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Amine oxidation in testing of ASCC in a pilot campaign at Technology Centre Mongstad

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Abstract

The University of Texas at Austin (UT) and Honeywell UOP conducted a four-month CO_2 capture pilot campaign at Technology Centre Mongstad (TCM) with 30% wt ASCC at ~12 MW_e scale. Two different flue gases were available for testing in both undiluted and diluted form (Table 1) over 2,650 hours of testing. A residual fluid catalytic cracker (RFCC) flue gas with high aerosols (8.5 X 10^4 1/cm^3) was tested in undiluted form to understand the impact of high CO_2 and aerosol content on solvent oxidation and emissions. This flue gas was also diluted with air to achieve natural gas combined cycle (NGCC) conditions (~4% CO_2). The second flue gas tested was derived from the Mongstad Heat Plant (MHP) which burns refinery fuel gas resulting in ~16 ppm NO_2. This flue gas source was also diluted to NGCC conditions with air. A major objective of the pilot campaign was to measure solvent degradation and emissions with the different flue gases. A secondary objective included the evaluation of reclaiming in removing solvent degradation products, lowering emissions, and lowering the energy requirement of the process at 96-98 % CO_2 capture rate. Other presentations will cover emissions data [1] and general operations [2].

Table 1. Flue gases tested at TCM

Flue gas type	CO_2 (v%)	O_2 (v%)	H_2O (v%)	NO_2 (ppm)
Residual fluid catalytic cracker (RFCC) average	14.7	2.5-3.5	5.5-7.5	0.5-1.5
Diluted RFCC average	4	16	5.8	0.3
Mongstad Heat Plant (MHP) average	9.9	3.8	6.2	15.7
Dilute MHP average	4	14	5.4	5.8

The presence and concentration of both O_2 and NO_2 in the flue gases were monitored closely throughout the campaign. Both constituents are known to oxidize amine solvents including AM91, the main constituent in aqueous ASCC. Oxygen in the incoming flue gas will dissolve into the solvent as it passes through the absorber packing creating dissolved oxygen (DO) that will participate in free radical reactions and oxidize solvent. An Endress+Hauser

Memosens COS81E DO sensor was installed in the line downstream of the rich amine pump in the plant for continuous online measurements throughout the campaign.

Variations in the oxygen content of the flue gas and changes in the extent of solvent degradation directly impacted the amount of DO in the solvent throughout the campaign. The DO drifted downward from >1 to <0.1 mg/L during the period of accelerated solvent degradation when MHP flue gas was fed to the absorber (670 to 1000 hours). MHP flue gas has high NO_2 compared to RFCC flue gas (Table 1), resulting in accelerated solvent oxidation. As the DO in rich amine drifted downward through its consumption, the NH_3 concentration in the absorber outlet gas increased to >30 ppm. The flue gas was switched to diluted RFCC flue gas with 16% O_2 and 0.3 ppm NO_2 at ~935 hours followed by the implementation of thermal reclaiming starting at 1,000 hours. The DO increased to 5-6 mg/L reflecting the much higher concentration of O_2 in the dilute RFCC flue gas and the slower consumption of DO resulting from the removal of degradation intermediates by reclaiming. At approximately 1,350 hours, the flue gas dilution rate was changed to achieve 10% CO_2, resulting in a corresponding drop in the flue gas O_2 to 10% and a drop in DO to ~3.5 mg/L.

As listed in Table 1, the flue gas changes impacted CO_2, O_2, and NO_2 content. Changes in NO_2 were recorded throughout the campaign as depicted in Figure 2. When operating with MHP flue gas starting at 670 and again at 1,700 hours, the high concentration of NO_2 (16 ppm) resulted in an immediate increase in the rate of solvent oxidation, and the evolution of NH_3 in the water wash outlet (Figure 2). The ratio of moles NH_3 formed to NO_2 absorbed into the solvent was estimated as ~2.4 through the first 1,850 hours of the campaign which was consistent with the ratio measured in previous campaigns with ASCC.

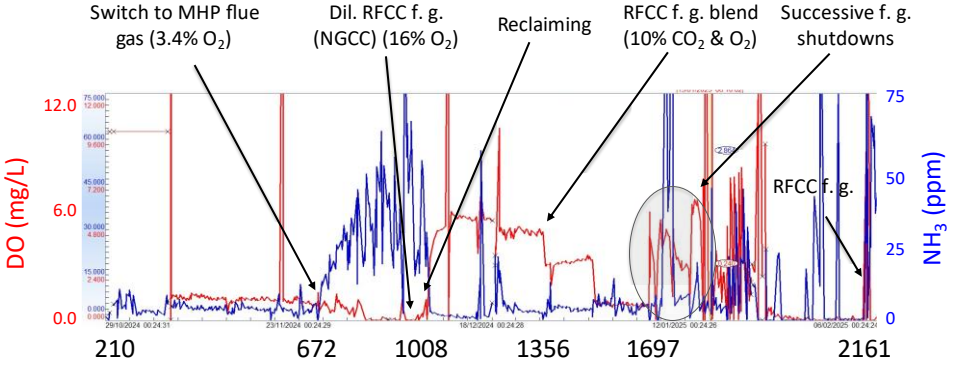

Figure 1. DO in rich amine coplotted with NH_3 in absorber outlet by FTIR at TCM

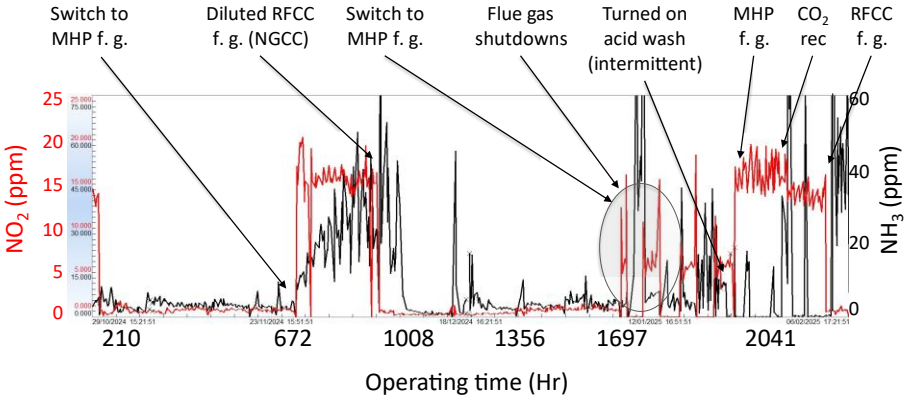

Figure 2. NO_2 in gas inlet coplotted with NH_3 in absorber outlet by FTIR at TCM

Liquid samples were collected daily throughout the campaign and analysed using onsite liquid chromatography/mass spectrometry (LC/MS) for key amine degradation species including AM93, AM95, AM96, and AM98 (Figure 3). AM93, AM95, and AM96 all experienced accelerated formation when feeding MHP flue gas with its high NO_2 (16 ppm) to the absorber, with a levelling off in their rate of formation when switching to diluted RFCC flue gas ~935 hours into the campaign (12/6/2024). These compounds were removed by ~90 and 70%, when reclaiming was implemented at 1,000 and 2,185 hours, respectively.

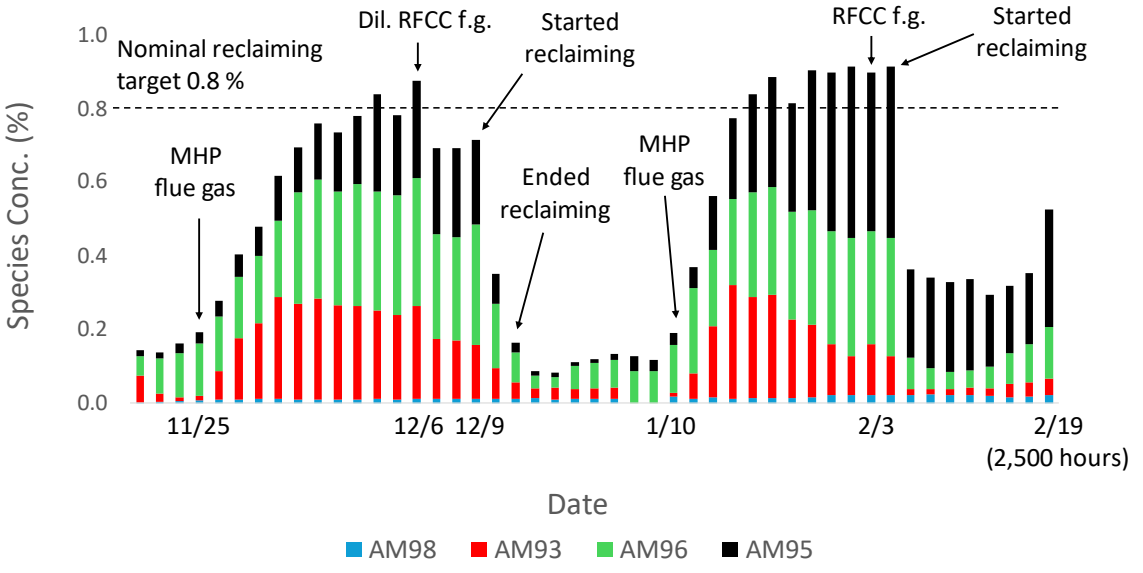

Figure 3. LC/MS results from TCM campaign

These results indicate:

- High NO_2 accelerated oxidation of the solvent and degradation products resulting in low residual DO;
- Rich amine DO changed with flue gas O_2 content; 16% O_2 in diluted RFCC flue gas resulted in >5 mg/L DO;
- Single stage thermal reclaiming removed 70 - 90% of oxidation products from the solvent; and
- The DO measurement will be a reliable online indicator of solvent health/oxidation in pilot and commercial CO_2 capture plants.

A more comprehensive review of the analytical data including amino acids will be provided at the conference. Other papers will be presented at PCCC8 covering topics including emissions data collected by a proton-transfer time-of-flight mass spectrometer (PTR-ToF-MS) [1] and general operations including the energy requirement necessary for high CO_2 removal [2].

References cited

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2. C. Stevens, F. Closmann, G.T. Rochelle. Results of testing ASCC at Technology Centre Mongstad. Presented at PCCC-8, 2025.

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Keywords: CO_2 capture; post-combustion capture; amines; oxidation; reclaiming; TCM; MHP; RFCC.