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Technologie Carbon Capture and Storage

Carbon Capture and Storage Technologies

Summary

The Carbon Capture and Storage (CCS) technology is a tool for active contribution to decreasing humankind-produced CO_2 emissions into the atmosphere, above all as a result of combustion processes for energy generation and thermal industrial processes. The technology as whole consists of three parts – capture, transport and safe long-time storage. The capture part is reviewed in this text. There are three different approaches to CCS depending on the stage of fuel conversion at which the CO_2 is captured. – post-combustion, pre-combustion and oxyfuel combustion.

Generally, the post-combustion CCS represents conventional air combustion of a fuel, and flue gas cleaning. This is followed by a technology which is able to remove the CO_2, typically at low concentration, from high flow rate of the off-gas. This removal is based on physical or chemical absorption by solvents (e.g. ammonia or ethanolamines).

The pre-combustion CCS is applied in an integrated gasification combined cycle (IGCC). The fuel is initially converted into a mixture of CO, CO_2 and H_2. The technology set-up remains similar to a conventional IGCC, there is just a process modification enabling CO_2 separation in the stage of acid gases scrubbing. A new part is a water-gas shift reactor that converts CO to CO_2 and H_2. The final product is hydrogen – a carbon-free fuel – that follows a standard pathway in the IGCC system to a gas turbine.

Oxyfuel combustion is based on replacing air by pure oxygen in a standard combustion process. The result is a flue gas free from nitrogen, thus increasing the CO_2 concentration up to 45-50 %. The second major component (about 40-50 %) is water vapour. The flue gas undergoes cleaning from trace pollutants and finally enters a condenser, removing the water vapour. Outgoing stream is 90-95 % CO_2.

Souhrn

Technologie Carbon Capture and Storage (CCS) je v současnosti jedním z nástrojů pro aktivní příspěvek ke snižování člověkem produkovaného CO_2 do ovzduší ze spalování zejména fosilních uhlíkatých paliv. Jedná se především o zařízení pro výrobu energie a o tepelné průmyslové procesy. Technologie CCS se jako celek skládá ze tří částí – záchyt, transport a dlouhodobé bezpečné uložení. V textu je dále rozebrána pouze část záchytu. Existují tři rozdílné přístupy k záchytu, které se liší podle toho, ve které fázi termochemické konverze paliva jsou realizovány – jedná se o technologii post-combustion, pre-combustion a oxyfuel spalování.

Post-combustion CCS technologie je obecně reprezentována konvenčním spalovacím procesem se standardním čištěním spalin. Tento konvenční systém je doplněn technologií schopnou separovat CO_2 v nízké koncentraci z velkého objemu spalin. Typicky je tato separace zajištěna fyzikální nebo chemickou absorpcí pomocí vhodných rozpouštědel (např. amoniak nebo etanolaminy).

Technologie pre-combustion je realizována ve standardním integrovaném paroplynovém cyklu se zplyněním (IGCC). Vstupní palivo je nejdříve pomocí zplyňování převedeno na směs hořlavých plynů, především CO, CO_2 a H_2. Technologie zůstává prakticky shodná s konvenčním IGCC, je zde pouze procesní modifikace v kroku separace kyselých plynů tak, aby zde došlo k záchytu i CO_2. Nově je do technologie zařazena jednotka konverze vodního plynu, která převádí CO na CO_2 a H_2. Konečným produktem je vodík, tj. bezuhlíkaté palivo, které pokračuje standardní cestou v IGCC do plynové turbíny.

Oxyfuel spalování je založeno na náhradě spalovacího vzduchu čistým kyslíkem v běžném spalovacím procesu. Výstupem jsou spaliny neobsahující dusík, čímž stoupne koncentrace CO_2 na 45-50 %. Druhou hlavní složkou je vodní pára v koncentraci cca 40-50 %. Spaliny procházejí běžným systémem čištění a vstupují do kondenzátoru, kde se odstraní vodní pára. Výstupem je 90-95 % CO_2.

Keywords

CCS; post-combustion; ammonia scrubbing; pre-combustion; Ca-looping; oxyfuel combustion

Klíčová slova

CCS; post-combustion; amoniaková vypírka; pre-combustion; karbonátová smyčka; oxyfuel spalování

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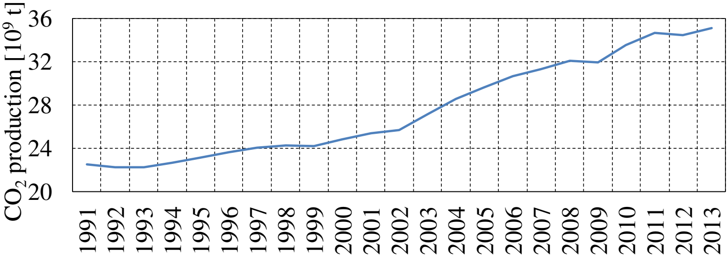
1. INTRODUCTION

The development of the Carbon Capture and Storage (so-called CCS) technologies is a response to a presumption, that a release of humankind-produced carbon dioxide (CO_2) from energy conversion of carbon-based fuels and industry is causing an increase of CO_2 in the atmosphere, which is in consequence playing an important role in global climate change, specifically in the increase of the global temperature on Earth by strengthening the greenhouse effect. The majority of CO_2 emissions come from burning fossil fuels, most of it from power and heat production and other thermal industrial processes, e.g. iron and steel production, cement production, natural gas processing and petroleum refining. Global emissions of CO_2 from fossil fuels have been increasing by 2.7 % annually over the past decade and are now about 60 % above 1990 level, the reference year for the Kyoto Protocol [1]. Details of the development of CO_2 production are shown in Figure 1.

Figure 1: Development of CO_2 emissions, data from [2]



Although there are many different opinions in the scientific world, whether the statement above, generally speaking, is true or untrue, and whether we do or don't have enough reliable data to correctly evaluate this statement, it is without any doubt that the "CO_2-global warming" issue has become a strong topic in political decisions. One of the most recent political decisions on global CO_2 emission reduction has been adopted at the 2015 United Nations Climate Change Conference in Paris [3]. At this conference, a Paris agreement has been signed that concerns the following aim: "Holding the increase in the global average temperature to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5°C above pre-industrial levels, recognizing that this would significantly reduce the risks and impacts of climate change” [4].

There are various approaches to how to reduce CO_2 emissions into the atmosphere, regardless of the energy conversion mechanism or source. One group represents reduction of CO_2 production by general means of increasing energy conversion efficiency, using fossil fuels with a low specific CO_2 emission or using renewable carbon-free or carbon-neutral energy sources. The second group represents active decreasing of CO_2 production by removing it before or after an energy conversion process of a carbon-based fuel or an industrial process, and its storage in a suitable location where it is unable to escape and can be safely stored for a long period of time. These technologies are called Carbon Capture and Storage (CCS) [5].

2. CCS TECHNOLOGIES IN GENERAL

The CCS technologies comprise in general of three technologic parts – CO_2 capture, transport and storage. This text reviews the part concerning CO_2 capture; the transport and storage parts are not further discussed. The capture part of CCS can be further divided according to the point where the CO_2 is sequestrated. These are the following:

a) post-combustion capture technology; in principle, the CO_2 is captured from final outgoing off-gas after the combustion process of a fuel had been completed.

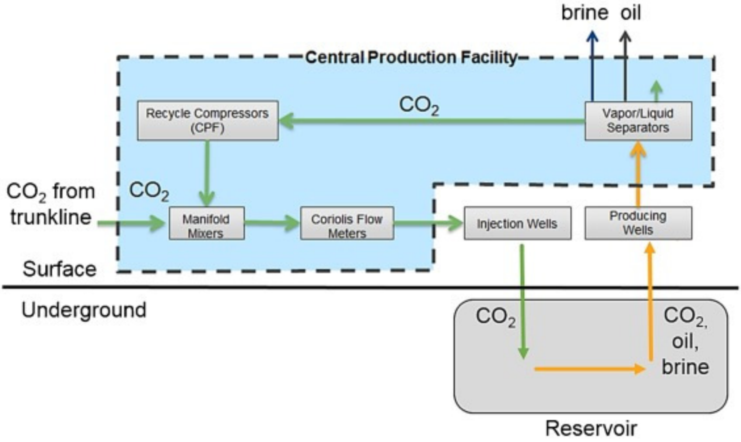
b) pre-combustion capture technology; any fuel entering this process is firstly converted to a mixture of CO, CO_2 and H_2 using a gasification process. CO is then converted to CO_2 and separated from hydrogen, which is the final carbon-free fuel.

c) oxyfuel combustion technology; a fuel is combusted with pure oxygen instead of air with a flue gas recirculation. Flue gas leaving this process contains majority of CO_2 with presence of minor components that need to be separated.

After the capture part of the technology, the separated CO_2 can optionally undergo a final cleaning and subsequently a compression or liquefaction. At this point, the CO_2 is ready for transport, either by pipeline (in gas phase) or by ship or rail (in liquid phase). The final stage is the storage in a safe and long-time stable storage place. Typically, the storage place is a geological structure or oceans. An alternative option are exploited gas or oil fields that have suitable conditions for storage [5], [6], [7].

Recently, the CO_2 storage is mostly discussed through the so-called Enhanced Oil Recovery processes (CO_2 EOR), enabling exploitation of residual oil in reservoirs in the 3rd phase of production, i.e. in a situation when the fluid pressure is reduced and water injection for the 2nd oil production phase is no more efficient. Injected CO_2 changes the oil properties and allows it to flow more freely within the reservoir. The CO_2 EOR originally came into application in 1980s mostly in the USA. At that time, however, the CO_2 was produced just for the EOR purpose without any link to CCS [8]. A scheme of the EOR principle is shown in the following figure.

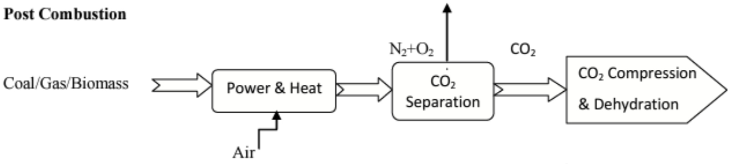
Figure 2: Principle scheme of EOR [9]



3. POST-COMBUSTION CAPTURE

The scheme of a post-combustion system is shown in the following Figure 3.

Figure 3: General scheme of a post-combustion CCS system [10]



Post-conversion capture involves separation of CO_2 from flue gas streams after the conversion of the carbon source to CO_2 – for example from combustion of fossil fuels. The processes of CO_2 separation from the flue gas are generally based on adsorption, absorption or chemisorption processes, alternatively on membrane separation or cryogenic separation. An overview of the possible methods is given in the following Table 1 [1], [11].

Table 1: Overview of post-combustion CO_2 separation technologies

Separation technology	**Technology principle**
Absorption – liquid solvents with chemical reaction	1) amine-based solvents, e.g. monoethanolamine (MEA) or diethanol amine (DEA) – amine scrubbing 2) ammonia solvent – ammonia scrubbing 3) alkaline solvents, e.g. NaOH
Adsorption – solid sorbents with/without chemical reaction	1) Ca-based sorbents, e.g. limestone $CaCO_3$ – Ca-looping system 2) Alkali metal carbonates, e.g. Na_2CO_3 3) Special sorbents or molecular sieves – e.g. zeolites, activated carbon
Membrane separation	1) Polymeric membranes 2) Inorganic and hybrid membranes

Recently, the mostly developed technologies, some of them already in full demonstration scale, are amine- or ammonia-based scrubbing and Ca-looping systems. These are described in more details in the following chapters. The other technologies are under different stages of research and development.

3.1 Amine and ammonia scrubbing

In principle, this process includes two main steps – absorption of the CO_2 by a solvent in an absorber and transport of the saturated solvent to a desorption unit where the solvent is regenerated and CO_2 released as a pure stream. In the case of amines and ammonia as solvents, both processes are chemisorption, i.e. a chemical reaction takes place. For the case of monoethanolamine (MEA), the general chemical reaction is:

$$HOCH_2CH_2-NH_2+CO_2+H_2O \rightarrow HOCH_2CH_2-NH_3^+ + HCO_3^-$$

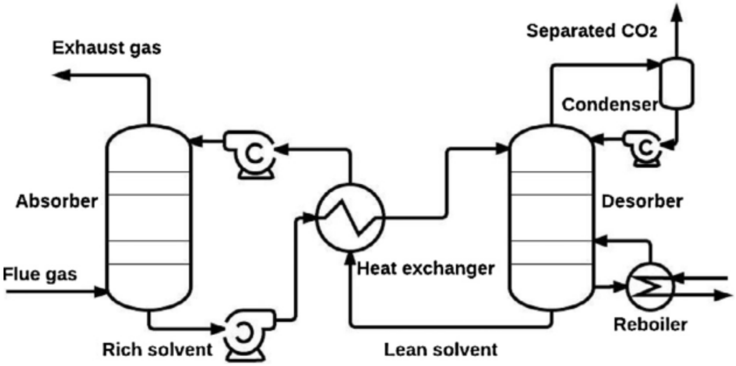
The absorption capacity of MEA solution for CO_2 is relatively low and therefore requires large specific amounts of the solvent, which translates into a large equipment size and intensive energy input, and leads to unfeasible process economy. To follow optimal conditions of the process in terms of the sorption capacity, the process is carried out usually at ambient temperature. Regeneration takes place at elevated temperatures at about 100-200°C. Steam is required for regeneration. Besides the low sorption capacity, an important disadvantage is degradation and decomposition of the solvent, leading to its higher consumption than required by the stoichiometry.

The ammonia scrubbing uses liquid ammonia, and the overall chemical reaction is:

$$NH_3(l)+CO_2(g)+H_2O(l) \rightarrow NH_4HCO_3(s)$$

This process requires more cooling compared to the amine scrubbing, normally a temperature of 5-10°C is required. Therefore, an extra cooling power is needed. An advantage of the ammonia scrubbing is a significantly higher sorption capacity, which is about 1.2 g CO_2/g NH_3 (compared to 0.4 g CO_2/g MEA), practically no risk of solvent degradation, and a lower temperature for regeneration is sufficient. Scheme of the process is illustrated in the following Figure 4.

Figure 4: Process scheme of a MEA scrubbing [12]



Generally, the solvent absorption processes bring a great energy penalty to the whole energy generation process due to the requirements for electricity and steam consumption. The main types of consumption are the following:

- electricity needs of main drives (compressor, flue gas fan, compression cooling, solvent pumps),

- steam supply for desorption,

- demi water consumption required for filling into the absorber to sustain required concentration and amount of the solvent.

For example, an overall impact of implementation of ammonia scrubbing on a reference 250 MWe coal-fired power plant is shown in the following Table 2.

Table 2: Impact of ammonia scrubbing post-combustion capture on a reference 250 MWe coal-fired power plant [11]

Parameter	**Unit**	**Current situation**	**With post-combustion CCS (ammonia)**
Power output	MWe	250	238
Coal consumption	t/h	214	214
Energy in fuel	MWt	588	588
Self-consumption	MWe	24	24
CO_2 production	t/h	211	211
Captured CO_2	t/h	0	190
Emissions of CO_2	t/h	211	21
Consumption of CCS	MWe	0	50
Net el. generation	MWe	226	164
Total efficiency	%	**38.4**	**27.9**
Efficiency decrease	**% pts.**	**0**	**10.5**

Table 2 clearly shows the energy penalty associated with addition of the ammonia scrubbing post-combustion technology, which makes about 10.5 percent points reduction in net electricity generation efficiency [1], [11].

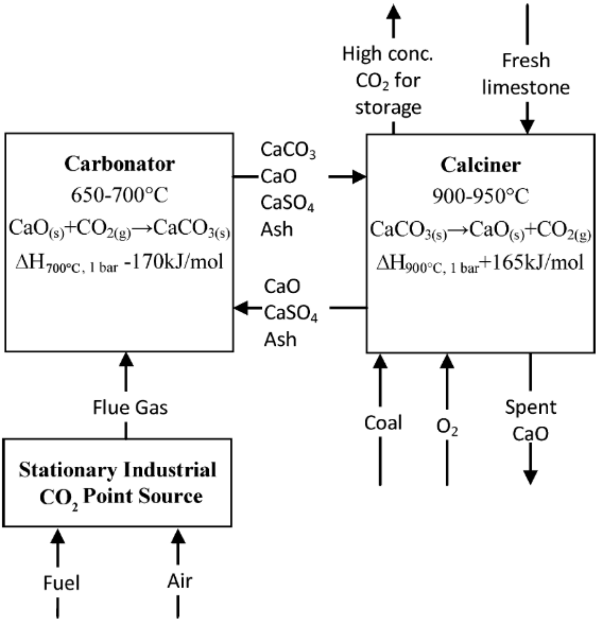
3.2 Carbonate loop

The carbonate loop, sometimes referred as Ca-looping system, is based on reversible chemical reaction between CO_2 and a sorbent containing CaO, as shown in the following equation:

$$CaO + CO_2 \leftrightarrow CaCO_3$$

In practice, the system consists of two reactors, so-called carbonator and calciner. In the carbonator, the CO_2 is captured by calcium oxide CaO at temperature of about 650°C and $CaCO_3$ is formed, which is then transported to the calciner, where the $CaCO_3$ is decomposed (calcined) to CaO, and stream of pure CO_2 is released. The Ca-looping is schematically shown in Figure 5.

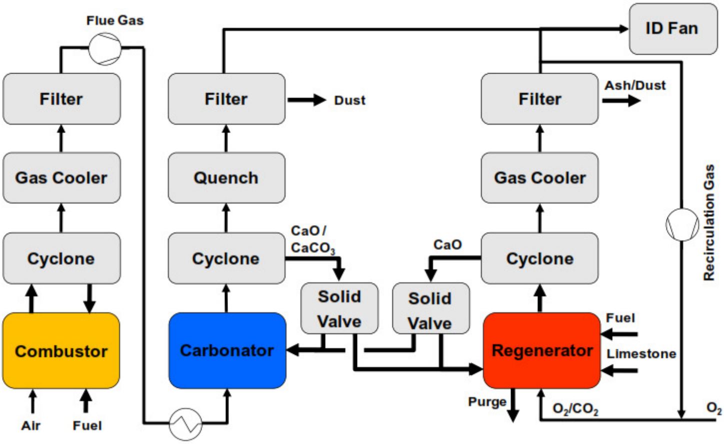
Figure 5: Scheme of a Ca-looping process [13]



As shown in the Figure 5, into the carbonator enters the flue gas from conventional air combustion of a fuel of any kind (solid, liquid, gaseous, etc.) containing CO_2 in a low concentration. For example, in air-fired coal combustion, this concentration is about 15 % vol. in dry flue gas. The carbonator leaves a CO_2-lean off gas, containing particularly nitrogen and water vapour from original flue gas. Residual CO_2 concentration in this stream is given by the carbonation efficiency. In calciner, the $CaCO_3$ is decomposed and CO_2-rich off gas leaves the calciner for subsequent treatment and compression.

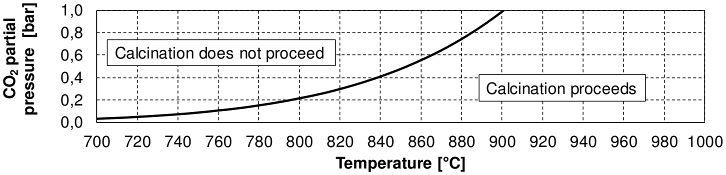
There are several important points in real implementation of this process. The first one is the issue of transporting ("looping") the regenerated and spent sorbent between the calciner and the carbonator. In practice, this is realized by operating both reactors as fluidized bed systems, very closely related to fluidized bed combustion systems. This system is known as a dual-FBC and its process scheme is illustrated in the following Figure 6.

Figure 6: Process scheme of a dual-FBC system for Ca-looping [14]



Besides ensuring the possibility of transport of solids between the reactors, the fluidized bed operation allows intensive mixing and thus intensive heat and mass transport, enhancing the reaction rates of the heterogeneous reactions between the sorbent and CO_2. The second important issue are operation temperatures. They are fixed by the chemical equilibrium of the calcination reaction and by the temperature dependence on the reaction kinetics. The optimum temperature required for carbonation is about 650°C, balancing the equilibrium, kinetics and structural stability of the sorbent. The optimum temperature for calcination is about 880-920°C and is given by the equilibrium curve of the calcination reaction. This is shown in Figure 7.

Figure 7: Equilibrium of calcination [15]



As shown in the Figure 7, the calcination depends on temperature and partial pressure (concentration) of CO_2 in the calciner. In principle, a higher CO_2 concentration implies a higher temperature for calcination.

Ensuring the proper temperatures in both reactors is one of the key issues of the Ca-looping system. Flue gas from the air-fired boiler enters the carbonator at about 60-100°C, thus requires a heat-up. The temperature in the carbonator is sustained by exothermic carbonation reaction and supply of hot sorbent from the calciner. Overall thermal balance is positive and the CO_2-lean off gas leaves the carbonator at elevated temperature about 500-600°C. However, the calciner needs an energy supply to heat up the spent sorbent from carbonator to the decomposition temperature. This is ensured by oxyfuel combustion (process description is given in chapter 5) carried out in the fluidized bed calciner, either of the same fuel as is used in the boiler or a different fuel, e.g. natural gas. The oxyfuel combustion ensures that the major flue gas component is CO_2, thus not diluting the CO_2 from regeneration of the sorbent. At the outlet of the calciner is therefore a stream of CO_2 that comes from calcination and oxyfuel combustion. Residual components in the stream are other products of the oxyfuel combustion in the calciner, particularly water vapour, residual oxygen and trace pollutants, typically oxides of nitrogen and sulphur.

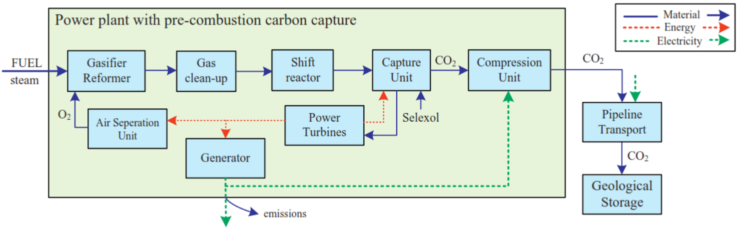
Advantage of the Ca-looping system is a robust and reliable construction and cheap and widely available sorbent. Both gas streams from carbonator and calciner are at high temperature and the energy carried by these streams can be efficiently recovered to electricity/heat production, thus not creating an extra energy penalty in additional unrecoverable heating or cooling, as in the scrubbing systems. An important advantage is load flexibility.

Disadvantage of the Ca-looping system is a requirement of an air separation unit for the calciner that brings an energy penalty of about 5-6 percent points on the electricity generation efficiency in the original power plant. This is about half of the penalty in comparison to oxygen consumption of oxyfuel combustion in the calciner, because about half of the power of the primary CO_2 source is required for calcination. A further important disadvantage is a loss of sorption capacity of the sorbent during the cycles, in which the sorbent passes between carbonator and calciner. The loss of capacity is caused by fragmentation, competing reaction with sulphur oxides, contamination of the sorbent by inert ash in calciner and destruction of porous system of the sorbent [16], [17], [18], [19].

4. PRE-COMBUSTION CAPTURE

This capture system is based on the consequent steps of gasification of input fuel to a mixture of combustible gases, particularly CO and H_2. These two major gases are accompanied by other gases, typically CH_4 and CO_2. CH_4 formation can be avoided during the gasification step. CO is possible to convert to CO_2 that can be subsequently removed from the produced syngas. The result of this process is hydrogen as a carbon-free fuel which can be used e.g. in a gas turbine. Generally, the process is called IGCC (integrated gasification combined cycle) and without CO_2 capture is generally used in practice [20]. The pre-combustion system is shown in the following Figure 8.

Figure 8: Process scheme of a pre-combustion CCS [21]



The gasification is a thermo-chemical process at about 800-1000°C in which a hydrocarbon-based material is converted by a so-called gasification medium to a mixture of combustible gases. These major gases are hydrogen, carbon monoxide and methane. The produced gas contains other inert or unwanted components, however. For example, these components are nitrogen, carbon dioxide, hydrogen sulphide or ammonia.

The choice of the gasification medium and pressure of the process determines the composition of the outgoing gas, particularly the share of the three major combustible components. An overview of the most typical options is given in Table 3 [22].

Table 3: Gasification process [22]

Gasification medium	**Pressure**	**Product**
air	atmospheric; elevated not used	lean gas, majority of N_2, low share of CO
air oxygen enhanced	atmospheric; elevated not used	lean gas, higher share of CO
air + steam	atmospheric; elevated not used	lean gas, higher share of CO and H_2
steam	atmospheric; elevated not used	water gas, $CO+H_2$ diluted by N_2
steam + oxygen	atmospheric	process gas, majority of CO, H_2 and CO_2
steam + oxygen	pressurized >2 MPa	syngas, majority of CO, H_2, CH_4 and CO_2

The Table 3 presents the required conditions for the gasification process. In the pre-combustion CCS, the only option is to use any air-free gasification medium (most typically oxygen-steam mixture) in order to avoid N_2 dilution of the output gas. The requirement of oxygen for the gasification medium imposes the necessity of an air separation unit. The pressure in gasification can control the share of methane and when using atmospheric gasification, production of methane can be nearly completely avoided.

The next key step after the gasification and produced gas cleaning (e.g. tar, dust or phenol removal) is a conversion of the CO in the gas to CO_2 by the so-called water gas shift reaction. It can be described as follows [23]:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

This reaction takes place in the "Shift reactor" shown in the Figure 8. The reaction normally takes two steps – low temperature shift (LTS) and high temperature shift (HTS). The LTS operates at 150-300°C and the HTS at 350 to 600°C. The reaction requires catalysts, whose composition can vary according to specifications and requirements of the shift reaction. A typical catalyst is ZnO/Al_2O_3 or Fe_2O_3/CrO. The process is usually pressurized. This step is the greatest energy penalty to the pre-combustion process, besides the oxygen required for gasification, due to the requirement of extensive heat-up of the gas.

Final step is a separation of CO_2 from the produced gas; alternatively, the water-gas shift and CO_2 separation can be altered, both options are possible. The CO_2 separation requires a highly selective process. The following table gives an overview of industrially available processes.

Table 4: Processes for CO_2 separation from gas from gasification [1], [24]

Procedure	**Process name**	**Specification**
Physical absorption	Selexol/ Coastal AGR	Solvent mixture of dimethyl ethers and propylene glycol (DEPG); ambient temperature
	Rectisol/ Ifpexol	Solvent methanol, sub-cooled at -20 to -60°C; application in IGCC
	Purisol	Solvent N-methyl-pyrollidone (NMP), chilled to -15°C; application in IGCC
	FluorSolvent	Solvent propylene carbonate; chilled to -18°C
Chemical absorption	MEA	Solvent mono-ethanolamine, application in ammonia production

It is important to note that the above mentioned physical solvent absorption processes have been originally developed for acid gas removal from gasification for IGCCs, typically a separation of H_2S, COS and HCN, but due to the acidic character of CO_2 they can be applied for its separation as well. Other options of CO_2 removal from the produced gas are similar to the post-combustion capture, e.g. cryogenic separation or membrane separation.

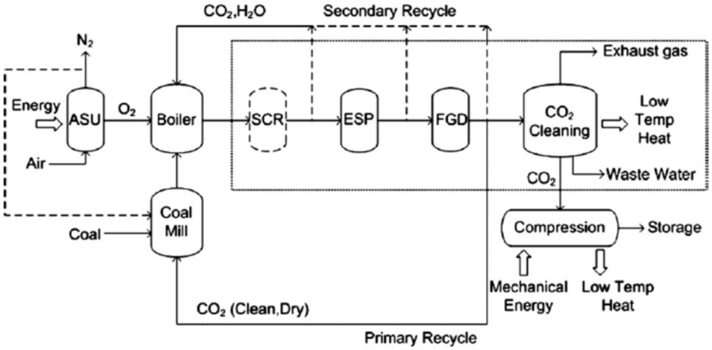
The advantage of the pre-combustion CCS is technical maturity of the IGCC technology that can be relatively easily adapted for CO_2 capture by modification of operation conditions of the acid gas separation units (e.g. Rectisol needs to operate at somewhat lower temperature than for just acid gases separation). The technologic challenge is however combustion of pure hydrogen in a specific gas turbine. Significant quantity of hydrogen in fuel has the benefit of high calorific value by mass, but by volume is nearly identical to carbon monoxide. There are also significantly different flame speeds, short reaction times and high flame temperatures. The hydrogen needs to be therefore diluted, either by nitrogen from air separation unit, or by injection of water steam [25], [26].

Recently, some IGCCs with CCS are already under construction or under operation, mostly in USA, UK and China. The electric capacity ranges roughly from 300 to 900 MWe [27].

5. OXYFUEL COMBUSTION

The concept of the oxyfuel combustion was firstly adopted in various industrial applications like cement or glass production. The oxyfuel combustion was also proposed already in 1980's in the context of providing CO_2-rich flue gas for enhanced crude oil recovery (EOR), as mentioned in chapter 2. The principle of the oxyfuel combustion is based on replacing air as an oxidizer by pure oxygen in conventional combustion systems. This enables removing nitrogen from the flue gas, which is a major flue gas component in conventional air combustion [6]. The scheme of the oxyfuel combustion is shown in Figure 9.

Figure 9: Configuration of an oxyfuel combustion plant [28]



The oxyfuel combustion system requires an air separation unit (ASU) to provide oxygen for combustion. This is also the greatest energy penalty for the oxyfuel CCS. As shown in the Figure 8, there are other conventional technologies applied, e.g. desulphurization (FGD) or deNOx (SCR) unit to remove sulphur and nitrogen oxides. The following step is a separation of water from CO_2 before it is ready for compression and transport. The following Table 5 shows the difference in composition of flue gas in air and oxyfuel combustion of the same sort of coal.

Table 5: Flue gas from air and oxyfuel combustion for a sort of lignite coal, 20 % oxygen excess [6]

	air-fired	**oxyfuel**	**unit**
excess oxygen ratio	1.24	1.10	-
O_2 in flue gas	4	5.4	%
concentrations of flue gas components (wet/dry), normal conditions			
CO_2	**13.2/15.3**	**47.9/88.9**	% vol.
H_2O	**14.0/0.0**	**46.1/0.0**	% vol.
N_2	68.4/79.6	0.3/0.5	% vol.
SO_2	0.08/0.09	0.3/0.5	% vol.
O_2	3.5/4.1	5.4/10.1	% vol.
noble gases (Ar)	0.8/0.9	0.0/0.0	% vol.

As shown in the Table 5, in full oxyfuel mode, the CO_2 concentration can reach up to about 90 vol. % in dry flue gas. For a higher grade fuels, it can exceed 90 % in dry flue gas and reach up to 95 %. The second major component is water vapour that can be as high as 50 % in share, depending on moisture of the fuel. The third major component is oxygen from its necessary excess in the combustion process.

A specific feature is the necessity of extensive flue gas recirculation (FGR), meaning return of major part of the outgoing CO_2-rich flue gas to the oxygen input. Without FGR, the flame temperature could be as high as 3000°C, since there is not enough heat carrier to carry away the heat released by the combustion process. Mixing the recycled flue gas with the pure oxygen is necessary because materials of construction currently available cannot withstand such a high temperature resulting from coal combustion in pure oxygen. There are also other limitations, for example ash fusion temperatures in case of coal combustion. The amount of the outgoing flue gas from oxyfuel combustion is about 70-80 % relative lower compared to conventional air combustion.

The oxyfuel combustion has some specific features compared to air-fired combustion. These features are primarily determined by the replacement of nitrogen by CO_2 in the primary mixture by massive recirculated flow of flue gas. Significant effect is on the adiabatic flame temperature. Due to different specific heat capacities, it is necessary that the O_2 proportion of the gases passing through the combustion zone is higher, typically 30 %, than that for air (of 21 % O_2), necessitating that about 60 % of the flue gas is recycled, in order to attain a similar adiabatic flame temperature. The high proportions of CO_2 and H_2O in the flue gas result in higher gas emissivity, so that similar radiative heat transfer for a boiler that would be eventually converted to oxyfuel would be attained when the O_2 proportion of the gases passing through the burner is less than the 30 % required for the same adiabatic flame temperature [6], [29], [30].

A strong advantage of the oxyfuel combustion is technical maturity and possible application on retrofitted combustion systems without the need of construction of additional space-consuming facilities, like in e.g. post-combustion CCS. The oxyfuel combustion disadvantage is a great energy penalty given by the need for oxygen supply for the process, however.

5.1 Trace pollutants in oxyfuel combustion

The oxyfuel combustion is also specific in formation of trace pollutants that need to be separated from the CO_2 stream before water condensation. The pollutants that need to be removed are carbon monoxide, nitrogen oxides and sulphur oxides. Other pollutants, if present, are in negligible concentrations.

The carbon monoxide is referred to as a product of incomplete oxidation of hydrocarbons in fuel. However, at high concentrations of CO_2 in the gas phase, which is typical for oxyfuel combustion, the CO can be also produced by dissociation of CO_2. CO levels in the flame zone are generally reported to increase significantly in oxyfuel combustion compared to air-firing. Even though the high CO_2 levels prevent CO from being oxidized at high temperatures, complete conversion is expected when excess oxygen is present during cool-down of the flue gas. Because of its severe toxicity it is important that oxyfuel combustion does not lead to an increased CO emission when the combustion is completed.

For the NOx formation, three known pathways are generally accepted – thermal (Zeldovich), prompt (Fenimore) and fuel-N type nitrogen oxides. The significance of these pathways differ according to the type of the combustion system. In the air-fired pulverized coal combustion, about 20 % of NOx is formed through the thermal mechanism and the rest is formed from fuel-N while the prompt mechanism is negligible. In the air-fired fluidized bed combustion, almost 100 % of NOx is formed from fuel-N and the other mechanisms have negligible significance due to generally lower combustion temperatures. Generally, a lack of nitrogen in the oxyfuel combustion mode prevents the thermal pathway of NOx formation. In addition, the equilibrium of the Zeldovich reaction can be affected by excessive NO concentration compared to N_2 concentration that always occur in the oxyfuel regime. Therefore, the Zeldovich reaction is supposed to be reversed to reduce NO to N_2. To benefit from this reduction, it is important to keep nearly stoichiometric conditions in the primary combustion zone and ingress of a false air must be prevented. An important reduction factor for the NOx emissions is the flue gas recirculation that causes the NOx to pass through the fuel-rich regions and to undergo reduction reactions to N_2.

Formation of sulphur is fundamentally similar to the air-fired conditions. Similar to the conventional air-fired combustion, the level of SO_2 emissions in case of oxyfuel combustion is strongly dependent on the coal's sulphur content. A key difference in comparison to air-fired combustion is however in significant increase of sulphur in the gas phase due to high ratio of flue gas recirculation. There is also a significant effect of enhancement of the sulphur retention, which is relatively about 20-30 % higher in the oxyfuel mode. An important aspect in oxyfuel combustion is a change of oxygen concentration that can cause increase of conversion of SO_2 to SO_3. The increase can be up to about 5 % while in the air-firing conditions this conversion is normally around 1 %. A higher SO_3 content is a potential risk for higher corrosion issues [28], [29], [31], [32], [33].

6. CONCLUSION

The technology of Carbon Capture and Storage is recently under strong development as a response to political decisions of reduction of humankind-produced CO_2, despite the fact that there are many opposing opinions concerning this issue. At the moment, there are already full scale demonstration units in operation worldwide. The research and development is also now focused on transport and storage parts of CCS technologies, since this has not yet been reliably resolved. The CO_2 is recently mostly considered for EOR, but this cannot resolve the storage of potential amounts that are considered to be captured. The research in seawater or in underground onshore storage is currently ongoing.

The capture part of the CCS technology is recently the most advanced. Some of the technologies are already in full demonstration scale, e.g. post-combustion ammonia scrubbing or oxyfuel combustion, others are under different stages of development. However, all CCS technologies struggle with additional energy demands. The technologies using pure oxygen (pre-combustion, oxyfuel combustion, Ca-looping) require an air separation unit, which brings a penalty in electricity consumption for driving compressors in the cooling loops. Other CCS technologies have various different energy penalties, mostly unrecoverable, e.g. pressure losses in membrane separation or solvent regeneration in ammonia scrubbing. A general penalty for any CCS application is CO_2 compression or liquefaction before transport.

For example, when considering a current state-of-the-art of the fossil fuel fired power plant, application of a CCS technologies in such a plant always means a decrease of net power production efficiency, which is an unavoidable trade-off with capturing the produced CO_2. This efficiency decrease can typically range from approx. 5 to 15 percent points. The future of CCS application in power production and industry will therefore probably not be on fully commercial basis, but will have to be supported by national policies and subsidies connected to adopted CO_2 reduction targets.

7. REFERENCES

1. **Cuellar-Franca, R.M. and Azapagic, A.** Carbon capture, storage and utilisation technologies: A critical analysis. *Journal of CO2 utilization.* 2015, Vol. 9, pp. 82-102.

2. **World Bank.** CO2 Emissions (Total) in the World. 2016.

3. 2015 United Nations Climate Change Conference. [Online] United Nations Framework on Climate Change, 2015. [Cited: 13 7 2016.] http://unfccc.int/meetings/paris_nov_2015/meeting/8926.php.

4. **United Nations Framework on Climate Change.** Paris Agreement, Decision 1/CP.21, Article 17. [Online] [Cited: 13 7 2016.] http://unfccc.int/resource/docs/2015/cop21/eng/10a01.pdf.

5. **Wennersten, R., Sun, Q. and Li, H.** The future potential for Carbon Capture and Storage in climate change mitigation e an overview from perspectives of technology, economy and risk. *Journal of Cleaner Production.* 2015, Vol. 103, pp. 724-736.

6. **Hrdlicka, J., et al.** Oxyfuel combustion in a bubbling fluidized bed combustor. *Energy Procedia.* 2016, Vol. 86, pp. 116-123.

7. **Tan, Y., et al.** Property impacts on Carbon Capture and Storage (CCS) processes: A review. *Energy Conversion and Management.* 2016, Vol. 118, pp. 204-222.

8. **Melzer, L.S.** *Carbon Dioxide Enhanced Oil Recovery (CO2 EOR)factors Involved in Adding Carbon Capture, Utilization and Storage (CCUS) to Enhanced Oil Recovery.* Midland Melzer Consulting, 2012.

9. **Fukai, I., Mishra, S. and Moody, M.A.** Economic analysis of CO2-enhanced oil recovery in Ohio: Implications for carbon capture, utilization, and storage in the Appalachian Basin region. *International Journal of Greenhouse Gas Control.* 2016, Vol. 52, pp. 357-377.

10. **Surampalli, R.Y., et al.** *Carbon Capture and Storage Physical, Chemical, and Biological Methods* . Reston : American Society of Civil Engineers, 2015. ISBN: 978-0-7844-7891-2.

11. **Pilar, L. and Hrdlicka, J.** Research and development of CO2 capture and storage technologies in fossil fuel power plants. *Acta Polytechnica.* 2012, Vol. 52, pp. 93-96.

12. **Nagy, T. and Miszey, P.** Model verification and analysis of the CO_2-MEA absorber-desorber system. *International Journal of Greenhouse Gas Control.* 2015, Vol. 39, pp. 236-244.

13. **Dean, C.C., et al.** The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research and Design.* 2011, Vol. 89, pp. 836-855.

14. **Hawthorne, C., et al.** CO_2 Capture with CaO in a 200 kWth Dual Fluidized Bed Pilot Plant. *Energy Procedia.* 2011, Vol. 4, pp. 441-448.

15. **Baker, E.H.** The calcium oxide-carbon dioxide system in the pressure range 1-300 atmospheres. *Journal of the Chemical Society.* 1962, pp. 464-470.

16. **Dieter, H., et al.** Development of the calcium looping CO_2 capture technology from lab to pilot scale at IFK, University of Stuttgart. *Fuel.* 2014, Vol. 127, pp. 23-37.

17. **Hughes, R.W., et al.** Design, process simulation and construction of an atmospheric dual fluidized bed combustion system for in situ CO_2 capture using high-temperature sorbents. *Fuel Processing Technology.* 2005, Vol. 86, pp. 1523-1531.

18. **Sánchez-Biezma, A., et al.** Postcombustion CO_2 capture with CaO. Status of the technology and next steps towards large scale demonstration. *Energy Procedia.* 2011, Vol. 4, pp. 852-859.

19. **Dieter, H., et al.** Efficiency and flexibility potential of Calcium Looping CO_2 Capture. *Energy Procedia.* 2014, Vol. 63, pp. 2129-2137.

20. **Sahraei, M.H., et al.** A survey on current advanced IGCC power plant technologies, sensors and control systems. *Fuel.* 2014, Vol. 173, pp. 245-259.

21. **Singh, B., Stroemman, A.H. and Hertwich, E.G.** Comparative life cycle environmental assessment of CCS technologies. *International Journal of Greenhouse Gas Control.* 2011, Vol. 5, pp. 911-921.

22. **Koutský, B.** *Základy zpracování a využití pevných a plynných paliv.* Praha : VŠCHT v Praze, 2005.

23. **Callaghan, C.A.** *Kinetics and Catalysis of the Water-Gas-Shift Reaction: A Microkinetic and Graph Theoretic Approach.* Worcester : Worcester Polytechnic Institute, 2006.

24. **Hochgesand, G.** Rectisol and Purisol. *Industrial and Engineering Chemistry.* 1970, Vol. 62.

25. **EU-FP7 Low Emission Gas Turbine Technology for Hydrogen-rich Syngas.** H2-IGCC, SubProject 4, WP1-System Analysis. *IGCC State-of-the-art report.* 2010.

26. **Al-attab, K.A. and Zainal, Z.A.** Externally fired gas turbine technology: A review. *Applied Energy.* 2015, Vol. 138, pp. 474-487.

27. **Mills, S.** *Coal-fired CCS demonstration plants, 2012.* London : IEA Clean Coal Centre, 2012.

28. **Toftegaard, M.B., et al.** Oxy-fuel combustion of solid fuels. *Progress in Energy and Combustion Science.* 2010, Vol. 36, pp. 581-625.

29. **Scheffknecht, G., et al.** Oxy-fuel coal combustion—A review of the current state-of-the-art. *International Journal of Greenhouse Gas Control.* 2011, Vol. 5S, pp. S16-S35.

30. **Wall, T.F.** Combustion processes for carbon capture. *Proceedings of the Combustion Institute.* 2007, Vol. 31, pp. 31-47.

31. **Maier, J., et al.** Impact of recycled gas species (SO2, NOx) on emission behaviour and fly ash quality during oxy-coal combustion. *Proceedings of the 33rd international technical conference on coal utilization and fuel systems* . Clearwater, Florida : s.n., 2008.

32. **Croiset, E., Thambimuthu, K. and Palmer, A.** Coal Combustion in O2/CO2 mixtures compared with air. *The Canadian Journal of Chemical Engineering.* 2000, Vol. 78, pp. 402-407.

33. **Skopec, P., et al.** NOx emissions from bubbling fluidized bed combustion of lignite coal. *Acta Polytechnica.* 2014, Vol. 55, pp. 275-281.

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Work experiences

2007-	Research assistant and assistant professor, Department of Energy Engineering, CTU in Prague
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Fellowships, scholarships

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Professional skills

- combustion processes
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- emission control
- CCS (oxyfuel combustion, chemical looping)
- energy conversion of biomass, alternative fuels and energy sources
- industrial energy sources

Projects

2015-	Study of pilot CCS technologies for coal power sources in CZ. Norway grants project, partner: NTNU Trondheim, Norway
2015-	Czech-Icelandic Clean Energy Cooperation. EEA grants project, partner: Reykjavík university
2015-	Research of high temperature CO2 sorption from flue gas using carbonate loop. Norway grants project, coordinator: UCT Prague, CTU as partner
2013-2016	Research of oxyfuel combustion in fluidized bed for CCS technologies; national project (TAČR Alfa 3)
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Most important publications

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Hrdlicka, J., Skopec, P., Dlouhy, T.: Emission factors of gaseous pollutants from small scale combustion of biofuels. Fuel 165 (2016), pp. 68-74

Hrdlicka, J.; Polak, M.: The Validation of a Calculation Model for Biomass Combustion Using CO2 Measurement. International Journal Of Green Energy 12 (2015) pp: 603-609

Skopec, P., Hrdlička, J., Opatřil, J., Štefanica, J.: NOx emissions from bubbling fluidized bed combustion of lignite coal. Acta Polytechnica 55 (2015), pp. 275-281

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