Techno-Economic Assessment of Polymeric, Ceramic and Metallic Membranes Integration in an Advanced IGCC Process for H_2 Production and CO_2 Capture

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In the present study, the integration of membrane technology in an Integrated Gasification Combined Cycle (IGCC) system has been considered, in order to reduce the power plant's CO_2 emissions. In this respect three different membrane materials was examined (polymeric, ceramic and metallic) taking into account the latest advances in membranes' development. The simulation of membranes separation performance was conducted in a Visual Fortran code and this was incorporated in an Aspen Plus flow diagram for the overall performance assessment. The energy analysis of the alternative cases show that CO_2 capture in this hybrid IGCC scheme is technically feasible but with an accompanying energy penalty in the power plant's output. Taking into account both technical and economic issues the most promising scenario seems to be the integration of a 2-staged ceramic membranes system for H_2 separation and CO_2 capture.

1. Introduction

The global warming potential, caused by the increased concentrations of CO_2 in the atmosphere can irreversibly affect the climate and the ecological systems. Considering the above there is a global awareness in order to find ways to reduce the anthropogenic CO_2 emissions. The latter is not only a social responsibility issue, but also a fact of political life, playing a growing role in business competition, since greenhouse gas emissions will be increasingly scrutinized, regulated and priced. Toward this direction CO_2 capture in power plants will probably be necessary in the near future. Literature studies have shown that Integrated Gasification Combined Cycle (IGCC) systems have the highest energy efficiency and the lowest environmental impact among the available technologies for coal-based electric power generation (Sadhukhan and Zhu, 2002). Carbon dioxide capture combined with IGCC power systems can be met by various technologies. Conventional methods such as chemical stripping, physical adsorption and cryogenics have been extensively examined in terms of overall process energy efficiency and cost. The main disadvantage of the conventional CO_2 capture methods is that they are energy intensive and reduce significantly the efficiency of the power plant, while at the same time increase the system's complexity. It is therefore necessary to examine new, less energy-intensive methods of pre-combustion CO_2 separation. A potential candidate method seems to be the application of different types of membranes, allowing the separation of gases at different temperatures depending on the type of membrane (Skorek-Osikowska and Janusz-Szymanska, 2012).
Membrane technology can offer several advantages compared to the conventional gas separation methods, such as low energy consumption, small size, simplicity of operation and maintenance,

compatibility and diversity. Moreover, membrane technology has significant environmental benefits, since its application does not result in pollutant by-products, such as spent solutions and solids, requiring further treatment and disposal. The use of membranes for various gas separation processes is an expanding field, which showed a major breakthrough in the 1970's due to the development of new polymeric membrane materials. Currently, industrial applications of gas separation polymeric membranes focus mainly on hydrogen recovery in oil refineries, natural gas purification and oxygen separation from air (Scott, 1990). The main disadvantage of polymeric membranes is their limited chemical and thermal stability. Thus, the last two decades have seen an important shift in research and development towards inorganic membranes (e.g. microporous ceramic and metallic membranes). These membranes exhibit high selectivities and high stability at elevated temperatures and in chemically aggressive atmospheres. Furthermore, their application in membrane reactors has proven to be very promising in order to enhance conversion in thermodynamically limited reactions (Hsieh, 1996). Although gas separation inorganic membranes are still immature for large scale application in energy systems, it is more and more often considered as potential candidates for H_2 separation and CO_2 capture in IGCC process schemes. Several investigators presented interesting results on various membrane materials for possible application in IGCC process. Diniz da Costa et al. (2009) examined the use of a cobalt doped silica membrane for the separation of H_2, Anantharaman et al., 2011 the use of oxygen transport membranes and Günther et al. (2013) the use of zeolite membranes. Amelio et al., 2007, showed that an integrated gasification gas combined cycle plant with membrane reactor is more convenient that a typical IGCC plant with Shift reactor. This conclusion is intensified by a later study of Franz and Scherer, 2011, in which the expected energy loss is calculated to 6.7 %. Schiebahn et al. (2012) showed that with the use of recirculation gas the energy loss drops to 4.5 %. Lima et al. (2012) conducted an optimization analysis of IGCC and membranes process examining various scenarios with respect to maximization of reactor performance and membrane use.

In a previous study (Kaldis et al., 2004) we conducted an energy and capital cost analysis of CO_2 capture in coal IGCC processes via gas separation membranes. We performed an overall process simulation using the Aspen Plus software package and we evaluated the impact of polymeric and ceramic membranes incorporation in the overall process efficiency. The results revealed that significant amounts of CO_2 emitted from future IGCC power stations in the atmosphere could be captured and mitigated, especially with the use of polymeric membranes. However, the energy penalty was estimated about 8–14 % units of total output (depending on the pressure and membrane stages) and a significant increased capital cost was indicated, especially for the ceramic membranes. It was concluded that additional improvements could be realized by the development of advanced materials for polymeric and ceramic membranes, which could further improve the competitiveness of membrane technologies. Since then, after about ten years of focused R&D, significant progress has been realized, especially in the field of inorganic membranes. The novel membrane production methods proposed the last decade, including the new innovative methods developed recently from our group for preparation of high-quality microporous ceramic membranes (Koutsonikolas et al., 2009, Koutsonikolas et al., 2011), turned much more efficient membranes. The recent advances in membranes' performance and cost, especially for ceramic and metallic membranes, may have significantly affected the results of previous studies. Therefore, in this study the new data (permeance, selectivity and cost) of state-of-the-art membranes were taken into account and the impact of CO_2 capture, via gas separation membranes, in a coal IGCC process' efficiency and economics was re-assessed.

2. Process simulation

Fig. 1 shows a simplified simulation diagram of the examined hybrid IGCC scheme. The coal gasifier is assumed to operate at conditions similar to the ones of the Puertollano Power Plant (1600 $^{\circ}$C and 16 bar). The process model formulation and material and energy balance computations were performed with the ASPEN PLUS software package in which each equipment is represented by selected unit operations blocks. Finally, for the membrane separation block, an algorithm was developed and incorporated into the ASPEN PLUS package, to simulate membrane module operation under a variety of temperatures, pressures, feed compositions and gas permeances (Kaldis et al., 1998, Kaldis et al., 2000). More details regarding the process simulation can be found in our previous study (Kaldis et al., 2004). Table 1 shows the basic membrane characteristics which were used in the present study. Polymeric membranes represent state-of-the-art H_2-selective polyetherimide membranes, assuming 0.2 μm film thickness, (Franz and Scherer, 2011), Ceramic membranes represent the state-of-the-art silica membranes used in our previous study (Kaldis et al., 2004), Ceramic (ALD) membranes represent the novel silica membranes developed recently from our group (Koutsonikolas et al., 2011) and Metallic membranes represent state of

the art Pd-based membranes, assuming a selectivity of 10,000 instead of infinity to account for micro-leakage diffusion, (Dolan et al., 2010).

Table 1: Basic membrane characteristics

	Polymeric	Ceramic	Ceramic (ALD)	Metallic
H_2 permeance	13.10-9 mol/(m2.s.Pa)	19.10-7 mol/(m2.s.Pa)	5.10-7 mol.m-2.s.Pa	6.10-4 mol/(m2.s.Pa0.5)
H_2/ N_2 selectivity	166	24	155	10,000
H_2/ CO_2 selectivity	5.9	3	100	10,000
H_2/CO selectivity	166	22	250	10,000

Figure 1: IGCC simulation diagram with Shift reactor and membrane separation

3. Results and discussion

The estimated gasifier product composition in mol fraction is H_2:0.238, CO_2:0.038, N_2:0.125, CO:0.526 and H_2O:0.073. This stream undergoes shift reaction, and the resulting gas stream (H_2:0.514, CO_2:0.374, N_2:0.112, in mol fraction free of water) is driven into the membranes. In Table 2 the mass balance results, which describe the composition of permeate and residue streams of various membrane scenarios are presented. In must be noted that these results are based on the maximum recovery of H_2 in the permeate stream and CO_2 in the residue stream for maximum energy exploitation and CO_2 removal respectively. It is obvious that these values are higher for the ceramic modified with ALD membranes and the metallic membranes where the H_2 recovery reaches about 90 % of the total feed H_2. The CO_2 recovery is much higher in the case of metallic membranes reaching almost 100 % of the total CO_2 fed. This drastic increase is accompanied, in both cases, with considerable increase in H_2 and CO_2 purity in permeate and residue streams respectively, due to the higher selectivity of the specific membranes. However, the reduction of the permeate production for the high selectivity membranes, as it is shown in the obtained stage cut values, is expected to have a direct impact in energy output.

In order to recover additional quantity of energy-exploitable gas in the permeate stream an additional membrane stage is introduced for the case of ceramic membranes modified with ALD. In this 2-stage scheme the residue stream of one stage is fed to the next. With this configuration there are no energy needs for gas compression and the operating cost is thus minimized. In this case, the H_2 recovery in the permeate stream increases substantially compared to both single stage ceramic (ALD) and metallic membranes.

At the same time CO_2 recovery decreases but it is counterbalanced by the fact that the subsequent CO_2 purity in the residue stream reaches concentration levels well above the mitigation acceptable limits, which is estimated to be around 70 % (Van Der Sluijs et al., 1992). The basis of this estimate is not clearly stated in the original reference. However, thermodynamic calculations on CO_2-N_2 vapor-liquid equilibria, using the ASPEN PLUS database, show that CO_2 liquefaction is not possible at 10-20°C and 60-100 bar if the gas mixture contains less than about 70 % CO_2. These temperature and pressure values are typical for deep ocean and geological disposal of liquefied CO_2.

Table 2: Mass balance analysis of various membrane scenarios performance

	Polymeric	Ceramic	Ceramic (ALD)	Ceramic (ALD) 2-stages	Metallic
H_2 permeate purity, mol fraction	0.756	0.644	0.969	0.875	0.999
H_2 permeate recovery, %	92.9	95.5	90.0	93.0	90.5
CO_2 residue purity, mol fraction	0.603	0.498	0.692	0.753	0.699
CO_2 residue recovery, %	59.3	31.6	96.7	92.6	99.9
Stage cut, permeate to feed fraction	0.632	0.763	0.478	0.584	0.465

Table 3 shows an energy analysis of the various scenarios. For comparison, a base case is also presented, corresponding to a 440 MWe IGCC power station operating at 16 bar. The net energy output of the process is the sum of the gas turbine power and the steam turbine power. The steam turbine power is calculated from the heat produced in the gasifier, the shift reactor and the burner, with a 37.5 % net steam cycle efficiency.

The introduction of the shift reactor reduces the total process energy output by 52 MW, mainly due to the consumption of some of the produced stream for the specific reaction. The estimated energy efficiency drop due to the use of membranes (76-110 MW) is attributed mainly to: (i) The energy consumption for membrane permeate stream re-compression before it enters the gas turbine, and (ii) the lower steam cycle output, due to lower gas quantities exploited.

The use of polymeric membranes gives high gas turbine power due to the higher permeate stream driven in the turbine (c.f. stage cut in Table 2) and the relatively high permeate purity. It is evident that in the case of simple ceramic membranes the gas turbine power is lower than that of polymerics because of the lower H_2 purity although they deliver higher amount of permeate. Consequently in the cases of ceramic-ALD and metallic membranes the gas turbine power is slightly lower due to the lower stage cut, although the permeate H_2 purity is higher. In the case of 2-stage ceramic membranes the produced power is substantially increased due to the improvement of the stage cut. The use of ceramic and metallic membranes, gives a better gas turbine power output due to the higher temperature of the gases. At the same time, however, more energy is required for permeate re-compression due to the higher quantity of this stream. Thus, it is obvious that the higher stage cut does not necessarily leads to higher gas turbine power. There is an optimum value, which is met in the case of 2-stage ceramic ALD membranes.

In the case of steam turbine power the lower values are observed in the cases of ceramic-ALD and metallic membranes due to the lower stage cuts and subsequent lower quantities of gas streams exploited in the burner. This is more clear in the case of 2-stage ceramic-ALD membranes where an increase of the stage cut leads to substantial improvement of the steam turbine power.

The total power output is higher in the case of 2-stage ceramic-ALD membranes, which leads us to the conclusion that the specific membrane material and configuration is the optimum in terms of energy production. However, this option requires higher membrane area, which is directly proportional to membranes investment cost.

The required membrane area (relative to the area of polymeric membranes) for each different scenario is also included in Table 3. The calculated membrane are depends mainly on membrane's permeance as well as the developed concentration profiles in the membrane module. It is obvious that polymeric ic

membranes requires the highest membrane area, mainly due to the low membrane's permeance. The required membrane area is about 160, 33, 4.8 and 14.4 times lower for the ceramic, ceramic-ALD, 2-stages ceramic ALD and metallic membranes respectively. However, one should note that the cost of polymeric, ceramic and metallic membranes has exactly the opposite order regarding their permeance., with metallic membranes to be the most expensive membranes, ceramic membranes to be about 5 times cheaper and polymeric membranes to be about 100 times cheaper. In any case it should be noted that membranes offer lower operating, labor and land cost relative to the conventional separation technologies, because of the compactness and simplicity of this technology and their operation at the pressure of the gasifier output stream without further compression requirements. Indicatively, the operating of cost polymeric membranes per year is about 35 % of their capital cost, including membrane replacement cost (Van Der Sluijs et al., 1992). For the inorganic membranes this figure is considerably higher reaching almost a 100 % of the membrane capital cost per year (Griscuoli et al., 2001).

Table 3: Energy analysis and capital cost estimation of various membrane scenarios.

	Base case	Base case & Shift	Polymeric	Ceramic	Ceramic (ALD)	Ceramic (ALD) 2-stages	Metallic
Gas turbine power, MW	293	249	214	205	210	234	212
Steam turbine power, MW	147	139	136	130	120	130	121
Total power, MW	440	388	350	335	330	364	333
Required membrane area	-	-	A	$6.25 \cdot 10^{-3} \cdot A$	$0.03 \cdot A$	$0.21 \cdot A$	$0.07 \cdot A$

4. Conclusions

The results of this study clearly showed that CO_2 removal in IGCC processes schemes is technically feasible. Significant amounts of CO_2 emitted from future IGCC power stations in the atmosphere can be captured and mitigated, especially with the use of presently available, state of the art inorganic membranes, which can be used for attaining both high H_2 and CO_2 recoveries, as well as the required CO_2 purity for the subsequent CO_2 storage. Taking into account both technical and economic issues the most promising scenario seems to be the integration of a 2-staged ceramic membranes system for H_2 separation and CO_2 capture. However, the energy penalty is substantial and its reduction should be further examined. In this direction it seems that the inorganic membranes' materials performance is adequate and therefore more sophisticated steam cycle and gas turbine designs as well as membrane separation designs (e.g. use of sweep gas or higher pressures) must be considered in order to achieve a lower energy penalty.

Acknowledgements

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