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Membrane technology application in the framework of zero emission concept

The Zero emissions concept envisages all industrial inputs being used in final products or converted into value-added inputs for other industries or processes. In this way, industries are reorganized into clusters such that each industry's wastes / by-products are fully matched with the input requirements of another industry, and the integrated whole produces no waste of any kind. This technique is based on the well-established economic analysis tool known as the input/output approach. In the framework of the zero emission concept capture of CO_2 plays an important role. CO_2 can be captured and permanently stored, or it can be re-used.

Carbon sequestration is a two-step process where the capture of CO_2 from a gas stream is followed by its permanent storage. The capture step contributes 75% to the overall carbon sequestration process cost. For this reason, the scientific community has paid a great attention to the development of new processes for CO_2 capture. Currently, there is a wide range of technologies to separate CO_2 from gas streams. They are based on different physical and chemical processes including absorption, adsorption, cryogenics and membrane technology. The choice of a suitable technology depends on the characteristics of the flue gas stream and, as a consequence, on the power plant technology. As an alternative to conventional processes for CO_2 separation and capture, membrane technology shows great potentiality for CO_2 capture owing to its easy applicability, efficiency, flexibility, ability to maintain high CO_2 pressure and to perform separations at low energy penalties. CO2-selective membranes allow separation of CO_2 from different gas streams, such as: flue gas (post-combustion system), natural gas (natural gas processing) and hydrogen (pre-combustion systems) or oxygen from nitrogen (in an oxyfuel combustion system).

In the framework of zero emission concept, this paper gives an overview and analysis of the types of membranes used and membrane technology application in CO_2 capture from the point of cost and energy consumption.

Keywords: *zero emission, membrane technology, CO_2 capture*

INTRODUCTION

Zero Emissions represents a shift from the traditional industrial model in which wastes are considered the norm, to integrated systems in which everything has its use. It advocates an industrial transformation whereby businesses emulate the sustainable cycles found in nature and where society minimizes the load it imposes on the natural resource base and learns to do more with what the earth produces.

The Zero Emissions concept envisages all industrial inputs being used in final products or converted into value-added inputs for other industries or processes. In this way, industries are reorganized into clusters such that each industry's wastes/by-products are fully matched with the input requirements of another industry, and the integrated whole produces no waste of any kind. This technique is based on the well-established economic analysis tool known as the input/output approach.

From an environmental perspective, the elimination of waste represents the ultimate solution to pollution problems that threaten ecosystems at global, national and local levels. In addition, full use of raw materials, accompanied by a shift towards renewable sources, means that utilization of the earth's resources can be brought back to sustainable levels.

One of the most important cornerstones of a sustainable society consists in an industry that uses zero waste, zero emissions processes. These processes require complete recycling or re-use of all raw and auxiliary materials that are not contained in the final product as well as of all operating materials and energy flows. The goal of this kind of production is to extract only those materials from the natural environment that form part of the final product or of by-products. In addition, a sustainable economy also requires that the whole product life from the extraction of raw materials to the disposal of the product be taken into account. Finally, it will be essential to develop a multitude of innovative services, which would make it unnecessary to own certain products.

Today's ideals in the industry are modern and innovative processes that aim to reduce emissions and waste by an efficient and careful input of raw materials. The necessity of using zero emission

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processes becomes evident if one considers the true costs caused by waste and emissions generated in manufacturing processes. The waste produced has to be purchased in the form of raw materials and has to be accounted for in overall production costs (personnel, equipment, disposal). This demonstrates the great potential for savings, which could be realized through the prevention and recycling of emissions.

The strong anthropogenic increase in the emission of CO_2 and the related environmental consequences force the developments in the direction of sustainability and Carbon Capture and Storage (CCS). Fossil fuels are with 86% the dominant energy source utilized in the world . More than one third of the CO_2 emissions come from the combustion of fossil fuels in power plants worldwide [2-3] and also the emission of CO_2 associated with the use of CH_4 is more than significant. The combustion of gaseous fuels (e.g. natural gas) accounted for 1521 million metric tons of carbon in 2006, which equals 18.5% of the total emissions from fossil fuels . In addition, also the emission of CO_2 associated with the exploration and production of natural gas is more than significant . The number of easy accessible, low CO_2 containing natural gas sources is only limited, urging the exploration of natural gas sources with high(er) concentrations of CO_2.

Next to its environmental impact, CO_2 reduces the heating value of the CH_4 gas streams in power plants . Due to its acidic character, the presence of CO_2 can lead to corrosion in equipment and pipelines. Pipeline specifications for natural gases give a maximum value of 2-5% for the CO_2 content while the CO_2 content for liquefied natural gas (LNG) even needs to be reduced to 50-100 ppm. This makes the removal of CO_2 from natural gas of crucial importance. After capturing, the removed CO_2 can be reused for different applications in the oil, food and chemical industry. Enhanced oil recovery as well as algae biofixation, where CO_2 is used for microalgaes as carbon source, are important applications. Smaller fields of application, like CO_2 enrichment in greenhouses, where the increase in CO2 concentration from 350 ppm to 500 ppm results in a production increase of 25% for certain bulk crops are of additional interest. Although several possibilities for reuse of CO_2 exist, the total capacity of the different options for the reuse of CO_2 do not match with the current production and, to reduce the emission of CO_2 into the atmosphere, additional storage of CO_2 is currently inevitable. Possibilities to store CO_2 include ocean sequestrations, geological sequestrations and the sequestrations of CO_2 in saline aquifers. In life cycle investigations, Khoo et al. determined the effectiveness of the different CO_2 sequestration ways and the potential environmental impact. The results showed geological sequestration methods to be the safest methods with the least environmental burdens.

In coal-based power production usually there are three ways for CO_2 capture considered:

1. post-combustion CO_2 capture from power plant flue gas,

2. pre-combustion CO_2 capture from gasified coal synthesis gas,and

3. oxy-combustion, which separates oxygen from air prior to combustion and produces a nearly sequestration-ready CO_2 effluent

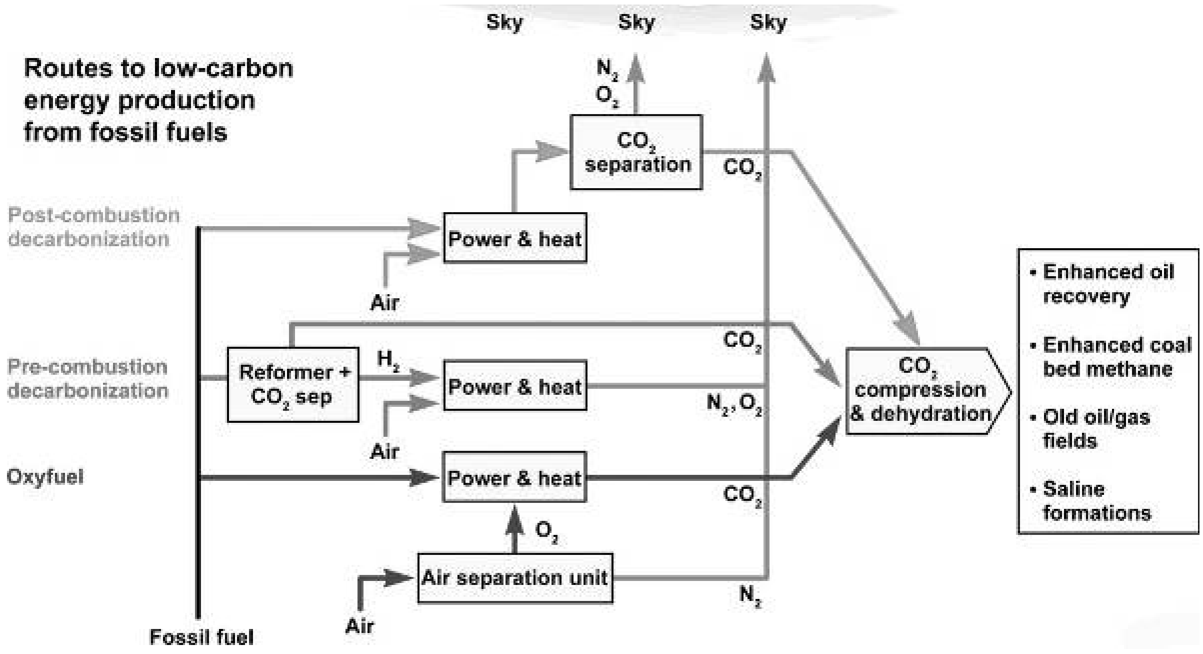

Figure 1 - Approaches to power generation with fossil fuels (coal, oil and natural gas) that include carbon dioxide capture and sequestration (CCS).

SEPARATION METHODS

Traditional methods used to separate CO_2 from gas mixtures are pressure swing adsorption, cryogenic distillation and the most frequently used method amine absorption. Also membrane processes are frequently used for gas separation. Examples are e.g. the separation of oxygen and nitrogen from air to produce nitrogen enriched air, but also for the separation of CO_2 from CH_4 . The main limitation of currently existing membranes is the occurrence of severe plasticization of the membrane in the presence of (high) pressure CO_2. Due to excessive swelling of the polymer membrane upon exposure to CO_2, the performance (selectivity) decreases significantly, thus reducing the purity of the CO_2 and consequently reducing the possibilities for reuse of the gas. Energy requirements on the other hand significantly benefit the use of membrane technology over other technologies: membrane technology uses 70-75 kWh per ton of recovered CO2 compared to significantly higher values for pressure swing adsorption (160-180 kWh), cryogenic distillation (600-800 kWh) or amine absorption (330-340 kWh) , making membrane technology an attractive alternative.

MEMBRANE TECHNOLOGY

Membrane technology is an attractive and competitive alternative to conventional absorption technology. It has a high energy efficiency, is easy to scale-up because of its modular design and it has a high area-to-volume ratio. A limitation can be found in the permeability-selectivity tradeoff relation: more permeable membrane materials are generally less selective and vice versa. Since 1980s gas separation with membranes has emerged into a commercially viable method. Nowadays, several hundreds of plants use membrane technology for the separation of gases.

Most plants use cellulose-acetate membranes, which have CO_2/CH_4 selectivities of only 15 According to Baker , the competiveness of membranes for the separation of CO_2/CH_4 would strongly increase if stable membranes with a selectivity of 40 during operation would become available. Due to plasticization in the presence of CO_2, membranes often lose their performance at elevated pressure. Swelling stresses on the polymer network and an increase in free volume and segmental mobility upon exposure to CO_2 cause a rise in permeability for all components, and especially the permeability of the low permeating component, consequently resulting in a decrease in selectivity . The development of polymeric membranes and membrane processes with improved plasticization resistance that maintain selectivity and permeability, even at higher CO_2 partial feed pressures is crucial and an important field of research.

MEMBRANE MODULES FOR CO_2 SEQUESTRATION

Conventionally, the membrane must be packed in a proper device called a 'membrane module', which should offer:

- low production costs
- high packing density
- low energy consumption
- good control of concentration polarization.

For the application of the membranes in gas separation processes, several configurations are conventionally used for the membrane housing such as hollow and capillary fibre systems and spiral wounds.

It should be stated that the commercial membrane modules available today are specifically designed for a specific membrane process application. However, the choice of a module configuration depends on:

- type of separation problem
- ease of cleaning
- ease of maintenance
- ease of operation
- compactness of the system
- scale
- possibility of membrane replacement.

MODULES BASED ON HOLLOW FIBRE MEMBRANES

Hollow fibre membranes are made from extremely thin polymeric tubes, with a diameter of 50–200 μm . The selective layer is on the outside surface of the fibres, facing the high-pressure gas. A hollow fibre membrane module normally contains tens of thousands of parallel fibres deposited at both ends in epoxy tube sheets . These kinds of membrane play an important role in gas separation owing to their high separation area and selectivity. Hollow fibres are stable and show high flux with moderate selectivity in a full scale system. The high flux of hollow fibres is due to the combination of high transfer or separation areas and a thin membrane wall.Moreover, they also possess a low surface energy.

MODULES BASED ON CAPILLARY FIBRE MEMBRANES

Capillary fibres are produced using similar equipment to hollow fibres, but they have a larger diameter, typically, 200–400 μm . The selective layer is formed on the inside surface of the fibres.

The free ends of the capillaries are potted agents such as epoxy resins, polyurethanes. In a capillary fibre module, the feed gas flows through the bore of the fibres.

The pressure difference feed-to-permeate, which capillary fibres can support, is limited and typically it does not exceed 10–15 bar. Higher pressures may rupture fibres and even a single defective fibre can seriously degrade the separation capability of the module. Capillary embrane modules are not as expensive or compact as hollow fibre modules, but they are still very economical. Their principal drawback is the pressure that the fibres can support. This limitation means capillary modules cannot be used at the high pressures that are necessary for hydrogen or natural-gas processing applications .

SPIRAL WOUND MODULES

Generally, sheets of membrane 1–2 m long are cut and folded and then packaged as spiral wound modules . A single module may contain as many as 30 membranes. Spiral wound elements are generally the most economical to operate .

Spiral systems are:

- Compact – high membrane packing density results in more efficient utilization of floor space;
- Energy efficient – lower power consumption compared to other membrane configurations;
- Lower capital cost, when extensive feed pretreatment is not required;
- Robust – high pressure spiral elements can withstand pressures in excess of 1000 psi (6.89 MPa).

COMPARISON BETWEEN DIFFERENT MEMBRANE MODULES

It is difficult to quantify correctly the cost of a module because the same module design varies widely depending on the application considered. Generally, hollow fibre modules are cheaper than the others even if they are produced for very high-volume applications in order to justify the expense of developing and building the spinning and module fabrication equipment.

Hollow-fibre and spiral-wound modules are very common mainly owing to their higher area to volume ratio. Spiral-wound modules have distinct advantages over the hollow-fibre elements in important applications, although the latter can offer higher packing density.

DESIGN FOR POWER PLANT INTEGRATION

The design of power stations requires simultaneous consideration of heat integration and power generation. Simulation models for gas separation membranes have to consider, generally, an equation describing the gas transport across the membrane, a mass balance equation for each component of the gas mixture, the pressure drops occurring on both sides of the membrane and the boundary conditions The major impediment to the engineering analysis of membrane processes in CO_2 separation is the large number and range of process variables. The mixture is often treated as a binary system (generally CO_2 and H_2) and, therefore, the role of impurities (water, SO_2, NO_x, particles, etc.) has not yet been investigated in detail. Another common assumption is that the constant feed mixture temperature is either close to or slightly above ambient temperature (e.g. 40°C). Moreover, the most important parameter, that must be considered, is the efficiency of a membrane separation process. The efficiency depends on three major variables:

- the membrane selectivity
- the pressure ratio between feed and permeate streams;
- the stage cut, the ratio of permeate flow rate to feed flow rate.

Particular attention is paid to the calculation of the CO_2 recovery ratio, the fraction of CO_2 in the feed captured in the permeate side:

$$R = \theta \frac{y_p}{y_{in}} \tag{1}$$

where y_p is the mole fraction of CO_2 in the permeate and x_{in} is the mole fraction of CO_2 in the feed. In general, an increase in θ (and so an increase of the membrane area) is not linear with the recovery of CO_2. For this reason, in a problem like CO_2 capture, one major objective of scientific studies is to determine the relationship between the CO_2 recovery ratio (R) and the corresponding permeate composition (y_p).

The International Energy Agency (IEA) guidelines require R to be above 80% or 90% (Davison and Thambimuthu, 2004), because values below this do not offer a sufficient decrease in CO_2 released to the atmosphere. The permeate CO_2 mole fraction y_p must also be in the range 0.8–0.95, both to minimize the compression and transportation costs and to prevent problems related to deep ocean or geological disposal. Unfortunately, the recovery ratio R and permeate composition yp seem to be inversely related, such that an increase in R implies a decrease in y_p and vice versa.

COST CONSIDERATIONS AND MEMBRANE TECHNOLOGY AT THE INDUSTRIAL SCALE

Economic analysis includes not only the costs for capture, but also the costs of injection and storage into a geological site, allowing a full comparison processes depend on the fixed charges and the repayment of the plant investment cost and of operating costs (energy, membrane replacement, maintenance).

In particular, quantitative analysis of the costs strongly depends on the specific application, plant and location as well as on the characteristics of membranes and modules. In fact, the costs of capture using gas separation membrane systems can be reduced by increasing the membrane permeability and selectivity.

Improvements in the permeability reduce the capture cost because less membrane area is required for the same CO_2 recovery rate. By increasing the CO_2/N_2 selectivity, the mole fraction of CO_2 in the permeate increases. As the capture cost includes the compression of CO_2 after separation, a higher CO_2 fraction in the permeate stream requires less compression and, thus, less energy; therefore, both the capital expenditure and operating costs are lower.

In contrast, the cost of membranes affects only marginally the capture costs . Therefore, reductions in membrane costs will improve the overall competitiveness of gas separation membrane systems slightly.

Another important aspect of CO_2 separation costs is the driving force, which, by using embrane technology, depends on the partial pressure difference between both sides of the membrane. By increasing the pressure across the membrane or reducing the feed gas pressure, the capture cost decreases.

This is because a lower feed pressure requires a smaller compressor, thereby reducing both the capital costs and the total energy consumption . Nevertheless, decreasing the feed pressure, the driving force across the membrane decreases. Therefore, to obtain the same CO_2 recovery from the feed gas, the membrane area required must increase. Globally, it is better to increase the costs of the membrane than to use a bigger compressor.

Moreover, just to give a very brief overview of the work in CO_2 capture direction, some European projects (in the UE FP6 and FP7 only) are reported in the following:

- Innovative CO_2 capture (iCap: 2010–2013). This project is coordinated by the Norwegian University of Science and Technology. The aim of the project is to develop breakthrough technologies that can be applied to post-combustion CO_2 capture. These technologies include the use of phase change solvents, the combination of SO_2 and CO_2 absorption, the use of CO_2-selective low-temperature membranes and the development of new energy production cycles with CO_2 capture.
- CO_2 enhanced separation and recovery (CESAR: 2008–2011. For: CESAR: http://www.co2cesar.eu/index.php). This aims for a breakthrough in the development of low-cost post-combustion CO_2 capture technology in order to provide an economically feasible solution for both new large scale power plants and retrofit of existing power plants. For this project, the research is charged with the development of new membrane contactors, development carried out by SME Polymem and ENSIC-Nancy.
- Nanoglowa is a project based on CO_2 capture trough nanostructured membranes (http://www.nanoglowa.com). In this project, the application of nanostructured membranes for CO_2 capture and separation brings down the energy penalty related to conventional absorption with amines.

CONCLUSIONS

Membrane-based technology has several advantages over conventional separation approaches for CO_2 capture, such as:

- lower capital cost
- ease of skid-mounted installation
- lower energy consumption
- ability to be applied in remote areas, especially offshore flexibility.

Nevertheless, there are many relevant factors determining the appropriateness of each membrane type for each specific application. When selecting a suitable membrane for CO_2 separation, the operating temperature and pressure are of paramount importance since they directly affect the separation performance of the membrane. In addition, the composition of the gas mixture to be separated, the material and fabrication costs of the membranes as well as the overall process design need to be taken into account. Moreover, the energy reduction required and the corresponding costs must be addressed. Currently, chemical modification of polymeric membranes is one of the most promising approaches for greatly enhancing separation performance. Therefore, further development of existing modification methods (e.g. identifying better cross-linking agents) or the invention of new modification techniques for existing gas-separation materials may accelerate the commercialization of polymeric membranes for CO_2 separation. However, long term stability and performance of polymeric membranes at elevated temperatures are necessary to maintain the robustness of the membrane-based systems. In addition to membrane materials selection, membrane configuration and module design are important considerations for industrial applications.

Membrane separation is an attractive and promising technology, which can be applied in combination in all types of power plants. Nevertheless, although membrane technology is widely applied for gas separation, it is not yet used on the scale of power plants. For this reason, a potential objective could be the development of innovative membrane-based technologies capable of reducing the cost of CO_2 capture, producing, for example, hydrogen from natural gas fuel. This could be, for example, obtained by producing higher selective membranes, such as hybrid membrane–absorbent (or solvent) systems, which use very high surface area to volume ratios for mass exchange between a gas stream and a solvent, resulting in a very compact system. Overall, even though the separation of CO_2 using polymer-based membranes is a complex undertaking, it is necessary to address the challenges and continue approaches that will produce the next generation of high performance membranes.

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IZVOD

PRIMENA MEMBRANSKE TEHNOLOGIJE U OKVIRU POJMA NULTE EMISIJE

Koncept nulte emisije predviđa sve industrijske inpute koji se koriste u finalnoj proizvodnji ili pretvorene u inpute koji ulaze u dodatnu vrednost za druge industrije ili procese. Na ovaj način, industrije se reorganizuju u klastere tako da se otpad svake industrije, sporedni proizvod, u potpunosti poklapa sa ulaznim zahtevima drugih industrije, a integrisana celina ne proizvodi otpad bilo koje vrste. Ova tehnika se zasniva na dobro utvrđenim ekonomskim analizama alata poznatim kao ulazno / izlazni pristupi . U okviru koncepta nulte emisije hvatanje CO_2 igra važnu ulogu. CO_2 se može uhvatiti i trajno čuvati, ili se može ponovo koristiti.

Sekvestracija ugljenika je proces u dva koraka, gde je hvatanje CO_2 iz gasne struje praćeno njegovim stalnim skladištenjem. Proces prikupljanja doprinosi 75% na ukupne troškove proces zaplena ugljena. Iz tog razloga, naučna zajednica je posvetila veliku pažnju razvoju novih procesa za prikupljanje CO_2. Trenutno, postoji širok spektar tehnologija za separaciju CO_2 iz gasnih struja. Oni su zasnovani na različitim fizičkim i hemijskim procesima, uključujući apsorpcije, adsorpciji i membranske tehnologije. Izbor odgovarajuće tehnologije zavisi od karakteristika protoka dimnih gasova i, kao posledica toga, na tehnologiji elektrane. Kao alternativa konvencionalnim procesima za separaciju i hvatanje CO_2, membranska tehnologija pokazuje veliki potencijal za CO_2 zbog njegove lakoća postavljanja, efikasnost, fleksibilnost, mogućnost održavanja visokog pritiska CO_2 i obavljanja razdvajanja na niskim vrednostima energije. CO_2- selektivna membrana dozvoljava odvajanje CO_2 iz različitih gasnih struja, kao što su: dimnih gasova (sistem posle sagorevanja), prirodni gas (prerada prirodnog gasa) i vodonika (sistemi pre sagorevanja) ili kiseonika od azota (u sistemu "oksifuel" sagorevanje).

U okviru koncepta nulte emisije, ovaj rad daje pregled i analizu vrsta membrana koje se koriste i primenjenih membranskih tehnologija za prihvatanje CO_2 sa stanovišta troškova i energetske potrošnje.

Ključne reči: *nulta emisija, membranska tehnologija, prihvatanje CO_2*

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