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ScienceDirect

Energy Procedia 114 (2017) 1022 – 1025

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

A sampling line artifact in stack emission measurement of alkanolamine-enabled carbon capture facility: surface reaction of amines with formaldehyde

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Abstract

Laboratory experiments were carried out to study Schiff-base condensation reactions between amines and formaldehyde that occur on inlet lines of emission monitoring instruments. Primary amines and formaldehyde were found to quickly react on inlet surfaces to form the respective Schiff-base condensation products. Secondary and tertiary amines did not react with formaldehyde. Schiff-base condensation reactions between primary amines and formaldehyde were also observed to occur on the ~110 m long inlet line that connects the absorber stack of the amine-based PCCC facility at Mongstad to the FT-IR and PTR-ToF-MS emission monitors. Emissions of primary amines and formaldehyde may be underestimated if condensation reactions of these species in inlet lines are not taken into account. The PTR-ToF-MS monitor does, however, also quantitatively detect the Schiff-base condensation products, making it straightforward to derive the correct amine and formaldehyde concentrations in the amine wash gas.

Keywords: post-combustion carbon capture; amine; PTR-MS; emission measurement; Mongstad

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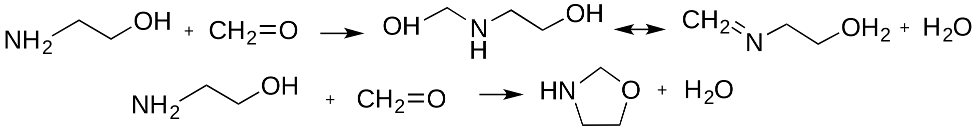
1. Introduction

Amine and formaldehyde emissions from the amine-based PCCC facility at Mongstad are continuously monitored by FT-IR and at times also by PTR-ToF-MS instruments.[1] Both analyzers sample from the absorber stack through a common ~110 m long line. It is a well-known phenomenon that amines are detected with a significant delay when sampled through a long inlet line. Surfaces of inlet lines need to be coated with amines before these “sticky”

doi:10.1016/j.egypro.2017.03.1247

molecules are quantitatively transmitted to the analyzer. Different line materials and line temperatures have been tested at TCM for minimizing this delay.[2] Surface adsorption and desorption processes are purely physical in nature. Chemical losses have hitherto not been considered.

Formaldehyde, a common amine degradation product, reacts rapidly with primary amines such as MEA to form either an imine or oxazolidine (Schiff-base condensation mechanism, Scheme 1).[3]



Scheme 1. Schiff-condensation of MEA with formaldehyde

In this work, we report the results from laboratory studies on surface reactions between formaldehyde and a series of amines. We show that amine-formaldehyde condensation reactions in instrument inlet lines may cause a significant underestimation of primary amine and formaldehyde concentrations in the amine wash gas.

Nomenclature

AB	4-Amino-1-butanol
AMP	2-Amino-2-methyl-1-propanol
AP	3-Amino-1-propanol
DMA	Dimethylamine
EA	Ethylamine
EDA	Ethylenediamine
FT-IR	Fourier Transform Infrared Spectroscopy
MAPA	3-(Methylamino)-propylamine
MA	Methylamine
MEA	2-Amino-Ethanol
m/z	mass number to charge number ratio
NAEP	N-(2-Aminoethyl)-piperazine
PCCC	post-combustion carbon capture
ppbV	parts per billion by volume
PTR-ToF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
sccm	standard cubic centimeters per minute
TCM	Technology Centre Mongstad
VMR	Volume Mixing Ratio

2. Methods

A flow of air containing an amine at variable mixing ratio (123-615 ppbV) was mixed with a flow of air containing formaldehyde at a constant mixing ratio (1230 ppbV). The mixing ratios resemble upper emission levels at TCM. The mixture was flushed through a 2 m long, heated (100 °C), Silcosteel®-coated stainless steel tube (1/4" OD) at a flow rate of 850 sccm. Apart from the length, the tube resembles the inlet tube at TCM. The outflow was fed to a PTR-TOF 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) which was run in its routine mode of operation.[1]

3. Results

Table 1 summarizes the loss of amine and formaldehyde, respectively, which occurred in the inlet tube. Equal amounts of amine and formaldehyde were lost in the tube as expected from the mechanism presented in Scheme 1.

The fraction of amine lost was found to be dependent upon the amount of amine that was injected into the tube.

Table 1. Injected amounts of amine (first column) and formaldehyde (second column), the amount of amine lost in the inlet tube (third column), the amount of formaldehyde lost in the inlet tube (fourth column) and the percentage of the injected amine lost in the inlet tube (fifth column)

Amine (ppbV)	Formaldehyde (ppbV)	ΔAmine (ppbV)	ΔFormaldehyde (ppbV)	Amine lost
615	1230	378.1	395.8	61.5%
492	1230	336.0	340.8	68.3%
369	1230	280.7	277.4	76.1%
246	1230	208.4	199.6	84.7%
123	1230	114.5	104.5	93.1%

Table 2 summarizes the results from a series of experiments with different amines. A 1:1 amine-formaldehyde consumption was observed for all primary amines including NAEP, which contains one primary, one secondary and one tertiary amino group. In the case of EDA, which contains two primary amino groups, single condensation was found to prevail over double condensation. Some condensation products fragment in the PTR-ToF-MS instrument, which complicates the interpretation of mass spectra, especially if real emission streams are measured.

Table 2. List of amines and corresponding condensation by-products

Amine	VMR (ppbV)	Formaldehyde (ppbV)	Condensation product	Fragment	Amine lost
MA	112	1230	$C_2H_6N^+$, *m/z* 44.050	-	31.9%
DMA	123	1230	-	-	0%
EA	138	1230	$C_3H_8N^+$, *m/z* 58.067	-	22.5%
MEA	123	1230	$C_3H_8NO^+$, *m/z* 74.063	*m/z* 56.050 *m/z* 44.050	65.4%
AP	123	1230	$C_4H_{10}NO^+$, *m/z* 88.076	*m/z* 44.050	93.1%
AB	123	1230	$C_5H_{12}NO^+$, *m/z* 102.092	*m/z* 84.081	66.5%
AMP	123	1230	$C_5H_{12}NO^+$, *m/z* 102.092	-	67.2%
MAPA	123	1230	$C_5H_{13}N_2^+$, *m/z* 101.108	*m/z* 99.092 *m/z* 58.067	99.8%
NAEP	123	1230	$C_7H_{16}N_3^+$, *m/z* 142.134	-	74.8%
EDA	123	1230	$C_3H_9N_2^+$, *m/z* 73.076 (90%) $C_4H_9N_2^+$, *m/z* 85.076 (10%)	-	60.6%

4. Discussion

Figure 1a shows the mixing ratios of two amines (AmX and AmY) and formaldehyde as measured at the end of a ~110 m long inlet line. Emission spikes in amines are accompanied by a drop in formaldehyde and a concurrent increase in the two respective amine-formaldehyde condensation products, AmXCP and AmYCP. Given that these were identified and quantified by PTR-ToF-MS, it was possible to add the amount of condensed amine and formaldehyde to the measured amount of these species. Figures 1b and 1c show the time traces of the apparent (measured) and corrected mixing ratios of formaldehyde and amines, respectively. For the period shown, emissions of AmX, AmY and formaldehyde increase by a factor of 70, 2 and 1.3, respectively.

5. Conclusions

Primary amines and formaldehyde condense in the inlet lines of measurement instruments. This leads to a significant underestimation of emissions of these substances from amine-based PCCC facilities. PTR-ToF-MS sensors also detect the condensation products, which make it straightforward to derive the correct amine and formaldehyde concentrations in the amine wash gas.

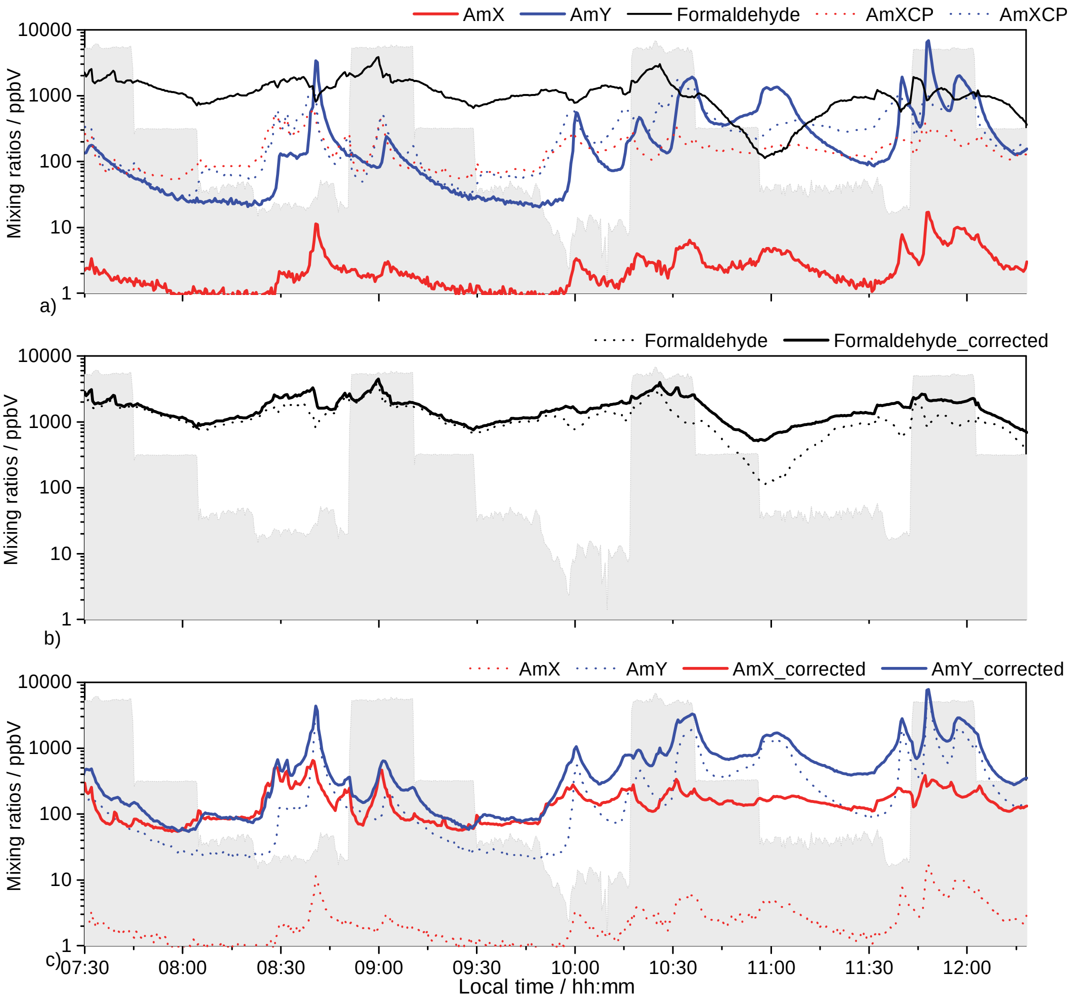


Figure 1. Time series of AmX, AmY, formaldehyde and the respective condensation products AmXCP and AmYCP as measured at the end of a ~110 m long inlet line (upper panel)). The time traces of the apparent (i.e. measured) and corrected mixing ratios of formaldehyde and amines are shown in the middle and lower panel, respectively. The grey shaded area is proportional to the CO_2 mixing ratio in the stripper, inflow and absorber streams.

Acknowledgements

The authors are grateful to the colleagues at TCM.

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