

Developments in Integrated Pollutant Removal for Low-Emission Oxy-Fuel Combustion

S. Gerdemann¹, C. Summers¹, D. Oryshchyn¹, B. Patrick², T. Ochs¹

Abstract

A complete coal combustion and flue gas treatment scheme was designed, constructed, and operated at bench scale as a product of cooperative research between USDOE's Albany Research Center (ARC) and Jupiter Oxygen Corporation. The products of combustion generated using this oxy-fuel coal combustion process were effectively captured using an integrated pollutant removal (IPR) process. Supporting laboratory-scale research focuses on elements of IPR such as extraction of particulates, SO₂, and mercury, and on the character of the liquid and vapor phase compositions for the CO₂ - N₂ - O₂ mixture at the temperature and pressure conditions found at the end of the process. Future pilot-scale work will be necessary to generate economic and engineering data that will apply to full-scale oxy-fuel/IPR systems.

Introduction

Oxy-Fuel Combustion

Traditional boiler design is based on the idea that the oxygen supply for combustion systems is air. Air is approximately 20.7% oxygen and the remaining 79.3% (mostly nitrogen) comes along for the ride, producing NO_x, lowering the flame temperature, and increasing the volume of combustion products. However, technology using air has become highly optimized with respect to utilizing both radiant and convective heat transfer throughout the boiler.

Firing a fossil-fueled power plant with oxygen-enriched air and recycled flue gas – oxy-fuel combustion – has significant advantages over traditional air-fired plants (Ochs et al, 2005a). Among these are:

- Greatly reduced nitrogen concentration in the burners decreases NO_x production;
- Greatly reduced nitrogen concentration in primary and secondary 'air' means less heat lost to non-reactive gas;
- Combustion product volume and mass are decreased;
- Exhaust contains a higher concentration of CO₂;
- Exhaust contains greater concentrations of all pollutants; and
- Most of the flue gases are condensable, making compression separation possible.

Other potential advantages, that could be utilized in modified, more efficient boiler designs (Ochs et al., 2005a), include:

- Increased radiant heat transfer in the boiler; and

¹ Albany Research Center, US Department of Energy, 1450 Queen Ave SW, Albany, OR 97321

² Jupiter Oxygen Corporation, 4825 N. Scott St., Suite 200, Schiller Park, IL 60176

- Oxygen concentration as a design variable.

The high cost of oxygen production once made oxy-fuel systems economically unattractive, but the growing interest in carbon sequestration, along with the opportunity, during CO₂ capture, of avoiding or removing other pollutants, is offsetting some of the economic concerns. For example, post-combustion NO_x levels in an oxy-fuel system have been recorded below 0.09 pounds per million Btu (lb/10⁶ Btu), lower than currently achievable using expensive SCR or NSCR technology. Computer modeling (Ochs et al., 2005a) indicates that an advanced oxy-fuel system using denitrified air (96% oxygen) and recycle of the combustion gas produces a combustion product that is 61% CO₂ and 33% water (figure 1). The water can easily be condensed, leaving a CO₂-rich combustion product gas. Existing technology may be applied to this gas to separate CO₂.

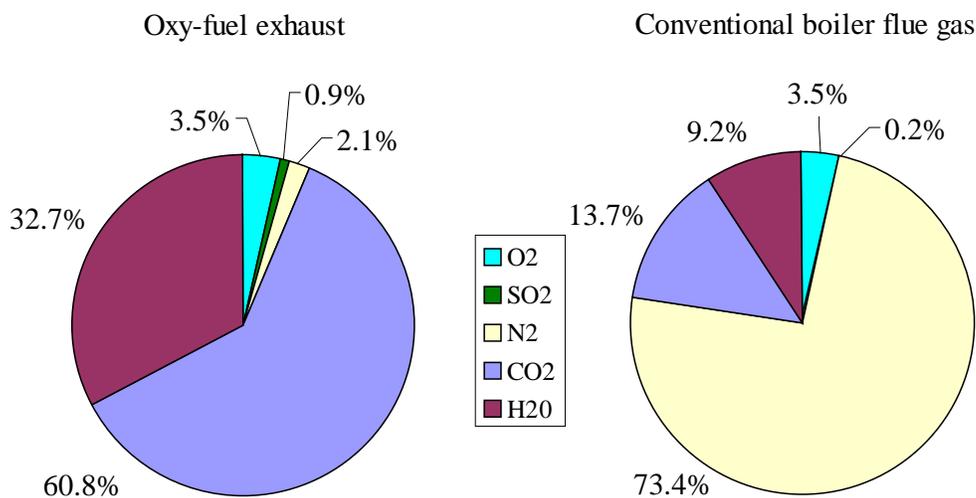


Figure 1 – Composition of an oxy-fuel exhaust compared to conventional air-fired boiler flue gas.

Economic analysis of a modeled oxy-fuel system using a 96% oxygen stream input, recycling the boiler flue gas stream, and capturing 99% of the CO₂ as liquid indicated that the approach is competitive with other zero-emissions power plant designs (Ochs, 2004). In the model, capturing and liquefying the CO₂ lowers the efficiency of a 500 MWE power plant approximately 1%, excluding the energy cost of oxygen. The energy cost of oxygen production for the plant is approximately 85 MW. However, approximately 50 MW of that can be recovered downstream in an integrated pollutant removal (IPR) system. In analyses done for this study, after producing oxygen, capturing CO₂ and SO₂ in IPR, and recovering the costs of the FGD and SCR units (which are no longer needed), the net loss to the boiler system is about 10%.

Integrated Pollutant Removal (IPR)

IPR for multi-pollutant capture and CO₂ separation is a post-combustion exhaust treatment scheme. The basis of the process is the separation of condensable vapors (such as water and CO₂) from non-condensable gases (such as O₂ and N₂) using compression and cooling. Heat energy is recovered from condensation of vapors and by expansion of pressurized non-

condensable flue gases. In the process, pollutants such as SO_x , NO_x , and particulates are removed with the condensate streams. The recovered energy is integrated back into the energy cycle of the power plant. The IPR process is possible in oxy-fuel systems because recycling the flue gas results in a bleed stream that comprises approximately 95% condensable gases (water vapor, CO_2 and SO_2).

Previous work has shown that the two component sections of the system can work together to allow fossil fuel combustion with near-zero emissions. Both systems can be constructed using existing technology applied in novel ways, and no breakthrough technologies are required (Ochs et al., 2005b). Additionally, none of the components require extensive re-design work. The system can be assembled using standard chemical engineering and mechanical engineering processes adapted in unique ways.

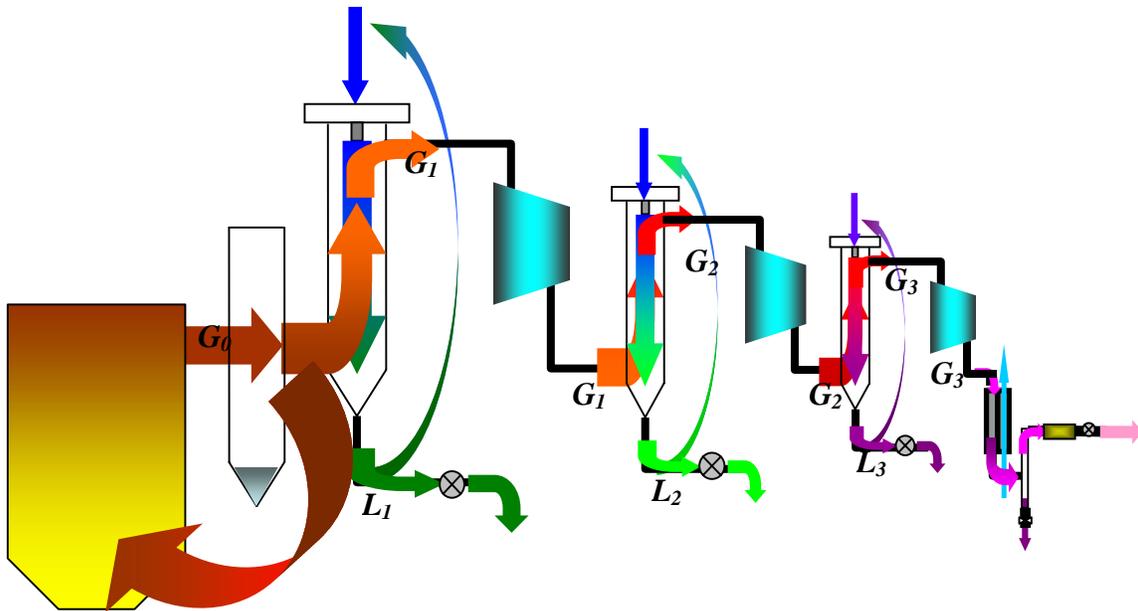


Figure 2 – Schematic diagram of the operational steps in IPR.

Figure 2 is a simplified flow diagram of the IPR process, not depicting steam routing and power production. Combustion gas (G_0) passes through a baghouse or cyclone for gross particle removal. This gas then flows through a counter-flow, direct-contact heat exchanger (DCHX). In this heat exchanger column, the gas comes into contact with cooler liquid. Cooling allows vapors in G_0 to condense. This condensed vapor and the cooling liquid both dissolve and entrain soluble pollutants and fine particles. Exiting this column are a cleaner gas (G_1) and a pollutant-laden liquid (L_1). The liquid, L_1 is split into two streams: the stream used for coolant (shown by the arrow leading back to the top of the column) is cleaned to enable dissolution and entrainment of pollutants on re-injection; the exiting stream is cleaned completely and is ready for use in the power plant, or for release. The gas, G_1 , is compressed and then brought through another DCHX. The condensed liquid at this stage repeats the same process as L_1 , but at higher pressure.

Table 1 shows the expected gas compositions of G_0 , G_1 , G_2 and G_3 based on computer modeling with GateCycle³. After the third condensation, when pressures and temperatures are close to the critical point of CO₂, the gas is cooled to condense CO₂ liquid. Ideally, the product of this condensation is a sequestration-ready liquid CO₂ product.

Table 1 - Compositions of IPR-treated oxy-fuel gas

	Flue gas (G_0)	After first condensation (G_1)	After second condensation (G_2)	After third condensation (G_3)
	Flue gas	After first condensation	After second condensation	After third condensation
CO ₂ %	60.8	87.1	91.4	71.0
O ₂ %	3.5	5.0	5.3	18.2
N ₂ %	2.1	2.9	3.1	10.7
H ₂ O %	32.7	3.7	.2	.1
SO ₂ %	0.9	1.3	0.0	0.0
Pressure (psia)	15	15	180	1,200
Mass (lb/hr)	935,000	789,000	762,000	207,000

Construction of an Oxy-Fuel/IPR Bench-Scale System

In August of 2004, Jupiter Oxygen Corporation issued a challenge to USDOE/ARC to help design and build a functioning Oxy-Fuel/IPR system using technology which could be readily acquired. Previous experimental work had been limited to the design and testing of small subsets of the total system. Following the system modeling process, there appeared to be no fundamental obstacles to building a functioning system, and it was determined that a proof-of-concept demonstration apparatus could, in fact, be assembled using “off-the-shelf” components and standard engineering practices. ARC agreed and the two organizations rapidly put together the complex of systems. The resulting activity produced a successful demonstration of the combined technologies in November 2004 (figure 3).

Initial designs for the system came from a GateCycle computer model of a 400 MW power plant. The model included the steam generator as well as the power production turbines and their auxiliary equipment. However, for the proof-of-concept system it was clear that it was not necessary to produce power or even to generate steam. The goal was to show that IPR could be successfully integrated with an oxy-fuel system. Work concentrated on capture of the combustion products after they had given up most of their energy through heat transfer to the power plant working fluid.

Estimation of flows for this small system came from other GateCycle computer models of a 250,000 Btu/hr coal combustion system with an attached IPR system. The software is good at modeling the initial combustion products; however, there are no commercial software systems

³ Commercial products mentioned in this paper are neither endorsed nor recommended by the USDOE. The USDOE does not endorse or recommend commercial equipment, processes, or software.

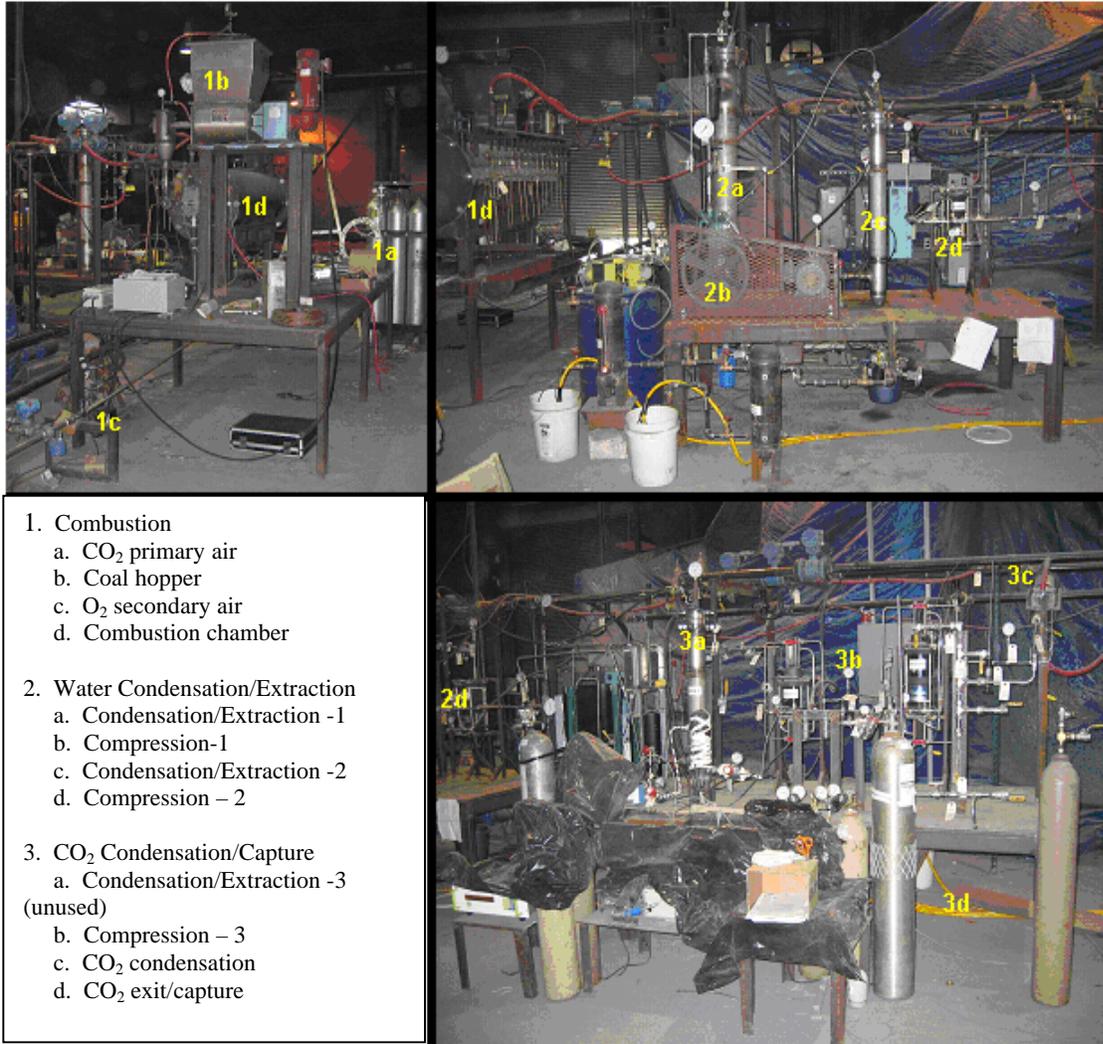


Figure 3 – Proof-of-concept experimental section

that are good at estimating the behavior of those combustion products under high-pressure IPR conditions. In the models combining thermophysical property calculations with the GateCycle base, the exit stream from IPR was calculated to consist predominantly of liquid CO₂, with N₂ and O₂ either dissolved in the liquid CO₂ or carried on as gas. Estimations of optimal pressures and temperatures for final fluid capture are also problematic to calculate using standard software.

The proof-of-concept system was operated, and successfully captured liquefied CO₂ at the end of the process. Particulates, SO₂, and oxidized mercury were effectively removed from the flue gas, and elemental mercury was concentrated in the final gas stream. Only 1000 to 1500 psig was required for full capture of the condensed CO₂ and remaining gases. It was surmised that there was significant dissolution of N₂ and O₂ in the condensed CO₂.

Near-Critical Phase Determination Experimentation

CO₂ at the highest pressures of the IPR process exists near the critical point, due to the temperature of cooling water at power plants. The exit stream from IPR was calculated to

consist predominantly of liquid CO₂. It is possible that significant solubility of tramp gases (primarily N₂ and O₂) in the CO₂ will result in little or no gas released to the atmosphere (all gases would be “squeezed” into the liquid CO₂). In fact, the full capture of the final IPR product during proof-of-concept operations indicates that this occurred.

Estimations of liquid and vapor phase compositions for near-critical compressed CO₂ are difficult. Minimal binary and ternary experimental data are available, and standard equations of state are unreliable near the critical point of vapors. Attempts to predict the actual partitioning of the non-condensable gases between the vapor and liquid phases were made using thermodynamic software and complex equations of state (Muirbrook and Prausnitz, 1965; Stoll et al., 2003). These efforts gave inconsistent results and proved inaccurate when checked against available experimental data.

Experiments are currently underway to determine the distribution of oxygen and nitrogen in carbon dioxide in the PT realm of late-stage IPR (Oryshchyn et al., 2005). A pressure vessel was designed to accept a super-critical mixture of CO₂, O₂, and N₂ in proportions predicted by computer modeling to be characteristic of the late, high-pressure stages of IPR. The mixture is cooled and condensation determined by examining the pressure vs. temperature curve during cooling. Once equilibrium is established, the liquid and vapor phases are isolated in six sample cells, and their compositions and relative quantities determined. These experiments will begin to answer the question of the proportion of CO₂ captured in liquid form at various pressures and temperatures, and its purity. From these data, it will be possible to determine the compression needed to provide an appropriate CO₂ product.

Inquiries and literature searches identified existing data (Muirbrook, 1964; Zenner and Dana, 1963). Data for this ternary system were available for temperatures near 0 °C, and for the binary systems (CO₂ + X; X = N₂ or O₂) at higher temperatures. Binary data indicated that temperatures below 15 degrees would be necessary to condense liquid from a gas containing more than 20% N₂+O₂. Ternary data from NIST at 0 °C supported this (see figure 4).

Initial experiments examined the pure CO₂ system as a baseline; subsequent experiments with two-component and three-component mixtures are providing checkpoints and data for the ternary phase diagram in the region of interest.

Three tests were done with a gas mix containing 18% O₂, 10% N₂, and the balance CO₂. In the first of these tests, the gas was compressed to 1500 psi in the pressure vessel at 34 °C. The vessel was chilled in a water and ice bath to 15 °C, and no evidence of separation was seen. In a second test, starting conditions were 1500 psi and 25 °C. The third test began at 1800 psia and 25 °C. For the latter two tests, the vessel was chilled to 0.4 °C; vessel pressure and water bath temperature were tracked during cooling. Once the vessel was chilled and had been held at 0.4 degrees C for about 3 hours, the vapor and liquid in the vessel were isolated and sampled with a gas chromatograph (GC). Relative densities of the material contained in the liquid and vapor sample cells were determined by venting at constant mass flow rate, and showed that condensation had occurred. Preliminary GC data for the vapor and liquid indicated that the liquid was enriched in CO₂. A number of additional experiments will be done to characterize the condensation behavior of CO₂-rich gases in the IPR system.

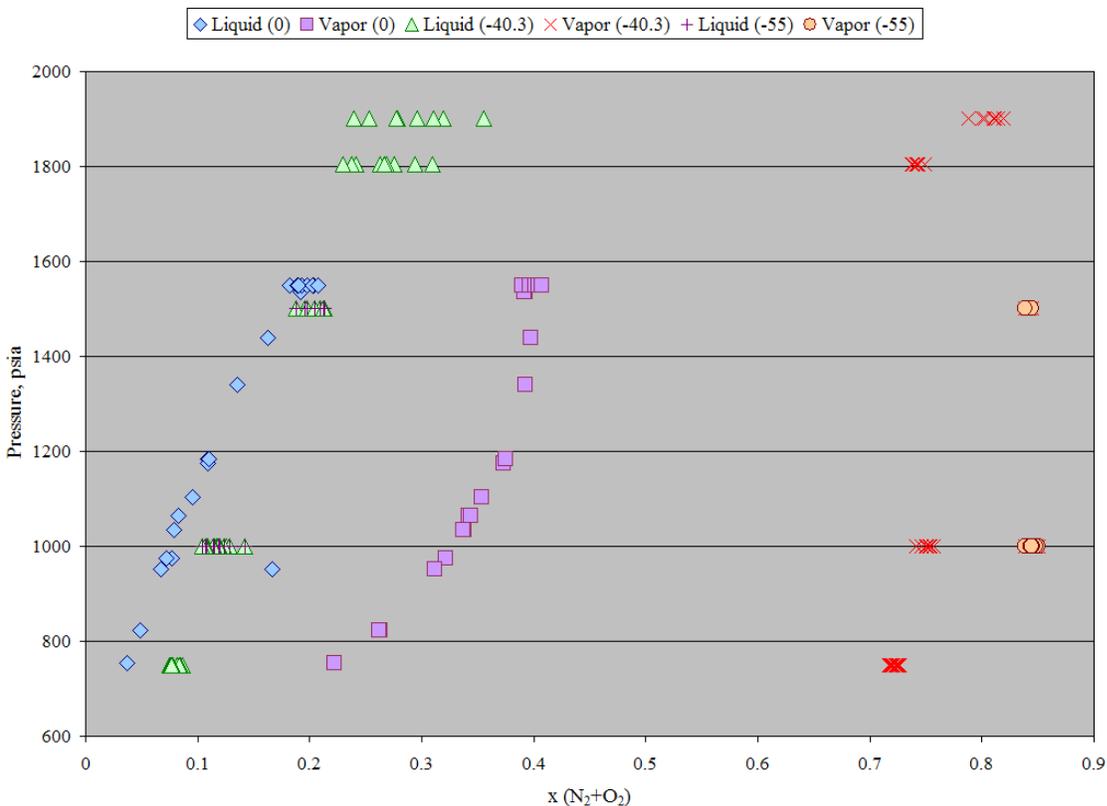


Figure 4 – Fraction of N₂ plus O₂ dissolved in CO₂ at 0 °C (Muirbrook, 1964; Zenner and Dana, 1963), -40.3 and -55 °C (Zenner and Dana, 1963) and various pressures. Experiments for the IPR system are focusing on the zero degree range.

Results and Conclusions

Standard approaches to the elimination of pollutants in flue gas rely on numerous separate processes, each of which uses a distinct method for removal. The USDOE/Albany Research Center and Jupiter Oxygen Corporation developed and demonstrated a package of control technologies that effectively removes virtually all of the pollutants from the flue gas. The technique involves flue gas recirculation, oxy-fuel combustion, and the condensation of the vapors in the flue gas to remove all of the pollutants, including particulates, CO₂, SO_x and NO_x, as well as mercury and fine particulate matter. This practical removal of carbon dioxide adds a new dimension to the science of flue gas treatment and handling.

During the demonstration, combustion gas tests showed NO_x levels at 0.088 lb/10⁶ Btu, well below the target of 0.1 lb/10⁶ Btu. With the addition of the Integrated Pollutant Removal system, liquid carbon dioxide and 99% of the SO_x and particulates were captured. Particle-bound mercury was efficiently removed from the flue gas, and mercury vapor was concentrated at the end of the process. Based upon the results of these tests and subsequent laboratory research, it is anticipated that future optimization of the combined systems could capture a liquid product comprising 80% CO₂, and more than 90% of the mercury, while maintaining ultra-low NO_x emissions.

The projected fuel savings and other increased efficiencies are such that the cost of this combined process could be competitive with other technologies that capture CO₂ for sequestration. Cost estimates for the combined ARC/Jupiter Oxygen system are on the order of 5.1 cents/kWh with amortized capital expenses including a production cost of 1.7 cents/kWh (Ochs et al., 2005b). Both figures are lower than traditional air-fired power plants. However, further testing and demonstration on a commercial scale are needed to prove out the system.

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