

Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂

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While Carbon Capture and Storage (CCS) technologies are being developed with the focus of capturing and storing CO₂ in huge quantities, new methods for the chemical exploitation of carbon dioxide (CCU) are being developed in parallel. The intensified chemical or physical utilization of CO₂ is targeted at generating value from a limited part of the CO₂ stream and developing better and more efficient chemical processes with reduced CO₂ footprint. Here, we compare the status of the three main lines of CCS technologies with respect to efficiency, energy consumption, and technical feasibility as well as the implications of CCS on the efficiency and structure of the energy supply chain.

Introduction

The CO₂-footprint of the materials used in everyday life is a new measure to evaluate the CO₂ emissions linked with their production and utilization. Reflecting the efficiency of the use of fossil resources, the CO₂-footprint receives a lot of attention in the light of the current climate discussion. By 2050, a business as usual policy would lead to an increase of CO₂ emissions by

24 Gt.¹ However, a reduction of 50% of the global CO₂ emissions appears necessary to limit the long-term global average temperature rise to between 2 °C and 2.4 °C by the year 2050.² The Blue Map Scenario of the International Energy Agency (IEA) proposes a wide range of measures to achieve a CO₂ emission cap of 14 Gt to meet the 2 °C target. Carbon capture and storage (CCS) is seen as one of the most important single reduction measures worldwide contributing with 8.2 Gt (Fig. 1). It is a reduction option suitable for large stationary CO₂ point sources, such as fossil power plants, cement industry, and refineries.

Parallel to the introduction of CCS technologies, Carbon Capture and Utilization (CCU) is aimed at using CO₂ as a carbon source for chemical production and generating value from a readily available feedstock.^{3,4} Exploiting a limited amount of the CO₂ as raw material for chemical synthesis or for direct use as gas or liquid can complement its storage in geological rock formations.⁴ This includes the utilization of CO₂ for producing platform and bulk chemicals, as well as increased utilization for

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Broader context

The CO₂ footprint of our everyday consumer products gives a measure of the intensity with which fossil energy carriers are employed for their production and during their typical lifetime. Reducing the CO₂ footprint seems mandatory, as the limited availability of fossil energy carriers and the rising level of carbon dioxide in the atmosphere due to the CO₂ emissions caused by combustion of fossil energy carriers is a matter of growing public concern. However, until renewable energy sources become available to a greater extent, the combustion of fossil energy carriers will continue and increased combustion of coal may even be necessary as a transition technology. To counter this effect, CO₂ capture technologies are being adjusted to the large scale of commercial power stations, which are one of the major contributors to the global CO₂ emissions. Once the CO₂ is separated, the question arises of how to store the captured CO₂ for long periods of time or to make use of it as sustainable resource and feedstock. The latter means that, in essence, we are entering into an anthropogenic carbon cycle. The present review discusses the status of CCS and CCU contributing with scientific and technological information to the decision finding process that is needed in society and politics.

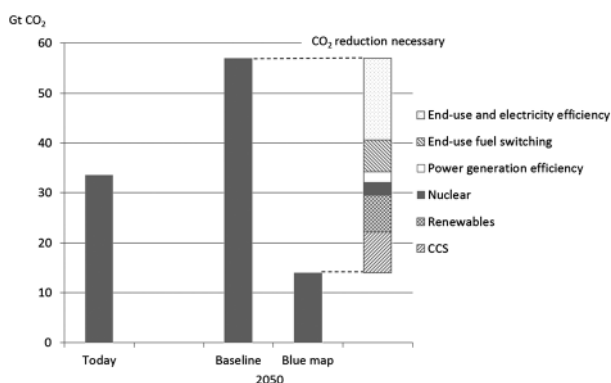
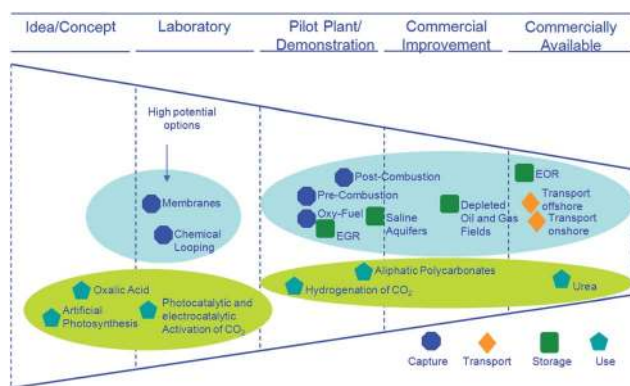


Fig. 1 CO₂ reduction measures in the IEA Blue Map Scenario, data from ref. 1.



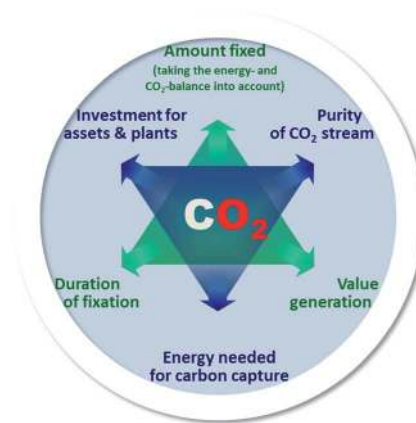
Scheme 1 Innovation phases of technologies for collecting, transporting, storing and exploiting CO₂, adapted from ref. 6.

manufacturing polymers⁵ and fine chemicals.⁴ Moreover, the physical use of CO₂, e.g., in the petroleum and gas industry (Enhanced Oil Recovery (EOR), Enhanced Gas Recovery (EGR), and Enhanced Coal Bed Methane (ECBM)), may become important applications in the energy supply field.

Carbon dioxide can be captured from CO₂ containing gases by using technologies, which are commercially available (Scheme 1) and established in chemical processing. Because of other framework requirements, the application of CCS technologies in power plants needs a modification of existing technologies and the development of improved capture technologies. The main challenges are the large flue gas flows, the chemical composition of flue gases, a high degree of CO₂ purity and the CO₂ capture rate. Worldwide, activities are focusing at present on identifying energy and cost efficient capture solutions.

The purity of the CO₂-stream[†] after separation is decisive for how much energy is needed for the capture of CO₂ but also is a significant aspect for the transport, storage and exploitation of the carbon dioxide stream (Scheme 2). With increasing requirements regarding the purity of the CO₂, its capture is more expensive and requires more energy, whereas with regard to compression, transport and storage, there may be advantages

[†] The CO₂-stream here is denoted as the gas obtained after separation of the CO₂. It consists mostly of CO₂, but can also contain other components.



Scheme 2 Criteria for making CO₂ available by carbon capture (blue) and evaluating the use of CO₂ as raw material and gas (green).

concerning the necessary energy expenditure and storage capacities. A high purity grade of the CO₂-stream is generally required in downstream processing in the chemical industry, as catalysts, employed in chemical conversion, may be poisoned by impurities, while impurities incorporated in the products may impair certain applications (e.g., in the pharmaceutical industry).⁴

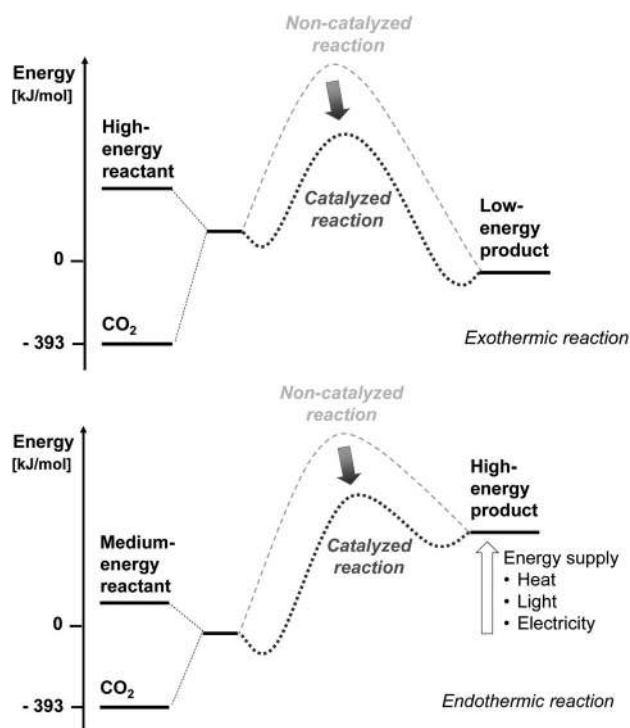
The transport of carbon dioxide has been commercially realized. Worldwide, currently over 4000 kilometres of CO₂ pipelines (mainly in the U.S. and Canada) are in operation. Many of these pipelines have been built in the 1980's. The CO₂ is transported to oil exploration sites and is used for enhanced oil recovery (EOR). However, there are still other transport options, as e.g. truck, train and ship.⁷

The use of a limited part of the CO₂ supply by means of fixation and transformation can complement its storage in geological rock formations. This includes the utilization of CO₂ for producing, e.g., platform and bulk chemicals,[‡] polymers and fine chemicals.^{4,5} There is an industrial policy perspective for the utilization of CO₂,⁸ but it may not be regarded a single solution for the huge amounts of CO₂ released by energy conversion processes, which characterizes the *Teraton Challenge*.⁹

For the utilization of CO₂ as chemical feedstock, the low energy level of CO₂ needs to be taken into account. For chemical transformation of CO₂, energy is required, which can be supplied directly by using energy-rich reaction partners or indirectly as heat, light or electricity (Scheme 3).^{4,10} The energy supply may likewise coincide with emissions of carbon dioxide. To minimize the CO₂-footprint, the utilization of energy from renewable resources (e.g., electricity from wind power stations) is particularly interesting. To evaluate the overall concept, a comprehensive assessment of the different options necessitates product-based complete CO₂- and energy-balances that account for the utilization of CO₂ as well as the supply of energy, separation and transport.

Whereas the storage of CO₂ in geological rock formations is set for long periods, the period of CO₂-fixation in products varies greatly. Most attractive are uses, where large amounts of CO₂ are

[‡] Bulk chemicals are basic chemicals produced in quantities of more than 10 000 t per annum.



Scheme 3 Energy balance for the reaction of CO₂ with high-energy reactants to low-energy products (top) and of CO₂ with medium-energy reactants to high-energy products (bottom).

fixed in products, which are used for long periods and whereby added value is generated by the utilization of CO₂ (Scheme 2). Feasible uses with a short CO₂-fixation time are only relevant in terms of net reduction of CO₂ emissions, if the use is repeated very often and substantial amounts of carbon dioxide are fixed in an anthropogenic carbon cycle.

The CCS and CCU technologies are found in very different stages of innovation (Scheme 1).^{4,6,11,12} While certain technologies have been commercially implemented (EOR, production of urea and methanol), others are found in the pilot stage or at the threshold of demonstration (Oxyfuel, production of aliphatic polycarbonates^{13,14}). Yet others are found in a very early stage of technical development or in the conceptualization stage (CO₂-membranes and artificial photosynthesis).

In this paper, we examine the status of research and development of CO₂-capture, transport and utilization as well as the perspectives of the corresponding technologies. We will begin with an overview on the worldwide status of CCS-technologies and assess innovative industrially applicable approaches regarding CCS, while we will only touch upon the physical and chemical exploitation of CO₂ including the organo-chemical utilization of CO₂ as the C1-building block. Concerning a detailed description and the fundamental aspects of the various process concepts of CCS, we refer the reader to the literature (see, e.g. ref. 7, 15 and 16). The focus lies on the discussion of technology aspects like energy efficiency, capture rates, degree of impurities and environmental impacts. The analysis comprises

§ CO₂ as a C1-building block concerns chemical synthesis routes in which CO₂ is used as a carbon source.

also a cost analysis for different capture and transport options. Also, the environmental impact of CCS technologies is analysed. Last but not least, the worldwide state of development for CCS and CO₂-utilization is summarized (see also ref. 17–22). Even though CO₂-storage is not the priority of this paper, it is briefly reviewed for the sake of completeness. For a detailed analysis about storage options, the state of the art, monitoring techniques, etc., the reader is referred to the literature.^{6,23–25}

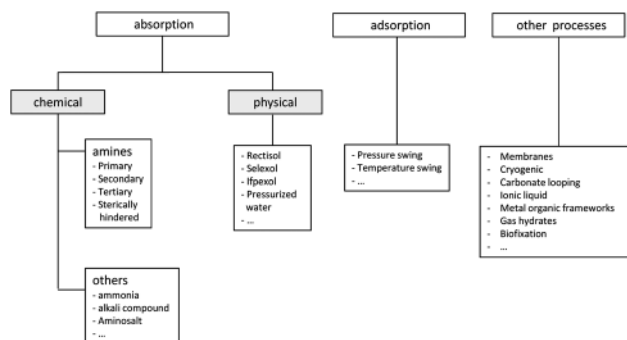
Carbon capture technologies

There are different commercial technologies to capture carbon dioxide from gases. In chemical processing, there are many examples, where the separation of CO₂ from gas streams is implemented on a large scale. The production of synthesis gas, hydrogen and ammonia are just some examples.⁴ Technologies like chemical absorption, physical absorption and membranes are used today (Scheme 4).^{7,26,27} Detailed information about these options can be found in the literature.^{7,28}

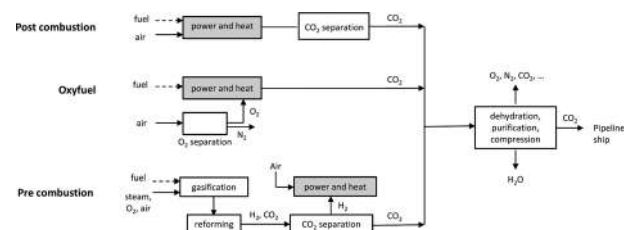
Yet the large-scale implementation of CO₂-capture in power plants is linked to many technical challenges, in particular, in the area of system integration (energy and stream management, incorporation into the power plant process).^{29,30} Three technology routes^{15,16,28,30} are currently most intensively discussed (Scheme 5):

- CO₂-capture from the flue gas stream after combustion (*Post-combustion*);
- Use of nearly pure oxygen for fuel combustion instead of air, which increases the CO₂-concentration of the flue gas (*Oxyfuel*); and
- CO₂-capture from the reformed synthesis gas of an upstream gasification unit (*Pre-combustion*).

All the process families need an additional energy input for gas separation, capture, conditioning and compression/liquefaction of the carbon dioxide.



Scheme 4 Underlying principles for the capture of carbon dioxide.



Scheme 5 Currently favoured CCS-process families.

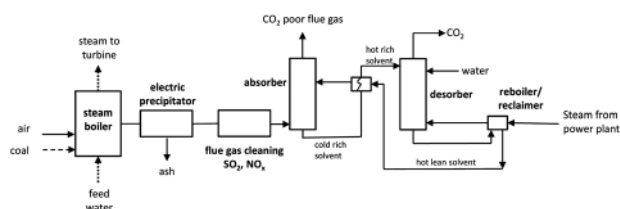
The energy penalty is reflected in a decrease in power plant efficiency of typically 10 to 14% points. Post-combustion processes are assessed with an efficiency loss of 10–12% points,^{7,31} while an efficiency loss of *ca.* 10% points is currently stated for the Oxyfuel process.¹⁶ Yet considerable efficiency potentials are seen for all technologies. In the mid- and long-term, losses in efficiency, ranging from 8–10% points, may be possible. Further increases in efficiency may be possible by instituting CCS-technologies of the second generation, such as new gas separation processes based on the use of membranes and chemical looping as alternative method for supplying oxygen (*vide infra*).

CO₂-capture after combustion: post-combustion processes

When carbon dioxide is captured after the combustion process, including the subsequent flue gas cleaning (removal of dust, sulfur and nitrogen compounds), the process line is described as ‘post-combustion’.³² From a current point of view, the most promising methods are the so-called ‘chemical absorption’ processes that are often denoted as chemical washes. The solvents favoured nowadays are those based on amines, or those containing ammonia or alkali. Another technical variant is the use of amino acid salts. After the absorption, the CO₂ is removed from the solvent by a regeneration process induced by a temperature increase and/or pressure decrease. The solvent is then recirculated and the separated CO₂ processed for the transport and subsequent storage.

Development line. The absorption in liquid solvents is an industrially tested and widely applied CO₂-separation technique, with which high purities and degrees of separation can be attained. Currently, the most developed technique is the amine-based separation method. In particular, monoethanolamine (MEA) and other amines have found widespread use. In connection with the particular requirements associated with the power plant processes and flue gas compositions, the stability of the solvents as well as the energy efficiency of the adsorption–desorption cycle need to be further improved.¹⁸

A possible processing scheme of a plant for post-combustion capture of CO₂ is shown in Scheme 6.^{33,34} After the flue gas is cooled, the absorption takes place at a temperature of about 40 °C to 60 °C. The CO₂-loaded liquid is then directed to a regenerator (stripper). The low-pressure steam for the necessary temperature change for the regeneration of the washing liquid is taken from the power plant process at a temperature of about 100–140 °C. Since the steam is no longer available for electricity generation, this leads to considerable decrease in the efficiency of the power plant.



Scheme 6 Processing scheme of a CO₂-capture from the flue gas (post-combustion).

The most important parameters for operating a post-combustion CO₂-capture unit are:

- Flue gas volume stream (this is decisive for the size and thus the investment costs of an absorber),
- CO₂-content of the flue gas as well as the partial pressure of the CO₂ (the partial pressure of the CO₂ typically lies in the range of 3–15 kPa, at which the chemical absorption represents the most suitable method),
- Degree of the CO₂-separation (typical degrees of separation are about 80–95%; higher degrees of separation require a larger dimensioning of the separator and cause a greater loss in efficiency),
- Solvent volume stream (essentially determines the dimensioning of the components found behind the actual absorption unit),
- Purity of the captured CO₂.

State-of-the-art. Within the framework of smaller pilot-scale projects and initial commercial applications, several power plants implementing CO₂-capture from the flue gas have been built throughout the world. One of the worldwide largest CO₂-washes in connection with a power plant process (320 MW_{el}) is currently operated at Shady Point (Oklahoma, USA) for producing CO₂ for the food industry. The amine-based chemical washes attain a separation capacity of 800 t CO₂ per day, which corresponds to about 15% of the total CO₂-quantity of the power plant. Another example for the chemical absorption based on amines is the Sleipner Project in Norway. On a natural gas offshore platform in the North Sea, each year about 1 million tonnes of CO₂ are captured from the recovered natural gas *via* a chemical wash and then pressed into a geological reservoir (Utsira field).

Technical and scientific challenges. Chemical washing processes based on monoethanolamine (MEA) and other solvents are associated with technical as well as fundamental constraints:

Decomposition of the solvent in the presence of oxygen and other foreign substances (dust): due to the less complex flue gas composition, the requirements of the chemical washes used today in the chemical industry are less stringent compared to those of wash solutions intended for the cleaning of power plant flue gases. The relatively high oxygen content in power plant flue gases causes degradation of the amines, which can be prevented by adding so-called inhibitors. Residual dust may block the filling body and thus impair the operation of the corresponding unit components.

Solvent degradation by reaction with sulfur dioxide or nitrogen oxide from the flue gas: by reaction with SO_x and NO_x, amines form salts that have to be precipitated at high temperatures in special units (reclaimers). This can be avoided by lowering the residual SO₂-content of the flue gas. At about 10 ppm SO₂, the salt formation can be prevented.³⁵ This value lies considerably below the legally prescribed limit for flue gases released into the atmosphere (70 ppm or 200 mg m⁻³ SO₂ for new plants in Europe).

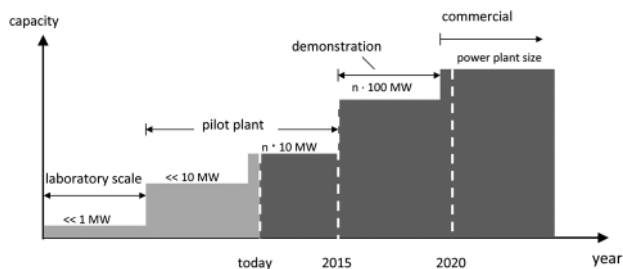
Higher energy demand for the solvent regeneration: the energy input required for regenerating the solvent is decisive for the overall efficiency of the post-combustion technique. The energy

consumption (low-pressure steam) amounts to about 4 GJ per tonne CO₂ captured, whereby about 40–50% of the entire low-pressure steam is needed for the regeneration step.³⁶ Presumably, the energy consumption can be cut by 50% by using more efficient washing liquids. Further potential savings can be obtained by optimal design and switching of the individual unit components as well as optimisation of the entire system in order to approach the thermodynamic limit.

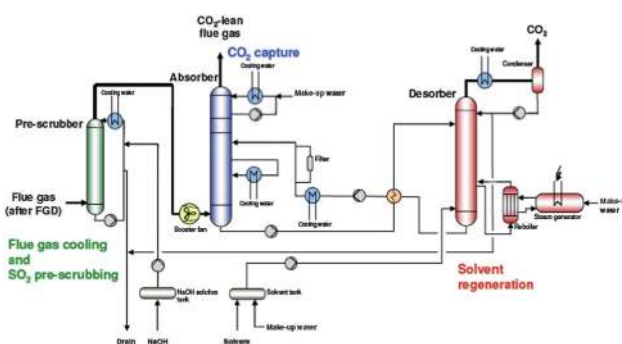
State-of-the-art and pilot plants. Currently there are an increasing number of post-combustion pilot plants, whereby the captured CO₂ is in a range of 0.125 to 500 tons per day.³⁷ Even though amine-based CO₂-washes have been implemented on an industrial scale, these units have not reached the necessary size for a power plant. Consequently, an essential challenge is their optimal thermodynamic design and incorporation into the power plant process, namely, the “scaling up” of such pilot plants (Scheme 7). The volume streams of the flue gas treated in today’s pilot plants and their corresponding power of below 1 MW_{el}³⁷ are minimal compared to that of an entire power plant. The next step is the construction of demonstration plants with a power rating of >10 MW_{el} up to 250 MW_{el}³⁰ before the data can be transferred to today’s conventional power plants with a capacity of 500–1000 MW_{el}.

A pilot plant, which cleans a partial stream of the flue gas, is currently being operated on the basis of an amine wash (MEA 30 wt%) at the coal power plant in Esbjerg (Denmark).^{38,39} The CO₂-capture capacity is *ca.* 1 t h⁻¹ at a MEA-volume stream of about 40 m³ h⁻¹. This unit comprises all the required components including a reclaimer and has been in operation since 2006.³⁸ After about 1000 h of operation (500 h thereof in permanent operation), experience on the interplay of the unit components as well as the influence of SO₂ has been gained. During the first runs, the energy consumption of the pilot plant was 4.4 GJ t⁻¹ CO₂, and the required solvent quantity was 2.4 kg t⁻¹ CO₂.^{38,39} In a second project phase, the energy consumption has been reduced to 3.7 GJ t⁻¹ CO₂.³⁷ It is one of the main objectives to further reduce the energy consumption⁴⁰ aiming at a heat consumption of 2 GJ t⁻¹ CO₂-captured (at a capture rate of 90% and capture costs of 20–30 € per t CO₂).

In 2010, a post-combustion pilot plant started operation at the power-plant site Niederaußem, Germany (Scheme 8).^{41,42} An amine-based wash is being tested there, whereby steam is withdrawn for regenerating the CO₂-loaded liquid from the preliminary heat stretch. A carbon capture of 90% is aimed for; the CO₂ stream is 7.2 t per day. The first test runs showed a purity of *ca.* 94 vol% CO₂. The objective is to obtain purities of over 99 vol%



Scheme 7 Scale-up phases for CCS technology development.



Scheme 8 Process diagram of the post-combustion pilot plant in Niederaußem.^{41,42}

with a water content of less than 500 ppm. The primary aim is to develop a post-combustion method with an efficiency loss (including CO₂-processing) of less than 10% points. In a next step, the construction of a larger amine wash-based demonstration plant is planned at the site Eemshaven (The Netherlands), where 200 000 tonnes CO₂ per year will be captured.^{41,42}

One German electricity supplier (E.ON AG) has internally set its aim to equip all power plants built after 2020 with CO₂-capture technology. The post-combustion technology is favoured due to the possibility of a retrofitting of existing power plants, the proven technical feasibility as well as the relatively few changes required to the actual power plant process. Moreover, there are still considerable efficiency potentials and cost-cutting possibilities. The target is to reach efficiency losses of less than 10% points as well as CO₂-avoidance costs of *ca.* 30 € per t CO₂. In the long term, even an efficiency loss of only about 8% points is considered feasible. At the same time, it is aimed to raise the efficiency of conventional hard coal-fired power plants to 50% (Project 50plus, power plant Wilhelmshaven). In a first step, altogether 7 smaller post-combustion pilot plants will be built onto existing power plants with a power rating of <10 MW_{el} (Table 1).^{43,44}

Future developments. More efficient solvents for absorption of CO₂ will enable to significantly reduce the energy input for the regeneration and to decrease the solvent degeneration. The current amine-based washes require a high-energy expense, which is incurred for desorption of the CO₂-loaded solvent. The use of sterically hindered or tertiary amines (amDEA, MDEA, and KS-1), frequently in combination with activators for accelerating the reaction, seems to be promising, as they need less energy for desorption as well as for operating the pumps and compressors. Moreover, the risk of corrosion can be reduced. Another option is utilizing amino acid salt solutions that are characterized by a low absorption enthalpy and a low vapour pressure. Moreover, they exhibit high selectivity, low degradation and high capacities. Furthermore, they allow high purities of the CO₂-stream to be attained.⁴⁵ A key factor for the applicability of an absorption solvent is an extended lifetime and it is anticipated that significant advances will come from increased understanding of the degradation mechanisms (oxidative and thermal degradation, reaction with acidic gases, and side reactions with CO₂).

The application of aqueous carbonate solutions (*e.g.*, K₂CO₃) represents another interesting option, since they are especially distinguished by a high thermal stability, resistance to oxygen as

Table 1 Planned CCS-pilot plants of a German electricity supplier (E.ON AG)^a

Place	Technology	Plant size	Amount of CO ₂	Commissioning
Maasvlakte (NL)	Amine ("CORAL")	0.3 MW _{el}	2 kt per annum	2008
Karlshamn (SWE)	Chilled ammonia	3 MW _{el}	15 kt per annum	2008
Datteln (D)	Chilled ammonia	n.a.	n.a.	2009
Heyden (D)	Amine	7.5 MW _{el}	45 kt per annum	2010
Staudinger (D)	Amine	0.4 MW _{el}	n.a.	2009
Wilhelmshaven (D)	Amine	5 MW _{el}	n.a.	2010
n.a. (D)	Amine (K1-S Solution)	7.5 MW _{el}	n.a.	2010

^a n.a. not available.

well as by relatively low absorption and desorption heat values. A disadvantage is the low reaction rate, which can be raised by using additives. An alternative is the so-called "chilled ammonia" method, in which the CO₂ is bound *via* ammonia and water. This method is marked by a low intrinsic energy demand for absorption and desorption. In addition, ammonia represents an absorbent that can be produced inexpensively on a large scale.^{40,46–50}

Carbonate looping. The 'carbonate looping' (often denoted as 'dry sorption') represents one further post-combustion technique. Here, calcium oxide (CaO) is carbonized in a reversible and exothermic reaction at 600–700 °C and the formed calcium carbonate (CaCO₃) calcination in an endothermic reaction at *ca.* 900 °C. The core element of the carbonate looping process is a dual fluidized-bed reactor (Scheme 9), in which the absorber material is cyclically transported between the carbonator (CO₂-absorption) and the regenerator (CO₂-desorption).⁵¹ The regeneration of the calcium oxide can be enhanced under reduced pressure.^{8,52} The released carbon dioxide stream can attain a high degree of purity.

Carbonate looping using CaO/CaCO₃ as the absorbing material is distinguished by the inexpensive and high availability of the starting materials. The absorbing material deactivates relatively fast, and permanent and considerable amounts are needed to replace the deactivated material. Although fresh CaCO₃ has to be continuously added to the process, CaCO₃ is sufficiently available and the deactivated CaCO₃ is recycled readily, *e.g.*, by reusing it as a construction material.⁸

The energy input and the process costs are linked mainly to the reactivation step. Unlike the classical washing techniques, the heat of absorption can be integrated in the power plant process resulting in lower losses in efficiency. Starting from a coal-fired

base process with an efficiency of about 46%, the loss in efficiency is estimated to be ≤7.2% points (including CO₂-compression and CO₂-processing).^{52–55} This method is also principally feasible as a retrofitting option for existing power plants.

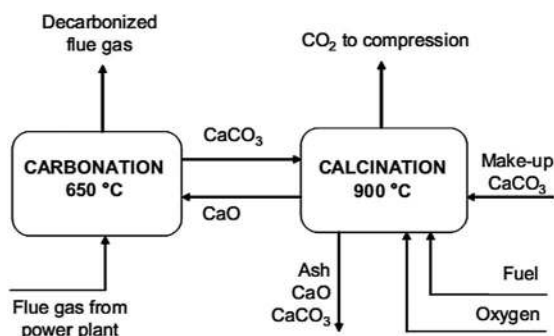
Reduced efficiency. Efficiency losses are in a range of 10 to 14% points including capturing and compression of the CO₂,^{7,28,56} whereby the efficiency losses due to compression and liquefaction of CO₂ amount to 2–3% points.⁵⁷ Options to reduce the energy losses include the development of new solvents, optimization of the scrubber process (absorption/desorption) and improved heat integration of the scrubber and compression process into the overall power plant process. In the most optimistic scenario, which considers the use of highly developed solvents, all possibilities to reduce the heat demand for regeneration and the implementation of all economically feasible heat integration methods, energy losses of 9.1% points were calculated (including compression and liquefaction and assuming a capture rate of 90%).²⁸

Comparative evaluation of post-combustion technology. There are various advantages, which might promote the application of post-combustion technology:

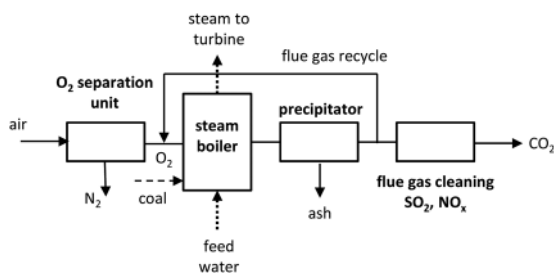
- Chemical absorption processes are well known;
 - High optimization potential to reduce energy losses;
 - Retrofitting of existing power plants is possible;
 - No fundamental changes of the original power plant process are necessary;
 - Highest purity of the CO₂ (>99.99%) of all carbon capture technology routes.
- Disadvantages of the post-combustion technology are:
- High costs;
 - Comparably large environmental impact; and
 - Flexible operation mode has yet to be demonstrated.

Combustion in pure oxygen: Oxyfuel process

The term "Oxyfuel process" denotes the combustion of carbon-containing fuels with pure oxygen (Scheme 10). After the flue gas cleaning and washing, the flue gas essentially consists of a mixture of carbon dioxide and steam. Unlike conventional power plants, for which the CO₂-content in the flue gas ranges from 12–15 vol%, the carbon dioxide content in Oxyfuel plants lies at about 89 vol%. By condensing the steam, one obtains a pure CO₂ flue gas, which, after being first demineralized, dried and compressed, can be transported to the storage site.



Scheme 9 Carbonate looping process.



Scheme 10 Processing scheme of CO₂-capture (Oxyfuel).

Development line. Nowadays, the oxygen for the combustion process is supplied by means of cryogenic air separation units, in which oxygen is separated from the air by condensation at low temperatures ($< -182\text{ }^{\circ}\text{C}$). This method is being applied worldwide on a large scale in the steel industry and in ‘gas-to-liquid’ plants (fuel from natural gas). The oxygen quantities of the currently largest planned units are in the range of $800\,000\text{ m}^3\text{ h}^{-1}$.⁵⁸ By comparison, a hard coal-fired power plant unit with an electrical power capacity of 500 MW and an efficiency of 43% requires, with stoichiometric combustion, an oxygen quantity of approx. $270\,000\text{ m}^3\text{ h}^{-1}$. Combustion with excess oxygen (today’s excess air coefficients of large plants lie at about 1.15) raises the necessary O₂-quantity accordingly.

When fuel is burned with pure oxygen, the combustion temperature is higher than that in conventional combustion and requires—due to the different heat- and flow-specific limiting conditions—a modification of the steam generator as well as measures for limiting the combustion temperature, as the heat stability of the applied materials is limited. Thus, a large fraction of the CO₂-rich combustion gas (about two-thirds of the volume stream of the flue gas) is directed back into the combustion chamber (Scheme 10). Furthermore, unreacted oxygen is recycled back into the oxidation process, thereby decreasing the residual oxygen content in the flue gas. The combustion with pure oxygen leads to largely reduced amounts of flue gas and to a changed radiation heat transfer of the flue gases (due to the altered CO₂- and H₂O-concentration), thereby necessitating a new design of heat-exchanger surfaces, a modification of burners, combustion chamber geometries as well as the implementation of an optimized flue-gas canal system.^{28,59}

Technical and scientific challenges. The recycling of a considerable fraction of the flue gas stream back into the combustion chamber as well as the changed amount of excess air presents numerous challenges. For example, the reduced amount of excess oxygen causes burning out problems and corrosion on the combustion chamber walls. Another important point is the optimal thermodynamic integration of the CO₂-processing into the actual power plant process to reduce efficiency losses. This means, e.g., to improve the heat balance by integration of multi-staged CO₂-condensers. Further challenges are:^{16,28,59–62}

Air-separation methods: the air separation requires a high-energy input, which decisively influences the losses in efficiency of the Oxyfuel power plant. Hence, increasing the efficiency is an important target parameter. The required purity of the necessary oxygen is about 99.5 vol% (remainder: N₂, Ar). This standard is to be maintained upon further increasing the efficiency of the air

separation. Otherwise, a lower degree of purity would lead to higher residual gas concentrations, which, in turn, would mean a higher energy consumption of the subsequent components (e.g., CO₂-liquefaction). Thus, an optimum has to be found for the entire process.^{28,59}

Steam generator: in general, the excess of oxygen during the combustion process has to be minimized. Today’s power plants run with an air excess of about 15% or more in order to ensure complete combustion and to minimise corrosion.^{63,64} Excessive residual oxygen after the combustion adversely affects the energy consumption of the flue gas processing, like purification and compression. Some components related to air and flue gas are operated below atmospheric pressure to prevent the slip of hot flue gas to the atmosphere. Unregulated air ingress can amount to several percent (2–4%) of the entire flue gas volume. In an Oxyfuel plant, such an infiltration would cause the required CO₂-purity not being reached and would lead to additional energy costs.^{59,64}

Denitrification and desulfurization: the nitrogen contained in the fuel is responsible for the formation of nitrogen oxides. Through the lower flue gas volume streams (no atmospheric nitrogen), the nitrogen oxide concentrations are higher than in a conventional power plant. Whereas typical lignite-fired power plants maintain the NO_x-limit values (200 mg m^{-3}) with the help of primary measures (e.g., sub-stoichiometric combustion), secondary measures may be necessary (selective catalytic reduction in DENOX-units) in lignite-fired power plants with CCS-technology. To prevent the degradation of the MEA-solvents, the residual SO₂-concentrations have to be reduced significantly compared to today’s coal power plants (*vide supra*).

State-of-the-art and pilot plants. In 2008, a pilot plant began operation at the lignite power plant site Schwarze Pumpe, Germany, for testing the Oxyfuel method. Having a thermal power rating of 30 MW_{th} (coal input: 5.2 t h^{-1} , O₂: 10 t h^{-1}), it is currently the worldwide largest Oxyfuel pilot plant.^{65,66} Since the combustion process runs at very high combustion temperatures, nitrogen oxides are formed in significant amounts. Whereas conventional lignite-fired power plants forego the taking of NO_x-secondary measures, the use of denitrification units (selective catalytic reduction) is necessary to maintain the required emission limits. Until June 2009, 1200 operating hours have been run in the Oxyfuel mode and about 1000 t CO₂ were captured with a purity of 99.7%, and a degree of carbon capture of 90%. Moreover, one goal is to realize the advanced ultra-supercritical 700 °C-power plant technology (live steam temperature 700 °C, efficiency without CCS: 50%) with the Oxyfuel method. Current estimates assume an efficiency loss of 8–10% points, whereby about 6% points of the efficiency losses result from the air separation unit.

Further important projects on Oxyfuel are being conducted in Canada (CANMET Project, $0.3\text{ MW}_{\text{th}}$), Japan ($1.2\text{ MW}_{\text{th}}$) and the USA ($1.5\text{ MW}_{\text{th}}$). Moreover, the Australian Callide research project has been running since 2006, whereby the work on the pilot plant (2 MW_{th}) has been finished. Currently, construction of an Oxyfuel unit with a power rating of about 30 MW_{el} is being prepared in the Callide coal power plant (Unit A) and should start up this year. In Europe, further Oxyfuel pilot plants are currently being operated in the Netherlands ($2.5\text{ MW}_{\text{th}}$) as well

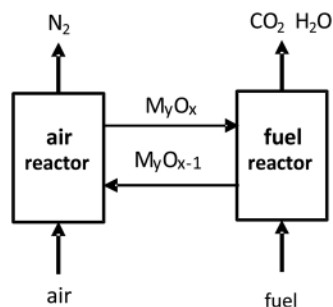
as in Great Britain (3 MW_{th}). Within the European CCS demonstration programme a 250 MW_{el} demonstration plant is planned sited in Compostilla (Spain).³⁰

Future developments. The production of pure oxygen with conventional cryogenic techniques reduces the power plant efficiency by *ca.* 7% points. The capture as well as the processing of the CO₂ intended for transport cost additional 3% points. Besides optimizing the whole system, the potential to raise the efficiency mainly lies in oxygen production. From today's perspective, possible ways to increase efficiency are:

- technically improving the cryogenic process (*e.g.*, by implementing the three-column process), thereby cutting the energy demand for the air separation by about 20%,^{28,67} and
- separating oxygen from the air with other methods, such as by using ceramic membranes or chemical looping.

Membranes. Advances in the process for producing pure oxygen by means of new high-temperature membranes can improve the efficiency and cost-effectiveness of the whole plant due to improved integration in the thermodynamic process of the power plant.⁶⁸ A key component is the high-temperature air separation membrane, which is permeable to oxygen ions above a material-dependent temperature (mostly >700 °C). The mass stream of the separated oxygen hereby depends on the partial pressure difference over the membrane, the membrane thickness and the temperature. Since only oxygen penetrates the membrane, a high purity can be obtained provided that leaks within the membrane module are avoided.^{8,69,70} Basic prerequisites for a large-scale utilization of membrane techniques in power plants are adequate membrane materials, an optimal process design and a sufficient mechanical strength of the membranes.

Chemical looping. Chemical looping offers another possibility to supply the oxygen by using metal oxides as O₂-carrier (Scheme 11). Here, in the reactor the fuel is oxidized not by molecular oxygen but rather by the oxygen carrier. The metal oxide is then regenerated in another reactor by using air as the oxidation agent. With the help of the metal oxide, the nitrogen contained in the air is not directed to the combustion process. Accordingly, a CO₂-rich flue gas can be produced after condensing the water. Concerning the oxygen carriers, very high requirements are placed on the reactivity and the regeneration capability in repeated oxidation–reduction cycles.^{8,71} Laboratory-scale and pilot-scale tests are running worldwide to identify suitable materials with the necessary long-term stability.



Scheme 11 Illustration of chemical looping combustion.

Reduced efficiency. It seems to be possible to achieve a CO₂ purity of 99.5 vol% using a downstream rectification process, which enables to reduce the fractions of Ar, NO_x and O₂. According to calculations of Kather and Klostermann⁵⁹ energy losses amount to 10% points (net, LHV) if state-of-the-art cryogenic technologies for air separation and gas processing are used. An optimized heat balance (*e.g.* integration of compressors) can reduce the efficiency losses to 9% points. Using optimized cryogenic air separation processes (*e.g.* multi-column process) reduces the energy losses to approximately 8% points. However, the additional energy demand of the Oxyfuel process depends strongly on parameters like O₂ purity, capture rate and air ingress. For obtaining higher oxygen purity, higher capture rate and lower air ingress, increased technical effort is required, which will lead to higher costs.

Mixed ion electron conducting membranes technology (MIEC) seems to be a promising candidate for the air separation, which could reduce the energy losses further. Energy losses in a range of 6 to 10% points seem to be possible.^{64,72–74} Chemical looping research is actually focusing on investigating suitable materials. Efficiency losses are estimated to be approximately 8% points.⁵⁴ Membrane and chemical looping technology are in very early stages of research and development. They are far away from commercial application. They have to be regarded as capture technologies of 2nd CCS generation.

Comparative evaluation of Oxyfuel technology. There are several advantages, which might promote the application of Oxyfuel technology. These are:

- Environmental impacts are low;
- Cryogenic air separation technology is well known;
- High potential to reduce energy losses.

Disadvantages are:

- Modification of burners and boiler design are necessary;
- Probably no retrofitting option; as well as
- High costs.

Decarbonisation of the combustion gas: pre-combustion processes

The method for capturing CO₂ from the fuel gas exploits the combination of converting the fuel to a hydrogen-rich synthesis gas and capturing the resulting CO₂ from the fuel gas. The decarbonized fuel gas is then directed to a combined gas and steam turbine cycle process for generating electricity. The CO₂-capture takes place after the fuel gas production and the conversion of the carbon monoxide to CO₂ and H₂.

Development line. The conversion of fossil fuels to synthesis gas occurs by partial oxidation in a gasification process. The use of coal or heavy oil requires cleaning of the synthesis gas in order to remove ash particles, alkali and sulfur compounds as well as other impurities. By a subsequent catalytic conversion, the CO is reacted with steam as oxidant to form carbon dioxide and hydrogen (CO-shift reaction). Since the fuel gas is available after the CO-shift at high pressure and consists of high H₂-fractions, the CO₂-capture is advantageous by using physical solvents. This type of gas separation is marked by moderate reductions in efficiency and costs. It is being commercially used in some

branches of the chemical industry and is, thus, state-of-the-art technology.⁷⁵ An air separation unit is placed before the gasification process in order to increase the yield in the gasification step, to keep atmospheric nitrogen out of the synthesis gas process, as well as to minimize the volume streams and, hence, the unit components. After the conversion of the CO, the fuel gas produced in this way consists almost exclusively of carbon dioxide and hydrogen (Scheme 12).⁷⁶

State-of-the-art and pilot plants. Since the 1980s, 'Integrated Gasification Combined Cycle' (IGCC) power plants without CO₂-capture have been built, which operate with coal, residual oil and petroleum coke. However, only five coal fired IGCC power plants have been built worldwide since the mid-1990s (Buggenum 253 MW, Wabash River 262 MW, Tampa 250 MW, Puertollano 300 MW and Nakoso 250 MW).⁷⁷ So far, IGCC power plants are less reliable compared to conventional coal fired power plants. Long start-up periods and low availability are related to high operational and maintenance costs.²⁸ The technical shortfalls of the plant in Puertollano, *e.g.*, were caused mainly by the gasification unit.⁷⁸

For gasifying coal on a large scale, gasifier types based on a solid-bed process are being applied worldwide. The solid-bed gasification process according to the Sasol–Lurgi method currently has a market share of over 75%.⁷⁹ Fluidized-bed gasifiers and entrained-bed gasifiers are particularly suited for the operation of an IGCC-power plant. Entrained-bed gasifiers allow higher coal throughputs, which allow the construction of units with a higher capacity. Moreover, a wide spectrum of coal types can be exploited (*e.g.*, lignite coal and hard coal). For converting the carbon monoxide in synthesis gas to CO₂ and H₂, the acid–gas shift method and the desulfurized synthesis gas shift are utilized currently. The former method necessitates the use of sulfur-resistant catalysts in the CO-shift reactor, as the desulfurization takes place only after the CO-shift reaction.

Physical washes can be used for the CO₂-capture process due to the favourable partial pressure of CO₂ and the higher overall pressure. Nowadays, the use of physical solvents (*e.g.*, rectisol) is

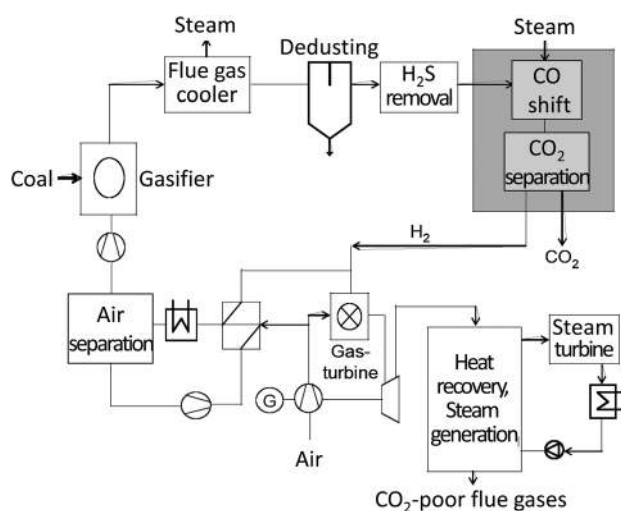
favoured, as H₂S and COS can also be removed from the fuel gas. A methanol-based absorbent serves as the solvent, which can be regenerated with the help of nitrogen and a temperature change. The advantage of these washes is the possibility to combine the fuel gas desulfurization with the CO₂-capture. After the washes, the H₂S and COS fractions in the fuel gas are less than 1 ppm.⁸⁰

Another technology to separate H₂ and CO₂ is the pressure swing adsorption (PSA), where CO₂ is selectively absorbed in a set of switching beds containing layers of solid adsorbents such as activated carbon, alumina and zeolites.⁸¹ The process is built around adsorptive separations of cyclic character, with two basic steps: adsorption, in which the more absorbable species are selectively removed from the feed gas, and regeneration (desorption), when these species are removed from the adsorbent so that it can be ready for the next cycle.

Operating gas turbines with synthesis gas is state-of-the-art. The operation with hydrogen-rich fuel gas, however, demands changes of the operation mode, adaptations of the combustion chambers as well as other burner concepts. The fuel gas is diluted with nitrogen from the air-separation unit or with process steam for increasing the power and limiting the work temperatures. Thus the formation of nitrogen oxides is countered.⁸²

Technical and scientific challenges. The efficiencies of IGCC-power plants are comparable to those of conventional steam power plants.^{7,28,56} Nonetheless, the required availabilities could not be attained with some of the existing IGCC-plants. Moreover, such power plants are more complex and the investment costs are clearly higher than those of conventional power plants.⁸³ Consequently in the past, only few coal-fired IGCC-power plants have been built. Thus, the essential challenges are improving the availability as well as reducing the costs. Compared to conventional power plants, those with CCS-technology might be advantageous because of the high product flexibility. Thus, the synthesis gas might also be used for producing chemicals or fuels (*e.g.*, methanol) or the produced hydrogen can be used for other applications (*e.g.* fuel cells). This possibility to manufacture other products besides electricity and heat (poly-generation) might also lead to a higher plant utilization and greater flexibility.

State-of-the-art and pilot plants. Coal fired IGCC plants with CCS-technology are generating great interest, although many plans to invest in IGCC power plants have been cancelled. One planned project is the IGCC plant in Hatfield (Great Britain), with a power rating of 900 MW_{el} and a capture rate of more than 90%, which has been approved for funding within the European CCS demonstration programme.³⁰ The construction of a demonstration plant with a capacity of 270 MW_{el} is also planned in Canada, where the start-up of this unit is expected in 2015. Since 2006, construction of a coal-fired IGCC plant with CCS-technology has planned at the power plant site Hürth. The heart of this power plant is an entrained-bed gasifier (40 bar, complete quench), which is suitable for the use of lignite and hard coal. A target efficiency of *ca.* 44% is stated for the optimized power plant with CCS-technology. The degree of carbon capture is about 92%, and the specific emissions value is 107 g CO₂ per kW h.



Scheme 12 Schematic representation of an IGCC-plant with CO₂-capture.⁷⁶

Future developments. The use of fuel gas in a gas turbine places great demands on the fuel gas cleaning, in particular the removal of dust. Hydrogen-rich fuel gases (hydrogen fraction of over 50%) are currently used in gas turbines of a smaller power rating in refineries.⁸⁴ The utilization of hydrogen-rich gases in heavy-duty gas turbines (F-class) is the current focus. The feasibility of the combustion of hydrogen-rich gases in gas turbines has been shown in a large-scale demonstrator of a combustion chamber. However, the design of the compressors, turbines and burners has to be further developed and optimized.⁷⁵ Plans for pilot projects are currently concentrating on the thermodynamic optimal integration of CO₂-capture into the overall process. The first step involves proving the principal technical feasibility of IGCC-power plants with CO₂-capture. Since oxygen is required for the gasification process, the costs for such IGCC-power plants are higher and the plants individually consume more energy. A more energy-efficient supply of oxygen for the pre-combustion power plants can contribute considerably towards improving the respective efficiency and reducing operation costs.

Efficiency losses. Efficiency losses in commercially operated coal fired IGCC plants caused by carbon capture with physical scrubbing processes are in the range of 9 to 12% points.^{28,57,85–88} A combined CO₂ separation and water gas shift reaction could lead to further reduction of energy losses.⁸⁹ Substituting physical scrubbing processes by application of polymeric membranes could reduce the energy losses to 8% points.^{28,85} The capture rate of today's IGCC power plants with physical washes might be lower compared to that of other power plant concepts with CCS because some CO₂ is needed for stable gas turbine operation and meeting NO_x requirements.²⁸

Comparative evaluation of the IGCC technology. There are some advantages, which might favour implementation of the IGCC technology:

- High efficiency potential;
- Poly-generation of electricity and hydrogen gives flexibility.

Disadvantages of the IGCC technology are:

- High investment costs;
- Lower availability and reliability so far;
- Less technology experience compared with conventional power plant technologies.

Classification of CO₂-capture approaches for retrofitting of power plants

It is anticipated that the CCS-technology will be commercially available at the earliest as of 2020. Even though the power plants built until this date should exhibit the highest efficiencies, they will not have CCS-technology. Since 2005, approximately 350 GW new coal fired power plants have been built worldwide. Additionally, old coal fired power plants have been substituted by new coal fired power plants.^{90–93} According to the actual energy projections of the International Energy Agency (IEA), the capacity demand of coal-fired power plants will increase until 2020 in a range of 350 to 675 GW. Consequently, retrofitting of existing power plants with CCS technology is an important option. To minimize the losses of efficiency as well as to keep costs low, a prospective 'capture-ready' concept for power plants

is being discussed nowadays for those plants that will be built in the near future. This concept infers that for a later retrofitting with CCS technology, certain unit components should be designed accordingly already in the planning stage (refer to ref. 94).

From experience, the efficiency of a retrofitted power plant is lower than that of an optimally designed new power plant. Considering the substantial losses in efficiency of power plants with combined CCS, the decision for a CCS-retrofitting is determined by the remaining economic lifetime and may be worthwhile for relatively new plants. Another important criterion is the additional need for space for installation of CCS-units. Thus, it is estimated that, *e.g.*, for a MEA-wash, including the components for the subsequent CO₂-processing (liquefaction and compression), an additional 50% of the original total area is needed.⁷⁶ How far a CCS-retrofitting changes the power dynamics and thus deviates from the optimal running mode of a power plant is an important question from the viewpoint of the power plant operator and cannot yet be answered. The high efficiency losses upon retrofitting cause a reduction in the original power supply. Consequently, the energy supplier has to decide whether to compensate for these energy shortfalls by either building more power capacity or buying this additional power on the market.

Among the most favourable CCS-technology lines, only those applying the post-combustion process (*e.g.*, amine scrubbers) are considered suitable for a retrofitting. For the other technology lines, practically no operation experience exists or fundamental technical problems have to be solved first. A suitability of the Oxyfuel method for a retrofitting of existing power plants has not yet been clarified. First model-supported simulations (see ref. 95) show that a power plant operation with oxygen and air might be feasible. Nonetheless, it is unknown how far high-temperature corrosion or carbonization effects of the boiler material may impair the function or life span of the boiler. A complete replacement of a steam generator, which represents one of the most expensive construction components, would equal the costs of building a completely new power plant. Since the pre-combustion variant represents an entirely different technology line compared to a conventional steam power plant, it is not suitable for retrofitting. Even though the retrofitting of existing IGCC-plants with CCS-units is being discussed internationally, it does not play a role due to the low number of such power plants existing throughout the world. Hence, only the retrofitting with the post-combustion method is discussed in the following.

As mentioned above, high residual concentrations of SO₂ in the flue gas degrade the amine-based solvents used today. Moreover, it is still unclear, which degree of purity is required for the transport and storage of CO₂. Hence, the SO₂-concentrations must be clearly reduced below current levels, making it necessary to enlarge the SO₂-stripping units. For an existing power plant, this means that the existing flue gas stripper would have to be modified. An alternative is to exchange the degraded solvent more often.

Large quantities of low-pressure steam are needed to desorb the CO₂-rich amine liquid. As this steam is no longer available for the electricity generation, its removal is decisively responsible for the substantial losses in efficiency. Thermodynamic calculations⁹⁶ show that about 65% of the complete low-pressure steam

of a coal-fired steam power plant is needed for the desorption process. A retrofitting requires modifications of the low-pressure turbine part, of the preheaters (heat exchangers before the steam generator), of the condenser as well as of the cooling water pumps. Since the low-pressure part of the turbine can only be supplied with one-third of the steam, two stages of a three-stage designed low-pressure steam turbine cannot be used. From pilot plant experiments, it is known that a pressure of about 3.2 bar is necessary for regenerating the CO₂-rich amine solvent. As this pressure would fall below this level during a partial-capacity operating mode, the required steam would have to be taken from the mid-pressure part of the turbine at a very much higher pressure level, which, in turn, would lead to additional losses in efficiency.⁹⁶

A retrofitting with a MEA-unit leads to a 30% higher cooling water demand than that of a conventional power plant with CCS.⁹⁶ The higher water consumption is essentially attributed to the components amine wash, flue gas cooling as well as CO₂-compression. In particular, the flue gas cooling before the absorber causes a clear increase in the total heat load to be removed. Which 'capture-ready' measures should be taken depends on the cooling water system. Thus, in a closed cooling circuit, additional space has to be planned for cooling towers. With freshwater cooling, it has to be guaranteed that an additional take-up of fresh water is possible.³⁶

About 25% of the total losses in efficiency are attributed to the processing of the carbon dioxide, before it is transported to the storage site.⁹⁶ Incorporating the heat resulting from the compression of the CO₂ intended for transport is highly significant for improving the energy balance by decreasing these efficiency losses.

One advantage of amine-based units is that, in the case of a malfunction of the washes, the power plant can continue to be operated. Moreover, there is the possibility to enter step-wise into the CO₂-capture process by determining the CO₂-partial streams or to hereby set constant flue gas streams as a function of time.⁷⁶ Furthermore the possibility of a better flexibility of power plants with wash liquid-based CCS is notable. In the context of a liberalized electricity market with corresponding electricity price deviations, the regeneration of wash liquids could be done in time periods, in which the electricity prices are relatively low.⁹⁷

Limiting conditions and testing criteria have been formulated about whether a power plant is suited for a CCS-retrofitting.^{97,98} Besides the aforementioned need for space, additional cooling water, and the availability of CO₂ storage, the concept comprises the turbine design, heat-exchanger designs, incorporation of compression heat into the heat balance as well as the absorber/desorber unit design.⁹⁷ The efficiency of retrofitting a 'capture-ready' power plant may be by about 1.5% points higher as opposed to that of an unprepared power plant.³⁶ The additional specific construction costs of a plant retrofitted with a MEA-unit are more than 20% higher than the costs for a new, optimized power plant equipped with MEA.^{62,99}

CO₂-transport

For logistic and economic reasons, CO₂ must be transported at high densities. The phase diagram with the melting and vapour pressure curves of pure CO₂ is given in Fig. 2. Since CO₂-

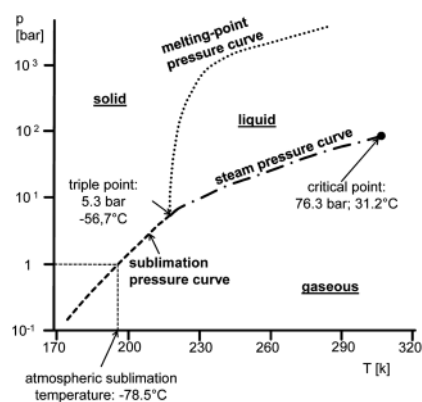


Fig. 2 Schematic phase diagram of pure CO₂.

pipelines are generally not actively cooled, the ambient temperature is (besides the pressure) decisive for the aggregate state of the carbon dioxide during the transport. Above the critical temperature of 304.2 K (31.2 °C), the CO₂ is in supercritical state and resembles a liquid with respect to its density and flow behaviour. Because of its high dissolution capability for many hydrophobic substances, supercritical CO₂ is used as a solvent (e.g., in the food industry and petrochemical industry).¹⁰⁰⁻¹⁰² Another important property is that CO₂ readily dissolves in water. Under standard conditions, about 0.9 l gaseous CO₂ dissolves itself in one litre water in the form of carbonic acid. Note that the pH value of the aqueous carbonic acid can be tuned by adjusting the CO₂ pressure.^{103,104}

For choosing the appropriate transport option, the required capacities, the geographical location, security issues and the technical facilities need to be considered. For discontinuous transport, as by truck, train or ship an intermediate storage option has to be planned for matching the continuous capture of CO₂ from the power plant. Currently, CO₂ is transported by truck, ship or pipeline. The transport by truck and train in pressure vessels is feasible for small amounts (up to a few thousand tons CO₂ per year) to be transported over short distances. The preferred option for the transport of large CO₂-quantities (e.g., for EOR) is currently *via* pipelines. Worldwide, there are over 4000 kilometres of CO₂-pipelines (mainly in the USA and Canada), although the covered areas and the lengths of the networks are not comparable with natural gas or petroleum networks. Existing CO₂-pipelines (mostly built in the 1980s) transport primarily CO₂ used for enhanced oil recovery. The existing pipelines have been operated reliably and safely for more than two decades and can be regarded as state-of-the-art technology.^{24,105,106} A statistical analysis of incidents in the USA points out that there have been no serious accidents.¹⁰⁷ Few CO₂-pipeline damages were caused by problems with overpressure valves and seals, poor welding seams as well as corrosion damages. Typical costs for the transport of CO₂ in pipelines are onshore 1–7 Euro per tonne CO₂ and 100 km, whereas the offshore transport costs 1–11 Euro per tonne CO₂ and 100 km.^{24,105,106}

CO₂-storage

Worldwide, the options to store CO₂ in geological storage formations are being discussed intensively. The storage of CO₂ in

the ocean is connected with negative impacts on the oceanic flora and fauna and prohibited according to international agreements (OSPAR, London Convention). In geological storage options, the carbon dioxide is trapped in gas-tight rock formations, whereby the following options are discussed:

- Deep-lying, unused brine-containing porous rock layers so-called 'saline aquifers' onshore, as well as below the ocean bottom,

- Depleted natural gas- and petroleum reservoirs including almost depleted reservoirs, whereby the amounts of oil and gas extracted can be increased by CO₂-injection (Enhanced Oil Recovery, EOR; Enhanced Gas Recovery, EGR), as well as

- Coal seams possibly combined with the recovery of coal seam gas (Enhanced Coal Bed Methane, ECBM).

The CO₂ is stored by structurally trapping it below a gas-tight barrier rock formation (*e.g.*, clay stone or salt) with a convex shape or without structural encapsulation in extensive storage reservoirs. At typical pressures and temperatures in saline aquifers, the density of the CO₂ is lower than that of the ambient rock formation water. Because of its power to rise up, the CO₂-phase is encapsulated below the convex, gas-tight rock layer. In the medium term, a considerable amount of carbon dioxide is dissolved in the rock formation water, and becomes mineralized in the long term.¹⁰⁸ Typically, only storage reservoirs located at depths of more than 800 m are suitable for storage of CO₂.

Worldwide, the largest CO₂-storage potential is ascribed to saline aquifers (see Table 2).^{6,24,109} Because of their high salt concentrations, the water content of these rock layers is otherwise not economically exploitable. Exhausted natural gas and petroleum fields also represent a considerable potential. Injected into nearly depleted reservoirs, the supercritical CO₂ mobilizes the remaining hydrocarbons and simultaneously increases the pressure there. Both processes lead to an increased petroleum and natural gas yield. Such hydrocarbon reserves have inherently proven their gas-tightness, because otherwise they could not have stored oil or gas there over geological eras. For EOR, EGR and ECBM, there are big uncertainties of the safety and duration of underground CO₂ storage. The adsorption processes in coal seams can be used to store CO₂, too. In this case, the released methane has to be captured in order not to imperil the climate protecting effect.

The as yet largest, currently operated CO₂-storage reservoir in an aquifer is located below the North Sea. Above the Sleipner natural gas field in the Norwegian Sector, *ca.* 1 million t CO₂ per year are being separated as byproduct from the recovered natural gas and injected into the Utsira sandstone formation located at a depth of about 1000 metres. Besides the technical demonstration and economic feasibility, methods for monitoring the injected CO₂ are explored. A selection of currently running CO₂-

storage projects worldwide is shown in Table 3.^{24,105} The annually stored CO₂-quantities vary from a few thousand tonnes up to a million tonnes CO₂ (for comparison: a new generation 500 MW hard coal unit emits *ca.* 2.4 million tonnes CO₂ per year). An analysis of the storage capacities in Germany shows that the onshore potential is sufficient for only a few power-plant generations.

Aspects of CO₂-purity with respect to CCS-technologies

After the carbon dioxide is captured, the gas stream still contains impurities. Different requirements may be placed on the purity of the carbon dioxide regarding its transport, storage or utilization. In general, the stricter the purity requirements are, the greater the technical complexity and energy expenditure and, hence, the costs for CO₂-capture and its processing. Therefore, it is important to find a technically and economically feasible optimum over the entire chain (power plant as well as the capture, treatment, transport, storage and/or utilization of CO₂). As no consensus has been reached yet about the necessary CO₂ purity, they cannot be stipulated at present. This uncertainty is reflected in the current CCS-directive of the European Union, which states that the gas mixture to be stored should 'overwhelmingly' contain CO₂. Possible dangers are considered insofar as the respective concentrations of the substances in the CO₂-stream are required to be below a level that would harm the integrity of the transport infrastructure or the storage reservoir and that would pose a significant environmental and health risk. In consequence, the composition of the impurities, which ultimately cause the undesired side effects (*e.g.*, corrosion), needs to be evaluated. Since the materials applied to construct CO₂-pipelines are known and many years of experience have been acquired, the technical requirements for the material in combination with the impurities can be specified clearly. The effects concerning CO₂-storage are still the focus of research. Here, one has to differentiate between the possible interactions with the geological storage surroundings as well as the requirements resulting from the storage periphery (*e.g.*, pipe materials, cement) at the conditions of the injection.

Purity grade and flue gas processing. How the impurities affect the energy costs of the subsequent flue gas treatment (compression) depends on the respective contaminants. This will be illustrated using the following simplified comparison of pure carbon dioxide and a CO₂-stream with impurities. The assumed CO₂-purities were selected exemplarily in order to analyse the principal effects of individual contaminants on the compression work. It is assumed that the carbon dioxide to be stored is compressed to a pressure of 120 bar by using a two-step

Table 2 Estimations of CO₂-storage capacities (10⁹ t CO₂)^a

CO ₂ storage	Global ²⁴	Europe ⁶	Germany ¹⁰⁹
Deep saline aquifer	1000–10 000	30–500	12–28
Oil/natural gas field	600–1200	10–15	3
Non-exploitable coal seams/ECBM	3–200	n.a.	0.4–1.7

^a n.a.: no information available.

Table 3 Classification of realized and planned storage projects

Project (location)	CO ₂ -source	Type of storage	Amount of CO ₂
In Salah (Algeria)	CO ₂ -separation from natural gas	Natural gas field/saline aquifer	1200 kt per annum (since 2004)
Sleipner (Norway)	CO ₂ -separation from natural gas	Saline aquifer in maritime area	1000 kt per annum (since 1996)
Weyburn (Canada/USA)	Coal	Natural oil field (EOR)	1000 kt per annum since 2000
K12b (Netherlands)	CO ₂ -separation from natural gas	Natural gas field (EGR)	100 kt per annum (since 2004)
Otway (Australia)	Natural gas separation	Depleted gas field	50 kt per annum (2007–2009)
Snohvit (Norway-offshore)	CO ₂ -separation from natural gas	Natural gas field/saline aquifer	0.75 kt per annum (since 2007)
Permian Basin (USA)	Natural deposits, industry	Several oil fields (EOR)	500 000 kt (since 1972)
Gorgon (Australia -offshore)	CO ₂ -separation from natural gas	Saline aquifer	129 000 kt (2008–2010)
Lacq (France)	Oxyfuel power station	Depleted gas field	150 kt (2010–2012)
Ketzin (Germany)	External delivery	Saline aquifer	60 kt planned (start in 2008)
Nagaoka (Japan)	Industrial production	Saline aquifer	10 kt (2004–2005)
Frio Brine (USA)	Industrial production	Saline aquifer	3 kt (2005–2006)
Quinshu (China)	Industrial production	ECBM (pilot project)	200 t

compressor with intermediate cooling, which compresses the carbon dioxide in several stages to 58 bar. The completely condensed carbon dioxide is then raised to a pressure level of 120 bar by using pumps (see Scheme 13 and Fig. 3).

The respective physical-state points (1, 2, 3, 4) are found in both images. The necessary compression work to raise the pressure of the pure carbon dioxide is 0.089 kW h kg⁻¹. The density of the compressed CO₂ is calculated at 564 kg m⁻³. In the case of impure carbon dioxide, a higher amount of compression and pump work is necessary due to the different properties (critical pressure and critical temperature) and because a two-phase area has to be passed through during the compression. From a process-engineering point of view, it has to be ensured that the mixture has first been completely condensed before the pressure is raised by the pumps. Since the individual components have other properties than carbon dioxide, the amount of work for the compression depends on the composition of the impurities. The following shows how single components influence this process, whereby impurities of 5% and 10% are assumed exemplarily in order to better illustrate the relationships (Table 4).¹¹⁰

To be able to recognize the effects of the individual substances, the extra compression work for each respective impurity was compared with the aforementioned case of a pure CO₂-stream (Fig. 4).¹¹⁰ If the contamination, *e.g.*, consists only of nitrogen, the compression work is 9% and 15% greater due to the higher boiling point of the particular gas mixture (with 5% and 10% impurities, respectively). Most impurity components cause an increase on the compression work. An exception is sulfur dioxide, as it has a lower boiling point than that of carbon dioxide and, thus, requires less compression work.

Moreover, the presence of impurities affects the density of the gas mixture. All impurity components cause a reduction of the density and, hence, of the storage capacity (Fig. 5).¹¹⁰ For example, in the case of a 5% or 10% N₂-contamination, approx. 30% or 40% less carbon dioxide, respectively, can be stored at

a given storage volume than that possible for storing pure carbon dioxide.

The following gives an estimate of the effect of carbon dioxide mixtures consisting of several impurities. Two mixtures are listed exemplarily in Table 5 to illustrate the influence of impurities on the compression work.¹¹⁰ Note that they are not to be equated to mixtures that actually occur for CCS demonstration plants.

The energy demand for the compression is essentially determined by the compressor work. Although the purity of mixture A1 (89.3 vol%) is lower than that of A2 (92.3 vol%), the specific compression work is less for A1 than for A2 (Fig. 6).¹¹⁰ This is attributed to the specific physical properties of the components and their respective concentrations in the gas mixture. For both mixtures, the densities are depicted in Fig. 7,¹¹⁰ which both lie clearly below that of pure carbon dioxide, which infers that a higher storage capacity is needed.

In practice, it is attempted to separate the components of the contamination as far as possible before the liquid pump. Typical purities of the carbon dioxide to be stored are in the range 93–98% CO₂. However, with respect to energy consumption, the separation is disadvantageous. With this in mind, one has to find an optimum regarding purity, degree of carbon dioxide captured and energy expense, which meets economic criteria, ensures safety and the purity requirements prescribed for storage.¹¹⁰

Purity grade and CO₂-transport. The composition of the cleaned flue gas depends on the actual power plant process as

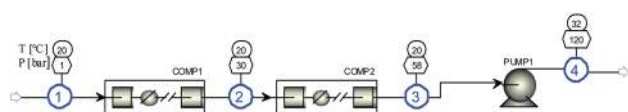
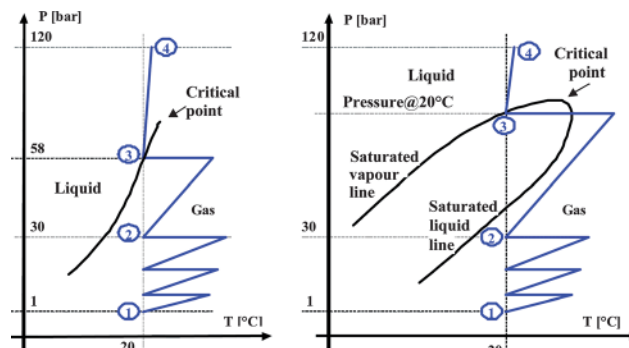
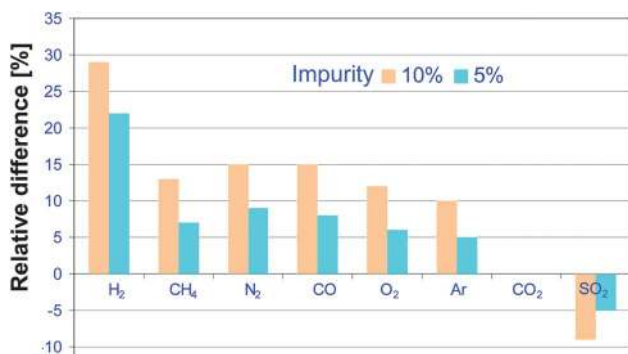
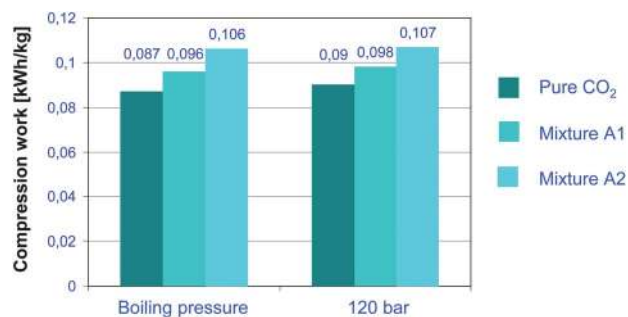
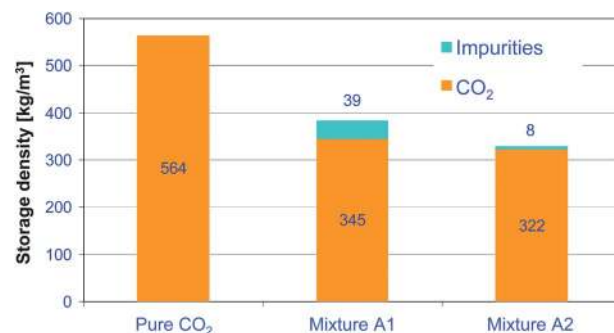
**Scheme 13** Simplified CO₂-compression system.**Fig. 3** Compression of a pure (left) and contaminated CO₂-stream (right).

Table 4 Boiling pressures and molar masses of binary CO₂-mixtures (90% and 95% purity)

		Contaminant							
		H ₂	CH ₄	N ₂	CO	O ₂	Ar	CO ₂	SO ₂
Molecular mass	kg kmol ⁻¹	2	16	28	28	32	40	44	64
<i>95% CO₂-5% Contaminants</i>									
Molecular mass—mixture	kg kmol ⁻¹	41.9	42.6	43.2	43.2	43.4	43.8	44.0	45.0
Boiling pressure	Bar	127	67	79	77	72	72	58	53
<i>90% CO₂-10% Contaminants</i>									
Molecular mass—mixture	kg kmol ⁻¹	39.8	41.2	42.4	42.4	42.8	43.6	44.0	46.0
Boiling pressure	Bar	143	75	94	91	84	83	58	50

**Fig. 4** Effect of impurities on the compression work (1 to 120 bar) in comparison to pure CO₂.**Fig. 5** Effect of impurities on the storage density in comparison to pure CO₂ (120 bar).**Table 5** Composition of flue gases (dry) after the capture assumed in the analysis of the storage capacity

Constituents [vol%]	Pure CO ₂	Mixture A1	Mixture A2
CO ₂	100.0	89.3	92.3
Ar	—	5.7	0.1
N ₂	—	0.3	2.9
H ₂	—	—	4.1
CH ₄	—	—	0.5
CO	—	—	0.1
SO ₂	—	1.6	—
O ₂	—	3.1	—
Molar mass [kg kmol ⁻¹]	44.0	43.7	41.7
SP pressure [bar]	58	82	100

**Fig. 6** Effects of impurities of flue gases (CO₂-mixtures) on the compression work.**Fig. 7** Effects of flue gas impurities on the storage density (120 bar, 40 °C).

well as on the respective CO₂-capture method. Typical impurities for the respective CCS technology lines differentiated according to the energy sources are listed in Table 6.^{111,112} Whereas the fractions of argon and nitrogen dominate in the Oxyfuel techniques due to air penetration, the contaminants CH₄ and H₂ occurring in the pre-combustion process result from the actual gasification process. Also SO₂, NO_x, CO and O₂ are found in the power-plant flue gases.

The composition of the transported gases in a selection of U.S. CO₂-pipelines is depicted in Table 7.¹¹² The anthropogenic sources deal with the synthesis gas production, which explains the H₂S-content as well as the fraction of hydrocarbons with a lower molecular mass. Upon comparing the compositions from Tables 6 and 7, the differences in the respective compositions of the impurities are obvious.

In general, it applies that the impurities cause a higher loss in transport pressure compared to the transport of pure CO₂.¹¹²

Table 6 Typical impurities of flue gases^{7,111,112}

CCS technology line	Component	Coal (vol%)	Natural gas (vol%)
Post-combustion	SO ₂	<0.01	<0.01
	NO _x	<0.01	<0.01
	N ₂ /Ar/O ₂	0.01	0.01
Pre-combustion	H ₂ S	0.01–0.6	<0.01
	H ₂	0.8–2.0	1
	CO	0.03–0.4	0.04
	CH ₄	0.01	2
Oxyfuel	SO ₂	0.5	<0.01
	NO _x	0.01	<0.01
	N ₂ /Ar/O ₂	3.7	4.1

Due to the differing properties of the components, the pressure loss varies greatly. In practice, this means that the pressure at the beginning of the transport has to be much higher than that necessary for the actual CO₂-storage. An alternative option is to integrate additional CO₂-pumps or CO₂-compressors along the course of the pipeline.

Quality criteria for the pipeline transport. The U.S. company Kinder Morgan, which builds and operates CO₂-pipelines, has set standards for the CO₂-mixtures to be transported (Table 8).¹¹³ There are different reasons for setting such criteria. Thus, a minimum purity of 95% CO₂ is required in order to guarantee the mixability with petroleum. Substances such as sulfur, nitrogen and nitrogen oxides adversely affect the mixability, whereas H₂S and hydrocarbons of low molecular weight positively affect it. This also explains the relatively high threshold for hydrocarbons. Further reasons for limiting the respective impurities concern material, corrosion and safety aspects.

These standards can be applied only partially to the transport of CO₂-mixtures originating from power plant processes. The recommended limits ¶ for CO₂-pipelines operating with power plant CO₂ mixtures (from pre-combustion- or post-combustion units) are given in Table 9.^{113,114}

Some of the reasons for limiting the individual substances are likewise found in Table 9.^{107,113,115} For instance, excessive water content in the CO₂-mixture is disadvantageous to the pipeline transport, as this would promote corrosion and the formation of hydrates. If solid hydrates accumulate, there is a risk of blockages and damage to the pipeline periphery (*e.g.*, valves). A danger of corrosion results from the formation of carbonic acid, in particular in combination with other components (such as SO₂ and H₂S). The formation of free water, which would boost the corrosion risk, is also problematic. An excessive water fraction is generally undesired, since it reduces the energy efficiency of the entire process. Moreover, there is the danger that the properties of the pipeline material (carbon steel) would be adversely affected, *e.g.*, by becoming brittle. Likewise undesired is oxygen as an impurity, since together with water, it can accelerate oxidation reactions, which may lead to corrosive damage.

¶ Limits set within the framework of the EU project “DYNAMIS”, www.dynamis-hypogen.com

CCS as an option for climate protection

Stringent targets to minimize greenhouse gases demand a wide spectrum of corresponding measures, which comprise all energy sectors as well as industry, commerce, transport as well as households. Over 40% of the worldwide CO₂-emissions are caused by electricity generation in fossil fuel power plants. Thus, this becomes especially relevant in the context of reducing greenhouse gas emissions. Measures to be taken regarding fossil fuel power plants constitute substituting carbon-rich with carbon-poor energy sources, raising the efficiency of power plants as well as capturing carbon dioxide and subsequently storing it, which is accompanied by an overhaul of the power plant parks.

As current energy scenarios of the International Energy Agency (IEA) show, CCS technologies are particularly significant within the scope of worldwide strategies to reduce greenhouse gases.¹¹⁶ The IEA projects an increase in today's CO₂ emissions of around 29 billion t per annum to about 62 billion t per annum until the year 2050.¹⁰⁵ This goes hand in hand with an increase in atmospheric CO₂ concentrations to *ca.* 550 ppm and a mean temperature increase of 3–4 °C. In two scenarios, a period until 2050 was evaluated. In the first scenario (ACT Map scenario), a clear CO₂ reduction is attained, so that by 2050, about 35 billion tonnes less CO₂ will be emitted annually compared to today's emissions. This would correspond to a CO₂ concentration of about 485 ppm in 2050 (Fig. 8).¹⁰⁵ The second IEA reduction scenario (BLUE Map scenario) predicts a decrease in carbon dioxide emissions to about 48 billion t CO₂ per annum. Compared to the typical emissions scenario, this would correspond to a reduction of about 77% and, accordingly, to a CO₂ concentration of about 445 ppm in 2050.

For both scenarios, the particular contributions of the individual sectors in reducing carbon dioxide emissions are shown in Fig. 8.¹⁰⁵ In both cases, the energy generation sector contributes the greatest towards minimizing CO₂ emissions. In both scenarios, CCS represents the single measure that contributes most towards reducing CO₂ emissions. The CCS-fraction of the total reduction in carbon dioxide due to energy generation is *ca.* 21% and *ca.* 26% for the ACT and BLUE map scenarios, respectively. These results illustrate the importance of CCS-technology in a global context and show that CCS is becoming an increasingly attractive option for reducing carbon dioxide emissions.

Economic perspective

As mentioned above, there are tendencies to make CCS technologies commercially available from the year 2020 onwards. CCS-technologies may be an important option upon stipulating stringent reduction targets on the CO₂ emissions.¹¹⁷ As there are many power plants being planned or in construction,¹¹⁸ it may be necessary to retrofit plants built before 2020 without CCS-technology. The European CCS-directive envisions a CCS-retrofitting of power plants with a power rating of greater than 300 MW, whose construction has been begun since 2009. The new construction of CCS-power plants depends on the energy cost-effectiveness as well as political framework conditions that decisively influence the investment decisions of the energy supply

Table 7 Gas compositions in existing pipelines¹¹²

	CO ₂	CH ₄	N ₂	H ₂ S	C ₂ H _n	CO	O ₂	Source
Canyon Reef	95%	5%	<0.5%	100 ppm	—	—	—	Anthropogenic
Central Basin	98.5%	0.2%	1.3%	—	—	—	—	Natural
Sheep Mountain	96.8%	1.7%	0.9%	—	0.6%	—	—	Natural
Bravo Dome	99.7%	—	0.3%	—	—	—	—	Natural
Weyburn	96%	0.7%	<300 ppm	0.9%	2.3%	0.1%	<50 ppm	Anthropogenic

Table 8 Quality requirements for CO₂-pipelines in the USA¹¹³

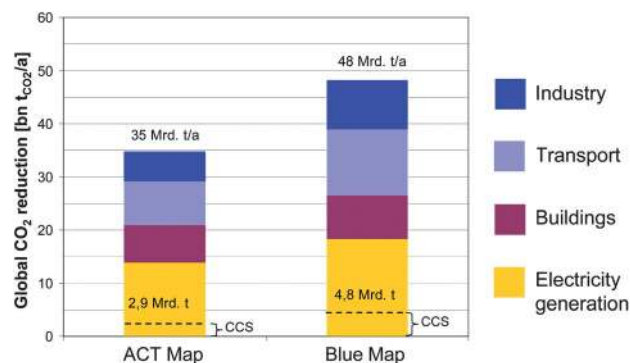
Component	Concentration	Criterion
CO ₂	>95%	Mixability
N ₂	<4%	Mixability
C _m H _n	<5%	Mixability
H ₂ O	<480 mg m ⁻³	Corrosion
O ₂	<10 ppm	Corrosion
H ₂ S	<10–200 ppm	Safety
Glycol	<0.04 ppmv	Operation
Temperature	<50 °C	Material

companies. Such framework conditions include the further development of the emissions trade, policies on renewable energies, as well as the future development of primary energy-carrier prices.

Additional fuel demand upon implementation of CCS-technologies. Due to the necessity of gas separation, the efficiency of a power plant with CCS is always lower than that without CCS. Decisive for the greater fuel demand of such a power plant is the ratio of the efficiency without and with CCS. The additional power needed to compensate for this stems from the ratio of the efficiency without (η_{old}) and that with CCS (η_{new}). The additionally required power amounts to $[(\eta_{old}/\eta_{new}) - 1] \times 100$ (in %). In the case of an exemplary hard coal power plant with an efficiency of $\eta_{old} = 46\%$ and a post-combustion plant with efficiency losses of 12% points, approximately 35% more fuel is needed. If one succeeds in reducing the efficiency losses to 8% points, the amount of additionally needed fuel is diminished to ca. 21%.

Table 9 Recommended limits for CO₂-streams for pipeline transport^{113,114}

Component	Concentration	Criterion
H ₂ O	500 ppm	Technical: below solubility limit of H ₂ O in CO ₂ . No significant cross-effect of H ₂ O and H ₂ S, cross-effect of H ₂ O and CH ₄ is significant but within limits for water solubility
H ₂ S	200 ppm	Health and safety considerations
CO	2000 ppm	Health and safety considerations
O ₂	Aquifer < 4 vol%, EOR 100–1000 ppm	Technical: range for EOR, because lack of practical experience on effects of O ₂ underground
CH ₄	Aquifer < 4 vol%, EOR < 2 vol%	As proposed in ENCAP project
N ₂	<4 vol% (all condensable gases)	As proposed in ENCAP project
Ar	<4 vol% (all condensable gases)	As proposed in ENCAP project
H ₂	<4 vol% (all condensable gases)	Further reduction of H ₂ is recommended because of its energy content
SO _x	100 ppm	Health and safety considerations
NO _x	100 ppm	Health and safety considerations
CO ₂	>95.5%	Balanced with other compounds in CO ₂

**Fig. 8** Global CO₂-reduction in the scenarios of IEA for 2050.

Cost-effectiveness of CCS: costs for generating power and avoiding CO₂. To project the cost-effectiveness of CCS technologies, it is relevant to view the costs to generate power (LCOE) and, concerning the reduction in CO₂-emissions, the costs to avoid CO₂ (CAC). The electricity generation costs with CCS specify the costs of the power production chain comprising the power plant with CO₂-capture, transport and storage of CO₂ and thus allow a comparison with other technologies for electricity generation. The parameter here is one unit of electricity, which flows into the grid, e.g., one MWh. In contrast, the CO₂-avoidance costs denote those expenses that result for the CO₂-quantities, which are not released into the atmosphere and, hence are 'avoided'. Here, the parameter is one unit of CO₂, e.g., one tonne CO₂. The avoidance costs are figured by comparing the reference technology without CCS with the corresponding technology using CCS. One has to differentiate between the CO₂-avoidance costs and the CO₂-capture costs. The former are always higher

than the CO₂-capture costs because of the reduction in efficiency and the necessary compensation by a higher power and a higher fuel input.

The costs to generate electricity or respectively to avoid CO₂ result from several factors, which are essentially delineated by the technology, the energy carrier prices and other factors affected by the environmental and climate-political framework (*e.g.*, the price for CO₂-certificates) as well as by the time-line. Due to the long lifetimes of power plants and the corresponding long-term binding of capital, these framework conditions are particularly significant for investment decisions.

The certificate costs result from the remaining CO₂-emissions (without or with CCS), for which a certificate has to be made available, and the certificate price, which reflects the market price for CO₂. Independent of the mechanism of the first allocation of certificates (so-called 'grandfathering' vs. auctioning) it is sensible and necessary to consider the certificate costs for the electricity supply to completely represent the economic situation. If a power plant does not own certificates, the certificates actually have to be bought. If a power plant does own certificates, opportunity costs are incurred, since certificates that are needed are not available for sale. Thus, the allocation mechanism affects the profit situation and liquidity.

Electricity generation costs and CO₂-avoidance costs. In recent years, a number of studies focusing on costs of CCS were published.^{6,7,119–122} Here, CCS and reference plants without CCS are considered. Post-combustion, pre-combustion and Oxyfuel concepts are assumed for the fuels lignite and hard coal, whereas a post-combustion plant is assumed for natural gas. The electricity generation costs are based on assumptions of efficiencies, investment costs, and levels of CO₂-capture, among others, compiled within the scope of the current public literature (Table 10). The cost calculations are based on an economic life span of 40 years (coal), 25 years (natural gas), and an interest rate of 5%. The number of full load hours is gaining importance, as in the case of increased integration of renewable energies the number of full load hours is expected to decrease. The depicted electricity generation costs also contain the expenses for the compression/liquefaction of carbon dioxide for a pipeline transport of 350 km and for the storage in a saline aquifer at a depth of 1000 metres, including the monitoring costs. For transport and storage of CO₂, average cost of 5 €₂₀₁₁ per t CO₂

Table 10 Basic data for calculation of LCOE and CAC

Fuel price	€ ₂₀₁₁ per GJ	Ref.
Lignite	1.52	
Hard coal	2.63	123
Natural gas	6.39	123
Transport and storage costs	€ ₂₀₁₁ per t CO ₂	
	5.00	
Escalation	% per annum	Ref.
Fuel price	1.20	123
Operation and maintenance	1.50	
Transport and storage costs	1.50	

was assumed. A moderate price escalation was assumed for the energy carrier development.

At first, the electricity generation costs were calculated without figuring in the costs of certificates. This would correspond to a (theoretical) situation without certificate trade, whereby CCS, *e.g.*, would be legally stipulated. The direct comparison of power plant variants allows conclusions to be drawn about the change in the origination costs without the cost-effectiveness of plants being already answered upon consideration of a certificate market. A clear increase in the electricity generation costs through CCS can be determined for the different variants (Fig. 9). As a whole, the electricity generation costs are the lowest for lignite-fuelled power plants and are the highest for natural gas-fuelled power plants. Upon introducing CCS, the electricity generation costs rise by 37% (natural gas), 58–65% (hard coal) and 71–81% (lignite). Here it is obvious that the power plants with high capital costs show the strongest increase of the electricity generation costs. This again underscores the importance of the additional investment costs for CCS. Even though slight advantages may arise for Oxyfuel power plants with carbon capture that are fuelled with lignite or hard coal, the results show that, for the individual fuels, no clear preference for a CCS-technology line can be derived.

Breakdown of the generation costs according to the individual types of expenses underscores the argumentation (Fig. 9). Of central importance is the increase in capital costs upon introducing CCS for coal-fired power plants. Compared to power plants without CCS-technology, the additional investment costs for those with CCS-technology are essentially attributed to investments for carbon capture. Additionally, the importance of fuel costs becomes clear: the higher the energy penalty (due to the efficiency loss), the higher the increase in fuel costs.

Regarding natural gas, the electricity generation cost depends more strongly on the higher natural gas supply prices and the lower investments compared to those for coal-fired power plants. For all power plant variants with CO₂-capture, however, the expenses for the transport and storage of CO₂ are low compared to the CO₂-capture costs as well as to the entire electricity

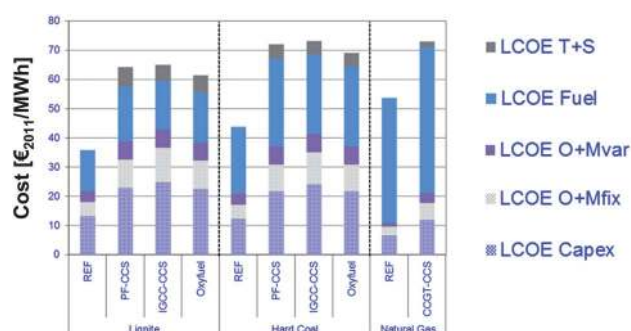


Fig. 9 Electricity generation costs (LCOE) of fossil fuel power plants for 2020 and cost structure (T + S: transport and storage; fuel; O + M: operation and variable and fixed cost for maintenance; Capex: capital expenditure) for a reference power plant without carbon capture (REF) and with carbon capture (other variants) for 7500 h full load hours. Certificate costs were not considered (basic data adapted from ref. 119). PF: pulverized fuel; IGCC: integrated gasification combined cycle; CCGT: combined cycle gas turbine.

generation costs. Altogether, the analyses clearly show that potential cost-saving measures have to focus on the power plant base process and the CO₂-capture.

Comparison of the CO₂-avoidance costs shows that these costs are lowest for lignite-fired power plants and highest for natural gas-fired power plants (Fig. 10).¹²⁴ Regarding natural gas, this is essentially attributed to the fact that even without CCS, the natural gas-fired power plants clearly show lower specific CO₂-emissions. Hence, successful savings have then to be 'bought' by high expenditures. The CO₂-avoidance costs run at 35–40 € per t (lignite) und 42–44 € per t (hard coal) and thus slightly favour the lignite-fired variants. Also in this case, this slight advantage is related to the high specific CO₂-emissions of the lignite-fired power plants without CCS.

The MIT study "The Future of Coal"¹²² quotes individually calculated CO₂-avoidance costs for coal-fired power plants, which are much lower than those cited in ref. 125. For hard coal-IGCC plants, these cost estimates of 20 \$ per t CO₂ may be due to optimistic expectations regarding the investment costs. The McKinsey study "Carbon Capture and Storage: Assessing the Economics" states CO₂-avoidance costs of 33–50 € per t for power plants at the beginning of the commercial use of CCS.⁶ Upon considering the cited CO₂-avoidance costs of 35–40 € per t (lignite) and of 42–44 € per t (hard coal), this applies largely for coal-fired CCS power plants. Note that technical and economic base parameters (such as power plant efficiency, power, fuel prices, and fixed costs) were estimated differently and different calculation methods and limiting criteria were applied.

Environmental relevance

While the application of CCS in power generation leads to a reduction in CO₂-emissions and thereby to a reduction in the global warming potential (GWP),¹²⁶ a more comprehensive investigation is necessary to account for other environmental effects.^{19,127,128} Beside direct emissions at the power plant itself, other major contributors are upstream processes for coal supply or solvent production (post-/pre-combustion), oxygen supply (Oxyfuel), and downstream processes such as waste treatment but also transport and storage. The holistic approach of Life Cycle Assessment (LCA) opens up the field of vision to additional fuel supply, changed waste composition and amounts as well as the environmental impact of chemicals (see, e.g.

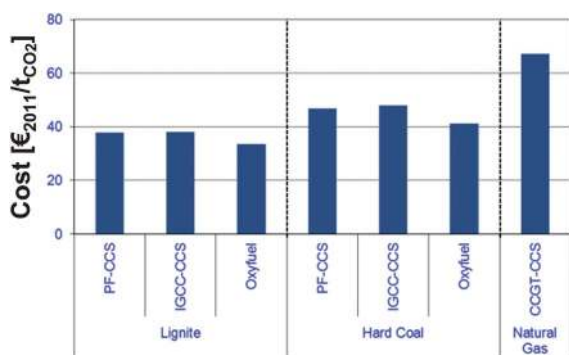


Fig. 10 CO₂ avoidance costs (CAC) for CCS-power plants for 2020 for 7500 h full load hours. Certificate costs were not considered. Basic data adapted from ref. 119.

ref. 129–137). Most studies consider the post-combustion capture route with coal as fuel and MEA scrubbing. More recent studies include the Oxyfuel route, while pre-combustion is underrepresented. New, second generation capture technologies, such as chilled ammonia or membranes, have not yet been subject of a LCA analysis.

Underlying assumptions have a considerable impact on the outcome of the LCA analyses.¹²⁸ A significant aspect concerns the efficiencies of today's and future power plants. For hard coal, the assumed efficiencies for a power plant without CCS vary from 37% up to 54%, representing diverse stages of technology, but also different technology concepts. Assumptions concerning the efficiency losses due to the capture system vary between 6 and 18% points. Other parameters with considerable impact on the results are capture efficiency and quality of CO₂ captured. Variation in CO₂ removal efficiency by ±5% points results in changed values for the GWP by ±20%.¹³⁰ Independent of the capture technology, the type of fuel has the highest impact on the results.

In the first step, an inventory of all inputs and outputs of the entire system was evaluated. These values were then categorised and assigned to a specific environmental impact, whereby each impact is characterised by a specific impact equivalent. The absolute impact equivalents per kWh of electricity produced for each impact category are presented in Fig. 11. As it is sometimes difficult to interpret these absolute values, each effect is benchmarked in a normalisation step against the known overall effect for this class, whereby the world average is chosen as reference system. All data are related to the total global emissions for the year 2000, where the global hard coal electricity generation was 5136 TWh.¹³⁸

For the pulverised hard coal combustion technology without capture (Fig. 11), the *Global Warming Potential* (GWP, expressed in kg CO₂-equivalent) varies from 765 g CO₂-eq. per kWh (future plant of 2025)¹²⁹ to 1092 g CO₂-eq. per kWh (old PC plant of 2000).¹³⁰ The values for the *Acidification Potential* (AP, in kg SO₂-equivalent) scatter between 0.39 g SO₂-eq. per kWh¹⁴⁰ and 2.76 g SO₂-eq. per kWh.¹³⁰ Most important here is the assumed flue gas treatment, but also the coal composition. The *Eutrophication Potential* (EP, in kg PO₄³⁻-equivalent) and *Photochemical Oxidation Potential* (POCP, in kg C₂H₄-equivalent) vary with the efficiency.

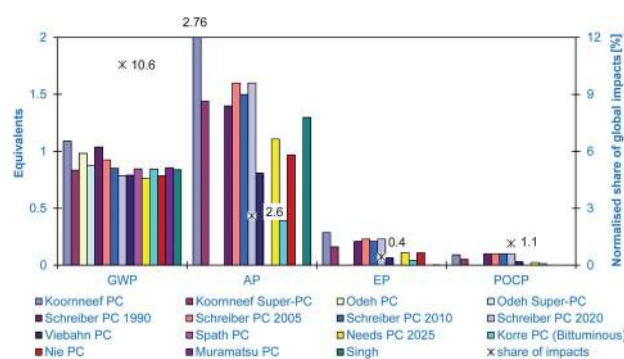


Fig. 11 Environmental impacts of hard coal combustion without capture, normalised to total global emissions in 2000 (adapted from ref. 139).

To estimate the relative importance of the environmental effects, the data were normalised. Hard coal power generation has a considerable share of the global GWP with 10.6%, while the share of global AP is small (2.6%). The effects on the EP and POCP are even smaller.

Upon introduction of a MEA-based post-combustion capture technology, the GWP is substantially reduced (Fig. 12). Note that the reduction is less than the proportion of CO₂ captured (in most studies 90%), which is explained readily by the higher amount of CO₂ to be captured for CCS systems due to efficiency losses and, consequently, increased coal consumption. Additionally, this higher coal demand results in an increase of methane emissions during mining and transport of the hard coal.

All LCA analyses show an increase in all other impact categories. The AP and EP of a MEA post-combustion system increase even though further reductions of SO₂ and NO_x emissions by improved flue gas desulfurization (FGD) and selective catalytic reduction (SCR), respectively, are assumed. The underlying reason is the emission of ammonia during MEA production and degradation^{130,141} as well as ammonia slip from the SCR. Furthermore, more SO₂ and NO_x are emitted during coal transport by ship, typically by heavy-oil-fuelled freighters; the latter also causing an increase in POCP.

One impact category, which is significantly affected by post-combustion technology, is the *Human Toxicity Potential* (HTP), which may increase up to 200% for post-combustion systems. This follows from heavy metal and organic emissions into air and water, mainly ethylene oxide emissions from the MEA supply,^{130,135} and heavy metal and phosphate emissions into water from landfilling coal ash.

Normalisation shows that by CCS power generation the GWP goes down to 2.6%. The contribution to the share in the global AP increases from 2.6% to 3.2%, while the contribution to EP, POCP and HTP is small. It has to be pointed out, that AP is a regional impact and CCS shifts the acidification potential from the region of power production to regions of coal mining and transport.

The environmental effects of the Oxyfuel process (Fig. 13) are similar. While the GWP decreases, the values for AP lie between -38% and 40%, for EP between -43% and 58% and for POCP between 23% and 123%. The reason for the large scatter might be in the differences concerning the assumptions on efficiency and

energy penalty, improvement of flue gas treatment, and the distribution of SO₂ and NO_x in the compressed CO₂ stream vs. flue gas emissions.¹⁴² The environmental effects of IGCC power plants have been little investigated. Values for GWP between 692 g CO₂-eq. per kWh and 862 g CO₂-eq. per kWh and for AP between 0.5 g SO₂-eq. per kWh and 0.9 g SO₂-eq. per kWh have been quoted. GWP decreases from 11.5% to 2.9%, while the share of AP on the global impact increases from 1.5% to 1.8%. EP and POCP remain rather low compared to the global values.

Status of development of CCS, CO₂-exploitation and -recycling

Currently running and planned large-scale CCS projects

Currently, there are a considerable number of pilot-scale plants worldwide, with which the various CCS-technologies are being evaluated, whereby post-combustion plants clearly predominate.^{143,144} Planned large-scale projects as well as larger pilot-scale power plants that are differentiated according to their respective input energy sources, power ratings as well as the technology routes are listed in Scheme 14.¹⁴⁵

For the CO₂-capture in gas power plants, the Mongstad project is aimed at CO₂-capture in combination with a gas power plant (Karsto, 280 MW_{el}, maximum heat decoupling 350 MW_{th}) and a refinery. For the first stage, the capture of 100 000 t CO₂ per year is planned; afterwards the plant shall be developed to reach an annual capture capacity of 1 million tonnes CO₂. The currently largest Oxyfuel pilot-scale power plant in the world is found at the German lignite-fired power plant site "Schwarze Pumpe" with a power rating of 30 MW_{th}. Within the scope of the Australian CCS research initiative, an Oxyfuel plant is being built at the coal power plant site Callide (Queensland). Within the framework of the Spanish Ciuden project, the construction of a coal-fired Oxyfuel plant (20 MW_{th}) is currently being pushed. Also to be mentioned are the activities at the power plant site 'Mountaineer' (U.S.), where a post-combustion plant (chilled ammonia) with a power rating of 54 MW_{th} is currently being built.

Whereas power plants of a lower power rating (<50 MW) are being built or already being operated, large-scale power plants are in planning. In Europe, numerous large-scale projects are being planned that are targeted at the actual capture, transport as well as storage of carbon dioxide. These include the coal power-plant projects Kingsnorth (2 × 400 MW), Ferrybridge (480 MW)

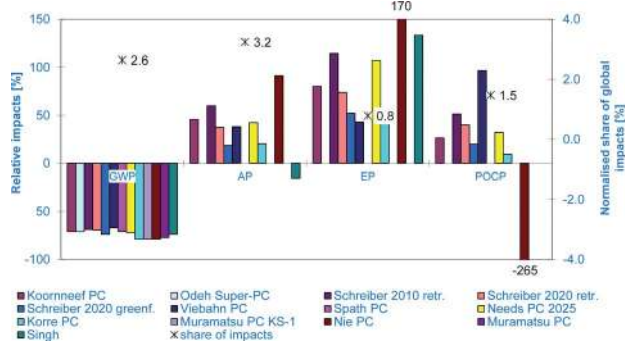


Fig. 12 Relative environmental impacts of hard coal combustion with MEA capture, normalised to the total global emissions in 2000 (adapted from ref. 139).

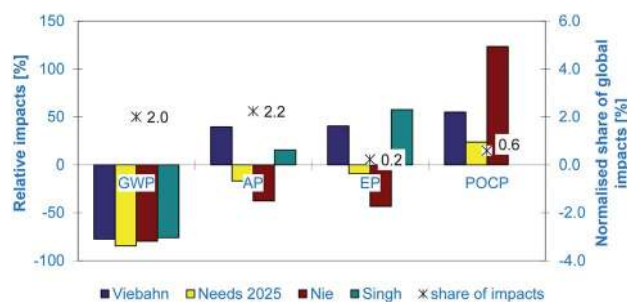
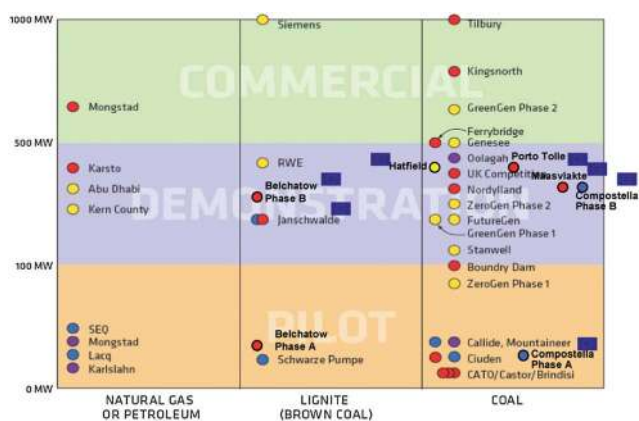


Fig. 13 Relative environmental impacts of hard coal Oxyfuel technology, normalised to the total global emissions in 2000 (adapted from ref. 139).



Scheme 14 Overview on CCS-projects (Status 2010) with amine (red circles) and ammonia (purple circles) based post-combustion, pre-combustion (yellow circles) and Oxyfuel process (blue circles). The flag marks projects supported by the EU.

and Tilbury (1600 MW) in Great Britain, for which feasibility studies are presently being developed. Moreover, construction of a coal-fired power plant (411 MW_{el}, heat decoupling 411 MJ s⁻¹) equipped with a post-combustion unit is planned at the Danish coal power plant site Nordjylland. At the Canadian power plant site 'Boundary Dam', the retrofitting of a coal power plant (100 MW_{el}) with a post-combustion washing unit is being planned. The carbon dioxide captured there is to be used in petroleum exploration. Furthermore, the German activities comprise the construction of post-combustion plants (Wilhelmshaven and Janschwalde), a pre-combustion plant at the site Hürth and the building of an Oxyfuel plant at the power-plant site Janschwalde.

Table 11 Worldwide largest realized CCS-projects

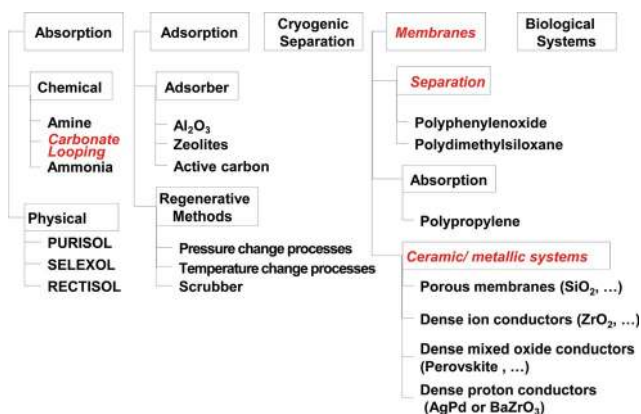
Project/Plant	Criterion
Bellingham Cogeneration Facility	Separation > 100 kt per annum
CASTOR Project	Separation (from exhaust gas) > 10 kt per annum
Great Plains Synfuel Plant	Separation > 100 kt per annum
In Salah	Injection > 10 kt per annum, separation > 100 kt per annum
K12-B	Injection > 10 kt per annum
Ketzin	Injection > 10 kt per annum
MRCSP Michigan Basin	Injection > 10 kt per annum
Nagaoka	Injection > 10 kt per annum
Otway Basin Project	Injection > 10 kt per annum
Pembina Cardium Project	EOR Monitoring > 10 kt per annum
Petrona Fertilizer Plant	Separation (from exhaust gas) > 10 kt per annum
IFFCO CO ₂ Recovery Plant Phulpur	Separation > 100 kt per annum, separation (from exhaust gas) > 10 kt per annum
Chemical Co. "A" CO ₂ Recovery Plant	Separation > 100 kt per annum, separation (from exhaust gas) > 10 kt per annum
IFFCO CO ₂ Recovery Plant Aonla	Separation > 100 kt per annum, separation (from exhaust gas) > 10 kt per annum
Prosint Methanol Plant	Separation (from exhaust gas) > 10 kt per annum
Rangely CO ₂ Project	EOR monitoring > 10 kt per annum
SECARB-Cranfield II	EOR monitoring > 10 kt per annum
Shady Point Power Plant	Separation (from exhaust gas) > 10 kt per annum
Sleipner	Separation > 100 kt per annum, injection > 10 kt per annum
Snøhvit LNG Project	Separation > 100 kt per annum, injection > 10 kt per annum
Schwarze Pumpe	Separation (from exhaust gas) > 10 kt per annum
IMC Global Soda Plant	Separation > 100 kt per annum, separation (from exhaust gas) > 10 kt per annum
SRCSF Aneth EOR Pradox Basin	EOR monitoring > 10 kt per annum
SRCSF San Juan Basin	Storage in coal seam > 10 kt CO ₂
Sumitomo Chemicals Plant	Separation (from exhaust gas) > 10 kt per annum
Warrior Run Power Plant	Separation (from exhaust gas) > 10 kt per annum
Weyburn	EOR monitoring > 10 kt per annum
ZAMA EOR Project	EOR monitoring > 10 kt per annum

Presently in the world, there are four large projects in which the capture, transport and storage of carbon dioxide are being simultaneously demonstrated. They are the projects Sleipner (Norway), Weyburn (USA–Canada), In Salah (Algeria) and Snøhvit (Norway). The amount of stored carbon dioxide of the four projects totals to about 7 million t per annum. Also to be mentioned here are the EOR-activities in Rangeley (USA), where CO₂ has been utilized for petroleum exploration for 20 years. Furthermore, numerous other large storage projects are being planned, in particular, in the U.S. and Canada. It is estimated that the amount of CO₂ stored will rise to 24 million tonnes CO₂ until the year 2012.

Within the scope of the GHG-program of the IEA, a survey was begun with the aim of compiling and summarizing the experiences gained from so-called CCS 'grand' projects. Such projects infer large pilot plants, demonstration plants as well as commercial chemical plants and storage projects. In all, 28 projects or plants (Table 11) were identified.¹⁴³ The largest CCS-plants are commercial chemical plants, which are implemented, e.g., in the context of producing ammonia and hydrogen as well as for processing Liquefied Natural Gas (LNG).

CO₂-capture methods of the second generation

Besides the previously described methods to capture CO₂ and separate air in power plants, there are many other innovative technical possibilities to achieve this. Membrane-based methods as well as the dry sorption of CO₂ (carbonate looping) are currently the most promising techniques (Scheme 15) for realization on the large-scale.^{146,147} Moreover, the 'chemical looping'

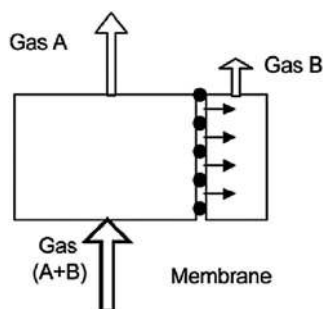


Scheme 15 Overview of gas separation processes.

method represents an alternative variant for supplying oxygen. As all these methods are still found in the early stage of development, these methods are often characterized as CCS-methods of the “second generation”.

Membranes are materials that selectively allow gases to permeate through them (Scheme 16). The membrane-based capture of gases is employed on a large scale for separating CO₂ from natural gas.⁷ Currently, worldwide efforts concentrate on developing dense, porous, or ion-/electron-conducting membranes for capturing CO₂ in power plant processes. The selectivity of the membranes for the permeability of various gases essentially depends on the membrane material and transport mechanisms. The stream of the gas through the membrane is decisively determined by the partial pressure difference of the gases between the permeated side and the retention side. Hence, the use of membranes is a technique particularly suitable for separation at high gas pressures.

The membrane-based separation has the potential to enable improved efficiency and the cost-effectiveness of the whole plant. The use of membranes is particularly interesting for H₂/CO₂-separation¹⁴⁸ because of the large difference in the physico-chemical properties of the two gases. Here, one can choose between separating hydrogen or carbon dioxide. Also for the production of pure oxygen for the Oxyfuel method membranes are an interesting option as the conventional cryogenic techniques are essentially responsible for the losses in efficiency and the efficiency potential mainly concerns the oxygen production (*vide supra*).



Scheme 16 Illustration of gas separation with membranes.

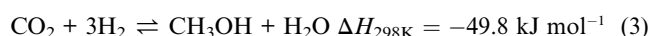
Physical and chemical utilization of CO₂

The physical utilization of carbon dioxide ranges from its application as a coolant and refrigerant to uses in fire extinguishers and cleaning processes to its use in the petroleum and natural gas industry for Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR). In recent years, numerous application areas have been developed and intensively studied. These include the extraction of natural materials, the processing and recycling of polymer and rubber products as well as the impregnation of wood.

The chemical utilization of CO₂ as a C1-building block in synthesis offers the possibility of incorporating it into products and materials either permanently or at least for a longer period. This option reflects an emerging anthropogenic carbon cycle similar to that of photosynthesis. The thermodynamic stability of CO₂ (end production of combustion) and its kinetic inertia (low reactivity) can be overcome by using energy-rich starting materials as reaction partners and the use of suitable catalysts, respectively, as has been proven by existing industrial processes and manifold research results. Alternative to energy-rich starting materials, an endergonic process may be driven by incorporation of heat, electricity or light. The highest reduction in CO₂ footprint is achieved, when the energy for chemical processing is supplied from renewable resources, such as wind power, solar collectors or panels.

The options for chemically exploiting CO₂ vary with respect to the maturity of the technologies. With existing technologies, carbon dioxide is used as a raw material in numerous important chemical processes. Currently, the most important applications are for the production of urea (107 million t per annum), methanol (2 million t per annum), cyclic carbonates (0.04 million t per annum) and salicylic acid (0.025 million t per annum).

Several innovative technologies are on the cusp of industrial realization. The synthesis of carbonates and polycarbonates from CO₂^{5,13,149,150} allows immediate accessibility to many markets in the chemistry and polymer sector.¹⁴ The hydrogenation of CO₂ to important chemical products such as methanol and formic acid¹⁵¹ and their derivatives is being intensively studied. Also the Reverse Water Gas Shift (RWGS) reaction (eqn (1)) is a feasible option for access into the chemical value chain *via* CO. Since hydrogen is nowadays produced practically only from fossil resources, a reduction in the CO₂-emission could be realized by using H₂ from other sources (*e.g.*, wind power or biomass). The utilization of H₂, for example, for producing methanol (*via* the reactions given in eqn (2) and (3)) would then have to be weighed accordingly:



Especially attractive in chemical utilization of CO₂ is the aspect that CO₂ has unlimited availability. There are various sources of carbon dioxide for its chemical utilization. In the chemical industry, carbon dioxide is produced in relatively pure form. Thus, about 120 million metric tons of CO₂ are formed yearly as a byproduct during the synthesis of ammonia.

Furthermore, CO₂ is formed during ethylene oxide production, in refineries and during the cleaning of natural gas. Moreover, carbon dioxide results as a byproduct during the production of synthesis gas as well as during fermentation processes. The grade of purity of carbon dioxide from ammonia production and from fermentation suffices for practically all synthesis purposes.

Carbon dioxide captured from power plants can likewise be used as a raw material. Nonetheless, due to possible impurities in the CO₂-stream in the power plant, scrubbing might first be necessary before the CO₂ can be materially used. The various impurities in the flue gases include O₂, N₂, H₂O, H₂S, CO, CO₂, SO₂, NO_x, heavy metals as well as other hydrocarbons. Certain criteria have to be met upon cleaning the CO₂-streams. From a chemical point of view, the stability of the applied catalysts towards catalyst poisons plays a particularly important role and has to be controlled. Also impurities incorporated into the products may restrict the use in certain fields of application (e.g., as pharmaceuticals). In contrast to classical chemical syntheses, where other cleaning steps typically follow the incorporation of CO₂, the purity of CO₂ is essential for its direct physical utilization. Since CO₂ is often used without further processing steps, e.g., in the food and beverage industries, CO₂-impurities can play a decisive role here. Since further cleaning of the carbon dioxide accrues costs, one likewise has to consider the economic balance. Moreover, from an ecological viewpoint, the additional energy expenditure for the CO₂-cleaning is likewise significant.

There are numerous reactions, where CO₂ can be employed for chemical synthesis (see, e.g. ref. 4,152–159). Active catalysts are available for coupling carbon dioxide with energy-rich unsaturated substrates such as epoxides,¹³ butadiene or acetylene. Direct carboxylation of hydrocarbons by inserting CO₂ into the C–H bond of alkanes, aromatics or olefins is regarded as a door for “dream reactions” of modern catalyst research;¹⁶⁰ this would open up an elegant route for producing fine chemicals. This pathway would allow the conversion of methane and CO₂ to acetic acid, benzene and CO₂ to benzoic acid, and ethylene and CO₂ to acrylic acid. Other options are further along the development path. The electro-catalytic and, in particular, the photocatalytic reduction of CO₂¹⁶¹ would be the most elegant way to exploit carbon dioxide, since it mimics the synthesis performance of nature in photosynthesis. However, current heterogeneous and homogeneous catalysts as well as the technical systems still need to be improved before they can attain technically viable efficiencies.

Conclusions

As current energy scenarios show, CCS-technologies are becoming a highly important option within the scope of worldwide strategies to reduce greenhouse gas emissions. Whereas carbon capture is already being commercially applied in certain branches of industry, e.g. in natural gas processing and chemical production, the use of these technologies in power plants has not yet reached such a level of maturity. In particular, with regard to the capture process as well as CO₂-processing, it is important to reduce efficiency losses and investment costs further in order to satisfy economic and environmental demands. Here, it is especially important to build demonstration units to reach market maturity in 10 to 15 years. Additional future technologies

like gas separation by membranes, methods for producing oxygen, chemical looping as well as dry sorption (carbonate looping) are regarded as the most promising candidates for a long-term implementation of carbon capture. As all these technologies are still in the early research and development stage, a large-scale application in power plants is expected only later on in the future. They are thus often called CCS-processes of the “second generation”.

A clear increase of the electricity generation costs through CCS can be expected. The increase is highest for lignite-based power plants (71–81%) and lowest for natural gas-based power plants (37%). The costs are linked closely to the capital expenditure. Additionally, the importance of fuel costs becomes clear: the higher the energy penalty (efficiency loss), the more fuel is consumed and the more the cost increase. Although optimistic costs parameters are expected for the IGCC concept, there is no clear preference for a single CCS technology line. The CO₂ avoidance costs range between 34 and 38 € (lignite) and more than 60 € per ton CO₂ (natural gas). In a regime with increasing share of renewable energies, where the level of full load hours is expected to decrease, the power generation costs and the CO₂ avoidance costs are expected to increase considerably. The increase is higher for those power plants with a high share of investment costs.

The introduction of CO₂ reduction technologies goes along with an increase of environmental impact (except the global warming potential (GWP)) regardless of the process routes or fuel used. This is related to the loss in efficiency and the corresponding additional demand for fuel, operating materials (e.g. solvents) and increasing waste. Therefore, an extensive further optimisation at the power plant alone will not have a recognisable effect. Reduced environmental impacts can be achieved by improving upstream processes. When solvents are used in the process, the toxicological impact on humans and the environment increases. Beside that the acidification potential (AP) increases noticeably, shifting the impact from the power plant to the extraction and transportation of fuel. In comparison to other industries the central impact for power production is the GWP, which will be decreased.

Parallel to the implementation of CCS, the technical and, in particular, chemical exploitation of carbon dioxide (CCU) can offer an interesting though limited contribution to the reduction of CO₂ emissions. Here, the captured CO₂ is a raw material, which can be made use of in the value creation chain of the chemical industry. Increased utilization of CO₂ may lead to a reduced carbon footprint of the products. The fixation period and fixation quantity are decisive for climate protection. Nevertheless, the utilization of carbon dioxide is an important option in the total strategy of ‘carbon management’. In particular, it offers an attractive alternative to the geological storage of carbon dioxide, enabling us to exploit CO₂ as a valuable resource in many different applications.

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