MULTIVARIATE CALIBRATION OF CO_2 SOLUBILITY IN METHYLDIETHANOLAMINE (MDEA) USING RAMAN SPECTROSCOPY

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Dissertation submitted in partial fulfilment of
the requirements for the
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Perak.

CERTIFICATION OF APPROVAL

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Approved by,

(Ir. Dr. Abdul Halim Shah Bin Maulud)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK.

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original works is my own except as specified in the references and acknowledgements, and that the originals work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD HAFIZ BIN MOKHTAR KAMIL

ABSTRACT

For decades, Carbon dioxide (CO_2) capturing process had been an important issues since it is one of the major greenhouse gas (GHG) contributors which leads to the global warming. Alkanolamines such as Methyldiethanolamine (MDEA) had been widely used for CO_2 capturing by absorption process. A study on carbon dioxide (CO_2) solubility was done inside aqueous MDEA solution by using Raman Spectroscopy with the goal of calculating the CO_2 loading. This is because, there was still no direct measurement to calculate the CO_2 loading inside the MDEA solution. Therefore, a sensor or a measurement device is needed to calculate the CO_2 loading. After a three careful experiment had been run on three different MDEA concentrations which are 10%, 20% and 30% concentration, the raw data from the Raman Spectrum had been obtained. Matlab simulation was used to construct a statistical calibration and validation models between the CO_2 loading and the peak of Raman Shift by using Partial Least-Squares method (PLS). Results shows that lower MDEA concentration produce better Coefficient of Determination (R^2) and Mean Square Error (MSE) for calibration models while the combination of the three MDEA concentrations has found as a good fit with R2 of 0.9651 and MSE of 0.0347 in CO_2 loading prediction.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Lately, it is widely known that the main cause of global warming is greenhouse gases, mainly CO_2, emitted into the environment. The major sources of CO_2 emissions are combustion of fossil fuel power plants, automobiles and other industrial sources. Among the greenhouse gases, CO_2 contributes more than 60% to global warming because of its huge emission amount (Cheng-Hsiu Yu 2012).

Therefore, several efforts have been made recently to develop new cleaner technologies to mitigate the harmful impact of CO_2 emissions on climate change (Rodríguez, Mussati, & Scenna, 2011). To prevent the global warming by the greenhouse effect it is crucial to develop energy saving absorbents for capturing and separating CO_2 from its large point sources. Aqueous solutions of alkanolamines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams (Hamborg, Derks, van Elk, & Versteeg, 2011). CO_2 capture by chemical absorption using an aqueous solution of alkanolamine as based absorbents is a common industrial process and has, in many cases, been found to be the most practical solution compared with other processes (Chowdhury, Okabe, Yamada, Onoda, & Fujioka, 2011). The alkanolamines as a solvent are classified into primary, secondary, and tertiary amines. The most commonly used alkanolamines solvent are asmonoethanolamine (MEA), diethanolamine (DEA), Methyldiethanolamine (MDEA).

In an industrial plant, a conventional acid gas removal plant is operated with an acid gas absorption/desorption cycle (Hamborg, van Aken, & Versteeg, 2010) . In the process of CO_2 capturing, the CO_2 is chemically absorbed by the alkanolamine solvent under low pressure and high temperature to ease the absorption process. A titration metd choan be used to measure the CO_2 loading but it is not conventional because it requires a longer time and produces many errors. So, it is a requirement to measure the CO_2 loading instantaneously to properly control the process.

Therefore, different types of spectroscopy techniques had been used for the measurement of CO_2 loading in alkanolamines such as Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) and Raman Spectroscopy. These spectroscopy techniques are used for instantaneous measurement of CO_2 concentrations to properly control the process as well as increase the efficiency (Bakeev, K.A., 2010). Raman spectroscopy had been considered as a better technique for vibrational spectroscopy technique and a complementary to the also well-established infrared spectroscopy (Eberhardt.K et al., 2015). This is because it gives weak spectrum for water and facilitates in identification of reactant or product spectrum peaks. Thus, Raman spectroscopy had been tested for the measurement of CO_2 absorption in aqueous MDEA solution.

1.2 Problem Statement

The process of CO_2 absorption inside alkanolamines had been executed many times but still there is no direct measurement for the CO_2 loading. The measurement of CO_2 loading is essential to ensure the process operate in better efficiency. Other than that, the CO_2 loading measurement is also important for process optimization. As a result, a sensor or measurement device is needed to detect CO_2 concentration inside the alkanolamines. To overcome this problem, different types of spectroscopy technique for measurement had been use widely for direct measurement of CO_2 loading. For example, Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) and Raman Spectroscopy. Raman spectroscopy proves to be a better technique because it had a better advantage to be use in aqueous solutions (Alexander, 2008). Raman spectroscopy works by producing inelastic scattering of light from molecules which is called the Raman Spectrum. So, all that is required for the collection of spectrum is to place the sample into the excitation beam and collect the scatter light. However, the Raman spectrums produce a lot of peak to be process. Therefore, different multivariate calibration technique had been used such as Principle Component Analysis (PCA), Principle Component Regression (PCR) and Partially Least Square (PLS) regression. The PLS had proven to predict better than PCR because it's correlation with the y variables are sought in determining the scores and PLS loading are more readily interpreted (Montoto, 2002). As a result, a calibration models can be construct by using Partially Least Square (PLS) regression technique.

1.3 Objective of study

The main objectives of this study are:

1. To obtain carbon dioxide (CO_2) loading data in aqueous Methyldiethanolamine (MDEA) solution and their respective Raman spectrum by using different MDEA concentration.
2. To construct calibration models between the carbon dioxide (CO_2) loading and spectrum by using Partially Least Square regression (PLS) method.
3. To evaluate the performance of the constructed calibration model.

1.4 Scope of Study

For the scope of study, this project starts from obtaining the parameters of interest which is the carbon dioxide (CO_2) loading data in MDEA aqueous solution and the Raman spectrum. The MDEA aqueous solution will be prepared in different concentrations to observe their effect on CO_2 loading. From the CO_2 loading and Raman spectrum data, a calibration model can be constructed using Partially Least Square regression (PLS) and will be constructed in Mat lab simulation.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon dioxide (CO_2) absorption in Methyldiethanolamine (MDEA).

For decades, climate changes and carbon dioxide (CO_2) emission have attracted attentions worldwide and the reduction of CO_2 has become a hot issue. This is due to the exploitation of natural gas resource and the improvement of people living standard, the demand of natural gas is growing year by year (Tang et al., 2014). Natural gas filtration, separation, desulfurization, decarbonization, dehydration and other pretreatment processes are needed to ensure the safety of natural gas storage, transportation and utility. The widely used technology for CO_2 capture is chemical absorption using alkanolamine aqueous solutions as absorbents (Fu & Zhang, 2015). The chemical absorption has been found to be the most viable solution compared with other processes (Chowdhury, Okabe, Yamada, Onoda, & Fujioka, 2011) . The alkanolamines as a solvent are classified into primary, secondary, and tertiary amines such asmonoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), respectively (Shojaeian & Haghtalab, 2013). The most commonly used alkanolamines is Methyldiethanolamine (MDEA). The advantage of using these tertiary amines is that the regeneration energy is significantly lower than the regeneration energy of primary and secondary amines (Penders-van Elk, Derks, Fradette, & Versteeg, 2012). As a result, the lower energy means the lower the cost for stripping. An ideal solution would be a combination of fast absorption and low regeneration energy such as activated tertiary amine solutions.

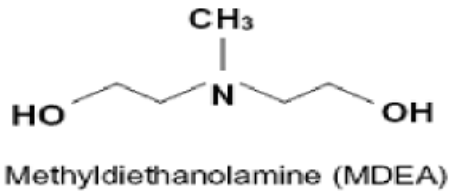

Figure 2.1 Molecular structure for MDEA

Theoretically, according to Kierzkowska-Pawlak and Chacuk (2010), the reaction mechanism which stated that Methyldiethanolamine (MDEA) does not react directly with Carbon dioxide. In accordance with the convention used in the amine literature, MDEA is represented as R1R2R3N, where R1 = R2 = CH2CH2OH and R3 = CH3. When CO_2 is absorbed in aqueous solution, the reaction mechanism is as shown below and the following reactions m occurs in the liquid phase.

$$CO_2 + R_1R_2R_3N + H_2O \longleftrightarrow R_1R_2R_3NH^+ + HCO_3^- \quad (1)$$

$$CO_2 + OH^- \longleftrightarrow HCO_3^- \quad (2)$$

$$HCO_3 - + OH \longleftrightarrow CO_3^{2-} + H_2O \quad (3)$$

$$R_1R_2R_3NH^+ + OH^- \longleftrightarrow R_1R_2R_3N + H_2O \quad (4)$$

$$2H_2O \longleftrightarrow OH^- + H3O^+ \quad (5)$$

In addition, Seagraves and Weiland (2009) stated that the reason MDEA react indirectly with CO_2 is because MDEA is tertiary amine whose amine groups lacks the single proton that need to react directly. Thus, the reaction mechanism does not produce or form carbomate that resulted when using primary and secondary amines. For tertiary amine reaction mechanism, it only produces carbonate and bicarbonate ions. In terms of its chemistry, the most that MDEA can do is providing a sink for the hydrogen ions produced when CO_2 hydrolyses in water.

2.2 Raman Spectroscopy.

Recently**,** Raman spectroscopy had become an important analytical tool across a number of industries and application. As Raman spectroscopy enables rapid, non-destructive measurements, the technique appears a most promising tool for on-line process monitoring and analysis. Raman scattering spectroscopy is also a very well-known spectroscopic tool for measuring gas-phase temperature and species concentration in reacting flows (Roy, Wrzesinski, Pestov, Dantus, & Gord, 2010). Basically, Raman spectroscopy is the phenomenon of inelastic scattering (T. Vankeirsbilck, 2002). Raman spectroscopies are concerned with measuring associated molecular vibration and rotational energy changes. When using Raman spectroscopy, monochromatic radiation of frequency is incident on a sample, some of the radiation is scattered and this is called Raman scattering (Kudelski, 2008). In the scattered radiation, in addition to radiation with the same frequency as the incident radiation it is described as an elastically scattered radiation or Rayleigh radiation. But, the main focus is on the radiation of different frequencies or inelastic scattered radiation which is the Raman spectrum (Kudelski, 2008). Typically, total Raman scattering cross-section is $10{-}29$ cm^2 per molecule, whereas typical cross-sections for absorption in ultraviolet and infrared are $10{-}18$ and $10{-}21$ cm^2 (Kudelski, 2008). Therefore, to record conventional Raman spectra, analytical concentrations greater than 0.01M are usually required.

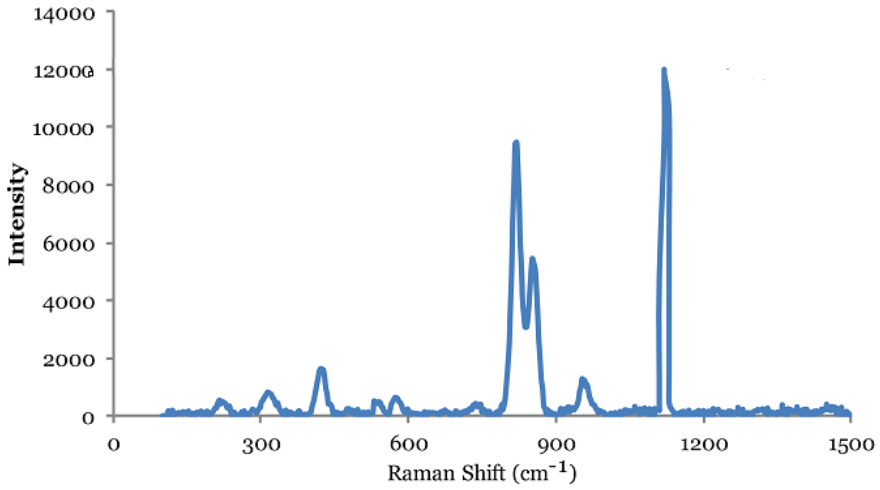

Figure 2.2 A Raman spectrum plots against light intensity

2.3 Partial Least Square Regression (PLS) technique.

The partial least squares regression (PLSR) was developed by Wold in the late 1960s for econometrics (Wold, 1975) and then, it was introduced as a tool to analyze data from chemical applications in the late 1970s. A major objective in process data analysis is to establish regression models and predicting product quality from experimental or historical data (Kim, Lee, & Lee, 2005). However, the high dimensionality of such data makes it difficult or, in some cases, impossible to reliably measure the product quality. The need to describe the quality of the final product from such data has led to the advancement of multivariate calibration models such as partial least squares (PLS) (Kim et al., 2005).The PLS concept is defined as dimensional reduction technique that finds a set of latent variables through the projection of the variables X and variables Y onto new subspaces by maximizing the covariance between the two variables simultaneously. PLS produces more stable results with regard to the identification of the relevant variables and their magnitudes of influence independent of the sample size in the analysis, a situation in which other regression approaches fail (Carrascal, Galván, & Gordo, 2009). The examples of other regression approaches are

principle component analysis (PCA) and Principle component regression (PCR). In addition, the probability of correctly rejecting the false null hypothesis, and thus accepting the alternative true hypothesis , was higher in the PLS analysis (Carrascal et al., 2009).Moreover, PLS also had been shown to be a powerful technique for process modeling and calibration in systems where the predictor variables are collinear or have high dimensional data set (Kim et al., 2005). It is important to model the set of modification more precisely, therefore PLS calibration technique was used (N. Dupuy, 2002).According to Kim et al., (2005). PLS also decompose X and Y matrices with mean zero in the form of:

$$X = TP^T + E \quad (1)$$

$$Y = UQ^T + F \quad (2)$$

The PLS regression model can be expressed with regression coefficient B and residual matrix R as follows:

$$Y = XB + R \quad (3)$$

$$B = W (P^T W)^{-1} C^T \quad (4)$$

Where P (N*k) is the matrix consisting of loading vectors $pi = X^T ti / (ti^T ti)$ i =1. . . ,k.
After derivation with equation below:

$$W = X^T U \quad (5)$$

$$P = X^T T (T^T T)^{-1} \quad (6)$$

$$C = Y^T T (T^T T)^{-1} \quad (7)$$

Then, matrix B can write in the following form to make prediction in PLS regression:

$$B = X^T U (T^T X X^T U)^{-1} T^T Y \quad (8)$$

CHAPTER 3

METHODOLOGY

3.1 Materials and Tools.

The materials and tools used throughout the project are as stated below:

1. Methyldiethanolamine (MDEA) with a purity of 99% the alkanolamines in aqueous solution.
2. Distilled water for the preparation of solution.
3. Carbon dioxide (CO_2) was supply into the absorption vessel under high pressure and low temperature.
4. Portable Raman spectrometer manufactured by Stellar Net.
5. Software Spectra Wiz is use to capture Raman spectrum.
6. Matlab software is used to calibrate between the CO_2 loading and Raman Spectrum.
7. Partially least square regression (PLS) methods is use which is a mathematical tools to calibration between the CO_2 loading and Raman Spectrum.

3.2 Project Methodology

3.2.1 Experimental Methods:

3.2.1.1 Carbon Dioxide (CO2) in absorption cell.

The CO_2 absorption cell is contained in a feed tank absorption vessel, having a volume of 435 cm^3 and 465 cm^3 respectively. The methyldiethanolamine (MDEA) aqueous solution was prepared and charged into the absorption vessel. The CO_2 will be supply into the absorption vessel through pressure drop method and the high pressure will also ease the absorption process.

3.2.1.2 Raman spectroscopy.

The portable Raman Spectrometer manufactured by Stellar Net was used. The laser source had wavelength of 785 nm and power of 500 mW. The spectrometer had resolution of 4cm^{-1} and signal to noise ratio of 1000:1.The Spectra Wiz software was used to capture the Raman spectrum after an optical fiber probe of Raman spectrometer was connected with the CO_2 absorption cell. The result will show the covariance on CO_2 loading because the software detects all the peak ratio gives out by the Raman spectrum.

3.2.2 Simulation Methods.

3.2.2.1 Partial Least Square (PLS) Regression

After the data was obtained and tabulated, a measurement of CO_2 loading by using multivariate calibration technique is used. One of the techniques is Partial Least Square Regression (PLS). In this project, PLS technique is used because it had proven to be a better multivariate calibration technique when it eliminates the dimension of the Raman spectrum on the CO_2 loading by correlating the normalized x and y variables simultaneously. However, before developing calibration models, the data have been divided into two types of data set, calibration and validation data set. The calibration data set will be used to construct few calibration models while the validation data set will be used to evaluate the performance of the constructed models.

3.2.2.2 Matlab Simulation.

In this project, modeling of the PLS regression was done by using MATLAB software to predict the CO_2 loading. Then, the evaluation of prediction calibration models will be evaluated by using coefficient of determination (R^2) and Mean square error (MSE). R^2 is defined as how well the data is fitted while MSE defined as the mean square difference between predicting and original data. After that, proceed with the validation model. Therefore, comparison can be made and the performance of the models can be verified.

The steps for Matlab simulation are as shown below:

1. Before proceed with PLS models, the raw data set need to be normalized by using zscore command.

   Example: [Xn,meanX,stdX]=zscore(x); (1)

[Yn,meanY,stdY]=zscore(y); (2)

2. In Matlab software, use ‘plsregress’ command to perform PLS regression with the same number of components as predictors.
   Example: [XL,yl,XS,YS,beta,PCTVAR]= plsregress(xcalib,ycalib,8).
3. Then plot the percentage variance explained in the response as a function of the number of components.
   Example: plot (1:8,cumsum(100*PCTVAR(2,:)),'-bo');
   xlabel('Number of PLS components');
   ylabel('Percent Variance Explained in y');
4. Using the percent variance explained in Y calibration, precede to computes the ‘number of variance contribution’-component model.
   Example:
   [XL,yl,XS,YS,beta,PCTVAR,MSE,stats]=
   plsregress(xvalid,yvalid,6);
   yfit = [ones(size(X,1),1) X]*beta;
   plot(y,yfit,'o').

5. Proceed to calculate the R^2 statistic.
   Example: TSS = sum((y-mean(y)).^2);
   RSS = sum((y-yfit).^2);
   Rsquared = 1 - RSS/TSS
6. Repeat step 1 until 4 by using data for x validation and y validation data set.

3.3 Process Flow of the project.

This is the process flow for this research project that must be follow so that the objectives of the study can be successfully achieved.

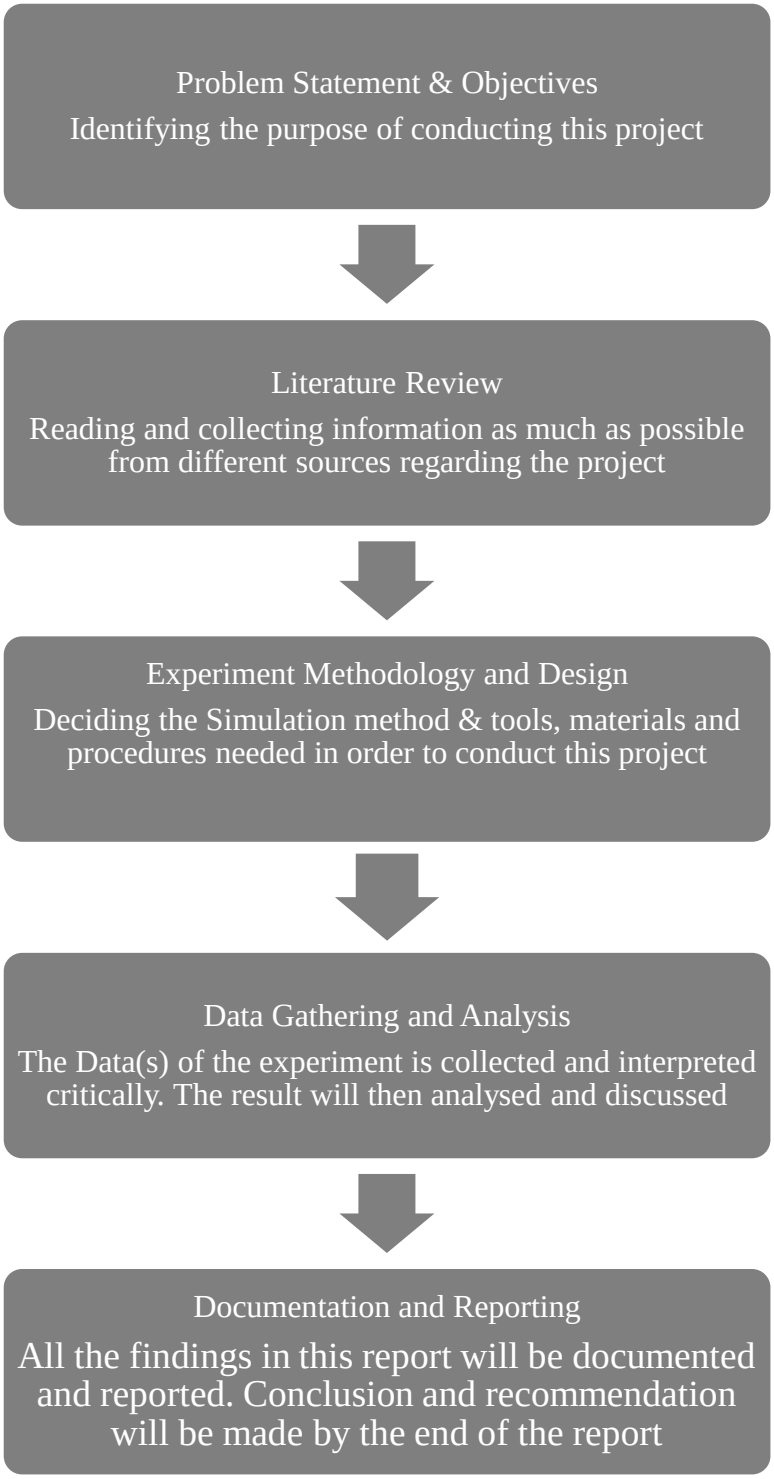

Figure 3.1 Project Flow

3.4 Gantt Chart and Key Milestone

No	DETAILS/WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Discussion with supervisor to proceed on FYP2.														
2	Critical analysis of literature review addition.														
3	Constructing the Calibration models.														
4	Constructing validation models														
5	Upgrading and testing the results.														
6	Development of new models.														
7	Preparation of Report progression.														
8	Submission progress report.														

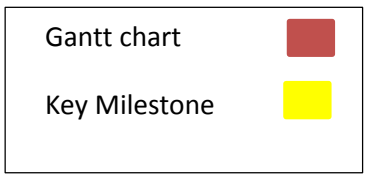

Table 3.1 Project Gantt chart and Key Milestone.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Raman Shift based on CO_2 Solubility.

After completing conducting the experiment, the Raman spectrum had been obtained successfully after the absorption process occurs inside Methyldiethanolamine (MDEA) solution. There were three different MDEA concentrations that had been used while conducting the experiment which are 10%, 20% and 30%. The results of the experiment are as shown below.

Experiment A: Determination of Raman Shift (cm^{-1}) in 10% MDEA concentration.

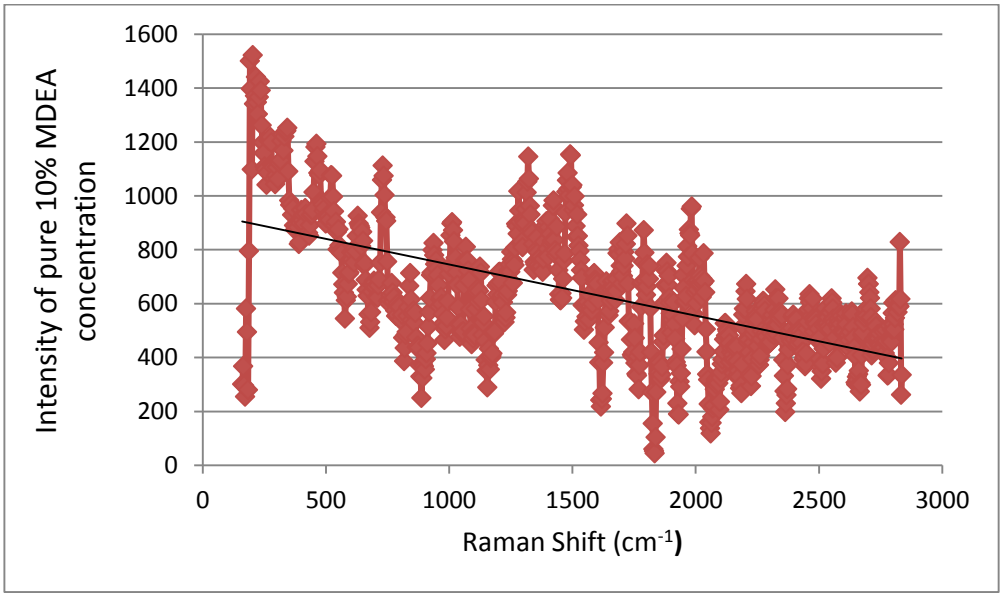

Figure 4.1 Raman Shift (cm-1) vs. Intensity of 10% pure MDEA

Experiment B: Determination of Raman Shift (cm-1) in 20% MDEA concentration.

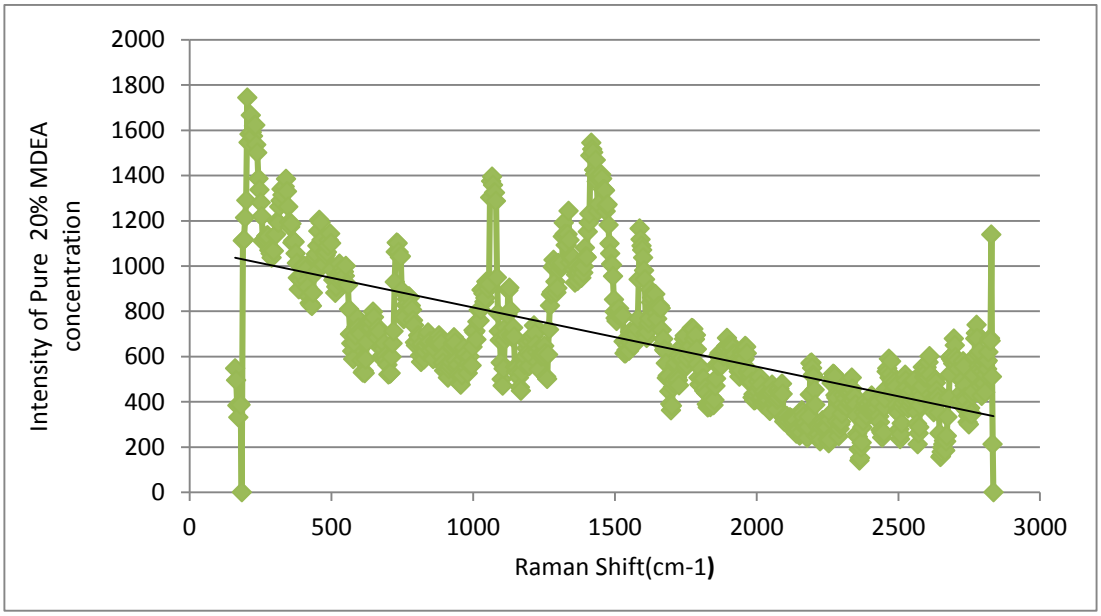

Figure 4.2 Raman Shift (cm-1) vs. Intensity of 20% pure MDEA

Experiment C: Determination of Raman Shift (cm-1) in 30% MDEA concentration.

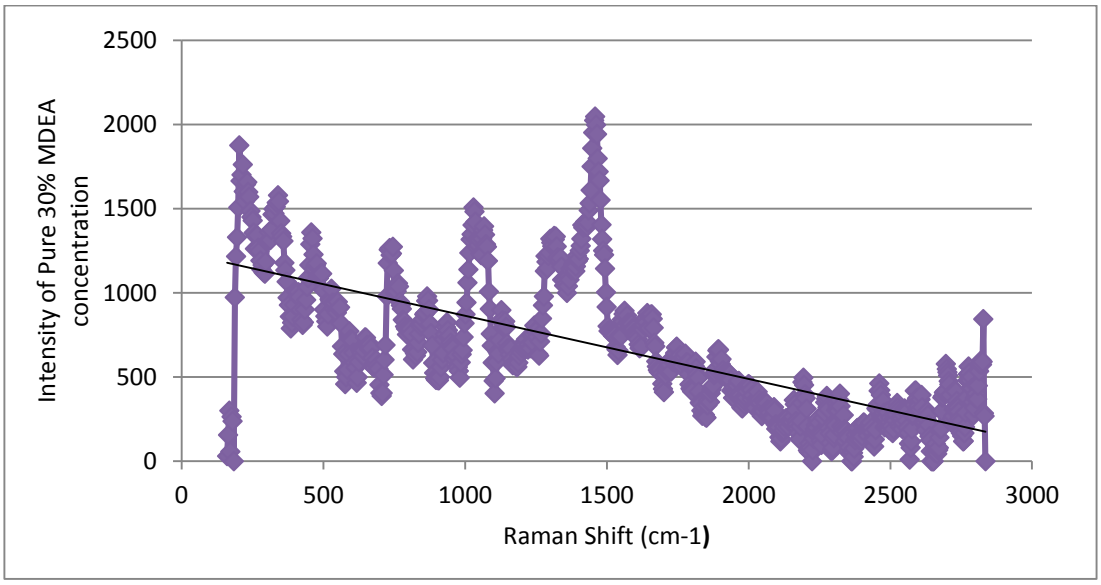

Figure 4.3 Raman Shift (cm-1) vs. Intensity of 30% pure MDEA

Based on graph 4, 5 and 6, each concentration has Raman Shift ranging from 1 until 2800 cm^{-1}. In other words, the Raman Shift represents the values of CO_2 loading based on the peaks. But, with just the experimentation process, the CO_2 loading cannot determine. This is because the data point is huge and the CO_2 cannot be read through the graph. One of the ways to obtain the CO_2 loading is through multivariate calibration. Thus, it proves that Partial Least Squares (PLS) regression technique is needed to be done to construct a statistical modeling. The Matlab simulation was used to execute the PLS regression which acts as a medium.

From the Matlab simulation, PLS regression can be used to construct a statistical calibration and validation models. The Coefficient of determination (R^2) and Mean Square Error (MSE) can also be calculated. Therefore, how much the CO_2 loading that had been soluble inside the MDEA solution can be determined.

4.2 The constructed calibration and validation models.

The data obtain from the Raman Shift had been divided into two parts. One part is 70% of the data that represent the calibration data and the other 30% represent the validation data. At first, the calibration and validation models were constructed individually. By using the 10% Methyldiethanolamine (MDEA) concentration data the models was constructed and the Coefficient of determination (R^2) as well as Mean Square Error (MSE) was calculated. After that, proceed the methods with 20%, 30% and the combination of the three MDEA concentrations. The results of the constructed models are as shown below.

Models 1**:** CO_2 absorption inside MDEA with 10% concentration.

Calibration models:

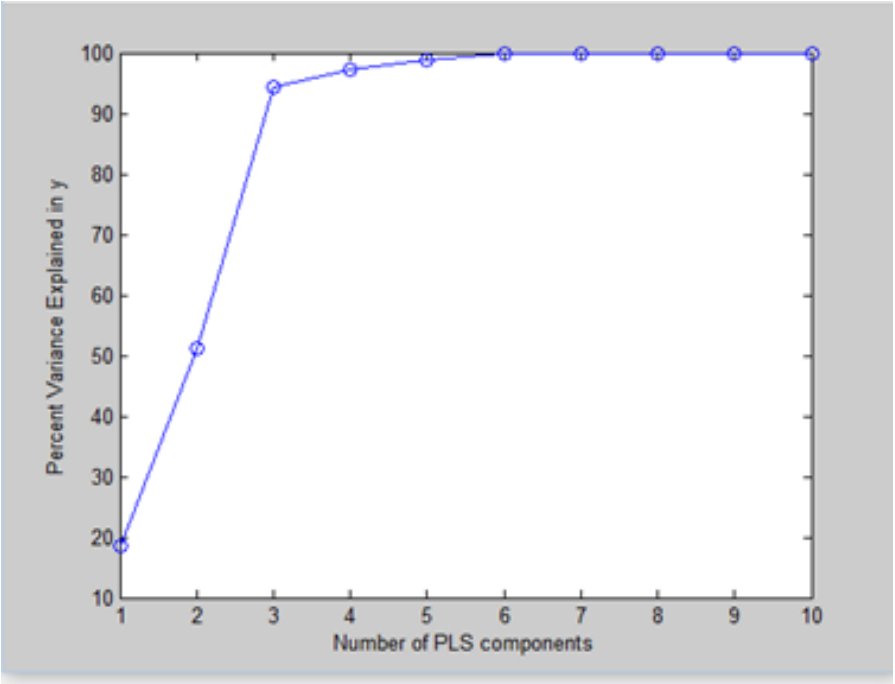

Figure 4.4 Number of PLS components vs. Percent variance Explained in y.

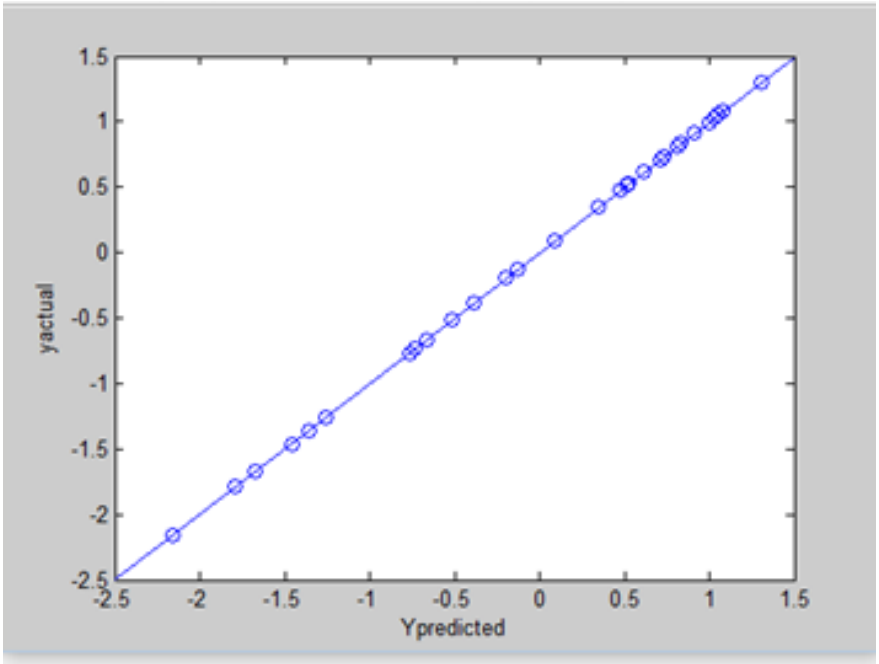

Figure 4.5 Y predicted vs. Y actual

Validation model:

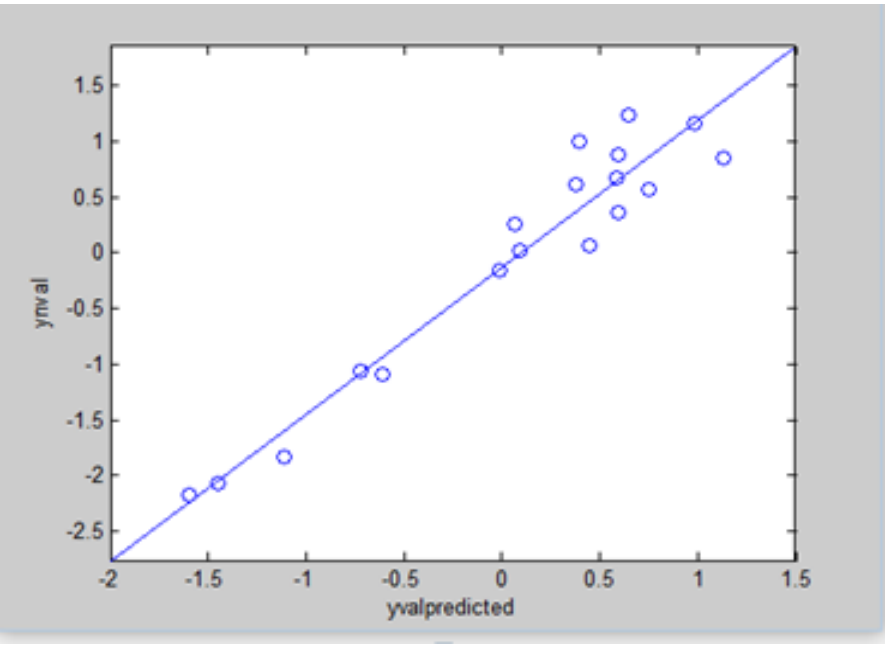

Figure 4.6 Y validation predicted vs. Y validation actual.

The first graph of the calibration models shows the covariance from the number of PLS components that contribute the most important part for the data to the CO_2 loading based on the Raman Shift. The second calibration graphs represent a new set of transform variables from the projection of variables X (Raman Shift) and Y (CO_2 loading). The value shows a better best fit line because we only take the value that contributes the most from the variance before. As for the validation models, the validation data will be used to justify the calibration models by normalize the data from the mean and standard deviation from the calibration data set.

4.2.1 Coefficient of determination (R2) and Mean Square Error (MSE) results.

Table 4.1 Models for 10% MDEA concentration.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8666
Mean Square Error (MSE)	1.0587e-006	0.1587

Table 4.2 Models for 20% MDEA concentration.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	0.9999	0.9333
Mean Square Error (MSE)	1.0972e-004	0.0639

Table 4.3 Models for 30% MDEA concentration.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	0.9998	0.9274
Mean Square Error (MSE)	1.6493e-004	0.0901

Table 4.4 Models for three combinations of MDEA concentrations.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	0.9651	0.6831
Mean Square Error (MSE)	0.0347	0.3599

Further calculation on R^2 statistic and Mean Square Error (MSE) will be proceeded to justify the graphs. R^2 is a statistical measure of how well the regression line approximates the real data points. An R^2 of 1 indicates the regression line perfectly fits the data point. So, the focus point of this project is to achieve a statistical modelling almost reaching to 1. While MSE is measurement of how close a fitted line is to data points. For every data point, you take the distance vertically from the point to the corresponding y value on the curve fit (the error). MSE of 0 indicates the error is almost zero. Therefore, the MSE targeted results for the model is zero.

From the tables, the highest R^2 for calibration models is 1.000 and the lowest is for the combination of the three concentrations which only reaching 0.9651. This shows that for 10% MDEA concentration it is the best fit line obtained. For validation models, the highest R^2 is 0.9333 and the lowest is 0.6831. This shows that the results for the

combination of the three concentrations were only reaching 70% and further improvement are needed to be done.

For Mean Square Error (MSE), the calibration model shows a good result when the highest value is 0.0347 and for validation models the highest is 0.3599 meaning that the error almost to zero but the validation results can still be improved for better results.

4.3 Modified calibration and validation models.

The modified calibration and validation model was constructed to strengthen the results of the models. But, the modified will be focusing on individual concentration for example on 10% Methyldiethanolamine (MDEA) concentration. This is because, the validation results for 10% MDEA is the weakest. Inside 10% MDEA Raman Shift data, further specification on trial and testing on the data was done to identify the effects on the models. For instance, the Raman Shift between 1000cm^{-1} until 1100 cm^{-1} was taken and identified as 'A' and 'B' is the Raman Shift ranging from 1100 until 1200 cm^{-1} . The A was chosen to be analyzing because in range A, it is where the bicarbonate and carbonate produce the highest peaks while B is where the water peaks shows the highest. Then, a calibration and validation models were constructed as usual for further development so that it can be learned and analyze to improve the combination models results.

10% MDEA concentration

Table 4.5 Model A- 1000-1100(cm^{-1}) Raman Shift.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	0.9389	0.0194
Mean Square Error (MSE)	0.0592	1.1664

Table 4.6 Model B- 1100-1200(cm^{-1}) Raman Shift.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	0.8461	-0.5499
Mean Square Error (MSE)	0.1490	1.8435

Modified models based on A.

Table 4.7 Model 1- 10% MDEA+A.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8702
Mean Square Error (MSE)	1.5838e-006	0.1543

Table 4.8 Model 2- 10% MDEA+A^2.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8652
Mean Square Error (MSE)	1.8089e-006	0.1603

Table 4.9 Model 3- 10% MDEA+A^3.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8608
Mean Square Error (MSE)	3.4775e-006	0.1656

Table 4.10 Model 4- 10% MDEA+1/A.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8795
Mean Square Error (MSE)	2.3361e-006	0.1433

Table 4.11 Model 5- 10% MDEA+1/A^2.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8833
Mean Square Error (MSE)	2.5846e-006	0.1389

Table 4.12 Model 6- 10% MDEA+1/A^3.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8853
Mean Square Error (MSE)	2.8478e-006	0.1364

Modified models based on B:

Table 4.13 Model 7- 10% MDEA+B.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8695
Mean Square Error (MSE)	1.3369e-006	0.1553

Table 4.14 Model 8- 10% MDEA+B^2.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8693
Mean Square Error (MSE)	1.5952e-006	0.1555

Table 4.15 Model 9- 10% MDEA+B^3.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8719
Mean Square Error (MSE)	2.4780e-006	0.1523

Table 4.16 Model 10- 10% MDEA+1/B.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8779
Mean Square Error (MSE)	2.6046e-006	0.1452

Table 4.17 Model 11- 10% MDEA+1/B^2.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8795
Mean Square Error (MSE)	3.2032e-006	0.1433

Table 4.18 Model 12- 10% MDEA+1/B^3.

	Calibration Model	Validation Model
Coefficient of determination(R^2)	1.0000	0.8799
Mean Square Error (MSE)	3.6041e-006	0.1428

For modified models based on ‘A’, Model 6 shows an improvement on Coefficient of determination (R^2) from before when it reach 0.8853 for the validation models. Before this, the Coefficient of determination (R^2) was only 0.8666 meaning that the modified model is a success. Moreover, for the Mean Square Error (MSE), the results also decrease. The lowest MSE from modified models is 0.1364 and before this for 10% MDEA was 0.1587. These prove that the error is reducing after gone through the modified process, meaning that the results can be improved.

Proceed to modified models based on ‘B’, Model 12 shows the highest improvement of Coefficient of determination (R^2) for validation models when it reached 0.8799. For MSE, it decreases from 0.1587 to 0.1428. From these two modified models basis, the modified models based on ‘A’ shows a better improvement rather than based on ‘B’.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion.

In this sub-chapter, a few major conclusions have been identified throughout this research project.

For the three different Methyldiethanolamine (MDEA) concentrations, based on the Raman Shift, the Carbon Dioxide (CO_2) loading reacts differently based on the graph represent. The peaks which represents the CO_2 loading proves that CO_2 reacts differently in different MDEA concentration but it does not shows that the higher concentration have the better results.

Moving on to the constructed calibration and validation models, the statistical modelling of the models can be used to identify the CO_2 loading and the Coefficient of determination (R^2) as well as the Mean Square Error (MSE). Results indicates that the models can be used. The R^2 illustrate the best fit line for the models while the MSE point out the least errors obtained.

Last but not least, the modified models prove an improvement can be done to improve the results. Thus, further testing and simulation can be done to ensure the results can be used to strengthen the models.

In conclusion, when dealing with CO_2 capturing process, the first step towards handling the CO_2 is to measure the CO_2 loading so that it can operate in better

efficiency. Thus, process optimization can be achieved. After the calibration models was constructed by using partially least square regression (PLS) technique, the CO_2 loading can be identify and obtained. The constructed models will be evaluated to check its performance by using the validation data set. The scatter results based on reasonable correlation between fitted and observed responses will be confirmed by the R^2 statistic.

5.2 Recommendation.

As for recommendation, further simulation testing especially on the modified models need to be done to ensure a better coefficient if determination (R^2) and mean square error (MSE) results. Below are a few recommendations on this research project:

1. The raw data can be further study and analyze to learn how the effect on Raman Shift towards the CO_2 loading.
2. Provide a new basis for modified models such as produce a new basis for 'C'.
3. Run the simulation testing base on the new basis produced.

After undergone the further recommendation, proceed with the three combination models and calculate the coefficient if determination (R^2) and mean square error (MSE). Then, identify the data effects and take a new action to improve the results.

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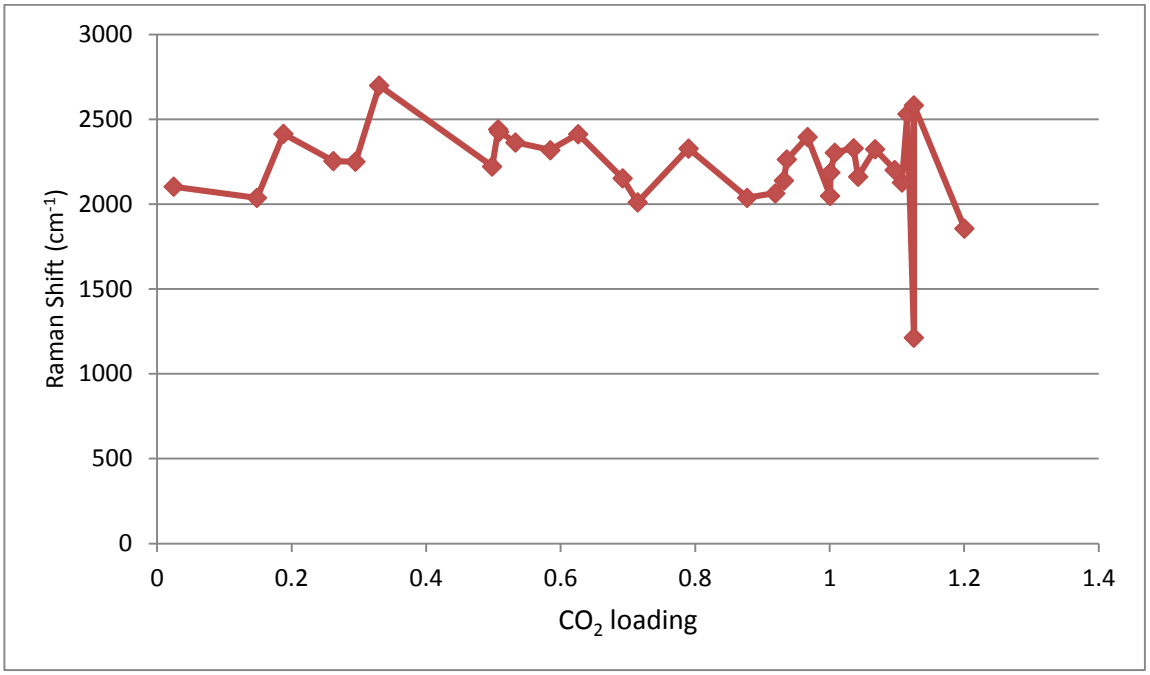
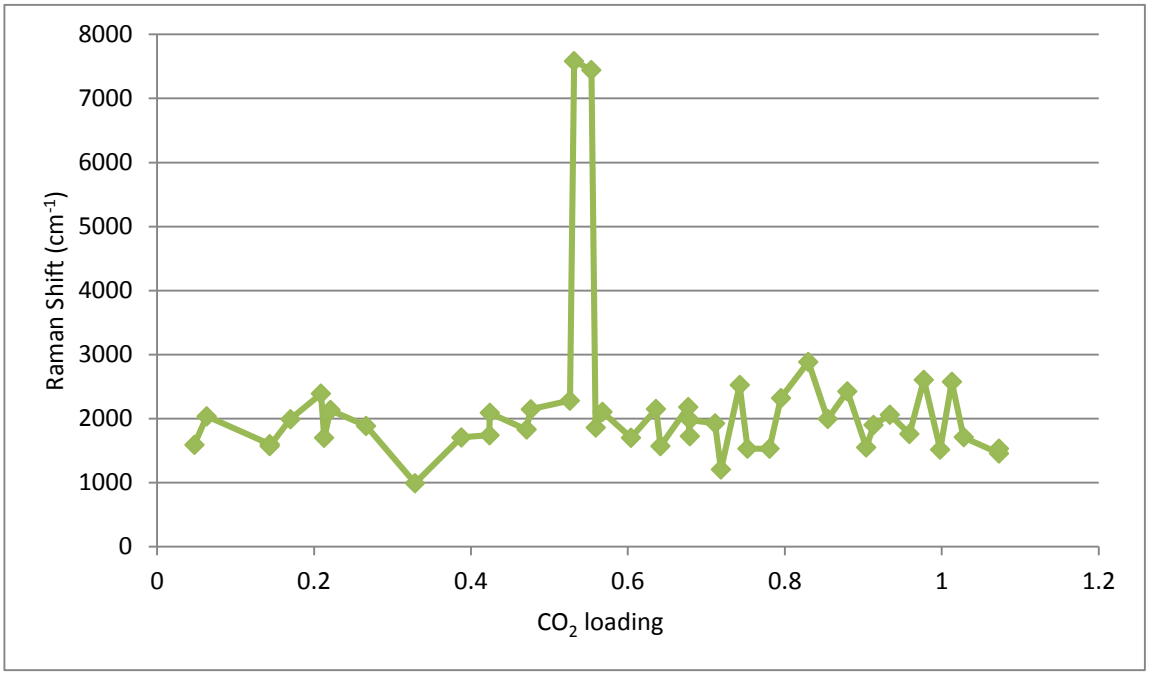
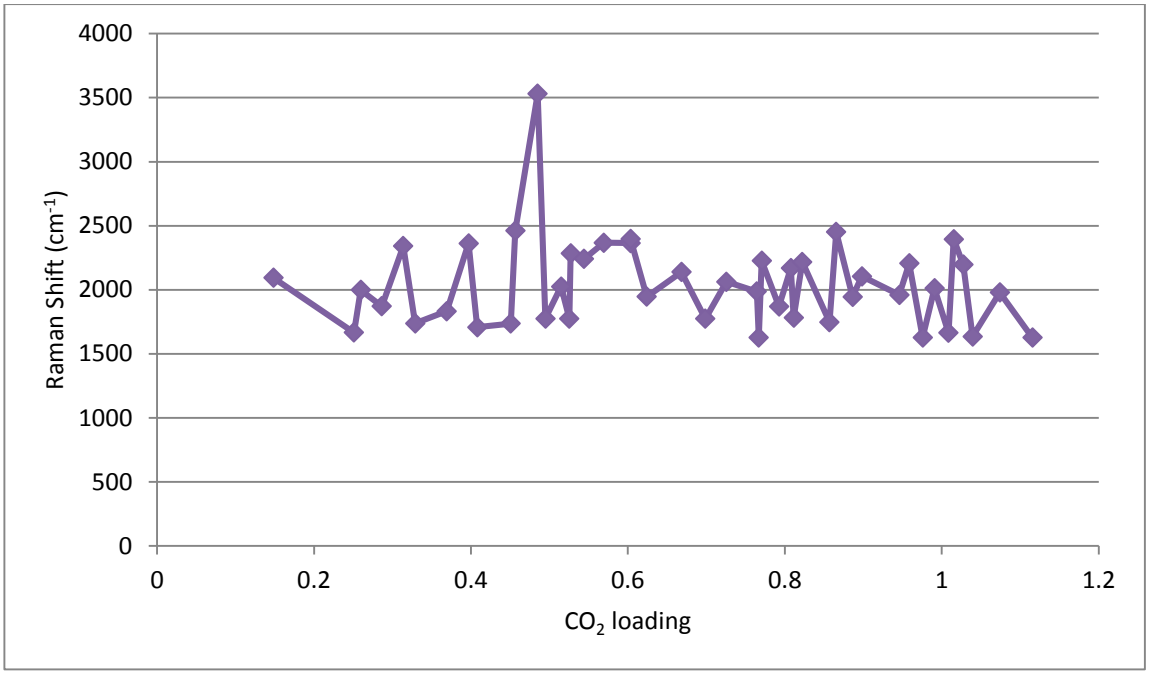
APPENDICES



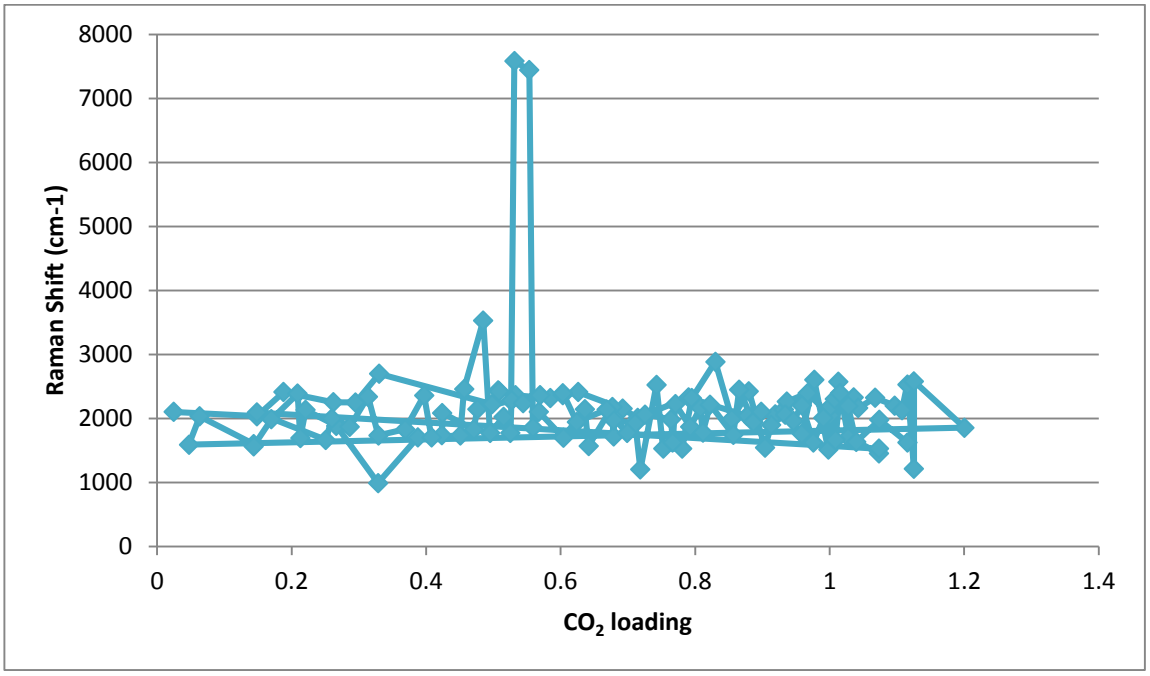
Appendix 1 Raman Shift (cm-1) vs. CO_2 loading in 10% MDEA concentration for calibration.



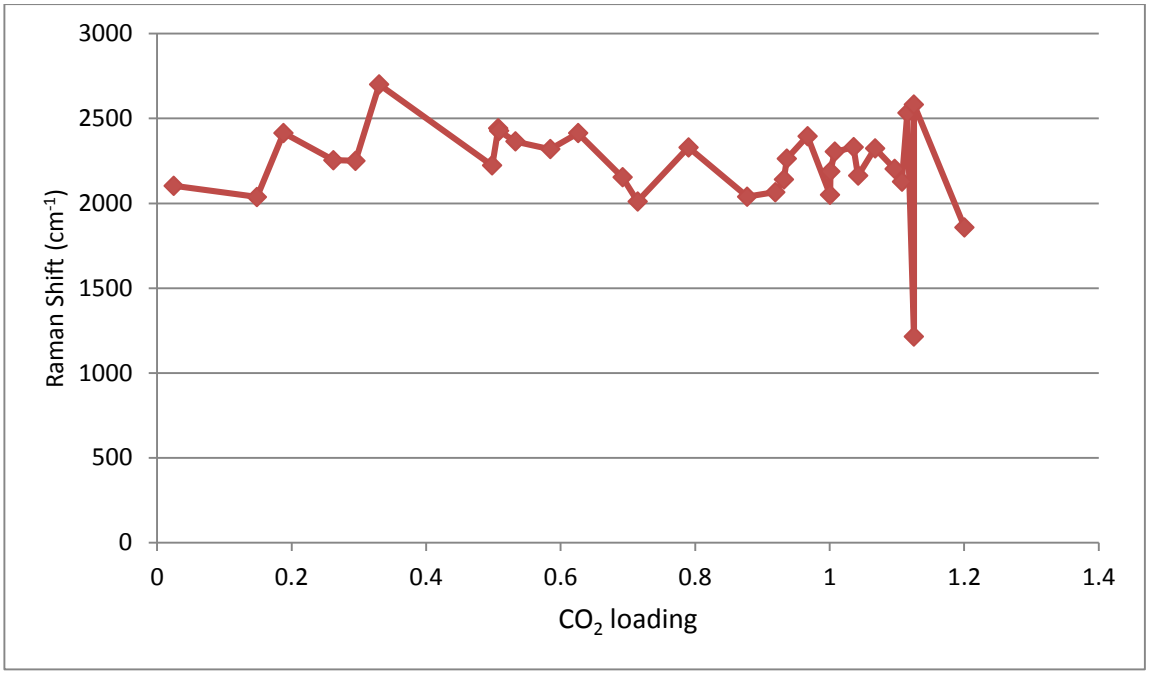
Appendix 2 Raman Shift (cm-1) vs. CO_2 loading in 20% MDEA concentration for calibration.



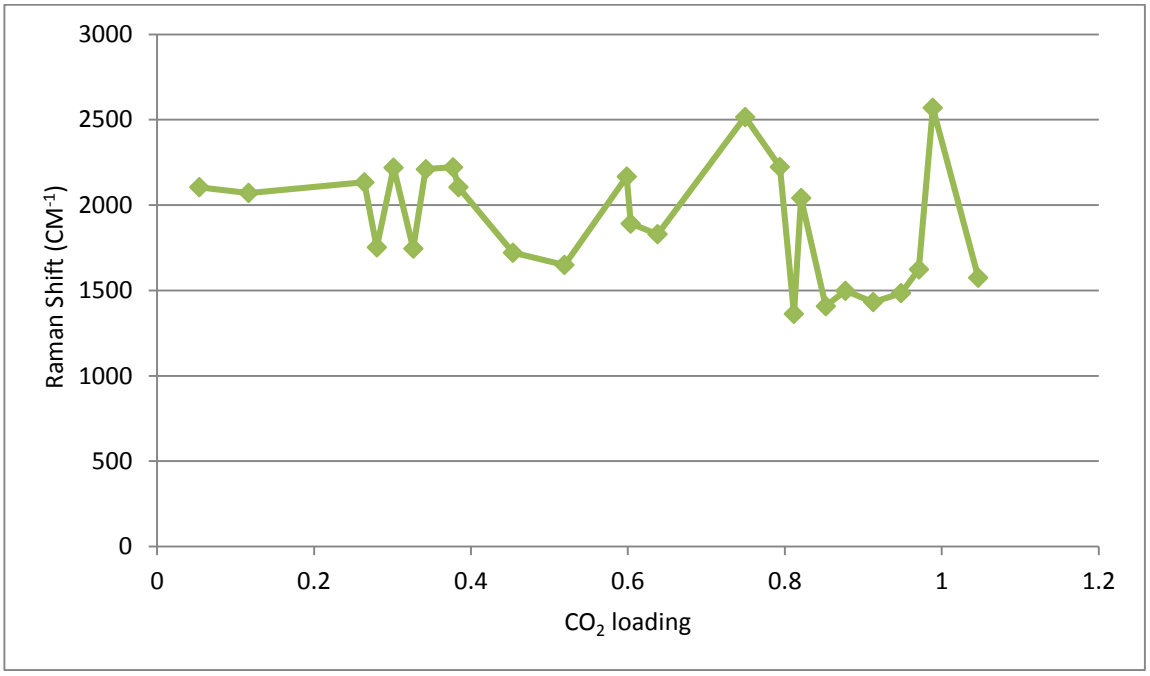
Appendix 3 Raman Shift (cm-1) vs. CO_2 loading in 30% MDEA concentration for calibration.



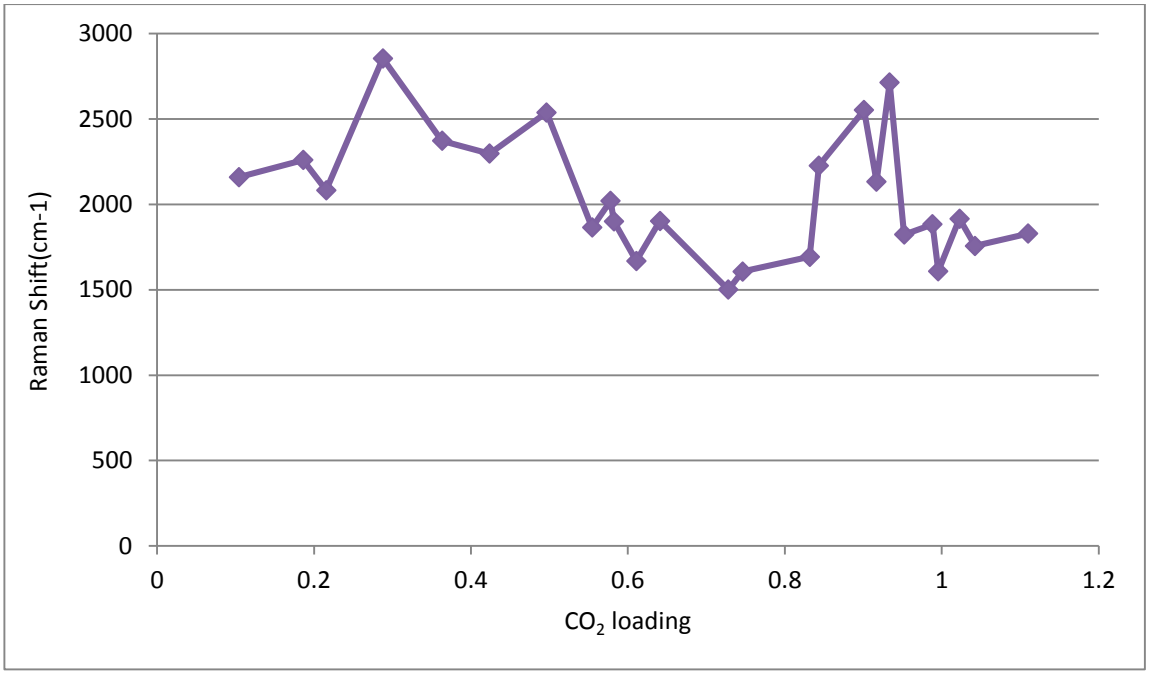
Appendix 4 Raman Shift (cm-1) vs. CO_2 loading in three different MDEA concentrations for calibration.



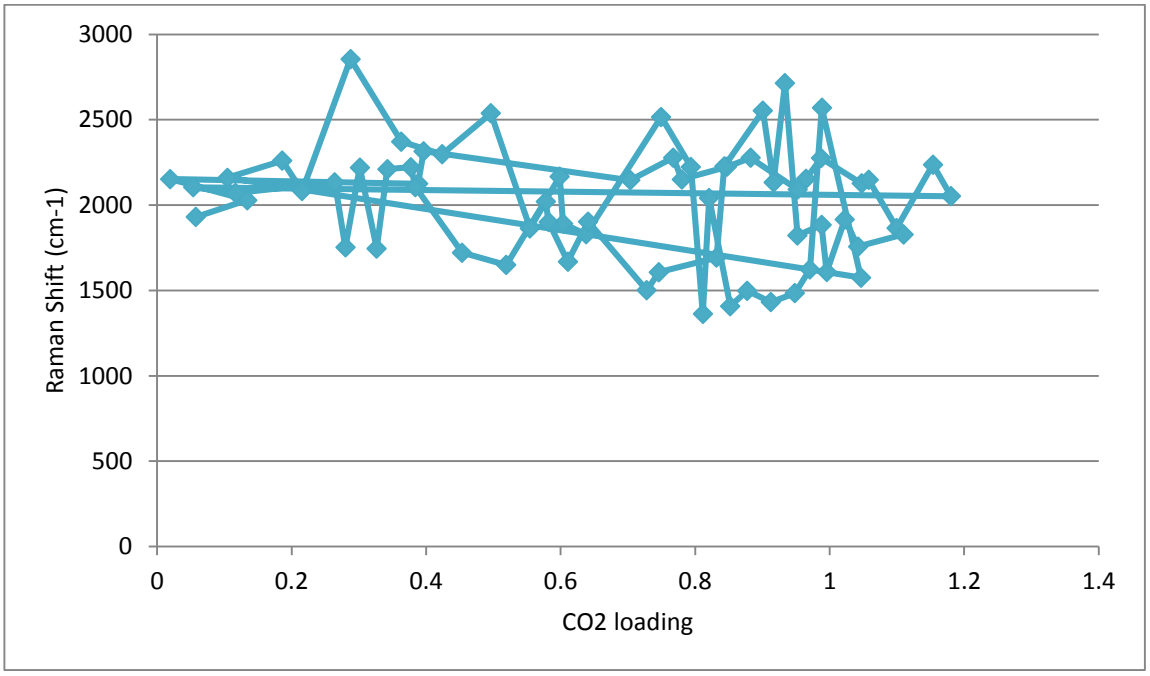
Appendix 5 Raman Shift (cm-1) vs. CO_2 loading in 10% MDEA concentration for validation.



Appendix 6 Raman Shift (cm-1) vs. CO_2 loading in 20% MDEA concentration for validation.



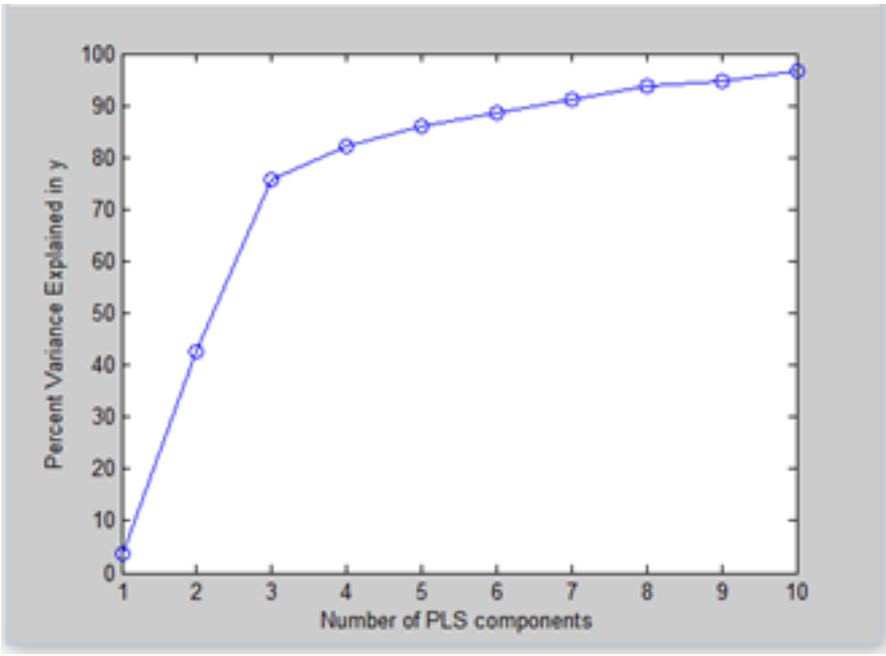
Appendix 7 Raman Shift (cm-1) vs. CO_2 loading in 30% MDEA concentration for validation.



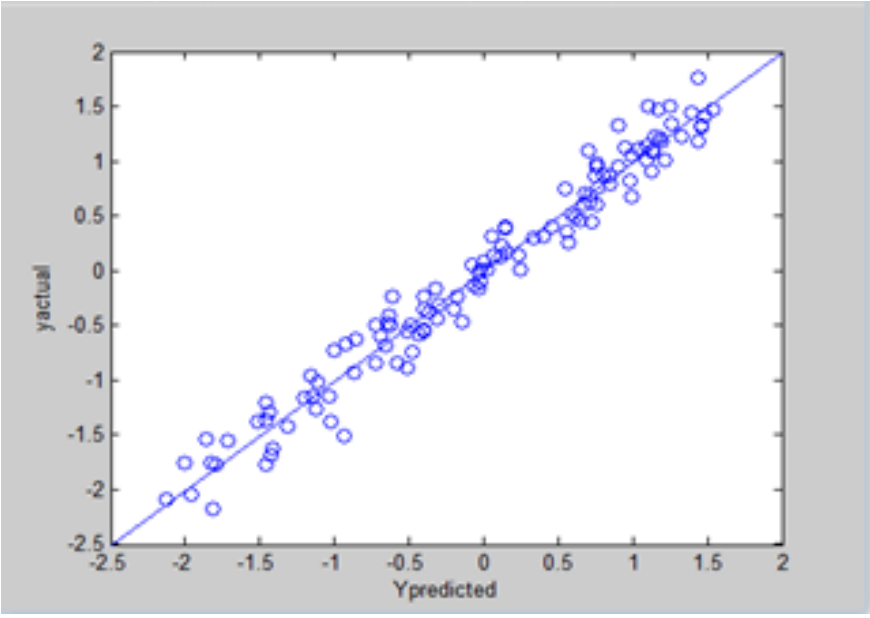
Appendix 8 Raman Shift (cm-1) vs. CO_2 loading in three different MDEA concentrations for validation.

Models 2 CO_2 absorption inside MDEA with the combination of 20% concentration.

Calibration models.

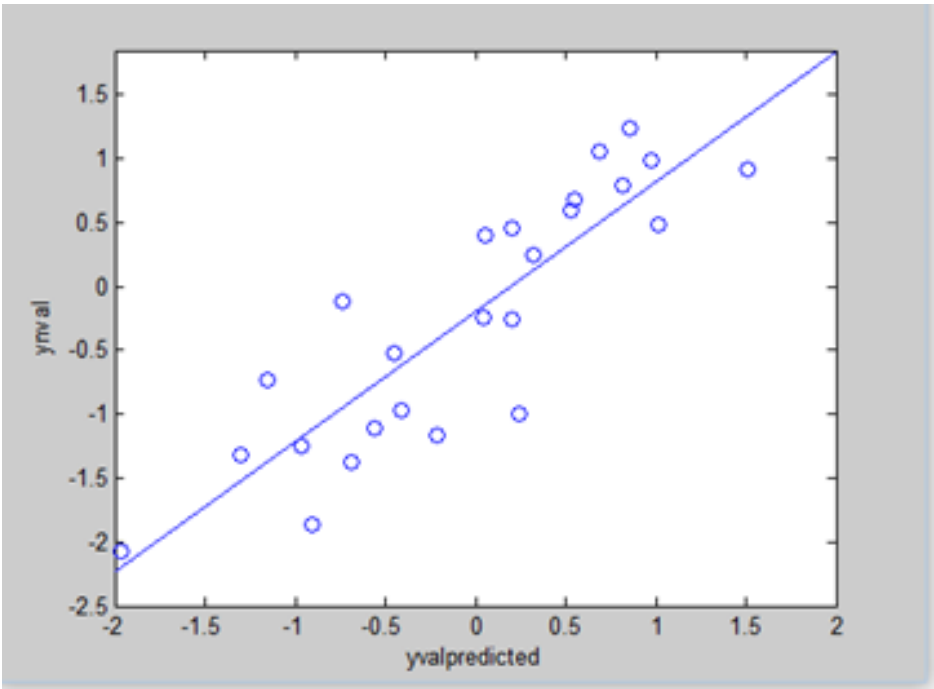


Appendix 9 Number of PLS components vs. Percent variance Explained in Y.



Appendix 10 Y predicted vs. Y actual.

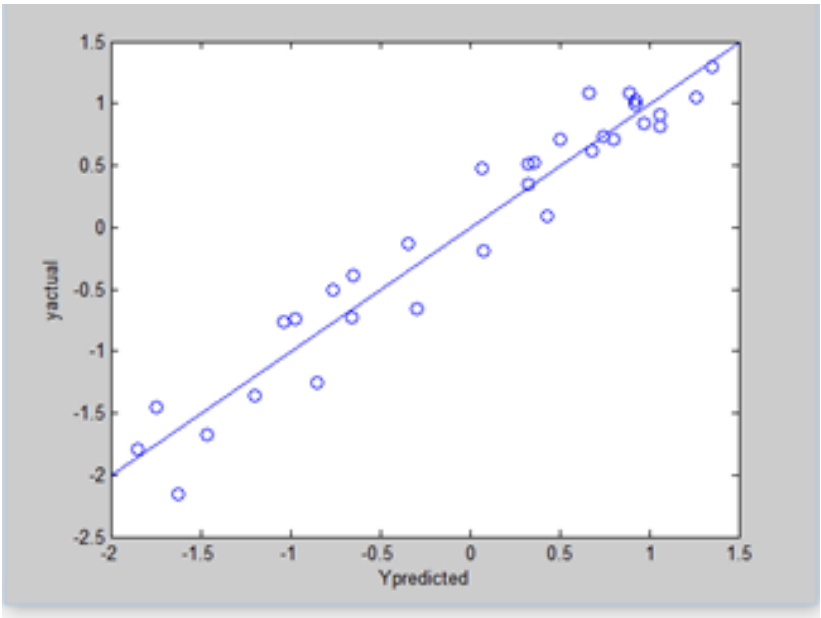
Validation models.



Appendix 11 Y validation predicted vs Y validation actual

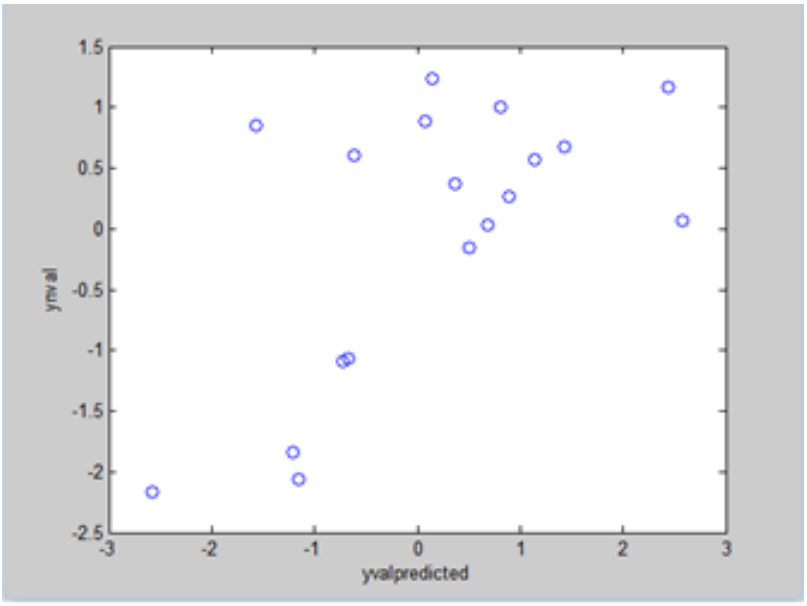
Models A

Calibration Models.



Appendix 12 Y predicted vs. Y actual.

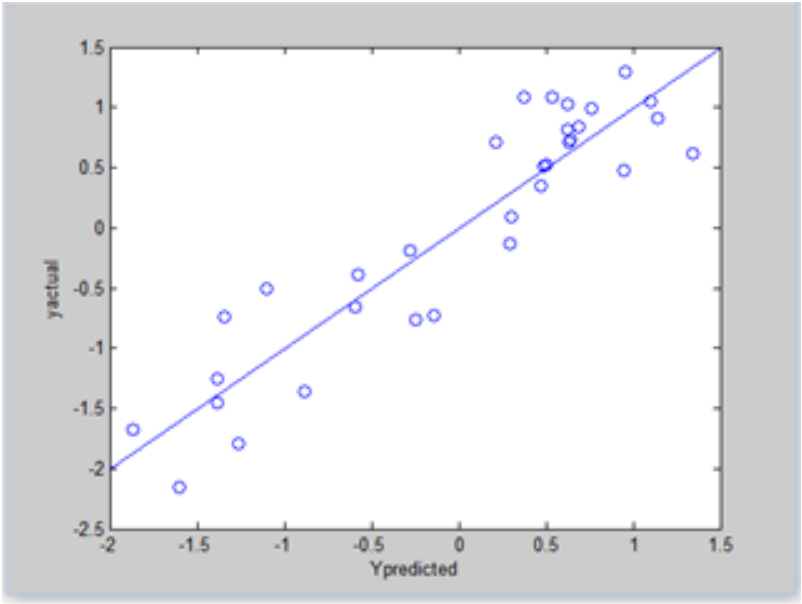
Validation Models.



Appendix 13 Y validation predicted vs Y validation actual.

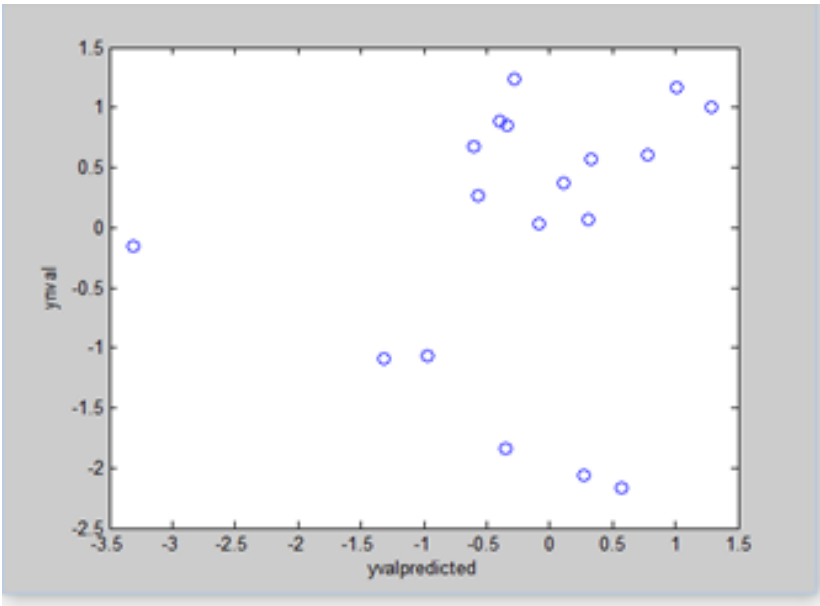
Models B

Calibration Models.



Appendix 14 Y predicted vs. Y actual.

Validation Models.



Appendix 15 Y validation predicted vs Y validation actual.