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Evaluation of Oxygen-Enriched Air Combustion Process Integrated with CO_2 Post-Combustion Capture

Adewale Adeosun, Aravind Muthiah, Mohammad R. M. Abu-Zahra*

Separation Technology Laboratory, Masdar Institute of Science and Technology, P.O. Box 54224, Abu Dhabi, United Arab Emirates

Abstract

A novel concept combining membrane-based technology for air enrichment combustion process integrated with solvent-based post-combustion capture is evaluated using Aspen Plus® process simulation tool. The aim of this integrated concept is to reduce the amount of Nitrogen used in the combustion process and as a result increase the CO_2 concentration in the flue gas. The effects of the increased CO_2 concentration on liquid-to-gas molar flow ratio, solvent flow rate, reboiler duty and washing water requirement are evaluated. Based on the cost analysis for the air separation unit and the CO_2 capture solvent flow rate and washing water requirement, the optimum enrichment level of air was found to be 35% O_2. However, in term of CO_2 mole concentration in the flue gas and liquid-gas molar ratio in the absorption process, 40% enrichment shows highest value of 28.22% and 7.15, respectively. No significant benefit is observed in terms of reboiler duty as expected due to the fixed amount of CO_2 captured and the limited increase in the solvent rich loading. On the other hand, the flue gas flow rate was reduced dramatically at higher CO_2 concentration, which will result in a smaller absorption tower and consequently a lower capital investment. In addition, with improved membrane technology that can work at lower air inlet pressure and with higher oxygen permeability and selectivity, the target energy reduction is achievable. These results encourage a full scale economic evaluation of the novel process of combining enriched air combustion and AMP-solvent based post-combustion capture to be conducted in order to weigh enrichment costs to absorber size reduction economic benefits.

Keywords: *Carbon Capture, Post Combustion, Membrane, Coal power plant, Simulation*

1. Introduction

The impact of climate change is becoming increasingly evident, posing significant challenge, both in the political and scientific arenas. The emission of greenhouse gases has been reported to be the main cause of global warming [1,2,3]. To mitigate impacts, carbon dioxide capture and storage (CCS) is expected to play significant role [4]. Since power plants, transportation, cement, metallurgical industries among others constitute the largest source of greenhouse gas emission [5], it becomes vivid why technology research is focused on capturing CO_2 emissions from stationary sources.

Three key technologies are currently available for CCS, an overview of which is described in Figure 1 [6]. Post-combustion capture technology is focused on separating carbon dioxide from the flue gas using conventional chemical absorption or other novel options such as adsorption. Pre-combustion capture technology is centered on fuel gasification, syngas shifting and extracting hydrogen from fuel through gasification. Oxyfuel combustion technology involves the combustion of fuel in pure oxygen, leading to high purity CO_2 effluent. However, techno-economic evaluations of the various technologies indicate that there is yet to be found the winning technology [7,8]. The winning technology will be one which meets the roadmap targets in terms of operating energy penalty, low cost of CO_2 avoided and a reduction on capital investment [9].

Novel process involving membrane-based air enrichment, integrated with post-combustion capture technology is attracting attention [10, 11]. In fact, energy penalty reduction by 35% is reported to be achievable [12]. In this work, Aspen Plus is used to evaluate air enrichment, fuel combustion using the enriched air and the post-combustion capture with a view to evaluating enrichment impacts on flue gas composition, liquid-to-gas ratio, washing water requirement and reboiler duty. The novel evaluated concept is illustrated in the block diagram shown in Figure 2.

* Corresponding author. Tel.: +97128109181
E-mail: mabuzahra@masdar.ac.ae

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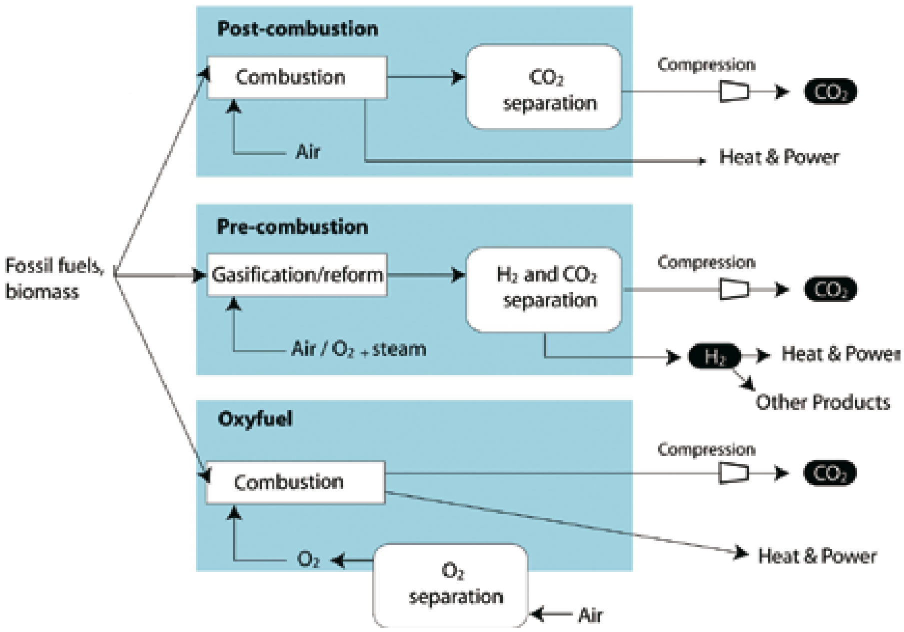

Fig.1. Schematic representation of the different capture systems [6]

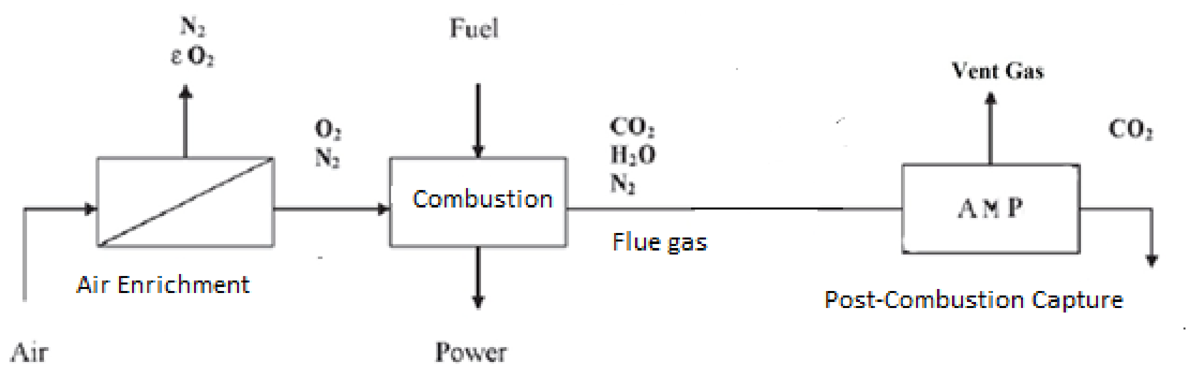

Fig.2. Block diagram of enriched air combustion with AMP-solvent based CO_2 capture

2. Background

Global dependence on fossil fuel is expected to increase until the middle of the century, especially from the emerging economies in Asia and Africa. New coal- and gas-fired power plants will be built in order to meet the growing demand for electricity and other industrial needs. To ensure that 50% CO_2 reduction target is met, key technologies including CCS, nuclear energy, improved energy/process efficiency, fuel switching and renewable energy utilization are promoted by International Energy Agency [4]. For CCS, Post-combustion technology is the near term option for industrial deployment due to its retrofitability to existing power plants, suitability to low CO_2 partial pressure systems and process maturity, as applied to gas sweetening [13]. However, large scale implementation for CO_2 capture is plagued with high energy penalty and the capital intensive nature of the capture plant for the monoethanolamine (MEA)-based chemical absorption. This leads to increased power generation cost.

Efforts have been made to improve the process for economic viability. For example, major energy savings are reported through parametric optimizations involving lean solvent loading, amine solvent concentration, stripper operating pressure, capture ratio, process temperature and pressure [9,14]. However, MEA-based PCC has been identified to have low absorption capacity, low cyclic capacity, high degradation rate, high equipment corrosion rate and high regeneration energy requirement [15]. This has necessitated research into other classes of amines including sterically-hindered-amines (e.g. AMP), secondary, tertiary amines and heterocyclic amines including piperazine.

In addition, smart process design, novel integration and advanced solvents are to be investigated to make CO_2 capture economically feasible for industrial deployment [9]. Other efforts consider the option of increasing the CO_2 concentration in the flue gas stream either by recycling the flue gas with fresh air over the boiler or by utilizing the concept of air enrichment [16,17,25]. Both options are expected to be beneficial to the overall capture scenario due to expected reduction in flue gas flow rate. Thus, smaller absorber/desorber columns will be required under these conditions. The capital investment cost, cost of CO_2 avoided and the cost of electricity will be reduced. Based on these aforementioned benefits, this work evaluates membrane-based air enrichment integrated with post-combustion capture is applied to a coal-fired power plant using Aspen Plus simulations.

3. Process and Simulation Description

3.1. Air Enrichment

Cryogenic separation has been the choice for high purity oxygen production for large scale production among the various available technologies as depicted in Table 1 [18]. However, the energy penalty associated with the subzero operations with the attending high capital investment in terms of equipment size and waste energy has led to finding alternatives. Modern membrane engineering has been seen as one of the future technologies to meet the roadmap targets for high CO_2 flue gas concentration; hence the need for enriched air combustion [19, 20].

Table 1. Oxygen production technology alternatives[18].

Process	Status	Byproduct Capability	Purity (vol%)
Cryogenic	Mature	Excellent	99+
Adsorption	Semi-mature	Poor	95
Polymeric membrane	Semi-mature	Poor	≈40
Chemical	Developing	Poor	99+
Ceramic Membrane	Developing	Poor	99+

The choice of membrane in this work is based on permeability, selectivity, material structure and thickness and operating temperature. Recent work of Robeson [21] showed that membranes made of polymers of intrinsic microporosity (PIM) have better material properties and better trade-offs between oxygen permeability and oxygen-nitrogen selectivity. The properties needed for the simulation is presented in Table 2.

As a pressure-driven process, compressor with isentropic efficiency of 85% and mechanical efficiency of 95% was selected for the simulation with outlet pressure values of 3, 5, 10, 15, 20 and 30 bar for the parametric studies. For each of these pressure values, the corresponding membrane area is determined using the mathematical relation in Equation 1 [12] and the compressor cost is determined from the electrical energy consumption as obtained from simulations.

Table 2. Membrane Modeling Fixed Parameters

Parameter	Value	Unit	Reference
Oxygen Permeability	100	Barrer	[23]
Thickness of membrane	2.00E-06	m	[24]
Pressure on permeate side	1.013	bar	
Cost of membrane	45	$/m^2	

$$\frac{Q_p y_A}{A_m} = \frac{P_A}{l}(p_h x_A - p_l y_A) \tag{1}$$

The optimum pressure is determined from total capital cost plot against the pressure. The capital cost accounts to the membrane and compression costs only. Separator unit was chosen to model the membrane in the simulation and the process considers 25%, 30%, 35% and 40% air enrichment subjected to the limitation for polymeric membranes as indicated in Table 1. Economic evaluation is restricted to the enrichment section.

3.2. Power Plant Description

The conventional power plants, novel and advance combustion processes and their related gaseous emissions are well established technology as discussed intensively in open literature [26, 27, 28, 29]. Figure 3 shows the power plant simulation with the enrichment section. The power plant simulation involves coal crushing, enriched air combustion, steam turbine electricity production, flue gas cooling and recirculation section. Due to the pressure gradient and the higher selectivity and permeability of the chosen membrane, enriched air is produced and pumped into combustion furnace. Assumptions for power plant simulations include the following:

- Fuel rate of 3kg/s is considered in all cases.
- Lean fuel combustion at 5% excess oxygen in the hot gas from the furnace. This is essentially set to justify complete combustion of coal assumption.
- Since increased oxygen relative to nitrogen composition is expected to lead to higher combustion temperature, flue gas is recirculated with fresh enriched air to keep the boiler temperature at 1400°C. This temperature is well below the fuel adiabatic flame temperature and therefore hinders the thermal NOx formation which is promoted beyond1800°C [22].

Coal typically delivered at the power plant as non-pulverized and characterized with different sizes that can reach several centimeters. Therefore, crushing of the coal is important to increase the specific surface area per unit volume. Also, complete combustion of the fuel can be achieved when the particle size distribution is within the range of 180 to 360 microns. Multistage crushing model is used; with multiple screens to sieve the coal particles to the appropriate size. To ensure a reduction in the power consumption by the crushing process as a result of solid transport, the coal particles are mixed with water. This leads to addition in the coal particle moisture content up to 15wt%.

In Aspen Plus simulation, the final coal particles were separated from the conveying water stream through a SEP2 unit. The coal properties were established on chemical species associated with both conventional and non-conventional feedstock specifications. For the physical property, Peng-Robinson with Mathias modification was used to model gas phase behavior. Elemental composition reactions are used to represent coal combustion summary of the coal proximate and ultimate properties, the coal fuel feed composition is given in Table 3. At this combustion temperature and particle size, the burner is modeled with RGibbs reactor, achieving equilibrium achieved through the Gibbs free energy minimization. After combustion, the particulate matters are separated from the flue gas using SSplit model as an electrostatic precipitator. The hot gas stream is then used to produce superheated steam at 500°C and 35atm pressure, modeled using two heater unit operations. This is subsequently used to be expanded in a steam turbine which is coupled with electric generator for electricity production. Before the flue gas is channeled to the stack, it is subjected to desulphurization and it is modeled using separator and cooler units.

Table 3. Coal Feed Composition [30]

Component	weight %
Moisture	9.535
Fixed carbon	50.909
Volatile matter	39.452
Ash	9.639

3.3. Post-Combustion Capture Description

Though, AMP has lower reaction kinetics than MEA, it is appropriate for enriched air post-combustion capture simulation. This is because the potential higher cyclic loading of AMP that can be harnessed, compared to MEA at higher CO_2 partial pressure [25]. This will lead to lower solvent rate and higher liquid-to-gas ratio, thus smaller absorber size. A reduction in the condenser water rate is expected due to AMP low vapour pressure. This can ultimately lead to elimination of washing section, and reducing further the capital expenditure.

The process flow sheet diagram is presented in Figure 4. The flue gas is set to 1.2 bar pressure and 50°C temperature. Each of the obtained flue gas streams is simulated for the scrubbing using Radfrac unit as the absorber, with 4 stages and a pressure drop of 10kPa. The rich solvent from the bottoms of the absorber is pumped to 2.3 bar pressure to enhance the CO_2 desorption in the stripper. The pressurized rich solvent stream passes through a cross heat exchanger where it receives heat from the stripper bottom outlet stream. This cross heat exchanger is an important heat integration option to reduce the amount of thermal energy required for the feed stream entering the stripper for regeneration. The stripper is modeled using Radfrac with 6 stages, 1.8 bar column bottom pressure and 30kPa column pressure drop.

The constraints used for the simulation is 90% CO_2 recovery by mole and less than 97% CO_2 mass fraction in the CO_2 stream from the top of the stripper. The simulation is done with a heat exchanger design given by the difference in the hot stream outlet temperature and the cold stream outlet temperature. In this case, 5°C is chosen.

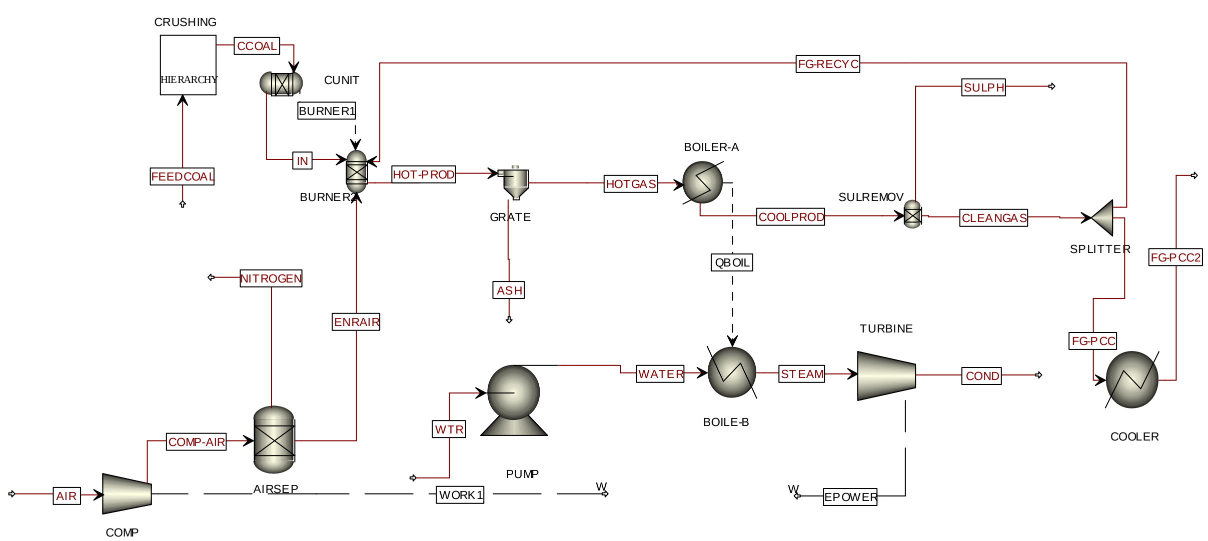

Fig. 3. Coal-fired power plant with air enrichment section simulation process flow sheet

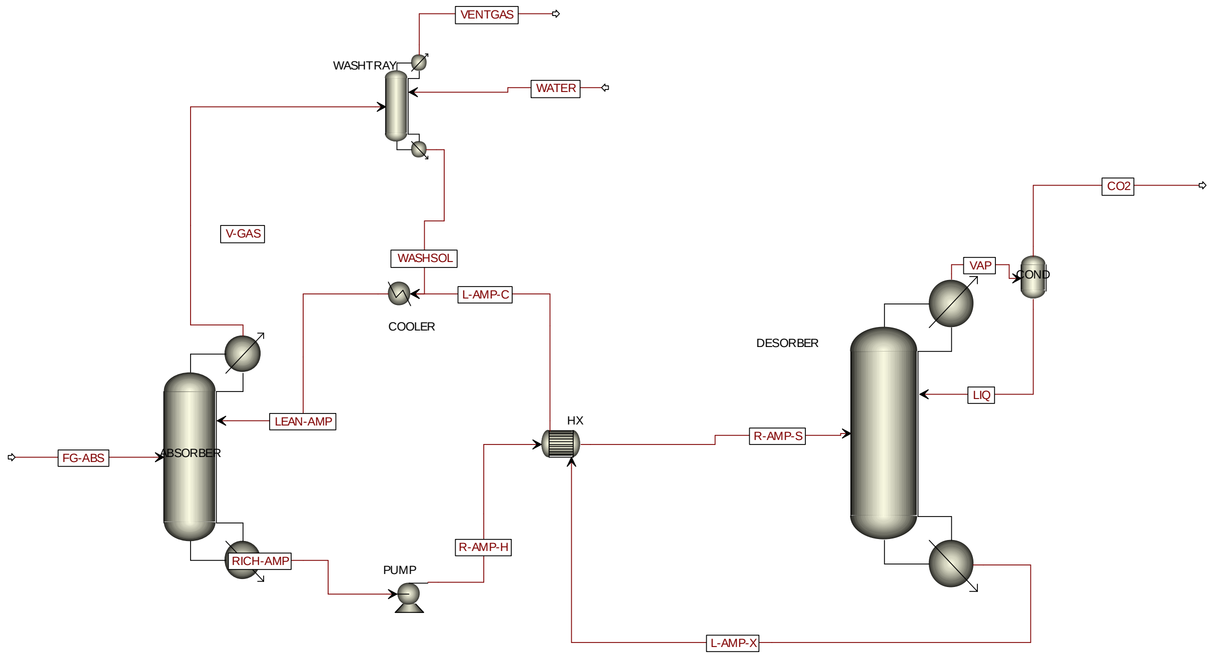

Fig. 4. Post-combustion CO_2 capture simulation process flow sheet.

4. Results and Discussion

4.1. Air Enrichment Result

Figure 5 shows the total cost against pressure for four oxygen enrichments levels. It is observed that the cost is higher at low pressure and as the enrichment percentage increases. However, at higher compression, the cost flattens out for pressure above 19 bars. The observed result implies that increasing the air inlet compression cost is counterbalanced by reduction in membrane cost of the same order of magnitude as a result of a smaller membrane area requirement. Figure 6 elaborates on one of the oxygen enrichment as an example of 25% enrichment. The optimum pressure in this specific case is found to be 11.5 bar, giving a total membrane and compression cost of US$180 million. Figure 7 shows a plot of optimum pressure against total cost and the enrichment. As expected, the minimum cost at optimum membrane inlet pressure increases with increasing enrichment ratio. At 40% air enrichment, carbon dioxide mole percent rises to 28.22% with optimum pressure of 17.5bar. This CO_2 concentration is about twice the observed concentration for conventional air combustion process.

4.2. Combustion Result

The combustion process is simulated with flue gas recirculation in other to avoid increased NOx concentrations due to higher oxygen concentrations from enrichment. Flue gas is recycled to achieve 1400°C hot gas temperature from the furnace. Table 5 gives the recycle ratio required to obtain the temperature set value. The result shows that significant amount of the flue gas must be recycled. In the case of 40% enrichment, above 60% is recycled, about twice the requirement in the case of convention combustion process. This reiterates the significant importance of nitrogen as a diluent in combustion process. With this air enriched concept, more detailed study should be carried out to evaluate the effect on the combustion process efficiency, operation and emissions.

4.3. Post-Combustion Capture Result

Table 4 shows liquid-to-gas ratios and reboiler duties while Table 6 presents the solvent flow rates and washing water flow rate requirements for various enrichments. In both tables, values are compared with AMP-based post-combustion capture values using conventional air of 21% oxygen by mole. The liquid-to-gas flow rates increase with increasing air enrichment. This is expected due to the reduction in the gas flow rate from air enrichment. With the same amount of fuel used in combustion process and same amount of CO_2 to be captured, the liquid flow rate requirement is marginal in difference for various enrichments. In terms of the reboiler duty, there is marginal decrease as the enrichment proportion increases, which directly connected with the increase in the solvent rich loading. With the air enrichment (N_2 decrease), the CO_2 concentration increases in the flue gas, the composition of the rich solvent to the stripper is also increased. This is the critical factor that determines the reboiler duty. From table 5, it is observed that 35% air enrichment has the lowest solvent flow rate of 15.36 L/kg-CO_2 and lowest washing water requirement of 0.02 L/kg-CO_2. Essentially, 40% air enrichment is expected to have smallest absorber size reduction due to its lower liquid-gas ratio. When compared to the reference case of conventional air combustion with AMP scrubbing with 4.38 liquid-to-gas ratio, air enrichment of 40%. shows 44% decrease in flue gas flow rate, leading to 63% increase in liquid-to-gas ratio. Since absorber typically represents 50% of purchased equipment cost and gas path equipment constitutes 75% of total capture equipment cost [9], a significant reduction in absorber size is expected at constant liquid flow. 25%, 30% and 35% enrichments show 14.8%, 27% and 37% reduction in flue gas flow rates respectively, indicating expected benefits in terms of reduced equipment cost from smaller absorber size.

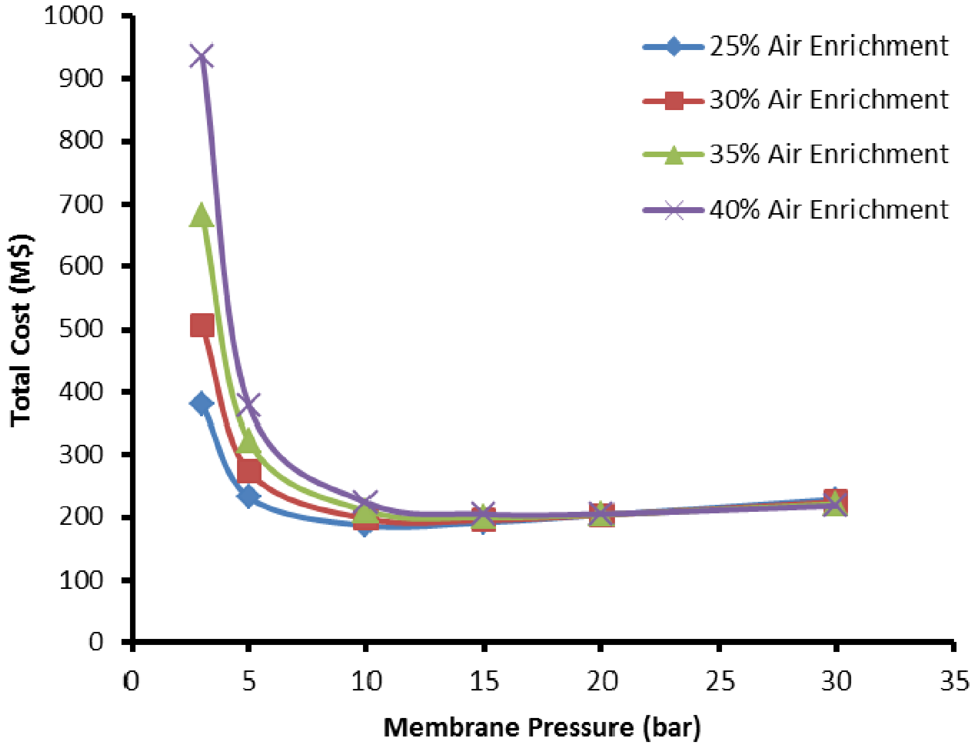

Fig. 5. Plot of total cost against membrane pressure

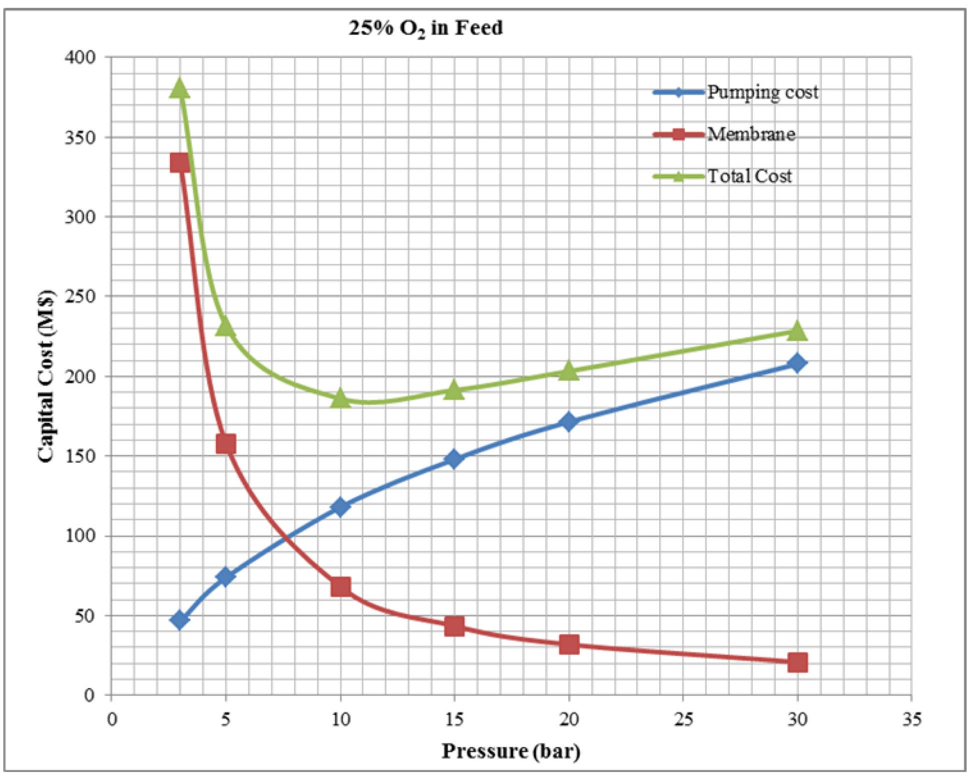

Fig. 6. Cost vs. membrane inlet pressure plot for 25% enrichment.

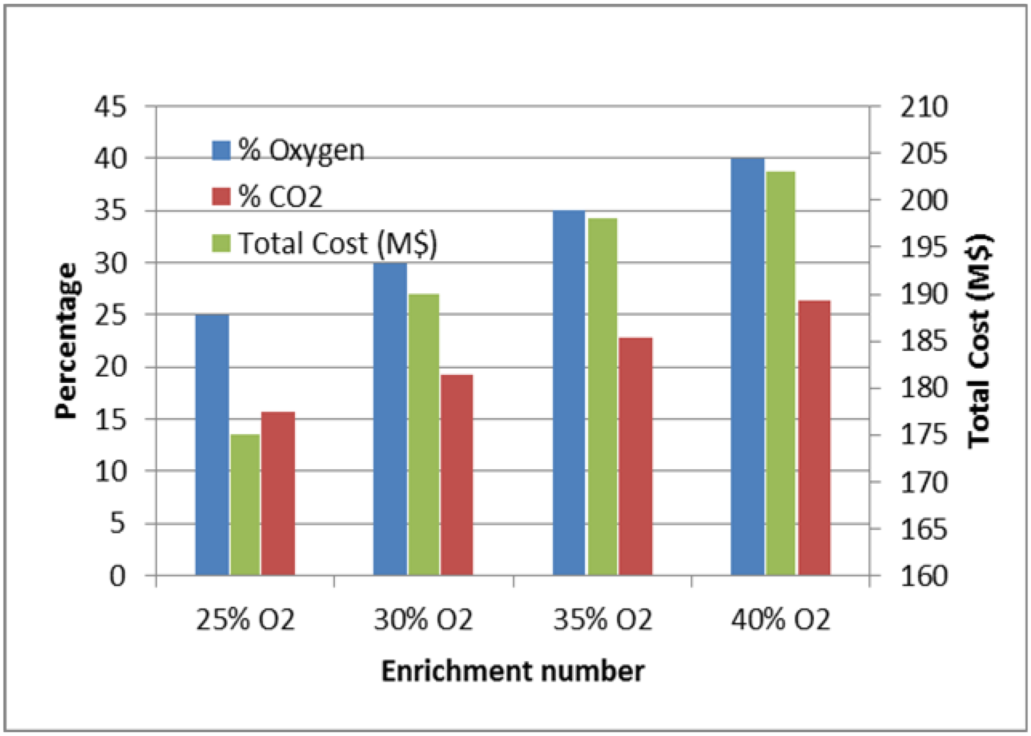

Fig. 7. CO_2 concentration and total cost results for air enrichments

Table 4. Flue gas recirculation vs. enrichment ratio

Oxygen Enrichment (%)	Recycle Ratio
21	0.334
25	0.427
30	0.507
35	0.564
40	0.605

Table 5. Liquid-to-gas ratio and reboiler duty simulation result for enrichments

Oxygen Enrichment (%)	L/G Ratio (mol/mol)	Reboiler Duty (GJth/ton-CO2)	Rich loading) (mol/mol
25	5.54	3.126	0.497
30	5.76	3.093	0.523
35	6.12	3.067	0.542
40	7.15	3.047	0.541

Table 6. Solvent flow rate and washing water requirement

Oxygen Enrichment (%)	Solvent Flowrate ($L/kg-CO_2$)	Washing Water rate ($L/kg-CO_2$)
21	16.93	0.16
25	17.38	0.06
30	16.10	0.05
35	15.36	0.02
40	15.50	0.05

5. Conclusion

Air enrichment combustion process integrated with CO_2 post-combustion capture in coal-fired power plant was evaluated. Membrane made of polymers of intrinsic microporosity is used for the enrichment due to its permeability and selectivity for oxygen. The optimum pressures for 25%, 30%, 35% and 40% enrichment are determined using the minimum total cost of compression and membrane. The combustion process is designed to produce hot gas at 1400°C, using flue gas recirculation and 5% excess oxygen design specifications. The flue gas CO_2 composition increased to 28% on molar basis for 40% oxygen enrichment. 35% oxygen enrichment shows lowest solvent flow rate and washing water requirement.

The result shows that the main benefit of the enrichment on post-combustion capture is the reduction of the flue gas flow rate, which clearly results in a reduction in the absorber size, introspectively leading to reduced capital cost. The increase in the solvent rich loading and the decrease in the solvent regeneration energy were found to be very marginal. With advances in membrane technology, greater reduction in cost can be expected in the enrichment section. As more advanced solvents are developed, enriched air combustion with post-combustion capture will lead to more significant cost reduction.

As a future research work, a full scale economic evaluation of this novel process combining enriched air combustion and post-combustion capture will be conducted to weigh the enrichment cost to absorber size reduction economic benefits.

Nomenclature

Q_p	air volumetric flow rate
y_a	oxygen outlet mole fraction.
A_m	membrane area.
P_A	oxygen permeability.
p_h	inlet air pressure
p_l	outlet air pressure
x_A	oxygen inlet mole fraction.
L	membrane thickness

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