Developments in oxyfuel combustion of coal

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Preface

This report has been produced by IEA Clean Coal Centre and is based on a survey and analysis of published literature, and on information gathered in discussions with interested organisations and individuals. Their assistance is gratefully acknowledged. It should be understood that the views expressed in this report are our own, and are not necessarily shared by those who supplied the information, nor by our member countries.

IEA Clean Coal Centre is an organisation set up under the auspices of the International EnergyAgency (IEA) which was itself founded in 1974 by member countries of the Organisation for Economic Co-operation and Development (OECD). The purpose of the IEA is to explore means bywhich countries interested in minimising their dependence on imported oil can co-operate. In the field of Research, Development and Demonstration over fifty individual projects have been established in partnership between member countries of the IEA.

IEA Clean Coal Centre began in 1975 and has contracting parties and sponsors from: Australia, Austria, Canada, China, the European Commission, Germany, India, Italy, Japan, New Zealand, Russia, South Africa, Thailand, the UK and the USA. The Service provides information and assessments on all aspects of coal from supply and transport, through markets and end-use technologies, to environmental issues and waste utilisation.

Abstract

In oxyfuel combustion, coal is fired in a mixture of oxygen and recycled flue gases to produce a concentrated stream of CO_2 which can be purified for sequestration through physical separation processes. Despite the successful operation of a 30 MWth pilot plant since 2008, oxyfuel capture has yet to progress to the demonstration phase, however, the recent commissioning of a 100 MWth retrofit project and a 30 MWth oxyfuel circulating fluidised bed represent major steps for the technology. A number of new demonstration projects have also progressed to advanced stages of planning, of which the 168 MW FutureGen 2.0 plant could commence construction this year. With operation at the pilot-scale well-established, ongoing oxyfuel research has focused on clarifying the complex effect of the altered gas composition on combustion, heat transfer, and corrosion mechanisms in the boiler. As overall plant efficiency is limited by the substantial auxiliary loads required for oxygen production and purification of the CO_2 product, optimisation of these processes is also key to future scale up. Commercial cryogenic air separation units can be thermally integrated with the plant's steam cycle for higher efficiencies, or potentially replaced by membrane-based processes currently in early stages of development. New technologies trialled for CO_2 purification have focused primarily on improving SOx and NOx removal and achieving almost complete CO_2 capture. This report will review technological progress in each element of the oxyfuel plant, as well as presenting the latest results from large pilot projects and demonstration Front-End Engineering Design (FEED) studies. Finally, recent analyses of the potential efficiency and economic performance of future commercial-scale plant are compared.

Acronyms and abbreviations

AC	activated carbon
ALIVE	air liquide innovative variable energy
ANL	ANL Argonne National Laboratory
ASU	air separation unit
BAM	Bundesanstalt für Materialforschung und prüfung (Federal Institute for Materials Research and Testing)
CAPEX	capital expenses
CDS	circulating dry scrubber
CFB	circulating fluidised bed
CFBC	circulating fluidised bed combustion
CFD	computational fluid dynamics
Ciuden	Fundacion Ciudad de la Energia
COE	cost of electricity
CPU	compression and purification unit
DCCPS	direction contact cooler/polishing scrubber
DTF	drop tube furnace
ECO	economiser
EDF	Electricité de France
EFT	entrained flow reactor
EOR	enhanced oil recovery
EPRI	Electric Power Research Institute (USA)
FEED	Front End Engineering Design
FF	fabric filters
FG	flue gas
FGC	flue gas condenser
FGCC	flue gas cooler and condenser
FGD	flue gas desulphurisation
FGLPH	flue gas low-pressure heater
FID	final investment decission
GCCSI	Global Carbon Capture and Storage Institute
GAN	gaseous nitrogen
GRF	gas recirculation fan
GOX	gaseous oxygen
GPU	gas processing unit
GHE	gas heat exchanger
HEX	heat exchanger
HTC	heat transfer coefficient
HUST	Huazhong University of Science and Technology
HP	high pressure
ID	induction draught
IDF	induction draught fan
IEA	International Energy Agency
IFK	Institut für Feuerungs und Kraftwerkstechnik (Institute of Combustion and Power Plant Technology)
IP	intermediate pressure
IR	infrared
IGCC	integrated gasification combined cycle

ITM	ion transport membrane
LCOE	levelised cost of electricity
LE	large efficient (ASU)
LICONOX	Linde cold deNOx
LIN	liquid nitrogen
LOX	liquid oxygen
LP	low pressure
MCR	maximum continuous rating
MIT	Massachusetts Institute of Technology
MP	medium pressure
NG	natural gas
NGCC	natural gas combined cycle
NETL	National Energy Technology Laboratory
NTNU	Norwegian University of Science and Technology
O&M	operating and maintenance
OPEX	operating expenses
PAH	primary air heater
PC	pulverised coal
PCC	pulverised coal combustion
PJFF	pulsed jet fabric filters
PM	particulate matter
PSA	pressure swing adsorption
RFG	recycled flue gas
SAH	secondary air heater
SC	supercritical
SH	superheater
SWRI	Southwest Research Institute
TGA	thermogravimetric analysis
TIPS	ThermoEnergy’s integrated pressurised system
tCO_2	tonnes of CO_2
tO_2	tonnes of oxygen
t/d	tonnes per day
TU	Technical University
USC	ultra-supercritical
US DOE	United States Department of Energy
VPSA	vacuum pressure swing adsorption
WMR	wire mesh reactor
XLE	extra large efficient (ASU)
ZEP	zero-emissions platform

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1 Introduction

Continual growth in fossil fuel combustion worldwide since the start of the industrial era has increased atmospheric CO_2 to levels of 400 ppm which are unprecendented in human history. The observed warming effect of this greenhouse gas on the Earth's climate is expected to have an irreversible ecological and economic impact if CO_2 levels are allowed to increase beyond 450 ppm (IEA, 2011). Despite the growing use of alternative energy sources, fossil fuels currently represent over 81% of global energy consumption, and are forecast to remain a majority energy source for the rest of this century due to their widespread availability and capacity to provide dispatchable and economic energy. With huge global abundance and relatively low cost, coal in particular is expected to form a significant part of any future energy scenario, and massive growth in coal capacity is ongoing in developing and populous nations such as China and India.

Carbon capture and storage (CCS), in which CO_2 is extracted at source and transported to geological reservoirs, has therefore been proposed as the only means of decarbonising fossil fuel combustion. Despite the substantial additional technology and infrastructure required by this process, IEA analysis has estimated that the cost of halving CO_2 emissions by 2050 would increase by 70% without application of CCS (IEA, 2013). This is in large part due to the significant 'locked in' emissions from recently built coal capacity, for which retrofitting with CCS is the most effective means of abatement.

Three distinct strategies for carbon capture from coal plant have reached an advanced stage of development: Post-combustion capture, developed from existing natural gas purification processes, uses CO_2-reactive solvents such as amines to scrub CO_2 from flue gases; pre-combustion capture, where coal is first gasified and CO_2 is removed prior to combustion of the remaining H_2 in a gas turbine, and oxyfuel combustion, in which coal is combusted in a blend of pure oxygen and recycled flue gases in order to produce a more concentrated stream of CO_2 which can be captured without use of chemical solvents. As large-scale post- and pre-combustion capture are currently nearing completion, oxyfuel can be considered the least established of the three approaches, but has nevertheless undergone rapid development in the last ten years, and is likely to reach demonstration scale in the next few years, with a few large-scale plants having reached advanced stages of planning.

The principle behind the oxyfuel process is to aid the capture of CO_2 from flue gases by eliminating nitrogen from combustion, thus producing a flue gas consisting mainly of CO_2 and water, from which the latter can be easily removed by condensation. Instead of air, combustion is carried out in a mixture of nearly pure oxygen and the CO_2-enriched recycled flue gases, usually in a proportion which best mimics the properties of air combustion. The recycled flue gas is required to moderate the temperature of a pure oxygen flame, and provide sufficient volume to carry heat into the convective pass of the boiler. Besides the facility for flue gas recycle, this process requires the significant additions to a standard coal plant of an air separation unit (ASU) for production of oxygen and a compression and purification unit (CPU) for removing remaining impurities from the CO_2-rich flue gases and compressing it for transportation.

The energetic cost to this strategy is associated primarily with the air separation process required to produce pure oxygen, and partly with the compression and purification of the CO_2 product and fans for flue gas recycle. However, some current estimates suggest that this energy penalty has the potential to improve on that of post-combustion capture, with a loss of 6–8% points achievable for a full-scale, integrated oxyfuel plant (*see* Chapter 9). Furthermore, very high capture rates of up to 99% are possible in oxyfuel which are difficult to achieve in other forms of capture, thus lowering the energetic and economic cost per tonne of CO_2. Dispensing with the chemical-based capture plant used in post-combustion capture also circumvents problems of waste disposal and fugitive emissions of toxic compounds. Other advantages particular to oxyfuel include a reduced flue gas volume which could translate into smaller and more economical boiler island equipment and potentially facilitate the removal of conventional coal pollutants. Oxyfuel combustion also appears to improve combustion efficiency and reduce unburnt carbon in ash (Tranier and others, 2013; Uchida and others, 2013).

The origins of oxyfuel combustion lie in the early 1980s, when it was conceived as a way of producing pure CO_2 for enhanced oil recovery. As an approach to carbon capture from power plants it has initially lagged behind post-combustion technology which was well-established as an industrial process in natural gas purification. However, with growing interest in CCS in the 1990s, early pilot-scale studies were performed, leading to increased interest from boiler manufacturers and gradual scale-up of pilots (Chen and others, 2012). In 2008, the first full-chain oxyfuel process (including ASU and CPU) was demonstrated at Vattenfall's 30 MWth Schwarze Pumpe pilot plant in Germany, representing an important landmark for oxyfuel technology. Since then, other large pilots have followed, including a 30 MWth oxyfuel circulating fluidised bed plant in Spain and, most recently, a 100 MWth oxyfuel retrofit of an existing pulverised coal plant in Australia, which is also the first to generate electricity to the grid. Several plants at the demonstration scale have been proposed and had FEED studies completed, but none have been realised to date, primarily due to the lack of political and financial support required for a first-of-a-kind project. Currently, the only large projects remaining active are the 168 MW FutureGen 2.0 plant in the USA, for which a final investment decision will be taken this year, the 426 MW White Rose project in the UK, scheduled to complete a FEED study in 2015, and a 200 MW retrofit of a plant in Shenmu, China, which is also undergoing FEED work.

The earliest challenges presented by the oxyfuel process related to optimising coal combustion in a mixture of oxygen, CO_2, and water vapour which has thermal and chemical properties that are considerably altered from those of air. Achieving stable combustion with good stoichiometric ratios in these conditions is now fairly routine through use of both the adjustable oxygen concentration and conventional flame stabilisation techniques, although the development of accurate oxyfuel-specific computational models for combustion and heat transfer is ongoing. Other challenges are associated with understanding the changes to SOx and NOx formation, and managing the increased concentrations of these species which arise from recycling flue gas to the boiler. Elevated SOx and H_2O levels lead to a greatly enhanced risk of low-temperature corrosion and, together with high CO_2 levels, these species also have the potential to accelerate high-temperature corrosion mechanisms.

Although these areas of fundamental research are still highly active, this review will present a brief summary of their current status, before focusing on progress at the industrial-scale, including the state-of-the-art of ASU and CPU technology and results from the larger pilot plants currently operating. Air separation via cryogenic distillation of air is well-established in several industries, and yet it is a highly energy intensive process which remains a limiting factor in oxyfuel plant efficiency. In the last few years, commercial gas manufacturers have made progress in reducing the energy penalty of air separation for oxyfuel by up to 20%, and further savings may be possible through better thermal integration of the process with the plant's steam cycle. Alternatively, ion transport membranes are thought to present a lower energy solution for air separation and are approaching commercialisation. CPU prototypes have less basis in existing commercial technology, essentially consisting of a collection of gas purification processes corresponding to each flue gas contaminant. In particular, achieiving sufficient removal of the acid gases SOx and NOx has given rise to a range of technological solutions, including some entirely new concepts.

This report will also review some 'second generation' oxyfuel concepts which have departed from mimicry of conventional air combustion and attempted to exploit some of the benefits unique to oxyfuel. In particular, the suitability of pressurised oxyfuel combustion to reduce the energy penalty through recovery of the latent heat in water vapour has made it the subject of much research. Often in combination with pressurised combustion, several emerging technologies have also attempted to lower equipment costs by reducing or eliminating the need to recycle flue gases.

Finally, a brief review of recent cost analyses of oxyfuel capture will be presented, both in comparison to conventional coal plant and post-combution capture plant. As for energetic cost, the oxygen demand of an oxyfuel plant also represents a significant economic penalty but, within the sizeable margin of error, most estimates place a similar or slightly lower price on oxyfuel capture to post-combustion capture. Moreover, as a large proportion of existing plant equipment can be retained for oxyfuel capture, the technology may be particularly cost effective for retrofit.

2 Boiler island

It is possible for oxyfuel combustion to sufficiently mimic the heat transfer properties of an air-fired furnace for little adaption of conventional boiler design to be required, although for optimum performance new burners and potentially some modification of heat exchange duty in the convective pass may be necessary. On the other hand, a new build oxyfuel boiler design may be able to exploit reduced flue gas volumes by scaling down equipment. For both new build and retrofit, the principal addition to a conventional boiler island is the facility for recycling flue gas to replace both primary and secondary air, which can comprise ducting, additional fans, and a gas-gas heat exchanger for preheating the recycle streams.

The replacement of nitrogen with recycled flue gases has several important repercussions on boiler operation which will form the basis of this chapter. Foremost amongst these is a significant effect on the combustion behaviour of pulverised coal, together with the radiative and convective heat transfer properties of the flue gas. Achieving a sufficient understanding of combustion under oxyfuel conditions for optimum boiler operation and accurate modelling has been the focus of considerable research effort to date. Besides creating such challenges for boiler operation, recycling flue gas introduces a range of new variables to the system such as the proportion and composition of the flue gas used. Although more efficient, recycling untreated flue gas will lead to high concentrations of potentially corrosive species such as SOx throughout the boiler and ductwork, which will react with metals via corrosion mechanisms that can be substantially altered in the CO_2-rich environment. Lastly, preserving the CO_2 purity of this atmosphere against infiltration of outside air is another principal concern, not only for the boiler but throughout most of the plant.

2.1 Flue gas recycle

2.1.1 Location

In most forms of oxyfuel coal combustion, recycled flue gases are used to dilute pure oxygen and keep combustion temperatures similar to those of air firing. There are several possible locations from which flue gas can be taken for recycle to the oxyfuel boiler, and two streams are required to replace both the primary and secondary air in a conventional plant. As shown in Figure 1, the principal options are before the flue gas desulphurisation (FGD) equipment (3), after the FGD (2), and after the flue gas condenser (FGC) which removes water prior to further CO_2 purification steps (1). As removal of particulates prior to the recycle is considered essential to prevent severe erosion, all these locations are downstream of the flue gas filters. The further along the path the recycle stream is taken, the cooler the flue gas, and more reheating is necessary before it is returned to the boiler; this represents an efficiency penalty for the plant. On the other hand, recycling untreated flue gas could lead to significant operational problems. Recycle before desulphurisation (known as hot or warm recycle) will raise the concentrations of SOx in the boiler and potentially increase the risk of low and high temperature corrosion mechanisms associated with sulphur species. Recycle of flue gases prior to the condensation step avoids this problem but may remain unsuitable as a replacement for primary air, as the high moisture content hinders coal drying and can cause coal agglomeration problems. This is often referred to as dry flue gas recycle, in contrast to wet flue gas recycle taken from before the FGC.

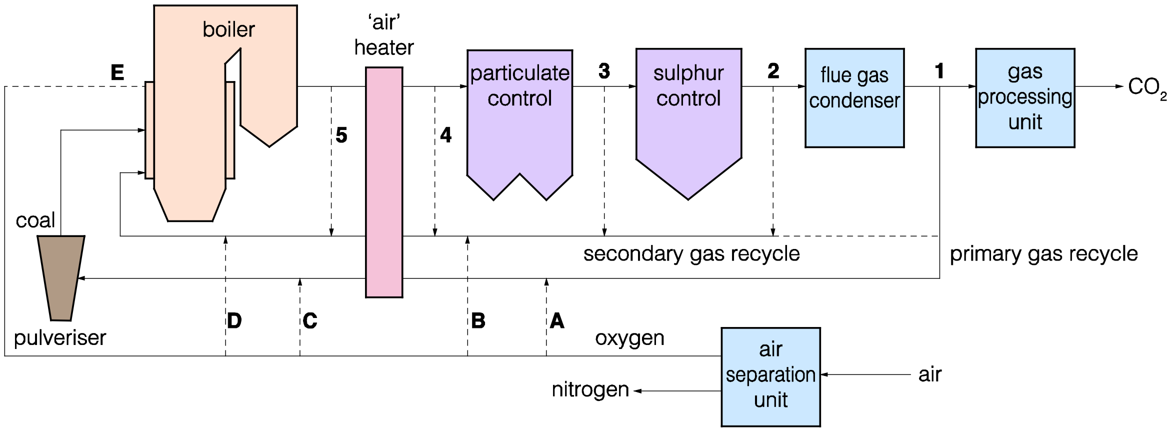


Figure 1 Possible flue gas recycle options in an oxyfuel plant (Davidson and Santos, 2010)

Most oxyfuel plant designs are obliged to use dry flue gases recycled from after the FGC as the primary stream for coal transportation and drying. Having been cooled to less than 30°C in the FGC, the stream first requires heating to around 250–300°C to dry the coal feed effectively (Mancuso and others, 2013). Whether the secondary recycle stream is taken from before or after the FGD will depend to a large extent on the sulphur content of the coal used. The increased corrosion risk under the high levels of SO_2, CO_2, and H_2O created by recycling flue gas is a subject of considerable ongoing research (see Section 2.4), and several oxyfuel pilot and demonstration plant designs have therefore followed a conservative approach of secondary recycle after wet FGD, despite the efficiency penalty incurred. A useful compromise for all but very high sulphur coal is to use a form of semi-dry FGD or even dry sorbent injection, which can mitigate or eliminate the efficiency penalty whilst achieving sufficient SOx removal to prevent corrosion (McDonald, 2013). However, the inclusion of wet FGD may also be necessary for plants intended to switch between oxyfuel and normal air firing. An alternative solution is to allow a combination of flue gas from both recycle locations, and to adjust the composition according to the sulphur level of the coal used. Carrying out any kind of flue gas treatment after the recycle point has the added benefit of treating a reduced volume, and could allow for significant reductions in equipment size (Riedl, 2014).

A study by Air Products and Foster Wheeler finds that, as a general rule, no FGD would be required for an oxyfuel plant firing coal with less than 5% sulphur content, and suggests SOx levels should be less than 2000–3000 ppm in the boiler (Mancuso and others, 2013). A low level of sulphur removal such as dry sorbent injection should be sufficient for the secondary stream with coals up to 2% sulphur. Babcock and Wilcox have also suggested increasing levels of FGD according to coal sulphur content, and note that, as semi-dry scrubbing precedes particulate filters, separate particulate control would be needed for a secondary stream taken before the FGD (McDonald, 2013). Taking both recycle streams from after flue gas condensation is suggested for the highest sulphur coals.

As for combustion air in a conventional plant, both primary and secondary recycle streams can be reheated against flue gases exiting the boiler in a gas-gas heat exchanger. Flue gases are cooled to around 200°C in this process, so further heat can be recovered for use in the steam cycle, depending on the acid dew point.

2.1.2 Recycle ratio

One of the most important parameters in oxyfuel combustion is the proportion of flue gas which is recycled and used to dilute the pure oxygen, often referred to as the recycle ratio. As discussed in the following section, this is one of the primary means of adjusting the coal combustion and heat transfer properties of the furnace. Whilst oxyfuel tests frequently refer to the volume percentages of oxygen and recycled flue gas in the gas mixture supplied to the furnace, the recycle ratio will be somewhat lower than the level of dilution ultimately obtained. This is largely due to moisture content in the coal, which adds to the volume of diluent available in the flue gases, but coal rank and air-fuel ratio are also factors. For a bituminous coal with 1% moisture, a recycle ratio of around 66% may be sufficient to dilute oxygen to 30%, compared to around 62% for a subbituminous coal with 20% moisture (Hu, 2011). In dry recycle, the removal of moisture means that the recycle ratio is much closer to the final percentage of diluent.

Recycle ratios which offer a lesser degree of oxygen dilution than in air result in less gas entering the furnace than in air firing, and a smaller volume of flue gas for the boiler and ducts to accommodate. This introduces the potential for smaller and cheaper boiler equipment, unless the ability to operate under air firing at maximum output needs to be retained.

The primary, secondary, and potentially tertiary streams can, in principle, be supplied with gas with various recycle ratios, and this is frequently applied in practice. There is an incentive to keep oxygen in the primary stream to below air-equivalent levels in order to minimise the risk of mill fires, though this means that the recycle ratio needs to be correspondingly increased in the secondary stream (Mine and others, 2011). Whilst injection of oxygen to the primary stream is beneficial for flame stability, it is not a necessity, and the Schwarze Pumpe and Callide pilot plants have both operated successfully without.

2.2 Oxyfuel combustion

Replacing combustion air with a mixture of oxygen and recycled flue gases has a significant impact on the combustion and heat transfer properties of a coal-fired boiler. Achieving a stable pulverised coal flame and, particularly for retrofit cases, similar heat transfer profiles to air combustion have therefore been important challenges for oxyfuel research. Oxyfuel conditions have a complex effect on combustion and heat transfer due to the fact that, as a larger, triatomic molecule, CO_2 differs from nitrogen in a number of important physical and chemical properties. Most thermodynamically relevant of these are its greater density (1.7 x higher) and molar heat capacity (1.6 x higher), but also influential are its strong activity in the infrared spectrum and low mass diffusivity for other gases such as oxygen (Figure 2). CO_2 is also much more chemically active than the inert nitrogen, and is able to participate in reactions such as the gasification of solid carbon (the Boudouard reaction). Fortunately, the ability to control the ratio of oxygen to recycled flue gases introduces a convenient additional degree of freedom with which to optimise the combustion process. However, the additional influence of this parameter and the altered gas density on mass flows and burner aerodynamics must also be taken into account.

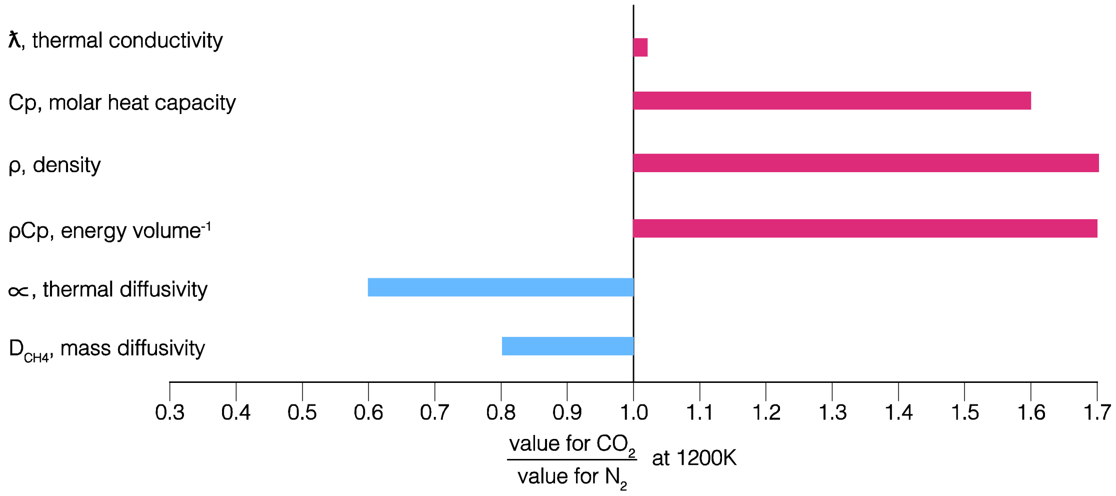


Figure 2 Ratios of combustion relevant properties of CO_2 and N_2 (Shaddix, 2012)

2.2.1 Heat transfer

Heat transfer in a coal-fired boiler can be divided into the radiative transfer to water walls which occurs in the initial stage of the furnace, and the convective transfer to superheaters, reheaters, and economisers, which takes place in the convective pass section. With both of these processes largely dependent on gas temperatures, the adiabatic flame temperature can be used as a useful fundamental parameter with which to optimise oxyfuel combustion to conventional heat transfer. As a result of the greater specific heat of CO_2, oxyfuel flame temperatures are lower for a given release of heat energy, but can be raised by lowering the recycle ratio to give an oxygen concentration above that of air. An oxygen percentage of around 28% in wet recycle flue gas is theoretically required to match air flame temperatures, or 35% for dry recycled flue gas (Wall and others, 2009). However, CO_2 and H_2O are both strongly active in the infrared and, unlike nitrogen, contribute to the radiation of heat energy to the furnace walls. Although this factor is less significant than either the temperature (on which radiation is dependent to the fourth power) and particulate radiation (~70% of total thermal radiation), it does have the effect of slightly lowering the flame temperature required to match the radiative heat transfer of air firing (Chen and others, 2012) (Figure 3). As a result, slightly higher recycle ratios are often applied which leave around 25–27% oxygen (Hayashi and others, 2011).

The greater contribution of gas radiation in oxyfuel furnaces means that accurate heat transfer modelling will require a thorough treatment of the true gas emission spectrum, rather than the wavelength-independent ‘grey gas’ approximation used for air combustion (Becher and others, 2011). Although computationally more demanding, such full spectral models of the gas radiation have been shown to result in 50% less error in prediction of oxyfuel flue gas exit temperatures (Pourkashanian and others, 2014).

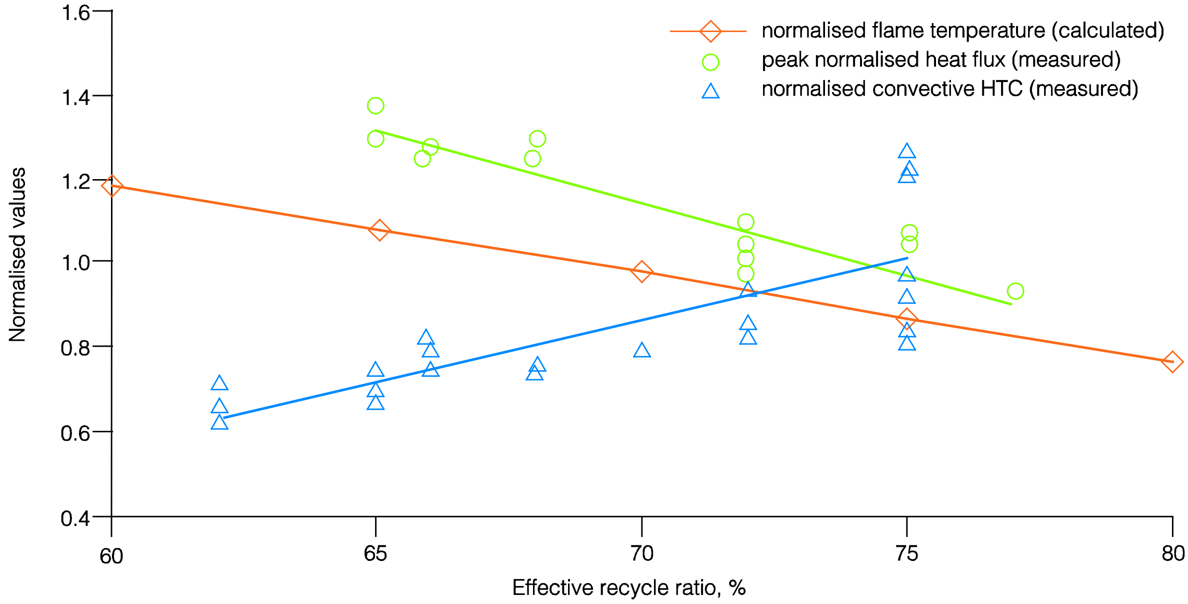


Figure 3 The effect of recycle ratio on adiabatic flame temperature, radiative heat flux, and the convective heat transfer coefficient (Smart and others, 2010)

Convective heat transfer is governed by both the temperature of flue gases and a heat transfer coefficient which is, in turn, largely dependent on the mass flow of gas through the boiler. Increasing the reycle ratio results in higher mass flows and greater convective heat transfer, with the coefficient conveniently approaching that of air firing at a similar recycle ratio as that required to match radiative heat transfer (Figure 3). Although the optimum ratio for matching both kinds of heat transfer will depend on the design of heat exchange surface in a given boiler, there nonetheless exists an acceptable range of recycle ratios (70–75%) at which a boiler can be operated close to air firing conditions without modification. Whilst this is significant for oxyfuel retrofit and boilers designed to operate in both firing modes, it is suggested that lower recycle ratios of less than 70% could be applied for new build boilers designed specifically for oxyfuel operation (Smart and others, 2010; Pourkashanian and others, 2014).

2.2.2 Flame stabilisation and burner design

Initial tests with oxyfuel combustion experienced difficulties in achieving a stable, well-defined flame. Indeed, theoretical models clearly show that replacing nitrogen with CO_2-rich flue gases results in an inherently less stable flame which exists within a narrower range of air-fuel ratios and level of oxygen dilution (Chen and others, 2012). Furthermore, the laminar flame speed of an oxyfuel flame is much lower than in air, contributing to ignition delay and making the flame more susceptible to detaching from the burner and blowing out (Suda and others, 2007; Molina and Shaddix, 2007). These altered properties again stem fundamentally from the greater specific heat of CO_2 or, more specifically, the still greater heat capacity per unit volume (ρCp) which lowers the reaction temperature and thus the reaction rate via the Arrhenius law (Molina and Shaddix, 2007). Experimental measurements of flame propagation in coal dust clouds have shown that the burning velocity can be a factor of six slower when nitrogen is replaced by CO_2, depending on coal volatile content (Figure 4). The process has also been simulated with theoretical models, usually using methane gas as replacement for coal volatiles. Such studies have shown up to ten times higher flame speed in air than in CO_2 with 21% oxygen (Vagelopoulos and others, 1994; Zhu and others, 1989).

Besides the physical effect of CO_2, there is a small chemical influence due to reactions between CO_2 and radicals such as O, H, and CH, which take part in combustion reactions. Reducing the concentration of these species also makes a small contribution to the reduction in the rate of fuel consumption and flame speed (Liu and others, 2003). One model of methane combustion in oxyfuel conditions has used a simulated chemically inactive CO_2 species to clarify that this chemical effect has roughly a twofold reduction on flame speed, compared to the almost tenfold influence from physical properties of the gas.

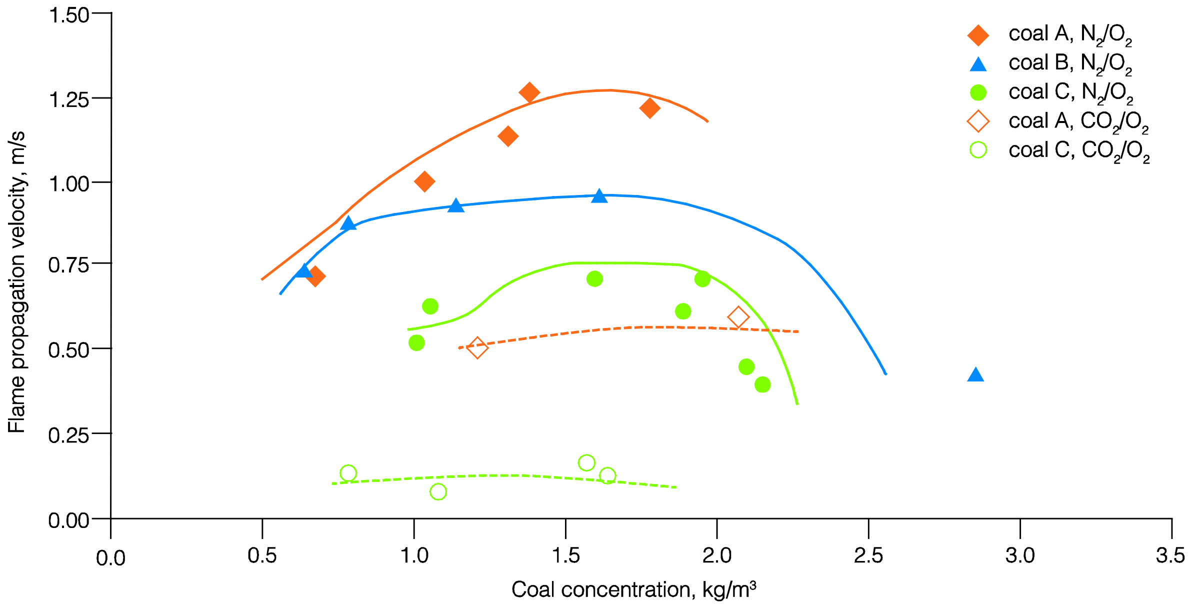


Figure 4 Flame propagation velocity in air and simulated oxyfuel atmosphere. Coal A is higher in volatile matter than Coal C (Suda and others, 2007)

Approaches to stabilising an oxyfuel flame are therefore usually based on increasing the combustion reaction rate, and thus the burning velocity, either by increasing the available oxygen or raising the temperature of the unburnt gases. Both these strategies can be effected in several ways. Simply reducing the reycle ratio to give higher-than-air oxygen levels is familiar from earlier discussion and 27% O_2 is again found to be sufficient to produce a stable flame in many cases. This is unsurprising given that the flame temperature will approach that of air and the reaction rate will increase accordingly. Whilst some retrofit studies using conventional coal burners have obtained stable, air-like flames by reducing the recycle ratio, new oxyfuel burner designs are needed to achieve optimal oxyfuel combustion performance, including good turndown capability and burnout, and minimal excess oxygen. A number of such tailor-made burners have been produced by research institutes and manufacturers such as IHI, Alstom, Doosan Power Systems, and Siemens (Chen and others, 2012; Grathwohl and others, 2011; Burchhardt and others, 2013).

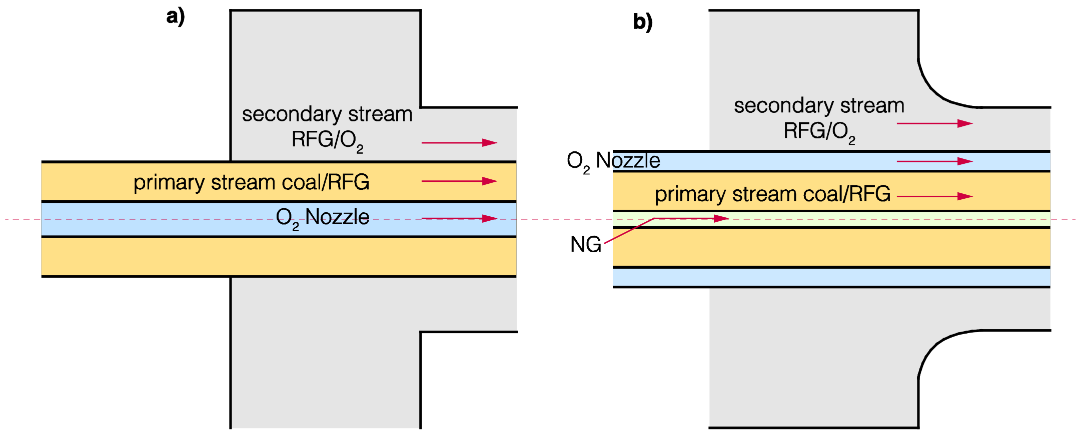


Figure 5 Oxyfuel burner designs with direct O_2 injection from a) IHI and b) Canmet (Chen and others, 2012)

Flame stability can be particularly sensitive to oxygen in the primary stream, which is consumed in initial volatile ignition and fixes the flame to the burner. However, high levels of oxygen in the primary stream are also undesirable due to the risk of autoignition, and the oxygen is frequently added entirely to the secondary stream, with the added benefit of simplified mixing. This means that more advanced burner designs can be required to compensate for the lack of primary oxygen. One method of directing the oxygen to where it can be most effective is to inject a proportion of in pure form, through lances usually located along on the burner axis or between the primary and secondary streams (Figure 5). This has been shown in several studies to be effective at producing a more compact, stable flame, which is more easily localised to a desired region of the furnace. Praxair have experimented with direct injection of fairly small quantities of oxygen (5–10% of the total) through different nozzle geometries, demonstrating how angling the oxygen away from the flame promotes mixing close to the burner and fixes the flame (Bool and others, 2010). Oxygen lances mounted within the secondary air inlet were employed by Alstom and IFK Stuttgart for the 500 kWth IFK oxyfuel rig, and subsquently for Alstom's first burner design trialled at the Schwarze Pumpe pilot plant (Maier and others, 2013).

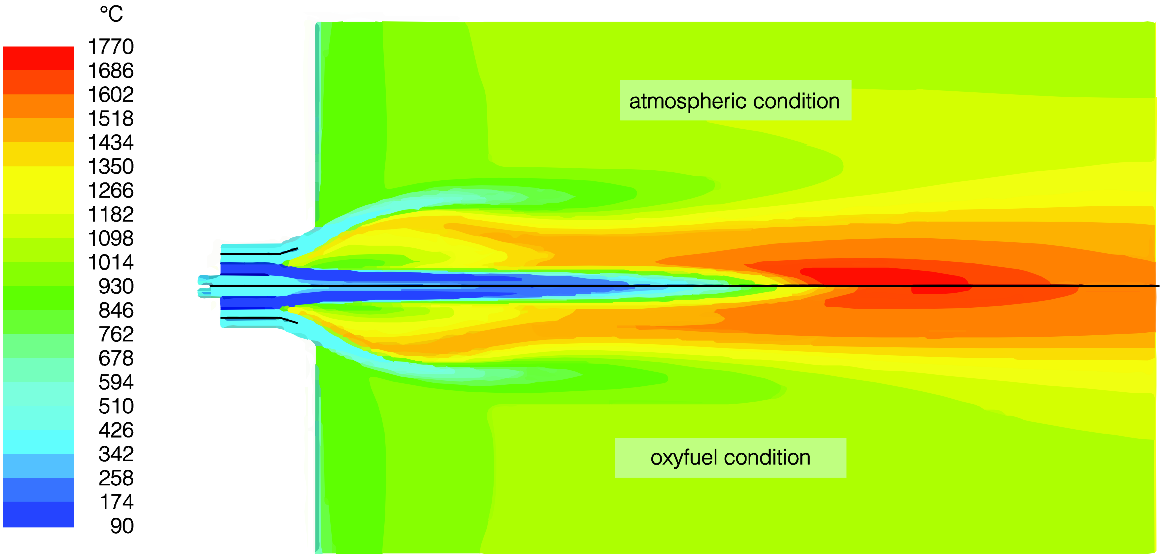


Figure 6 Temperature profiles of Hitachi's low NOx burner under air and oxyfuel conditions in which the O_2 concentration and momentum flows have been adjusted to match the air profile (Tigges and others, 2008)

The second strategy, raising the pre-ignition temperature of the oxyfuel gases, is best approached by promoting internal recirculation of the hot combustion products (Habermehl and others, 2012). The swirl feature which already achieves this in air burners by adding angular momentum to the secondary air, has therefore also proved highly useful for stabilising oxyfuel flames, and a high level of swirl has effectively become standard for burners tailored to oxyfuel firing. Early work at RWTH Aachen designed an oxyfuel burner based on redesigning quarl geometry to promote internal recirculation, achieving a stable flame even at 18% oxygen (Toporov and others, 2007; Heil and others, 2009). Reducing the mass flow through the burner was also found to help increase the proportion of recirculated combustion products, generating under-stoichiometric conditions and increasing the flame temperature near to the burner.

Building on this research through a collaborative project, tests at Siemens demonstrated that oxygen in the primary stream can be lowered to 2.7% (equivalent to residual levels in the recycled flue gas) when using the Siemens-REI swirl burner (Fry and others, 2010). Particularly when optimising aerodynamic effects such as swirl, it is important to take into account the significantly altered mass flow rates which arise from the lower total gas volumes generally used in oxyfuel combustion. As the primary velocity is often kept at air-fired levels to ensure coal is kept in suspension, secondary mass flow is proportionally reduced in oxyfuel, and the primary to secondary momentum ratio can increase from 0.13 to 0.73. This decreases the swirl effect and generally changes the flow regime from that which the burner was designed to produce. Hitachi have demonstrated that maintaining the air combustion momentum ratio by increasing the secondary flow rate in oxyfuel is sufficient for restoring the flowfields and temperature distribution (Tigges and others, 2008) (Figure 6). Alternativey, there is actually greater scope for lowering the primary velocity in oxyfuel, as the higher density of CO_2 allows coal to be kept in suspension at lower flow rates (Chen and others, 2012).

Doosan Power Systems have also developed an oxyfuel burner based on a low NOx swirl burner, of which a 40 MWth demonstration at Renfrew, UK, remains the largest oxyfuel burner tested and was able to maintaining a stable flame at 40% turndown (Sturgeon and others, 2013). A slightly scaled-down 30 MWth model of the burner was also trialled at the Schwarze Pumpe pilot plant.

2.2.3 Coal combustion chemistry

To obtain a complete understanding of the effect of oxyfuel conditions on coal combustion, it is necessary to elucidate the effect of recycled flue gas on the fundamental chemical and physical processes occurring in the flame. These are conventionally divided into four successive stages:

- drying of the coal particle;
- release of volatiles by pyrolysis (devolatilisation);
- ignition and burning of volatiles;
- combustion of the solid char.

The combustion of volatiles and char usually occurs separately for higher-rank coals (homogeneous ignition), but for lower rank coals the two can occur together, often with the char fragmenting during the process (heterogeneous ignition). Fundamentally, the altered combustion properties in oxyfuel stem from the impact of CO_2 on each of these steps, at which scale the effects of lower mass diffusivity and CO_2 chemistry become evident in addition to the elevated heat capacity. A clearer understanding of exactly how these processes take place in oxyfuel combustion should allow more accurate submodels for computational fluid dynamics (CFD) to be developed, which can in turn provide a detailed picture of boiler heat profiles and flame profiles. Research in this area generally relies on small-scale combustion analysis techniques such as thermogravimetric analysis (TGA), drop tube furnaces (DTF), and entrained flow reactors (ETF), which allow changes in each step of pulverised coal combustion to be elucidated (Tognotti, 2013).

Coal is dried by the hot primary gas stream during in the milling process and then upon contact with hot furnace gases. The drying rate depends primarily on the gas temperature and has been shown to be little affected by a CO_2-rich environment (Chen and others, 2012).

Pyrolysis of the coal particles, or devolatilisation, commences as they reach higher temperatures. Some studies have shown that the total yield of volatiles produced in oxyfuel conditions is greater than in air, and attributed this to the result of gasification reactions between CO_2 or H_2O and the char (Rathnam and others, 2009). Other studies have shown no difference, and equivalent rates of devolatilisation in both conditions (Brix and others, 2010; Chen and others, 2012). It has been proposed that this discrepancy in the literature is due to largely to varying experimental procedures and conditions. It is likely that gasification reactions become influential only at high gas temperatures and long residence times. On the other hand, the rate of devolatilisation is slightly slower than in air due to the reduced mass diffusivity (Shaddix and Molina, 2009).

As the volatile species meet hot oxidising gases they ignite and burn as a flame enveloping the coal particle. The time taken for ignition to occur defines the start of the visible coal flame, and is therefore a key parameter in stabilising the flame and inherently related to the discussion of flame speed above. Many oxyfuel studies have observed a signficant ignition delay in oxyfuel firing, which can contribute to a detached, unstable flame. This would be unsurprising for air-like oxygen concentrations which give a lower flame temperature in oxyfuel and therefore slow the heating rate, but smaller ignition delays have also been observed in experiments with equivalent gas temperature profiles. In experiments with an entrained flow reactor at set temperatures, Shaddix and others measured ignition delays of up to around 50% with CO_2 as the diluent, depending on coal type (Shaddix and Molina, 2009). Like flame speed, the ignition delay has a linear dependence on the heat capacity per unit volume, which slows down the temperature rise associated with chemically released heat, and is therefore increased in the CO_2-rich environment. Again, the suppression of radicals by CO_2 also exerts a small influence. The ignition delay can be reduced using the techniques discussed above for flame stabilisation; either by increasing O_2 concentration or raising the temperature of the unburnt gases via internal recirculation. Research by the same group also showed that time taken for volatiles to burn is extended when CO_2 is used as the diluent gas (Molina and Shaddix, 2007). Unrelated to the change in heat capacity, this effect stems instead from the reduced diffusivity of volatiles and oxygen in CO_2 compared to nitrogen.

In combustion of bituminous coal, oxidation of the char commences only after the volatiles are completely burnt and oxygen can reach the char surface. A principal point of oxyfuel research has been to determine the extent of the effect of gasification reactions between CO_2 or H_2O and the char:

$$CO_2 + C \rightarrow 2CO \tag{1}$$

$$H_2O + C \rightarrow CO + H_2 \tag{2}$$

As these reactions both have much higher activation energies (around 250 kJ/mol for CO_2 gasification) than the char oxidation reaction (~160 kJ/mol), they are now only thought to become significant at high temperatures and low partial pressures of oxygen, at which gasification is sufficiently accelerated but oxidation inhibited by the shortage of oxygen (Shaddix and others, 2013). Researchers at MIT have proposed three separate regimes for char oxidation experiments, which help explain the diverse range of results found in the literature (Figure 7) (Chen and others, 2012). In Region A of the plot, at low temperature and any amount of O_2, gasification reactions are too slow to have any impact, and the oxidation reaction is kinetically controlled (known as Zone I combustion in air). TGA experiments usually operate in this regime, and so show similar reaction rates for air and oxyfuel conditions. At the high O_2 and high temperatures of Region B, char oxidation is still dominant, but reaction kinetics are sufficiently fast for the reaction to be diffusion controlled (Zone II combustion). Here, the impeded diffusion of O_2 in CO_2 comes into play, and char consumption is reduced in oxyfuel conditions, as reflected in the DTF and EFR experiments which tend to operate in this regime. In Region C, at low O_2 and high temperatures, the gasification reactions become significant. However, as CO_2 gasification is highly endothermic, the reaction acts to lower the char temperature and slow the oxidation reaction. As a result, the additional char consumption by CO_2 is almost completely negated.

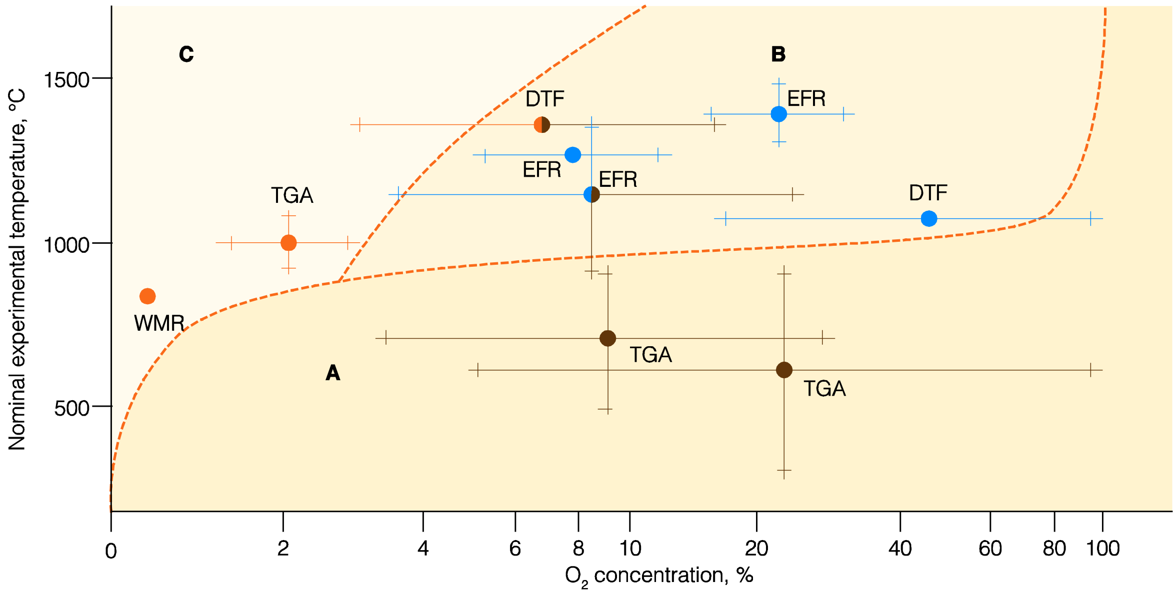


Figure 7 The effect of O_2 concentration and temperature on the relative influence of char gasification reactions. The experimental conditions of various studies from the literature are colour-coded to indicate whether an unchanged (black), decreased (blue), or increased (orange) char consumption rate was observed (Chen and others, 2012).

Detailed modelling of char combustion at the Combustion Research Facility has provided a quantitative analysis of the gasification effect at various oxygen concentrations (Shaddix, 2012). Using a model known as SKIPPY (surface kinetics in porous particles), it was confirmed that gasification reactions can significantly lower reaction temperature (by up to 400°C), to a large extent countering the additional char consumption they contribute. The researchers found that gasification by CO_2 contributed to 21% of char consumption in wet recycle oxyfuel conditions at 25% O_2, with water vapour gasification contributing a further 7.4%.

2.2.4 Oxyfuel circulating fluidised bed combustion

In circulating fluidised bed combustion (CFBC), coal is combusted in a hot bed of inert material which is given fluid-like properties by the injection of high-pressure air from the furnace floor. Finer particles become entrained with the high velocity flue gas and are returned to the furnace by cyclone separators. As there is no flame or burner used, many of the challenges presented by oxyfuel pulverised coal combustion are absent. Owing to this and other potential advantages, it has been suggested that CFBC may be well-suited to oxyfuel combustion of coal. While flame stability is not an issue, approximating the heat transfer profile of an air-fired CFB still requires an appropriate recycle ratio, and elevated oxygen levels of over 25% are again found to produce air-like parameters (Hack and others, 2009). However, in CFBC a large proportion of heat is recovered from hot solid material as it is circulated back to the lower furnace, providing an alternative means of moderating combustion temperature and allowing greater potential for reduction of the flue gas recycle ratio (Jukkola and others, 2005). As the main developers of oxyfuel CFB technology, Foster Wheeler have proposed that an increase in oxygen levels to 40% would be possible, bringing advantages of reduced fan power and boiler size and cost. It would not be possible for such a boiler to operate in air mode, and as such this is considered a second generation technology (Hotta, 2013).

2.3 Pollutant formation

The importance of pollutants such as NOx, SOx, and mercury is fundamentally altered in oxyfuel combustion, as these species are not generally released to the atmosphere and are instead almost completely removed in the downstream purification of CO_2. The range of processes used to remove these contaminants is discussed in detail in Chapter 4, but in most cases SOx, NOx, and mercury are dissolved and removed as liquid condensates. Understanding the altered rates of formation of these species is nevertheless useful for determining the demand on both conventional flue gas treatment processes and removal in the CPU. Most importantly, levels of SOx in particular have a significant impact on low and high temperature corrosion in the boiler and flue gas ducts. In oxyfuel combustion this is exacerbated by flue gas recycle, which has the effect of concentrating all flue gas contaminants to a level equivalent to combustion in pure oxygen. The extent of concentration therefore depends mainly on the proportion of diluting water vapour in flue gases, and can range from three to four times that of air levels (equivalent to 5% to 20% moisture) (Figure 8). A much smaller concentrating effect (typically a factor of 1.3) stems from the lower total volume of flue gas usually found in oxyfuel due to higher-than-air oxygen concentrations (Stanger and Wall, 2011; Bordenet and others, 2014a). Only this effect is observed for species removed before the recycle point. In discussion of oxyfuel contanimant concentrations it is therefore important to distinguish between the concentrated levels found in the boiler, and their actual rates of formation relative to air firing.

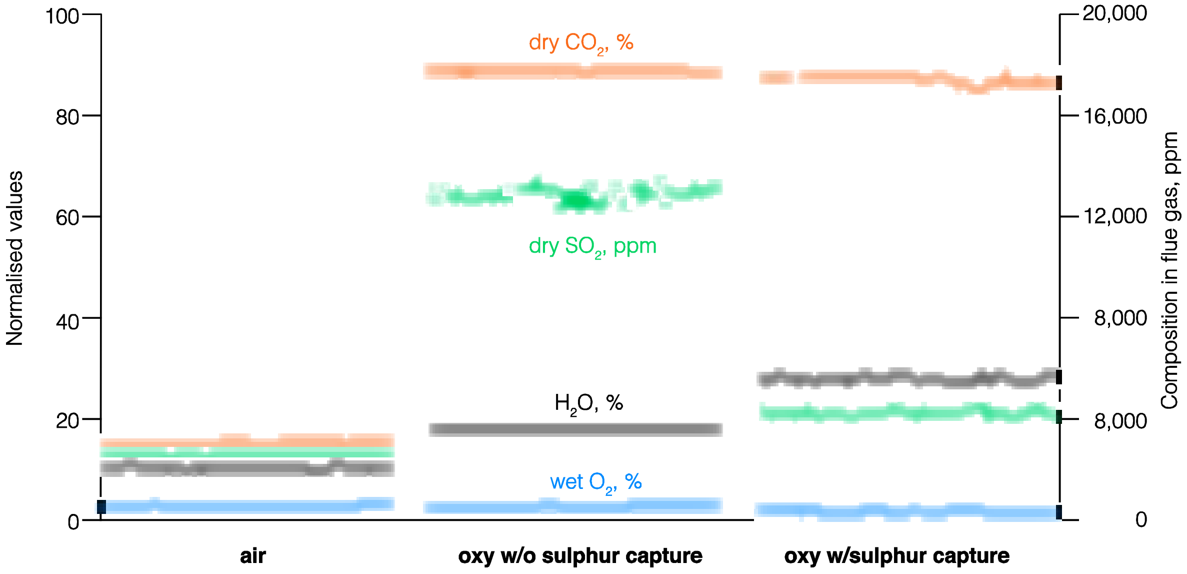


Figure 8 Typical concentrations of flue gas constituents in oxyfuel boilers with recycle of flue gas from before and after desulphurisation (Bordenet and others, 2014a)

2.3.1 SOx

SOx formation has an important bearing on oxyfuel plant operation, as the concentrating effect of recycling flue gases considerably raises the risk of sulphur-related corrosion mechanisms (discussed in detail in Section 2.4). Several studies have shown that SO_2 formation in oxyfuel furnaces is moderated by a higher rate of conversion to sulphur-containing salts in ash deposits, with formation rates that can be up to a third lower than air firing, although greatly varying results show this to be highly case-specific (Fleig and others, 2009; Stanger and Wall, 2011; Spörl and Maier, 2013). This effect is due to the concentrated levels of SO_2 in the boiler which stabilise and favour the formation of sulphates of calcium and other alkali metals, leading to increased retention of sulphur in oxyfuel ash (Spörl and others, 2013). Some studies have identified a correlation between the efficiency of this ash desulphurisation effect and the alkali metal content of the coal fired (Liu and Okazaki, 2003; Scheffknecht and others, 2011; Spörl and Maier, 2013). Simulated oxyfuel tests in oxygen and CO_2 without flue gas recycle have indicated that SO_2 formation rates may actually be slightly increased when the concentrating effect is absent, although reduced flue gas volumes in oxyfuel should also be expected to increase residence time and thus desulphurisation by ash (Croiset and Thambimuthu, 2001; Spörl and others, 2013)

The formation rate of SO_3 is significant for low temperature corrosion, but it is highly case-specific and much harder to determine due to challenges in measuring SO_3 levels. Whilst the higher partial pressures of SO_2 and also of oxygen found in oxyfuel boilers can be expected to lead to higher rates of conversion to SO_3, the capture of SO_3 by ash species is also enhanced in a similar fashion to SO_2. Indeed, increased conversion to SO_3 prior to capture by ash is also a proposed mechanism for reduced SO_2 formation in oxyfuel. However, with boiler-specific factors such as fuel, flue gas temperature, and residence times crucial to SO_3 formation rates, the effect of oxyfuel firing appears to be less significant and highly variable between tests (Spörl and others, 2013). Pilot-scale tests by Stanger and Wall observed similar SO_2 to SO_3 conversion rates in air and oxyfuel firing, and a review of pilot-scale results in the same work shows variable SO_3 formation rates which can be more or less than those of air (Stanger and Wall, 2011) (Figure 9). Other researchers have found higher conversion to SO_3 and suggested that high partial pressures of oxygen are mainly responsible (Stein-Brzozowska, 2013a).

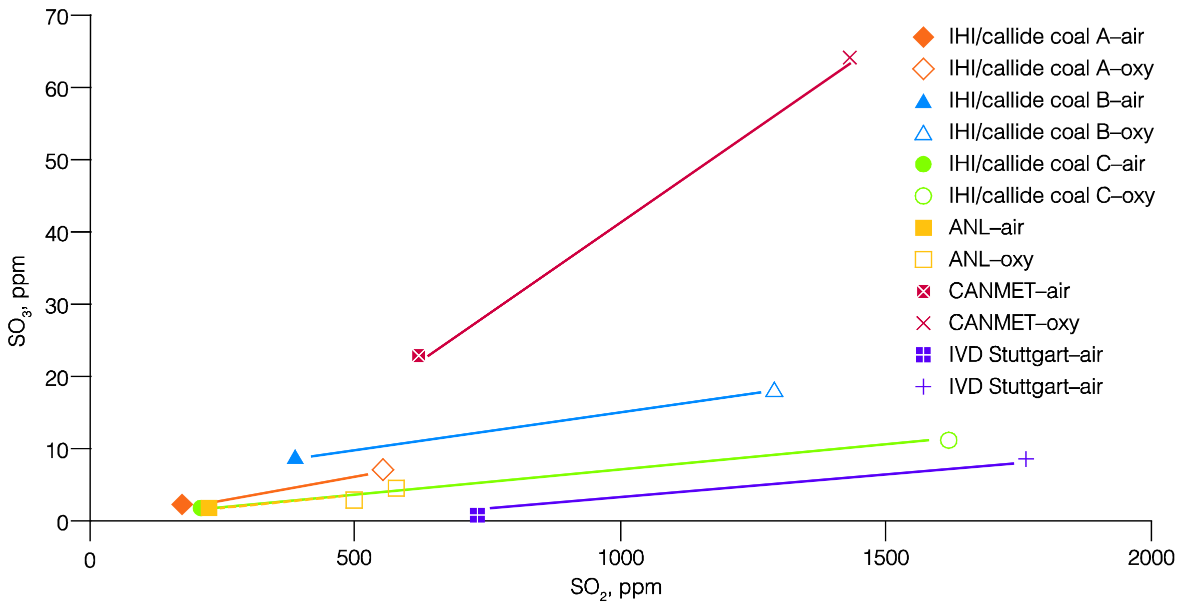


Figure 9 A review of SO_2/SO_3 formation in oxyfuel pilots (Stanger and Wall, 2011)

2.3.2 NOx

NOx formation in oxyfuel combustion has been widely shown to be susbstantially reduced in comparison to air firing, by a factor of around three to four (Figure 10). This is partly due to the absence of nitrogen gas, which effectively eliminates thermal NOx, but more significant is the reburning of recycled NO in the combustion zone. The extent of the reburning effect has been demonstrated by oxyfuel tests in which the recycled flue gas is replaced with an uncontaminated mixture of CO_2 and H_2O. In such tests, NOx levels are only 0.6 to 0.8 times air-fired levels. Studies without flue gas recycle have also shown that, in addition to almost eliminating thermal NOx, fuel NOx conversion is also lower in oxyfuel. This is thought to be related to higher concentrations of CO in the combustion zone (Chen and others, 2012).

The reburning mechanism which is dominant in NO removal has also been studied in isolation using oxy-methane combustion, which demonstrates removal of 40–70%, depending on equivalence ratio (Okazaki and Ando, 1997). In coal combustion, the extent of NO removal due to reburning is independent of temperature and NO concentration, depending only on coal reactivity, equivalence ratio, and the recycle ratio. The reburning effect has been shown to be even more pronounced in oxyfuel firing than in an equivalent air-fired system with recycled flue gas (Liu and others, 2003).

Primary NOx reduction measures such as low NOx burners and overfire air have been shown to also work effectively in oxyfuel combustion (Kluger and others, 2011).

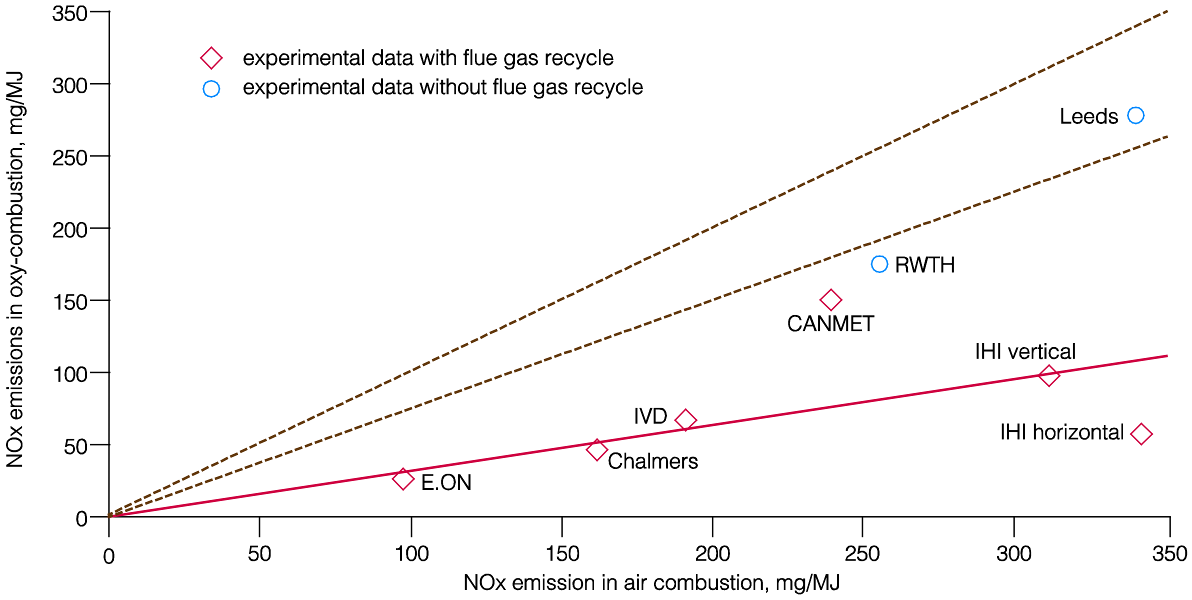


Figure 10 A review of NOx emissions data from oxyfuel pilot tests (Chen and others, 2012)

2.3.3 Pollutants in oxyfuel CFB

The effect of oxyfuel conditions on SOx formation in CFBC is more complex, as desulphurisation is carried out by the addition of limestone sorbent directly to the furnace. The limestone is calcined to CaO at the furnace operating temperature and goes on to react with SO_2 to form $CaSO_3$. The much higher levels of CO_2 in the furnace in oxyfuel combustion have the effect of much higher temperatures being required for significant calcination to occur (Wall and others, 2012). While SO_2 is able to react directly with limestone, the reaction is much slower, and it is preferable for an oxyfuel CFB to operate at bed temperatures of up to 100°C greater than those of air firing to allow the standard 'indirect desulphurisation' via CaO to take place. In this case, desulphurisation is actually improved due to the concentrating effect of flue gas recycle (Gomez and others, 2013a).

Air-fired CFBC already produces lower levels of NOx than pulverised coal combustion due to lower combustion temperatures and a reducing atmosphere. In oxyfuel CFB pilot studies, this effect has been shown to be further magnified under oxyfuel conditions, with up to three times less NOx than in air firing possible (Gomez and others, 2013a).

2.4 Corrosion

Metal corrosion is an important issue for oxyfuel combustion, as the increased concentration in the boiler and flue gases of species such as SOx and water vapour are likely to produce highly corrosive conditions relative to air combustion. It is well-established that the combined high levels of water vapour and SO_3 found in oxyfuel result in a significant increase in acid dew point which carries the risk of low-temperature corrosion in cool parts of the system, and existing oxyfuel pilots have been obliged to account for and seek to minimise this threat. The effect of the altered gas composition on high temperature corrosion mechanisms at superheat surface is less well understood and a highly active topic of research, with higher levels of CO_2, H_2O, and SO_2 all proposed to play signficant roles. These corrosion effects therefore have an important bearing on whether flue gas is recycled from before or after an FGD unit and the extent of desulphurisation required.

2.4.1 Low-temperature corrosion

Recycle of flue gases prior to desulphurisation typically concentrates SO_3 levels to up to four times those of air firing which, combined with up to 20% water vapour, can result in increases of the acid dew point by 20–30°C (Fleig, 2009; Hjornhede, 2010) (Figure 11). This puts low temperature areas of the plant such as the economiser, preheater, FGD, and FGC at higher risk of corrosion from acidic condensates, and means that unwanted cooling in sections of flue gas ductwork needs to be prevented as much as possible. Corrosion tests at the Schwarze Pumpe pilot estimated an acid dew point of 153°C in oxyfuel mode compared to 124°C in air firing, resulting in high levels of corrosion at 170°C as sulphuric acid starts to condense. A peak corrosion temperature exists at around 20–30°C below the acid dew point as increased water condensation at lower temperatures acts to dilute acidity (Hjornhede, 2010). Corrosion deposits enriched in sulphur compounds are formed in regions within the susceptible temperature range.

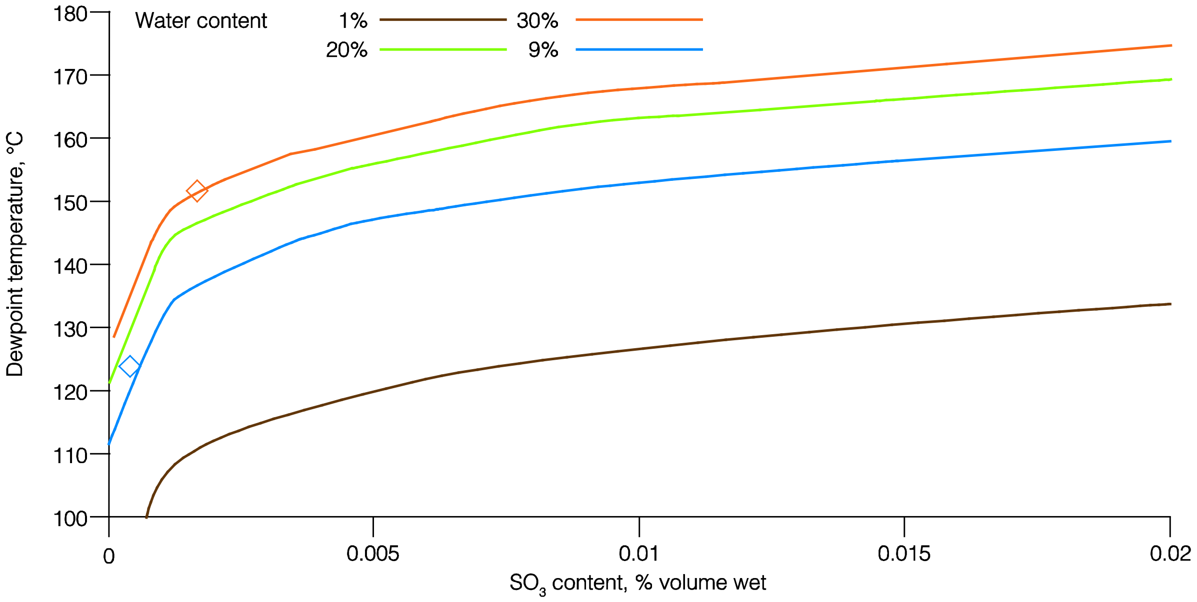


Figure 11 The effect of SO_3 and water vapour on acid dew point at Schwarze Pumpe (Hjornede, 2010)

Areas of flue gas ductwork can also undergo unwanted cooling due to ‘dead legs’ where flue gas stagnates or poor sealing which allows infiltration of ambient air. Both these problems were experienced at the Ciuden oxyfuel pilot, where purging of flue gas lines and more stringent sealing have been employed as corrective measures (*see also* Section 2.5) (Alvarez and others, 2013). At the Callide 100 MWth pilot plant a plate heat exchanger used for drying primary air was subjected to highly aggressive low temperature corrosion, particularly when low levels of chlorides were also present (Spero, 2013). Both plants have also had to make use of more corrosion resistant materials such as high chromium duplex and super duplex steels for ductwork below the acid dew point. Anticorrosive coatings have also been employed at

Ciuden. Avoiding acid condensation will be imperative in full-scale plant, and will require appropriate treatment of flue gas recycle streams and insulation of areas which are at risk of cooling below the acid dew-point (Bordenet and others, 2014a).

In the FGC and other parts of the CPU, condensation becomes an integral part of the purification process and SO_2 and NO_2 start to condense at these lower temperatures. Consequently, highly acid resistant materials have been employed for some exposed sections, such as the lower section of FGC cooling columns. Materials used include plastics, protective metal coatings, and corrosion resistant nickel alloys (Lockwood and others, 2013, Spero, 2013) (*see* Chapter 4).

2.4.2 High-temperature corrosion

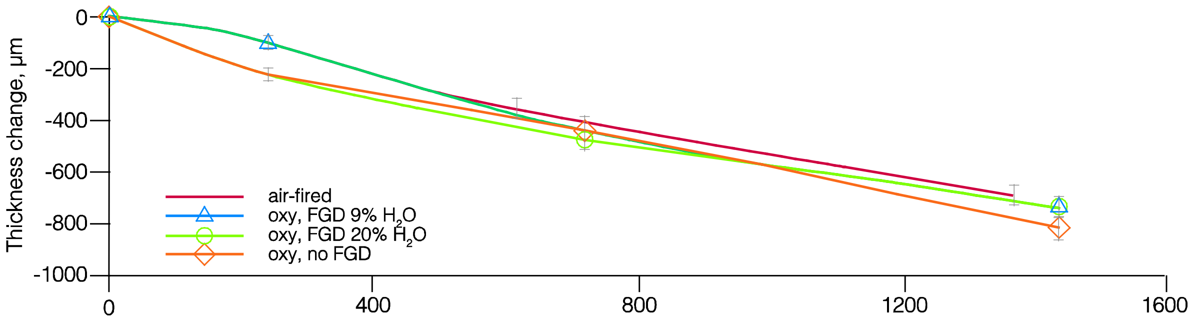
In regions of the boiler which experience temperatures of over 500°C, a wide range of reactions between combustion products and metals are sufficiently accelerated to lead to degradation of the metal surface. This is primarily a concern for superheaters, which can reach temperatures of 700°C, but waterwall materials may also be under threat if exposed to overheating or reducing conditions. The ferritic steels generally used for waterwalls and the more corrosion resistant martensitic or austenitic steels used for superheaters form surface scales of chromium and iron oxides which should present a thin and impermeable barrier to further oxidation and loss of material. However, in the presence of coal flue gases and the ash deposits which build up on boiler surfaces, this scale can become porous and thicken, eventually leading to spallation and further oxidation of the metal beneath. As well as oxidative attack by species such as oxygen and water vapour, sulphidation and carburisation reactions can take place in the presence of SOx and CO_2 which result in formation of unprotective sulphates, sulphides, and carbides of the alloy components. In the presence of a weak or slow-growing scale, corrosive reactions may also take place within the base metal beneath. This is known as internal oxidation or sulphidation and often occurs preferentially along the metal grain boundaries (Young, 2008).

A particularly aggressive form of attack is known as 'hot corrosion', in which the formation of molten salt species in the ash deposit leads to dissolution of the protective scale and reprecipitation of a porous mixture of the metal oxide and salt. In coal furnaces, this is usually due to the formation of alkali iron trisulphates (Na, K)$FeSO_4$, which are molten and stable within the range of superheater temperatures (550–650°C) and can form in the presence of alkali metals and SOx (Abang and others, 2013).

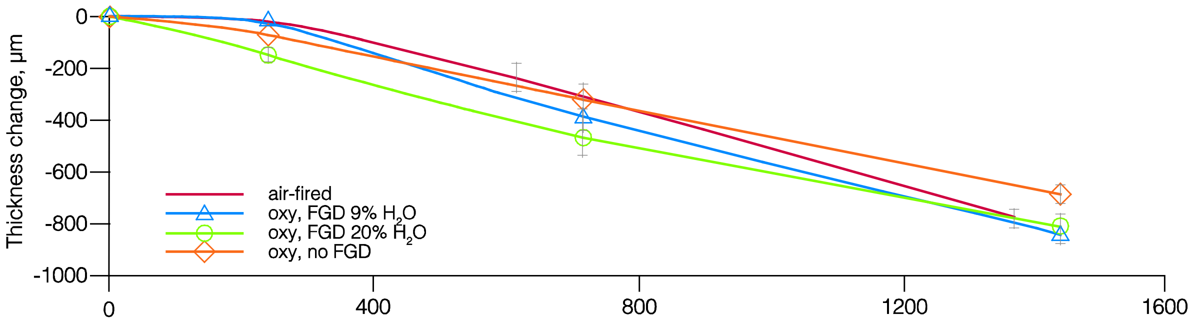
Effect of oxyfuel firing

Particularly where recycled flue gases have undergone minimal treatment, the conditions in an oxyfuel furnace include increased levels of several gas species which could potentially exacerbate high temperature corrosion. As for low temperature corrosion, concentrated levels of SOx are the principal concern due to their role in sulphidation and hot corrosion mechanisms involving molten sulphates. Much research has therefore been conducted into clarifying the extent of high-temperature corrosion under oxyfuel conditions and whether it constitutes a limiting factor for the process. However, effectively simulating long term corrosion of boiler materials can be challenging, as they are subjected to a complex chemical environment in the form of flue gases and ash deposits on the fireside, as well as high-temperature steam on the steam side. Whilst oxyfuel pilots rarely offer extended periods of operation under constant conditions, longer term laboratory tests may not always provide a realistic approximation of the boiler environment.

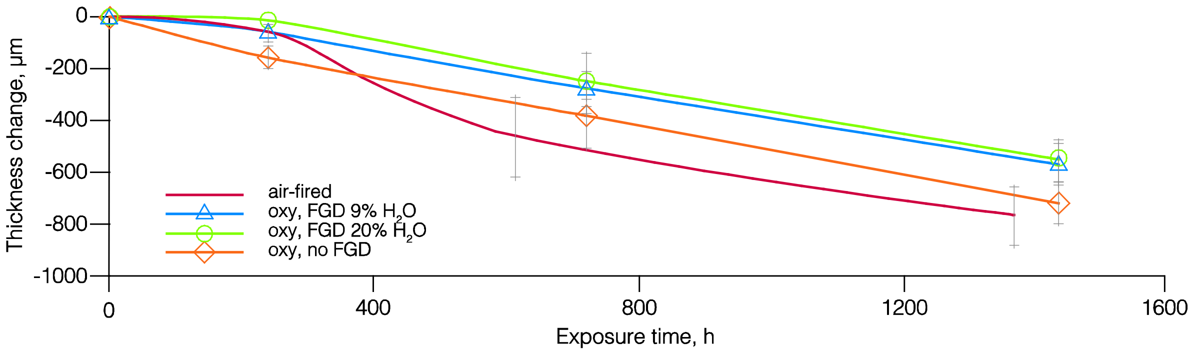
The wide range of conditions and methods used in corrosion testing has led to some uncertainty over the true influence of the oxyfuel gas composition. Whilst some early studies have shown worse corrosion in oxyfuel (Holcomb and others, 2012; Hjornhede and others, 2009; Kull and others, 2009; Abang and others, 2011), other results, including long-term experience at the Schwarze Pumpe pilot plant, have shown little difference to air firing (Gerhardt and others, 2013; Bordenet and others, 2014b; Hawk and others, 2014; Pint and others, 2014) (Figure 12). Indeed, there is now some consensus that high-temperature corrosion in oxyfuel boilers is not significantly different from air firing, and is governed by the same fundamental mechanisms. Although hot flue gas recycle will lead to high levels of SOx, this essentially creates a corrosive environment similar to that encountered when using high sulphur coals, and the presence of high levels of SOx alone does not guarantee particularly severe corrosion. Given the key role played by ash chemistry in high temperature corrosion, this similarity between air and oxyfuel corrosion mechanisms is in keeping with the widespread observation that both firing modes produce ash deposits of similar composition, although hot recycle in oxyfuel does result in higher levels of SOx in ash (Oakey, 2014; Bordenet and others, 2014a).



T91 700°C oxidative



TP347 700°C oxidative



617 700°C oxidative

Figure 12 1400 hour corrosion tests of a martensitic steel (T91), an austenitic steel (TP347), and a nickel alloy (617) in gas environments simulating air firing and oxyfuel with different kinds of flue gas recycle (Hawk, 2014)

Effect of SOx

High concentrations of SOx in the boiler can lead to severe high-temperature corrosion through a variety of mechanisms, including sulphidation of the base metal and formation of corrosive melts of iron alkali trisulphates. Several studies have observed thicker oxide scales in martensitic steels or incomplete chromia scale for austenitics under gas conditions which simulate oxyfuel boilers with hot recycle (Stein-Brzozowska and others, 2011; Otsuka, 2013; Abang and others, 2013). Some low chromium nickel alloys have also shown very high levels of corrosion in these conditions, with internal sulphidation of Cr leading to worse corrosion than the austenitic steels (Hawk, 2014, Matsunaga and others, 2013, Stein-Brzozowska and others, 2013b). When ash deposits containing alkali metals are present, higher levels of SO_3 stabilise molten sulphates to higher temperatures, broadening the temperature range for hot corrosion and raising the temperature at which maximum corrosion occurs (Figure 13) (Oakey and others, 2013; Matsunaga and others, 2013).

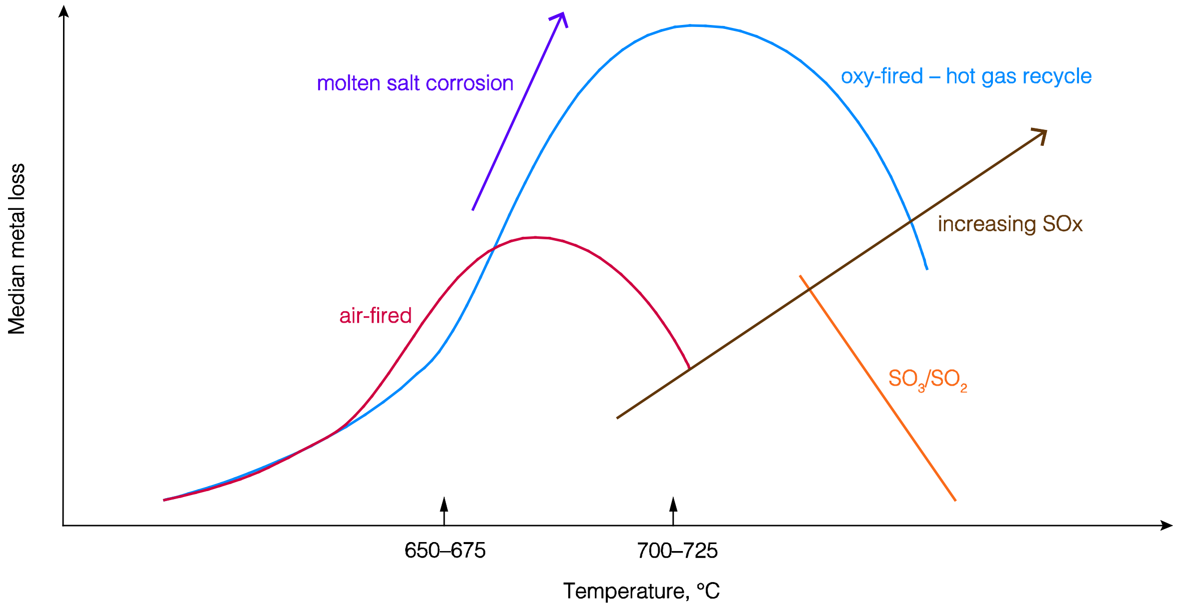


Figure 13 The broadening of the temperature range for hot corrosion caused by high levels of SOx, as found in oxyfuel furnaces with hot recycle (Simms and others, 2014)

On the other hand, sulphur-related corrosion is highly dependent on factors such as metal temperature and ash composition, and high levels of SOx have in many cases been shown to have little detrimental effect. Where stable sulphates of Ca and Mg are able to form, they can act as a non-corrosive sink for SOx within the ash deposit (Stein-Brzozowska and others, 2013a). Internal oxidation has also been shown to be mitigated by high levels of SOx, possibly as a result of reduced oxygen solubility or Cr sulphide formation (Huczkowski and others, 2013). Even where hot corrosion takes place, alkali metal sulphates can be a less damaging alternative to formation of chlorides of the same species (Paneru and others, 2013). Extensive corrosion tests by Babcock and Wilcox have even shown significantly reduced hot corrosion in oxyfuel conditions over air for a wide range of metals and using three coal types (Kung, 2013). A number of factors were thought to contribute to this effect, including the reduced mass diffusivity in oxyfuel gases, the early formation of carbonates delaying the availability of sulphates, and the base-neutralising effect of the acidic gases CO_2 and HCl.

Water vapour

Nevertheless, there have been observations of slightly worse corrosion in oxyfuel even with equivalent levels of SOx, particularly for ferritic and martensitic steels (Bordenet and others, 2014b). Indeed, some laboratory studies have indicated that high water levels could be the more influential factor in oxyfuel boilers with wet flue gas recycle (Holcomb and others, 2013; Otsuka, 2013; Quaddakers and others, 2014; Paneru and others, 2014). Water can enhance the diffusivity of other species through oxide scales and, in conjunction with oxygen, leads to the formation of the volatile species $CrO_2(OH)_2$ which greatly impedes the formation of protective chromia (Ani and others, 2009; Mu and others, 2013). Although this mechanism can be highly damaging for the 'chromia-forming' austenitic steels, it also appears to be effectively mitigated by the presence of ash deposit and also of SO_2, which adsorbs to the metal in preference to water (Asteman and others, 2014; Quaddakers and others, 2014).

Carburisation

The much higher levels of CO_2 found in any oxyfuel configuration were early on highlighted as presenting a risk of metal carburisation, but relatively few studies have actually observed significant carbide formation under oxyfuel conditions (Kull and others, 2009; Stein-Brzozowska and others, 2011; Kranzmann and others, 2011). In these cases, ferritic and martensitic steels have been particularly affected, with chromia or alumina forming materials thought to resist the diffusion of CO_2 into the base metal. The failure to observe carburisation in many other oxyfuel corrosion tests has led to the suggestion that the reaction of CO_2 with the metal is effectively mitigated in the presence of water vapour and oxygen (Hjornhede and others, 2010; Quaddakers and others, 2014). However, carburisation may still pose a threat in regions of the boiler exposed to reducing conditions, such as in the vicinity of burners.

Impact on full-scale plant

The risk of increased corrosion in oxyfuel furnaces is likely to restrict the use of hot recycle to low sulphur coals so as to keep SOx levels to within the experience range of air-fired boilers (as discussed in Section 2.1.1) (Davis, 2014; Bordenet and others, 2014a; Kung, 2014). As risk minimisation is particularly important for first-of-a-kind units, all planned demonstration plants have incorporated some kind of desulphurisation prior to flue gas recycle, although an additional drying step is generally reserved only for the primary recycle stream. Further understanding of corrosion under oxyfuel conditions is likely to require experience from such a demonstration plant, although there is also increasing interest in studying oxyfuel corrosion at the higher temperatures that would be encountered in advanced ultra-supercritical (USC) plant.

2.5 Preventing air ingress

The ingress of air into the boiler or any part of the flue gas stream presents a major problem to an oxyfuel plant, as it increases the energy demand of CO_2 purification. Several oxyfuel pilot projects have found that effective sealing of the boiler and accessories is one of the principal challenges of plant operation, although it should be noted that this effect would be diminished in larger units. At the Ciuden 30 MWth pilot in Spain, areas vulnerable to air infiltration were found to include textile expansion joints, flange unions, and moving parts such as fans (Alvarez and others, 2013). Corrective measures involved the use of metal expansion joints, welded flanges rather than bolted, and the use of dynamic sealing for fans. The recycle of cold flue gases to shield moving parts from air, or as backup to other seals, has been trialled at Ciuden and at Vattenfall’s Schwarze Pumpe pilot unit (Burchhardt and Griebe, 2013). At Schwarze Pumpe, the inclusion of wet FGD in the flue gas path presents a further challenge, as the forced oxidation tank, into which air necessarily flows, must be physically seperated from the primary reaction vessel. This measure was found to be effective but could carry a high capital cost for larger plants. Other preventative measures taken by the Vattenfall pilot include integrating the start burner into the main burner to prevent ingress via this route. Artificial air ingress tests at the plant have also led to the development of a statistical method for quickly detecting and locating leakages based on the measurement of relatively few parameters (Preusche and others, 2011).

Air ingress is likely to be a much more significant issue for oxyfuel retrofit projects, as new-build oxyfuel plant can be designed to minimise infiltration (Perrin and others, 2013). CFB boilers may also be less affected by air ingress, as the boiler pressure is usually above atmospheric (Wall and others, 2012).

3 Oxygen production

A utility-scale oxyfuel plant requires a constant supply of large volumes of oxygen on a scale comparable to some of the largest existing oxygen-consuming industrial installments. Cryogenic air separation is the standard industrial process for oxygen production at such large scales, and is widely used throughout industries such as glass, steel, and chemical manufacture, with the largest single units producing over 4000 t/d of oxygen. As an oxyfuel plant is expected to consume roughly 20 t/d per MW of net generation, plant in excess of 500 MW is likely to require multiple units on an even larger scale, making the ASU the most costly addition to a conventional plant (Terrien and others, 2013). Whilst relatively low purity oxygen (>95%) can be used for oxyfuel combustion, cryogenic air separation is also a highly energy intensive process and represents the most significant efficiency penalty to the plant (10–15% of gross power output). Growing interest in oxyfuel carbon capture over the last ten years has therefore led ASU manufacturers to focus on developing new large units with high efficiency. Although cryogenic ASU is the only technology currently capable of producing oxygen at the necessary scale for oxyfuel plant, air separation using oxygen-conducting ceramic membranes is an emerging alternative technology which has some potential to provide a less energy intensive oxygen supply for second generation oxyfuel plant. This chapter reviews the state-of-the-art in cryogenic air separation as well as the current status of ceramic membrane technologies. Other methods of oxygen production, such as pressure swing adsorption and polymer membranes, have been used for much smaller scales or lower purities and are not currently considered suitable for oxyfuel plant.

3.1 Cryogenic air separation

In cryogenic separation, air is separated into its principal constituents based on the difference in their boiling points (oxygen, -183°C and nitrogen, -195°C). This requires the air to be compressed and cooled to close to saturation point (roughly 4–6 bar and below -170°C) before separation in a continuous distillation process. The technology has existed in some form since the start of the 20th century, and is established for oxygen production on the commercial scale. In such applications the additional removal of argon to achieve oxygen purities of more than 99.5% is usually implemented, partly due to the high value of the argon itself. However, the high value of power in a power plant and the option of removing argon and other impurities in the CPU mean that lower purities (95–97%) are more suitable for oxyfuel combustion. The compression of large volumes of air, combined with significant energetic losses in the separation process, make ASUs highly energy intensive. Large units developed for integrated gasification combined cycle (IGCC) plant during the 1990s consume roughly 200 kWh/t of oxygen produced, but the last decade has seen the development of oxyfuel dedicated units which have achieved significant reductions in energy consumption of the process to approach 160 kWh/t (Perrin and others, 2013). However, as this still represents around 10% of gross plant output, efforts to further reduce the power consumption of the ASU through optimisation and new process concepts remain at the forefront of oxyfuel research.

Manufacturers have also responded to the large oxygen demand of oxyfuel plant by designing single units with increased outputs (White and others, 2009). Whilst large oxyfuel plant will still require multiple ASU trains, units of 5000 t/d are now commercially available, producing sufficient oxygen for a 250 MW net plant. The Compostilla CFB300 demonstration has incorporated a single large ASU from Air Liquide into its design (Terrien and others, 2013).

At the pilot-scale, several oxyfuel units have used commercially supplied oxygen rather than an ASU, given that the technology is already mature and can be impractical at the small scales of current pilots. However, the 30 MWth oxyfuel pilot at Schwarze Pumpe was supplied by an ASU and has provided some useful results on how the unit can be coupled to the operation of the plant. The 100 MWth pilot at Callide also operates two ASU trains, primarily due to the remote location of the plant, and research has not focussed on ASU operation.

3.1.1 Process description

Compression, cleaning, and cooling

Atmospheric air is first filtered for particulates before compression to 4–6 bar. This usually takes place over two stages with water cooling of the air after each. The air is then precooled to around 12°C in a direct contact tower with chilled water obtained by cooling against a stream of waste nitrogen. Temperature swing adsorption (TSA) is used to remove water and CO_2 from the cold, compressed air, as these species would otherwise freeze and block the cold sections downstream (Figure 14). The TSA process uses dual beds of adsorbent materials such as alumina or molecular sieves which adsorb water and CO_2 at lower temperatures and release them when heated. Once the adsorbent in one bed is saturated, the air is switched to the other bed while the adsorbent is regenerated with more nitrogen waste which has first been heated with low-pressure steam.

The air is further cooled to approaching saturation point (~-172°C for air at 6 bar) in a brazed aluminium plate fin heat exchanger against the countercurrent flow of cold, gaseous nitrogen product. Cooled against waste streams of nitrogen-rich vapour, most or all of the air remains gaseous, but a proportion may be condensed to liquid air against vaporising a liquid oxygen product. These separate streams are used as the feed to a dual distillation column which performs the separation into the component gases and forms the core of the process.

Distillation and refrigeration

The cooled and compressed air is fed continuously to a distillation column at a height determined by the composition of air and other column parameters. The column is packed with high surface area material on which air separates into more nitrogen-rich vapour and more oxygen-rich condensate, with increasingly pure oxygen condensate produced towards the cooler column base and increasingly pure nitrogen vapour towards the warmer top. A portion of the nitrogen-rich vapour exiting at the top (the overhead product) is condensed and passed back down the column as reflux and conversely, some of the bottoms product of oxygen-rich liquid is vaporised in a reboiler and passed back up the column. Efficient production of the cold required to condense sufficient nitrogen reflux is a fundamental challenge of cryogenic distillation, and a key early development was to recover the high quality cold in the liquid oxygen product for this purpose. As liquid oxygen will only vaporise at temperatures necessary to condense nitrogen if the nitrogen is under pressure, a pressurised column must be used, with the oxygen product first expanded and then vaporised against condensing overhead product.

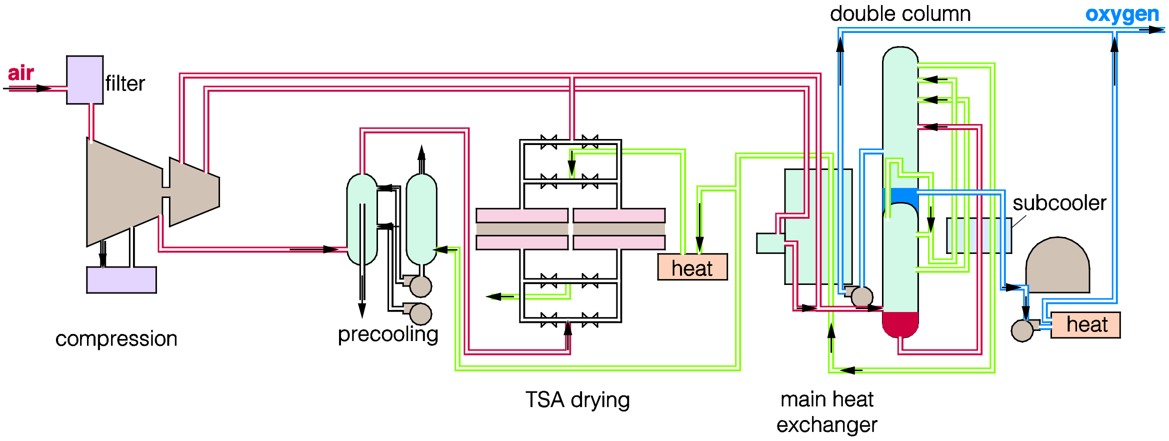


Figure 14 Process configuration of a standard ASU showing air compression, precooling, drying, cryogenic cooling and a double column distillation (White and others, 2009)

A refinement of this idea is the dual column process developed by Linde in the early 20th century, which still forms the basis of modern cryogenic air separation (Linde, ND). In this process, air is fed both to a high-pressure (HP) and low-pressure (LP, slightly above atmospheric) column which share a common condenser/reboiler and are usually housed within a common shell (Figure 14). The HP column produces nitrogen-rich vapour at sufficient pressure to condense above the boiling point of oxygen, and is thus able to vaporise oxygen at the bottom of the LP column, yielding a high purity nitrogen condensate used as reflux in both columns. The oxygen-rich bottoms product of the HP column is also sent as feed to the LP column, which produces the high purity oxygen product at its base. This can be extracted as either gaseous or liquid oxygen, but liquid is preferred as it allows for slightly higher process efficiency (*see* Section 3.1.2) (Higginbotham and White, 2013). Both oxygen and nitrogen product streams provide cooling duty in the main heat exchanger.

The overhead product from the LP column is a third stream of low purity waste nitrogen which is first sent to an additional heat exchanger called the subcooler (Figures 14 and 18). Here, all inlet streams to the LP column are cooled to approach the lower saturation temperature of the LP column in order to minimise the flash formation of vapour with the drop in pressure, which reduces the amount of liquid reflux obtained. The waste nitrogen stream is then also used for cooling in the main heat exchanger, before finally being used for production of cooling water for pre-cooling and regeneration of TSA adsorbent.

Although this separation process resembles a refrigeration cycle, additional cold is required to counter imperfect heat transfer and the ingress of ambient heat into the system. Rather than further compressing the entire air feed to supply this energy, cryogenic ASU include a separate refrigeration cycle using only a portion of the compressed air (Dawson and others, 2004). This is further compressed in a booster compressor and cooled in the main heat exchanger to a lessser extent than the main air feed, before further cooling in an expansion turbine which is usually mechanically coupled to the booster compressor (Figures 14 and 18). This cooled air (around -188°C) is fed to the LP column. Alternatively, this cycle can be operated using the pure nitrogen byproduct, which is also cooled in an expansion turbine to recover some energy (Goloubev and others, 2013).

Modern ASU have developed highly complex variants on this basic format, which minimise energy loss by using multiple air feeds and flows from each column to maximise the heat exchange efficiency between the two columns. These are discussed in the next section.

3.1.2 Process optimisation

The deployment of IGCC plant from the 1990s and the more recent development of oxyfuel technology have both provided impetus for ASU manufacturers to produce more efficient, larger units for producing lower purity oxygen of 95–97% (Figure 15) (Beysel and Schueller, 2010; Perrin and others, 2011; Goloubev, 2012). The relatively high value of electric power in power plant projects means that large capital investment in a more efficient ASU is easily compensated by the increased generation output and reduced cost of CO_2 abatement. From a base energy cost of around 200 kWh/t of oxygen for a conventional unit in 2000, development work by the industrial gas providers, Air Liquide, Air Products, Linde, and Praxair, have enabled the process to approach 160 kWh/t. Several of these manufacturers have targetted further optimisation to 140–150 kWh/t in the next few years, with up to 120 kWh/t expected by 2020 (Terrien and others, 2013; Paufique and others, 2013; Prosser and Shah, 2011; Higginbotham and others, 2011).

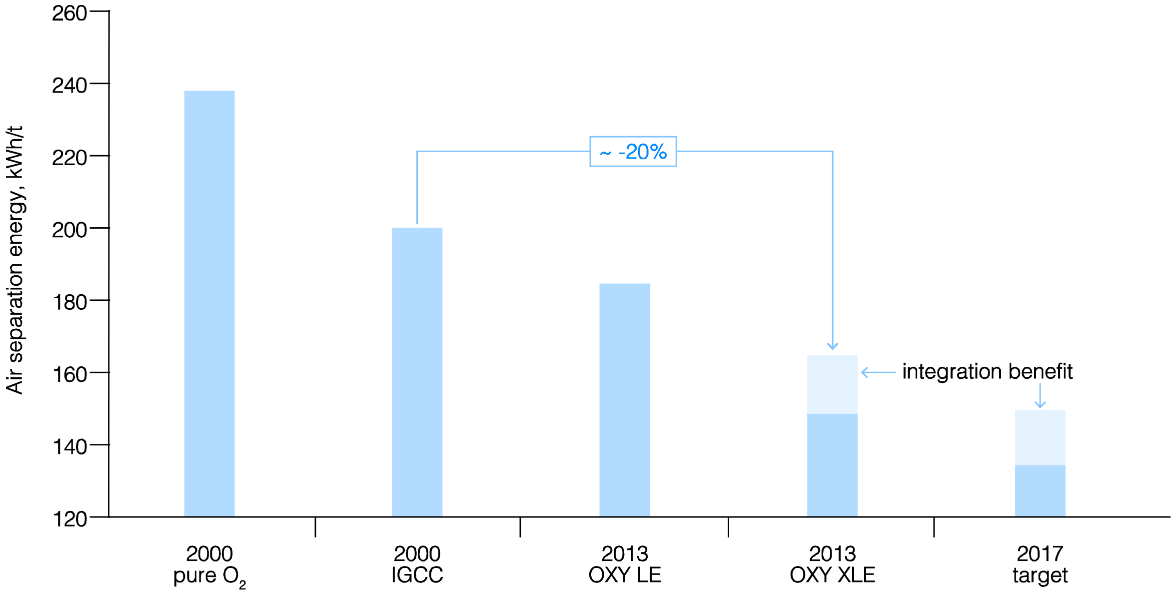


Figure 15 The reduction in air separation energy (kWh/t) over time in Air Liquide ASU

As the intrinisic separation energy of oxygen from air is around 50 kWh/t, it is clear that the current optimised processes still have some room for improvement (Tranier, 2013). Almost all the energy supplied to the ASU is the used to drive the air compressors, apart from a small amount of heat energy required to regenerate adsorbents which is provided by low-pressure steam. The turbocompressors used are inherently around 75% efficient, meaning that 25% of the supplied power is immediately lost to heating the compressed air (in an adiabatic process). However, energy is also lost throughout the cleaning, refrigeration, and distillation process due to irreversibilities such as pressure drops and thermal losses in heat exchange. This is also ultimately expressed as increased power consumption at the main compressor, which must reach higher air pressures to counter the losses. Exergy analysis of the process steps indicate that the greatest losses occur in the distillation process, with around half the total ASU losses (Fu and others, 2013; Shafeen and others, 2013) (Figure 16). Smaller losses occur in prepurification, the main heat exchanger, and with the byproduct streams.

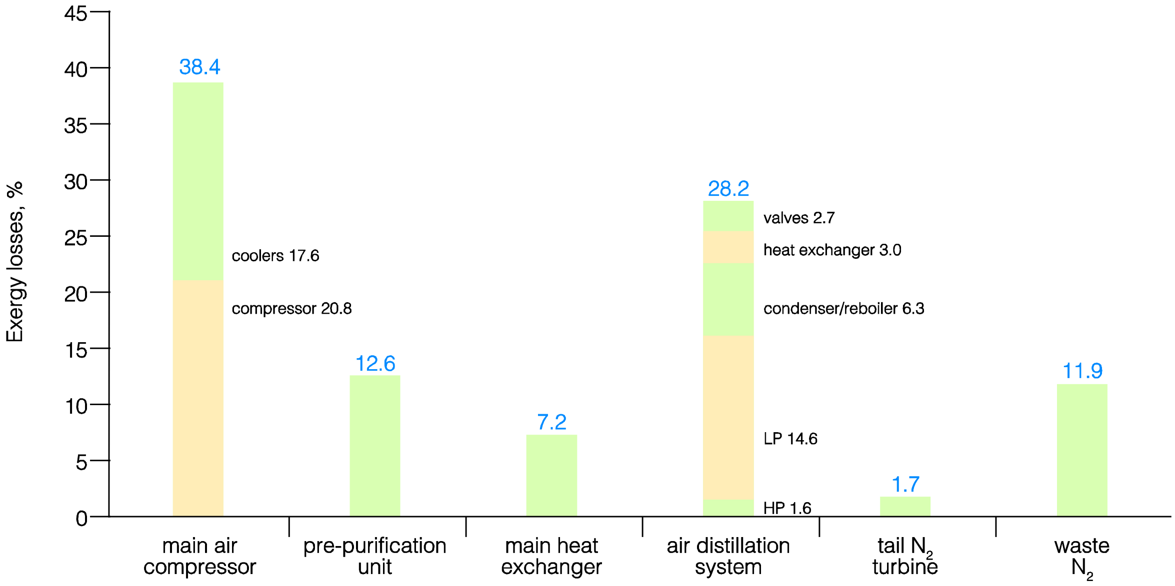


Figure 16 Exergy losses in cryogenic air separation (Fu and others, 2013)

Advances in ASU optimisation have therefore focused on reducing irreversibilities, both by technological advantages in apparatus to reduce pressure drops and enable more efficient heat exchange, and by designing increasingly complex distillation processes which optimise use of the available exergy. Whilst most improvement to date has been through the latter approach, equipment optimisation is likely to play more of a role in the next few years. An additional strategy for efficiency gain is possible for ASU for oxyfuel power plant, as there exists the potential for recovering the heat lost in compression by thermal integration with the power plant steam cycle. As they are highly plant specific, energetic gains derived from this route are usually considered separately from the fundamental ASU efficiency.

Optimising equipment

The large air compressors used by an oxyfuel ASU can be of either axial or centrifugal design. While axial compressors can reach higher pressures in a single stage and are higher efficiency, they are also carry a much greater capital cost. For this reason, two centrifugal compressors in series, with intercooling after each, are often used to reach the required air pressure. Both types of compressor are already highly optimised, but further gains may be possible through advanced modelling of their aerodynamic design. In 2011, 5–7% of further ASU energy saving was estimated to be achievable from compressor optimisation, although it is not clear how much progress has been made in this respect (White and others, 2009; Prosser and Shah, 2011) (Figure 17). Air compressors are usually electrically powered, but can also be mechanically driven by steam or gas turbines.

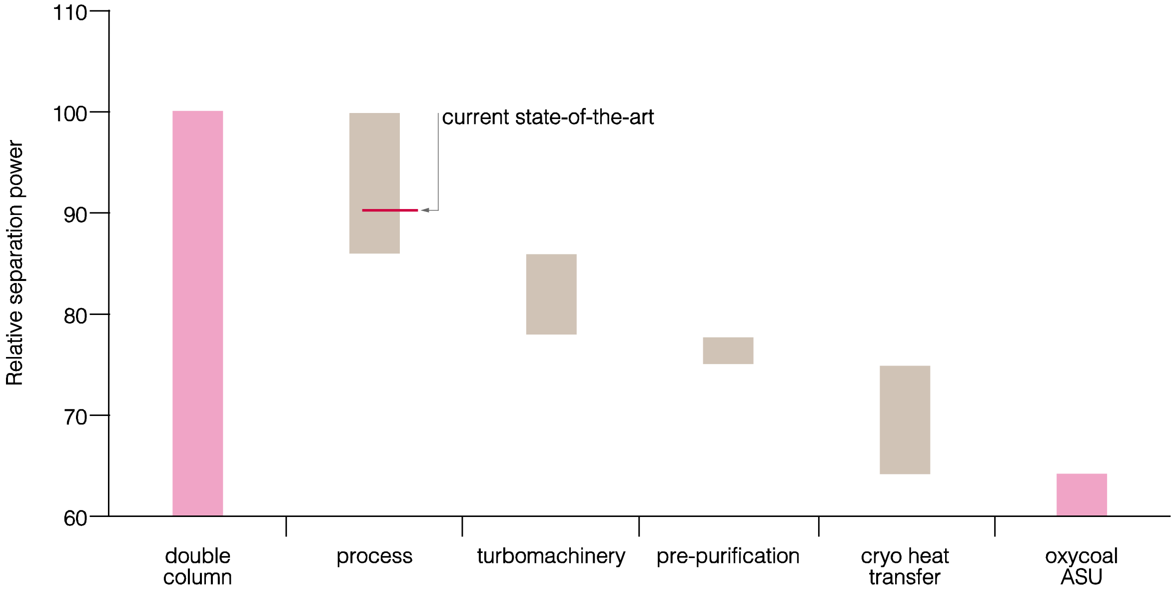


Figure 17 Praxair estimates of the energy optimisation potential in each aspect of ASU design (Prosser and Shah, 2011)

Energy consumption in prepurification is relatively small, but the TSA process in particular is open to process and material optimisation and overall process efficiency gains of 2–3% are thought to be achievable (White and others, 2009; Prosser and Shah, 2011). Manufacturers have aimed to reduce the pressure drop across the adsorber vessel, as well as reducing the heat energy required for regeneration of the adsorbent. Air Liquide have implemented a novel, radial design of adsorber vessel, in which the process gas enters axially and passes through the packed adsorbent through a series of radial channels (Perrin and others, 2011). A similar design has been produced by Air Products, in the form of their multi-layer horizontal adsorbers formed from vertical cylindrical units with annular beds (Dillon and others, 2005). This design allows the use of lower pressure steam or hot condensate for regeneration heating to minimise the impact on the power generation cycle. The adsorbent beds are made up of mixed layers of alumina or silica gel and layers of zeolite.

Improvements in cryogenic heat exchange technology are likely to hold the largest potential for energy gains, with overall process improvements of around 10% estimated (Prosser and Shah, 2011; White and others, 2009). The main heat exchanger used to cool the feed air uses state-of-the-art brazed aluminium plate-fin cores, which can be manifolded together in large numbers to achieve more efficient heat transfer.

For the reboiler/condensers in the distillation process, a downflow or film vaporiser design has been adopted instead of bath immersion to minimise temperature approaches (Tranier, 2013).

First introduced in the 1980s, the use of structured packing for distillation columns as an alternative to sieve trays is a principal approach for improving column efficiency by lowering the pressure drop while maximising contact between the vapour and liquid phases. These highly optimised packings are generally proprietary designs.

All these routes have contributed to ASU optimisation since its first application, and many of the technologies developed are proprietary and cannot be discussed in detail here. The obtainable efficiency gains are to a large extent dependent on the capital investment made; for instance large diameter ducts and vessels can reduce pressure drops but do not tend to follow economies of scale (White and others, 2009).

Optimising the process cycle

Manufacturers have developed the original dual column distillation design into more complex processes designed to reduce irreversibilities in the distillation and thus minimise the air pressure required to achieve separation. Such process cycle improvements represent the most significant efficiency savings which have been made in oxyfuel ASU to date, and while many designs are proprietary, some underlying principles can be addressed here.

The principal strategy in optimising distillation efficiency is to improve the integration between the high- and low-pressure columns, generally using an approach known as distributed reboiling. Instead of supplying all the heat for LP column reboil duty in one reboiler at the column base, a portion of the vapour reflux can be produced higher up the column, where the less pure liquid vaporises at lower temperatures (Prosser and Shah, 2011). In a basic dual reboiler process, a lower reboiler uses a stream of air as its condensing fluid, whilst the upper reboiler condenses the overhead vapour from the high-pressure column. As the impure liquid vapourised by the upper reboiler boils at a lower temperature than pure oxygen, the nitrogen product can be condensed at lower pressure than in a standard process to provide sufficient heat. This translates into a reduction in HP column pressure and main air compression energy.

A variation on this design is the three column process, in which an additional column at intermediate pressure (IP) is introduced (Higginbotham and others, 2011) (Figure 18). The nitrogen product from this column is condensed in the upper of the two LP column reboilers, whilst the higher pressure overhead product from the HP column can be condensed in the lower reboiler. Both these condensed streams contribute to the cold reflux for the LP column, as well as providing the reflux for their respective higher pressure columns of origin. The bottoms products of both HP and IP columns provide feed for the LP column, usually in addition to liquid air reflux taken from an intermediate position on one of the columns.

Either the HP or IP column is housed separately from the standard dual column shell, depending on manufacturer-specific design. Having a column at intermediate pressure reduces the requirement for high-pressure air for the HP column, and saves on compression power. The main air compressor produces air at the intermediate pressure of around 3.5 bar, whilst the high-pressure air is produced by additional booster compressor to over 5 bar prior to the main heat exchanger. In the Air Products three column design, these two streams actually undergo separate precooling and drying steps, with a view to using smaller volume cooling and drying vessels and saving on capital (Dillon and others, 2005).

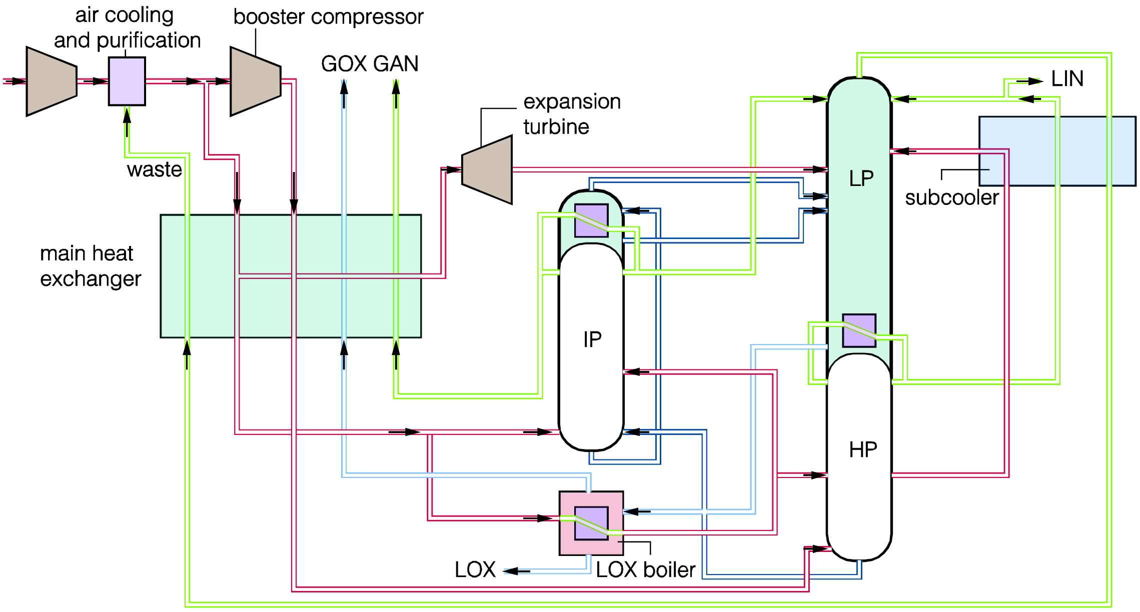


Figure 18 A triple column distillation process from Air Products (Higginbotham and others, 2011)

A third approach to reducing the pressure of the HP column is to introduce a cold compression stage for the nitrogen product from the column. This provides a means of reaching the required nitrogen pressure for reboiling oxygen without having to pressurise the entire column to the same extent (Prosser and Shah, 2011).

In most modern ASU, a liquid rather than gaseous oxygen product is taken from the low-pressure column, as this can be vaporised against condensing air in a separate liquid oxygen (LOX) boiler and provide an additional source of liquid air reflux. This is estimated to achieve a 1–3%pts increase in energy efficiency (Higginbotham and White, 2013), as well as providing the option of retaining the liquid oxygen for storage (*see* Section 3.1.6).

Such designs ultimately allow reductions in the air pressures required for the distillation process. For example, Air Liquide's optimised process claims to require air compression to only <4 bara (Terrien and others, 2013). An efficiency gain of around 10% is obtainable from a dual reboiler process compared to a standard double column. The triple column is estimated to gain a further 3–5%pts, and cold compression an additional 1%pt (Prosser and Shah, 2011; Higginbotham and others, 2011). Increasingly complex processes are likely to be able to achieve even greater gains, but with diminishing returns for the investment required. Additional columns and compression steps are capital intensive and the most suitable process will depend heavily on the case-specific value of power.

Recuperative vapour recompression

An advanced concept, at the research stage, is to avoid compressing the oxygen component of the air, which is essentially wasted energy given that the oxygen product is nearly at atmospheric pressure. A process known as recuperative vapour recompression developed by the Norwegian University of Science and Technology, introduces air to the distillation column after minimal compression, and instead compresses the nitrogen produced at the top of the column to produce the liquid reflux stream (Fu and Gundersen, 2013a). The nitrogen product is compressed, cooled and condensed against the boiling oxygen at the bottom of the column. This design could produce 95% pure O_2 at 17% less energy than a traditional dual column, although the need for additional compressors and water removal at low pressure could translate to higher capital costs.

3.1.3 Steam cycle integration

Around 25% of the power used to drive the main air compressor is lost as heat to the process air (Dawson and others, 2010; Goloubev and others, 2013). Conventionally, air exiting the compressors is water-cooled in heat exchangers, but an oxyfuel power plant presents the possibility of replacing the cooling water with boiler feedwater, recovering the heat energy as preheating duty. Boiler condensate is usually preheated in several stages with steam bled from the high-pressure and intermediate-pressure turbines, so replacing any of these stages with an alternative heat source reduces the steam used and increases power generation at the turbine. The potential increase in ASU efficiency from this approach is case-specific, but ASU manufacturers have estimated gains from 7 to 9%pts to be possible with thermal integration (Terrien and others, 2013; Higginbotham and others, 2011; Goloubev and others, 2013).

For the most efficient use of the compression energy, it is favourable to heat the air to as high a temperature as possible by use of an initial axial compressor instead of two centrifugal compressors with intercooling stages. However, heating feedwater with the compressed air still requires a heat exchanger with much more stringent specifications than those used for intercooling, as a large amount of heat needs to be transferred across a relatively small temperature difference (10–15°C) and with minimum loss of pressure in the air stream (<100 mbar) (Goloubev and others, 2013). Linde have proposed the use of a coil-wound heat exchanger as an appropriate technology for this purpose. In general, higher temperature heat recovery is more efficiently performed at lower pressure compression, so initial lower temperature feedwater heating is also carried as the air is further compressed for the IP column (Figure 19). In the Linde design, feedwater could be heated from 30°C to 120–140°C with minimal increase in compressor power.

Air Liquide suggest that 150 kWh/tO_2 is achievable based on an integrated version of their current process (otherwise 164 kWh/t), while Air Products quote 162 kWh/t for an integrated triple column process. Based on the 426 MW White Rose demonstration project, Linde have calculated a 7% reduction in ASU power consumption, or 4.15 MW from 47.2 MW.

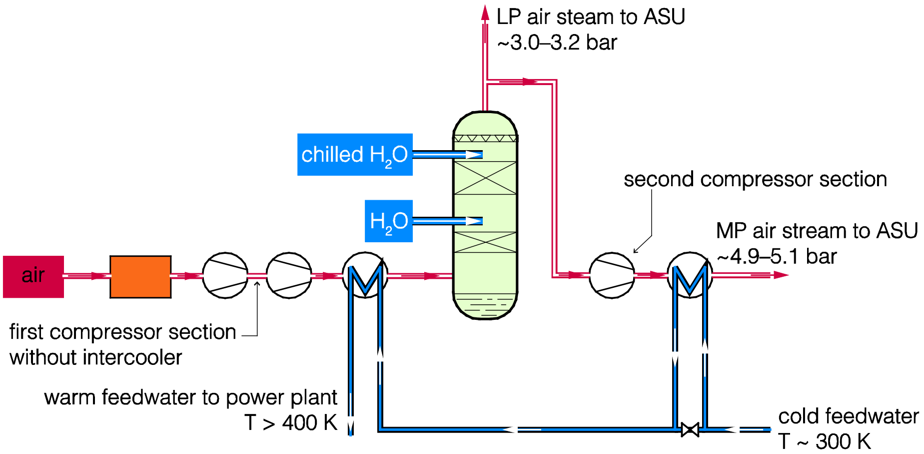


Figure 19 Linde schematic of integration of the ASU with feedwater heating (Goloubev and others, 2013)

3.1.4 Oxygen purity optimisation

For an oxyfuel plant there exists an optimum oxygen purity at which the ASU energy saving for any further purity reduction is outweighed by the additional energy consumed in the CPU to remove the impurities. With a boiling point between those of nitrogen and oxygen, argon is much easier to remove from the CO_2 product, so this purification step is always eliminated from an oxyfuel ASU. Furthermore, some air ingress to the boiler and flue gas train is inevitable, so some facility for N_2 and Ar removal from flue gases will always be required to achieve high purity CO_2. Optimum O_2 purity will depend on the specifics of the ASU, CPU, and plant design, but is generally estimated to be in the range 96–97%. In an Alstom model for optimising a large oxyfuel plant (900 MW gross), a purity of 96.3% was calculated to provide a 1.4 MW energy saving for the plant compared to a reference case of 95% (Pourchot and Granier, 2013).

3.1.5 Producing oxygen at higher pressures

The high-pressure oxygen required for pressurised oxyfuel processes (Section 7.1) can be produced in two main ways. In a ‘pumped LOX’ process, liquid oxygen is taken from the column and pumped to the required pressure pressures before vaporisation against a condensing stream of compressed air from a booster compressor. The liquid air produced can be used for refrigeration by expansion in a dense fluid expander, before being added to the LP column. Alternatively, a gaseous oxygen product is taken from the LP column and compressed outside the coldbox.

The pumped LOX process is generally preferred due to improved flexibility and availability, as well as concerns over the safety of gaseous oxygen compression. However, Air Products calculate that pumped LOX can range from between 3% more or less efficient than GOX compression depending on the product pressure required and the plant configuration (Higginbotham and White, 2013). The oxygen compression energy is effectively balanced by the booster air compressor power needed for the pumped process, and ignition risk in the gaseous process can be managed with care over minimum clearance in compressors and material selection. Both processes are vulnerable to CO_2 and N_2O freezing, so breakthrough of these species from the upstream TSA process needs to be strictly limited.

3.1.6 Liquid oxygen storage

Several ASU manufacturers have suggested that the facility to store liquid oxygen could provide a means of reducing operating costs for an oxyfuel plant in a liberalised energy market. During times of low energy demand, the ASU could be kept running on relatively cheap power and the oxygen liquefied and stored on site. This store could then be used as a cheap oxygen supply during peak energy demand, and the ASU taken offline instead of running it on more expensive energy. This strategy results in a lower average energy efficiency, as energy storage is not 100% efficient, but the operating cost is lower, and cost of electricity could be reduced.

Linde suggest several alternative means of using the stored liquid oxygen as opposed to a basic vaporisation against low-pressure steam, which has an energy storage efficiency of only 27% and would require a very high liquefaction capacity to have a significant impact on peak-time oxygen consumption (Goloubev and others, 2013). Alternatively, the liquid oxygen can be used to provide refrigeration in the ASU 'cold integration', replacing the nitrogen cold turbine used for cold generation in the standard Linde ASU design. During LOX refrigeration, the by-product N_2 would instead be preheated and used to generate additional power with an expansion turbine. In this scenario, the amount of LOX injected into the ASU is limited by refrigeration demand and efficiency of storage is increased to around 55%. However, only 10% of ASU power consumption could be saved during peak time.

The LOX injection can be used more efficiently in combination with a cold compressor cycle (described in Section 3.1.2), which allows for better heat integration with the plant. In normal operation, the cold compressor would operate at minimum load, but during peak times liquid oxygen is vapourised against condensing air from the main heat exchanger to produce liquid air reflux for the low-pressure column. This enables shifting of heat loads between the reboilers and a reduction in compression energy. In this scheme, energy storage is 65% efficient and 20% of ASU power is saved during peak time.

In Linde's 'Varox' system, both liquid nitrogen (peak times) and oxygen (off-peak) are stored, with nitrogen injection during off-peak and oxygen injection at peak. This method allows the separation energy to be stored but not the energy of liquefaction, so significant amounts of LOX need to be stored to have an effect on power saving. Although the energy storage efficiency is 90%, only 11–12% of ASU power consumption is saved during peak time. The Varox concept would therefore be most suitable for regions with large changes in power demand, whereas the cold compressor concept is better for a smaller spread in demand (Figure 20).

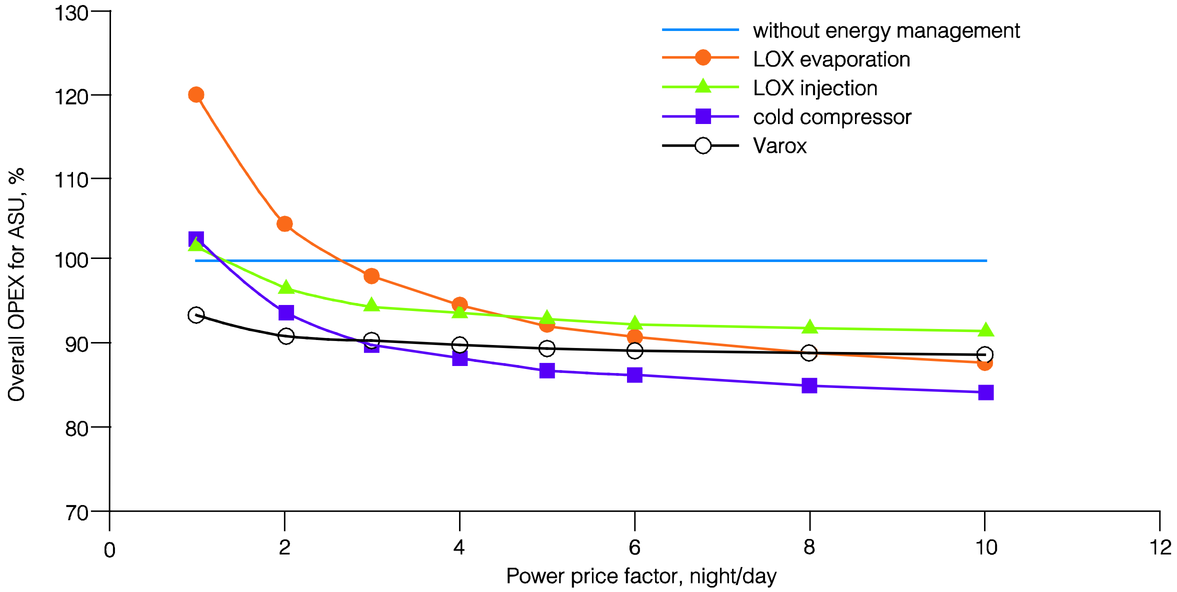


Figure 20 OPEX savings for various Linde oxygen storage concepts relative to power price spread (Goloubev and others, 2013)

Air Liquide's oxygen storage concept is known as ALIVE, or 'Air Liquide innovative variable energy', and was incorporated in the FEED study for Endesa's oxyfuel demonstration at Compostilla. While little technical detail of this process is available, it is based on a highly efficient transfer of liquefaction energy between the oxygen and nitrogen products, offering an energy storage efficiency of >95% and a capacity of 200–300 MWh. Two variants of the concept have been proposed for the optimisation either the operating or capital cost of the plant. In the OPEX optimised model for a 575 MW plant, the ASU is sized according to the plant's maximum oxygen demand and a 10% saving in oxygen production costs can be obtained for a 40 €/MWh spread in cost of electricity. In the CAPEX optimised model for the same scenario, a smaller ASU is matched to the plant's average oxygen demand to gain a 15% saving in capital investment but only a 3% saving in production costs (Dubettier and Guillard, 2011).

In a similar concept, Air Products have suggested coupling liquid air storage system with LOX storage (Higginbotham and others, 2011); when oxygen production is below demand, the storage LOX can be evaporated against air to continue making liquid air. Then if oxygen supply is above demand, stored liquid air can be used to provide refrigeration to convert the gaseous oxgyen to liquid for storage

3.1.7 ASU flexibility

Modern power plant operation in liberalised grids can require rapid ramping of output which an ASU must be capable of following. In addition, the need to switch between air and oxyfuel modes will be present at least in first generation plants, so the plant ASU will be required to shut-down and start-up quickly. Experience at Schwarze Pumpe has shown that starting up a cryogenic ASU from 'warm' can take up to three days, and can be significantly quicker if cold liquid reflux remains in the columns or is stored (Anheden and others, 2011). Conversely, plant start-up may be negatively affected if the ASU is thermally integrated with the plant, as the low grade compression heat will not be available until the ASU has started up (White and others, 2009).

On the other hand, turndown of an ASU in response to plant ramping is limited by the air compressors rather than the cold box (White and others, 2009). For maximum efficiency, the ASU should be operated at above 75% load, but using dual compressor trains can reduce this limitation to 50% simply by switching to a single compressor at full load. Correspondingly, three trains will allow efficient turndown to 35% (Prosser and Shah, 2011) (Figure 21). A utility-scale oxyfuel plant would require multiple compressor trains in any case, as oxygen demand is likely to surpass the largest compressors currently available. Use of liquid oxygen storage would also improve ASU turndown capability, as compressors can be maintained at high load and the oxygen produced stored instead of being vented (Dubettier and Guillard, 2011). Although ASU ramp rates of 2% of oxygen output per minute are typical, use of advanced control systems and liquid oxygen storage can improve this to the 4%/min applied in the FEED study for the Compostilla demonstration plant (Section 6.2) (White and others, 2009; Endesa and others, 2013).

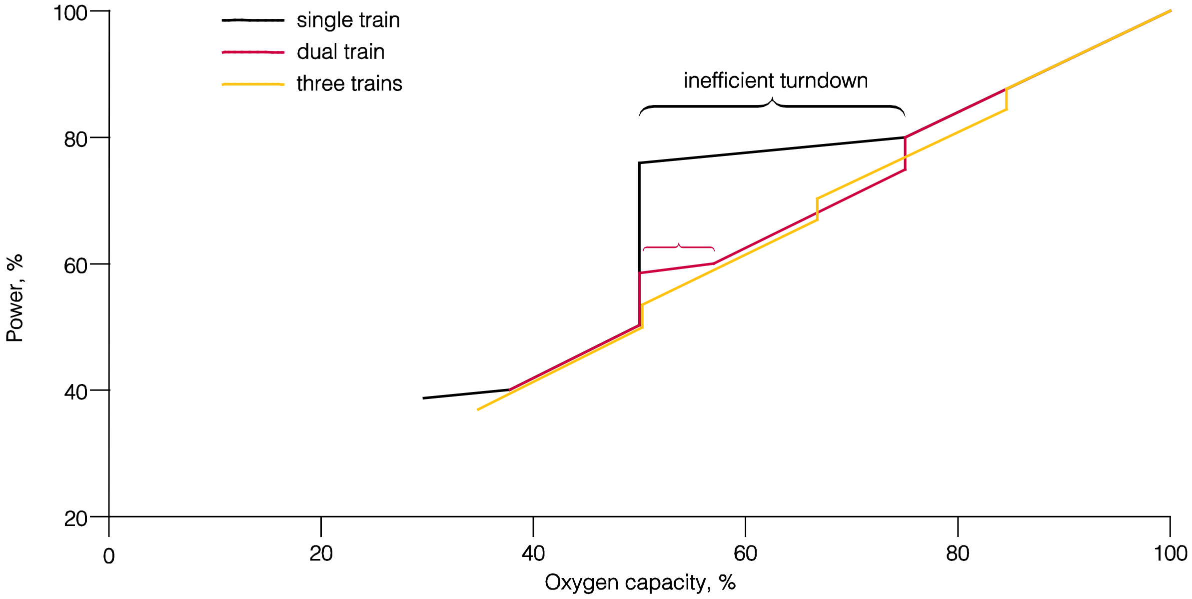


Figure 21 Improved ASU turndown capability with multiple compressor trains (Prosser and Shah, 2011)

3.2 Ion transport membranes

Air separation using ion transport membranes is emerging as a potentially viable means of producing oxygen at the purity and volumes required by oxyfuel with significantly lower energy consumption than cryogenic ASU. These membranes are based on various classes of dense ceramic materials whose ability to conduct oxygen ions allows them to separate oxygen from air at high temperatures (800–900°C) and in the presence of an oxygen pressure gradient. Amongst a number of potential materials, perovskites have drawn the most attention for their added ability to conduct electrons in the opposite direction to the oxygen ions, meaning that no external circuitry is required for the process. Once depleted of oxygen, the hot, pressurised feed gas can be used for further work, allowing for potential efficiency gains relative to cryogenic ASUs.

Whilst a number of research institutes and gas companies have investigated membranes for ASU, Air Products, with support from the US government, have taken the first major steps towards commercialisation of the technology. Using a design based on stacks of flat wafer-like membranes, the company commissioned a plant producing 5 t/d in 2010, and have scheduled a 100 t/d plant for start-up this year (Repasky and others, 2012).

3.2.1 Materials and design

Oxygen ion conduction through a membrane requires five distinct processes: Adsorption of an oxygen molecule on the air-exposed side of the membrane, dissociation and reduction by electrons to the O^{2-} ion, diffusion of the ion to the opposite side, and finally oxidation by release of electrons and desorption as an oxygen molecule. Suitable materials must therefore allow conduction of oxygen ions, usually via defects and oxygen vacancies in their crystal structure, and be able to electrocatalyse the surface reactions. The processes require relatively high temperatures (>750°C) to achieve sufficient rates of oxygen transport. A gradient of oxygen partial pressure across the membrane is also clearly necessary for net transport to occur in one direction and achieve selective separation of feed air (Da Costa and others, 2013).

Perovskites, which are ceramics with the general formula ABO_3, are the most studied ITM due to their additional ability to conduct electrons, which allows oxygen transport to take place without an external circuit to transport electrons from one surface to the other. Several high performance perovskites have been identified, including BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$), which has high oxygen fluxes but poor stability at low temperatures, and LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) which has lower fluxes but better stability. BCFZ ($BaCo_xFe_yZr_zO_{3-\delta}$) is another alternative which has produced very stable membranes, operated for up to 2200 hours. Interest in other ceramic materials such as fluorites has stemmed primarily from concerns over the stability of perovskites in CO_2- and water-rich environments, despite the fact that fluorites do not conduct electrons and thus require a fuel cell-like design (Da Costa and others, 2013).

The maximum oxygen flux possible with a given membrane depends not only on the inherent properties of the material but also on the membrane thickness. For most materials and temperatures used, the oxygen transport is diffusion limited except for very thin membranes which are not usually mechanically stable. It is therefore important to identify high performance materials from which as thin as possible structures may be fabricated. Hollow fibre or capillary structures are popular candidates for high oxygen flux membranes, as they can be fabricated with wall thicknesses below 1 mm whilst retaining structural stability (Da Costa and others, 2013). Flat membranes on the other hand, are exposed to the highly brittle nature of the ceramic, and present additional problems for sealing the open edges. Effective sealing is a principal challenge in ITM technology, as disparities in thermal expansion coefficients can cause problems at the high temperatures used. Any membrane assembly must present an airtight barrier between the inlet air and oxygen sides whilst subjected to a substantial pressure gradient. This gradient can be created by pressurising the feed air, creating a vacuum on the oxygen side, or a combination of both, with higher oxygen capture rates achievable at higher pressure differentials. An alternative aimed at oxyfuel combustion is to supply a CO_2-rich stream to the product side, diluting the oxygen and lowering its partial pressure. ITM lends itself to modular design as large-scale fabrication of stable ceramic membranes would be difficult.

The key to the proposed efficiency gains possible with ITM over cryogenic air separation is that the energy in the compressed, hot air supplied to the membrane can be retained, unlike in a cryogenic ASU where the air is cooled by necessity. An ITM module can be designed so there is little pressure drop in the feed air, and only a portion of the heat is lost to the ceramic and oxygen products. Oxygen removal from the feed air is incomplete, so the depleted air may be fed to a combustion process such as a gas turbine and the remaining energy used. ITM air separation requires a high level of integration with plant processes to maximise its efficiency potential, and may be particularly compatible with natural gas combined cycle plant. A separate heating system such as a gas-fired heater is also required to heat the feed air to the operating temperature of the membrane (Repasky and others, 2013).

3.2.2 Air Products ITM

With support from the US DOE, Air Products have developed their ITM technology to a pilot-scale stage, with commercialisation possible in the next few years. In 2001, a first phase of the project identified a suitable perovskite material based on high oxygen flux, resistance to contaminants, and compatibility with standard ceramic processing techniques (Repasky and others, 2012). The membrane design developed for the material is based on flat wafers with a layered structure, all produced from the same ceramic in order to minimise problems of thermal expansion. The roughly 20 cm square wafer structures consist of two membranes supported by a porous ceramic layer and enclosing a hollow space into which the permeate oxygen flows (Figure 22). A large number of these wafers are stacked around a common oxygen collection tube (also ceramic) to form modules with outputs of 0.5 to 1 t/d of oxygen, depending on the stack height. In 2010, Air Products commissioned a pilot facility which can employ up to six of these modules to produce up to 5 t/d oxygen. The modules are connected to a common oxygen manifold and enclosed within a vessel into which compressed, heated air at over 13 bars and 800–900°C is passed parallel to the wafers in order to minimise the pressure drop. The air pressure on both sides of the wafers also helps to stabilise the structures. The permeate side of the module is pumped to less than 1 atm pressure to achieve the necessary oxygen partial pressure gradient across the membranes.

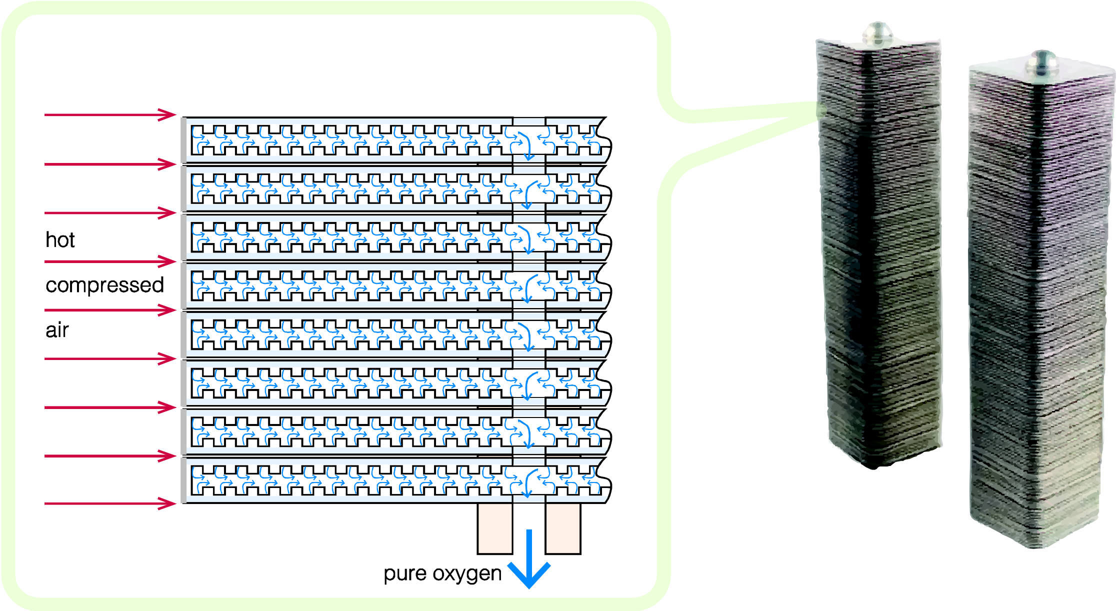


Figure 22 Air Products ITM design (left) and assembled 1 t/d modules (right) (Repasky and others, 2012)

Various test campaigns have been conducted at the pilot facility with a view to further scale-up of the technology. Most importantly, high oxygen purity levels of over 99% have been achieved with flux rates beyond those expected for the modules. In normal operation, the conditions in the pressurised vessel are slowly brought to the required pressure and temperature, however, the stability and performance of the modules has also been tested under cycling and emergency shutdowns to mimic power plant operation. The modules were found to maintain oxygen purity levels even under temperature and pressure cycling, with patented techniques employed to modify the concentration gradients experienced and minimise stresses in the material. Other tests were conducted on the ceramic–metal seals used where the modules connect to the oxygen manifold, on auto-shutoff valves attached to each module to maintain overall oxygen purity in case of individual damage, and on getters for removing contaminants from the feed air (Repasky and others, 2012).

A 100 t/d facility based on the same design was scheduled to start-up in 2013. This plant will integrate the oxygen production process with a gas-fired power generation process. The plant is designed to be separated into two relatively independent units: An oxygen producing section and a power producing section (Figure 23). The power generating side adds fuel to the oxygen depleted process gas which is combusted in the remaining oxygen (~10 mol%) and the resulting hot gas expanded in a turbine. The hot exhaust from the turbine is also coupled to the inlet process air for preheating duty. The inlet compressed air is further preheated by the depleted gas (before combustion), and finally heated to 800–900°C in a separate gas-fired heater.

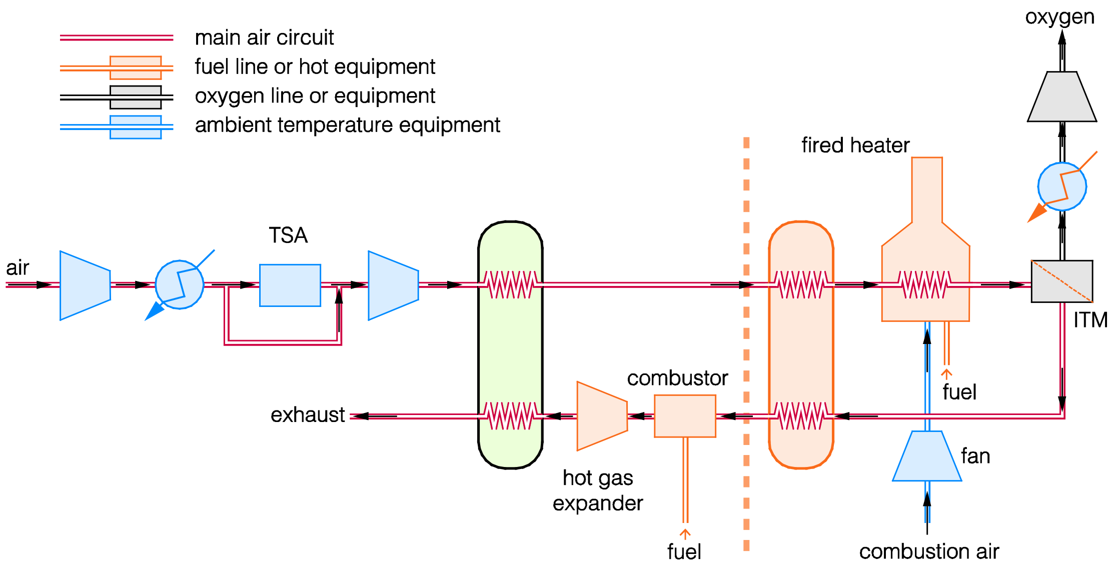


Figure 23 The design of Air Products 100 t/d ITM plant (Repasky and others, 2012)

To support further development of the technology, Air Products have also started construction of a plant dedicated to the fabrication of the ceramic wafers, capable of producing module assemblies on the 2000 t/d scale. The wafer manufacture is based on conventional tape-casting and lamination techniques for ceramic processing, using near-commercial-scale equipment. Precision machining of features such as the slotted inner layers is carried out by laser. Partly conceived as a means to test large-scale production lines of the material and wafers, the facility is scheduled to start-up in 2014. The company envisage that ITM could become fully-commercial by 2017.

A detailed analysis has been carried out by the manufcaturer to compare the performance of the membranes with cryogenic ASU in various oxyfuel plant scenarios (Repasky and others, 2013). The ITM can be applied either as a simple one-stage process, or as two coupled units, in which an initial partial capture of oxygen at low pressure gradient is followed by a second, more complete capture in which a vacuum is applied to the product side. Combination of the two product streams provides heated oxygen, from which the thermal energy is used in the combustion process, raising efficiency. A separate gas-fired heater used to heat the feed air produces its own CO_2 which needs to be included in the plant's carbon account. Either these emissions are left unabated, and total carbon capture is reduced from 90% to 73%, or the facility to add this stream to the CPU is added at greater capital cost. For this 90% case, the ITM plant gained 2.5%pts efficiency advantage and 18% lower capital cost and 5% reduction in levelised cost of electricity (LCOE).

An assessment by the US DOE has estimated that the ITM technology has the potential for achieving a 14% reduction in oxygen production cost over cryogenic ASU (Quintrell and Foster, 2011).

3.2.3 Tubular membranes

Whilst Air Products' process is based on flat membranes, tubular membrane structures have been the subject of much research due to their potentially superior mechanical properties and reduced sealing requirements. An EU funded research project for developing highly efficient tubular membranes for oxycombustion (HETMOC) is being led by TU Denmark in collaboration with industrial and academic partners such as Air Liquide and Sintef, and is scheduled to run from 2011 to 2015 (EU, 2014). The project aims to build a proof of concept trial module consisting of 25 tubes of 1 m in length which will be trialled for over 1000 hours. A conceptual design for a 100 t/d assembly will also be produced.

4 Compression and purification unit

The portion of flue gas remaining after the recycle streams have been drawn off is fed into a compression and purification unit (CPU), where it is processed into a pure CO_2 product and compressed to a dense phase for transportation by pipeline. Although oxyfuel combustion flue gases are enriched to at least 65% CO_2 (wet basis), they still contain significant proportions of N_2, O_2, H_2O, and various other impurities in smaller amounts, many of which need to be removed in the CPU. The series of purification steps involved in this process make the CPU the most complex oxyfuel addition to a conventional plant, drawing on a collection of gas processing technologies. Consequently, a number of different approaches to CPU design have been implemented or proposed. This chapter will discuss the basic principles common to all CPU designs, before looking at specific processes as conceived by the five principal CPU manufacturers.

4.1 CO_2 purity

The primary consideration for CO_2 purity from the CPU is suitability of the product for transportation by pipeline as a supercritical fluid (usually over 100 bar). In this respect, water content is the first concern, as even low levels of water in supercritical CO_2 result in the formation of carbonic acid which is highly corrosive to the low-alloy steels used in pipelines. Existing pipeline spefications for CO_2 transport in the USA reflect this in specifying a maximum water content of 640 ppm, which necessitates flue gas drying beyond what can be achieved in a straightforward condensation by cooling (Doctor and others, 2006; GCCSI, 2012a) (Table 1). Excessive levels of the light gases N_2, O_2, and Ar are also problematic, as they add to the pressure required to reach a supercritical fluid without the risk of two-phase flow occurring. As existing CO_2 transport networks in the USA are for enhanced oil recovery (EOR), pipeline specifications also reflect the strict requirement for minimal O_2 for this use (<0.0014%), where it can lead to unwanted oxidation of the extracted hydrocarbons (GCCSI, 2012a). Early CPU development has therefore had a tendency to aim for as high purity CO_2 product as possible, both to demonstrate the absolute capabilities of the technology and to meet the strictest possible specifications for applications such as EOR. In reality, storage of CO_2 in geological formations such as saline aquifers would allow higher levels of O_2, and simplified processes could be possible for such projects. Indeed, the early gas-fired oxyfuel capture and storage project at Lacq, France, demonstrated storage of CO_2 after dehydration only (Total, 2013). However, it is generally accepted that some additional removal of the non-condensable gases is optimum for the whole process, as costs are outweighed by economising on compression energy and the reduced volume for compression, transportation, and storage (*see* Section 4.4).

Table 1 Kinder Morgan CO_2 pipeline specifications (GCCSI, 2012a)

Component	Specifications
CO_2, %	≥95
Water, %	0.064
H_2S, %	0.00127–0.0254
N_2, %	≤4
CH_4, %	≤5
O_2, %	≤0.00136

Separation of CO_2 from the inert gases and oxygen is carried out by a partial condensation of the process gas at cryogenic temperatures. This step forms the core process of any CPU, and involves both an initial compression step and cooling to temperatures approaching the triple point of CO_2. The CO_2-rich liquid obtained can then be further purified by flash separation and distillation steps. These compression and cooling steps required for liquefaction impose their own secondary purity requirements, as they can be seriously impeded by other flue gas impurities. Cooling to -70°C necessitates not only dehydration but removal of NO_2, which freezes at -11.2°C. Furthermore, high efficiency cooling is performed by brazed aluminium heat exchangers which can react with any mercury left in the process gas to form a brittle amalgam. Compressors may also need to be protected from particulate matter and the highly acidic condensates which result from compression in the presence of water and SOx or NOx. Consequently, most CPU process designs have implemented a chain of steps to remove SO_2, NOx, particulates, and Hg prior to the cooling step. These additional steps are the principal distinction between CPU pilots designed by different manufacturers, as there are a number of ways in which they can be carried out or combined with flue gas condensation or compression.

Besides these material and process limitations on gas purity, the high-pressure and reduced-volume gas stream found in the CPU present the possibility of more efficient pollutant removal than in conventional flue gas cleaning equipment, particularly for SOx, NOx, and mercury (Tranier and Perrin, 2011). Purity requirements for the secondary recycle stream necessitate at least particulate filters and possibly some form of FGD upstream of the CPU, but future oxyfuel plant designs are likely to aim to maximise the proportion of flue gas cleaning performed in the CPU. This is potentially a significant means of cost reduction in oxyfuel over alternative capture processes, and as such is another motivation for CPU manufacturers to incorporate efficient pollutant removal equipment in their designs.

4.2 Process

4.2.1 Flue gas condensation

The majority of water vapour (around 80%) is removed in a flue gas condenser (FGC) or quench, sometimes considered separately from the CPU as a dry primary recycle stream is usually drawn from after this step (Yan and others, 2009). The flue gas is rapidly water-cooled to around 30°C in either a direct or indirect contact heat exchanger. As acidic condensates are necessarily produced in cooling below the acid dew point, corrosion resistant materials must be selected for the vessel.

4.2.2 Acid gas removal

As mentioned, approaches to removal of SOx and NOx in CPU are highly specific to each manufacturer and are discussed below, but some general principles can be noted here. All CPU involve several condensation steps in which the soluble species SO_3 and NO_2 can react with water and be removed as acidic condensates (Yan and others, 2013). Although NO comprises the majority of flue gas NOx, during compression it is largely oxidised to NO_2 and is thus easier to remove in condensates; a property that is widely exploited in strategies for NOx removal in the CPU. Whilst SOx treatment can occur before or after compression, NOx removal is therefore almost always carried out after or during compression. Removal of both SOx and NOx with condensates can be enhanced by scrubbing with alkaline solutions and using packed columns to increase contact between the liquid and gas phases. Promoting acidic condensation in this manner again leads to important material considerations, and the need for carefully chosen corrosion resistant materials. Alternatively, high surface area adsorbents such as activated carbon can be used to adsorb the gases.

4.2.3 Compression

In the CPU of a full-scale oxyfuel plant, two distinct compression processes would take place: An initial compression to around 30 bar as part of CO_2 purification by condensation, and a final, dry compression of the pure CO_2 product to a supercritical fluid at ~100 bar for pipeline transportation. However, the dry compression is not usually demonstrated in pilot-scale CPU, as a well-established technology whose energetic penalty and cost will depend only on the product purity achieved by the upstream process. Furthermore, with pipelines not usually present, most projects have preferred to produce a liquid CO_2 which can be more easily transported by vehicle to storage test sites or other end uses.

Upstream of process gas cooling and usually also of dehydration, the initial compression is normally in two stages with inter-stage cooling. The pressure to be reached is essentially determined by the proportion of CO_2 needed to condense in the partial condensation step, based on subsequent cooling to temperatures close to the CO_2 triple point. Most pilots have identified 90% CO_2 condensation as a practical benchmark, for which around 30 bar pressure is required in wet compression. Whilst screw and reciprocating compressors have been used for pilot-scale CPU of up to 30 MWth, for much larger volumes of gas these cease to be viable and centrifugal-type turbocompressors become necessary. As a larger volume of gas is involved in the intial compression, this is the most energy consuming step in the CPU.

4.2.4 Drying

As a well-established technology for dehydration of air and natural gas, temperature swing adsorption (TSA) is the preferred technology for drying the process gas to ppm levels of water prior to cooling. TSA employs columns packed with beads of water adsorbent materials from which water is driven of at higher temperatures. Several colums are normally used, so that while one column adsorbs moisture from the process gas, the other undergoes adsorbent regeneration. Regeneration is carried out by purging with hot dry gases, which are often taken from the N_2-rich vent stream of the distillation column. A colder purge stream is then required to cool the sorbent in preparation for the moisture adsorption phase. Ideally, the adsorbent should remain active without regeneration for as long as possible, generally lasting several hours.

Typically used for adsorbents are highly porous materials such as silica gels, zeolites, and activated alumina, which have the property of adsorbing gases at moderate temperatures (~40°C) and releasing them at higher temperatures (>120°C). The presence of residual contaminants such as SOx, NOx, and mercury in the process gas can interfere with the process by adsorbing to the adsorbent material, in some cases irreversibly. This is another motivation for achieving high levels of removal of these species upstream in the process.

4.2.5 Mercury

Mercury which is present in flue gases in the oxidised form Hg^{2+} is largely dissolved in condensates during the flue gas quench (Spero, 2014; Stanger and others, 2012). Elemental mercury, on the other hand, could also be substantially removed in the nitric acid-rich condensates which form during flue gas compression according to the reaction:

$$Hg + 2HNO_3 \rightarrow Hg(NO_3)_2 + H_2 \qquad (3)$$

A final wall of defense known as a guard bed is often employed to protect the aluminium heat exchangers. Guard beds are based on non-regenerable mercury-reactive sorbents such as sulphur-impregnated activated carbon, which reacts with mercury to form HgS. However, mercury capture in upstream processes such as condensation, compression, and drying, may actually be sufficient to dispense with any dedicated mercury removal (Béasse and others, 2013).

4.2.6 Partial condensation and distillation

The heavily insulated container in which all low temperature processes occur is referred to as the cold box. Here, a brazed aluminium heat exchanger is employed to cool the compressed process gas against a countercurrent flow of refrigerant, partially condensing it into a CO_2-rich liquid and an N_2-rich gas. The refrigerant is usually CO_2, which permits the cooling to approach the triple point of CO_2 at which the highest proportion of CO_2 can be liquefied, but ammonia has also been used, allowing cooling to -30°C. Refrigeration with CO_2 can employ either a separate working cycle of CO_2 or make use of the purified flue gas CO_2 itself in a process known as autorefrigeration. Most manufacturers have identified autorefrigeration as the optimum process for CO_2 liquefaction due to its relative simplicity, lower cost and energy use, and higher CO_2 capture rate, although it may be avoided for pilot projects as it produces a gaseous CO_2 product when often a liquid product is preferred at this scale (Shah and others, 2011, White and others, 2013a). In an oxyfuel plant producing CO_2 for pipeline transportation, this product would be recompressed to a supercritical state, and loss of pressure in the transition to gaseous state needs to be made up during compression. A concern when operating close to the CO_2 triple point is the risk of CO_2 freezing and causing equipment blockages, although no serious problems have been reported by the CPU pilots currently operational.

The condensed liquid can contain over 95% CO_2, but is normally subjected to further purification in the form of a flash separation (a rapid pressure reduction through a nozzle) or distillation. Distillation is required to reach the high purities (>99%) for which most pilot projects have been designed. At least one distillation column is employed, producing a CO_2-rich liquid as the bottoms product and a mixture of the lighter gases as the overhead product.

4.2.7 Vent gas separation

A futher refinement to CPU design is the addition of a unit for extraction of the CO_2 remaining in the 'vent gases' released from the cold box processes, allowing standard capture rates of around 90% to be increased to up to 98% (Figure 24). The extra capital cost of such a process can therefore be outweighed by a significant reduction in the cost per tonne of CO_2 captured (Leclerc and others, 2013). Manufacturers have employed either membrane-based systems or pressure swing adsorption for this purpose. The gas separating membranes are based on collections of fibres through which different gases permeate at different rates. Slower diffusing gases can be drawn off at higher concentrations near the beginning of the fibre bundle, with faster gases exiting at the end (Air Products, 2014). Whilst this technology would be far too expensive for handling larger volumes of gas, it is well-suited to processing the small volume of vent gas. Pressure swing adsorption is similar to TSA, but uses adsorbents which adsorb CO_2 at higher pressures, then release the gas when the pressure is dropped to approach a vacuum.

The separated CO_2 can be returned to the process gas upstream of the CPU compression, whilst the remaining vent gases can still be used to regenerate the dehydration sorbent. Alternatively, CO_2 and O_2 can be captured together and both recycled to the ASU, thus limiting oxygen loss and reducing the demand on the ASU (White and others, 2013a).

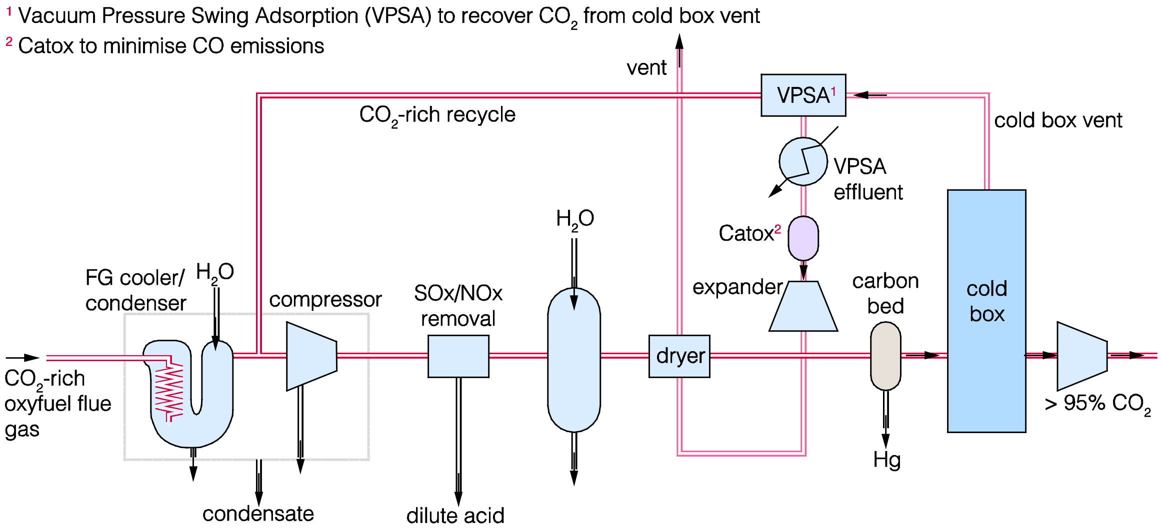


Figure 24 Praxair CPU schematic showing vacuum pressure swing adsorption (VPSA) and catalytic oxidation (Catox) for vent gas purification (Shah and others, 2011)

A further purification step aimed at achieving negligible emissions of pollutant to the atmosphere is to also eliminate CO in the vent gases. For this purpose, catalytic oxidation can be used to convert CO to CO_2 in vent gases prior to the CO_2 separation step (Shah and others, 2011).

Table 2 **Technologies used or proposed by the five main CPU manufacturers for each stage of purification** (Kluger, 2013; Stallmann, 2014; Shah and others, 2011; White and others, 2013a; Béasse and others, 2013; Ritter, 2011)

Process	Alstom	Air Liquide	Air Products	Linde	Praxair
deSOx	LP alkali scrub	LP alkali scrub	Sour compression	LP Alkali scrub	AC bed
deNOx	Selective catalytic reduction	Distillation	Sour compression	LICONOX alkali scrub at pressure	AC bed
Drying	TSA post-compression	TSA pre- or post-compression	TSA post-compression	TSA post-compression	TSA post-compression
Hg	AC pre-drying	Adsorption or cryoseparation proposed	None	AC guard bed	AC guard bed
Vent gas capture	None described	Membranes	Membranes	PSA	VPSA
Cold box	Ammonia or autorefrigeration, flash or distillation	Autorefrigeration, distillation	Autorefregieration, distillation	Autorefrigeration, distillation	Autorefrigeration, distillation

4.3 CPU by manufacturer

4.3.1 Alstom

Alstom CO_2 purification technology, known as a gas purification unit or GPU, was tested on a flue gas slipstream from the company's 15 MWth oxyfuel pilot in Windsor, USA, during 2012 (Wang and others, 2013). Little detail is available on the technologies used in this test facility, but the process chain proposed by Alstom for commercial units is fairly standard, with a direct contact condenser followed by compression to >28 bar, mercury removal, and adsorbent drying prior to the cold box (Kluger, 2013; Stallman and others, 2013). Presumably through use of an alkaline scrub, 98% removal of SO_2 is achieved in the direct contact condenser, while ppm levels of NOx can be obtained in the CO_2 product and vent gases through an undescribed process (Kluger, 2013). More recently, Alstom have patented an SCR-based process for NOx removal in the CPU, for which the flue gas is reheated by a catalytic oxidation reaction between residual oxygen and a fuel added to the stream (Stallmann, 2014).

A significant feature of the design offered by Alstom, is that two alternative cold box processes are offered depending on the purity of CO_2 required by the project. A simple flash purification of the condensed flue gases is proposed to achieve >95% purity CO_2 (including <1% O_2) for saline aquifer storage, with the more complex distillation process reserved for projects requiring high purity CO_2 (<0.01% O_2) for EOR. Both autorefrigeration and external refrigeration of ammonia are also offered, with the latter proposed as most suitable for hot climates. Current details of the overall process chain indicate:

- direct contact cooling (reduces H2O to less than 5%);
- multistage compression to >28 bar;
- activated carbon for mercury removal;
- TSA drying (regeneration with vent gases);
- partial condensation of CO_2 via autorefrigeration (90% capture) or ammonia refrigeration (80% capture);
- flash separation (saline aquifer storage) or distillation (EOR).

A large-scale Alstom GPU design will be incorporated in the ongoing FEED study for the White Rose 426 MW oxyfuel project at Drax power station in the UK. Aimed at saline aquifer storage, this project is presumably targeting around 95% purity CO_2.

4.3.2 Air Liquide

Air Liquide have been involved with major oxyfuel projects from an early stage, having proposed a CPU design for a cancelled Saskpower oxyfuel demonstration, and the CO_2 driers for the 30 MWth oxyfuel gas-fired plant at Lacq. In 2012, two large Air Liquide designed CPU became operational at the Ciuden and Callide pilot projects, each demonstrating some new process technologies. Both plants share key features of the Air Liquide process (registered as Cryocap™) including a low-pressure alkaline scrub for SO_2 removal, which can be combined with the initial flue gas quench or condensation step or occur just after. The units at both pilots can potentially be exposed to high levels of SO_2, so a dedicated removal technology is a necessity. NOx removal is also relatively unique, as a second distillation column is employed in the cold box to remove any remaining NO_2. Air Liquide also employ dedicated particulate filters after the low-pressure scrub to protect downstream equipment, although at both plants the majority of particulates are removed during scrubbing. These filters are regenerated by back pulsing the process gas.

Ciuden

At the Ciuden pilot, the entire flue gas flow of 8000 kg/h is scrubbed and dried in the CPU, but only a portion of this is then compressed and distilled, producing up to 420 kg/h of high purity liquid CO_2 or 10 t/d (Lockwood, 2013; Ciuden, 2013). Flue gas treatment at the plant can include wet FGD, but most research to date has been performed with the 30 MWth CFB boiler in which desulphurisation is carried out by limestone addition to the furnace. In the course of testing this process under oxyfuel conditions, SO_2 in flue gases can reach relatively high levels of up to 500 mg/m^3. The unit includes:

- direct contact quench with water;
- two columns scrubbing with sodium carbonate solution;
- particulate filter;
- pre-compression;
- TSA driers (3 vessels);
- main compression;
- partial condensation via a separate CO_2 cycle;
- O_2, N_2, Ar distillation;
- NO_2 distillation.

To protect against acidic condensates, the quench is carried out in a nickel alloy vessel, and the alkaline scrub in two plastic columns which produce a waste solution of around pH 6–7. Transients in SO_2 concentration can result in acid condensation, particularly at the flue gas inlet, which is coated with corrosion resistant Corrothane XP. The scrub achieves SO_2 levels of below 1 ppm, although spikes of up to

10 ppm are observed when inlet concentrations increase. A significant technology demonstrated in the Ciuden CPU is the use of low-pressure TSA driers as opposed to the usual post-compression adsorption; a move aimed at protecting the compressors from any acidic condensates, with the dew point reduced to -100°C in drying. A separate CO_2 refrigerant cycle is used to cool the gases close to the CO_2 triple point, prior to distillation columns for removal of NO_2 and non-condensable gases.

Callide

A similar unit at Callide is used to purify around 15% of the flue gas remaining after recycle, processing 4090 m^3/h into 75 t/d of liquid CO_2. The Callide pilot presents the additional challenge of no flue gas desulphurisation upstream of the CPU, resulting in up to 0.07% SOx as well as 0.14% NOx at the unit's inlet. Along with optimising performance and cost in a large unit, this project is aimed specifically at a detailed study of corrosion, ageing, and behaviour of impurities throughout the process chain (Spero and others, 2013a; Béasse and others, 2013; Court and others, 2011) (Figure 25). The Callide process follows:

- direct contact quench with NaOH solution;
- second NaOH scrub column;
- particulate filter;
- compression (centrifugally geared);
- scrub with chilled water;
- TSA driers (three vessels);
- partial condensation with ammonia;
- O_2 distillation by autorefrigeration;
- NO_2 distillation.

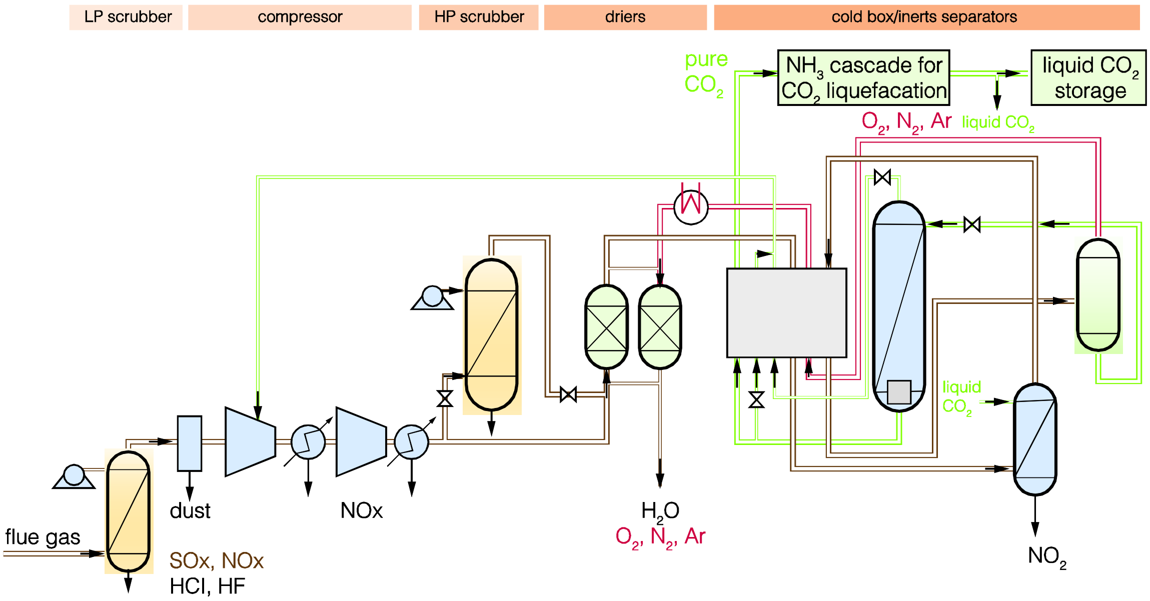


Figure 25 Process flow of the Callide CPU (Spero and others, 2013a)

At Callide, the alkaline scrub also acts as the initial flue gas quench as the primary recycle stream has already been taken off and is dried separately. This quench from 145°C to <40°C is followed by another scrubbing column connected to the same circuit of condensate and fresh solution. Here, NaOH is used as an alternative to the sodium carbonate at Ciuden, perhaps due to the higher SOx levels experienced. This achieves a reduction in SOx from over 800 ppm to less than 10 ppm (Table 3). The following compression at Callide is notable for being the first demonstration of centrifugal compressors in a CPU, which are the technology any large-scale plant would be obliged to use to accommodate the volume of process gas. A compression to 25 bar takes place over four stages before a further scrub, this time with chilled water (7°C), partly to promote NO_2 removal and partly to cool the compressed gases. In the cold box, an autorefrigeration cycle is used, although the gaseous CO_2 product is then liquefied with ammonia for storage or transport by road.

Typical NOx behaviour is for 10% to be removed in the low-pressure alkaline scrub, 55% in condensates after compression, 15% in the dryers, and a final 26% in the cryogenic distillation. Future designs will be adapted to prevent any remaining NOx emissions to the atmosphere. Mercury is mainly removed in condensates throughout the low-pressure area, reaching less than 0.1 µg/m^3 by the cold box inlet. No corrosion of materials or damage to compressors has been observed.

Table 3 Process gas composition at stages of the Callide CPU (Spero and others, 2013a)

Species	From boiler	LP outlet	Product
CO_2, mol%	50–57	58–67	>99.95
H_2O, mol%	19–22	5-7	<20 ppm
O_2, mol%	3–5	3.5–6	30 ppm
CO, ppm	20–>200	25–>200	<10
NO, ppm	500–700	580–820	<2.5
NO_2, ppm	20–40	Nil	14
SO_2, ppm	800–1000	<10	<0.1
SO_3, ppm	10–15	<0.1	<0.1
N_2 (+Ar)	Balance	Balance	Trace
Hg, µg/m^3	2.7–4.9	0.4–0.9	<0.0002
Particulates, mg/m^3	150–250	<0.02	Nil

Zero emissions

Air Liquide propose a membrane-based process for recovering CO_2 from vent gases, consisting of a bundle of polymer membrane fibres, contained in a pressurised cylindrical vessel (Leclerc and others, 2013) (Figure 26). One 30 cm diameter bundle contains 1.2 million fibres, representing 750 miles of length. This technology has not yet been implemented on either of the large pilots, but calculations predict that an increase in capture rate from 90% to 98% could be effected, with the associated reduction in cost per tonne of CO_2 compensating for the necessary capital expense. As part of a wider strategy towards zero emissions, the addition of catalytic oxidation to the vent gas stream has also been proposed to achieve 98% reduction of CO, as well as a cryogenic separation of Hg impurities (Leclerc and others, 2013).

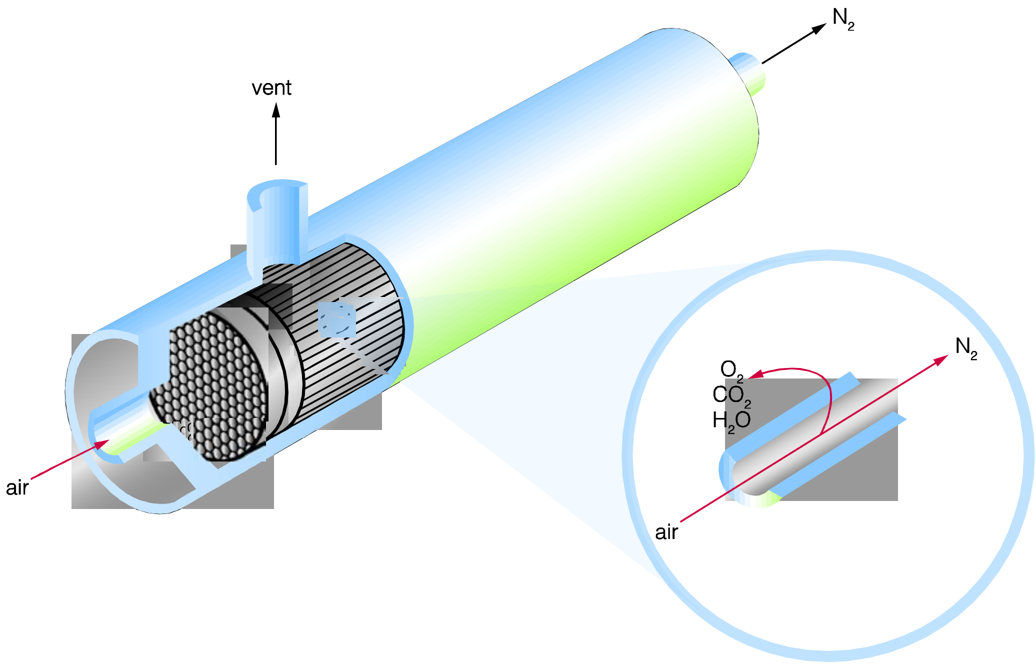


Figure 26 Air Liquide's polymer membrane-based technology for vent gas purification (Tranier, 2013)

In 2010, Air Liquide was selected to provide ASU and CPU for the FutureGen 2.0 oxyfuel demonstration. The CPU for this 168 MW plant is to be designed to produce 3200 tCO_2/d at a 98% capture rate, presumably using membrane technology to augment the capture rate.

4.3.3 Air Products

Early work by Air Products into oxyfuel flue gas purification was conducted in collaboration with Imperial College London, during which several key concepts were developed. This work was followed by installation of units equivalent to 6 kWt at the Doosan oxyfuel pilot at Renfrew and on a 0.3 MWth equivalent slipstream at the Alstom pilot in Windsor, USA. From 2011, an Air Products designed CPU was operated as a secondary CO_2 capture plant at the Schwarze Pumpe pilot plant, where it treated a flue gas slipstream equivalent to 1 MWth (White and others, 2013a). This pilot CPU was designed primarily to demonstrate three principal concepts in the CO_2 process chain: 'Sour compression' of acid gases SOx and NOx, autorefrigerated partial condensation, and membrane-based recovery of CO_2 from the vent gases. These are combined with some well-established processes in this sequence:

- direct contact flue gas cooler;
- sour compression removal of NOx and SOx;
- TSA drying;
- mercury guard bed;
- partial condensation via autorefrigeration;
- optional distillation;
- optional membrane-based CO_2 capture from vent gases.

Sour compression

Of the new processes demonstrated, sour compression is of particular interest as a quite distinct method of SOx and NOx removal which does not require chemical agents (White and others, 2013a; Torrente Murciano and others, 2009). This technology exploits the chemistry between the two species under pressure and in the presence of water to maximise their conversion to the soluble acids HNO_3 and H_2SO_4 which can be removed in condensates. In essence, this chemistry resembles the lead chamber process originally used for the production of sulphuric acid, where NO_2 is hydrated to HNO_2 before acting as an oxidising agent in the conversion of SO_2 to SO_3/H_2SO_4:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (4)$$

$$2HNO_2 + SO_2 \rightarrow 2NO + H_2SO_4 \qquad (5)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (6)$$

However, the detailed chemistry is understood to be rather more complex as numerous pathways are available to the reacting species (Murciano and others, 2009, White and others, 2013b). The desired pathway depends on the redox reaction producing NO rather than nitrous oxide, as NO can then be oxidised to NO_2 and repeat the process, effectively catalysing the production of SO_3. Nitrous oxide, on the other hand, terminates this redox cycle. In addition to the redox active HNO_2 species, the hydration of NO_2 forms the unreactive HNO_3 by which the NO_2 is eventually also condensed out.

Promoting the chemistry involved in sour compression requires a prolonged contact time between the pressurised gases and water. As shown in Figure 27, at the Schwarze Pumpe pilot unit this is achieved with two packed columns, one at 15 bar and the other at 30 bar, through which condensate water is circulated together with a proportion of fresh makeup water (White and others, 2013a). Before each column the process gas is compressed with diaphragm compressors followed by interstage cooling. Even before compression, 10–20% of SO_2 is removed in the condensate of the FGCC, but no NOx. During the initial two-stage compression to 15 bar, the expected conversion of some NO to NO_2 is observed and a significant proportion of SO_2 is removed in the interstage condensates. Comparison of the process with and without SO_2 reveals less NO_2 in the presence of SO_2, indicating that some NO_2 is already reacting with SO_2 at this step. Measurements after the 15 bar packed column show around 80% removal of both SO_2 and NOx, with the remainder removed in the second column at 30 bar.

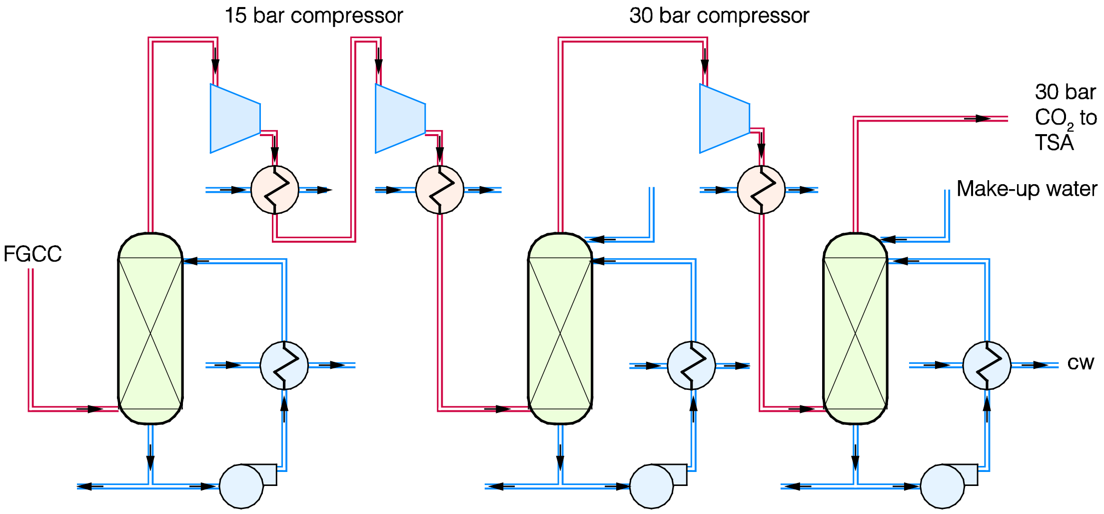


Figure 27 The sour compression process (White and others, 2013a)

A third phase of testing started in May 2012 looked at the effect of various parameters on sour compression, including pressure, residence time, and SO_2/NOx ratio (White and others, 2013a). Whilst the levels of NOx entering the CPU are relatively fixed by the operation of the boiler, SO_2 levels can be adjusted by mixing flue gas from before and after the pilot plant's FGD unit in varying proportions, allowing up to a maximum of 2500 ppm. NOx levels also varied naturally between 260 and 360 ppm over the course of the tests. Within these restrictions, the effect of the ratio of the two species was studied, and showed a clear reduction in SO_2 removal with increasing SO_2/NOx ratio, with removal by the first column more than halved in increasing the ratio from 2 to 8. This highlights the importance of NOx in sour compression, meaning that overzealous reduction of NOx from the boiler could be seriously detrimental to optimising SO_2 removal. High SO_2/NOx ratios are also thought to lead to unwanted formation of N_2O, which can have a significant negative influence on NOx removal. As could be expected, increasing pressure, residence time, and fresh make-up water flow in the first column all had strong positive influences on the extent of SO_2 removal.

Residual SO_2 was found to impede the performance of the TSA drying by irrervisbly binding to the sorbent and blocking the openings of the microporous crystals. No adverse effect was observed from NOx, which evidently adsorbs reversibly to the material.

Autorefrigeration and distillation

In the autorefrigerated main heat exchanger, product CO_2 at low and medium pressures are evaporated to provide cooling to the process gas (White and others, 2013a). Variation in the CO_2 composition of the flue gas affects the temperature and pressure at which condensation occurs, so the pressures of the evaporating refrigerant CO_2 must be altered using a feed forward control system to optimise heat transfer.

The CPU has been tested both with a distillation for high purity CO_2 (99.9%) CO_2 and without for lower purity CO_2 (97.4%) containing over 1% each of N_2 and O_2. Capture rates of 87.3% and 81.4% could be achieved for low and high product purity respectively, although higher rates are expected with an optimised plant.

Vent gas separation

A series of membrane modules is installed to recover both CO_2 and O_2 from the cold box vent gas and return them to the boiler, improving capture rate and lowering the O_2 demand on the ASU. Using Air Products' own PRISM® membrane technology, these modules consist of high-pressure vessels containing thousands of polymer membrane fibres though which the pressurised gas mixture is forced (White and others, 2013a; Air Products, 2014).

4.3.4 Linde

A prominent demonstration of Linde's CO_2 purification technology was the main CPU operating at Schwarze Pumpe, which accommodated the entire 30 MWth flue gas flow and produced up to 10 t/h of CO_2 at over 99.7% purity (Holling and others, 2009). When commissioned in September 2008, this unit was the first industrial-scale oxyfuel CPU to be built, and remains the largest capacity unit operated. Since start-up, this CPU underwent significant upgrading consistent with the technological advances that have been made during that time. As with other pilot-scale CPU, the principal distinguishing feature of the Linde pilot is the manner in which SO_2 and NOx are removed from the process gas. Although the original design of the unit used only an activated carbon filter combined with the SO_2 and NOx removal inherent in two-stage compression with interstage cooling, specially developed deNOx technology has since been added to the process. When decommisioned in 2014, the process flow consisted of:

- flue gas cooler and condenser;
- NaOH or $NH_3(OH)$ scrub;
- activated carbon filter for removal of SOx, HCl, and heavy metals;
- two-stage compression with interstage cooling and condensate separators;
- LICONOX process: alkaline scrub for NOx removal (Added 2010);
- temperature swing adsorption dryers (molecular sieves);
- liquefaction via separate CO_2 cycle;
- distillation.

Inlet levels of SOx are already quite low at Schwarze Pumpe due to the presence of wet FGD upstream. An average input of 100 mg/m^3 SO_2 is reduced to 20 mg/m^3 by the NaOH scrub, and the majority of the remainder is removed with condensates throughout the rest of the process (Table 4). The loss of some CO_2 in the condesate has the negative effect of adding to NaOH consumption (Stromberg, 2011).

Before the dedicated NOx removal was added, an NO_2 concentration of 11.1 ppm could still be obtained (Yan and others, 2011). Around 33% of the 600–700 mg/m^3 inlet NOx was removed with condensate after the last compression stage, with smaller amounts removed by the activated carbon and flue gas quench. Remaining trace amounts of both pollutants were finally adsorbed in the dryers and thus removed in the regeneration process with the vent gases.

Table 4 Process gas compositions at Schwarze Pumpe and the Linde designed CPU (Ritter and others, 2009; Burchhardt and others, 2011; Yan and others, 2011)

Species	FGD outlet	After FGC	Product
CO_2, %	>58	>88	>99.9
H_2O, %	30	~4	<5 ppm
O_2, %	<4	<4	<0.001
N_2, %	<3	<3	<0.01
Ar, %			
SO_2, mg/m^3	<100	<20	<2.6
SO_3, mg/m^3	<20	<5	<0.1
NO, mg/m^3	–	<630	<6.1
NO_2, mg/m^3	–	<10	<9.4

LICONOX (Linde cold deNOx technology)

In 2010, a new deNOx process was installed in the Linde CPU after the wet compression and before drying, comprising an alkali scrub which has been tested with either ammonia water or sodium hydroxide solution (Ritter and others, 2013) (Figure 28). Through a series of possible reactions, these reagents convert NOx to nitrites and nitrates of either ammonium or sodium, with ammonia water also reacting with SO_2 and SO_3 to form ammonium sulphite and sulphate. A NOx removal rate of 97% has been demonstrated with the unit at a pressure 15 bar. The resulting salt solution is neutral and removed as aqueous waste, for which two possible disposal strategies have been proposed and tested. Heating to 60°C can convert ammonium nitrite to nitrogen and water; a path which relies on first directing the neutralisation reaction to nitrites rather than nitrates by careful control of pressure, temperature, and NO/NO_2 ratio. Alternatively, the waste can be converted to entirely ammonium nitrates which have value as a fertiliser. Other advantages of the process are the avoidance of corrisive, acidic condensates and the fact that SO_2 adsorption can occur independently of NOx kinetics and without prior oxidation to SO_3.

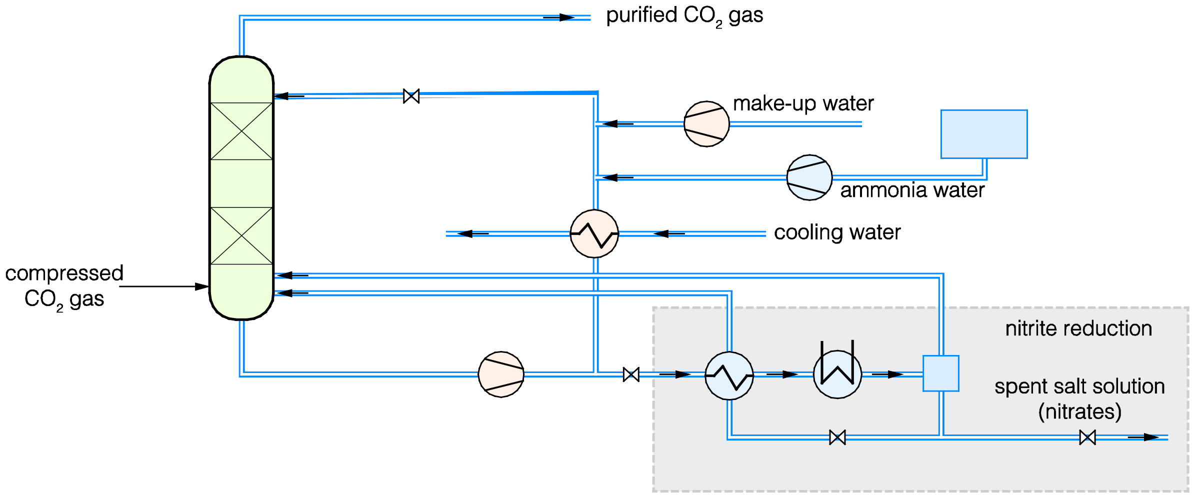


Figure 28 The Linde LICONOX process (Ritter and others, 2013)

Future optimisation

The LICONOX system is one of a number of additional processes that Linde proposed in their design for the, now cancelled, demonstration plant at Jänschwalde which give an indication of future Linde plans for larger CPU (Ritter, 2011; Vattenfall, 2012). The Jänschwalde CPU incorporated further mercury removal in the form of dual regenerable beds of activated carbon after the driers, as well as CO_2 capture from vent gases based on pressure swing adsorption. Other planned upgrades considered standard for large-scale CPU are the move to turbocompressors and autorefrigeration. This process was designed for a capture rate of over 90% and greater than 96% product purity.

4.3.5 Praxair

From 2009 to 2012, Praxair carried out detailed bench-scale tests and simulation of their CPU technology as part of a wider oxyfuel study with Foster Wheeler for the US DOE (Shah and others, 2012). This design employs a regenerable activated carbon-based process for removal of SOx and NOx, and has a focus on achieving near zero emissions via vent gas purification.

The SOx and NOx removal process consists of at least two packed beds of activated carbon which alternate between adsorption and regeneration modes. When a bed becomes saturated with contaminants regeneration is carried out by water washing, generating a dilute acid stream which can be partly recycled to minimise waste. A stream of heated nitrogen is then used for drying the sorbent. Batch tests of this process at 20°C and 15 bar achieved 99.9% SOx removal and up to 98% NOx removal from inlet concentrations of 4000 ppm and 400 ppm respectively. In tests of the continuous process similar removal rates were achieved, though some loss of activity of the sorbent was experienced over the 40 day test period. Tests on a related process aimed at recycling the pollutants as sulphuric and nitric acids were deemed unsuccessful due to the impracticality of separating residual sulphuric acid from the nitric acid stream.

To achieve near-zero emissions, Praxair have tested vent gas purification using catalytic oxidation for conversion of CO to CO_2 followed by vacuum pressure swing adsorption (VPSA) for CO_2 capture. Using commercially available sorbents, tests on the VPSA step have sought to optimise the process, with a six bed unit chosen as the best compromise of performance and capital cost. With a simulated vent gas feed of around 30% CO_2, this design was able to achieve more than 90% capture of CO_2, producing an 80% pure stream which is returned to upstream in the CPU.

4.4 CPU energy consumption

In contrast to the ASU, the majority of energy consumed by the CPU goes into compressing the high-pressure CO_2 product, with a smaller proportion of energy required for the separation of impurities. The energy required for this separation is also much closer to its theoretical limit than in the oxygen production process, and as a consequence, further optimisation of the CPU process is more challenging (Fu and Gundersen, 2013b). Of the two compression processes in the CPU, the initial 'wet' compression for liquefaction of the flue gases consumes a larger proportion of the total energy than the 'dry' compression of the purified CO_2 product, due to the larger gas volume and presence of much more volatile gases. Consequently, CPU energy consumption depends largely on the concentration of CO_2 in the flue gases (Figure 29). Achieving high levels of CO_2 by minimising air ingress is therefore crucial to maximising plant efficiency.

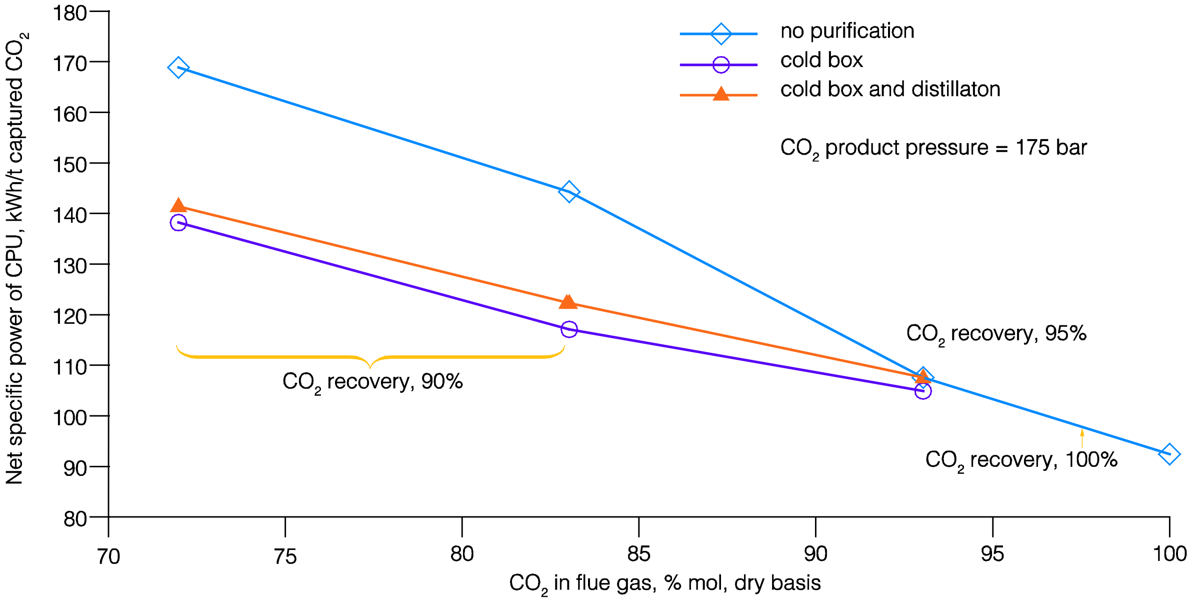


Figure 29 The effect of flue gas CO_2 content and purification method on CPU power consumption (Perrin and others, 2011)

As can be seen in Figure 29, introducing a flue gas liquefaction step actually reduces CPU energy consumption for all but the purest flue gases, as the compression to pipeline pressure is much less energy intensive once the light gas impurities have been removed. On the other hand, the addition of a distillation step to reach even higher purities introduces inefficiencies and the energy consumption of the unit is increased by several percent. An optimised CPU energy consumption of 120 kWh/tCO_2 is targetted by Air Liquide over the next five years (Paufique and others, 2013), although models of large oxyfuel plant have used values as low as 113 kWh/t (Hagi and others, 2014). The unit typically consumes from 8% to 12% of a large-scale plant's gross power output.

5 Industrial-scale pilot projects

The commissioning in 2008 of a 30 MWth oxyfuel pilot at Schwarze Pumpe power plant in Germany represented an important landmark in the development of oxyfuel technology, as the first demonstration of the full process chain including air separation and CO_2 purification. However, this unit was preceded by combustion tests at Babcock and Wilcox's 30 MWth pilot furnace. Since these, a number of similarly sized and larger projects have been completed, although none so far which are considered of demonstration scale (Figure 30). In 2009, a 40 MWth burner test was commissioned by Doosan Babcock, although without ASU or CPU. In 2011, a 30 MWth oxyfuel-fired CFB unit started operations near the Compostilla power plant in Spain, accompanied by a 20 MWth PC unit at the same site. The largest project currently operating is the oxyfuel retrofit of a 30 MWe (100 MWth) PC boiler at Callide, Australia, which is also the first oxyfuel plant to generate electricity directly to the grid. It is noteworthy that these projects have been funded by a wide range of organisations, including utilities (Vattenfall, CS Energy), boiler manufacturers (B&W, Doosan, Foster Wheeler, IHI), mining companies (Xstrata) and national governments (Spain, Australia, Japan); often in the form of consortia of all interested parties.

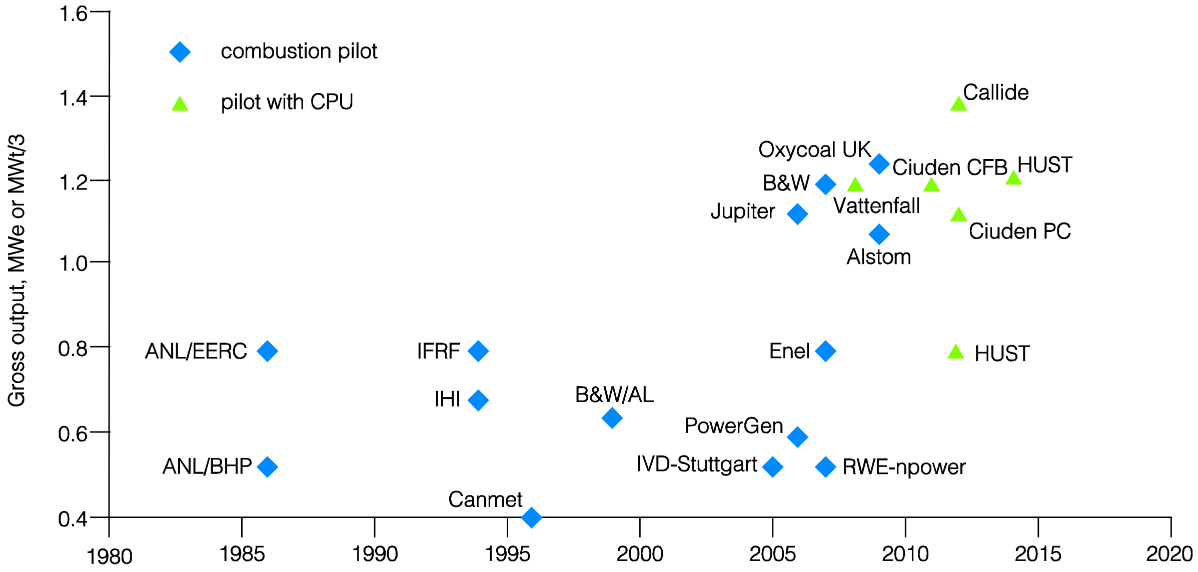


Figure 30 Historical scale-up of oxyfuel pilot plants (adapted from Wall and others, 2009)

Pilot studies at this scale (>10 MWth) are a crucial step between laboratory-scale studies and future demonstration units upwards of 100 MW. Testing in such facilities can yield important information on the transition between firing modes, burner design and combustion, materials and corrosion, and the fate of ash and slag (Chen and others, 2012). Moreover, units which incorporate ASU or CPU gas processing steps can provide invaluable information on how these processes interact with the boiler and environmental island, and how the process chain responds as a whole to inputs such as cycling, fuel switching, shut-downs, and air/oxy switching. A common feature of all pilot plants is the ability to switch between air- and oxy-firing modes, achieving stable operation under air before undergoing a step-based transition to oxyfuel. This reflects the likelihood that early full-scale oxyfuel plants will be expected to be able to operate flexibly between the two modes, in case of ASU or CPU faults or to allow higher net power output when required. Most pilots at this scale are also intended to support plans for larger demonstration projects which are discussed in the next chapter.

5.1 Schwarze Pumpe

The Schwarze Pumpe oxyfuel project was developed by Swedish utility Vattenfall in order to validate and improve technology around carbon capture. Construction of the 30 MWth PC plant at the site of an existing lignite-fired plant in south-east Brandenburg began in May 2006, with first power generation achieved in September 2008 (Burchhardt, 2009). As of September 2013, the project had recorded 13,200 hours of operation under oxyfuel mode and 3800 hours of air firing, producing 10,660 tonnes of liquid CO_2 in the process (Burchhardt and Griebe, 2013). However, following the cancellation of the Jänschwalde oxyfuel demonstration plant and Vattenfall withdrawing their interest in CCS research, the pilot plant concluded operations in April 2014.

The plant's Alstom-designed boiler fired primarily dried local lignite, using a single ceiling-mounted burner which permitted trials of alternative burner designs (Figure 31). A transition time between air and oxyfuel modes of 20 minutes exceeded orginal expectations for the plant. The flue gas underwent standard processing for a modern European coal plant, passing through ESP and FGD, and with an optional SCR pathway on leaving the boiler. Primary recycled flue gas was taken from after the FGC, whilst the secondary recycle could be taken either prior to or following desulphurisation, but usually operating in the latter mode. Significantly, the entire O_2 supply was provided by a cryogenic ASU, and all the non-recycled flue gas flow could be processed by the CPU, which captured 90% of the CO_2 to produce a maximum of 9 t/h of liquid CO_2 at 99.7% purity. Storage tests in a saline aquifer at Ketzin ran successfully from May to June 2011, with 1500 tCO_2 transported by road.

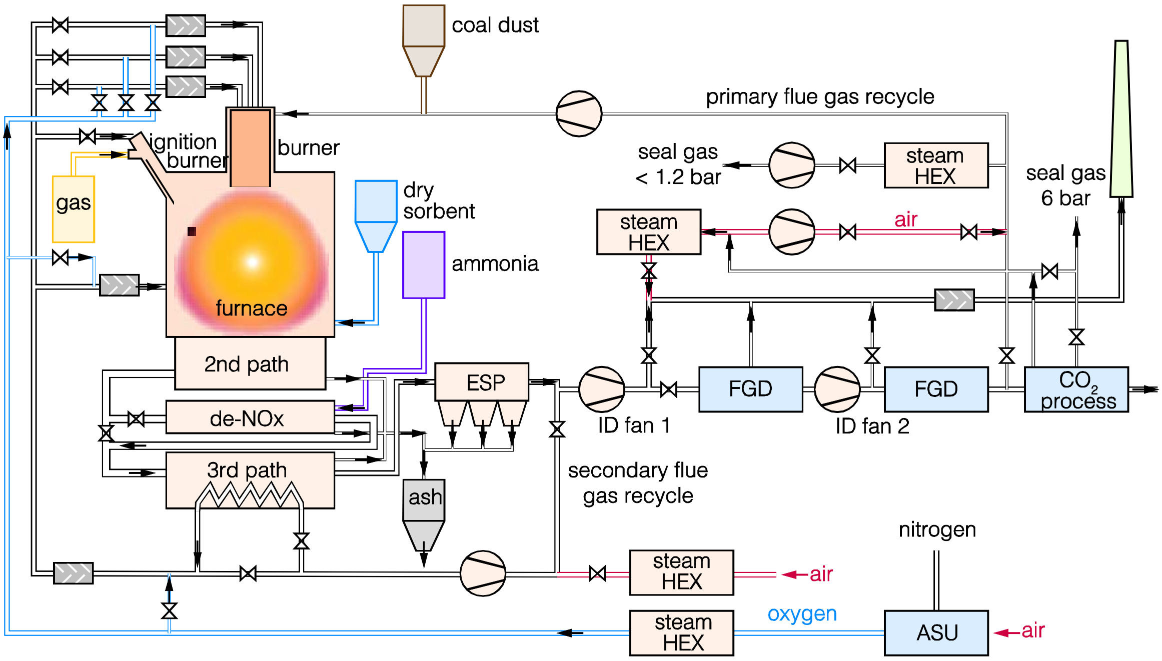


Figure 31 Schematic of the Schwarze Pumpe pilot plant (Burchhardt and Griebe, 2013)

A principal test variable at Schwarze Pumpe was burner design, used in combination with varying recycle ratio and oxygen–flue gas mixing techniques to optimise combustion parameters such as excess oxygen and ignition delay (Burchhardt and others, 2013; Stromberg, 2013). Since its commissioning, five different burners from four manufacturers were tested, including two Alstom burners, Doosan Babcock's 'Oxycoal' burner, and a Hitachi burner. The majority of these were pure swirl burners, with only the original Alstom burner employing a combination of jet and swirl. Swirl is a key requirement for producing a stable oxyfuel flame, which can also be adjusted when the plant transitions between firing modes. Stable flames were achieved with all burner designs in this manner, with 28% O_2 providing the most similar flame temperatures to air firing (Burchhardt and Lindgren, 2011). Ignition was achieved by a separate propane-fired starter burner at an angle to the main burner, or through a burner axially integrated into the main burner, depending on the design. Reduced power consumption on ignition may be possible through use of an axial plasma flame lance, trialled during later burner tests.

Different approaches to introducing oxygen to the secondary recycle stream were designated 'pre-mixed mode', in which the oxygen is added before the stream is split at the burner, 'expert mode', where the amount added to each burner register is controlled (including the overfire air outlet), and 'hybrid mode' in which both these approaches are combined. It was found that premixing the oxygen places a lower limit on both the excess oxygen needed (3.5%) and the proportion of total oxygen which can be used (22%). In expert mode, a much wider range of these parameters is possible, down to 2.5% of excess oxygen at 18% total oxygen, which is even lower than possible in air firing (Burchhardt and others, 2013). However, the tests also concluded that the pre-mixed mode would also be sufficient for operation of a commercial plant. Varying the proportion of overfire air also had an effect on combustion behaviour and, as in a conventional boiler, could be used to reduce NOx and CO.

The furnace was usually operated with hot recycle of flue gas from before the FGD for the secondary stream, which provided roughly 1%pt additional efficiency over recycle from downstream of the FGD (Burchhardt and Griebe, 2013). Operating under these high sulphur conditions did not appear to result in observable exacerbation of material corrosion, although long-term material studies were rendered difficult by constantly changing operation parameters and cycling associated with other tests.

A network of analysers for temperature, pressure, and flue gas flow rate and composition throughout the boiler was combined with process modelling to produce a detailed picture of heat and mass transfer (Burchhardt and Griebe, 2013). Radiant heat transfer in the evaporative section is only slightly lower in oxyfuel mode, and tends to approach the air values with increasing oxygen ratio or at lower boiler loads (Figure 32). Heat transfer in the convective pass is also similar in both modes, although the larger volume of combustion air preheated in air mode requires more heat from flue gases in the gas heat exchanger. This is balanced by a greater heat loss for oxyfuel flue gases at the second superheater. Carbon burnout, fouling and slagging were similar in both firing modes.

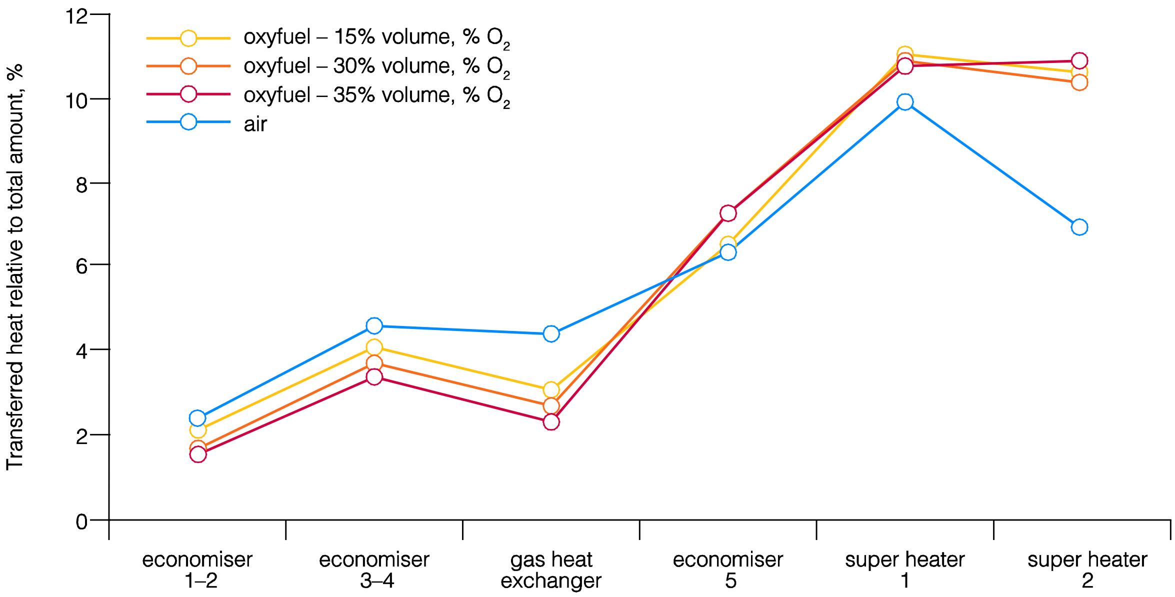


Figure 32 Heat transfer at heat exchange sections of the Schwarze Pumpe pilot (Burchhardt and Griebe, 2013)

5.1.1 Emissions

As expected for oxyfuel combustion, NOx formation was significantly lower at less than half that of air firing. This could be further decreased through use of overfire air or low NOx burners, but air-staging measures also led to increased CO (Kluger and others, 2011).

SO_2 and SO_3 formation was roughly the same as for air firing, but hot flue gas recycle resulted in boiler concentrations of around four times those of air firing (Kluger and others, 2011). Alstom conducted SO_3 measurements via the controlled condensation method and found around 40–60 mg/m^3 and 10 mg/m^3

SO_3 in dry gas for high and low sulphur coals respectively. The SO_3/SO_2 ratio is relatively low at 0.15–0.45%.

In general, no fundamental problems were encountered with the wet FGD under oxyfuel conditions, with 99.5% removal rates achieved even at high levels of SO_2, and a comparable quality of gypsum produced. The pH of the reaction vessel is slightly lower in oxyfuel, but the high partial pressure of CO_2 did not appear to be detrimental to limestone dissolution and SO_2 absorption (Anheden and others, 2011; Yan and others, 2009). Higher water content in the flue gases can lead to higher operating temperatures, so water condensation in the unit needs to be avoided. Forced oxidation of the product suspension to gypsum was conducted in a separate vessel to avoid contamination of the flue gas.

5.1.2 CO_2 processing and plant balance

Flue gas upstream of the FGD contained around 64% CO_2, with the 31% water reduced to 4% in the flue gas condenser before further processing in the Linde-designed CPU which was capable of processing the entire 30 MWth flue gas flow (*see* Section 4.3.4) (Anheden and others, 2011). This pilot CPU could achieve a removal rate of greater than 92%, with the majority of the escaped CO_2 leaving as vent gases (7%) from the CPU distillation, and smaller amounts (around 1%) lost in the FGD. The liquid CO_2 product had a purity of >99.7% which is in excess of what would realistically be required for a full-scale oxyfuel plant (~96%) (Burchhardt and Griebe, 2013). Measures taken to reduce air ingress and maintain high levels of CO_2 in the flue gas included the use of two flue gas fans so the under pressures are closer to atmospheric, and recirculation of cold flue gases for sealing critical points and moving parts.

Since 2011, an alternative CPU pilot designed by Air Products was trialled at the plant, taking a flue gas slipstream equivalent to around 1 MWth (*see* Section 4.3.3).

5.1.3 ASU

The Schwarze Pumpe cryogenic ASU was a commercial GOX6600 from Linde AG which produced oxygen at 99.5% purity and with less energy efficiency than would be expected of an optimised large-scale oxyfuel ASU (~330 kWh/t). This energy consumption was further increased in warmer weather or at reduced operating load. The unit was usually operated under stationary operating conditions with automated start-up, shut-down and load-changing procedures. However, start-up of the ASU at ambient conditions and without liquid in the distillation columns could take around three days, although if cold reflux is still present in the columns this time could be reduced to 22 hours. Load change rates while maintaining O_2 purity were found to be significantly higher than specified (Anheden and other, 2011).

5.2 Callide

Currently the largest oxyfuel pilot operating, the Callide plant is a 100 MWth retrofit of an existing PC boiler located in Central Queensland, Australia. The project is a joint venture of six organisations: Regional state-owned utility CS energy, IHI, JPower, Mitsui, Schlumberger, and Xstrata Coal, managed by a company created for the purpose, Callide Oxyfuel Services Limited (COSPL). Funding has also been provided by the governments of Australia, Queensland (through CS Energy), and Japan (through the

Japanese partners) (Spero, 2009). Construction of the plant began in 2010, with first oxyfuel firing in March 2012 and start-up of the CPU six months later. The existing boiler, dating from the 1960s but refurbished in the late 90s, was retrofitted by IHI for oxyfuel operation by replacement of two of the six burners and installation of extensive ducting for flue gas recycle, including some additional heat exchange equipment (Spero, 2011, 2014) (Figure 33). Notably, existing flue gas treatment equipment comprises only fabric filters for particulate control and no FGD, as is typical for Australian coal plant. This means that both primary and secondary recycle streams are SO_2-rich, with both streams taken off at the same point, before flue gas condensation. The primary recycle is therefore dried in a separate water condensation unit based on a plate heat exchanger, before being preheated against boiler exit gases in a retrofitted heat exchanger. As reheating recycled flue gas takes less heat from the boiler exit gases than heating ambient air, a new feedwater heater was necessary to further cool oxyfuel flue gases to a temperature compatible with the fabric filters. Oxygen is provided by two cryogenic ASU (330 t/d each), whilst the CPU purifies around 75 t/d of liquid CO_2 from a slipstream of roughly 12% of the flue gas remaining after recycle, with the rest released to the stack. Both these gas processing pilots are supplied by Air Liquide. A key feature of the Callide plant is that it is the first oxyfuel pilot to use the steam generated to supply electricity directly to the grid (Spero, 2013).

A second stage of the project has characterised the CO_2 storage potential in the region, consisting of depleted gas fields and saline aquifers in the Northern Denison Trough and the Surat Basin. This has included trial injection of quantities of liquid CO_2 transported by road from the plant.

On completion of the planned three year project duration, the Callide pilot plant is scheduled to be decommissioned in December 2014.

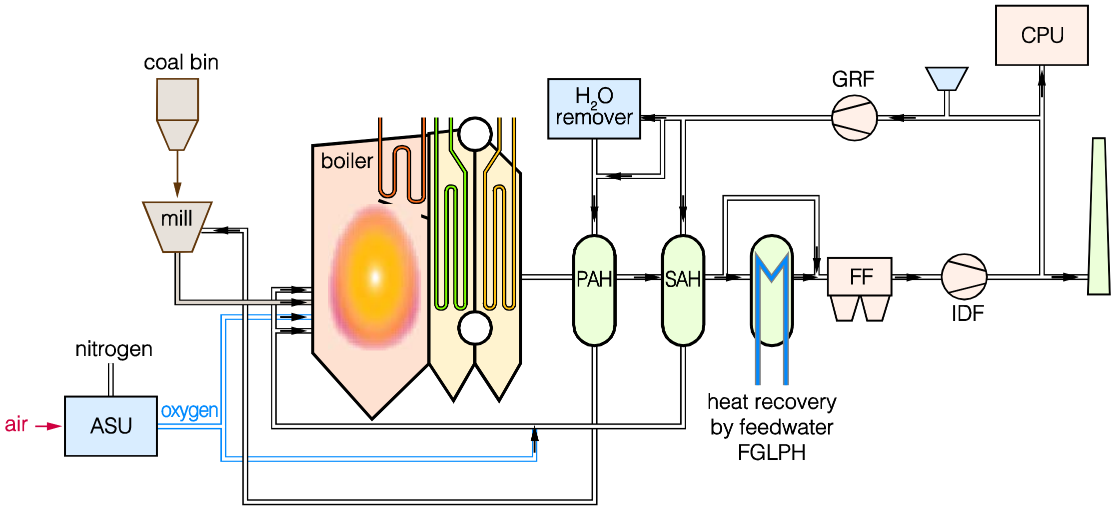


Figure 33 The Callide oxyfuel pilot process (Spero, 2013)

5.2.1 Combustion and heat transfer

The plant fires primarily local 'Callide' subbituminous coal, though blends with a semi-anthracite and a medium volatile bituminous coal have also been trialled. In oxyfuel mode at full load, flue gases contain over 70% CO_2, which is higher than originally targetted for the plant. A reliable, automated transition between firing modes, lasting at least 90 minutes, involves an initial introduction of oxygen, prior to a simultaenous gradual reduction in air supply and increase in flow of recycled flue gas (Spero, 2014). The combustion efficiency is enhanced in oxyfuel mode, as indicated by lower levels of CO and significantly lower levels of carbon in ash (Spero and others, 2013a). At 27% oxygen, the heat balance between boiler sections is almost equivalent to air, with 80% absorbed in the evaporator and 20% by superheaters, but the overall heat duty is slightly reduced due to greater heat recovery in feedwater heating (Yamada and others, 2013). In practice the plant operates with oxygen levels of 24–30%, and is capable of ramping at 1%/min and turndown to 55% whilst in oxyfuel mode (Spero, 2014).

Other combustion tests completed include the trialling of direct oxygen injection through lances around the burners, and using wet flue gas recycle by bypassing the water remover unit (Spero and others, 2013b).

5.2.2 Emissions

As for the Schwarze Pumpe pilot, NOx formation rates in oxyfuel are less than half those of air firing, accompanied by a shift towards a higher proportion of NO_2. The concentrating effect of flue gas recycle results in SOx levels 4–5 times higher in oxyfuel, although SOx formation rates can be slightly less than in air firing due to higher absorption of sulphur species by fly ash. On the other hand, SO_3 comprises 1–2% of total SOx, compared with less than 1% in air. These elevated levels of sulphur species lead to sulphate deposits throughout the ductwork which can create blockages at pressure tapping points. A slightly lower yield of fly ash particulates is produced under oxyfuel conditions, and boiler slagging is also reduced (Spero, 2013).

5.2.3 Acid corrosion

Although Callide coal is relatively low in sulphur, the lack of FGD for either recycle stream leads to high concentrations of SO_2 throughout the boiler and duct work (1000–1500 ppm). Combined with water levels of 18–25% this creates highly corrosive conditions for areas which are below the acid dew point such as the primary air heater and coal transport pipes (Uchida, 2011). In these places the plant has employed corrosion-resistant duplex and super-duplex (high Cr) stainless steels (Spero, 2013). Sulphate deposits are also formed throughout the duct work, and can block outlets such as condensate drains. The plate heat exchanger cooler used to remove water from the primary flue gas stream has been subjected to particularly severe corrosion from combined sulphuric acid and chlorides, and has been replaced with more chloride-corrosion resistant SMO254 steel (Spero, 2013). In the CPU, SO_2 is removed in the flue gas quench, so nitric acid is main problem downstream, producing very acidic condensates of pH <1.5 and favouring use of the nitric acid-passivated steels.

Corrosion probes of advanced alloys at the superheaters have been installed as part of ongoing investigation into high-temperature corrosion of materials for supercritical and USC plant.

5.2.4 Plant control and trouble-shooting

Substantial work has been carried out on optimisation of the process logic of the oxyfuel boiler and CPU. Operation of the plant relies on continuous monitoring of emissions and various condensates, relying on numerous chemical analysers which can be challenging to run and need regular calibration. Control of the oxygen mixing mechanism and balance of the primary and secondary gas pressures have also required careful attention to achieve optimum combustion conditions. Measures to reduce significant air ingress of around 7% relative to the total flow have included modification of the fabric filter hatch seals (Spero and others, 2013b). Having resolved most of these commissioning issues, the plant has been operating steadily since August 2013.

5.3 es.CO_2-Ciuden

The es.CO_2 oxyfuel pilot is the flagship research site of Ciudad de la Energia or 'Ciuden', a non-profit institution set up by the Spanish government for research into CCS technology. Situated near the Compostilla coal plant in the El Bierzo region of northern Spain, the site houses both a pioneering 30 MWth oxyfuel CFB unit designed by Foster Wheeler and a 20 MWth PC unit, sharing much of the same auxiliary equipment and a CPU. The first oxyfuel firing of the CFB boiler was achieved in November 2011, with first CO_2 capture almost a year later (Otero, 2013). As of September 2013, this unit had been operating for 3500 hours, and early tests on the PC boiler had recently begun. Although an FGD unit was originally planned for use with PC flue gases, it has not been installed, and the CFB boiler uses limestone for in-situ desulphurisation in the furnace. Hot recycle is therefore used for the secondary recycle stream, and the primary stream is also hot and undried, with potential problems for solids handling (Figure 34). Unlike the Vattenfall and Callide pilots, commercially supplied oxygen is used in place of an ASU, largely because this technology is considered well-established and not in need of demonstration. A CPU designed by Air Liquide carries out dehydration of the entire flue gas flow, although only 6% of this is further purified to 99% pure liquid CO_2 which can be taken by road to a storage demonstration site at Hontomin near Burgos. The es.CO_2 site also includes an oxyfuel biomass gasifier, a 3 km long CO_2 transport test rig, and a facility for studying the effect of escaped CO_2 on plants (Lupion, 2011a).

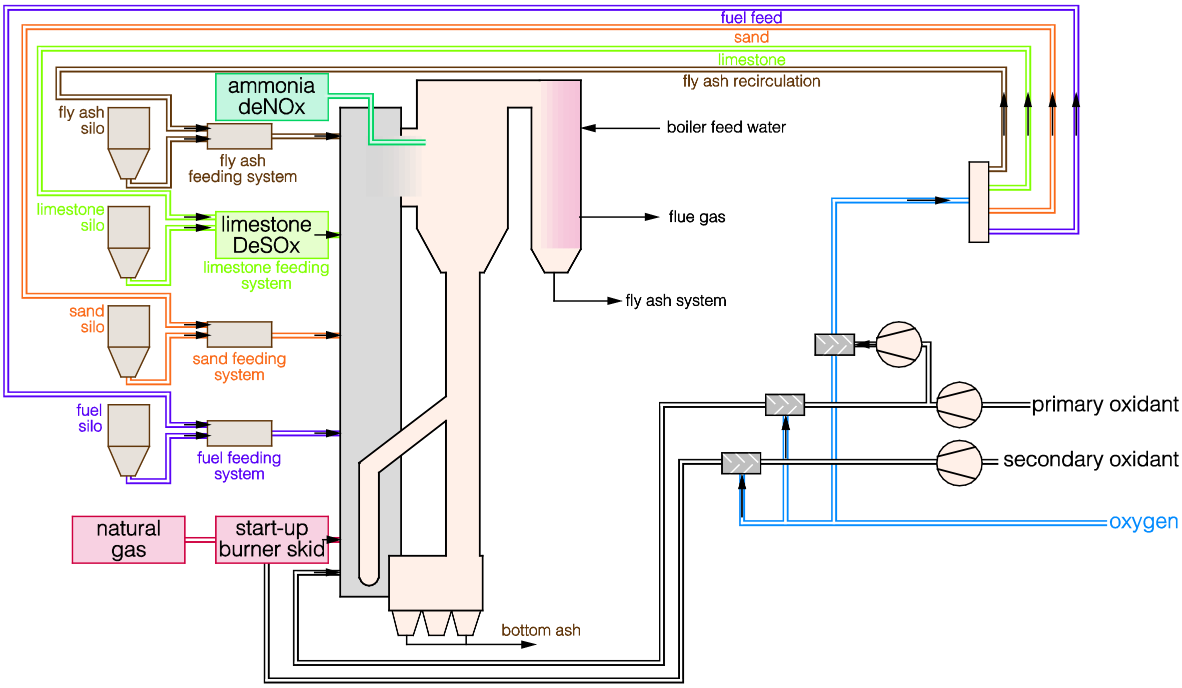


Figure 34 Schematic of the es.CO_2 oxyfuel CFB pilot (Alvarez and others, 2013)

Combustion

The CFB boiler forms a major part of research into Foster Wheeler's oxyfuel CFB technology, registered as 'Flexiburn^{TM}' due to the inherent fuel flexibility of CFB as well as the capacity to switch between oxyfuel and air modes (Hotta, 2011). In order to study how well fuel flexibility is retained in oxyfuel mode, the Ciuden test campaigns include various blends of the local anthracite with petcoke and biomass, as well as a subbituminous coal alone. In addition to the fuel and limestone feeds, the boiler is equipped with silos for feeding sand and ash to act as inert bed materials.

The maximum power output the boiler can achieve in oxyfuel mode is actually double the 15 MWth rating when air-fired (Table 5). This represents the fact that in oxyfuel mode the oxygen concentration is raised by increasing the oxygen flow and keeping the total gas flow constant, rather than by only reducing the volume of recycled flue gases. Furthermore, a key advantage of oxyfuel CFB is that very high levels of oxygen can be used without risk of overheating, as combustion temperatures are lower and more uniform than in a PC boiler, and heat can be recovered from circulating solids as well as flue gases. At a maximum oxygen concentration of 40% therefore, the boiler attains its full load of 30 MWth. The transition between the two firing modes takes roughly 40 minutes through an automated sequence of steps. In oxyfuel mode, combustion efficiency appears to be slightly negatively affected, with marginally higher CO and carbon in ash levels observed, though there is also a dependence on boiler loading (Kuivalainen and others, 2013).

Objectives of the Ciuden test programme include clarifying the effect of bed temperature, excess oxygen levels, flue gas recycle ratio, fluidisation velocity, and bed inventory, and monitoring of emissions, desulphurisation performance, corrosion, fouling, and bed agglomeration (Hotta, 2013).

Table 5 Design parameters of the Ciuden CFB boiler (Kuivalainen and others, 2013, Lupion, 2011b)

Furnace dimensions, m	20 x 2.9 x 1.7
Air output, MWth	15
Max oxyfuel output, MWth	30
O_2 consumption, kg/h	8775
Flue gas recycle, kg/h	28880
Coal consumption, kg/h	5469
Limestone feed, kg/h	720
Max steam flow, t/h	47.5
Superheat temperature, °C	250
Superheat pressure, bar	30
Feedwater temperature, °C	135
Boiler outlet gas temperature, °C	350–425

Emissions

Initial results from the CFB boiler indicated the commonly observed decrease in NOx emissions when switching to oxyfuel mode (Lupion and others, 2013). However, more recent data suggests that similarly low levels (<140 mg/m^3) are achievable in air firing, and that other factors such as bed temperature and limestone addition are more influential on NOx emissions (Gomez and others, 2013b). At higher temperatures and rates of limestone addition levels of NO (the dominant species) are increased. Due to their generally higher levels in CFB combustion, N_2O emissions were also studied and found to be unaffected by firing mode but reduced at lower bed temperatures. The boiler is equipped with SNCR, which was effective in abating NO emissions, although N_2O was unaffected.

An important concern when applying oxyfuel to CFB boilers is the effect on the in-situ desulphurisation process, which relies on limestone being calcined to more reactive lime before reaction with SO_2 takes place. In the high CO_2 partial pressures created by oxyfuel combustion, the equilibrium of the calcination reaction is shifted, so higher temperatures are required before lime formation becomes favourable. SO_2 can also react directly with limestone, but the kinetics of this 'direct reaction' are much slower than those of the standard 'indirect reaction'. This phenomenon has been observed at the Ciuden CFB, where SO_2 capture rates in oxyfuel are greatly reduced at temperatures optimal for SO_2 capture in air combustion. On the other hand, if the bed temperature is raised to 870°C, sufficient calcination can take place in oxyfuel conditions and peak SO_2 capture rates are in fact considerably higher than in air, due to the much higher levels of SO_2 created by flue gas recycle (Gomez and others, 2013a; Ramos and others, 2013a). This requirement for high bed temperatures for effective SO_2 capture may, however, present problems for operating the boiler at low loadings. A related concern for oxyfuel CFB is that the large proportion of lime in the fly ash may be recarbonised to limestone as it cools and coat upstream surfaces, but no evidence of this has been observed at Ciuden (Kuivalainen, 2013).

Corrosion and sealing

As for other oxyfuel pilots, low temperature corrosion from sulphuric acid condensation has posed a significant problem at the Ciuden facility. High levels of corrosion have been experienced in areas of the flue gas pathway which receive unwanted cooling, including poorly sealed joints and 'dead-legs' or sections of duct where the flue gas is allowed to stagnate. Measures for improving sealing at joints, which have the important added benefit of reducing air ingress, include employing metal expansion joints (as opposed to textile) and using welded flanges instead of bolted, and stainless steels with anti-corrosion coatings have been used in vulnerable places. Heat tracing and purge lines have also been implemented to prevent flue gas stagnation, and removable insulation used to avoid unwanted cooling (Alvarez and others, 2013). These methods have been particularly important in avoiding cooling in solids transport lines, where condensation can lead to agglomeration and blockages. Gas sampling in the CPU has determined that significant air ingress occurs in the low-pressure scrub for SOx polishing (Ramos and others, 2013b).

CPU integration

The cold box of the CPU receives only 6% of the flue gas flow at full load, but lower loadings have been used to investigate the interaction between the two parts of the plant without venting any flue gas to the stack. These tests have demonstrated that a valve is immediately able to transfer flue gas flow to the stack in the event of the CPU suddenly coming offline (Ramos and others, 2013b). The CPU is also able to respond to varying flue gas volume flow as the boiler is ramped up and down.

PC boiler

The 20 MWth PC boiler is providing a key test platform for the EU-funded 'RELCOM' research project, aimed at ensuring reliable scale-up of oxyfuel combustion through collaborative experimental and modelling work between industry and academia. Although smaller than the Schwarze Pumpe pilot, the unit is equipped with four burners and pendant superheaters, enabling a study of multiple burner interaction and radiant heat transfer which is highly applicable to a full-scale plant (Hesselmann, 2014). Ongoing tests at the facility have included trialling of new burners.

6 Demonstration projects

There is no clear definition of what scale of plant constitutes a demonstration of new plant technology, and some pilot-scale projects such as that at Callide have been referred to as demonstrations. However, it is generally accepted that a demonstration of at least 100 MW capacity is necessary before the technology can make the crucial step to commercial viability. A complete carbon capture demonstration is also expected to be integrated with CO_2 pipeline transportation and storage. The capital cost of such first-of-a-kind plant and installation of an entirely new CO_2 transport and storage infrastructure will necessarily be much greater than that of later commercial plant, and will require substantial state funding. Equally challenging can be the allocation of project liability and insuring the risk of CO_2 transport and storage for long after the planned lifetime of the plant. As a consequence of these difficulties, several demonstration projects which have reached advanced stages of planning in the last few years have met with cancellation, and only three major projects currently remain active. Nevertheless, these active projects are able to benefit greatly from experience and results obtained in FEED studies which were not progressed, often through the involvement of the same technology providers.

6.1 Stalled or cancelled demonstration projects

6.1.1 Jänschwalde

The 250 MW gross (167 MW net) Jänschwalde oxyfuel plant was planned by Vattenfall based on the success of the Schwarze Pumpe pilot, and was to also incorporate an even larger post-combustion demonstration boiler. Having completed the FEED study, this project was cancelled in late 2011 due to the failure of the German government to pass the EU CCS directive, as well as a lack of public support and regional opposition to the CO_2 pipeline. The lignite-fired oxyfuel plant planned to use state-of-the-art lignite drying to achieve a high efficiency of 35–36% and produce flue gas with 45–58% CO_2 (Vattenfall, 2012). The plant was to consume 165 t/h of 95% pure O_2 from an ASU which would consume 28–34 MW of the plant's gross output. The CPU was designed to process 450 t/h of flue gas into 175 t/h of 95% pure CO_2 at a capture rate of 90-93%, using 23 MW of output (further details in Chapter 4). The product CO_2 was to be transported by pipeline to an onshore saline aquifer storage site. The project was estimated to require 1.5 billion euros of funding.

6.1.2 Compostilla OxyCFB300

Spanish utility Endesa's oxyfuel project at Compostilla in north-west Spain envisaged a 345 MW gross supercritical oxyfuel CFB boiler, to be designed by Foster Wheeler based on experience from the nearby Ciuden pilot plant (Martinez and Gutierrez, 2013). Like the Ciuden unit, the greater fuel flexibility of CFBC would be exploited for firing blends of petcoke and local anthracite, with wood pellet cofiring also possible. The 5500 t/d (1.3 Mt/y) of CO_2 produced by the plant was to be transported by a 147 km underground pipeline to deep saline formations at the Duero and Ebro basins. Having completed a FEED study of the full process chain and subsurface characterisation of the storage site, the project has attempted to secure financial support in addition to the funding it has secured from the European Energy Program for Recovery, but received a negative FID in 2013.

Based on Foster Wheeler's supercritical CFB design for plants such as Łagsiza in Poland, the boiler was designed with Benson once-through low mass flux waterwalls and Intrex superheaters (Eriksson and Gutierrez, 2013). Although designed to operate in both firing modes, the gross output of the plant is actually reduced under air firing as the steam cycle is optimised for oxyfuel operation. However, the high auxiliary loads associated with the ASU (38.5 MW) and CPU (34.2 MW) result in a lower net power output in oxyfuel mode and an efficiency penalty of 5.7%pts over the air-fired plant (Table 6).

Table 6 Design data for the Compostilla CFB300 demonstration (Martinez and Gutierrez, 2013)

	Air mode	Oxyfuel mode
Coal, kg/s	28.5	30.9
Limestone, kg/s	7.44	7.99
Air/O_2 consumption, kg/s	272	58.4
Gross power, MW	299.8	345.2
ASU, MW	–	38.5
CPU w/o compression, MW	–	19.2
CO_2 compression, MW	–	15
Others, MW	29.8	34.8
Net power, MW	270	237.7
Net efficiency, %	41.1	33.3
CO_2 captured, %	–	91
CO_2 captured, t/y	–	1287
CO_2 emitted, t/y	–	89.8
CO_2 avoided, t/y	–	766.8

The plant design incorporates two ASU compression trains which share a common cold box, and a gaseous oxygen buffer is used to smooth fluctuations in oxygen supply. In the event of the unit going offline, liquid oxygen storage would provide back-up for up to 3 hours. The unit can be kept cold for over two days, allowing a restart time of 6 hours, but start-up from warm would take up to three days. The design also allows for turndown to 40% MCR boiler load and ramping at 4% of O_2 consumption/min (Endesa and others, 2013).

Following a single FGC and alkaline polishing scrub, the CPU is also split into two trains for compression and drying steps, before flue gases are combined in a single cold box and distillation which achieve a capture rate of 91%. The product CO_2 at 97.5% purity is also split into two streams for compression to pipeline pressure. Both the ASU and CPU would be integrated with the steam cycle through recovery of compression heat and use of low-pressure steam for heating sorbent regeneration gases (Endesa and others, 2013).

Identifaction of the most suitable storage site proceeded via prescreening and ranking of a range of sites, including the drilling of five test wells and a three-dimensional seismic survey. A mechanical and geochemical model of the reservoirs was developed to confirm the durability of the caprock seal, and CO_2 flow simulations conducted. The project would employ three wells for CO_2 injection at the chosen site in the Duero basin, as well as five wells for monitoring purposes (Martinez and Gutierrez, 2013).

6.1.3 Young Dong

The plan for a 100 MW oxyfuel retrofit of a boiler at Young Dong power station, South Korea, was initiated in 2007 by the governement research body KEPRI in collaboration with manufacturers Doosan and the plant owners, KOSEP (Kuczynski and others, 2013). Using experience from Doosan's 40 MWth OxyCoal burner tests, the project only aimed to operate for one year in oxyfuel mode, and has not included detailed plans for transport and storage. A FEED study for the plant was completed in 2013, but the project was recently put on hold by the Korean government due to uncertainties over CO_2 storage and support of operation costs.

The existing unit 1 at the Young Dong plant is a 125 MW downshot boiler built in 1973 for firing Korean anthracite. The dwindling supply of this domestic fuel requires upgrading of the plant for firing imported bituminous and subbituminous coals, of which the oxyfuel project would form a part. The chosen strategy for the oxyfuel upgrade was to install 16 wall-fired burners into the existing furnace, along with appropriate redistribution of heat transfer surface. Furnace modelling determined a recycle rate of 67.4% to be optimum for obtaining similar heat transfer to air firing, and a stable flame rooted to the burner. This furnace retrofit is estimated to make up around 21% of the total project cost.

A double column ASU from Daesung was to produce 20000 m^3/h of 95% pure oxygen, or an equivalent quantity of liquid oxygen for storage when the plant is operating in air mode. Also designed by Daesung, the CPU would incorporate flue gas condensation by alkaline wash for desulphurisation, producing 95% pure CO_2 at a capture rate of 90%.

6.1.4 Other

Several early demonstrations proposals in the USA did not reach the design phase due to lack of DOE funding, including a 50 MW CFB unit at Jamestown, NY, and Babcock and Wilcox's 100 MW Black Hills unit in Wyoming. An oxyfuel project planned by Saskpower in Canada was sidelined in 2007 in favour of a post-combustion capture plant. In Australia, AES and Aviva's Coolimba plant based on two 200 MW oxyfuel CFB units had investment withdrawn in 2009 (GCCSI, 2014; ZeroCO2, 2014).

In China, there are two major oxyfuel projects which appear not to have been progressed to a construction phase, both involving collaborations between multinational manufacturers and Chinese utilities. An oxyfuel retrofit of two 350 MW CHP units in Daqing was planned by the Datang Heliongjiang Power Gen Co and Alstom China, and a proposal for a new 350 MW supercritical plant at Taiyuan was led by Shanxi International Energy Group and Air Products.

6.2 Active demonstration projects

6.2.1 FutureGen 2.0

Centred on a 168 MW gross (99 MW net) oxyfuel retrofit of an existing unit at Meredosia power plant, Illinois, the FutureGen 2.0 project appears to be on course to become the first full-scale demonstration of oxyfuel technology (Humphreys, 2013). If successful, the plant will produce 1.1 Mt CO_2/yr to be sent 48 km by pipeline for storage in an onshore saline aquifer. Orginally conceived in 2008, a consortium known as FutureGen Alliance was set up to manage and fund the project, consisting of the energy and mining companies Alpha Natural Resources, AngloAmerican, Peabody Energy, Joyglobal, and GlencoreXstrata. The venture has also received considerable backing from the US government, in the form of $1 billion towards an estimated capital cost of US$1.65 billion, with the Alliance members providing the remainder. The FEED study and final design for the plant and CO_2 storage were completed in Spring 2014, following a formal record of decision by the US DOE signalling approval of the project. A FID for the project is expected in October 2014 which, if favourable, could lead to commissioning of the plant in 2017.

The Meredosia Energy Center is a recently idled plant consisting of four steam turbines in good condition and eight pulverised coal boilers, of which the 200 MW gross Unit 4 is to be repowered as an oxyfuel unit designed by Babcock and Wilcox (McDonald and others, 2013) (Figure 35). The plant is being maintained in working order preparation for the retrofit, and much of the plant including coal handling and transmission infrastructure is fit for incorporation into the new design. The oxyfuel plant will fire a blend of 40% of the high sulphur, local Illinois coal and 60% Powder River Basin coal, and operate with steam conditions of 537°C and 14.5 MPa, yielding a net efficiency of 21.5% HHV (Table 7). Use of a circulating dry scrubber will permit desulphurisation of the secondary recycle stream without raising sulphur corrosion issues in the boiler, whilst primary recycle gases are taken from after the flue gas condenser. One large ASU (3200 t/d) and a CPU (3500 t/d) are to be provided by Air Liquide, with a high capture rate of 98% yielding 99.8% purity CO_2 with less than 110 ppm O_2 and 1 ppm water, presumably employing membrane technology for CO_2 recovery from cold box vent gases.

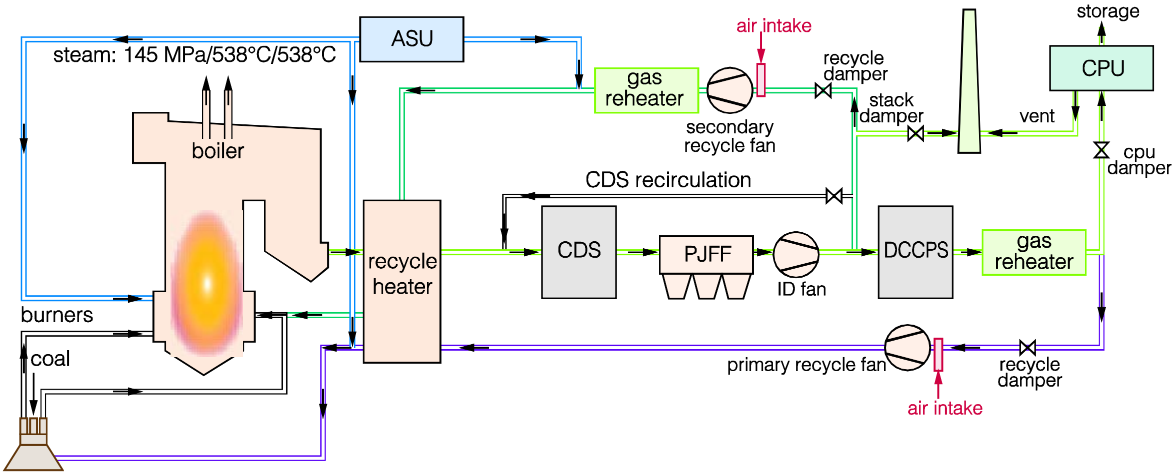


Figure 35 Proposed process configuration for FutureGen 2.0 (McDonald and others, 2013)

Table 7 Design data for FutureGen 2.0 (McDonald and others, 2013)

Gross output, MW	168
Net generation, MW	99
Boiler efficiency, %	87.25
Fuel input, MJ/h (HHV)	1445
Net plant efficiency, %	21.5

The CO_2 will be injected into a saline aquifer in the Mt Simon formation via a 1372 m deep well, from which four 762 m long horizontal legs extend to increase dispersion throughout the pore space. Detailed modelling of the CO_2 injection plume in the formation has been completed, and a monitoring strategy has been conceived for the 20 years of the plant's operational lifetime, followed by another 50 years. Seismic and hydrologic testing of the site has also been carried out. A liability management framework for the CO_2 storage has been created, in which low level damages are protected by project resources, followed by insurance, trust funds, and ultimately the state government for damages of over US$100m (Humphreys, 2013).

The project has made particular efforts to gain community support and involve stakeholders. For the area covering the storage site, landowners have been brought in as business partners, whilst those holding the properties crossed by the new 48 km pipeline will be compensated for easements. Outreach initiatives to the local communities such as open houses, event sponsorship and radio slots, have enabled the project to attain a good level of public acceptance (Humphreys, 2013).

Besides the substantial assistance from the federal government towards capital costs, a mechanism has been provided by the Illinois state government to aid in covering the elevated operating costs which will be incurred by the plant over those of a conventional plant. A purchase agreement has been completed for the power generated by the plant, which is to be transmitted directly to the state grid (Humphreys, 2013).

6.2.2 White Rose

White Rose is an oxyfuel demonstration proposed for Drax power station in North Yorkshire, UK, which would be based on a new USC 426 MWe PC boiler and send 2 Mt/y of CO_2 for storage in a North Sea saline aquifer (Emery, 2013; Marion and others, 2013). The project consortium comprises the Drax energy group, Alstom (suppliers of the boiler and CPU), and BOC (part of the Linde group and suppliers of the ASU), with NationalGrid to manage the transport and CO_2 storage as a subcontractor. In December, 2013, the UK government awarded the project a contract to commence a FEED study, naming White Rose as one of two preferred bidders for £1 billion of government funding under the UK's CCS Commercialisation Programme. In June 2014, the project also received 300 million euros in funding from the EU's NER300 scheme for investing in low carbon energy projects.

Though little technical detail of the project is currently available, there is strong potential for the plant to achieve negative emissions by combining oxyfuel operation with biomass cofiring, as a third of the existing Drax power station has already been converted to biomass. A high degree of flexibility is also a key target in order to accomodate increasing intermittent wind power on the UK grid. As the CO_2 produced is destined for geological sequestration rather than EOR, the plant's CPU is likely to employ Alstom's low CO_2 purity technology, with flash separation as opposed to a distillation of the liquefied flue gases. The plant is estimated to use 25% of its gross output for auxiliary power in oxyfuel mode, suggesting an actual net output of around 340 MW.

The CO_2 transport aspect of the project has been a principal aspect of its success in the UK CCS funding competition. Situated in a heavily industrialised area of the UK and close to the known massive storage capacity of north North Sea aquifers, the project proposes a CO_2 trunk pipeline to which future capture projects could connect, thus greatly reducing the cost of further CCS development. Planning of the route of this pipeline is currently in the public consultation phase and an R&D programme into dense phase transport is ongoing. After a regional assessment of 257 possible well locations in the storage area, a shortlist of potential sites has been draw up, from which two front-runners will be identified.

In addition to commencing its preFEED study, White Rose is over a year into a permitting process likely to last more than two years, and has negotiated a contract to support a two year risk reduction phase. A FID for the project is expected in late 2015.

6.2.3 Guohua Shenmu Power

The State Key Laboratory of Coal Combustion at Huazhong University of Science and Technology (HUST) in Hubei has placed a strong focus on oxyfuel research, operating a 3 MWth pilot since 2012 and with a 35 MWth unit also scheduled to be commissioned in 2014. The Laboratory is also participating in a FEED study for a 200 MW demonstration in collaboration with Shenhua Group and Dongfang Boiler Works (Zheng, 2013, Liu, 2013). This plant is to be a retrofit project at an existing plant in Shenmu County, Shanxi, with potential CO_2 storage options including saline aquifers and oil fields of the Erdos Basin.

7 Advanced oxyfuel technologies

Whilst first generation oxyfuel coal plant is likely to simulate air-fired pulverised coal combustion to minimise uncertainty and risk for the new process, a number of more novel approaches to oxyfuel combustion have been researched with a view to exploiting benefits specific to oxyfuel. Foremost amongst such 'second-generation technologies', pressurised coal combustion appears to possess several characteristics which are uniquely compatible with an efficient oxyfuel process, and consequently has been the focus of much research effort to the pilot scale. Other approaches include the use of much higher levels of oxygen with associated reductions in equipment size, or moderating flame temperature with steam instead of recycled flue gases. This chapter will review the status of such processes which are still based on the standard Rankine steam cycle model of power generation, with Brayton cycle approaches based on syngas reserved for a future report. Also often considered as a variety of oxyfuel combustion, chemical looping combustion has been covered in a recent IEA CCC report (Henderson, 2010).

7.1 Pressurised oxyfuel

Several characteristics of oxyfuel combustion render it particularly suitable for incorporation with a high-pressure system. Under pressure, water vapour condenses at higher temperatures, allowing useful, high quality heat to be recovered with a condensing heat exchanger which can be used for feedwater heating instead of bleeding steam from the turbines. The high proportion of water vapour in oxyfuel flue gases further increases the dew point and the amount of thermal energy which can be recovered in this fashion (Hong and others, 2009). In addition, the energy penalty associated with pressurising the oxygen feed to the system is compensated for by reducing the compression required in the CPU, essentially replacing the compression of a large volume of flue gases with a smaller volume of oxygen. The demand on the CPU is also further reduced by the elimination of air ingress into the pressurised system. Lastly, the fan power used for flue gas recirculation at high pressure is diminished due to the lower compression ratios required. These combined energy gains are estimated to correspond to between 3%pts and 5%pts absolute efficiency advantage over an atmopsheric oxyfuel boiler. Furthermore, the reduction in boiler and auxiliary equipment size derived from the reduction in flue gas volume enables a saving on capital costs, with only a condensing heat exchanger and deaerator required as additional equipment. Other advantages may include increased combustion efficiency and higher heat transfer.

Much of the early development of pressurised oxyfuel technology was carried out by the Italy-based ITEA (part of Sofinter) in collaboration with ENEL, and US-based ThermoEnergy, leading to distinct process concepts. These firms have now formed the joint venture Unity Power Alliance with the aim of promoting pressurised oxyfuel for repowering ageing coal plant in the USA with CCS. The US DOE has also given strong backing to pressurised oxyfuel technology research, with five pressurised oxyfuel projects selected in a 2012 award for the development advanced oxyfuel concepts. Besides the relatively advanced ITEA technology, these projects include novel concepts still at the research stage.

7.1.1 TIPS process

ThermoEnergy's integrated pressurised system (TIPS), jointly developed with Canmet, uses a coal slurry fed to a refractory-lined pressurised combustor with pressurised oxygen and recycled flue gases. Use of coal slurry avoids the need to pressurise the fuel reservoir, as the fluid can be pumped to pressure, while energy lost in water vaporisation is recovered at the condensing heat exchanger (Fassbender and others, 2009).

Hot flue gases leaving the combustor are then fed through successive radiative and convective heat transfer sections, before water is removed in two condensing heat exchangers. Coal slurries are often incorporated with pressurised combustion systems such as these, as the additional water merely adds to the energy recoverable at the condenser. The TIPS process condenser uses a temperature difference of more than 100°C between the flue gases and the heated feedwater in order to ensure high heat flux and reduce the heat exchanger size. The flue gas outlet temperature is between 120°C and 260°C. Canmet's analysis of the system concludes that the most efficiency is gained for flue gas pressures up to 20.7 bar, after which the increase is much more gradual (Chen and others, 2012; Cairns, 2013). An efficiency gain of 5 %pts is achieved over air combustion at a pressure of 8 bars (25–29% absolute). A cost of electricity analysis calculated only a 25% increase over air combustion compared to 60% for oxyfuel at ambient pressures (Canmet, 2013). Canmet are currently seeking partners with which to develop the high-pressure technology, although as ThermoEnergy have joined forces with pressurised oxyfuel competitor ITEA, it is unclear whether this technology remains viable.

7.1.2 Isotherm flameless pressurised oxyfuel

In the Isotherm technology developed by ITEA with support from ENEL and MIT, coal is also fed as a slurry to a pressurised combustor where it meets a premixed stream of pressurised oxygen and recycled flue gases (Figure 36). The fuel is combusted throughout the reactor volume with no flame front, yielding uniformly high temperatures of 1400–1700°C at ~10 bars of pressure (Saponaro and others, 2007). The reactor is refractory lined and minimal heat transfer occurs; instead, the hot flue gases are sent to a separate steam generation vessel in which the evaporative and superheating heat exchange surface is placed. Unlike the TIPS process, there is no radiative heat transfer section, with flue gases leaving the combustor quenched to 800°C against cooler downstream flue gases as they are recycled to the combustor. Flue gases are then sent to an acid condenser where the moisture content is condensed to provide heat for feedwater heating. A much smaller temperature difference of about 20°C is applied in the FGC than in the TIPS process, with a flue gas outlet temperature of around 50°C. This means that most of the latent heat can then be recovered at ~10 bar, but requires a large heat exchanger. To optimise equipment size and reduce cost, it was proposed to maintain the same flue gas velocity in the convective heat exchangers while increasing pressure (Chen and others, 2012).

Since 2007, the Isotherm process has been tested at a 5 MWth pilot facility at Gioia del Colle in southern Italy (Malavasi, 2012). This unit operates at a pressure of 4 bar as opposed to the full-scale plant design at

10 bar. A waste incinerator based on the Isotherm process has also been operating in Singapore since 2009 (Unity Power Alliance, 2013).

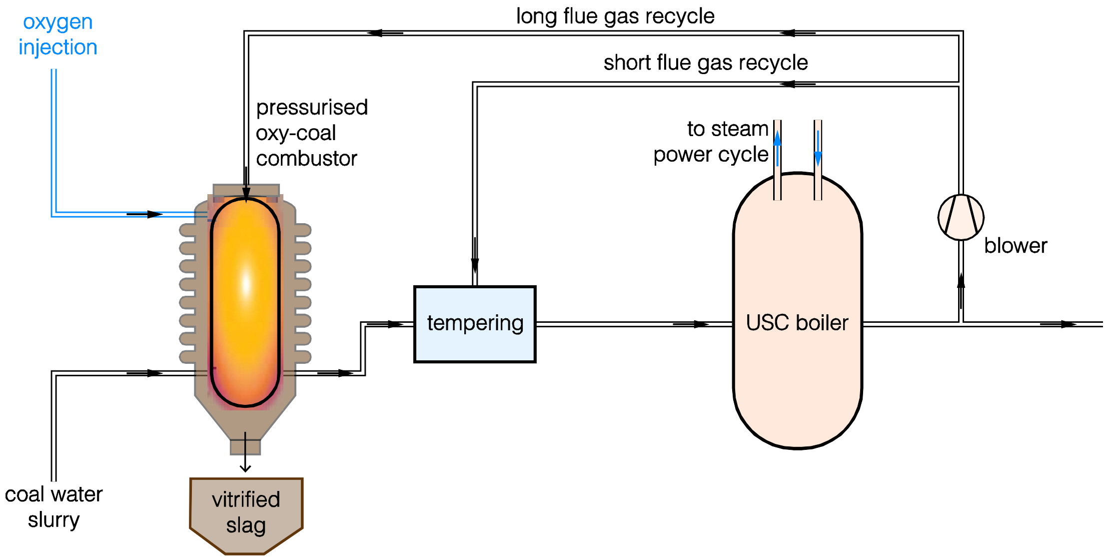


Figure 36 A schematic of the Isotherm process (Unity Power Alliance, 2013)

This flameless pressurised process is aimed at reducing problems of high erosion and corrosion which can occur in conventional pressurised combustion. The high combustion temperatures throughout the reactor cause ash to melt and flow out into water, where it is rapidly cooled and vitrified to glassy beads (Malavasi, 2012; Benelli, 2013). Flameless combustion also produces very low levels of NOx, and heavy metals tend to segregate out with the slag. As a result, the exhaust gases leaving the combustor are exceptionally clean, containing <10 mg/m³ of particulates and greatly reducing problems of erosion and corrosion to the heat exchange surfaces downstream (Table 8). Significant additional benefits of these low levels of flue gas contaminants are the ability to recycle flue gases without any treatment steps and the potential for simplifying the CPU process. Untreated flue gases are in fact recycled in two loops: A long loop which goes to the combustor and is mixed with oxygen, and a short loop which is added to the combustor exit gases in a tempering step to control their temperature (Benelli, 2013).

Table 8 Emissions data for the Isotherm process (Unity Power Alliance, 2013)

Species	Concentration
CO, mg/m^3	<1
NOx, mg/m^3	<100
SOx, mg/m^3	<30
Particulates, mg/m^3	<1
$PM_{2.5}$, µg/m^3	<10
Heavy metals, mg/m^3	<0.1
CO_2 in flue gas, % dry	>93

In 2009, researchers at MIT conducted a detailed technical and economic analysis of the ITEA system, based on a supercritical unit of 875 MWth gross and including ASU and a CPU employing flash separation

(Hong and others, 2009). A coal water slurry with 35% water by mass is injected with steam from the high-pressure turbine to atomise the coal particles and fed to the refractory-lined reactor. Combustion takes place at 10 bar and 1400°C to 1600°C, and the 2% of heat lost from the reactor is used to preheat feedwater. The flue gases leaving the combustor are nearly 48% water by volume compared to 8.7% in air, condensing at 150°C compared 80°C at atmospheric pressure. The heat recovered in the condenser allows 63% less steam to be taken from the low-pressure turbine for feedwater heating. To produce the pressurised oxygen supply, energy consumption in the ASU is 4%pts more of gross power output, but the CPU energy demand is more than halved due to the pre-pressurised flue gases. Fan power consumption also drops by 7.6 MW.

Enel and ITEA have conducted their own feasibility study of planned scale-up to a 50 MWth pilot and 320 MW (net) demonstration plant, both using systems at 10 bar (Malavasi, 2013; Unity Power Alliance, 2013). The larger plant is designed to have a gross power output of 430 MW and net efficiency of 35.4%, using supercritical steam conditions of 25 MPa and 605°C (Table 9). A cost analysis calculated a total capital cost of 930 million US dollars, with the highest proportion for coal logistics and slurrying, followed by the pressurised system and the ASU. A cost of electricity (COE) of 93 US$/MWh is targeted by the plant. With its high capability for dealing with low melting point ash and high moisture, the plant is particularly aimed at use of low quality fuels.

More recently, the governments of Italy and Sardinia have agreed to fund a 50 MWth pilot project based on pressurised oxyfuel technology in south-west Sardinia, with a view to collecting data for construction of a 350 MW plant at the same site. The construction and operation of both plants would be managed by the Sardinia-based research institute Sotacarbo (Pettinau, 2014).

Table 9 Design data for Enel's 320 MW net pressurised oxyfuel demonstration (Unity Power Alliance, 2013)

Net fuel input, MW	903
Gross power, MW	430
Gross efficiency, %	47.6
ASU, MW	75
CPU, MW	17
Other auxiliaries, MW	18
Net power, MW	320
Net efficiency, %	35.4

7.1.3 US DOE funded pressurised oxyfuel research projects

In July 2012, the US DOE awarded US$7 million to eight oxyfuel research projects identified as potentially 'transformational' including two chemical looping projects and five pressurised concepts of which the Isotherm design is one (NETL, 2014). Little detail is available on several of the remaining project concepts, as they are based on proprietary designs, but the information currently available is described here.

Supercritical CO_2 power cycle

Recently completed research carried out by Southwest Research Institute and Thar Energy LLC investigated combining a pressurised oxyfuel system with a supercritical CO_2 power cycle. Both a single loop cycle, in which the CO_2 combustion product itself is used in the power generation cycle, and a dual loop with a separate CO_2 power cycle were originally proposed, with the dual loop identified as the most practical solution due to the challenges of adequate flue gas cleaning and inconsistent CO_2 content (SWRI and Thar energy, 2014). Coal slurry is fed with oxygen into a CO_2-cooled pressurised combustion chamber, producing supercritical combustion products from which particulates are removed in a cyclone separator. In the dual loop cycle, these hot gases are then used to heat supercritical CO_2 in a microchannel heat exchanger. The heated CO_2 is passed through a turboexpander in which it changes to a non-supercritical gas, before compression and cooling converts it to liquid form. This liquid CO_2 is then pumped to supercritical pressures in a cryopump and returned to the main heat exchanger.

The process is estimated to be capable of 40% efficiency and 99% carbon capture, although a 49% increase in COE over conventionl plant exceeds the NETL target of 35% minimum. A proposed second phase of research would investigate replacing the coal–water slurry with a supercritical CO_2 slurry, and improvement of heat exchanger and particulate removal design.

Pressurised oxyFBC

Led by Pratt and Whitney Rocketdyne in collaboration with Linde and Pennsylvania State University, this research will validate a pressurised fluidised bed combustion process (NETL, 2013). Advantages include the standard benefits of pressurised combustion, together with the low NOx and in-furnace SOx control offered by FBC. The concept is estimated to potentially yield 33% plant efficiency (HHV) and 98% CO_2 capture with only a 30% increase in the COE over conventional plant. Planned activities include the development of a design basis for a 550 MW supercritical new-build plant and a plant retrofit of at least 275 MW. Systems and process engineering will be performed to determine the process performance and economics.

Pressurised oxycombustion based on a molten bed combustor

A first phase of a research programme into incorporation of the Gas Technology Institute's submerged combustion melting process with pressurised oxyfuel firing has been completed (NETL, 2012, Gas Technology Institute, 2012). In a molten bed combustor, burners in the furnace base are used to fire coal and oxygen into a pool of hot molten slag, leading to intense high-temperature combustion. Heat is transferred by the molten slag to waterwalls which are protected by a thin layer of refractory and solid slag. The principal advantage of this process for oxyfuel is the potential to reduce flue gas recycle by 85% to 100%, as the molten slag itself acts to redistribute the heat released by combustion. Eliminating flue gas recycle is estimated to allow a 3–4% increase in net plant efficiency and a 70% decrease in combustor size and cost. Other advantages include the recovery of a high proportion of ash as vitrified slag, high fuel flexibility, the potential for SOx mitigation via additives in the molten bed, and lower demands on waterwall materials, which experience lower fireside temperatures than in conventional boilers.

Technical challenges include the elutriation of slag into the convective pass, although this is not expected to excede that of a conventional slagging boiler.

The first phase of research has included burner testing at Brigham Young University and corrosion tests at Reaction Engineering International, as well as CFD modelling and a technical and economic analysis of a plant based on the technology.

Pressurised oxyfuel incorporating fuel staged combustion

This research led by Washington University aims to combine pressurised oxyfuel with a staged combustion process which allows for almost no flue gas recycle to be used. Coal is added to the combustor in stages of incrementally increasing stoichiometric ratio, using a gas mixture with reduced levels of oxygen at each stage (Axelbaum and others, 2012; Kumfer, 2013). The high stoichiometric ratio in initial stages serves to reduce the flame temperature, while combustion products from these stages are cooled and used to moderate the temperature of later stages rather than recycling flue gases from upstream of the combustor. Although somewhat higher adiabatic temperatures are reached in the earlier stages, greater radiative heat loss should yield a constant mean temperature at each combustion stage. Eliminating flue gas recycle in this way aims to further reduce the flue gas volume and thus also the size of equipment and pump power consumption of the pressurised plant. Radiative heat transfer is also expected to be improved by the higher peak temperatures, and the oxygen demand is reduced. A dry pulverised coal feed was chosen as opposed to a coal slurry for its lower excess oxygen requirement. Challenges for the process include avoiding hot spots and flame impingement, as well as selection of materials able to perform under high partial pressures of oxygen.

The project has conducted CFD modelling of furnace heat trasnfer and Aspen plant simulation. Ongoing work will include model validation in a laboratory-scale furnace and detailed specification and cost analysis for a full-scale plant. The aim is to develop a process capable of 90% CO_2 capture at no more than a 35% increase in COE and less than 25 US\$/tCO_2 captured.

7.2 Reduced flue gas recycle

As lowering the quantity of recycled flue gas needed for oxyfuel combustion can translate into reduced equipment sizes and lower plant costs, this has been the aim of several oxyfuel research routes including the molten bed reactor and staged combustion concepts detailed in the previous section. The earliest large-scale development of this idea was from the Jupiter Oxygen Corporation, whose technology employs a high temperature flame fed with pure oxygen rather than attempting to replicate air flame temperatures (Ochs and others, 2005; Ochs and others, 2008;). Recycled flue gas is still used to convey coal to the burner, and is added to the boiler outside of the flame envelope in order to control the temperature and volume of flue gas for heat duty in the convective section. The untempered flame reaches extremely high temperatures of over 2760°C, resulting in high heat transfer in the radiative section and higher boiler efficiency, as well as lower NOx. The total proportion of recycled flue gas is lower than in a standard oxyfuel process, providing a more concentrated stream of CO_2. The process has been applied to both natural gas and pulverised coal, and brings additional challenges of flame stability and balancing the heat duty between the radiative and convective zones, particularly for retrofit. Despite the high flame temperatures, the technology is suitable for retrofit without changes to boiler materials.

The high oxygen technology was originally employed commercially for aluminium remelt furnaces, following small-scale tests with natural gas and coal in a retrofitted d-type boiler. A 15 MWth pilot using the Jupiter technology has been operating since 2007 at the Corporation's research facility in Indiana, USA. Several burner designs have been tested at the pilot, including a second generation burner which employs four tangential oxygen nozzles to promote mixing with the primary stream and designed to deliver an overall level of 40% oxygen. The flue gases are purified to the CO_2 product using integrated pollutant removal (IPR) technology developed by the NETL.

The Jupiter Corporation is currently undertaking the retrofit of a supercritical boiler in China, in collaboration with Xinjian Guanghui New Energy (at their carbinol plant in Xinjian) (Schoenfield and Chen Jing, 2013). The relatively large existing furnace renders it well-suited to the high evaporative duty required, and retrofit measures will include replacement of burners, the induction draught fan, ducting, and control systems. The burners, developed by Maxon, use a proprietary nozzle design for efficient and safe mixing of the coal and oxygen streams. A cryogenic ASU will be added to the plant, capable of providing 3360 Mt/d of 97.5% oxygen to the boiler.

7.3 Oxy-steam combustion

Oxy-steam or 'hydroxyfuel' combustion, uses water vapour instead of recycled flue gases to dilute oxygen in order to simplify the purification of CO_2 from flue gases. The concept was first proposed in 2007 by Canmet, who have operated a 0.3 MWth oxyfuel test facility in oxy-steam mode (Salvador and others, 2009; Zou and others, 2014).

8 Economic analysis

The principal barrier to the adoption of oxyfuel or any CO_2 capture technology is economic. In the absence of significant carbon pricing or other form of government support, the high capital and operating costs of a demonstration plant make for an unfavourable investment. The costs for a first-of-a-kind capture plant are also likely to be substantially larger than for successive generations which would benefit from technological optimisation and a shared CO_2 transport and storage infrastructure. Despite this, on a levelised cost of electricity (LCOE) basis, most studies estimate fossil fuel plant with carbon capture to be generally more competitive than both photovoltaic solar power and offshore wind, suggesting that development of CCS on the same scale of these technologies should be possible in the right economic environment (GCCSI, 2012a). However, unlike renewable plant which can be deployed gradually in a modular fashion, a utility-scale capture and storage plant would require a one-off significant capital investment. Investment must therefore be informed by accurate economic analysis of the additional costs incurred for each capture technology, although cost estimates for non-commercial technologies such as carbon capture plant are highly challenging and will include large margins of error.

A number of costing indices can be used to both compare power plant economics and the relative value of carbon abatement technologies. The LCOE, which takes into account both the recuperation of financed capital cost over the lifetime of the plant and yearly operating costs, is the most widely used device for comparing different power generation technologies. As the major contributor to the LCOE, it can also be useful to consider separately the overnight capital cost of the plant. The value of a capture plant for CO_2 abatement can be considered in either of two ways: CO_2 avoided cost and CO_2 capture cost. Whilst the captured cost values the total CO_2 captured based on the increase in electricity price, the avoided cost accounts only for the CO_2 which would have been emitted by a conventional plant of equivalent capacity, thus avoiding valuing the increased fuel consumption of the capture plant. This chapter will review the various cost estimates that have been made for new build and retrofitted oxyfuel coal plant in the last few years, including estimates for other capture technologies for comparison.

8.1 Additional costs of oxyfuel plant

The ASU represents by far the biggest investment for an oxyfuel plant over the conventional plant equipment and has been estimated to amount to 14% to 20% of the total plant cost (NETL, 2010; Mancuso and others, 2013; Leandri and others, 2011; Li and others, 2012) (Figure 38). While cost reductions may be possible as the technology is optimised and scaled up for use with oxyfuel plant, the need for more efficient units may equally push costs in the other direction (Figure 37). The substantial power demand of the ASU means that the cost of this energy outweighs the capital cost to the plant, and optimising the unit through use of larger equipment or more complex process cycles is likely to be more economic than cheaper units over the lifetime of the plant. Despite this, ASU manufacturer Air Liquide have aimed to reduce ASU costs by 20% (Tranier and others, 2009). A sensitivity analysis of oxyfuel costs by Alstom estimates that reducing ASU power consumption from 150 to 140 kWh/tO_2 would result in a 1.1% drop in the LCOE (Leandri and others, 2013).

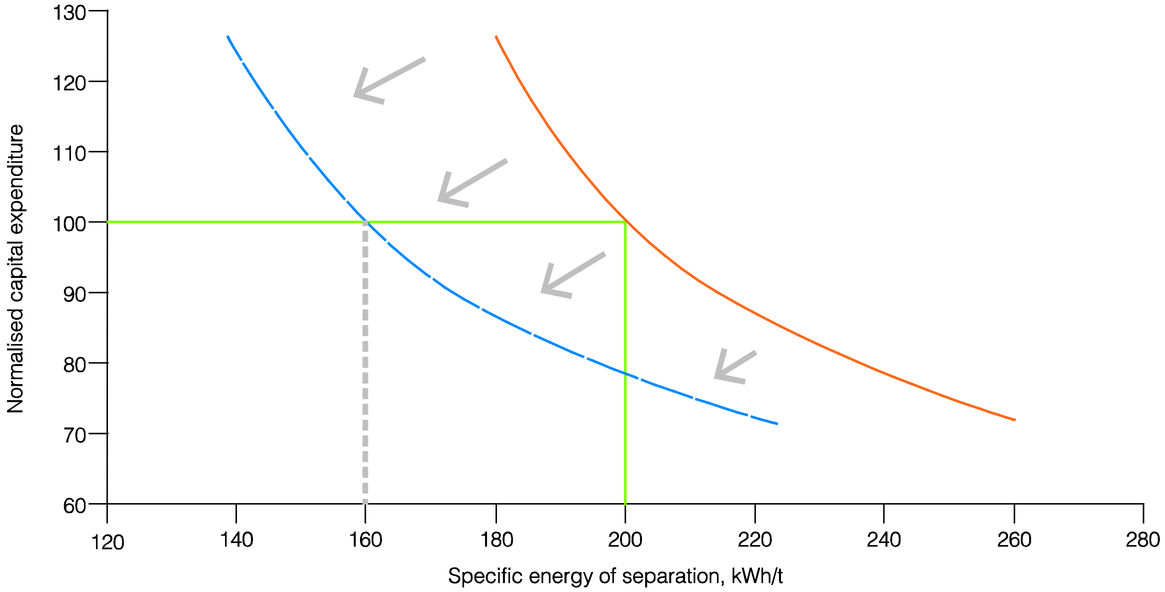


Figure 37 Increase in ASU capital cost with improving unit efficiency for previous Air Liquide design (red line) and state-of-the-art (dashed blue line) (Tranier and others, 2009)

A few studies have looked at the cost reduction potential of oxygen production via membranes. Although an early NETL study of various oxyfuel plant scenarios found ITM to yield significantly greater costs largely due to the need for natural gas to heat feed air to the unit, more recent EPRI analysis estimates similar COE to cryogenic ASU plant, and a 14% lower capital cost (NETL, 2008; Quintrell and Foster, 2011). The advantage of ITM is considerably enhanced with lower natural gas costs.

The CPU is the next largest investment specific to oxyfuel plant, and is usually estimated to amount to around half the ASU cost, or 7–10% of total plant cost (NETL, 2010; Bouillion, 2009; Mancuso and others, 2913) (Figure 38). Cost estimates may vary widely for CPU due to lack of agreement on the extent of flue gas purification necessary for CO_2 transport and storage, and the existence of several emerging technologies. Several early analyses have assumed flue gas dehydration alone could be sufficient, or that cosequestration of SOx, NOx, and non-condensable gases may be possible. Current thinking has tended to favour a conservative approach of producing relatively high purity CO_2 of at least 97%, which necessarily incorporates flue gas liquefaction followed by either flash separation or distillation to remove the majority of light gases. Higher capital and operating costs associated with this process may therefore contribute to increased CPU cost estimates in later studies. Whilst variable operating and maintenance (O&M) costs for oxyfuel plant have been estimated as similar to conventional plant, use of chemicals for polishing scrubs at the CPU could alter this assessment. On the other hand, CPU manufacturers such as Air Liquide suggest that added capital investment to achieve higher capture rates are easily outweighed by the reduced cost of capture per tonne of CO_2 (Leclerc and others, 2013). Fixed O&M costs for oxyfuel plant have been estimated to be around 35% higher than conventional plant (NETL, 2010; ZEP, 2011).

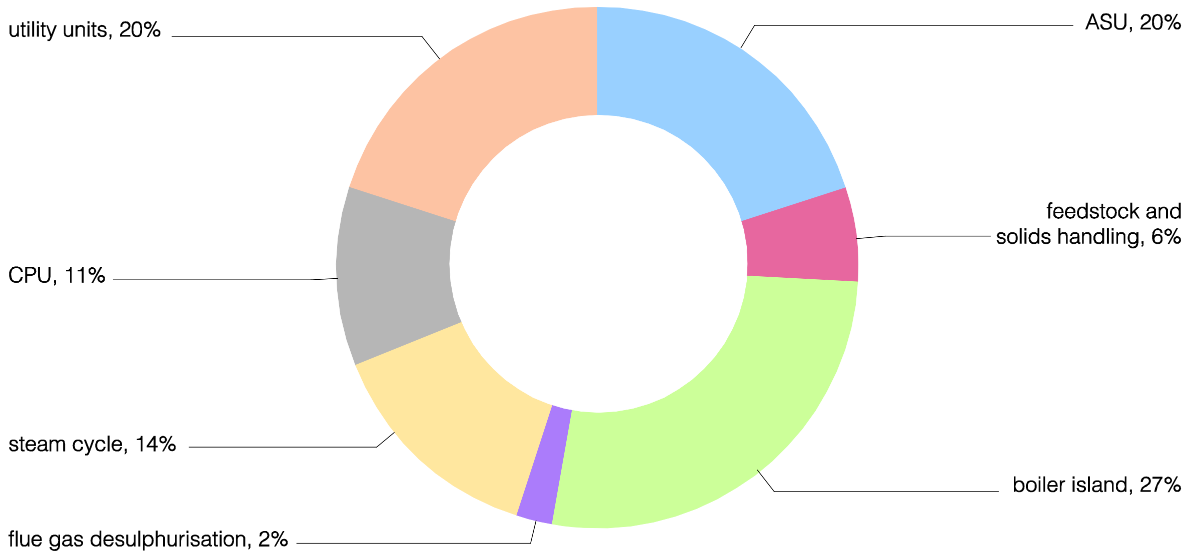


Figure 38 Breakdown of oxyfuel plant costs (Mancuso and others, 2013)

On the other hand, there is potential for oxyfuel plant to economise on conventional flue gas treatment equipment such as SCR and FGD. As discussed in Section 2.1, recycle of flue gas prior to desulphurisation leaves a reduced volume for treatment and FGD equipment can be correspondingly smaller, provided the plant operates exclusively in oxyfuel mode. Several studies have assumed that this would be a realistic option only for low sulphur coals (<1% sulphur) for which the risk of boiler corrosion is low (Li and others, 2012; Mancuso and others, 2013). Reagent-free sulphur removal processes at the CPU such as sour compression would also reduce the demand on upstream desulphurisation and potentially allow for the elimination of wet FGD or replacement with lower cost processes such as dry sorbent injection. An NETL analysis calculated that dispensing with the wet FGD from an oxyfuel plant would save over 7% of the capital cost, and allow an 8% reduction in LCOE (NETL, 2008). Low NOx formation in oxyfuel combustion should also avoid the need for installation of costly SCR, particularly as the remaining deNOx requitement can also be effectively transferred to the CPU. Removal of mercury is also likely to be more economically achieved in the CPU.

A comprehensive review by the IEA in 2011 assembled the findings of the major carbon capture costing studies conducted prior to its publication, converting all data to 2010 US dollars for comparison (Finkenrath, 2011) (Table 10). The studies included cover primarily the EU and the USA, with one analysis of a plant in China. The review calculates a 74% average increase in overnight plant cost over all estimates, a 64% increase in LCOE, and an average cost of 50 US$/t$CO_2$ avoided. The model plants considered apply efficiency penalties relative to reference coal plant from 7.9% to 12.2%, and capture rates between 90% and 100%.

Two separate NETL cost analysis of 550 MW net oxyfuel plant using bituminous and low rank coal plant provide the majority of data for the IEA review, and are worth considering separately as they provide detailed cost breakdowns for each plant (NETL, 2008) (Table 10). The analysis of bituminous coal plant is the earlier of the two studies, and as a result it allows for relatively basic CO_2 purification scenarios, ranging from flue gas dehydration to flash separation to >95% purity. In the highest purity case, total plant cost for a supercritical unit is 72% higher and LCOE 62% higher than the reference plant. For a USC plant these increases are reduced to 63% and 53% respectively, as the lower gross output required to meet the net target is associated with a relative decrease in oxyfuel costs.

The low rank coal study considers both subbituminous coal and lignite and CFBC plant in addition to pulverised coal (NETL, 2010). The cost increases over air-fired reference plant are greater than for bituminous coals as again, much larger gross capacity is required to produce the same net output. CFBC EPC costs are actually slightly lower than PCC costs, but added contingencies for the less established technology result in higher final costs (for a full analysis *see* Lockwood, 2013). This more recent report considers flue gas distillation as the base CPU technology, but basic dehydration and flash separation to ~1% oxygen are also considered, with the latter allowing for a 0.6% reduction in LCOE.

More recently, a cost analysis was performed for the Zero Emissions Protocol (ZEP) of the European Union which looked at all three capture technologies for a generic new plant in Northern Europe and considered three different coal prices (ZEP, 2011) (Table 10). This study also considers a 'base case' with conservative cost estimates based on existing technology and an optimised case accounting for potential cost reductions derived from technological improvement and economies of scale. The cost estimates for oxyfuel cover a wide range of values, denoting a high degree of uncertainty for the relatively new capture technology. Whilst the base case has a 113% greater EPC cost than the reference plant and 10.6%pts lower efficiency, the optimised case costs 81% more and has an 8.7%pts efficiency penalty. Estimates of the increase in LCOE range from 76% to 87% over reference coal plant costs. Variable costs are similar to the reference plant, but fixed O&M are widely variable from 21% to a more than 50% increase. The optimised case allows for the possbility of replacing full-scale FGD equipment with removal of SOx in the CPU, which allows minor cost and efficiency gains, but future improvements in ASU efficiency are not considered.

8.2 Comparison with post-combustion capture

It is particularly useful to compare the cost of oxyfuel capture to the two main alternative carbon capture technologies, known as post-combustion and pre-combustion capture. Post-combustion capture uses CO_2-reactive solvents such as amines to capture CO_2 directly from the flue gas stream as produced by a standard air-fired power plant. The main additional cost is therefore the installation of a substantial chemical plant for carrying out this process. As the solvent is regenerated thermally with steam bled from the low-pressure turbine, some plant modification is also required to facilitate this. Pre-combustion capture is based on the gasification of coal and combustion in an IGCC, so is less directly comparable with a pulverised coal oxyfuel process. In general, cost and efficiency estimates for new build oxyfuel and post-combustion capture plant are very similar, whereas slightly higher effiency and lower capital costs have been estimated for pre-combustion, but this technology is based on relatively unestablished IGCC technology and is unsuitable for retrofit (NETL, 2008; Finkenrath, 2011; Leandri and others, 2011). Which technology is most suitable is therefore likely to depend largely on site-specific factors. On the other hand, oxyfuel has been identified by several studies as more economic for retrofit cases as an oxyfuel plant would be able to reuse most of existing plant equipment (GCCSI, 2010; MIT, 2007). Conversely, the need to extract large amounts of low-pressure steam from the steam cycle for solvent regeneration (roughly 1.5/tCO_2) presents a challenge in post-combustion retrofit. Carrying out this steam extraction on an existing plant will result in the low-pressure turbine running significantly below design efficiency. In general, post-combustion capture costs are affected by the large capital investment associated with the CO_2 capture plant, in addition to relatively high variable costs from replenishing capture solvent and other chemicals such as caustic soda for SOx polishing. Post-combustion capture rates can be slightly more limited than oxyfuel, and rates of less than 90% are often assumed in plant models, compared to oxyfuel rates which could approach 100% (Finkenrath, 2011). The efficiency penalty associated with installation of both post-combustion and oxyfuel are usually considered to be within a similar range of 8–10%pts.

Table 10 Review of oxyfuel and post-combustion capture cost estimates (NETL, 2008; GCCSI, 2010; Finkenrath, 2011; ZEP, 2011; Leandri and others, 2011; WorleyParsons and others, 2011)

	NETL (SC bitumin-ous), US$	NETL (SC lignite), US$	IEA (average of studies 2007-11), US$	GCCSI (standard plant + retrofit), US$	GCCSI (capture ready plant + retrofit), US$	GCCSI (new SC plant), US$	ZEP (base case), euros	ZEP (optimised case), euros	Alstom (European plant 2015), euros	Alstom (European plant 2030), euros
Oxyfuel Capex, /kW	2715	3163	3959	2974	2858	4500	3325	2200	-	-
Oxyfuel Capex increase over ref. plant, %	71	58	74	89	81	73	113	81	61	45
Post-combustion Capex increase over ref. plant, %	81	–	63	145	82	81	67	48	71	47
Oxyfuel LCOE, /MWh	102.6	106	102	–	–	121	81.9	63–69.1	79	73
Oxyfuel LCOE increase over ref. plant, %	62	60	64	–	–	60	84	54	58	46
Post-combustion LCOE increase over ref. plant, %	73	–	75	–	–	72	54	41	70	48
Oxyfuel CO_2 avoidance cost, /t	54	58	52	–	–	57	56.6	28.5	–	–
Post-combustion CO_2 avoidance cost, /t	68	–	58	–	–	81	36	27.5	–	–

Post-combustion capture is also considered in the NETL evaluation of 550 MW bituminous coal oxyfuel plant detailed above (NETL, 2008). The total plant cost and LCOE are both around 4–6% more expensive than equivalent oxyfuel capture cases, due to a considerably higher cost for the amine plant than the ASU and CPU combined, and despite a slightly lower boiler cost. Variable operating costs are also up to 37% greater in the post-combustion cases due to the cost of solvent and other chemicals used in the capture plant. A lower capture rate in the post-combustion case results in significantly higher costs of CO_2 captured and avoided than in oxyfuel (100% capture), with a 31% increase over oxyfuel in the supercritical plant case. Avoided costs are more similar when considering oxyfuel plant with ITM oxygen production, due to unabated emissions from the gas-fired air heater.

A study by GCCSI in 2010 looked specifically at the retrofit costs of postcombustion and oxyfuel capture plant, based on plant with varying degrees of capture readiness (GCCSI, 2010) (Table 10). Capture-ready plant is essentially a means of using relatively small additional investment in a non-capture plant to significantly reduce later costs when retrofit for carbon capture may become a legal or economic requirement. Based on a reference plant costing 1575 US$/kW, the oxyfuel capture-ready scenarios include a basic case in which the plant has necessary land available and FEED work conducted, a case in with a larger generator is installed to allow for increased gross power output when low grade heat is recovered from the ASU and CPU, and a related case with additional increased steam turbine and cooling water capacity which would allow for a maximum 5% of increased capacity from low grade heat recovery.

These scenarios only add from 3 to 13 US$/kW to the reference plant cost. Including the cost of retrofit, the final oxyfuel plant is estimated to cost 2858 US$/kW for the most capture ready case, representing a 4% saving on retrofit of a standard plant.

Using the same reference plant, three capture ready cases are also proposed for postcombustion retrofit. These include simply extracting steam through a throttle valve between turbines, installing a clutch to decouple the low-pressure turbine, and starting with an oversized boiler and turbine which are then derated without loss of efficiency upon retrofit. The final cost of a retrofitted plant would be 3865 US$ for a non-ready case, or 2871 US$ for the most capture-ready scenario. For retrofit of an unmodified plant, oxyfuel is therefore 23% cheaper than post-combustion, but unsurprisingly the retrofit costs approach each other for the most capture-ready scenarios.

Alstom's 2011 comparison of capture technology costs plots their decline through an early commercial phase from 2015–20 and a mature market phase on to 2030, as well as considering three global regions (Leandri and others, 2011). Whilst oxyfuel is assessed to be initially the cheaper technology, with a 60% increase over conventional LCOE compared to 70% for post-combustion (including transport and storage), the two costs converge in 2030 as each technology reaches maturity (Table 10). This trend is followed in all regions, albeit with lower overall prices in South-East Asia, and with both low and high rank coals.

The ZEP analysis presents a much more uncertain view of oxyfuel plant costs than other capture technologies, and provides a large range of estimates spanning from slightly below post-combustion costs to much greater values (LCOE = 63–86.7 €/MWh) (ZEP, 2011). Even for an optimised oxyfuel plant, EPC costs relative to non-capture plant are estimated to be substantially greater than for post-combustion, but are offset by lower O&M costs. In the post-combustion case variable costs are tripled compared to that of the reference plant, whilst oxyfuel costs are relatively unchanged. However, as for most other analyses, it is emphasised that there is little difference discernible between the costs of each technology within the certainty of the estimates.

A less favourable assessment of oxyfuel was presented in a recent study which investigated the effect of parameters such as CO_2 and oxygen purity, CPU and ASU performance and cost, and coal composition on the competitivity of 550 MW net oxyfuel plant with an equivalent post-combustion capture plant (Borgert and Rubin, 2013). A principal conclusion is that increasing restrictions on CO_2 pipeline purity will have a relatively great effect on CO_2 avoidance costs for oxyfuel plant, as further processing becomes required in the CPU. Avoidance costs were shown to increase by up to 20% as CO_2 exit purity varies from 88.3% to 99.9%, with high sulphur coals adding roughly another 20% for all CO_2 purities. Because of this effect, comparison with a modelled post-combustion system found that oyfuel struggled to compete on avoidance cost with anything other than low sulphur coals and cosequestration of flue gas contaminants.

In general, most cost studies have stressed that little difference in costs has yet to be discerned for either oxyfuel or post-combustion capture, and that both technologies should therefore be pursued to maturity.

9 Efficiency of commercial plant

All forms of carbon capture are energy intensive processes which will impose a significant efficiency penalty on conventional coal plant, increasing the cost of fuel and the CO_2 capture cost. While efforts to reduce this energy penalty are therefore a principal aim of oxyfuel research, evaluating the efficiency of future full-scale oxyfuel plant based on current pilot-scale technology is not straightforward, and a wide range of performances have been proposed. With a growing number of FEED studies completed for demonstration-scale plant, and numerous industry and academic models of future commercial oxyfuel plant, it is informative to review the current trend in efficiency estimates. Furthermore, maximising the power output of a commercial plant will necessitate not just optimising the efficiency of component processes in isolation (ASU, CPU, and flue gas recycle), but achieving high level of integration between each process. A principal example of this is the thermal integration of ASU air compression heat with feedwater heating, discussed in Section 3.6. Several more recent evaluations have attempted to determine the performance of USC commercial plant which has been fully optimised and integrated with oxyfuel processes. Such estimates provide a useful lower limit for the efficiency penalty that can be expected for future plant.

9.1 Review of efficiency penalty estimates

The efficiency penalty imposed by the oxyfuel process on a conventional plant depends to a great extent on the size and efficiency of the plant considered, as well as other assumptions such as cooling water temperature. Estimates generally range from 7.5 to 10%pts, with the upper limit frequently taken as a reference point for an unoptimised, unintegrated commercial oxyfuel plant (Shafeen and others, 2013; Fu and Gundersen, 2013b; Hagi and others, 2014) (Table 11). More ambitious projections which account for potential technology improvements such as the use of membranes can approach 6%pts or lower (Fu and Gundersen, 2013b; Paufique and others, 2013). As discussed in previous chapters, this energy penalty is associated with the ASU and, to a slightly lesser extent, the CPU, as well as other small increases such as fan power for recycling flue gas. Recent estimates of ASU auxiliary load (without thermal integration) range from 9.5% to 15% of the gross power output, with average values of 12.8% and 12.4% used in the FEED studies for the Endesa and Vattenfall demonstration plants respectively (Dubettier and Guillard, 2011; Martinez and Gutierrez, 2013; Hagi and others, 2014; Vattenfall, 2012; Shafeen and others, 2013; NETL, 2010). The proportion of gross power comsumed by the CPU varies from 8% to 12% of gross output, with a strong dependence on flue gas purity, itself dependent on factors such as coal type and extent of air ingress.

Table 11 Oxyfuel efficiency estimates for demonstration and commercial-scale plant (Vattenfall, 2012; Endesa and others, 2013; Malavasi, 2012; McDonald, 2013; Paufique and others, 2013; Pourchot and others, 2013; Hagi and others, 2014; Shafeen and others, 2013; Fu and Gundersen, 2013b; EPRI, 2011; GCCSI, 2012b; NETL, 2010)

Study	Date	Oxyfuel output, MW gross	Oxyfuel plant net efficiency (**optimised case**), %	Air plant net efficiency, %	Efficiency penalty, (**optimised case**), %pts	Steam conditions, MPa/°C/°C	ASU power, MW	CPU power, MW	Other auxiliary power, MW	Notes
NETL	2010	746	32.4 (HHV)	39.9	7.5	27.6/649/649	91	62	–	
EPRI	2011	700	39 (HHV)	32	7	USC	91	59	46	
Jänschwalde FEED	2012	250	35–36 (LHV)	n/a	n/a	28.6/600	28–34	23–35	–	
Compostilla FEED	2013	345	33.3 (LHV)	41.1	7.8	Supercritical	38.5	34.2	34.8	CFB
Enel feasibility study	2013	430	35.44 (LHV)	–	n/a	25/605	75	17	18	Pressurised
FutureGen FEED	2013	168	21.5 (HHV)	n/a	n/a	–	–	–	–	
Air Liquide	2013	1000	41.9 (**44.0**) (LHV)	49.6	7.7 (**5.6**)	28/600/620	–	–	–	
Alstom	2013	900	33.4 (**37.1**) (LHV)	46.2	12.7 (**9**)	27.5/600/620	–	–	–	
EDF	2013	1100	36.1 (**38.3**) (LHV)	46.1	10 (**7.8**)	30/600/620	124	74	–	
Canmet	2013	786	–	–	–	–	111	98	–	
NTNU	2013	–	29.8 (**31.2**) (HHV)	39.8	10 (**8.6**)	–	–	–	–	

9.2 Plant integration and optimisation

Efforts to reduce the energy penalty of oxyfuel plant have more recently been directed at optimising thermal integration of all plant processes, rather than attempting to reduce the consumption of each component in isolation. The principal strategy for improving integration is to make use of the heat produced in the compression in steps in both the ASU and CPU, with the ASU receiving particuar attention due to its greater losses. The compressed gas is usually cooled between each compressor stage by indirect heat exchangers in which the cooling water can be replaced with boiler feedwater in order to recover the heat lost as useful work in the steam cycle. Other potential sites for integration with the steam cycle are residual flue gas heat (greater in oxyfuel than air-fired plant due to the raised acid dew point) and the flue gas condenser. The most common efficiency optimisation strategies considered include:

- high efficiency plant (reduces absolute efficiency penalty);
- plant heat integration (heat sources are ASU and CPU compressors and flue gas);
- O_2 purity optimisation and preheating;
- sealing (reduces demand on ASU and CPU);
- minimising CO_2 purity (according to application);
- optimising flue gas recycle and desulphurisation;
- O_2 production via membranes.

Studies into optimising plant by thermal integration are often conducted by exergy analysis, which accounts for all energy losses which could potentially be turned into useful work (Shafeen and others, 2013; Hagi and others, 2014; Fu and Gundersen, 2013b; Fu, 2013). In this way, it is possible to quantify the potential benefit of integrating the main heat sources (ASU and CPU compressors and flue gas) with condensate and feedwater heating. A 2013 study by EDF used this method for a model 1100 MW gross plant and found a reference efficiency penalty of 10%pts could be reduced to 7.8%pts via thermal integration.

Other research has sought to evaluate the potential efficiency and costs of commercial oxyfuel plant which is fully integrated and optimised in all possible ways, often accounting for future technological improvements. A study by Alstom looked at the costs and efficiency benefits associated with a range of optimisation strategies in a model 900 MW gross USC oxyfuel plant, with a 12.8%pts penalty on air firing in the unintegrated reference case (Table 12) (Pourchot and others, 2013). Heat integration of the steam cycle with the gas compressors and flue gas condenser yields the largest return in additional energy generated, producing 25.7 MW. Optimisation of the ASU process itself, including the use of a triple column distillation and multiple reboilers, allowed a further 13.3 MW to be obtained. Other energy saving measures included optimising the recycle path, O_2 and CO_2 purity, improving boiler sealing, and using steam from the steam cycle to regenerate drying sorbents. The fully optimised and integrated plant could achieve 37.1% efficiency, equating to a penalty of only 9.1%pts, for an estimated additional investment of 359 million euros.

Table 12 Oxyfuel efficiency estimates for demonstration and commercial-scale plant (Pourchot and others, 2013)

	Net power (MW)	Net efficiency (%)	Power value (million euros)
Air-fired reference	836	46.2	–
Unintegrated oxyfuel ref.	606	33.4	–
High efficiency ASU	+13.3	+0.7	+71
Integrated flue gas path	+23.5	+1.2	+125
ASU dryer steam supply	+5.1	+0.3	+27
Optimal heat integration	+25.7	+1.4	+136
Integrated plant	673	37.1	+359

Air Liquide have performed a similar analysis of the potential for minimising energy losses throughout the plant (Paufique and others, 2013). The small efficiency penalties found here stem partly from the high air-fired reference efficiency of a 1 GW USC plant with double reheat. An initial oxyfuel penalty of 7.7%pts was reduced to an estimated 5.6%pts by the various measures considered (Figure 39). Implementation of Air Liquide's future ASU target design provides the most benefit to the plant, based on a reduced energy demand of 120 kWh/t and including integration with the steam cycle. Projected optimisation of the CPU and implementation of 'warm flue gas recycle' (before FGD) also lead to significant gains. Unusually, the possibility of even higher temperature flue gas recycle is also considered, using high temperature particulate filtering and providing 0.2%pts efficiency gain.

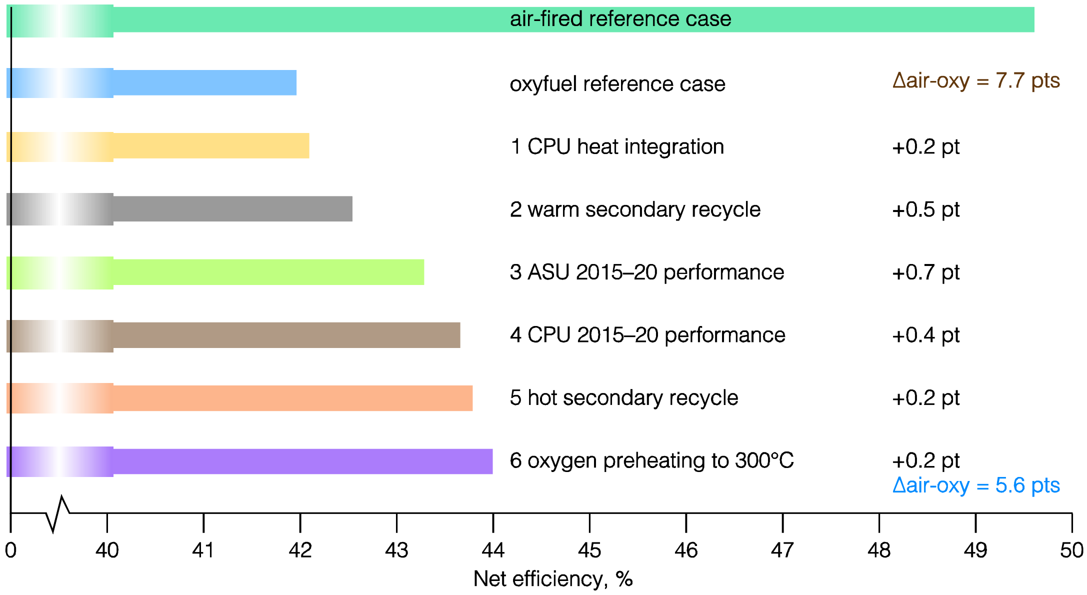


Figure 39 Potential energy savings in future oxyfuel plant calculated by Air Liquide (Paufique and others, 2013)

A study performed for the IEA greenhouse gas programme by Foster Wheeler and Air Products, scheduled for release in 2014, looks at integration of oxyfuel processes with a 1100 MW gross supercritical plant (Mancuso and others, 2013). Early results from this research indicate that 35.7% (LHV) net efficiency is achievable in the optimised plant, which uses hot secondary flue gas recycle and an Air Products CPU with sour compression. Thermal integration of the plant includes the use of CPU compression heat to heat the cold box vent gases, which are sent to an expander for energy recovery.

10 Conclusions

In the last five years, oxyfuel combustion has benefitted from successful full-chain pilot tests to cement its status amongst the viable options for CCS with coal plant. The technology is now widely considered to be ready for scale-up to a demonstration phase in which its suitability for commercial deployment can be assessed by the operation of a large-scale oxyfuel plant. While no major technological barriers have been encountered in developing oxyfuel to the scale of large pilot plants, the scope for research has only continued to grow as efforts have focussed on further optimisation of plant performance and new means of reducing the efficiency penalty imposed by the capture process.

Drawing on both lab-based and pilot-scale tests, considerable research experience has now been acquired in the altered behaviour of coal combustion in an atmosphere of oxygen and recycled flue gases. Whilst the destabilising effect of the increased heat capacity can in large part be countered by raising oxygen levels to 27–30%, new burner designs have been introduced by several manufacturers in order to optimise combustion and increase the possible range of operating parameters. These are usually based on swirl burners which promote a high degree of recirculation of hot exhaust, sometimes in conjunction with injection of pure oxygen via oxygen lances; both of which act to accelerate ignition close to the burner. Improved understanding of the combustion behaviour at the level of the coal particle is also important for developing accurate CFD simulations tailored to oxyfuel combustion. Ongoing research in this area aims to ensure that the performance of pilot-scale combustion can be reliably translated to operation of a full-scale plant.

Recycle of flue gases before FGD or drying steps is an attractive option for raising plant efficiency, but may carry considerable added risk of both low- and high-temperature corrosion. Increased levels of water vapour and SO_3 found in hot recycle schemes are known to raise the acid dew point and therefore require flue gas ductwork to be maintained above this temperature in order to avoid severe corrosion. The influence of oxyfuel conditions on high-temperature corrosion of superheaters and waterwalls is harder to elucidate, and often contradictory results have been obtained from laboratory and pilot studies. However, corrosion in oxyfuel furnaces appears to adhere to familiar air firing mechanisms, with the recycle of SOx-rich flue gases presenting a similar risk to the use of high sulphur coals. Although increased water vapour levels increase corrosion rates of some alloys, metal carburisation due to CO_2 appears to be effectively mitigated under oxidative conditions. It is likely that the corrosion risk will limit early oxyfuel plants to either less problematic fuels or more conservative flue gas recycle configurations with FGD.

As the most energy intensive plant process, the cryogenic air separation unit (ASU) is particularly in need of further development and adaptations specific to oxyfuel plant such as larger, more efficient, and more flexible units. In the last five years ASU manufacturers have reduced energy consumption of the unit by around 20%, primarily through use of more complex distillation process cycles such as three column or cold compression cycles, as well as implementing improved heat transfer and drying adsorbent technologies. Whilst cryogenic ASU still has potential for further efficiency optimisation, the recovery of air compression heat for feedwater preheating is another useful means of minimising the overall efficiency penalty to the plant. Other developments include new technologies for the efficient storage of liquid oxygen, providing a cheap alternative to costly operation of the ASU during times of peak energy demand. Although the ASU may prove to be a limiting factor in oxyfuel plant flexibility, as start-up of the unit from 'warm' can take days and air compressors have limited turndown, this could also be mitigted by the use of multiple compressor trains and stored oxygen. Ceramic membranes are a potentially higher efficiency alternative means of oxygen production, in which the absence of cryogenic cooling means that the energy of the hot, compressed air feed can be recovered after the oxygen is extracted. This technology has reached the pilot-scale but is not yet a commercial reality.

Although oxyfuel combustion can produce dried flue gases with over 90% CO_2, the remaining fraction is largely made up of the light gases N_2, O_2, and Ar which would significantly raise the energy required to compress the product gas to pipeline pressures, as well as potentially exceeding the limits set by existing pipeline and EOR specifications. The partial condensation of the flue gases required to remove these species also imposes its own strict limits on flue gas contaminants in order to avoid damage to the sensitive compressors and cryogenic equipment. Temperature swing adsorption is used for deep flue gas dehydration, while a variety of means for polishing of SOx, NOx and mercury to trace levels have been trialled at the lab-scale or in CPU operating at large oxyfuel pilots. These include conventional alkaline scrubs, pressure swing adsoprtion, distillation of NO_2, and a novel sour compression process in which the chemistry of SOx and NOx at high pressure is exploited to promote their removal as condensates. CPU pilots have successfully demonstrated that achieving very high product CO_2 purities is possible with a distillation step, although for future CO_2-storage purposes a simpler flash separation may provide sufficient purity.

A disadvantage to conducting oxyfuel research at the pilot-scale is the necessary investment in a dedicated oxyfuel boiler, as opposed to the power plant slip-stream tests which are possible for post-combustion capture pilots, and deployment of large oxyfuel pilots has therefore been less widespread. However, a number of pilots of over 20 MWth capacity have now been commissioned, with several including commercial ASU or pilot CPU in addition to the oxyfuel boiler. Such pilots are able to provide invaluable experience in controlling the interaction of each of the plant processes in addition to standard boiler tests. As the largest oxyfuel pilot currently operating, commisioning of the 100 MWth Callide unit has demonstrated the importance of managing the array of chemical analysers in a full-chain oxyfuel process, as well as minimising the acidic corrosion and air ingress issues encountered by most pilots. Also in the early stages of planned test campaigns, the 30 MWth CFB unit at Ciuden is a unique facility for assessing the potential of oxyfuel CFBC, including the use of high levels of oxygen and the performance of in-situ desulphurisation.

Although several demonstration projects have reached advanced stages of design and planning, most have been hindered by the strong dependence on political and financial support inherent to all large-scale carbon abatement projects. However, with growing support from several national governments, current projects may meet with more succes. Of these, the proposed 168 MW FutureGen 2.0 plant in the USA is nearest to realisation, having reached an advanced stage of design and storage permitting. Other, less advanced projects in the UK and China may also receive sufficient government support to progress although, as with other capture projects, the deployment of a safe transport and storage infrastructure may present more of a barrier than the plant technology.

Amongst second-generation oxyfuel combustion concepts, pressurised combustion has attracted particular attention due to the high proportion of latent heat of water vapour which can be recovered, the reduction in air ingress, and the fact that some compression energy is saved in the CPU. In the most developed pressurised technology, currently operating at the 5 MWth scale, the high-temperature flameless combustion of coal slurry also has the advantage of significantly reduced emissions. Other advanced oxyfuel processes have sought to reduce or eliminate flue gas recycle in order to reduce boiler size and improve combustion. Concepts at the research stage which combine both pressurised and low flue gas recycle include molten bed combustion and staged combustion, and development of such novel approaches is likely to continue.

Without experience from demonstration projects, assessing the techno-economic performance of future commercial oxyfuel plant bears a high degree of uncertainty. Despite this, results of current analyses are in broad agreement that oxyfuel is at least economically competitive with other capture technologies to within the level of accuracy. For retrofit purposes, oxyfuel may be a particularly suitable approach, as it avoids downgrading the steam turbine and can use a high proportion of existing plant equipment. Large-scale oxyfuel plant is variously estimated to impose an efficiency penalty of 6–10%pts on conventional coal plant, with the lower end of the range associated with a high degree of thermal integration of the three component processes and assuming ongoing progress in the optimisation of ASU and CPU efficiencies. Consequently, oxyfuel combustion could constitute a relatively efficient technology for a first generation coal CCS plant, and should be retained as a viable option alongside other capture processes by progression to a demonstration-scale.

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