

## Oxy-fuel Combustion and Integrated Pollutant Removal as Retrofit Technologies for Removing CO<sub>2</sub> from Coal Fired Power Plants

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### INTRODUCTION

One third of the US installed capacity is coal-fired, producing 49.7% of net electric generation in 2005<sup>1</sup>. Any approach to curbing CO<sub>2</sub> production must consider the installed capacity and provide a mechanism for preserving this resource while meeting CO<sub>2</sub> reduction goals. One promising approach to both new generation and retrofit is oxy-fuel combustion. Using oxygen instead of air as the oxidizer in a boiler provides a concentrated CO<sub>2</sub> combustion product for processing into a sequestration-ready fluid.

The processing of the CO<sub>2</sub>-rich combustion products from oxy-combustion provides an opportunity for removing multiple pollutants in a single integrated process. The integrated pollutant removal (IPR)<sup>2</sup> approach provides a mechanism for saving both energy and capital cost over the approach of using multiple pieces of equipment – one for each specific pollutant. The unit processes involved in oxy-fuel combustion and IPR are based on commonly-used, mature technologies from other industries (e.g., petrochemicals and gas separation), now applied in new contexts for the electric power sector.

Oxy-fuel/IPR systems are being designed for a number of green-field configurations where the full complement of technologies can be applied to produce an integrated system. It is more difficult to retrofit these technologies to coal-fired boilers that may be more than 20 years old (as is true with most of the US fleet). However, choices can be made during oxy-fuel/IPR retrofit that can make a significant difference in thermal efficiency, capital cost, and performance. NETL is modeling performance of an oxy-fuel/IPR system for retrofit with variation in: 1) oxygen purity, 2) recycle rate, 3) cooling of recycled gas, 4) FGD of recycled gas, 5) recovery of heat from compression, 6) infiltration, 7) material interaction with combustion products, and 8) excess oxygen<sup>3</sup>. The impact of these parameters is estimated using computer models to weight the importance of each parameter in retrofit design for retrofit experiments and demonstrations.

The USDOE has recognized three broad categories for carbon capture:

1. Pre combustion carbon capture (IGCC). IGCC plants will be new construction only, and are not a strategy for retrofit to pc combustion.
2. Post combustion carbon capture (absorption, dissolution, chemical reaction).
3. Oxy-fuel combustion.

Post-combustion carbon capture and oxy-fuel combustion paired with a compression capture technology such as IPR are both candidates for retrofitting pc combustion plants to meet carbon emission limits. This paper will focus on oxy-fuel combustion as applied to existing coal power plants.

## METHODS

The integration of combustion, pollutant removal, carbon capture, and energy recovery dictates a systems approach to design of upgrades to existing power plants while limiting capital and operational costs. To better understand the impact of identified enabling technologies, the NETL has modeled multiple retrofit scenarios for a typical subcritical PC power plant with single reheat (2400 psig, 1000°F, 1000°F) using GE GateCycle power plant modeling software version 5.61. Retrofits to oxy-combustion will almost certainly require flue gas recycling to maintain flame temperatures within design tolerances of the boiler. In this study, the International Flame Research Foundation definition of flue gas recycle ratio (R) is used<sup>4</sup>:

$$R = \frac{FG_{rcrc}}{FG_{tot}}$$

Where R = recirculation ratio;  $FG_{rcrc}$  = mass of the recirculated flue gas being recirculated;  $FG_{tot}$  = total mass of the flue gas including both the portion recirculated and the portion sent to the IPR<sup>TM</sup> system.

Two base cases were modeled:

1. Baseline air combustion system (400 MW sub-critical PC single reheat power plant)
2. Baseline oxy-combustion system (240 kWh/ton 99% O<sub>2</sub>, heat recovery, 3.5% excess O<sub>2</sub>, R = 0.58) with NETL's Integrated Pollutant Removal IPR<sup>TM</sup> and energy recovery.

Analysis involved application of a number of technology changes to the baseline oxy-combustion system in the models, and subsequent comparisons of the modified oxy-fuel system to the baseline oxy-fuel and baseline air combustion cases. Technological changes evaluated included:

- a. Lower-energy (improved) oxygen production (advanced technologies entering the market)
- b. Reduced excess O<sub>2</sub> in oxy-fueled exhaust products (from 3.5% wet to 1.0% wet)
- c. Reduced flue gas recirculation to the boiler from R = 0.58 to R = 0.34 (increasing O<sub>2</sub> concentration in the comburent from 38% to 61% O<sub>2</sub>). This option requires heat transfer surface modifications in a retrofit system.
- d. Reduced unburned carbon through improved carbon burnout (from 1% unburned carbon to 0.5%)
- e. Reduced oxygen purity to 95.5%
- f. Removal of heat recovery from the IPR<sup>TM</sup> system
- g. Addition of flue gas desulfurization (FGD) during recycle

## RESULTS AND DISCUSSION

### Modeling Results

The technological changes modeled clearly impacted the performance of the modeled systems. Figure 1 shows the thermal efficiencies of the models; each can be compared with the baseline air case (far left) and the baseline oxy-combustion/IPR<sup>TM</sup> case (second from left). As with any models, the absolute values of the efficiencies should not be the primary focus. Instead the incremental differences between the models give us an indication of the impact of each particular technology. Since a particular power plant was used as the design basis for the models, it is unlikely that any other power plant will have exactly the same performance characteristics. However, the implementation of the technologies can be expected to result in similar impacts for other sub-critical PC single reheat power plants.

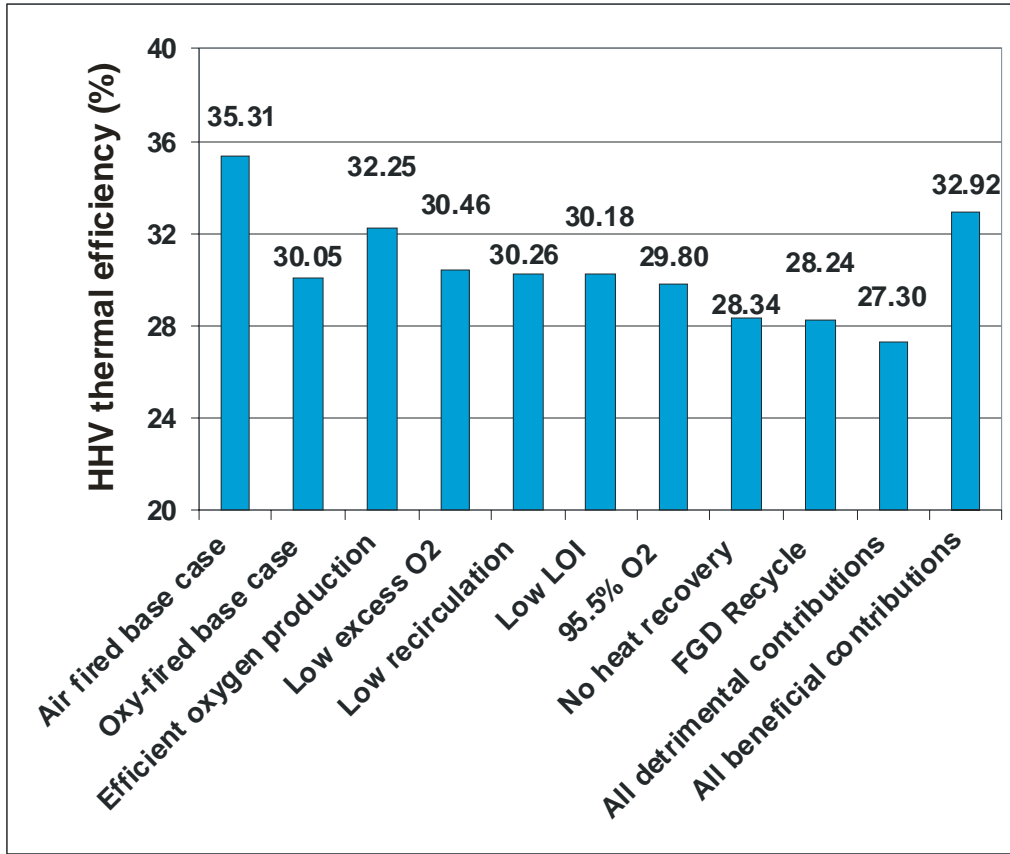
The results of the modeling efforts show that thermal efficiency (Figure 1) can vary broadly depending on the technologies being used. A ranking of the impact of the technologies has been developed<sup>3</sup>. In order, according to these modeling exercises, the greatest improvements in heat rate can be achieved through:

1. Lower energy O<sub>2</sub> production
2. Elimination of FGD during recycle
3. Improvement of heat recovery in exhaust gas processing
4. Reducing excess O<sub>2</sub>
5. Using high purity O<sub>2</sub>
6. Reducing recirculation
7. Reducing unburned carbon

### Energy balances

The transition from an air fired boiler to an oxy-combustion upgrade requires a careful examination of each potential change. As can be seen by the ordered list of technologies shown above and in Figure 1, these changes can make a significant difference in the performance of a system. Sankey diagrams were used to compare show energy flows in the baseline air-fired (Figure 2) and oxy-combustion (Figure 3) systems. The two models considered perform at the same main-steam production rate (based on the design limits of the existing HP turbine). Electrical losses to parasitic loads (such as feedwater pumps) are shown as a difference between gross generated power and net delivered power.

While these are diagrams for a specific sub-critical 400 MW single reheat power plant, the general relationship will be similar for other PC systems but flows will vary in absolute magnitude for every different power plant. The predominant avoidable losses



**Figure 1: Thermal efficiencies for power plant computer models using oxy-combustion and IPR capture using varying technologies.**

of energy (thermodynamic losses are not avoidable) in the air fired system (Figure 2) are direct losses due to hot combustion products being expelled to the atmosphere (sensible and latent losses through exhaust) and losses through the boiler walls. In reality, air fired boilers are well designed to get the maximum amount of heat transferred from the burning fuel to the steam and convert on the order of 90% of the chemical energy to thermal energy in the steam. Therefore, since boilers are designed to be safe and economical, exhaust losses and losses through the boiler walls, while considered avoidable, are not generally profitable to recover.

*Heat loss/recovery at the boiler stack:* The most obvious difference between the two Sankey diagrams is the loop at the bottom of the oxy-combustion diagram (Figure 3) wherein exhaust energy (sensible and latent heat as well as compression energy required to compress the CO<sub>2</sub> to pipeline pressure of approximately 2,100 psig) undergoes a partial recovery step. Also, in an oxy-combustion boiler there are new energy demands that reduce the final electric product, including the major demand of oxygen production shown at the top right of Figure 3.

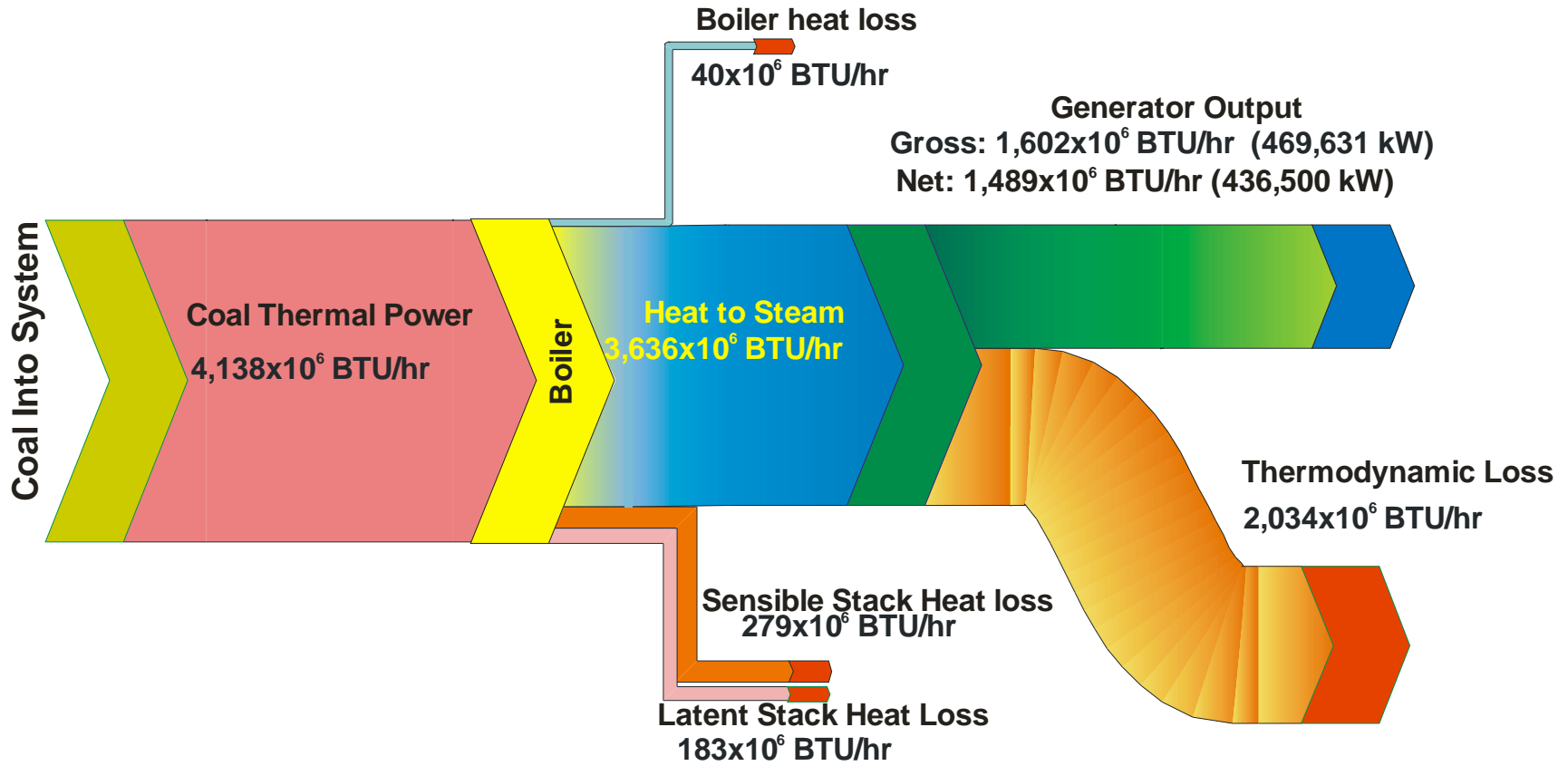


Figure 2: Air fired sub-critical PC power boiler heat distribution.

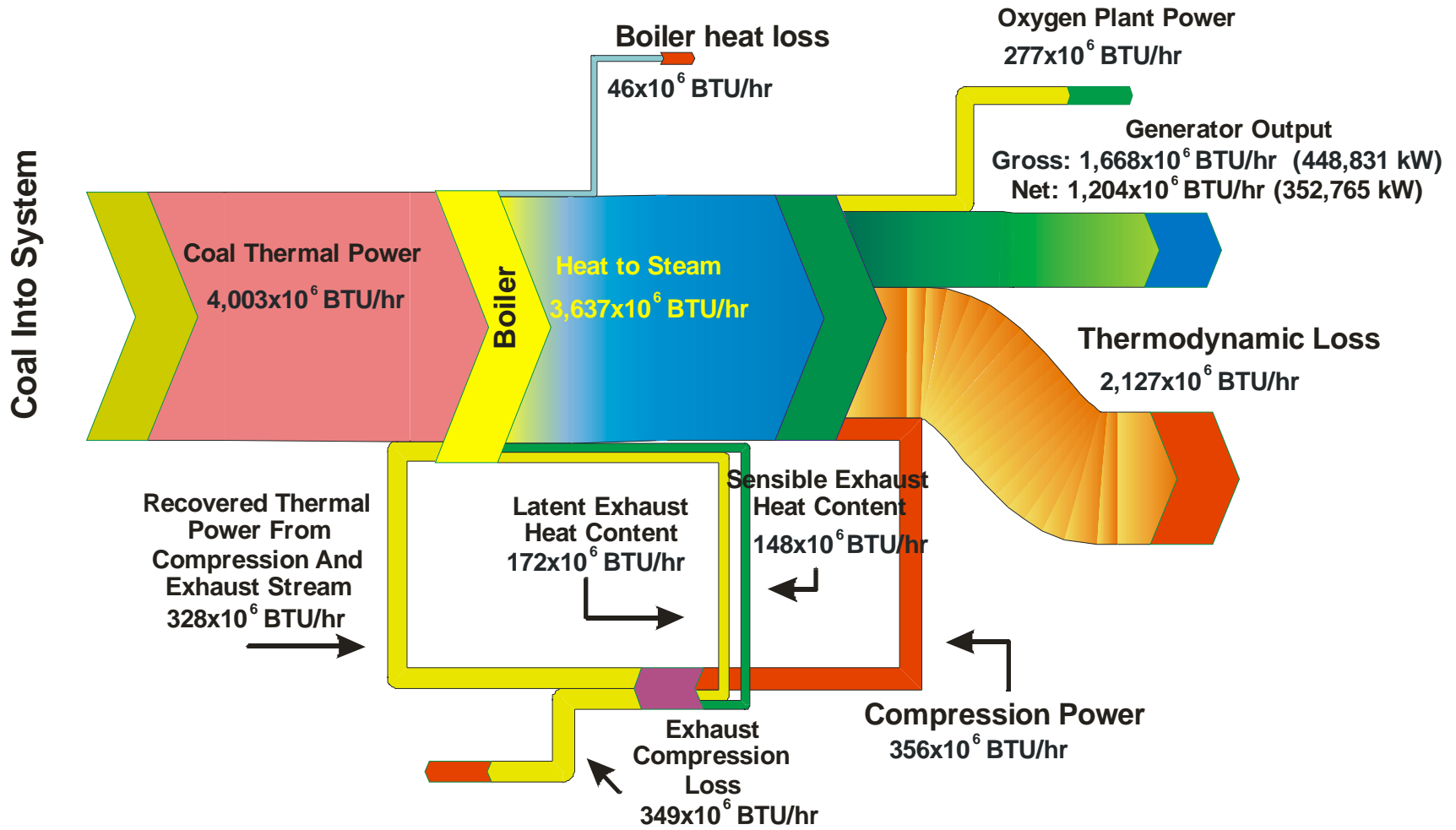


Figure 3: Oxy-combustion subcritical 400 MW PC power boiler heat distribution.

Comparing the inputs in the Sankey diagrams shows that there is about 3% less coal used to produce the same amount of steam in the oxy-combustion system. Further examination of the diagrams shows that the sensible heat being carried out of the oxy-combustion boiler is less by about  $131 \times 10^6$  BTU/hr. The reason for the difference is that there is no nitrogen to carry out additional sensible heat. In air based combustion systems the nitrogen is an inert carrier of energy instead of an active participant in energy generation (as are carbon dioxide and water vapor). There is also a lower limit to the discharge temperature of the combustion products to prevent condensation of  $H_2SO_4$  and to promote lofting of the stack gases.

The Sankey diagrams also indicate that the amount of latent heat in both cases is very similar (within  $11 \times 10^6$  BTU/hr). The reason is that the latent heat content in the water vapor is directly related to the amount of coal burned (which is similar in the two systems). In oxy-combustion systems with  $CO_2$  capture there is no need to prevent the exhaust discharge temperature dipping below the dew point for  $H_2SO_4$ ; there is also no need to maintain buoyancy of the combustion products since they are captured. The result is a slight reduction in the latent heat carried out of the boiler and a large reduction in the amount of sensible heat carried out.

*Oxygen separation power:* Downstream of the exhaust discharge in Figure 3, the oxygen plant and the power driving the compressors have a major impact on the output of the power plant. In the list of technologies with impacts on oxy-combustion power plant performance, reducing the energy required for oxygen production is ranked number 1. Presently there are significant efforts underway to reduce the energy cost of oxygen production. In the past 5 years (2002 – 2007) there has been a reduction from about 240 kWh/ton of 99%  $O_2$  to 220 kWh/ton. That reduction has taken place based on evolutionary improvements in the cryogenic separation process. Advanced, revolutionary, air separation technologies such as the use of membranes are showing considerable progress and early demonstrations indicate that energy requirements as low as 150 kWh/ton 99.9%  $O_2$  are feasible; these are projected to become commercially available as early as 2012<sup>5,6</sup>. If the power use for oxygen production can be reduced, the arrow showing that as a loss of energy in the system will become smaller. There is also active research into the possibility of incorporating the oxygen plant into the power plant to allow exchange of energy between the two, which would be represented on the Sankey diagram by another loop exchanging heat between unit processes.

*Recovery of Heat of Compression:* At the bottom of Figure 3, heat from the exhaust and the heat equivalent of compression power comprise two streams: a loop shows energy recovered while a second stream shows compression power lost as heat to the environment. Without heat recovery in the compression steps, thermal efficiency and power generated from the given rate of produced steam both drop considerably (“No heat recovery” bars in Figure 1 and Figure 4). Thermal efficiency decreases from 30.05% to 28.34% (a difference of 2.16%) and output drops from 353 MW to 333 MW. The impact of the other technologies in the ranked list can be evaluated in a similar fashion.

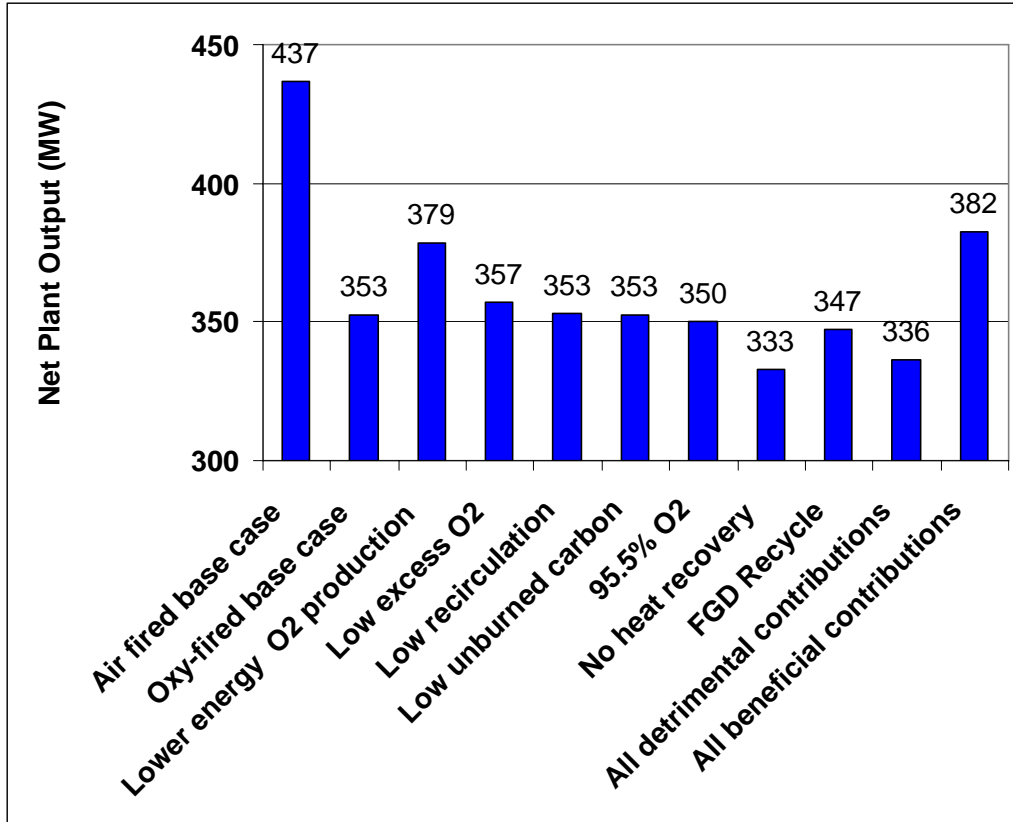


Figure 4: Net power plant output using different technologies.

## Other Impacts Considered

### Boiler air leakage

Another important factor that was not modeled in these activities is the impact of infiltration. Boilers are large and complicated and it is virtually impossible to imagine a fully sealed boiler. The amount of leakage is expected to vary widely between power plants with older plants having more leakage. Under severe leakage conditions enough air can leak into a system to add to the ID fan load and cause combustion problems due to an incorrect indication of operating excess air. During retrofit every effort should be expended to minimize leakage.

In existing air-fired systems, air in-leakage can decrease the thermal efficiency if the amount of air being heated is significantly greater than that necessary for combustion. In oxy-combustion systems, the air leaking in causes two problems not seen in air fired systems. First, the incoming air brings nitrogen into an environment that has low nitrogen levels, providing the raw material for thermal NO<sub>x</sub> production. Second, the air being introduced is a contaminant for the CO<sub>2</sub> product. So called “permanent” gases such as N<sub>2</sub>, O<sub>2</sub>, and Ar dissolve in CO<sub>2</sub> and depress its critical point preventing it from becoming a liquid (if pure liquid CO<sub>2</sub> is the desired product). If the sequestration mode requires separation of N<sub>2</sub>, O<sub>2</sub>, and Ar from CO<sub>2</sub>, increases in those permanent gases will



mean increased energy required for separation, and more CO<sub>2</sub> lost during the process. Even if the sequestration processes can tolerate limited tramp gases in the mixture, limiting impurities is best done by limiting contaminant intake rather than increasing contaminant removal.

The importance of infiltration to oxy-combustion systems with CO<sub>2</sub> capture brings up the interesting question of pressure of operation. Most PC boilers in the world operate at a slight negative pressure (for a number of valid reasons) and the industry is understandably reluctant to change the circumstances. However, if oxy-combustion becomes an important technology there could be an inherent competitive advantage in developing safe slightly positive pressure boiler systems.

### **Materials challenges**

At each step in the evolution of power generation, materials have been pushed to their limits. The move from air fired systems to oxy-combustion appears to have some potential challenges ahead. The term “potential” is being used because it is not clear yet if these challenges will materialize and, if so, under which conditions. The materials challenge most discussed is the possibility of increased corrosion in an oxy-coal system. In these discussions, higher corrosion rates are connected to an increase in mole fraction of trace gases (such as SO<sub>2</sub>) in an oxy-combustion system. This increase in concentration of SO<sub>2</sub> is, many times, incorrectly attributed to flue gas recirculation (see Text box explanation).

The materials concern points to a possibility that materials designed for operation in a lower SO<sub>x</sub> concentration (air-firing) could suffer accelerated corrosion in oxy-firing practice. Materials research programs are underway to determine the performance of materials in the nitrogen free oxy-coal combustion environment.

**The concentration of trace contaminants in oxy-coal combustion products:** There is a misconception that recirculation causes a “build-up” of trace contaminants in recirculating boilers. The reasoning used to come to this conclusion is that most of the combustion products are recirculated back into the boiler and, therefore, with most of the contaminants being returning to the boiler the concentration builds up. This is wrong.

There is an increase in the “relative concentration” of all the combustion products. However, it is not related to recirculation. Instead, in air combustion, the gas entering the boiler has approximately 71% nitrogen and so the active gas (oxygen) is diluted with nitrogen. In oxy-combustion, when the oxygen in the air reacts with the coal to form combustion products they are all at relatively higher concentrations due to the absence of nitrogen to dilute them.

From a mathematical standpoint, if 71% of the gas (N<sub>2</sub>) going into the boiler is missing, then the gases that are left (in their same relative proportions) are increased by the ratio of the remaining volume to the starting volume due to the missing nitrogen.

In the case of low-sulfur coal, the oxy-firing concentration of SO<sub>x</sub> stays within the region of accepted limits for most materials of construction. However, the atmosphere in an oxy-combustion system has much higher concentrations of CO<sub>2</sub> and H<sub>2</sub>O. It is not clear what role the oxy-firing concentrations of those components might play at any concentration of SO<sub>x</sub>. At present, there is no experimental evidence to either sustain or refute the possibility of accelerated corrosion in retrofit boilers. Experiments should be providing answers within the next few years. In new construction boilers any more aggressive environment can be mitigated by the use of materials selected to operate under the new conditions.

## SUMMARY

If there are carbon dioxide constraints applied to power generation, the combination of oxy-combustion and Integrated Pollutant Removal is a viable technology for retrofit. The approach could be applied using existing technologies and experience from other industries using the technologies. However, there is significant room for improvement and engineering studies are underway to better understand the implications of integrating both oxygen production and CO<sub>2</sub> processing into the power plant infrastructure. This integration is more complex when applied to retrofit because a prime goal of retrofit is to minimize capital costs. The ordered list of technologies and their potential impact provides a framework for efforts over the next few years to prepare the industry for the potential of carbon constraints.

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