysis of CO_2 Hydrogenation to Methanol

The reaction needed to synthesize methanol through CO_2 hydrogenation from synthesis gas releases heat (exothermic reaction). Moreover, because of its chemically inert nature, CO_2 requires high activation energy in order to generate CH_3OH. For the above reasons, relatively high temperature (above 240°C) is essential for the reaction to be carried out. However, in such high temperatures the reverse water gas shift (RWGS) reaction occurs, generating CO out of CO_2 and, as an endothermic reaction, reducing CH_3OH production yield. To adjust the RWGS reaction, lower temperatures and higher pressure is needed.

Water is also an important factor to restrain the reaction speed of CH_3OH production by CO_2 reduction [102]. Firstly, local water sorption was reported by researchers for CO_2 hydrogenation [103]. It was recently noted that in order to lessen thermodynamic obstacles, methanol yield is 1.3 times higher for water sorption enhanced hydrogenation compared to common hydrogenation of CO_2 inside a temperature scope of 220–270°C. Nevertheless, as previously said, high temperatures result in CO formation (RWGS reaction takes place) and so water sorption at higher temperatures cause a drop in methanol generation. Same thing is observed at high pressure values, while methanol selectivity increases with pressure changes, at the same time the more dominating RWGS reaction causes methanol selectivity to drop due to equilibrium disturbance [104]. More recently, researchers met with the conclusion that the hydrogenation reaction of CO_2 can be improved if the final product, in our case CH_3OH, is condensed. As shown in the equation bellow, low temperatures and specific pressure value with the addition of H_2O, is followed by considerable improvement in CO_2 conversion [105], for the reason that the reverse water gas shift reaction balance is regulated.

$$CH_3OH + CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

6.2.5. Challenges in Reduction of CO_2 to Methanol

Keeping in mind that CO_2 is an inert molecule, thanks to the two double bonds that bind carbon and oxygen together. Due to that fact, reducing CO_2 to methanol demands high energy levels. The first step to all catalytic conversion reactions is the reduction of CO_2 to CO and, as it is widely known, this reaction occurs in metal surfaces of catalysts [94, 95]. For the formation of value-added products, a highly active and stable catalyst is needed for the hydrogenation of CO_2 [108]. Post CO_2 reduction reaction synthesized H_2O, resulted in fast sintering and deactivation of the usually used Cu and ZnO catalyst [109]. Temperature-wise, if the CO_2 hydrogenation reaction takes place at high temperatures, then the same issue suggest itself through RWGS endothermic reaction that turns CO_2 into CO and H_2O. On the other hand, low reaction temperature results in slow catalytic activity. Consequently, regulating the CO_2 reduction reaction temperature to be low enough to prevent the reverse water gas shit reaction and at the same time high enough so the catalytic activity of the catalyst remains intact all the way through the reaction, is a major challenge in the reduction [110].

6.3. The Catalysis of Methanol Synthesis

6.3.1. Catalysts for the Synthesis of Methanol

Generally, there are three main needs for catalyst performance: selectivity, stability and activity. Many variables affect a catalysts performance in methanol synthesis.

High-Pressure Methanol Synthesis Catalysts

Ever since industrial methanol was first synthesized, in the 1920s, it was produced in a zinc oxide based catalytic system, stabilized by chromium oxide with a synthesis gas under 25-35MPa of pressure and in 300-400°C [99, 100]. A more active catalyst based on copper was already known at that time, but the zinc/chromium oxide based catalyst was significantly more stable than copper catalyst for the sulphur and chlorine composites that were in synthesis gas back then [101, 102]. Later, during the 1950s, higher purity synthesis gas was available and so, a new generation of higher activity and better selectivity copper based catalysts replaced the high-pressure zinc/chromium oxide catalytic process [115].

Low-Pressure Methanol Synthesis Catalysts

The vast majority of low temperature methanol synthesis catalysts are made of copper composites (copper, zinc and aluminium). An alternative to that, are Cu-based catalytic schemes that can be realized by aluminium leaching from Cu/Al alloys, resulting in Raney-Cu catalysts with large surface areas [114]. Other catalytic methods for methanol synthesis are based on noble metals, initially developed during the 1980s, but these systems have not yet managed to draw industrial development attention [116]. The reason for the lack of commercial interest lies in the significantly high cost of a noble metal catalyst, the same time that it offers no improvements in performance compared to other catalytic systems. Researchers have developed single-crystal and polycrystalline copper catalysts and, in both theoretical and experimental level, CO_2 and H_2 reagents over pure Cu result in CH_3OH synthesis, although it needs to be said that the academically developed catalytic model bares little relevance with the performance of industrial scale commercial catalysts [117].

Other, noble metal based catalysts have been developed as well, especially those based on palladium (Pd). Also, another kind of catalysts that is based on molybdenum disulfide (MoS_2) supported by alkali metals has shown good reactivity for methanol synthesis, and shows an attractive synthetic for high alcohol applications. A low-pressure methanol synthesis catalyst for industrial production was initiated by the Imperial Chemical Industries Ltd in 1966, which revealed a method of manufacturing adequately stable copper-based catalysts. The said catalyst, based on copper oxide and zinc oxide, was thermally stabilised with alumina and utilized in synthesis gas to methanol conversion [118]. To apply such a catalyst, the synthesis gas needs to be stripped of any sulphur and chlorine composites. In addition to the increased performance and thus the industrial profit of this catalytic system, a significant advancement for the use of this catalyst system was made by new purification systems and reforming technologies that developed simultaneously and satisfied the required purity of the syngas feed.

The methanol synthesis with this exceptionally active catalytic system can be held at 220–230°C and 5 MPa, therefore aging caused by copper sintering at high reaction temperatures is avoided. The low-pressure methanol synthesis catalytic system provides methanol purity higher than 99.5 % thanks to its high selectivity. Also, because of the low operating temperature of the method, the development of by-products (e.g. dimethyl ether, carbonyl complexes and methane) was notably reduced.

Properties of Catalysts for Low-pressure Synthesis of Methanol

All low-pressure catalysts in the industry today contain copper oxide and zinc oxide with a single or multiple stabilizing additives. Today's industrial catalysts are, for the most part, based on a Cu–Zn-Al arrangement and manufactured by coprecipitation, on an atomic ratio of Cu/Zn ranging in 2-3 and a small part of alumina [119]. Prime examples are the MK-121 catalyst from Topsøe [120] and the Megamax series catalysts from Clariant (formerly Süd-Chemie) which are also said to be made of $CuO/ZnO/Al_2O_3$ [121]. One of the most common compositions is an atomic ratio of Cu/Zn ranging from 2.8:1 to 3.8:1, as defined in U.S. Patent 4.535.071 [122].

Catalysts for industrial use are usually produced into tablets of 6x4 mm (MEGAMAX-800 and MK-121) or otherwise 5.3x5.1 mm (Katalco 51-9). The bulk density (i.e. the catalyst mass per volume of oxidic catalyst) is in the level of 1,200kg/l, though occasionally it may reach 1,300 kg/l (Katalco 51-9). Prior to the use, the oxidic catalyst requires reduction (normally post loading) by conventional methods [77].

The growing diversity of types of converters, the raw material of the current methanol production industry and its operating conditions has resulted in a need for suitable catalysts. However, due to the elevated business risk of the large-scale methanol production, custom-made catalysts remain still in the process of being developed.

Active Site of Catalysts

There have been many discussions as to why copper, zinc and aluminium ions containing catalysts are better than other arrangements. The main reason for that is the nature of the Cu/ZnO based catalyst's active site. Researchers have demonstrated how to classify the crucial atomic structure pattern for an industrial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst by means of experimental data from bulk, surface-sensitive and imaging methods collected on real high-performance catalytic systems along with density functional theory calculations [100]. In the figure bellow, there is a high-resolution transmission electron micrograph of a catalyst analysed by the Behrens group [124]. As said by the authors, the active site is mainly made of Cu steps alloyed with Zn atoms, all stabilized by bulk defects like stacking faults or twin boundaries terminating at the surface.
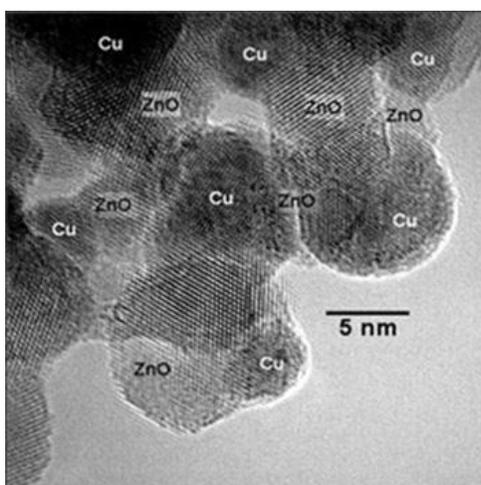

Figure 6.4 High resolution transmission electron microscope image of a conventionally prepared Cu/Zn/Al catalyst [124]

The Cu/ZnO catalyst's chemistry that was investigated in simple, carefully calculated model systems is very unlike the commercial catalyst utilized in chemical reactors in the industry. The industrial scale catalyst is a sponge-like assembly of myriads of small, copper and zinc spheres sized up to 10 nm with some percentage of alumina. Up until recently, the common knowledge was that the catalytic reaction occurs exclusively on copper's surface and thus, the goal was for copper to have a large area so the reactivity increases. In order to prevent copper atoms to cluster together into a larger sphere, zinc oxide was thought to play the role of a spacer. With a high-resolution transmission electron microscope, separate copper and zinc atoms can be observed within a minor segment of the cluster. It is known that the catalyst works properly when it has pattern defects. Slight defects in the crystal web of the copper particles manifest themselves as valleys and peaks on the surface.

These defects help bind the reagents and intermediates of the methanol synthesis in an optimal manner to ultimately yield methanol. Nevertheless, an analysis of a copper-zinc sponge-like atom has further established an occasional proposal that suggests that zinc oxide is not only found in nanoparticles of the stabilizing stage, where it puts space between the copper particles, but is also detected over some copper atoms, as a messy deposition of atomic layers. Separate zinc particles can even transport to the copper net. As it has been calculated, the oxygen-rich intermediates in the methanol reaction, bond better to zinc compared to copper atoms. As a result of the high stability of intermediates, they are easily formed. Therefore, the performance of the catalyst increases owing to the fact that the energy barrier from the intermediates to the starting molecules has reached higher levels than the final result [77].

The various catalysts with copper, zinc and alumina phases exhibit minimal differences in overall technical performance. However, on large scale, in large methanol plants, small differences in technical performance translate into costly differences in value.

6.3.2. Catalytic Mechanism

The mechanism of methanol synthesis catalysis can be generally described by the following equations, the second of which is commonly recognized as reverse water gas shift reaction (RWGS):

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta_R H_{298K,50bar} = -90.7 \text{ kJ/mol}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{R298K,50bar} = -40.\frac{9 \text{ kJ}}{mol}$$

In both of the reactions, H_2O and CO directly affect catalyst performance as the main by-products. That is because water reduces the catalytic activity by getting in the way of coordinatively unsaturated binding sites [78] while carbon monoxide is strongly chemisorbed on catalysts of palladium [113, 114, 115]. Additional by-products such as dimethyl ether, methyl formate, methane or higher alcohols are also found, but their total selectivity is usually not as much of 0.1%. In order to improve the selectivity for methanol synthesis by carbon dioxide, an in-depth understanding of the reaction mechanism is necessary. Today, the so-called forming pathway (Figure 6.5) is the predominant reaction pathway for describing the mechanism and therefore the key steps of the formate route are described below.
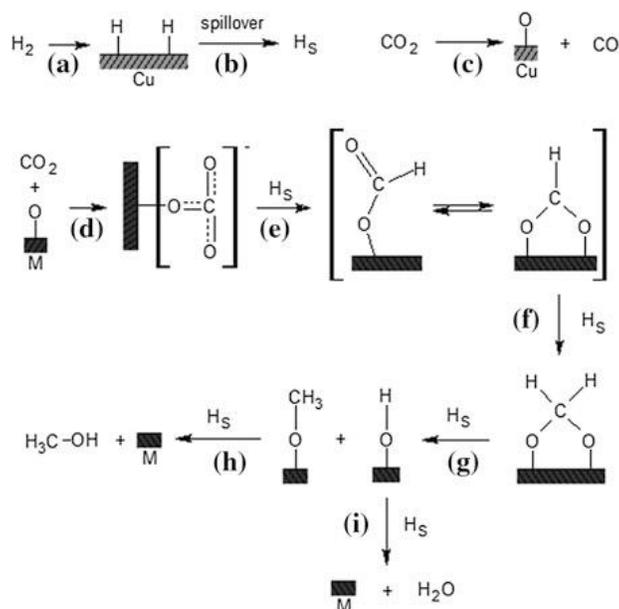

Figure 6.5 Mechanism of methanol synthesis [77]

As shown in the Figure 6.5, the reaction initiates with H adsorption on the Cu surface followed by a homogenous splitting (a), which offers atomic hydrogen as overflow (b). The hydrogen overflow is presented as travelling H atoms over the Cu surface that set up new bonds to the nearest Cu atoms [128]. This travelling carries on until the H atoms pass the Cu/metal oxide limit. When the limit is surpassed, the H atoms are offered for CO2 reduction. At the same time, CO_2 latches onto the catalyst surface, yielding two competitive reactions. The dissociative adsorption (c) is one component of the RWGS reaction and it yields CO and adsorbed oxygen. Then again, CO_2 attaches on the catalyst surface, where a reaction with adsorbed oxygen takes place, in order to yield a carbonate-like shift state (d). Having in mind that CO_2 also adsorbs on metal oxides such as ZnO, ZrO_2, or Ga_2O_3, consequently M symbolizes a placeholder in place of specific chemical bodies.

In the next step, hydrogen supplied by spill over reduces the transition state (d), yielding formate being bound in two different ways to the catalyst surface (e). Of these entities, only the bidentate formate reacts with atomic hydrogen (f). The resulting methylenediol group undergoes a further reduction to a catalyst bound methoxy and hydroxy group each (g). The methoxy species undergoes a final reaction with hydrogen to give methanol, which desorbs as methanol in subsequent course (h). In a consecutive reaction, the remaining hydroxy species is converted to water (i). The rate-determining step of the mechanism is the reduction of the bidentate methyl formate [77].

In addition, catalysts made of mainly Pd and supported by gallium (III) trioxide (Ga_2O_3) show similar potential to those based on Cu [105, 107, 108]. The Pd catalysts varies in some aspects from the Cu based catalyst, mainly because the CO_2 hydrogenation occurs in Ga_2O_3 surface while atomic hydrogen leaks through Pd [129]. The consequent reduction stages give in only methoxy groups, so the Pd is needed for the sufficient hydrogen supply in order to reduce CO_2 to methanol [107, 108]. Another variation from the Cu-catalysts refers to the RWGS reaction, which occurs on gallium (III) trioxide as shown in Figure 6.6 [105, 109].
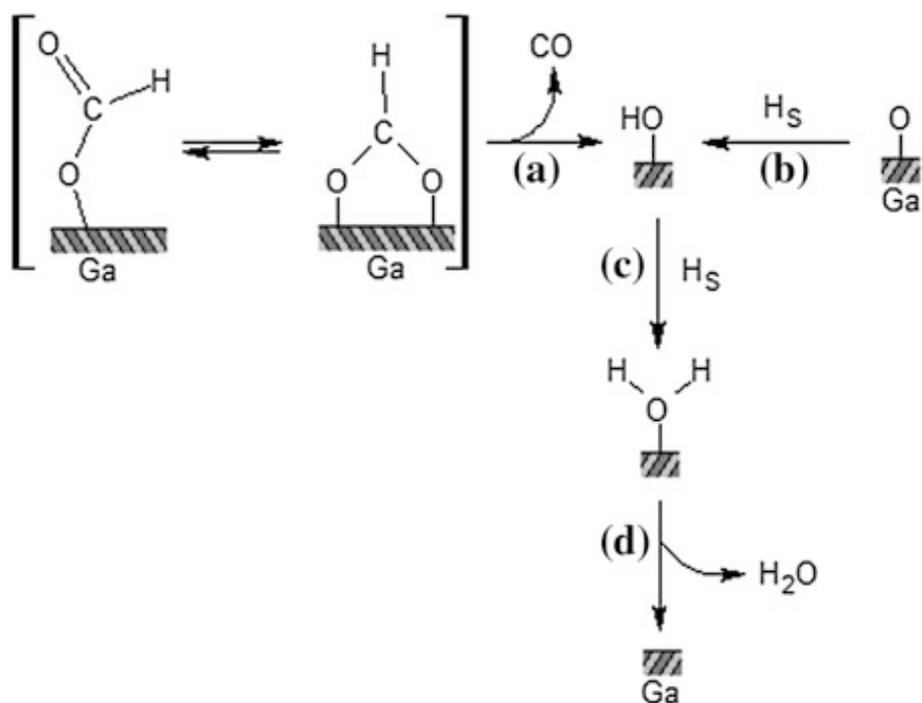
Figure 6.6 RWGS reaction on a Pd-Ga$_2$O$_3$ catalyst [77]

6.3.3. Catalyst Compositions

Many of the catalytic synthesis used for CO_2 hydrogenation are utilized as well in methanol production due to similar reaction conditions, mechanisms and the fact that minor CO_2 concentration in the syngas mix aids methanol yield. There has been a variety of catalysts tested for selectivity, durable stability and reactivity for methanol production processes [80, 109–116].

Table 6.4 Most common hydrogenation catalysts [77]

Process	Catalyst composition (wt %)	Reaction conditions	Reference/patent filing date
Shell International Research	Cu-Zn-M 40:18:4[b]	300°C, 53 bar, 10,900 h^{-1}	[137](1971)
Mitsubishi Gas Chemical Company	Cu-Zn-Al 62:31.5:6.5[c]	240°C, 88 bar, 30,000 h^{-1}	[138](2010)
Ammonia Casale	Cu-Zn-Cr–Al 30:50:16:3	250°C, 100 bar, 12,500 h^{-1}	[139] (1982)
Süd-Chemie AG	Cu-Zn-Al 65.2:23.8:11	300°C, 100 bar, 4,000 h^{-1}	[132] (1984)
Süd-Chemie AG	Cu-Zn-Al 63:27:10	250°C, 60 bar, 22,000 h^{-1}	[133](2001)
Lonza AG	Cu-Zn-Zr 40:20:40	250°C, 50 bar, 8,000 l/kg h^{-1}	[134](1996)
AIST, RITE[a]	Cu-Zn-Al-Zr-Si 45.2:27.1:4.5:22.6:0.6	250°C, 50 bar, 10,000 h^{-1}	[102](1998)
Mitsubishi Gas Chemical Company	Cu-Zn-Al-Zr[d] 57.6:29.5:9.2:3.7	250°C, 49 bar, 4,000 h^{-1}	[135](1973)
YYK Corp[a]	Cu-Zn-Al 76.3:11:12.7	250°C, 50 bar, 1.7 g/h mol	[136](1998)
Kang et al.	Cu-Zn-Al-Zr 60.5:30.1:7.6:1.8	250°C, 50 bar, 4,000 h^{-1}	[140](2009)

M = Mixture of two or more rare earth elements (except Ce) in their natural ratio
a = The full list of all proprietors is published in the patent
b = Weight portion of the metal oxides
c = Molar ratio
d = A Ce/Zr-oxide support was used with a catalyst/support weight ratio of 5:1

Usually, conventional catalysts are used as research fundamentals and are further improved by additions. The majority of catalytic systems have a noble metal component, such as Cu, Re, Pt, Pd, Ag or Au in addition some less noble metal oxides, like ZnO, ZrO_2, Ga_2O_3 or Al_2O_3. Depending on the construction technique, SiO_2, further metal oxides, or carbon structures aid in supporting the catalyst even further. In spite of the great variety of metal oxides combinations for catalytic processes, Cu catalysts lead over the rest. Aside catalyst synthesis, the manufacture technique and the catalyst pre-treatment that determine the size of the catalyst's active surface are equally important since they directly affect catalytic activity.

Methanol catalyst synthesis and production methods are very much alike the ones used for synthesis gas conversion catalysis. Pure CO_2 hydrogenation has some characteristics that demand the procedures to be customized. The main difference between CO_2/H_2 and synthesis gas is the water production in stoichiometric quantities taking place in CO_2 hydrogenation. The side-product formation generally reflects in weakening of the catalyst activity because it blocks unsaturated bonding sites [103, 107], 121]. In this perspective, the CO_2/H_2 converting catalysts have to be more stable and more active to sustain methanol synthesis from syngas catalysis. Thus, improvements in catalysts synthesis present great potential. There are many metal oxides useful for upgrading catalytic properties and often more than one of them are employed to do so. Table 6.5 presents how catalyst properties can be upgraded from a binary to a ternary structure.

Table 6.5 Changes in catalyst properties caused by metal oxides [77]

Catalyst (molar ratio)	X_{CO2}(%)	S_{MeOH} (%)	S_{CO} (%)	Y_{MeOH} (%)
Cu/ZnO (50/50)	27.3	31.9	68.1	8.7
Cu/ZnO/MgO (47/47/6)	19.1	57.0	43.0	9.0
Cu/ZnO/Al_2O_3 (47/47/6)	35.3	64.7	35.3	22.8

Reaction conditions H_2/CO_2 = 3, temperature = 493 K, pressure = 13 bar, space velocity = $3.600h^{-1}$

Nearly all metal oxides studied for catalyst promoters are alkali metals, alkaline earth metals, rare earth metals, transition metals, or main group III metals of the boron group. Nevertheless, few of them are appropriate as catalyst components. Some metal oxides weaken catalyst properties and others (the majority of the rare earth oxides) are simply too expensive. Generally, the most frequent metal oxides used are ZnO, ZrO_2, Al_2O_3 and Ga_2O_3.

ZnO is found in most copper based catalysts. It makes possible for Cu particles to be better dispersed and as a result widens the catalytic surface area [110, 115, 130, 131]. As said before, ZnO partakes in addition in the catalytic mechanism, which makes ZnO a key catalytic factor. Additionally, ZnO is able to store small quantities of sulphides, which may contribute to avoid catalyst deactivation [113, 132].

Al_2O_3 signifies another commonly used metal oxide. Specifically, combining ZnO and Al_2O_3 presents a cooperative effect that causes a significant delay of the unavoidable sintering of Cu particles in the course of long-term operations [130–132]. Alumina aids as well in Cu particle disperse, although that phenomenon does not occur in Re or Pd based catalysts. On the contrary, Al_2O_3 can severely damage a Re or Pd based catalyst's selectivity and reactivity [110, 113, 132].

At times **ZrO_2** instead of alumina is used in ternary catalytic compositions. That is due to the fact that zirconia containing catalysts have been proved to adsorb a reduced amount of water onto the catalyst surface than the ones containing alumina [127]. Similar to the rest, ZrO_2 can also enhance copper particle dispersion. However it is not as effective as ZnO [130, 131, 133].

Ga_2O_3 structured as monoclinic b-Ga_2O_3 is frequently used in arrangement with Pd as noble metal component, where it is essential for CO_2 adsorption [134–136]. Gallia, as an additive in Cu catalysts, prevents sintering [127]. In addition to that, gallia interacts with copper during methanol synthesis and regulates Cu^0/Cu^+-ratio.

Additionally, recent findings show that **Cu/CeO_2** supported catalysts are very promising in the field of methanol synthesis, although with CO as feed gas. In particular, researchers supported that Cu/CeO_2 catalysts show greater activity in CO hydrogenation than conventional Cu/ZnO catalysts [128]. The in situ formation of copper ions (Cu^+),

stabilized on catalyst surface via Cu–Ceria interactions, were considered to be accountable for high methanol synthesis activity [149]. Moreover, in the subject of CO_2 hydrogenation to methanol, Cu/CeO_2 catalysts have been recently highlighted [138, 139]. Rodriguez and collaborators showed by theoretical calculations and experimental results that the blend of metal and oxides in the Cu/CeO_2 boundary aids the CO_2 conversion to methanol [151]. This is significantly important bearing in mind the difficulties associated with the chemical inertness of CO_2 [149].

6.4.   Methanol from Synthesis Gas

6.4.1. Chemistry of Methanol Synthesis

Stoichiometry

The following are the main reactions responsible for methanol production from synthesis gas:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{R(298K,50bar)} = -90.7 \text{ kJ/mol}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{R(298K,50bar)} = -40.9 \text{ kJ/mol}$$

The production of methanol from carbon monoxide and carbon dioxide are connected via the water gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{R(298K,50bar)} = -42 \text{ kJ/mol}$$
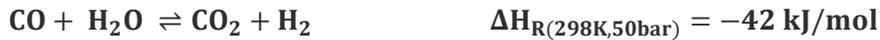
The reaction enthalpy $\Delta H_{R(298k, 50bar)}$ [152] mentions 298 K and 50 bar, while the typical enthalpy of reaction (indicated as $\Delta_R H^-$) is the enthalpy change that happens in a system when 1 mol of matter is transformed by a chemical reaction under standard conditions. Methanol production from synthesis gas reactions are exothermic and come with by a volume drop. Water gas shift reaction with carbon dioxide and hydrogen by-products is slightly exothermic. Technically, increase in pressure and decrease in temperature favours methanol formation, with the highest conversion depending on the equilibrium composition.

Actual supply is not only out of CO and H_2. One way to account for the water gas shift reaction is to classify a stoichiometric number SN as:

$$SN = \frac{mol_{H_2} - mol_{CO_2}}{mol_{CO} + mol_{CO_2}}$$

The stoichiometric number (SN) of the methanol production syngas should be 2.0, which differs from the molar ratio of H_2/CO. Nonetheless, a small hydrogen addition can raise the SN to 2.05-2.08 and has been noticed to improve catalytic performance [153]. In principle, the synthesis gas generated from different sources covers a variety of feed gas

compositions (CO-free, CO-rich, or hydrogen-rich syngas), and thus the stoichiometric value has to be attuned by the water gas shift reaction. The synthesis gas coming from gasification (e.g. of coal) is loaded in CO. The most favourable syngas composition can be found if CO is partially converted by high-temperature water gas shift and CO_2 is subsequently removed or if H_2 is added from synthesis purge gas. Due to the fact that the rate of methanol synthesis can be enhanced by extra CO_2 in the synthesis gas mix, balancing the stoichiometry of the makeup gas (MUG) can elevate the performance of methanol production and selectivity.

6.4.2. By-product formation

All common liquid phase methanol synthesis $Cu/Zn/Al_2O_3$ catalysts produce methanol with nearly 99% selectivity. However, along with direct CO hydrogenation process, some other reaction by-products are to be expected [154]. This is notable since all of the by-products usually found, except for formaldehyde and formic acid, are a lot more thermodynamically favoured compared to methanol. That shows how important the catalysts' properties (physical, chemical and topological) are. All of the direct CO hydrogenation reactions release heat (exothermic) and are equilibrium reactions. The direct reactions of hydrogenation have various values of activation energy, which limits the reaction rate, under the same temperature/pressure conditions. It is apparent that the favourable by-product formation can be achieved since catalysts directly affect the activation energy.

Other by-products that form in carbon oxides hydrogenation catalysis are ketones and ethers, primarily dimethyl ether [134–136]. However, water present in reaction products strongly prevents dimethyl ether to form and ketones appear in minor concentrations in unrefined methanol. Formation of above mentioned by-products can be supported by impurities in the catalyst, such as alkali, iron, nickel and cobalt (through usual Fischer-Tropsch reactions). For example, if the catalysts' alumina component is very acidic, methanol formation reaction can proceed to produce dimethyl ether.

Table 6.6 By-products through direct CO hydrogenation reactions [158]

	CO:H_2 Ratio	Loss (%) as H_2O
CO + 2H_2 → methanol	1:2	-
2CO + 2H_2 → acetic acid	1:1	-
2CO + 2H_2 → methyl formate	1:1	-
2CO + 4H_2 → ethanol	1:2	28
3CO + 6H_2 → propanol	1:2	38
2CO + 3H_2 → ethylene glycol	2:3	-
4CO + 8H_2 → isobutanol	1:2	50
2CO + 4H_2 → ethylene	1:2	56
16CO + 33H_2 → n-hexadecane, representative for Fischer-Tropsch	1:1.2	56

6.4.3. Catalyst Deactivation

Catalytic process conditions directly affect the catalysts structural properties. In methanol synthesis catalysis, physical and chemical aspects of the environment are crucial for the catalysts activity and longevity. However, the above properties are significantly affected and varied by the conditions prevailing in the process [137–139].

Poisoning

The main mechanism for deactivating the catalyst in methanol synthesis is its poisoning with traces of sulphur and chlorides potentially present in the feed gas, because all of the methanol synthesis catalysts are predominantly copper. Therefore, any component contained in the feed gas and reacts with copper will poison the catalyst. Synthesis gas (or nitrogen flow) must have a sulphur content of less than 0.05 ppmv H_2S. The catalyst is completely deactivated if the sulphur exceeds 0.8% by weight of the catalyst. Chloride also in any form, such as Cl_2, HCl or R-Cl, is a powerful poison for the methanol catalyst. Copper chloride agglomerates rapidly, which in turn reduces the active surface of the catalyst. Therefore, the content of chlorine in the synthesis gas must be undetectable. The chlorides found in concentrations above 500 ppmw completely inactivate the catalyst.

Additionally, various solid particles in the feed such as dust deposited on the surface of the catalyst inhibit the catalytic process and lead to early inactivation of the catalyst. If iron in the form of iron carbonyls is carried onto the methanol synthesis catalyst, this catalyses the Fischer–Tropsch reaction and consequently by-product formation increases. Iron and other heavy metals also block the active sites of the catalyst, thus reducing activity.

Nickel has a similar deleterious effect on the catalyst performance. Any carryover of lubricating oil should be avoided because it is a fact that these heavy hydrocarbons can deactivate methanol synthesis catalysts [77].

Methanol synthesis catalyst has to steer away from steaming because it directs to an accelerated increase of copper crystals and thus causes the catalyst to deactivate prematurely. In CO_2-rich syngas, the deactivation is a follow-up by water, formed via the RWGS reaction. The higher partial pressure caused by water devastates the matrix of the catalyst, which allows the copper crystallites to sinter more swiftly [158].

Oxygen may also poison the catalyst because contact of oxygen with the reduced catalyst is followed by partial re-oxidation and consequent reduction by the process gas. These redox reactions affect the catalyst structure and lead to premature loss in crushing resistance as well as a rapid increase in pressure drop. This can also cause thermal sintering, with the result of active copper surface area loss.

Thermal Damage

In a small degree, the catalyst can also be deactivated by alterations in the copper crystals due to thermal stress. Such alterations can be large copper crystallites that form because of sintering. Even if no poisoning occurs, methanol synthesis catalysts suffer by rather fast deactivation. Over one-third of the activity is lost in the course of the first 1,000h of operation [160]. Specifically, the catalyst is sensitive to high temperature and therefore demands controlled conditions during the process in order to stay away from changes of the active site or speedy sintering of the copper particles [123]. In general, the life span of an industrial catalyst for methanol synthesis is found in practice to be no less than 4 years. The catalyst lifetime is directly connected to the operational expenses of a methanol plant [141, 142].

7. Conclusion

The purpose of the present work was to highlight the production of methanol from CO_2 with the aim of exploiting CO_2 as a raw material and producing methanol as a pure form of energy.

CO_2 is a greenhouse gas and its increased emissions due to human activity make it imperative to remove. At the same time, fossil energy sources are rapidly depleted and humanity is called upon to find forms of energy to replace them. In this context, there has been extensive literature review on CO_2 post-combustion and oxy-fuel combustion capture, sequestration and hydrogenation methods together with a presentation of recent developments in the production of methanol from syngas with its main constituents, CO_2 and H_2. In addition, hydrogen production methods were analyzed by both conventional and pioneering methods.

Particular emphasis was placed on the production of methanol from the hydrogenation of bound CO_2. To this end, the potential ways of producing hydrogen have been explored in depth, especially with the use of renewable energy sources. From the standpoint of the present thesis, the production of hydrogen from renewable sources fills a necessary gap in the widespread application of RES. In this way, energy generated by air, sun, waves and other sources can directly operate water electrolysis technologies and be used to produce hydrogen. This hydrogen can then be stored, transported or fed to a carbon dioxide hydrogenation unit to provide methanol and other alcohols as a final product.

The above shows that the future of methanol production from CO_2 seems very promising in terms of achieving sustainable development. However, there are still many paths to be explored to render production more efficient and to reach a point where widespread application of post-combustion CO_2 capture (conventional or oxy-fuel) and CO_2 hydrogenation plants to methanol can be achieved.

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