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Purification of oxy-combustion flue gas for SOx/NOx removal and high CO_2 recovery

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1. Introduction

Oxyfuel combustion produces CO_2-rich flue gas that can be compressed and purified for sequestration. Praxair is developing a near zero emissions technology that will achieve near zero stack emissions, produce CO_2 that is nearly free of trace impurities and achieve high CO_2 capture rates while reducing the cost of CO_2 capture. Two key elements of this technology are SOx/NOx removal and enhanced CO_2 recovery.

Removing SOx and NOx from the flue gas in the CO_2 purification unit (CPU) offers several benefits. The reduced level of SOx/NOx in flue gas will reduce or eliminate the adverse effects of these impurities on some of the downstream equipment in the CPU such as dryer, mercury removal beds and cold box. It will alleviate public safety concerns arising from transporting CO_2 through pipelines. Above all, the cost of CO_2 capture can be reduced if expensive SOx/NOx removal systems can be eliminated from the power plant.

Other feature of this technology uses cold box-VPSA (vacuum pressure swing adsorption) hybrid separation process to achieve high CO_2 recovery. The concentration of CO_2 in the oxy-combustion flue gas is likely to be ~80% (by volume on a dry basis). If only cold box is used in the CPU, 90 - 92% of the CO_2 in the flue gas can be captured. The remainder of CO_2 in the cold box vent is still at high pressure. It can be recovered using VPSA with minimal additional energy and recycled back to the front end of the process to improve overall CO_2 recovery to > 99%. Even when power plant has high air ingress rates, this hybrid process can achieve >95% CO_2 recovery. The overall CO_2 capture costs actually decreases when high CO_2 recovery is achieved due to better utilization of ASU capital and operating costs.

This paper will present the experimental results for the SOx/NOx removal and VPSA processes and next steps for technology scale-up.

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2. Process Description

Praxair is working on two SOx/NOx removal processes resulting in two CPU design options. Both of these options incorporate VPSA for enhanced CO_2 recovery. Figure 1 shows the process schematics of the CPU based on the activated carbon process for SOx/NOx removal. The raw CO_2-rich flue gas from the oxyfuel boiler is cooled by first indirect contact and then by direct contact with water in the flue gas cooler/condenser. A majority of water soluble impurities are expected to dissolve in the condensate. The cooled raw CO_2 gas is then compressed to 25 to 35 bar (a) in a multi-stage centrifugal compressor that includes intercoolers and knock-out drums. The condensate collected from the compression train will include additional water soluble impurities. The compressed raw CO_2 gas is then sent to the activated carbon process for SOx/NOx removal.

The SO_2 and NO in the flue gas are oxidized to SO_3 and NO_2. At least two beds are used such that one bed is on feed while the other is being regenerated. When the carbon bed is saturated with SOx and NOx, it is regenerated by washing the activated carbon bed with water, which reacts with the SO_3 and NO_2 to form sulphuric and nitric acid. The dilute acid generated from activated carbon system can be disposed off using known methods. After water wash step, if needed, the carbon bed can be dried by passing regeneration gas over it.

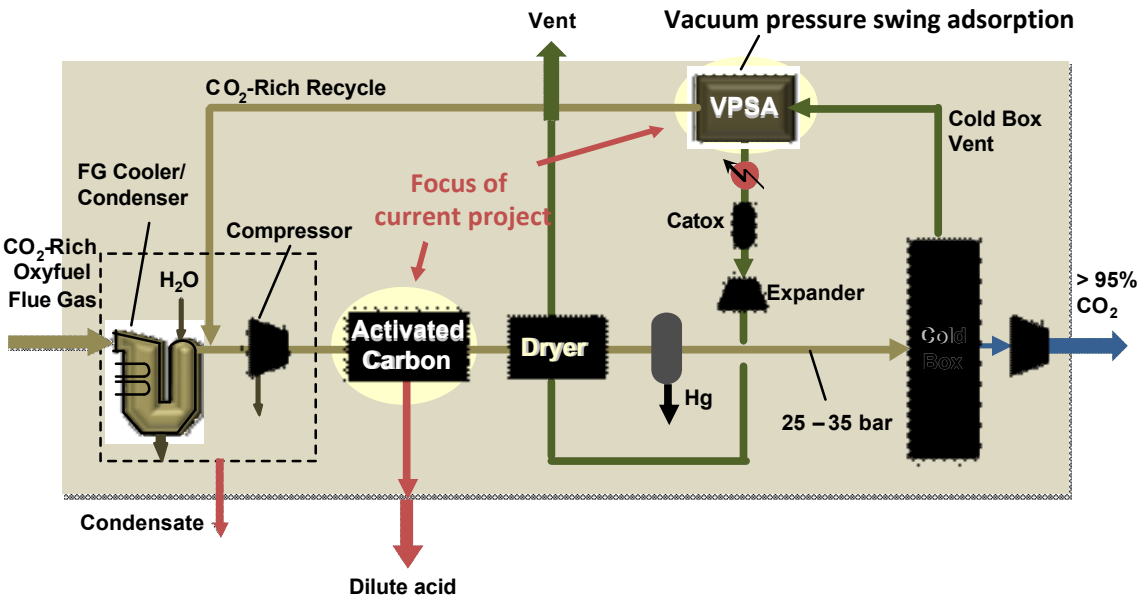

Figure 1. Near zero emissions CPU based on activated carbon process

The SOx-NOx depleted flue gas is dried in a dryer unit and then passed through a carbon bed designed for mercury removal. The cleaned and compressed raw CO_2 gas is fed to the cold box for producing purified CO_2. Within the cold box, atmospheric gases and carbon monoxide (CO) are separated from CO_2 and removed in the cold box vent stream. About 10% of CO_2 fed to the cold box also remains in the cold box vent stream. The vent stream, which is obtained at 24 – 34 bar (a) is processed in the VPSA unit for recovering additional CO_2. The VPSA unit produces a CO_2-rich stream at near atmospheric pressure while rejecting the CO_2-depleted effluent at elevated pressure. The CO_2-rich stream from the VPSA is recycled and mixed with the raw CO_2 gas upstream of the raw CO_2 compressor. The effluent from the VPSA is heated and passed through a catox (catalytic oxidation) reactor to convert CO into CO_2. The CO-depleted stream is expanded to recover power and then used as a regeneration gas in the dryer. The vent stream from the CPU will contain mainly atmospheric gases, moisture and CO_2 and traces of CO, SOx and NOx. The purified CO_2 from the cold box is compressed to supercritical pressures for pipeline transport.

Second SOx/NOx removal option is based on the concentrated sulfuric acid process. This process is a modified lead chamber process adapted for high pressure operation. It will produce saleable sulfuric acid and nitric acid as by-products. In this process, compressed flue gas is contacted with concentrated sulfuric acid in a series of towers to remove mercury, SOx and NOx from the flue gas. The cleaned flue gas is then processed in the cold box and VPSA as shown in Figure 1.

3. Results

The activated carbon tests with synthetic flue gas containing SOx only, NOx only and the mixtures of SOx and NOx at elevated pressures and ambient temperatures showed that activated carbon is able to remove SOx and NOx when fed individually or together. Investigation of various operating conditions showed that the process has better performance at ambient temperature (~20 ^{o}C) compared to temperatures above ambient. The presence of moisture had a beneficial effect on the retention of SOx. Higher operating pressure (220 psig vs. 50 psig) significantly improved the process performance, especially for NOx removal. The process achieved simultaneous removal of SOx and NOx from flue gas with the removal efficiency of > 99 % for SOx and > 96 % for NOx.

The sulfuric acid tests for NOx removal have been completed. The NOx absorption was best when NO:NO_2 ratio was slightly greater than 1:1. Up to 98% NOx removal efficiency was achieved. However, removal of NOx from the acid appears to be challenging. As a result, the quality of sulfuric acid will not meet the commercial grade specifications. Although this will result in lower or no market value for sulfuric acid, it can still offer some of the benefits of removing SOx/NOx within CPU that were discussed earlier. The SOx removal tests have been completed. The data are being analyzed to assess the effectiveness of this process for SOx removal. After completing technoeconomic analysis and weighing commercial implications, a go/no go decision on this technology will be taken.

The VPSA is being tested at the pilot scale. The results show that the VPSA is able to recover >90% of the CO_2 from the simulated cold box vent stream and produce CO_2 at purity equal to higher than the purity of the raw flue gas from the boiler. Based on these results, we are able to project the overall CO_2 recovery of >99%.

Process simulations have shown that the stack emissions for all the major pollutants (SOx, NOx, Hg, CO and particulate matter) and CO_2 are reduced by >99% compared to the air-based power plant with a state of the art pollution control equipment. The cost of CO_2 capture can be reduced by $2 - $8/tonne in various scenarios that were analyzed.

4. Conclusions

The near zero emissions CPU process based on the activated carbon process and VPSA has met the performance targets. It will achieve near zero stack emissions, produce CO_2 that is nearly free of trace impurities and achieve high CO_2 capture rates while reducing the cost of CO_2 capture. This technology is now ready for scale up to a pilot demonstration.