



## Evaluation of Emissions of 2-Amino-2-Methyl-1-Propanol Degradation Products by adding Degradation Reactions to the Carbon Dioxide Capture Unit

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**ABSTRACT:** Degradation is a major problem which poses lots of emission risk during chemical absorption process with amine solvents. Degradation occurs through irreversible side reactions with CO<sub>2</sub> and other flue gas components, forming into products that cannot easily regenerate. The degradation products then react with amines to form thermally stable salts, which accumulate in the system over time. The problems associated with degradation include decreased plant equipment life, foaming, corrosion, high solution viscosity, and increased operating cost. Amines capture about 70 - 90% CO<sub>2</sub> from commercial power stations. These high removal rates have many environmental impacts due to their degradation products. Researchers have therefore shown interest in characterising and quantifying atmospheric emissions of amines and their degradation products. In this study, 2-Amino-2-Methyl-1-Propanol (AMP) degradation reactions were included into a large-scale capture plant model to evaluate the influence of process variables, the emissions of AMP and its degradation products. Steady-state simulations were performed using Aspen Plus® V8.4 software to provide a full assessment of the degradation products and their impact on the capture process. This assessment is important because it identifies and quantifies all pollutants emitted from the process plant. The results of the simulation indicate that AMP emissions are 3.04E+03mg/Nm<sup>3</sup> of CO<sub>2</sub> lean flue gas, while the quantity of AMP lost due to degradation was 37.88kg/s for the large-scale capture plant. The results further showed that among the gases emitted, ammonia was highest, while acetone was the highest gas formed. In this study, 2-amino-2-methyl-1-propanol (AMP) degradation reactions were included into a large-scale carbon dioxide (CO<sub>2</sub>) capture plant model to evaluate the influence of process variables, AMP emissions and its degradation products. Steady-state simulations were performed using Aspen Plus® V8.4 software to provide a full assessment of the degradation products and their impact on the large-scale AMP capture process. The results of the equilibrium model developed in this study revealed that AMP emissions are 3.04E+03mg/Nm<sup>3</sup> of CO<sub>2</sub> lean flue gas, while the quantity of AMP lost due to degradation was 37.88kg/s for the large-scale capture plant. More importantly, the emissions obtained from the PWOD and PWD are 7.80E+03 mg/Nm<sup>3</sup> and 9.82E+03 mg/Nm<sup>3</sup> of CO<sub>2</sub> respectively.

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### Nomenclature

AMP	2-Amino-2-Methyl-1-Propanol
PCC	Post-Combustion Capture
CCS	Carbon, Capture, and Storage
MEA	Monoethanolamine
NGCC	Natural gas combined cycle
NRTL	Non-Random Two-Liquid
NETL	National Energy Technology
MDEA	Laboratory
PZ	Methyldiethanolamine
DMOZD	Piperazine
DGAQFM	4,4 dimethyl-2-oxazolidinone
PWD	Gibbs free energy of formation
PWOD	Process with degradation reactions Process without degradation reactions

The most important objective for carbon, capture, and storage (CCS) is the capture of CO<sub>2</sub> from the exhaust gases of power generation systems. There are various stages of CO<sub>2</sub> separation technologies. However, the most promising one is the use of amine solvents for the

reduction of CO<sub>2</sub> emissions, particularly from natural gas combined cycle (NGCC) power plants. Amines capture plant about 70-90% CO<sub>2</sub> from commercial power stations (IEAGHG, 2012), these high removal

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rates have many environmental impacts due to their degradation products.

During the process of CO<sub>2</sub> removal from a power plant, two types of degradation occur. (1) Thermal degradation: This is caused by heat (mainly at temperatures that exceed 200 °C). (2) Oxidative degradation which is activated by oxygen (based on radical reactions, is catalysed by metal ions, and results in oxidized fragments of the solvent) (Bedell, 2009). Thermal degradation occurs mostly in the regenerator (stripper), due to high temperatures during the stripping of CO<sub>2</sub>. At this temperature, enhanced solvent loss occurs. This is because the kinetic rates of the degradation reactions increase. Furthermore, due to the presence of steric hindrance, 2-amino-2-methyl-1-propanol (AMP), is less liable to thermal degradation than monoethanolamine (MEA) (Bedell, 2009; Davis, 2009; Eide-Haugmo *et al.*, 2011). This leads to an increment in the cost of amine replacement and causes environmental issues leading to health effects and the reactivity of volatile products (Lepaumier *et al.*, 2009; Nguyen *et al.*, 2010). Oxidative degradation mainly occurs in the absorber. It involves the reaction of oxygen with the amine solution that enters the system mainly through the flue gas stream. Oxidative degradation rates of amines are dependent on temperature, dissolved oxygen, a solution of CO<sub>2</sub> and the concentration of impurities such as SO<sub>x</sub> present in the flue gas (Lepaumier, 2009). AMP produce emissions and degradation products, which are harmful to the environment. The evaluation of these emissions is required to implement control strategies (IEAGHG, 2012). Thus, the focus of solvent degradation is mainly the environmental balance such as the emissions of volatile degradation products. The various degradation products of AMP are 4,4 dimethyl-2-oxazolidinone, acetone, ammonia, formic acid, 2,4 lutidine, nitrite, nitrate being secondary oxidation products originating from NH<sub>3</sub>, while acidic, glycolic- and oxalic acid are thought to be the secondary oxidation products of acetone (Vega *et al.*, 2014). 2, 4-Lutidine is proposed to be formed by the reaction of acetone, formaldehyde and dimethylamine, the latter two molecules are suggested to be transient intermediate products. 4, 4-dimethyl oxazolidine is expected to be formed by the reaction of the total oxidation product; CO<sub>2</sub> with AMP. The main oxidative degradation products of AMP are acetone, 2, 4 lutidine, 4, 4 dimethyl-2-oxazolidinone, and their reaction mechanisms are described in literature (Wang, and Jens, 2012). The oxidative degradation of AMP results in gas and liquid phase impurities, which reduces the absorption capacity of the solvent and produces compounds whose emission is hazardous to the environment. These impurities are emitted in the CO<sub>2</sub>-lean gas from the top of the absorber. The extent

of degradation of the solvent depends on the operating conditions of the process. The concentrations of the product present as vapour in the exiting CO<sub>2</sub> emitted from the absorber to the atmosphere depends on the vapour pressure of gas and liquid, and the temperature of the absorber. From the top of the absorber, CO<sub>2</sub> lean flue gas is released to the atmosphere. Due to degradation reactions taking place in the absorber and stripper, chemical compounds are produced forming heat stable salts in which some are recycled in the process and others are released to the atmosphere. However, the un-emitted degradation products in the system are removed via a reclaimers. Experimental studies by Wang and Jens, (2012) showed that oxidative degradation of AMP is more significant than thermal degradation. Oxidative degradation is a critical problem because of its high impact on the environment, process economics, and corrosion problems, leading to a decrease in equipment life. The majority of studies on AMP were experimentally based; there is not much research on simulation-based. Thus, this study evaluates the emissions of AMP and its degradation products by adding degradation reactions to the CO<sub>2</sub> capture unit using Aspen Plus® V8.4.

## MATERIALS AND METHODS

*AMP capture plant description:* Fig. 1 shows a pictorial view of the flowsheet for the aqueous AMP-based post-combustion CO<sub>2</sub> capture (PCC) plant, which is the Aspen Plus® process simulation presented in this study. The AMP-based PCC is a steady-state process which consists of two columns (absorber and stripper). The absorber helps absorb CO<sub>2</sub> by the amine solvent (AMP), while the stripper separates the CO<sub>2</sub> from the AMP solution. The temperature of the flue gas from the NGCC is reduced in the blower and further reduction occurs in the direct contact cooler (DCC) so that the temperature of the flue gas is slightly close to atmospheric. The rich and lean pumps are used to pump the rich solvent (more of CO<sub>2</sub> in solution), and the lean solvent (more of amine solution) respectively. Also, the cross heat exchanger is used to exchange the hot fluid coming from the absorber with the cold fluid from the stripper, and the water and solvent makeups help to ensure process convergence. Lastly, the AMP PCC plant uses a water washer in the first two stages of the column after the absorption of CO<sub>2</sub>. This is to enable further reduction in the temperature of the exit flue gas, to recover the concentration of AMP, and to prevent volatile solvent products in the treated gas to be released to the environment. This is very important since the temperature in and out of the absorber affects the levels of volatile compounds, and this reduces CO<sub>2</sub>

emissions from the solvent and its degradation products.

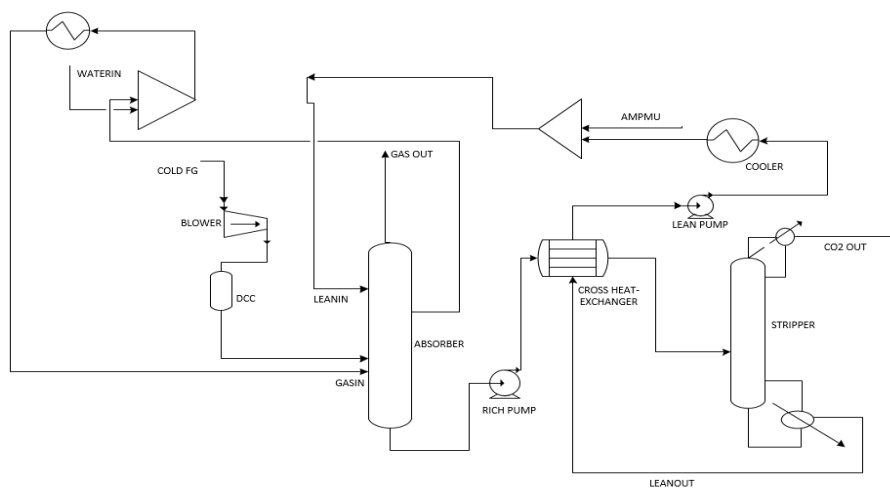


Fig. 1: Process flowsheet of AMP PCC capture process

*Thermodynamics and design parameters:* The AMP PCC plant model is developed using default parameters in Aspen Plus® V8.4 at pilot (small) scale and the model is validated against experimental data from studies reported by Gabrielsen *et al.*, (2007). The model built is rate-based; the thermophysical properties and reaction kinetics implemented into the model is based on experimental studies (Austgen *et al.*, 1989). Transport property models and parameters are validated against experimental data available in the literature (Aspen Technology, 2008). The absorber and stripper are designed based on chemical kinetics and mass transfer operations. Electrolyte Non-Random Two Liquid (NRTL) present in Aspen data bank (Aspen Technology, 2010) was used to describe the ionic species and determine the overall physical properties of the process streams in the CO<sub>2</sub> absorption/desorption process, while the Redlich-

Kwong equation of state is used for vapour phase (Redlich and Kwong, 1949). The equilibrium equations and the kinetic reactions which describe the absorption chemistry of AMP are given in study (Aspen Technology, 2008). The AMP PCC plant model is scaled up to handle the exhaust gas from an NGCC power plant. This study assumes that the flue gas is pretreated to reduce the concentration of O<sub>2</sub> and also negligible concentration of sulphur dioxide (SO<sub>2</sub>) and nitrogen dioxide (NO<sub>2</sub>) in the flue gas. Similar assumptions have also been made in previous studies (Canepa *et al.*, 2014; NETL, 2010). The flue gas composition from a 474 MWe NGCC power plant before treatment obtained from the literature (NETL, 2010) is given in Table 1. Preliminary design and operations data for the capture plant are presented in Tables 2 and 3.

Table 1. Exhaust gas composition (NETL, 2010)

Flue gas	Composition	Composition after treating
O <sub>2</sub> (mol/mol)	0.1209	0.001209
N <sub>2</sub> (mol/mol)	0.7432	0.7432
H <sub>2</sub> O (mol/mol)	0.0867	0.0867
CO <sub>2</sub> (mol/mol)	0.0404	0.0404
Argon (mol/mol)	0.0089	0.0089
Mass flowrate (kg/s)	897.4	897.4

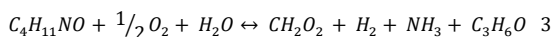
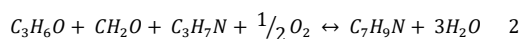
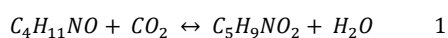
Table 2. Capture plant operating conditions (Rao and Rubin, 2002; Gabrielsen *et al.*, 2007).

Parameters	Value
Absorber pressure (°C)	1.013
Flue gas inlet temperature at absorber (°C)	40
CO <sub>2</sub> loading (mol/mol)	0.2
Concentration (% <sub>wt</sub> )	30
CO <sub>2</sub> capture efficiency (%)	90

Table 3. AMP large-scale plant preliminary design

Parameters	Value
Absorber diameter (m)	12.5
Absorber packing height (m)	30
Stripper column diameter (m)	8
Stripper packing height (m)	30
Absorber column number	4
Stripper column number	1
Absorber cross-sectional area (m <sup>2</sup> )	490.87
Stripper cross-sectional area (m <sup>2</sup> )	50.27

*Modelling and simulation of degradation products in Aspen Plus®:* The degradation reactions of AMP are added into the Aspen Plus® model. The oxidative degradation of AMP has data based on experiments and the equilibrium data chosen for modelling the degradation reactions are the inbuilt parameters present in Aspen model, and this is relied on. At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, and at a given temperature, the mass expression is a constant known as equilibrium constant. Thus, at a temperature of 120 °C, the concentration data for the degradation products (5 mol/kg, at 250 kPa O<sub>2</sub>) (Wang and Jens, 2012) was used. The equilibrium equations which describes the chemistry for the degradation products are defined by equations (Osagie *et al.*, 2017) (1)-(3):



Gibb's free energy given in equation 4. Gibbs free energy of formation (DGAQFM); also an inbuilt correlation in Aspen Plus®, is used in the estimation of Gibbs free energy using the empirical relation developed in Aspen Technology (Aspen Technology, 2000).

$$\Delta G = -RT \ln K \quad 4$$

The component data of the degradation reactions; acetone and 4,4 dimethyl-2-oxazolidinone were retrieved from Aspen Plus® databases, while 2,4 lutidine had no data available but was estimated by Aspen based on molecular structure and weight. In addition, thermodynamic data for 2,4 lutidine from the literature Reference (Chemical Book, 2017) presented in Table 4, were input specifications in the equilibrium model. Table 4 shows the results for the vapour phase emissions of AMP and its degradation products after the water wash column. The mass and heat balance that occurs in the AMP PCC process is because of chemical reactions taking place during absorption. Thus, the temperature stream leaving the absorber needs to be lowered so as to reduce the water wash column load. This is shown in the absorber temperature profile in Fig. 2, where the temperature bulge occurs at 58 °C and reduced to 50 °C. However, with the water wash system, potentials for chemical emissions still exist. Thus, emissions can be lowered at a point where they can be considered negligible. The maximum values calculated from the simulations are shown and presented in Table 5. The results show that ammonia

is the main degradation product emitted. Very low emissions of 4, 4 dimethyl-2-oxazolidinone and formic acid were estimated, this could be due to the model used in this study which does not consider the kinetic reactions for the degradation products.

**Table 4.** Physical properties data for 2, 4 Lutidine (Chemical Book, 2017)

Input specification	Value
CAS NO	108-47-4
Molecular weight	107.15
Boiling point (°C)	432
$\Delta_f H_{liquid}$ (J/mol)	16100
$S_{liquid}$ (J/molK)	248.50
$\Delta G = \Delta_f H - T\Delta S$ (J/mol)	57990

Degradation products are expected to be mostly present in the liquid phase as shown in Table 5. These products are not emitted as much but they reduce the amount of AMP solvent available. As observed in Table 6, four degradation products of AMP are observed to be formed with a considerable amount present in the liquid phase. The most readily formed degradation product is acetone, while the least formed is 4, 4 dimethyl-2-oxazolidinone.

**Table 5.** Emissions of AMP and its degradation products

Chemical emissions	After wash water (mg/Nm <sup>3</sup> of flue gas)
AMP	3.04E+03
4,4 dimethyl-2-Oxazolidinone	1.67E-16
Acetone	3.60E+02
Ammonia	1.74E+03
Formic acid	2.90E-05

**Table 6.** Formation of chemical compounds

Degradation products	Approximate concentration in liquid phase (mg/Nm <sup>3</sup> of flue gas)
AMP	4.70E+08
4,4 dimethyl-2-Oxazolidinone	3.52E-10
Acetone	3.08E+06
Ammonia	4.66E+04
Formic acid	2.59E+06

In order to determine the impact of the degradation products on the capture plant process, there is need to make a comparison between the process with degradation reactions (PWD) and the process without degradation reactions (PWOD). The PWD is also designed using specifications given in Table 2. Furthermore, Figs. 2 and 3 present the temperature profiles of the PWD and PWOD respectively. It is important to evaluate the degradation effects of the heat of absorption in the system. This is to observe the increase or decrease in the amount of heat present in the system as a result of the degradation reactions. The properties such as the rich loading, density etc. before

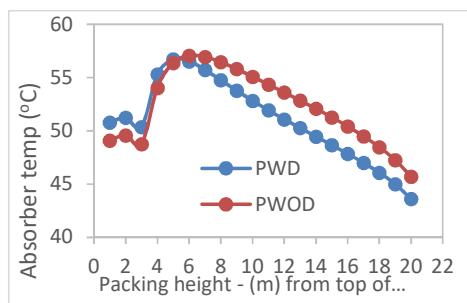
and after the addition of degradation reactions are given in Table 7.

**Table 7.** Comparison of the capture plant with and without degradation

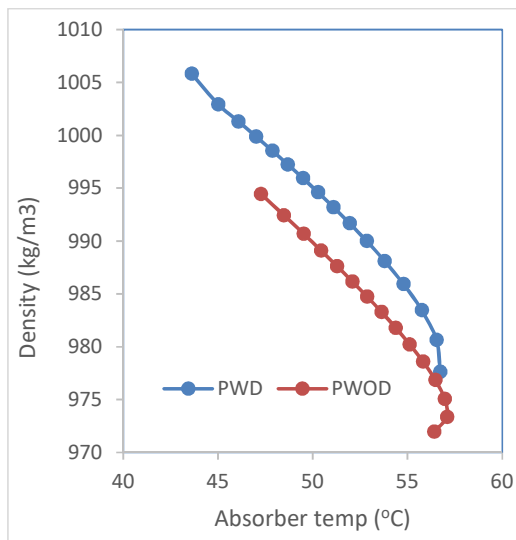
Properties	PWOD	PWD
AMP degradation (kg/s)	262.91	225.03
Solvent make-up flowrate (kg/s)	0.620	0.625
Density (kg/m <sup>3</sup> )	997.55	1005.84

In Table 6, the result shows that the AMP flowrate reduced from 262.91 kg/s to 225.03 kg/s, leading to a loss of 37.88 kg/s of AMP. However, the AMP considered to be lost is converted to the secondary parts, referred to as degradation parts. As a result of this, the solvent make-up flowrate increases for the PWD compared to that of the PWOD. CO<sub>2</sub> emissions increased from 7.80E+03 mg/Nm<sup>3</sup> to 9.82E+03 mg/Nm<sup>3</sup>, with the addition of degradation reactions. This is expected since the presence of degradation products introduces more emissions to the process. Furthermore, rich loading increased from 0.123 mol/mol to 0.145 mol/mol with degradation. This is because the degradation products reduce the moles of AMP, and loading will invariably increase. Also shown in Table 6, is the density, which increases from 998 kg/m<sup>3</sup> to 1006 kg/m<sup>3</sup> for the PWD. A reason for this is due to the higher densities of the degradation products, which can be observed in Fig 3, and this turn leads to lower temperature profiles for the PWD compared to the PWOD as shown in Fig 2.

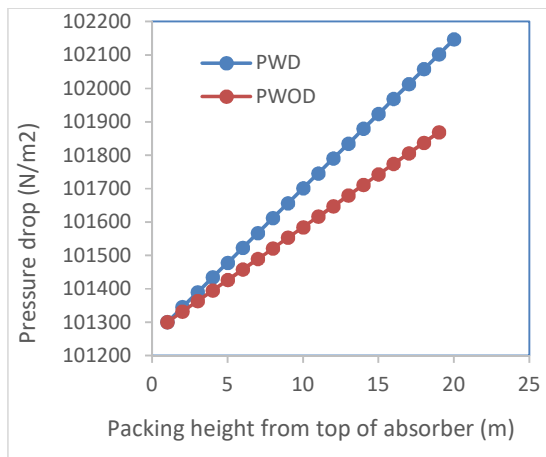
Reboiler duty, which is affected by the heat capacity, is 3.45 MJ/kgCO<sub>2</sub> for the PWD and 3.72 MJ/kgCO<sub>2</sub> for the PWOD. Thus, the amount of heat needed to raise the temperature (heat capacity) for the PWD is less. It should be noted that the presence of oxidative products is also responsible for foaming, which results in the increase in pressure drop across the absorber. This is observed in the pressure profile presented in Fig 4. Results show that the pressure drop for the PWOD is lower than that of the PWD; this is due to the higher foaming index for the PWD as shown in Fig 5, which in turn enhances vapour phase emissions for the PWD, as shown in Table 6.



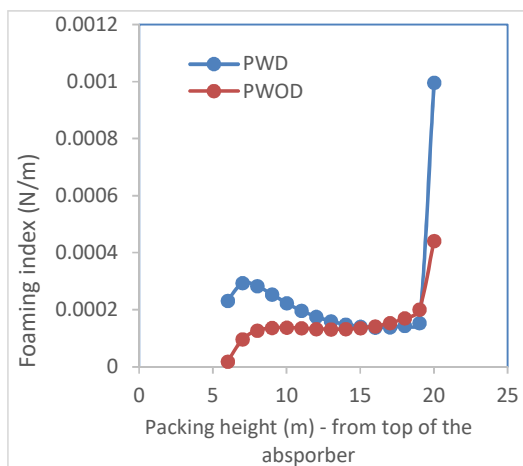
**Fig. 2:** A plot of packing height against absorber temperature



**Fig. 3:** A plot of absorber temperature against density



**Fig. 4:** A plot of packing height against absorber pressure



**Fig. 5:** A plot of packing height against foaming index

An equilibrium model to evaluate the emissions of AMP and its degradation products for a large-scale capture plant has been developed using Aspen Plus® V8.4. Further research into emission and measurements are required and more experiments needed to model the kinetic reactions of AMP degradation. Also, the degradation of AMP results in loss of solvent, which requires replacement and affects the operating cost. Therefore, economic analysis is important in assessing how much impact the degradation has on the AMP capture process.

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