

CARBON DIOXIDE ABSORPTION SEPARATION METHODS

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Abstract: The paper deals with carbon dioxide separation methods. Although there are many carbon dioxide separation methods, this paper focuses on post-combustion absorption methods. Several existing absorption methods provide acceptable results. The article evaluates absorption methods listing advantages and drawbacks of available solvents.

Keywords: Carbon dioxide absorption methods, Post-combustion capture, Carbon dioxide capture

1. INTRODUCTION

According to Kyoto protocol, many countries are involved in reduction of carbon dioxide emissions. Carbon dioxide production became financially penalized and CO₂ emission savings is economically supported by national governments. Carbon capture and storage (CCS) can help to reduce emitted carbon dioxide. Carbon dioxide capture and storage deal with an idea of carbon dioxide separation, transport and geological storage.

2. CARBON CAPTURE TECHNOLOGY

There are generally recognized three technology options. One essential and two another, which were developed to reduce energy needed for carbon dioxide separation and make whole process more efficient.

2.1. POST-COMBUSTION CAPTURE

Post combustion capture is based on separation from flue gas, which has low carbon dioxide concentrations. Concentration of CO₂ for coal power plants is about 12 % to 15 % [3], for coal fired power plants with integrated gasification combined cycle about 9 % [1] and for natural gas fired power station as low as 4 % to 8 % [3]. These low concentrations are inconvenient for separation and directly handicap some separation methods (e.g. distillation, cryogenics).

Contrary this technology doesn't require large reconstruction actions and is more compatible to existing power stations. Modifications are usually needed in fly-ash, NO_x and SO_x separation. Technology itself also require construction number of heat exchangers and other technological devices (e.g. absorbers, strippers, membrane separation units, etc.).

For separation process can be used membranes, chemical absorption, adsorption, etc. [1]

2.2. PRE-COMBUSTION CAPTURE

Pre-combustion capture is based on carbon dioxide separation before combustion. Essential technological part is gasification unit which uses solid, liquid or even gaseous fuel transforming energy of carbon to energy of hydrogen.

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 CO₂ and H₂. Carbon dioxide is now separated and hydrogen is used as a fuel. Significant advantage is that hydrogen can be utilized in gas turbines, which is much efficient than classic steam turbine cycle.

Reliability of low ranked coal gasification still hasn't been found as technologically feasible. Another fuel for pre-combustion capture can be biomass and natural gas. As gasification of biomass is similar to IGCC, for gasification of natural gas there are used several methods. Hydrogen seems to be reliable 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.

2.3. OXYFUEL COMBUSTION CAPTURE

Oxy-fuel is actually modified post combustion method, which deals with low concentration of carbon dioxide in flue gas. Fuel is combusted in almost pure oxygen instead of air, which results in high concentration of CO₂ in flue gases. Main reason for oxyfuel combustion is to make CO₂ separation easier. For this method is suitable cryogenic separation. Disadvantage is necessity of oxygen production. For oxygen separation there is used cryogenic air separation unit (ASU) or more efficient oxygen transport membranes. [1][4]

Combustion in carbon dioxide provides no NO_x emissions, which is also significant advantage. Absence of nitrogen provides low volume of gases and so reduced size of entire process.

3. CHEMICAL ABSORPTION

3.1. AMINE SCRUBBING

There is a long term experience with amine scrubbing in chemical industry, though the technology is developed. For practical applications is commonly used mono-ethanolamine (MEA). It is aqueous solution with formula NH₂-CH₂-CH₂-OH. It provides recovery of 98 % of CO₂ from flue gases with higher purity than 99 %. Main disadvantage of MEA is relatively high amount of energy required for regeneration. Possibility of improvement can be brought by sterically-hindered amines which have good absorption and desorption characteristics. The sterically-hindered amines have larger molecules than MEA and improves CO₂ load during absorption. The hindered amine process needs less energy, because solvents consume less heat for regeneration than MEA solvents. Only drawback is in lower reaction speeds than for MEA.

Amine based absorption has also problems with oxidizing environment, which 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 NO₂ or SO_x into stable salts which are irreversible. Therefore recommended concentration of SO_x is between 1 and 10 ppm. [2][4][5]

3.2. AMMONIA ABSORPTION

Ammonia scrubbing is relatively new technology, which offers many advantages in comparison with amine scrubbing. Ammonia absorption uses NH₃ which has acceptable cost. Absorption can proceed at room temperature and regeneration temperature can be as low as 60 °C. The CO₂ loading capacity of ammonia solution can be three times higher than in mono-ethanolamine scrubbing. Ammonia absorption is also used for flue gas SO₂ and NO₂ removal, so these reactions doesn't cause solvent degradation. There are several pilot scale tests being constructed and planned. [1][5]

3.3. CALCIUM ABSORPTION

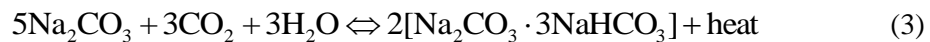
Flue gases are passed through lime extraction and CO₂ chemically reacts to lime. Result product, limestone is later heated to temperatures about 850 °C for calcium oxide recovery. Both reactions are described by following equation (1).



Calcium oxide also reacts to sulphuric oxides. This technology is quite costly, because for CO₂ drive off there is needed relatively high temperature.

3.4. SODIUM HYDROXIDE ABSORPTION

Sodium hydroxide reacts with carbon dioxide and steam, which makes sodium bicarbonate (eq. 2) or Wegscheider's salt (eq. 3). For CO₂ releasing are reverse reactions. [6]



Solvent name	Solvent type	Conditions
MEA	2, 5n monoethanolamine	40°C, intermediate pressures
Amine guard	5n monoethanolamone	40°C, intermediate pressures
Ecoamine	6n diglycolamine	80 to 120°C, 6,3 MPa
ADIP	2-4n disopropanolamine	35-40°C, >0,1 MPa
MDEA	2n methyldiethanolamine	
Flexsorb, KS-1, KS-2, KS-3	Hiderend amine	
Benfield and versions	Potassium carbonate and catalysts	70 to 120 °C, 2,2 to 7 MPa

Table 1: Absorption solvents review [3]

4. SUMMARY

Carbon dioxide absorption methods are mostly used for post-combustion capture technologies, where CO₂ is needs to be separated from flue gas. There are three key requirements for efficient solvent – fast reaction rate, low regeneration energy and high loading capacity [5]. However these requirements are important, chosen solvent must also has acceptable price. Another quality is absorption selectivity, which prevents solvent from degradation.

All mentioned absorber qualities influences technology size and structure, absorption energy and solvent consumption, which directly affects absorption economy.

Even calcium scrubbing has is being used for long time and the experience is proven, amine scrubbing and ammonia scrubbing seems to be most reliable. It provides lower heat for solvent regeneration and thus also lower energy penalty for whole technology.

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