CO_2 Capture via Oxyfuel Firing: Optimisation of a Retrofit Design Concept for a Refinery Power Station Boiler

Michael B Wilkinson (wilkinmb@bp.com; +44 1932 763369)
John C Boden (bodenjc@bp.com; +44 1932 762783)
BP
Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK

Raghbir S Panesar (rpanesar@mitsuibabcock.com; +44 141 885 3921)
Mitsui Babcock
Technology Centre, High Street, Renfrew, PA4 8UW, Scotland, UK

Rodney J Allam (allamrj@apci.com; +44 1932 249935)
Air Products
Hersham Place, Molesey Road, Walton-on-Thames, Surrey, KT12 4RZ, UK

ABSTRACT

A previous study by the present authors demonstrated that the capture of carbon dioxide (CO_2) from an existing large refinery power station boiler by conversion to oxygen firing with flue gas recycle is feasible and could be based on proven, available equipment. The study covered the systems for air separation, firing, boiler operation and CO_2 separation and compression, and predicted the overall performance of the plant, the requirements for major new items of equipment and budget capital and operating costs. Further work has now been carried out to resolve key remaining uncertainties and to optimise the design.

The new work reported here has considered in more detail the sensitivity of the plant performance and costs of conversion to such critical factors as the purity of the oxygen supply and the extent to which the boiler plant can be sealed against air ingress (tramp air). The effect of different levels of furnace modelling and the potential for plant integration have been reviewed. Significant opportunities for cost reduction compared with the previous study have been identified and the results will allow more cost effective oxyfuel plant designs and more reliable comparisons with alternative CO_2 capture technologies.

INTRODUCTION

In order to understand the practicalities and costs of applying oxyfuel for CO_2 capture within its own operations, BP joined with Mitsui Babcock and Air Products to carry out a detailed feasibility study on a specific oil and gas-fired refinery power station boiler, concentrating on the firing of refinery off-gas (1). This study demonstrated the feasibility of the conversion using available equipment. It also highlighted the requirement for further studies to reduce uncertainties and overall costs. These new studies are reported here.

Combustion with oxygen instead of air is one of the more promising techniques for CO_2 capture from boiler plant. CO_2 is easily separated from the flue gas, which is largely CO_2 and water, and the technology is applicable to any fossil fuel. In order to allow conventional combustion equipment to be used, the combustion temperatures have to be moderated by recycling a proportion

of the flue gases and mixing this with the incoming oxygen. Pilot and laboratory scale studies, firing coal, have indicated that the technique is feasible (2-5). There have also been theoretical studies of its possible application to coal-fired power stations (6, 7), but there has been no commercial installation and little work on fuels other than coal. Hence it was decided to carry out these studies.

OBJECTIVE

The earlier study identified the following areas where further work could either improve the performance predictions or reduce overall costs. The objective of the present work was to address these issues.

- More detailed furnace thermal performance modelling.
- Sensitivity to burner flame luminosity and furnace flue gas emissivity.
- Boiler performance on turndown.
- Heavy fuel oil firing.
- Sealing the boiler against tramp air ingress.
- Supply oxygen purity.
- Energy enhancement through plant integration.
- Materials selection for the flue gas carbon dioxide treatment process.

PROJECT DESCRIPTION AND RESULTS

Boiler Type and Oxyfuel Process

The refinery power station boiler used as a basis for these studies has an evaporation rate of 500,000 lb/hr at maximum continuous rating (MCR) and generates superheat steam at $518^{o}C$, 129 bar abs. The steam is used to cogenerate power and process steam for the site. The boiler is a natural circulation, radiant, two-pass unit and is designed to fire two fuels, heavy oil and gas.

Figure 1 is a simplified representation of the oxyfuel process concept. The flue gas leaving the boiler is split into two streams. Approximately one third of the boiler exit flue gas provides the exhaust stream to feed the CO_2 compression and inerts removal system via the gas cooler. The remaining two-thirds is returned to the boiler unit by a flue gas recycle (FGR) fan to moderate the combustion temperatures. The quality of the CO_2 product was specified for transportation by pipeline and injection into a generic oil reservoir for enhanced oil recovery (EOR). Water was limited to <50 ppm molar to minimise corrosion in the transportation system. Reservoir engineers advised that the nitrogen plus argon should typically be limited to <3% by weight. No restrictions were placed on NOx, SOx, hydrocarbons, carbon monoxide or oxygen. The pressure was defined as 101 bar abs. The study assumed a refinery fuel gas molar composition of H_2 27.0%, C_1 13.0%, C_2 20.3%, C_3 27.7%, C_4 7.0%, C_5 3.0%, H_2S 1.0% and N_2 1.0%.

More Detailed Furnace Modelling

Previously, detailed furnace and boiler models were set up using Mitsui Babcock's proprietary boiler design programs. The furnace model calculated heat transfer within the firebox. The boiler model included, in addition, the heat transfer within the convection sections and the performance of the steam system. These models were used to analyse the impact of heat transfer on furnace and boiler performance for oxyfuel firing of refinery fuel gas.

The furnace heat transfer model was retained for the present work. The grid employed, which incorporated 170 gas zones, is shown in Figure 2. In order to improve the accuracy of the prediction of local furnace heat fluxes and hence overall furnace performance, a computational fluid dynamics (CFD) modelling package was now used to generate the furnace flue gas flow-field data for input to this furnace heat transfer model. The use of CFD enabled a more detailed prediction of the flow pattern data and hence overcame the limitation of the less rigorous flow-field information used in the original calculations. Figure 3 presents an isometric view of the CFD isothermal furnace model. Typical furnace flue gas flow patterns predicted under oxyfuel firing conditions are shown in Figure 4.

At near 100% MCR boiler operating conditions, the performance change from air firing to oxyfuel firing using CFD derived flue gas flow pattern data was very similar to the performance change predicted from the original flow pattern data. In general, the furnace absorption was seen to increase by some 10% due to an increase in radiative power of the hot flue gas and as a result the furnace exit gas temperature is reduced by some 50°C. For the same fuel gas firing rate, the boiler steam output with oxyfuel firing was projected to be higher by some 5% due to the increase in evaporation rate, with a slight increase in boiler efficiency. The increase in the furnace heat flux together with the increased evaporation rate will have minimal effect on the furnace tube wall metal temperature, and hence will lead to little or no reduction in operating life.

Sensitivity to Flame Luminosity and Flue Gas Emissivity
One of the uncertainties in characterising oxyfuel flames with flue gas recycle is the flame luminosity, which will have an impact on the furnace heat transfer. As a first approximation, the original study assumed the burner flames under oxyfuel firing conditions to be luminous. The sensitivity of the furnace performance to this parameter was examined by varying the original flame luminosity by ± 25% and also by considering the case of a non-luminous flame, which might be approached with some burner types. Outside the burner region the non-luminous flue gas emissivity was calculated using the partial pressures of the strongly radiating gaseous components, carbon dioxide and water vapour, together with the furnace geometry, and as a further check the sensitivity of the boiler performance to variations of ± 10% in this emissivity was assessed.

It was found that the furnace performance was relatively insensitive to both these parameters within the ranges considered, except for the case of a non-luminous burner flame where demand in the superheat spray could exceed the capacity of the existing attemperators. Attemperators are designed to control the final steam conditions by means of a water spray into the steam between the primary and secondary superheaters, and in this case it may be necessary to modify the attemperator by increasing the capacity of the attemperator nozzle and its associated control valve.

Boiler Turndown Operation
Boiler operation at the full turndown condition of 30% MCR was examined to identify any further operational issues and to assess the risk of low temperature corrosion in the flue gas recycle system. The furnace and boiler performance models showed that the change in performance in converting to oxyfuel operation at a load of 30% of MCR was similar in trend to that at near full boiler load conditions described above, ie an increased evaporation rate and a reduced furnace exit gas temperature. A similar proportion (two-thirds) of flue gas recycle was necessary to maintain the same adiabatic flame temperature as that of 30% MCR air-firing.

One of the main concerns when operating the boiler in oxyfuel firing mode at the turndown condition is the possibility of low temperature corrosion. The boiler exit flue gas temperature was found to be close to the acid dew point of the flue gas. However, the comburant (i.e. recycled flue gas mixed with oxygen) temperature was some 10°C below the dew point. One possible method of increasing the flue gas temperature at the boiler exit (and hence the comburant temperature) is to

increase the amount of flue gas recirculation (from 67% to some 75-85%). With the higher recycle rates, burner stability becomes more of an issue and this would need to be taken into consideration at the burner design stage. Another solution would be to increase the boiler feedwater temperature by integration with the air separation unit (ASU), which is discussed below. The level of increase in feedwater temperature required should not present any problems to boiler performance, provided the economiser outlet water temperature is low enough to avoid water evaporation within the economiser.

Oil Firing

As a follow on to the work based on refinery gas firing, a brief review was carried out to list the additional issues which need to be considered in the conversion of heavy fuel oil firing to oxyfuel operation. The main areas requiring future work are fuel quality issues, burner performance, boiler performance, high- and low- temperature corrosion, the possibility of increased deposits/fouling and the impact of particulates on the downstream CO_2 treatment plant.

Boiler Sealing against Tramp Air Ingress

If the current level of boiler plant tramp air ingress could be reduced by about 75%, then the process to separate inerts (permanent gases) from the CO_2 product could be eliminated whilst still achieving the specified level of 3% inerts by weight. This reduction may be possible, although significant effort would need to be spent on boiler refurbishment. However, with envisaged sealing techniques, deterioration can be expected over time. In order to confirm the minimum air ingress levels realistically achievable over the lifetime of the retrofitted boiler plant, plant testing and the development of an on-line monitoring technique are proposed as activities for future work. The costs of sealing have not been estimated, as they are very specific to a particular boiler and are beyond the scope of the present study. These conclusions apply to balanced draught boilers, such as this one, with furnaces operating at slightly sub-atmospheric pressure. For pressurised boilers, designed to operate fully sealed at a slightly elevated pressure, air inleakage would not be an issue.

Oxygen Purity

The effect of changes in the oxygen supply purity from the level of 95% by volume used in the original study was examined to assess its impact on the process economics. A high purity of 99.5% was included in this study because if the boiler were sealed against tramp air and the inerts separation stage eliminated as described above, this level of oxygen purity would be needed to achieve the required level of inerts in the CO_2 product.

The base case for the original design study used a simple liquid oxygen (LOX) boil cycle for the air separation unit (ASU) as shown in Figure 5, operating at an oxygen purity of 95% by volume.

Figure 6 shows the impact of varying oxygen purity on the capital costs and power requirements of both the ASU and the CO_2 treatment and compression process. It also shows the effect on the overall cost for CO_2 capture in $/tonne, compared with the base cost of $20.9/tonne calculated in the original study. Where costs for CO_2 capture are presented these are based on annual costs calculated as annual operating costs plus 10% of capital costs, the latter being vendors' installed, inside battery limits, costs. No account is taken of CO_2 produced in the generation of the electric power imported. It should be noted that the percentage of CO_2 recovered increases progressively as the oxygen purity increases and reaches effectively 100% for the sealed boiler case and the effect of this has been included in the CO_2 capture costs presented in Figure 6.

Operation at purities below 95% oxygen reduces the air separation power, but the capital cost of the ASU increases because of the larger equipment sizes, caused by the lower pressures in the system.

Operation at higher oxygen purities leads to increased power consumption up to 97% oxygen. At this point the separation in the main low pressure distillation column changes from oxygen-nitrogen to oxygen-argon, which is well known to increase both capital and operating costs sharply.

The best ASU cycle to be used for the 99.5% case is the simple LOX boil cycle shown in Figure 5. It consists of an air compressor, in which the air is raised in pressure to 5.6 bar abs, followed by an air purifier in which water, CO_2 and hydrocarbon impurities are removed in a pair of switching adsorber vessels packed with alumina and molecular sieve. The air enters an insulated cold box, where it is cooled in a bank of aluminium plate-fin heat exchangers against returning product and waste streams, before entering the lower section of a double column distillation system. Liquid oxygen product is withdrawn from the sump of the upper low pressure column and vaporised against a condensing air stream before entering the main heat exchanger. Waste nitrogen leaves the top of the upper column. Reflux for the upper and lower columns is produced by condensing nitrogen in the reboiler condenser which separates the two columns.

There are many possible cycles which can be used if boiler sealing is not possible and operation at 95% purity is selected. One of these cycles is shown in Figure 7. It utilises a double reboiler and a double high pressure column. Part of the air stream is boosted in pressure to 5 bar abs following purification while the remaining air enters the cold box, enclosing the cryogenic equipment, at 3.7 bar abs. The lower reboiler operates by condensing nitrogen from the boosted air circuit producing 95% oxygen liquid plus the column boil-up, while the upper reboiler boils an intermediate impure oxygen liquid from the upper column against a condensing nitrogen stream from the HP column operating at the 3.7 bar abs pressure level. The more complex cycle results in an increase in capital cost but there is a reduction in power consumption of 6.5% which leads to an overall reduction in the recovery cost of the CO_2 of $0.28/tonne.

Carbon Dioxide Compression and Purification
Optimisation of the carbon dioxide compression system depends on the level of inerts in the crude flue gas stream from the boiler which in turn is a function of the degree of boiler tramp air ingress and the purity of oxygen used in the process, as discussed above. It is estimated that where the boiler is sealed, elimination of the inerts removal process and setting the supply oxygen purity at 99.5% would result in a net reduction of CO_2 capture cost of $1.7/tonne.

In the cases where there is tramp air ingress or the oxygen purity is below 99.5%, a low temperature inerts removal system is necessary, and the refrigeration required for its operation is obtained by recycling CO_2 gas around one of the stages of the nine stage centrifugal CO_2 compression train (Figure 8). The inerts are removed by phase separation at a temperature which is fixed at an approach to the triple point temperature of CO_2 (-56.6°C). Operating as cold as possible will minimise loss of CO_2 with the inert waste gas but will consume more power. For the design case, a reduction in temperature of 2°C at the cold end results in an increase of 0.27 tonne/hr of CO_2 captured with an extra 100 kW_e power consumption. This is equivalent to 370 kW_eh/tonne of CO_2, giving a marginal cost for the extra CO_2 captured of $16.1/tonne CO_2 (at an electricity cost of 4.35 c/kWh) compared with an overall cost of $20.9/tonne of CO_2, making the selection of the lowest possible operating temperature the best option.

Waste Gas Energy Recovery
In the original design case, the inerts separation was carried out at a pressure of 34 bar abs. This means that the inerts stream leaving the low temperature separator has a significant internal energy which can be released by expansion of the gas in a turbine producing shaft power (see Figure 8).

Preheating of the inert gas waste stream prior to expansion will increase the power produced. Table 1 shows the effect of preheating using final boiler product steam which gives an increase in

power output from 268 kW to 560 kW for the consumption of 715 kW of steam and reduces the overall CO_2 capture cost by \$0.2/tonne. Note that expansion of the inerts from ambient temperature gives an exit temperature of -113°C. An intermediate case, which looks more attractive, is to preheat the inert stream to a temperature of about 140°C against the product flue gas leaving the boiler at 220°C. The expander exit gas can then be used as a refrigeration stream in the low temperature inerts separation unit. This will reduce the power consumption of the recycle refrigeration section of the CO_2 compressor by about 60kW giving an overall net power benefit of about 440 kW. This has not been costed, but is believed to be the most attractive option for efficient use of the high pressure inerts stream.

Heat Recovery from Gas Compression
An oxyfuel boiler recycles the bulk (in this case approximately two-thirds) of the flue gas back to the burners at an elevated temperature above the acid dewpoint. In the present study, the boiler exit flue gas temperature is 220°C. This characteristic of oxyfuel boilers allows the option of recovering the heat of compression from the main air and CO_2 compressors, operating adiabatically instead of in the usual intercooled mode, to preheat boiler feedwater prior to evaporation and superheating in the boiler. This would not be possible in a conventional boiler because raising the boiler feed water temperature would simply raise the flue gas exit temperature and hence increase the dry gas heat loss by an equivalent amount.

Operation of the main air compressor of the ASU adiabatically results in an air exit temperature of about 222°C at a pressure of about 5.6 bar abs for the 99.5% oxygen case. The carbon dioxide product compressor, for the case of the sealed boiler with no inerts removal, could also be operated adiabatically at 101 bar abs discharge with a single intercooler. The drier would then be at the 10 bar abs pressure level. In the case of the unsealed boiler with inerts removal, the selection of adiabatic pressure levels depends on the operating pressures in the inerts removal unit.

The operation of three parallel stages of boiler feedwater preheating, against cooling air and two cooling CO_2 streams, is possible because the total heat capacity of the air and CO_2 streams is less than the heat capacity of the boiler feedwater stream.

In the present case, preheating of the boiler feedwater will reduce the amount of steam consumed by the existing feedwater preheaters. For example, the heat released by the ASU main air stream is up to about 13 MW for an increase in shaft power of about 1.1 MW. Indeed in the case of operation at 30% MCR it would be desirable to use the heat to increase the temperature of the pre-heated boiler feedwater from the normal 146°C to 168°C. This has the effect of increasing the flue gas exit temperature by a further margin above the acid dew point and avoiding the potential corrosion problems discussed above.

Although not specifically studied, it is believed that in very large oxyfuel systems (eg over 3,000 tpd O_2), there would be a significant reduction in the installed cost of adiabatic compressors compared with isothermal, plus a reduction in the cooling water requirements, making this an attractive option to consider.

Materials Selection
There are significant corrosion issues which must be addressed when specifying the materials to be used in the CO_2 separation and compression section of the plant.

With an H_2S content of 1% in the refinery fuel gas to the boiler, the compositions of the net flue gas from the boiler together with the cooled gas prior to and after compression are shown in Table 2. The gas must be cooled from 220°C to the compressor suction temperature of 31°C. The main cooling procedure is by direct contact with cooling water in a tower with a plastic packing. Suitable

material for the tower shell would be glass-reinforced plastic (GRP) with a polyvinylidine fluoride plastic such as KYNAR for the packing and with internal supports and water distribution in stainless steel grades 316 or 904L.

In order to reduce the temperature of the gas to a level of around 100°C suitable for the scrub tower, a first stage cooler comprising a venturi water scrubber is used which also serves to remove any dust entering the system. This could be constructed of stainless steel 316 or 904L, but the inlet side where water droplets could splash onto hot surfaces and evaporate, thus concentrating the acid components, may need to be coated with a more resistant material such as tantalum. The line from the boiler to the venturi scrubber would be carbon steel suitably insulated to prevent condensation.

The CO_2 compressor can be considered as two sections divided by the gas drier, which ensures that the high pressure section of the machine and the downstream delivery pipeline can be constructed of carbon steel, which will not corrode in spite of the acid components since the dewpoint will be below -40°C. However, the low pressure end of the machine is subject to the corrosive effects of wet CO_2 and SO_2 gas with the likelihood of a small quantity of SO_3 acid mist. These conditions can be handled by the use of grades of stainless steel such as G X5 Cr Ni 13.4 (1.4313) for casting the volutes and X 6 Cr Ni Ti 8.10 (1.4541) for the intercooler shells and tubes and the piping. All impellers would be standard 13% chrome, 4% nickel ferritic stainless steel.

SAFETY

Safety was reviewed in the original study and the new work has not altered the conclusion that the issues with oxyfuel firing are similar to those successfully managed elsewhere in the process industry. For the boiler control systems and the plant trip systems, all of the additional control functions and safety interlocks to accommodate oxyfuel firing can be implemented using well established technology.

CONCLUSIONS AND BENEFITS

This study has increased confidence in the original predictions that the specified refinery power station boiler could be converted to oxyfuel operation for CO_2 capture, without changes in the costly steam pressure parts and without loss of duty. By considering a specific plant in detail, the work provides an indication of the potential of oxyfuel conversion. It is believed that the technology could be applied widely to boilers and process heaters, where there is reasonable sealing against furnace air ingress.

Since more than 80% of the $20.9/tonne CO_2 capture cost estimated in the original study was associated with the ASU and the CO_2 purification system, attention was given in this study to varying the purity of the O2 from the 95% used previously and seeing the effect on overall CO_2 capture cost. It was found that there is an inverse relationship between the purity of the O_2 and the capture cost, with the cost increasing quite markedly at lower O_2 purities (eg 17% increase at 80% O_2). Above 95%, however, the cost decrease is only small, with the minimum cost (a 1% reduction) being found at 97% O_2.

Initial findings indicate that there may be an additional 2% cost reduction available through the recovery of the pressure energy in the inerts disposal stream, coupled with the use of a more efficient ASU.

A more significant cost reduction would be available if it were possible to seal the boiler against tramp air ingress – although this may not be practicable in all plants. In this case, by using 99.5% O_2 there is no need for the inerts removal section of the CO_2 system and an overall cost reduction of some 8% may be achieved.

It is considered that the main remaining uncertainties lie in the performance of large-scale gas and oil burners using oxygen and recycled fuel gas, and in the prediction of flame properties. Testing of the appropriate type of burner on a realistic scale is therefore recommended as the next stage, before proceeding to a plant demonstration.

ACKNOWLEDGEMENT

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TABLES

		Let-Down Valve	Expander without Pre-Heater	Expander with Steam Pre-Heater	Expander with Flue Gas Pre-Heater
Flue gas flow	Nm^3/hr	5732	5732	5732	5732
Flue gas temp ex cold box	^{o}C	17	17	17	17
Pre-heater thermal duty	kW	N/A	N/A	715	280
Pre-heater exit temp	^{o}C	N/A	N/A	330	140
Expander generated power	kW	N/A	268	560	380
Vent temperature	^{o}C	2.3	-113	33	-54

Table 1. Comparison of options for reducing flue gas inerts pressure from 34 bar abs to atmospheric

	Flue Gas (% by weight)	CO_2 Compressor Suction (% by weight)	CO_2 Compressor Discharge (% by weight)
CO_2	54.39	81.53	95.67
H_2O	34.59	1.96	0.00
N_2	6.09	9.19	1.65
O_2	1.68	2.51	0.57
SO_2	0.45	0.62	0.76
Argon	2.81	4.19	1.35
Temp ^{o}C	220.6	30.6	38
Mass Flow kg/s	20.07	13.36	10.58
Pressure bar abs	1.03	1.01	101

Table 2. CO_2 stream compositions

FIGURES
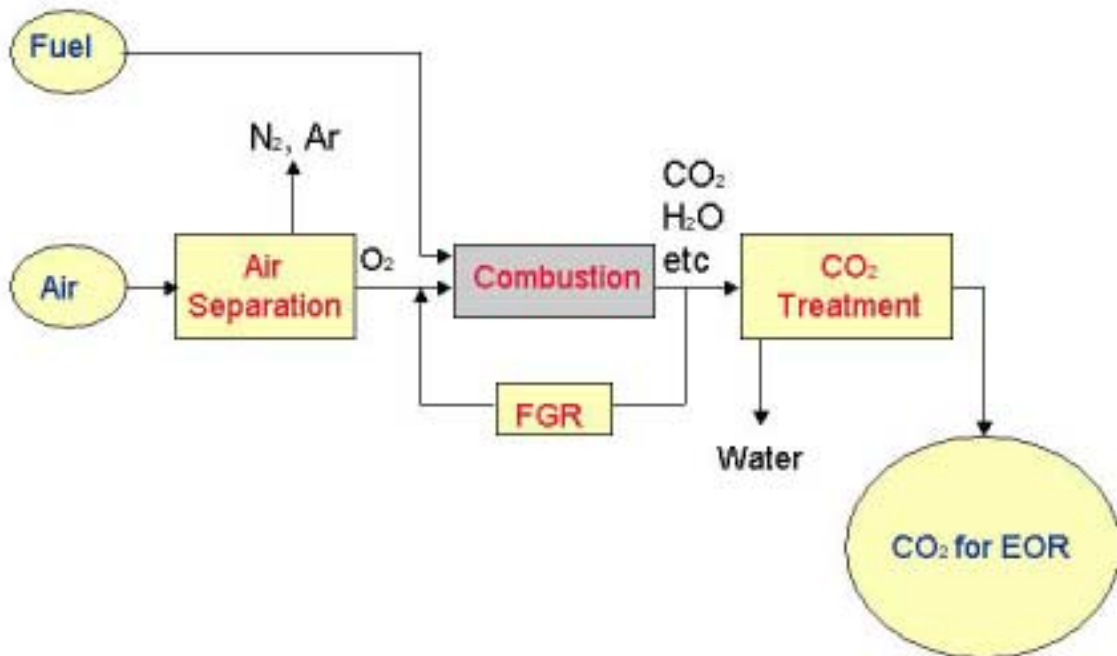
Figure 1. Simplified oxyfuel firing arrangement

NOT TO SCALE
All Dimensions in metres
'X' Denotes Burners
Boiler Width = 6.706 m
No.of Gas Zones = 34
No. of Planes = 5
Total No. Gas Zones = 170
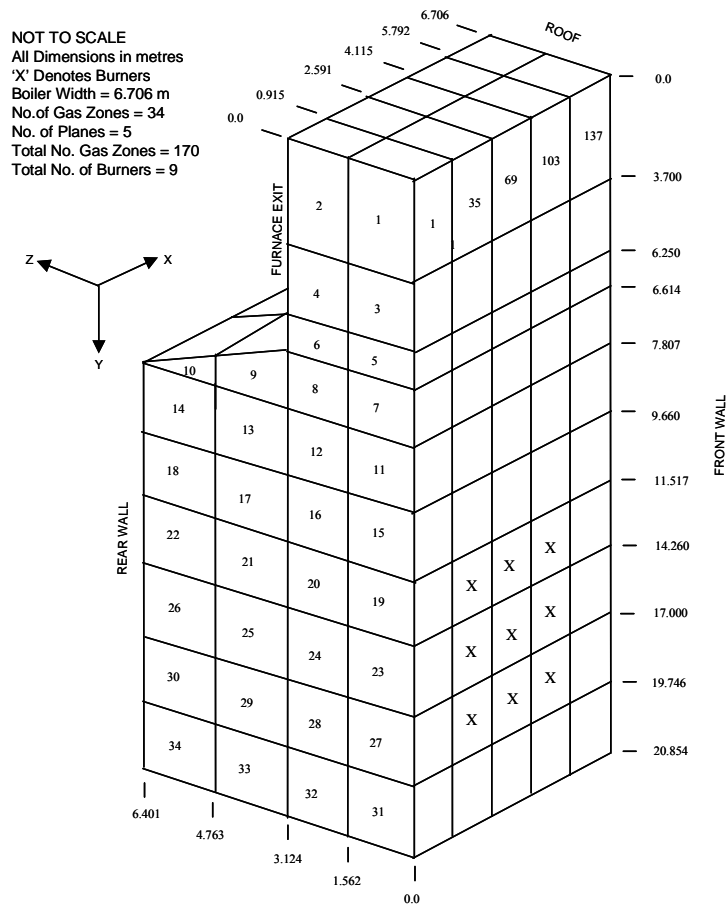Total No. of Burners = 9

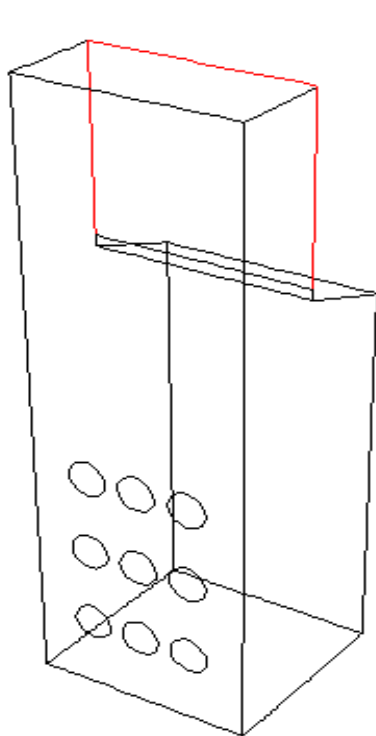**Figure 2. Furnace heat transfer model**
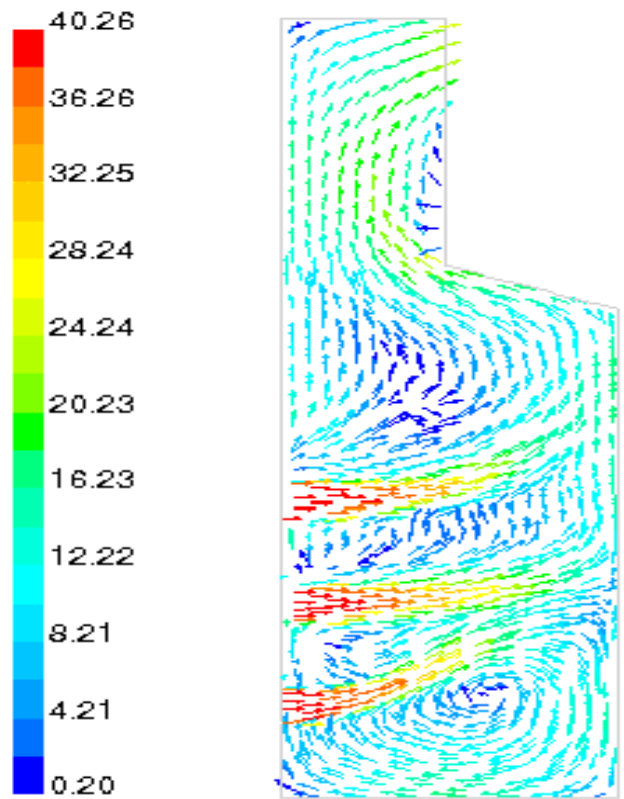

Figure 3. CFD isothermal furnace model

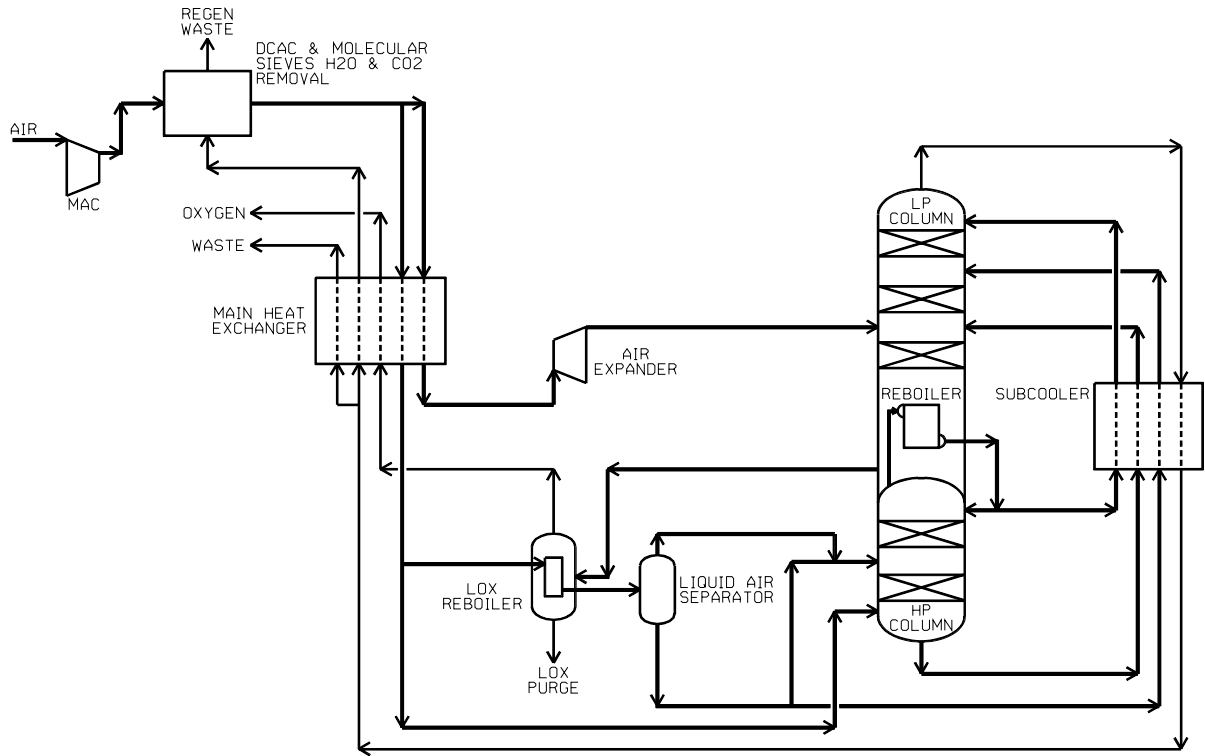**Figure 4. CFD flue gas flow patterns
showing velocities in m/s**
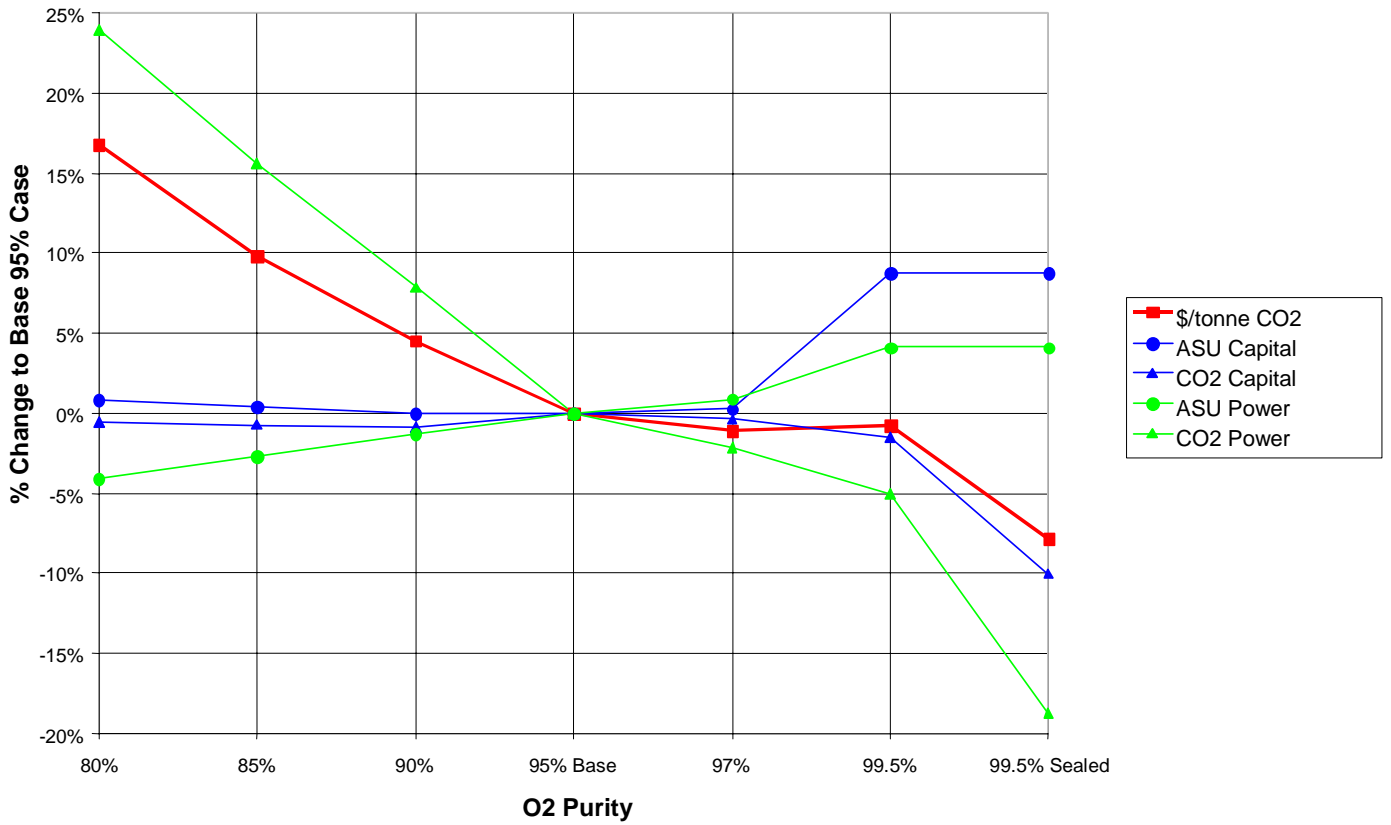
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Figure 5. Air separation unit. Basic LOX boil cycle

Figure 6. Effect of oxygen purity on CO$_2$ capture economics - capital costs and power

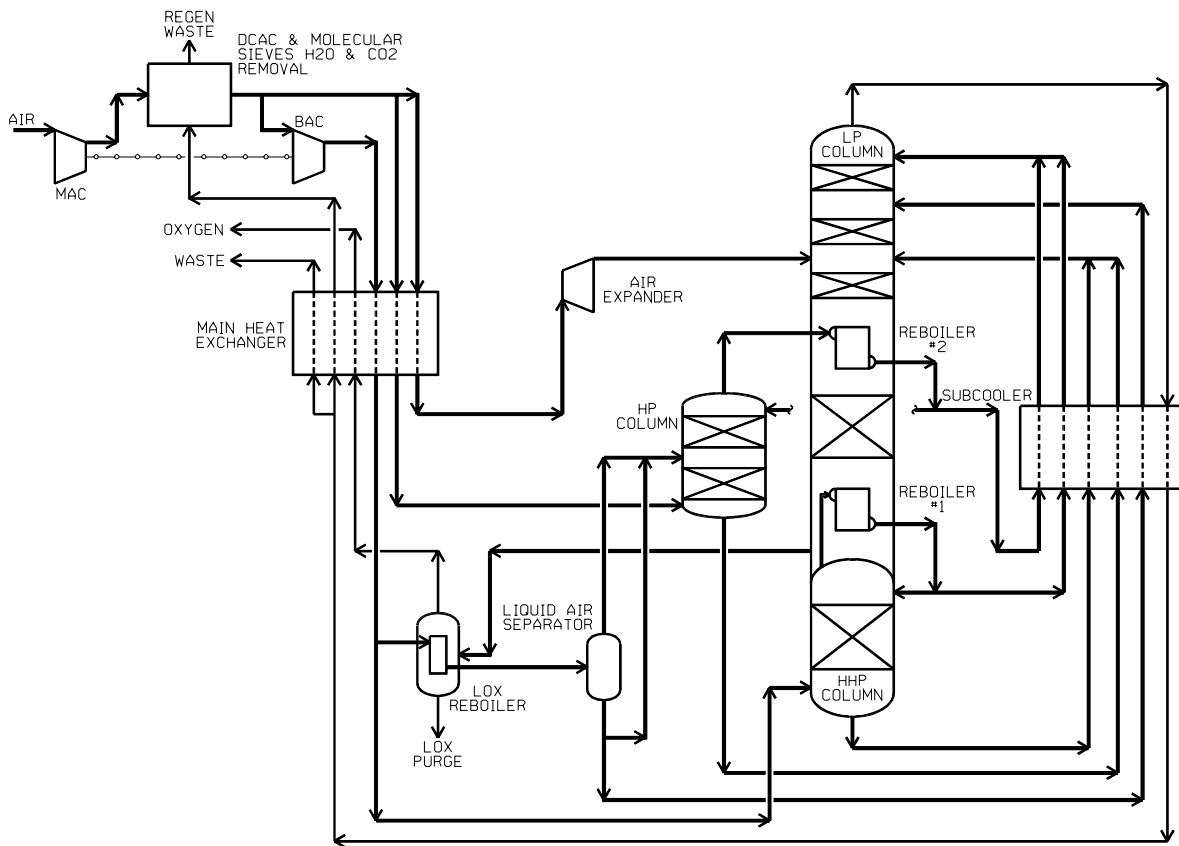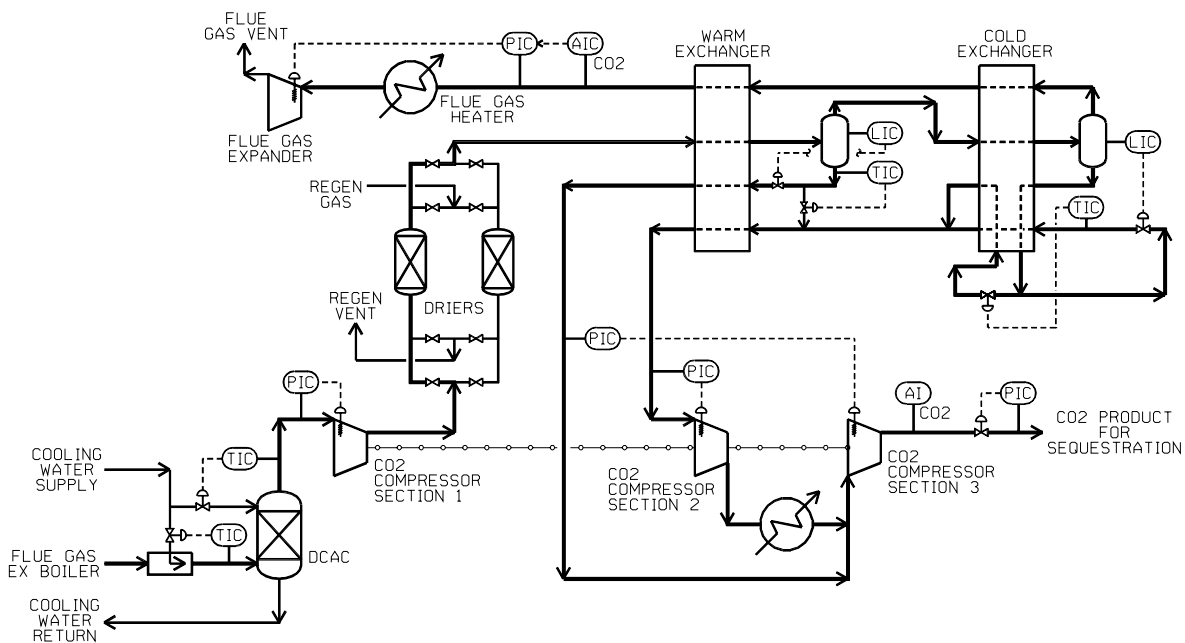**Figure 7. Air separation unit. Dual LP column with dual HP column**

Figure 8. Basic CO₂ removal flowsheet with optional flue gas expander