

Investigation of the Liquid/Vapor Composition of Compressed Liquid CO₂ with N₂ and O₂ in Integrated Pollutant Removal Systems for Coal Combustion

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ABSTRACT

Accurate prediction of the processes in Integrated Pollutant Removal (IPR) using compression and condensation of coal combustion products requires an understanding of the liquid/vapor ternary CO₂/O₂/N₂ system. At conditions close to the critical point of CO₂ the existing equations of state deviate from the sparse measured results available in the literature. Building on existing data and procedures, the USDOE/Albany Research Center has designed an apparatus for examining compositions in this region. The design of the apparatus and planned initial experiments are presented.

BACKGROUND

The Integrated Pollutant Removal process for multipollutant capture including CO₂ is a post combustion exhaust treatment process in which heat transfer necessary for capture of pollutants is integrated into the energy cycle of the power generation plant. The energy balance for IPR in a power generation system is a combination of energy used for compression of flue gas and energy released by the cooling of that compressed gas to enable condensation of the vapor components of the exhaust stream. Pollutants are removed in the condensate streams. The final condensate, CO₂, is captured as a liquid or supercritical fluid amenable to sequestration [1].

During a proof-of-concept (POC) experiment [2] treating the exhaust of a 250,000 BTU/hr oxy-coal combustion unit, it was determined that there is significant dissolution of N₂ and O₂ in the condensed CO₂ flowing through the higher pressure stages of IPR. During operation of the experimental system, maximum pressures required for full capture of the final-stage exhaust stream were between 1,000 and 1,500 psig. This was lower than the pressures occurring in the computer models of IPR. These models were built assuming negligible solubility of N₂ and O₂ in liquid CO₂ at these pressures.

Figure 1 shows a simplified flow diagram for the integrated pollutant removal process. This diagram is derived from the simplified process implemented for proof-of-concept. In this figure, the integration of removal of the full spectrum of pollutants is the focus.

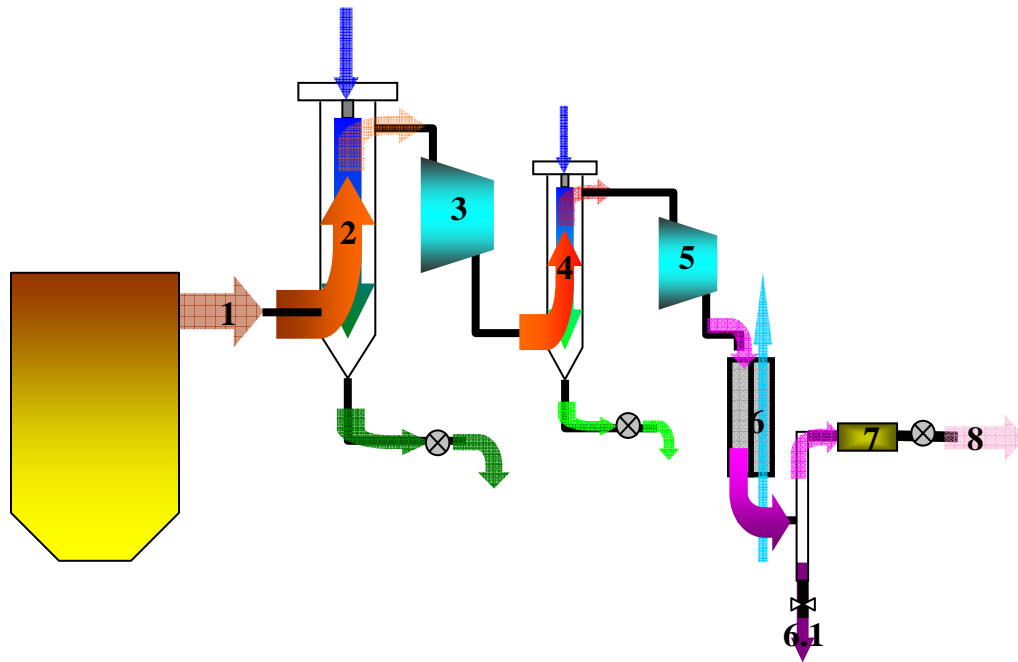


Figure 1: Flow diagram for IPR. Note, power plant steam cycle is not shown here.

1. Oxy-coal combustion produces low-nitrogen exhaust.
2. Direct contact with high-pH water spray condenses H₂O, removes SO_x and particles at ambient pressure.
3. Cooled, cleaner gas is pressurized.
4. Direct contact with high-pH water spray condenses H₂O, removes SO_x and fine particles and absorbs CO₂ at intermediate pressure.
5. Cooled, even cleaner gas is pressurized.
6. Shell-and-tube heat exchanger cools gas (CO₂, O₂, N₂ and uncaptured Hg) at high pressure. CO₂ condenses for capture (6.1).
7. Remaining uncondensed gas flows through mercury trap.
8. Decompress and release cleaned gas (O₂ and N₂).

It is important to note that IPR is also integrated with the power plant through the general intra-power-plant energy transfer. IPR process energy transfer is integrated into the more general process of power generation through interactions used for feedwater heating, primary air heating and expansion. The heat-based transfers are most effective when the temperature difference across which heat flows is greatest.

Now that the concept of IPR has been proven, closer focus on design decisions is occurring as the project moves toward larger, more scaleable formats. The capabilities of the system for elimination of SO_x and NO_x being fairly well understood, capture of the final stream of CO₂ remains. How much CO₂ is left uncaptured after the high pressure N₂/O₂/CO₂ stream is cooled? Oxygen and nitrogen are soluble in liquid carbon dioxide, but the extent to which they dissolve depends on the temperature of the liquid CO₂. Design decisions balancing the amount of energy to be used cooling the CO₂/N₂/O₂

stream and the CO₂ capture technologies best applied to the varying final vapor stream will be made more clear with a better understanding of the effect of temperature and pressure on the composition of this final vapor stream. The main constraint on cooling in this IPR regime is the temperature of the cooling water available to the plant. Water available to plants located in tropical areas, for example, is typically as high as 85° F. This is above the 83° F temperature at which CO₂ will boil at these pressures. Under these high cooling water temperatures there is a need for active cooling of the supercritical CO₂ streams. Since dissolved gases are evolved from a liquid on boiling, the extent to which the stream could be brought below its boiling point is expected to have a significant effect on the composition, and therefore the treatment, of the fluid exiting the cooling stage of the high pressure regime of IPR.

Previous computer modeling studies predicted the compositions of treated flue gas as it progressed through sequential compression and condensation stages of IPR [3]. Gas compositions expected in late-stage IPR are shown in Table 1. The mixture used for the first set of experiments is in the column “After third condensation”.

Table 1: Expected gas compositions in the IPR process [2]

	Flue gas bleed	After first condensation	After second condensation	After third condensation	After fourth condensation	After fifth condensation
CO ₂	0.6085	0.8711	0.9143	0.71	0.39	0.085
O ₂	0.035	0.0501	0.0526	0.1821	0.383	0.5765
N ₂	0.0206	0.0294	0.0309	0.1069	0.2249	0.3384
H ₂ O	0.3269	0.0365	0.0022	0.001	0.0021	0.0001
SO ₂	0.009	0.0129	0	0	0	0
Pressure (psia)	15	15	180	1,200	2,500	5,000 to 2,000
Mass (lb/hr)	935,000	789,000	762,000	207,000	87,800	51,700

Pressures and temperatures in these regimes approximate the critical point of CO₂, the primary component of the mixture. Because of the instability of states near fluid critical points, data predicting the distribution of the components in this regime are difficult to obtain. State models [4, 5] are not consistent in their predictions of near-critical phase distributions of this system. Experimental work with this ternary system has been done in regimes not near the critical point of CO₂ [4, 5, 6]. Extrapolation of these experimental results to near-critical pressures and temperatures is also not reliable.

The USDOE/Albany Research Center is in the process of gathering data to characterize the phase distributions of the N₂/O₂/CO₂ ternary system at compositions similar to those in Table 1, at pressures and temperatures expected in the higher-pressure regimes of the process. A series of experiments will generate initial empirical data, which are expected to clarify the behavior of the final exhaust flows of coal-fired power plants employing IPR. The ensuing discussion will cover the impact of the behavior of the N₂/O₂/CO₂

system on compression capture of CO₂ from coal-fired combustion flue gas, models developed thus far for the behavior of the ternary system, design of the experimental test apparatus, and a discussion of the scope and expectations for this and future studies.

SCOPE OF INITIAL STUDY

Observation of the N₂/O₂/CO₂ system at ARC will focus on gas compositions and pressure-temperature regimes surrounding those predicted by computer modeling for the high-pressure stages of IPR (Table 1). Results of the ARC study should help to define the phase distribution of mixtures on the order of 18% O₂, 12% N₂, balance CO₂ at temperatures between 14 and 31° C and pressures ranging from the mixtures' dew points to approximately 130 bar. Results from the ARC study of this composition will clarify what future compositions will be studied at ARC and, hopefully, focus the field of inquiry for further, general study of the N₂/O₂/CO₂ ternary system. Water vapor and argon are predicted by the computer model to be present in only trace amounts in this stream, and are eliminated from the study for simplicity.

Experiments will begin using the pressures and temperatures occurring in the proof-of-concept system. From the results in the POC regime, experiments will then continue at higher temperatures until the critical point of this system is found. This is the upper bound of interest, because, beyond these temperatures, the supercritical mixture will not fractionate for further processing in IPR. Treating and/or sequestering this supercritical mixture is one avenue along which further IPR/CO₂ sequestration research design may proceed. Since it is expected that the critical point of the ternary system will be below that of pure CO₂ [7], the prospect of this supercritical mixture as a product of IPR is a real possibility.

After finding the critical temperature for this mixture, lower temperature experiments will continue to collect data to apply to plants in cooler climes with lower temperature cooling water. The temperature differential may not be the only factor involved in optimizing IPR for cooler geographical areas. The accompanying change in the composition of the high-pressure IPR stream may affect design decisions dealing with the necessity of further compression and final capture methods.

DESIGN OF THE TEST SECTION

The method of testing used for these experiments is characterized in the Christov, Dohrn review of methods for high pressure fluid phase equilibria [8] as an "Analytical, Isothermal" method. "Analytical methods...involve the determination of the compositions of coexisting phases." In an isothermal method, "[a]fter the desired temperature has been reached, the mixture is kept at a constant temperature." The pressure will change in response to temperature adjustment and possibly also as equilibrium is achieved in the test vessel.

The experimental apparatus for these experiments accepts and compresses a given amount of premixed gas at a temperature above the critical temperature for CO₂. It

allows the gas to cool and condense slowly, and to separate into vapor and liquid components. During cooling, the vessel is repeatedly inverted to prevent stratification and speed the approach to equilibrium. The gas is held at a constant temperature after cooling, as an equilibrium phase distribution is reached. Multiple samples of gas and liquid are captured and transferred directly to a gas chromatograph for analysis. Figure 2 shows a schematic view of the test section.

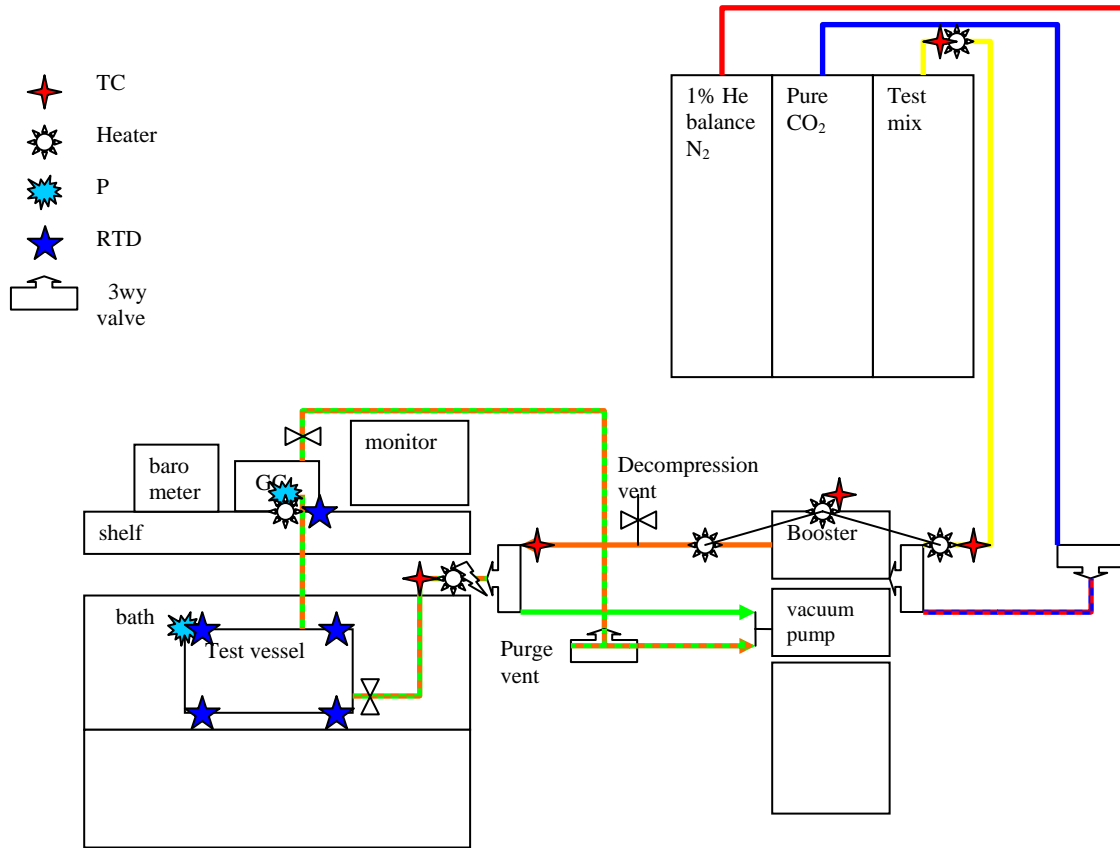


Figure 2: Test section for initial studies of the $N_2/O_2/CO_2$ ternary system near its critical point

Equilibrium vessel

The vessel in which gas mixtures will be contained is built of stainless steel tubing and fittings. Its volume is approximately 0.6 L. Fifteen percent of this volume is made up of two series' of sample chambers – one for liquid capture, the other for gas capture. Separating these cells are ball valves which, when open, allow gas and liquid to flow freely. The relatively large volume of the vessel shown in Figure 3 allows for phase separation throughout the pressure vessel, including the sample-capture sections. This volume also minimizes whatever effect the isolation of samples will have on the pressure, and so phase distribution in the vessel. The sample capture sections of the vessel are made up of series' of tees and ball-valves. The internal diameter of the tees and valves is large to allow gravity-driven, two-phase counter-flow.

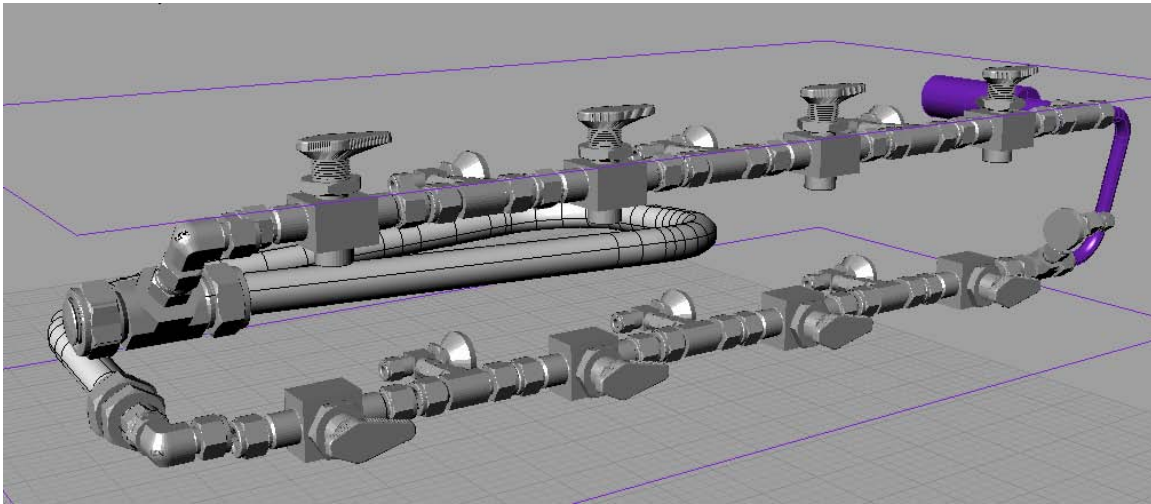


Figure 3: For clearer viewing, the test vessel is shown here without feed or sampling tubing.

Gas Loading

The gas mixtures tested in these experiments are made commercially to Albany Research Center specifications. The delivered mixtures have been analyzed for precise composition. The gas loading sequence consists of a leak-check and cleaning step, a blanking-test step and a filling/compression step. In the first step, the vessel, feed lines and sample lines are checked for leaks using bubbling indicator and a helium leak detector. After assurance of a tight vessel for the experiment, the helium-spiked nitrogen for leak testing is removed using a vacuum pump. This gas is replaced with pure CO₂ to displace and dilute any remaining leak-test gas. After flushing three times with pure CO₂, the vessel is again evacuated, and the empty, clean vessel is then filled with the test gas. These cleaning and filling/compression steps occur at approximately 90 °F. The test gas enters the equilibrium vessel for blanking at 100 psig and 90 °F. Samples at the extreme ends of the test vessel are isolated and analyzed. The composition analyses of these samples are expected to match each other as well as the commercial composition description.

The vessel is then emptied of this blanking mixture and refilled with the premixed gas, compressing as necessary to achieve the desired pre-separation pressure. Compression is done by a double-acting, air-driven pressure-booster pump. The pump is controlled by a pressure switch to allow the desired pressure to be attained automatically.

Temperature Control and Measurement

In order that the gas be well-mixed as it enters and is compressed into the test vessel, it is kept at a temperature above the critical temperature of CO₂. This ensures that, even as the gas is compressed, it will not begin prematurely to condense and fractionate. Tubing which carries the gas from its storage bottle to the compressor and test vessel is kept at a temperature between 90 and 100° F. Delivery tubing is heated using electrical heat-tape

powered via a proportional-integral-derivative (PID) feedback temperature controller. The vessel itself is held at temperature in a water bath. Sample delivery lines, carrying post-equilibrium phases to the gas chromatograph are also heated above 90° F, using warm air to help prevent differential vaporization of captured samples during analysis. The water-bath is large and so requires a long time to change temperature. This is a help in achieving full separation and equilibration of phases in the test vessel.

Temperatures are measured along the gas-feed line, at locations along the test vessel itself, and at the delivery point to the gas chromatograph. These temperatures are logged electronically using commercial data acquisition software to read a set of thermocouples and a set of four-wire platinum resistance temperature detector (RTD).

Pressure measurement and control

Coarse pressure control is given to an automatic pressure switch. Fine pressure control is achieved by the manual control of valves involved in feeding the test vessel and compressor with test gas and driving air, respectively. As the time to reach equilibrium would be lengthened should gas enter or leave the test vessel during phase separation, the initial vessel pressure, seen at supercritical temperatures, is constrained to the desired pressure to be reached at the cooler-than-supercritical temperature ordered for a given experiment. Electronic pressure transducers are used to measure vessel pressure.

Sampling

After the phases have fully separated, all valves in the sample series' are closed, trapping samples of liquid and vapor in place. The samples are then allowed, one by one, to pass through a narrow delivery tube to a gas regulator which reduces the delivery pressure of the gas to safe limits for the gas chromatograph. To minimize the chance of differential vaporization, especially of the samples taken from the liquid sample series, the vessel, after valves are closed to trap fluid, is warmed above 90° F again. It is expected that the liquid series samples will be homogeneous, and that the vapor series may show some variation in composition as the experiment works at temperatures and pressures that maximize the solubility of N₂ and O₂ in the liquid CO₂. In these situations, the volume of pure vapor may be even smaller than the ten percent of total vessel volume allowed for this sample series. Replication of samples from the same test will give us an idea of homogeneity.

FUTURE WORK

The study of this ternary system is of benefit, not only to further design of the IPR process, but also to the food processing and brewing industries [4] and any other industries in which CO₂ is processed in the presence of tramp oxygen and nitrogen. Following the results of experimentation at the Albany Research Center, further work is planned to more precisely define the phase diagram for this system near its critical point. This work would use a combination of molecular modeling and experimentation to attain an understanding of this regime. Data made available near the critical point of this

system will combine with data already available at low temperatures to improve models already under construction [4, 5, 6].

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