Oxyfuel combustion of pulverised coal

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Abstract

This report concentrates on the oxyfuel combustion of pulverised coal with recycled flue gas. Oxyfuel combustion is one of the leading options for power generation with CO_2 capture. It can be simply described as a process that eliminates nitrogen from the oxidant or comburent by burning the fuel in either nearly pure oxygen or a mixture of nearly pure oxygen and a CO_2-rich recycled flue gas (RFG) resulting in a product flue gas from the boiler containing mainly carbon dioxide and water vapour. Pulverised coal is burned with a mixture of CO_2-rich recycled flue gas or steam (to act as diluents replacing nitrogen in order to moderate the temperature) in addition to the oxygen from an air separation unit. In the current design of the oxyfuel combustion for pulverised coal fired boilers, the CO_2-rich recycled flue gas is used as the diluent. The contents of this report include: a discussion of ignition and flame propagation, combustion and burnout, and heat transfer. This is followed by a chapter on oxyfuel burner and boiler design. 'Conventional' pollutants from coal combustion will be considered: particulates and ash, sulphur oxides, nitrogen oxides, and trace elements, in particular mercury. Slagging, fouling, and corrosion issues are addressed followed by a brief update on the status of pilot and demonstration projects of oxyfuel technology. The final chapter before the conclusions provides an account of the findings of techno-economic analyses of oxyfuel combustion and some competing technologies.

Acknowledgements

Acronyms and abbreviations

CCS	carbon capture and storage
CFD	computational fluid dynamics
COE	cost of electricity
db	dry basis
DTF	drop tube furnace
DOE	Department of Energy, USA
ESP	electrostatic precipitator
FGD	flue gas desulphurisation
IEA GHG	IEA Greenhouse Gas R&D Programme
IGCC	integrated gasification combined cycle
LHV	lower heating value
MEA	monoethanolamine
mol%	molar percentage
NGCC	natural gas combined cycle
NOx	nitrogen oxides (NO + NO_2)
OFA	overfire air
ppm	parts per million
RFG	recycled flue gas
TGA	thermal gravimetric analysis/analyser
VM	volatile matter
UBC	unburnt carbon
vol%	percentage by volume
wt%	weight percentage
XRD	X-ray diffraction

Contents

1 Introduction

Oxyfuel combustion is one of the leading options for power generation with CO_2 capture. It can be simply described as a process that eliminates nitrogen from the oxidant or comburent by burning the fuel in either nearly pure oxygen or a mixture of nearly pure oxygen and a CO_2-rich recycled flue gas (RFG) resulting in a product flue gas from the boiler containing mainly carbon dioxide and water vapour. Burning of fuel with pure or nearly pure oxygen is typically applied to high temperature processes such as reheating furnaces or glass tank furnaces; whereas for steam generation applications such as pulverised coal boilers, lower combustion temperatures are necessary. Therefore, fuels are burned with a mixture of CO_2-rich recycled flue gas or steam (to act as diluents replacing nitrogen in order to moderate the temperature) in addition to the oxygen from an air separation unit. In the current design of the oxyfuel combustion for pulverised coal fired boilers, the CO_2-rich recycled flue gas is used as the diluent. This report will be limited to that design. A schematic of an oxyfuel fired pulverised coal power plant is shown in Figure 1.

The combustion products (or flue gas) consist mainly of carbon dioxide and water vapour together with excess oxygen required to ensure complete combustion of the fuel. The flue gas exiting from the boiler will also contain other components such as reactive and inert components derived from the fuel such as SOx, NOx, fly ash, trace metals, etc), any inert components from the oxygen stream supplied (Ar, N_2), any inert components from the air in-leakage (N_2, Ar, H_2O) and any additional chemicals that are added in the post-combustion treatment of the flue gas (such as NH_3 from selective catalytic reduction). The typical range of percentages (wet basis) of the composition of the oxidant or comburent gases in the windbox entering the furnace for both air and oxyfuel combustion are given in Table 1 together with data for the composition of the most common major components of the flue gas exiting the boiler (Makino, 2006).

The net flue gas after condensing all the water vapour can typically contain about 80–95% (db) CO_2 for any coal fired oxyfuel boiler depending on coal type, excess oxygen, air in-leakage and flue gas processing employed. Tan and others (2005) have reported that CO_2 concentration in the flue gas

from various industrial scale oxyfuel pilot plant experiments undertaken between 1980 and 2000 have achieved concentrations greater than 90% (db) and have reached as high as 95% (db); with the balance mainly consisting of the nitrogen, argon derived from the air in-leakage, NOx and SOx derived from the fuel sulphur and nitrogen during combustion, and excess oxygen supplied. Buhre and others (2005) have noted that the CO_2 concentration in the flue gas of a pulverised coal boiler could reach concentrations higher than 95%; however, it should be noted that this concentration could only be achieved if operating in a lean combustion condition and very minimal air in-leakage.

The high partial pressure (or concentration) of CO_2 in the oxyfuel flue gas removes the need to apply expensive and energy intensive absorption units to strip out the CO_2, such as in post-combustion capture. This concentrated CO_2-rich flue gas from the boiler is further purified, dried and compressed before delivery into a pipeline for storage.

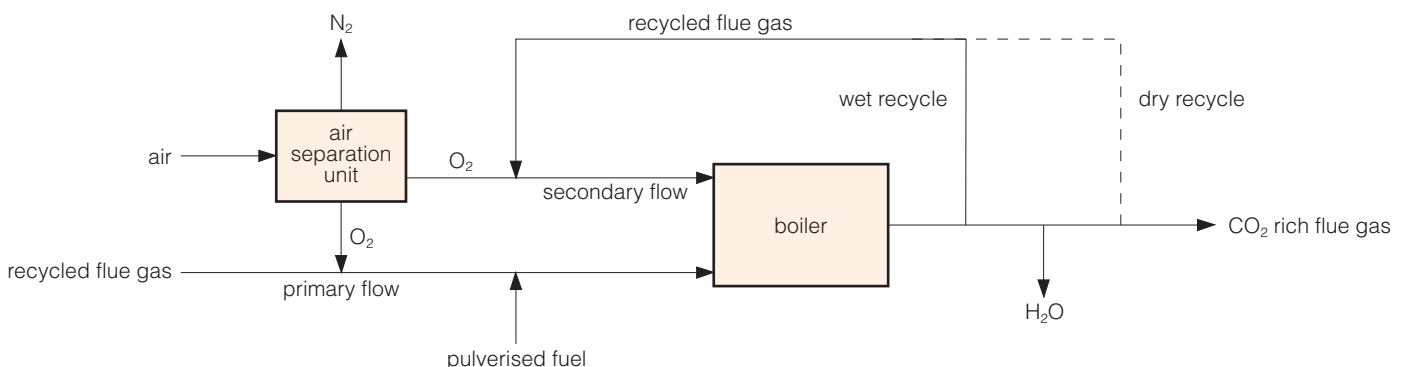| Table 1	Comparison of the gases in the combustion chamber and in the flue gas (Makino, 2006)		
		Gas constituents, % (wet basis)	
		Combustion with air	Combustion with O_2
Windbox	O_2	21	21–30
	N_2	79	0–10
	CO_2	0	40–50
	H_2O	small	10–20
	others	–	NOx, SO_2
Flue gas	O_2	3–4	3–4
	N_2	70–75	0–10
	CO_2	12–14	60–70
	H_2O	10–15	20–25
	others	NOx, SO_2,	NOx, SO_2

Figure 1   Schematic of an oxyfuel pulverised coal fired power plant

Zheng and others (2005b) noted that, in general, there are four components of the oxyfuel combustion process:

1 the air separation unit (ASU), which provides oxygen for combustion;
2 the combustor, which can be either a boiler, or a furnace, or a turbine;
3 the integrated emissions control;
4 the product recovery train (PRT), which produces a product CO_2 stream.

The production technologies for oxygen have been reviewed by Anheden and others (2005) and more recently examined in a report for the IEA Greenhouse Gas R&D Programme by Allam (2007, 2009) so they will not be included in this report which will concentrate on the oxyfuel combustion of pulverised coal with recycled flue gas (RFG). Allam (2007) pointed out that oxygen production is a major part of the energy consumption and capital cost of oxyfuel combustion with CO_2 capture. The current oxygen production process is the cryogenic separation of air by distillation and this method will still have a potential in the future for specific applications, particularly coal fired oxyfuel power stations.

The starting point of this review will be several literature reviews produced in 2005 and the inaugural meeting of the IEA Greenhouse Gas R&D Programme's *International Oxy-combustion Network for CO_2 Capture* in November 2005 (IEA GHG, 2006). Literature produced prior to 2005 will not be included.

One review was performed by Tan and others (2005); *see also* Santos and Haines, 2006; Santos and Davison, 2006; Santos and others, 2006) for the International Flame Research Foundation. They concluded that one of the promising technologies for carbon capture and sequestration in coal utilisation for power generation industry is by ultra-supercritical boilers using oxygen combustion and recycle flue gas. Further, it was concluded that the technology is technically feasible and should be further developed initially for demonstration then for implementation.

The following points were noted:
● oxyfuel coal firing should be viewed either as a technology to be developed for retrofitting of current coal-fired boilers or as a technology to be developed for the next generation boilers;
● the key factor for this technology is to understand how to control the heat transfer profile of the combustion process and at the same time reaching a CO_2 concentration in the flue gas of at least greater than 80% (db);
● the second important challenge for this technology to succeed is how to reduce the cost of oxygen and the cost of transporting of the product flue gas.

From the review, the following are some of the key conclusions regarding this technology:
● the flue gas recycle ratio is the most important parameter in controlling the heat transfer profile of the oxyfuel coal combustion process;
● the amount of water vapour in the flue gas seems to have a strong effect on the optimum level recycled flue gas in

order to have a combustion characteristic similar to a conventional air fired case;
● air ingress should be minimised to reach the desired level of CO_2 in the flue gas.

Some gaps in the knowledge of this technology were identified:
● *Optimum recycle ratio* – the amount of recycled flue gas to achieve similar combustion and heat transfer characteristics to an air fired operation still required further elucidation. Likewise, the effect of air ingress on determination of amount of recycled flue gas is not well established. It is only the effect of water vapour in the recycled flue gas that has been studied in depth.
● *Carbon burnout* – experimental data obtained from various pilot-scale studies have been reported but these data were limited to only a certain range of coal.
● *Ash formation, slagging and fouling* – there is also some question on the effect of CO_2-rich atmosphere on ash formation. It was noted that vaporisation of mineral oxides in the coal will be suppressed, resulting in altered particle size distribution and potential problems with ash deposition. Slagging and fouling problems have been found to be worse in CO_2/RFG firing than in air combustion, in part due to reducing conditions and decreased velocity or flow rate of combustion products at optimal recycle ratios.
● *Fine particulates, SO_3, trace metal emissions* – experimental results indicate reduced conversion of fuel-S to SO_2 compared with air combustion; a number of explanations for the reduction have been suggested, including conversion to other sulphurous gases or SO_3, and sulphur retention in ash, unburned carbon or condensate. This clearly indicated that mechanisms of sulphur conversion during combustion with high level of CO_2 and H_2O were not yet well understood. It was suggested that SO_3 will surely have an impact on fine particulates but studies on this topic have been very limited. Mercury emissions were reported to be reduced by about 50%, although the mechanism had not yet been determined nor predicted by thermodynamic modelling.
● *Radiative heat flux measurements* – the review noted that most radiative heat flux measurements are taken using ellipsoidal radiometers, which do not eliminate the effect of radiation from the wall. For the purpose of developing radiation for oxyfuel combustion, the use of a Narrow Angle Radiometer was highly recommended to determine the flame radiation and the contribution of char to the radiation.

It was also recommended that the next generation of boilers should be developed to operate at the conditions found in oxy-coal firing since there is significant potential for reduction in boiler size and cost – it was estimated that oxyfuel combustion could reduce required heat transfer area by as much as 50% compared with air firing.

Oxyfuel combustion technology for coal-fired power generation has also been comprehensively reviewed by Buhre and others (2005; *see also* Wall and others, 2005; Wall, 2006). They identified four areas that needed to be addressed in more detail to obtain a more fundamental understanding of the

changes between oxyfuel combustion and conventional air fired combustion:

- the heat transfer performance of new and retrofitted plant and the impact of oxygen feed concentration and CO_2 recycle ratio;
- the gas cleaning required;
- the assessment of retrofits for electricity cost and cost of CO_2 avoided;
- the combustion of coal in an O_2/CO_2 atmosphere, including ignition, burnout, and emissions.

The techno-economic studies reviewed had revealed that oxyfuel combustion was a cost-effective method of CO_2 capture. More important, the studies indicated that oxyfuel combustion was technically feasible with current technologies, reducing the risks associated with the implementation of new technologies.

Another, briefer, review was produced by Croiset and others (2005) in which they concluded that oxyfuel combustion represents a viable solution for capturing CO_2 from pulverised coal plants being technically feasible not only for new plants but also for retrofit application. Recently, a wide ranging review has been produced by Toftegaard and others (2010).

A study for the IEA GHG led by Mitsui Babcock (now Doosan Babcock) found that specific areas of oxyfuel combustion technology requiring development included:

- plant start up and control systems;
- burner and flame characterisation;
- materials issues (IEA GHG, 2005).

In addition to oxyfuel combustion being a potential retrofit technology for existing fossil fuel power plants, a study by Dillon and others (2005) suggested that oxyfuel combustion lends itself to accommodating a staged approach for the implementation of CO_2 capture into new build power plants as 'capture ready'. Capture ready plants would be specifically designed for easy retrofit of CO_2 capture. It was suggested that, as part of the development and demonstration of an advanced supercritical oxyfuel combustion 'capture ready' plant, the key areas to be addressed included:

- the successful demonstration of full-scale burners under conditions of combustion in oxygen and recycle flue gas;
- full appraisal of the slagging and fouling nature of the ash arising from the oxyfuel combustion process and their impact on boiler heating surface arrangement and choice of boiler materials;
- the impact of radiant and convective heat transfer from the novel flue gas on boiler plant design;
- general issues associated with materials, corrosion, and requirements for plant start-up, shut-down, oxyfuel combustion boiler control systems, recycle flue gas duct purging and the effect of plant trips on the boiler system;
- further process optimisation, integration and automation to reduce cost, improve performance and increase energy efficiency.

In a presentation to the second meeting of the oxyfuel network, Sarofim (2007) considered the progress and remaining issues of oxyfuel combustion. He concluded that laboratory- and pilot-scale studies have demonstrated the feasibility of near-term commercial implementation of oxyfuel combustion for CO_2 production. It had the advantages to industry of reliability, availability, and familiarity although there was a need to develop a 'clean coal' image for oxyfuel combustion.

The European Technology Platform for Zero Emission Power Plants (ZEP) has published recommendations for research and development activities within the European Unions's FP7 programme (ZEP, 2008). Some topics relevant to the content of this report include:

- Intensify laboratory research into combustion, heat transfer, formation of pollutants, excess oxygen, ash compositions and properties, slagging, fouling and corrosivity of flue gases. It is important to investigate the implications of oxyfuel combustion for a large spectrum of solid fuels covering ranges of fuel properties, such as high contents of sulphur, high contents of chlorine, calcium oxide-rich ashes.
- Develop, based on research results, and adapt engineering and design tools for scale-up, such as computerised fluid dynamics (CFD) and other advanced tools. Validate developed tools against laboratory and pilot-plant testing.
- Pilot-plant tests (10s of MWth) of full oxyfuel pulverised fuel (PF) process, to validate results from scale-up based on laboratory tests.
- Development of PF burner designs and piloting in 10s of MWth scale.
- Investigations of start-up and shut-down procedures, transient conditions and performance during part-load operation, to be performed as combinations of dynamic simulations;
- Verifications in pilot plants.

ZEP expects that these R&D actions will create a validated, firm basis for design of oxyfuel boilers to be used in large-scale demonstrations (100s of MWth) of oxyfuel power plants. The list of recommendations has since been updated by the publication of recommendations for beyond 2020 (ZEP, 2010).

As noted above, this report will concentrate on the oxyfuel combustion of pulverised coal with recycled flue gas, concentrating on the combustion processes, which covers one technology block within the oxyfuel process for carbon capture and storage (CCS), the others being oxygen separation, fuel preparation, steam cycle, flue gas recycle and O_2 mixing, flue gas treatment and cooling, and CO_2 purification and compression (ZEP, 2010). It is admitted that this topic is difficult to treat in isolation, as clearly the technology blocks will influence one another.

The chapter following this introduction will discuss ignition, combustion, and heat transfer. *Chemical looping combustion* using metal oxides to provide oxygen is not discussed here but will be the subject of a companion Clean Coal Centre (CCC) report by Henderson (2010). The chapter on combustion will be followed by a chapter discussing burner and boiler design. The next four chapters will discuss the formation of particulates and ash, sulphur oxides, nitrogen oxides, and trace elements, in particular mercury. Flue gas

cleaning will not be addressed but that topic is covered in another CCC report on *Flue gas treatment for CO$_2$ capture* (Adams, 2010) in which she concludes that the issue of optimum product CO$_2$ purity is a question that, at the moment, does not have a satisfactory answer. Slagging, fouling, and corrosion issues will be addressed followed by a brief update on the status of pilot and demonstration projects of oxyfuel technology. The final chapter before the conclusions will provide an account of the findings of techno-economic analyses of oxyfuel combustion and some competing technologies.

2 Ignition, combustion, and heat transfer

Buhre and others (2005) have pointed out that there is a need for a more fundamental understanding of the effects of combustion of coal in an O_2/CO_2 atmosphere on the ignition and burnout. Changes in combustion characteristics may be partly attributed to the lower combustion temperatures caused by the replacement of nitrogen with higher heat capacity carbon dioxide gas, 57.83 kJ/mol at 1400 K and constant atmospheric pressure for CO_2 compared with 34.18 kJ/mol for N_2 (Khare and others, 2008). Other factors can also affect combustion, in addition to the higher heat capacity of the CO_2, Tappe and Krautz (2009a) list:

● hindering the diffusion of CO_2 from the particle to the ambient gas atmosphere;
● hindering the diffusion of oxygen to the char surface;
● the Boudouard reaction between CO_2 and carbon may result in higher combustion rates.

2.1 Ignition, flame propagation and stability

Buhre and others (2005) reported that the flame propagation speed in an O_2/CO_2 environment was lower than in O_2/N_2 and that this was related to the higher heat capacity of CO_2 compared with that of N_2. The delayed flame ignition in oxyfuel combustion was also attributed to the higher heat capacity. Flame ignition is also delayed in oxyfuel combustion but this was related to changed burner velocities for a retrofit where secondary velocities will be reduced (that is, where the air burner is unchanged).

Experiments in a combustion-driven laminar entrained flow reactor by Molina and Shaddix (2005) and Shaddix and Molina (2006) suggested that the presence of CO_2 retards coal and char ignition, but has a negligible effect on the duration of devolatilisation. The change in the particle ignition time was minor. Shaddix and Molina (2006) and Molina and Shaddix (2007) pointed out that particle ignition and devolatilisation properties in a mixture of 30% O_2 in CO_2 were very similar to those in air. Shaddix and Molina (2009) reported that increasing oxygen concentration accelerated particle ignition for both N_2 and CO_2 atmospheres. The effect of O_2 concentration and diluent gas on the particle ignition process was attributed to the effect of O_2 on local mixture reactivity and the higher specific heat and/or the reduced radical pool associated with CO_2. Particle devolatilisation proceeds more rapidly with higher O_2 concentrations and decreases with the use of CO_2 diluent because of the influence of these two species on the mass diffusion rates of O_2 and fuel volatiles. It was concluded that an increased oxygen concentration for CO_2 recycle combustion, if correctly selected, should produce ignition times and volatile flames similar to those obtained under coal/air combustion.

The effects of enhanced oxygen and of CO_2 on the ignition of a 'cloud' of pulverised coal particles has been studied by Shaddix and others (2009b). Photographs of the group particle ignition and subsequent combustion in the entrained flow reactor at 1200 K for both N_2 and CO_2 diluents were obtained together with corresponding optical data comparing mean optical emission intensity of the particles as a function of reactor height. It was found that the particles ignite earlier and burn hotter in the nitrogen environment. These results are qualitatively consistent with what had been previously determined for isolated particle ignition and combustion: namely, ignition is strongly controlled by oxygen concentration (for a given ambient temperature) and is also retarded by using a CO_2 diluent. Molina and others (2009) reported that experiments at 1650 K demonstrated the same trend with oxygen concentration as observed at 1200 K but with a much reduced variation in ignition delay (as measured by the standoff distance from the coal flame to the flat flame burner). They also observed that, at 1650 K a higher oxygen concentration had a detrimental effect on flame stability. It was noted that this was a surprising result that requires verification with further experiments.

Tan and others (2006) have reported studies in a 0.3 MWth vertical combustor test facility. When the combustion feed gas was composed of 21% of O_2 (similar to air) with the rest being RFG, the flame temperature was found to be significantly lower than combustion in air and, in certain cases, it was not even possible to maintain stable flames. It was thus necessary to increase the concentration of O_2 in the feed gas to raise the flame temperature and maintain stable flames.

Man and others (2007) have described ignition tests on pulverised coal suspensions using a suite of coals of different rank and from different countries of origin and over a range of oxygen and coal concentrations of interest for oxyfuel combustion. The ignition tests were carried out using the (US) National Institute for Occupational Safety and Health (NIOSH) 20 litre explosion chamber. The coals included one US bituminous coal (Pocahontas) with volatile matter (VM) content of about 18 wt% dry basis and five low volatile coals (VM roughly between 6 and 13 wt% db). Apart from the lowest volatile coal, which did not ignite, all the coals ignited in O_2 in CO_2 at some point. The concentration of O_2 in CO_2, which gave ignition comparable to that in air, was established to be between 30 to 35 vol% consistent with the data reported by Tan and others (2006).

Thermal gravimetric analysis (TGA) of three Chinese pulverised coals has shown that combustion was more difficult as the rank increased (Niu and others, 2009). To improve the combustion process, sufficient oxygen must be provided and 10% O_2 concentration was inadequate. But, once the concentration. Increasing the oxygen concentration up to 40% favoured the combustion process but the effect levelled off at higher O_2 concentrations. Shaddix and others (2009a) have also reported the expected rank dependence of burning rate, with the lowest rank coals burning faster than those of higher rank. At a temperature representative of pulverised coal furnaces (1650 K), they found that, for low or middle rank coals, the char particles burn at lower temperatures when in the presence of CO_2 instead of N_2. No meaningful difference was observed for the anthracite sample studied.

Based on experimental data from the Chalmers University 100 kW combustion test unit, three different lignite fired oxyfuel flames were investigated by Hjärtstam and others (2007, 2009). The oxyfuel flames contained 25, 27, and 29 vol% O_2 with the remainder being RFG (dry recycle). The air fired case and the 25% O_2 case showed strong similarity in terms of flame stability indicating the possibility of establishing an oxyfuel flame with a flame structure almost identical to one in air firing. From an operational point of view, the flames with 27 and 29 vol% O_2 were the most stable. It was also found that an increase in the O_2 content from air to oxyfuel firing in the feed gas (from 21 to 27 vol%) enabled an improved ignition sequence for the coal particles in the O_2/CO_2 mixture compared with air firing.

The effect of CO_2 on flame propagation velocity was studied by Suda and others (2007) both experimentally and numerically. The results showed that the flame propagation velocity has a maximum value with an upper and lower limit of coal concentration. The distance between particles at the maximum flame propagation velocity was of the same order as the flame radius of each particle. In CO_2/O_2 mixture gas, flame propagation velocity decreased to about one third to one fifth compared with that of N_2/O_2 mixture gas mainly due to the greater heat capacity of CO_2. Using an Ar/O_2 gas mixture gas, it was revealed that the thermal diffusivity of the gas seems to have a large effect on flame propagation velocity since Ar has the greatest thermal diffusivity among the three gases. This was clarified by the numerical analysis concerning detailed radiation heat transfer using the Monte Carlo method.

Khare and others (2007, 2008; *see also* Wall and others, 2009a) note that, for a retrofit, changes to the mass flows and velocities of the primary and secondary streams due to the different heat capacity and densities of the main gases (N_2 and CO_2) will change burner aerodynamics, thereby influencing flame ignition and flame shape. The density of CO_2 at 1400 K and atmospheric pressure is 0.383 kg/m^3 compared with 0.244 kg/m^3 for N_2. Combustion tests were performed in a vertical pilot-scale furnace (1.2 MWth) at the IHI test facility in Aioi, Japan, to compare the performance of an air fired swirl burner retrofitted to oxyfuel fired pf coal combustion with the oxyfuel fired feed conditions established to match the furnace heat transfer for the air fired case. The study suggested that changes in jet aerodynamics, due to burner primary and secondary velocity differences (and hence the momentum flux ratio of the flows) influence flame shape and type. These changes are found when furnace radiative heat transfer is matched, and are due to differences in gas density and heat capacity. For the oxyfuel retrofit considered, the higher momentum flux of the primary stream of the oxyfuel burner caused the predicted ignition to be delayed and occur further away from the burner nozzle, with the difference being accentuated at low load. However, it was pointed out that the experimental flames were low swirl with no internal recirculation as opposed to the higher swirl flames (with internal recirculation) more common in industry.

Arias and others (2008) have also reported an increase in the ignition temperature in CO_2/O_2 mixtures when the oxygen concentration was the same as that of the air. The ignition of the samples under a mixture of 79% CO_2/21% O_2 is delayed with respect to air and there is a shift to higher temperatures. Again, this was explained as being due to the difference in the specific heats of the gases. CO_2 has a higher specific heat, and so more heat is needed to increase the temperature when coal is being oxidised during ignition. This causes a delay in ignition in rich CO_2 atmospheres. However, at an oxygen concentration of 30% or higher, an improvement in ignition was observed; ignition takes place at lower temperatures. This was attributed to the reaction rate increasing which in turn increases the release of heat.

A 100 kW downfired oxyfuel combustion test furnace has been used by Zhang and others (2008, 2009) to study the effect on flame stability of partial pressure of O_2 within the O_2/CO_2 mixture. The furnace consists of an oxyfuel combustion chamber, followed by downstream controlled temperature cooling to simulate practical furnace conditions. The burner applied in the tests is a coaxial, none-swirl one, with transport stream and coal jet in the centre pipe and secondary stream in the annular sleeve. A new methodology was developed to quantify flame length, flame stability, and ignition behaviour in the near burner zone. This involved an image processing technique and statistical analysis, which allowed quantification of the precision in experiments. Preliminary results have shown that, at similar adiabatic flame temperatures, the mean luminosity of an oxyfuel coal flame was somewhat lower than that of the equivalent O_2/N_2 flame. Experimental data show how flame attachment increased with P_{O2} in the secondary oxidant streams.

Smart and others (2009) defined the recycle ratio as the ratio of the recycled flue gas to the sum of the recycled flue gas and the net furnace product flue gas. Using RWE npower's Combustion Test Facility (CTF), Smart and others (2010a) investigated the impact of combustion on flame characteristics through the application of digital imaging and image processing techniques. The characteristic parameters of the flame were derived from flame images that were captured using a vision-based flame monitoring system. Different flue gas recycle ratios and furnace oxygen levels were created for the Russian and South African coals studied. It was found that the flame temperature decreased with the recycle ratio for both test coals, suggesting that the flame temperature is effectively controlled by the flue gas recycle ratio. The decrease in flame temperature with the flue gas recycle ratio showed a steeper gradient for the high O_2 level setting and was considered likely to be attributable to the differences in CO_2 and O_2 inputs. It was also found that the differences in coal properties had an impact on the flame temperature. High flame temperatures were observed for high volatile content Russian coal at high recycle ratios compared with those for the low volatile content South African coal. In addition, the flame oscillation frequency decreases with the recycle ratio, indicating that a high recycle ratio has an adverse effect on the flame stability. In most cases, the flame oscillation frequency in the root region was lower than that in the middle region, indicating ignition problems under oxyfuel firing conditions. Comparisons between oxyfuel and air firing conditions also suggested that, to maintain equivalent flame temperatures in oxyfuel combustion and air combustion, the feeding gas needs to be around 32–35 vol% oxygen and 65–68 vol% dry recycled CO_2.

2.2   Combustion and burnout

Experiments were carried out in a 20 kW down-fired combustor by Liu and others (2005). They found that simply replacing the N_2 in the combustion air with CO_2 will result in a significant decrease in the combustion gas temperatures. Temperatures may be elevated, however, by increasing the input partial pressure of oxygen in the gas beyond that found in air. It was concluded that, to keep a similar temperature profile for coal combustion in air and for coal combustion in O_2/CO_2, the oxygen concentration in O_2/CO_2 mixture has to be increased to 30% or more. This produced better char burnout. Andersson (2006) reported that coal-fired tests had shown that temperatures reached for a lower concentration of 27% oxygen in the oxyfuel were comparable to the air firing case.

Bejarano and Levendis (2007a; Levendis and Bejarano, 2006) studied the effect of oxygen concentrations by burning single bituminous coal char particles in a drop tube furnace, electrically heated to 1300–1500 K, in 21%, 50%, and 100% oxygen in a balance of nitrogen. Average char surface temperatures increased from 1600–1800 K in air, to 2100–2300 K in 50% O_2, to 2300–2400 K in 100% O_2. Combustion duration decreased from 25–45 ms in air, to 8–17 ms in 50% O_2, to 6–13 ms in 100% O_2. Thus, average particle temperatures increased by up to 45%, whereas burnout times decreased by up to 87% as combustion was progressively enriched in O_2 until 100% was attained. The apparent and intrinsic reactivity of the chars burning at 1500 K gas temperature was found to increase by factors of to 8 and 35, respectively, as the oxygen mole fraction increased by a factor of five, from 21% to 100%.

Although increasing the fraction of oxygen reduces burnout times, the replacement of nitrogen with carbon dioxide may have the opposite effect. Alvarez and others (2005) found that a higher amount of O_2 in CO_2 than in N_2 was needed to achieve similar burnout levels. Experimental results reported by Borrego and Alvarez (2007) suggested that CO_2 could be involved in cross-linking at the char surface.

Naredi and Pisupati (2007a) reported that their computational predictions had indicated that the char burnout will be higher for combustion in a blend of O_2/CO_2 than combustion in air. They then reported an increase in char burnout values in 21% O_2/CO_2 compared with combustion in air and suggested a significant effect of gasification reactions (Naredi and Pisupati, 2007b). However, in a later paper, bituminous coal char burnout in 21% O_2/CO_2 was reported to be much lower than combustion in air (Naredi and Pisupati, 2008). This was attributed to the lower gas temperatures despite the contribution from the char-CO_2 reaction. A significant increase in a bituminous coal char burnout in 30% O_2/CO_2 compared with combustion in air was also observed, attributed to the higher oxygen partial pressure with some minor contribution from the char gasification reaction.

Arias and others (2007, 2008) have reported that the burnout of coals with a mixture of 79% CO_2/21% O_2 is lower than in air, but an improvement is achieved when the oxygen concentration is 30% or 35%. They defined 'fuel ratio' as the ratio between the coal mass flow rate used and the stoichiometric value and found that there was a worsening of coal burnout as this fuel ratio increased because the availability of oxygen is more restricted. The results are shown in Figure 2.
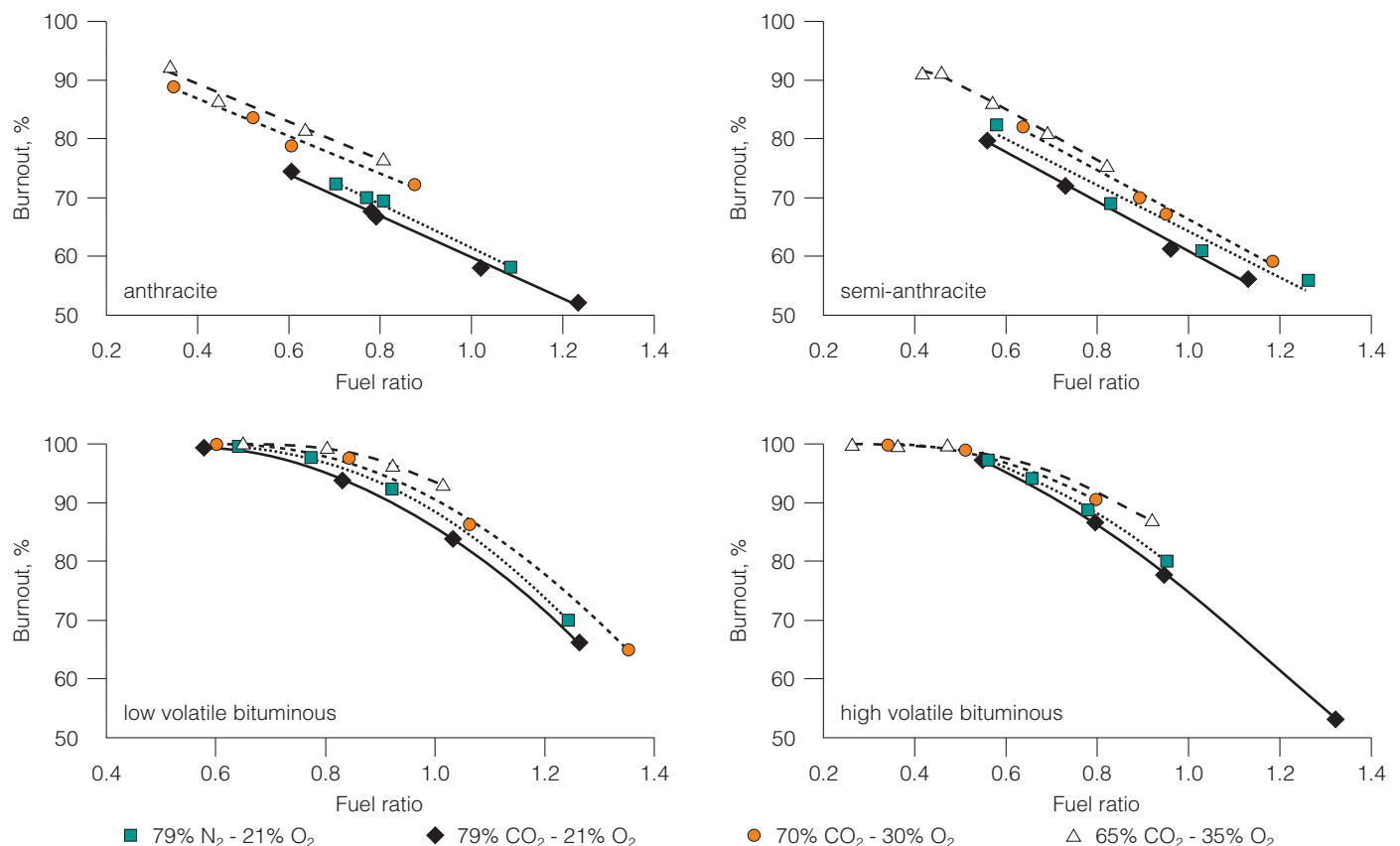

Figure 2   Burnouts at different fuel ratios (Arias and others, 2008)

Sethi and others (2007) found similar results; the unburnt carbon (UBC) from a bituminous coal in air was 4.9% which increased to 33.1% with 21% oxyfuel combustion. At 27% O_2 however, the UBC was 5.8%.

The impact of replacing N_2 with CO_2 on particle combustion behaviour has also been studied by Bejarano and Levendis (2007b, 2008) who burned pulverised bituminous coal and lignite in a vertical drop tube furnace under two different gas mixtures, O_2/N_2 and O_2/CO_2, at varying O_2 partial pressures. Their goal was to obtain temperature-time profiles throughout the luminous combustion history of single free-falling particles. The experimental results revealed that coal particles burned at higher mean temperatures and shorter combustion times in O_2/N_2 than in O_2/CO_2 environments at the same oxygen mole fractions. The replacement of N_2 with CO_2 reduced the bituminous coal flame temperatures by as much as 250 K and increased the volatile flame duration times and luminous char burnout times by as much as a factor of two at analogous O_2 mole fractions. In the case of the bituminous coal and for the experimental combustion conditions tested, measured volatile and char temperatures as in air (21% O_2) were attained with an oxygen content in the CO_2 mixtures about 30%. Bituminous coal volatile and char burnout times comparable to those in air (21% O_2) were attained with oxygen content in the CO_2 mixtures in the range of 30–35%. In the case of the lignite, the corresponding differences in oxygen mole fractions, which result in similar particle temperatures and burnout times in the two different gas mixtures, were less pronounced. Particle size had little difference on the temperature of the volatile flames and char surfaces although smaller char particles clearly burned faster. In a study using two lignites from North Dakota and Texas, Levandis and Joshi (2008) observed that the particle temperatures increased with partial pressure of oxygen and the burnout time decreased. Both lignites burned at higher temperatures and faster in O_2/N_2 than in O_2/CO_2.

Combustion characteristics of oxyfuel combustion of a Kleinkopje coal and a Lusatian (Lausitz) lignite were obtained in a 20 kWth electrically heated laboratory reactor by Scheffknecht and Maier (2008). They compared combustion in air and O_2/CO_2 ratios of 21/79 and 27/73 vol%. The system was operated in such a way that constant gas flows occurred in the combustion reactor. The concentration profiles for O_2 in air and 27 vol% O_2 were found to be similar. The course of the combustion in 21 vol% O_2 was delayed. Similar burnout was also seen in the case of air and with the 27 vol% oxyfuel case.

The combustion rates of char particles from a Canadian subbituminous coal and a high volatile eastern US bituminous coal have been measured by Murphy and Shaddix (2006) over oxygen concentrations ranging from 6% to 36 mol% and gas temperatures of 1320–1800 K. They found that, as the bulk oxygen concentration increases, devolatilisation occurs more rapidly and incandescence from the burning char particles is visible lower in the combustion reactor. The char particle combustion temperature increases as the oxygen concentration increases, and char burnout occurs much faster. The apparent enhancement of the devolatilisation rate with increasing oxygen content was explained by two factors: the

closer proximity of the volatiles flame to the coal particle and the higher temperature of the volatiles flame. Shaddix and Molina (2007, 2008) investigated the oxyfuel combustion of a Pittsburgh bituminous coal and a Black Thunder subbituminous coal in a combustion-driven entrained flow reactor. The oxygen content varied from 12 to 36 vol%. The char particle temperatures were observed to be consistently lower in the CO_2 environment even though the surface burning rates were essentially identical for combustion in O_2/N_2 and O_2/CO_2. It was suggested that the sole influence of CO_2 is through the approximately 20% slower diffusion of O_2 through the CO_2-rich boundary layer surrounding the reacting char particle. Single particle computations supported this conclusion and indicated that the higher volumetric specific heat of CO_2 does not significantly influence char combustion.

Gani and others (2009) have also reported that devolatilisation and char combustion are delayed and that the calculated particle temperatures are lower in the presence of CO_2. This was attributed to the differences in the thermal and transport properties of N_2 and CO_2. The burnout time and particle temperature similar to those in air conditions can be achieved by increasing the oxygen concentration above 21% in oxyfuel conditions.

Coal particle temperatures for one hard coal at three different residence times have been measured by Schiemann and others (2009) with an imaging two-colour pyrometer in a flat flame burner. The burner was operated with air as well as under oxyfuel conditions. Oxygen concentration was 3 vol% at temperatures of 1510 K to compare the effects of nitrogen and carbon dioxide as major components of the gas phase. For the oxyfuel experiments measurements with 9 vol% O_2 were also carried out to investigate the effect of the oxygen concentration. The measured particle temperatures were approximately 2000 K in N_2 and 1900 K in CO_2 diluted gas for the lower oxygen concentration and 1970 K in the oxygen-enriched gas. It was concluded that the difference in combustion temperatures is mainly caused by differences in heat capacity and heat conduction between carbon dioxide and nitrogen and the increased reaction rates in the presence of higher amounts of oxygen.

Up to this point it would seem that there is a fair degree of unanimity that the oxygen content in oxyfuel combustion has to be around 30% to be comparable with combustion in air. However, there is contrary evidence; Elliott and others (2005) have pointed out that, although the C-CO_2 reaction is significantly slower than the C-O_2 reaction, the elevated concentrations of CO_2 in oxyfuel conditions are such that the C-CO_2 reaction will have an impact on the combustion rate resulting in higher burnout levels than expected in an O_2/N_2 environment. They found that the char reactivity was slightly greater in the CO_2 environment. Their experimental data also indicated that the burnout improvement is determined primarily by changes on operation rather than the reactivity differences. It was noted above that Naredi and Pisupati (2008) only found a minor contribution from the char-CO_2 reaction. Shaddix and Molina (2008) have pointed out that direct gasification of char carbon by CO_2 could contribute to the overall gasification of the char surface, increasing the burn rate at a given temperature. However, the endothermicity of

the Boudouard reaction would tend to lower the char temperature and thereby lower the overall burning rate. This could provide an alternative to the suggestion by Borrego and Alvarez (2007) that CO_2 could be involved in cross-linking at the char surface.

SKIPPY (Surface Kinetics in Porous Particles) modelling by Shaddix and others (2009b) has demonstrated that the high endothermicity of the reaction of CO_2 with char has a strong impact on the char particle temperature, even for assumed reaction rates that fail to yield substantial flux for CO_2 gasification. When the char particle is otherwise burning at a high temperature relative to the surrounding (as, for example, during oxygen-enriched combustion), this decrease in char temperature results in a strong decrease in the overall char consumption rate. For conditions in which the char particle temperature is close to ambient (for example, during combustion in vitiated air), activation of the CO_2 gasification reaction results in an augmented char consumption rate, even as the char temperature drops substantially.

Rathnam and others (2006) suggest that the differences in their observations compared with those reported by Liu and others (2005) and Alvarez and others (2005) could be due to the higher gas temperatures (1400°C) and that this could be the reason for the higher gasification rates and hence slightly higher burnouts. However, Brix and others (2009) also conducted experiments at 1400°C and concluded that gasification of char by CO_2 does not seem to affect conversion even at high temperatures and low oxygen concentrations. Although, at these conditions the lower diffusion coefficient of oxygen in CO_2 appears to slow down the reaction rate compared to combustion in N_2.

Rathnam and others (2007) found that the char gasification process was significant and occurs at temperatures above 800°C. It was also especially significant at very low O_2 levels (2%). They suggested that char gasification will aid the better burnout of char during the later stages of combustion in a practical combustion environment furnace. No significant differences were observed between the air and oxyfuel cases at higher O_2 levels (10% and 21%). Rathnam and others (2009b) have pointed out that, while a lower reactivity is expected in O_2/CO_2 conditions due to the lower O_2 diffusion rate in CO_2, a higher reactivity as seen in their study of three coals means that the char-CO_2 gasification reaction contributes significantly to the higher reactivity in O_2/CO_2 conditions. In turn, the higher reactivity in O_2/CO_2 conditions means that burnout similar to in O_2/N_2 conditions may be obtained with lower oxygen consumption. Reduction in the oxygen consumption reduces the oxyfuel plant operating costs.

Rathnam and others (2009a) have measured the reactivity of four pulverised Australian coals under simulated air (O_2/N_2) and oxyfuel (O_2/CO_2) environments using a drop tube furnace (DTF) maintained at 1673 K and a TGA run under non-isothermal (heating) conditions at temperatures up to 1473 K. The oxygen content was varied from 3 to 21 vol% in O_2/N_2 and 5 to 30 vol% in O_2/CO_2. The apparent volatile yield measured in CO_2 in the DTF was greater than in N_2 for all the coals studied. Pyrolysis experiments in the TGA also
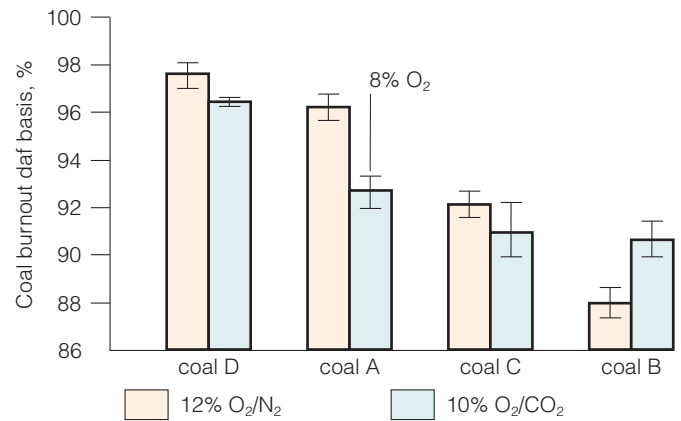

Figure 3 **Burnouts in air and oxyfuel conditions in DTF at 1673 K** (Rathnam and others, 2009)

revealed mass loss in a CO_2 atmosphere, not observed in a N_2 atmosphere, at relatively high temperatures. The coal burnout measured in the DTF at several O_2 concentrations revealed significantly higher burnouts for two coals (A and B) and similar burnouts for the other two coals (C and D) in oxyfuel conditions. TGA experiments with char also revealed higher reactivity at high temperatures and low O_2 concentration. It was concluded that the results were consistent with a char-CO_2 reaction during the volatile yield experiments, but additional experiments were necessary to resolve the mechanisms determining differences in coal burnout. In addition, it was clearly pointed out that the results were specific for the four coals tested at the temperatures considered. Considering the data provided, the only obvious difference in the two coals with significant improvements (A and B) is their lower volatile matter content, 25.6 and 24.5 wt% compared with 40.5 and 33.8 wt% in the other two coals. Coal B was also a high ash coal. The coal ranking for percentage increase in apparent volatile yield in CO_2 compared with N_2 matched the ranking observed in coal burnout but not the differences observed in air and oxyfuel conditions. Figure 3 shows the coal burnout values at fairly low O_2 concentrations and suggests that oxyfuel combustion may significantly enhance the burnout of lower reactivity coals such as coal B.

Some support for this tentative conclusion comes from a study of oxyfuel combustion of high rank coals by Borrego and others (2007a,b) using a drop tube furnace at 1300°C with an oxygen concentration in CO_2 ranging from 0% to 30% to prepare chars. The comparison of the burnouts under air (21% O_2 in N_2) against the burnout data for 21% O_2 in CO_2 indicated rather similar burnouts for most of the samples under both operating conditions except for the highest rank anthracites that showed better performance in an oxyfuel atmosphere. This is shown in Figure 4 in which the burnouts in air (21% O_2 in N_2) are plotted versus the burnout data for 21% O_2 in CO_2. The results indicate that the blend (BL) and the lowest rank anthracite (AA) had rather similar conversion under oxyfuel and air atmospheres whereas the highest rank anthracites (AB and AC) burned comparatively better under oxyfuel conditions. This is a different result from that observed for high volatile bituminous coals using the same device and conditions by Alvarez and others (2005) in which lower burnouts for oxyfuel chars were observed.
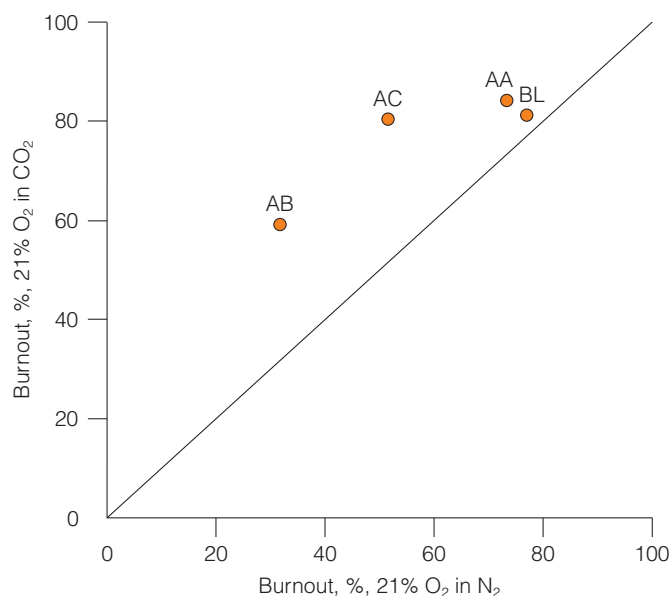
Oxyfuel combustion of pulverised coal

Figure 4   Burnouts in air and oxyfuel conditions at similar oxygen concentrations (Borrego and others, 2007a)

Results obtained by TGA and a drop tube furnace by Naredi and Pisupati (2009) have also suggested that a low volatile rank coal is more reactive towards CO_2 compared with a high volatile rank coal. A slightly higher CO emission was observed during combustion in a 21% O_2/CO_2 mixture due to char-CO_2 reaction. A computational fluid dynamics combustion model was able to describe both the CO emission and char burnout. Higher reactivity of the low volatile coal towards CO_2 and higher activation energy for char-CO_2 reaction suggests that oxyfuel coal combustion may be more suitable for specific coal types.

Against this must be set the report from another paper by Rathnam and others (2008) that a significantly higher burnout was observed for a lignite coal under oxyfuel conditions. The effect of coal rank probably needs further study. Babcock and Wilcox has used an entrained flow reactor to study the chars formed from different rank coals under oxyfuel combustion conditions (Zeng and others, 2008). They found that, compared with a nitrogen atmosphere, coal devolatilisation under a CO_2 atmosphere is greatly affected by the CO_2 gasification reaction, which leads to a higher mass release. The effect of CO_2 gasification is coal rank dependent. For the Illinois No 6 bituminous coal, CO_2 gasification affects devolatilisation in the early stage before cross-linking reactions occur, and the effect diminishes with increasing pyrolysis temperature. For the lower rank coals including Powder River Basin (PRB) coal and Saskatchewan lignite, the CO_2 gasification effect is significant at high pyrolysis temperatures where catalytic gasification by the minerals is important. At high temperatures, the gasification rate of lower rank chars could increase despite the possibility of having low non-catalytic reactivity. The effect was more marked in the higher ash lignite (13.4% dry) than in the subbituminous PRB coal (6.2% dry). Using a DTF, Sun and Snape (2009) have also found that coal devolatilisation under oxyfuel firing conditions at 1300ºC produces significantly higher yields (5–20 wt%) of volatiles than in air firing. They also attributed this to CO_2 char gasification reactions. The increase in

volatiles varied considerably, the largest increase (~20 wt%) being for the subbituminous Indonesian Kideco coal, the most reactive of the six coals studied (five bituminous and the Kideco subbituminous). The lowest increases were around 5–8 wt% for the less reactive South African Kleinkopje and the UK Thoresby coals. At 900ºC and 1100ºC the effects of oxyfuel firing on volatile yields was negligible. DTF char re-firing tests demonstrated that at 1300ºC, char burnout is faster in oxyfuel conditions than in air, again attributed to the CO_2 char gasification reactions. However, at 900ºC and 1100ºC, CO_2 generally retarded char burnout, attributed to the lower diffusivity of O_2 in CO_2 than in N_2. It was noted that the different oxyfuel char combustion behaviour for different coals was indicative of both mineral and petrographic effects and requires further investigation.

Rehfeldt and others (2009) have reported that the CO concentration in the flame is particularly high in the case of oxyfuel combustion of Lusatian lignite as a result of gasification reactions in the oxygen lean flame regions. The CO concentration was however similar for both air fired and oxyfuel combustion of South African Tselentis bituminous coal. Al-Makhadmeh and others (2009) have also found that, when Lusatian lignite is pyrolysed in a CO_2 environment, the CO concentration is significantly higher than the H_2 gas concentration. This was attributed to the Boudouard and CO shift reactions. At temperatures above 850ºC, the overall mass release during pyrolysis in a CO_2 environment is higher than in a nitrogen environment, again attributable to the char-CO_2 gasification reaction. As expected, the volatile release decreases as the rank of the coal increases in both environments.

Using TGA, Kaß and others (2009) investigated the combustion behaviour of a predried lignite. They found that, with increasing combustion temperatures the combustion time decreased. Despite the same oxygen concentrations in the combustion gas the combustion time in an O_2/CO_2 atmosphere was apparently shorter than in air for temperatures higher than 1100 K. They suggested that in air only oxygen acts as a reactant but in an O_2/CO_2 atmosphere the carbon dioxide reacts with the carbon as well. Especially in oxygen lean atmospheres as occurring on the bottom of the combustion crucible the Boudouard reaction increases the mass lost of char. Tappe and Krautz (2009a) studied two types of dry lignite burned in different gas mixtures consisting of various O_2/CO_2 concentrations. They found that the ratio of combustion time in an O_2/CO_2 atmosphere to that in air was in the range 0.425–1.03. They attributed this to the Boudouard reaction of CO_2 with the lignite carbon. Figure 5 shows an Arrhenius diagram for one of the lignites. For oxygen concentrations lower than 21 vol% and temperatures between 1073–1273 K (7.9 x 10^{-4} – 9.3 x 10^{-4} K^{-1}), the chemical reaction appears to dominate the combustion process, as the combustion velocity is strongly influenced by temperature. At higher temperatures (1273–1353 K), the combustion times depend less on the temperature. This indicates that in this region diffusion procedures are limiting the combustion process and therefore the combustion velocity. For oxygen concentrations higher than 21 vol% the combustion times were influenced by the temperature in the whole investigated region. There is no change in the slope of
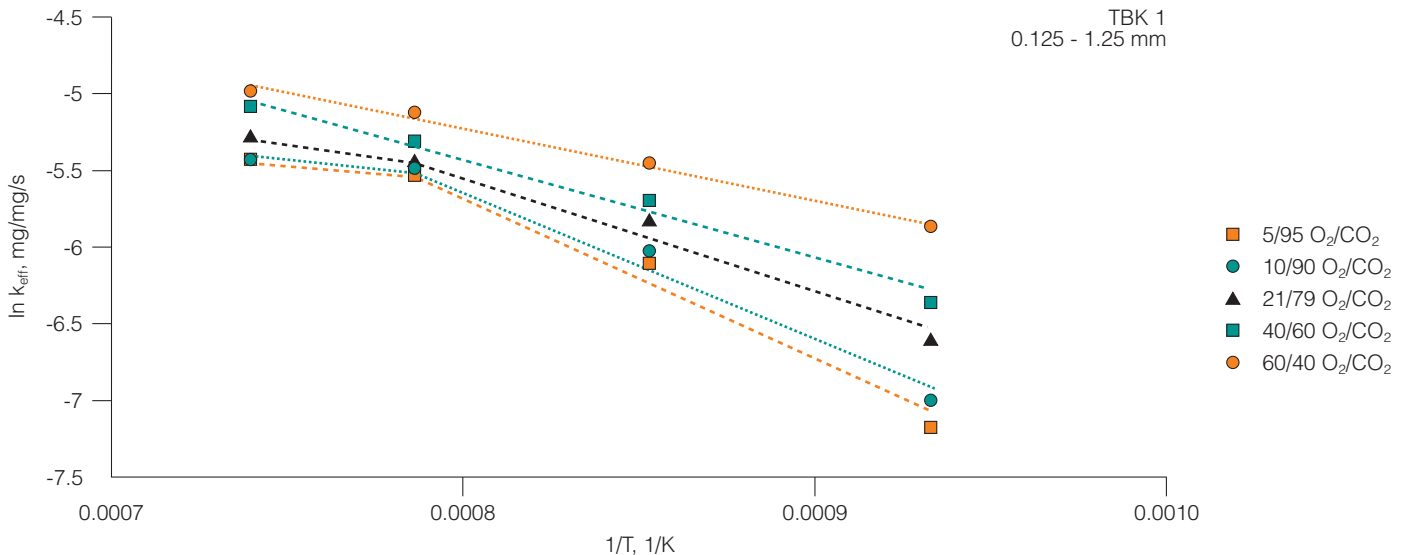
Figure 5   Arrhenius diagram for TBK1 lignite (Tappe and Krautz, 2009a)

the lines at 1273 K as in the lower oxygen concentrations. Thus, the combustion is controlled by chemical reaction even at high temperatures. At high oxygen concentrations, the driving forces for diffusion are high such that even at high temperatures the molecular mass flow is adequate and does not limit the combustion. This trend was observed for both lignites.

In a further study using bituminous coals in addition to the lignites, Tappe and Krautz (2009b,c) found that lignites had shorter combustion times than the bituminous coals. Tappe and Krautz (2009c) explained the reduction of burnout time by the reaction mechanisms which are taking part. As well as oxygen, the CO_2 is acting as a second oxidiser of the fixed carbon so that CO is produced. Thus, the time until the fixed carbon is oxidised is shortened. Gas analysis confirmed that increased CO concentrations in the flue gas were present during combustion in O_2/CO_2 atmospheres.

2.3   Heat transfer

Buhre and others (2005) point out that the major contributor of the heat transfer from a flame from conventional fuels (and conventional combustion) is thermal radiation from water vapour, carbon dioxide, soot, and carbon monoxide. In oxyfuel combustion with RFG the concentration of carbon dioxide and water vapor is increased significantly, the radiative heat transfer from the flame will change. Carbon dioxide and water have high thermal capacities compared with nitrogen which will lead to an increase in the heat transfer in the convective section of the boiler. This is offset by the lower amount of gas passing through and the increased heat transfer in the radiative section of the boiler. The differences in heat transfer in oxyfuel combustion and conventional combustion have not yet been fully resolved. Khare and others (2005) calculated that oxygen concentrations at the burner inlet should range from 25–38 vol% to achieve similar predicted furnace heat transfer as the air case (21% O_2). Makino (2006) reported that the furnace heat absorption in the air case was matched in the oxyfuel case at an O_2 concentration of 30%.

Tan and others (2006) have reported studies in a 0.3 MWth vertical combustor test facility in which heat transfer was evaluated by measuring heat flux in the furnace using a specialised probe. It was found that with an O_2 concentration of 35% in the combustion feed gas with the rest being mainly CO_2, the O_2/RFG combustion produced slightly higher heat flux and in-furnace temperatures compared with air firing at the same heat input. This enhancement of heat transfer resulted directly from the higher O_2 concentration in the feed gas and, by simply reducing the O_2 concentration slightly, the measured heat flux and temperature profiles with O_2/RFG combustion could be made to match those for air firing. In O_2/RFG tests with 28% of O_2 in the feed gas, the measured heat flux and temperature profiles were slightly lower than air firing. It was suggested that this is an advantage of oxyfuel firing, since it could allow a somewhat more flexible selection of fuels, especially for coal-fired power plants.

Radiative heat transfer in lignite fired oxyfuel flames has been studied by Andersson and others (2008b) in the Chalmers University 100 kW test facility. The flue gas recycle rate was varied to keep the stoichiometry the same in all cases but the oxygen fraction in the RFG ranged from 25 vol% to 29 vol%. It was found that the temperature, and thereby the total radiation intensity of the oxyfuel flames, increased with decreasing flue gas recycle rate. The ratio of gas and total radiation intensities increased under oxyfuel conditions compared with air firing. However, when radiation overlap between gas and particles was considered the ratios for air firing and oxyfuel conditions became more similar, since the gas-particle overlap is increased in the CO_2-rich atmosphere. A large fraction of the radiation in the lignite flames studied was emitted by particles whose radiation was not significantly influenced by oxyfuel operation. Therefore, an increment of gas radiation due to higher CO_2 concentration was not evident because of the background of particle radiation and the total radiation intensities are similar during oxyfuel and air fuel operation as long as the temperature distributions are similar.

Calculations by Liu and others (2008) have indicated that, in order to achieve the same radiation heat transfer quantity (RHTQ) as in air combustion, the inlet oxygen concentration

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should be 29.2% with dry cycle of RFG (only CO_2 and O_2) or 28.4% with wet cycle (RFG contains H_2O).

Radiative and convective heat transfer in oxyfuel combustion of coal was investigated in a once through system by Smart and others (2009, 2010b). The experimental furnace used for the work was the RWE npower's Combustion Test Facility (CTF) with a 0.5 MWth burner operated without using its low NOx capability. For all experiments, the O_2 concentration in the primary transport stream was maintained at 21 vol%. For the majority of tests, the furnace exit O_2 was driven to 3 vol% and 6 vol% for all recycle ratios studied. Each of the experimental Russian and South African coals were also fired on air for comparative baseline data acquisition. The effects of varying the recycle ratio were studied. It was varied between 65% and 75% over the course of the experimental programme. The obtained data clearly showed that the radiative heat flux profiles can be significantly manipulated by varying the recycle ratio. For the coals studied, the peak radiative heat flux increased significantly as recycle ratio decreased. The data also showed that a radiative heat flux profile similar to air firing can be obtained for recycle ratios between 72% and 75%. Rossi and others (2009) have also studied the effect of the recycle ratio and found, in agreement with Smart and others (2009, 2010b), that the effect of increasing R is to decrease the heat transfer efficiency. At 68% R the heat transfer properties of the oxyfuel flames, are close to that of baseline flame in air.

Figure 6 shows a plot of peak radiative heat flux, convective heat flux and calculated adiabatic flame temperature against recycle ratio for two coals. The data are normalised to air operation by taking the ratio of peak radiative heat fluxes under recycled conditions to that of air. It is apparent from the data that the radiative and convective heat transfer

components of the combustion and heat transfer process cannot be matched precisely in terms of an optimum recycle ratio compared with the performance in air firing. However, it was suggested that there is a good indication that an acceptable operational range exists in terms of matching the radiative and convective heat transfer components on oxyfuel. Although there is a certain degree of scatter in the data, possibly due to furnace ash buildup, particularly at the higher recycle ratios, the results indicate that a recycle ratio of between 72% and 74% gives a similar radiative and convective heat flux component. In the presentation slides it was suggested that recycle ratios in the area between 70% and 75% could be suitable for retrofit applications but that new build oxyfuel power plants could use ratios below 70%. Recycle ratios above 75% should be avoided in all cases.

Detailed process analysis and calculations have been performed by Zhou and Moyeda (2010) to evaluate the potentials of converting a conventional boiler to an oxyfuel boiler with flue gas recycle. The study indicated that the optimal wet flue gas recycle ratio depends on the existing boiler exit O_2 and fuel properties and is in general around 0.7–0.75, in agreement with Smart and others (2010a).

2.4   Comments

This chapter has considered the effects that oxyfuel firing has on the combustion of pulverised coal. It is generally agreed that ignition is retarded but that this can be countered by increasing the oxygen content of the comburent gases. There can also be a lower flame propagation velocity due to the higher specific heat of CO_2 compared with N_2. The effects on burnout are less clear cut – in general, it has been found that burnout is lower in oxyfuel conditions but, again, this can be
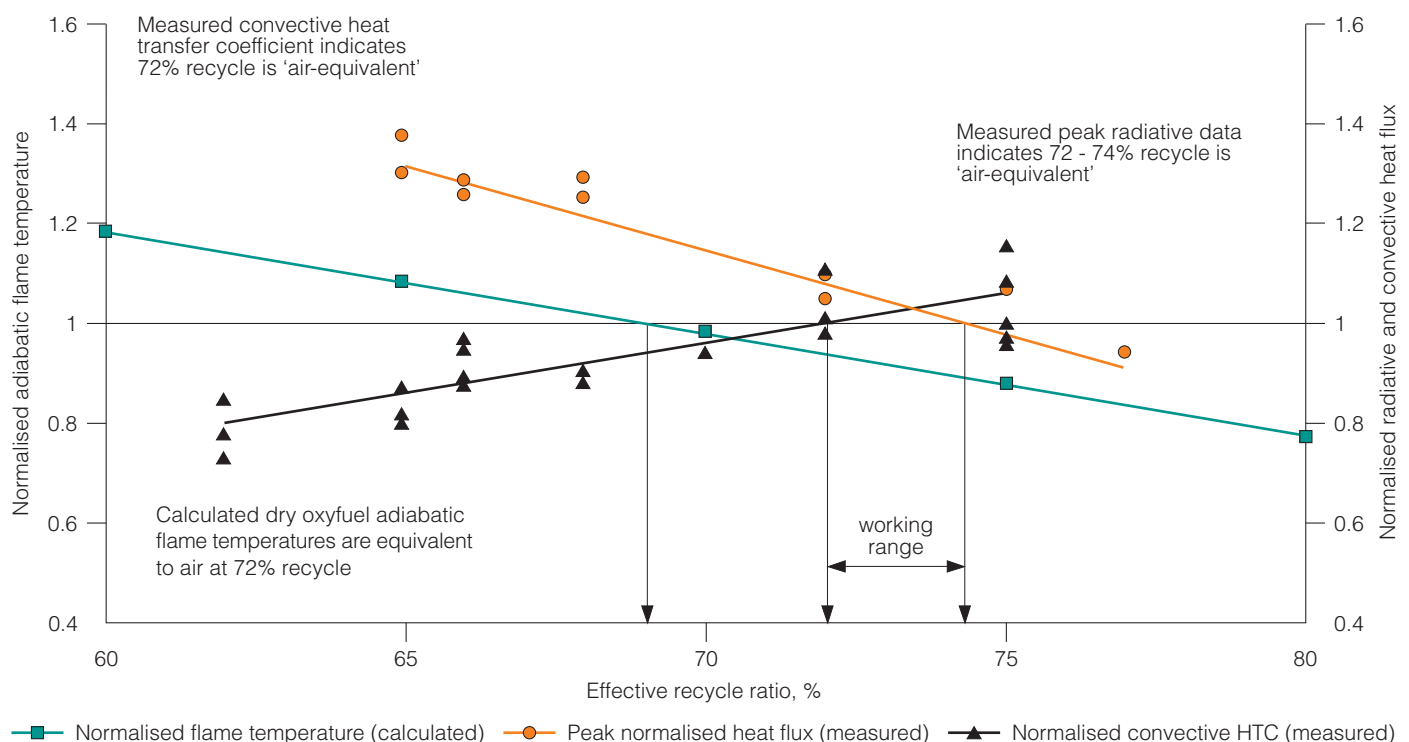

Figure 6   Peak radiative heat flux, convective heat flux and calculated adiabatic flame temperature versus recycle ratio for two coals (Smart and others, 2009)

remedied by increasing the amount of oxygen. However, there is evidence that burnout may be enhanced for lower reactivity coals. There is evidence for char-CO_2 gasification reactions that may also be coal dependent but it is also difficult to assess how important these reactions are. Heat transfer has been found to be influenced by the flue gas recycle ratio (R); the effect of increasing R is to decrease the heat transfer efficiency.

3   Burner and boiler design

The recycling of flue gas and the injection of the oxygen as comburent (oxidant) add extra complexity to the design and operation of the oxyfuel burners and boilers.

Tan and others (2005), Marion and others (2009), and Farzan and others (2009) have all reported that the following factors are critical to the design and operation of the oxyfuel burners and boilers:
- flue gas recycle ratio (flue gas recycle flow rate);
- flue gas composition;
- manner of flue gas recycling (windbox and OFA design);
- oxygen injection (method of injection and manner of distribution)
- oxygen (comburent) heating.

Marion and others (2009) also noted additional parameters that should also be considered in the design of tangential burners, including:
- burner tilt angle;
- burner throat gas velocity.

These variations would therefore require an understanding of the effects of the recycling of the flue gas and the oxygen concentration of the comburent on the following:
- oxygen concentration of the flue gas;
- unburned carbon in ash;
- emissions (SOx, NOx, CO);
- flame shape and length;
- heat transfer profile.

3.1   Oxyfuel burner types

The current generation of burners for oxyfuel fired power plants can be generally classified into two types based on the manner of how the oxygen and recycled flue gas are introduced.

The first type of oxyfuel burners are burners designed with the main comburent consisting of a mixture of recycled flue gas and oxygen prior to the introduction to the windbox – premixed oxygen injection. The oxygen content in the

windbox could normally be operated between 28 and 40 vol% (wet basis) and could be higher depending on the burner operation and coal type. However, the overall stoichiometry through the boiler would depend on the heat transfer profile. As discussed in Chapter 2, it has been reported that an overall stoichiometry through the boiler having about 28–30 vol% O_2 (wet basis) would provide a flame and heat transfer profile very similar to that of conventional air fired burners.

The second type of oxyfuel burners are burners in which the oxygen are introduced separately via separate channels – direct oxygen injection. It should also be expected that the overall stoichiometry through the boiler would be dependent on the heat transfer profile of the boiler. Tan and others (2005) reported on the early work of IHI in which part of the oxygen required was introduced through a direct oxygen lance in the centre of the burner which resulted in lower CO emissions and unburned carbon in ash. Alstom have produced a burner with direct oxygen channels surrounding the primary air/coal feeding port (Kruger and Marion, 2008).

3.2   Flue gas take off points

Figure 7 illustrates five possible locations where flue gas could be recycled (points 1–5) and five possible locations where oxygen could be injected into the boiler (points A–E).

In an oxyfuel combustion system, at least two streams of flue gas to be recycled are required. These are primary RFG and the secondary RFG. Additionally, where the oxyfuel burners and boilers require tertiary air or overfire air, then additional streams of recycled flue gas are necessary.

The choice of location on where the flue gas could be taken and recycled to the boiler can affect the operation of the burner and boiler. This could eventually affect the thermal efficiency of the power plant due to the required preheating and flue gas processing steps. The report produced by Mitsui Babcock for the IEA GHG (2005) has described in detail their evaluation of the choice of the location of the take off point of
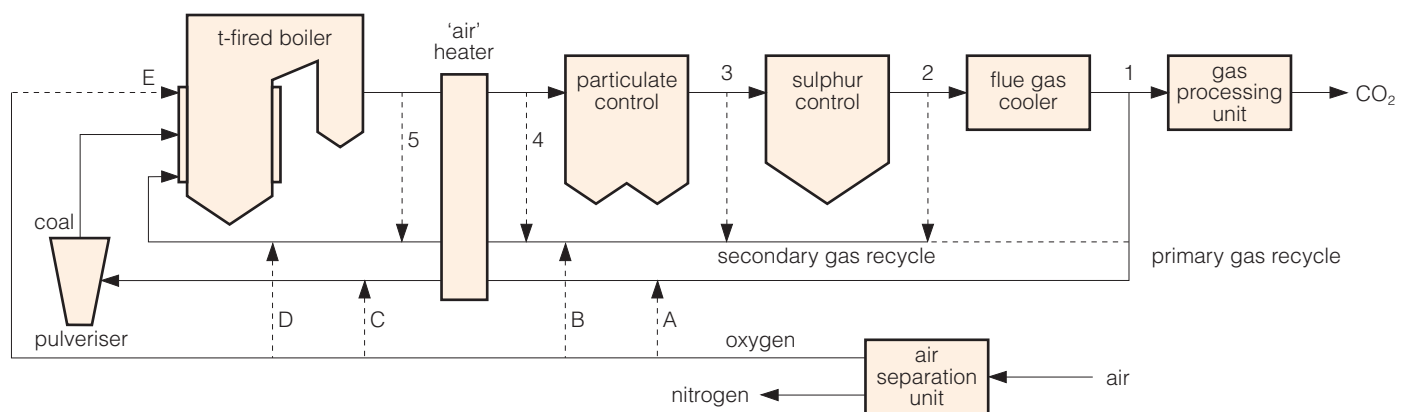

Figure 7   Flue gas off take and oxygen injection points which affect the design of the oxyfuel burner and boiler (Marion and others, 2009)

the flue gas to be recycled for both the primary and secondary RFG.

Flue gas recycled at point 1 is partially dried by employing direct contact coolers. This is generally used as primary recycled flue gas replacing air for the transport gas of the coal mills. The amount of flue gas taken and deliver to the coal mill is totally dependent on the minimum amount of transport gas required. Generally, after the cooler, the flue gas is saturated at around 30–40ºC and would have most of its SO_3 and HCl effectively removed whilst the level of SO_2 would depend on whether flue gas desulphurisation was employed. Prior to being introduced into the coal mill, the primary RFG is normally preheated to dry the coal but, in oxyfuel combustion, it is also necessary to ensure that it is above the dew point temperature.

Farzan and others (2009) have studied the performance of their coal mill when operating under oxyfuel conditions and concluded that there could be a possibility of reducing the primary flow with respect to the coal flow as shown in Figure 8. It should be noted that this reduction in flow of the primary flow is dependent to the degree of dryness of the primary recycled flue gas.

If the flue gas at point 1 is also used as the main comburent (that is, as secondary RFG), then significant heat is needed to preheat the flue gas, consequently reducing the efficiency of the power plant. However, this would also reduce significantly the various acid gases and moisture content present in the flue gas thus minimising any corrosion problem in the boiler and along the ducts of the recycled flue gas.

Thermodynamically, the recycling of flue gas at points 4 and 5 could be more efficient due to less preheating and flue gas processing required. However, this would be impractical due to the high dust loading.
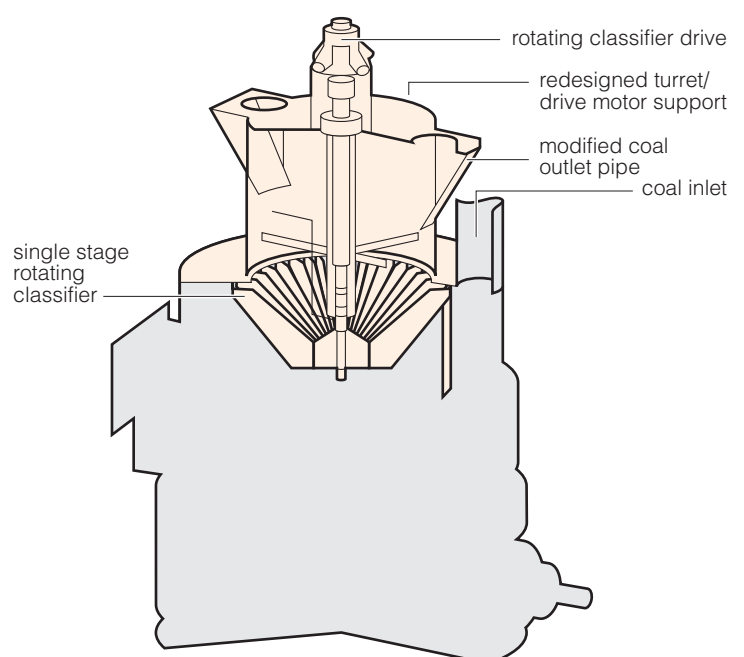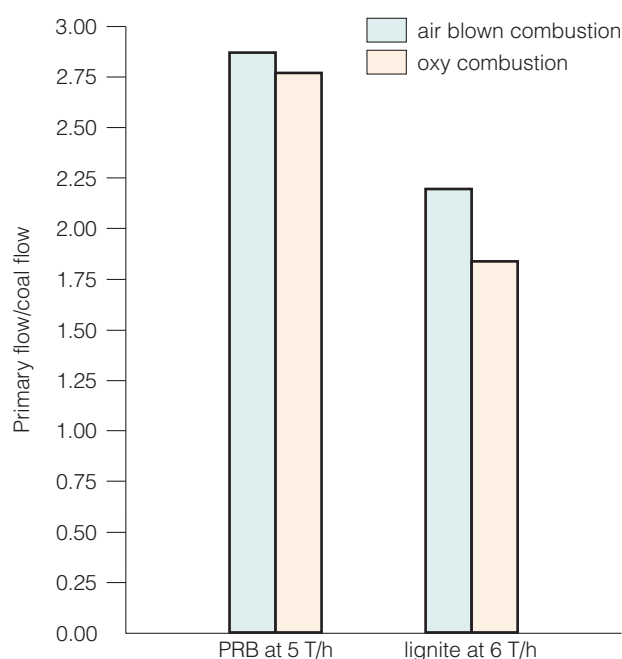
Points 2 and 3 would be the typical take off points for the recycled flue gas for the secondary/tertiary RFG or OFA streams. At point 2, most of the sulphur species would be removed. The impact of a lower amount of sulphur species in the recycle flue gas stream has been described in the presentations by Wang and Grubbström (2009), Dernjatin and Fukuda (2009), and Kawasaki and others (2009).

Some variations to the flue gas off take position should be expected. For example, flue gas desulphurisation is not used in coal-fired power plants in Australia, therefore having the recycled flue gas take off location limited to points 1 and 3 are the only possible options.

3.3   Oxygen injection

To ensure complete combustion as in any air fired coal burner, excess oxygen should be introduced into the boiler. The fundamental principle is to maintain lower overall stoichiometry to reduce oxygen demand from the air separation unit. Similar to an air fired coal furnace/boiler, it is expected that first generation of oxyfuel boilers would operate an overall stoichiometry through the furnace/boiler of 1.15 to 1.20 as it is highly dependent on the boiler and burner design.

Current work done by Alstom at their Boiler Simulation Facility has shown that the overall stoichiometry through the furnace/boiler during oxyfuel combustion could be operated as low as 1.07 and as high as 1.15. It was found that maintaining the same O_2 concentration at the flue gas exit but varying the global O_2 in the oxidant will also vary the overall stoichiometry. Therefore, it is essential to note that maintaining the same stoichiometry through the furnace/boiler as air firing would lead to higher outlet O_2 concentration at the flue gas exit depending on the recycle rate (Nsakala, 2010).

Figure 8   Primary flow/coal flow for a single stage rotating classifier type coal mill (Farzan and others, 2009)

Additionally, since it is desirable to operate the oxyfuel burner with lowest possible overall stoichiometry through the furnace/boiler in order to reduce oxygen supplied, nonetheless, this parameter would be limited by the level of CO emissions and loss of ignition (carbon in ash).

However the manner on how the oxygen is introduced has produced variations in the design and operation of the burners. It should be expected that control systems would be more complex than for typical air fired burners. This should consider factors such as:

- excess oxygen level (the percentage O_2 content at the boiler exit);
- flame shape and length criteria;
- ignition and flame stability criteria;
- heat transfer profile criteria;
- CO emission;
- unburnt carbon in ash.

One of the major differences between air fired burners and oxyfuel burners is the cost of the oxygen which has to be produced in the air separation unit. The cost of the produced oxygen means that it is desirable that excess oxygen level is kept as low as possible without affecting the performance and safety of the boiler.

As illustrated in Figure 7, Marion and others (2009) presented five possible locations where oxygen could be introduced. One of several factors to be considered during oxyfuel combustion would be the mixing property of the recycled flue gas and oxygen.

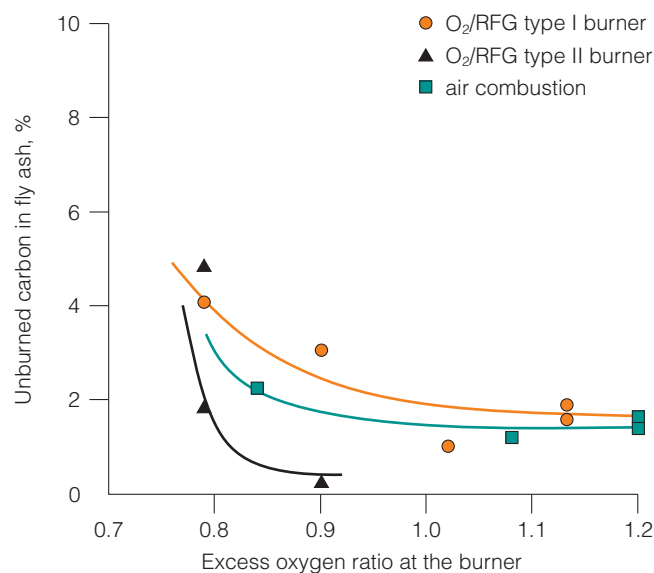At points A and C, oxygen is premixed with the primary RFG.
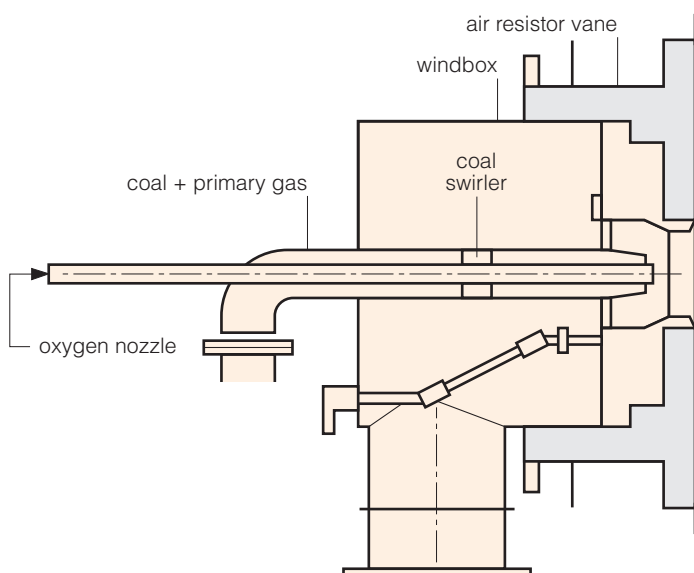
However, the amount of oxygen that could be introduced at this point would be limited by safety considerations since the primary RFG will be used in the coal mill as 'transport gas'. Typically, this would be limited to a maximum of 21–25 vol% (db). At point A, the oxygen introduced would be preheated together with the primary RFG, whilst at point C, oxygen is not preheated and therefore could effectively lower the final temperature of the RFG after the gas-gas heater.

At points B and D, oxygen is premixed with the secondary RFG. The amount of oxygen added to this stream would be determined by design of the burner. Typical oxygen concentration on these streams should be between 30 and 40 vol% (wet basis). It is generally observed that if less oxygen has been introduced into the primary RFG, the addition of more oxygen through the secondary RFG becomes necessary to ensure better flame stability and intensity. The addition of oxygen at point D (just after the gas-gas heater) could affect the final temperature of the comburent introduced into the secondary ports. It is always desirable to maintain higher temperature in the secondary RFG to ensure better ignition and flame stability, thus it should be expected that comburent temperature would be higher at point B than at point D). However, the benefit of preheating the oxygen together with the secondary RFG should be balanced with the loss in the overall thermal efficiency of the power plant versus the flame stability.

At point E, it should be expected that oxygen has been introduced as 100% through oxygen lances. This could be introduced in an annulus surrounding the coal injection port or an oxygen lance central to the coal injection port (for example the IHI burner) or introduced in various oxygen lances within the annulus of the secondary port surrounding

combustion conditions
coal: coal A
coal feed rate: 100 kg/h
flue gas oxygen: 3.5%
wind box oxygen: 30% (O_2/RFG combustion)
pure oxygen flow rate: 20 m³/h (O_2/RFG combustion)

burner type (O_2/RFG combustion)
type I: pure oxygen supply from the centre of the burner
type II: pure oxygen swirly supply from the centre of the burner

Figure 9   Impact of the oxygen lancing at the centre of the burner on the performance of the IHI burner
(Makino, 2006; Tan and others, 2005)

air operation   oxyfuel operation
pre-mixed oxygen   oxyfuel operation
direct oxygen injection

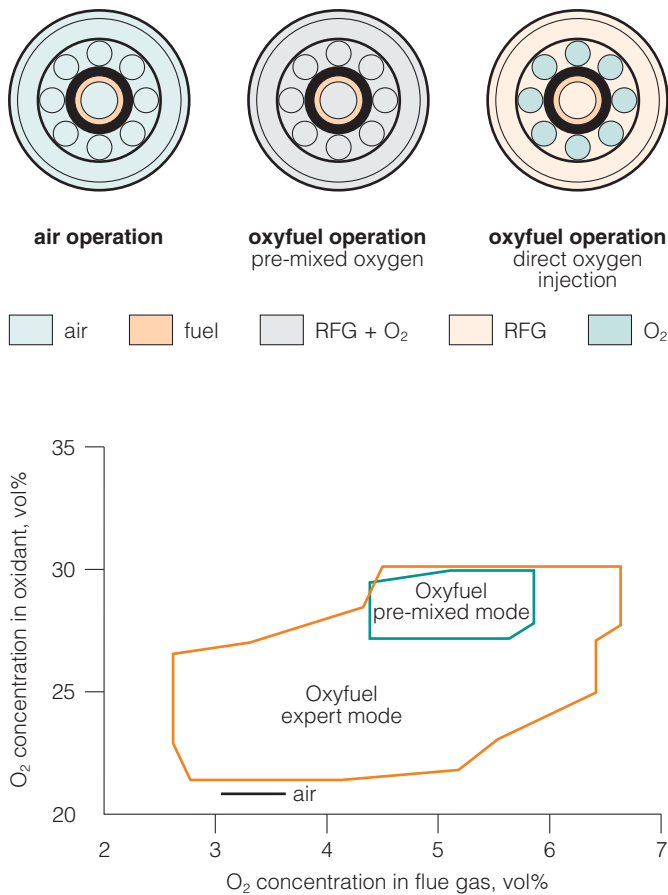air   fuel   RFG + O_2 RFG O_2

Figure 10 Operating envelope of the Alstom burner in premix mode (Kluger and others, 2009)

the coal injection port (for example, Alstom's 'Type 1' burner used at Schwarze Pumpe).

Tan and others (2005) reported earlier work done by International Flame Research Foundation which found that the heat transfer profile was not affected by the oxygen concentration of the primary RFG. The results showed no discernible differences between 3.3 vol% (db) and 16 vol% (db). However, the good stability of the flame achieve from the experimental campaign and its intensity was compensated by higher oxygen concentration in the secondary RFG. It was noted that secondary RFG needed to have an oxygen concentration of ~48 vol% (db) when operating under oxyfuel mode in order to achieve a similar heat transfer profile to the air fired operation mode.

Uchida and others (2008) presented their work on oxyfuel indicating an overall stoichiometry having 27 vol% (wet basis) oxygen through the boiler, but the composition of the secondary RFG was about 33 vol% (wet basis). The earlier work performed by IHI as reported by Makino (2006) and Tan and others (2005) had found that the use of oxygen lancing significantly improved the burner performance and achieving better burnout once the amount of oxygen was increased (as shown in Figure 9).

Kluger and others (2009) reported the operating envelope of their burner operation with three different operating modes using their type 1 burner in which oxygen is premixed with RFG. Figure 10 illustrates the operating envelope indicating

the oxygen content of the flue gas exiting the boiler and oxygen content of the secondary RFG comburent.

3.4   Amount of recycled flue gas

Tan and others (2005) and Buhre and others (2005) have noted that one of the primary considerations in retrofitting boilers for oxyfuel operation is to match the heat transfer profile in the radiative and convective sections of the boiler. This could be affected by the amount of flue gas recycled, the moisture content and temperature of the recycle flue gas.

The review of Tan and others (2005) described the impact of the amount of recycled flue gas on the flame shape and length as shown in Figure 11. They have clearly indicated that there exists a limit of how much flue gas could be recycled and the start of flame lift off and instability. It was also described in the report that when the recycled flue gas is reduced, the flame length becomes shorter and more intense. However, it should be noted that these observations were made when the velocity of the comburent through the burner during oxyfuel combustion was maintained at the same velocity when operating under air firing conditions. The observation regarding the impact of the level of the amount of recycled flue gas as described by Tan and others (2005) has been confirmed by Smart and others (2009) as discussed in Section 2.3 and shown in Figure 6.

3.5   Burner aerodynamics

A general view is that, if a burner which has been optimised for coal combustion is used for oxyfuel combustion, then this will lead to flame instability and poor burnout. This, as has been discussed earlier, can be improved by increasing the oxygen concentration to achieve similar reaction rates and temperature levels to a pulverised fuel flame in air. However, as Toporov and others (2007) have pointed out, this could also be achieved by modifications to the burner aerodynamics. Using computational fluid dynamics (CFD) modelling, they studied two different burner designs. The modelling demonstrated the possibility of burning pulverised coal successfully with lower than 21 vol% O_2 content in the CO_2/O_2 mixture. Tests using an experimental burner had shown that the ratio between the incoming cold coal-gas mixture and the recirculated internally hot flue gases was critical for the flame stabilisation. The higher specific heat (c_p) of the gas mixture delays the heating of the pulverised coal-gas mixture thus influencing the particle devolatilisation, ignition and combustion. The oxyfuel burner design and operating conditions were modified in such a way that appropriate aerodynamic interactions in the near burner region were created in order to develop conditions for enhanced particle ignition, namely:
- fast particle heating, volatile release and ignition;
- stabilisation of the Boudouard reaction;
- compensation for high c_p of the oxidising mixture.

It was considered that the combined effect of stronger internal recirculation and a smaller amount (but large enough to create the recirculation zone) of highly swirled secondary flow
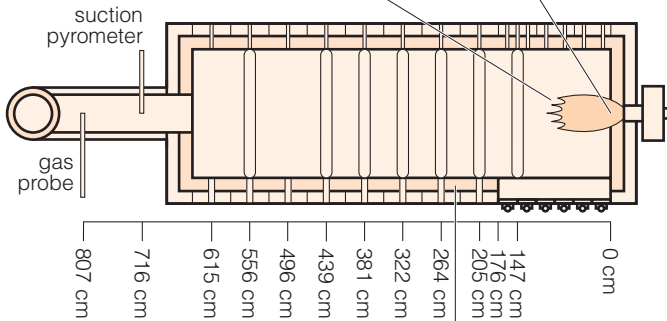
Oxyfuel combustion of pulverised coal

normal air fired operation

combustion region
- inflame measurements indicate flame length to be approximately $x/D_O = 4$ (≈1 m from quarl throat)

ignition region
- short, intense type 2 flame stabilised on the quarl with closed internal recirculation zone
- swirl number = 1.0
- very stable flame

suction pyrometer

gas probe

807 cm | 716 cm | 615 cm | 556 cm | 496 cm | 439 cm | 381 cm | 322 cm | 264 cm | 205 cm | 176 cm | 147 cm | 0 cm

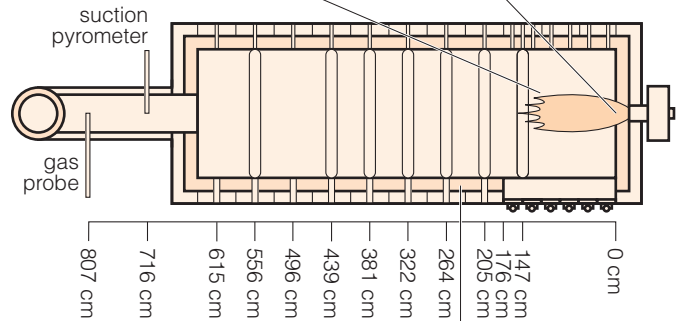- total heat extraction efficiency measured to be 54.5%

O$_2$-RFG flame with recycle ratio = 0.58

combustion region
- observations indicate flame length slightly longer than baseline (could be due to lower swirl number)
- measurements indicate combustion completed at approximately $x/D_O = 4$ (≈1.0 m)

ignition region
- stable flame igniting inside quarl
- internal recirculation zone more clearly defined than at higher recycle ratios
- flame comparable to type II, however, not as compact
- intensity comparable to baseline due to similar flame temperature

suction pyrometer

gas probe

807 cm | 716 cm | 615 cm | 556 cm | 496 cm | 439 cm | 381 cm | 322 cm | 264 cm | 205 cm | 176 cm | 147 cm | 0 cm

- total heat extraction efficiency measured to be 57.4%
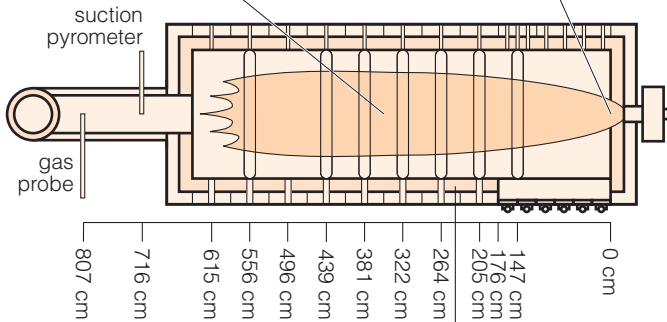- wall temperature stable and comparable to baseline condition

O$_2$-RFG flame with recycle ratio = 0.76

combustion region
- flame length difficult to define combustion occurring throughout entire length of furnace
- evidence of combustion in chimney
- poor combustion efficiency

ignition region
- unstable flame detached from quarl
- weak internal recirculation zone
- low intensity due to low temperature

suction pyrometer

gas probe

807 cm | 716 cm | 615 cm | 556 cm | 496 cm | 439 cm | 381 cm | 322 cm | 264 cm | 205 cm | 176 cm | 147 cm | 0 cm

wall temperatures
- well below baseline condition
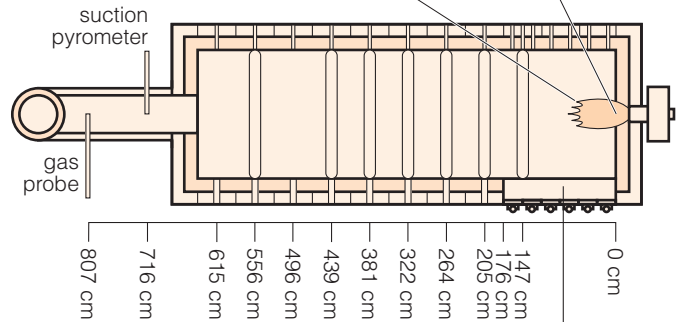- continually decreased, which adversely effected combustion performance

O$_2$-RFG flame with recycle ratio = 0.52

combustion region
- flame length significantly shorter than baseline (even though lower swirl number)

ignition region
- very stable flame igniting inside quarl
- strong internal recirculation zone clearly defined
- flame temperature higher than baseline

suction pyrometer

gas probe

807 cm | 716 cm | 615 cm | 556 cm | 496 cm | 439 cm | 381 cm | 322 cm | 264 cm | 205 cm | 176 cm | 147 cm | 0 cm

wall temperatures
- higher than baseline near burner region

Figure 11 Impact of the amount of recycled flue gas (Tan and others, 2005)

should create the appropriate conditions for fast ignition and flame stabilisation in a CO_2/O_2 atmosphere without increasing the O_2 concentration. The CFD modelling showed that a slight modification to the burner opening (the quarl) could generate a larger and stronger internal recirculation zone compared with the unmodified burner. This allows the hot recirculated gases to enter closer to the burner. The reverse flow draws hot combustion products back toward the burner inlet providing the high heat input required to compensate the higher c_p of the incoming fresh gas mixture. As a result, faster

release and ignition of the volatiles as well as enhanced particle ignition and gasification could be achieved. A modified burner was built and tested under oxyfuel conditions in which a stable flame and good burnout at an O_2 content in the secondary stream of ~23 vol% were obtained. However, further decrease of the O_2 concentration in the burning mixture kept the flame stabilised at the burner, but made the burnout worse. CFD was used intensively as a design tool in order to find the optimal geometry and operating conditions in a redesigned burner which could operate at lower O_2

concentrations. The revised design provided a much bigger internal recirculation zone thus promoting faster particle ignition and flame stabilisation near the burner. Again, a burner was built and tested and a stable flame and good burnout was obtained at an O_2 content in the secondary stream of ~21 vol%. The results of detailed numerical and experimental investigations of a stable oxyfuel fired pulverised coal swirl flame obtained with a 21 vol% O_2 concentration have been reported by Toporov and others (2008). The combustion tests were performed in a vertical pilot-scale furnace (100 kWth).

CFD modelling of a 125 MWth pulverised coal power plant by Chae and others (2009) indicates that it is more difficult to apply oxyfuel combustion of pulverised coal in a corner fired boiler than in a wall fired boiler, mainly due to the low inlet velocity. The inlet velocity in the oxyfuel case is only 70% of the air case and that adversely affects the aerodynamics in the furnace since burner inlet velocities are key parameters for maintaining stable combustion.

3.6   Furnace size

Zheng and others (2005a) have noted that furnace volume is limited more by heat transfer requirements than by those for complete combustion but that, to avoid furnace slagging, it is generally unfeasible to reduce the furnace heat transfer surface significantly. They added that the potential to reduce furnace size of supercritical boilers is much less than for subcritical boilers because they operate at higher temperatures. Supercritical boilers are designed to use more expensive alloys with high service temperature for wall construction to withstand these higher temperatures and increasing the wall temperature could be difficult. Such a high radiant heat flux could very likely cause severe slagging problems in the furnace.

However, modelling studies for a 460 MW bituminous coal fired plant carried out by Seltzer and others (2005) had produced, for the air fired design, a total surface area of all convective banks of 27324 m² compared with 20039 m² for the oxygen fired design. A reduction of nearly 27%. Selzer and others (2006a,b) also calculated that, compared with a supercritical air fired furnace, an oxyfuel furnace with a flue gas recycle flow rate of 56% requires only 65% of the surface area and 45% of the volume. Seltzer and others (2009) point out that oxyfuel combustion is adaptable to a new boiler or a retrofit of an existing boiler. The only boiler modifications that are needed are the addition of a low pressure economiser, gas recirculation duct and fans, O_2 feeding duct, and dampers for O_2 and recirculation flow control. They refer to a conceptual Flexi-Burn™ boiler design developed by Foster Wheeler based on a 780 MWe (gross) supercritical power plant which has been simulated using three-dimensional CFD modelling.

Kakaras and others (2007a) have noted that the dominating factors that affect the dimensioning of an oxyfuel lignite fired boiler are the higher radiative heat transfer due to the high concentrations of CO_2 and H_2O in the flue gas, and the different flue gas mass flow, compared with a conventional air

fired boiler. They formulated a modified boiler design based on a modern Greek air fired plant. The oxyfuel boiler of the same heat input has a furnace cross section slightly smaller compared to the air fired case while the height is larger and the total heat exchange surface is about 8.5% smaller.

Zheng and others (2009) believe that it is questionable whether large boiler size reductions and concomitant savings can be realised in practice. However, they note that optimisation opportunities exist in terms of flue gas recycle location. For coals with low sulphur content, they recommend that a warm, wet recycle be used after the electrostatic precipitator (ESP) to reduce blower wear and operation costs, and to increase the overall power generation efficiency. There is a slight increase in plant efficiency due to a reduction in auxiliary power requirements. A cold, dry recycle is probably the best option for high sulphur coal.

4 Particulates and ash

Yan and others (2006) have pointed out that oxyfuel plants may require higher removal efficiency for ash particles and that there is a need to investigate if ash properties are affected by oxyfuel combustion.

Suriyawong and others (2005) point out that, since fly ash particles are formed by means of nucleation of vaporised ash components and growth by coagulation and heterogeneous condensation, under oxyfuel combustion conditions, the formation mechanisms of fly ash and their aerosol characteristics could be altered, and may eventually affect their removal efficiency in particle control devices. They studied submicron (<0.5 μm) particle formation under oxyfuel combustion of subbituminous Powder River Basin coals with a mean particle size of 50 μm. It was found that the geometric mean size of fly ash formed under higher CO_2/O_2 ratios is smaller than the geometric mean size of fly ash formed by conventional combustion at all three temperatures studied (800, 1000, and 1200ºC). A later report confirmed the reduction in mean size together with a decrease in the total number concentration of particles when nitrogen is replaced with carbon dioxide in the combustor in both drop tube and flame reactors (Suriyawong and others, 2006a). Suriyawong and others (2006b) reported that the total mass of the particles in the submicron mode of ash was smaller. Correspondingly, the geometric mean size of the submicron aerosol was smaller by approximately 28%. When the O_2:CO_2 ratio was increased from 1:4 to 4:4, the geometric mean size of the submicron mode increased from 29 to 54 nm due to a faster vaporisation rate as a result of a higher coal particle temperature. This was attributed to the increase in oxygen volume fraction from 20% to 50%, which increased the particle surface temperature from 1772 to 2679 K. It was suggested that the temperature plays an important role in the vaporisation process of metals and mineral inherent in the coal particle. O_2/CO_2 combustion may affect only the vaporisation process and may not influence other aerosol growth mechanisms. An increase in the geometric mean size was observed on increasing the N_2:CO_2 ratio at a fixed O_2 concentration for the same reason. The shape of the primary particles was spherical in all the tests, indicating that a vapour to particle transformation pathway was prevalent.

Ash formation in oxyfuel combustion has been studied by Sheng and others (2007a,b; Sheng and Li, 2008). Sheng and others (2007a) studied the burning of a high-aluminium Chinese coal in a drop tube furnace (DTF). They reported that, compared with air combustion, O_2/CO_2 combustion did not affect the species of mineral phases formed in the ashes of the coal studied but did affect the relative amounts of the phases. O_2/CO_2 combustion had an impact on the coal particle combustion temperature and consequently on the ash mineral composition. O_2/CO_2 combustion decreased the yields of the fine ash particles in both the submicron fume region and fine fragmentation region compared with air combustion with the same O_2 concentration due to the decrease in the particle combustion temperature, while an increasing O_2 concentration enhanced the formation of both region particles.

The mode size of submicron particles formed in O_2/CO_2 combustion was found to shift to a smaller size when compared with that in air combustion. It was admitted that, since the study involved a single high-aluminium coal, a further experimental study with more coals was needed for obtaining more general conclusions.

Consequently, Sheng and others (2007b) extended their studies to three typical Chinese coals. It was found that O_2/CO_2 combustion did not significantly affect the size distribution of the residue ash particles but significantly affected the size distribution of submicron particles. O_2/CO_2 combustion at the same oxygen concentration shifted the size of the submicron mode centre to a smaller size and decreased the yield of the submicron particles compared with air combustion, while increasing the oxygen concentration decreased the difference between the two combustion atmospheres. O_2/CO_2 combustion also had a significant impact on the composition size distribution of the submicron ash particles but did not affect the mechanism of submicron particle formation. Enrichment of CaO and Fe_2O_3 was observed in the fine fragmentation mode, which confirmed the contribution of fragmentation to the formation of fine ash particles. Compared with O_2/N_2 combustion, increasing the oxygen concentration in O_2/CO_2 combustion had more significant impacts on the formation of the fine ash particles under both the submicron mode and the fine fragmentation mode.

Sheng and Li (2008) studied four Chinese thermal coals and characterised the ash samples with X-ray diffraction (XRD) analysis and ^{57}Fe Mössbauer spectroscopy. Qualitative XRD analysis showed that, compared with O_2/N_2 combustion, O_2/CO_2 combustion did not significantly change the main crystalline phases formed in residue ashes, implying no significant impacts on the ash formation behaviour of the main coal minerals. Mössbauer spectroscopic analysis indicated that the variation between O_2/CO_2 combustion and O_2/N_2 combustion did not affect the ash formation mechanisms of iron-bearing minerals, but did affect the relative percentages of iron species formed in the ashes. In general, O_2/CO_2 combustion resulted in more iron melting into glass silicates and less iron oxides formed because the lower char combustion temperatures and the high CO concentration within the particles slowed the transformations of included pyrite and siderite to oxides while favouring their transformations to form the iron glass. The differences observed in the ashes formed in two atmospheres were attributed to the impact of combustion gas atmosphere on coal char combustion temperatures, which influenced the ash formation behaviour of the included minerals.

Sheng and others (2008) also studied a Chinese lignite and found that the mass fraction of very fine particles smaller than ~0.1 μm formed in O_2/CO_2 combustion was higher while that of the particles between 0.1 and 0.5 μm was lower than those formed in O_2/N_2 combustion at a same oxygen concentration. No apparent shift of the submicron mode centre was observed

when changing the environment. While the particles collected on two smallest size stages were observed to have same elemental composition (dominated by Na and Mg), the elemental composition of the submicron particles of 0.06–0.5 μm between O_2/N_2 and O_2/CO_2 combustion were significantly different. Changing the combustion environment from O_2/N_2 to O_2/CO_2 combustion as well as changing the oxygen concentration had impacts on the size distributions of the major elements in the submicron particles. In term of the elemental size distribution, the submicron particles formed by combustion in an $O_2:CO_2$ ratio of 3:7 combustion of the lignite studied matched those formed in an $O_2:N_2$ ratio of 1:4.

Wall and others (2009a) have reported that due to the reduced gas volume in oxyfuel combustion, the dust concentration measured is 1.5 times greater than during air combustion, with no significant difference in the dust particle size distribution. The particle diameter of fly ash was approximately 5 μm for coal A and coal C, and approximately 8–10 μm for coal B when produced during both air and oxyfuel combustion. The chemical composition of ash appeared to be only affected if changes in the flame temperature alter the character of particles which affects ash deposition. The chemistry of collected deposit samples indicated oxyfuel deposits contained more sulphur than air deposits, though fly ash samples from both combustion modes had similar sulphur contents. The bottom ash from coal A and coal C was finer when produced in oxyfuel conditions due to the reduced gas flow (lower gas velocity) which would not be able to support larger ash particles. This indicates that the amount of bottom ash produced in oxyfuel combustion will increase compared with the quantity produced in air combustion.

Zhou and others (2009) studied the combustion of a Chinese lignite in a laboratory drop tube furnace. They found that the particulate matter (PM) was trimodally distributed with respect to particle size, and the condition changes had no impact on the trend of size distribution. Compared with the O_2/N_2 conditions, both the inhalable particulate matter (PM_{10}) and submicron particles (PM_1) production were reduced under the O_2/CO_2 conditions because the vaporisation of the mineral elements was lower and the vaporisation of refractory elements was lower than that of the volatile elements. The vaporisation of the mineral elements was affected by both the particle burning temperature and reducing atmosphere in oxyfuel combustion, showing a trend of decrease first and then an increase as the O_2 concentration increased.

A Chinese Datong brown coal was studied by Liu and others (2009). The coal is high ash as well as high in iron and sulphur. In agreement with Sheng and others (2007a), it was confirmed that O_2/CO_2 combustion did not affect the species of mineral phases formed in the ashes of the coal studied but did affect the relative amounts of the phases. However, since the char combustion temperature is lower in oxyfuel combustion than in air, the vaporisation of refractory oxides can be 'drastically decreased'. With an oxygen concentration of 30%, the yield and chemical composition of submicron particles are comparable to those from air combustion. It was suggested that, if flame stabilisation could be achieved at a relatively low oxygen fraction, for example 20%, then it may

be possible to reduce submicron particulate matter emissions from oxyfuel combustion.

The submicron ash particles formed in oxyfuel combustion with $O_2:CO_2 = 1:4$ were sulphate (Liu and others, 2009). Stam and others (2009) also found that a higher amount of calcium sulphate was found in the ash from oxyfuel firing of both coal and coal/biomass mixtures. This was attributed to the elevated levels of sulphur found in oxyfuel combustion (*see* Chapter 5).

5 Sulphur oxides

In their review of oxyfuel combustion of coal, Croiset and others (2005) point out that there is a decrease in the conversion of sulphur into sulphur dioxide (SO_2) in oxyfuel combustion compared with air firing and more so with flue gas recycling. This was attributed to conversion of SO_2 to sulphur trioxide (SO_3) or reaction of SO_2 with the ash. They noted that details about the fate of sulphur were not clear. Sarofim (2007) has noted that the sulphur removal has been explained by higher kinetics of sulphation of ash due to higher concentrations of SO_2. He also pointed out that an additional factor may be the direct sulphation of $CaCO_3$:

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 + CO_2$$
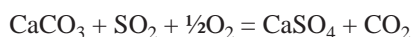
Fleig and others (2009a) have shown the lower conversion of sulphur in coal to SO_2 as reported in previously published work as shown in Figure 12.

Recently, Santos (2009) has reviewed the current state of understanding of the fate of sulphur during oxyfuel combustion with RFG. He pointed out that understanding the fate of sulphur is very critical to the design and operation of the oxyfuel coal fired power plant with CO_2 capture. It could impact on various aspects of the power plant in terms of the process design, plant construction principles, and operations such as:
- location of where to draw out the primary and secondary recycle flue gas;
- the choice of materials for the furnace, convective bank of tubes, air heater, economisers, electrostatic precipitators (ESP) and recycle flue gas conduits;
- soot blowing;
- location of the flue gas desulphurisation (FGD) and its operation;
- choice of SO_3 removal equipment.

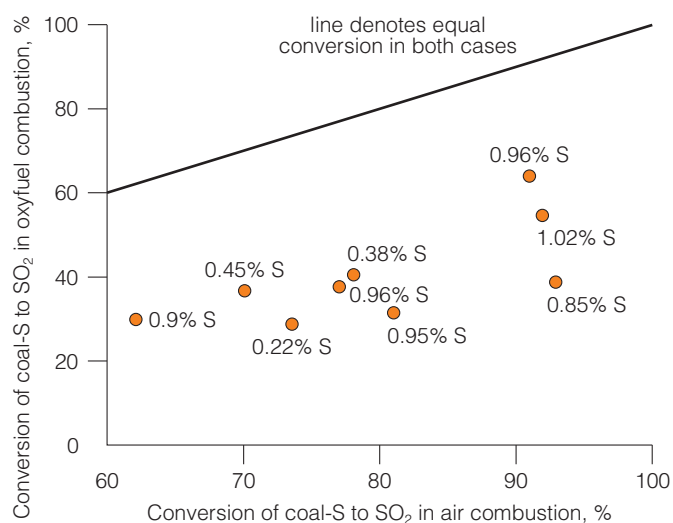The work reviewed shows that the SO_2 concentration is two to

Figure 12 Conversion of sulphur in coal to SO_2 as reported in previously published work (Fleig and others, 2009a)

five times higher in the oxyfuel flue gas than in the air fired flue. However, in terms of specific mass per energy input the SO_2 emissions in oxyfuel combustion are about 30–40% lower than in air fired combustion. This lower emission is attributed to retention of sulphur in the ash primarily due to its high temperature direct sulphation and the inhibition of decomposition of calcium sulphate at high temperatures. However, Santos (2009) also suggests that additional sulphur capture in ash could be promoted by increased formation of SO_3 and subsequent deposition.

Andersson and others (2006) found that the gas emission profile measurements, performed in their 20 kW coal-fired unit, showed that the SO_2 formation in the air and 27% O_2 oxyfuel case were similar for both coals tested. The results were in line with what was expected since the 20 kW unit is a once through reactor without flue gas recycling. Given that the emission profiles are similar it would seem that reduced SO_2 emissions are most likely a result of the flue gas recycling.

Using a 500 kW pulverised fuel combustion facility modified for operation under oxyfuel conditions with recirculation of flue gas, Mönckert and others (2007) found that, although the concentration of the SO_2 emission increased from 583 ppm in air firing conditions to 1145 ppm in oxyfuel conditions, on specific mass to energy basis the emission fell about 22% from 480 mg/MJ to 373 mg/MJ. 50.4% of the sulphur in the Lusatian pre-dried lignite used as the fuel was converted into SO_2 in air firing but this was reduced to 39.1% in oxyfuel conditions.

The SO_2 capture potential by the ash of two brown coals and two bituminous coals was determined by Maier and others (2008) under air firing and oxyfuel (27% O_2) conditions. SO_2 capture in the flue gas was compared with SO_2 measured at the end of the radiative section of the furnace. The difference between to two firing modes were not that apparent; in both, the SO_2 captured in the flue gas path increased with increase in SO_2 concentration at the end of the radiative section. A plateau was reached for all coals studied after a certain concentration of SO_2 was reached at the end of the radiative section. This indicated that the SO_2 capture capacity becomes exhausted. It was suggested that the capture capacity showed a weak dependency on the Ca/S molar ratio although it was likely that the form of the calcium in the ash plays a more important role in SO_2 capture. The finding that the SO_2 retained by the ash increases with increase in SO_2 concentration up to a certain limit indicates that the sulphur retained by the ash will be higher during oxyfuel combustion due to the higher concentrations of SO_2 in the RFG.

It was also found that the H_2S/SO_2 formation mechanism in the near flame zone is fundamentally similar during air firing and oxyfuel combustion. However, from a corrosion point-of-view, the concentration of H_2S was higher during oxyfuel combustion with RFG and also much higher for high volatile coals compared with medium volatile coals. This will
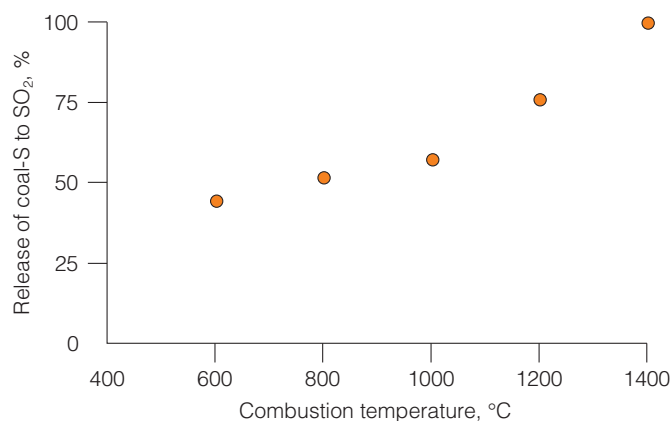
Figure 13 Release of SO₂ from Lusatian lignite at different temperatures in pure O₂under laboratory conditions (Fleig and others, 2009a)

be discussed further in Chapter 8 on slagging, fouling, and corrosion. The conversion rate of SO_2 to SO_3 also increased from 1.1% in air fired conditions to 4.7% in oxyfuel conditions. It was suggested that future investigation should focus on changes in the SO_2/SO_3 conversion rate under oxyfuel conditions.

Fleig and others (2009a) studied the fate of sulphur during oxyfuel combustion of Lusatian lignite. They burned a small lignite sample under a pure oxygen atmosphere at constant temperature, and the SO_2 content of the flue gas was measured. They also considered published experimental data and the gas-phase reactions and the formation of SO_3 and H_2S were investigated by means of a combustion model. Three cases were investigated by modelling: air firing, oxyfuel combustion with dry recycle, and oxyfuel combustion with wet recycle. Figure 13 shows the release of coal-S to SO_2 from the lignite at different temperatures under laboratory conditions. The sulphur release is closely related to temperature, and at 1200ºC, for example, only 76% of the total sulphur is released. Below 600ºC the dominant sources of sulphur release are organically bound sulphur and pyrite. Thus, the combustion temperature is critical to the sulphur release. However, part of the SOx formed is captured and bound to inorganic compounds in the ashes downstream of the combustor. Another part of the fuel sulphur is bound in the minerals without being released. In principle, Lusatian lignite contains enough calcium to capture all the sulphur as $CaSO_4$. However, in practice, all the calcium is not available to capture sulphur, since it is also bound in inactive species such as silicate minerals.

The sulphur mass balance in the oxyfuel combustion of pulverised lignite was investigated by Fleig and others (2009b). They compared the amount of emitted SO_2 in air and oxyfuel combustion for both wet and dry flue gas recycle. The amounts of sulphur in the ash and also in the water of the flue gas condenser were determined to make a mass balance and to verify the measured amount of SO_2 in the flue gas. It was found that the mass flow of sulphur in the ash was higher in oxyfuel combustion compared with air combustion due to slightly higher average sulphur content in the ash and a higher amount of bottom and residual ash in the oxyfuel cases. The

sulphur content in the condenser water was also higher in oxyfuel combustion but had only a low influence on the mass balance. However, the increase in the ash sulphur content was not sufficient to explain the lower SO_2 concentration in the flue gas. While verifying that the conversion of fuel S to SO_2 is lower in oxyfuel firing compared with air combustion, the lowered conversion was not reflected by equivalent higher S contents in the ashes. The fuel S mass flow was higher than the estimated S mass flows leaving with the flue gas, ash, and condenser water. The reasons for this gap in the sulphur mass balance remain to be clarified.

Fleig and others' (2009a) modelling studies showed that the outlet concentration of SO_3 in oxyfuel combustion is about four times the concentration in air firing when the gas follows a predefined temperature profile typical for a coal-fired power plant. SO_3 is primarily formed during the cooling of the flue gas in the temperature range around 1300ºC to 900ºC. Note that Santos (2009) states that maximum conversion of SO_2 to SO_3 should occur around 700–800ºC. Fleig and others (2009a) suggested that the increase in SO_3 is caused by three properties of the oxyfuel process in decreasing relative importance:

- the oxidiser in oxyfuel combustion contains SO_2, which increases the amount of sulphur present during combustion;
- the oxidiser in oxyfuel combustion has a higher concentration of O_2, which decreases the volume flow through the furnace and, thus, increases the concentration of SO_3;
- the change from N_2 to CO_2 increases the SO_3/SO_2 ratio – simulations showed that, similar to an air fired furnace, the cooling rate (or residence time in the crucial temperature range) and the stoichiometric ratio during the cooling are of great importance for SO_3 formation, while the influence of the peak temperature is negligible.

Fleig and others (2009a) also suggested that an increase in acid dew point temperature by 20 to 30 K was expected due to higher SO_3 and H_2O concentrations.

It is worth noting that there can be difficulties in measuring SO_3. Maier (2010) has stated that, at the University of Stuttgart Institute of Combustion and Power Plant Technology, they have performed more than 150 measurements and SO_3 still seems to be challenging to measure. If anything in the boundary conditions have changed it is necessary to perform several measurements to detect SO_3 and reduce the level of uncertainty. The problems get even worse if measuring in the high dust area and with a fuel which has a high potential to form sulphates.

Wall and others (2009a,b) have reported results using three Australian bituminous coals in the 150 kg/h IHI combustion test facility. The SO_2 in the flue gas (in ppm) of the pilot-scale experiments was directly proportional to the fuel sulphur content in both oxyfuel and air combustion, but it was three times greater in oxyfuel combustion compared with air combustion. The concentration did not change significantly with increasing recycle ratio. As shown in Figure 14, the total mass (mg/MJ) of sulphur emitted during oxyfuel combustion was two thirds of the total sulphur in the flue gas of air
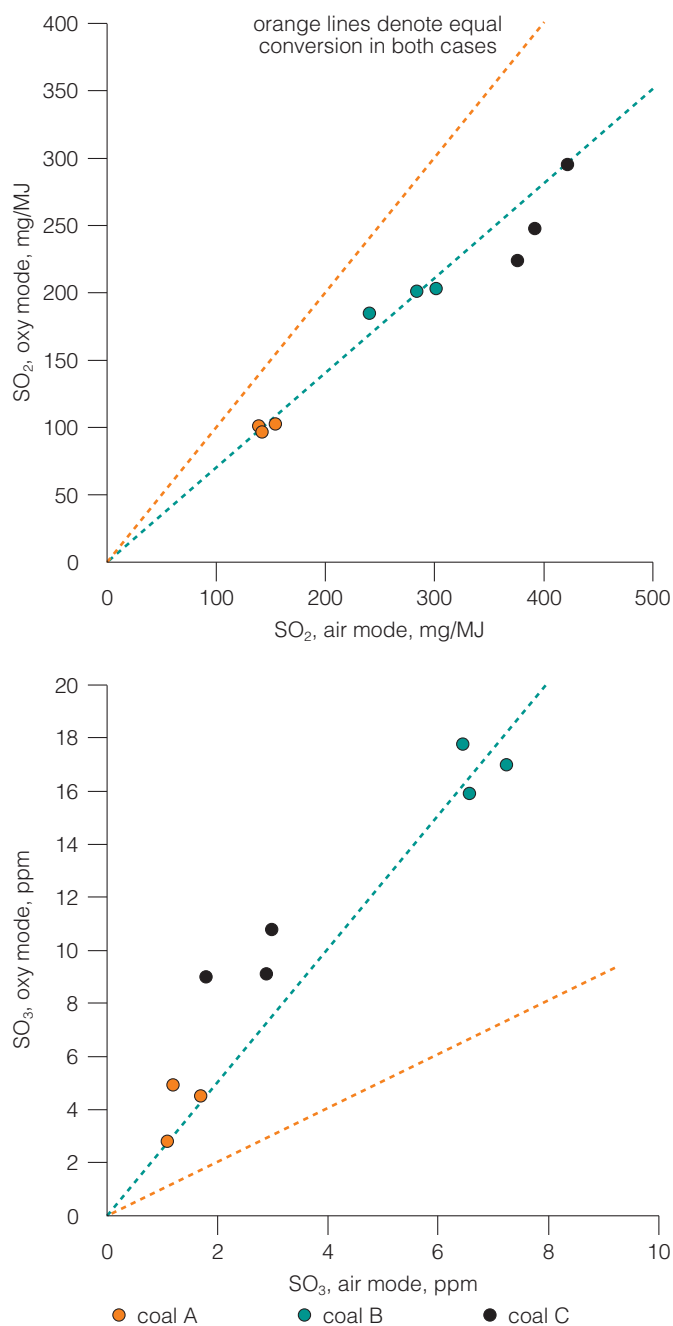
Figure 14 Comparisons of SOx for air and oxyfuel firing (Wall and others, 2009)

combustion, and a very small additional decrease in mass of sulphur was observed when the recycle of flue gas through the furnace was increased. Figure 14 also shows that the SO_3 concentration (in ppm) was approximately two and a half (2.5) to three (3.0) times higher in oxyfuel combustion than in air combustion. The dashed lines in Figure 14 shows where the concentration values would lie if there were no differences between the air and oxyfuel firing cases. Stanger and Wall (2010) have noted that, despite the higher SO_3 concentrations, the conversion of SO_2 to SO_3 was comparable in both air fired and oxyfuel conditions.

In general, the fly ash produced during oxyfuel combustion contained slightly more sulphur and the furnace deposits contained significantly more sulphur compared with air combustion samples. However, the mass balance of the coal ash could not be closed because a significant proportion of the

ash was not accounted for in the experiment. Apparently, ash was depositing throughout the furnace, or lost in ducts, which contained a significant proportion of the coal sulphur. Again, the acid dew point was shown to be increased under oxyfuel combustion conditions increasing the potential corrosion during operation, which may result in the need for desulphurisation of the flue gas before recycle or limit oxyfuel combustion to low sulphur coals.

Using the 50 kWth pulverised coal combustion test facility at the University of Dresden, Grahl and others (2009) studied the effect of varying excess oxygen at the end of the combustion chamber on the levels of SO_2 in the flue gas from oxyfuel combustion of lignite. This is shown for two cases (4 and 8 vol%) in Figure 15. The concentrations of SO_2 in the flue gas show two major effects. First, at 4 vol%, in contrast to the comparable points from 8 vol% residual oxygen in dry flue gas at the end of the combustion chamber, higher adiabatic reaction temperatures are reached, which is why in the 4 vol% case emissions of SO_2 are generally higher. The second effect is the variation of the flue gas recirculation. When the oxygen concentration at the burner head is 17 or 20 vol% (oxyfuel points 17 to 20) significantly more flue gas is recirculated than in the oxyfuel 30 to 33 cases, and thus at lower oxyfuel points the adiabatic reaction temperature decreases. The result is a higher SO_2 reduction potential at lower concentrations of oxygen at the combustion chamber entry for the same residual oxygen at the end of the combustion chamber. The effects of air in-leakage were also studied which also showed the dependence of SO_2 formation on the adiabatic reaction temperature. This was reduced due to the dilution effect of atmospheric nitrogen from the in-leaked air resulting in generally lower SO_2 concentrations.

The SO_2 formation behaviour during the combustion of Chinese Xuzhou bituminous coal combustion in O_2/N_2 and O_2/CO_2 atmospheres has been investigated by Duan and others (2009). It was found that replacing N_2 with CO_2 enhances the SO_2 release rate. SO_2 emission increases first and then decreases as the O_2 fraction increases in the O_2/CO_2 mixture. X-ray photoelectron spectroscopy (XPS) studies of the ash after combustion indicated that a higher O_2 concentration elevates the sulphur retention ability of the mineral matter in the coal, mainly calcite. When the temperature is above 1000 K, sulphate in the CO_2 atmosphere begins to decompose attributed to the reduction effect of CO produced by CO_2 gasification of the coal. Their results also showed that COS is preferentially formed during the coal pyrolysis process in a CO_2 atmosphere rather than in a N_2 atmosphere in which only negligible amounts were detected. It was suggested that the COS is formed by both gas phase secondary reactions:

$$H_2S + CO \rightarrow COS + H_2$$

$$H_2S + CO_2 \rightarrow COS + H_2O$$
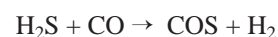
and a gas-solid reaction with pyrite:

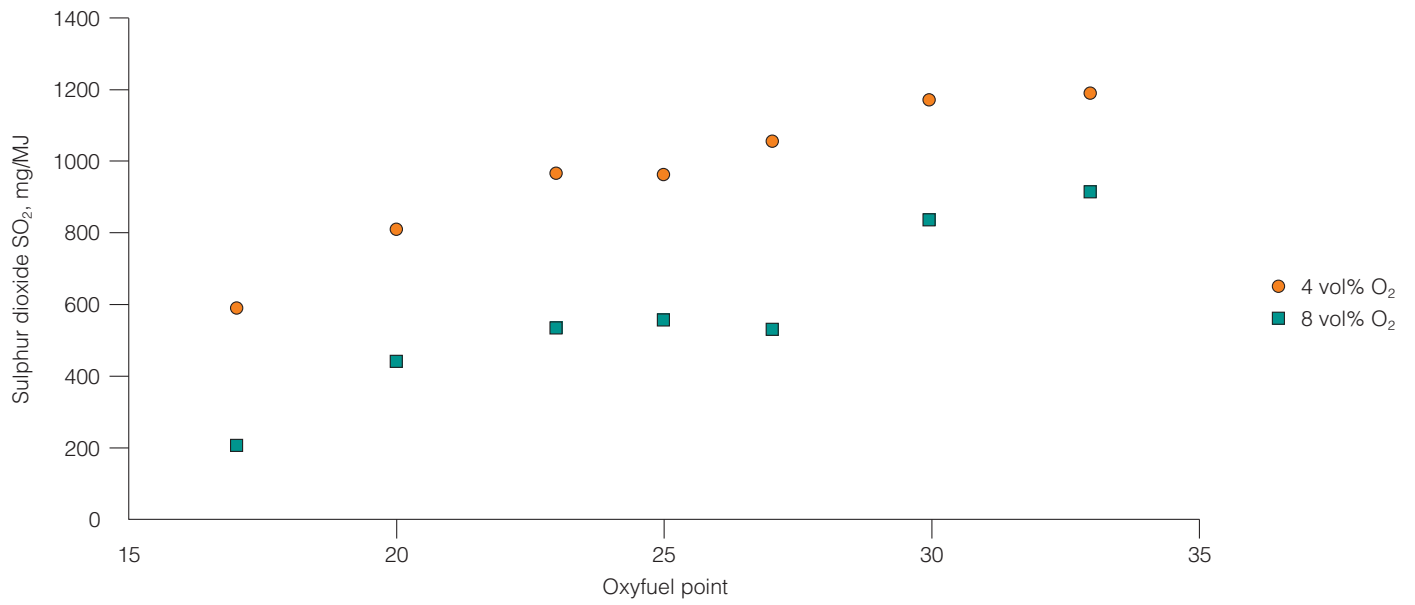$$FeS_2 + CO \rightarrow FeS + COS$$
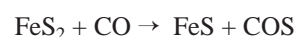
Figure 15 Dependence of SO$_2$ concentration on varying excess oxygen (Grahl and others, 2009)

6   Nitrogen oxides

Buhre and others (2005) have pointed out that, in the USA, the reduction in nitrogen oxides (NOx) formation has been an important driver for research into oxyfuel combustion. Indeed, the use of oxygen enriched combustion has been proposed as a retrofit for NOx control (for example, Châtel-Pélage and others, 2005a,b). The technology consists of injection of 5% or 10% oxygen enriched air into an existing coal-fired boiler to promote the conversion of fuel-bound nitrogen into molecular nitrogen and to limit its conversion into NOx. It requires the installation of proprietary oxygen injection equipment. Air remains the main oxidiser in the retrofitted boiler, with more than 90% of the oxygen molecules needed for complete coal burnout being provided by ordinary combustion air. Less than 10% of the stoichiometry, or less than 10% of the total oxygen molecules, is provided by pure oxygen. Results obtained in pilot-scale tests (1.5 MWth and 30 MWth) with two very different types of coal showed up to 30% NOx emission reductions from an air-staged baseline. These results were very sensitive to the O_2 introduction arrangement and to the O_2 enrichment level.

The 1.5 MWth boiler was also used to test oxyfuel combustion of a low sulphur subbituminous coal. It was found that the NOx emissions were reduced by an average of 65% in the oxyfuel combustion versus the air-blown baseline. It is obvious that there should be a decrease in thermal NOx as a consequence of the very low amount of nitrogen entering the burners. However, a reduction of 65% strongly implies that is not due simply to the disappearance of thermal NOx since the fuel NOx usually accounts for around 80% of the total. Châtel-Pélage and others (2005a,b) attributed such significant NOx reduction to the combined effect of flue gas recycle, burner stoichiometry, and oxygen injection in the primary air zone. They suggested that no selective catalytic reduction (SCR) would be necessary for implementing oxyfuel combustion.

Tan and Croiset (2005) have pointed out that, even though NOx emissions from oxyfuel combustion can be reduced significantly, this can only be achieved through good O_2 management. It is still important to adopt low NOx burners specifically designed for oxygen firing. Tan and others (2006) studied three Canadian coals in a 0.3 MWth test facility – a lignite, subbituminous, and bituminous coal. The concentration of NO in the flue gas increased in the oxyfuel firing case compared with the air fired case for the bituminous coal and the subbituminous coal (by a factor of two) but this was a consequence of the reduced flue gas volume in oxyfuel combustion. The mass emission rate (ng/J) slightly increased by about 10% for the bituminous coal but fell by 37% for the subbituminous coal. The most noticeable decrease in NOx levels, both in concentration and mass emission rate was for the lignite where the mass emission rate was reduced by nearly 75%. However, for the lignite, an improved burner optimised for O_2 firing was used.

Sarofim (2007), reviewing previous research, has pointed out that the reduction in NOx is consistent with:
● reburning due to the recirculation of the flue gas;

● a decrease of fuel nitrogen conversion with increased NO concentration.

Mackrory and others (2007; Mackrory and Tree, 2008; Tree and others, 2009) have provided a useful checklist of ten possible reasons for NOx reduction in oxyfuel and oxygen enhanced combustion:
● near elimination of thermal and prompt NOx;
● more attached flame;
● high NO concentrations limiting the conversion of fuel-N to NO;
● reduction of recycled NOx in the fuel-rich flame zone;
● temperature changes;
● longer residence times in fuel-rich regions;
● equilibrium amount of NOx being significantly lower in oxyfuel combustion;
● increased volatile yields leading to reduced NO formation from char;
● heterogeneous reburning enhanced by higher CO concentrations and possibly altered soot concentrations;
● increased importance of gasification reactions.

Mackrory and Tree (2008) suggest that 'the length of the list indicates the present lack of understanding of nitrogen chemistry under oxyfuel conditions'.

Liu and others (2005), using a laboratory burner, found that the conversion of coal-N to NOx for coal combustion in any of the O_2/CO_2 mixtures investigated was smaller than that for coal combustion in air. The conversion of coal-N to NOx increased with the O_2 concentration in O_2/CO_2 mixture due to the higher gas temperatures promoting both homogeneous and heterogeneous NOx formation. The explanation of these findings involved the higher concentrations of CO (ppmv) and higher concentrations of NO (ppmv) which were found in the main combustion zone in 30% O_2/70% CO_2 mixtures. In addition, within the vicinity of a combusting coal particle, more CO and NO are expected to be present with 30% O_2/70% CO_2 than air as the combustion media, partly due to less dilution for 30% O_2/70% CO_2 combustion. The higher CO concentrations inside the combustion zone and within the vicinity of combusting particles result in more reduction of NOx. With higher background concentrations of NOx, more NOx formed from char combustion can be reduced on the char surface and in the gas phase with 30% O_2/70% CO_2 combustion and hence there will be a lower conversion of coal-N to NOx. It was also found that air/oxidant staging is a very effective method in reducing NOx emissions for both coal combustion in air and coal combustion in 30% O_2/70% CO_2. For coal combustion in air, air staging can reduce the conversion of coal-N to NOx from 27.6 to 10%, while for coal combustion in 30% O_2/70% CO_2, oxidant staging can reduce the conversion of coal-N to NOx from 22.6 to 7.5%.

The amount of NO released per unit energy released has been reported to be reduced to 25–30% of the emission levels during air fired conditions by Andersson and others (2007, 2008a). They concluded that the absence of free N_2 in oxyfuel

combustion is not an important factor in the overall reduction of NO under their experimental conditions in a 100 kW test unit burning lignite. Results from modelling studies indicated that the reduction is caused by an increased destruction of formed and recycled NO. The model also indicated that the conversion of coal-N to NO is similar or slightly higher than for air firing. Increasing the volume of oxygen from 25 to 29 vol% had only a negligible effect. Similarly, if the air-fuel ratio was increased from 1.18 to 1.41 while keeping the O_2 fraction constant at 27 vol% there was only a small increase in NO emissions. Increasing the N_2 content in the feed gas from about 1% to 15% again had only a small effect on NO formation during oxyfuel combustion.

Thermal NOx is produced from N_2 and O_2 by the extended Zeldovitch mechanism:

$$N_2 + O \rightarrow NO + N$$
$$N + O_2 \rightarrow NO + O \; N$$
$$N + OH \rightarrow NO + H \; N$$
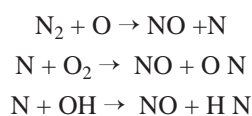
Andersson and others (2008a) found that their gas phase reaction modelling also showed that oxyfuel combustion has a potential for reduction of NO at high temperature: the absence (or near-zero level) of airborne N_2 enables the reverse Zeldovich mechanism to destroy NO at high temperatures. Therefore, in contrast to today's low NOx concepts, an optimised oxyfuel combustor may be designed for operation at high temperatures. This suggestion was further examined by Normann and others (2008) who examined the sensitivity of high temperature NOx reduction to critical parameters. Their modelling indicated that, at temperatures below 1400°C, the Zeldovitch mechanism was not active and NOx reduction was due to the reburning mechanism. At higher temperatures the reverse Zeldovich mechanism dominates the NO reduction. However, as the N_2 concentration increases the thermal mechanism no longer acts in the reverse direction and thermal NOx is produced. To achieve maximum NO reduction in the combustor via the reverse Zeldovich mechanism, the temperature profile should be high but fall throughout the combustion zone. The optimal temperature profile depends on parameters like residence time, oxygen concentration, and amount of nitrogen supplied by fuel, oxygen and air ingress into the combustion chamber. It was concluded that the possibility of high temperature reduction of NOx avoids the traditional tradeoff between low NOx and low UBC in boiler and burner design. Instead, issues related to high temperature corrosion and melting of ashes become important.

Mackrory and others (2007) burned pulverised Illinois No 6 bituminous coal in a once through laminar flow reactor to study the evolution of NOx in air and oxyfuel combustion at 25% and 30% oxygen. In unstaged combustion conditions, when the overall oxygen to fuel ratio was held constant at a slightly fuel lean condition, reductions in NOx were not observed. However, in staged conditions with the primary burnout zone overall fuel-rich, the initial conversion of fuel-N to NOx was comparable for all the oxidisers but the oxyfuel mixtures exhibited more rapid destruction of NOx in the reducing zone that followed. Several factors were identified as potential contributors to the higher reduction rate:
- the longer residence time created by the lower

- volumetric flow rates of oxyfuel combustion;
- the higher concentrations of NOx existing in the reactor;
- the equilibrium amount of NOx in oxyfuel combustion being much lower than in air combustion.

The final levels of NOx in staged oxyfuel combustion were observed to be lower than in staged air combustion.

Mackrory and Tree (2007) suspected that reduction of NO by CO catalysed by char may be the cause of the NOx reductions seen in their measurements and noted that a char oxidation model including accurate reaction rates for CO and NO required further investigation. Subsequently, Tree and Mackrory (2008) performed modelling studies which indicated that the measured NOx reductions were not due to equilibrium considerations, differences in volatile yields, differences in formation and destruction residence times, or higher temperatures. They concluded that the higher rates of NOx reduction observed in oxyfuel combustion could not be explained by the current state-of-the-art gas phase kinetic models. They found that the concentration of CO in their oxyfuel experiments was elevated well above and moving in a trend opposite to their model. They suggested that CO was being formed presumably by char reaction with CO_2 when the char was in a reducing environment. Additional studies on three coals have been reported by Mackrory and Tree (2008) and in a final report by Tree and others (2009). This work focused on oxidiser-staged combustion where a reducing zone was formed near the burner to simulate the performance of a low NOx combustion system. The pulverised coals were subbituminous, and bituminous Illinois No 6 and Pittsburgh seam coal. An attempt was made to close the nitrogen balance by analysing the char for residual nitrogen and using these data in combination with NOx measurements. Lower NOx emissions, as a percentage of the fuel nitrogen entering the reactor, were obtained for all three coals under oxyfuel conditions although there were qualitative differences. A summary of the test results is shown in Figure 16.
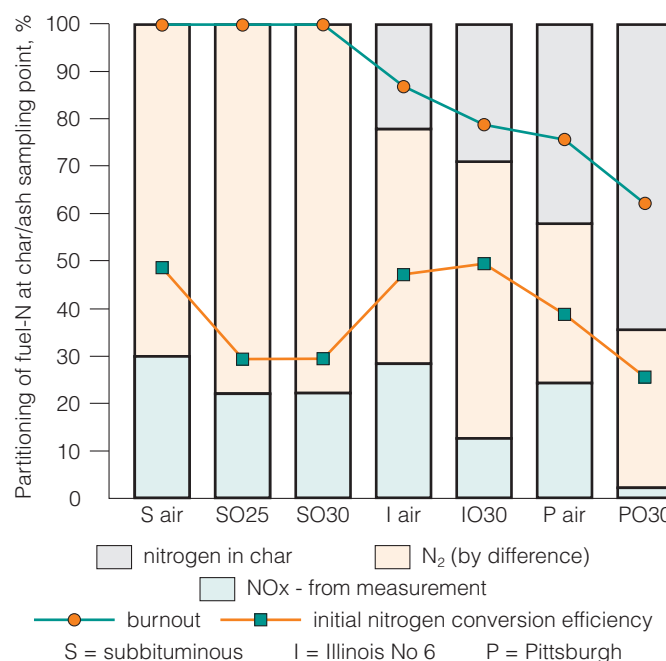

Figure 16 Fate of fuel nitrogen (Mackrory and Tree, 2008)

The oxyfuel flames were characterised by higher CO concentrations in fuel-rich regions than equivalent air flames. Thus, in agreement with Liu and others (2005) it was suggested that CO is an important species in producing faster NOx destruction under oxyfuel conditions. Modelling studies indicated that the high CO levels were associated primarily with thermal dissociation of CO_2 above about 1500 K and that char gasification by CO_2 was less significant. The computational model also predicted the suppression of initial NO formation and faster NOx destruction when there is NO in the recycle stream. However, the NOx destruction rates were underpredicted indicating that some mechanism may be missing from the model. In agreement with Andersson and others (2008a) and Normann and others (2008), Tree and Mackrory's (2009; *also* Mackrory and Tree, 2009) modelling studies suggested that the majority of NOx reduction is attributable to thermal NOx destruction or movement towards equilibrium. On the other hand, the experimental data suggest that reburning (CH_4, C_2H_4) and advanced reburning (HCN, NH_3) species are available and responsible for NOx reduction. Specifically, the model was unable to predict a fuel-rich region containing unburned hydrocarbons and nitrogen intermediates that were measured in experiments. Based on measured hydrocarbons, HCN, and NH_3 data, this pathway was believed to be the dominant means of NOx destruction observed in the experiments (Tree and others, 2009). This would be consistent with Wall and others' (2009a) conclusion that NOx reduction is consistent with the NOx in the recycled gas being reburnt as it contacts the flame generated hydrocarbons and the reducing atmosphere near the flame.

Mackrory and Tree (2009) attributed the failure of the model to predict NO reburning not to the gas phase kinetics, but rather to a need to model a size distribution of particles and thereby create a fuel-rich gas phase containing NO from combustion of small particles prior to release of volatiles suitable for reburning reactions from larger particles. Modelling a range of particle sizes was also expected to predict significant levels of nitrogen-intermediate species that may form NO as additional oxidiser is injected, a phenomenon noted in the experimental data that was not reflected by the model.

It is also possible that the gases in an oxyfuel environment can react with the char nitrogen directly. This possibility has been addressed by Sánchez and others (2007). They noted that, in coal combustion, NOx is primarily formed by oxidation of HCN and NH_3 in the gas phase. One possible route for HCN desorption in a highly oxidised char surface can be explained by the presence of epoxy groups promoting HCN formation from a pyridinic nitrogen complex. HCN has been central to experimental and modelling studies carried out by Giménez-López and others (2009, 2010). HCN is the main intermediate product generated during the NO reduction reburning process. The aim of the studies has been to evaluate the oxidation behaviour of HCN under oxyfuel combustion conditions through an experimental and kinetic modelling study of the oxidation of HCN (1000 ppm) under CO_2 diluted conditions, in the 900–1450 K temperature range and for different stoichiometries. The modelling studies were based on a model of HCN oxidation in air fired conditions but this was modified by including a number of reactions involving

CO_2 species which did not appear in the initial model but may be important during the HCN oxidation process under oxyfuel conditions have been included, together with a revision of the rate constants of the most sensitive reactions from the mechanism under the specific conditions studied. The modifications were made in an attempt to attain a better prediction of the experimental results. It was concluded that the high levels of CO_2 present compete with O_2 for atomic hydrogen, through the $CO_2 + H \leftrightarrow CO + OH$ reaction, reducing the formation of chain carriers via $O_2 + H \leftrightarrow O + OH$, which results in an inhibition of HCN oxidation. The lower HCN burning rate observed in a CO_2 atmosphere is accompanied by a higher CO and HNCO formation and lower NO and N_2O concentrations compared with air combustion. Similar trends were observed for all stoichiometries analysed. With regard to the stoichiometry influence under high CO_2 concentration conditions, the higher availability of oxygen increases the HCN conversion, due to the increased radical pool. HCN is mainly consumed through reactions with OH and O radicals, and to a lesser extent with NCO and its isomerisation to HNC. The increase in the HCN oxidation with the O_2 concentration results in a greater formation of the main products (including CO, NO, N_2 and N_2O). Nevertheless, the onset temperature for reaction is similar at any stoichiometry studied.

The formation of HCN has been incorporated into a CFD model by Cao and others (2010). They used the De Soete mechanism in which it is assumed that volatile N is released as HCN, then the HCN subsequently decays to form NH_3, which undergoes further reaction to produce either NO or N_2. Both experimental results and predictions showed that NO emission in oxyfuel conditions, which comes from fuel NO and recycled NO, can be reduced to a level less than that of air combustion. It was observed that higher nitrogen intermediate species during the combustion zone in oxyfuel conditions is favourable for NO reduction. The results showed that the NO formation rate could be suppressed by NOx recycling back to the furnace.

Tests in an electrically heated once through 20 kW furnace have been carried out by Dhungel and others (2005) and Maier and others (2006) at the Institute of Power Plant Technology (IVD) at the University of Stuttgart (since renamed as the Institute of Combustion and Power Plant Technology – IFK). Tests reported by Dhungel and others (2007a,b) and Scheffknecht and Maier (2008) have strongly indicated that fuel-NOx formation mechanism in fuel-rich conditions during oxyfuel coal combustion is similar to air-blown combustion. For unstaged combustion of South African Kleinkopje bituminous coal it was found that the decrease in NOx emission due to the absence of thermal NOx was outweighed by an increase in fuel NOx when the oxygen concentration was higher than 27%.The fate of flue gas components recycled back into the furnace during staged as well as unstaged combustion was investigated by injecting known concentrations of NO into the furnace. There was firm evidence that the reduction of recycled (injected) NOx is completely dependent on burner stoichiometry and residence time in the reduction zone. The percentage reduction of recycled NO decreased with an increase in burner stoichiometry. For a burner stoichiometry of 0.75, the

percentage reduction of recycled NO was almost 100% for both Kleinkopje coal and Lusatian brown coal and then decreased with increase in burner stoichiometry. This was attributed to a higher concentration of hydrocarbon radicals available in near burner region for lower burner stoichiometry, which enhances the reduction of recycled NO. The reduction potential was almost independent of the coal rank. Dhungel and others (2007b) add that recycled NO injected via the burner shows more reduction potential than NO injected with the overfire oxidant. Overall, during oxyfuel combustion with RFG, 70–80% of the flue gas is recycled back into the furnace resulting in much lower emission rate at the stack and, if 70% of flue gas is recirculated back to the furnace, NOx at the end of the system will be 69–77% lower than during air-blown combustion (Dhungel and others, 2007c).

At the IVD, a 500 kWth pulverised fuel combustion facility has been modified and retrofitted for operation under oxyfuel conditions (Mönckert and others, 2007). Tests have been conducted using Lusatian brown coal and the NOx emission rate was reduced from 187 mg/MJ for air firing to 63 mg/MJ for oxyfuel firing; a reduction of 66%. The tests were carried out for an unstaged flame and without preheating the combustion gas. The reduction was attributed to increased combustion temperatures, either due to lower recycle rates or higher recirculation gas temperatures facilitating cracking of the recirculated NOx.

Although reductions in NOx were achieved in tests conducted by Sethi and others (2007) on a lignite, subbituminous coal, and a bituminous coal, it was reported that the magnitude of the reductions was not as large as that previously reported by other research groups. This was attributed to the lack of any optimisation of staging during the oxyfuel combustion tests. However, there were some indications that the reduction might be coal dependent. The reduction in NOx emissions on a mass per unit energy basis decreased by 17.6% for a lignite burned in 27% O_2/73% CO_2 compared with air firing but the comparable figures for a subbituminous and a bituminous coal were 20.8% and 58.8% respectively.

Grahl and others (2009) and Wilhem and others (2009) compared NO formation in the oxyfuel process with and without air in-leakage (4 vol% from combustion chamber flow rate) and with combustion in air. Their results showed that the lower the in-leakage air, the lower is the nitrogen oxide formation and the higher the flue gas recirculation, the greater is the reduction of NO formation. For further investigations a series of experiments with a single flame were carried out in the combustion chamber of the 50 kWth pulverised coal combustion test facility. The reaction progress and the nitrogen release from coal was evaluated by sampling the particles along the combustion chamber at different radial positions and by subsequent elementary analysis. At the same time, emission measurements at the same sampling positions were carried out. The conversion rate NO/NO_{max} indicates the mass ratio of the actual formed NO to the maximum NO which could be formed when all the existing fuel nitrogen is converted into NO. As expected, the high temperatures at the combustion chamber for oxyfuel firing compared with air firing caused a rapid release of the fuel nitrogen. For both cases, after 200 mm about 97–98% of the fuel nitrogen was

Table 2	Percentage amount of NO_2 compared with NO formation (Wilhelm and others, 2009)		
$f_{NO_2/(NO + NO_2)}$ = (NO_2[mg/MJ]/NO[mg/MJ + NO_2[mg/MJ])*100			
In-leakage air amount, %	Factor $f_{NO_2/(NO + NO_2)}$		
	air	oxyfuel 17	oxyfuel 25	oxyfuel 33
0	6.75	9.4	21.2	27.9
4		17.3	21.5	19.4

released. The conversion rate of NO/NO_{max} in air firing was higher than for oxyfuel firing. Wilhelm and others (2009) also studied the formation of NO_2 in oxyfuel combustion and found that the fraction of NO_2 formation from the total NOx production was higher in the oxyfuel experimental tests than in the air comparison cases due to the higher NO supply from the flue gas recirculation. This was also associated with the longer residence time and the higher oxygen partial pressure. Their results are given in Table 2.

The rapid release of fuel nitrogen is possibly associated with the release of higher yields of volatiles at high temperature reported by Sun and Snape (2009) and discussed in Section 2.2. They also reported that, under oxyfuel firing conditions, higher proportions of nitrogen were released into volatiles, but they are similarly proportional to the yields of volatiles as observed in air firing. This means that less nitrogen remains behind in the chars. In addition, the DTF studies revealed that, compared with air firing, nitrogen release is slightly retarded under oxyfuel conditions such that higher proportions of nitrogen are retained in the unburnt chars. It was suggested that the probable cause of this was the CO_2 char gasification reaction favouring carbon rather than char nitrogen.

The recycle ratio (R) can also affect NOx concentrations. Rossi and others (2009) observed that an increase in R leads to an increase of NOx emissions. The injection of oxygen into the primary duct also causes an increase in NOx emissions which depend strongly on the amount of O_2 injected.

Recently, Normann and others (2009a) have reviewed the technology status of NOx control systems for the oxyfuel combustion process. They report that flue gas recirculation alone, an important part of the oxyfuel combustion process, can achieve a 65% reduction in NOx emission. High temperature combustion, achievable under oxyfuel conditions, could reduce NOx emissions by 95%. A summary of the performance of NOx control measures reviewed is provided in Table 3. Note that the achievable reduction is for the measure concerned and not for addition or multiplication of measures.

Normann and others (2009b) point out that NOx control has constrained the design of combustion in air for a long time. In their opinion it is therefore important not to imitate combustion in air but to utilise the opportunities given by oxyfuel combustion to find the optimal performance, both with respect to NOx and combustion efficiency.

Table 3 Summary of the performance of NOx control measures (Normann and others, 2009a)			
	Advantages	Disadvantages/tendencies	Achievable reduction, %
Primary measures			
Reburning	conventional technology	(natural gas consumption) high temperature corrosion	60*
Staging	conventional technology	reduced combustion efficiency high temperature corrosion	40*
Low NOx burner	conventional technology	reduced combustion efficiency high temperature corrosion	60*
Flue gas recirculation	included in the oxyfuel process		65†
High temperature	improved combustion efficiency Small and compact furnace	melting of ashes requires low N_2 concentration high temperature corrosion	90‡
Secondary measures			
Selective catalytic reduction	conventional technology	melting of ashes ammonia consumption extra units ammonia slip	95*
Selective non-catalytic reduction	conventional technology	ammonia consumption ammonia slip	50*
Absorption	simultaneous removal of SO_2	placed in high pressure part extra units waste (weak nitric acid)	90‡
Co-storage	included in the oxyfuel process	pollution of the CO_2	95‡
Distillation	simultaneous removal of SO_2 placed in high pressure part	power consumption extra units waste (liquid NOx)	95‡

*   based on practical experience under air fired conditions
†   based on experiments under oxyfuel conditions
‡   based on modelling of the oxyfuel process

7 Trace elements and mercury

Tan and Croiset (2005) found that *trace elements* measured in the flue gas stream upstream of a fabric filter were almost exactly the same whether coal was fired in air or in oxyfuel. However, Suriyawong and others (2008) have pointed out that ash particles in the ultrafine and submicron size regimes are enriched in toxic heavy metals, and efficient removal of these particles from combustion exhaust flow is extremely important. Since the collection efficiency of electrostatic precipitators (ESP) is size dependent, a smaller geometric mean size of the ash particles will have implications on their performance. To minimise ultrafine and submicron particle emissions, power plants operating electrostatic precipitators with positive applied voltages, as is common for two-stage ESP would need to increase the applied voltage to the ESP and therefore power consumption to reach corona inception and a desired current level if oxyfuel combustion is used. The gas mixtures used in the experiments to simulate oxyfuel flue gas were mixtures of O_2 and CO_2; no moisture was present. It was estimated that, for example, a 15% increase in power would be needed to operate a positive corona at 10 µA in 80% CO_2/20% O_2 compared with air. Even at the same current level, numerical simulations revealed that the ion concentration of positive ions in pure O_2/CO_2 systems is lower than in pure O_2/N_2 systems, thus decreasing the diffusion charging efficiency within ESPs and greatly increasing particle penetration. The effects of O_2/CO_2 gas mixtures on ESP performance could lead to a substantially greater number concentration of particles emitted from power plants using O_2/CO_2 combustion and applying positive voltages to their electrostatic precipitators. However, if negative applied voltages are used, the effects of using O_2/CO_2 in coal combustion on the performance of electrostatic precipitators will be minimised.

Stam and others (2009) have reported that the concentration of gaseous trace elements is higher in oxyfuel combustion due to the recycling of the flue gases, although this is moderated for certain elements that condense on the fly ash that is assumed not to be recycled. Equilibrium calculations indicated no change in speciation for oxyfuel firing compared with air firing for the most hazardous elements (Hg, Se, Cr, and As).

Wall and others (2009a) have found that there are different trends for trace element emissions during oxyfuel and air combustion. In particular, the proportion of mercury that reported to the ash for two coals studied increased during oxyfuel combustion. None of this mercury appeared to be leachable.

The anthropogenic emissions of mercury from any coal-fired power plants have been a primary environmental concern. However, for oxyfuel combustion power plant with CO_2 capture, the presentation by Santos (2008) during the third meeting of the Oxy-Combustion Network in Yokohama pointed out that this is now an operational issue especially for the CO_2 processing unit. He noted that any species of mercury, if not removed sufficiently, could cause failure to

any aluminium based equipment within the CO_2 processing unit. He laid down the following discussion points:

- What are the acceptable limits to any mercury emissions that could be tolerated the CO_2 processing unit? Is the standard limit of less than 0.01 µg/m³ set by the natural gas industry appropriate?
- Is there any change to the speciation of Hg during oxyfuel combustion compared with conventional coal-fired power plant?
- What could be the impact of higher chlorine species concentration on the level of mercury oxidation?
- What could be the impact of higher NOx and SO_3 concentrations on any activated carbon based Hg removal system?
- What could be effectiveness of Hg removal during the sour compression process?

Santos (2006) had noted that in the natural gas processing industry, it is general practice that mercury should be limited to less than 0.01 µg/m³. In natural gas processing a failure of aluminium based equipment could cause an explosion due to the release of combustible natural gas. Thus, the natural gas standard is probably too strict for an oxyfuel coal combustion power plant simply because the release of any CO_2-rich flue gases would not cause an explosion. He also noted that standard set by the natural gas industry could be practically achievable since they are dealing with the removal of mercury in a reducing environment. However, for an oxyfuel combustion power plant, it is not yet well established what the impact may be of higher concentrations of NOx and SOx on any activated carbon bed typically used for mercury removal. The NOx species of the oxyfuel combustion flue gas could also have an impact on any regenerative type mercury removal system (in particular, silver based adsorbents). Furthermore, the impact of sulphur species, particularly SO_3, in relation to the effectiveness of the activated carbon adsorbent is not yet well established.

Work done by Babcock and Wilcox at their CEDF facility firing lignite under oxyfuel conditions was reported by Farzan and others (2009). Using an online analyser, they have reported that the total mercury emissions measured during air firing in the flue gas leaving the boiler was about 13.4 µg/m³. They also observed an increase in the concentration of total mercury measured under oxyfuel combustion which corresponded to the removal of nitrogen. Furthermore, they have reported an increase in the oxidation of Hg^0 to Hg^{2+} by 25–30% which they expect to be mostly captured in the wet FGD system.

Gharebaghi and others (2009, 2010) modelled the mechanisms of mercury chlorination in flue gases under oxyfuel conditions. They have identified through their model the possible mercury transformation path under O_2/CO_2 enriched environment between 400 and 1800 K. The mercury adsorption on the fly ash is evaluated using carbon burnout kinetic model. It was noted that retention of mercury in the fly ash is dependent on temperature, burnout and particle size. A

combined homogeneous/heterogeneous model for prediction of mercury speciation in flue gas was developed under air fired condition and validated with various experimental data. This combined model then was adapted to evaluate speciation under oxyfuel combustion conditions. It was concluded that experimental data of mercury emissions and partitioning under oxyfuel conditions are necessary to further validate the model.

Guo and others (2009) tested the release of mercury during thermal decomposition from three different types of coals (anthracite, bituminous and lignite) using a fixed bed quartz tube reactor under three different environments (nitrogen, air, and CO_2) and temperatures between 800°C and 1100°C. They observed that the rate of release of total mercury under CO_2 conditions has a strong dependence to volatile yield and temperature for all types of coal. It was also found that the rate of release of total mercury from bituminous coal was very similar under air and CO_2 environments. Also they noted that, for anthracite, the release rate of elemental mercury was higher in the CO_2 environment than in the air environment at 1100°C. They reported that, under oxidising conditions, mercury conversion from Hg^0 to Hg^{2+} is higher.

Sethi and others (2007) have performed experiments on the performance of and emissions from oxyfuel combustion using a 250,000 Btu/h (~75 kWth/h) combustion test furnace at the Western Research Institute. They used three types of coal – bituminous, subbituminous and lignite. They reported that the total mercury emissions during oxyfuel firing conditions (using a synthetic mixture of 73% CO_2 and 27% O_2 as comburent) compared with air fired conditions for bituminous and subbituminous coal fell from 1.2 down to 0.2 $\mu g/m^3$ and 1.5 down to 0.9 $\mu g/m^3$ respectively. In contrast, they found that there was no change in total mercury emissions for lignite which remained at 3.3 $\mu g/m^3$.

As discussed in Chapter 4, Suriyawong and others (2005, 2006b) performed experimental trials determining the characteristics of the submicron mode of ash and mercury speciation of coal in O_2/CO_2 fired conditions and air fired conditions. The experiments were conducted at different $O_2:CO_2$ and $O_2:CO_2:N_2$ mixture ratios in an alumina reactor tube. They found that with 20:80 and 25:75 $O_2:CO_2$ conditions, the results indicated that the total gaseous concentration under O_2/CO_2 conditions is about the same as that of air, indicating that the O_2/CO_2 system has no effect on the vaporisation of mercury. The ratios of elemental to oxidised mercury (approximately 4:1) were found to be similar for O_2/CO_2 and air combustion. It was also noted that speciation is not affected by the different $O_2:CO_2$ ratios of 20:80 and 25:75.

8 Slagging, fouling, and corrosion

In a recent IEA Clean Coal Centre report, Barnes (2009) briefly discussed slagging and fouling in oxyfuel combustion. He had contacted some industry professionals and summarised their opinion that oxyfuel combustion 'represents largely unknown territory in respect of the impact of the modified combustion environment on ash slagging and fouling and associated effects such as tube corrosion'.

Bordenet (2008) points out that the deposit chemistry may be changed under the oxyfuel gas composition which could lead to higher metal wastages. Due to the high content of CO_2 in the flue gas, a change in deposit chemistry is assumed, and the formation of carbonates in the deposit could be possible. As carbonate deposits are very corrosive, the metal wastage rate could increase. Carbonate formation has, in fact, been observed by Scheffknecht and Maier (2008). Bordenet (2008) also mentions the possibility of locally reducing environments in oxyfuel combustion. This would seem to be highly likely; Dhungel and others (2005) and Maier and others (2006) found that the concentration of CO during oxyfuel combustion was much higher than during combustion with air. For Kleinkopje coal a higher CO emission was detected at the exit of the furnace and also a much higher peak at the near burner zone. They concluded that corrosion may become an issue at the near burner zone since the high CO peaks observed during the oxyfuel runs indicated highly reducing local atmospheres. However, Hjärtstam and others (2007, 2009) have found that, despite significant differences in local CO concentrations in the flame, the stack emissions of CO were comparable. They also found that the CO concentrations in the flame for air firing and oxyfuel firing with 25 vol% O_2 were similar leading them to conclude that in-flame CO concentrations are not necessarily higher in oxyfuel combustion.

In Chapter 4 on ash formation, it was noted that Sheng and Li (2008) found that the variation between O_2/CO_2 combustion and O_2/N_2 combustion did not affect the ash formation mechanisms of iron-bearing minerals, but did affect the relative percentages of iron species formed in the ashes. In general, O_2/CO_2 combustion resulted in more iron melting into glass silicates and less iron oxides formed because the lower char combustion temperatures and the high CO concentration within the particles slowed the transformations of included pyrite and siderite to oxides while favouring their transformations to form the iron glass. The differences observed in the ashes formed in two atmospheres were attributed to the impact of combustion gas atmosphere on coal char combustion temperatures, which influenced the ash formation behaviour of the included minerals. It was pointed out that the increase in iron glass silicates implies that more ash particles formed in oxyfuel combustion are melting and sticky. Therefore, if a coal contains a considerable amount of included pyrite and/or siderite, its slagging propensity may be expected to increase during oxyfuel combustion.

Ash deposition behaviour in oxyfuel combustion was studied by Grahl and others (2009) by installing uncooled ceramic specimen holders at the end of the chamber of their 50 kWh test facility. The experiments shown in Figure 17 show that, compared with conventional combustion, in oxyfuel combustion the slagging grade increases with decreasing flue gas recirculation volume flow with increasing oxygen content. As less flue gas is recirculated the combustion temperature increases resulting in complete slagging at 30 vol% O_2. Although the ash melting temperature (T_S) from 20% O_2 to 30% O_2 increases because there are mineral losses due to reactions with the gas phase, the outlet temperature from the combustion chamber increases even more, which leads to slagging on the uncooled specimen holder. At 20% O_2, where the operation mode is similar to the conventional air firing, no major changes were expected and the ash melting point was at a similar temperature level.

A comprehensive suite of ash deposits has been collected during oxyfuel combustion trials of two coals on the 1 MW combustion test facility (CTF) at E.ON UK by Wigley and Goh (2009). Combustion parameters that they have investigated include firing mode (air or oxyfuel), excess oxygen level, proportion of air staging and degree of oxygen enrichment. Scanning electron microscopy examination of the samples revealed that, compared with air fired deposits, the oxyfuel deposits:
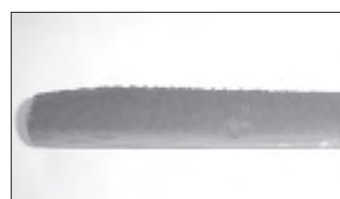
Conventional combustion - 4 vol% residual oxygen

- loose overlay of the ash
- no slagging

ash melting point:
T_S=1099°C

Oxyfuel 20 - 4 vol% residual oxygen

- loose overlay of the ash
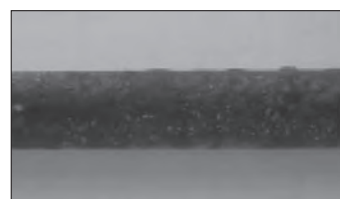- no slagging

ash melting point:
T_S=1074°C

Oxyfuel 25 - 4 vol% residual oxygen

- loose overlay of the ash
- light slagging on certain points

ash melting point:
T_S=1173°C

Oxyfuel 30 - 4 vol% residual oxygen

- complete slagging
- no loose fraction

ash melting point:
T_S=1280°C

Figure 17 Ash crust behaviour from oxyfuel combustion of lignite (Grahl and others, 2009)

- were smaller and had a different (wedge) shape;
- were more densely packed;
- had similar particle size;
- were less well sintered and more friable;
- contained particles that were less rounded;
- were richer in clay-derived particles that were not fully fused.

It was suggested that the different shape and denser packing in the oxyfuel fired deposits are probably caused by the greater density of CO_2-rich flue gas, and may be general features of oxyfuel firing. As the O_2 concentration in the secondary recycled flue gas increased, oxyfuel fired deposits became larger but showed no significant changes in microstructure. Deposit structure was not significantly affected by the level of excess oxygen or the proportion of overfire air (OFA). It was pointed out that the current uncertainty about ash behaviour during oxyfuel combustion of coal arises mainly from the unknown combustion conditions. Once the combustion conditions (and therefore time-temperature history) for oxyfuel firing are specified, ash behaviour in the radiative section of the boiler should be largely predictable from current knowledge.

Recently, there have been a few studies on corrosion reported. Covino Jr and others (2007) conducted corrosion exposure tests at elevated temperatures on three alloy corrosion coupons covered with a synthetic ash (Standard Corrosion Mixture, SCM) and exposed to two different gaseous mixtures representative of air fired and wet recycle oxyfuel/RFG fired coal combustion. At a superheater temperature of 675°C the corrosion rates were found to be high with a consistent increase in the oxyfuel/RFG fired environment compared with the air fired environment.

Huenert and others (2008) have studied the corrosion of steels with chromium contents ranging from 1% to 24% in H_2O/CO_2 atmospheres at temperatures between 500°C and 700°C. They found that the corrosion mechanisms and observed oxide-scale compositions in a flowing H_2O/CO_2 atmosphere at different temperatures are changed compared with the corrosion results in pure H_2O, CO_2, and O_2 respectively. In particular, steels with chromium contents below 12% did not form a dense and therefore protective Cr_2O_3 layer. The oxide-scale thickness increased strongly with temperature and decreased with increased chromium content.

Hünert and others (2009) also studied corrosion in $CO_2/H_2O/O_2$ which corresponds to the atmosphere in oxyfuel combustion (with wet flue gas recycle). At 600°C the formation of carbides and carburisation of the steels was observed in low alloyed steels. Carburisation was observed in all ferritic and ferritic-martensitic steels investigated in the study but was limited when a dense Cr-oxide or Fe-Cr-spinel layer was formed. Carburisation changes the mechanical properties such as ductility and may have an impact on the lifetime and the reliability of components. As a consequence of carburisation, the excess carbon can change the properties of the materials and support crack formation during thermal cycling. Chromium is consumed during the formation and growth of metal carbides leading to loss of oxidation

resistance. A deeper corrosion could be the effect. Kranzmann and others (2009) suggest that steels with Cr content higher than 20% can be used in the temperature regime above 570°C in a carburising environment and perhaps 14–15% could be sufficient (Kranzmann, 2010). The working temperature limit for 9 to 12% Cr steels under load and with the requirement for long lifetime of the component may decrease in high CO_2 containing atmospheres to below 550°C.

Abellán and others (2010) have also studied the oxidation behaviour of a ferritic-martensitic 9% Cr steel using a model gas mixture containing 70% CO_2/30% H_2O in the temperature range 550–650°C. The results were compared with the behaviour in air, Ar/CO_2 and Ar/H_2O. In the CO_2-rich gases and/or H_2O-rich gases, the steel formed iron-rich oxide-scales which possess substantially higher growth rates than the Cr-rich surface scales formed during air exposure. The explanation of this was that the iron-rich oxide-scales are formed as a result of a decreased flux of chromium in the bulk alloy toward the surface. This is the result of enhanced internal oxidation of chromium in the H_2O-containing gases and carburisation in the CO_2 gases. The oxide-scales allow molecular transport of CO_2 towards the metallic surface, resulting in carburisation of the alloy. The presence of water vapour induced buckling in the outer haematite layer, apparently as a result of compressive oxide growth stresses. Buckling did not occur in the H_2O-free gas. Thus there is potential for H_2O to increase growth stresses and accelerate crack propagation. Overall, the oxidation rates in CO_2/H_2O did not seem to be higher than those observed in flue gases of conventional fossil fuel-fired power plants.

Abellán and others (2010) also pointed out that in H_2O-rich gases incorporation of hydrogen in the steel results in a higher oxygen solubility and/or diffusivity and consequently, in enhanced internal oxidation of chromium. The diffusion of hydrogen and carbon produced in the corrosion process can also change the corrosion mechanism on the steam side of the superheater. According to Hünert and others (2009) this effect produces an additional unknown influence on the total corrosion impact. The effects of the dual atmosphere – the combustion gas and the air/steam on the opposite surface – have been reported by Huenert and others (2009). The corrosion behaviour of ferritic-martensitic steels under such dual atmospheres was investigated in specially designed test equipment between 500°C and 620°C. The power plant conditions were simulated with a flowing and pressurised (8 MPa) combustion gas on the inner side of the tube which mainly consists of H_2O and/or CO_2. On the outer side, the tube material was exposed to air. It was discovered that under similar temperatures the oxides formed on the air side under dual atmosphere conditions were significantly different from the oxide scales formed when the alloy was exposed to air only. A faster corrosion of the air side under dual atmospheres was also observed. It was assumed that the anomalous corrosion behaviour during the dual atmosphere exposure was due to hydrogen transport through the bulk alloy from the combustion gas side to the air side.

A combined corrosion and deposit exposure test was undertaken in a 500 kW oxyfuel test rig (KSVA) at IVD, University of Stuttgart (Hjörnhede and others, 2009). A broad

spectrum of alloys from low alloyed steels to nickel-based alloys were mounted on a internally cooled probe exposed in the rig at a metal temperature of 630ºC for up to 40 hours with Lusatian lignite as the fuel and for 26 hours with South African hard coal (Kleinkopje) as the fuel. Exposures with both with oxyfuel firing with recirculation of flue gas and conventional firing have been conducted to compare the corrosion attack and deposit composition for lignite, while only oxyfuel tests were performed with hard coal. It was found that, generally, the mass gain rates were similar between the different tests for the same material. No major difference could be detected between air firing and oxyfuel firing. Further long term tests (672 hours) were performed for some selected samples using a tube furnace at the Swedish High-Temperature Competence Center (HTC) at Chalmers University, with a synthetic oxyfuel flue gas composition to simulate long term corrosion effects. Samples from the tests in the IVD KSVA-rig, on which a deposit layer had formed, were exposed in Chalmers tube furnace. The corrosion mechanisms detected were similar for both the long term and short term exposures. However, in the conference presentation, it was concluded, at least for nickel based alloys, that there was a strong indication of a higher material wastage rate in oxyfuel conditions and there was evidence for increased sulphur concentration at the corrosion front. The effects of sulphur on corrosion in oxyfuel plants will be considered in the next section.

8.1   Sulphur-related corrosion

In Chapter 5 on sulphur oxides, it was noted that Maier and others (2008) had found that the concentration of H_2S was higher during oxyfuel combustion with RFG and also much higher for high volatile coals compared with medium volatile coals. It was suggested that careful attention should be given to high volatile and high sulphur coals such as low rank high sulphur coals. Fleig and others (2009a) have pointed out that formation of H_2S can be considerable under substoichiometric conditions (λ <1) combined with temperatures between 1100ºC and 1600ºC, conditions typically occurring in a flame. If oxygen is in excess with quantities typical for pulverised coal combustors, the outlet concentration of H_2S is negligible. An increased H_2S concentration can be anticipated in an oxyfuel flame, due to the SO_2 content in the oxidiser. Furthermore, the recycle rate in oxyfuel operation can directly influence the H_2S concentration since the flame temperature has a considerable influence on the formation under substoichiometric conditions.

In Chapter 5 it was noted that the outlet concentration of SO_3 could be about four times the concentration in air firing (Fleig and others, 2009a). In the presence of higher SO_3 concentrations under wet flue gas conditions, the increase in the water vapour concentration can lead to substantial increases in the acid dew point (Maier and others, 2008). The SO_3 concentration was initially reported to be 85 ppm in oxyfuel conditions, an order of magnitude higher than the 8 ppm in air fired conditions. These figures were both ten times too high and were later correctly reported by Scheffknecht and Meier (2008), but that does not affect the order of magnitude difference. Fleig and others (2009a)
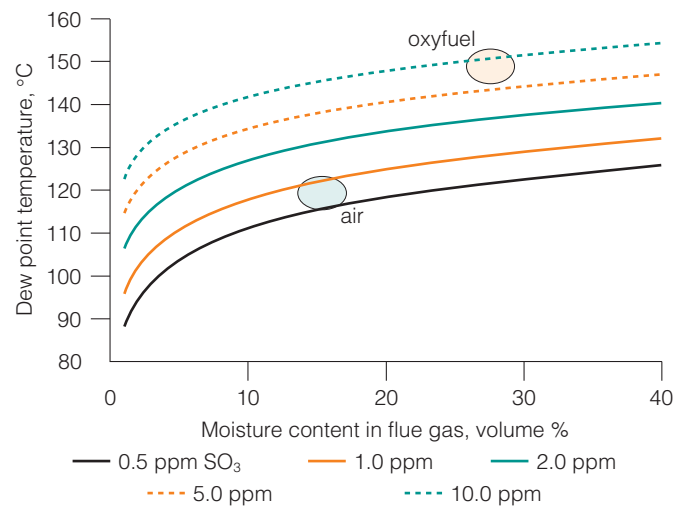

Figure 18   Dew point temperature as a function of SO_3 and moisture concentration (Scheffknecht and Maier, 2008)

suggested that an increase in acid dew point temperature by 20 to 30 K was expected in oxyfuel conditions due to higher SO_3 and H_2O concentrations. Figure 18 shows the calculated increase in dew point temperature as a function of SO_3 and moisture concentration (Scheffknecht and Maier, 2008).

Stanger and Wall (2010) have pointed out that, in air fired pulverised coal combustion, the SO_3 concentration in the flue gas is generally accepted to be coal and boiler specific and dependent on temperature. The concentrations of SO_3 and H_2O are important factors in determining the acid dew point of the flue gas. At temperatures below the acid dew point the liquid H_2SO_4 begins to condense on surfaces and can be a major corrosion issue if not accounted for. In oxyfuel combustion, the higher SO_2 and H_2O concentrations resulting from recycled flue gas and lower gas volumes are expected to produce a higher concentration of SO_3 and hence a higher acid dew point. Correlations using measured SO_3 levels for three coals produced an estimated increase in acid dew points of 14.0–21.6ºC compared with the air fired case.

Schnurrer and others (2008), on the basis of thermodynamic modelling studies, had found that, compared with combustion in air, oxyfuel combustion of pulverised coal alters the flue gas composition significantly. The elevated SOx concentrations result in a drastically increased formation of sulphuric acid, strongly indicating higher corrosion potential. Additionally, larger parts of the air heater may be affected by acidic corrosion due to an increase in acid dew point temperature of about 30ºC in oxyfuel combustion. This led Wall and others (2009a) to suggest that there could be a need for desulphurisation of the flue gas or oxyfuel combustion being limited to low sulphur coals. Schnurrer and others (2008) also suggested a second option to counter the increased acidic corrosion – the removal of H_2O from the recycled flue gas stream. This dry recycle results in less water content in the flue gas and thus would decrease the amount of H_2SO_4 formed.

Zheng and others (2009) also believe that a cold, dry flue gas recycle is probably the best option for high sulphur coal. The

El Cerrejon oxyfuel
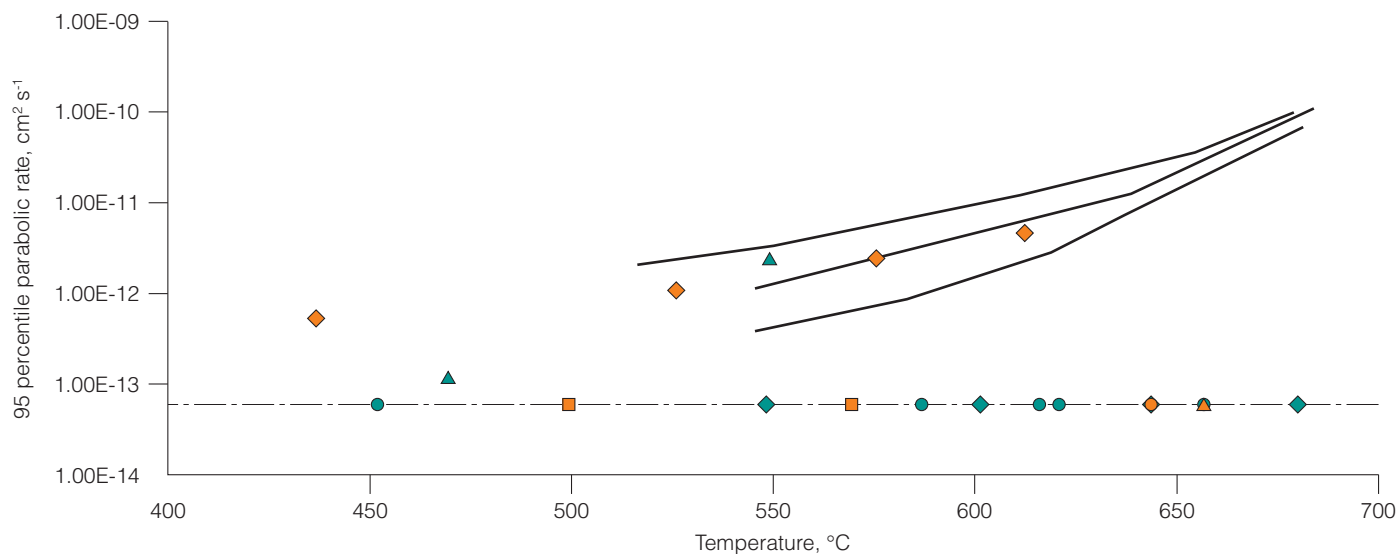
low sulphur, low chlorine

Thoresby oxyfuel
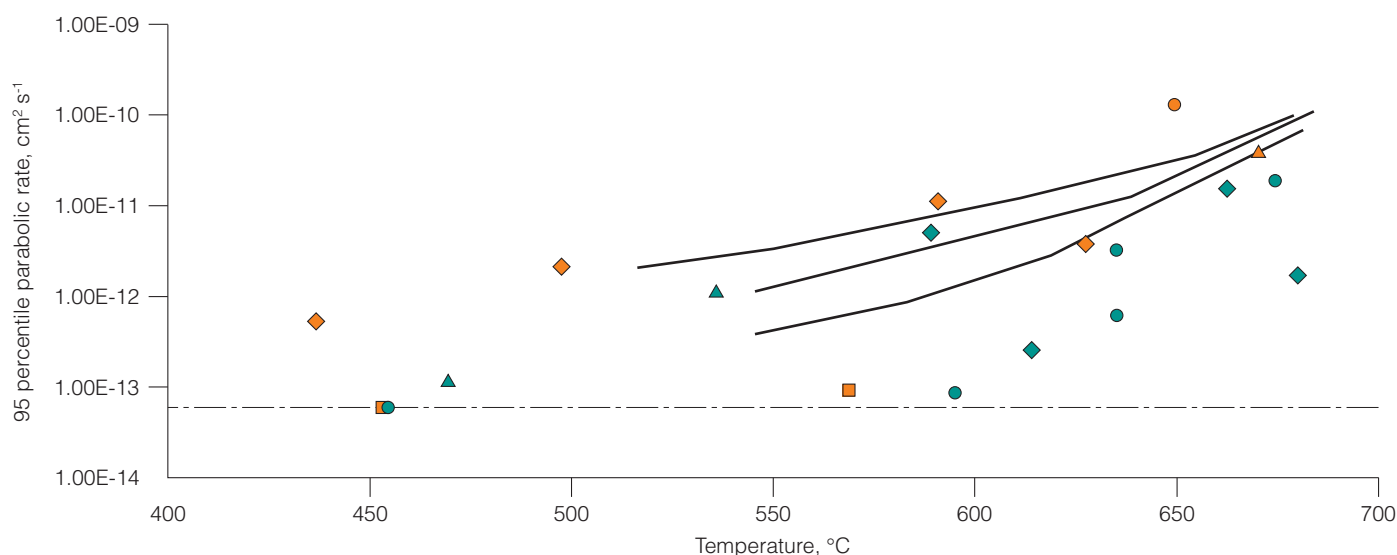
high sulphur, high chlorine

◆ T22 ▲ T91 ■ E1250 ● TP347HFG ◆ HR3C ▲ San25 ● IN740

Figure 19 Effects of sulphur and chlorine on corrosion (Irons, 2009)

recycled flue gas is usually extracted downstream of an FGD and a flue gas condenser so that most of the SOx has been removed. Therefore, the accumulation of SOx in the recycle loop will be greatly reduced. A warm, wet recycle before the FGD would be expected to increase boiler corrosion.

Calculations by Stam and others (2009) indicated the formation of significant levels of calcium sulphate in oxyfuel conditions, again probably related to the higher levels of sulphur. The presence of calcium sulphate could lead to higher levels of fouling.

The influence of the atmosphere from oxyfuel combustion of Lusatian lignite on the surface of selected superheater materials was studied by Kull and others (2009) and subsequently compared with the influence caused by the conventional combustion atmosphere. The investigation was focussed on the impacts of sulphur caused corrosion. Increased corrosion caused by sulphur was observed in samples exposed to the oxyfuel combustion atmosphere. A higher depth of corrosive attack of the oxyfuel samples was observed and might be explained by a higher partial pressure of SO_2 due to the flue gas recirculation. The oxyfuel samples were exposed to much higher partial pressures of carbon dioxide compared with the air firing case leading apparently to rapid and massive carburisation of the metal surfaces.

Holcomb and Huckaby (2009) have pointed out that oxyfuel firing affects the sulphur content of the ash. The sodium and potassium sulphates that are formed tend to increase corrosion and molten phases promote hot corrosion. Also, oxyfuel firing affects the iron speciation of the ash in which unreduced FeS

could be a corrosion concern. However, initial experiments had revealed that the ash-covered corrosion rates in air and oxyfuel environments appeared to be similar. Thermodynamic modelling studies by Schnurrer and others (2008) have indicated that higher amounts of alkali sulphate form in oxyfuel combustion for two of the three Australian coals studied, so oxyfuel combustion may not lead to higher sulphate values, but coal composition has to be taken into account. Slagging and fouling propensity is expected to rise with increasing alkali sulphate presence, as they are responsible for deposit creation. However, the overall amount of melt phase (includes slags, molten solutions and liquids) was found to be almost the same in both air and oxyfuel firing.

The effects of both sulphur and chlorine on corrosion in an oxyfuel environment have been reported by Irons (2009) based on studies of Colombian El Cerrejon coal (moderate sulphur content, near zero chlorine) and UK Thoresby coal (~2% S, 0.4–0.5% Cl) and ten materials. With El Cerrejon coal in an oxyfuel environment, the observed corrosion was comparable to that observed in air firing. In contrast, the corrosion observed with Thoresby coal in an oxyfuel environment was much more marked. The difference can be seen in Figure 19. There is potential for a severe increase in corrosion when using high sulphur and chlorine coals especially for high chromium content alloys.

9 Pilot and demonstration plants

Although a comprehensive overview of oxyfuel demonstration projects has been produced by Wall and Yu (2009), some more recent details of pilot and demonstration plants and plans for future ones will be included in this chapter, again limited to pulverised coal firing technologies but also to facilities that are in operation or under construction. Most of the information included here was presented at the first Oxyfuel Combustion Conference, 8-11 September 2009, in Cottbus, Germany.

Vattenfall's 30 MW Schwarze Pumpe pilot plant

http://www.vattenfall.com/en/ccs/schwarze-pumpe_73203.htm

An update on this plant has been provided by Altmann and others (2009) and Paelinck and Altmann, 2010). The project started in July 2005 and the plant was inaugurated on 9 September 2009 although oxyfuel operation had started a year earlier. The basic purpose of the plant is to provide operating information to make it possible to scale-up the technology to a 400–600 MW demonstration power plant. The plant operates with a complete process of coal input and oxygen production up to separation of CO_2. It is possible to operate on full load both in air firing mode and oxyfuel mode. The present plant is designed to operate on lignite and in a second phase on bituminous coal.

Until August 2009 the plant had operated using lignite for over 3000 hours with slightly more that half of this time in the oxyfuel mode. In that time 1400 tonnes of CO_2 had been captured. It is possible to change from air firing to oxyfuel firing in 20 minutes. Good flame stability has been obtained at oxygen concentrations above 21 wt% but different burner swirls are necessary for air and oxyfuel operation. Some combustion tests still to be carried out include:
- variation of coal quality (moisture, sulphur content, particle size);
- different burners with integrated ignition burner;
- material tests for demonstration plants and 700°C technology under an oxyfuel atmosphere;
- cofiring biomass and bituminous coal;
- deNOx tests.

Figure 20 shows a schematic of the pilot plant.

Kluger and others (2009) confirm that the burner operates in premixed mode in a stable and reliable way with an oxygen concentration of 28 vol%. Limits for emissions are kept easily for the oxyfuel mode of operation. Indeed, primary measures for NOx reduction were not required, typical emissions being <700 mg/m^3 (dry). Burnout was good with low unburnt carbon in the fly ash and slag. However, in the oxyfuel mode
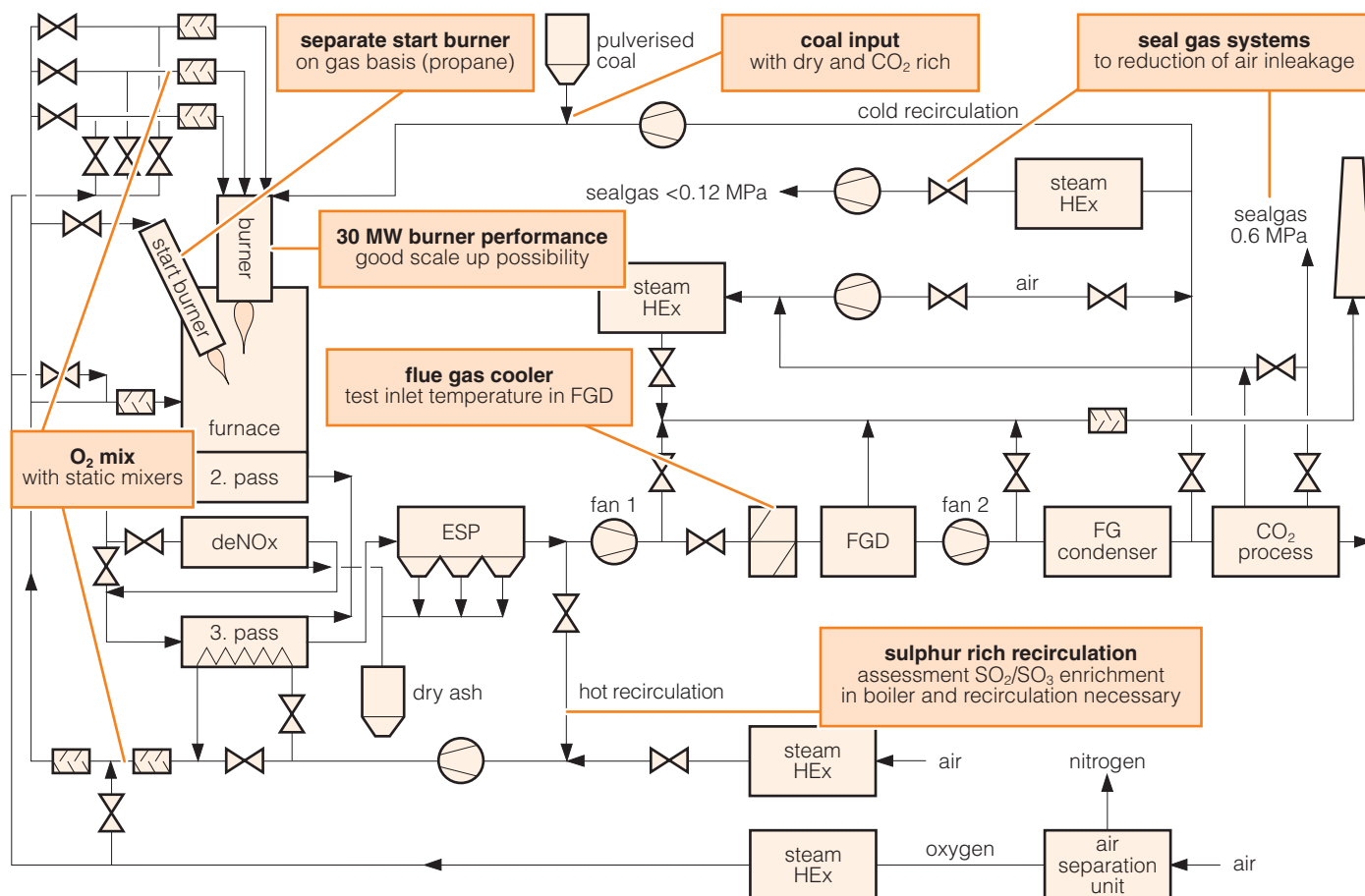
Figure 20 Schematic of the Schwarze Pumpe pilot plant (Altmann and others, 2009)

there is a longer response time due to the flue gas recirculation. The mode switch from air mode to oxyfuel mode and vice versa works more easily than originally anticipated. CO_2 concentrations in the flue gas downstream of the boiler are >85 vol% (dry).

Meyer and others (2009) note that one of the challenges facing the pilot plant is in-leakage of air since it is crucial for the CO_2 capture process that the concentration of CO_2 is as high as possible. Thus dilution with nitrogen (ambient air) is to be avoided. The solutions for this involved two induced draught (ID) fans to maintain the underpressure in the flue gas path, but keep it low and avoid points of too high underpressure. There is also a CO_2 sealing system in which critical points for air in-leakage are to be sealed with a 'mantle' of CO_2. Jacoby and others (2009) confirm that air ingress into the steam generator is low and that, additionally, all measurement ports have been equipped with ball valves and seals to minimise air ingress.

The Schwarze Pumpe plant is a step towards a 250 MW lignite-fired plant planned to be built around 2015 at Jänschwalde which will incorporate both an oxyfuel boiler and post-combustion amine scrubbing.

Callide Oxyfuel Project

http://www.callideoxyfuel.com

The Callide 'A' power station in central Queensland, Australia, has been refurbished to act as a 30 MWe oxyfuel pilot plant (Spero, 2009a). The contract for the oxygen and CO_2 plant earthworks was awarded in August 2009 so the plant is not yet operational. The Callide oxyfuel boiler is based on a nominal 70% RFG rate. About 40% of the RFG is dried by cooling and used as primary gas through the mills; the balance is wet secondary gas to the windbox. The longer term design issues relate to:

- the need or otherwise to dry the primary gas to the mills;
- materials in the RFG circuit to minimise the impact of dew point corrosion;
- burner design (in the context of relative flows/velocity between primary gas through the burner and secondary gas around the burner registers);
- integration of heat recovery with traditional feedwater heating systems;
- process control especially regarding run-up and master fuel trips.

In the Callide Oxyfuel Project, IHI Corporation (Japan) have responsibility for the retrofit work to oxyfuel of the Callide 'A' boiler. Some risks have been identified and some studies have been conducted in the process of design progress, considering the commercialisation, safety and reliable operation (Yamada and others, 2009). The risks identified were the possibilities of:

- ignition of fly ash at the high temperature and high O_2 concentration on the duct wall;
- unbalanced O_2 concentration at the burner windbox inlet, resulting in a different or uncontrollable flame temperature in the four burners;
- change of boiler heat balance;
- a back stream of RFG.

Reliable performance of the flame detector was also identified as necessary.

Tests carried out showed that the possibility of ignition of fly ash at Callide 'A' conditions is very low. By the optimisation of the O_2 injection nozzle, it was found that the possibility of higher O_2 concentration on the duct is low, the risk of ignition of the fly ash on the duct is very low, and the risk of unbalanced O_2 distribution at the burner inlet is lower.

The Callide plant will be the first integrated oxyfuel demonstration plant with electrical generation; this means that it will demonstrate the ability of an oxyfuel plant to operate with real time load following in an open market. Additionally, the coal mill will be an online coal mill, rather than the pre-milled material used in the Schwarze Pumpe plant and other facilities to date. Thus this is the second online issue yet to be demonstrated. The plant will be operating without the use of an SCR or FGD, and thus the effects of higher NOx and SOx during the compression plant, and within the primary recycle lines will be demonstrated. How this reacts with the coal mill will have real relevance for larger-scale operations. The plant will be the first full chain retrofit application to be demonstrated in oxyfuel, rather than new build. It will operate with two air separation units, a likely practical situation (Wall and Stanger, 2010)

CIUDEN 20 MWth pulverised coal boiler

http://www.ciuden.es/

The CIUDEN CO_2 capture programme incorporates not only the 20 MWth pulverised coal boiler but also a 30 MWth circulating fluidised bed boiler when working in full oxyfuel mode (Lupion and others, 2009). The plant is located in northwest Spain in the province of León, close to the Compostilla power plant. Investment in the plant is €84 million. The pulverised coal unit was dimensioned following the criteria generally used in commercial boilers, taking into account the peculiarities of a pilot plant in order to generate data/information in the experimental unit for a comparison between full-scale operation. The combustor has been designed to operate with air whilst taking into account all necessary constraints in order to allow the unit to operate with oxygen such as limits of flammability, fuel injection, flame temperature, and furnace behaviour and heat transfer surfaces, providing the pilot boiler the necessary flexibility to achieve the testing objectives sought with oxyfuel combustion.

Babcock & Wilcox CEDF

During 2007 and early 2008 the Babcock & Wilcox Company's (B&W) Power Generation Group together with Air Liquide tested oxyfuel combustion in a 30 MWth Clean Environment Development Facility (CEDF) in Alliance, Ohio, USA (McDonald and others, 2009a; Farzan and others, 2009). The CEDF used three burners, one for bituminous coal, a new design for lignite and subbituminous coal, and an enhanced ignition burner for the Powder River Basin subbituminous coal. The feasibility of switching from air to O_2 enriched recycle gas operation was demonstrated, and an operating procedure for smooth transition from air to oxyfuel firing then back to air firing modes was developed. The oxyfuel firing flame was adjusted via burner hardware and oxygen input to

obtain a stable and attached flame. It was found that the flame stability and shape were strongly dependent on the oxygen concentrations in the primary zone and coal and recycle gas moisture contents. Moisture levels well in excess of 35% in the secondary recycle gas were tested. Furnace exit gas temperature (FEGT), flame temperature, and furnace heat fluxes were lower with oxyfuel combustion and were ascribed to the density and emissivity impact of high CO_2 levels and the moisture impact on flame temperature.

Except for SO_2 emissions which were the same for air and oxyfuel firing (somewhat surprising given the discussion in Chapter 5), the oxyfuel firing emission levels were lower than emissions under air firing for all fuels and were dependent on the firing conditions. For example, the NOx emissions were approximately 50% lower in oxyfuel firing conditions than the baseline for lignite (on a kg/MWth basis). NOx emissions, flame length, and unburned combustibles were a strong function of burner configuration. NOx emissions were affected by the burner design and the method through which oxygen was introduced into the boiler. Figure 21 shows the effect of the strategic oxygen introduction into the process. With the optimum oxyfuel firing configuration NOx emissions were 70% lower than the air firing conditions using bituminous coal.

Although emission characteristics of oxyfuel firing were favourable when compared with air firing for all three coals tested, CO could be very high with oxyfuel firing in a non-optimised situation but CO emissions were mostly lower in oxyfuel firing when oxygen was introduced in an appropriate fashion. Unburnt combustibles were typically low for air firing and oxyfuel firing in optimum conditions. Mercury concentration significantly increased due to removal of nitrogen but oxidation also increased. Since the same mass of Hg must be removed with air or oxyfuel firing, the higher concentration and ionic portion should improve removal in the environmental equipment.

B&W and Air Liquide are now pursuing commercial demonstration of a 100 MWe net oxyfuel coal plant with CCS to confirm the cost and performance expectations and demonstrate the operability and reliability of the design (McCauley, 2009); McDonald and others, 2009b). The Black Hills demonstration plant will be located in Campbell County, Wyoming, firing Powder River Basin subbituminous coal.

Doosan Babcock 40 MWth OxyCoal™ combustion system

Doosan Babcock is leading a number of UK Government supported collaborative projects that are developing oxyfuel combustion technology, including the £7.4 million UK Department of Energy and Climate Change (DECC) collaborative project, *Demonstration of an Oxyfuel Combustion System (OxyCoal 2)*, which will demonstrate the Doosan Babcock 40 MWt OxyCoal™ full-scale utility power plant burner (Cameron and others, 2009, 2010). The burner will be based on the existing 90 MWt Multi-fuel Burner Test Facility (MBTF). Eight ambient vaporisers to supply gaseous oxygen for injection into primary and secondary FGR streams are being installed. The primary and secondary FGR streams will replace the primary air and main combustion air respectively, each having a dedicated fan. Work commenced in the summer of 2009. The OxyCoal™ burner design is based on current low NOx air fired burner technology. It is compatible with existing plant for retrofit purposes and exploits a range of potential operating conditions for both oxyfuel and air firing. The facility is able to fire a wide variety of fuels; coals (low volatile semi-anthracites – 8% volatile matter to high volatile bituminous coals with 50% volatile matter, up to 35% ash, and up to 20% inherent moisture), heavy fuel oil and natural gas. For oxyfuel operation the volumetric flow rate and oxygen content of the primary gas is maintained as per air firing. The overall stoichiometry is 1.2, and the flue gas recycle rate chosen to give an adiabatic equivalent to air operation. Preliminary test
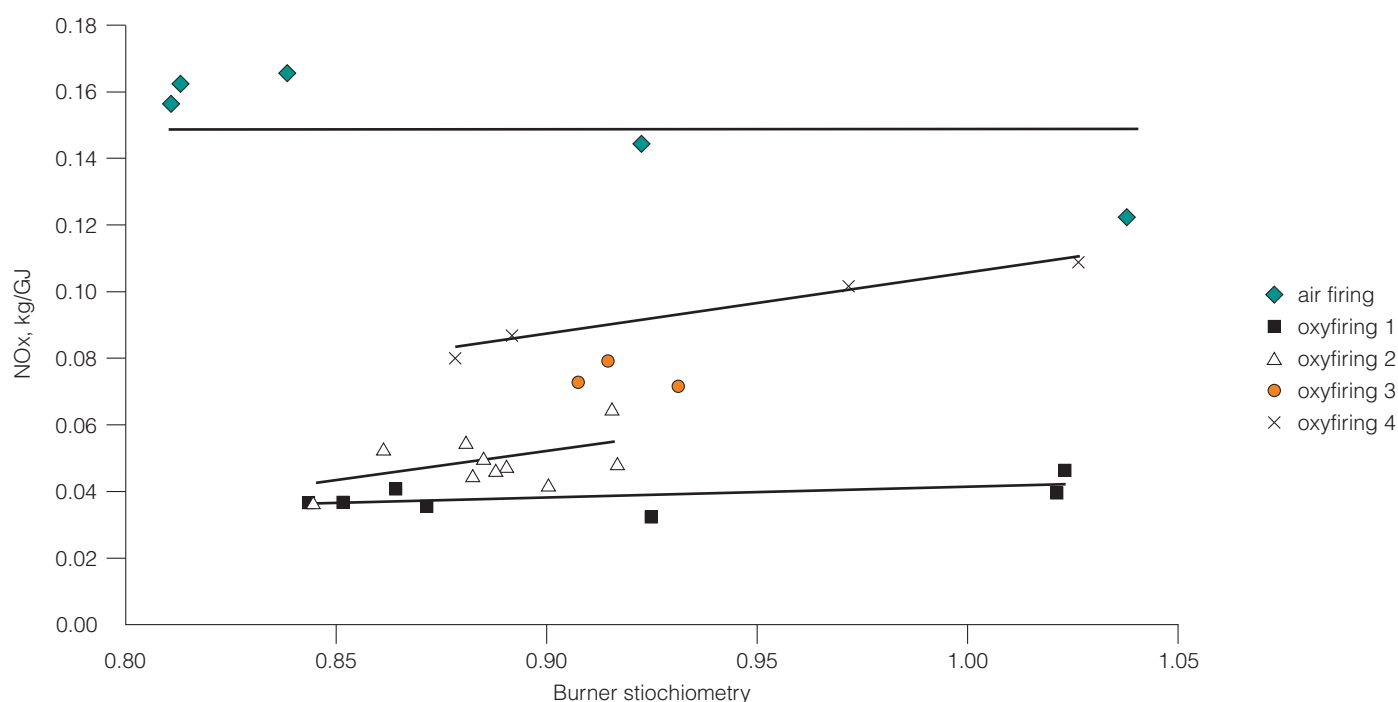

Figure 21 Effect of the strategic oxygen introduction (1b/MMBtu = 1.548 kg/MWh) (Farzan and others, 2009)

results for wall heat flux are shown in Figure 22. Oxyfuel has lower heat flux with less peaky distribution due to FGR dilution effect in the flame. There is similar FEGT and heat flux towards the furnace exit.

Tests have shown that the transition from coal firing on air to oxyfuel is safe and smooth and that a stable oxyfuel flame is achievable. The oxyfuel coal flame is visually practically indistinguishable from the flame obtained during air firing. Importance of air ingress has been investigated. Initially air ingress resulted in a CO_2 concentration of around 50 vol% (db) when at full load oxyfuel operation. However, air ingress minimisation has resulted in a CO_2 concentration of around 85 vol% (db) when at full load oxyfuel operation. By balancing pressures in the draught plant it is possible to control the air in-leakage.
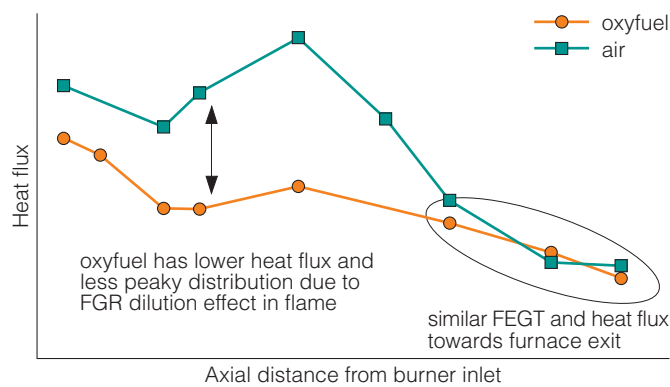

Figure 22 Test results for wall heat flux in the OxyCoal™ burner (Cameron and others, 2009)

Jupiter Oxygen Corporation large-scale boiler test facility

Jupiter Oxygen has designed, built and operated a 15 MWth boiler test facility in Hammond, Indiana, USA (Gross and others, 2009). Most of the reported tests have been carried out using natural gas but initial testing since August 2008 has also used coal (Illinois No 6). Jupiter's approach is to maintain the purity of the oxidant in order to have a flame with a high concentration of oxygen at the burner tip, thereby producing a very stable flame (Ochs and others, 2009). Coal has been used with oxygen (with and without FGR) resulting in a high flame temperature in the boiler (~2760°C) without any evidence of tube or refractory damage in a 1984 boiler with original tube and wall materials. Test data indicate that heat deposition (transfer of heat from the hot combustion products to the water/steam) in the boiler can be controlled by the use of recycled flue gases. In Jupiter's approach, these recycled gases are not mixed with the oxygen or the flame. The recycle is outside the flame envelope to maintain high flame temperature. The initial coal test have shown that the burner has excellent turndown and stability and sustained operation of burner has been achieved with excess oxygen levels of 2.5% or less. Preliminary results show no issues with slagging or fouling.

Future developments

Figure 23, prepared by the IEA GHG, shows the progress towards larger-scale demonstration plants and possible commercialisation by 2020. By the end of 2010-11, power plant operators will have six burner manufacturers fully-demonstrating utility-size large-scale burners (not all based on pulverised coal firing). Successful operation of these plants should provide a high level of confidence for demonstration on a larger scale.
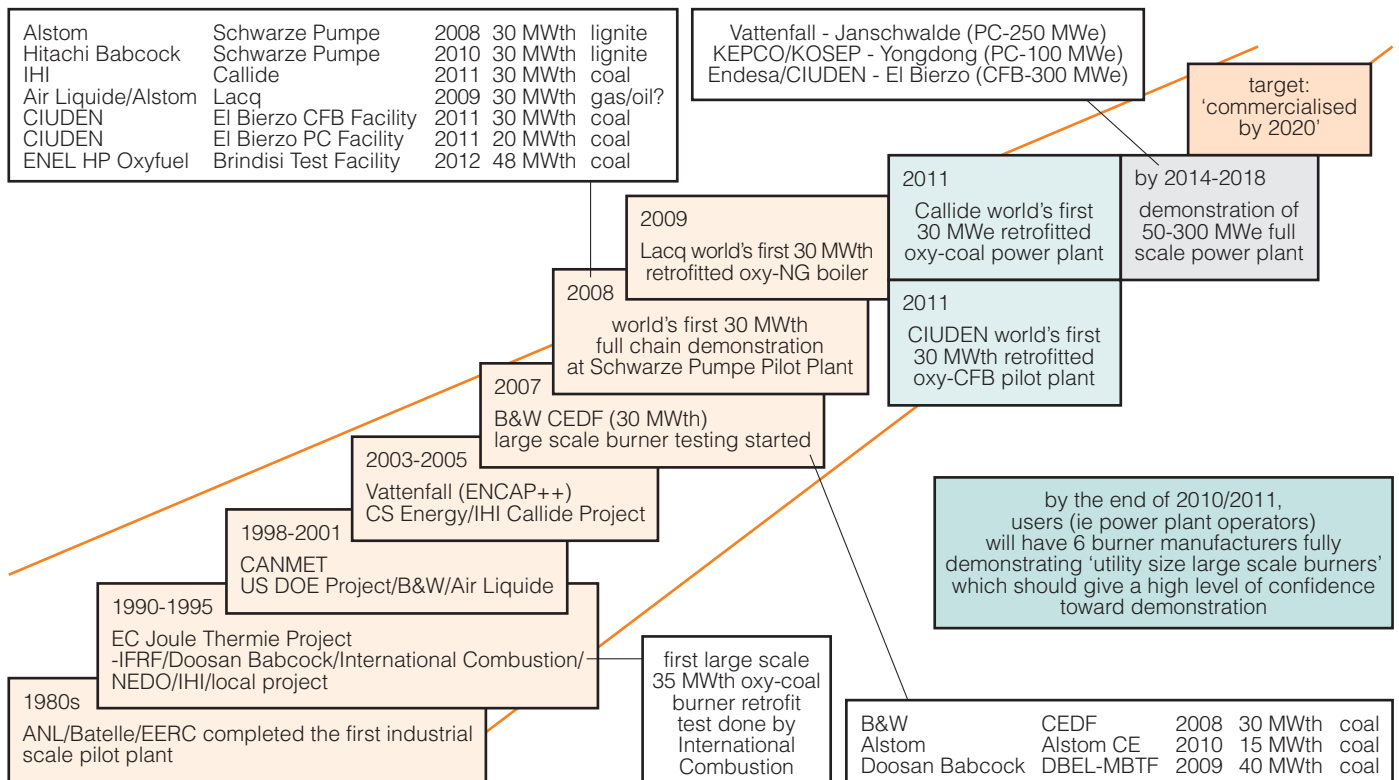

Figure 23 Progress towards larger-scale demonstration plants and possible commercialisation by 2020

However, Wall and Stanger (2010) have commented that, at its current state of maturity, oxyfuel technology may be considered pre-commercial, in that, even if a unit was economically viable and could be provided by a vendor, the generator and vendor would need to share the technical risk. This is because guarantees could not at present be provided for operating characteristics associated with mature technologies such as reliability, emissions, ramp rate and spray control. This is due to the maturity of the technology associated with the capability of vendors and associated design and operational uncertainties, associated with a lack of plant experience at semi-commercial and commercial scale. The experience required for a mature technology is for units of a scale justifying high efficiency using high temperature steam conditions, typically >250 MWe, rather than a number of demonstration units currently proposed of a scale of 100 MWe. This is because the efficiency penalty has a greater impact on low efficiency units. There is only one pulverised coal plant planned to be of this scale – the 250 MW lignite-fired plant planned to be built around 2015 at Jänschwalde, Germany. In addition, there is also the CIUDEN 300 MWe circulating fluidised bed plant planned to be built around the same time near Compostilla, Spain.

10 Techno-economic studies

It is not the intention of this chapter to provide an authoritative techno-economic assessment of oxyfuel combustion of pulverised coal as means of CO_2 capture but, rather, simply to report on the limited number of assessments that have been made in this area where there are very few data available on which to base economic assessments. There is no doubt that oxyfuel combustion of pulverised coal will be more expensive than an air fired plant without capture. The IEA GHG report of 2005 estimated that, for a plant with 500 MWe net power output, the oxyfuel case would have a cost of electricity (COE) of 7.28 US ¢/kWh compared with 4.9 ¢/kWh for the base case. The cost of CO_2 avoided would be ~41 $/t while the plant thermal efficiency would decrease from 44.2 % LHV (net) to 35.4%.

Some studies performed prior to 2005 have been reviewed by Gupta and others (2005a) who concluded that, by taking into account the by-product credits such as N_2 and CO_2, oxyfuel combustion could be more attractive than other competing technologies. Based on studies carried out on behalf of the IEA GHG, Gupta and others (2005b) concluded that oxyfuel combustion (with and without CO_2 capture) could be a very cost competitive technology option for future plants. Without carbon capture, oxyfuel combustion was compared with conventional air fired pulverised coal combustion and was found be to very competitive in terms of cost and integrated control of air pollutants. With carbon capture, it was observed that oxyfuel combustion offers a very competitive technology option.

Andersson and others (2005) evaluated the fixed and running costs associated with an 865 MWe lignite-fired oxyfuel power plant in order to obtain the CO_2 avoidance cost for a new state-of-the-art capture plant. With a lignite price of 43 €/MWh and an interest rate of 5% an avoidance cost of about 15 €/tonne CO_2 was obtained compared with the 865 MW lignite-fired reference plant. In a later paper Andersson and Johnsson (2006) produced revised figures. Based on a lignite price of 5.2 $/MWh (4.0 €/MWh) and an interest rate of 10%, the electricity generation cost increased from 42.1 to 64.3 $/MWh, corresponding to a CO_2 avoidance cost of ~29 $/t CO_2 (or ~22 €/t CO_2). With all integration possibilities considered, the net efficiency of the oxyfuel plant was approximately 33.5% compared with 42.6% in the reference plant.

An economic analysis was conducted by Seltzer and others (2005, 2006a,b) to determine capital and operating costs of an oxyfuel fired pulverised coal power plant as well as for the equivalent conventional air fired plant. A conceptual design of a CO_2 sequestration-ready oxygen based subcritical 460 MWe (gross) pulverised coal boiler plant was developed. The optimised oxyfuel fired design case has a net cycle efficiency of 30.3% compared with the air fired system efficiency of 36.7%. The levelised cost of electricity (COE) was calculated to be 4.61 ¢/kWh for the reference conventional air fired plant and 6.41 ¢/kWh for the oxyfuel plant. The CO_2 mitigation cost of the oxyfuel plant was calculated at 21.4 $/tonne.

Table 4	Effects of air leak (95% O_2) (Shah, 2006)			
Air leak, %	1	3	5	10
% CO_2 in flue gas (dry basis)	85.0	78.4	72.7	61.4
% CO_2 avoided	92.3	86.9	81.2	65.3
cost of CO_2 avoided, $/t	38.8	42.5	47.2	62.3
COE, $/MWh	70.9	71.7	72.7	74.4

Seltzer and Robinson (2006) have also pointed out that the oxygen supply and the CO_2 gas processing systems have a major impact on the economics and efficiency of oxyfuel plants. Seltzer and others (2008) considered the Flex-Burn™ oxyfuel boiler design in which includes several modifications to minimise the power plant derating and CO_2 removal penalty. The levelised COE was calculated to be 7.0 ¢/kWh for the reference conventional air fired plant and 6.41 ¢/kWh for the Flexi-Burn™ plant. The CO_2 mitigation cost of the oxyfuel plant was calculated at 45.3 $/tonne.

Parameters such as oxygen purity, air in-leak, and CO_2 purity can affect the economics of oxyfuel combustion. This was addressed by Shah (2006) who found that, as the oxygen purity increased from 90 to 99.5%, the COE rose from 72.1 to 73.9 $/MWh and the cost of CO_2 avoided decreased from 41.1 to 39.7 $/ton. The base case was a supercritical pulverised coal plant with a nominal output of 450 MW and 44% efficiency (LHV). The effects of air leakage were even more marked as shown in Table 4, especially the effects on the cost of the CO_2 avoided.

A thermodynamic (second law) study of oxyfuel combustion was performed by Simpson and Simon (2007). They found that the current second law efficiencies of 13% and 22% for carbon separation units and air separation units, respectively, are not sufficient for CO_2 capture to be implemented into the market. It was pointed out that a post-combustion carbon separation unit may still be required in an oxyfuel plant due to impurities in the oxygen-rich combustion stream and/or fuel stream. This would only be used if the flue gas stream exiting the boiler does not meet the CO_2 concentration requirement for storage. The conclusion was that for oxyfuel combustion systems to be competitive, air separation efficiency needs to increase enough to offset the additional cost and inefficiency of requiring a carbon separation unit on the back end.

Kakaras and others (2007b) have examined the economic implications for oxyfuel application in a lignite-fired power plant. They found that the application of CO_2 capture technologies in a power plant is highly costly in terms of efficiency and net power output reduction. The cost of electricity is increased significantly. For the case studied, an oxyfuel power plant that uses low rank coal such as Greek lignite is expected to have CO_2 avoidance cost more than 20 €/t of CO_2. It was also noted that despite the increase in gross power output for the oxyfuel power plant and despite

the integration of heat that would otherwise be wasted, the huge demand for auxiliary power results in a significant penalty in the power plant performance ($\approx 8.5\%$ points). This penalty is for a new plant in which the penalties in efficiency and power output can be reduced if heat that would otherwise be wasted is integrated. Kakaras and others (2007c) calculated that, for a retrofit oxyfuel power plant, there is an efficiency reduction of about 12.7% points compared with the reference plant.

A techno-economic evaluation of subcritical and supercritical pulverised fuel boilers in connection with oxyfuel based CO_2 capture facilities was performed by Rezvani and others (2007) using the ECLIPSE process simulation package. They pointed out that the technical features of supercritical plants such as higher efficiency, lower fuel consumption and lower specific emissions make these systems predestined for CO_2 capture. Nonetheless, the subcritical cycle simulated showed satisfactory economics. Thus oxyfuel technology should be considered for retrofit options if economic and technical conditions are appropriate. It was concluded that the economics depend strongly on the financial background and technical viability of the system such as high capacity factors, low government supported discounted cash flow rates and low operating cost. If these are adequate, even subcritical systems can be techno-economically sensible options.

10.1 Technology comparisons

One important consideration is how oxyfuel combustion compares with post-combustion capture. In their review of coal oxyfuel combustion, Croiset and others (2005) reported that, for retrofit applications, the cost of CO_2 avoidance for oxyfuel combustion were systematically lower (by about 15–20%) than that for amine scrubbing. For new plants, the studies reviewed produced more variable results which Croiset and others (2005) considered could be due to the use of assumptions that were unfavourable to the oxyfuel case. Châtel-Pélage and others (2005a,b) found that pulverised coal oxyfuel combustion technology was more cost effective than competitive amine scrubbing technology being about 25–40% cheaper for a 500 MWe (net) plant. The cost of CO_2 avoided was around ~40 \$/t for the new oxyfuel cases, about ~53 \$/t on a retrofit case, and ~57 \$/t to ~71 \$/t for the post-combustion new and retrofit cases, respectively. Those numbers were calculated for subcritical units and included the cost of CO_2 compression.

Stromberg (2005) noted that numerous different views on costs for technologies exist but that internal Vattenfall studies pointed to oxyfuel as the least expensive. Vattenfall had investigated integrated gasification combined cycle (IGCC) technology thoroughly and did not see it as competitive unless under very specific conditions. Although post-combustion capture is commercially available for plants up to 500 MW, it needed the energy consumption for regenerating the absorbent to come down considerably to make it competitive. A final argument favouring oxyfuel was the good experience Vattenfall had with pulverised coal technology.

Seltzer and others (2005, 2006a,b) presented an economic comparison of oxyfuel combustion with other CO_2 removal. Compared with the COE of the oxyfuel pulverised coal plant, the COE for the other technologies was 45% higher for the air fired power plant with post-combustion removal, 40% higher for the natural gas combined cycle (NGCC) with post-combustion removal, and 6% higher for the IGCC with pre-combustion CO_2 removal. Compared with the CO_2 mitigation costs of the oxyfuel plant, the costs for the other technologies were 250% higher for NGCC, 160% higher for the air fired plant, and 17% higher for IGCC. Compared with the COE of the later Flexi-Burn™ design, the COE of the competing technologies was 16% higher for the air fired power plant with post-combustion removal, and 6% higher for the integrated gasification combined cycle (IGCC) with pre-combustion CO_2 removal. Compared with the CO_2 mitigation costs of the oxyfuel plant, the costs for the other technologies were 76% higher for the air fired plant, and 5% higher for IGCC.

Process simulations have been carried out by Varagani and others (2005; Châtel-Pélage and others, 2005a,b) comparing oxyfuel combustion, post-combustion amine scrubbing and IGCC fitted with the Selexol process. Cost models were developed to estimate the capital, operating, electricity, and the CO_2 avoidance costs for each technology. The economic analysis showed that the COE for the oxyfuel plant increased by about 60%, the amine scrubbing plant by 79% and the IGCC plant by 43%, compared with the pulverised coal plant without CO_2 capture. The CO_2 avoidance costs are shown in Figure 24 in which it can be seen that for the new and retrofit oxyfuel plants, the costs are 25–30% lower than the amine scrubbing costs.

Ciferno (2006) has stated that conservative cost estimates indicate a 25% improvement in CO_2 avoided costs compared with monoethanolamine (MEA) scrubbing. He also suggests that applying cost reductions may result in a 50% improvement. For MEA scrubbing he quoted a figure of 52 \$/tonne of CO_2 avoided compared with \$35 for supercritical oxyfuel and \$37 for ultra-supercritical oxyfuel. An additional analysis was performed by Babcock & Wilcox which evaluated the various capture alternatives from an investment standpoint, namely net present value (NPV) and internal rate of return (IRR) (Farzan and others, 2007a,b; Varagani and others, 2007). From this it emerged that no single combustion technology appeared to dominate the returns at this early stage of development although gasification was the least attractive due to a higher capital cost and lower availability. It was concluded that oxyfuel combustion is an economically viable technology for retrofitting existing boilers as well as new pulverised coal boilers.

Based on information from studies carried out by the IEA GHG, Davison (2007) found that the net efficiencies of post-combustion capture and oxyfuel plants were similar and in the range 34.8–35.4% (LHV) and the COE and costs of CO_2 avoided were also similar (31–36 \$/tonne of CO_2 avoided). Bouillon and others (2009) have also found that oxyfuel and post-combustion processes lead to similar CO_2 penalties: around 44 €/tonne of CO_2 for post-combustion capture and 46 €/tCO_2 for the oxyfuel process. The COE from
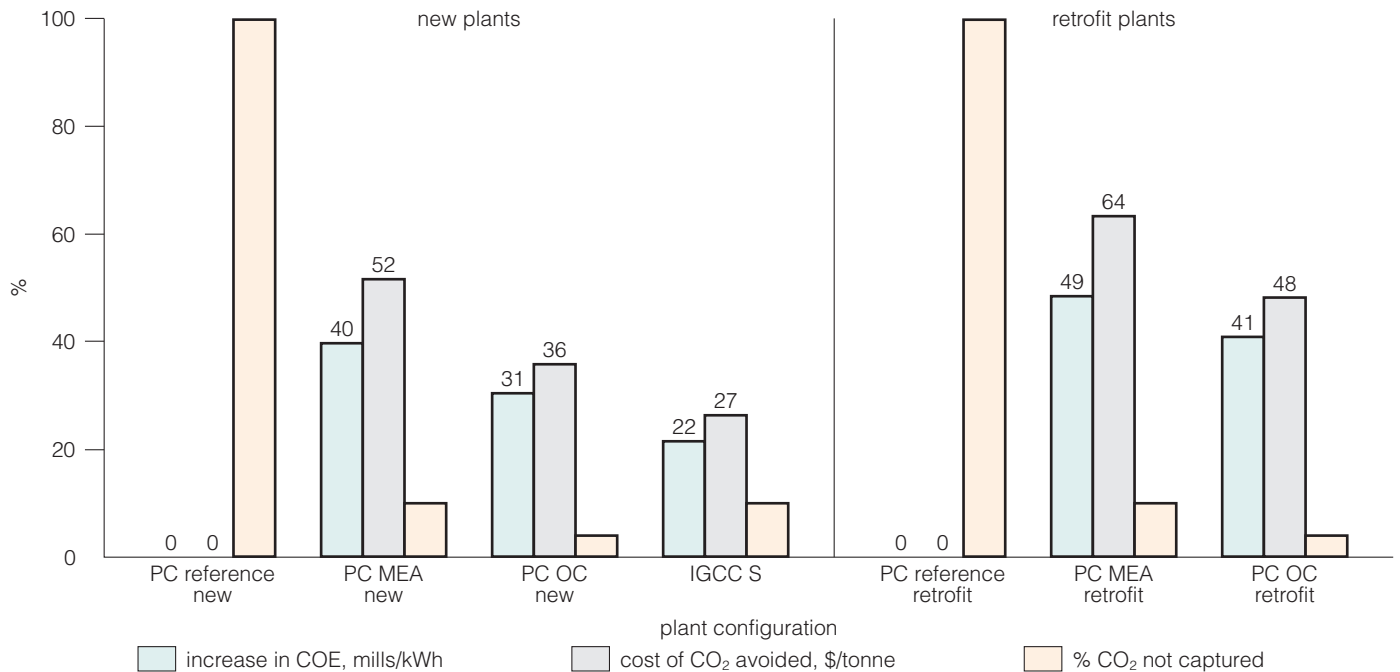
Figure 24 CO$_2$ avoidance and electricity costs (Varagani and others, 2005)

each process was calculated to be around 66 €/MWh and 67 €/MWh respectively. The analysis was based on a 630 MWe (net) circulating fluidised bed plant rather than a pulverised fuel plant.

The US Department of Energy (DOE) has a goal of achieving CO$_2$ capture with no more than a 20% increase in levelised COE. Its National Energy Technology Laboratory has produced a report with the objective of establishing a cost and performance baseline for the oxyfuel combustion process that can be used as a basis for comparison with past and future studies (NETL, 2008). Twelve cases were examined including four conventional air-based combustion cases for reference (with and without post-combustion CO$_2$ control), six oxyfuel combustion cases with O$_2$ provided by a cryogenic distillation process and two oxyfuel combustion cases with O$_2$ provided by an ion transport membrane process. Both supercritical and ultra-supercritical (USC) steam cycles were analysed. In summary, none of the cases achieved the DOE's goal. For the oxyfuel combustion cases, the increase in levelised COE relative to the air fired base case ranged from 52% to 63% (excluding the cost of CO$_2$ transport, storage, and monitoring). These values were lower than the corresponding values of nearly 75% for the amine scrubbing cases. An ultra-supercritical oxyfuel plant had the lowest cost of CO$_2$ avoided of 34/t compared with $56 and $67 for the amine scrubber cases.

A thermo-economic comparison of oxyfuel and post-combustion CO$_2$ capture has been carried out by Liszka and Ziębik (2008; 2010) referring to Silesian (southern Poland) conditions. The calculated drop of efficiency of a supercritical pulverised coal unit caused by CO$_2$ separation amounted to 11.1 percentage points in the case of post-combustion CO$_2$ absorption using MEA and to 10.3 percentage points in the case of oxyfuel combustion. The increase in the cumulative primary energy consumption for electricity production, due to post-combustion CO$_2$ removal

using MEA, was calculated to be 34%. In the case of oxyfuel combustion the value of this parameter depends on the fate of the nitrogen produced in the air separation unit. If nitrogen is treated as waste, the oxyfuel cumulative energy consumption is greater by 29.5% compared with the reference pulverised fuel plant without capture. If it were possible to use nitrogen for external processes as a power unit by-product, the cumulative energy consumption would decrease by 25.3% compared with the reference plant. These results led to the conclusion that if it were possible to use nitrogen for external processes then oxyfuel technology would be thermodynamically more efficient than air combustion systems, as the by-product nitrogen replaces nitrogen produced in a dedicated stand-alone. It was admitted that the idea of joint electricity and nitrogen generation is obviously limited by potential nitrogen demand which is expected to be much lower than oxyfuel nitrogen production. On the other hand more nitrogen is used by customers than any other industrial gas. It is used in a broad range of industries, including chemicals, pharmaceuticals, petroleum processing, glass and ceramic manufacture, steelmaking and other metals refining. The cost of electricity was similar for both options studied, however oxyfuel combustion was found to be more promising based on its higher removal efficiency and potential for integration with nitrogen-consuming industry.

Doukelis and others (2009) have produced economic evaluations of retrofit post-combustion and oxyfuel plants compared with reference cases of a 330 MWe Greek lignite-fired power plant. In their calculations the increase in electricity generation costs is 70.18% for a plant fitted with post-combustion capture and 65.32% for an oxyfuel plant. The differences in the increase in electricity generation cost per gross electric production were calculated to be 50.13% for the post-combustion plant compared with 29.69% for the oxyfuel plant.

Ekström and others' (2009) compared oxyfuel technology

with pre-combustion CO_2 capture using integrated gasification combined cycle (IGCC) power plants. Their calculations produced almost the same cost increases for all lignite-fired systems compared with their respective reference cases. However, for the bituminous coal fired systems, the electricity generation costs were lower for the oxyfuel compared with pre-combustion capture. It was pointed out that the cost differences were within the ranges of uncertainty that could be expected at the current level of development.

A cost-benefit analysis was conducted for the estimation of the electricity unit cost and CO_2 avoidance cost of a pulverised coal oxyfuel combustion technology plant and compared with four different CCS technologies by Hadjipaschalis and others (2009). The technologies compared were pre-combustion IGCC plant, post-combustion pulverised coal plant, and both the pre- and post-combustion natural gas combined cycle plants. The results showed that the oxyfuel combustion plant was a competitive technology. However, in contrast to the findings of Ekström and others' (2009), it was slightly more expensive than the IGCC with pre-combustion CCS integration technology which had the lowest electricity unit costs and lower CO_2 avoidance costs.

The Global CCS Institute (2009) recently commissioned a strategic analysis of the global status of carbon capture and storage undertaken by a WorleyParsons led consortium of Schlumberger, Baker & McKenzie and the Electric Power Research Institute (EPRI). In the report the effects of CO_2 credit value breakpoint was considered for the case of the US Gulf Coast region. Emissions of CO_2 will impose a cost on future power generation systems as either a share price in a cap and trade system or as a CO_2 tax. This CO_2 credit value will be an input to be considered by owners and utilities in determining whether to pursue the installation of CCS technologies or, alternatively, purchase credits. The CO_2 credit value breakpoint refers to the CO_2 credit value, expressed as $/tonne of CO_2 emitted. This has the potential to drive the economics in favour of systems with CCS over those without. Below the breakpoint, project proponents and utility owners are likely to conclude that it is more economically favourable to operate the system without CCS, and pay for the emissions in the form of a tax or purchased credits rather than building and operating a system with CCS. The oxyfuel combustion technologies were estimated to have the lowest CO_2 credit value breakpoint, approximately $60/tonne of CO_2. This was related to eliminating solvent capture of CO_2 from the gas stream. However, oxyfuel technology was not considered demonstrated at a commercial scale for power generation.

- many studies are considering a retrofit rather than a new situation.

A major weakness in the techno-economic assessments that have been carried out is the uncertainty simply due to the fact that there is no experience of constructing or operating full-scale plants.

10.2 Comments

Although many of the techno-economic studies that have been carried out have been disinterested in promoting one technology over another, it may be worth looking at Stromberg's (2005) reasons for the different cost estimations:
- many data are biased – almost all papers want to show something;
- many reports are based on marketing of products;
- there are different ways of handling the loss of energy output;

11 Conclusions

In his final remarks at the first Oxyfuel Combustion Conference, Hesselman (2009) concluded that considerable progress has been made in the development of oxyfuel technology:

- the process is technically viable;
- the process is reasonably well understood;
- the process has been demonstrated at pilot scale;
- the process is being demonstrated at large scale (30 MWth +);
- most of the individual components are in commercial operation at the required scale.

He noted that even though oxyfuel combustion is economically competitive with alternative technologies, there is a perception that post-combustion is 'easier' and that pre-combustion is also seeing heavy R&D investment and is being promoted strongly. However, several utilities are making or planning significant investments in oxyfuel technology with large-scale testing and plant demonstration. Finally, he stressed that the time is right for the full-scale demonstration of oxyfuel.

At the same meeting Spero (2009b) agreed that post-combustion capture is seen by many as a quick fix and in some respects the oxyfuel option has lost ground because it cannot easily be partially applied so the investment dollars are higher. Contrary to this opinion though, a recent CCC report has concluded that although partial capture may be possible, it is probably politically and economically unattractive as an option. It is possible that the only acceptable version of partial capture is full capture on one or more units of a multi-unit plant (Adams, 2009).

Why post-combustion capture should be seen as a more attractive option does not seem to be obvious from any technical viewpoint though. The Global CCS Institute (2009) grouped CCS technologies into different levels of technical readiness, the highest being full-scale commercial deployment, which has been achieved by pre-combustion technologies. Post-combustion was graded only slightly higher than oxyfuel combustion at the pilot-lant stage while oxyfuel combustion was graded at both component prototype demonstration and pilot plant.

Spero (2009b) also pointed out that there are still there are process optimisations to be made by looking at:

- flame stability, radiative heat transfer and gas composition as a function of O_2 injection and distribution;
- the behaviour of H_2O, SO_2/SO_3, and trace elements;
- material selection where SO_3 dew point corrosion is likely to occur.

Wall and Stanger (2010) have commented that market, economic, public acceptability and legal issues are more significant than technical issues as barriers to the commercial deployment of oxyfuel technology. These non-technical barriers probably apply equally to all CCS technologies.

Indeed, oxyfuel combustion may have an advantage in that it does not use chemical reagents such as the amines used in post-combustion capture. Our knowledge of the environmental impacts of solvent scrubbing of CO_2 is quite limited at present and cannot be quantified with any degree of accuracy (Davidson, 2007).

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