REVIEW OF TECHOLOGICAL METHODS FOR FLUE GASES CARBON DIOXIDE REMOVAL IN POWER PLANTS

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Abstract: Intensive scientific research in past 20 years provide clear evidence that climate changes and increase of green house gases concentration in atmosphere are caused by human activities. Energy sector plays main role in these processes with overall emission of carbon dioxide between 60 and 70 % mainly due to combustion of solid, liquid and gas fossil fuels. Similar case is characteristic for energy sector of Republic of Serbia, which emitted around 60% of overall carbon dioxide during 1990s. Republic of Serbia has been a member of United Nations Convention on Climate Change and Kyoto Protocol since 2008 with no green house gasses emission reduction commitments as a developing country. Nevertheless, increase in power supply demand from year to year and expected rise of industrial activities indicate rise of fossil fuels consumption and because of that, raise of green house gases emissions. Previous mentioned facts implicate that energy sector is crucial sector in which establishment and implementation of measures and activities will take place with green house gases emission reduction as main task. Main goal of this paper is to provide review of currently available methods for carbon dioxide removal from which some are commercially available, while others are under development. Special attention will be given through detailed description of methods based on hemi sorption with aqueous solutions of alkanol amines, which found wide commercial use in industry. Choice of appropriate absorbent, process equipment, methods, working parameters, combustion process etc. are some of key points that will be presented within this work with main goal for providing clear picture about possibilities and limitations of carbon dioxide removal methods.

Key words: removal, carbon dioxide, green house gases, hemi sorption, flue gases

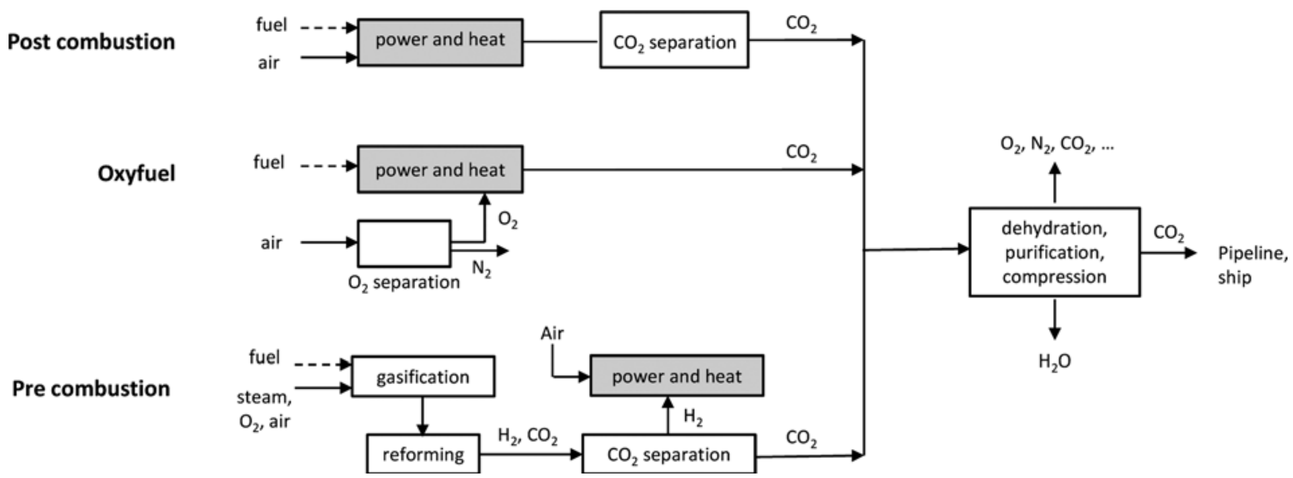
1. INTRODUCTION

It is becoming clear now that in order to accomplish reduction of green houses gases (GHG) emission, use of wide spectrum of corresponding measures, which must comprise all energy sectors as well as industry, commerce and transport is needed. Over 40% of the worldwide CO_2-emissions are caused by electricity generation in fossil fuel power plants. Climate shift changes are affecting weather systems causing negative effects on human health, agriculture, and global economy, which resulted in serious environmental concerns deriving from the need to reduce GHG emissions from industrial resources. Since carbon dioxide (CO_2) accounts for the largest portion of the world's annual emissions of GHG's, its emissions from industrial waste gases have become major target for reduction, especially flue gasses from coal power stations as main emitters of carbon dioxide. Main goal of this paper is to provide clear picture regarding status of research and development of CO_2-capture, transport and utilization as well as perspectives of corresponding technologies.

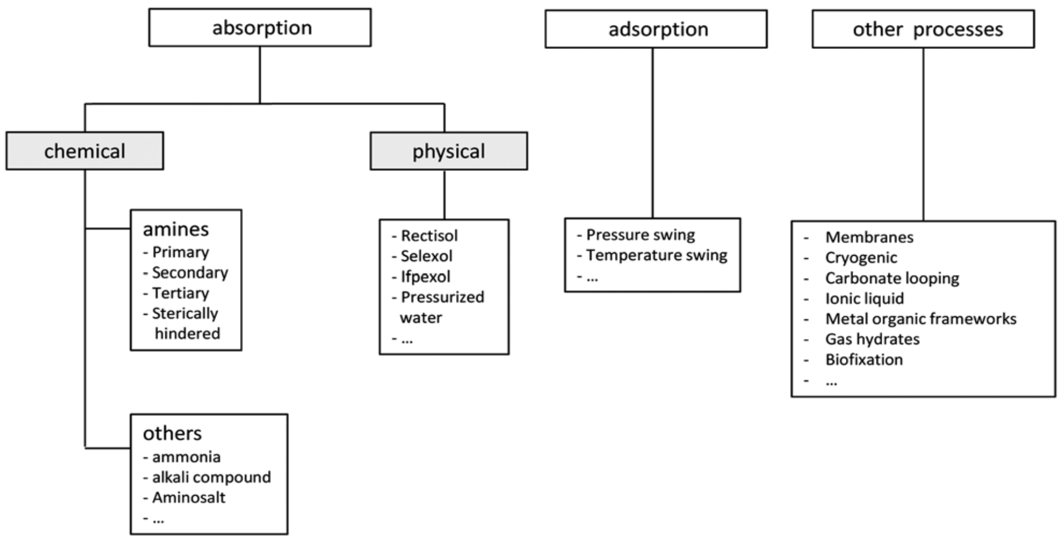
2. CARBON CAPTURE TECHNOLOGIES

Carbon capture technologies are pretty mature taking into account pioneer works in early 1960's. Although those early works set primary goals for carbon capture for use in other industries, rather than mitigation of green house gases, its contribution in forming foundation for future development of carbon capture is undisputable. Industrial implementation in those days was set mainly on purification of gases emitted from petrochemical and oil industries or, generation of derivates that can be synthesized and effectively used for other purposes. In early 1990's first pilot plants and large laboratory installations are emerging with task for removal of carbon dioxide from flue gases. As worldwide attention increases with clear connection between negative effects on climate change and increase of concentration of CO_2 in atmosphere, international community set main rules and emission quotas for different gases that contribute to green house effect. This key point opened up opportunities for commercialization of emission quotas trading system followed by increase investments in development of carbon dioxide removal technologies. In past ten years we are witnessing implementation of full scale industrial units in USA and Germany as world leaders in this field, followed by other countries.

Nowadays, there are numerous technologies for treatment of flue gases. Although, they are different at first look, a general division can be set. Currently, there are three main routes for development of carbon dioxide removal process that are presented on Scheme 1. First include process for CO_2 capture from the flue gas stream after combustion (*Post-combustion*). Other process include CO_2 capture from the reformed synthesis gas of an upstream gasification unit (*Pre-combustion*). The youngest, but not least promising, is newly developed use of nearly pure oxygen for combustion instead of air which offers increase of CO_2 concentration within flue gases stream (*Oxyfuel*). All routes use main principles which are in operating use or under development (Scheme 2.)



Scheme 1. Main routes for development of carbon dioxide capture technologies



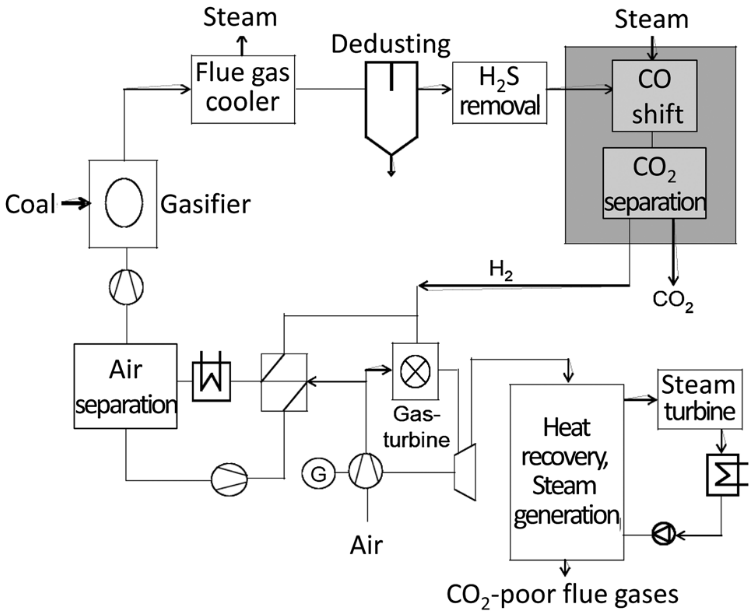
Scheme 2. Main principles for carbon dioxide capture in use or under development

Listed processes require additional energy input for gas separation, regeneration of absorbents, capture, conditioning, storage and transportation of the carbon dioxide. Therefore, when speaking about carbon dioxide removal, it becomes clear that negative side effect is decrease of energy efficiency of power plants of 10 to 14 % points. Concerning post-combustion process, this efficiency loses are assessed from 10 to 12 % points by some authors [1], while oxyfuel process take 10 % points efficiency loss [2]. Besides that, there is significant space for reduction in energy requirements for carbon dioxide removal. Majority of energy requirements are needed for absorbent regeneration (around 60 % of overall energy requirement) and additional 20 to 30 % for compression, storage and transportation of carbon dioxide. New research data are showing promising results for use of so called stericaly hindered amines and blends of amines which are characterized by increase loading capacity for CO_2 with simultaneous decrease in energy requirements for its regeneration [3,4]. Additional savings can be made by use of waste heat (heat loses from cooling of flue gases before entry point into carbon dioxide removal plant, but also heat gains from exothermic reactions between absorbents and flue gases). Efficiency loses of 8 % points are feasible and can be easily achieved in near future.

2.1. Pre-combustion processes

Two dominant pre-combustion technologies under development are production of synthesis gas and pressure swing adsorption (PSA). First process includes partial oxidation of fuel in gasification unit and generation of CO rich stream. After gasification, through catalytic CO-shift reaction, CO reacts with steam as oxidant where CO_2 and H_2 rich stream is generated. Since such generated fuel gas is under high pressure and consists of rich content of H_2, carbon dioxide removal methods based on physical adsorption becomes advantageous.

This process needs additional requirements for cleaning of synthesis gas from ash particles, alkali and sulfur components and other impurities. In order to yield gasification step, reduce volume flow of gases and thus costs of required equipments, air separator unit is needed before gasification unit. The CO_2 capture takes place after conversion of carbon monoxide into CO_2 and H_2 and generation of fuel gas. Such decarbonized fuel gas is then directed to combined gas and steam turbine cycle for generation of electricity. Overall process of IGCC plant with CO_2 capture is given in Scheme 3.



Scheme 3. IGCC plant with carbon dioxide capture

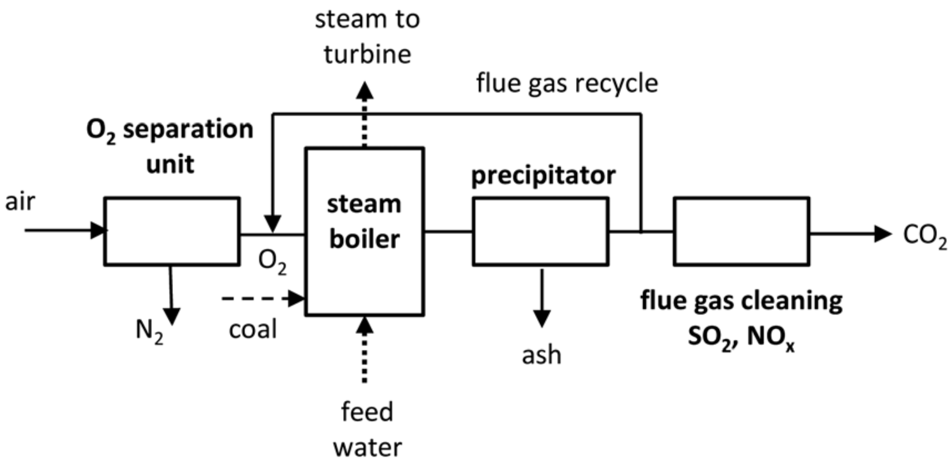
Pressure swing adsorption comprise use of physical adsorbents such as carbon, zeolites or alumina [5], which selectively absorb carbon dioxide passing flue gases through layers of beds. Process consists of two step cycle. In first, adsorbent selectively adsorbs carbon dioxide from feed gas, under high pressure conditions, while in second step, carbon dioxide is usually removed from adsorbent by reduction of pressure, enabling regeneration of adsorbent and use in next cycle. Beside production of synthesis gas and PSA methods, scrubbing procedure with physical sorbents can be used, offering possibility for simultaneous removal of H_2S and COS. Methanol based solvents can be effectively used for scrubbing of fuel gases and easily regenerated using nitrogen and change of temperature. Positive side of scrubbing process is that CO_2 can be removed together with H_2S and COS. Downside is necessity for high pressure operating conditions which limits implication of mentioned technologies into pulverized coal power plans, operating at lower pressures.

Evaluation of use of IGCC technology is showing some clear advantages and disadvantages regarding carbon dioxide removal. Advantages are: high efficiency potential and poly generation of electricity and hydrogen. When speaking about poly generation, synthesis gas can be effectively used for production of other chemicals and fuels (methanol, hydrogen for fuel cells), leading to greater flexibility, higher plant utilization and reduction of operating cost. High investment, operational and maintenance cost followed by technical shortfalls manifested through long startup periods are some of disadvantages which drove much of current research attention. With currently only 5 operational IGCC power plants in the world [6], new power plants in plan for construction in England and Canada and more energy-efficient supply of oxygen for the precombustion power plants, significan contributions are being made towards improving the respective efficiency and reduction of operation costs.

2.2. Oxyfuel process

Oxyfuel process use stream of pure oxygen for combustion of coal. Flue gases, after cleaning and washing consist of high CO_2 concentration (around 90 % by volume), compared to conventional power plants (7 - 15 % vol). Such pure CO_2 stream can be easily compressed and transported to storage site after being first demoisturized. Supply of pure oxygen stream is achieved by “gas to liquid” cryogenic air separation units (at temperatures around -180 °C). Currently, the largest planed unit for generation of pure oxygen will supply around 800.000 m^3/h [7]. Taking into account for example that 500 MW unit with efficiency of 43 % requires by stoichiometry around 270.000 m^3/h of pure oxygen, great attention must be given for development of new methods that will assure steady and continuous supply of pure oxygen with reasonable operating costs.

Combustion process with stream of pure oxygen is causing altering of temperature within steam generator unit. High altering of temperature field must be limited due to limitations in properties of applied materials in combustion chamber. In order to achieve this, large portion of CO_2 rich stream (around two-thirds of flue gases volume flow) is directed back to combustion chamber. Entire process is presented in scheme 4.

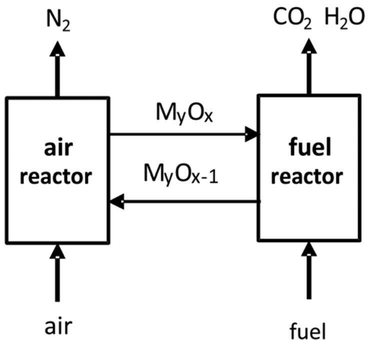


Scheme 4. Process scheme of CO_2 capture with oxyfuel combustion

Scientific challenges that yet have to be solved include improvements of air separation method and units, steam generator and process of denitrification and desulphurization. Air separation unit consumes largest portion of energy (from overall 10 % energy consumption, 7 % is required for process of air separation and additional 3 % for carbon compression and storage). Additionally, required purity of oxygen stream that must be achieved is 99.5 % by volume. Complete purity can not be achieved due to presence of hard separation components (nitrogen and argon from air). Bearing this in mind, it becomes clear that main reductions of energy consumption can be received by optimization and improvements in air separation methods. Current and future development [8], in this field, is set on usage of mixed ion electron conducting membrane technology and chemical looping technology.

Main concept behind membrane separation technique lays in usage of ceramic or other advanced materials that are showing property of selective permeability toward different gas components. Air stream under high temperature (above 700 °C) passes through membrane. Membrane selectivity allows only transport of oxygen, preventing other components to pass by. Present limitations of wider usage of membranes on large scale industrial units are due to problems caused by temperature membrane stability and mechanical strength property.

Chemical looping process includes use of metal oxides for combustion with fuel, instead of pure oxygen. After combustion, these metal oxides are regenerated in another reactor with air, limiting input of air nitrogen as it is presented in Scheme 5. Current laboratory and pilot scale test have main goal to identify most suitable materials as metal oxygen carriers. At this point, these oxygen generation methods are still in early stage of development, so much that can be classified as second generation carbon capture and storage technologies.



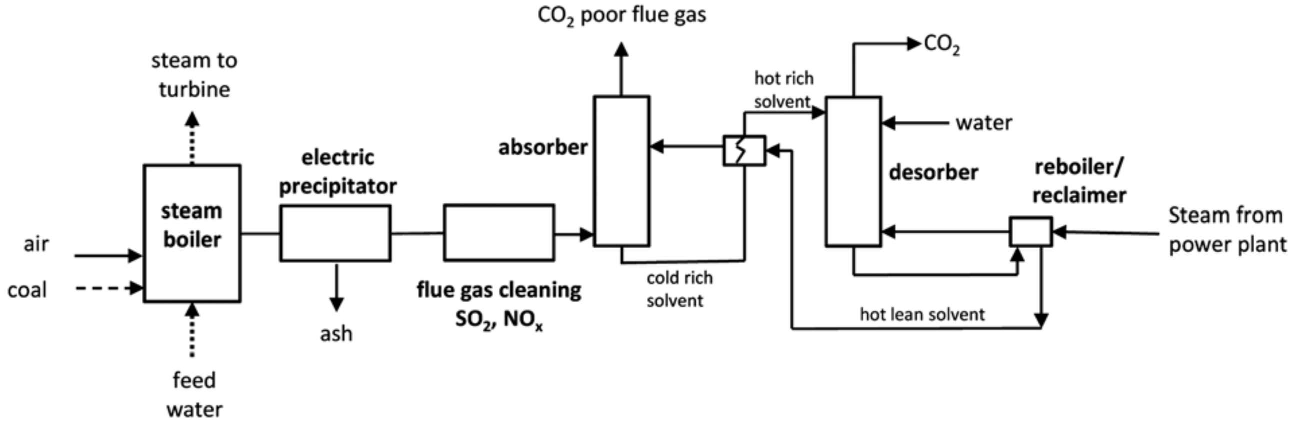
Scheme 5. Oxygen chemical looping

Important projects regarding use of oxyfuel are conducted in Canada (CANMET Project, 0.3 MW_{th} unit), Japan (1.2 MW_{th} unit) and USA (1.5 MW_{th} unit). Australian Callide Project, started at 2006, planed and finished construction of 30 MW_{el} unit that will use oxyfuel with scheduled start by end of 2012. Research is also conducted in Europe with pilot plants in Netherland (2.5 MW_{th}), Great Britain (3 MW_{th}) and future plans for construction of 250 MW_{el} units at Compostilia site (Spain).

Advantages of oxyfuel technology are low environmental impact, well known air cryogenic separation technology with high potential for further energy requirements reduction through implementation of new separation methods. Different heat and flow conditions produce necessity for new design of heat exchanger surfaces, burner's modification, combustion chamber geometries which present clear disadvantages with little or no possibility for retrofitting.

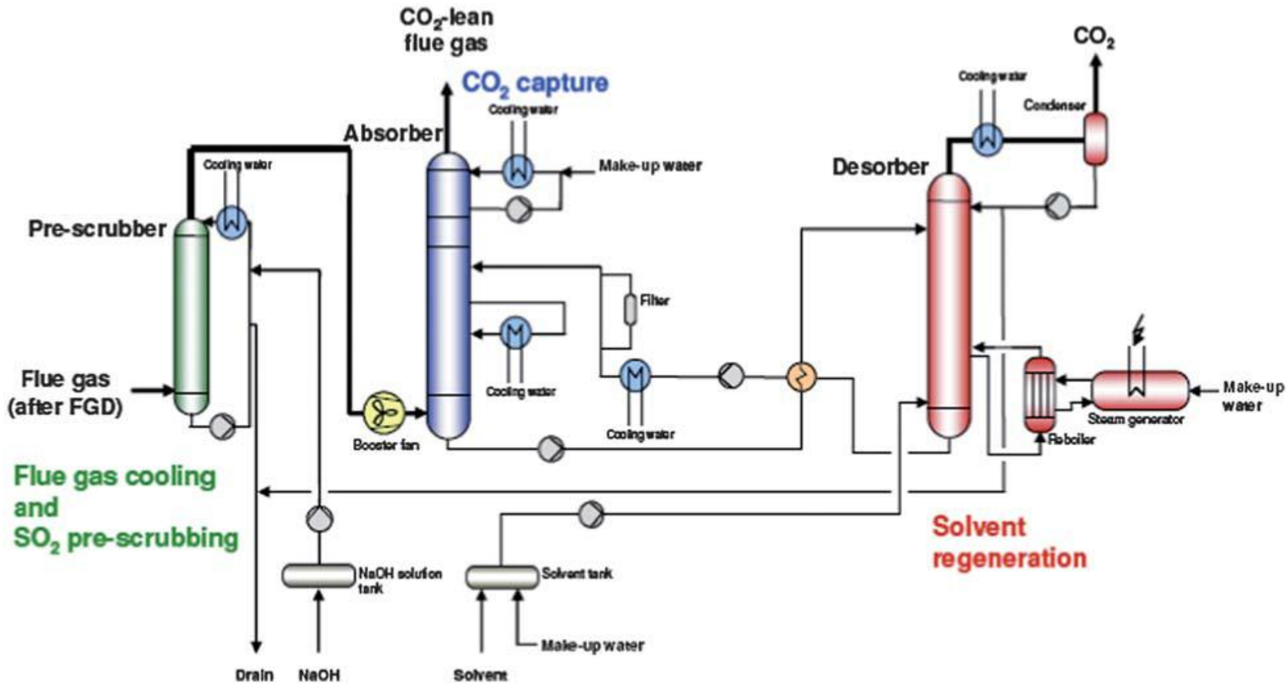
2.3. Post-combustion process

Post-combustion process includes treatment of flue gases after combustion is completed. Most widely used process include so called chemical washing with amine based solvents. This technology offer many advantages that will be described later on. Main process includes two columns (an absorber and stripper column). Flue gases, after precipitator, are cooled to temperature between 40 and 60 °C and entered into bottom of absorption column. Amine based solvent is entered at the top of the column. Gas-liquid contact is achieved either by tray or packed columns. Chemical reaction that occurs, bonds molecules of CO_2 with amine solvent, followed by release of heat. This heat must be effectively prevented because of decrease of CO_2 solubility in amine solvent with increase of temperature. CO_2 rich stream at the bottom of absorber column is carried to stripper column where at elevated temperatures around 120 °C process of solvent regeneration and release of CO_2 take place. Steam used for this process is taken from low pressure power plant steam, thus reducing potential for generation of electricity. Chemical bonds between CO_2 and amine solvent are unbonded, leaving pure stream of CO_2 (99,9%) which is transported from stripper column, dried, compressed and ready for transportation to storage site. Regenerated amine solvent is returned to absorption column after passing through heat exchanger used for preheating of CO_2 rich stream. Amine based chemical washing method is followed by some constraints that require additional researching efforts. Originally, chemical washing was designed and effectively used for scrubbing of flue gases from petrochemical industries. High level of oxygen in flue gases in power plants can cause amine solvent degradation, which can be prevented by use of some chemical inhibitors. Further, high efficiency of precipitator units must be achieved due to problems regarding blocking of packed column, disabling effective work of process equipment. Levels of NO_x and SO_x must be reduced due to solvent degradation, since they can react with them by salt formation. For example, 10 ppm SO_x is target concentration upon which salt formation is avoided [9]. Most challenging problem, yet to be resolved is reduction of energy requirements of stripper column since almost 50 % of overall energy needed for CO_2 capture goes to process of solvent regeneration. Entire process optimization is required so thermodynamic limits can be achieved. Recent development offer solvents with significant increase in loading capacity of CO_2 with decrease in energy requirements for its regeneration [10]. Content of moisture must be also reduced since significant content can cause increased negative effects on process equipment such as corrosion problems. Integrated system which compensates all this effects is presented in scheme 6.



Scheme 6. Integrated system for post combustion CO_2 capture using amine washing

Concerning operational units, currently largest operating unit in connection with power plant is located in USA (Shady Point, Oklahoma). This plant removes around 800 t of CO_2 per day from power plant unit (320 MW_{el}). Removed CO_2 is used for food industries. Another example of effective removal and storage system in same site is located in off shore natural gas platform in Norway (Utsira field). At this site, CO_2 is removed from natural gas and stored back to geological reservoir into the sea bed. In 2010, post combustion unit started operation in Germany (Niederaussem site). Plans are for 99% CO_2 removal with less than 10 % energy efficiency loses [11]. Process scheme for this unit is presented on scheme 7.



Scheme 7. Niederaubem carbon dioxide capture facility

Conclusion that can be made is that post combustion carbon dioxide capture process are offering some clear advantages such as highest purity of CO_2 (99.9%) that can be achieved of all other carbon dioxide capture technologies. No fundamental changes of the original power plant process are required, which enables retrofitting of existing power plants with ease. There is also high potential for further improvements and reduction in energy efficiency loses by utilization of advanced solvents and overall process optimization. Still, high costs and flexibility of such plants that yet have to be tested limit wider use of this method for carbon dioxide removal.

3. CONCLUSION

Carbon dioxide capture technologies although mature in field of petro-chemical industries application, are still in early phase of development in regard to treatment of flue gases in power plants. This paper presented main routes for treatment of carbon capture with clear advantages, but also technical problems that need to be resolved. Due to economical limitations, it is becoming clear that focus in near future will be on increase of efficiency of already built power plants with further delay in construction of new power plant units (IGCC). Concerning this, amine based washing of flue gases will remain dominant technology in treatment of flue gases, with ease possibility for retrofitting. Pre combustion process, although effective, are still too expensive to find wide commercial use. Small number of currently installed units based on IGCC technology, prevents significant contribution of this technology in reduction of carbon dioxide emission. In order for carbon dioxide removal technologies to become "less expensive" simple storage of carbon dioxide must be gradually replaced by use of removed CO_2 in other industries (food industry, chemical production, hydrogen production, production of fertilizers etc.). New developments in field of selective membranes, physical absorption and new energy efficient advanced absorbents, will further lower costs regarding flue gases treatment. Increase in energy demand will undoubtedly contribute to emission of carbon dioxide, so implementation of these measures as standalone concept will not be sufficient. For global reduction in emission of greenhouse gases to happen, battle must be fought on several fronts, simultaneously. First, installment of carbon capture units in new and retrofitting in old power plant units must be conducted, followed by implementation of measures and activities that will have goal to increase energy efficiency of power plants (more energy output from same amount of fuel) and finally, gradual replacement of coal based power plants with renewable resources over time.

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