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Review of Membrane Oxygen Enrichment for Efficient Combustion

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Abstract. Oxygen enrichment from air is a simple way of increasing the efficiency of combustion process, as in oxy-combustion. Oxy-combustion has become one of the most attracting combustion technologies because of its potential to address both pollutant reduction and CO_2 capture. In oxy-combustion, the fuel and recycled flue gas are combusted with oxygen enriched air (OEA). By using OEA, many benefits can be obtained, such as increasing available heat, improving ignition characteristics, flue gas reduction, increasing productivity, energy efficiency, turndown ratio, and flame stability. Membrane-based gas separation for OEA production becomes an attractive technology over the conventional technology due to the some advantages, including low capital cost, low energy consumption, compact size, and modularity. A single pass through membrane usually can enrich O_2 concentration in the air up to 35% and a 50% concentration can be achieved with a double pass of membrane. The use of OEA in the combustion process eliminates the presence of nitrogen in the flue gas. Hence, the flue gas is mainly composed of CO_2 and condensable water that can be easily separated. This paper gives an overview of oxy-combustion with membrane technology for oxygen enrichment process. Special attention is given to OEA production and the effect of OEA to the efficiency of combustion.

1. Introduction

Coal is a combustible sedimentary rock with a high amount of carbon and hydrocarbons. Coal contains the energy stored by plants that lived hundreds of millions of years ago. Therefore, coal becomes the primary fuel, especially for electricity generation. Currently, about 40% of the world's electricity is generated with coal [1]. Demand for coal resources is expected to continue to increase worldwide because of increasing energy demand in the future. However, coal as an energy source has a number of negative environmental impacts, including the release of particle matter (PM), oxides of sulphur and nitrogen (SO_x and NO_x), carbon monoxide (CO), and trace metals such as mercury [1-4]. Therefore, Coal combustion presents challenges for reducing emissions of air pollutants and carbon dioxide (CO_2). In response to these challenges, a number of technologies have been developed with further prospective developments toward 'near zero emission' power plants. One of the promising technologies for emissions reduction is by using oxy-combustion.

Oxy-combustion has become one of the most attracting combustion technologies in the last decade [5]. In Oxy-Combustion, the fuel and recycled flue gas are combusted with oxygen enriched air (OEA) with the result that the flue gas consists mainly of CO_2 and water vapor. The net flue gas contains about 80–95% CO_2 depending on the fuel used and the particular oxy-fuel combustion process [6]. The water can be removed easily by condensation and the remaining CO_2 can be purified relatively inexpensively. This process is having numerous environmental benefits as well as improved energy efficiency and productivity. Using oxygen enriched air (OEA) as the feed to the power plant ensures that the flue gas contains nearly pure CO_2, which eliminates the expensive CO_2/N_2 separation necessary for capture and sequestration [7, 8].

To establish oxy combustion, it needs oxygen enrichment process. There are three methods that usually used in oxygen enrichment: distillation, adsorption, and membrane technology. Some reviews relating to oxygen enrichment have been published. However, the reviews more focused on cryogenic distillation process. None of them focus on the membrane oxygen enrichment for oxy combustion. Therefore, this paper provides an overview of oxy-combustion with membrane technology for oxygen enrichment process. Special attention is given to OEA production and the effect of OEA to the efficiency of combustion.

2. Oxy combustion

Oxy combustion is recognized as an effective process for coal-fired power plants to continue operation in a carbon-constrained world. In 1982 oxy-coal combustion was originally proposed to produce CO_2 for Enhanced Oil Recovery (EOR) [2, 6, 9, 10]. But lately, interest has been paid to oxy-coal combustion as a means to reduce pollutant emission and create a CO_2 gas stream that can easily be removed. The core concept of oxy-combustion is the use of a high purity oxidant stream for the combustion process. The aim is to obtain a carbon dioxide-rich stream that is ready for sequestration, after removing water vapor and other impurities. Replacing combustion air with a mixture of oxygen and recycled flue gases has a significant impact on the combustion, such as increase efficiency, lower emissions, improve temperature stability and heat transfer, increase productivity, improve ignition characteristics, and low risk [5, 11, 12].

$$\boldsymbol{Coal + O_2 + 3.76N_2 \rightarrow \underbrace{CO_2 + H_2O}_{\text{unavoidable}} + \underbrace{3.76N_2}_{\text{unnecessary}} + \underbrace{(CO, unburned\ coal, NO_x)}_{\text{undesirable}} + \underbrace{Heat}_{\text{needed}}} \quad (1)$$

Combusting the fuel using oxygen enriched air at near-stoichiometric conditions creates a flue gas consisting mainly of CO_2 (80-95 % on a dry basis), water vapour and minor amounts of noble gases and, depending on fuel composition [13]. Due to its high concentrations, CO_2 can be recovered relatively easily and economically with the flue gas compression train [2]. After the water in the flue gas is condensed and the small amounts of impurities such as SO_x, NO_x, O_2, noble gases, metals and particulates are removed to meet transport and storage requirements [3, 8, 14]. In addition, for safety and environmental requirements, the CO_2 can be sent to storage.

3. Oxygen enrichment

One of the most important processes in oxy combustion is oxygen enrichment from air. Some technologies have been developed to meet high concentration of oxygen to improve combustion efficiency. Three methods that currently exist to separate oxygen from the air include distillation, adsorption, and membranes [15, 16]. Distillation is the most mature of the three technologies and allows for both high purities (>99%) and large scale productions [13, 17]. Adsorption is able to reach purities of up to 95% oxygen but the requirement of solvents limits its size capacity due primarily to capital costs [18]. Membrane technology is the most recent method for oxygen enrichment, which includes polymeric and high temperature ion transport membranes. Polymeric membranes can produce oxygen enriched air of various concentrations, meanwhile ion transport membranes can produce purities of close to 100% [19].

A commercial-scale coal-fired oxy-combustion power plant would require thousands of tons of oxygen each day. Cryogenic distillation is one of technology that commercially available today to produce such large quantities of O_2 economically [20]. Cryogenic distillation is a technology that has been around since the early 1900s when the Linde process was developed [21]. Gases such as oxygen and nitrogen, the primary constituents of air, decrease in temperature and condense when throttled because they have a positive Joules–Thompson coefficient. By controlling how much the temperature decreases through pressurizing and throttling the air, oxygen and nitrogen can be separated by phase as they have different boiling temperatures [19].

Table 1. Oxygen production technology alternatives [18, 22]

Process	Status	Purity (vol%)
Cryogenic distillation	Mature	> 99
Pressure Swing Adsorption	Semi-mature	95
Polymer membrane	Semi-mature	> 99
Ion transport membrane	Developing	> 99

Beside cryogenic distillation, oxygen enrichment can be obtained by pressure wings adsorption (PSA). In PSA, the regeneration of the adsorbent is performed by reducing the total pressure of the system, the total pressure of the system “swings” between high pressure in feed and low pressure in regeneration. Zeolites A and X are the most common used adsorbate for air separation [18, 23-25]. Compressed air enters the adsorption bed at a high pressure. Since nitrogen is adsorbed appreciably more than oxygen at high pressure, oxygen-enriched air can be easily obtained at the outlet. The bed is then blown down to a lower pressure to desorb the nitrogen in zeolite [25-27].

Both cryogenic distillation and PSA are energy intensive, which limits further development of the oxy combustion technique. Therefore, membrane process becomes one of the attractive technologies to replace both processes. Membrane offers some benefits, such as simple separation, continuous nature of the process, and operation at near ambient conditions [16, 18]. With an induced pressure difference, an O_2/N_2 selective polymeric membrane can partly separate oxygen from air by having properties that allow oxygen molecules to pass through the membrane easier than nitrogen molecules. However, the membrane cannot fully separate oxygen from the air; it can only be used to increase the concentration of oxygen as some nitrogen molecules will also flow through the membrane [19].

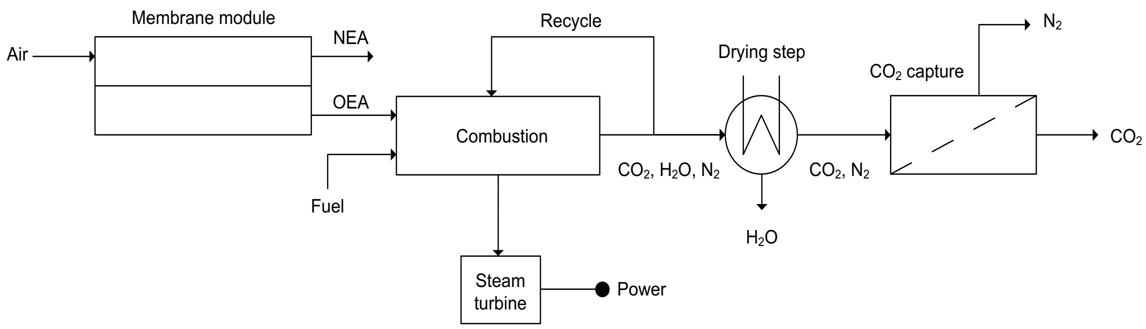

Figure 1. Oxy combustion with membrane as oxygen enrichment process, adapted from [28, 29]

Recently, some studies have reported the oxygen production by membrane processes. Smith and Klosek [18] used inorganic oxide ceramic materials to produce oxygen by the passage of oxygen ions through the ceramic crystal structure. These systems operated at high temperatures, over 11008°F. Oxygen molecules were converted to oxygen ions at the surface of the membrane and transported through the membrane by an applied electric voltage or oxygen partial pressure difference, then reform oxygen molecules after passing through the membrane material. The oxygen ions travel through the inorganic oxide ceramic materials at very high flow rates and produce nearly pure oxygen on the permeate side of the membrane.

Meanwhile, Clark and Rowan [30] studied an efficient method to enrich the oxygen concentration of the air stream by passing the incoming air through a series of polymeric membranes where there is a preferential diffusion rate for oxygen through the membrane over the other gases in the air. A single pass through membranes can enrich the oxygen concentration in the air to 35% and a 50% concentration can be achieved with a double pass of membrane. Later, Murali et al. [28] also used polymeric membrane based separation for O_2 production. Production of pure O_2 is difficult because a little quantity of N_2 always permeates through the membranes, resulting in oxygen enriched air (OEA) rather than pure O_2.

Besides by polymeric membrane, oxygen enrichment can be obtained by using an integrated oxygen ion transport membrane (ITM). Oxy-fuel combustion with ITM is a thermodynamically attractive concept that seeks to mitigate the penalties associated with CO_2 capture from power plants. ITM utilizes a high-temperature mixed-conducting (ionic and electronic) ceramic membrane to separate oxygen from air, and in some cases counter-currently oxidize a fuel within the same unit. ITM systems operate at relatively high temperatures, typically 800-1000°C [9, 31, 32].

Ion transport membranes (ITMs) offer promising oxygen production technology with high purity (up to 99%) without adversely affecting the efficiency of the oxy-fired plants. The separation rate of such ITMs can be increased by replacing the conventional inert sweep gas with a reactant/diluent mixture (e.g. CO_2, CH_4) as this reduces the permeate partial pressure on the permeate side of the membrane, which, along with the temperature, governs the permeation flux [33].

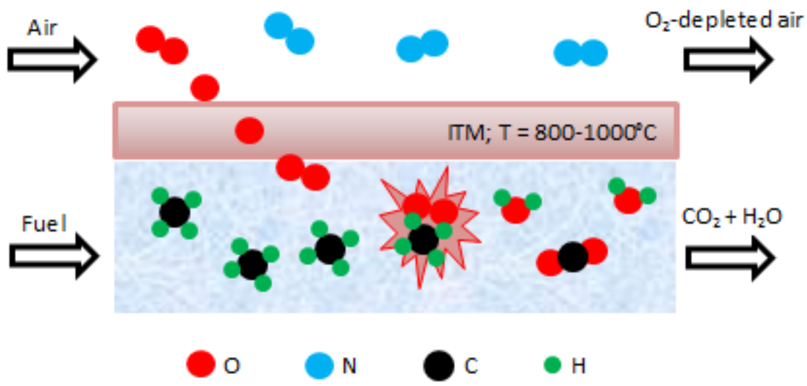

Figure 2. ITM counter-currently oxidize a fuel within the same unit, adapted from [6, 34, 35]

Ceramic membranes are selected as materials of ITM to maximize the oxygen permeation rate while keeping the membrane temperature within the operating limits [36]. Perovskites (ABO_3) are the most studied ITM materials due to their additional ability to conduct electrons, which allows oxygen transport to take place without an external circuit to transport electrons from one surface to the other. There are three types of perovskites for ITM, including BSCF (Ba0.5Sr0.5Co0.2Fe0.8O3), which has high oxygen fluxes but poor stability at low temperatures, LSCF (La0.6Sr0.4Co0.2Fe0.8O3−δ) which has lower fluxes but better stability, and BCFZ (BaCoxFeyZrzO3−δ) which has produced very stable membranes, operated for up to 2200 hours [9, 37].

4. Effect of OEA on oxy combustion

Using oxy-combustion for specific applications may improve efficiency, depending on the exhaust gas temperature and percentage of oxygen in the combustion air. In the past decades, intense research efforts have been directed to the development and improvement of ceramic and polymeric membranes for oxygen separation from air at high temperature operations. The result showed that by increasing oxygen flux, the combustion process is improved slightly and the maximum temperature inside the reaction zone is increased a little bit [10, 38].

Increasing the concentration of oxygen in combustion air also allows a reduction in fuel usage. This energy savings is due to the fact that nitrogen is not necessary for the combustion process and energy is lost as the inert nitrogen is heated during combustion and exhausted to the atmosphere [39]. As the oxygen concentration in the combustion air increases, more energy is available from the combustion thus less fuel is required. When oxygen concentration increases from 21% to 40%, energy saving of 60% can be achieved with the assumption that the exhaust temperature is constant, while in the real case it increases and thus there will be reduced savings.

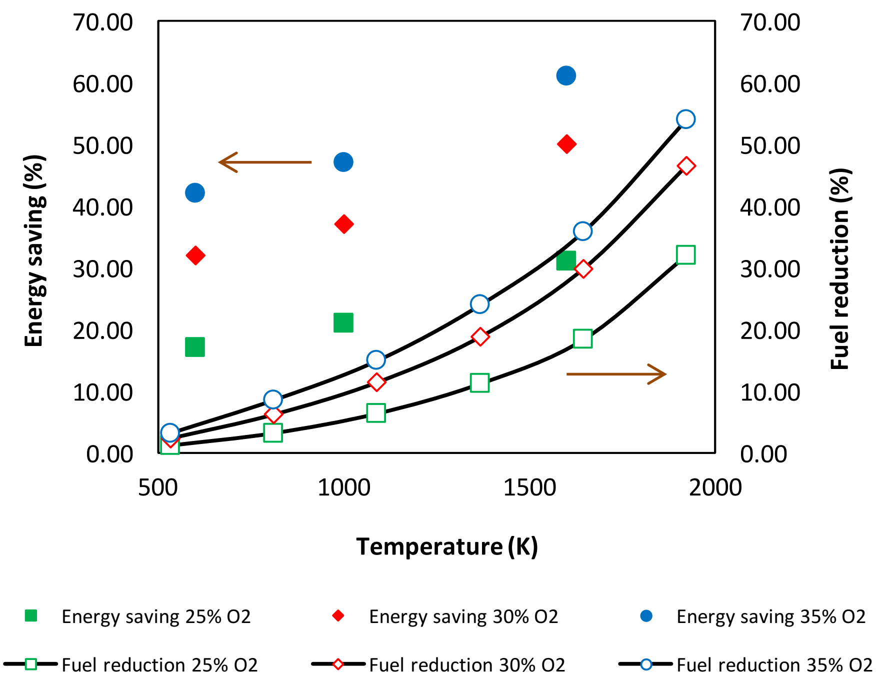

Figure 3. Effect of oxygen concentration and temperature on energy saving and fuel reduction, adapted from [11, 40]

The oxy-fuel efficiency can be increased by an optimisation of membrane operation parameters, such as oxygen separation degree, partial pressure ratio, and total pressure ratio. For example, the overall efficiency can be increased to 40.8% by reducing the mass flow in the recirculation which reduces the mean partial pressure ratio to 17 [35]. A reduction of the partial pressure ratio is only possible by increasing the area of the membrane. With this partial pressure ratio the upper temperature difference of the air preheater reaches a limit. Therefore, a further reduction of the partial pressure ratio requires changes to other parameters as well.

5. Commercial oxy combustion

There are a number of pilot-scale facilities around the world, typically ranging in size from about 0.3-3.0 MW that has been used to characterise the combustion performance of coals under oxy-fuel combustion conditions. A number of demonstration projects ranging in size from 30 MW to 300 MW have been proposed [41-43].

Furthermore, large oxy-combustion plant analyses and configurations also have been completed. The Babcock & Wilcox Company (B&W), through its Power Generation Group, and Air Liquide (AL) have been actively involved in the development of oxy-coal technologies for power generation throughout the past decade [4, 44]. During 2007 and 2008, B&W successfully demonstrated oxy-combustion by using eastern bituminous, sub-bituminous and lignite coals. The oxy-combustion emission levels were all lower than emissions under air-blown combustion for all fuels. From 2009, B&W has been actively pursuing projects and partners for demonstrating CCS with oxy-combustion in the range of 50MW to 150MW. This size provided for commercial scale testing and also generated up to 1 million tons/year of CO_2 [45].

Other company that develop oxy combustion is Alstom. They started with lab scale (<3 MW) in 1990s. In 2012, they successfully demonstrated large pilot plant by using pulverized coal with capacity of 150-400 MW [46]. Nowadays, by using scale up modelling, they try to design full scale oxy combustion plant that will be operated in 2018/2019 with capacity of 600-1100 MW. Besides, there are some other large scale demonstration projects of oxy combustion that have or will be developed, such as Vattenfall's Jaenschwalde 30 MW Project (Germany), CIUDEN/Endessa's Compostilla OxyCFB300 Project (Spain), KEPCO's Young Dong Project (South Korea), FutureGen 2.0 Project (USA), and White Rose Project (UK).

6. Conclusion

Oxy-combustion has become one of the most attracting combustion technologies where the fuel and recycled flue gas are combusted with oxygen enriched air with the result that the flue gas consists mainly of CO_2 and water vapor. Some benefits can be obtained by oxy-combustion, such as increase efficiency, lower emissions, improve temperature stability and heat transfer, increase productivity, improve ignition characteristics, and low risk. Three branches of technologies have been developed to meet high concentration of oxygen to improve combustion efficiency, include distillation, adsorption, and membranes. A single pass through membranes can enrich the oxygen concentration in the air to 35% and a 50% concentration can be achieved with a double pass of membrane.

By increasing oxygen flux, the combustion process is improved slightly and the maximum temperature inside the reaction zone is increased a little bit. Besides, increasing the concentration of oxygen in combustion air allows a reduction in fuel usage. When oxygen concentration increases from 21% to 40%, energy saving of 60% can be achieved.

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