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CCS Membrane Development at CIUDEN's Technology Development Centre for CO_2 Capture

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Abstract

CO_2 concentration to the atmosphere has risen faster than ever in the last century. This is highly due to fossil fuel combustion which is the major anthropogenic CO_2 source. Membrane technology is an important alternative for reliability, flexibility and economically competitiveness for Carbon Capture and Storage (CCS) processes. The use of membranes has applicability to CCS technologies mainly for CO_2, O_2 or H_2 separation, although most of the membrane studies for CO_2/O_2 production have been carried out at laboratory scale and will require a step further for commercial scale. This paper will present current membranes R & D needs when applied to CCS systems and CIUDEN capabilities for membrane technological development and testing under real conditions. It covers from O_2 separation membrane integration in the process, and applied to the oxy-combustion CO_2 capture, to post-combustion technologies for membrane CO_2 separation, tested under real conditions or H_2 production catalytic-membranes through gasification. At CIUDEN CCS facility important membrane evaluations can be carried out for the module integration, testing of materials performance and behavior under real conditions.

Keywords

CCS, Membrane, Carbon Capture, Oxy-Fuel, CIUDEN

1. Introduction

CO_2 concentration to the atmosphere has risen faster than ever in the last century. This is highly due to fossil fuel combustion which is the major anthropogenic CO_2 source. The IEA CCS Roadmap highlighted the significance that will need to be attached to CCS (Carbon Capture and Storage) in achieving an atmospheric

CO_2 concentration stabilization of 450 ppm in 2050 [1].

The EU has adopted ambitious targets for reducing the emissions of greenhouse gases in the coming decades. The targets for 2020 are:

1) to reduce greenhouse gas emissions by 20%;
2) to ensure 20% of renewable energy sources in the EU energy mix;
3) to reduce EU global primary energy use by 20% by 2020.

In particular, to reduce CO_2 emissions the EU member states will promote the commercial use of technologies for CO_2 capture, transport and storage through demonstration at industrial scale, including whole system efficiency and advanced research as included in the European Energy Roadmap 2050. Therefore, the EU plans are to set up a network of CCS demonstration plants on the short-term to test their viability, with the aim of commercial scale up of CCS technologies on the mid-term.

CCS consists of four major parts: capture, compression, transport and storage of CO_2. There are three main routes to capturing CO_2 from power processes: post-combustion, oxy-fuel combustion and pre-combustion.

Membrane technology is an important alternative for reliability, flexibility and economically competitiveness for two CCS process options: post-combustion and oxy-combustion. The use of membranes has applicability to CCS technologies mainly for CO_2 and O_2 separation, although most of the membrane studies for CO_2/O_2 production have been carried out at laboratory scale and will require a step further for commercial scale.

The application of membranes in fossil fuel power plants demands large superficial area membranes that can be maintained and repaired efficiently. Moreover, the membranes have to withstand pollution, fouling as well as temperature and pressure changes, conditions that cannot be endured by today's membrane technology. The development of cheaper and more robust membrane modules high permeability and selectivity is also foreseen. For example, the O_2 separation technology with membranes has been studied as an alternative way to produce O_2 to the cryogenics, VPSA, etc. with promising results. Fundacion Ciudad de la Energia (CIUDEN) esCO_2 centre is divided in two main facilities:

1) Technology Development Centre for CO_2 Capture and the Technology Development Plant for CO_2 Geological Storage.
2) CIUDEN Technology Development Plant for CO_2 Geological Storage, situated in Hontomin (N Spain), allows carrying out experiments in real scale in saline formations to develop CO_2 storage knowledge.

The Technology Development Centre for CO_2 Capture is a flexible, modular and integrated installation ready to test and validate membrane technologies (either CO_2 or O_2 and H_2) under a wide range of conditions in controlled industrial environment. Aerial view of the centre can be seen in **Figure 1**.

The capabilities of CIUDEN for membrane technology development and testing at different conditions and purposes go from O_2 membrane production integration in the energy production process, applied to the oxy-combustion facility mode, to post-combustion technologies for CO_2 separation membranes,

Figure 1. Aerial view of CIUDEN's Technology Development Centre for CO_2 Capture.

tested under real conditions, or even H_2 separation from syngas after gasification. Furthermore, ancillary equipment is considered a key player on the development of this technology. Due to the high stresses that will suffer the materials and the special needs of the membranes (dust removal at high temperatures, cleaning system control, fouling control, etc.), further study and development should be taken into account and the CIUDEN's CCS facility promotes the evaluation of the integration and testing of the system, understood as the membrane, ancillary equipment and structural components, both in materials performance and behavior, and process control optimization.

2. CIUDEN CO_2 Capture and Transport Programme

CIUDEN) is a state owned, public R & D institution created by the Spanish Government in 2006. It was conceived to foster economic and social development in Spain through activities related to the energy and environmental sectors.

The es.CO_2 Technology Development Centre for CO_2 Capture is located in Cubillos del Sil (Leon, Spain). It aims to develop CO_2 capture and transport technologies feasibility to reach the industrial scale. It is a semi-industrial size facility for experimental purposes, which includes the following systems:

- Fuel Preparation System
- Pulverized Coal Boiler 20 MW_{th} (PC)
- Circulating Fluidized Bed Boiler 30 MW_{th} (CFB)
- Flue Gas Cleaning System
- Oxidant preparation system
- CO_2 Compression and Purification Unit (CPU)
- CO_2 Transport Test rig
- Biomass Gasifier 3 MW_{th}

The main systems and novelty equipments and advances will be described very briefly in this section.

2.1. PC Boiler

The Pulverized Coal Boiler is a 20 MW_{th} unit focused on research demonstration and technological development. It can operate in air and oxy mode for different types of fuels (anthracite, bituminous, sub-bituminous, petcoke/anthracite mixture). It is a vertical water tube boiler with natural water circulation and balanced draft, equipped with different burners configurations.

2.2. CFB Boiler

The Circulating Fluidized Bed Boiler (30 MW_{th}) is a natural circulation, balanced draft, circulating fluidized bed boiler, designed to test CFB combustion under air and oxy-combustion conditions. Foster Wheeler is the technology supplier.

Design fuel is anthracite, but it is able to burn bituminous coal, sub-bituminous coal, pet coke, biomass and its blends, etc.

The oxidant stream required for oxy-combustion is obtained from mixing oxygen with recirculation gas in order to temper combustion. The O_2 concentration design parameters in the oxidant streams vary from 30% to 70%.

2.3. Flue Gas Cleaning System and Oxidant Preparation System

Coal and biomass combustion and oxy-combustion produces particulate matter and gaseous contaminants which need to be treated.

The flue gas cleaning system is aimed to treat flue gases emissions from the boilers to meet environmental legislative requirements and to reduce impurities to the maximum levels that can be treated at the CO_2 Compression and Purification Unit (CPU). The system includes the following main equipment: Cyclones, Selective catalytic reduction of NO_x (SCR) and Bag filter.

2.4. Capture and Purification Unit (CPU)

As result of the oxy-combustion process a flue gas highly concentrated in CO_2 is produced almost ready for transport and storage; nevertheless some contaminants need to be removed. Main contaminants form oxy-combustion for transport and storage are: water, O_2, NO_x, SO_x and particulates.

The Compression and Purification Unit (CPU) is aimed to treat oxy-combustion flue gases remaining impurities, which have not been removed at the Flue Gas Cleaning System, to get CO_2 ready for transport and storage.

2.5. CO_2 Transport Experimental Facility

Once CO_2 is captured, it needs to be transported to the geological storage site. One of the most suitable ways, from a technical and economical point of view, to transport high quantities of CO_2, is doing it by pipeline. The transport is usually performed in dense or supercritical phase.

The CO_2 Transport Experimental Facility at CIUDEN es.CO_2 is a first-of-its-kind facility aimed to test CO_2 behavior in transport by pipelines.

The core of the facility consists on ten coiled pipe racks, with a length of 300 m each (total length of 3000 m) and 2" diameter. Between these racks, there are six experimental areas: Depressurization, Leakage, Fracture, Corrosion, Instrumentation testing and Pressure Drop.

2.6. Biomass Gasifier (3 MW_t)

CIUDEN's es.CO_2 Bubbling Bed Biomass Gasifier is an industrial scale facility that can achieve a gross power of 3 MW_{th}.

It is aimed to test biomass gasification and coal—biomass co-gasification by bubbling bed and atmospheric pressure gasifier.

Simplified process diagram of the full centre can be seen in Figure 2.

3. Membrane R & D Needs for CCS Implementation

Nowadays, a transition to a low carbon energy generation is taking place. Nevertheless, it is foreseen that in the future the trend is to continue using fossil fuels. This contemplates the need of CCS industry and different feasible technology approaches to be implemented. The strategy to reduce CO_2 emissions by CCS technologies is necessary in order to counteract global warming regarding to Kyoto Protocol.

The task of CCS installation involves firstly the separation of CO_2 and further the preparation of carbon dioxide for transportation to the storage site. Currently, it is considered that purity of CO_2 for transport should be greater than 95%, and transported CO_2 should be free of water [2]. This requires:

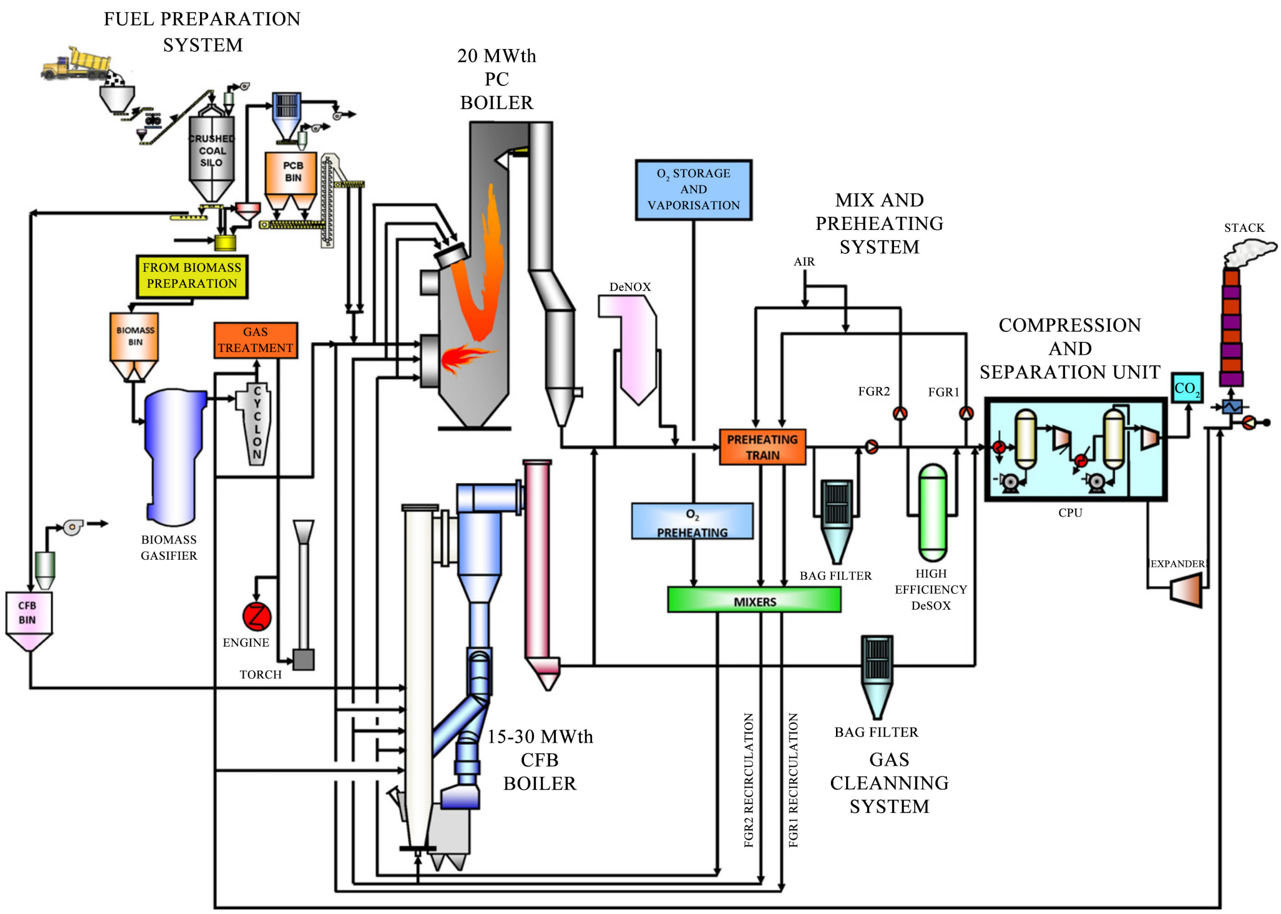

Figure 2. Simplified process diagram.

- No free water to prevent corrosion, hydrate formation and two phase flow, <500 ppm.
- Limited concentration of contaminants (SO_2, H_2S, and O_2) for safety and acceptance reasons.
- Limited concentration of non-condensable gases (N_2, NO_x, CH_4, Ar and H_2); they should not exceed in total 4%, (two phase flow at higher pressure).

There are three approaches to integrate CO_2 capture in power plants:

1) Post-combustion capture of flue gas CO_2 via chemical treatment, usually sorbent (amine) washing, but there are other approach as the calcium looping.
2) Oxy-combustion or oxy-fuel systems that produce a flue gas with high CO_2 concentrations amenable to capture without a post-combustion chemical process.
3) Pre-combustion, chemical removal of CO_2 from the synthesis gas produced in an integrated coal gasification combined cycle (IGCC) power plant.

The first generation technologies for the three capture options (post-combustion, pre-combustion and oxy-combustion) in the power sector have already been tested at large pilot scale facilities and are now ready for the large scale demonstration. However, CO_2 capture is still an emerging technology and significant advances are possible through well planned R & D programs.

The application of CCS installations in the power sector implies a significant loss of energy production efficiency due to their high energy consumption. The optimization of current and next-generation technologies is essential to: reduce costs and build public and investor's confidence to accelerate deployment of CCS technologies.

The use of membranes in fossil fuel power plants requires large membranes that should be maintained and repaired on site. Resistance to pollution, fouling and temperature and pressure changes are key characteristics for membranes operation in large industrial installations. These properties cannot be accomplished delivered nowadays by membrane technology. Furthermore, it is necessary the development of cheaper and more robust membrane modules with high permeability and selectivity.

Membranes could be applied to the three CO_2 capture options in different ways, and with different purposes. These membranes will have specific requirements from the application to singular conditions which will give R & D needs. For example, the O_2 separation technology with membranes has been studied as an alternative way to produce O_2 to the cryogenics, VPSA, etc. with promising results.

3.1. Post-Combustion Technologies Membrane R & D Needs

In post-combustion CO_2 capture, flue gases produced during combustion of primary fuel with air are treated to separate the CO_2. Post-combustion methods have been proposed to separate CO_2 from the flue gas stream in large point-sources, such as coal-fired power plants and energy intensive industries; in which CO_2 concentration varies from typically around 3% vol (dry) for a natural gas combined cycle plant to 35% vol (dry) in cement industry, and about 15% vol (dry) for a pulverized coal fired power plant.

These capture technologies can be applied to flue gases from all kinds of industrial processes, in particular power production from fossil fuels and biomass, cement, steel and aluminum production. Selection of the preferred capture technology depends on the flue gas properties (temperature, pressure, concentration and volume flow rate). These methods may be classified according separation principles into absorption, adsorption, cryogenics and membranes.

Among these technologies, amine chemical absorption is the most developed since there is great experience in the chemical and oil industries for the removal of CO_2 from gas streams. However, this process has a significant energy penalty due to the high energy requirements in the regeneration step. Large sorbent make-up flow is also required because of the chemical and oxidative degradation of the amines. The implementation of this technology for CO_2 capture from power plants is limited by its high costs derived given by the high energy penalties.

The accomplishment of lower energy penalties in the CO_2 capture process is crucial to the achievements of the goal of CCS deployment at industrial scale. CO_2 membrane separation is considered to be one of the most promising technologies to reduce energy penalty and cost of capture.

CO_2 membrane technology has been developed for removing CO_2 from mixtures with light gases such as CH_4, N_2 and H_2. Nevertheless, nowadays current membrane technology has to be developed to achieve good performance under a real post-combustion flue gas. The R & D needs are focused on the development of cheaper and more robust membrane modules with higher permeability and selectivity [3].

Membrane structure and property guidelines have been extensively studying explored in an effort to improve the separation performances for gas separation (*i.e.* diffusivity and selectivity) [4] [5]. However, good selectivity has not been fully pursued as a route to enhance gas separation properties.

3.2. Oxy-Combustion Membrane R & D Needs

In an oxy-fuel power plant, pure oxygen is used in the combustion process instead of air which results in a flue gas highly concentrated in CO_2, more than 85% db, making easier the CO_2 separation and reducing the operating costs. To perform the combustion, very large volumes of oxygen are needed, which involves a large and costly air separation unit. Currently, the main commercial available technology to separate oxygen from air is cryogenic distillation (ASU). Nevertheless, cryogenic air distillation has the important inconvenient of the high energy demand needed, contributing to more than half of the energy penalty of the whole CCS processes. Another drawback is the fact that cryogenic distillation plants are only economically viable for very large oxygen productions, what makes more difficult its implantation in small applications. Typical ASU plants present a daily production between 50 - 4000 tons of oxygen, so, according to this, production rates below 50 ton/day are not viable.

For the 1st large scale demonstrations of oxy-fuel power plants, and the first commercial generations, cryogenic air separation will be the only viable air separation technology due to the large scale. In longer time perspectives, other air separation technologies based on membranes or adsorbents are seen as potential candidates.

Being O_2 production the main drawback of the oxy-combustion, one of the main purposes to develop cost efficiency oxy-combustion technology is to reduce specific energy consumption of today cryogenic processes, what is today in the range of 160 - 220 kWh/ton. A long term R & D target should be to reduce this to the range 120 - 140 kWh/ton for improved cryogenic processes. Other technologies could aim further, going down the range 90 - 120 kWh/ton such as membrane or sorbent based technologies.

Oxygen transport membrane (OTM) technology are then a substitutive way for O_2 production, reducing O_2 production costs and making in consequence, oxy-fuel combustion technology for CO_2 capture more economically attractive option than the others. Oxygen transport in these membranes consists on the oxygen diffusion through vacancies in the crystal lattice and simultaneous transport of electrons in the opposite direction, thus obviating the need for an external electrical short circuit. It can reach O_2 purity higher than 99% and can reduce efficiency drop to 5% - 6% in a power plant when CCS is implemented. The oxygen separation process follows three phases which can be identified:

- Molecular oxygen in air is adsorbed, reduced and dissociated on surface of the membrane in the feed side to form oxygen-ions which are incorporated into the material lattice.
- Oxygen ions (O_2-) diffuse selectively through the membrane under the driving force of a gradient in oxygen chemical potential. The flux of O_2- is charge compensated by a simultaneous flux of electrons or electron holes.
- Lattice oxygen ions are desorbed and form oxygen atoms by oxidation reaction at the permeate side membrane surface.

System integration is one of the key factors to achieve the best efficiency high-temperature oxygen separating membranes. Another key challenge that nowadays technology present is the improvement of further materials with better flux, selectivity and upgraded performance at lower temperatures (below 700˚C).

Oxy-combustion produces a flue gas with higher concentration of pollutants, especially SO_x and NO_x, due to the absence of N_2 in all the system. It implies the development of new materials (or integrated ancillary equipment) able to tolerate these higher concentrations of pollutants. Membrane materials for oxy-fuel should be stable at sour conditions and to gas with high CO_2 concentrations.

For the implementation of OTM membranes in an oxy-fuel plant the technology should be scaled-up and knowledge on manufacturing a reactor design should be increased. Furthermore, for in any large scale application, industrial fabrication methods should be developed and, maintenance and reparation strategies defined precisely.

3.3. Pre-Combustion and Gasification Membrane R & D Needs

IGCC is based on the gasification of coal at elevated pressures (10 - 80 bar) and temperatures (950˚C - 2000˚C) with oxygen and steam as gasification agents [6]. The raw gas stream produced consists mainly of CO and H_2. It has to be cooled for the downstream process; the cooling can be done by using recirculated cold raw gas or by a wet quench injecting water into the gas stream. An intensive cleaning of the gas, eliminating dust and gaseous pollutants as HF, COS, H_2S, etc., in the gas conditioning part of the power plant finalizes the syngas production. The syngas produced is then fed to a combined cycle: to a combustion chamber of a gas turbine and the exhaust gases to a heat recovery steam generator.

Regarding membrane application, the IGCC process presents two advantageous operation conditions, high absolute pressure of the syngas and high partial pressure of the gas species of interest. Another advantage of the IGCC process is that between gasifier and the gas turbine island there are different temperature levels which allow implementing different membrane types with different working characteristics.

O_2, CO_2 and H_2 selective membrane can be applied to an IGCC system. H_2 selective membranes are the most specific to IGCC systems.

Process schemes may be obtained by integration of components and/or material development. Typically by combining a membrane into a catalytic process, to shift the equilibrium of the water-gas-shift reaction, $H_2O + CO \rightarrow H_2 + CO_2$, in the direction of completion thus making following separation and/or purification steps redundant. The most challenging is to develop membranes with high flux, selectivity and stability at temperatures and elevated pressure.

The four main locations for H_2 membrane integration in an IGCC system were described and presented by Marano [7]. Integration options can be seen at scheme 2, these are:

- Post WGS H_2 Recovery
- CO_2 Compressor Interstage H_2 Recovery
- WGS Interstage H_2 Recovery
- WGS Membrane Reactor

Oxygen transport membrane reactors (OTM) may find applications in large scale processes for oxygen production, for chemical production (syngas produced from autothermal reforming—ATR or partial oxidation—POX) and for energy conversion (Coal to liquid, coal to gas, oxycombustion and IGCC processes). OTM membranes applied to IGCC systems will have similar approaches to the one performed in oxy-combustion. OTM membranes are seen as an alternative to reduce energy consumption for oxygen production. Main membranes R & D challenges are similar to oxy-combustion, but integration options and specific pollutants will be particular for IGCC systems. Locations for H_2 membrane integration in an IGCC system are studied also by Marano J.J. and Cifinero J.P [7].

4. Membrane Technological Development at CIUDEN

Membrane technology is seen as an important alternative for increasing reliability, flexibility and economic competitiveness of CCS processes. The use of membranes has applicability to CCS technologies mainly by CO_2 and O_2 separation, although most of the membrane studies for CO_2/O_2 production have been carried out at laboratory scale and will require a step further for commercial scale.

CIUDEN Technology Development Centre for CO_2 Capture semi-industrial facility given its flexibility, modularity and integration is ready to test and validate membrane technologies either CO_2, O_2 or H_2 under a wide range of real conditions. Large scale of the centre generates conditions similar to the real ones, which will be necessary for any development before reaching a larger scale.

The capabilities of the TDC es.CO_2 for membrane testing at different conditions and purposes go from O_2 membrane production integration in the system and applied to the oxy-combustion facility mode to post-combustion technologies for membrane CO_2 separation, tested under real conditions.

4.1. Oxy-Combustion Membrane Development at CIUDEN

Oxygen production process is the main source of efficiency penalty in oxy-fuel plants and it has high capital cost. Dense electrolytic high temperature Oxygen Transport Membranes (OTM), based on mixed ions-electrons conducting materials, are a promising alternative to cryogenic ASUs, when integrated in power plants.

OTM are being developed to operate at high temperature, typically greater than 700˚C. High-temperature air separation process has better synergy with power generation systems. Commercial-scale OTM oxygen modules have been fabricated by Air Products (0.5 ton/day of oxygen); this technology requires 35% less capital (much simpler flow sheet) and 35% - 60% less energy (less compression energy associated with oxygen separation) than cryogenic air separation. [8].

To reach satisfactory results in the scaling-up of the OTM technology, several stages of the whole process should be developed such as membrane materials manufacture, membrane module design and built, energetic system integration in an oxyfuel process, ancillary equipment design, etc. The membrane technology should go through several phases prior to the final development/demonstration at industrial scale between laboratory activities and pilot and demonstration.

Integrated OTM membranes in an oxy-combustion system will have to withstand several contaminants. The development of new membranes resistant to these contaminants is a major issue which is under being investigated. The most concentrated hazardous contaminants are SO_2, NO_x and CO_2. Other trace elements such as NH_3 can affect membrane stability too. Typical oxy-combustion contaminants concentrations, which have been analyzed at CIUDEN facility, can be seen in **Table 1**.

Testing of membrane materials under real conditions is a major issue for the scaling up of membrane and for the application to industrial environment. Membranes have to be adapted from laboratory ideal conditions to industrial hostile environments.

Considering all the aspects aforementioned, it will be necessary to ensure a suitable composition of the flue gas in contact with the membrane. Aiming to re-circulate a fraction of this stream to be used as sweep gas, ashes and other compounds like SO_x should be removed from the gas stream. Thus, it is necessary to consider the inclusion of ash filters and, depending on the membrane characteristics, sulphur oxides scavengers/filter too.

Due to the fact that it is very important to keep the gas in the operating temperature range, both the filter and the SO_x removal system must operate at these temperatures (typically above 1000˚C). For the case of ash removal, ceramic filters or the so-called ceramic candles are available for operation at such high temperatures (1000˚C - 900˚C), although only few commercial products fit these strong requirements. Consequently, it is envisaged that an important research and development task is necessary to address ash filtering.

Regarding to SO_X, the utilization of a variety of methods consisting mainly in wet and spray-dry scrubbing techniques, dry sorbent injection systems, and flue gas desulfurization using recycled sodium carbonate seem the most appropriate. Nevertheless, the applicability of these techniques might be limited by the maximum operation temperature since the membrane operation required maintaining the stream temperature as high as possible during the hot gas cleaning. Most common desulphurization processes operate in a low temperature range (e.g.

Table 1. Typical oxy-combustion flue gas composition.

Compound	Concentration	Unit
O_2	2 - 4	%-wet
CO_2	55 - 65	%-wet
H_2O	7 - 15	%-wet
N_2 + Ar	7 - 10	%-wet
CO	45 - 70	ppm
SO_2	50 - 240	ppm
NO_x	50 - 70	ppm
Others: NH_3, HCl, C_2H_4, CHOH, etc.		

200˚C - 500˚C) due to either the lack of need to recycle the gas stream or process temperature. The use of CFB boilers, where SO_x removal can be done inside the boiler, will be more appropriate for membrane systems and their integration. SO_x removal in CFB boilers is accomplished by limestone injection in the furnace, showing the operation at temperatures of 900˚C - 1000˚C.

Ancillary equipment is considered a key player on the development of this technology. Due to the high stresses that will suffer the materials and the special needs of the membranes (dust removal at high temperatures, cleaning system control, fouling control, etc.), further study and development should be taken into account and the CIUDEN's CCS facility can achieve important evaluations for the integration and testing of the system, both in materials performance and behavior, and distributed control system of the process.

Integration of membranes in the different boilers can have different special features. Fluidized bed boiler steam cycle plants, carry out desulfurization directly inside the bed, release an exhaust stream poor in SO_X, making easy the integration with high temperature membranes, while pulverized coal boiler steam cycle plants are at the moment the most widely adopted solution for power generation from coal.

Membrane integration can be done according to different module configurations:

- Cross-flow (3 ends) module that minimizes the connection problems with the rest of the plant.
- Counter-flow (4 ends) module (with a sweep stream) that introduces additional problems of integration but it allows the plant to achieve a higher efficiency.

The best thermodynamic performance configurations have to be identified. Such configurations may require different levels of R & D and of technological risk to be implemented in full-scale power plants. The maximum energy integration of oxygen separation system is the integration of the membrane system inside the boiler itself. However, this task would be very ambitious since it would entail strong modifications in the boiler design.

The integration of N_2 membranes inside the capture system is another option of application of membranes. The two possibilities for integration are the N_2/CO_2 separation after capture or N_2 separation from air to carry out partial oxy-combustion tests.

4.2. Post-Combustion and Pre-Combustion Membrane Development at CIUDEN

Although CIUDEN special feature is the developing of oxy-combustion capture, post-combustion and pre-combustion technological development can be carried out at CIUDEN facility.

Given that the installation can work under air combustion conditions, any kind of combustion flue gas can be reached to test post-combustion systems.

Pre-combustion needs a complete singular installation. Nevertheless some aspects of pre-combustion can be studied at CIUDEN through the use of the biomass/coal gasifier.

4.2.1. Post-Combustion Membrane Development at CIUDEN

Membrane technology has been mainly investigated for removing CO_2 from mixtures with light gases such as CH_4, N_2 and H_2 by the oil industry. Optimal membranes with high CO_2 permeability and high CO_2/light gas selectivity were of great interest. However, the application of membranes to coal combustion flue gas presents peculiarities which make the technology development more challenging.

Apart from the gas composition, the process drawbacks to capture CO_2 with membranes are the low CO_2 concentration, the low pressure of the feed gas and the huge gas flows to be treated. The huge volumetric flowrate of a power plant flue gas stream means plants with very large membrane areas are required.

The identification of the best capture process for post-combustion systems application requires a definition of the composition of the mixture to be treated, together with the target specifications, namely the CO_2 purity and maximal tolerable range of concentrations of the different species of the feed mixture (outlet boundary conditions).

The CO_2 content (volume basis) can be as low as 4% in a gas turbine plant, around 15% for coal power plants, and more concentrated (~20% - 30%) for cement and steel production plants. Larger concentrations can occasionally be found in some special situations such as ammonia, syngas or biofuels plants [9]. Additionally, different compounds are found; for instance N_2, O_2, NOx, SOx.

CIUDEN boilers, CFB and PC, have been running under air combustion conditions. Pollutants concentrations have varied from the ones in CFB oxy-combustion, these have been summarized in **Table 2**.

However, producing membranes materials for this application is not the principal problem preventing adoption of post-combustion membrane systems for CO_2 treatment. The more difficult problems to overcome are the scale of the process and the very large, expensive, and energy-consuming compression equipment needed.

4.2.2. Pre-Combustion Membrane Development at CIUDEN

Membranes are attractive integrated into a number of locations in the IGCC process. Membrane applications to IGCC systems that can be developed and validated at CIUDEN are mainly focused on OTM and H_2 membranes.

Table 2. Environmental data taken at CIUDEN on the Oxy-CFB Boiler.

Item	Oxy- vs. Air-firing	Comments
CO	Slightly higher	
NO_X	Equal/lower	Lower at high load/high temperature
SO_2	Higher	Higher in oxy-combustion due to higher SO_2 concentration

OTM membranes will present similar problems that the expected to oxy-combustion. The differences would be the integration options and the gas mixture at each point.

The most specific membranes for IGCC systems are the H_2 membranes, which can be studied at CIUDEN after by the use of the gasifier. Pre-combustion technology implies a first step of gasification of the fuel (coal/biomass) to produce a syngas which main. Syngas cleaning and treatment is one of the keys of the pre-combustion systems. It will depends on syngas composition of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and typically a range of hydrocarbons such as methane (CH_4) with nitrogen from the air.

Since CO_2 will need to be further compressed to 150 bar, it is desirable to recover CO_2 at high pressures; therefore, a H_2 selective membrane is preferred.

Aiming to increase H_2 recovery, H_2 membranes should be placed at locations with high H_2 partial pressures, either high total pressures or high H_2 concentrations [7].

As CIUDEN biomass/coal gasifier still being commissioned, syngas compositions to be treated by the membrane system are not representative enough. The average composition to be treated is expected to be the following [10]:

- Hydrogen (% vol. dry): 4.55
- Oxygen (% vol. dry): 0.5
- Nitrogen (% vol. dry): 65.97
- Carbon monoxide (% vol. dry): 0.97
- Methane (% vol. dry): 7.12
- Carbon dioxide (% vol. dry): 20.25
- Ethane (% vol. dry): 0.15
- Ethylene (% vol. dry): 0.27
- Propane (% vol. dry): 0.2
- TAR (% vol. dry): 0.0027
- GCV (MJ/Nm^3 dry): 4.34

These values, especially the H_2 value which is the one of interest for the membrane application may vary due to different gasification processes. H_2 composition could reach more than 20% vol. dry [11].

5. Conclusions

Membrane possibilities in the field of Carbon Capture and Storage have been studied. The three ways of carbon capture from industrial sources, pre-combustion, post-combustion and oxy-combustion have been introduced. In addition, the main R & D tasks to focus membrane application to any of these three industrial sources were revised.

Nowadays membrane technology is still far from fulfilling the total capacities of industrial applications. However, some development activities can be carried out to increase the scale of actual laboratory and pilot scale systems.

Furthermore, membrane research has to be carried out taking into account necessities and limitations of the final use under real conditions. Research focused and considering the real application will have more options to be successful and productive in the medium and long term.

Main results at CIUDEN Technology Development Centre for CO_2 Capture Circulating Fluidized Bed Boiler were given, in particular regarding SO_x and NO_x emissions, main contaminants in the general system and in the particular membrane scheme. That is helpful to introduce real flue gas conditions to be considered in the future and technological development necessities. In addition, it will help to focus short term objectives to be settled by membrane developers.

CIUDEN as a technology development centre is aiming to validate and demonstrate real CCS systems in a representative size to be scaled-up and reduce technological risks. CIUDEN characteristics and R & D capabilities and advances were explained.

Membrane R & D needs were compared and matched to CIUDEN capabilities to introduce main work to be developed and validated facing CCS membrane development at CIUDEN's technology development centre for CO_2 capture.

R & D in identified areas must be initiated and/or continued now and in the years to come in order to reach estimated maturity at the defined time-scales. Development steps considered: laboratory—pilot plants—semi industrial—industrial—pre-commercial scales are essential for the continuity from the EU in supporting developing technologies.

In this perspective, it is important to know the need for medium sized pilot plants which are less risky and costly for new developments [12].

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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