# PROCESS MONITORING OF $CO_2$ ABSORPTION IN DIETHANOLAMINE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

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NORHASHIMA BINTI MOKHTAR B. ENG. (CHEMICAL) 2013 UMP

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

# SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature:

Name of Supervisor: NUR AMINATULMIMI BT ISMAIL

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Date:

## STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :

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Date : JANUARY 2013

*Special dedication to my supervisor, my family members,*

*my friends, my fellow colleague and all faculty members*

*for all your care, support and believe in me.*

# ACKNOWLEDGEMENT

In order to complete this project, I met a number of people, namely lecturers and professional. All of them have assisted me in many ways towards completing this research. I would like to thank several people who have contributed either directly or indirectly to the completion of this final year project 2. I would like to express my sincere appreciation to my supervisor, Miss Nur Aminatulmimi Binti Ismail for her valuable guidance, advices, constant support and her valuable time towards finishing my final year project 2. Following her guidance, I am able to understand more about this research where to collect the information that is needed and how to use the information properly to produce successful report. I am really thankful and indebted with her for all her cooperation, tolerance and commitment in assisting me to make this project success.

I also would like to thanks the personnel of Faculty of Chemical Engineering and Natural Resources (FKKSA), especially lecturers, for their assistance and corporation and also to FKKSA laboratory staff. Not to be forgotten, my biggest thanks to Dr Ramesh, Dr Kamal and Tuan Haji Mohd Noor as my panels for their comments during the final year project 1 presentation in order to improve the study. Lastly, I am also obliged to express my appreciation towards my beloved family members for their moral supports due to complete this project. Special thanks to all my friends that also entitled for an appreciation, as they have been all very supportive and always assist me in various occasions. Thanks to all of you for everything. Alhamdulillah.

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| | |
|---|---|
| ATR | Attenuated Total Reflectance |
| $CO_2$ | Carbon dioxide |
| DEA | Diethanolamine |
| $DEACOO^-$ | Carbamate |
| FTIR | Fourier Transform Infrared Spectroscopy |
| $H_2O$ | Water |
| MDEA | Methyldiethanolamine |
| MEA | Monoethanolamine |
| MSPC | Multivariate Statistical Process Control |
| PCs | Principal Component |
| PCA | Principal Component Analysis |
| PLS | Partial Least Squares |
| SNR | Signal noise-to-noise ratio |

# LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| $\lambda$ | Latent |
| *atm* | Atmospheric |
| *ml* | Mililiter |
| $M$ | Molarity |
| *ppmv* | Part Per Million By Volume |
| $p$ | Loading Vector |
| $t$ | Score Vector |
| $t$ | Time |
| $X$ | Matrix |

# PROSES PEMANTAUAN PENYERAPAN $CO_2$ DALAM DIETHANOLAMIN MENGGUNAKAN SPEKTROSKOPI INFRAMERAH TRANSFORMASI FOURIER (FTIR)

## ABSTRAK

Penyelidikan ini adalah tentang pemantauan penyerapan proses karbon dioksida ($CO_2$) dalam larutan alkanolamin, Diethanolamin (DEA) oleh Spektroskopi Inframerah Transformasi Fourier (FTIR). Ia adalah penting untuk menangkap gas $CO_2$ dari gas serombong untuk mengurangkan pelepasan gas dalam atmosfera. Hari ini, penyerapan $CO_2$ oleh pelbagai jenis larutan alkanolamin adalah salah satu proses dominan perindustrian untuk menyelesaikan peningkatan pelepasan gas rumah hijau. Dalam kajian ini, DEA digunakan sebagai penyerap dalam penyerapan $CO_2$. Objektif utama kajian ini adalah untuk mendapatkan spektrum FTIR bagi sistem $CO_2$-DEA pada kepekatan dan kadar aliran $CO_2$ yang berbeza. Kepekatan DEA adalah 2M, 4M dan 6M. Kadar aliran $CO_2$ adalah 100 dan 200 ml/min. Eksperimen telah dijalankan pada kelajuan pengacau yang tetap, 120rpm. Objektif kedua kajian ini adalah untuk mensintesis spektrum FTIR untuk mencirikan sistem menggunakan Analisis Komponen Utama (PCA). Eksperimen telah dijalankan dengan mengambil sampel bagi setiap 1, 2, 3, 4, 5, 6 dan 7 jam selepas penambahan $CO_2$ dalam DEA. Sampel dianalisis menggunakan FTIR. Sebagai kesimpulan, Spektra FTIR bagi sistem $CO_2$-DEA berjaya diperolehi. FTIR sesuai untuk digunakan bagi memantau proses penyerapan $CO_2$ dalam kepekatan DEA dan kadar alir $CO_2$ yang berbeza kerana ia memberi analisis yang cepat dan pengukuran yang boleh dipercayai. Teknik PCA boleh digunakan untuk mencirikan tingkah laku penyerapan dengan menggunakan spektrum yang diperolehi dari eksperimen. Dengan itu disyorkan, lebih analisis perlu dilakukan untuk mendapat data yang lebih baik dalam membuat perbandingan setiap sistem.

# PROCESS MONITORING OF $CO_2$ ABSORPTION IN DIETHANOLAMINE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

## ABSTRACT

The research is about the process monitoring of carbon dioxide ($CO_2$) absorption in alkanolamine aqueous solution, Diethanolamine (DEA) by Fourier Transform Infrared Spectroscopy (FTIR). The $CO_2$ gas level in the atmosphere is rising fast because of the human activities and industry process. It is important to capture $CO_2$ gas from the flue gas to reduce the emission of gasses in atmosphere. Today, absorption of $CO_2$ by various alkanolamine solutions is the dominant industrial process for solving the increasing of greenhouse gas emission. In this study, DEA is use as an absorbent in absorption of $CO_2$. The first objective of the study is to obtain the FTIR spectrum of $CO_2$-DEA system at different DEA concentration and $CO_2$ flow rate. The concentrations of DEA are 2M, 4M and 6M. The $CO_2$ flow rate is 100 and 200 ml/min. The experiment was performed at the constant stirrer speed, 120rpm. The second objective of the study is to synthesize FTIR spectrum to characterize the system using Principal Component Analysis (PCA). The experiment were be conducted by taking the sample for every 1h, 2h, 3h, 4h, 5h, 6h and 7h after $CO_2$ addition in DEA solution. The samples were analyzed using FTIR. As the conclusion, FTIR spectra for $CO_2$-DEA system are successfully obtained. FTIR are feasible to be used to monitor the absorption process of $CO_2$ in different DEA concentration and $CO_2$ flowrate because it gives a fast analysis and reliable measurement. The multivariate technique of Principal Component Analysis (PCA) can be applied to characterize the absorption behavior by resulting the spectrum obtained from the experiment. As the recommendation, the more analysis should be done to have better data in making comparison of each system. Besides that, the other variable also can be observed like temperature and pressure. The other amine also can be used as an absorbent like AMP and blending of MDEA with DEA.

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# CHAPTER 1

# INTRODUCTION

This chapter provide the general ideas on the subject that are going to be study including background of proposed study, problem statement, research objectives, scope of proposed study, expected outcome and significance of proposed study.

## 1.1 Research Background

Carbon dioxide ($CO_2$) is the most abundant gas contained in the atmosphere. The amount of $CO_2$ released in the atmosphere is increasing day by day due to the human activity which is burning the fossil fuels, producing cement, combustion activities and gas flaring in the industry (Chiari and Zecca, 2011). The scenario of the $CO_2$ emissions level is shown in Figure 1.1 which is the $CO_2$ emission is getting higher on 2050 if there is no action taken. The carbon dioxide removal from the atmosphere that cause by the consumption of large amount of fossil fuels has become one of the most serious environmental problems which is now being paid attention by public authorities worldwide (Delgado et al., 2009). According to Wang et al., (2003), 80% of the world total primary energy sources and 60% of the world electricity was supplied by the fossil fuels but the burning of fossil fuels itself in industry is the main contribution to the increment of $CO_2$ emission which is the most important. As stated by Fernandes et al., (2012), the power generation from the fossil fuels, estimated for approximately 25% of global $CO_2$ emission and this are set to increase dramatically over the next 25 years. The coal-fired power plant produces and released $CO_2$ to the atmosphere, a major greenhouse gas. The greenhouses gasses will bring to the environmental global climate change. As stated by Thitakamol et al,. (2007), the coal combustion could contribute approximately 41% of the total world $CO_2$ emissions (43,676 million metric tonnes of $CO_2$) in 2030. It is important to capture $CO_2$ gas from the flue gas to reduce the emission of gasses in atmosphere. Today, absorption of $CO_2$ by various alkanolamine solution is the dominant industrial process for solving the increasing of greenhouse gas emission (Sulaiman et al., 1998). Monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) is the commonly three type of alkanolamine were used in the industry as an absorbent in removal of $CO_2$. In this study, DEA is used as an absorbent in the analysis due to the advantages to remove $CO_2$ gas. The absorption of the $CO_2$ in DEA solution will be analysed using Fourier Transform Infrared Spectroscopy (FTIR).

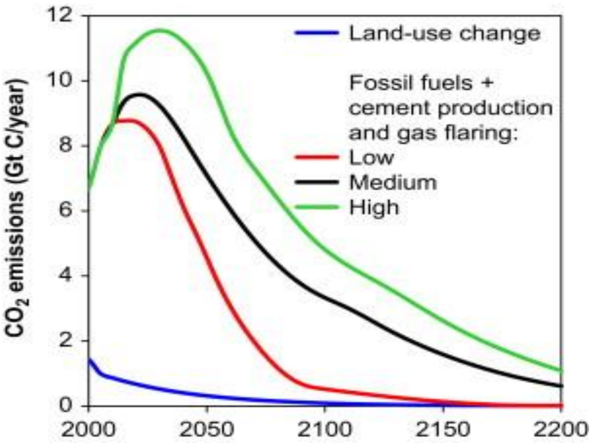


**Figure 1.1** Anthropogenic $CO_2$ emissions from fossil fuels, cement production, gas flaring and land-use changes: the present Low, Medium and High scenarios are shown

(Sources: Chiari and Zecca, 2011).

## 1.2 Problem Statement

Increase in $CO_2$ gas emission in atmosphere was brought to the global environmental problem which is increase in greenhouse gases. According to UNEP (2005), global concentrations of $CO_2$ in the atmosphere have increased from pre-industrialisation levels of approximately 280 parts per million by volume (ppmv) to approximately 316 ppmv in 1958 and rapidly increased to approximately 369 ppmv today. Global $CO_2$ concentration is estimated to increase above 750 ppmv by 2100 if there is no action is taken to solve the current situation. According to Freund, (2003), power generation from fossil fuel fired-plant which is coal and natural gas is one of the main sources of $CO_2$ emission. However, the fossil fuel-fired plant plays an important role in supply the energy and electricity to the world. The fossil fuel fired-plant should be operated flexibly in fulfil the all demand from the world. The increasing of the atmospheric concentration of greenhouse gases, the effective $CO_2$ emission strategies which are $CO_2$ capture are required to solve the problem. The $CO_2$ absorption is well suited for $CO_2$ capture in industry.

Gas treating using alkanolamines has been practiced in industry for over half a century. However, the method that we have for analysing $CO_2$ gas concentration is not sufficient and not achieves the good measurement. According to Vogt et al,. (2011), an effective solvent analysis which is considered the characteristic parameters such as the actual loading of solvent during absorption and regeneration is necessary. Today in petroleum industry, a continuous control of the capture efficiency was performed through a balance of gaseous phase by observing the $CO_2$ concentration in raw and cleaned gas which is this technique is not effective. Furthermore the operator also need to apply the empirical knowledge by enhancing the solvent flow ratio, application of additives, partial exchanges of the solvent or elevating the regenerator temperature and this all action will caused the higher operation cost and a long of time is needed in identified the main cause of the inefficiency of the $CO_2$ capture in order to optimized the process. From the problem that had faced by the industry, a new fast and effective absorption measurement is needed in obtaining the accurate and effective result.

The method based on infrared ray absorption has been found to passes the wide measuring range and fast response. In this study, the experimental of $CO_2$ absorption in DEA solution will be measured using FTIR which is the fast analysis. By investigate the FTIR spectrum of $CO_2$-DEA system at different process variables by produces a molecular fingerprint of the sample with absorption peaks, industry will have a reference from data of the system for making the predictive models without time consuming.

## 1.3 Research Objectives

The objectives of this study are:

1.3.1 To obtain the FTIR spectrum of $CO_2$-DEA system at different process variables which is amine concentration and $CO_2$ gas flow rate.

1.3.2 To synthesize FTIR spectrum to characterize the system.

## 1.4 Research Questions/Hypothesis

1.4.1 What is the measurement of $CO_2$ absorption obtaining at different process variables using FTIR analysis?

1.4.2 How the system is characterised by using FTIR spectrum?

## 1.5 Scope of Proposed Study

This study provides a state of the art of the research work carried out in $CO_2$ capture with chemical absorption. The first scope of the proposed study is to perform the experiment of $CO_2$ gas absorption in alkanolamine solution which is DEA. The experiment will be run at atmospheric pressure, 1 atm, at room temperature, $25^oC$ and at different process variables which is the concentration of DEA and $CO_2$ flow rate. The concentrations of DEA are 2, 4 and 6M and the $CO_2$ flow rate are 100 and 200 ml/min. The experiment will be performed at constant stirrer speed which is 120 rpm. Then, the amine solution, DEA will be analyzed to $CO_2$ using FTIR which is a fast analysis instrument and more sensitive than any older dispersive instrument. The characterization will be done by using multivariate method of Principal Component Analysis (PCA).

## 1.6 Expected Outcome

The absorption of $CO_2$ in DEA solution, a secondary amine is able to be detected using FTIR which is fast analysis, high sensitivity and good selectivity. The FTIR spectrum of $CO_2$-DEA system will able to be obtained at different process variables which is at different DEA concentration and $CO_2$ gas flow rate which will be used in characterized the system. The chemical absorption process occurred during the absorption of $CO_2$ in DEA solution. Then, PCA is feasible to characterize the system based on the data obtained from the $CO_2$-DEA spectrum in the experiment that represents the molecular absorption and transmission, creating a molecular fingerprint of the sample with absorption peaks. The data analysis obtain will able to be used in the processing control, chemical analysis, laboratory analysis and system control application.

## 1.7 Significance of Proposed Study

Study the process monitoring of $CO_2$ absorption using DEA by FTIR will bring the benefits towards environment and industry. According to Kierzkowska-Pawlak and Chacuk (2010), the absorption of $CO_2$ from flue gas will reduces the emission of greenhouse gasses, which is the solution of the alkanolamine, DEA play an important role in capture the $CO_2$ gas. Global warming is caused by emission of greenhouse gases which is 72% of the totally emitted greenhouse gases is $CO_2$. By $CO_2$ capture in reducing the $CO_2$ emission will result in minimizing the climate change. Besides that, by action taking to decrease $CO_2$ concentration in atmosphere will reduce the potential burdens to human health.

FTIR spectrum of $CO_2$-DEA system at different process variables which is DEA concentration and $CO_2$ gas flow rate will be obtained using FTIR as to detect $CO_2$ in DEA solution. Jackson et al., (2009) state that FTIR brought the faster analysis of chemical analysis to be carried out. $CO_2$ can be detected very fast using FTIR with the method based on radiation. The FTIR spectrum is synthesize to characterize the system using PCA. Besides that, process monitoring of $CO_2$ absorption using DEA by FTIR will give the benefit towards industry which is based on the result obtain in the experiment, it can be used in industry as a reference to capture the $CO_2$ in reducing the emission of $CO_2$ in the atmosphere that produced by the industry activity and also can be used in control system application (Zhang and Wu, 2004).

## 1.8 Concluding remarks

The chapter already review the introduction of absorption of $CO_2$ by using alkanolamine which is DEA solution. It also reviewed about the scope and the significance of the study. The next chapter will discuss more about the literature and theoretical of the research about the absorption of $CO_2$, the reaction mechanism, the analysis of $CO_2$ detection, FTIR, the type of alkanolamine that used as an absorbent and review of PCA.

# CHAPTER 2

# LITERATURE REVIEW

This chapter provide the general ideals on the subject that are going to be study including introduction, absorption principle which is physical and chemical absorption, reaction mechanism of $CO_2$ absorption in DEA, Fourier Transform Infrared Spectroscopy (FTIR) Analysis, Principal Component Analysis (PCA) and the type of absorbent.

## 2.1 Introduction

The $CO_2$ gas level in the atmosphere is rising fast because of the human activities and industry process. Increases in amounts of greenhouse gases and other harmful gases into the atmosphere are caused by the fossil fuel usage (Chiari and Zecca, 2011). Scientist realized that a gas in the atmosphere is the main cause of the greenhouse effect which brought to the effects of earth's temperature. The greenhouse effect refers to the phenomenon whereas the gases in the upper atmosphere absorb a portion of the heat radiated by the earth. The earth's temperature is estimated in range of 33$^{o}$C warmer than it would be if this energy were instead transmitted to space (Cooper and Alley, 1994). Absorption into liquid solvents, adsorption on solids, cryogenic capture and permeating via membrane are the examples of the separation technologies that are available for the removal of $CO_2$ gas nowadays but absorption is most efficient based on the researcher's opinion (Ajibola, 2010). According to Lawal at al., (2011), there are two type of absorption include in the separation technologies for $CO_2$ removal which is physical and chemical absorption. As discussed by Jamal and Meisen, (2001), this type of absorption is the dominant industrial process for the separation of acid gases such as $CO_2$ and $H_2S$, from mixtures in natural gas processing. DEA is the secondary type of amine which is popular commercially used absorbent. Principal component analysis (PCA) will be used to characterise the system which is generally considered to be the working horse of multivariate data analysis.

## 2.2 $CO_2$ Absorption/Desorption In Aqueous Amine

Amine-based $CO_2$ capture has been widely considered as a feasible ideal technology for reducing large-scale $CO_2$ emissions and mitigating global warming (Zhou et al., 2011). Sholeh et al., (2007) stated that the amine-based $CO_2$ capture process has become a common method for $CO_2$ removal because it is energy efficient which is in the amine-based $CO_2$ capture process, an amine solvent is used to absorb $CO_2$ from the flue gas, and $CO_2$ is subsequently extracted from the amine solvent, which can then be regenerated and reused. $CO_2$ capture using aqueous amine is a well-established technology which has been used to separate $CO_2$ from $H_2$ or $CH_4$ and currently used in ammonia production and in natural gas processing.

As stated by Jamal et al., (2006), absorption rate are decreases from MEA to DEA to MDEA. Figure 2.1 shows a comparison of the predicted and experimentally observed absorption rates for the three alkanolamine system which is DEA-$H_2O$, MEA-$H_2O$ and MDEA-$H_2O$. From the literature, MEA is a primary amine with very high reactivity towards $CO_2$ in aqueous solution, DEA is a secondary amine with intermediate reactivity with $CO_2$ and MDEA is a tertiary amine with very low reactivity towards $CO_2$. Figure 2.1 clearly showed the decreasing of the absorption rate between three alkanolamine solution.

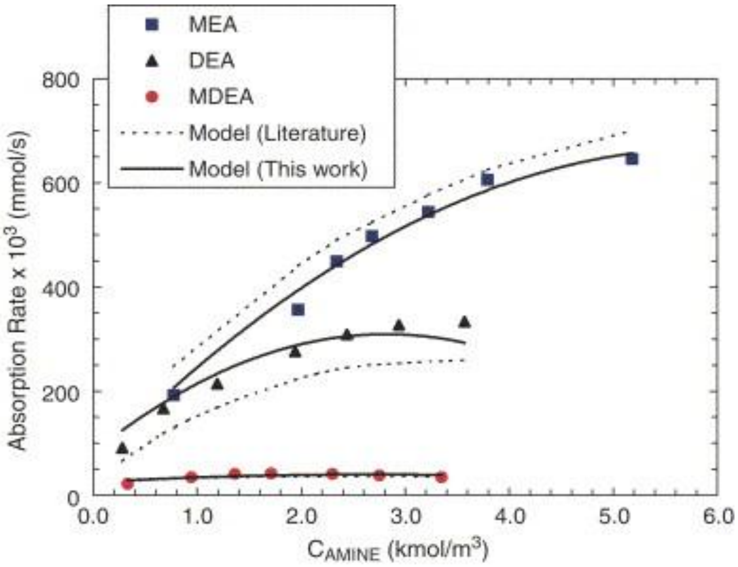


**Figure 2.1** Absorption rates of $CO_2$ in aqueous solution of MEA, DEA and MDEA, (Sources: Jamal et al., 2006).

## 2.3 Absorption Principle

Gas absorption which is known as scrubbing is an operation or process in which a gas mixture in contacted with a liquid for a purpose of preferentially dissolving one or more components of the gas mixture and to provide a solution of them in the liquid. Mass transfer occurred in the gas absorption when the solute is removed from the gaseous stream by dissolve it in solvent. Absorption into liquid solvents (chemical and physical absorption), adsorption on solids, cryogenic capture and permeating via membrane is the kind of separation technologist of $CO_2$ removal from a mixture of gases (Wang et al., 2011). The important criteria that should be considered in gas separation process are capture effectiveness, economy process, energy consumption, technical and operational issues. However, chemical and physical absorption is the type of process that use in the separation of $CO_2$ gas in the petroleum, natural gas and chemical industries actually (Gupta et al., 2003). According to Ma'mun (2005), physical absorption is more referred to physical solubility whereas the chemical absorption is more on the reactions occurred between solute and solvent. Both of the processes have their own advantages and disadvantages. Both of the type of absorption is depend on whether there is any chemical reaction between the solute and solvent as an absorbent.

### 2.3.1 Physical Absorption

Physical absorption is the absorption when there is no chemical reactions occur between the solute and the solvent (absorbent), for an example when water and hydrocarbon oils are used as an absorbents. Physical absorption is rarely used because of its inefficiency (Ajibola, 2010). The binding between the $CO_2$ molecules with solvent molecules is weaker than the binding in chemical absorption. However, for the physical absorption, the regeneration process is easier and less energy demanding but the solvent capacity is strongly depending on the partial pressure (Ma'mun, 2005).

The amount of gas absorbed during physical absorption is directly proportional to its partial pressure which is obeyed Henry Law. Physical absorption processes are temperature and pressure dependent which is absorption favored at high pressure in above 5-10 atm (Kohl and Nielsen, 1997; Ma'mun, 2005), and low temperature, the lower the temperature the more gas is absorbed. Chakravati et al., (2001) stated physical absorption is not economical for flue gas streams with $CO_2$ partial pressure lower than 15vol% whereas physical absorption will be more efficient when the partial pressure of gas to be absorbed is high.

### 2.3.2 Chemical Absorption

Chemical absorption also known as reactive absorption which is occurs when aqueous solution is used as an absorbent to dissolve an acid gas. The method usually used for removing $CO_2$ from the other gases such as methane, hydrogen and others. Chemical absorption used the different reactivity of various gases with absorbent to separate them such as alkali carbonate, aqueous ammonia and alkanolamines. In this study, chemical absorption refers to a process where a gas, $CO_2$ is absorbed in a liquid solvent by formation of a chemically bonded compound (Herzog and Golomb, 2004). The chemical absorption is the most popular method for gas separation because it absorbs and reacts with the gas. The binding between the absorbent and $CO_2$ are strong and this make the reaction become fast and effective removal of $CO_2$ in one stage of absorption but the strong binding between the absorbent and $CO_2$ will produce the high regeneration energy requirement.

The important of chemical absorption processes is its give the higher absorption rate and higher absorption capacity but its regeneration process requires more energy consumption. In addition, as stated by Lawal (2011), the selectivity of this kind of separation is relatively high. Chemical absorption is suitable for $CO_2$ capture for industrial flue gases because a relatively pure $CO_2$ stream could be produced. In chemical absorption, it’s favored at lower partial pressure (Ma’mun, 2005). Consequently, in the $CO_2$ process removal, chemical absorption is more preferred because the chemical reaction between $CO_2$ and amines increases the separation of $CO_2$ even at low partial pressures of $CO_2$. Chemical absorption with alkanolamine is the technology that generally used for the $CO_2$ removal today (Ma'mun, 2005).

## 2.4 Reaction Mechanism of $CO_2$ Absorption in DEA

Primary and secondary amines react with $CO_2$ forming carbamate species whereas tertiary amines groups cannot react with $CO_2$ directly to form a carbamate, because these amines lack a free proton. Hence, tertiary amines act as a base and catalyze the hydration of $CO_2$, leading to the formation of bicarbonate. The amount of each product is directly related to the absorption rate and the energy requirement for absorbent regeneration. Singh (2011), stated as the main parameters in determining the absorption capacity and regeneration energy requirement are the carbamate stability and basicity.

DEA is an industrially accepted alkanolamine for the removal of $CO_2$ and the well-established zwitterion mechanism, resulting the producing in formation of carbamate ions, and can explain the reaction with $CO_2$. The reaction between $CO_2$ and DEA ($C_4H_{11}NO_2$) can be interpreted by using the zwitterions mechanism proposed by Caplow (Benamor et al., 2007). There are two step sequence described by the zwitterions mechanism for the reaction of primary or secondary amines with dissolved $CO_2$ (Wang et al., 2003). In this study, the reaction mechanism for the secondary amine DEA with $CO_2$ can be described as follows. The first step is the formation of intermediate zwitterions, $DEAH^+COO^-$ ($R_1R_2NH^+COO^-$) which is:

$$CO_2 + DEA \leftrightarrow DEAH^+COO^- \qquad (2.1)$$

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+COO^-$$

Then the second step, the zwitterions is deprotonated by the bases present in the solution, where B is $H_2O$, OH- and $R_1R_2NH$ (NH $(CH_2CH_2OH)_2$) in aqueous amine solution, respectively. Then it forms a carbamate ($DEACOO^-$ or $R_1R_2NCOO^-$) ion and a protonated base which is:

$$DEAH^+COO^- + B \leftrightarrow DEACOO^- + BH^+ \qquad (2.2)$$

$$R_1R_2NH^+COO^- + B \leftrightarrow R_1R_2NCOO^- + BH^+$$

In aqueous solution, the corresponding reactions are as follow:

$$DEAH^+COO^- + DEA \leftrightarrow DEACOO^- + DEAH \qquad (2.3)$$

$$R_1R_2NH^+COO^- + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$$

$$DEAH^+COO^- + H_2O \leftrightarrow DEACOO^- + H_3O^+ \qquad (2.4)$$

$$R_1R_2NH^+COO^- + H_2O \leftrightarrow R_1R_2NCOO^- + H_3O^+$$

$$DEAH^+COO^- + OH^- \leftrightarrow DEACOO^- + H_2O \qquad (2.5)$$

$$R_1R_2NH^+COO^- + OH^- \leftrightarrow R_1R_2NCOO^- + H_2O$$

DEA carbamate reversion:

$$DEACOO^- + H_2O \leftrightarrow DEA + HCO_3^- \qquad (2.6)$$

$$R_1R_2NCOO^- + H_2O \leftrightarrow R_1R_2NH + HCO_3^-$$

DEA deprotonation:

$$R_1R_2NH_2^+ + OH^- \leftrightarrow R_1R_2NH + H_2O \qquad (2.7)$$

The other reaction considered in $CO_2$-DEA-$H_2O$ system is:

$$2H_2O \leftrightarrow OH^- + H_3O^+ \qquad (2.8)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (2.9)$$

$$HCO_3- + OH^- \leftrightarrow CO_3^{2-} + H_2O \qquad (2.10)$$

Equation (2.8) is water dissociation whereas equation (2.9) and (2.10) is bicarbonate formation and carbonate formation.

## 2.5 Analysis

Process information concerning to the $CO_2$ loading (mol $CO_2$/mol amine) and the amine concentration of solvents for $CO_2$ capture are significant for amine based carbon capture plant operation and in various experimental apparatuses studying $CO_2$ absorption. These liquid analyses usually have been performed manually by the use of relatively time-demanding methods (Einbu et al,. 2012). Manual off-line liquid analysis does not provide input data for real-time process control and optimization. The methods used are generally labour-intensive and is not practical for studies of transient conditions during dynamic changes in a process. Both from a scientific and an operational aspect, real-time data of $CO_2$ loading and amine concentration during operation of experimental equipment and $CO_2$ capture plants would provide much useful information for process characterization and control.

There are several type of infrared spectroscopy used in the world but the most widely used are FTIR (Smith, 2011). As found by Einbu et al,. (2012), Fourier Transform Infrared Spectroscopy (FTIR) has a large potential for scientific purposes and as a quantitative quality control tool for the industry. Besides that, recent advances in FTIR spectroscopy have allowed for rapid and accurate analysis of liquid samples in conjunction with Attenuated Total Reflectance (ATR) technology. FTIR-ATR liquid analysis of $CO_2$ absorption in amine solutions has showed that both carbamate and carbonate formation can be monitored using this technique. The advantage of choosing FTIR as a quantitative technique lies in its ability to readily carry out multi-component analysis in association with multivariate analysis methods such as Partial Least Squares (PLS) regression or Principal Component Analysis (PCA).

### 2.5.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Carbamate and bicarbonate species are formed during the amine scrubbing of $CO_2$ from the flue gas. The fast calibration-free spectroscopic techniques of $CO_2$-alkanolamine system in determining the amine protonation carbamate ion were studied.

FTIR stands for Fourier Transform Infrared, is the preferred method of infrared spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) is the most useful for identifying the chemicals that are either organic or inorganic and also can be used to identify some components of an unknown mixture. As stated by Richner and Puxty (2012), there are two types of FTIR analysis which is qualitative and quantitative analysis. FTIR is widely used for quantitative as well as for qualitative analysis in almost all fields (Sawant et al., 2011). Infrared monitoring also allows a quantitative measurement which is according to Beer-Lambert Law, the absorbance changes linearly with species concentrations. With $CO_2$-$H_2O$ alkanolamine system, these calibrations are based on a single peak evaluation. For an example the amplitude of the absorbance peak at certain wavenumber is due to one species only. The sums of individual contributions from multiple species (peak overlap) are not considered making such an evaluation inaccurate.

FTIR is one of the analytical methods widely used in chemistry for online reaction monitoring (Richner and Puxty, 2012). FTIR can be applied to the analysis of solids, liquids and also gases. It is the analysis which is the data is collected and then converted from an interference pattern to spectrum. According to Azom (2012), one of the function of the spectroscopic analysis is to determine the chemical functional groups in the sample like C=O, C-H or N-H. The compound exist at the peak can be known by make the comparison with the IR absorption frequencies of functional group as in table 2.1 and table 2.2 (Silversteion et al., 1981). The table 2.1 showed the characteristic IR absorption frequencies of organic functional groups whereas table 2.2 showed the IR absorption frequencies of functional groups containing a carbonyl (C=O).

**Table 2.1** Characteristic IR Absorption Frequencies of Organic Functional Group

| Characteristic IR Absorption Frequencies of Organic Functional Groups | | | |
|---|---|---|---|
| Functional Group | Type of Vibration | Characteristic Absorptions (cm$^{-1}$) | Intensity |
| Alcohol | | | |
| O-H | (stretch, H-bonded) | 3200-3600 | strong, broad |
| O-H | (stretch, free) | 3500-3700 | strong, sharp |
| C-O | (stretch) | 1050-1150 | strong |
| Alkane | | | |
| C-H | stretch | 2850-3000 | strong |
| -C-H | bending | 1350-1480 | variable |
| Alkene | | | |
| =C-H | stretch | 3010-3100 | medium |
| =C-H | bending | 675-1000 | strong |
| C=C | stretch | 1620-1680 | variable |
| Alkyl Halide | | | |
| C-F | stretch | 1000-1400 | strong |
| C-Cl | stretch | 600-800 | strong |
| C-Br | stretch | 500-600 | strong |
| C-I | stretch | 500 | strong |
| Alkyne | | | |
| C-H | stretch | 3300 | strong,sharp |
| $-C\equiv C-$ | stretch | 2100-2260 | variable, not present in symmetrical alkynes |
| Amine | | | |
| N-H | stretch | 3300-3500 | medium (primary amines have two bands; secondary have one band, often very weak) |
| C-N | stretch | 1080-1360 | medium-weak |

| | | | |
|---|---|---|---|
| N-H | bending | 1600 | medium |
| Aromatic | | | |
| C-H | stretch | 3000-3100 | medium |
| C=C | stretch | 1400-1600 | medium-weak, multiple bands |
| Analysis of C-H out of plane bending can often distinguish substitution patterns | | | |
| Carbonyl | Detailed Information on Carbonyl IR | | |
| C=O | stretch | 1670-1820 | strong |
| (conjugation moves absorptions to lower wave numbers) | | | |
| Ether | | | |
| C-O | stretch | 1000-1300<br>(1070-1150) | strong |
| Nitrile | | | |
| CN | stretch | 2210-2260 | medium |
| Nitro | | | |
| N-O | stretch | 1515-1560 & 1345-1385 | strong, two bands |

(Sources: Silverstein et al., 1981)

**Table 2.2** IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)

| IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O) | | | |
|---|---|---|---|
| Functional Group | Type of Vibration | Characteristic Absorptions (cm-1) | Intensity |
| Carbonyl | | | |
| C=O | stretch | 1670-1820 | strong |
| (conjugation moves absorptions to lower wave numbers) | | | |
| Acid | | | |
| C=O | stretch | 1700-1725 | strong |
| O-H | stretch | 2500-3300 | strong, very broad |
| C-O | stretch | 1210-1320 | strong |

| | | | |
|---|---|---|---|
| Aldehyde | | | |
| C=O | stretch | 1740-1720 | strong |
| =C-H | stretch | 2820-2850 & 2720-2750 | medium, two peaks |
| Amide | | | |
| C=O | stretch | 1640-1690 | strong |
| N-H | stretch | 3100-3500 | unsubstituted have two bands |
| N-H | bending | 1550-1640 | |
| Anhydride | | | |
| C=O | stretch | 1800-1830 & 1740-1775 | two bands |
| Ester | | | |
| C=O | stretch | 1735-1750 | strong |
| C-O | stretch | 1000-1300 | two bands or more |
| Ketone | | | |
| acyclic | stretch | 1705-1725 | strong |
| cyclic | stretch | 3-membered - 1850<br>4-membered - 1780<br>5-membered - 1745<br>6-membered - 1715<br>7-membered - 1705 | strong |
| A,β-unsaturated | stretch | 1665-1685 | strong |
| aryl ketone | stretch | 1680-1700 | strong |

(Sources: Silverstein et al., 1981)

### 2.5.2 The Advantages of FTIR

FTIR are now mostly used and has improved the quality of infrared spectra and minimized the time required to obtain data (Stuart, 2004). Sawant et al., (2011) stated FTIR spectroscopy can detect several compounds simultaneously and the monitoring can be performed continuously because as cited by Stuart (2004), FTIR spectroscopy did not use a slit or other restricting device, hence the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector, hence translating to higher signals and improved signal noise-to-noise ratio (SNR) which is measure the quality of a peak. The signal is determined by measuring the size of a peak. Higher signal noise-to-noise ratio (SNR) will increase the sensitivity of the instrument. This is known as Jacquinot's advantage.

According to Jackson et al., (2009), FTIR spectroscopy have allowed for the faster analysis of chemical species to be carried out which is the speed advantages. The spectra are substantially to be obtained on a millisecond timescale because the mirror has the ability to move short distances rapidly with the SNR improvements hence make it the analysis become fast. Besides that, FTIR also are more sensitive than the older dispersive instruments. Figure 2.2 is the FTIR instrument that used in varied of analysis application.

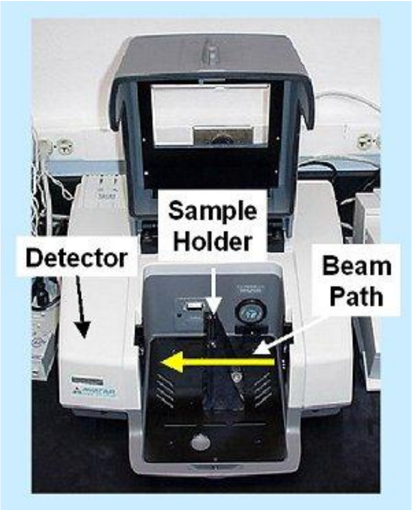


**Figure 2.2** FTIR instrument

(Source: http://chemlab.truman.edu)

### 2.5.3 Fundamentals of FTIR

FTIR spectroscopy is the interference of radiation between two beams to yield an interferogram. The signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier-transformation. The basic components of an FTIR spectroscopy are shown schematically in Figure 2.3 (Stuart as cited in Infrared Spectroscopy: Fundamentals and Applications, 2004, p 23).

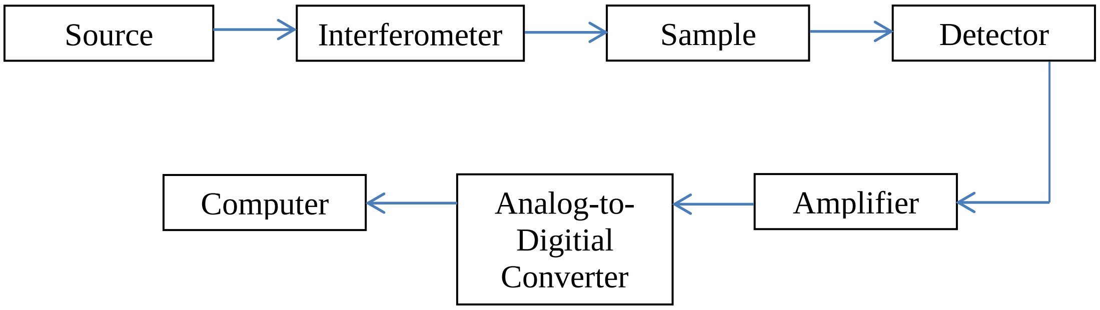


**Figure 2.3** Basic components of FTIR spectroscopy.

As in Figure 2.4, in FTIR, radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through as transmitted. The resulting spectrum represents the molecular absorption and transmission, produces the molecular fingerprint of the sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Like a fingerprint, there is no two unique molecular structures produce the same infrared spectrum. Bevis (1996) stated the benefits of the FTIR makes infrared spectroscopy useful for several types of analysis.

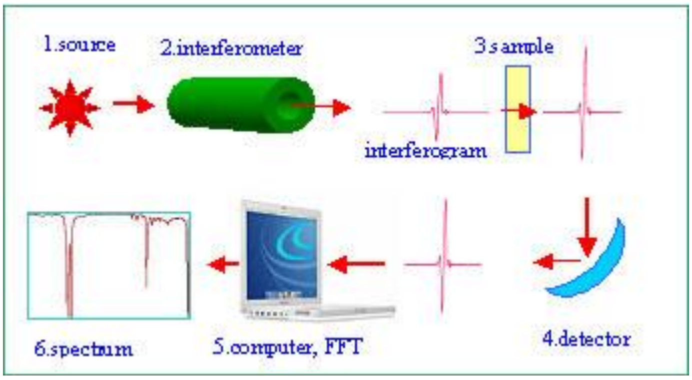


**Figure 2.4** The principle of FTIR.

(Sources: http://www.nuance.northwestern.edu)

The output from the instrument is referred to as a spectrum. Figure 2.5 showed the performance of the infrared spectrum of DEA solution charged with $CO_2$ using FTIR. As stated by Smith (2011), the peak from the infrared spectrum is related with the molecular structure and the reason why infrared spectroscopy are useful.

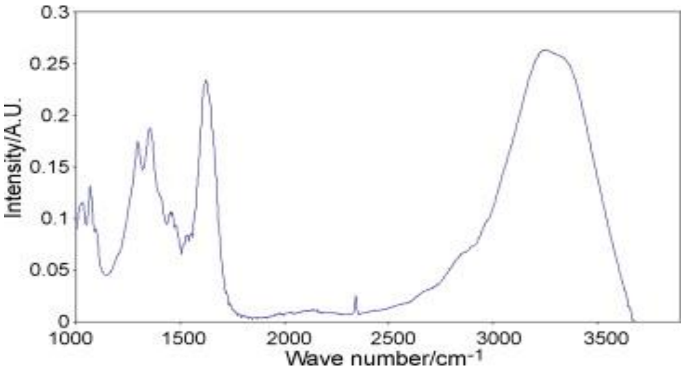


**Figure 2.5** Infrared spectrum of DEA solution charged with $CO_2$

(Sources: Archane et.all, 2008).

## 2.6 Principal Component Analysis (PCA)

Principal components analysis (PCA) and factor analysis (FA) are statistical techniques used for data reduction or structure detection (Tabachnik and Fidell, 2001). PCA is the method of choice for the researcher that interested in reducing large number of variables down to a smaller number of components. PCA analyses the variances whereas FA analyses the covariance (communality). The purpose of PCA to extract the maximum variance from a data set with a few orthogonal components whereas the purpose of FA is to reproduce the correlation matrix and scores on observed variables.

As stated by Kano et al., (2001), Principal Component Analysis (PCA) has been used successfully as a multivariate statistical process control (MSPC) tool for detecting faults in processes with highly correlated variables. PCA is about explaining the variations among the number of variables, as reflected in the dispersion matrix of the vector of variables, more precisely, the total variance of the variables, through a few linear combination of the original variables. As discussed by Mukhopadhyay (2009), an analysis of principal components frequently exposed the relationship among original variables that were not previously suspected and indirectly allows a new insight into the data. PCA is central to the study of multivariate data which is PCA is a technique from statistics for simplifying a data set. It was developed by Pearson (1901) and Hotelling (1933) who developed the technique for his work in educational psychology, while Jolliffe (2002) is the best modern reference. Its mathematical theory has been developed by Girshick (1939), Anderson (1936) and Geisser (1965) among the others.

As stated by Mukhopadhyay (2009), PCA is usually serves as an intermediate step in much larger investigations with data analysis. For example in regression analysis, a test may be not effective if the number of independent variables is large relative to the number of observations. Besides that, if the independent variables are highly correlated, the estimates of regression coefficient may be unstable.

### 2.6.1 Purposes of PCA

The main purposes of the method is to reduce the dimensionality of multivariate data while preserving as much of the relevant information as possible (Wendy and Angel, 2005). It is a form of unsupervised learning which is it relies entirely on the input data itself without reference to the corresponding target data and the criterion to be maximized is the variance. As stated by Tabachnick and Fidell (2001), PCA is going to extract maximum variance from the data set with each component. By using PCA, the data can be transforming to a new set of coordinates or variables that are linear combination of the original variables. The observations in the new principal component space are uncorrelated. According to Abdi and Williams (2010), the other aims of the method are to extract the important information from the table, to compress the size of the data set by keeping only this important information, to simplify the description of the data set and to analyse the structure of the observations and variables.

Below is the general form for the formula to compute scores on the first component extracted in a principal component analysis (Svensson et al., 1999):

$$X = t_1 p'_1 + t_2 p'_2 + \ldots.. + t_A p'_A + E \tag{2.11}$$

where

X = The original data in matrix form

t = Score vector

*p* = Loading vector

There are two vectors for each principal component (PC) which is score vector, t and loading vector, *p*. The score vectors contain a score value for each spectrum and tell how the spectrum is related to the other spectra in that particular component. The loading vector tells which spectra features in the original spectral that are captured by the component studied. The residual variation from X is denoted E. As stated by Svensson et al., (1999), the number of components (A) is usually much smaller than the number of original variables (k) and spectra (n). The collected spectra are placed as rows in a matrix X, with n rows represent a spectrum and k columns represent a single wavelength. The principal components is determined by using the princomp function in matlab with the command below

```
[coeff, score, latent] = princomp (X)
```

Coeff represents the loading matrix P whereas score represent the score vector T which holds the principal components (PCs) value and latent represents the eigenvalues of the covariance matrix of X. The latent values is expressed as a percentage of the total variance and were calculated by using the equation (2.7) which the value obtained will determine the PC that give the most explanation about the variability of the data.

$$\frac{\lambda_i}{\Sigma_{i=1}\lambda_i}\times 100\% \qquad (2.12)$$

## 2.7 Type of Absorbent

Amine scrubbing technology was developed over 60 years ago in the oil and chemical industries, for removal of hydrogen sulphide ($H_2S$), carbon dioxide ($CO_2$), carbonyl sulfide and others in gas mixtures from gas streams. Benamor et al., (2007) stated that the removal of acid gases like $CO_2$ and $H_2S$ from natural and refinery gases is an important process in the industrial process.

The present interest in energy conservation and pollution control has led to the search for more efficient and economical methods of removing acid gases (Ali, 2004). There are many absorption solvents commercially available for $CO_2$ capture either physical or chemical solvents. The physical solvents such as selexol and methanol are commonly used for the high pressure gas streams whereas the chemical solvent such as alkanolamine are commonly used for the treating gas streams that have low $CO_2$ partial pressure (Thitakamol, 2007). According to Ali (2004), the uses of physical solvents for the removal of $CO_2$, $H_2S$ and other sulfur compounds may give some advantages over the uses of chemical solvents such as working at lower absorber temperatures. Alkanolamines are usually used in the form of aqueous solution is the common chemical solvents used for $CO_2$ removal purposes. This type of solvent have their own advantages as they can dissolved in water as well as in organic liquid like ethanol, cyclohexanol and ethyleneglycol or the mixtures of these liquid (Ali, 2004). The required reaction rate can be obtained by an appropriate choice of the alkanolamine type. Normally, methyethanolamine (MEA), diethanolamine (DEA) and monoethanolamine (MDEA) as an alkanolamine-based solvent is use in gas treating technology. Alkanolamines can be classified into primary, secondary and tertiary types depending on the number of the alky groups attached to the nitrogen atom in the structure of the molecule (Haji-Sulaiman et al., 1998). Lawal et al., (2011) stated that the primary and secondary alkanolamines react rapidly in forming the carbamates.

As state by Davidson (2007), the ideal chemical solvent possesses the high reactivity with respect to $CO_2$, low regeneration cost requirements, high absorption capacity, low environmental impact, high thermal stability and reduced solvent degradation and low solvent costs.

### 2.7.1 MEA

MEA ($C_2H_7NO$ or $R_1NH_2$), as a primary amine is also has been used extensively as an absorbent for $CO_2$ removal in capture process (Ma’mun et al., 2007). MEA is low solvent cost, low molecular weight and high reactivity. As state by Davidson (2007), there are some problem encountered using MEA like degradation of solvents in the oxidising environment of flue gas, high energy consumption for regeneration of solvents. According to Kittel et al., (2009), MEA is more corrosive compared with the secondary and tertiary amines used for the gas treating.

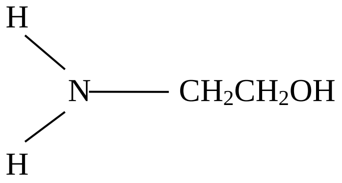


**Figure 2.6** Molecular structure of MEA

(Sources: Wang et al., 2011).

### 2.7.2 DEA

DEA ($C_4H_{11}NO_2$ or $R_1R_2NH$) is a secondary amine. As stated by Wang et al., (2011), primary and secondary alkanolamine react faster with $CO_2$ to form carbamates. According to Ali (2004), DEA is one of the industrially accepted in the separation of $CO_2$ from the flue gas and the well-established zwitterions mechanism, resulting in the formation of carbamate ion.

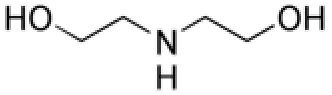


**Figure 2.7** Molecular structure of DEA

(Sources: Wang et al., 2004)

DEA is soluble in water, alcohol and benzene but insoluble in most other organic solvent. The physical and chemical properties of DEA are summarized in table 2.1.

DEA is more popular commercially used absorbent with two ethanol groups attached to the nitrogen atom. According to Wang et al. (2003), secondary amines are low solvent cost, less corrosive and require less heat to regenerate, as the additional ethanol group draws most of the free electron character away from the nitrogen atom compared with primary amines. Chemical absorption will be occurred between $CO_2$-DEA reactions.

Besides used as an absorbent, DEA is a major alkanolamine commonly used in various industries, consumer products and DEA conjugates are widely used in cosmetic formulations as emulsifiers, thickeners, wetting agents, detergents, and alkalizing agent (Knaak et al., 1997 & Kraeling et al., 2004).

**Table 2.3** Physical and chemical properties of DEA

| Properties | | Reference |
|---|---|---|
| Molecular formula | $C_4H_{11}NO_2$ | - |
| Molecular weight | 105.14 g $mol^{-1}$ | ChemFinder 2001 |
| Colour | Colourless to faintly coloured | NTP 1999a |
| Odor | Mild, ammonia-like | Budavari *et al.* 1996 |
| Physical state | Crystalline solid | Budavari *et al.* 1996 |
| Specific gravity | 1.092 | NTP 2001 |
| Density | 1.0966 $g/cm^3$ | Lide 1999 |
| Melting Point | 28 °C | Lide 1999 |
| Boiling Point | 268.8 °C | Lide 1999 |
| Flash point | 137 $^oC$ | NTP 2001 |
| Solubility in water | >100 mg/mL (at 14 °C) | NTP 2001 |
| Vapor Pressure | 0.00028 mmHG | Syracuse Research Corp. 2001 |
| Henry constant | $3.87\times10^{-11}$ ($25^oC$) | Syracuse Research Corp. 2001 |

(Sources: Report on Carcinogens Background Document for Diethanolamine, 2002)

### 2.7.3 MDEA

MDEA ($C_5H_{13}NO_2$ or $R_1R_2R_3N$), tertiary amine has two ethanol groups attached to the nitrogen atom along with a methyl group. Aqueous MDEA solutions are widely used for $H_2S$ removal. In a recent study, research indicates (Wang et al., 2004) aqueous MDEA are also normally used as an alternative to the primary and secondary amines in bulk $CO_2$ removal due to its lowest regeneration heat and lowest corrosives among three types of amines

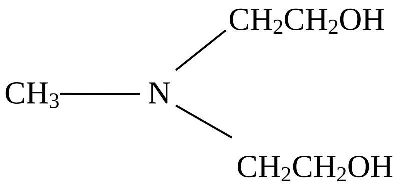


**Figure 2.8** Molecular structure of MDEA

(Sources: Wang et al., 2004).

## 2.8 Concluding Remarks

The chapter already review the literature or the theoretical of the research about the absorption of $CO_2$ using alkanolamine solution through the FTIR analysis to characterize the system. It also reviews about the reaction mechanism of $CO_2$ and DEA itself. The next chapter will discuss more about the experimental of how the research is going to be conducted, analysing sample and the experiment set up.

# CHAPTER 3

# METHODOLOGY

This chapter provide the methodology of the study that how the experiment is conducted to achieve the objective of the study. This chapter consist of experimental, material, equipment set up, procedure, analysing the sample and experiment set up.

## 3.1 Experimental

The experiment was conducted based on the process that were be carry out in absorption of $CO_2$ in amine solution, DEA using FTIR analysis to detect $CO_2$. The research was conducted in the laboratory by doing the experiment to obtain the data and details process.

### 3.1.1 Material

The chemical used in the experiment is 99% purity of DEA obtained from MERCK and commercially available 99% purity of $CO_2$.

#### 3.1.1.1 DEA

The 99% purity of DEA used in the experiment. The DEA solution, at different concentration of 2M, 4M and 6M was prepared using distilled water.

#### 3.1.1.2 $CO_2$

The 99% purity of $CO_2$ which commercially available used in the experiment. The $CO_2$ purged into DEA solution about 7 hours and were analysed to detect $CO_2$. The $CO_2$ flow rate was varied of 100 and 200 ml/min. The pressure is 1 atm.

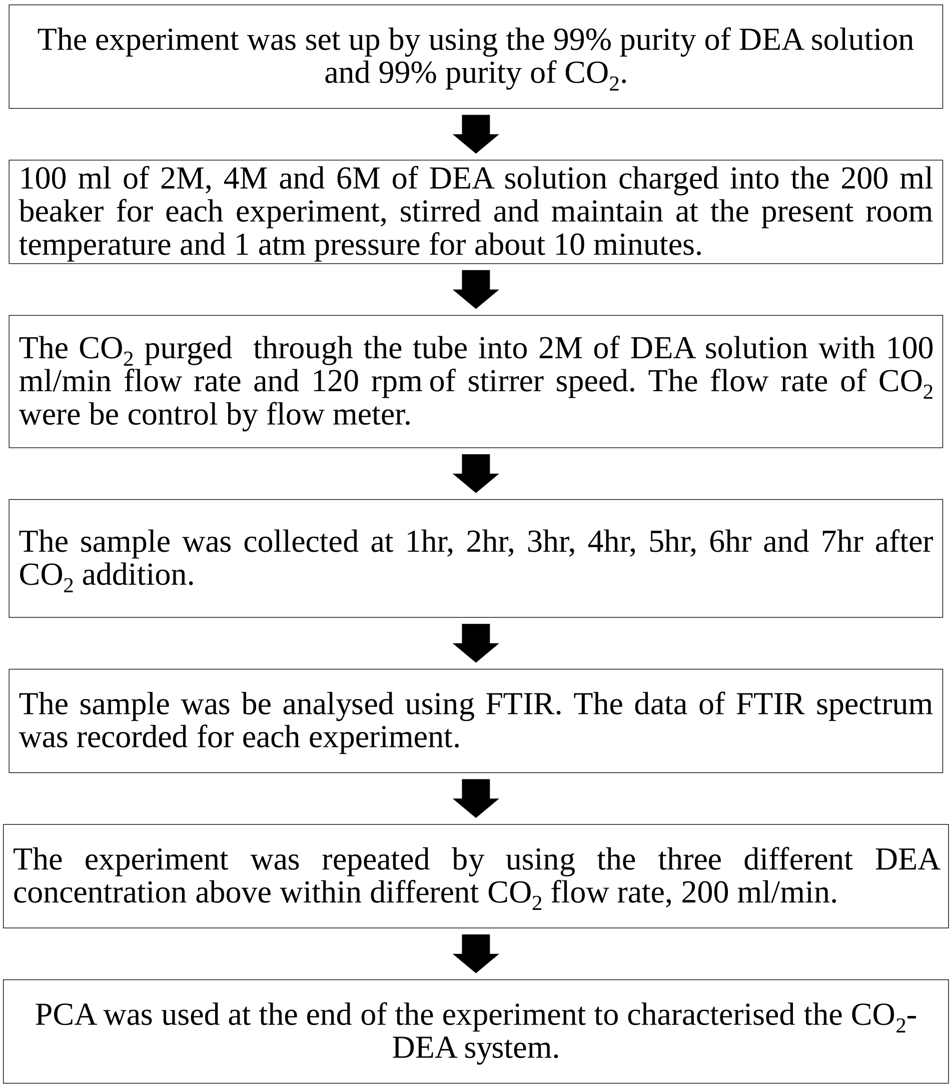
### 3.1.2 Equipment Set Up

The apparatus that used in the experiment is 200 ml beaker, tube, pressure regulator, flow meter, electronic magnetic stirrer, stirrer bar and vial or micro centrifugal tube. The 200 ml beaker is used to fill 100 ml of 2M, 4M and 6M DEA solutions in each experiment. Flow meter and pressure regulator are used to adjust the flow rate of

$CO_2$ and maintaining the pressure at 1 atm. Electronic magnetic stirrer and stirrer bar are used to get the homogeneous mixture. The vial or micro centrifugal tube is used to fill up 1.5 ml of the sample at the end of each run of the experiment.

### 3.1.3 Procedure

The experiment was conducted at atmospheric pressure, 1 atm and at room temperature, 25$^oC$. The FTIR spectrum of $CO_2$-DEA system analysed at different process variables which is amine concentration, 2M, 4M and 6M DEA and $CO_2$ gas flow rate, which is 100 and 200 ml/min. The experiment was conducted at the constant stirrer speed, 120 rpm. The total volume for DEA solution will be maintaining about 100 ml for each experiment. The $CO_2$ purged into DEA solution and analysed. The 1.5 ml of the sample is taken from the beaker at the end of time for each run of experiment at time 1hr, 2hr, 3hr, 4hr, 5hr, 6hr and 7hr for further analysis to determine the ion form during the reaction based on the spectrum produced using FTIR. The experiment was conducted in 7 hours to detect $CO_2$ in DEA solution using FTIR. The FTIR spectrum produce from the sample were used to characterize the system using Principal Component Analysis (PCA). The procedure of the experiment can be simplified as in flow chart in Figure 3.1.



The experiment was set up by using the 99% purity of DEA solution and 99% purity of $CO_2$.

100 ml of 2M, 4M and 6M of DEA solution charged into the 200 ml beaker for each experiment, stirred and maintain at the present room temperature and 1 atm pressure for about 10 minutes.

The $CO_2$ purged through the tube into 2M of DEA solution with 100 ml/min flow rate and 120 rpm of stirrer speed. The flow rate of $CO_2$ were be control by flow meter.

The sample was collected at 1hr, 2hr, 3hr, 4hr, 5hr, 6hr and 7hr after $CO_2$ addition.

The sample was be analysed using FTIR. The data of FTIR spectrum was recorded for each experiment.

The experiment was repeated by using the three different DEA concentration above within different $CO_2$ flow rate, 200 ml/min.

PCA was used at the end of the experiment to characterised the $CO_2$-DEA system.

**Figure 3.1** Procedure of the experiment

## 3.2 Sample Analysing

Sample of FTIR can be prepared in a number of ways. In this study, the liquid sample is analysed. At the end of the experiment, the sample with different DEA concentration, 2M, 4M and 6M with 100 and 200 ml/min $CO_2$ gas flow rate at constant stirrer speed for each experiment is analysed using FTIR. The sample was being collected using vial or micro centrifuge tube about 1.5 ml at each time set from each experiment for the further analysis. The plate was cleaned with the acetone before placed the sample. Then, the sample was placed into the plate of FTIR sample holder in FTIR instrument as shown in the Figure 3.1. In FTIR, the beam enters the sample compartment where it is transmitted through and the radiation or light is passed into the sample. On the other side of the sample is a detector which detects the light that is transmitted through the sample for the final measurement. The results of FTIR sample is a spectrum that is like a molecular fingerprint. After the spectrum data collected, the plate was removed from the sample holder and the plate was cleaned with acetone by dry with a clean tissue, returned them to their container and placed in the desiccator.

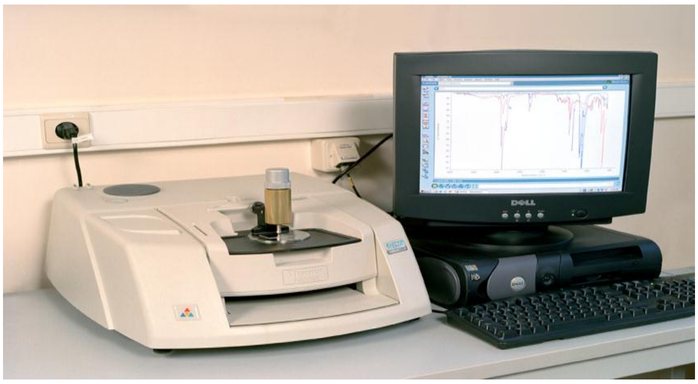


**Figure 3.2** Sample placed on the FTIR sample holder.

(Sources: http://maritzaperez6270.wordpress.com)/

## 3.3 Experiment Set Up

The experiment will be set up as in Figure 3.2 followed the procedure as discussed in 3.3.1.

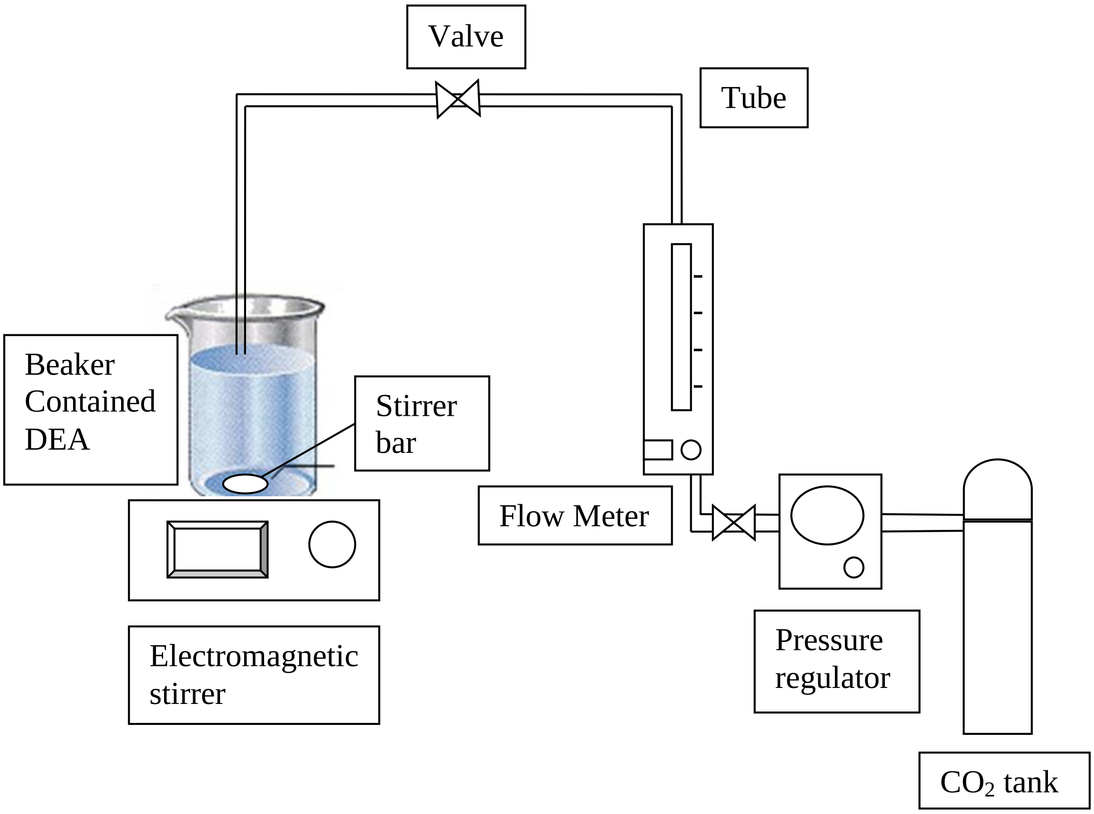


**Figure 3.3** Experimental set up.

# CHAPTER 4

# RESULT AND DISCUSSION

The experiment conducted to obtain the FTIR spectrum of $CO_2$-DEA system at different process variables which is different DEA concentration, 2M, 4M and 6M with 100 ml/min and 200 ml/min $CO_2$ flowrate. PCA were performed in order to characterize the system.

## 4.1 FTIR Spectra of $CO_2$ Absorption in DEA

In the experiment, FTIR spectra were recorded for $CO_2$ absorption in different concentration of 2M, 4M and 6M with different $CO_2$ flow rate of 100 and 200ml/min at different reaction time from 1hour to 7 hours. FTIR spectra were collected for 2M of 100 ml/min, 2M of 200 ml/min, 4M of 100 ml/min, 4M of 200 ml/min, 6M of 100 ml/min and 6M of 200 ml/min. The spectra were collected between 500 $cm^{-1}$ until 4000 $cm^{-1}$ but only 900 $cm^{-1}$ until 3500 $cm^{-1}$ were used in the data evaluation. The spectrum below 900 $cm^{-1}$ and more than 3500 $cm^{-1}$ is neglected in data evaluation. Figure 4.1, 4.2, 4.3, 4.4, 4.5, and 4.6 showed the spectrum for different concentration and different $CO_2$ flow rate. Based on the figures, the spectrum from 1900 $cm^{-1}$ until

2900 $cm^{-1}$ did not have the significant value. The absorption of $CO_2$ caused the increasing and decreasing of the spectrum either the wavelength or the absorbance. The increasing occurred can be related to the reaction products, possibly hydrogen carbonate ($HCO_3^-$), carbonate ($CO_3^{2-}$), protonated amine and carbamate while the decreasing occurred can be related to the reactant itself which is amine.

### 4.1.1 FTIR Spectra for 2M DEA with 100 ml/min $CO_2$ flowrate

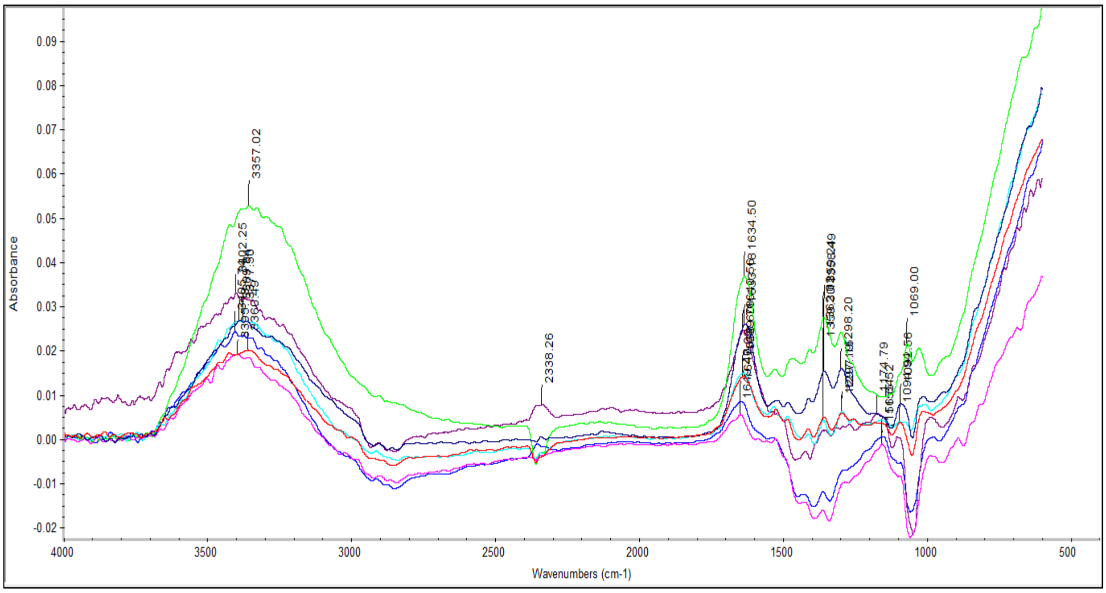


**Figure 4.1** FTIR Spectra for 2M DEA with 100 ml/min $CO_2$ flowrate

Figure 4.1 showed the overlapping of spectrum for 2M DEA with 100 ml/min flow rate $CO_2$ from t=1hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1300, 1200 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction times. During the absorption, the absorbance of the peak at 3300, 1600, 1300, 1200 and 1000 $cm^{-1}$ can be seen as in table 4.1.

### 4.1.2 FTIR Spectra for 2M DEA with 200 ml/min $CO_2$ flowrate

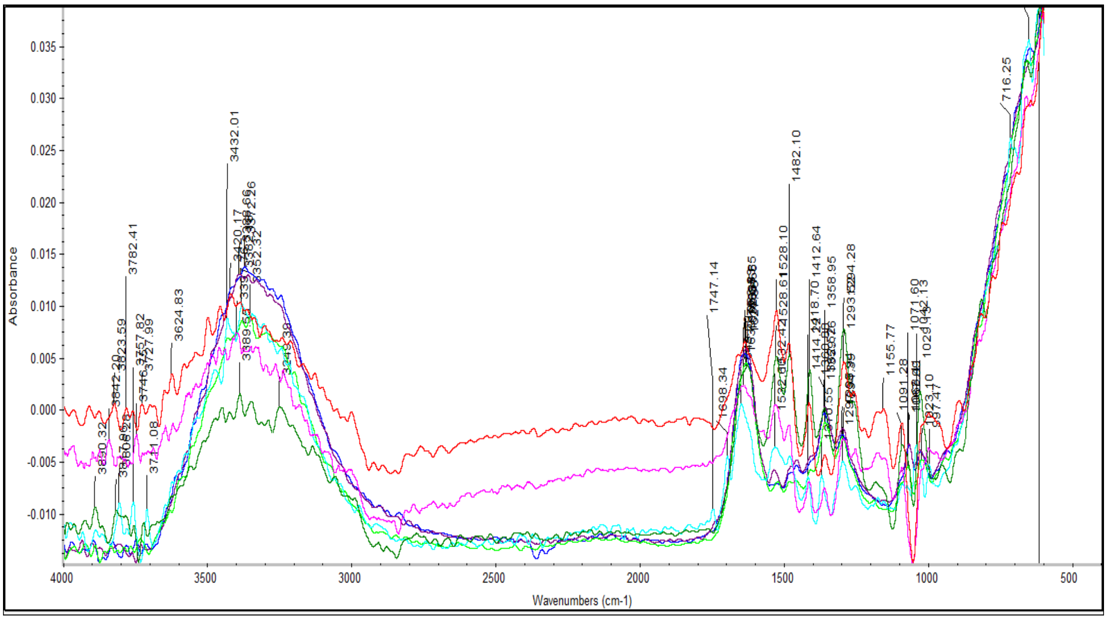


**Figure 4.2** FTIR Spectra for 2M DEA with 200 ml/min $CO_2$ flowrate

Figure 4.2 showed the overlapping of spectrum for 2M DEA with 200 ml/min flow rate $CO_2$ from t=1 hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction times. During the absorption, the absorbance of the peak at 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ can be seen as in table 4.2.

### 4.1.3 FTIR Spectra for 4M DEA with 100 ml/min $CO_2$ flowrate

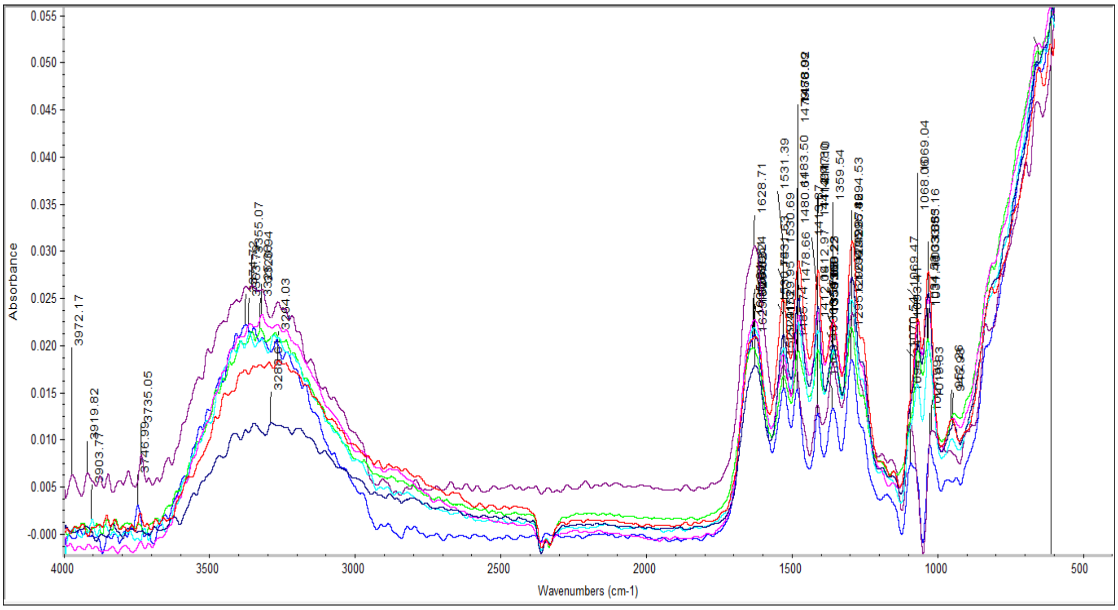


**Figure 4.3** FTIR Spectra for 4M DEA with 100 ml/min $CO_2$ flowrate

Figure 4.3 showed the overlapping of spectrum for 4M DEA with 100ml/min flow rate $CO_2$ from t=1 hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction time. During the absorption, the absorbance of the peak at 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ can be seen as in table 4.3.

### 4.1.4 FTIR Spectra for 4M DEA with 200 ml/min $CO_2$ flowrate

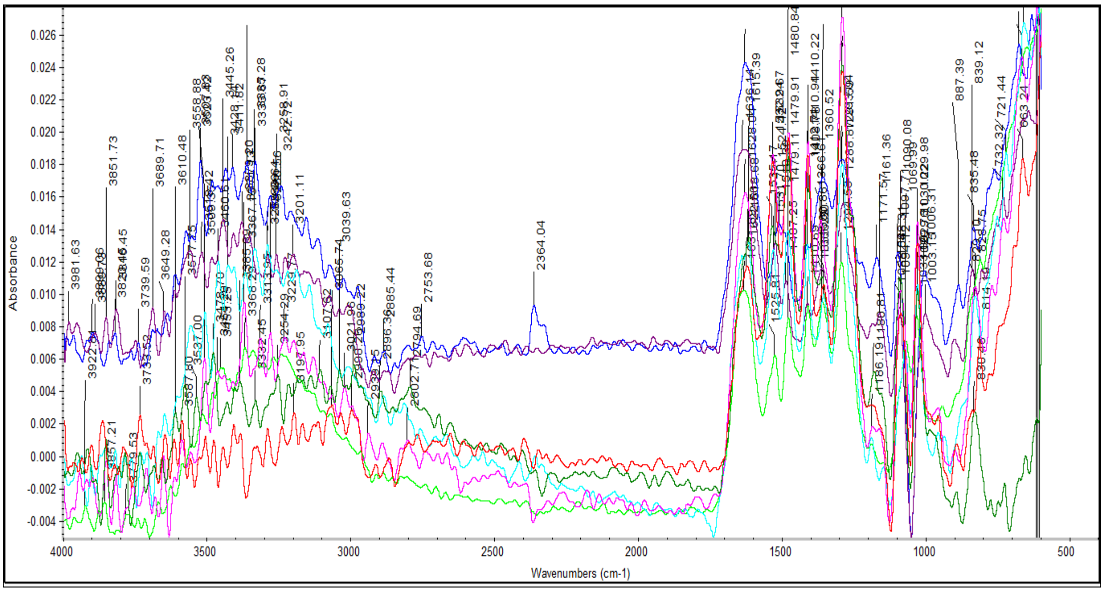


**Figure 4.4** FTIR Spectra for 4M DEA with 200 ml/min $CO_2$ flowrate

Figure 4.4 showed the overlapping of spectrum for 4M DEA with 200 ml/min flow rate $CO_2$ from t=1 hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction time. During the absorption, the absorbance of the peak at 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ can be seen as in table 4.4.

### 4.1.5 FTIR Spectra for 6M DEA with 100 ml/min $CO_2$ flowrate

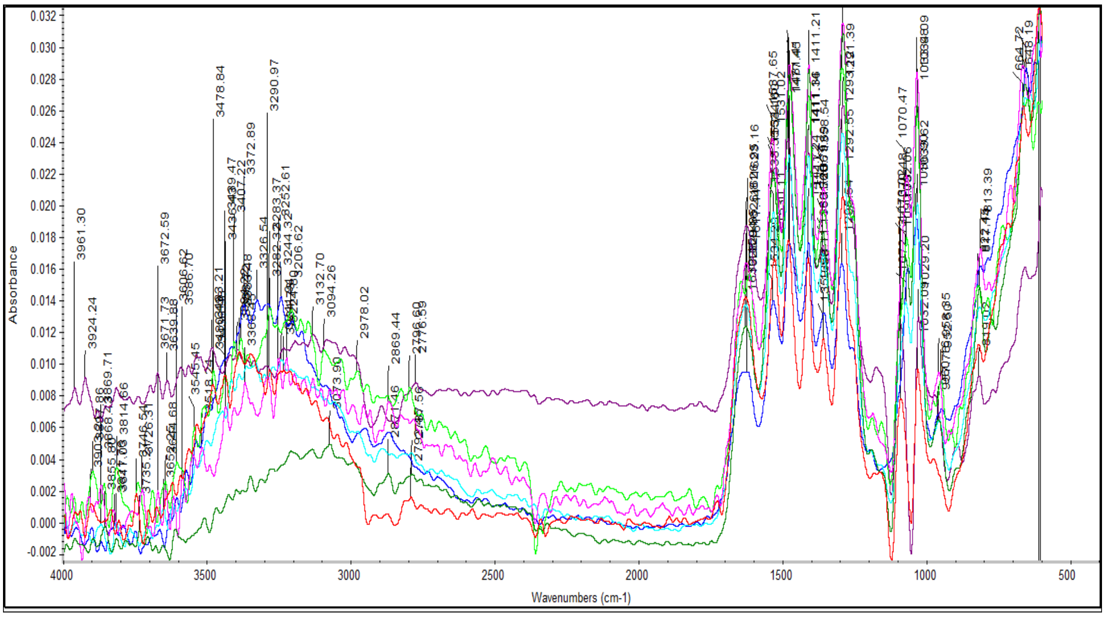


**Figure 4.5** FTIR Spectra for 6M DEA with 100 ml/min $CO_2$ flowrate

Figure 4.5 showed the overlapping of spectrum for 6M DEA with 200 ml/min flow rate $CO_2$ from t=1 hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction times. During the absorption, the absorbance of the peak at 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ can be seen as in table 4.5.

### 4.1.6 FTIR Spectra for 6M DEA with 200 ml/min $CO_2$ flowrate

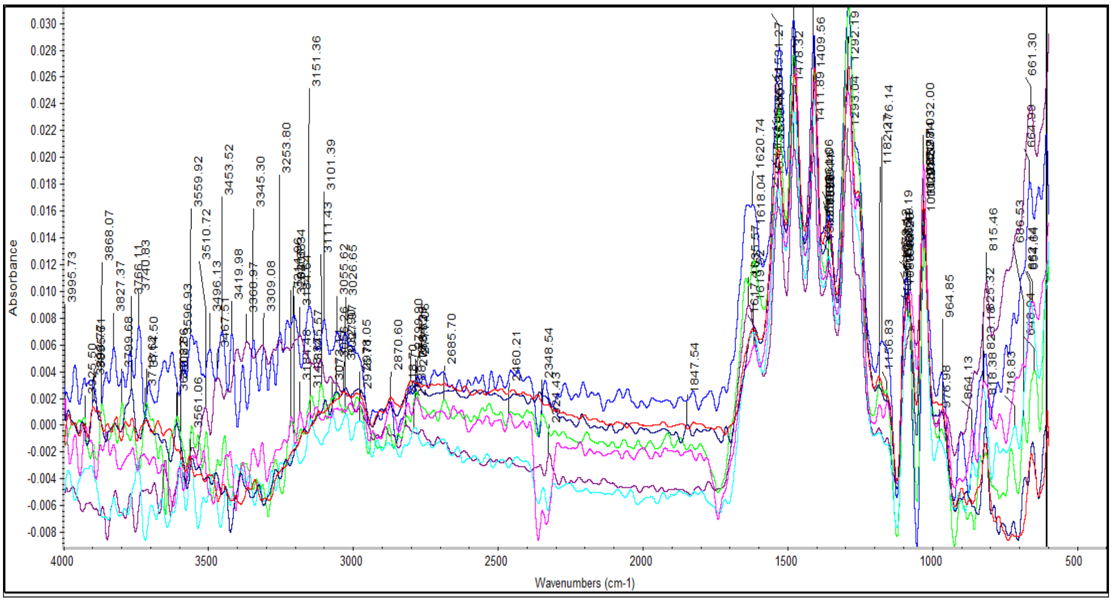


**Figure 4.6** FTIR Spectra for 6M DEA with 200 ml/min $CO_2$ flowrate

Figure 4.6 showed the overlapping of spectrum for 6M DEA with 200 ml/min flow rate $CO_2$ from t=1 hour to t=7 hours reaction times. Based on the figure above, the peak height and the absorbance is varies at different reaction time. The spectra are ranged between 4000 to 500 $cm^{-1}$ but there are no significant values from 1800 until 2900 of wavelength. The only peak of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ are observed and used in data evaluation. By continuous recording of spectra during $CO_2$ absorption, the applicability of FTIR spectroscopy for the qualitative monitoring of the reaction was proven. Based on the graph, the absorbance value is not increased or decreased consistently in 7 hours reaction times. During the absorption, the absorbance of the peak at 3500, 3000, 1600, 1500, 1400 and 1300 $cm^{-1}$ can be seen as in table 4.6.

## 4.2 Selection of Affected Peak

The FTIR spectra were recorded during the absorption process for 2M, 4M and 6M DEA with different $CO_2$ flowrate 100 ml/min and 200 ml/min for 7 hours reaction times as in figure 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6 in section 4.1 above. From the spectra obtained, the most important peaks which give the absorbance values are selected. According to the FTIR analysis result, the peaks with 3500, 3300, 1600, 1500, 1400, 1300, 1200 and 1000 $cm^{-1}$ are selected and the absorbance value were determined for DEA concentration of each peaks for 7 hours reaction times.

During the absorption process, the important spectra changes either peak absorbance or the wavelength were be increased or decreased in 7 hours of reaction times or shifting towards the new wavelength. The increasing of peak absorbance can be related to the reaction products which is mainly are carbamate, hydrogen carbonate ($HCO_3^-$), carbonate ($CO_3^{2-}$) and protonated amine while the decreasing of peak absorbance can be related to the reactant itself which is amine. The peaks selected were compared with the characteristic IR absorption frequencies of the functional group as in table 2.2 and table 2.3 in section 2.5.1. The trend for the peak absorbance of each peak selected with 7 hours reaction time is showed in Figure 4.7, 4.8, 4.9, 4.10. 4.11 and 4.12.

### 4.2.1 Selection the most affected peaks of 2M DEA with 100 ml/min $CO_2$ flowrate

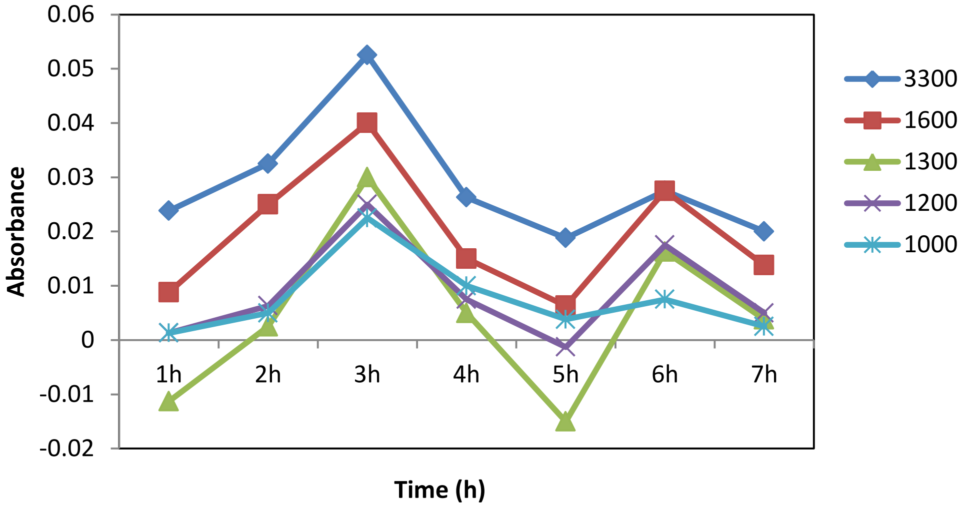


**Figure 4.7** Graph of absorbance versus time for 2M DEA with 100ml/min $CO_2$ flowrate

**Table 4.1** Absorbance for wavelength of 3300, 1600, 1300, 1200 and 1000 $cm^{-1}$ for 7 hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3300 | 1600 | 1300 | 1200 | 1000 |
|---|---|---|---|---|---|
| 1h | 0.0238 | 0.0088 | -0.0113 | 0.0013 | 0.0013 |
| 2h | 0.0325 | 0.0250 | 0.0025 | 0.0063 | 0.0050 |
| 3h | 0.0525 | 0.0400 | 0.0300 | 0.0250 | 0.0225 |
| 4h | 0.0263 | 0.0150 | 0.0050 | 0.0075 | 0.0100 |
| 5h | 0.0188 | 0.0063 | -0.0150 | -0.0013 | 0.0038 |
| 6h | 0.0275 | 0.0275 | 0.0163 | 0.0175 | 0.0075 |
| 7h | 0.0200 | 0.0138 | 0.0038 | 0.0050 | 0.0025 |

The FTIR spectra were recorded for 2M with 100 ml/min in 7 hours reaction times. The most affected peak was selected from the spectra obtained in Figure 4.1 consist of 3300, 1600, 1300, 1200 and 1000cm$^{-1}$ which gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 5 peaks selected from the previous section, the peak absorbance was determined as in table 4.1. The graph of absorbance versus time of 2M DEA with 100 ml/min $CO_2$ flowrate were plotted as in figure 4.7 based on the data from table 4.1 for 7 hours reaction times.

For 7 hours reaction time, the peak 3300 cm$^{-1}$ has highest absorbance whereas the peak 1300 cm$^{-1}$ has the lowest absorbance. As the reaction progress from 1 hour to 7 hour, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. Based on figure 4.7, at t=3h, the absorbance is highest at each selected peak. The peak 3300 cm$^{-1}$ (3500-3300 cm$^{1}$) has highest absorbance which regarded to N-H appeared in that region of the IR spectrum while the peak 1000 cm$^{-1}$ and 1300 cm$^{-1}$ (1020-1340 cm$^{-1}$), -HN-$CO_2$ (carbamate) appeared. The absorbance of 5 selected peaks is decreased with increasing the reaction time because as the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}$/$HCO_3^-$ system towards $HCO_3^-$.

### 4.2.2 Selection the most affected peaks of 2M DEA with 200 ml/min $CO_2$ flowrate

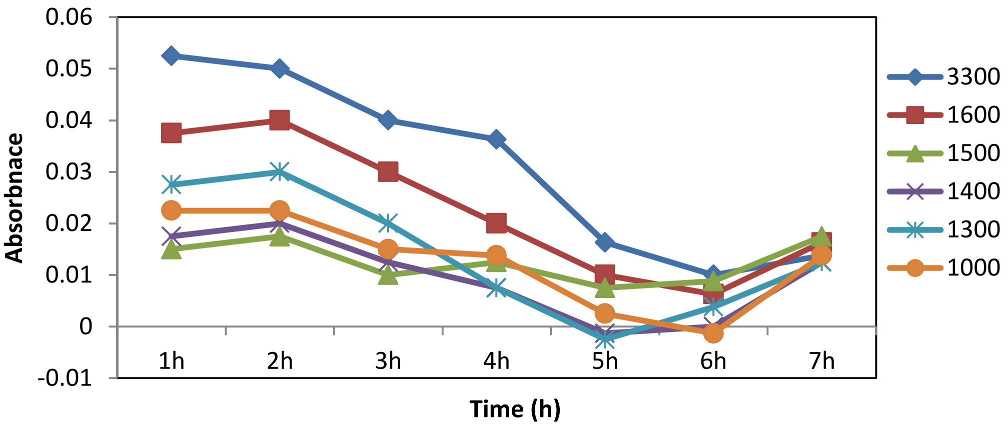


**Figure 4.8** Graph of absorbance versus time for 2M DEA with 200 ml/min $CO_2$ flowrate

**Table 4.2** Absorbance for wavelength of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ for 7 hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3300 | 1600 | 1500 | 1400 | 1300 | 1000 |
|---|---|---|---|---|---|---|
| 1h | 0.0525 | 0.0375 | 0.0150 | 0.0175 | 0.0275 | 0.0225 |
| 2h | 0.0500 | 0.0400 | 0.0175 | 0.0200 | 0.0300 | 0.0225 |
| 3h | 0.0400 | 0.0300 | 0.0100 | 0.0125 | 0.0200 | 0.0150 |
| 4h | 0.0363 | 0.0200 | 0.0125 | 0.0075 | 0.0075 | 0.0138 |
| 5h | 0.0163 | 0.0100 | 0.0075 | -0.0013 | -0.0025 | 0.0025 |
| 6h | 0.0100 | 0.0063 | 0.0088 | 0.0000 | 0.0038 | -0.0013 |
| 7h | 0.0138 | 0.0163 | 0.0175 | 0.0125 | 0.0125 | 0.0138 |

The FTIR spectra were recorded for 2M with 200 ml/min for 7 hours reaction times. The 6 most affected peak was selected from the spectra obtained in figure 4.2 consist of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ which gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 6 peaks selected from the previous section the peak absorbance was determined as in table 4.2. The graph of absorbance versus time of 2M DEA with 200 ml/min $CO_2$ flowrate were plotted as in figure 4.8 based on the data from table 4.2 for 7 hours reaction time.

Based on figure 4.8, at t=2h reaction time the absorbance is highest at each selected peak. For 7 hours reaction time, the peak 3300 $cm^{-1}$ has highest absorbance whereas the peak 1500 $cm^{-1}$ has the lowest absorbance. As the reaction progress from 1 hour to 7 hours, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. The absorbance at peak 3300 $cm^{-1}$ (3500-3300 $cm^{-1}$) is highest at t=1h reaction time which regarded to the highest of N-H appeared. The absorbance for the other 5 selected peaks is highest at t=2h reaction times. The highest $-HN-CO_2$ (carbamate) appeared at 1000$cm^{-1}$ and 1300 $cm^{-1}$ (1080-1360$cm^{-1}$) peaks at t=2h reaction time. The absorbance of 6 selected peaks is decreased with increasing the reaction time because as the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}/HCO_3^-$ system towards $HCO_3^-$ .

### 4.2.3 Selection the most affected peaks of 4M DEA with 100 ml/min $CO_2$ flowrate

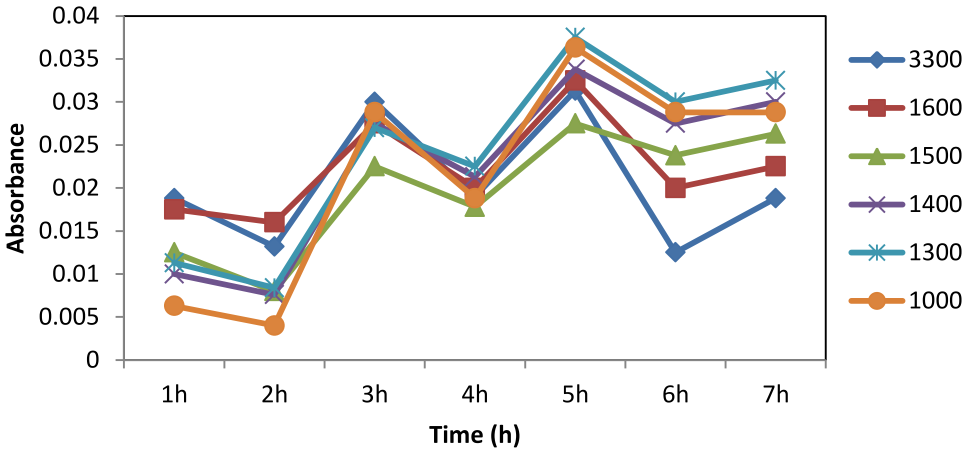


**Figure 4.9** Graph of absorbance versus time for 2M DEA with 100 ml/min $CO_2$ flowrate

**Table 4.3** Absorbance for wavelength of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ for 7 hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3300 | 1600 | 1500 | 1400 | 1300 | 1000 |
|---|---|---|---|---|---|---|
| 1h | 0.0188 | 0.0175 | 0.0125 | 0.0100 | 0.0113 | 0.0063 |
| 2h | 0.0132 | 0.0160 | 0.0080 | 0.0076 | 0.0084 | 0.0040 |
| 3h | 0.0300 | 0.0275 | 0.0225 | 0.0275 | 0.0270 | 0.0288 |
| 4h | 0.0190 | 0.0200 | 0.0178 | 0.0213 | 0.0225 | 0.0188 |
| 5h | 0.0313 | 0.0325 | 0.0275 | 0.0338 | 0.0375 | 0.0363 |
| 6h | 0.0125 | 0.0200 | 0.0238 | 0.0275 | 0.0300 | 0.0288 |
| 7h | 0.0188 | 0.0225 | 0.0263 | 0.0300 | 0.0325 | 0.0288 |

The FTIR spectra were recorded for 4M with 100 ml/min for 7 hours reaction times. The 6 most affected peak was selected from the spectra obtained in Figure 4.2 consist of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ which gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 6 peaks selected from the previous section the peak absorbance was determined as in table 4.3. The graph of absorbance versus time of 4M DEA with 100 ml/min $CO_2$ flowrate were plotted as in figure 4.9 based on the data from table 4.3 for 7 hours reaction times.

From the figure 4.9, the absorbance for 7 hours reaction time is highest at 1300 $cm^{-1}$ peak while the lowest absorbance peak is at 1500 $cm^{-1}$ peak. As the reaction progress from 1 hour to 7 hours, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. The absorbance at the peak 1300 $cm^{-1}$ (1080-1360 $cm^{-1}$) is highest at t=5h reaction times which regarded to the highest of -HN-$CO_2$ (carbamate) appeared in that region of IR spectra. Highest N-H appeared at peak 1500 $cm^{-1}$(1650-1580 $cm^{-1}$) at t=5h. The absorbance of 6 selected peaks is decreased with increasing the reaction time because as the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}/HCO_3^-$ system towards $HCO_3^-$.

### 4.2.4 Selection the most affected peaks of 4M DEA with 200 ml/min $CO_2$ flowrate

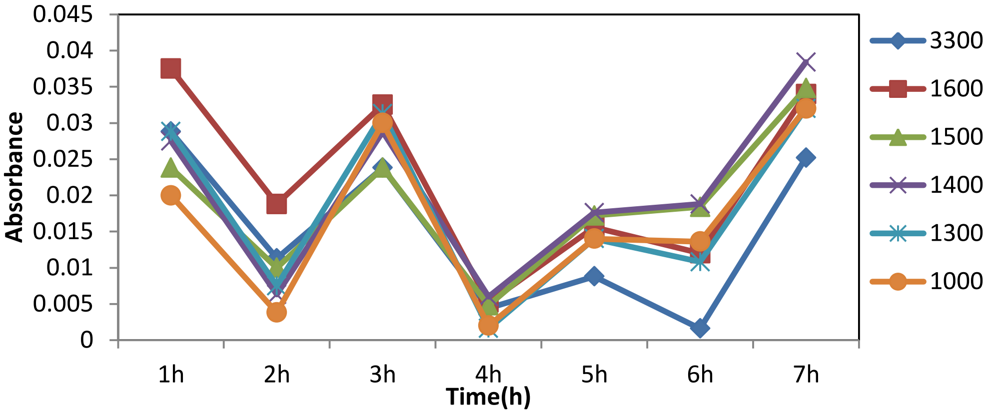


**Figure 4.10** Graph of absorbance versus time for 4M DEA with 200 ml/min $CO_2$ flowrate

**Table 4.4** Absorbance for wavelength of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ for 7hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3300 | 1600 | 1500 | 1400 | 1300 | 1000 |
|---|---|---|---|---|---|---|
| 1h | 0.0288 | 0.0375 | 0.0238 | 0.0275 | 0.0288 | 0.0200 |
| 2h | 0.0113 | 0.0188 | 0.0100 | 0.0063 | 0.0075 | 0.0038 |
| 3h | 0.0238 | 0.0325 | 0.0238 | 0.0288 | 0.0313 | 0.0300 |
| 4h | 0.0044 | 0.0052 | 0.0048 | 0.0060 | 0.0016 | 0.0020 |
| 5h | 0.0088 | 0.0156 | 0.0172 | 0.0176 | 0.0140 | 0.0140 |
| 6h | 0.0016 | 0.0120 | 0.0184 | 0.0188 | 0.0108 | 0.0136 |
| 7h | 0.0252 | 0.0340 | 0.0348 | 0.0384 | 0.0320 | 0.0320 |

The FTIR spectra were recorded for 4M with 200 ml/min for 7 hours reaction times. The 6 most affected peak was selected from the spectra obtained in Figure 4.2 consist of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ which gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 6 peaks selected from the previous section the peak absorbance was determined as in table 4.4. The graph of absorbance versus time of 4M DEA with 200 ml/min $CO_2$ flowrate were plotted as in figure 4.10 based on the data from table 4.4 for 7 hours reaction time.

As the reaction progress from 1 hour to 7 hours, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. The absorbance for the peak 1000 $cm^{-1}$ and 1300 $cm^{-1}$ (1020-1340 $cm^{-1}$) is highest at t=3h and t=7h reaction time. It regarded to the highest of NH-$CO_2$ (carbamate) appeared in that region of IR spectra. The absorbance peak at 3300 $cm^{-1}$ (3500-3300 $cm^{-1}$) is lowest in 7 hours reaction time which regarded to N-H appeared in that IR spectra region. The absorbance of 6 selected peaks is not constantly decreased with the reaction time. As the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}$/$HCO_3^-$ system towards $HCO_3^-$.

### 4.2.5 Selection the most affected peaks of 6M DEA with 100ml/min $CO_2$ flowrate

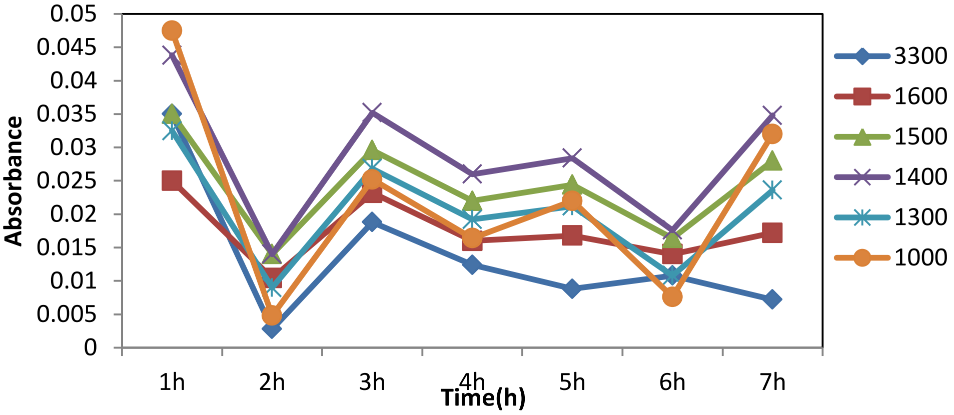


**Figure 4.11** Graph of absorbance versus time for 6M DEA with 100ml/min $CO_2$ flowrate

**Table 4.5** Absorbance for wavelength of 3300, 1600, 1500, 1400, 1300 and 1000 $cm^{-1}$ for 7hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3300 | 1600 | 1500 | 1400 | 1300 | 1000 |
|---|---|---|---|---|---|---|
| 1h | 0.0350 | 0.0250 | 0.0350 | 0.0438 | 0.0325 | 0.0475 |
| 2h | 0.0028 | 0.0104 | 0.0140 | 0.0140 | 0.0090 | 0.0048 |
| 3h | 0.0188 | 0.0232 | 0.0296 | 0.0352 | 0.0268 | 0.0252 |
| 4h | 0.0124 | 0.0160 | 0.0220 | 0.0260 | 0.0192 | 0.0164 |
| 5h | 0.0088 | 0.0168 | 0.0244 | 0.0284 | 0.0212 | 0.0220 |
| 6h | 0.0108 | 0.0140 | 0.0164 | 0.0176 | 0.0108 | 0.0076 |
| 7h | 0.0072 | 0.0172 | 0.0280 | 0.0348 | 0.0236 | 0.0320 |

The FTIR spectra were recorded for 6M with 100 ml/min for 7 hours reaction times. The 6 most affected peak was selected from the spectra obtained in Figure 4.2 consist of 3300, 1600, 1500, 1400, 1300 and 1000cm$^{-1}$ gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 6 peaks selected from the previous section the peak absorbance was determined as in table 4.5. The graph of absorbance versus time of 6M DEA with 100ml/min $CO_2$ flowrate were plotted as in figure 4.11 based on the data from table 4.5 for 7 hours reaction times.

From the figure 4.11, the absorbance for 7 hours reaction time is highest at 1400 cm$^{-1}$ peak whereas the lowest absorbance peak is at 3300 cm$^{-1}$ peak. As the reaction progress from 1 hour to 7 hours, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. The absorbance at the peak 1400 cm$^{-1}$ (1470-1350 cm$^{-1}$) is highest which regarded to the highest of C-H appeared while the absorbance peak at 3300cm$^{-1}$ is lowest in 7 hours reaction time which regarded to N-H appeared there. The highest -HN-$CO_2$ (carbamate) appeared at the peak 1000 cm$^{-1}$(1020-1340 cm$^{-1}$) at t=1h reaction times. The absorbance of 6 selected peaks is decreased with increasing the reaction time because as the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}$ /$HCO_3^-$ system towards $HCO_3^-$.

### 4.2.6 Selection the most affected peaks of 6M DEA with 200 ml/min $CO_2$ flowrate

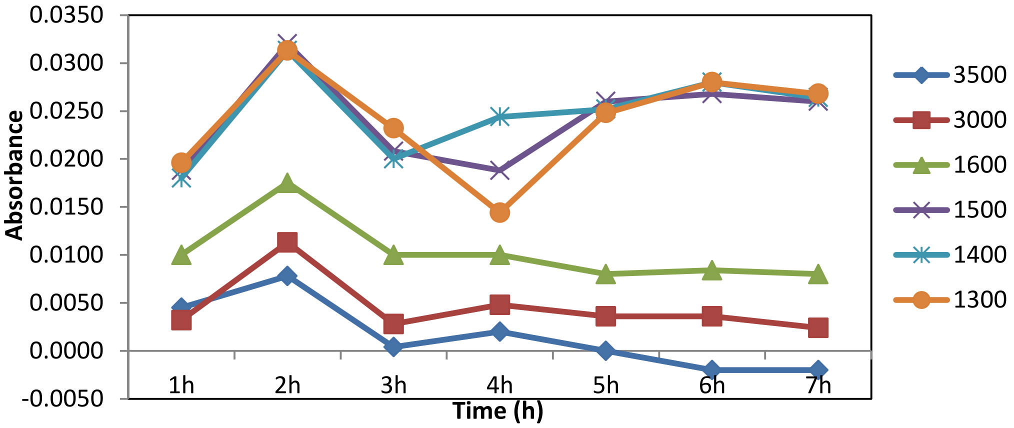


**Figure 4.12** Graph of absorbance versus time for 6M DEA with 200 ml/min $CO_2$ flowrate

**Table 4.6** Absorbance for wavelength of 3500, 3000, 1600, 1500, 1400 and 1300 $cm^{-1}$ for 7 hours reaction time

| Time(h)/Wavelength($cm^{-1}$) | 3500 | 3000 | 1600 | 1500 | 1400 | 1300 |
|---|---|---|---|---|---|---|
| 1h | 0.0045 | 0.0032 | 0.0100 | 0.0188 | 0.0180 | 0.0196 |
| 2h | 0.0078 | 0.0113 | 0.0175 | 0.0320 | 0.0313 | 0.0313 |
| 3h | 0.0004 | 0.0028 | 0.0100 | 0.0208 | 0.0200 | 0.0232 |
| 4h | 0.0020 | 0.0048 | 0.0100 | 0.0188 | 0.0244 | 0.0144 |
| 5h | 0.0000 | 0.0036 | 0.0080 | 0.0260 | 0.0252 | 0.0248 |
| 6h | -0.0020 | 0.0036 | 0.0084 | 0.0268 | 0.0280 | 0.0280 |
| 7h | -0.0020 | 0.0024 | 0.0080 | 0.0260 | 0.0264 | 0.0268 |

The FTIR spectra were recorded for 6M with 200 ml/min for 7 hours reaction times. The 6 most affected peak was selected from the spectra obtained in Figure 4.2 consist of 3500, 3000 1600, 1500, 1400 and 1300 $cm^{-1}$ gives the absorbance value that can be used to monitor evolution of $CO_2$-DEA reaction products. Based on the 6 peaks selected from the previous section the peak absorbance was determined as in table 4.6. The graph of absorbance versus time of 6M DEA with 100 ml/min $CO_2$ flowrate were plotted as in figure 4.12 based on the data from table 4.6 for 7 hours reaction times.

From the figure 4.12, for 7 hours reaction time the absorbance is highest at 1400 $cm^{-1}$ peak whereas the lowest absorbance peak is at 3500 $cm^{-1}$ peak. As the reaction progress from 1hours to 7 hours, all of the peaks are shift in frequency regarding to the product formation or the reactant itself. The absorbance for the peak 1400 $cm^{-1}$(1470-1350 $cm^{-1}$) is highest at t=2h reaction time which means highest of C-H appeared. The absorbance peak at 3500 $cm^{-1}$ (3300-3500 $cm^{-1}$) is lowest in 7 hours reaction time regarded to N-H appeared in that IR spectra region. The highest $NH-CO_2$ (carbamate) appeared at the peak 1300$cm^{-1}$(1020-1340 $cm^{-1}$) at t=2h. The absorbance of 6 selected peaks is decreased with increasing the reaction time because as the $CO_2$ loading of the reaction solution is increased, the pH of the solution is decreased from a high pH to low pH which is from 13 to 7pH. This shift the equilibrium in the $CO_3^{2-}/HCO_3^-$ system towards $HCO_3^-$.

## 4.3 Comparison between Different DEA Concentrations

### 4.3.1 Comparison between 2M, 4M and 6M DEA with 100 ml/min $CO_2$ Flowrate

The $CO_2$ absorption capacity was compared with different DEA concentration, 2M, 4M and 6M of 100 ml/min $CO_2$ flowrate based on the trend in section 4.2. The 4M of DEA concentration had higher $CO_2$ absorption capacity compared to 2M and 6M DEA. The 2M of DEA concentration had the lowest $CO_2$ absorption capacity compared with the other two DEA concentrations.

### 4.3.2 Comparison between 2M, 4M and 6M DEA with 200 ml/min $CO_2$ Flowrate

The $CO_2$ absorption capacity was compared with different DEA concentration, 2M, 4M and 6M of 200 ml/min $CO_2$ flowrate based on the trend in section 4.2. The 6M of DEA concentration had higher absorption capacity compared to 2M and 4M DEA. The 2M of DEA concentration had the lowest $CO_2$ absorption capacity compared with the other two DEA concentrations.

## 4.4 Principal Component Analysis (PCA)

PCA is the study of multivariate data which is a technique from statistics for simplifying a data set were used to characterize the DEA-$CO_2$ system. The purpose of PCA to extract the maximum variance from a data set with a few orthogonal components. In order to monitor the absorption progress of $CO_2$ loading process in DEA aqueous solution this experiment, PCA is used to extract and simplify the absorption behaviour of the system rather than selecting a specific peaks randomly. PCA was performed for each DEA concentration with different $CO_2$ flow rate for 2M with 100 ml/min, 2M with 200 ml/min, 4M with 100 ml/min, 4M with 200 ml/min, 6M with 100 ml/min and 6M with 200 ml/min. The calculation of PCA was performed using MATLAB software based on the original data of absorbance in matrix form X as in table 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6 above. The function used in MATLAB is princomp with command:

```
[Coeff, score, latent] = princomp(zscore(X))
```

Where coeff represents the loading matrix P, while score is the score vector T which hold the principal components (PCs) value and the latent is the eigenvalues of the covariance matrix of X. The coeff and score from PCA calculation for 2M, 4M and 6M with 100ml/min and 200ml/min showed in appendixes. The latent value obtained from PCA calculation are expressed as a percentage of the total variance and were calculated by using equation 4.1.

$$\frac{\lambda_i}{\Sigma_{i=1}\lambda_i}\times 100\% \qquad (4.1)$$

The percentage of each latent obtained will determine the PC which is represented the PC1, PC2, PC3 and so on that give the most explanation about the variability of the data. The first component which has captured the largest variation in the data matrix based on the latent value, λ more than 85% can be used to characterize the whole system. Results from calculation were tabulated in table 4.7, 4.8, 4.9, 4.10, 4.11 and 4.12. Then the selected PC was plotted in figure 4.13, 4.14, 4.15, 4.16, 4.17, 4.18 and 4.19. Then the trend of the graph for the selected PC was compared with the peak as in section 4.2 to identify the compound exists.

### 4.4.1 PCA of 2M DEA with 100 ml/min $CO_2$ flowrate

Table 4.7 showed the result for the latent values ($\lambda$) from PCA calculation for 2M DEA with 100 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 90.8% which mean a very large variation of data has been captured by the first principal component (PC1) followed by PC2 with 5.54% and PC3 with 2.86%. The $\lambda$ value for PC4 and PC5 are 0.47% and 0.29%.

**Table 4.7** PCA Latent value for spectra 2M DEA with 100 ml/min $CO_2$ flowrate

| PC | Latent value ($\boldsymbol{\lambda_i}$) | $\frac{\boldsymbol{\lambda_i}}{\boldsymbol{\lambda_{total}}}$ | Percentage (%) |
|---|---|---|---|
| 1 | 4.54239 | 0.90848 | 90.85 |
| 2 | 0.27711 | 0.05542 | 5.54 |
| 3 | 0.14283 | 0.02857 | 2.86 |
| 4 | 0.02326 | 0.00465 | 0.47 |
| 5 | 0.01441 | 0.00288 | 0.29 |

The first component which has captured the largest variation in the data matrix based on the latent value, $\lambda$ more than 85% can be used to characterize the whole system. With that, One PC is selected to represent the data for $CO_2$ absorption in 2M DEA with 100ml/min.

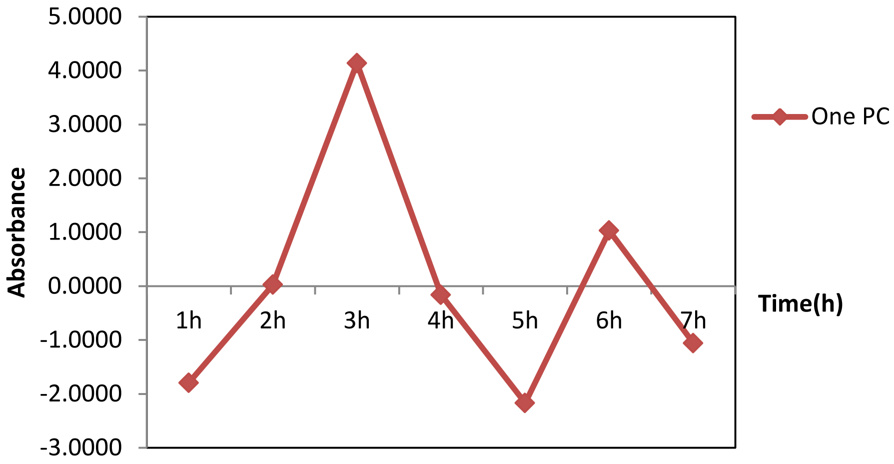


**Figure 4.13** One PC projection for $CO_2$ absorption in 2M DEA with 100 ml/min $CO_2$ flowrate at different reaction time

Then the trend for One PC in figure 4.13 is compared with the original trend as in figure 4.7. The peak that followed the same trend as One PC is the peak 1300 $cm^{-1}$ According to Silvestein et al.,(1981), the compound that was detected with this range value is $-HN-CO_2$ (carbamate). This could precisely describe by the reaction in section 2.4 where carbamate is the product of the reaction.

### 4.4.2 PCA of 2M DEA with 200 ml/min $CO_2$ flowrate

Table 4.8 showed the result for the latent values (λ) from PCA calculation for 2M DEA with 200 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 86.57% which mean a very large variation of data has been captured by the first principal component (PC1) followed by PC2 with 10.78% and PC3 with 2.04%. The λ value for PC4, PC5 and PC6 are 0.47%, 0.13% and 0.02%.

**Table 4.8** PCA Latent values for spectra 2M DEA with 200 ml/min $CO_2$ flowrate

| PC | Latent value ($\lambda_i$) | $\frac{\lambda_i}{\lambda_{total}}$ | Percentage (%) |
|---|---|---|---|
| 1 | 5.19404 | 0.86567 | 86.57 |
| 2 | 0.64662 | 0.10777 | 10.78 |
| 3 | 0.12239 | 0.02040 | 2.04 |
| 4 | 0.02828 | 0.00471 | 0.47 |
| 5 | 0.00755 | 0.00126 | 0.13 |
| 6 | 0.00112 | 0.00019 | 0.02 |

The first component which has captured the largest variation in the data matrix based on the latent value, λ more than 85% can be used to characterize the whole system. With that, One PC is selected to represent the data for $CO_2$ absorption in 2M DEA with 200ml/min.

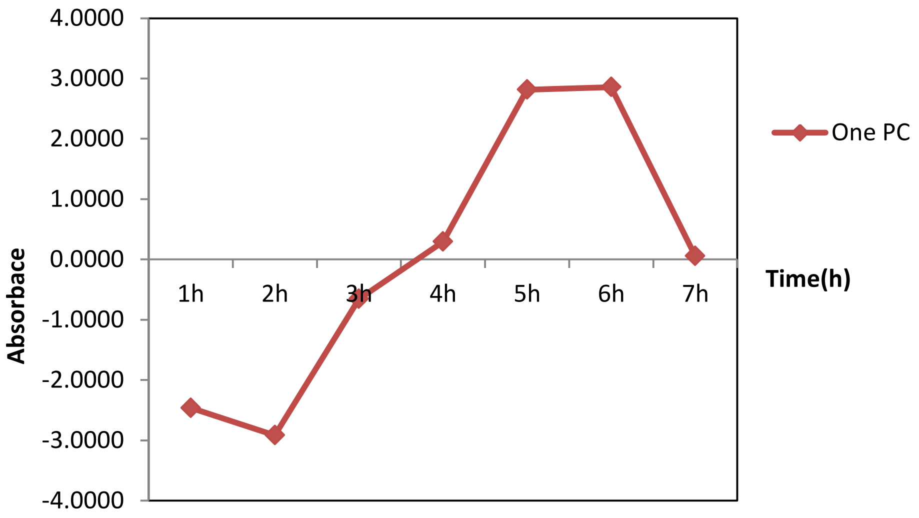


**Figure 4.14** One PC projection for $CO_2$ absorption in 2M DEA with 200 ml/min $CO_2$ flowrate at different reaction time

Then the trend for One PC in figure 4.14 is compared with the original trend as in figure 4.8. The peak that followed the same trend as One PC is the peak 1500 $cm^{-1}$ According to Silvestein et al.,(1981), the compound that was detected with this range value is N-H (amine). This could precisely describe by the reaction in section 2.4 where amine is the reactant of the reaction.

### 4.4.3 PCA of 4M DEA with 100 ml/min $CO_2$ flowrate

Table 4.9 showed the result for the latent values (λ) from PCA calculation for 4M DEA with 100 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 85.29% which mean a very large variation of data has been captured by the first principal component (PC1) followed by PC2 with 13.78% and PC3 with 0.59%. The λ value for PC4, PC5 and PC6 are 0.23%, 0.10% and 0.01%.

**Table 4.9** PCA Latent values for spectra 4M DEA with 100 ml/min $CO_2$ flowrate

| PC | Latent value ($\boldsymbol{\lambda}_i$) | $\frac{\boldsymbol{\lambda}_i}{\boldsymbol{\lambda}_{total}}$ | Percentage (%) |
|---|---|---|---|
| 1 | 5.11734 | 0.85289 | 85.29 |
| 2 | 0.82693 | 0.13782 | 13.78 |
| 3 | 0.03553 | 0.00592 | 0.59 |
| 4 | 0.01397 | 0.00233 | 0.23 |
| 5 | 0.00574 | 0.00096 | 0.10 |
| 6 | 0.00050 | 0.00008 | 0.01 |

The first component which has captured the largest variation in the data matrix based on the latent value, λ more than 85% can be used to characterize the whole system. With that, One PC is selected to represent the data for $CO_2$ absorption in 4M DEA with 100ml/min.

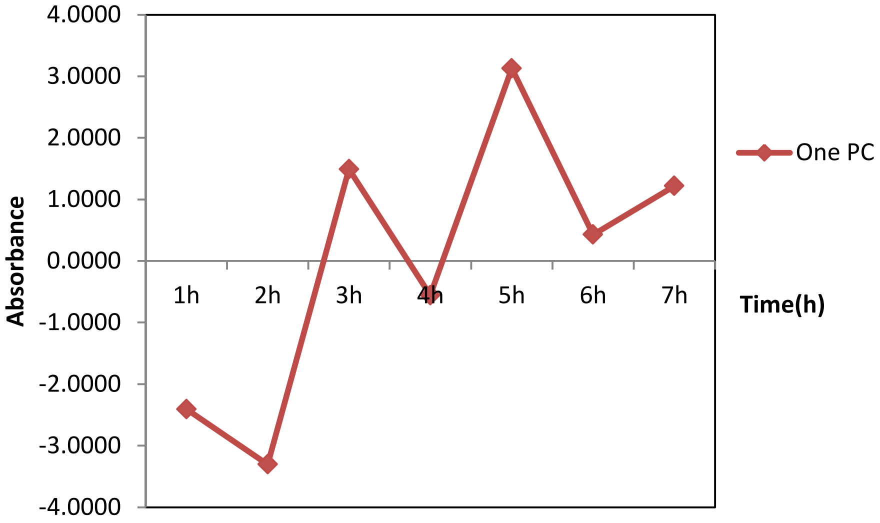


**Figure 4.15** One PC projection for $CO_2$ absorption in 4M DEA with 100 ml/min $CO_2$ flowrate at different reaction time

Then the trend for One PC in figure 4.15 is compared with the original trend as in figure 4.9. The peak that followed the same trend as One PC is the peak 1300 $cm^{-1}$ According to Silvestein et al.,(1981), the compound that was detected with this range value is $-HN-CO_2$ (carbamate). This could precisely describe by the reaction in section 2.4 where carbamate is the product of the reaction.

### 4.4.4 PCA of 4M DEA with 200 ml/min $CO_2$ flowrate

Table 4.10 showed the result for the latent values (λ) from PCA calculation for 4M DEA with 100 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 90.32% which mean a very large variation of data has been captured by the first principal component (PC1) followed by PC2 with 8.01% and PC3 with 1.12%. The λ value for PC4, PC5 and PC6 are 0.41%, 0.12% and 0.02%.

**Table 4.10** PCA Latent values for spectra 4M DEA with 200 ml/min $CO_2$ flowrate

| PC | Latent Value ($\boldsymbol{\lambda_i}$) | $\frac{\boldsymbol{\lambda_i}}{\boldsymbol{\lambda_{total}}}$ | Percentage (%) |
|---|---|---|---|
| 1 | 5.41908 | 0.903181 | 90.32 |
| 2 | 0.48086 | 0.080143 | 8.01 |
| 3 | 0.06723 | 0.011205 | 1.12 |
| 4 | 0.02451 | 0.004086 | 0.41 |
| 5 | 0.00740 | 0.001233 | 0.12 |
| 6 | 0.00091 | 0.000152 | 0.02 |

The first component which has captured the largest variation in the data matrix based on the latent value, λ more than 85% can be used to characterize the whole system. With that, One PC is selected to represent the data for $CO_2$ absorption in 4M DEA with 200ml/min.

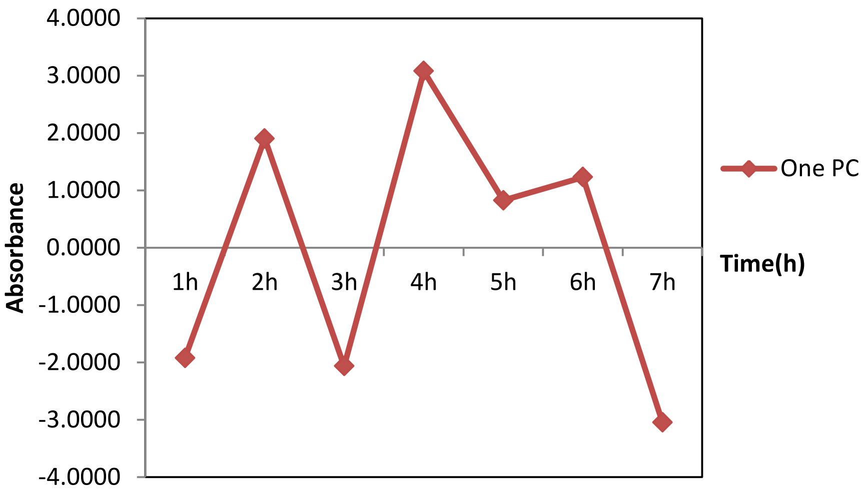


**Figure 4.16** One PC projection for $CO_2$ absorption in 4M DEA with 200 ml/min $CO_2$ flowrate at different reaction time

Then the trend for One PC in figure 4.16 is compared with the original trend as in figure 4.10. The peak that followed the same trend as One PC is the peak 1300 $cm^{-1}$ According to Silvestein et al.,(1981), the compound that was detected with this range value is $-HN-CO_2$ (carbamate). This could precisely describe by the reaction in section 2.4 where carbamate is the product of the reaction.

### 4.4.5 PCA of 6M DEA with 100 ml/min $CO_2$ flowrate

Table 4.10 showed the result for the latent values ($\lambda$) from PCA calculation for 6M DEA with 100 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 92.22% which mean a very large variation of data has been captured by the first principal component (PC1) followed by PC2 with 5.73% and PC3 with 1.84%. The $\lambda$ value for PC4, PC5 and PC6 are 0.17%, 0.03% and 0.00%.

**Table 4.11** PCA Latent values for spectra 6M DEA with 100 ml/min $CO_2$ flowrate

| PC | Latent value ($\lambda_i$) | $\frac{\lambda_i}{\lambda_{total}}$ | Percentage (%) |
|---|---|---|---|
| 1 | 5.53344 | 9E-01 | 92.22 |
| 2 | 0.34380 | 6E-02 | 5.73 |
| 3 | 0.11061 | 2E-02 | 1.84 |
| 4 | 0.01014 | 2E-03 | 0.17 |
| 5 | 0.00200 | 3E-04 | 0.03 |
| 6 | 0.00001 | 1E-06 | 0.00 |

The first component which has captured the largest variation in the data matrix based on the latent value, $\lambda$ more than 85% can be used to characterize the whole system. With that, One PC is selected to represent the data for $CO_2$ absorption in 6M DEA with 100ml/min.

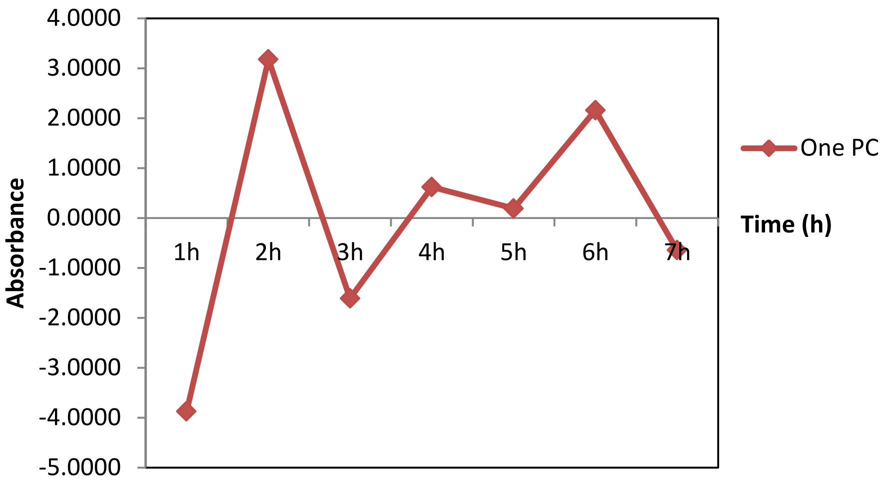


**Figure 4.17** One PC projection for $CO_2$ absorption in 6M DEA with 100 ml/min $CO_2$ flowrate at different reaction time

Then the trend for One PC in figure 4.17 is compared with the original trend as in figure 4.11. The peak that followed the same trend as One PC is the peak 1000 $cm^{-1}$ According to Silvestein et al.,(1981), the compound that was detected with this range value is -HN-$CO_2$ (carbamate). This could precisely describe by the reaction in section 2.4 where carbamate is the product of the reaction.

### 4.4.6 PCA of 6M DEA with 200 ml/min $CO_2$ flowrate

Table 4.12 showed the result for the latent values ($\lambda$) from PCA calculation for 6M DEA with 200 ml/min $CO_2$ flowrate. The $\lambda_1$ value obtained from the calculation give the highest percentage value with 64.10% followed by PC2 with 28.75% and PC3 with 6.07%. The $\lambda$ value for PC4, PC5 and PC6 are 0.91%, 0.12% and 0.05%.

**Table 4.12** PCA Latent values for spectra 6M DEA with 200ml/min $CO_2$ flowrate

| PC | Latent value ($\boldsymbol{\lambda_i}$) | $\frac{\boldsymbol{\lambda_i}}{\boldsymbol{\lambda_{total}}}$ | Percentage (%) | Accumulative Percentage (%) |
|---|---|---|---|---|
| 1 | 3.84616 | 0.64103 | 64.10 | 64.10 |
| 2 | 1.72504 | 0.28751 | 28.75 | 92.85 |
| 3 | 0.36428 | 0.06071 | 6.07 | 98.92 |
| 4 | 0.05463 | 0.00910 | 0.91 | 99.84 |
| 5 | 0.00708 | 0.00118 | 0.12 | 99.95 |
| 6 | 0.00281 | 0.00047 | 0.05 | 100.00 |

The $\lambda$ value obtained from the calculation is 64.1% which is less than 85%. Hence it cannot be explained by the first principal component (PC1). The second principal component, Two PC which is combined of PC1 and PC2 is determined. Two PC produced 92.85% that is very large variation of data compared with One PC. With that, Two PC is selected to represent the data for $CO_2$ absorption in 6M DEA with 200ml/min.

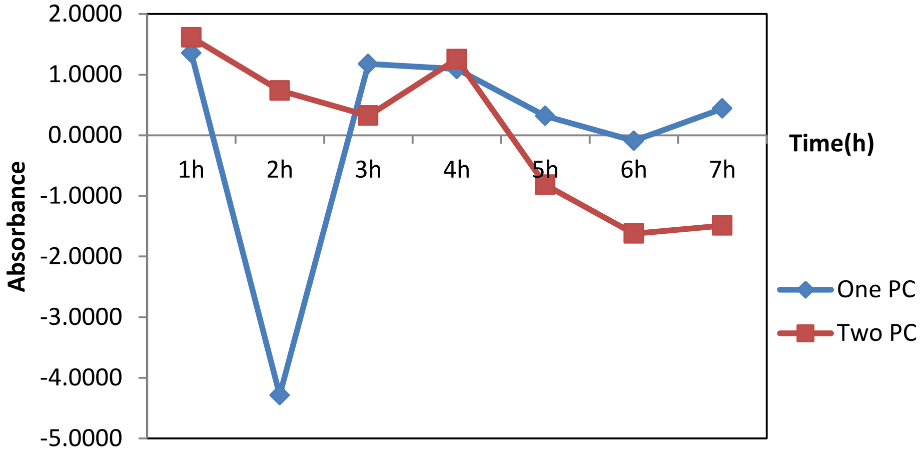


**Figure 4.18** One PC and Two PC projection for $CO_2$ absorption in 6M DEA with 200 ml/min $CO_2$ flowrate at different reaction time

Figure 4.18 showed the trend for One PC and Two PC. Then the trend for Two PC in figure 4.18 is compared with the original trend as in figure 4.12. The peak that followed the same trend as Two PC is the peak 1300 $cm^{-1}$. According to Silvestein et al.,(1981), the compound that was detected with this range value is -HN-$CO_2$ (carbamate). This could precisely describe by the reaction in section 2.4 where carbamate is the product of the reaction.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 CONCLUSION

The experiment for $CO_2$ absorption in different concentration of DEA, 2M, 4M and 6M with 100 ml/min and 200 ml/min $CO_2$ flowrate was successfully conducted. The samples collected during the experiment were being analysed using FTIR spectroscopy. As the conclusion, FTIR spectra for $CO_2$-DEA system are successfully obtained. FTIR are feasible to be used to monitor the absorption process of $CO_2$ in different DEA concentration and $CO_2$ flowrate because it gives a fast analysis and reliable measurement. The multivariate technique of PCA can be applied to characterize the absorption behavior by resulting the spectrum obtained from the experiment. Table 5.1 showed the summary of results obtained from $CO_2$-DEA behaviour.

**Table 5.1** Summary of results

| Case | Number of PC's | Characteristic peak |
|---|---|---|
| 2M DEA with 100ml/min $CO_2$ flowrate | 1 | Carbamate |
| 2M DEA with 200ml/min $CO_2$ flowrate | 1 | Amine |
| 4M DEA with 100ml/min $CO_2$ flowrate | 1 | Carbamate |
| 4M DEA with 200ml/min $CO_2$ flowrate | 1 | Carbamate |
| 6M DEA with 100ml/min $CO_2$ flowrate | 1 | Carbamate |
| 6M DEA with 200ml/min $CO_2$ flowrate | 2 | Carbamate |

## 5.2 RECOMMENDATION

As the recommendation, more analysis should be done to have better data in making comparison of each system. Besides that, the other variable also can be observed like temperature and pressure. The other types of amine also can be used as an absorbent like AMP and blending of MDEA with DEA.

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# APPENDIX A

## 1. Experimental

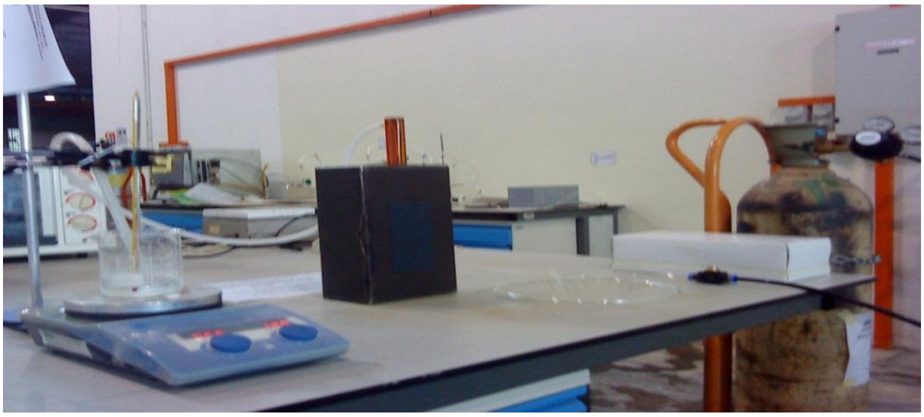

**Figure A-1** Experiment set up

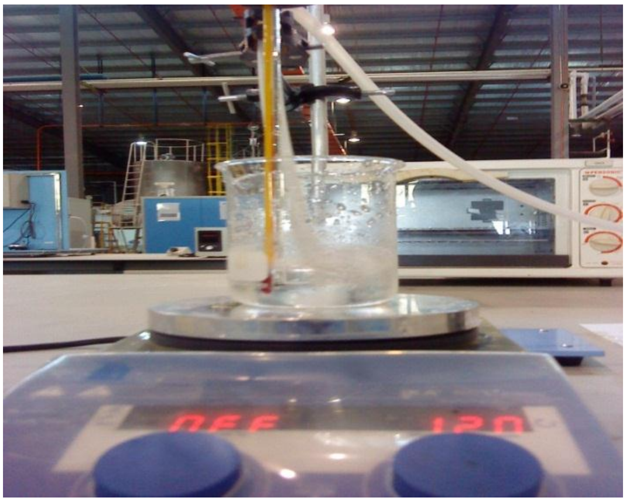

**Figure A-2** $CO_2$ purged into DEA aqueous solution at constant stirrer speed, 120 rpm

### 2. FTIR Spectra 2M DEA with 100ml/min $CO_2$ flowrate for 7 hours reaction time

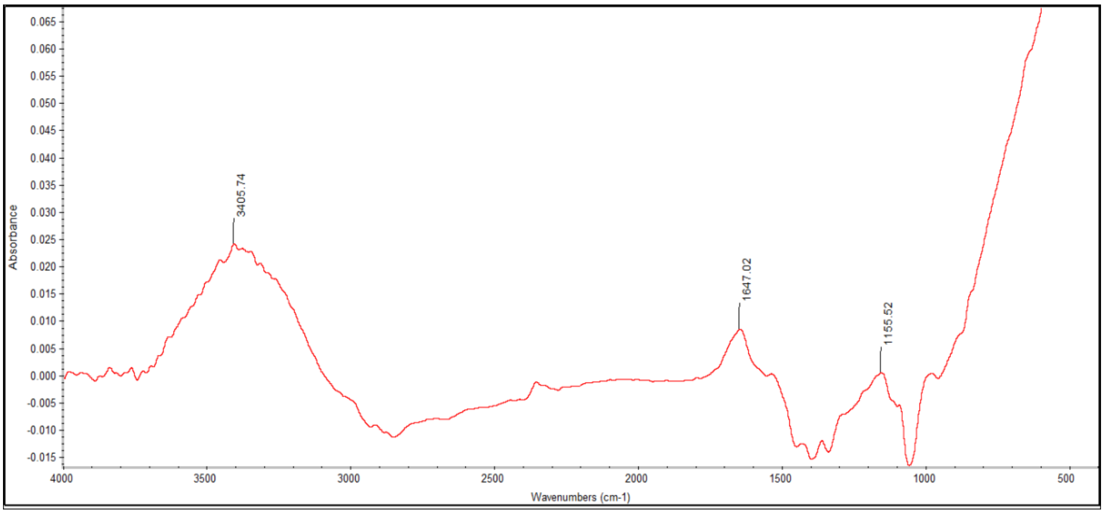

**Figure A-3** 1 hour reaction time

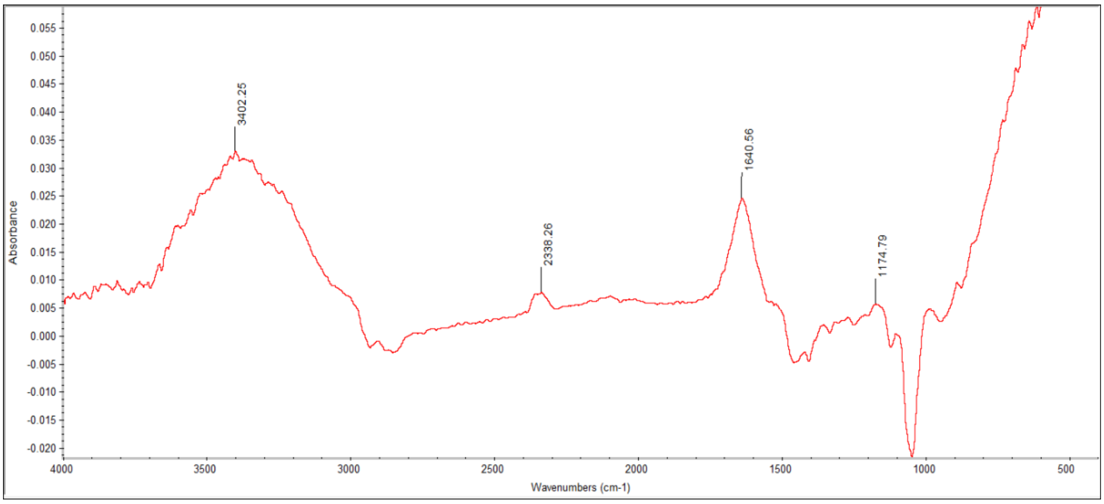

**Figure A-4** 2 hour reaction time

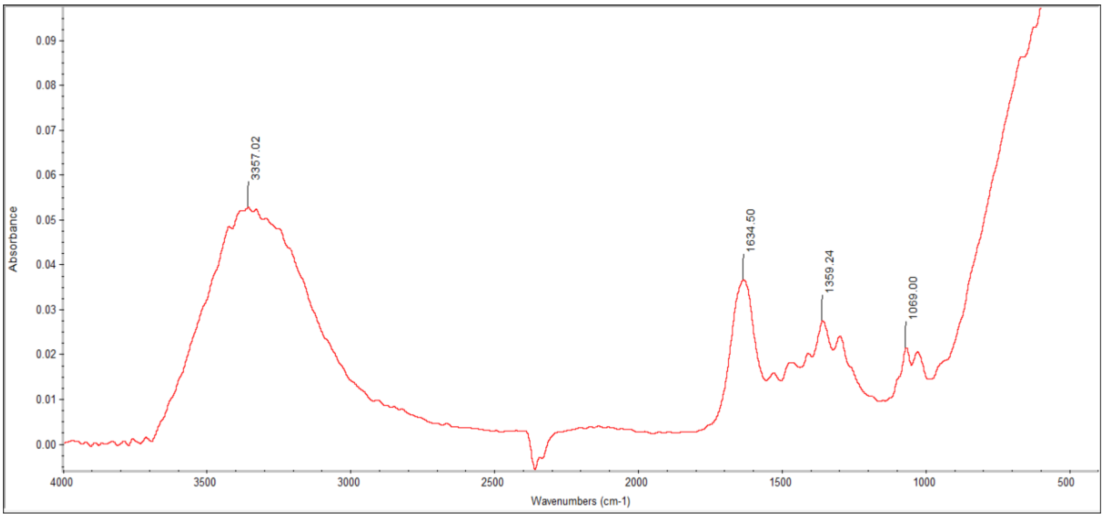

**Figure A-5** 3 hour reaction time

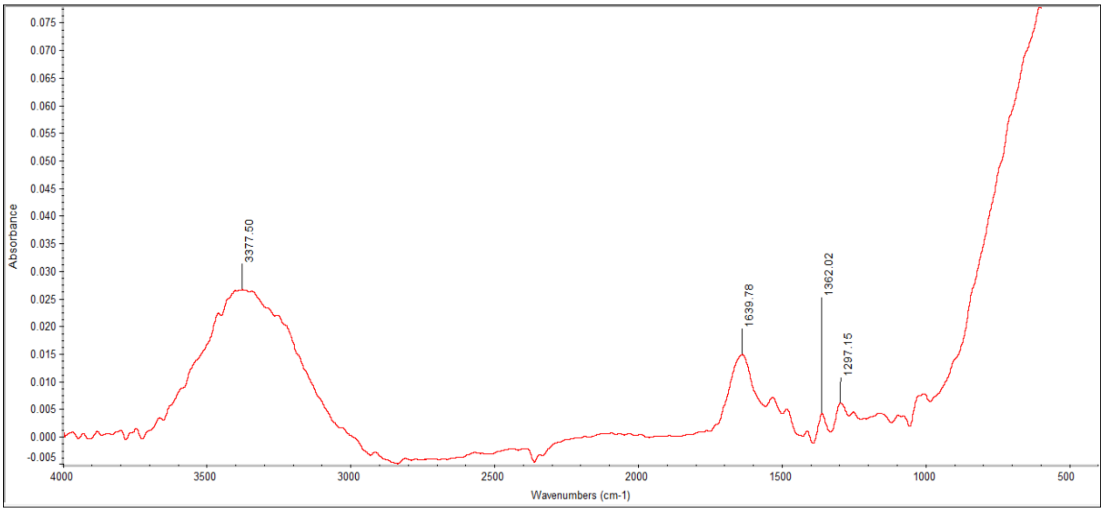

**Figure A-6** 4 hour reaction time

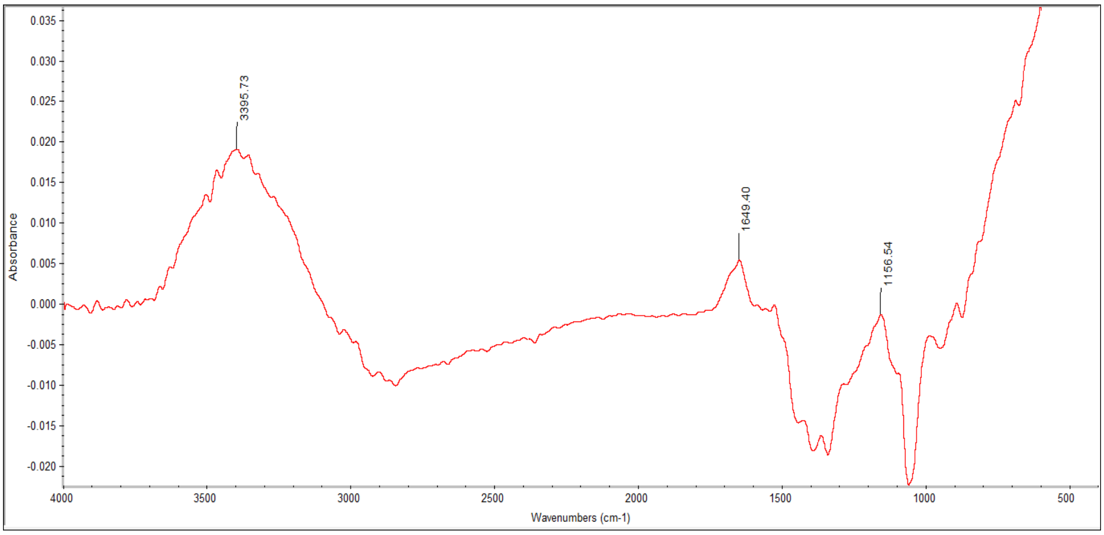

**Figure A-7** 5 hour reaction time

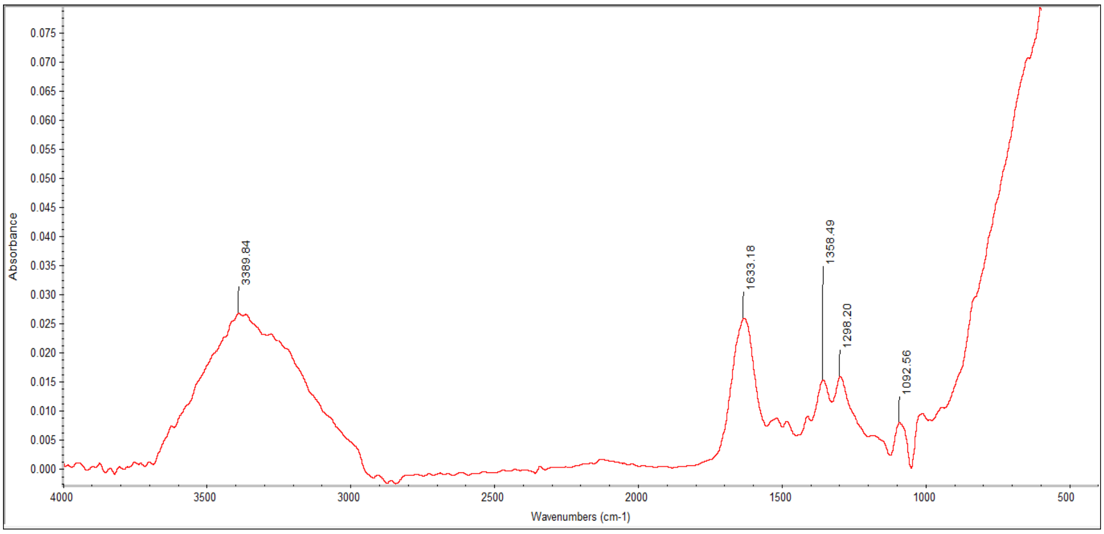

**Figure A-8** 6 hour reaction time

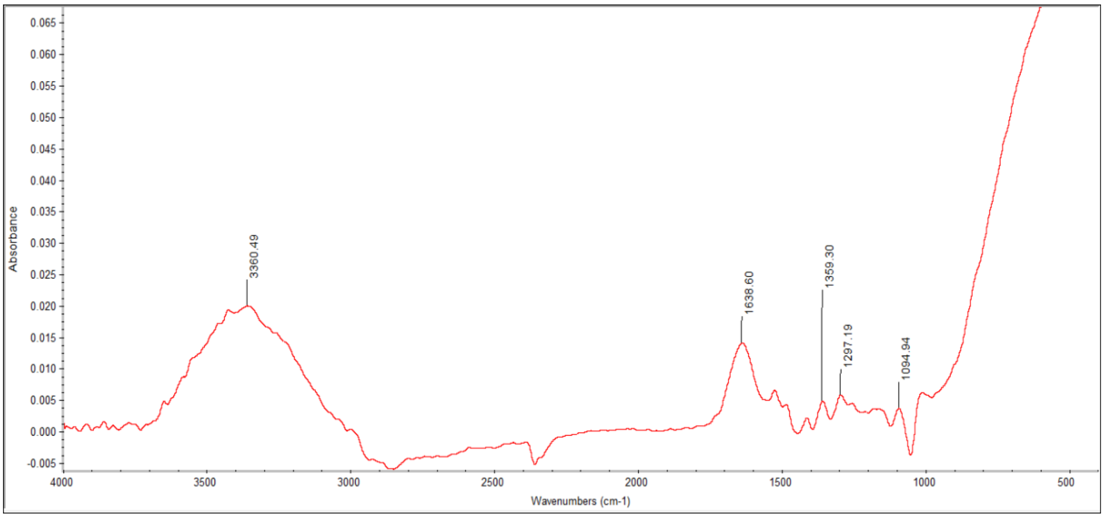

**Figure A-9** 7 hour reaction time

### 3. FTIR Spectra 4M DEA with 100ml/min $CO_2$ flowrate for 7 hours reaction time

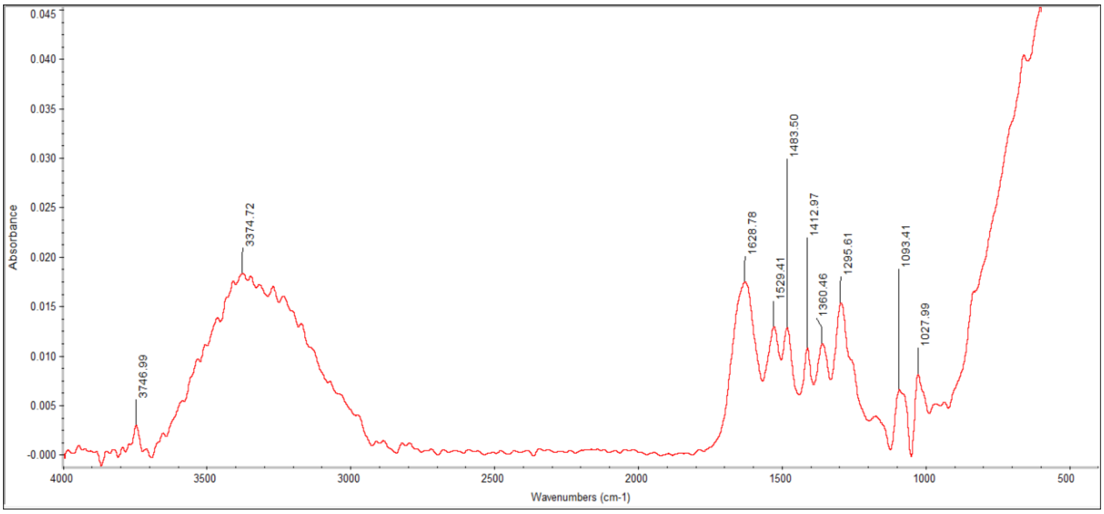

**Figure A-10** 1 hour reaction time

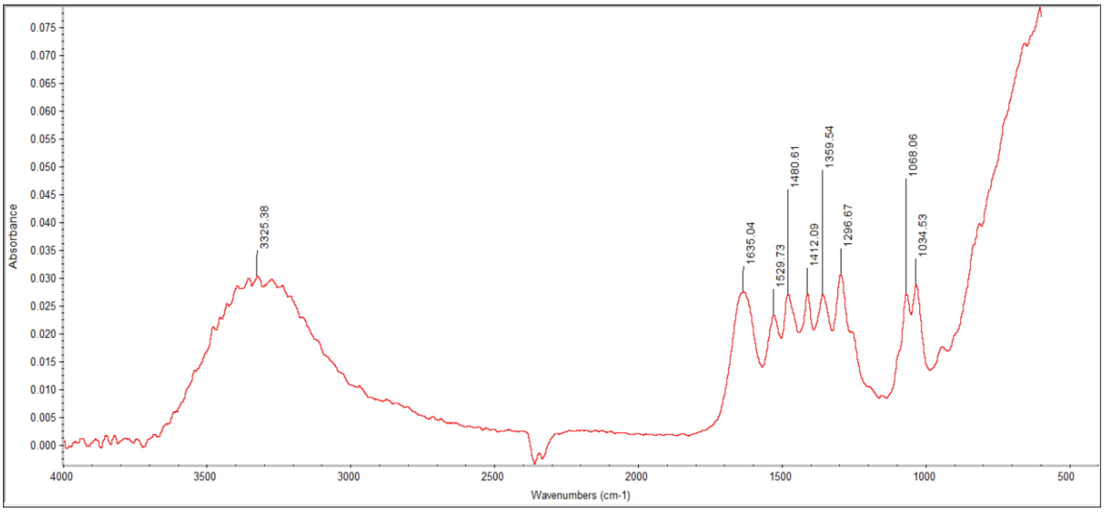

**Figure A-11** 2 hour reaction time

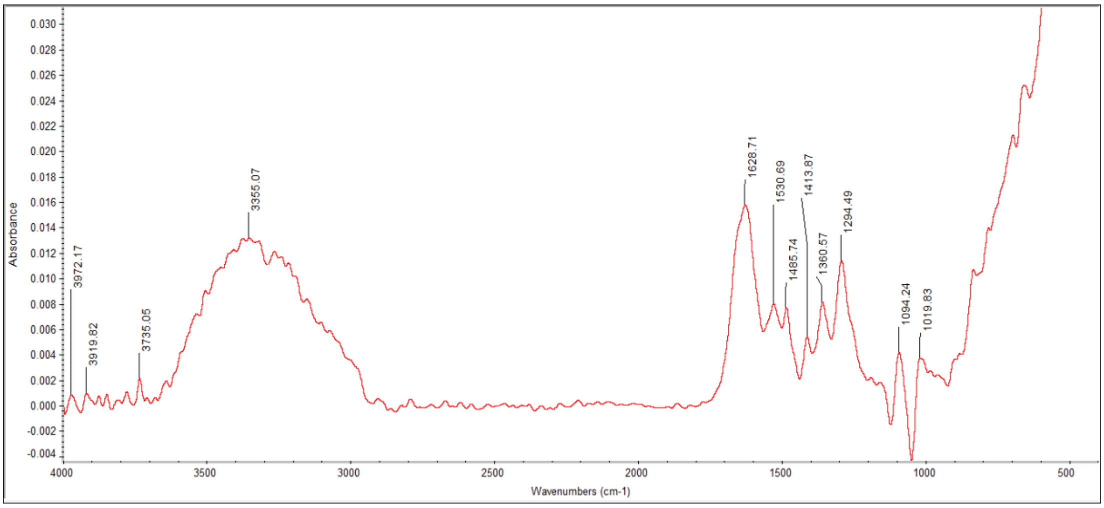

**Figure A-12** 3 hour reaction time

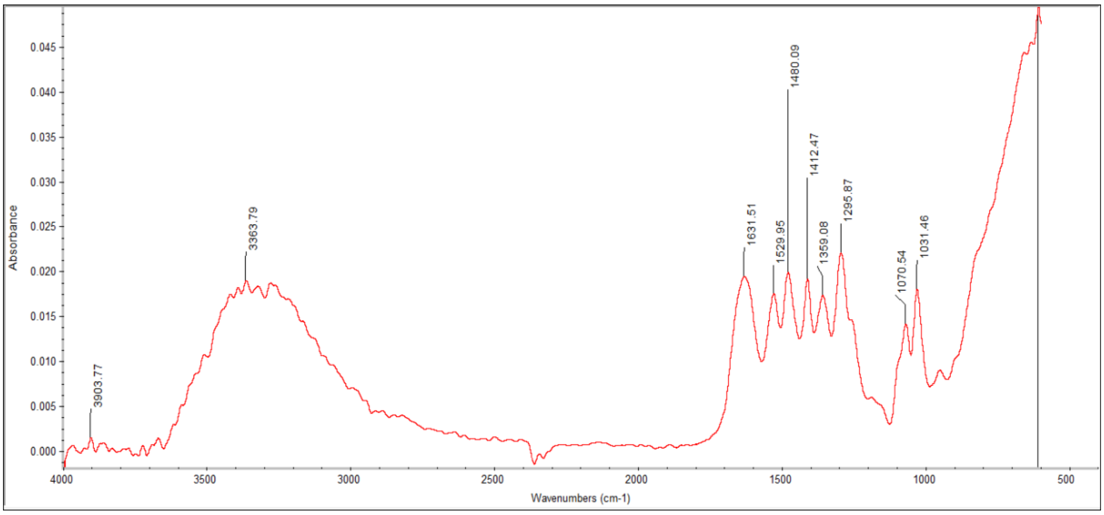

**Figure A-13** 4 hour reaction time

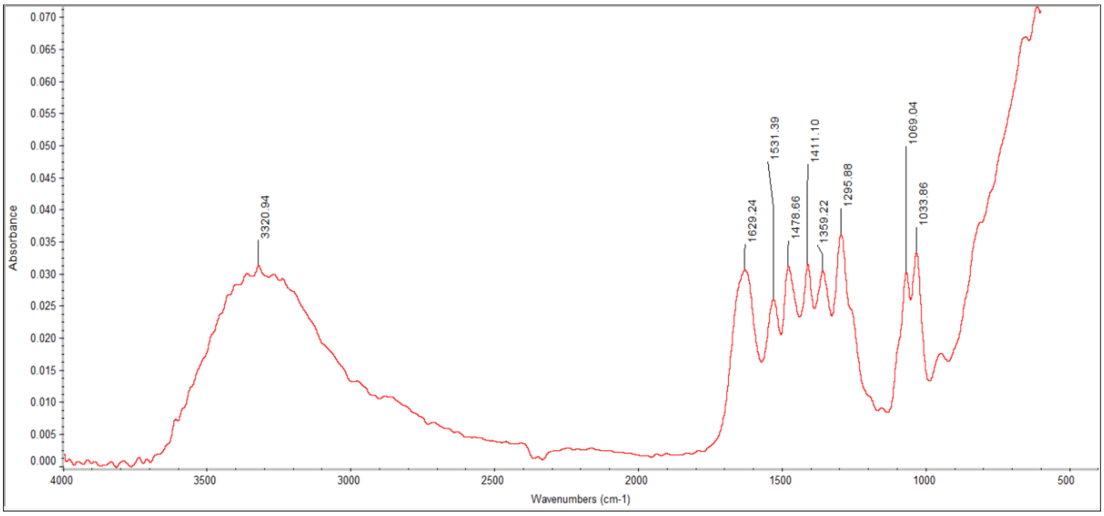

**Figure A-14** 5 hour reaction time

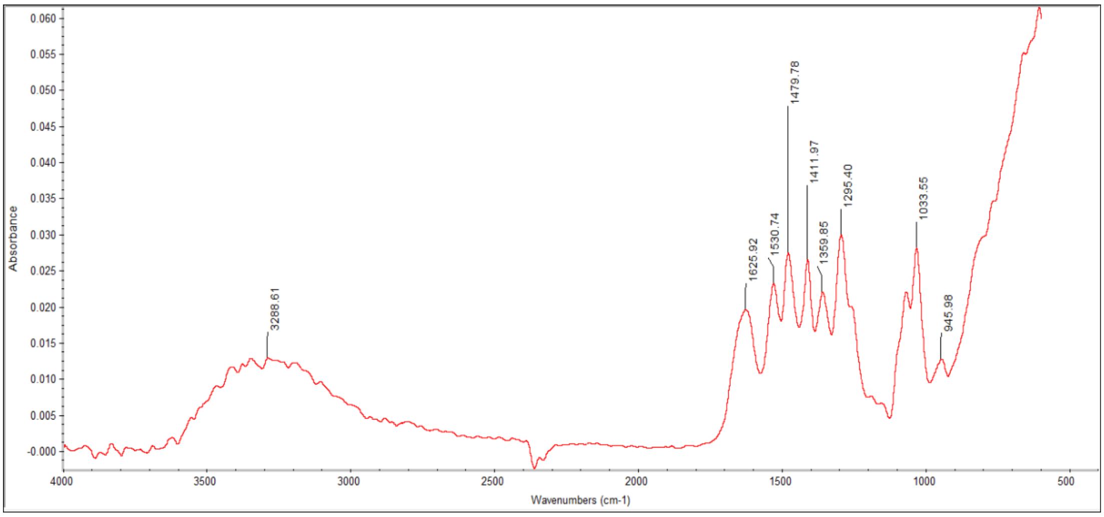

**Figure A-15** 6 hour reaction time

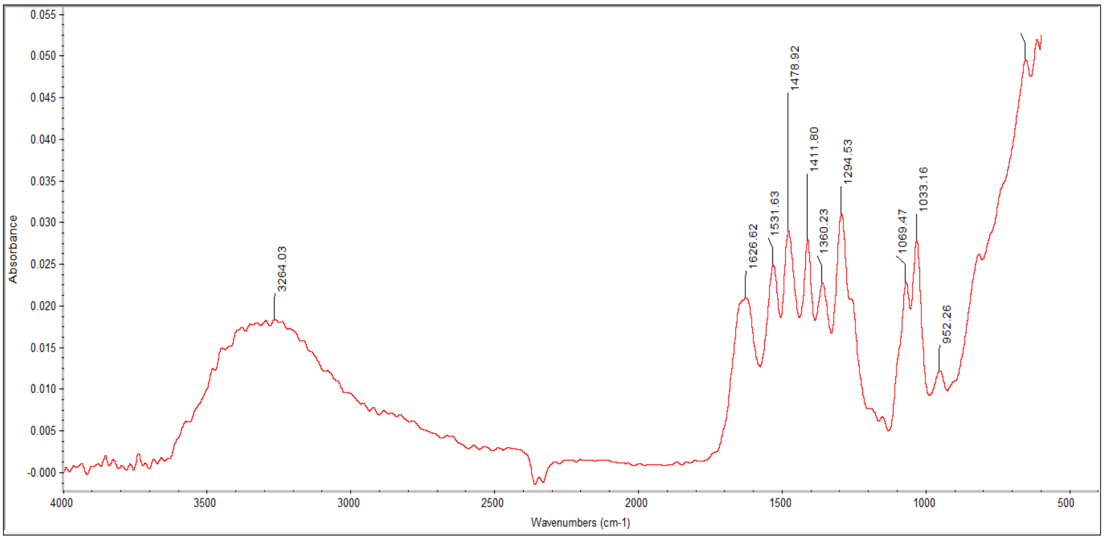

**Figure A-16** 7 hour reaction time

# APPENDIX B

## PCA 2M DEA with 100 ml/min $CO_2$ flowrate using MATLAB

**Table B-1** X matrix

| 0.0238 | 0.0088 | -0.0113 | 0.0013 | 0.0013 |
|---|---|---|---|---|
| 0.0325 | 0.0250 | 0.0025 | 0.0063 | 0.0050 |
| 0.0525 | 0.0400 | 0.0300 | 0.0250 | 0.0225 |
| 0.0263 | 0.0150 | 0.0050 | 0.0075 | 0.0100 |
| 0.0188 | 0.0063 | -0.0150 | -0.0013 | 0.0038 |
| 0.0275 | 0.0275 | 0.0163 | 0.0175 | 0.0075 |
| 0.0200 | 0.0138 | 0.0038 | 0.0050 | 0.0025 |

[coeff, score, latent] = princomp (X)

**Table B-2** Coeff

| 0.4399 | -0.5479 | -0.4890 | 0.0127 | -0.5168 |
|---|---|---|---|---|
| 0.4540 | 0.2289 | -0.5470 | -0.0893 | 0.6591 |
| 0.4500 | 0.4692 | 0.2409 | -0.6256 | -0.3578 |
| 0.4559 | 0.3596 | 0.2028 | 0.7708 | -0.1662 |
| 0.4360 | -0.5458 | 0.6022 | -0.0801 | 0.3781 |

**Table B-3**: Score

| -1.7977 | -0.2670 | -0.2243 | 0.1654 | -0.1900 |
|---|---|---|---|---|
| 0.0235 | -0.0384 | -0.7053 | -0.1329 | 0.0943 |
| 4.1361 | -0.4670 | 0.0463 | 0.0170 | -0.0403 |
| -0.1620 | -0.1875 | 0.4986 | -0.1224 | 0.0041 |
| -2.1699 | -0.4772 | 0.1972 | 0.0856 | 0.1607 |
| 1.0290 | 0.9139 | 0.0618 | 0.1832 | 0.0679 |
| -1.0590 | 0.5232 | 0.1257 | -0.1959 | -0.0967 |

**Table B-4**: Latent

| 4.54239 |
|---|
| 0.27711 |
| 0.14283 |
| 0.02326 |
| 0.01441 |

# APPENDIX C

## PCA 2M DEA with 200 ml/min $CO_2$ flowrate using MATLAB

**Table C-1** X matrix

| 0.0525 | 0.0375 | 0.0150 | 0.0175 | 0.0275 | 0.0225 |
|---|---|---|---|---|---|
| 0.0500 | 0.0400 | 0.0175 | 0.0200 | 0.0300 | 0.0225 |
| 0.0400 | 0.0300 | 0.0100 | 0.0125 | 0.0200 | 0.0150 |
| 0.0363 | 0.0200 | 0.0125 | 0.0075 | 0.0075 | 0.0138 |
| 0.0163 | 0.0100 | 0.0075 | -0.0013 | -0.0025 | 0.0025 |
| 0.0100 | 0.0063 | 0.0088 | 0.0000 | 0.0038 | -0.0013 |
| 0.0138 | 0.0163 | 0.0175 | 0.0125 | 0.0125 | 0.0138 |

[coeff, score, latent] = princomp (X)

**Table C-2** Coeff

| -0.3893 | 0.5337 | 0.4161 | 0.4941 | 0.3033 | -0.2333 |
|---|---|---|---|---|---|
| -0.4255 | 0.2864 | -0.0932 | -0.0316 | -0.8525 | 0.0235 |
| -0.3399 | -0.7738 | 0.2297 | 0.4639 | -0.1322 | 0.0172 |
| -0.4319 | -0.1731 | -0.2235 | -0.4171 | 0.1773 | -0.7267 |
| -0.4241 | 0.0560 | -0.7108 | 0.2080 | 0.3119 | 0.4139 |
| -0.4308 | -0.0361 | 0.4586 | -0.5679 | 0.1875 | 0.4952 |

**Table C-3** Score

| -2.4618 | 0.3794 | 0.0293 | 0.0445 | 0.0558 | 0.0604 |
|---|---|---|---|---|---|
| -2.9131 | -0.1547 | -0.1208 | 0.1668 | -0.1107 | -0.0289 |
| -0.6536 | 0.8849 | -0.2952 | -0.2580 | 0.0325 | -0.0268 |
| 0.2964 | 0.1385 | 0.6320 | 0.0619 | 0.0810 | -0.0304 |
| 2.8162 | 0.4478 | 0.2073 | -0.0562 | -0.1338 | 0.0230 |
| 2.8579 | -0.0508 | -0.4348 | 0.2015 | 0.0660 | -0.0032 |
| 0.0580 | -1.6451 | -0.0176 | -0.1605 | 0.0091 | 0.0060 |

**Table C-4** Latent

| 5.19404 |
|---|
| 0.64662 |
| 0.12239 |
| 0.02828 |
| 0.00755 |
| 0.00112 |

# APPENDIX D

## PCA 4M with 100ml/min $CO_2$ flowrate using MATLAB

**Table D-1** X matrix

| 0.0188 | 0.0175 | 0.0125 | 0.0100 | 0.0113 | 0.0063 |
|---|---|---|---|---|---|
| 0.0132 | 0.0160 | 0.0080 | 0.0076 | 0.0084 | 0.0040 |
| 0.0300 | 0.0275 | 0.0225 | 0.0275 | 0.0270 | 0.0288 |
| 0.0190 | 0.0200 | 0.0178 | 0.0213 | 0.0225 | 0.0188 |
| 0.0313 | 0.0325 | 0.0275 | 0.0338 | 0.0375 | 0.0363 |
| 0.0125 | 0.0200 | 0.0238 | 0.0275 | 0.0300 | 0.0288 |
| 0.0188 | 0.0225 | 0.0263 | 0.0300 | 0.0325 | 0.0288 |

[coeff, score, latent] = princomp (X)

**Table D-2** Coeff

| 0.3130 | -0.7700 | -0.4718 | -0.1520 | 0.1508 | 0.2017 |
|---|---|---|---|---|---|
| 0.4050 | -0.4174 | 0.6493 | 0.3234 | -0.2078 | -0.3041 |
| 0.4247 | 0.2760 | -0.5331 | 0.4245 | -0.5051 | -0.1548 |
| 0.4318 | 0.2255 | -0.0862 | -0.3891 | 0.4454 | -0.6368 |
| 0.4281 | 0.2639 | 0.1208 | 0.4009 | 0.5566 | 0.5118 |
| 0.4336 | 0.1902 | 0.2228 | -0.6164 | -0.4132 | 0.4189 |

**Table D-3** Score

| -2.4067 | -0.5830 | -0.2070 | 0.1191 | -0.0622 | 0.0187 |
|---|---|---|---|---|---|
| -3.3047 | -0.2253 | 0.2559 | -0.0112 | 0.0104 | -0.0231 |
| 1.4916 | -0.9628 | -0.1032 | -0.1869 | -0.0546 | -0.0115 |
| -0.5559 | 0.1335 | -0.0746 | -0.0812 | 0.1430 | 0.0208 |
| 3.1288 | -0.7554 | 0.2043 | 0.1265 | 0.0150 | 0.0094 |
| 0.4290 | 1.5065 | 0.1108 | -0.0587 | -0.0781 | 0.0188 |
| 1.2179 | 0.8866 | -0.1861 | 0.0923 | 0.0264 | -0.0330 |

**Table D-4** Latent

| 5.11734 |
|---|
| 0.82693 |
| 0.03553 |
| 0.01397 |
| 0.00574 |
| 0.00050 |

# APPENDIX E

## PCA 4M DEA with 200ml/min $CO_2$ flowrate using MATLAB

**Table E-1** X matrix

| 0.0288 | 0.0375 | 0.0238 | 0.0275 | 0.0288 | 0.0200 |
|---|---|---|---|---|---|
| 0.0113 | 0.0188 | 0.0100 | 0.0063 | 0.0075 | 0.0038 |
| 0.0238 | 0.0325 | 0.0238 | 0.0288 | 0.0313 | 0.0300 |
| 0.0044 | 0.0052 | 0.0048 | 0.0060 | 0.0016 | 0.0020 |
| 0.0088 | 0.0156 | 0.0172 | 0.0176 | 0.0140 | 0.0140 |
| 0.0016 | 0.0120 | 0.0184 | 0.0188 | 0.0108 | 0.0136 |
| 0.0252 | 0.0340 | 0.0348 | 0.0384 | 0.0320 | 0.0320 |

[coeff, score, latent] = princomp (X)

**Table E-2** Coeff

| -0.3858 | -0.6184 | 0.0244 | -0.5868 | 0.3417 | -0.0843 |
|---|---|---|---|---|---|
| -0.4042 | -0.4601 | -0.2475 | 0.5869 | -0.1545 | 0.4420 |
| -0.4069 | 0.3931 | -0.6349 | 0.1077 | 0.4031 | -0.3207 |
| -0.4138 | 0.3615 | -0.1325 | -0.4873 | -0.5467 | 0.3797 |
| -0.4270 | -0.0599 | 0.3317 | 0.1960 | -0.4460 | -0.6831 |
| -0.4107 | 0.3423 | 0.6383 | 0.1541 | 0.4462 | 0.2895 |

**Table E-3** Score

| -1.9237 | -0.8998 | -0.1833 | -0.0456 | -0.1270 | -0.0033 |
|---|---|---|---|---|---|
| 1.9014 | -0.7796 | -0.1754 | 0.1754 | 0.1027 | 0.0082 |
| -2.0660 | -0.1118 | 0.5028 | 0.1050 | 0.0116 | 0.0096 |
| 3.0772 | -0.1267 | 0.1636 | -0.2568 | -0.0013 | 0.0158 |
| 0.8258 | 0.3760 | 0.0228 | 0.0142 | 0.0004 | -0.0656 |
| 1.2295 | 1.0046 | -0.1191 | 0.1399 | -0.0867 | 0.0260 |
| -3.0443 | 0.5372 | -0.2115 | -0.1321 | 0.1003 | 0.0094 |

**Table E-4** Latent

| 5.41908 |
|---|
| 0.48086 |
| 0.06723 |
| 0.02451 |
| 0.00740 |
| 0.00091 |

# APPENDIX F

## PCA 6M DEA with 100ml/min $CO_2$ flowrate using MATLAB

**Table F-1** X matrix

| 0.0350 | 0.0250 | 0.0350 | 0.0438 | 0.0325 | 0.0475 |
|---|---|---|---|---|---|
| 0.0028 | 0.0104 | 0.0140 | 0.0140 | 0.0090 | 0.0048 |
| 0.0188 | 0.0232 | 0.0296 | 0.0352 | 0.0268 | 0.0252 |
| 0.0124 | 0.0160 | 0.0220 | 0.0260 | 0.0192 | 0.0164 |
| 0.0088 | 0.0168 | 0.0244 | 0.0284 | 0.0212 | 0.0220 |
| 0.0108 | 0.0140 | 0.0164 | 0.0176 | 0.0108 | 0.0076 |
| 0.0072 | 0.0172 | 0.0280 | 0.0348 | 0.0236 | 0.0320 |

[coeff, score, latent] = princomp (X)

**Table F-2** Coeff

| -0.3669 | -0.8452 | 0.2858 | -0.1901 | 0.1386 | 0.1180 |
|---|---|---|---|---|---|
| -0.4113 | -0.2249 | -0.6315 | 0.4954 | -0.2390 | -0.2808 |
| -0.4206 | 0.2393 | -0.1037 | 0.0948 | -0.0443 | 0.8626 |
| -0.4192 | 0.2756 | 0.0092 | 0.0509 | 0.8286 | -0.2429 |
| -0.4196 | 0.2096 | -0.2031 | -0.7775 | -0.2955 | -0.2169 |
| -0.4093 | 0.2405 | 0.6837 | 0.3199 | -0.3844 | -0.2390 |

**Table F-3** Score

| -3.8777 | -0.5639 | 0.3891 | -0.0053 | -0.0144 | 0.0005 |
|---|---|---|---|---|---|
| 3.1740 | -0.1012 | 0.1894 | -0.0196 | -0.0413 | 0.0042 |
| -1.6130 | -0.1020 | -0.6551 | 0.0410 | -0.0073 | 0.0022 |
| 0.6184 | -0.0948 | -0.0580 | -0.1768 | 0.0618 | -0.0004 |
| 0.1894 | 0.4392 | -0.0739 | -0.0552 | -0.0638 | -0.0043 |
| 2.1564 | -0.6351 | 0.0129 | 0.1311 | 0.0283 | -0.0029 |
| -0.6476 | 1.0578 | 0.1956 | 0.0850 | 0.0367 | 0.0008 |

**Table F-4** Latent

| 5.53344 |
|---|
| 0.34380 |
| 0.11061 |
| 0.01014 |
| 0.00200 |
| 0.00001 |

# APPENDIX G

## PCA 6M with 200ml/min $CO_2$ flowrate using MATLAB

**Table G-1** X matrix

| 0.0045 | 0.0032 | 0.0100 | 0.0188 | 0.0180 | 0.0196 |
|---|---|---|---|---|---|
| 0.0078 | 0.0113 | 0.0175 | 0.0320 | 0.0313 | 0.0313 |
| 0.0004 | 0.0028 | 0.0100 | 0.0208 | 0.0200 | 0.0232 |
| 0.0020 | 0.0048 | 0.0100 | 0.0188 | 0.0244 | 0.0144 |
| 0.0000 | 0.0036 | 0.0080 | 0.0260 | 0.0252 | 0.0248 |
| -0.0020 | 0.0036 | 0.0084 | 0.0268 | 0.0280 | 0.0280 |
| -0.0020 | 0.0024 | 0.0080 | 0.0260 | 0.0264 | 0.0268 |

[coeff, score, latent] = princomp (X)

**Table G-2** Coeff

| -0.3073 | 0.5907 | -0.1957 | 0.6021 | 0.3947 | -0.0012 |
|---|---|---|---|---|---|
| -0.4741 | 0.2534 | 0.2428 | -0.0487 | -0.5554 | -0.5842 |
| -0.4369 | 0.3706 | -0.1024 | -0.6689 | 0.0761 | 0.4562 |
| -0.4379 | -0.3787 | -0.1001 | 0.4083 | -0.4450 | 0.5386 |
| -0.4051 | -0.3418 | 0.6742 | 0.0110 | 0.5135 | -0.0284 |
| -0.3661 | -0.4350 | -0.6540 | -0.1447 | 0.2612 | -0.3997 |

**Table G-3** Score

| 1.3532 | 1.6141 | -0.6354 | 0.2247 | 0.0827 | -0.0211 |
|---|---|---|---|---|---|
| -4.2861 | 0.7386 | -0.0709 | -0.0257 | 0.0003 | 0.0083 |
| 1.1758 | 0.3217 | -0.6063 | -0.3795 | -0.0865 | 0.0077 |
| 1.0911 | 1.2553 | 1.1786 | -0.0718 | -0.0018 | 0.0058 |
| 0.3187 | -0.8172 | 0.0171 | 0.3480 | -0.1329 | 0.0073 |
| -0.0908 | -1.6219 | 0.1400 | -0.0777 | 0.0471 | -0.0940 |
| 0.4382 | -1.4906 | -0.0231 | -0.0180 | 0.0910 | 0.0860 |

**Table G-4** Latent

| 3.84616 |
|---|
| 1.72504 |
| 0.36428 |
| 0.05463 |
| 0.00708 |
| 0.00281 |