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Hybrid Heat Exchange for the Compression Capture of CO_2 from Recirculated Flue Gas

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ABSTRACT

An approach proposed for removal of CO_2 from flue gas cools and compresses a portion of a recirculated flue-gas stream, condensing its volatile materials for capture. Recirculating the flue gas concentrates SO_x, H_2O and CO_2 while dramatically reducing N_2 and NO_x, enabling this approach, which uses readily available industrial components. A hybrid system of indirect and direct-contact heat exchange performs heat and mass transfer for pollutant removal and energy recovery. Computer modeling and experimentation combine to investigate the thermodynamics, heat and mass transfer, chemistry and engineering design of this integrated pollutant removal (IPR) system.

INTRODUCTION

New, more stringent regulations have been proposed by EPA for the acid-producing pollutants SO_x and NO_x, as well as for particulate matter and mercury. It is also widely believed that CO_2 could be regulated for the first time in the foreseeable future. The use of oxygen-enriched recycled flue gas as combustion "air," coupled with liquefaction of flue gas for pollutant capture, is being examined at the ARC (USDOE, Albany Research Center). This Integrated Pollutant Removal (IPR) process is being studied through computer models and experimentation. The IPR process compresses a portion of the flue gas from a fossil-fueled boiler, dissolving or otherwise entraining non-condensable pollutants and producing liquid exit streams which may then be cleaned to remove those pollutants. This flue gas bleed stream is hereafter called "exhaust" to distinguish it from the remainder of the flue gas, which is recirculated to the boiler, and to describe this stream as exiting the boiler for the final time. Because the combustion process uses flue gas recirculation (FGR), the amount of nitrogen in the exhaust to be treated is markedly lower than in exhaust from combustion supported by air [1]. This exhaust, low in NO_x and relatively high in concentrations of other pollutants (SO_2, CO_2, and Hg), also has a higher H_2O content. The lack of nitrogen in this exhaust allows H_2O and CO_2 to be economically compressed for removal and recovery or disposal [2].

Similar processes being studied around the world are showing the feasibility of this technology. The largest cost lies in oxygen production [3]. At least one study, however, concludes that the use of an integrated approach, including the purchase of an air separation unit (ASU), would be less costly than a system that must use a separate desulfurization unit in its flue gas treatment [4]. Another study, examining solvent capture of CO_2, has identified a scrubbing column technology which may increase the flexibility and robustness of IPR for varying capacities [1].

Computer and physical models of the IPR process are being studied at the ARC. Computer modeling has been done on two fronts: the portion of the system concerning firing with FGR, and the treatment, or IPR system. Models have varied the volume of flue gas recirculated and consequently the percent of total oxygen for firing, resulting in the recognition of potential benefits to overall efficiency of the plant. Improved models of IPR have shown the need for further study in the area of SO_x capture. An experimental model of the IPR process is under construction and will demonstrate the actual behavior of flue gas experiencing the first, lowest pressure, stages of treatment. Experimental results will be used to validate modeling results.

This paper reviews the IPR process along with the computer models being used to study it. The characteristics of hybrid heat exchange are discussed as they relate to mass transfer and heat transfer. The experiments now underway at the USDOE/Albany Research Center (ARC) are introduced.

PROCESS OVERVIEW

Figure 1 shows the tandem processes involved in the FGR/IPR concept.

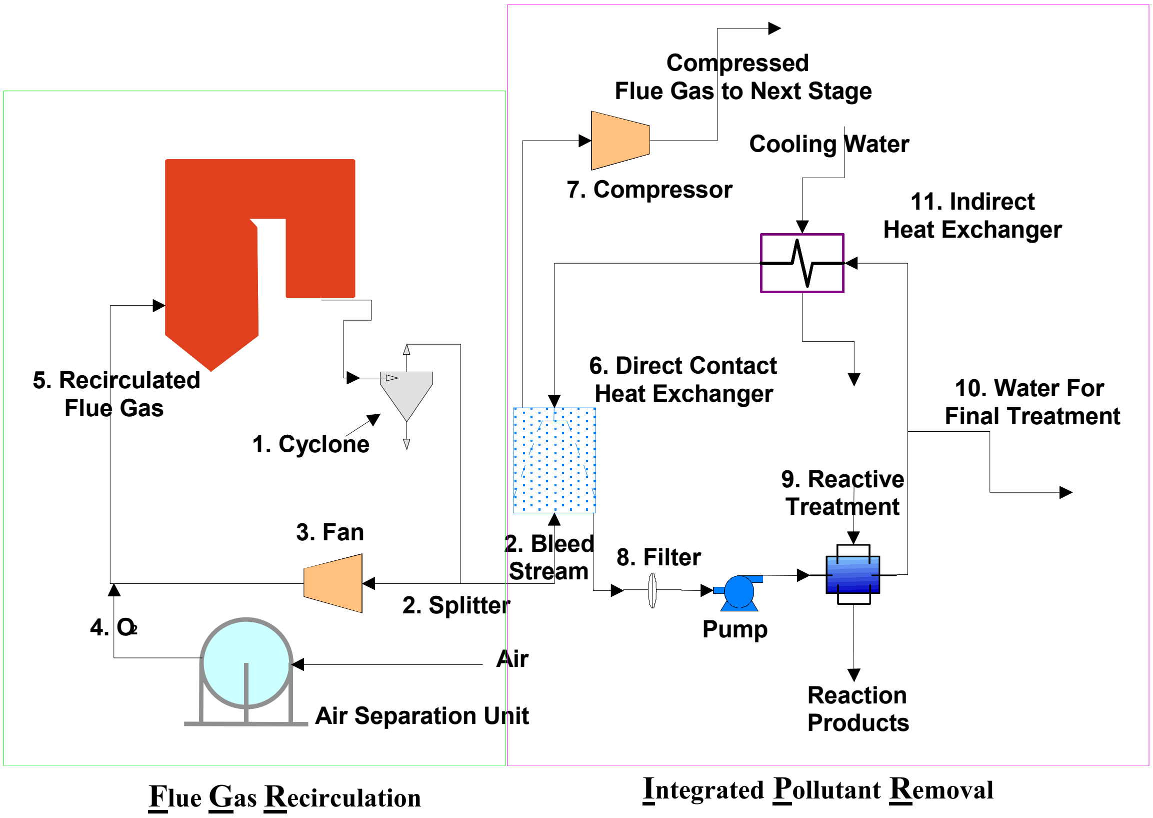

Figure 1: Overview of the FGR/IPR process [2].

Flue Gas Recirculation (FGR)

1. Flue gas from the boiler is fed through a cyclone to remove coarse particulates.
2. Enough flue gas is removed through the exhaust bleed stream to offset combustion products generated and the oxygen added to support combustion. As an example, for 21% oxygen in the combustion gas, approximately 25% of the combustion product stream is bled off.
3. A fan compresses the flue gas for injection into the boiler.
4. Oxygen produced by an air separation unit is injected into the returning flue gas so that it can support combustion.
5. "Oxyfuel" combustion occurs, where coal mixes with the synthetic "air" and is burned. (The term "oxyfuel" connotes the independent control and inclusion of oxygen in the combustion process, as opposed to the set oxygen concentration available in air-supported combustion.)

Integrated Pollutant Removal (IPR)

6. The exhaust bleed stream passes through a direct-contact heat exchanger (DCHX) where it comes into contact with cold liquid (water in this case) running counter-flow. Cooling of the exhaust causes some of the stream to condense. Both the condensate and counterflow liquid may entrain or dissolve other components of the exhaust stream (i.e. particulates, SO_2).
7. Uncondensed material exiting the top of the DCHX is compressed to ready it for subsequent direct contact cooling and the precipitation of more condensables.
8. Liquid material exiting the bottom of the DCHX comprises fresh condensate and coolant. It is filtered to remove entrained particulates.
9. The liquid stream is carried to a cleaning system where the bulk of solutes and remaining particulates are removed.
10. Part of the liquid is separated from the stream and continues to a final purification system for reuse elsewhere in the plant, or for release.
11. The balance of the liquid stream, now carrying lower concentrations of solubles and no particulates, is cooled in an indirect heat exchanger to the correct temperature for use as coolant for incoming exhaust gas in the DCHX.

Steps 6-11 are repeated in several subsequent stages. Step 7 increases the pressure of the exhaust stream at each repetition. As pressures increase, the dominant condensable constituent changes from water to CO_2. The CO_2 in the flue gas is removed and converted to liquid (or supercritical fluid) at pressures suitable for transmission through a pipeline (2,000 – 5,000 psi (13.8 – 34.5 MPa)) [3].

Computer Model

The basic models were built in GE GateCycle® software° and include a subcritical single reheat PC unit (2,400 psi (16.55 MPa), 1,004°F (540°C), 1,004°F) and a mildly supercritical double reheat PC unit (3,500 psi (24.13MPa), 1,050°F (566°C), 1,050°F, 1,050°F). These

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° The USDOE neither endorses nor recommends specific products. References to product names are for information purposes only and should not be interpreted as endorsement or recommendation.

computer models allow us to predict the effects of applying an IPR system to a full-scale plant.

Different cases, using different ratios of oxygen to recycled flue gas, have been modeled to observe the effect of oxygen ratio on combustion, heat exchange mechanisms in the boiler and plant capacity and efficiency [5]. The oxygen feed in the models is sufficient to support combustion of fuel without excessive O_2 exiting in the flue gas. Since the fuel rate is kept constant for each case studied, the oxygen feed is also constant. The O_2: flue-gas ratio and the volumetric percent O_2 change as the proportion of recycled flue gas changes.

RESULTS FROM COMPUTER MODELLING/EXAMINING HYBRID HEAT EXCHANGE

The composition of the flue gas used for the IPR study is typical for oxyfuel combustion (~21% O_2), similar to the amount of oxygen available in air [6]. Table 1 shows the predicted change in composition, mass flowrate and volume flowrate of the exhaust stream as it travels through the IPR process.

Table 1: Gas streams showing composition, pressure, mass- and volume-flowrate [2].

Gas composition, shown as mole fraction	Exhaust flue gas	After first H_2O condensation	After second H_2O condensation (Compression 1)	After first CO_2 condensation (Compression 2)	After second CO_2 condensation (Compression 3)	After third CO_2 condensation (Compression 4 and Expansion 1)
CO_2	0.6085	0.8711	0.9143	0.7100	0.3900	0.0850
O_2	0.0350	0.0501	0.0526	0.1821	0.3830	0.5765
N_2	0.0206	0.0294	0.0309	0.1069	0.2249	0.3384
H_2O	0.3269	0.0365	0.0022	0.0010	0.0021	0.0001
SO_2	0.0090	0.0129	0.0000	0.0000	0.0000	0.0000
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
Flow Rate (ft^3/s)	3378.50	2945.94	150.09	6.53	1.49	0.50

The compositions above are the predicted results for exhaust treatment using hybrid heat exchange. This hybrid heat exchange process combines direct-contact and indirect heat exchangers to effect both cooling and cleaning of the exhaust gas. As explained in Step 11 of the Process Overview, above, the condensate from the DCHX is partially cleaned and then used as the coolant for the exhaust gas in the DCHX. Hybrid heat exchange decreases the need for ‘clean’ cooling fluids and takes advantage of the potential scavenging effects of the impure fluid used to cool the incoming exhaust gas.

The first experiments will examine the ambient pressure stage of IPR in which water and, potentially, SO_2 are recovered. The solubility and hydrolysis of SO_2 in water are represented by the following equations:

$$SO_2\ (g) \leftrightarrow SO_2\ (aq) \qquad (1)$$

$$SO_2\ (aq) + H_2O \leftrightarrow H^+ + HSO_3^- \qquad (2)$$

In addition, in the presence of oxygen, small amounts of SO_2 are oxidized to SO_3, which is dissolved in water more readily than SO_2. Examination of the solubility of SO_2 in water shows that, at temperatures between 40 and 50 °C and at equilibrium concentrations, the capacity of the water condensate in this first stage is adequate to dissolve and hydrolyze nearly all of the SO_2 present in the gas stream. It is unlikely, however, that the hybrid heat exchange process will result in equilibrium conditions. Thus, one goal of the ARC experimental IPR system is to perform hybrid heat exchange in the lab to measure the amount of SO_2 captured under a set of baseline conditions, then investigate methods for improving SO_2 recovery in the water compression stage.

In the first stage DCHX, the chilled condensate (water) flows counter to the exhaust gas, cooling the gas, condensing more H_2O, and removing particulates and SO_2. At the liquid exit of the direct contact heat exchanger, the condensate approaches the temperature of the incoming flue gas and is nearing saturation with sulfur species.

The solubility of SO_2 in water drops as water temperature rises (Figure 2) and as the amount of dissolved SO_2 increases. For SO_2 removal from the gas to be effective, the concentration of SO_2 in the water must remain low so that, even at the condensate exit, the left side of equation 1 is not favored; i.e., there is no net loss of SO_2 from the condensate to gas. However, the greater the temperature of the condensate leaving the column, the greater the range of cooling streams that can be used to cool it (by indirect heat exchange) for re-injection.

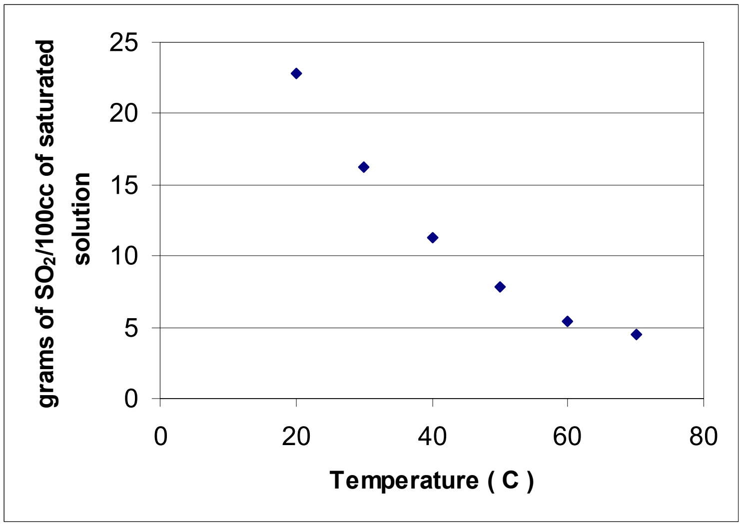

Figure 2: Grams of SO_2 in 0.1L of saturated solution at 1 atmosphere [7]

Using the condensate as the cooling fluid in the DCHX may enable optimization of SO_2 absorption and heat recovery. First, the cooling stream contains water and dissociated H_2SO_3 and H_2SO_4. A weak acid solution is more effective at absorbing SO_2 than pure water. Second, the recirculated coolant is treated in a reactor to reduce the concentrations of sulfuric and sulfurous acids before it is injected into the top of the absorption column (the DCHX). In this way, the dissolution and hydrolysis reactions will proceed toward removal of SO_2 from the gas. Catalytic oxidation is another treatment option that could be used to increase SO_2 dissolution for recovery [8]. Third, because the condensate exiting the column is always at a higher temperature than required for re-injection, all adjustments for inlet temperature occur by virtue of releasing energy to other parts of the plant, rather than by heating the coolant stream before entry.

Finally, there is the possibility of carrying SO_2 through the IPR process to the end and either separating it from the liquid CO_2 or using it to assist in the mineral sequestration of CO_2, a process which is being examined at ARC. Experiments have shown the addition of SO_2 to the CO_2 stream can help the carbonation of CO_2 in olivine [9]. The risk posed by SO_2 and also by CO_2 passing all the way through IPR is corrosion caused by the acids formed when these two materials dissolve in water. It would be important either to protect the IPR machinery from acid attack, or to remove essentially all the water from the flue gas as close to the beginning of the process as possible. Therefore, it may prove wise to insert a final drying step after the stages of water condensation. One promising method has been identified by researchers in Sweden [4].

Another consideration is the ratio of gas flow to coolant flow in the DCHX. A greater gas flow will increase the effectiveness of the column for absorbing SO_2 in the condensate [7]. A greater coolant flow, however, increases the rate of heat absorbed. Balancing these effects to provide the optimal combination of condensation and gas-liquid mass transfer is a complex process that will be investigated thoroughly in the laboratory.

Volumetric Flow Rates

A systems-level investigation of IPR and hybrid heat exchange looks at possible impacts of IPR fluid flows on fluid-moving machinery and heat transfer. The decreasing volume of exhaust being carried as IPR progresses allows the use of smaller machinery at the higher pressure stages – an advantage. Lower volumetric flow rates, however, also seem to give an advantage to heat exchange. Modeling internal and external heat flows for a shell-and-tube heat exchanger, it was seen that if the decrease in volumetric flow is accompanied by a decrease in heat exchanger tube diameter, the overall heat transfer coefficient is actually greater for the lower flow, another opportunity for improving heat recovery. Figure 3 compares the effect of halving the volumetric flow rate on the overall heat transfer coefficient (U). The figure is normalized against the larger flow in the larger tubing. The trends are repeated for any reduction in flow, the heat transfer benefit increasing with increased reductions from full flow.

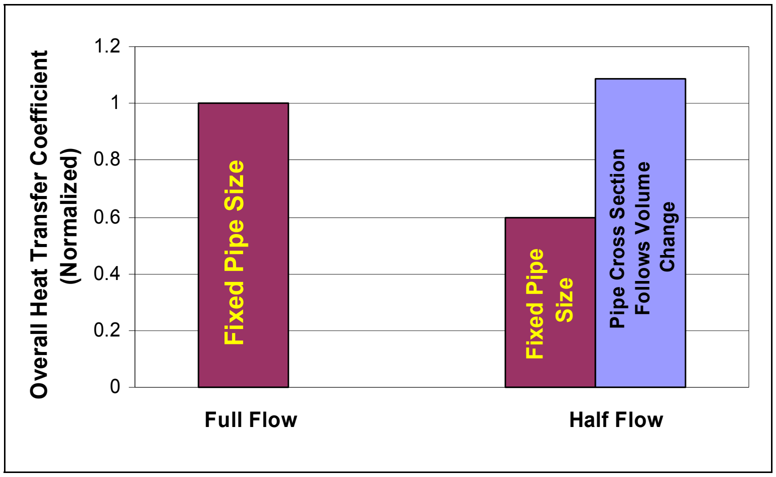

Figure 3: Effects of lower volumetric flow rates on heat transfer with and without changing pipe diameter

The liquids exiting the DCHXs will be split into two flows. The first is the coolant stream, set to a rate maximizing condensation and mass transfer in the DCHX. The second is routed to final purification; its volume will match the volume of condensables released in the column. The implication of the above heat transfer analysis is that more effective heat exchange will occur if the recirculated and exiting liquids are cooled after they are separated into two different streams.

HYBRID HEAT EXCHANGE EXPERIMENTS

A test facility has been constructed at the ARC to empirically evaluate the behavior of the hybrid heat exchange portion of the IPR process, and to make comparisons with the computer models. Exhaust compositions predicted for different stages of IPR by the models will be treated. From these tests, we will learn more about the effectiveness of hybrid heat exchange for condensation and energy recovery. We will also measure the mass transfer and reaction characteristics of this dynamic system.

In full-scale work, the DCHX will be a column in which the coolant will enter in its cleanest state at the top of the column and on reaching the bottom, will be near saturation with soluble and entrainable pollutants. The lab-scale section will model this column using a DCHX whose coolant is not cleaned before reinjection. Experiments will continue treating model flue-gas with the same coolant until the coolant is saturated with the soluble components. The coolant in the experimental DCHX is unlikely to attain concentrations found in equilibrium solubility experiments [7]. By controlling the input compositions to the experimental column, we hope to model a full-scale DCHX level by level, showing the maximum concentrations possible at different heights in the full-scale column.

To evaluate both the reactions of computer-predicted compositions and empirically recorded compositions, the hybrid heat exchange experiment feeds typical mixed flue gas components (H_2O, CO_2, N_2, O_2 and SO_2) into the absorption column. The composition, flow rate, temperature and pressure of the test gases are each independently controllable. Samples of the exhaust gas and condensate flows in this lab-scale section will be taken periodically. Experiments will begin with the computer modeled compositions shown above. Modeling and experimentation will then continue in tandem, using empirical and calculated results.

Besides testing condensabilities and solubilities, the experiments will provide information on material durability in the presence of the different compositions of gas and condensate in the different stages of IPR. Of special concern is the formation of acids from the combination of either SO_x or CO_2 with water. This will be one focus of the initial series of tests, which will be performed at near ambient pressure.

SUMMARY

The integrated pollutant removal (IPR) process treats the exhaust from a boiler which uses oxygenated flue gas (instead of air) to support combustion. Because of the lack of nitrogen and the high concentrations of pollutants and condensables, this exhaust lends itself to a process using compression and cooling to condense H_2O and CO_2 for removal from the exhaust stream. The process is referred to as Hybrid Heat Exchange because of the combined use of direct-contact and indirect heat exchange to effect heat and mass transfer from the boiler exhaust stream.

The resulting condensates are expected to dissolve and entrain SO_x and particulates, while the use of recirculated flue gas for combustion is expected to reduce the presence of NO_x in the exhaust. The flue gas recirculation (FGR) and IPR processes have been mapped and explained above. Still being investigated is the optimal method and location within the treatment process to remove SO_x from the exhaust stream. Solubility and absorption parameters such as flow rate and temperature of fluids passing through a direct contact heat exchanger (DCHX) have been examined, along with options for SO_x removal.

The decrease in volumetric flow rate of the exhaust fluids, both through component removal and through compression, raises the predicted overall heat transfer coefficients of heat exchangers that would typically be applied to the indirect exchange portion of hybrid heat exchange. The low volume flows also infer the possibility of minimizing the footprint of the IPR treatment system.

An experimental test section is performing first-stage, low-pressure hybrid heat exchange studies on model gas mixtures. Mass transfer rates and steady state saturations of the resulting liquid and gas streams will be determined. The results will be compiled to represent a model of the full scale hybrid heat exchange process as applied through the computer-modeled pressure range.

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