Optimization and Modelling of Carbon (II) Oxide Sequestration by Absorption Using Ammonia Solution

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Abstract—*Carbon (ii) oxide sequestration was carried out from a known emission source with the aid of a prototype laboratory absorber column. The power generating set was duly connected to the column for flow of the flue gas in to it and in contact with the absorbent in a counter current manner. Optimization, modelling and effect of process parameters were carried out with the aid of a Design Expert Software, with concentration of solvent, process/contact duration and volume of solvent as the variables considered for the capture process. The effect of process variables were analyzed using the response surface methodology for carbon (ii) oxide captured and removal efficiencies. Optimum yield for captured carbon (ii) oxide were obtained for concentration of solvent at 6 mol/dm3, contact time of 60 seconds, volume of solvent at 120 millilitre while optimum yield for removal efficiency was obtained at 80.37% for CO and also a quadratic model was developed as the best model for the capture process.*

Keywords— *Optimization, modelling, environment, carbon (ii) oxide sequestration, absorption, ammonia, concentration, volume, time.*

I. INTRODUCTION

Carbon (ii) oxide is a product of incomplete combustion as encountered in the operation of vehicles, heating, coal power generation, and biomass burning (Godish, 2003). Natural geographical events such as volcanic eruptions, emission of natural gases, degradation of vegetation and animals, and forest fires all contribute to atmospheric CO. Approximately 40% of global CO comes from these natural sources. Human intervention such as fossil fuel consumption, garbage disposal, tobacco smoke, and charcoal fires contribute to the remaining 60% of global CO (Vreman et al., 2000). Because human activity and density differ from place to place because of socioeconomic factors, atmospheric CO varies greatly from place to place. Global warming is the increase in the average temperature of the earth. This effect is caused by anthropogenic greenhouse gases released to the atmosphere. The control of these greenhouse gases is arguably the most challenging environmental policy issue facing most countries. An approach that is gaining widespread interest is to control carbon oxides emissions by capturing them from fossil fuels, to continue to be used without contributing significantly to greenhouse warming (Chukwu et. al, 2018). Post Combustion Capture (PCC) with ammonia solution is currently regarded as the most feasible technology to reduce the CO_2 and CO emission from fossil fuel and natural gas fired power plants (Derks and Versteeg, 2009). The focus on this research is the development of new technologies for the management of the challenge posed by the carbon oxide gases by use of chemicals in order to achieve this objective.

II. MATERIALS AND METHOD

2.1 Materials (A)

The ammonia solvent (analytical grade) was purchased at the chemical market with the prototype absorption column designed and fabricated to aid the carbon (ii) oxide sequestration.
- Ammonia
- Distilled water
- Sodium hydroxide

Equipment used (B)
- Prototype absorber column
- Power generating set
- Non-heat sensitive pipe
- Gas analyser (portable combustion analyser, PCA2)

2.2 Method

(A) Carbon (ii) oxide capture by absorption using ammonia solution

The method used for this work was absorption due to the nature of the equipment made of glassware and in order to control the experiment. Due to the nature of the research work, conditions of ambient temperature and atmospheric pressure were adopted for the process. There were three parameters/independent variables used such as concentration of solvent, contact time and volume of solvent. Experimental parameters for concentration of solvent were 2 to 10 mol/dm^3, process/time duration of 20 to 100 seconds and volume of solvent 40 to 200 millilitres. The chemical solution is charged into the column from the top and is evenly distributed across the inner surface of the column while in contact with the plates. The flue gas from the generating set enters through an opening at the base of the column and contacts in a counter-current form with the liquid as it flows up and reacts with the ammonia solution, this enables the CO and aqueous ammonia contact and react vigorously (Qing, et al., 2011).

(B) Determination of CO composition in flue gas and absorption column

A gas analyser (portable combustion analyser, PCA2) used to determine the composition of the gases. The equipment gas sensor was brought close to the gas exit point of the generating set and the readings taken while also taken to the gas exit point of the prototype absorption column set up in order to

detect the composition left over after the absorption process had taken place.

(C) Process Optimization

The Design Expert software was used in the regression statistical analysis of the results for the absorption process using ammonia solution. The results/data from the absorption process were used to analyse and generate parameters for optimization and statistical model development.

III. RESULTS AND DISCUSSIONS

Before the experiment in the absorption column was carried out, the gas analyzer was used to ascertain the initial conditions from the flue gas source (petrol electricity generating set).

The values obtained are:
- Average amount of CO initially present in the flue gas: 703.33ppm (0.0703%)
- Average amount of other gases: 85.2%

To ascertain the removal efficiency:

$$\% \text{ Removal Efficiency} = \frac{\text{Amount of gas leaving the column}}{\text{Amount of gas initially present in the flue gas source}} \times 100$$

3.1 Results for CO Capture Using Aqueous Ammonia

Effect of Concentration of Solvent on CO absorption/sequestration

The effect of concentration was determined in the absorption process with contact time of 60 seconds and volume of solvent at 120ml at different concentration intervals (2, 4, 6, 8 and 10 mol/dm^3). With the aid of specific gravity, percentage purity and molar mass, the desired quantity is prepared and made up with distilled water. The values obtained from the effect of concentration of ammonia solvent were plotted against the amount of CO absorbed/captured and removal efficiencies of CO.
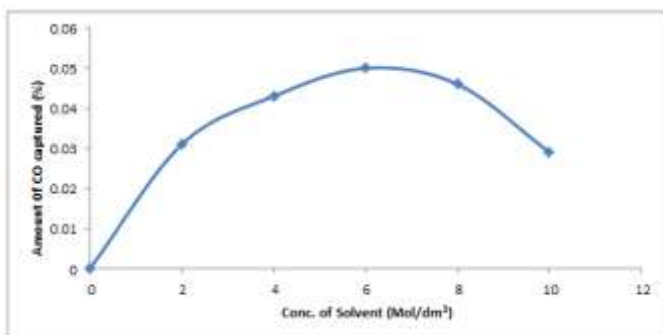

Fig. 1. Effect of concentration of solvent on capture of CO.

From the effect of concentration of aqueous ammonia on CO captured, it can be seen that aqueous ammonia concentration obviously had an impact on the absorption performance. As optimum value of CO captured was highest at 6 mol/dm^3 with 0.0498% (498.12 part per million) and removal efficiency of 70.48% as seen in Figure 1, there was a sharp drop in CO absorbed at 8 mol/dm^3 and further decrease at 10 mol/dm^3, this is similar to the work of Voitl and Rodriquez-Rivera (2004) were for their CO absorption efficiency, 82% of CO was captured with the NH$_3$ solution as absorbent this could be attributed to practical issues such as

ammonia volatilization and a decrease in the diffusion coefficient of the liquid phase as reported in the work of Liu et al. (2009) on CO$_2$ capture.

Effect of Contact Time on CO absorption/sequestration

The effect of contact time was determined in the experiment with concentration of solvent at 6 mol/dm^3 and volume of solvent at 120ml at different contact time intervals (20, 40, 60, 80 and 100 seconds) with the analyzer measuring the quantity CO present. The values obtained from the effect of contact/operating time were plotted against the amount of CO absorbed/captured and removal efficiencies of CO.
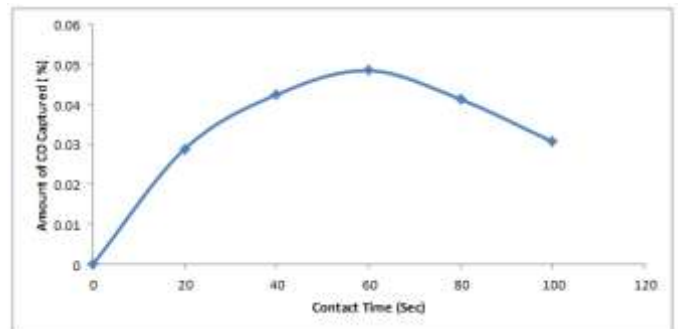

Fig. 2. Effect of contact time on capture of CO.

Figure 2 showed the effect of contact time on CO captured, it is well-known that a CO absorption process using amine solvent is an exothermic reversible reaction. It can be observed that CO capture and removal efficiency increases with increasing contact time from 20 to 60 seconds were the optimum values is obtained at 0.0485% CO captured. As shown in Figure 2, by increasing contact time from 20 to 60 seconds, the forward reaction was favoured with removal efficiency of 68.99%. This has resulted in a higher percentage of CO$_2$ removal and mass transfer coefficient. A similar observation was also obtained by Voitl and Rodriquez-Rivera (2004), in their study on the kinetic reaction between CO$_2$ and alkanolamines in aqueous solution at atmospheric conditions for the capture of CO$_2$ and CO; they obtained a removal efficiency of ranges 88 to 93%.

Effect of volume of solvent on CO absorption/sequestration

Effect of volume of solvent was determined in the absorption process while taking the effect of concentration at 6 mol/dm^3 and contact time at 60 seconds. The values obtained from the effect of volume of solvent were plotted against the amount of CO absorbed/captured.
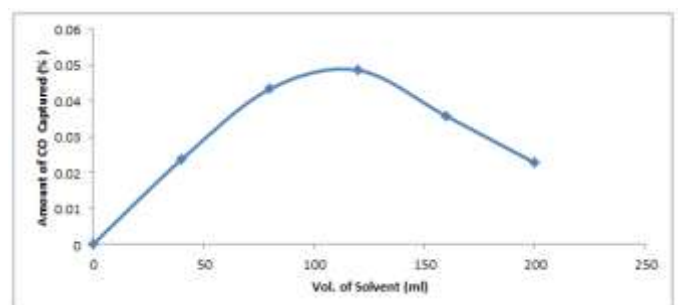

Fig. 3. Effect of volume of solvent on capture of CO.

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Figure 3 shows the effect of volume of solvent on CO captured. The captured CO increased with an increase in volume of solvent, from 40 to 120 millilitres were the optimum value was attained at 0.0358% (358ppm) and 69.13% removal efficiency as shown in Figure 3. This can be attributed to the increase in the heat of reaction between CO and NH$_3$ as a result of slow reaction and rate determining step. Similar trend were reported by Yeh and Bai (1999).

3.2 Results for CO Optimization, Modeling and Statistical Analysis

The design of the experiment (DOE) as shown in Table 1 was used to analyze and optimize the amount of Carbon (II) Oxide absorbed using ammonia solution. The coded and uncoded values of the capture were used and the percentage yield was presented in Table 1.

TABLE 1. Optimization results for the capture of CO in ammonia solution.

Std	Concentration of Solvent (Mol/dm^3)	Contact Time (Seconds)	Volume of Solvent (ml)	Amount of CO Captured (ppm)	Amount of CO Captured (%)	Removal Efficiency (%)
1	4	40	80	333	0.0333	47.37
2	8	40	80	372	0.0372	52.92
3	4	80	80	346	0.0346	49.22
4	8	80	80	435	0.0435	61.88
5	4	40	160	375	0.0375	53.34
6	8	40	160	297	0.0297	42.25
7	4	80	160	357	0.0357	50.78
8	8	80	160	367	0.0367	52.20
9	2	60	120	311	0.0311	44.24
10	10	60	120	332	0.0332	45.80
11	6	20	120	292	0.0292	41.54
12	6	100	120	375	0.0375	53.34
13	6	60	40	303	0.0303	43.10
14	6	60	200	277	0.0277	39.40
15	6	60	120	454	0.0454	64.58
16	6	60	120	501	0.0501	71.27
17	6	60	120	482	0.0482	68.56
18	6	60	120	565	0.0565	80.37
19	6	60	120	461	0.0461	65.58
20	6	60	120	493	0.0493	70.13

The empirical relationship between amount of Carbon (II) Oxide absorbed and three variables in coded values obtained by using the statistical package Design-Expert for determining the levels of factors which gives optimum percentage yield was given by Equation 1. The absorption result of the optimization process using ammonia solution is given in Table 2. It showed the combined effects of concentration of solvent (A), time (B) and volume of solvent (C). The highest percentage of CO absorbed was 0.0583 (85.38%) at a Concentration of solvent of 6mol/dm^3, Time of 60 seconds and Volume of solvent at 120ml. A quadratic regression equation that fitted the data is:

$$Y \ CO \ captured = 0.0490 + 0.0007A + 0.0020B - 0.0007C + 0.0020AB - 0.0021AC + 0.0011BC + 0.0045A^2 - 0.00041B^2 + 0.00051C^2 \quad (1)$$

Where Y is the response variable (amount of CO $_{absorbed}$) and A, B and C are the coded values of the independent variables. The above equation represents the quantitative effect of the factors (A, B and C) upon the response (Y). Coefficients with one factor represent the effect of that particular factor while the coefficients with more than one factor represent the interaction between those factors. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factor. The adequacy of the above proposed model was tested using the Design Expert sequential model sum of squares and the model test statistics. The model F-value of 23.37 implied that the model is significant. The low probability value (<0.0001) also indicated that the model is

significant. The value of the determination coefficient, R^2 being a measure of goodness of fit to the model indicated high degree of correlation between the observed value and predicted value. The predicted R^2 of 0.8908 is in reasonable agreement with the adjusted R^2 of 0.9138. Adequate precision measured the signal to noise ratio. A ratio > 4 is desirable. The ratio of 12.7332 in this process indicated an adequate signal. The ANOVA quadratic regression model demostrated that the model was highly significant, as was evident from the very low probability ($p < 0.0001$) of F-test and insignificant result from the lack of fit model. The coefficient of variation (CV) as the ratio of standard error of estimate to the mean value of the observed response is a measure of reproductibility of the model, generally a model can be considered reasonably reproducable if its CV is not greater than 10 percent. Hence, the low coefficient of variation, CV value (CV = 0.09) obtained indicated a high precision and reliability of the experiments. This test was shown in Table 2.

The ANOVA results for the model terms are given in Table 2. Analysis of variance (ANOVA) was applied for estimating the significance of the model at 5% significance level and shown in Table 2. A model is considered significant if the p-value (significance probability value) is less than 0.05.

TABLE 2. Significance of regression coefficients for the absorption of CO.

Source	Sum of Squares	df	Mean Square	F Value	P-value prob>F	
Model	0.0012	9	0.0001	23.37	<0.0001	significant
A-Conc. of Solvent	0.0015	1	0.0015	5.32	0.0021	
B-Contact Time	0.0001	1	0.0001	11.43	0.0570	
C-Vol. of Solvent	0.0018	1	0.0018	1.57	0.0023	
AB	0.0000	1	0.0000	5.93	0.0351	
AC	0.0000	1	0.0000	6.69	0.0271	
BC	0.0000	1	0.0000	0.0000	0.0780	
A^2	0.0005	1	0.0005	82.59	< 0.0001	
B^2	0.0004	1	0.0004	66.94	< 0.0001	
C^2	0.0006	1	0.0006	110.26	< 0.0001	
Residual	0.0001	10	0.0001			
Lack of Fit	9.002E-0.6	5	8.328E-06	0.0380	0.9517	not significant
Pure Error	0.0001	5	9.262E-06			
Cor Total	0.0012	19				

Std. Dev. = 0.0024; Mean = 0.0386; C.V.% = 0.09; PRESS = 0.001; R^2 = 0.9546; Adj. R^2 = 0.9138; Pred. R^2 = 0.8908; Adeq. Precision = 12.7332

From the p-values presented in Table 2, it can be deduced that the linear terms A and C, interaction terms AB, AC, and quadratic terms A^2, B^2 and C^2 are significant model terms. Based on this, the insignificant terms of the model B and BC were removed and the model reduced to the following equation:

Y CO captured = 0.0490 + 0.0007A − 0.0007C + 0.0020AB − 0.0021AC + 0.0045A^2 − 0.00041B^2 + 0.00051 C^2 (2)

The experimental data in Table 2 were also analyzed to check the correlation between the experimental and predicted CO_2 absorbed, and the normal probability and residual plot, and actual and predicted plot are shown in Figures 4 and 5 respectively. It can be seen from the Figures that the data points on the plot are reasonably distributed near the straight line, indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis is appropriate. The result also suggested that the selected quadratic model is adequate in predicting the response variables for the experimental data.
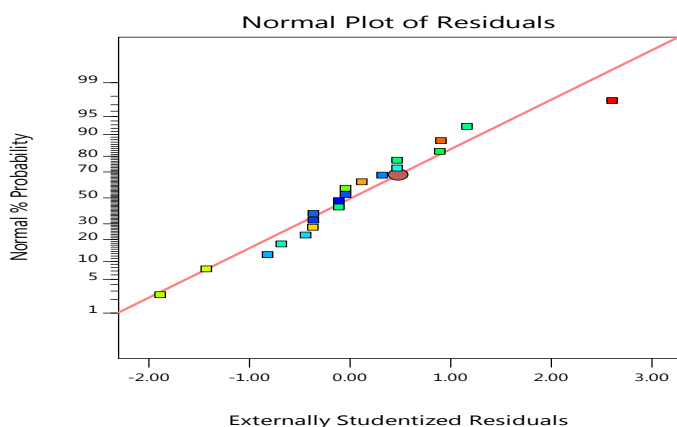

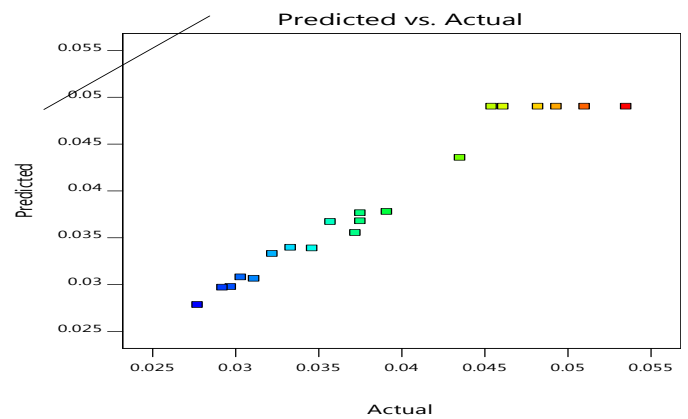Fig. 4. Plot of normal probability versus residuals for the captured CO.

Fig. 5. Plot of predicted versus actual for the captured CO.

Surface and contour Plots for Carbon (II) Oxide Capture yield

The 3D response surface and contour plots were generated to estimate the effect of the combinations of the independent variables on the amount of the captured Carbon (II) Oxide. The plots are shown in Figures 6 to 8. Figure 6 showed the dependency of amount of Carbon (II) Oxide captured on the interaction of concentration of solvent and contact time. The concentration of ammonia solution at 6mol/dm^3 and contact time of 60 seconds is observed as the optimum condition, as the amount of CO captured increased as both the concentration of ammonia solution and contact time increase up to the mid point and then sudden decrease takes place after that. This may be that beyond the midpoint of the variables, the conditions were no longer favourable for CO capture. Figure 7 showed the dependency of amount of Carbon (II) Oxide captured on the interaction of concentration of solvent and volume of solvent. As can be seen from the figure, amount of CO captured increased as both the concentration of solvent and volume of solvent increased up to the mid point of these variables with concentration at 6mol/dm^3 and volume at 120ml, and then decreased for volume of solvent but remained constant for concentration of solvent.
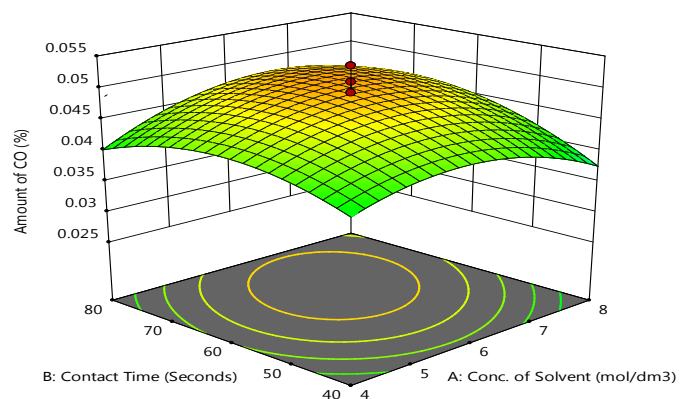

Fig. 6. 3D plot showing the effect of concentration of solvent and contact time on the amount of Carbon (II) Oxide captured.

This may be that the CO captured has attained it optimum level at volume of 120ml. Figure 8 showed the dependency of amount of Carbon (II) Oxide captured on the interaction of

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contact time and volume of solvent. As can be seen from the figure at contact time of 60 seconds and concentration of solvent at 6 mol/dm³, amount of CO captured is optimum at the midpoint level of the curvature. This may be that beyond the midpoints of these variables, the conditions were no longer favourable for CO capture.
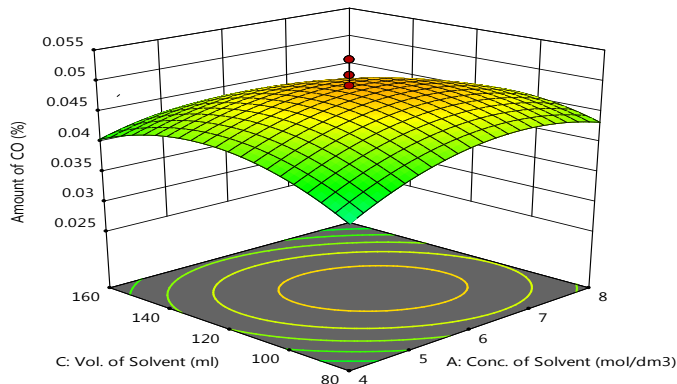

Fig. 7. 3D plot showing the effect of concentration of solvent and volume of solvent on the amount of Carbon (II) Oxide captured.
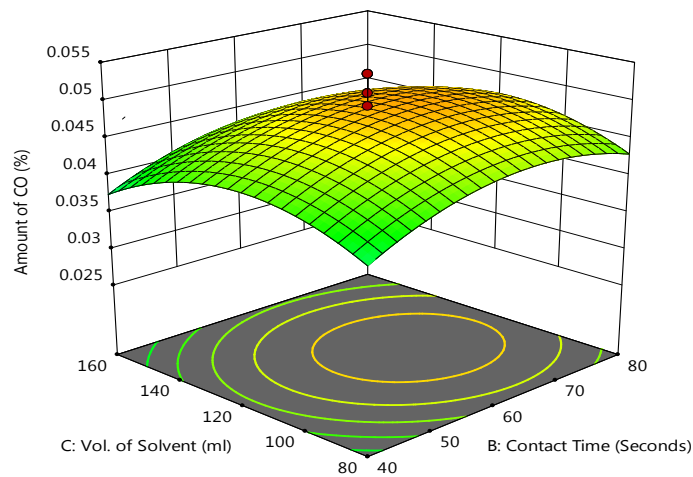

Fig. 8. 3D plot showing the effect of contact time and volume of solvent on the amount of Carbon (II) Oxide captured.

ANOVA analysis of the Carbon (II) oxide capture

Design Expert was used to analyze the results. The summary of P-values indicates that a quadratic model fitted the ANOVA analysis and hence it was suggested. The linear and 2FI models were not suggested. The Cubic model is always aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used hence all terms whose P-value are less than 0.05 are considered significant. The model summary test and the lack of fit test for the Carbon (II) Oxide capture were also presented in Tables 3 to 5.

In Table 3, the summary of P-values for CO captured indicated that a quadratic model fitted the ANOVA analysis because the adjusted R-squared value was very close to the value obtained for the predicted R-squared, also the P-value obtained in Lack of Fit was close to unity and therefore it was suggested. The linear and 2FI models were not suggested, the

cubic model is always aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used therefore sequential terms whose P-value are less than 0.05 are considered significant. In Table 4, quadratic model was suggested because of the closeness of the adjusted R-squared and predicted R-squared, with the cubic model aliased as a result of the CCD not having enough runs for a full cubic model. In Table 5, quadratic model was suggested because the p-value was close to unity and there was a good relationship between the sum of squares and mean square.

TABLE 3. Summary of P-values for carbon (II) oxide captured.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Remark
Linear	0.7761	0.0085	-0.1106	-0.3539	Not suggested
2FI	0.8370	0.0051	-0.2832	-0.4488	Not suggested
Quadratic	< 0.0001	0.9517	0.9132	0.8908	Suggested
Cubic	0.9097	0.6995	0.8756	0.6851	Aliased

TABLE 4. Model summary statistics for carbon (II) oxide captured.

Source	Std. Dev.	R-Squared	Adjusted R-Sq	Predicted R-Sq	Press	Remark
Linear	0.0084	0.0648	-0.1106	-0.3539	0.0016	Not suggested
2FI	0.0091	0.1220	-0.2832	-0.4488	0.0018	Not suggested
Quadratic	0.0024	0.9546	0.9138	0.8908	0.0001	Suggested
Cubic	0.0028	0.9607	0.8756	0.6851	0.0004	Aliased

TABLE 5. Lack of fit test for carbon (II) oxide captured.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Linear	0.0011	11	0.0011	10.73	0.0085	Not suggested
2FI	0.0010	8	0.0010	13.81	0.0051	Not suggested
Quadratic	9.002E-06	5	1.800E-06	0.1944	0.9517	Suggested
Cubic	1.549E-06	1	1.549E-06	0.1673	0.6995	Aliased
Pure Error	0.0000	5	9.262E-06			

IV. CONCLUSION

From this work it can be deduced that ammonia solution was a very good absorbent for the carbon (ii) oxide sequestration. Evident to this was the decrease in the carbon (ii) oxide composition therein in the flue gas during the capture process with ammonia. The effect of process variables were studied using the response surface methodology for the design of experiment for carbon (II) oxide capture and removal efficiencies. The obtained optimum yield were from experimental parameters for concentration of solvent ranging from 2 to 10 mol/dm³, process duration of 20 to 100 seconds and volume of solvent between 40 to 200 millilitres with standard operating conditions of ambient temperature and atmospheric pressure adopted for the research. The analyzer monitored the emission levels of CO in part per million (ppm) with the measured and calculated values displayed on its LCD.

From the optimization results obtained, about 80% reduction in flue gas carbon (ii) oxide contents was achieved by aqueous ammonia at concentration of solvent at 6 mol/dm^3, contact time of 60 seconds, volume of solvent at 120 millilitres. It is an indicator that aqueous ammonia with a high potential scrubbing capacity has a fast absorption rate.

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