CARBON DIOXIDE CAPTURE TECHNOLOGIES

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ABSTRACT

Carbon dioxide sequestration needs effective CO_2 capture technologies. This paper describes several methods of carbon dioxide capture from combustion processes. One technology known as post-combustion CO_2 capture applies several separation methods, which are mentioned in chapter 2. Next chapter describes pre-combustion method which uses different concept based on fuel gasification. This paper deals with oxyfuel combustion, which uses fuel combustion in nearly pure oxygen. Text is about advantages and disadvantages of mentioned methods. Finally, possibilities of carbon storage in Czech Republic are featured.

1. INTRODUCTION

High CO_2 capture efficiency at low costs is essential requirement for carbon capture and storage technologies. For operational industries the application of redevelopment is limited. Thus less reconstruction actions are needed, more compatible it is. There are three basic technologies being developed recently:

- Post-combustion capture,
- Pre-combustion capture,
- Oxyfuel combustion capture.

2. POST-COMBUSTION CARBON DIOXIDE CAPTURE

Post-combustion CO_2 capture is the most suitable method for almost all technologies used recently. It is technology which doesn't need large modifications in combustion system.

	CO_2 concentration in the flue gas [vol. %], approx.
Pulverized coal fired	14
Coal fired IGCC *(Integrated gasification combined cycle)*	9
Natural gas combined cycle	4

Table 1: Concentration of carbon dioxide in flue gases [1]

Post-combustion capture is based on removing CO_2 from flue gases. Unfortunately, concentration of carbon dioxide in flue gases is low (table 1). Membranes, adsorption or chemical solvents absorption is used for separation process [1].

2.1. MEMBRANES

Separation membranes are based on different permeation of gases through membrane. There are different gas separation membranes, e.g. inorganic membranes, palladium membranes, polymeric membranes and zeolites. As efficiency of membrane separation is low, multiple stages are needed. Solvent scrubbing combined with membranes has been found useful, and could bring best features. Much development is required for large scale applications [2].

2.2. ADSORPTION

In this process CO_2 is accumulated on surface of adsorbents (e.g. zeolites or activated carbon). One method is called pressure swing adsorption (PSA), where flue gas flows through a packed bed (tube filled with material) of adsorbent at higher pressure. For desorption there is used temperature swing adsorption (TSA), which regenerates the adsorbent. While rising the temperature, the carbon dioxide is separated from the adsorbent. PSA and TSA are commercially practiced, but not for large scale applications, as capacity and CO_2 selectivity of available adsorbents is low [2], [3].

2.3. AMINE SCRUBBING

There are long term experiences with amine scrubbing in chemical industry, though the technology is developed. For practical applications is used mono-ethanolamine (MEA). It provides recovery of 98% of CO_2 from flue gases with higher purity then 99%. Oxidizing environment can cause solvent degradation and equipment corrosion. Use of inhibitors can reduce these negative effects. Amine solvents are also degraded by nitrogen dioxide and sulphuric oxides. Amine solvents react with NO_2 or SO_x into stable salts which are irreversible. Therefore recommended concentration of SO_x is between 1 and 10 ppm. Another disadvantage is that amount of energy required for regeneration is relatively high. Possibility of improvement can be brought by sterically-hindered amines which have good absorption and desorption characteristics. The hindered amine process needs less energy, because solvents consume less heat for regeneration then MEA solvents [2],[4].

2.4. AMMONIA ABSORPTION

Ammonia scrubbing is relatively new technology, which offers many advantages in comparison with amine scrubbing. Ammonia absorption uses NH_3 which is cost acceptable. Absorption can proceeds at room temperature and regeneration temperature can be as low as 60 °C. The CO_2 loading capacity of ammonia solution can by three times higher than in mono-ethanolamine scrubbing. In addition NH_3 is tolerant toward SO_2 and NO_x. There are several pilot scale tests being constructed and planed [1].

2.5. CALCIUM CYCLE

Flue gases are passed through lime extraction and CO_2 chemically reacts to lime (described by equation (1). Result product, limestone is later heated for calcium oxide recovery. Calcium oxide also reacts to sulphuric oxides. This technology is quite costly, because there is needed relatively high temperature for CO_2 drive off.

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (1)$$

Post combustion capture doesn't affect any equipment of power plant except of exhaust system. Modifications may be needed just in fly-ash separation, and also NO_x and SO_x separation. These modifications must be made to allow the carbon dioxide capture technology to be included into capture system. Several different capture technologies have been listed above. There are specific requirements for each of those.

3. PRE-COMBUSTION CARBON DIOXIDE CAPTURE

Pre-combustion carbon capture is a technology, which is based on carbon dioxide capture while the fuel is gasified. Gasification provides gas mixture, which is called syngas and consists mostly of hydrogen and carbon monoxide. After that, syngas goes to shift reactor where it reacts with steam to create mixture of CO_2 and H_2. Carbon dioxide is now separated and hydrogen is used as a fuel. This technology is usually used for coal gasification (IGCC), however it could be applied to liquid and gaseous fuel. Typical reaction for IGCC is shown in following equations. Equation (2) is for carbon gasification and equation (3) makes syngas shift reaction [1], [4].

$$\begin{gathered} 2C + O_2 + H_2O \rightarrow H_2 + CO + CO_2 \\ C + H_2O \rightarrow H_2 + CO \end{gathered} \qquad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

Low ranked coal gasification still hasn't been found as technologically reliable. Biomass and natural gas can be also used for pre-combustion capture technology. As gasification of biomass is similar to IGCC, for gasification of natural gas there are used several methods (e.i. Steam reforming, Partial oxidation, Autothermal reforming). Steam reforming method converts CH_4 and water vapor into CO_2 and H_2 (4), this process is endothermic and needs temperatures from 700 °C to 850 °C. Partial oxidation uses exothermic reaction of oxygen and methane (eq5). Autothermal reforming is combination of both methods [5].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (4)$$

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \qquad (5)$$

After shift reaction, gas mixture is cooled and Selexol acid gas removal unit separates CO_2 and sulfur compound steams [4].

The profit of pre-combustion capture is based on transformation of carbon fuel to carbonless fuel. Gassification process uses chemical energy of carbon and transforms it to chemical energy of hydrogen. Hydrogen combustion doesn't emit any sulfur dioxide. Hydrogen seems to be useful fuel, as it could be used for gas boilers, gas turbines, fuel cells and other technologies. Combustion of pure hydrogen provides high temperatures, which could damage boiler or combustion chamber. Solution of this negative feature is in lowering hydrogen purity or using high temperature resistant materials for combustion chamber [1].

Figure 1: A modern coal fired power station [2]

4. OXYFUEL COMBUSTION CO_2 CAPTURE

Oxy-fuel is actually modified post combustion method. Fuel is combusted in almost pure oxygen instead of air, which results in high concentration of CO_2 in flue gases. Main reason for oxyfuel combustion is to make CO_2 separation easier. For this method the cryogenic separation seems to be suitable. Production of oxygen is necessary and also quite costly. For oxygen separation there is used cryogenic air separation unit (ASU) or more efficient oxygen transport membranes. [1][4]

Another advantage is the absence of nitrogen, which eliminates NO_x emissions. Absence of nitrogen provides low volume of gases and so reduced size of entire process. Oxy-fuel combustion results in high temperatures, which are inconvenient for boilers materials. To achieve required temperature characteristics, input oxygen can be mixed with output flue gas. There is also possibility to moderate temperature by hydroxy-fuel combustion [1], [4].

Oxyfuel combustion can be also retrofit on existing power plants, but all advantages of this method can be reached only by new facilities.

4.1. CRYOGENICS

Cryogenics are based on different condensation temperature of gases. This is widely used on high CO_2 concentrations. Since there is required high energy for refrigeration, it is not used on gases with low CO_2 concentrations. Water has to be removed before the gas is cooled, to prevent of blockages. The main advantage of cryogenic separation is that it provides CO_2 as a liquid, which is needed for transport and storage. [2]

5. CONCLUSION

Efficiency and convenience of mentioned technologies are usually characterized by energy penalty. Energy penalty represents additional energy which is needed for capture process regarding to energy produced excluding capture process. Energy penalty for post combustion are generally considered higher than pre-combustion and oxyfuel combustion capture systems. Even though, numbers vary in each solution.

Amine scrubbing and ammonia scrubbing seems to by most profitable for post-combustion capture. This technology can be applied on existing power plants. Gasification unit must be constructed for pre-combustion capture method. Gasification allows solid fuels, such as coal and biomass, to be used on most up to date gas turbines, which are highly reliable in electrical generation. Oxyfuel combustion significantly reduces carbon dioxide capture penalty. However oxygen production involves 8 % to 30 % energy penalty. Oxyfuel combustion is rather new technology, which still needs to be proven.

The Czech Republic produces over 70 % of electrical energy from fossil fuels. Czech Republic has signed Kjoto protocol. In addition it is a member of the European Union, which supports carbon capture and storage (CCS). For that reason cutback of CO_2 emissions is needed. CCS program possibilities in the Czech Republic seems to be wide. Capacity of storage places is relatively large. Storage may be possible in numerous salt aquifers and Silesia coal mines. Natural gas and crude oil fields in Southern Moravia are mostly depleted and they provide CO_2 storage place. Enhanced gas recovery (EGR) and enhanced oil recovery (EOR) may be applied on fields which haven't been depleted yet. EGR and EOR can help to reduce geological sequestration energy penalty and make it more useful.

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