# Prediction of Amines Thermal Degradation in CO2 Capture Process Using Intelligent Techniques


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*Keywords:* Amines, Carbon Dioxide Capture, intelligent model, thermal degradation, statistical analysis



*Abstract:*

Mitigation of carbon emissions is an important step to achieve the climate change goals. Amine-based post-combustion CO2 capture (PCC) process is a promising technology, and many commercial projects have been developed based on different capture mechanisms governing in various carbon capture and storage (CCS) processes. The thermally regenerative amine-based PCC is a traditional technology, which consists of an absorber to capture CO2 from the flue gas and a desorber to strip CO2 from the CO2-rich. Although there have been substantial improvements in the industrial applications of amines technology, further developments are still required owing to significant energy requirement, high capital cost, and amine degradation. One of the most critical issues in the amine-based PCC process is the degradation of solvent, which occurs by the transformation of amines into other chemical components by thermal degradation and oxidative degradation. In the thermal degradation, the amines react with CO2 to form com-pounds having high molecular weight, and in the oxidative degradation, the amines react with O2 to synthesize compounds having low molecular weight. In addition, the high stable salts are formed as a result of the reaction between the amines and the carboxylic acids. These high stable salts lead to considerable problems in the regeneration process, and increase the chance of corrosion in the process equipment. Monoethanolamine (MEA) is the most recognized solvent, which is considered a benchmark solvent in the solvent-based PCC processes. It has been confirmed that to absorb one molecule of CO2 two molecules of MEA are required, producing ion pair of MEACOO- (carbamate) and MEAH+ (protonated MEA). In this research, the MEA thermal degradation is investigated through employing hybrid intelligent techniques of artificial neural network-particle swarm optimization (ANN-PSO) and coupled simulated annealing-least square support vector machine (CSA-LSSVM). The models development is carried out utilizing experimental data, and the input parameters are MEA concentration, CO2 loading, temperature, and time, and the output is the remaining MEA concentration after experiencing the degradation phenome-non. The results can be employed for the further improvement of a solvent-based PCC process in terms of energy efficiency and operation cost. More importantly, the findings of this study can be used for the detailed and more accurate modeling and optimization of the corresponding processes.



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# Prediction of Amines Thermal Degradation in $CO_2$ Capture Process Using Intelligent Techniques

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## ABSTRACT

Mitigation of carbon emissions is an important step to achieve the climate change goals. Amine-based post-combustion $CO_2$ capture (PCC) process is a promising technology, and many commercial projects have been developed based on different capture mechanisms governing in various carbon capture and storage (CCS) processes. The thermally regenerative amine-based PCC is a traditional technology, which consists of an absorber to capture $CO_2$ from the flue gas and a desorber to strip $CO_2$ from the $CO_2$-rich. Although there have been substantial improvements in the industrial applications of amines technology, further developments are still required owing to significant energy requirement, high capital cost, and amine degradation. One of the most critical issues in the amine-based PCC process is the degradation of solvent, which occurs by the transformation of amines into other chemical components by thermal degradation and oxidative degradation. In the thermal degradation, the amines react with $CO_2$ to form compounds having high molecular weight, and in the oxidative degradation, the amines react with $O_2$ to synthesize compounds having low molecular weight. In addition, the high stable salts are formed as a result of the reaction between the amines and the carboxylic acids. These high stable salts lead to considerable problems in the regeneration process, and increase the chance of corrosion in the process equipment. Monoethanolamine (MEA) is the most recognized solvent, which is considered a benchmark solvent in the solvent-based PCC processes. It has been confirmed that to absorb one molecule of $CO_2$ two molecules of MEA are required, producing ion pair of $MEACOO^-$ (carbamate) and $MEAH^+$ (protonated MEA). In this research, the MEA thermal degradation is investigated through employing hybrid intelligent techniques of artificial neural network-particle swarm optimization (ANN-PSO) and coupled simulated annealing-least square support vector machine (CSA-LSSVM). The models development is carried out utilizing experimental data, and the input parameters are MEA concentration, $CO_2$ loading, temperature, and time, and the output is the remaining MEA concentration after experiencing the degradation phenomenon. The results can be employed for the further improvement of a solvent-based PCC process in terms of energy efficiency and operation cost. More importantly, the findings of this study can be used for the detailed and more accurate modeling and optimization of the corresponding processes.

**Keywords**: Amines, $CO_2$ capture, intelligent model, thermal degradation, statistical analysis

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## INTRODUCTION

Carbon capture and storage (CCS) is an unavoidable strategy to decelerate the climate change progress and meet the expectations of Paris Agreement [1-4]. Although there have been substantial developments in the industrial applications of amine technology, additional enhancements are still needed due to their high energy requirement, significant capital cost, and amine degradation [5, 6]. One of the most concerning issues in the amine-based PCC processes is the degradation of solvent, which occurs by the transformation of amines into other chemical components due to the chemical reactions. This adverse phenomenon takes place by the thermal degradation and oxidative degradation. In thermal degradation, the amines react with carbon dioxide to synthesize compounds having high molecular weight, and in oxidative degradation, the amines react with $O_2$ to form compounds having low molecular weight. In addition, high-stable salts are formed because of the reaction between the amines and the carboxylic acids. These high-stable salts create greater problems on the regeneration process and enhance the chance of corrosion in the process equipment [7]. Monoethanolamine (MEA) is the most common solvent, which is considered as a benchmark solvent, in the solvent-based PCC processes. In the capture process, MEA is wasted via thermal degradation, oxidative degradation, and volatility losses. Thermal degradation occurs by the polymerization of carbamate, causing high molecular weight by-products. Oxidative degradation, which takes place

in the stripper leading to the high-stable salts, is not a usual concern in the current applications of the amines absorption/stripping as oxygen is not in the system. The solvent losses due to the volatility in the absorber and stripper can be prevented through using a sophisticated control system [8]. In the $CO_2$ capture process, thermal degradation mostly occurs in the stripper, and significant research works have reported that high temperature in the presence of $CO_2$ is the key reason of degradation. Some studies stated that the thermal degradation occurs due to the high temperature in the absence of $CO_2$, emphasizing the essential role of heat. This type of degradation leads to dimerization, cyclization, and dealkylation. The main products of the thermal degradation of MEA are oxazolidine-2-one (OZD), N-(2-hydroxyethyl)imidazolidine-2-one (HEIA), N-(2-hydroxyethyl) ethylenediamine (HEEDA), and N,N'-bis-(2-hydroxyethyl)urea. Oxidative degradation normally occurs in the absorber, and the major reactions taking place are addition, piperazinones, and dealkylation. Some of the key products of the MEA oxidative degradation are ammonia, formaldehyde, acetaldehyde, methylamine, formamide, formic acid, glyoxal, and acetic acid [9]. There have been several research investigations on the solvents' degradation employed in the carbon capture processes. For instance, Davis and Rochelle [10] quantified the MEA thermal degradation as a function of $CO_2$ loading, temperature, and initial MEA concentration over the normal operating condition of the stripper. They concluded that most of the MEA loss happens in the formation of N,N'-bis-(2-hydroxyethyl)urea, HEEDA, and HEIA [10]. Thermal degradation and $CO_2$ removal capacity of various samples of MEA were evaluated at 160 °C over the period of 2-8 weeks. It was found that the concentration of MEA decreases by 95% because of the thermal degradation at 160 °C for 8 weeks ; however, the remaining solvent keeps its capacity at 22% to remove $CO_2$ [11]. Development of a $CO_2$ capture process model was carried out incorporating the degradation rate of MEA resulted from the experimental data. The model was used to assess the effect of the operating conditions on the process solvent loss. It was claimed that the major reason of solvent loss was the oxidative degradation in the absorber, while thermal degradation was not an important concern [12].

In another study, the researchers concluded that the developed method could be employed for the simultaneous quantification of various products of thermal degradation [13]. Molecular mechanisms demonstrating the thermal degradation of MEA were examined by employing molecular dynamic simulation as well as metadynamics sampling. It was found that the OZD formation as an intermediate and the main products of HEEDA and HEIA are thermodynamically favorable [14]. The literature review reveals that no investigation based on smart techniques has been carried out on the solvent thermal degradation analysis in a solvent-based PCC process. Thus, this research focuses on this gap employing the hybrid intelligent models. The models can offer an appropriate platform for the assessment of the solvent degradation in the proposed system, and the models can be utilized for the modeling and optimization of the solvent-based PCC processes.

# METHODOLOGY

## Data Processing

Adequate number of data is required for the accurate prediction of the solvent degradation. The key step of constructing a smart model is to determine the model input and output parameters. In this study, MEA initial concentration, time, $CO_2$ loading, and temperature are the input variables, and the MEA concentration left after particular period of time is the output variable. Thermal degradation greatly depends on the system temperature, and it happens at high temperatures. $CO_2$ loading increases the thermal degradation, and higher loading of $CO_2$ appears to enhance the thermal degradation either by improving the proton donors availability by catalyzing the dehydration or through the formation of more carbamate [15]. Concerning the effect of time, the products of thermal degradation usually increase over time [16]. Clearly, the solvent concentration in the system is a key parameter in the solvent thermal degradation. For example, an increase in the MEA concentration unexpectedly lowers the thermal degradation rate [8].

## Programming

MATLAB software is employed to build the models of artificial neural network-particle swarm optimization (ANN-PSO) and coupled simulated annealing-least square support vector machine (CSA-LSSVM). Various configurations of each model are used to obtain the reliable results. In the proposed models, the degradation of MEA is analyzed utilizing the input data and inputs. All data are normalized within the range of [-1 1] in order to prevent the numerical overflow in the program runs and achieve the required convergence. The following equation is used to normalize the data:

$$\hat{x} = 2\frac{x_i - x_{min}}{x_{max} - x_{min}} - 1 \quad (1)$$

where $\hat{x}$ refers to the normalized value of $x_i$, and $x_{min}$ and $x_{max}$ resemble the minimum and maximum values of the experimental data.

## Model Performance Assessment

The statistical parameters including mean square error (MSE), average absolute relative error percentage (AARE%), and coefficient of determination ($R^2$) are used to assess the precision and performance of the models. The following equations introduce the above-stated statistical measures [17-19]:

$$AARE\% = 100 \sum_{i=1}^{n} \left| \frac{x_d^i - x_m^i}{x_d^i} \right| / n \quad (2)$$

$$MSE = \frac{1}{n} \sum_{i=1}^{n} \left( x_d^i - x_m^i \right)^2 \quad (3)$$

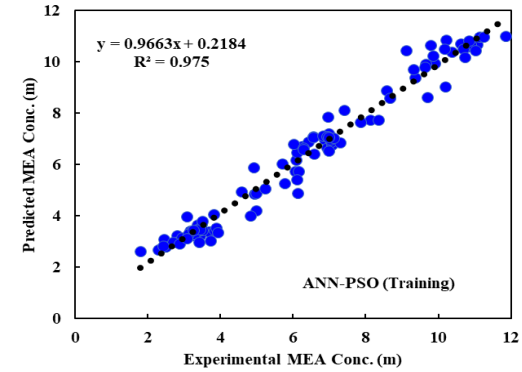
$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left( x_d^i - x_m^i \right)^2}{\sum_{i=1}^{n} \left( x_d^i - \bar{x} \right)^2} \quad (4)$$

where $x_d^i$ and $x_m^i$ are the amounts of the experimental data and predicted by the model; $\bar{x}$ stands fot the average value of the experimental data; and $n$ indicates the data number.

# RESULTS AND DISCUSSION

Various parameters are optimized to configure the most optimal ANN-PSO model, such as constants for *gBest* and

*pBest*, number of particles, number of maximum iterations, and number of neurons in the hidden layer. Figure 1 displays the performance of the ANN-PSO model for the data sets of training and testing. The values of AARE% for the training and testing phases are 6.57 and 5.33, respectively. The LSSVM model with the radial Kernel function contains two critical parameters of tuning ($\sigma^2$) and regularization ($\gamma$), and their optimal values are computed by CSA optimization algorithm. These two parameters substantially affect the model prediction accuracy. The estimated optimal values of $\sigma^2$ and $\gamma$ are 218.52 and $2.89\times10^5$, respectively. Figure 2 illustrates the performance of the CSA-LSSVM model in the training and testing phases. The AARE% values for the data sets of training and testing are 3.30 and 5.36, respectively.



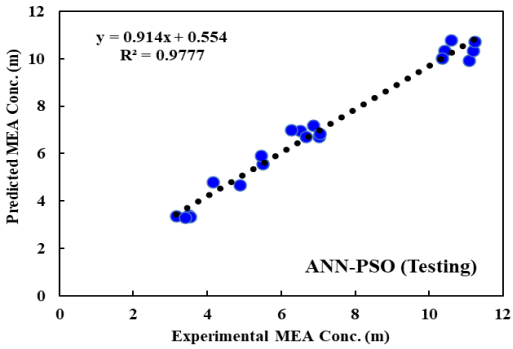
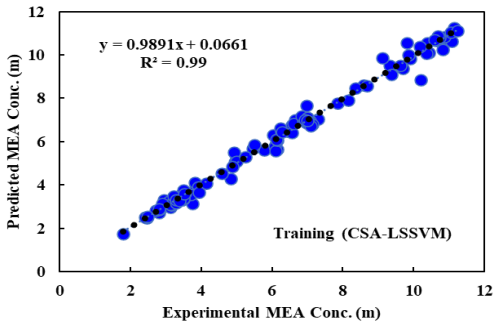




**Figure 1.** Performance of ANN-PSO.



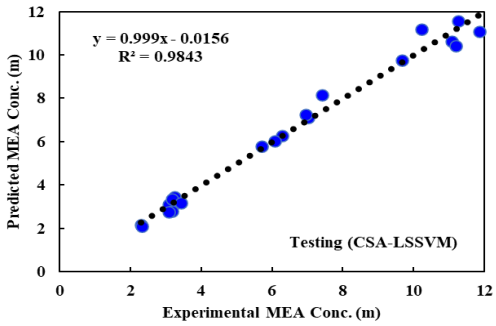
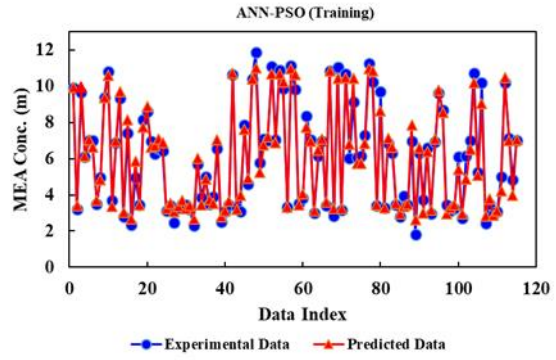
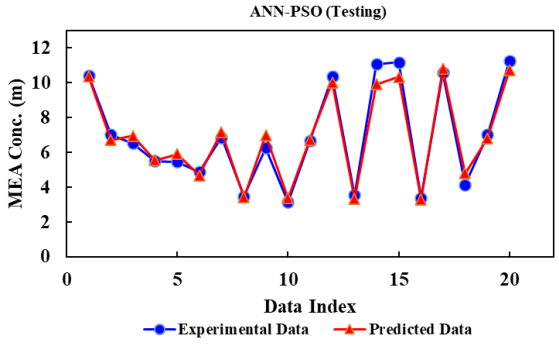




**Figure 2.** Performance of CSA-LSSVM.

## Comparison of Developed Models

The statistical criteria of $R^2$ (coefficient of determination), AARE%, and MSE are employed to assess the developed models performance. Figure 3 depicts the performance of ANN-PSO and CSA-LSSVM based on training and testing data sets. Table 1 reports the developed models performance based on the statistical criteria, revealing that CSA-LSSVM is a more accurate model.



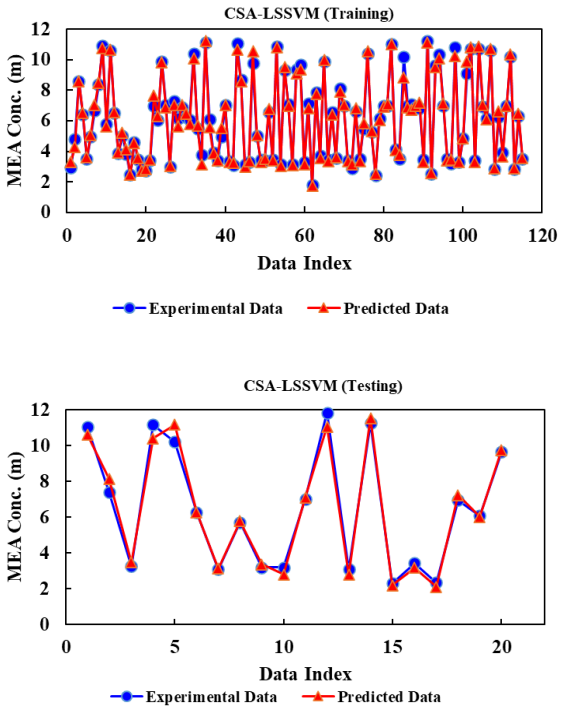



**Figure 3.** Performance of the models based on the training and testing phases.

**Table 1:** Performance of the developed models.

| Model | $R^2$ (Tr) | $R^2$ (Ts) | MSE (Tr) | MSE (Ts) | AARE % (Tr) | AARE % (Ts) |
|---|---|---|---|---|---|---|
| ANN-PSO | 0.975 | 0.977 | 0.195 | 0.211 | 6.57 | 5.33 |
| CSA-LSSVM | 0.990 | 0.984 | 0.073 | 0.176 | 3.30 | 5.36 |

## Parametric Sensitivity Analysis

Sensitivity analysis is performed to figure out the relationship between the input variables and the output variable. Correlation matrix theory can determine the degree of the linear relationship between two variables in a multi-variable system. Different approaches can be utilized to compute the strength of the linear relationship. The Pearson product-moment correlation coefficient is one of the most suitable techniques to do the correlation matrix analysis. The analysis reveals that the variables of temperature, loading, and time have a negative relationship with the output variable, indicating that an increase in these variables decreases the remaining concentration of the solvent in the system. Temperature has the strongest negative relationship with the target variable.

In the solvent-based PCC operation, it was claimed that 10% of the operation cost is associated with the solvent degradation [20]. This suggests the significance of understanding amine degradation in the performance analysis of the PCC processes. Moreover, the capacity of solvent to absorb $CO_2$ reduces when it faces the unfavorable phenomenon of degradation. The byproducts of the degradation should be removed from the system. They are hazardous wastes, and their quantity and specifications require to be determined for the more accurate control of the process. Moreover, a suitable model of the thermal degradation outside of the customary operating conditions is needed to optimize the system [21]. Increasing temperature accelerates the MEA degradation, and in a constant pressure system, lower $CO_2$ concentration leads to the elevated temperature of the reboiler, leading to the thermal degradation enhancement [8]. An increase in MEA concentration increases the risk of corrosion, and results in increased viscosity of the solution. Based on the results obtained by Davis [8], an increase in temperature results in more thermal degradation while increasing $CO_2$ loading and amine concentration reduces the thermal degradation. In this research, increase in temperature and $CO_2$ loading accelerates the thermal degradation while an increase in MEA concentration lowers the thermal degradation. Thus, there is a discrepancy between the two models with respect to the $CO_2$ loading. However, the results of this study regarding the influence of $CO_2$ loading on the thermal degradation agree with the models developed by Braakhuis, Høisæter [15] and Léonard, Toye [22].

## CONCLUSIONS

In this research, amines thermal degradation in the conventional solvent-based post-combustion $CO_2$ capture (PCC) process was analyzed by employing the hybrid intelligent models of ANN-PSO and CSA-LSSVM. Moreover, a correlation was introduced using the capability of the GEP based on the concept of maximum fitness and optimal evolution. The training phase reveals that CSA-LSSVM model is more accurate than ANN-PSO. The results indicate that increase in temperature, $CO_2$ loading, and time accelerate the thermal degradation, and an increase in initial the MEA concentration results in the reduction of the thermal degradation. Considering the global warming, together with the several solvents capable of absorbing $CO_2$ and extreme cost of experimental activities, this research offers a convenient groundwork for a systematic analysis of the thermal degradation mechanism of the solvents and more precise development of the optimization models. The developed methodology together with the developed models can be employed for the prediction of thermal and oxidative degradation of various solvents and the comparison of their capability in $CO_2$ absorption. The selected suitable solvent can be used to optimize the standard PCC processes employing the first principle models and/or intelligent techniques.

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