

# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Capture and Separation of Carbon Dioxide  
from Combustion Sources**

*Edited by*

**David C. Thomas**

*Senior Technical Advisor*

*Advanced Resources International, Inc.*

*4603 Clearwater Lane*

*Naperville, IL, USA*

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## Chapter 26

# THE OXYFUEL BASELINE: REVAMPING HEATERS AND BOILERS TO OXYFIRING BY CRYOGENIC AIR SEPARATION AND FLUE GAS RECYCLE

Rodney Allam<sup>1</sup>, Vince White<sup>1</sup>, Neil Ivens<sup>1</sup> and Mark Simmonds<sup>2</sup>

<sup>1</sup>Air Products PLC, Hersham, Surrey, UK

<sup>2</sup>BP, plc, Sunbury-on-Thames, UK

### ABSTRACT

This feasibility study involves the potential application of oxyfuel technology on a refinery-wide basis at the BP Grangemouth unit in Scotland. A total of seven boilers and 13 process heaters of various types, burning a mixture of refinery fuel gas and fuel oil resulting in the production of approximately 2.0 million tonnes per annum of CO<sub>2</sub>, form the basis of this study.

This work considers the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale air separation plants totalling up to 7400 tonne/day of oxygen plus a CO<sub>2</sub> compression and purification system on a congested site. In addition, we present the scheme for distributing the oxygen around the site and collecting the CO<sub>2</sub>-rich effluent from the combustion processes for purification, final compression, and delivery into a pipeline for enhanced oil recovery.

The basic case, Case 1, is presented and costed involves the supply of the complete oxyfuel system with installation and start-up and includes all required utilities. The electrical energy required for the system is provided by a GE 6FA gas turbine combined cycle cogeneration unit with 10.7 MW of excess power available as surplus. Two further cases are also presented. The first uses a GE 7EA gas turbine plus heat recovery steam generator producing steam primarily at the refinery condition of 127 barg 518 °C together with some additional supplies at 13.7 barg. The steam production from the existing boilers is reduced by a corresponding amount. The third case uses a similar 7EA gas turbine plus heat recovery steam generator, but in this case the fuel is hydrogen produced from an oxygen autothermal reformer with product steam generation and CO<sub>2</sub> removed using a methyl diethanolamine (MDEA) system. In each of these three cases the total quantity of CO<sub>2</sub> emission avoided and the quantity of CO<sub>2</sub> available for pipeline delivery is calculated, costed and presented in Table 1.

### INTRODUCTION

This Chapter presents the results of a feasibility study carried out on the oxyfuel conversion of steam raising boilers and process heaters in the Grangemouth refinery and petrochemical complex of BP, located in Scotland between Edinburgh and Glasgow. The sources of CO<sub>2</sub> emission at Grangemouth include utility boilers and process heaters which are fired using a combination of refinery fuel gas and sulphur containing fuel oil. Currently, BP Grangemouth emits about 4 million tonnes of CO<sub>2</sub> per year. The target of this study was to

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*Abbreviations:* ASU, Air separation unit; ATR, Autothermal reformer; CW, Cooling water; EOR, Enhanced oil recovery; FD, Forced draft; FGR, Flue gas recycle; GOX, Gaseous oxygen; GTCC, Gas turbine combined cycle; HRSG, Heat recovery steam generator; ID, Induced draft; J–T, Joule Thomson; LOX, Liquid oxygen; MAC, Main air compressor; MDEA, Methyl diethanolamine; PFD, Process flow diagram.

TABLE 1  
SUMMARY OF STUDY RESULTS

Case	Oxygen flow (tonne/day)	CO <sub>2</sub> captured (× 10 <sup>6</sup> tonne/year)	CO <sub>2</sub> avoided, (× 10 <sup>6</sup> tonne/year)	Cost CO <sub>2</sub> captured (\$/tonne)	Cost CO <sub>2</sub> avoided (\$/tonne)
1	6736	1.88	1.65	37.95	43.24
2	6034	1.69	1.57	- 5%	- 10%
3	6889	2.33	1.99	- 11%	- 9%

avoid emission of approximately 2 million tonnes of CO<sub>2</sub> by using the proposed oxyfuel conversions representing about 50% of the total Grangemouth emissions. The assumption in the study is that the captured CO<sub>2</sub> would be used for enhanced oil recovery (EOR) in the North Sea fields. For this application the CO<sub>2</sub> must have a maximum inerts content defined as total nitrogen plus argon not exceeding 3 mol%, minor quantities of excess oxygen and sulphur dioxide are permitted. The CO<sub>2</sub> must be compressed to 220 bar pressure, purified and dried to a water content less than 50 ppmv before delivery into a transmission pipeline.

Oxyfuel is pre-eminently suited to retrofit conversion of existing fossil fuel fired facilities. A number of studies have been published [1–3] indicating that conversion of existing steam boilers and process heaters to oxyfuel firing is feasible at low cost and often with improved performance. Projected overall costs which include oxygen supply and CO<sub>2</sub> processing and compression are competitive with other CO<sub>2</sub> capture technologies. One of the main objectives of this study was to consider the practical difficulties and real costs of carrying out a retrofit project for CO<sub>2</sub> removal using oxyfuel conversion of existing units in a real refinery location. The sources of CO<sub>2</sub> emission are scattered around a very congested site covering over 3 km<sup>2</sup>. CO<sub>2</sub> is collected at these scattered points and, after preliminary processing involving cooling, water knockout, compression and drying, the crude CO<sub>2</sub> streams are conveyed by pipeline to a central location for further purification and final compression. There are no spare utilities available on the site, so all additional power requirements will be provided by new natural gas fired gas turbine combined cycle cogeneration units. Additional cooling water will be provided from new induced draft cooling towers.

Two possible sources of oxygen were considered in this oxyfuel retrofit study: cryogenic air separation in two separate identical plants, reported in this chapter, and high temperature ion transport membranes integrated with two gas turbines, reported in Chapter 30. The study was coordinated by Air Products PLC who provide the overall system integration and costing and the detailed designs and specification for the oxygen system, CO<sub>2</sub> system, utilities, layout and performance. The detailed work on the boiler conversions was subcontracted to Mitsui-Babcock (Renfrew) and on the process heater conversions to Foster Wheeler (Reading).

### *Cases to be Studied*

The oxyfuel conversion study includes the provision of all additional site services required for this area including cooling water and power production. Power is required for the Air Separation Unit (ASU) compressors and the CO<sub>2</sub> compressors. This power will be provided using a gas turbine combined cycle system. Once a gas turbine model has been selected, the excess power can be fed into the refinery system. There are three options for dealing with the gas turbine CO<sub>2</sub> emissions and steam production.

*Case 1.* The gas turbine and associated steam production is all used for power production. In this case a 6FA gas turbine combined cycle system is used to generate power.

*Case 2.* The steam production is primarily at the 127 bar level and is used to replace part of the boiler steam, thus saving oxygen flow to the boilers. Here, a 7EA gas turbine is required but since steam produced in the heat recovery steam generator (HRSG) is backing out steam production from the boilers, no steam turbines are required. This option also saves on cooling water requirements since none is required for the power generation system and the ASU is smaller due to the reduction in firing of the boilers allowed by the generation of steam in the gas turbine HRSG.

*Case 3.* The gas turbine could be run in the precombustion decarbonisation mode with part of the oxygen being used for hydrogen production in an autothermal reformer and with shift conversion and CO<sub>2</sub> removal using a methyl diethanolamine (MDEA) system. For this case we have assumed excess steam production sent to the refinery turbines.

#### *Adiabatic compression*

Also considered as an option with each case is the use of adiabatic compression for the main air compressors (MACs) on the ASU. This allows boiler feed water to be preheated, saving 13.7 bar steam, and reduces the cooling water requirement.

## STUDY METHODOLOGY

### *Design Basis*

The task for this study is to consider the total equipment system including associated services for extra power, cooling water, etc. to convert a number of units in the BP Grangemouth refinery to oxyfuel firing.

The units which will be converted for oxyfuel firing are described below.

- Five Simon Carves boilers each supplying 300,000 lb/h steam. Typical fuel mix 40% gas, 60% oil by weight. These are linked to two stacks.
- Two Babcock steam boilers each supplying 500,000 lb/h steam. Average fuel mix 40% gas 60% oil by weight. These two boilers are linked to a single stack.

The steam conditions for all these boilers are 127.6 barg, 518 °C.

There are, in addition, a total of 12 process heaters of various types which have been specified for oxyfuel conversion—box, cabin or vertical cylindrical. Duties vary from 10.3–112.3 MW. Fuel is either gas alone or a combination of gas and fuel oil. In addition, there is a hydrogen producing steam/natural gas reformer furnace fired by fuel gas. Summary details of the heaters and boilers considered in this study are given in Table 2. This gives the CO<sub>2</sub> emissions with air firing, the CO<sub>2</sub> delivered to the pipeline when operating in the oxyfuel mode and the total oxygen consumptions. It is clear from these results that one of the benefits of oxyfuel firing is a reduction in fuel required, in this case 6%. This is the reason that the total CO<sub>2</sub> captured is below the 2.0 million tonne per year target.

TABLE 2  
GRANGEMOUTH HEATERS AND BOILERS

	Air Firing		Oxyfuel Firing – Asu		
	Total Fuel Consumption (kg/hr)	Total CO <sub>2</sub> Emitted (kg/hr)	Total Fuel Consumption (kg/hr)	Total O <sub>2</sub> Consumption (kg/hr)	Total CO <sub>2</sub> Captured (kg/hr)
Boilers B1–B7	54,810	164,270	52,520	179,835	145,290
Heaters H1–H12	26,511	73,827	24,303	90,339	62,676
Reformer H13	3,600	9,791	2,813	10,494	7,080
Totals	84,921 kg/hr	2.17 million tonnes/year	79,636 kg/hr	6,736 tonnes/day	1.88 million tonnes/year

### *CO<sub>2</sub> product composition*

The product specification for the CO<sub>2</sub> is as shown in Table 3. The post combustion baseline study used a slightly different specification for CO<sub>2</sub> where CO<sub>2</sub> purity was to be ≥97 mol%. However, in the CO<sub>2</sub>

purification system for this oxyfuel study the only other impurities other than the inerts, which are limited to 3 mol%, are O<sub>2</sub> and SO<sub>2</sub>, which are at around 0.5 mol%, making the CO<sub>2</sub> around 96.5 mol%.

TABLE 3  
CO<sub>2</sub> PRODUCT SPECIFICATION

Purity (dry basis)	90 mol % min
Pressure	220 barg
Inerts (N <sub>2</sub> and Ar)	3 mol % max.
NO <sub>x</sub> , SO <sub>x</sub> , CO, HC, O <sub>2</sub>	Unrestricted (mol %)
Temperature (BL)	50 °C max.
Moisture content	50 ppmv max.

#### *Oxidant composition*

The oxidant composition, i.e. the oxygen product from the ASU, is as shown in Table 4. The purity of the oxygen used in this study has been chosen as an economic trade-off between the cost of oxygen production and inerts removal. 95 mol% was found to be the economic optimum in previous retro-fit oxyfuel studies. This is because in retro-fitting heaters and boilers there will always be some air in-leakage. Therefore, the dried CO<sub>2</sub> will always require further purification to remove inerts (argon and nitrogen) to meet the CO<sub>2</sub> purity specification and so the extra capital and power to produce high purity (~99.5 mol%) oxygen would not give any advantage over low purity (95 mol%) oxygen. Should one consider a boiler or heater in which no air in-leakage is expected, such as in a new-build rather than a retro-fit, then high purity oxygen could be used, eliminating the need for an inerts removal system, which may present a better economic optimum.

TABLE 4  
OXIDANT COMPOSITION

Component	Mole %
Oxygen	95.0%
Argon	3.5%
Nitrogen	1.5%
Other impurities	Trace
Pressure	0.7 (barg) available

#### *Overall Process Description*

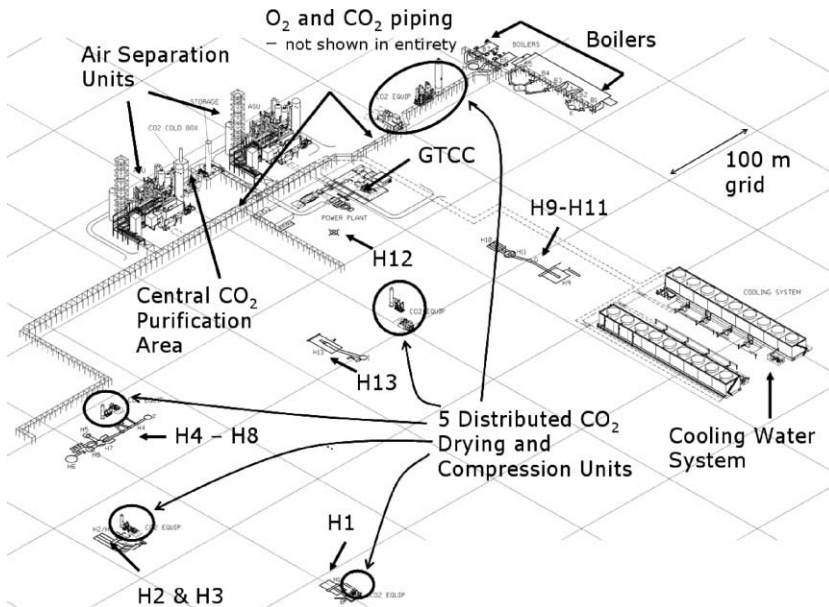
Figure 1 shows the layout of the site with the location of the boilers and heaters and the extra processing equipment required for the oxyfuel study. Below is a general description of the process steps that will be further expanded upon in subsequent sections.

#### *Oxygen generation*

Boilers and heaters normally firing on air are converted to oxyfuel firing by replacing the air feed with oxygen and recycling part of the hot flue gases. Therefore, a large ASU is required in order to generate sufficient quantities of oxygen. Here, we consider two trains of 3700 tonnes/day cryogenic ASUs. These are very large plants. Currently, the largest plants operating are around 3000 tonnes/day; however, 3500 tonnes/day plants are in construction.

#### *Oxygen distribution*

The units to be converted and the area of the site which could locate the extra equipment cover an area of around 600 m by 700 m. The oxygen must be distributed around this site to each unit. An economic study



**Figure 1:** Isometric view of site layout showing the relative location of the oxyfuel systems, the air separation units and the cooling towers, together with the CO<sub>2</sub> and oxygen piping runs.

has shown that oxygen distribution at low pressure (0.7 barg feed pressure) is the most favourable. In order to be able to use carbon steel piping it is essential to ensure that the velocity within the pipework is kept below a maximum so as to avoid the risk of fire caused by impingement of foreign objects within the piping against the pipe walls. In addition, the configuration of the piping should be such as to avoid situations in which impingement would be worse. Therefore, only long radius bends are used and T-junctions can only be used when flow goes from the main into the branch. Table 5 gives the details of the length of piping required for the network (standard gauge piping is used) and the interconnections.

#### *Heater and boiler conversion*

Each heater and boiler considered within the study must be converted to fire on oxygen rather than air, with air firing maintained as a backup. Foster Wheeler have considered the conversion of the heaters and Mitsui Babcock the boilers. Each unit produces a hot wet CO<sub>2</sub> stream that must be cooled, dried, purified and compressed.

#### *Local CO<sub>2</sub> collection and drying*

Due to the widely spread out nature of the site, the units to be converted are considered to be within one of five zones. Each of these zones takes the hot, wet CO<sub>2</sub> from the converted heaters or boilers, cools this stream and removes water by direct contact with cooling water. The crude CO<sub>2</sub> gas is then compressed and further dried down to a dew point of -60 °C.

#### *CO<sub>2</sub> collection*

The compressed dry CO<sub>2</sub> is transported at a pressure of 30 barg from each of the five local zones, by a carbon steel piping network, to a central zone for further purification and compression. The layout of this pipeline was also considered and where possible routed with the oxygen piping.



TABLE 5  
O<sub>2</sub> PIPING

Approx. pipe lengths		Approx. no of fittings			
Size (in.)	Length (m)	LRE 90	LRE 45	EQ TEES	Reducers
40	570	5	6	4	–
36	31	2	–	–	(40 × 36) = 1
30	463	7	–	1	(40 × 30) = 2; (36 × 30) = 1
24	8	–	–	–	(30 × 24) = 1
20	382	9	–	2	(30 × 20) = 1; (40 × 20) = 1 I
18	267	3	–	–	(20 × 18) = 1; (24 × 18) = 1; (30 × 18) = 1
16	299	6	–	–	(20 × 16) = 2
12	30	1	–	–	(18 × 12) = 1
10	233	4	–	–	(20 × 10) = 1
8	35	–	–	–	–
6	82	3	–	–	(20 × 6) = 1

#### *CO<sub>2</sub> purification and compression*

The central CO<sub>2</sub> purification and compression system takes the dried CO<sub>2</sub> from the distribution pipeline and removes inerts from this stream by cooling down to close to the triple point of CO<sub>2</sub> and separating out the uncondensed inerts. The purified gas is then further compressed to the delivery CO<sub>2</sub> pressure of 220 barg and transported by pipeline to the EOR site for disposal.

#### **Boiler and Heater Conversion Details**

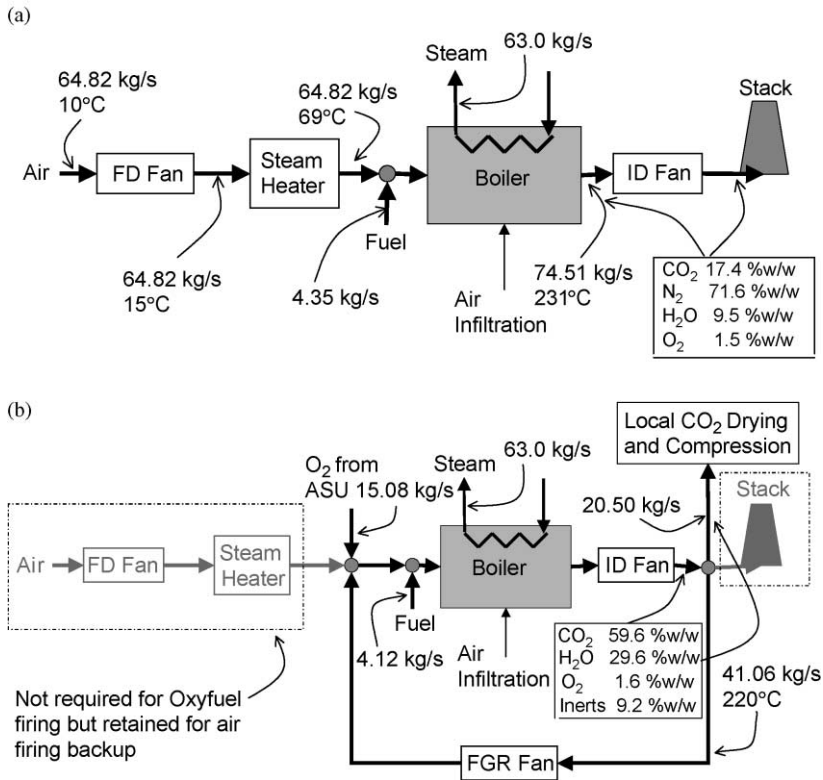
##### *Oxyfuel boiler conversion*

A detailed analysis of the conversion of one of the Babcock boilers at BP Grangemouth has been given in a previous paper [2,3]. Figure 2 shows diagrammatically the way in which the boiler conversion is carried out and the typical performance characteristics of the oxyfuel system. A critical parameter, which must be established by careful performance analysis on an existing boiler, is the amount of air in-leakage and the possibility of reducing this to a minimum by repairs. New equipment will include a recycle flue gas line and blower, 100% shutoff stack damper, oxygen injection and mixing system and possible burner modifications. The revised control system will allow air firing to be re-established in the event of an oxygen supply failure without tripping the boiler. This can be achieved with an liquid oxygen (LOX) instant demand back-up system that maintains oxygen supply pressure while the air fans are started.

##### *Oxyfuel heater conversion*

The conversion of process heaters to oxyfuel firing requires a similar modification to the system as that described for the boiler conversion [1]. A key criterion for the process heaters is to ensure that the peak heat flux to the tube surfaces is not increased. This is normally fixed by consideration of the thermal stability of process fluids to be heated or tube metallurgy. This constraint is maintained for the higher emissivity CO<sub>2</sub>- and H<sub>2</sub>O-rich gas in the furnace by setting the recycle to oxygen feed ratio to operate at below 21% oxygen concentration thus limiting flame temperature. The same overall duty is maintained in each case and also the same balance of radiant and convection section duties. The firing rate is reduced because of the lower heat loss in the smaller net flue gas flow.

The cases of the steam/natural gas reformer furnace (H13) and the heaters in the catalytic reforming area (H5–H8) are interesting as these only require radiant heat and thus the higher emissivity furnace gas allows the firing rate to be reduced by 15% and still maintain the same radiant heat flux. The lower firing rate reduces the excess steam production in the convection section. Some heaters have steam preheat of the air to the burners, resulting in a small saving in steam consumption for



**Figure 2:** Comparison of air and oxyfuel firing boiler. (a) Boiler with air firing (one of the 500,000 lb/hr Babcock boilers); (b) boiler converted to Oxyfuel firing.

the oxyfuel case. The resulting net steam deficit must be made up by producing extra steam from the boiler system. This is considered in this report by the addition of fuel to compensate for the reduction in steam.

It should be noted that some of these units share a convection section. That is, in air firing, the flue gases of H5, H7 and H8 combine and steam is generated in one convection section, and H10 and H11 flue gases combine before a convective process heater. In addition, H5–H8 share a forced draft (FD) fan. In order to simplify this study, these units have been considered as independent units each with their own FD fan. This gives conservative costing since savings would be made by converting the units together, with a single flue gas recycle (FGR) fan. This would mean that the units that are linked would either all be on air firing or all on oxyfuel firing.

#### *Flue gas inerts separation and CO<sub>2</sub> compression*

Due to the widely scattered location of the boilers and heaters in the refinery, it is necessary to collect the CO<sub>2</sub>-rich flue gas and pipe it to a central location for final purification and compression.

In general, each vent stack takes flue gas from one or more heaters or utility boilers. At each vent stack location we must collect the net flue gas during oxyfuel operation and prepare this for transmission to a central CO<sub>2</sub> purification and compression system.

We have analysed options for local flue gas treatment. There are two possibilities. The first is to cool the flue gas to knock out water vapour, compress the flue gas in a blower to, say, 1 barg and transport the wet flue gas in a duct made from corrosion proof material to the central CO<sub>2</sub> processing point. The second is to treat the flue gas locally in order to cool, compress and dry the flue gas and then transmit the compressed flue gas using small diameter carbon steel pipes, to the central processing location. We have chosen the second alternative as being more cost effective and allowing local operation and flexibility.

The flue gas product from each oxyfuel unit varies in temperature from 180 to 398 °C and contains about 30% water vapour. The ambient pressure flue gas is piped a short distance to a local collection point where it is cooled in a venturi water scrubber, to reduce the initial temperature to about 100 °C, followed by a direct contact packed tower containing polypropylene packing. The water vapour is condensed and leaves the base of the tower with the cooling water return flow. The flue gas is compressed in a centrifugal integrally geared compressor to 32 bara. The gas is then passed into a dual bed desiccant drier to reduce the water content to a dewpoint below -60 °C. The desiccant driers are filled with molecular sieve material to achieve the required -60 °C dewpoint. They are switched over at 8 h intervals. A closed cycled thermal swing CO<sub>2</sub> reactivation system is used. The dry CO<sub>2</sub> can now be piped in carbon steel lines to the central purification and final compression point.

### **Cryogenic Oxygen Production**

The maximum total oxygen demand of 7400 tonne/day, which includes a 10% flow margin, is provided by two cryogenic ASUs with single air compressors provided as two trains of 3700 tonne/day, which is close to the current largest plant size of 3500 tonne/day. The oxygen is delivered at 95% purity 0.7 barg into a pipeline system which runs to each of the oxyfuel use points. The plants utilise a cryogenic distillation system for air separation based on the use of an upper low pressure column in which the air is separated into a gaseous nitrogen stream leaving the top and a LOX stream leaving the base. The lower column is linked to the upper column through a reboiler-condenser in which N<sub>2</sub> separated from the air feed is condensed against boiling oxygen. The liquid nitrogen produced provides reflux for the upper and lower columns. A summary of the utility requirements is given in Table 6.

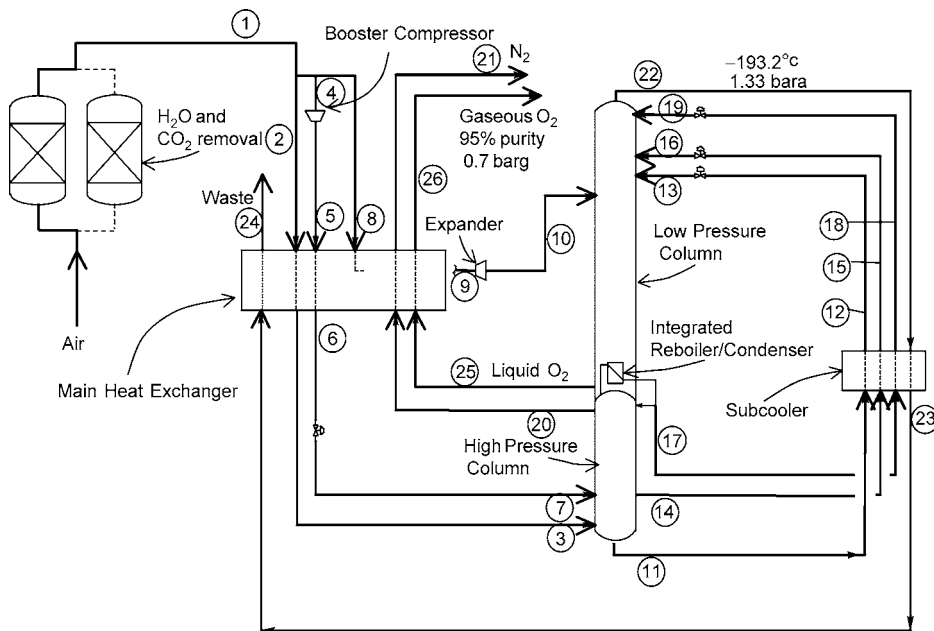
TABLE 6  
ASU PERFORMANCE COMPARISON WITH ADIABATIC AND ISOTHERMAL COMPRESSION

O <sub>2</sub> flow (tonne/day)	Air flow (Nm <sup>3</sup> /h)	Air pressure (bara)	Compressor type	Power (MW)	Cooling water flow (tonne/h)	Condensate flow (tonne/h)	13.7 barg steam turbine (MW)	Net power (MW)
6736	956,280	5.52	Isothermal	65.5	7289	0	0	65.5
6736	956,280	5.52	Adiabatic	75.5	0	573	14.6	60.9

### *ASU cycle process description—basic compressed LOX boil cycle*

This is one of the simplest cycles and benefits from a low capital cost. It is ideally suited to this application as the delivery pressure required is low. There is no requirement for either pumping the liquid O<sub>2</sub> or compressing the gaseous product. The plant consists of a compression system, an adsorption front-end air purification system, and a cold box containing the separation and the heat exchanger equipment. This process offers the benefits of high reliability, low maintenance cost, and it is simple to install and operate. A process flow diagram (PFD) of the process is given in Figure 3.

*Air compression and cooling.* Air is taken in through an inlet filter to remove dust and particulate matter prior to entering the MAC where it is compressed to 5.5 bara. Interstage cooling of the process air is provided by water-cooled intercoolers or alternatively an adiabatic compression arrangement can be used. The overall air separation system performance is shown in Table 6 for both cases. The air leaving the intercooled compressor is cooled in the Direct-Contact After Cooler (DCAC), in the lower section with

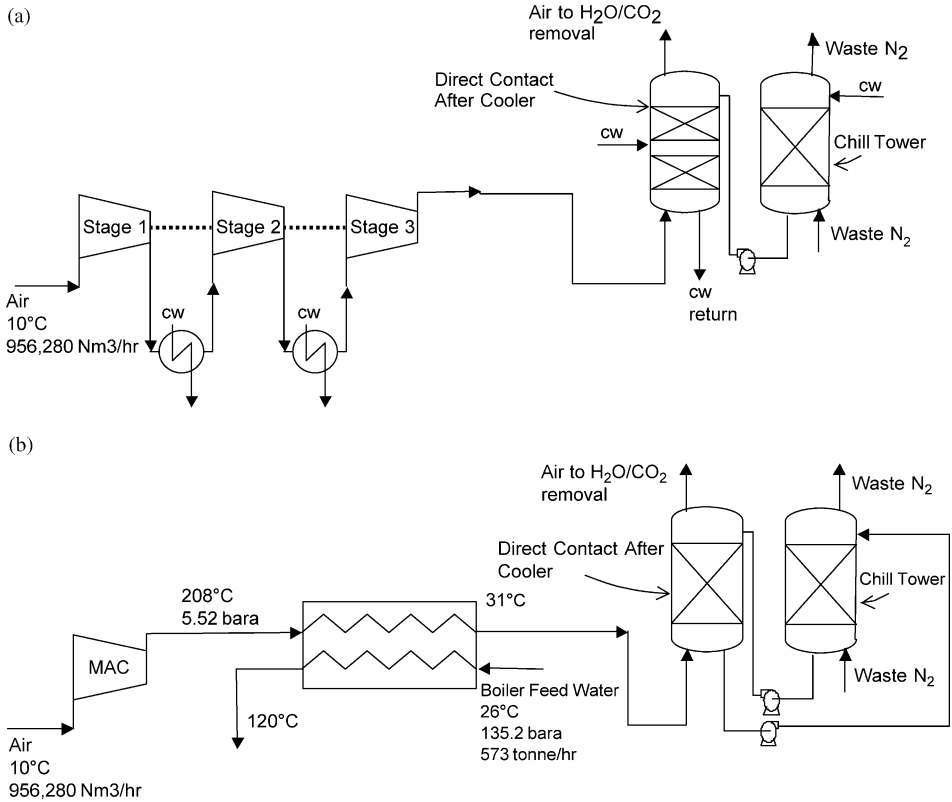


**Figure 3:** Cryogenic air separation plant.

cooling water and in the upper section with chilled water from the Chiller Tower. The air is cooled to a temperature of around 12 °C. The adiabatic MAC system only needs cooling water from the waste N<sub>2</sub>/water chiller tower for final air-cooling following the condensate heater. In both cases, which are shown diagrammatically in Figure 4, the MAC will be an in-line machine with a first stage axial compressor casing which is followed by two centrifugal stages and will be driven by an electric motor. Adiabatic compression will save 81 tonne/h of 13.7 barg steam at present used for preheating condensate feed to the boilers and is equivalent to a net saving in power of 6 MW. This steam can then be condensed to produce more power leading to a net reduction in the overall power requirement for the ASUs.

**Air cleanup.** Before the air is cooled to cryogenic temperatures, water vapour and carbon dioxide and other trace impurities such as hydrocarbons and nitrous oxide are removed in a dual bed adsorber. Removal of carbon dioxide and water avoids blockage of cryogenic equipment. The removal of impurities results in a clean, dry air stream free from contaminants which might cause blockages or safety problems in ASU operation. The adsorber operates on a staggered cycle, i.e. one vessel is adsorbing the contained impurities while the other is being reactivated by low pressure gaseous waste nitrogen using a temperature swing adsorber cycle. The nitrogen is heated to around 180 °C against condensing steam in a reactivation gas heater followed by a period in which the bed is cooled down with ambient temperature nitrogen which bypasses the heater. The adsorbents used are generally selected for optimum operation at the particular site. They consist of layers of alumina or silica gel plus layers of zeolite. The adsorber vessels are vertical cylindrical units having annular adsorbent beds.

**Principle of cryogenic air separation.** The industry standard method of cryogenic air separation consists of a double column distillation cycle comprising a high pressure and a low pressure column. The high pressure, higher temperature cryogenic distillation produces an overhead nitrogen product that is condensed against the low pressure, low temperature liquid O<sub>2</sub> in the LP Column sump. The plate-fin condenser–reboiler sits in the LP Column sump and thermally links the HP and LP Column. The HP column provides the boil up for



**Figure 4:** MAC (Main Air Compressor) options. (a) Isothermal Compression-cooling water; (b) Adiabatic Compression-integrated with condensate preheating for boiler feed.

the LP distillation column and the LP Column O<sub>2</sub> provides the condensing duty for the HP Column. Some of the condensed nitrogen returns to the high pressure column as reflux. The balance of the pure nitrogen reflux is cooled in the subcooler and flashed into the top of the low pressure column as reflux. The columns have aluminium structured packing optimised for cryogenic separation.

*Cooling and refrigeration.* Following the front end adsorber, the air stream (stream 1 in Figure 3) is split into three parts. The first and second are fed directly to the main heat exchanger. This consists of a number of parallel aluminium plate-fin heat exchanger blocks manifolded together. The first, larger portion, stream 2, is cooled close to its dew point (−175 °C) and fed to the bottom of the high pressure column. The second, stream 8, is removed from the middle of the main heat exchanger at an intermediate temperature (−146 °C, stream 9), then expanded in a centrifugal single wheel expansion turbine running on the same shaft as a single wheel centrifugal compressor which adsorbs the expander power. The expanded air, stream 10, is fed to the middle of the low pressure column at a pressure of about 1.38 bara and −181 °C to provide refrigeration for the operation of the ASU. The third part of the feed air stream, stream 4, is compressed in the compressor part of the expander and then cooled and condensed in the main heat exchanger against boiling oxygen. The resulting liquid air from the main exchanger, stream 6, is fed to the middle of the high pressure column.

*Distillation system.* In the HP column, the gaseous air feed is separated in the distillation packing into an overhead nitrogen vapour and an oxygen-enriched bottom liquid, stream 11. Part of the nitrogen vapour is

warmed in the main heat exchanger and taken as product, stream 21, whilst the remainder is condensed against boiling oxygen in the low pressure column sump, and split into two parts. The first part is returned to the high pressure column as reflux, whilst the second part, stream 17, is subcooled, reduced in pressure and fed to the low pressure column as reflux, stream 19. Crude LOX, stream 11, is withdrawn from the sump of the high pressure column, cooled in the subcooler against warming waste  $N_2$  and is flashed to the low pressure column as an intermediate feed, stream 13. A portion of liquid air, stream 14, is also withdrawn from the middle of the high pressure column. This liquid is subcooled in the subcooler and fed to the middle of the low pressure column, stream 16.

*Low pressure column.* The feeds to the low pressure column are separated into a waste nitrogen overhead vapour, stream 22, and an LOX bottom product, stream 25, which reaches the required purity of 95%. The waste nitrogen is withdrawn from the top of the low pressure column and warmed in the subcooler and the main heat exchanger. A portion of the nitrogen stream from the main exchanger is used for adsorber reactivation. The remaining dry nitrogen is vented through a Chilled Water Tower to produce chilled water by evaporative cooling. The chilled water is used to provide additional feed air cooling in the top section of the DCAC.

Pure LOX is withdrawn from the reboiler sump of the low pressure column, stream 25, and is returned to the main heat exchanger where it is vaporised and warmed up to ambient conditions against boosted air feed to the columns. The gaseous  $O_2$ , stream 26, is then regulated and supplied to the customer. The pressure in the low pressure column is typically 1.35 bara. The hydrostatic head between the sump of the LP Column and the LOX boil heat exchanger results in the  $O_2$  product being available at approximately 0.7 barg.

*Oxygen backup.* Each of the boilers and heaters will be designed in such a way as to allow air firing as a fall-back position should there be an interruption in supply from the ASUs. Therefore, enough backup for the ASUs should be provided in order to allow a controlled change-over to air-firing.

Both ASUs are supplied with independent MACs. It is, therefore, unlikely that both plants would need to be backed up at the same time. Consequently, should an interruption in supply occur from either ASU, only enough heaters and boilers need to be switched back to air in order to match the reduction in oxygen supply equivalent to one plant offline. Those that are chosen will be the ones that can most easily be switched back to air, most likely process heaters and the more modern Babcock boilers. Backup will be in the form of LOX enough of which will be stored on site to allow controlled changeover for the selected units to air firing.

### ***CO<sub>2</sub> Collection, Treatment and Compression***

The net flue gas from each oxyfuel fired boiler and heater must be cooled, dried and compressed, and inerts removed, before the resulting  $CO_2$  can be used for EOR. Due to the widely scattered location of the boilers and heaters in the refinery, it is necessary to collect the  $CO_2$ -rich flue gas and pipe it to a central location for final purification and compression. This is carried out in two stages. First, the net flue gas from one or more heaters and boilers is cooled, dried and compressed locally. Then the resulting dry gas is piped to one central area where inerts are removed and final compression takes place. A summary of the performance of this system is shown in Table 7.

TABLE 7  
PERFORMANCE SUMMARY FOR THE  $CO_2$  TREATMENT SYSTEM

Zone	Cooling water (tonne/h)	$CO_2$ compressor (MW)	Turbo expander (MW)
1	4128	14.55	–
2	1095	2.75	–
3	529	1.48	–
4	1339	2.13	–
5	179	0.56	–
Central zone	1767	9.10	4.27
Totals	9038 tonne/h		26.31 MW

*Local CO<sub>2</sub> collection, cooling, drying and compression*

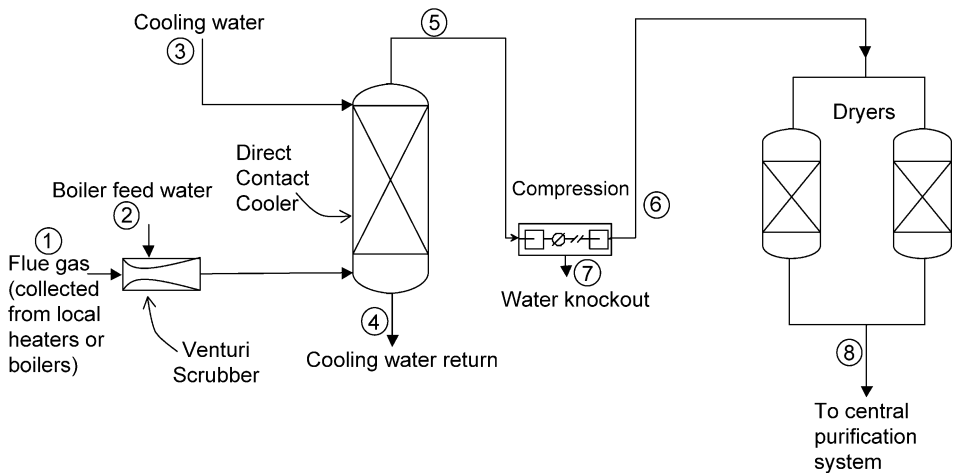
There are five local treatment zones distributed about the site, close to sources of CO<sub>2</sub>. These zones are numbered and the association between the boilers and heaters and the zones are given in Table 8.

TABLE 8  
DISTRIBUTED CO<sub>2</sub> TREATMENT ZONES

Zone	1							2					3				4			5
Unit	B1	B2	B3	B4	B5	B6	B7	H9	H10	H11	H12	H13	H4	H5	H6	H7	H8	H2	H3	H1

*Process description.* The distributed CO<sub>2</sub> drying and compression plants consist of: a venturi scrubber, a direct contact cooler, a compressor and a drier system. The flue gas product from each oxyfuel unit varies in temperature from 180 to 398 °C and contains about 30% water vapour. The ambient pressure flue gas is piped a short distance to a local collection point where it is cooled in a venturi water scrubber followed by a direct contact packed tower. The water vapour is condensed and the flue gas is compressed in a centrifugal integrally geared compressor to 32 bar. The gas is then passed into a dual bed desiccant drier to reduce the water content to a dewpoint below -60 °C.

A PFD for the local CO<sub>2</sub> dryer areas is shown in Figure 5 with the mass balance for the largest zone, Zone 1, given in Table 9, where the Design Flowrate corresponds to the average conditions and the Maximum Flow-rate corresponds to the sum of maximum net flue gas each boiler or heater within a zone can produce.



**Figure 5:** PFD of local distributed CO<sub>2</sub> compression and drying.

The flue gas enters the plant through insulated pipework to maintain the elevated temperature of the flue gas and keep it above its dew point of around 150 °C. This prevents corrosion of the pipe work. Firstly, the venturi mixer directly quenches the gas with cooling water reducing its temperature to around 100 °C before feeding directly into a water-fed DCAC for the final stage of cooling. The DCAC removes the bulk of the moisture in the flue gas by cooling the flue gas further to a temperature of around 30 °C. A cooling

TABLE 9  
MASS BALANCE FOR CO<sub>2</sub> TREATMENT ZONE 1

	Stream no.							
	1	2	3	4	5	6	7	8
<i>Composition (mol%)</i>								
Carbon dioxide	40.77	0.00	0.00	0.03	74.84	77.05	0.26	77.19
Oxygen	1.67	0.00	0.00	0.00	3.11	3.20	0.00	3.21
Argon	2.10	0.00	0.00	0.00	3.90	4.02	0.00	4.03
Nitrogen	8.08	0.00	0.00	0.00	15.02	15.47	0.00	15.49
Water	47.29	100.00	100.00	99.97	3.04	0.18	99.73	0.00
Sulphur dioxide	0.08	0.00	0.00	0.00	0.08	0.08	0.01	0.08
Molecular Weight (kg/kmol)	30.15	18.02	18.02	18.02	40.30	40.96	18.09	41.00
<i>Design flowrate</i>								
(kg/h)	264,665	12,266	2,617,643	2,704,303	190,271	187,819	2,453	187,671
(Nm <sup>3</sup> /h)	196,602	15,252	3,254,799	3,360,895	105,758	102,720	3,038	102,536
<i>Maximum flowrate</i>								
(kg/h)	373,594	17,315	3,694,999	3,817,326	268,582	265,120	3463	264,912
(Nm <sup>3</sup> /h)	277,519	21,530	4,594,393	4,744,157	149,285	144,997	4,288	144,738
<i>Phase</i>								
Pressure bar (a)	Vapour	Liquid	Liquid	Liquid	Vapour	Vapour	2 Phase	Vapour
Temperature (°C)	1.01	4.41	4.41	1.01	1.01	32.06	1.01	32.06
	196.70	34.00	24.00	44.00	24.30	30.00	29.55	30.00

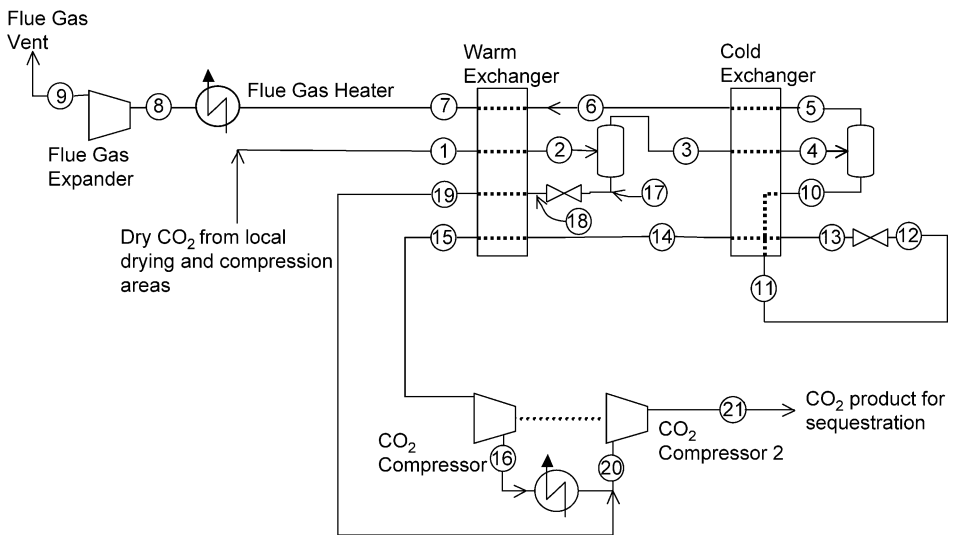


water temperature rise of 20 °C is used in the DCAC to reduce CO<sub>2</sub> losses in the cooling water. The water from the DCAC is slightly acidic, but can be mixed and diluted with the bulk cooling water returned from the plant. The flue gas is then passed through a multi-stage compressor with inter-cooling after each stage and an after cooler. Once compressed to the required pressure for transportation and final purification, the gas is dried in a silica gel/molecular sieve twin bed drier operated as a thermal swing cycle, using wet gas regeneration where the wet feed gas is heated and used to regenerate the beds. This desiccant dryer system prevents ice formation which could cause a blockage in the cold box as well as causing corrosion in the pipeline.

#### Central CO<sub>2</sub> purification and compression

The dry CO<sub>2</sub> from the distributed CO<sub>2</sub> treatment zones can then be piped in carbon steel lines to the central purification and final compression point.

*Process description.* Figure 6 shows the inert gas removal plant using CO<sub>2</sub> refrigeration, with the mass balance given in Table 10. This plant separates the inert gases from the CO<sub>2</sub> at a temperature of about -55 °C which is close to the CO<sub>2</sub> freezing temperature. At this point the CO<sub>2</sub> partial pressure in the vapour phase has been reduced to about 7 bar. The refrigeration is obtained by evaporating two streams of CO<sub>2</sub> at pressure levels of 9.4 and 18.3 bara and recycling the CO<sub>2</sub> gas in the main CO<sub>2</sub> compressor. The separated inert gas at 29 bar can be heated and passed through a power recovery turbine. It is possible to reach a CO<sub>2</sub> purity in excess of 96% using this method at inlet CO<sub>2</sub> concentrations as low as 77% with a CO<sub>2</sub> recovery of better than 90%.



**Figure 6:** Central CO<sub>2</sub> inerts removal and compression PFD.

The cold equipment is contained in a steel jacketed container or “cold box” with perlite granular insulation. The dry gas, stream 1, is fed to the cold box and is cooled by heat exchange to -26 °C with the returning product and the waste streams in the main exchanger. The main heat exchanger is a multi-stream plate-fin aluminium block. The cooled feed stream, stream 2, is sent to a separator pot, the stream is split into liquid and vapour, the liquid produced, stream 17, contains part of the required CO<sub>2</sub> product.

TABLE 10  
 MASS BALANCE FOR CENTRAL CO<sub>2</sub> INERTS REMOVAL AND COMPRESSION

	Stream no.																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
<i>Composition</i>																					
<i>(mol%)</i>																					
Carbon dioxide	77.03	77.03	62.71	62.71	25.09	25.09	25.09	25.09	25.09	95.04	95.04	95.04	95.04	95.04	95.04	95.04	97.12	97.12	97.12	96.23	96.23
Oxygen	4.14	4.14	6.73	6.73	13.49	13.49	13.49	13.49	13.49	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.51	0.51	0.51	0.69	0.69
Argon	4.48	4.48	7.12	7.12	13.62	13.62	13.62	13.62	13.62	1.53	1.53	1.53	1.53	1.53	1.53	1.53	0.79	0.79	0.79	1.11	1.11
Nitrogen	14.28	14.28	23.43	23.43	47.80	47.80	47.80	47.80	47.80	2.49	2.49	2.49	2.49	2.49	2.49	2.49	1.45	1.45	1.45	1.89	1.89
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulphur dioxide	0.06	0.06	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.13	0.13	0.13	0.09	0.09
Molecular Weight (kg/kmol)	41.06	41.06	39.17	39.17	34.19	34.19	34.19	34.19	34.19	43.44	43.44	43.44	43.44	43.44	43.44	43.44	43.71	43.71	43.71	43.60	43.60
<i>Design</i>																					
<i>Flowrate</i>																					
kg/h	277,391	277,391	154,448	154,448	62,320	62,320	62,320	62,320	62,320	92,128	92,128	92,128	92,128	92,128	92,128	92,128	122,943	122,943	122,943	215,071	215,071
Nm <sup>3</sup> /h	151,336	151,336	88,332	88,332	40,829	40,829	40,829	40,829	40,829	47,503	47,503	47,503	47,503	47,503	47,503	47,503	63,004	63,004	63,004	110,507	110,507
<i>Maximum</i>																					
<i>Flowrate</i>																					
kg/h	305,130	305,130	169,893	169,893	68,552	68,552	68,552	68,552	68,552	101,341	101,341	101,341	101,341	101,341	101,341	101,341	135,237	135,237	135,237	236,578	236,578
Nm <sup>3</sup> /h	166,469	166,469	97,165	97,165	44,912	44,912	44,912	44,912	44,912	52,253	52,253	52,253	52,253	52,253	52,253	52,253	69,304	69,304	69,304	121,557	121,557
<i>Phase</i>																					
Pressure bar(a)	Vapour	2 Phase	Vapour	2 Phase	Vapour	Vapour	Vapour	Vapour	Vapour	Liquid	2 Phase	2 Phase	2 Phase	Vapour	Vapour	Vapour	Liquid	2 Phase	Vapour	Vapour	Vapour
Temperature °C	29.17	28.89	28.89	28.62	28.62	28.34	28.07	28.07	1.05	28.62	28.41	28.41	9.43	9.23	9.02	18.23	28.89	18.33	18.13	18.13	221.01
Temperature °C	30.00	-26.10	-26.10	-54.72	-54.72	-43.27	18.83	302.81	35.00	-54.72	-45.39	-45.39	-55.71	-43.27	18.83	81.56	-26.10	-32.67	18.83	24.41	38.00

The vapour from the separator, stream 3, still contains a large proportion of CO<sub>2</sub>. In order to recover this CO<sub>2</sub> the vapour is cooled further to  $-55\text{ }^{\circ}\text{C}$  where it partially condenses, stream 4, and is passed to another separator pot. The pressure at this point is critical in controlling the process, cooling the vapour below  $-58\text{ }^{\circ}\text{C}$  would lead to the formation of solid carbon dioxide. The vapour from the second separator, stream 5, containing the separated inerts together with some CO<sub>2</sub> at a partial pressure of about 7 bara, is sent back to the heat exchanger where it is heated to  $19\text{ }^{\circ}\text{C}$ . This stream of inerts, which is at a pressure of 28 bara, is heated against hot flue gas in the boiler area, i.e. upstream of the venturi scrubber in Zone 1, and expanded in a power producing turbo-expander before being vented, stream 9.

Liquid, stream 17, from the first separator containing the CO<sub>2</sub> is expanded through a J-T valve to 18 bara and heated to  $19\text{ }^{\circ}\text{C}$ . The liquid from the second separator, stream 10, is heated, expanded to 9.4 bara to provide refrigeration and heated to  $19\text{ }^{\circ}\text{C}$ . The CO<sub>2</sub> stream is then compressed to the same pressure as the CO<sub>2</sub> stream from the first separator, stream 16. The two streams are combined and compressed to the required pressure of 220 barg. This machine is a five-stage unit which could be operated from the 18.3–220 bar level as either an intercooled compressor or as an adiabatic compressor with an after cooler used to heat condensate to  $120\text{ }^{\circ}\text{C}$ . In the latter case, no cooling water would be required for this section of the compressor.

#### Material selection

Compressor material selection for the wet CO<sub>2</sub> compression needs careful consideration due to the possibility of wet SO<sub>2</sub> being present. Previous studies have suggested doubling the nickel content in 316 stainless steel to 904 austenitic stainless steel to combat this problem. An appropriate material specification would be:

- Alloy 20Cb-3 (UNS No: NO8020)—20Cr2.2Mo34Ni3.5Cu austenitic stainless steel for impact areas or cold areas such as volutes, impeller, intercoolers and internals
- Alloy 2205—22Cr5Ni3Mo duplex stainless steel for shafting.

The central CO<sub>2</sub> product compressor needs no special materials of construction.

#### Dried raw CO<sub>2</sub> pipeline network

A summary of the required piping for the CO<sub>2</sub> network is shown in Table 11. Appropriate pipe sizes have been selected to meet a nominal pressure drop within the piping system of 2 bar. The layout of the piping is such that it uses existing pipe racks where possible. The pressure of the CO<sub>2</sub> pipeline network was chosen to be the pressure required at the inlet of the cold box in the central purification area. Any pressure up to this could have been chosen. However, the higher the pressure, the smaller are the local dryers and the pipe sizes required for distribution.

TABLE 11  
CO<sub>2</sub> PIPING

Approx. pipe lengths		Approx. no. of fittings			
Size (in.)	Length (m)	LRE 90	LRE 45	EQ TEES	Reducers
16	132	5	–	–	–
12	173	2	4	–	(16 × 12) = 1
10	374	3	–	–	(16 × 10) = 1
8	560	17	–	–	(10 × 6) = 1
6	64	4	2	–	–
4	239	4	–	–	(8 × 4) = 1

### **Site Layout**

One of the main challenges of this project was locating all of the new equipment required for the project on the site at Grangemouth. Constraints to be considered were:

- oxygen generation to be as close as possible to the main users of oxygen in order to minimise piping runs,
- available space was restricted and some areas were ear-marked for future process plant expansion,
- no equipment was allowed within a given safe distance of the flares, which are adjacent to the area allocated for the main process equipment required for the study,
- space was required within each of the five zones for the local drying and compressing equipment,
- space was required for the extra cooling water duty, although this did not have to be so close to the rest of the equipment,
- the power generating GTCC could also have been moved away from the main ASU to a more convenient location,
- the oxygen and carbon dioxide piping runs had to be routed so as to reflect what would be possible on the site. Existing pipe racks were used where appropriate.

Figure 1 shows the layout of the whole system in the refinery with the relative location of the oxyfuel systems, the ASUs and the cooling towers, together with the CO<sub>2</sub> and oxygen piping runs superimposed on a grid to show typical spacings and piping runs required.

## **RESULTS AND DISCUSSION**

### **Performance Summary**

#### *Terminology*

Before examining the results, some clarification of terms used in the tables that follow.

*CO<sub>2</sub> captured.* CO<sub>2</sub> captured is the amount of CO<sub>2</sub> collected from the oxyfuel converted boilers and heaters, purified, compressed and delivered into a pipeline.

*CO<sub>2</sub> avoided.* CO<sub>2</sub> avoided is the reduction in CO<sub>2</sub> emitted due to the conversion to oxyfuel firing. It is calculated by determining the net reduction in CO<sub>2</sub> emissions due to oxyfuel firing, i.e. CO<sub>2</sub> emissions from air firing *minus* CO<sub>2</sub> emissions from oxyfuel firing (i.e. CO<sub>2</sub> in the process vent plus CO<sub>2</sub> in the power generation gas turbine exhaust) *plus* a CO<sub>2</sub> credit for exported power.

*Reduction in fuel to heaters/boilers.* In converting to oxyfuel there is a reduction in the amount of fuel required to maintain a given duty. This is one of the advantages of oxyfuel firing. However, in the case of some of the heaters, this saving is further increased by accounting for the fuel that would have been used to raise the steam used for air pre-heating. Where the oxyfuel heater conversion results in less steam being produced in a downstream waste heat boiler, extra fuel must be included in the overall mass and heat balance to account for the makeup of this steam elsewhere on site. This is all accounted for in the fuel savings reported in these tables.

*Natural gas equivalent fuel.* The savings in fuel gas and/or oil to the heaters and boilers are converted to the equivalent amount of natural gas based on lower heating value. The gas turbine is powered by natural gas. Converting the fuel savings into equivalent natural gas savings allows the operating cost savings of oxyfuel to be fully accounted for, on the basis of the assumption that saving fuel oil or gas to the fired heaters or boilers will allow natural gas to be saved elsewhere on the site.

#### *Results*

The overall performance of the complete system for these options is given in Table 12 based on isothermal air and CO<sub>2</sub> compression. Table 13 gives the extra natural gas requirements and total equivalent fuel gas and fuel oil requirements for the system. Table 14 summarises the overall performance of these three cases, where Case 0 is air firing.

These results show, for each case that are discussed below.

TABLE 12  
COMPARISON OF DIFFERENT POWER GENERATION OPTIONS

Case	GT	Power (MW)		Fuel to power system (MW)	Reduction in fuel to boilers (MW)	Reduction in fuel to heaters <sup>1</sup> (MW)	CO <sub>2</sub> from GT exhaust (× 10 <sup>6</sup> tonne/year)	Boiler steam, (× 10 <sup>3</sup> lb/h)		Extra 13.7 barg steam	
		GT	ST					From boilers	From GT HRSG	tonne/h	MW
1	6FA	70.1	37.0	202	27.75	22.75	0.374	1771	0	0	0
2	7EA	85.4	0	260	135.26	22.75	0.455	1483	287.6	24.2	4.4
3	7EA	97.0	4.5	302	100.64	22.75	0.022	1576	195.0	37.9	6.8

Case	Total power generated (MW)	O <sub>2</sub> required (tonne/day)	O <sub>2</sub> to boilers (tonne/day)	Total power requirement (MW)	Export power (MW)	GTCC cooling water (tonne/h)	Total cooling water (tonne/h)	CO <sub>2</sub> captured (× 10 <sup>6</sup> tonne/year)	CO <sub>2</sub> avoided (× 10 <sup>6</sup> tonne/year)
1	107.1	6736	4316	96.4	10.7	6395	22,722	1.88	1.65
2	89.8	6034	3615	86.4	3.4	0	14,628	1.69	1.57
3	108.3	6889	3841	108.7	0.3	0	16,700	2.33	1.99

<sup>1</sup>Corrected for air pre-heating gain and steam generation steam loss.

TABLE 13  
FUEL REQUIREMENT SUMMARY

Case	Fuel gas/oil reduction (MW)	Fuel to GTCC (MW)	Nat. gas CV (MJ/kg)	Fuel to GTCC (tonne/h)	Nat. gas equiv. fuel gas/oil reduction (tonne/h)	Net equiv. nat. gas requirement (tonne/h)
1	50.5	202.1	48.16	15.11	3.77	11.33
2	158.0	260.4	48.16	19.46	11.81	7.65
3	123.4	301.9	48.16	22.57	9.22	13.34

TABLE 14  
FUEL AND POWER SUMMARY

Case	GT type	Total power generated (MW)	Export power (MW)	Total fuel, (MW)	O <sub>2</sub> required (tonne/day)	Total cooling water (tonne/h)	CO <sub>2</sub> captured, × 10 <sup>6</sup> (tonne/year)	CO <sub>2</sub> avoided, × 10 <sup>6</sup> (tonne/year)
0	n/a	n/a	0	1045.8	0	0	0	0
1	6FA	107	10.7	1197.4	6735	22,722	1.88	1.65
2	7EA	90	3.4	1148.2	6034	14,628	1.69	1.57
3	7EA	108	0.3	1124.3	6889	16,700	2.33	1.97

*Case 1.* This case requires the most oxygen and cooling water and gives a small export power. 1.88 million tonnes per annum is available for sequestration and the net reduction in CO<sub>2</sub> emitted is 1.65 million tonnes per year.

*Case 2.* In this case the power generation system is integrated with the existing boilers and steam turbines. Steam is produced in the HRSG of the gas turbine primarily at the 127 bar level and is used to replace part of the boiler steam, thus saving oxygen flow to the boilers. Here, a 7EA gas turbine is required but since steam produced in the HRSG is backing out steam production from the boilers, no steam turbines are required. This option also saves on cooling water requirements since none is required for the power generation system and the ASU is smaller due to the reduction in firing of the boilers allowed by the generation of steam in the gas turbine HRSG. This results in a lower amount of CO<sub>2</sub> available for sequestering since less CO<sub>2</sub> is available from the boiler system. The net reduction in CO<sub>2</sub> emitted is also reduced due to increased CO<sub>2</sub> from the gas turbine exhaust. However, total natural gas requirement is reduced from 11.33 tonne/h in Case 1 to 7.65 tonne/h in Case 2 and a smaller ASU is required.

*Case 3.* This case has the gas turbine operating in the pre-combustion decarbonisation mode with part of the oxygen from the ASU being used for hydrogen production in an autothermal reformer and with shift conversion and CO<sub>2</sub> removal using a MDEA system. Due to the fact that the CO<sub>2</sub> from the MDEA system is captured and compressed and also available for sequestration, this case has the highest amount of CO<sub>2</sub> for sequestering and also the highest net reduction in CO<sub>2</sub> emitted. For this case, we have assumed excess steam production is sent to the refinery turbines.

The results for Cases 1–3 have been reported with isothermal compression for the ASU and the main CO<sub>2</sub> compressor. However, further savings can be made by the use of adiabatic compression. As previously discussed, Table 6 shows the difference in performance of the ASU with both types of compression. One can

see a net reduction in power required of 4.6 MW and a reduction in total cooling water required of 7289 tonnes/h. This alteration is reflected in Table 15.

TABLE 15  
EFFECT OF ADIABATIC COMPRESSION ON CASES STUDIED

	Extra 13.7 barg steam		Total power generated (MW)	Total power requirement (MW)	Export power (MW)	Total cooling water (tonne/h)	CO <sub>2</sub> captured × 10 <sup>6</sup> (tonne/year)	CO <sub>2</sub> avoided × 10 <sup>6</sup> (tonne/year)
	(tonne/h)	(MW)						
Case 1 with adiabatic compressor	81.0	14.6	121.7	106.4	15.3	15,432	1.88	1.67
Case 2 with adiabatic compressor	105.2	19.0	104.4	95.3	9.1	8096	1.69	1.60
Case 3 with adiabatic compressor	118.9	21.4	122.9	118.9	4.0	9243	2.33	1.98

#### ***Cost Estimates and Overall Cost of CO<sub>2</sub> Removed***

This section summarises the estimate basis for initial capital investment and operating costs required to implement the base case scheme (Case 1). The section is divided into three main parts: capital costs, operating costs (including operating savings derived from oxyfuel operation of fired units) and an estimate of the cost per tonne of CO<sub>2</sub> captured and CO<sub>2</sub> avoided, for comparison with alternative methods of CO<sub>2</sub> capture. A final section aims to give the indicative cost impact for Cases 2 and 3, in order to quantify whether these alternatives would lead to an even lower cost of CO<sub>2</sub> capture.

The financial figures presented in this section and elsewhere in this report are presented as budgetary estimates for information only and do not constitute a commercial offer on behalf of Air Products, Mitsui Babcock, Foster Wheeler Energy, General Electric or any other potential suppliers of the scope of the study.

#### ***Capital cost estimate***

The overall estimate accuracy is ± 30%, although individual items may be more or less accurate. The Mitsui Babcock figures for refurbishment of the existing boilers have been quoted at ± 50%. Lower accuracy is typical for refurbishment type projects due to the higher technical risks associated with older equipment. The largest new capital investment items, the ASUs and the power cogeneration unit, are expected to be better than ± 30% accuracy.

The capital estimate is quoted on a lump sum turn-key basis and includes: site preparation, civil work and foundations; equipment and materials; transportation and logistics; fabrication, construction and installation labour; commissioning and start-up; 2-year operating spares and start-up spares and consumables; project management and procurement services; Engineering (excluding technology R&D); profit; royalties and licence fees.

The following items, most of which were given in the study remit, are specifically excluded: insurance; import duties and taxes; escalation; regulatory permits; cost of capital; cost of land; VAT; operator training; removal of contaminated land (no ground condition data is available); piling (no ground condition data is available).

Contingency of 20% has been included for direct comparison with previous work on benchmark technology.

The costs are presented in USD. Exchange rates of:

USD/GBP = 1.4

EUR/GBP = 1.6

have been used as realistic historical rates, and to give consistency with previous studies.

Costs are presented on a 2003 installation basis at the Grangemouth site in the UK. No allowance is made for escalation to a future actual project date. The capital estimate summary sheet is presented in Table 16.

#### *Operating cost estimate*

Estimates of the operating costs for Case 1 are given in Table 17.

#### *Cost of CO<sub>2</sub> capture*

One of the key measures for comparison with alternative methods of CO<sub>2</sub> capture is “cost per tonne of CO<sub>2</sub> captured or avoided”. This is a simple calculation, dividing the total annual costs attributable by the tonnes per year of CO<sub>2</sub> captured (or avoided).

To get a time-average annual cost for the significant capital investment, which must be made at the beginning of the life of the project, it is normal to derive a “capital multiplier” or “capital factor”. This takes into account: the operating or accounting life of the equipment, the cost of investment capital, tax rates in the country of investment and required return on investment criteria of the owner/operator. For this study a value of 0.1 or 10% has been used:

$$\begin{aligned} \text{Annual capital charge} &= \$490,931,000 \times 0.1 = \$49,093,100 \text{ per year} \\ \text{Therefore, total annual costs} &= \$49,093,100 + \text{£}22,246,100 = \$71,339,200. \end{aligned}$$

*Cost of CO<sub>2</sub> captured.* The CO<sub>2</sub> captured and available for sequestration is given in Table 12 for the base case, Case 1, as 1,880,000 tonne/year. Therefore, the cost per tonne of CO<sub>2</sub> Table 12 captured is:

$$\$71,339,200/1,880,000 = \$37.95 \text{ per tonne CO}_2 \text{ captured}$$

*Cost of CO<sub>2</sub> avoided (net reduction in CO<sub>2</sub> emissions).* The net CO<sub>2</sub> removed from potential emissions to the atmosphere is stated in Table 12 as 1,650,000 tonne/year. Therefore, the cost per tonne of CO<sub>2</sub> avoided is:

$$\$71,339,200/1,650,000 = \$43.24 \text{ per tonne CO}_2 \text{ avoided.}$$

It is likely that further development, integration and optimisation of the base case process will lead to a reduction in the CO<sub>2</sub> still emitted to atmosphere and, therefore, a further reduction in the cost of CO<sub>2</sub> avoided. For instance, methods of recovering the large quantity of additional CO<sub>2</sub> from the gas turbine exhaust have not been covered in this report.

#### *Alternatives to base case*

Indicative changes in the base case costing for the two alternative power generation schemes, Case 2 and Case 3, are presented in Table 18 and Table 19. As can be seen, both options will lead to a significant further reduction in cost per tonne of CO<sub>2</sub> capture. Case 2 would be preferred if the objective is to minimise the overall amount of CO<sub>2</sub> emitted, however, Case 3 would give a significant increase in the amount of CO<sub>2</sub> captured. The costs of all three cases are summarised in Table 1.



TABLE 16  
SUMMARY OF CAPITAL COST ESTIMATE

WBS No	Description	Materials	Sub-contracts	Total	Comments
100	Air separation units (2 × A3700)	58,113	36,219	94,331	
200	O <sub>2</sub> distribution and CO <sub>2</sub> gathering pipework	796	4787	5582	
300	CO <sub>2</sub> drying, compression and purification	45,802	23,718	69,520	Distributed and centralised
400	Cogeneration system			107,016	Turn-key GE 6FA package
500	Cooling water system			14,000	Constructed package
600	Boiler modifications	9030	8960	17,990	Mitsui Babcock estimate
700	Fired heater modifications			12,039	AP/FWE estimate
	<i>Total direct field costs</i>	113,740	73,683	320,478	
	Construction management			4913	
	Pre-commissioning/commissioning support			1891	
	Temporary facilities				Included in sub-contracts
	Vendor reps				Included in const mgt/comm support
	Heavy lift				Included in sub-contracts/freight
	Freight	10%		11,374	
	2 year operating spares	2%		2275	
	Commissioning spares	0.5%		569	
	<i>Total indirect field costs</i>			21,021	
	Project management, engineering and procurement			27,067	
	<i>Total home office costs</i>			27,067	
	<i>Total field and office costs</i>			368,567	
	Escalation			0	Excluded
	Reserve/contingency	20%		73,713	
	<i>Total capital cost</i>			442,280	
	Other costs				
	License fees				None
	Owners costs	10%		44,228	
	C.A.R insurance	1%		4423	
	<i>Overall total</i>			490,931	

All costs in × 10<sup>3</sup> USD.

TABLE 17  
SUMMARY OF ANNUAL OPERATING COSTS

Description	Annual cost ( × 10 <sup>3</sup> USD)	Comments
Combined cycle fuel cost	21,496.4	Natural gas at UK rate
Export power credit	– 2624.5	Exported to grid
Fired unit fuel reduction	– 5365.2	Natural gas equivalent value
Make-up water	2366.6	Possible to use condensed water from flue gases
Operator manpower	1450.0	
Maintenance	4422.8	
Consumables	500.0	
Total operating costs	22,246.1 per year	

TABLE 18  
COST DIFFERENCE FOR CASE 2

Item	Difference to base case costs	
	Case 2	Comments
Capital cost	– 12%	Steam integration of cogen. with fired units Less O <sub>2</sub> required by turned down boilers. Smaller ASU and CO <sub>2</sub> system. Simple cycle cogeneration system with HRSG, but no ST
Operating cost	– 19%	Higher fuel to cogen, but large amount of fuel saved in turned down boilers, by more efficient production of steam duty by cogen
Total annual costs	– 15%	
CO <sub>2</sub> captured	– 10%	Boilers turned down
Cost/tonne CO <sub>2</sub> captured	– 5%	
CO <sub>2</sub> avoided	– 5%	Higher CO <sub>2</sub> emissions from enlarged cogen
Cost/tonne CO <sub>2</sub> avoided	– 10%	

TABLE 19  
COST DIFFERENCE FOR CASE 3

Item	Difference to base case costs	
	Case 3	Comments
Capital cost	+ 4%	O <sub>2</sub> autothermal reformer (ATR) for hydrogen fuel More O <sub>2</sub> required for ATR, ATR capital itself and enlarged CO <sub>2</sub> system
Operating cost	22%	Higher fuel to cogen, no export power, larger fuel saving in fired units
Total annual costs	+ 10%	
CO <sub>2</sub> captured	+ 24%	
Cost/tonne CO <sub>2</sub> captured	– 11%	
CO <sub>2</sub> avoided	21%	
Cost/tonne CO <sub>2</sub> avoided	– 9%	

## CONCLUSIONS

This work has shown that it is feasible to apply oxyfuel technology to a complete refinery system with multiple CO<sub>2</sub> emission points spread out over a large area. This involves a centralised oxygen supply system and a CO<sub>2</sub> recovery, purification and compression facility.

It has been found that primary effluent gas cooling, compression and drying is best decentralised to be close to the emission points and an intermediate pressure CO<sub>2</sub> stream can then be routed to a centralised collection point for final purification and compression to pipeline pressure. The CO<sub>2</sub> purification system can be designed to handle practical levels of air leakage into boilers and process heaters to produce a purity of CO<sub>2</sub> suitable for geological sequestration.

The level of air leakage into boilers and heaters that are retrofitted for oxyfuel means that it is more economic to design the ASUs for only 95% purity and reject the associated argon and nitrogen in the CO<sub>2</sub> inert gas removal system.

It is possible to integrate the air separation system and the refinery steam system by using an adiabatic air compressor with boiler feed-water preheating in the compressor aftercooler. This minimises requirements for cooling water and also reduces overall power consumption.

A new gas turbine combined cycle system has been provided to provide power for the ASUs, the CO<sub>2</sub> purification and compression system, and the cooling water system. The combined cycle system can be specified with its own power producing steam system which will include a steam turbine and condenser, etc. or the gas turbine exhaust can discharge through a waste heat boiler producing steam at refinery conditions with resulting lower levels of steam production in the existing boilers and lower oxygen requirement for oxyfuel combustion.

It is possible to take this one step further and generate hydrogen to fuel the gas turbine and so avoid further CO<sub>2</sub> emissions. The natural gas fuel is decarbonised in an autothermal reformer fired with pure oxygen and using an MDEA system for CO<sub>2</sub> removal.

Costing all of the process alternatives discussed in this chapter leads to the conclusion that the lowest cost system is a hydrogen fired gas turbine with a HRSG integrated into the refinery steam system. Oxygen is supplied by two cryogenic ASUs which have adiabatic MACs, with aftercoolers being used to heat boiler feed water.

## RECOMMENDATIONS

Further work is required to allow a project of this type to proceed to the execution phase.

- Carry out necessary burner tests to verify the design of the oxyfuel burners and their likely performance in both air and oxyfuel firing.
- Further studies are required to properly integrate the gas turbine waste heat boiler and refinery steam system and the condensate heating in the adiabatic compressor aftercoolers.
- Dynamic simulation to verify the operability of the control system for oxygen supply, CO<sub>2</sub> management and boiler/heater response when changing over from oxyfuel to air operation.
- Specifically, for this refinery site it would be possible to identify further sources of CO<sub>2</sub> on the Grangemouth site suitable for capture—such as the CO<sub>2</sub> stack from the hydrogen reformer or other process heaters that could be converted to oxyfuel firing.

## REFERENCES

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