

Zero-emission coal power plants

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Introduction

The progressing global climate change induce atmospheric phenomena that negatively affect the environment and human life standards. The reason behind this is supposedly the growing level of carbon dioxide in the atmosphere, leading to aggravating greenhouse effect. In order to counteract climate change it has been established to set a specific, measurable goal, namely, not to exceed the temperature growth limit on Earth of 2°C [1]. The objective may only be fulfilled conditional upon a makeover of the global energy production that nowadays in nearly 80% relies on fossil fuel.

The solution may be to develop and implement technologies that allow for fossil fuel combustion without carbon dioxide emission to the atmosphere. One such technology is CCS (Carbon Capture and Storage) that involves the capture and depositing of carbon dioxide in geological formations [1, 2]. The said technologies are little known and require sophistication and development in order to be adopted for the purpose of the purification of exhaust from power or cement plants.

Among the fossil fuels used for energy production in Poland brown coal and hard coal prevail. Coal combustion that yields 1 GJ of energy produces approx. 100 kg of carbon dioxide, i.e. approx. twice the amount resulting from natural gas combustion.

From a technological standpoint, the formation of carbon dioxide following thermal and electric energy production considerably diminishes the performance of the power supply system. The applicable legal conditions also impose the necessity to reduce detrimental combustion product emissions to the atmosphere and apply solutions warranting zero-emission of carbon dioxide.

In pursuit of the objectives adopted as part of the energy-climate package, the European Union centres on the technological options including the post-process capture of carbon dioxide from exhaust gases (Fig. 1) [3]: coal combustion in air fuelled boilers; gasification and pre-combustion of the fuel obtained via gasification; coal combustion in oxygen-fuelled boilers with the recirculation of carbon dioxide.

to the chimney upon coal-fuel combustion. This is due to the fact that approx. 95% of electric energy is obtained in coal combustion in condensing boilers. The technologies of carbon dioxide separation base of absorption, adsorption as well as membrane and cryogenic separation processes. The choice of an adequate technology depends on the characteristics and volume of exhaust streams.

The capture of carbon dioxide prior to combustion consists in the gasification of coal fuel in oxygen to hydrogen gas and the release of carbon dioxide as a by-product. The most efficient process of carbon dioxide capture is physical absorption. Gaining popularity is the process of pure hydrogen emission by means of ceramic membranes.

The technology of the combustion or gasification of fuels in oxygen belongs to the solutions of the future. By virtue of oxygen application in the direct combustion, nitrogen is removed from exhaust gases, leaving a readily separable mixture of CO₂ and water vapour. This technology involves the recirculation of a part of exhaust gases with the content of CO₂ in order to reduce the temperature of the furnace and increase the level of carbon dioxide in exhaust gases.

Upon coal combustion in air, exhaust gases are diluted by means of nitrogen, which is why the level of carbon dioxide in exhaust gases usually does not exceed 16% of volume. Coal combustion processes in oxygen facilitate a higher level of carbon dioxide in exhaust gases, in the order of magnitude of 90%. Exhaust gases are not diluted with inert gases, so the amount thereof is approx. 6-fold lower. The said processes also require less excess air, leading to lower NO_x levels in exhaust gases.

Carbon dioxide sorption from combustion exhaust gases

The level of carbon dioxide in gases resulting from combustion processes varies within a broad range, depending on the applied technology of combustion (Tab. 1).

Table 1

The level of carbon dioxide in gases resulting from combustion processes

| Specification | Volumetric level of CO ₂ , % | Specification | Volumetric level of CO ₂ , % |
|------------------------------|---|---|---|
| Power plant exhaust gases | | Power plants with the pre-combustion capture of CO ₂ | |
| Coal-fuelled boilers | 14 | Coal gasification | 40 |
| Gas-fired boilers | 8< | Partial oxidation of flue gases | 24 |
| Natural gas (combined cycle) | 4 | | |
| Carbon combustion in oxygen | >80 | | |
| Mill proces gases | | Other | |
| Pre-combustion | 20 | Gases from cement combustion | 4–23 |
| Post-combustion | 27 | Petroleum industry and refineries | 8 |

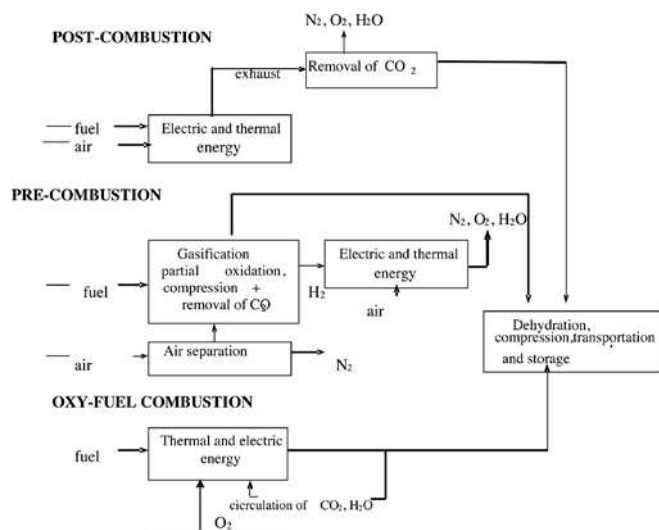


Fig. 1. Overview of CO₂ capture processes and systems

Of greatest importance in the energy industry in Poland is the method of carbon dioxide capture from exhaust gases directed

Post-combustion gases in power plants that implement coal-fuelled boilers the level of carbon dioxide amount to approx. volumetric 14% with respect to coal combustion in oxygen in exhaust gases with a volumetric content of CO₂ exceeding 80%.

Carbon dioxide separation from exhaust gases relies on the processes of adsorption, membrane and cryogenic separation as well as chemical and physical absorption, (Fig. 2) [4]. The choice of an adequate technology depends on the characteristics of exhaust gases (such as pressure, temperature, level of carbon dioxide) and volume of exhaust streams.

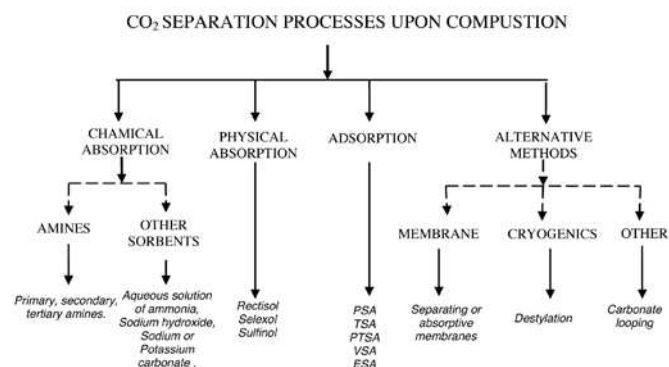


Fig. 2. Post-combustion technologies of carbon dioxide separation

The sorption carbon dioxide technique by means of chemical absorption is the most popular method of carbon dioxide separation from the boiler exhaust streams. Gas sweetening by means of amines shows the highest efficiency in bonding carbon dioxide. In this case, carbon dioxide absorption occurs in amine aqueous solutions (Fig. 3). The reactions underlying the chemical absorption of carbon dioxide with primary amines may be defined in the following formulas:

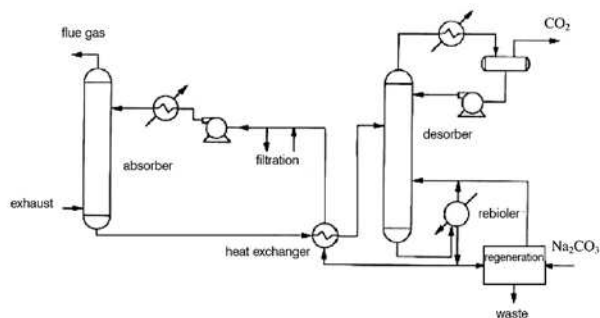
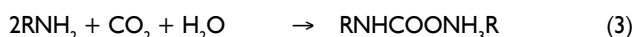
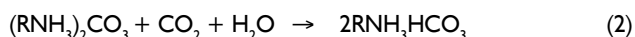
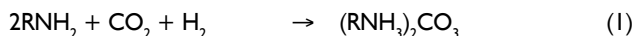


Fig. 3. Flow diagram of the plant for the chemical absorption process of CO₂ capture

The plant comprises an absorber that serves to remove carbon dioxide from exhaust gases and regenerator where CO₂ undergoes desorption at a high concentration and amine is recovered.

Gas separation on the separation membranes proceeds on account of chemical and physical differences between the components present in the gas mixture and the membrane material. The said differences are responsible for the non-uniform passage through the membrane of respective mixture components. The driving mechanism underlying sorption is the difference in contaminant molecular pressures on both sides of the membrane. The criteria to be met by an efficient separation membrane are selectivity and penetrability.

Cryogenic separation of carbon dioxide from the stream of boiler exhaust gases encompasses multiple-step compression and cooling to a desired temperature and subsequent separation of carbon dioxide in liquid form by means of distillation. It is recommended to adopt this method whenever the level of carbon dioxide in boiler exhaust gases exceeds volumetric 20%. Cryogenic methods for the capture of carbon dioxide may only be considered for the gasification and combustion plant in ambient oxygen medium and the recirculation of in carbon dioxide.

Adsorption methods involve the processes of the adsorption of the contaminants at the surface and in the voids of an adequately selected adsorbent. The said methods harvest the physical interactions between the gas and the active sites of a solid body. The main factor in the adsorption process is the choice of a sufficiently large sorption capacity with respect to carbon dioxide as captured from exhaust gases. The following may be counted among adsorbents: molecular sieves, clay and silica gel, active carbon, aluminium oxide, meso-porous molecular sieves and synthetic zeolites.

Chemical management of carbon dioxide

Carbon dioxide has been implemented in few production processes. It is applied in the nutritional industry to saturate drinks, produce dry ice for cooling facilities as well as in breweries.

In the chemical industry, carbon dioxide had been directly applied for the purpose of carbamide production. Research is underway concerning the implementation of carbon dioxide in a mixture of synthesized gases to produce methanol. Another application of this gas feature the neutralisation of alkali waste or inert gas production in production processes [5].

The demand for carbon dioxide used in these processes is, however, relatively low in contrast to the supply and other means of the mitigation of its effect must be sought.

Mineral carbonation method

One of the variants of carbon dioxide sequestration by chemical means is mineral carbonation. This sequestration method has not yet evolved past research stage. In mineral carbonation, carbon dioxide bonding is streamlined by means of minerals or waste minerals such as fly ashes and slag [6 ÷ 8]. By definition, mineral carbonation requires the reaction of carbon dioxide with metal oxides, leading to the formation of insoluble carbonates. Mineral carbonation may be performed by direct method, wherein a mineral undergoes carbonization, or indirect method, wherein the reactive components are initially extracted from the mineral matrix and subsequently subjected to the reaction with carbon dioxide (Fig. 4).

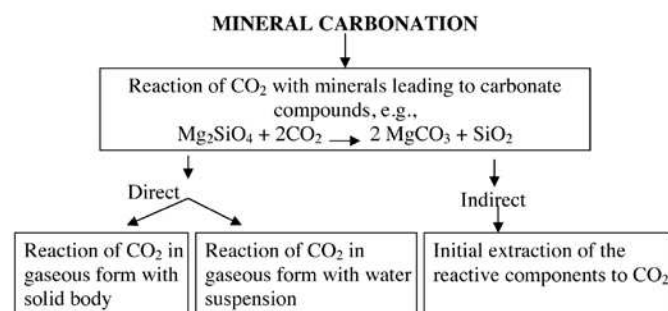
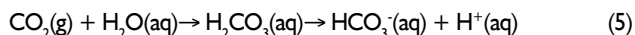


Fig. 4. Sequestration of carbon dioxide by mineral carbonation [9]

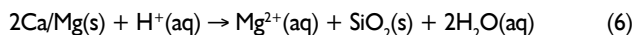
Direct carbonation may be achieved through the method of gaseous carbon dioxide reaction with a solid body such as calcium or magnesium silica:



or via the method of carbon dioxide reaction with water suspension containing calcium or magnesium silica. In this method, at the initial stage carbon dioxide dissolves in water and then dissociates into acidic carbonate and the ions of H^+ :



At the subsequent stage, Mg^{2+} ions are removed from the mineral matrix by the ions of H^+ :

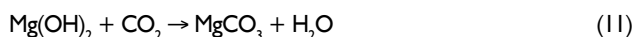
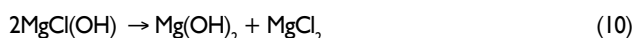
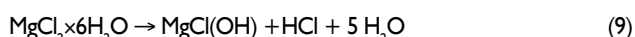
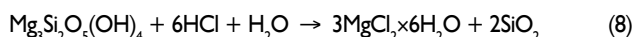


At the final stage, Mg^{2+} react with carbonate ions, forming magnesite:



Indirect carbonation method consists in the initial extraction of the components reactive with respect to carbon dioxide from the mineral matrix. The extraction may be conducted with the use of various substances such as hydrochloric acid, sulphuric acid, caustic soda and water vapour.

Described below are the chemical reactions that occur in the process of magnesium or calcium extraction from the mineral matrix with the use of hydrochloric acid:



Having regard to the application of mineral carbonation for the sequestration of carbon dioxide, two approaches may be adopted:

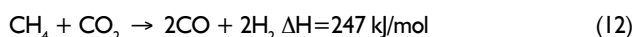
- *in situ* – underground mineral sequestration of carbon dioxide with geological storage
- *ex situ* – aboveground industrial process.

The bonding of carbon dioxide via mineral carbonation yields stable products that have a neutral effect on the environment.

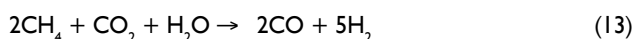
Carbon dioxide reforming of methane

The optimal carbon dioxide application in the chemical industry is the reaction of the dry methane reforming allowing for the transformation of carbon dioxide into syngas [10, 11].

The dry methane reforming reaction is an exothermic reaction, occurring according to the following formula:



The downside of dry reforming is the low volumetric ratio $\text{H}_2:\text{CO}$ in the syngas produced as well as the hazard of the contamination of metal catalysts by the so-called carbonization. The bi-reforming method combining steam and dry reforming yields a higher volumetric ratio H_2/CO , approx. 3.



Likewise with dry reforming, bi-reforming requires the enrichment of exhaust gases with carbon dioxide and the selection

of a suitable catalyst (Pt, Ni-based, on Al, zeolith carriers) and provide waste heat that may come from power station.

Tri-reforming spans the reactions of dry reforming, steam reforming and methane combustion in oxygen. The following reactions can be discerned within the process of tri-reforming:



The produced syngas may be used in the process of tri-generation for the synthesis of fuels and chemicals as well as the production of electricity. The advantage of tri-reforming is the application of exhaust gases containing carbon dioxide without the need for separation. Another upside is the possibility to harvest the waste heat from the power plant.

Geological sequestration

Since the market for the industrial applications of carbon dioxide is limited, most of the gas released must be neutralised in a different way. One option is to deposit carbon dioxide in deep geological formations such as mined-out oil or gas deposits, mined-out coal deposits or saline reservoirs. The process of storing carbon dioxide in suitable geological formations is called geological sequestration. Underground storage requires carbon dioxide to be deposited in deep and penetrable layers lined with impermeable material [12].

Geological storage of carbon dioxide is determined by several factors [13]. The period of storage must extend for several hundred years or longer and the costs of storage, along with transportation expenses from the source to the storage site, must be maintained at a minimum level. Other conditions are the elimination of emergency risk and minimization of the negative effect on the environment. It has been estimated that the available carbon dioxide storage capacity is as follows:

| | |
|--|--------------|
| • Oceans/seas | > 106 GtC |
| • Salt caverns | 100–1000 GtC |
| • Mined-out gas deposits | > 140 GtC |
| • Mined-out oil deposits | > 40 GtC |
| • Coal deposits | 10–100 GtC |
| • Injection with simultaneous oil recovery | 65 GtC. |

It is estimated that the global carbon dioxide emission amounts to approx. 25 Gt annually. The potential for carbon dioxide geological storage is much higher and so could be continued for many years to solve the problem of the anthropogenic carbon dioxide [13]. The costs of storage depend on the type of geological deposit wherein carbon dioxide is injected. The costs of storage in salt caverns and mined-out oil and gas deposits range from 10 to 20 EUR for 1 t of CO_2 . The costs of the transportation of carbon dioxide to the storage site also cannot be neglected. The said costs vary from 1 to 4 EUR for 1 t of CO_2 .

Conceptual project of zero-emission polygeneration coal power plant

The conceptual project of a zero-emission polygeneration coal power plant comprises the production of a synthesised gas (hydrogen) that is subsequently deployed as fuel for the generation of electric energy and as a material for the manufacture of methanol (Fig. 5).

The project has been developed by the Southern Energy Concern Company (Południowy Koncern Energetyczny) and ZAK SA in Kędzierzyn-Koźle and involves the process of coal gasification in oxygen in two production lines, the first yielding synthesised gas that

may be deployed for methanol, ammonia or Oxo alcohol production. Whereas, the other generates pure electric energy produced via combustion in hydrogen-powered turbine engines.

The polygeneration system ensures an energy balance of 60%. The 40% correspond to losses at the condenser.

According to the conceptual project, 20% of the carbon contained within the fuel subjected to gasification, shall be utilised as carbon dioxide for the synthesis of methanol, whereas 2.5 mln of Mg CO₂ shall undergo sequestration and underground storage (Fig. 6).

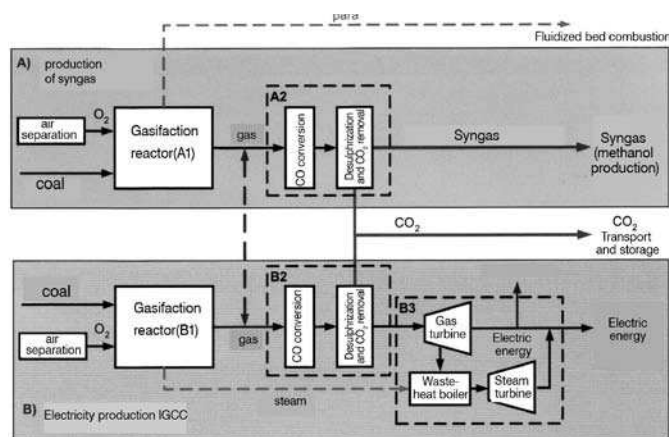


Fig. 5. Polygeneration power plant [14]

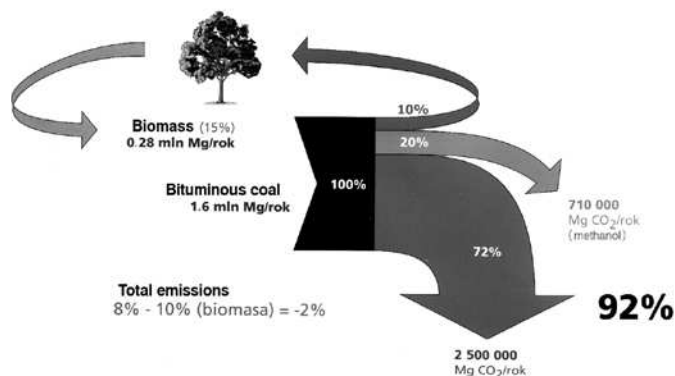


Fig. 6. Coal balance with respect to the example of the conceptual project of polygeneration power plant [14]

It is assumed that 10% of carbon dioxide shall be processed by plants that shall then serve as the material for the process of gasification. The total balance of carbon amounts to minus 2%, contributing to the reduction of carbon dioxide in the environment.

Conclusions

Zero-emission coal power plants seek to reduce carbon dioxide emissions accompanying electric energy production. The technologies of the capture of carbon dioxide from exhaust gases are based on the following processes: adsorption, absorption, membrane application and cryogenics. A part of the separated carbon dioxide may be used as the chemical material for the production of syngas or methanol. However, there are few chemical applications of CO₂. The bulk of the carbon dioxide released from the exhaust gases must therefore be stored in geological formations upon purification and compression.

It is recommended to reduce CO₂ emissions by means of the processes of coal combustion and gasification in oxygen. Such exhaust gases do not contain nitrogen, the content of CO₂ may even reach 90%. Hence, carbon dioxide capture is facilitated.

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