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Overview of Oxy-Combustion Technology for Utility Coal-Fired Boilers

by

Brian Vitalis
Manager, Project Engineer
Riley Power Inc.

Presented at

5th International Conference on Advance in Materials Technology for Fossil Power Plants
October 3-5, 2007
Marco Island, Florida

Riley Power Inc.
5 Neponset Street
Worcester, Massachusetts 01606
www.babcockpower.com

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ABSTRACT

With nearly half of the world's electricity generation fueled by coal and an increasing focus on limiting carbon dioxide emissions, several technologies are being evaluated and developed to capture and prevent such emissions while continuing to use this primary fossil energy resource. One method aimed at facilitating the capture and processing of the resulting carbon dioxide product is oxy-combustion. With appropriate adjustments to the process, the approach is applicable to both new and existing power plants.

In oxy-combustion, rather than introducing ambient air to the system for burning the fuel, oxygen is separated from the nitrogen and used alone. Without the nitrogen from the air to dilute the flue gas, the flue gas volume leaving the system is significantly reduced and consists primarily of carbon dioxide and water vapor. Once the water vapor is reduced by condensation, the purification and compression processes otherwise required for carbon dioxide transport and sequestration are significantly reduced.

As an introduction to and overview of this technology, the paper summarizes the basic concepts and system variations, for both new boiler and retrofit applications, and also serves as an organized review of subsystem issues identified in recent literature and publications. Topics such as the air separation units, flue gas recirculation, burners and combustion, furnace performance, emissions, air infiltration issues, and materials issues are introduced.

INTRODUCTION

With the goal of mitigating global warming, much research is focused on ways to capture the carbon dioxide (CO_2) produced from fossil fuels use. Roughly 85% of the world's energy needs are supplied by fossil fuels. While coal use represents only a quarter of worldwide energy release for all purposes, it is favored for use in large power plants and fuels roughly half of the electricity generated in the USA and worldwide. Being large stationary sources of emissions, power plants are excellent candidates for application of highly effective emissions control systems, and significant progress has been achieved in reducing the emissions of particulate, nitrogen oxides, sulfur dioxide, and mercury from coal-fired plants. Conceptually, there are three main approaches to capturing CO_2 from combustion of fossil fuels:

1. Pre-combustion, or decarbonization in IGCC applications with water-gas shift reaction
2. Post-combustion, such as amine scrubbing
3. Oxy-combustion, to produce CO_2-rich flue gas

Oxy-combustion is attractive because it essentially combines advantages of the other two: the cost of CO_2 capture and plant efficiency are comparable to IGCC, and it can be applied as a retrofit to many existing coal-fired plants. However, in all cases, capture of CO_2 will pose significant energy and economic penalties, and the pursuit of emissions capture should be balanced with sensitivity to the associated increase in direct heat release to surroundings, as well as the accelerated consumption of resources.

Oxy-combustion itself is not a new concept, in fact it was used for high temperature applications such as welding and metal cutting in the 1940's and moved into the aluminum, cement, and glass industries in the 1960's(1, 2). In the 1980's, Abraham proposed its use specifically to produce CO_2 for Enhanced Oil Recovery (EOR)(1) and in the 1990's it gained further attention for NO_x reduction(3). Until now, it has not been widely adopted because the energy requirement for oxygen separation makes implementation for these uses too expensive. However, now with the potential valuation of limiting CO_2 emissions, the economics are being changed again and oxy-combustion is seen as a way to produce a CO_2-rich flue gas that is easier to process for sequestration than conventional air-fired flue gas (4).

Oxy-Combustion — Basic Concepts

In conventional combustion, air (21% oxygen, balance mainly nitrogen) is used as the convenient oxygen source for burning of fuel. The nitrogen from the air is mostly inert in this process (a trace of it is oxidized to NO_x) and ends up mixed with the combustion products. As shown in Figure 1, typical flue gas from burning bituminous coal with air contains about 74% nitrogen, 14% carbon dioxide, and 8% water vapor, with other species. At the tremendous quantities of flue gas involved in power generation, if carbon dioxide is to be captured and sequestered, practical limitations dictate that it be separated from the other primary components considered benign. The basic premise of oxy-combustion for power plant application is to separate the nitrogen from the oxygen in the air rather than having to separate it from the carbon dioxide in the flue gas. Without the air-borne nitrogen diluting the flue gas, a concentrated CO_2 flue gas results which is also much less in volume. As shown in Figure 1, by using nearly pure oxygen as the oxidant instead of air, the resulting flue gas is primarily CO_2: 61% CO_2, 30% water vapor. Due to the relative absence of nitrogen, the net volume of flue gas (after any recycling) is reduced by 80% compared to the dilute, air-firing condition. After condensation of water vapor, the flue gas is further reduced in volume and about 88% CO_2. This stream is then much easier to process for CO_2 purification and compression than dilute, air-fired flue gas that would require significant scrubbing processes.

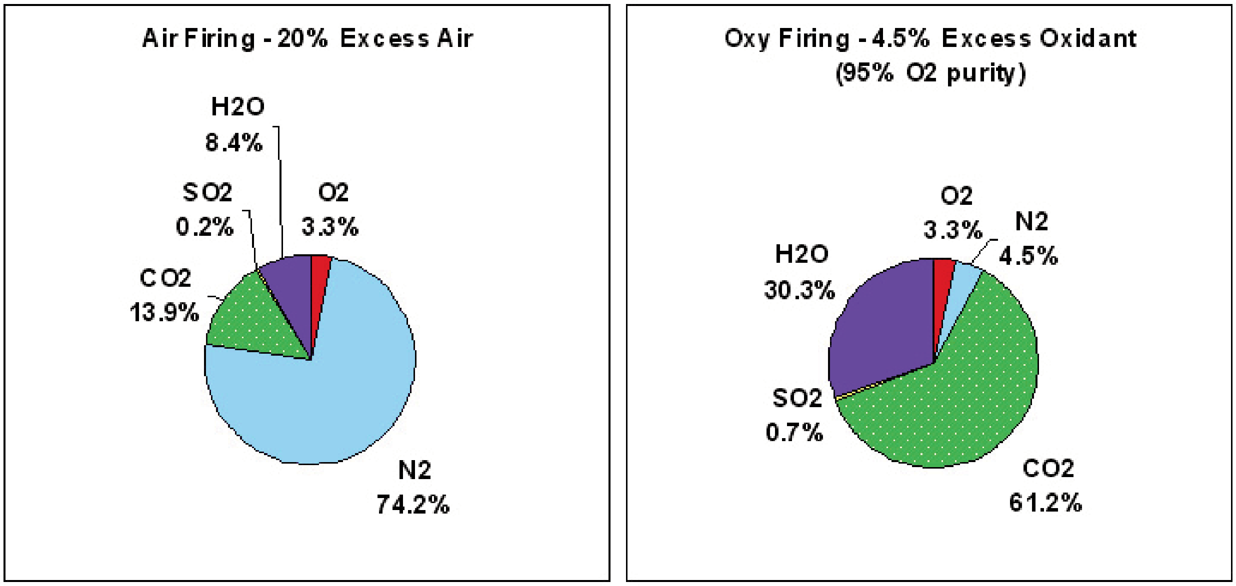

Figure 1. Comparison of Flue Gas Compositions

However, simply combining fuel with oxygen results in very hot flames and, at the scale of coal-fired power generation, some means of controlling furnace temperature is desired to permit use of economical materials and conventional designs. Retrofit of existing boilers is also a consideration, and is discussed later in this paper. In the near term, the use of various diluents (in place of nitrogen from air) is being considered. By far the most popular choice right now is recycled flue gas, which introduces no additional need for flue gas species separation and provides a means for coal drying and transport, though it does require some processing to avoid problems. Other means to control the flame temperature include water or steam injection(5), or more sophisticated burner zone oxygen staging can permit a reduced level of flue gas recirculation (FGR)(6).

A basic schematic of the oxy-combustion system with FGR is shown in Figure 2. In conventional air-firing, the combustion air is preheated in a regenerative heater, cooling the flue gas for heat recovery. In oxy-combustion systems, the air entering the air separation unit is not available for cooling of the flue gas since the air separation unit needs to begin with cool air and has a significant heat rejection load itself. Instead, significant plant integration of feedwater and process heating is needed, taking heat from both the flue gas stream and the air separation unit process. Oxygen is mixed with a diluent — generally FGR as shown here — and burns the fuel. Most proposed schemes have an Electrostatic Precipitator (ESP) handling the combined flue gas stream, so that the recycled gas is relatively clean. Downstream of the recycle take-off, the flue gas volume is much less than that from air-firing, and system equipment requirements vary primarily according to the purity requirements of the ultimate CO_2 sequestration use and destination. In some cases, and for low sulfur coal, conventional FGD and SCR systems may not be required at all and the minor pollutants are sequestered along with the CO_2.

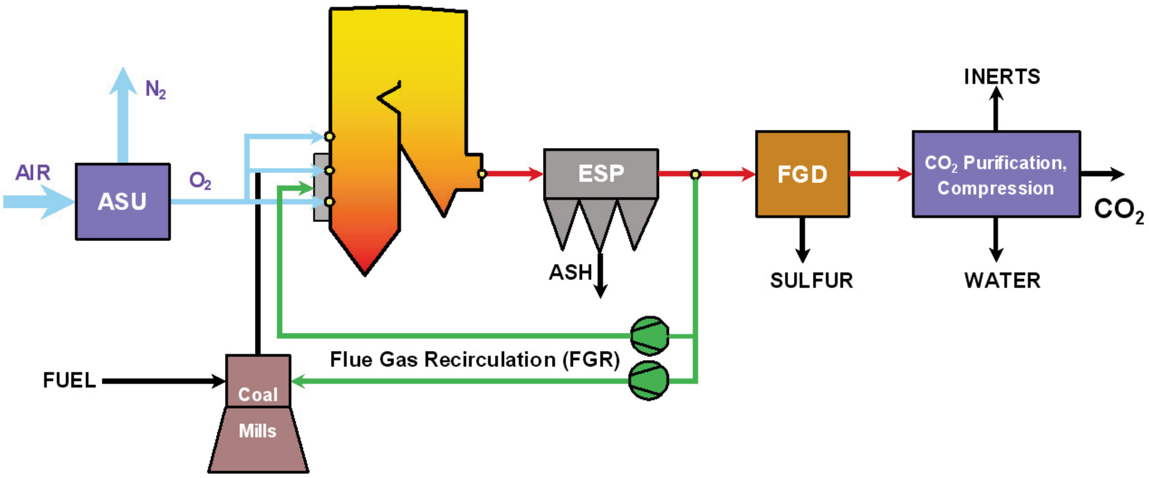

Figure 2. Basic Schematic of Oxy-Combustion Concept

Oxygen Source

At the quantities required for utility power production, the only commercially available oxygen production technology is cryogenic separation. Using this technology, the system is often referred to as an Air Separation Unit (ASU). A typical ASU consists of an air compressor, precooling system, purification unit, heat exchangers, and distillation column. Though it's a well-proven technology, the power involved (210-220 kWhr/ton O_2) is one of the primary barriers to implementation of oxy-combustion(7, 2, 4). Development continues for several novel, lower-power alternatives such as ceramic membranes (Oxygen Transport Membranes, Ion Transport Membranes, Mixed Conducting Membranes), Ceramic Autothermal Recovery systems, and Chemical Looping, with DOE funding for some of these activities, targeting commercialization by 2010.

Ideally, nitrogen should be entirely eliminated, but ASU energy requirements rise sharply when oxygen purity needs to be above 98% (3, 1), since argon-oxygen separation then becomes a factor. The operating economics must not only be optimized for the oxygen equipment alone, but require consideration of the ultimate CO_2 purity requirements and optimization with removal of the inerts by the CO_2 product recovery system. In general, when recognizing that at least some nominal amount of air infiltration to the boiler system is inevitable, most studies have determined that 95% purity oxygen provides the best economic balance when using an ASU (3, 8, 2, 1).

Flue Gas Recirculation (FGR)

Recycle flue gas is used to moderate the combustion temperatures and to maintain overall heat transfer characteristics, enabling oxy-combustion to be easily retrofitted to existing boilers, and permitting conventional design for new units. For new unit designs, the convective heating surfaces and flue gas handling equipment could be dramatically reduced if FGR could be omitted or reduced, however there are certain practical considerations for the flame and furnace that limit reductions in FGR, as further described in the section Combustion and Furnace Conditions, below.

When the recycled flue gas is mixed with the oxidant before entering the burners, the recycle rate has a corresponding diluting effect on the oxygen concentration at the burner. This is an interesting new variable available to the burner designer, as it opens up possibilities for different stoichiometries and oxygen concentrations in various parts of the burner and/or for various parts of the furnace, enabling further control of the flame and furnace conditions. By using such techniques, aided by CFD modeling and pilot-scale testing, there is the possibility of reducing overall FGR rates and the size of the boiler, while still controlling combustion conditions within practical limits.

Wet vs. Dry Recycle

While most of this and other introductory discussions presume that the recycled flue gas is the same condition and composition as that flowing from the boiler, the issue of water vapor removal should be mentioned. Wet vs. Dry FGR is illustrated in Figure 3 and described below.

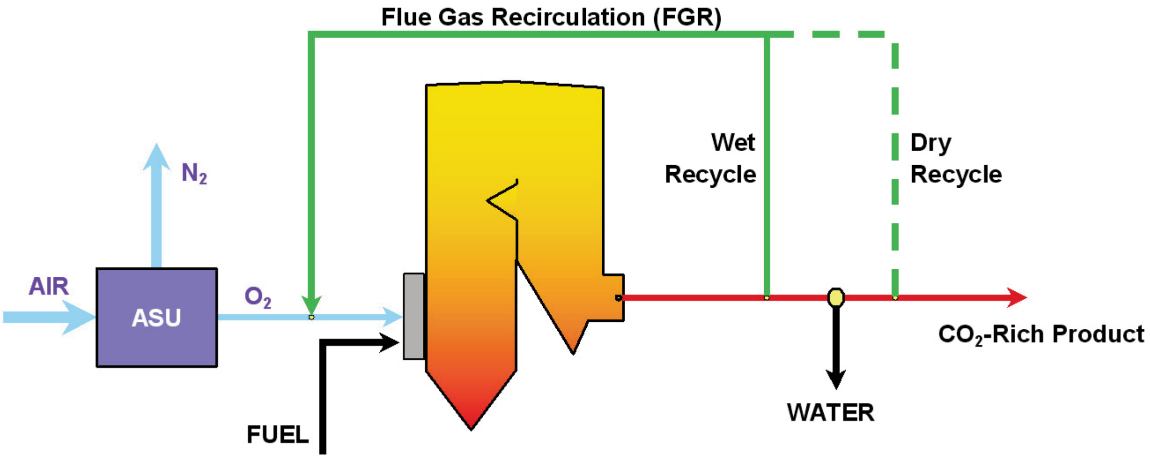

Figure 3. Wet vs. Dry Flue Gas Recirculation

Wet FGR: The recycle gas contains the full water vapor content of the main flue gas. Sometimes referred to as “the practical” approach to FGR, but the high moisture content may cause problems in the FGR duct, fan, and pulverizers.

Dry FGR: Some of the water vapor is removed from the recycle gas stream.

More development is needed in the area of pulverizer performance under a range of FGR conditions. The effect of wet vs. dry recycle does not end at the pulverizer or FGR circuit, but impacts furnace and overall boiler performance by altering the density, heat capacity, radiation, and convection properties of the flue gas mixture.

Regenerative Heating

An interesting combination of solutions is described in a 2005 report sponsored by the International Energy Administration (IEA Report 2005/9)(1). As shown in Figure 4, the system utilizes a regenerative gas-gas heat exchanger to cool the combined flue gas from 644°F to 518°F in order to optimize cost vs. efficiency of the ESP. The heat is transferred back to the recycled flue gas. The FGR is treated as two separate streams. The primary recycle, serving the pulverizers, gets cooled and dried, while the secondary recycle is "wet", and both are reheated by the gas-gas heat exchanger. Oxygen is introduced to the secondary recycle stream to bring the mixture oxygen content up to 23% oxygen, and the balance of oxygen is fed to the windbox / burner separately.

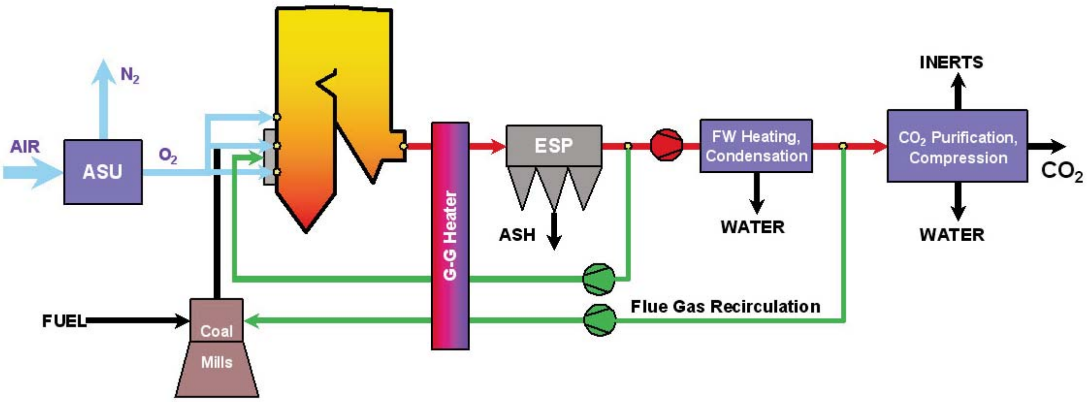

Figure 4: Oxy-Combustion System Schematic with G-G Heat Exchanger (Figure adapted from IEA Report 2005/9, via ref. (1))

Combustion and Furnace Conditions

Most combustion science and conventional furnace and heat transfer designs have been developed on the basis of air-firing. Research and test programs have started and are continuing to investigate fundamentals of oxy-combustion environments. At the macro level, oxy-combustion flame stability, overall heat transfer, and thermodynamic performance have been found to be comparable to well-known air-fired conditions (3, 1), confirming good potential for retrofit of existing units, but there are some differences that should be taken into account.

Excess Oxidant

Generally, the basic mechanics of ensuring complete combustion continue to require a modest amount of excess oxygen in the flue gas. The concept of "excess air" may be extended to "excess oxidant", but in any case the proven target of about 3-3.5% oxygen left over in the flue gas is a reasonable amount. Selective use of oxygen concentrations and stoichiometry staging at various burner levels may permit some reduction in the overall excess oxidant level. Experiments are continuing to determine how close an oxy flame can come to stoichiometric (4, 6). This has significant appeal considering that a primary penalty of oxy-combustion is the energy required to separate the oxygen from air in the first place.

Flame Temperature

Some initial insight to the differences in performance between the firing conditions can be gained by review of relevant gas properties. Figure 5 is a comparison of some of the relevant properties of the gas species; recall that N_2 is the dominant presence in air-firing, and CO_2 and H_2O dominate oxy-firing. In order to use conventional materials and designs — especially a requirement for retrofit applications, it is desired to achieve a conventional adiabatic flame temperature. If the air-fired and oxy-fired gas properties were the same, one might expect that a similar flame temperature would be produced if the oxygen concentration into the burner were diluted (via FGR) to about 21% (such as in air). But since the specific heat of CO_2 is greater than that of N_2, the adiabatic flame temperature is suppressed and less FGR dilution effect is needed. Several studies have shown that to match the flame temperature from air-firing, the oxygen at the burner should only be diluted to about 30%, requiring about 60% FGR (9, 1, 10).

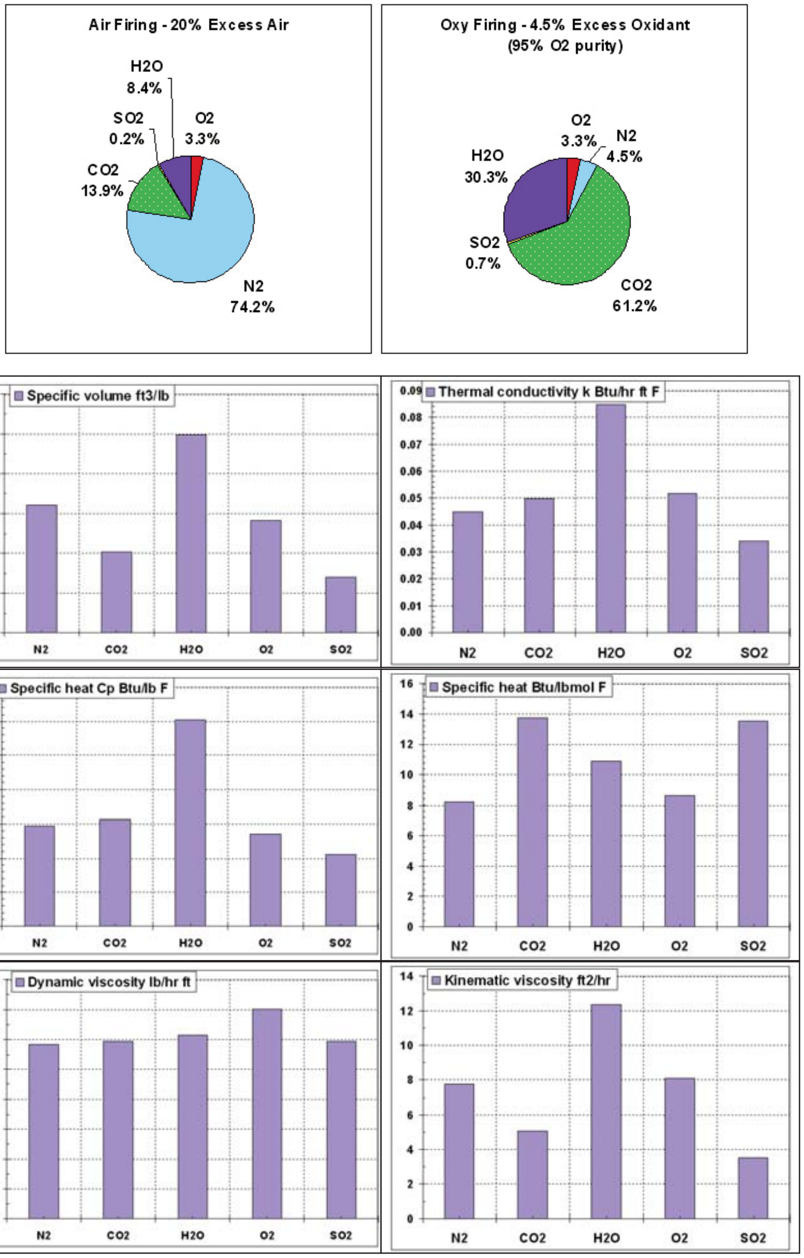

Figure 5. Properties of Gases at 2000°F, 1 atm

Radiation and Overall Furnace Performance

Another key furnace design parameter is the furnace exit gas temperature. The temperature at the furnace exit must be controlled below the particular coal's ash softening point in order to prevent significant ash fouling in the convection section. As discussed above for the flame temperature consideration, radiative heat transfer differences can be identified by review of gas properties and have been confirmed by lab and pilot-scale testing. Strongly radiating gases, CO_2 and H_2O, dominate the oxy-fired environment and this suggests that some further tempering of the flame temperature with FGR is appropriate. Several studies conclude that an oxygen concentration of 25-27% at the burner would result in matching the radiation heat transfer rate of air firing (9, 10, 7). The enhanced radiative properties of the oxy-fired gases must be accounted for in evaluating existing furnace wall materials in retrofits, and for properly predicting furnace wall temperatures in advanced UltraSuperCritical units, especially sliding pressure designs which require high furnace outlet steam enthalpies.

While the conditions described above match the radiation heat transfer rate in the burner zone, the furnace exit gas temperature will be less for oxy-combustion. With the denser flue gas and somewhat less mass flow from oxy-firing conditions, the residence time is increased and furnace exit gas temperature has been found to be 70-90 F° less than for air (9). Further evaluations of furnace performance and variations of wet vs. dry FGR and selective staging of burner levels will be facilitated by Computational Fluid Dynamic (CFD) modeling. Fundamental issues of gas modeling methods, coal devolatilization, and char burnout must be further investigated to support detailed modeling. Regarding unburned carbon, University of Newcastle trials suggest 20-60% reduction in unburned carbon loss, which might be explained since the combustion process begins at higher oxygen concentrations at the burner, and furnace residence time is longer due to reduced flue gas volume(9).

Emissions

NO_x

Various test programs have shown oxy-fired NO_x levels to be significantly lower than those from air-firing. With very little molecular nitrogen available at the flame, thermal NO_x is reduced. Further, some of the fuel NO_x in the recycled flue gas is reduced back to molecular nitrogen when it passes through the flame again. Tests with both staged and unstaged burning of coal indicate oxy-fired NO_x about 50-70% less than air-fired, suggesting that post-combustion controls would not be required even if the flue gas were to be released(3, 9, 11, 7). But at such low levels, any NO_x may ultimately be co-sequestered with the CO_2.

SO_x

In general, the fuel sulfur will be fully oxidized as in air-firing so there may not be any significant change due to oxy-firing mode, though the potential for SO_2 to SO_3 conversion still needs to be investigated. However, oxy-firing poses some opportunities for avoiding the cost of dedicated FGD equipment. First, use of low sulfur coal may bring the uncontrolled SO_2 level to within acceptable limits for co-sequestration with CO_2. In fact, small amounts of SO_x and H_2S help the EOR process by improving oil miscibility(11). Second, Buhre et al.(9) suggest the oxy-combustion environment may permit in-furnace desulfurization due to inhibition of $CaSO_4$ decomposition at higher temperatures and recirculation of flue gas (9).

Mercury

Some literature reports lower mercury emissions are possible with oxy-combustion(1). Thermodynamic analysis by CANMET (11) suggests that both oxidized and elemental mercury could be captured in the condensed CO_2 product and therefore not admitted to the atmosphere or handled separately.

Air Infiltration

Air infiltration may be a significant challenge depending on the CO_2 capture and sequestration requirements. Ochs et al.(4), report that if the tramp nitrogen can be tolerated in the sequestration scheme, then there should be no problem in the compression and delivery of the mixture, and that initial experiments suggest that geologic sites should be tolerant of minor constituents including SO_x. However, if high purity CO_2 is required and air infiltration is significant, then an additional distillation process is required to purify the CO_2, requiring significant energy and limiting the amount of CO_2 that can be economically captured(4).

A second aspect of air infiltration is its potential impact on NO_x production. Without infiltration, several studies and test programs indicate that NO_x from oxy-combustion can be very low and would generally be tolerated for most sequestration sites. However, further research is required to determine the impact of varying amounts of tramp nitrogen on the oxy-fuel NO_x production, and NO_x treatment systems could be required at some point.

Retrofit vs. New Unit

For new unit builds, the integration aspects described previously — especially for heat recovery from the ASU and the CO_2 recovery train — are important aspects to help offset these systems' considerable energy penalties. Further, the capital cost of new plants can take advantage of the potential reduced size of the boiler and omission of conventional, discrete emissions control equipment for both criteria and trace pollutants. The term "capture-ready" is sometimes used to refer to a plant that has essentially been fully designed for CO_2 capture (via oxy-combustion technology or other means), but some of the equipment is not initially purchased or installed and the plant operates in more conventional mode prior to CO_2 regulation or policy being firmly established.

In the case of retrofit to an existing coal-fired boiler, opportunities for full heat recovery and system integration may be limited, and the oxy-combustion system may need to be somewhat simplified. It is anticipated that many boilers will be able to be converted without making significant changes to the heat transfer surfaces or other pressure parts. Working with the existing furnace enclosure and arrangement, burner retrofits may be advisable. The significant additions to the plant would be the oxygen supply system, flue gas recirculation system (if not already present or sufficient), and of course the CO_2 product recovery system. In general, the existing air system would be left in place (and tied-into) to permit startup on air and transition to oxy-combustion at a stable load.

Materials Issues

Simply by nature of the absence of diluent nitrogen from the air, the concentration of all other combustion products are elevated in oxy-combustion. The comparison of air-fired and oxy-fired flue gas analyses of Figure 1 helps to illustrate this point. Based on the same 2% sulfur coal, and regardless of flue gas recirculation, the concentration of sulfur dioxide increases from 0.2% to 0.7% (vol, wet). More concentrated SO_2, SO_3, H_2O, and other trace species in the flue gas could result in greater corrosion rates.

The higher concentration of SO_2 and the higher concentration of oxygen passing through the burner may suggest the likelihood of greater SO_2 to SO_3 conversion, where SO_3 is a greater concern for corrosive attack. SO_3 reacts with metal surfaces to form low melting point components, such as alkali-iron trisulfates, that cause molten salt attack(12). However, the overall oxygen concentration from oxy-combustion will be the same or possibly less that that in air-fired flue gas, so the variations and potential for excess oxidant reductions should be considered in terms of corrosion potential as well as overall system optimization. Further research is required to confirm the detailed behaviors of SO_3 and various trace species in the denitrified environment.

As described in the furnace radiation discussion above, with high CO_2 and H_2O there is the possibility of increased radiative heat flux in the furnace resulting in slightly higher tube metal temperatures. This may aggravate the situation of high furnace metal temperatures generally present in sliding pressure supercritical and UltraSuperCritical boilers. Despite previous reasoning and separate test results indicating lower unburned carbon with oxy-firing, others suggest that the CO_2-rich environment could inhibit burnout and lead to CO and elevated carbon in the ash. The combination could result in more reducing conditions underneath the ash deposits, resulting in accelerated corrosion of boiler tubes (12, 13).

In several publications, flue gas recirculation (FGR) is blamed for accumulation of corrosive species. This requires some clarification. If the FGR is recycled "wet" — without any preferential separation or reduction of species other than removal of flyash — then it is of the same composition as the flue gas resulting from the combination of fuel and oxidant in the furnace. Mixing gases of the same composition will result in a mixture of the very same composition. However, in "dry" recirculation, much of the moisture is removed from the recycle stream, and a concentrating effect similar to that described for nitrogen above takes place. As an upper bound on this concentrating effect, Figure 6 shows the effect of removing all of the moisture from the recycle stream. Iterative calculations can then predict the feedback effects of this continual mixing and separation scheme. The interactions and path history of certain trace species require special review depending on specific system designs.

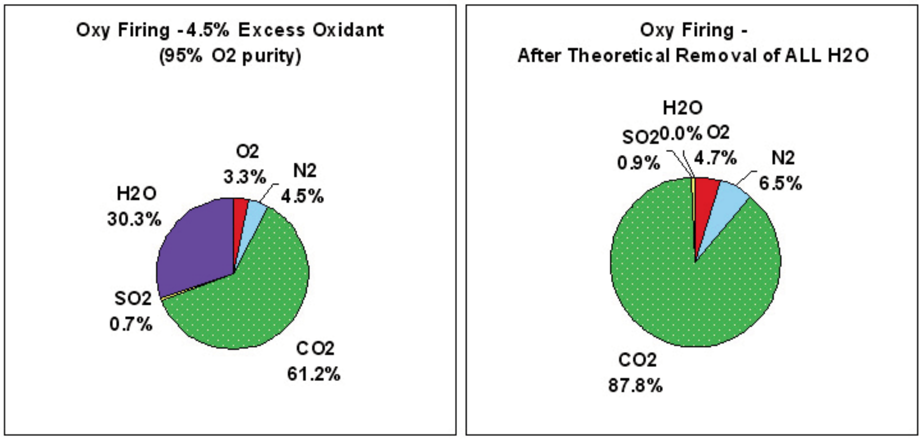

Figure 6. Concentrating Effect of Moisture Removal

Until more is known about the performance of materials in the oxy-combustion environment, several studies propose including sulfur-removing scrubbers (FGD) in the recycle path. This poses a significant capital cost as well as heat rate penalty, and the issue adds to the need to better understand the materials issues under the denitrified conditions(4).

Riley Power is involved in an industry consortium partly sponsored by the US DOE and Ohio Coal Development Office, investigating advanced materials issues for UltraSuperCritical (USC) coal-fired power plants. The group is beginning a second phase of the work, extending considerations into the application of oxy-combustion mode to USC power plants. The specific combinations of oxy-combustion gas and ash conditions and elevated metal temperatures will be investigated.

CLOSING REMARKS

Efforts to mitigate global warming should first be applied to two areas: improved economy — reduced use of energy throughout society — and higher efficiency. Gains in efficiency should span from the use of supercritical and ultrasupercritical steam cycles in central power stations, to improvements in vehicles and household appliances. Improvement in these areas not only prevents unnecessary production of CO_2, but also reduces the often-overlooked direct heat release into the environment and slows the depletion of key resources. Building on that presumed foundation, several technologies are being developed to capture and permanently store CO_2 emissions that result from responsible use of fossil fuel resources. Oxy-combustion is proposed for coal-fired boilers in order to yield a concentrated CO_2 flue gas that is relatively easy to capture, transport, and sequester. It is a promising technology in that it can be readily applied to the existing base of fossil-fired power plants, is relatively straightforward, and can offer significant cost advantages for new units including the potential avoidance of discrete emissions control equipment.

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