

**SAPO-34 Nanoparticles for CO₂ Capture:
Optimization of Synthesis Parameters**

by

Nur Afiqah Binti Adam 12798

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering Department)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

SAPO-34 Nanoparticles for CO₂ Capture – Optimization of Synthesis Parameters

by

Nur Afiqah Binti Adam

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

Dr. Yeong Yin Fong

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

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

NUR AFIQAH BINTI ADAM

ABSTRACT

Carbon dioxide is one of major greenhouse gaseous that lead to global warming. Besides, removing carbon dioxide has become a major key mostly in natural gas industry as carbon dioxide can reduce the heating value and energy content of the gas as well as corrosive in presence of water. Due to that, various technologies have been developed for CO₂ removal including amine absorption, membrane separation and adsorption. Adsorption is the most preferential technology mainly attributed to its ease of availability and economic efficiency. Literature showed that SAPO-34 has great potential in CO₂ adsorption as it has high selectivity of CO₂/CH₄ separation. However, synthesis of SAPO-34 nanoparticles is still a major concern in order to reduce the size of the particles and increase the CO₂ adsorption capability while retaining the morphology of the crystals. Therefore, this research work is focuses on the synthesis of SAPO-34 nanoparticles by using sonochemical treatment prior to synthesis. The synthesis parameters including ultrasonic pretreatment duration and synthesis time were varied and optimized using Design Expert software. The resulting particles characterized using TEM and FTIR shows that increasing in hydrothermal heating duration will increase the particle size of SAPO-34 and crystallinity. Meanwhile, surface area of SAPO-34 nanoparticles increased as the particle size decreases. The CO₂ adsorption characteristics of the resulting particles were tested using BELSORP. The effect of particle size on CO₂ adsorption was extensively studied and analyzed using Design Expert Software.

ACKNOWLEDGEMENT

First and foremost, I would like to praise God the Almighty for His guidance. Though difficulties occurred, His guidance gave me the chance to complete this challenging project successfully.

My sincere appreciation goes to my supervisor, Dr. Yeong Yin Fong for her valuable guidance and support towards the development of this project whenever necessary.

A very special recognition goes to my family, especially my mother and my father for the love and support they provided throughout my university career. My gratitude to all my friends that has gave a ton of feedback and helped through their useful idea and advice. To my education sponsor, PETRONAS for the endless support that had helped me throughout my campus life.

I really appreciate and pleased to all the hands given either direct or indirectly to complete this project. The time and energy spent in this project are highly appreciated. The experience gained throughout this project was so meaningful and I hope that this project could be used as reference for other students.

TABLE OF CONTENT

CERTIFICATION OF APPROVAL	i
CERTIFICATION OF ORIGINALITY	ii
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENT	v
LIST OF FIGURE	vi
LIST OF TABLE	vii
CHAPTER 1: INTRODUCTION	
1.1 Background of Study	1
1.2 Problem Statement	3
1.3 Objectives & Scope of Study	3
1.4 Relevancy and Feasibility of Project	4
CHAPTER 2: LITERATURE REVIEW	
2.1 Important of Removing CO ₂	5
2.2 Existing Technology in CO ₂ Removal	6
2.3 Zeolite: SAPO-34	7
2.4 Synthesis of SAPO-34 Nanoparticles	8
CHAPTER 3: METHODOLOGY	
3.1 Research Methodology	10
3.1.1 Identify Synthesis Parameters	11
3.1.2 Identify Range of Parameters	11
3.1.3 Design of Experiments	11
3.1.4 Synthesis of SAPO-34 Nanoparticles	16
3.1.5 Characterization Method	17
3.1.6 CO ₂ Adsorption of SAPO-34	19
3.2 Project Activities	19
3.2.1 Availability of Chemicals	19
3.2.2 Availability of Apparatus/Equipment	20

	3.2.3	Time Management	21
	3.3	Key Milestone	22
	3.4	Gantt Chart	23
CHAPTER 4:		RESULTS AND DISCUSSION	
	4.1	DOE Results	25
		4.1.1 Statistical Model Analysis	26
		4.1.2 Optimization	30
	4.2	Characterization of SAPO-34 Nanoparticles	32
		4.2.1 TEM	32
		4.2.2 FTIR	34
		4.2.3 BET (N ₂) Surface Area	35
CHAPTER 5:		CONCLUSION AND RECOMMENDATION	
	5.1	Conclusion	37
	5.2	Recommendation	38
REFERENCES			39

LIST OF FIGURE

Figure 1 Research methodology	10
Figure 2 DOE Response Surface design	13
Figure 3 DoE input data of independent variables	13
Figure 4 DoE input data of responses	14
Figure 5 DoE Experimental runs	14
Figure 6 Actual versus predicted Design-Expert Plot of average particle size	27
Figure 7 3D surface Design-Expert Plot of average particle size	27
Figure 8 Actual versus predicted DE Plot of CO ₂ adsorption capability	29
Figure 9 3D surface Design-Expert Plot of CO ₂ adsorption capability	30
Figure 10 TEM images	32
Figure 11 FTIR spectra	34
Figure 12 Sorption-Isotherm of S1, S2 and S3	35

LIST OF TABLE

Table 1 Characterization method used to study properties of SAPO-34	19
Table 2 Availability of chemicals	20
Table 3 Availability of apparatus/equipment	20
Table 4 Time planning for Experiment 1	21
Table 5 Key milestones	22
Table 6 Gantt chart for FYP 1	23
Table 7 Gantt chart for FYP II	24
Table 8 Experimental run	25
Table 9 ANOVA of average particle size, Y ₁	26
Table 10 ANOVA of CO ₂ adsorption capability, Y ₂	28
Table 11 Goal of criteria for optimization	31
Table 12 Solutions of numerical optimization by DOE	31
Table 9 BET results of samples	36

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Gavin Schmidt, climatologist at NASA's Goddard Institute for Space Studies stated that the reason why the earth temperature keeps increasing was because of people pumping increasing amounts of carbon dioxide into atmosphere (Hogue, Johnson & Kemsley, 2012). Due to that, various researches and studies have been conducted for effective removal of carbon dioxide in order to cater the greenhouse gas effect. Carbon dioxide is also undesirable in natural gas processing because it can reduce the heating value and energy content of the gas. Besides, CO₂ is acidic and therefore, it can induce corrosion and hydrate in the presence of water during the transportation and storage of natural gas (Li, Alvarado, Noble, & Falconer, 2005).

There are several methods introduced in removing carbon dioxide which include membrane separation, solvent absorption and sorbent adsorption. Membrane separation uses a membrane that made of polymers or ceramic that can selectively remove carbon dioxide from the gas streams (Baker, 2001). However, separation using polymeric membranes has not yet been well established on large scale process due to high pressure and temperature which limits of the membranes performance. This was because high partial pressures of CO₂ can plasticize polymer membranes and decrease their separation ability (Koros & Mahajan, 2000).

Solvent absorption uses liquid, typically amine, to absorb carbon dioxide from gas stream. The used liquid which has been contaminated with carbon dioxide is further processed in order to remove the carbon dioxide absorbed and the purified solvent is reused again (Baker, 2001). This method is widely used, but it needs a complex plant which is costly and energy intensive (Koros & Mahajan, 2000). Meanwhile, sorbent

adsorption method is one of the most desirable methods in carbon dioxide removal due to the availability of high CO₂ selective adsorbents including silica gel, activated alumina, carbons, zeolite, polymers and resins (Deng, 2008).

Microporous inorganic membranes with pore size between 0.2 and 0.8nm have been studied for gas separation due to its superior thermal and chemical stability, good erosion resistance and high pressure stability as compared to conventional polymer membranes (Li et al., 2004). Microporous silica (Tsai, Tam, Lu, & Brinker, 2000; Asaeda & Yamasaki, 2001), carbon molecular sieve (Vu, Koros, & Miller, 2002) and zeolite (van den Broeke, Kapteiji, & Mouijin, 1999; Kusakabe, Kuroda, Murate, & Morooka, 1997) membranes have been reported for their excellent performance in separation of CO₂ from CH₄.

Recently, there have been increasing interests on the study of SAPO-34, (SixAl₂Pz) O₂, which is a type of silicoaluminophosphate microporous zeolite. SAPO-34 is an excellent adsorbent as well as catalyst, known among the silicoaluminophosphates (SAPOs) due to its remarkable pore structure and thermal stability (Park, Lee, Kim, Hong, & Seo, 2008). SAPO-34 has been reported as a suitable adsorbent for CO₂/CH₄ separation due to its high selectivity of CO₂ over CH₄ on the basis competitive adsorption and diffusion mechanism. This was mainly due to the kinetic diameters of CO₂ (0.33nm) as compared to CH₄ (0.38nm). Therefore, CO₂ can enter the pore mouth of SAPO-34 crystals (0.34nm) (Li et al., 2008) selectively.

Due to its potential-application in adsorption of CO₂, synthesis of SAPO-34 has attracted much interest among the researchers and fine-tuning of synthesis method to obtain uniform particle size of SAPO-34 has become crucial. Investigations pointed out that enhancements in CO₂ adsorption activity and life time could depends on the size of the resulting SAPO-34 particles. Nevertheless, SAPO-34 nanoparticles can be obtained by manipulating synthesis template, silicon source, heating method, type and time of crystallization and synthesis temperature (Razavian, Halladj, & Askari, 2011). The resulting SAPO-34 particles in nanosize can subsequently increase the CO₂ adsorption capability due to the increase in effective surface area.

1.2 Problem Statement

Synthesizing of SAPO-34 has been a hot issue among the researches in order to find an effective route that will produce high quality nanoparticles with high surface area for CO₂ adsorption. From detail comparisons between the reported synthesizing method for SAPO-34 nanoparticles, sonochemical assisted hydrothermal synthesis was found to be the easiest and feasible synthesis method. However, this method is not well established in the literature because only Askari and coworkers (Askari & Halladj., 2012) reported on this method so far.

Besides, although previous study has been done to manipulate the synthesis parameters by trial and error, it was involved large number of experimental runs with only small ranges of parameters studied. Due to that, the optimization study of synthesis parameters in order to obtain nanoparticles of SAPO-34 and the effect of particle size on CO₂ adsorption capability is still remain a new task and has yet to be achieved.

1.3 Objectives & Scope of Study

The objectives and scopes of this project are:

1. To synthesis SAPO-34 nanoparticles using ultrasonic pretreatment and hydrothermal method.
2. To optimize synthesis parameters include ultrasonic pretreatment duration and synthesis duration using Design of Expert Software (DoE).
3. To characterize the SAPO-34 nanoparticles using Scanning Electron Microscope (SEM), Transmittance Electron Microscope (TEM) and Fourier Transform Infrared (FTIR).
4. To test the CO₂ adsorption characteristic of the synthesized SAPO-34 using CO₂ physisorption.

1.4 Relevancy and Feasibility of Project

The relevancy of this project in optimizing the parameters is to obtain a feasible method and optimum parameters for synthesis SAPO-34. By obtaining optimum synthesis parameters, the size of SAPO-34 can be reduced and thus the surface area for CO₂ adsorption will be increased.

By proper planning and execution, this project can be completed as per scope before the date of completion as the synthesis methods used do not consume much time. Besides, the used of DoE software to optimize the parameters make the project become more systematic with reduced number of experimental runs.

CHAPTER 2

LITERATURE REVIEW

2.1 Important of Removing CO₂

According to several new governments scientific reports issued recently (National Climate Assessment, 2013; Climate Commission, 2013), global warming is occurring due to the increasing greenhouse gases generated mostly by human activities. Carbon dioxide (CO₂) is the primary greenhouse gas emitted through human activities like combustion of fossil fuel, deforestation and agriculture (U.S. Environmental Protection Agency, 2012). Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle, both by adding more CO₂ to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO₂ from the atmosphere (Hogue, Johnson, & Kemsley, 2013).

In natural gas, the presence of CO₂ contaminants in the gas stream is as high as 70%. However, the pipeline specification for natural gas requires a CO₂ concentration below 2-3% (IPCC, 2005). Therefore, CO₂ must be removed from natural gas because it can reduce the heating value and energy content of the gas. Furthermore, CO₂ is an acidic gas that can corrode the pipeline in the presence of water. CO₂ can also block the cryogenic equipment due to the hydrate formation (solid crystalline) at a very low temperature which can result in overpressure and explosion (Bellusi et al., 2011). This can be a great concern in safety aspect which makes the CO₂ removal become a major key in the industry.

2.2 Existing technology in CO₂ removal

Separation of CO₂ from CH₄ is crucial in natural gas processing. Indicatively, a maximum limit for carbon dioxide in natural gas pipeline transmissions is below 2-3 % (IPCC, 2005). There are numerous technologies developed in order to separate carbon dioxide from natural gas. These technologies include absorption in a liquid or solid sorbent, permeation through a membrane and adsorption on a solid (Kohl & Nielsen, 1997; Seader & Henley, 2006).

Existing technology that is most widely used for CO₂ removal is aqueous amine absorption process whereby the CO₂ become carbonate salt once reacted with amine solution and the salt will then be heated in stripping columned reforming pure CO₂ and pure amine (Protea, n.d.). However, amine plants are complex and costly due to large amount of energy needed for regeneration of amine and the corrosive nature of amine that increase the cost of maintenance of equipment (Rufford et al., 2012). Meanwhile, the commercial membrane technologies employed in the natural gas industry are predominantly nonporous polymeric membranes that separate components by the solution-diffusion mechanism (Rufford et al., 2012). The main problems that limit the use of polymeric membrane are their poor performance stability at high pressure and in presence of highly sorbing components. For adsorption technology, it used porous solid adsorbents by selective adsorption in order to separate gas mixture. Adsorption-based processes have potential for energy and capital investment savings over the conventional CO₂ amine plant and polymeric membrane separation technology, but to date adsorption-based technologies have been limited to processing natural gas feed rates of only about 15 MMscfd (Rufford et al., 2012).

All technologies introduced have their advantages and disadvantages depending on the goal of the process. Therefore, apart from establishing new technologies, the exploration of capture materials with high separation performance and low capital cost are paramount importance (Songolzadeh, Ravanchi, & Soleimani, 2012). Among the various separation technologies, adsorption may be considered as a

competitive solution. Its major advantage is the ease of the adsorbent regeneration by thermal or pressure modulation (Thiruvengatachari, Su, An, & Yu, 2009). In addition, adsorption can reduce energy and cost of the capture or separation of CO₂ in post-combustion capture. However, the success of this approach is dependent on the development of an easily regenerated and durable adsorbent with high CO₂ selectivity and adsorption capacities (Li, Xiao, Webley, Zhang, & Singh, 2009).

2.3 Zeolite: SAPO-34

In general, the CO₂ adsorbent must have high selectivity and adsorption capacity, adequate adsorption/desorption kinetics, remain stable after several adsorption/desorption cycles, and possess good thermal and mechanical stability (Chaffee et al., 2007). Zeolites are crystalline materials with uniform-sized pores of molecular dimension. The unique properties of zeolites have made them suitable to be used in many different industrial processes including adsorption, separation, catalytic and ion-exchange (Hong, Funke, Falconer, & Noble, 2007).

SAPO-34 zeolite is a silicoaluminophosphate molecular sieve with CHA structure formed by introduction of Si atoms into neutral AlPO₄ framework. The chemical composition of SAPO-34 is (Si_xAl_yP_z) O₂ where, x=0.01-0.98, y=0.01- 0.60, z=0.01-0.52, and x+z=y. Its unique shape selectivity, molecular sieving property with pore diameter of 0.38 nm, near to CH₄ kinetic diameter, and strong CO₂ adsorption capacity, have attracted attention of the researchers, for separation of CO₂ from natural gas (Peydayesh, Asarehpour, Bakhtiari, & Mohammadi, 2010).

SAPO-34 molecular sieves are highly thermal stable up to 1100 °C which possess small crystalline pores of 0.38 nm. SAPO-34 can provide molecular sieving selectivity for the separation of H₂ or CO₂ from CH₄. SAPO-34 molecular sieves were also reported to adsorb more CO₂ than CH₄, which was favorable for achievement of high selectivity of CO₂ over CH₄ on the basis of a competitive adsorption separation mechanism. Ashraf et al. (2010), reported that the adsorption capacity of SAPO-34 on CO₂ was 14 mmol/g at 273K and 3000 kPa (Ashraf & Siamak, 2010). Meanwhile, commercialized synthetic zeolites 13X and 5A adsorbed

only adsorbed 6.82 mmol/g and 5.46 mmol/g of CO₂, respectively at 5°C (Ertan, 2004). These values were lower than that of CO₂ amount adsorbed in SAPO-34. This was mainly due to the kinetic diameter of CO₂ (0.33nm) as compared to CH₄ (0.38nm). Therefore, CO₂ can enter the pore mouth of SAPO-34 crystals (0.38nm) (Ashraf & Siamak, 2010).

2.4 Synthesis of SAPO-34 nanoparticles

There are many routes available for synthesizing of SAPO-34 nanoparticles which include using a hydrogel polymer, mixed template method, colloidal solutions and hydrothermal method. In 2005, Yao group reported new synthesis method to obtain fine dispersion of sub-micron or nanosized SAPO-34 crystals with good degree of crystallinity by exploiting three dimensional network structure of polymer hydrogel using Vapor Phase Transfer (VPT) process (Yao et al., 2005). Through VPT process, crystallization starts via the contact of initial gel with vapor obtained from the liquid mixture which has been poured into bottom of autoclave. The polymer hydrogel used is cross-linked polyacrylamide (C-PAM) in order to reduce the crystal size. SAPO-34 crystals size ranging from 3-5 µm can be obtained with appropriate amount of C-PAM ranging from 0.29-0.43 (Razavian et al., 2011).

Commonly, SAPO-34 particles are synthesized by using a single agent like morpholine or tetraethylammonium hydroxide (TEAOH) as structure directing agent (SDA) or template. In mixed template method, SAPO-34 was synthesized hydrothermally using the mixtures of morpholine and TEAOH (Razavian et al., 2011). This method resulted in the decrease in crystallinity of SAPO-34 and production of SAPO-5 when the concentration of TEAOH increased. Meanwhile, if only morpholine is used, the lifetime of the crystal decreased. Besides, by using mixed template, the size of particles was reduced to 1µm if compared to those particles synthesized using only TEAOH as template, which was 5-20µm. Although the size was reduced, however, no nanosized SAPO-34 crystals were formed by using this synthesis method (Razavian et al., 2011).

Synthesis of nanosized SAPO-34 from colloidal solution was another route which used different types of silicon source. van Heyden et al. (2004), reported that SAPO-34 with crystal sizes of 500 nm was obtained by using colloidal precursor solutions in the presence of TEAOH as a template (van Heyden, Mintova, & Bein, 2004).

By using microwave heating method, the synthesis duration can be effectively reduced from hours to minutes. Besides, the diameter of the resulting particles can be reduced to 100 nm, with fully crystalline and well defined cube-like morphology (van Heyden et al., 2004).

Recently, there has been a rapid increase in the application of unconventional hydrothermal method by using sonochemical method (Chen, Zhang, & Cai, 2003). Sonochemical method has been recently reported also by Askari et al. (2012). Sonochemical method is based on acoustic cavitations by the formation and collapsing of bubbles induced by ultrasonic irradiation. Study had shown that the increase in ultrasonic time can produce smaller particles of SAPO-34 (Askari et al., 2012). Ultrasonic treatment can influence the crystallization kinetics and the formation of crystal nuclei. Besides, ultrasonic treatment can enhance and alter dissolution processes, chemical reactions, nucleation and growth of precipitates.

So far, problems still exist and are challenging for determining the optimum parameters in synthesis of SAPO-34 with desirable morphology, porosity and particles size. Therefore, optimizing the synthesis parameters including the ultrasonic time and crystallization time and temperature are remain crucial not only to produce smaller crystals but also to maintain its morphology and crystallinity as well as to maximize the production of pure SAPO-34 with little by-product and waste output.

Optimize the synthesis parameters is a very complicated task as it involves numbers of synthesis variables which need to be manipulated. In order to reduce the complexity of synthesis, simulation software is introduced. In this project, Design Expert (DoE) Software is used to generate the experiments runs in order to identify the significant parameters for the synthesis of SAPO-34 nanoparticles. It has the most desirable variable settings for multiple responses simultaneously which can be

perfectly used in this project in order to find the optimum combination of parameters for synthesis of SAPO-34 nanoparticles (Buxton, n.d.). Besides, the interaction between the parameters as well as the effect of particles size on the CO₂ adsorption capability can be systematically analyzed.

CHAPTER 3 METHODOLOGY

3.1 Research Methodology

Figure 1 shows the research methodology for this project.

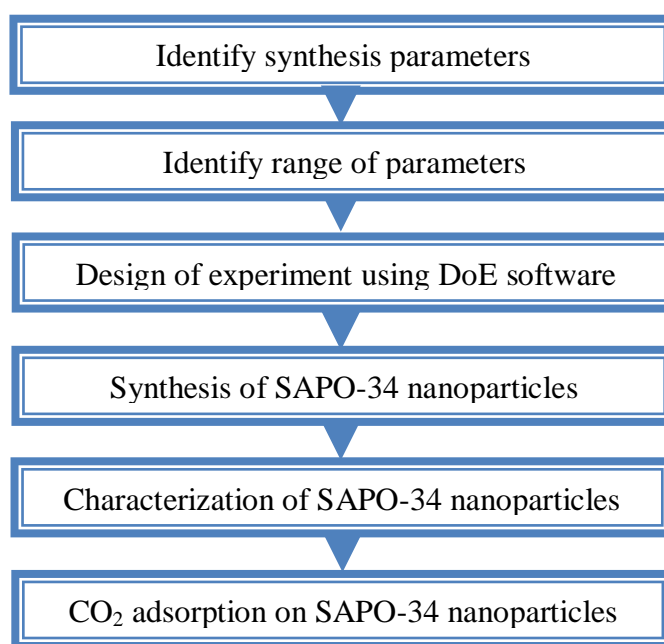


Figure 1: Research methodology

Based on Figure 1, there are several stages of activities that need to be performed in order to achieve the project objectives. The first stage is to identify the synthesis parameters of SAPO-34 nanoparticles and the second stage is to identify the range of parameters. Identification on the synthesis parameters and range are crucial for

process optimization of SAPO-34 nanoparticles synthesis. Then, third stage will focus on the design of experiment runs by using the DoE software. Based on the experimental design, in fourth stage, synthesis of SAPO-34 nanoparticles will be conducted. After that, in fifth stage, characterization will be done to the synthesized SAPO-34 nanoparticles for determination on its size, morphology and other characteristics by using TEM, FTIR and N₂-BET surface area analyzer. Lastly, the CO₂ adsorption on SAPO-34 nanoparticles will be tested in order to study the effect of particles size on the CO₂ adsorption capability. Details on each stage will further elaborated in the following section.

3.1.1 Identify Synthesis Parameters

In identifying the synthesis parameters, researches need to be done to verify the factors that can affect the synthesis of SAPO-34 nanoparticles. In this project, there are two synthesis parameters that have been identified for optimization of synthesis parameters, which includes:

1. Ultrasonic pretreatment duration
2. Hydrothermal heating duration

3.1.2 Identify Range of Parameters

After synthesis parameters have been identified, the ranges of the parameters need to be figured out. By referring to the literatures (Askari et al., 2012), the ranges of synthesis parameters are summarized as follow:

1. Ultrasonic pretreatment duration: 15 minutes to 45 minutes
2. Hydrothermal heating duration: 90 minutes to 180 minutes

The range of parameters then will be used as input data in the DoE software and the output data/responses are i) average size of SAPO-34 (nm) and ii) CO₂ adsorption capacity of SAPO-34 nanoparticles (mmol/g).

3.1.3 Design of Experiments

In designing experiment, DoE software will be used as a tool. Design Expert is software used to design and interpretation of multi-variable experiments such as the synthesis of SAPO-34 nanoparticles. The software offers a wide range of designs which can handle both response variable like size of particles and manipulated variables, such as synthesis time and temperature. Through the results and thorough analysis, the optimum synthesis parameters contributed to optimum particles size for optimum CO₂ adsorption capability can be obtained. Besides, through this simulation software, the analysing on the interaction between the parameters can be easier and time saving. Furthermore, wider range of synthesis data can be studied under minimum experimental runs.

By using Design Expert version 6.0.6, there will be three major steps involved in designing the experiment (Buxton, n.d.):

Constructing the design

Design Expert has a series of features that can be used to specify the information needed to construct the design - e.g. names and ranges of the variables and degree of replication. The steps in constructing the design are as follows:

1. Choose design method: RSM → CCD

Response Surface Methodology (RSM) is part of class designs available in the software. As this project is focusing on process optimization, RSM is a perfect method as it aimed for process optimization. Standard RSM design called Central Composite Design (CCD) and can be used to study the chemical process. Figure 2 shows the display of Response Surface design for DoE software.



Figure 2: DoE Response Surface design

2. Description of input data

After choosing the design method which is the Central Composite Design, description of input data into the software is performed for both independent variables and responses. Figure 3 shows input data entry of DoE software for independent variables of ultrasonic pre-treatment duration and hydrothermal heating duration.

Numeric Factors:		2	(2 to 10)	
Categorical Factors:		0	(0 to 10)	
	Name	Units	Low	High
A:	Ultrasonic Pref min		15	45
B:	Hydrothermal min		90	180

Figure 3: DoE input data of independent variables

Based on input data of variables shown, the numeric factors refer to number of input data which is in this case there are two numeric factors or input data (A and B) with categorical factor is set at default. The input data A and B are namely as ultrasonic pre-treatment duration and hydrothermal heating duration with both have unit of minutes. The lower and upper range of input data will be set up at “Low” and “High” column respectively.

Meanwhile, input data for responses consist of average particle size of SAPO-34 (nm) and CO₂ adsorption capability onto SAPO-34 nanoparticles (mmol/g). Figure 4 shows input data entry of DoE software for CCD.

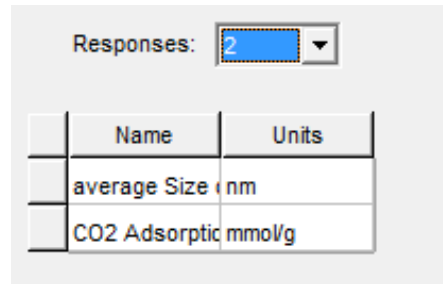


Figure 4: DoE output data responses

3. Generate experimental design

At the end of this step, Design Expert gives the design layout which lists the experimental settings to be used for each of the experimental runs. The order of the runs is randomised and this is the order in which the experiments should be carried out. Figure 5 shows 13 experimental runs generated by the DOE software that need to be conducted in order to get the result for the responses.

Std	Run	Block	Factor 1 A: Ultrasonic Power min	Factor 2 B: Hydrothermal min	Response 1 Average Size nm	Response 2 CO2 Adsorption mmol/g
7	1	Block 1	30.00	90.00		
8	2	Block 1	30.00	180.00		
9	3	Block 1	30.00	135.00		
13	4	Block 1	30.00	135.00		
11	5	Block 1	30.00	135.00		
1	6	Block 1	15.00	90.00		
3	7	Block 1	15.00	180.00		
5	8	Block 1	15.00	135.00		
6	9	Block 1	45.00	135.00		
4	10	Block 1	45.00	180.00		
10	11	Block 1	30.00	135.00		
12	12	Block 1	30.00	135.00		
2	13	Block 1	45.00	90.00		

Figure 5: DoE experimental runs

After the 13 experiments have been conducted, the results for average particle size and CO₂ adsorption capability were inserted in the DOE experimental design as shown in Figure 5. The size of the particles will be determined using transmittance electron microscope (TEM) while the CO₂ adsorption capacity will be tested using CO₂ analyzer (BELSORP).

Evaluating the design

The design model was analysed using a regression analysis program available in the DOE software which consist of evaluating tools like analysis of variance (ANOVA) and Design-expert plot. Both tools will estimate the error in the design, but the design-expert plot, the error is presented in graphical form. Therefore, by evaluating the design, it can determine whether the model design used for the effect of operating variables to responses are significant or not.

Generally, each responses may possess different type of model either linear or quadratic. For linear model of two factors (A and B), linear equation shown in reaction 1 (Khuri, 2001) was used to predict the response value and compared it with the experimental data.

$$Y = \beta_0 + \beta_i A + \beta_{ii} B \dots\dots\dots(1)$$

Where, Y = Measured response

β_0 = Intercept term coefficient

β_i = Coefficient of effect of variable A

β_{ii} = Coefficient of effect of variable B

Meanwhile, for quadratic model, equation 2 was used (Montgomery, 2001).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i A + \sum_{i=1}^k \beta_{ii} B + \sum \sum_{1 < j} \beta_{ij} AB + \varepsilon \dots\dots\dots(2)$$

Where, ε is the error.

Generally, DOE will provide suggested type of model for the response depending on ANOVA results and the variance of the predicted value and actual value.

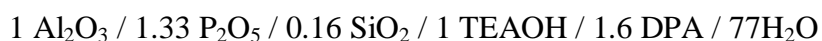
Optimization

Once the model have been verified its accuracy and validity, optimization on the results was proceeded. There are many ways to optimize the results either by numerical, graphical or point prediction. However, in this study, numerical optimization was used as it is easy to interpret by just setting the set of goal for each variables and responses. DOE software will generate possible solutions of optimum condition for the synthesis of SAPO-34 nanoparticles. Therefore, optimization can be achieved.

3.1.4 Synthesis of SAPO-34 Nanocrystals

The experimental procedures in synthesis of SAPO-34 are as follows:

1. Aluminium isopropoxide (6.8g) was added into solution containing phosphoric acid (3.85g) and de-ionized water (20g).
2. The mixture was stirred for 2 hours vigorously until homogeneous solution form.
3. LUDOX AS-40 colloidal silica (1.13g) was added to the solution and stirred for 0.5 hours.
4. Tetraethylammonium hydroxide (TEAOH) (7.02g) was then added into the mixture and stirred for another 0.5 hours.
5. After that, dipropylamine (1.37g) and cyclohexylamine (1.34g) was added to the solution and stirred for 24 hours. Final ratio of mixture is:



6. The solution was irradiated with ultrasound at temperature of 50°C.
7. Gel formed was transferred to an autoclave and heat in oven for hydrothermal growth of SAPO-34.
8. After synthesis, the seeds was centrifuged and washed with deionized water.

9. Step 8 was repeated three times.
10. SAPO-34 seeds were dried in an oven overnight at temperature 110 °C.
11. Lastly, the seeds were calcined in Protherm furnace at 550 °C for 6 hours to remove the template.
12. After removal of template, the seeds were stored in dessicator for characterization study.

Chemicals needed for synthesis of SAPO-34 are listed as follows:

1. Aluminium Isopropoxide ($\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$, >99.99%)
2. Phosphoric Acid (H_3PO_4 , 85wt%) Ammonia solution, NH_3
3. LUDOX AS-40 Colloidal Silica (SiO_2 , 40wt%)
4. Taetraethylammonium Hydroxide ($(\text{C}_2\text{H}_5)_4\text{NOH}$, 35wt%)
5. Dipropylamine ($\text{C}_6\text{H}_{15}\text{N}$, 99%)
6. Cyclohexylamine ($\text{C}_6\text{H}_{15}\text{N}$, 99%)

The apparatus needed for the experiments are listed as follows:

1. Beaker
2. Thermometer
3. Magnetic stirrer
4. Autoclave
5. Ultrasonic Bath
6. Centrifuge
7. Oven
8. Furnace

3.1.5 Characterization Method

The resulting SAPO-34 particles were characterized to determine the characteristics of SAPO-34 like size, shape, morphology and structural group. Tools used to characterize the SAPO-34 nanoparticles are as follows:

Transmission Electron Microscope

Transmission Electron Microscope (TEM) use electrons instead of light as “light source” and has much lower wavelength thus make it possible to get a resolution a thousand times better than light microscope. Images are recorded by detecting the electrons that pass through the sample to a system of electromagnetic lenses which focus and enlarge the image on a fluorescent screen, photographic film or digital camera. Therefore, the image of SAPO-34 nanocrystals as well as its particle sizes can be seen through this in order to analyze the morphology of the crystals (Kumar, 2010).

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) obtains infrared spectra by first collecting an interferogram (raw data) sample signal using interferometer. The interferogram collected will be sent to FTIR spectrometer to be digitized by performing Fourier Transform (FT) to obtain and display the spectrum. Wavelength of 4000cm^{-1} to 400cm^{-1} is used. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful in identifying unknown materials, quality or consistency and the amount of components in a mixture (Newport, n.d.).

N₂-BET Surface Area Analyzer

N₂-BET surface area analyzer used technology of nitrogen adsorption basically at a temperature of 77 K leads to a generation of adsorption isotherm data. It is sometimes referred to as Brunauer-Emmett-Teller (BET) isotherm, which is mostly measured over porous materials to determine the surface area of the particles. BET model aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the

measurement of the specific surface area of a material (Brunauer, Emmett, & Teller, 1938).

Table 1 lists the characterization methods and their respective properties.

Table 1: Characterization method used to study the properties of SAPO-34

Characterization Method	Properties
Transmission Electron Microscope (TEM)	Surface morphology and crystallinity and size of the particles
Fourier Transformed Infrared (FTIR)	Structural group verification
N ₂ -BET surface area analyzer	To study the surface area of the particles

3.1.6 CO₂ Adsorption on SAPO-34

Carbon dioxide adsorption capability of SAPO-34 will be analyzed using CO₂ physisorption analyzer, BELSORP. BELSORP is physisorption analyzer that is designed to identify adsorption isotherm for surface area and pore size distribution. From BELSORP, the CO₂ adsorption characterization can be determined. Basically, isotherm use in BELSORP is BET. The resulting SAPO-34 will be out gassed in vacuum for at least 24 hours before the sorption measurement. Instead of to measure CO₂ adsorption capability, BET model is also used to determine SAPO-34 surface area by nitrogen adsorption.

3.2 Project Activities

The project activity in FYP is mainly focuses on the experiment of synthesizing the SAPO-34 nanoparticles based on the experimental run conditions generated by the DoE software. Before experiment being conducted, proper planning needs to be done in term of availability of chemicals and equipment used. Besides, as one experiment need to be conducted more than one day, therefore, proper time planning is very crucial.

3.2.1 Availability of chemicals

Table 2 shows amount of chemicals needed for synthesis of SAPO-34 in each of the experiment run based on DoE.

Table 2: Availability of chemicals

Chemical Name	Chemical Formula	Mw (g/mol)	Amount (g)	Remark
Aluminium Isopropoxide >99.99% metal basis	$\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$	204.25	6.8	Available
Phosphoric Acid, 85 wt%	H_3PO_4	97.99	3.85	Available
Deionized water	H_2O	18.02	20	Available
LUDOX AS-40 Colloidal Silica 40 wt%	SiO_2	60.08	1.13	Available
Tetraethylammonium Hydroxide 35 wt%	$(\text{C}_2\text{H}_5)_4\text{NOH}$	144.61	7.02	Available
Dipropylamine 99%	$\text{C}_6\text{H}_{15}\text{N}$	101.19	1.37	Available
Cyclohexylamine 99%	$\text{C}_8\text{H}_{17}\text{NH}_2$	99.17	1.34	Available

3.2.2 Availability of Apparatus/Equipment

Table 3 shows the availability of apparatus/equipment.

Table 3: Availability of apparatus/equipment

Apparatus	Operating Parameter	Remarks
Beakers	-	Available in the laboratory
Chemical Bottle	-	Available in the laboratory
Measuring Cylinder	-	Available in the laboratory
Stirrer	-	Available in the laboratory
Ultrasound Bath	Temperature = 50°C Frequency = 24kHz Ultrasonic Duration: Refer to experimental condition generated by DoE software	Available in FYP Laboratory
Oven (Seeds growth)	Temperature=200°C Synthesis Duration=Refer to experimental condition generated by DoE software	Available in FYP Laboratory
Centrifuge	Speed = 7000 rpm	Available in block 04-02-07
Oven (Drying)	Temperature=110°C	Available in Physical

		Laboratory
Furnace	Temperature=500°C	Available in block 05-00-01

3.2.3 Time Management

Time management is important in conducting an experiment as this is to make sure that the experimental can be preceded smoothly without overlapping with other's schedule. Time planning is done on all experimental runs with different synthesis and ultrasonic durations. For example, experiment run for Experiment 1 requires ultrasonic duration of 30 minutes and synthesis duration of 90 minutes (Refer to Figure 5).

Table 4 shows the estimation time to complete Experiment 1.

Table 4: Time planning for Experiment 1

Date	Task	Duration	Start	End
1st day	Preparation of apparatus and chemicals	20 mins	8.00 am	8.20 am
	Weight chemicals	30 mins	8.20 am	8.50 am
	Stirred mixture of: (H ₂ O + Al ₂ O ₃ + H ₃ PO ₄ + LUDOX + TEAOH)	3 hrs	8.50 am	11.50 am
	Stirred Dipropylamine + Cyclohexylamine + mixture	24 hrs	11.50 am	11.50 am (2nd day)
2nd day	Set up of ultrasonic bath and oven	30 mins	11.20 am	11.50 am
	Ultrasound	30 mins	11.50 am	12.20 pm
	Oven for hydrothermal growth	90 mins	12.20 pm	1.50 pm
	Wash + Centrifuge	45 mins	1.50 pm	2.35 pm
	Drying in oven	24 hrs	2.35 pm	2.35 pm (3rd day)

Referring to Table 4, 3 days are needed to complete each experimental run if calcinations step is excluded (The sample will be kept in the dessicator after drying before the calcinations).

3.3 Key milestones

Table 5 shows the key milestones of FYP I and FYP II.

Table 5: Key milestones

Semester	Task	Completion
January 2013	Selection of FYP topic	Week 2
	Research for literature reviews	Week 6
	Submission first draft extended proposal	Week 7
	Submission second draft extended proposal	Week 8
	Proposal defense	Week 9
	Submission interim report draft	Week 13
	Submission final interim report	Week 14
May 2013	Synthesis and characterization of SAPO-34	Week 1 - 8
	Submission of progress report	Week 8
	DoE data input and analysis	Week 9-10
	Pre-SEDEX	Week 11
	Submission of draft report	Week 12
	Submission of dissertation (Soft bound)	Week 13
	Submission of technical paper	Week 13
	Oral Presentation	Week 14
	Submission of project dissertation (Hard bound)	Week 15

3.4 Gantt Chart

Table 6 and Table 7 show the Gantt chart for FYP 1 and FYP 11 respectively.



Table 6: Gantt chart for FYP 1

NO	DETAIL / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	First meeting with coordinator and supervisor	Process													
2	Problem statement and analysis of project		Process	Process											
3	Preliminary Research Work and Literature Review • Check availability of chemicals, labware and synthesis apparatus	Process	Process	Process	Process	Process	Process								
4	Submission of Extended Proposal Defense						Suggested Key Milestones								
5	Preparation for Oral Proposal Defense							Process	Process						
6	Oral Proposal Defense Presentation								Suggested Key Milestones						
7	Design of synthesis parameters (DoE study)									Process	Process				
8	Synthesis of SAPO-34									Process	Process	Process	Process		
9	Preparation of Interim Report										Process	Process			
10	Submission of Interim Draft Report												Suggested Key Milestones		
11	Submission of Interim Final Report														Suggested Key Milestones



Table 7: Gantt chart for FYP II

NO	DETAIL / WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
1	Synthesis and characterization of SAPO-34	Process	Process	Process	Process	Process	Process	Process									
2	Submission of progress report								Key Milestone								
3	DoE data input and analysis									Process	Process	Process					
4	Pre-SEDEX											Key Milestone					
5	Submission of draft report												Key Milestone				
6	Submission of dissertation (Soft bound)													Key Milestone			
7	Submission of technical paper														Key Milestone		
8	Oral Presentation															Key Milestone	
9	Submission of project dissertation (Hard bound)																Key Milestone

 Process
 Suggested Key Milestones

CHAPTER 4

RESULTS AND DISCUSSION

4.1 DOE Results

Table 8 shows the complete 13 number of experiment design for the ultrasonic pretreatment duration and hydrothermal heating duration and its corresponding responses.

Run	Ultrasonic Pretreatment Duration, A (min)	Hydrothermal Heating Duration, B (min)	Average Particle Size, Y_1 (nm)	CO ₂ Adsorption Capability, Y_2 (mmol/g)
1	30	90	12.5	0.20
2	30	180	27.5	0.11
3	30	135	20.5	0.16
4	30	135	20.0	0.15

Table 8: Experiment runs and responses

5	15	90	17.3	0.16
6	45	180	25.0	0.08
7	45	135	17.5	0.03
8	15	180	32.0	0.04
9	15	135	28.0	0.02
10	30	135	19.5	0.07
11	45	90	10.0	0.11
12	30	135	18.5	0.03
13	30	135	23.0	0.06

4.1.1 Statistical Model Analysis

Model analysis is required in order to determine the model is valid for both responses or not. By conforming the validity of the model, optimization can be proceeded.

Average Particle Size, Response Y_1

For the effect of operating variables on average particle size, linear model was recommended by the DOE software with F-value of 85.58 and “Prob > F” is less than 0.0001 which means that there was only less than 0.01% chance that the model F-value is due to noise. This indicates the model was significant as the values of “Prob > F” is less than 0.05.

Besides, for a model to be reliable, the response should be predicted with reasonable accuracy by the model and compared with the experimental data. From the comparison, it was found that the value of the correlation coefficient, R^2 was 0.9448 which confirms the accuracy of the model as the R^2 value is more than 0.8. Table 9 shows the ANOVA for 2^2 full CCD of average particle size, Y_1 .

Table 9: ANOVA of average particle size, Y_1

Source	Sum of Squares	d.f.	Mean Square	F-value	Prob > F
Model	435.52	2	217.76	85.58	<0.0001
A	102.51	1	102.51	40.28	<0.0001
B	333.01	1	333.01	130.87	<0.0001

The linear model used for Y_1 was described in Equation 3 as follows:

$$Y_1 = 6.7859 - 0.2756A + 0.1656B \dots \dots \dots (3)$$

Figure 6 shows Design-Expert plot for average particle size, response Y_1 of actual versus predicted values whereby the straight line indicates the predicted value.

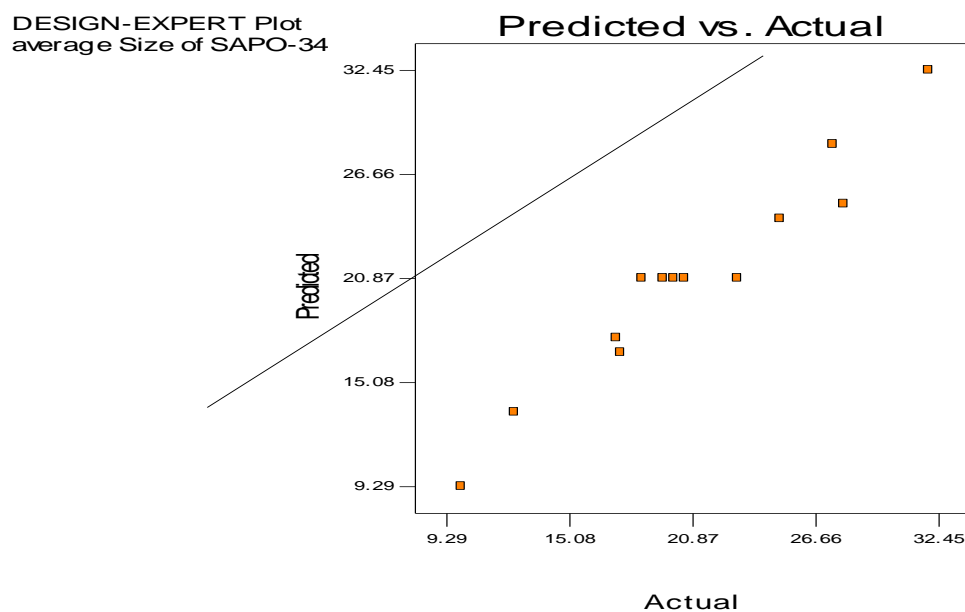


Figure 6: Actual versus predicted Design-Expert Plot of average particle size

From the Figure 6, it shows that the model used for Y_1 is adequate for predicting the average particle size as most actual values located near to the straight line. Meanwhile, to study the effect of the operating variables to the average particle size, Figure 7 shows the 3D surface of Design-Expert plot for the average particle size Y_1 .

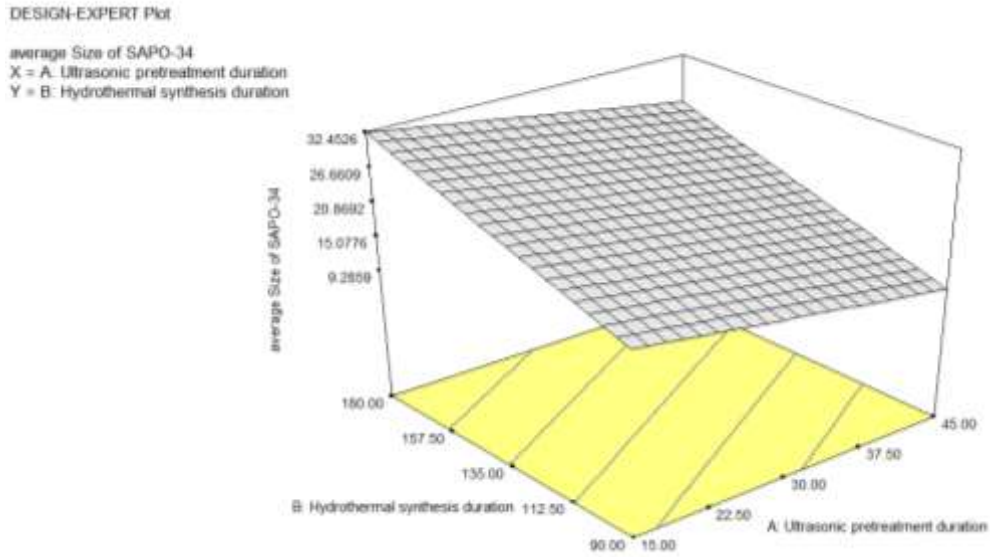


Figure 7: 3D surface Design-Expert Plot of average particle size

The 3D plot (Figure 7) shows that average particle size of the resulting SAPO-34 increase as the hydrothermal synthesis duration increase. The average particle sizes of the SAPO-34 formed were in the range from 10 nm to 32 nm.

Referring to Figure 7 also, the average particle size of SAPO-34 decreases when ultrasonic pre-treatment duration decreases. This is because ultrasonic can initiate seeding and control of crystal growth. Ultrasonic treatment can induced bubbles in solution and once the bubbles collapse, it will creates high temperature and pressure in the solution (Chen et. al., 2003). This phenomenon is called as cavitation. Cavitation bubbles acts as nuclei for crystals growth and disrupt the present nuclei from growing in size and into its cubic shape thus changed the morphology of complete crystal from cubic to spherical shape and reduce crystal size. Besides, the collapsing bubbles prevents the particles from agglomerate to bigger size (Askari et. al., 2009 & Talebi et. al., 2010).

CO₂ Adsorption Capability, Response Y₂

Table 10 shows the ANOVA for 2² CCD of the CO₂ adsorption capability, Y₂.

Table 10: ANOVA of CO₂ adsorption capability, Y₂

Source	Sum of Squares	d.f.	Mean Square	F-value	Prob > F
Model	0.029	5	5.7E-003	2.95	0.0957
A	0	1	0	0	1
B	9.6E-003	1	9.6E-003	4.96	0.0613
A ²	0.011	1	0.011	5.74	0.0478
B ²	0.012	1	0.012	6.31	0.0402
AB	2.03E-003	1	2.03E-003	1.05	0.3406

From Table 10, it shows that the model used for the Y_2 is not significant with F-value of 2.95 and “Prob > F” of 0.0957 which is more than 0.05. Besides, the R^2 of the model was 0.6779 which is below 0.8 that indicates also the accuracy of the model is not significant. The insignificant of the model is due to the inconsistency in results of CO_2 adsorption capability. The inconsistency of the response can be resulted from the error and incomplete crystallization of the SAPO-34. Although modification on the model has been done to increase the R^2 , but the model was remain insignificant. Therefore, as per suggested by DOE, quadratic model is chosen as the model shows the highest F-value with lowest “Prob > F” value and highest R^2 value. The quadratic model used for Y_2 is shown in Equation 4 as follows:

$$Y_2 = 0.6926 + 0.0124A - 0.0108B - 2.8199A^2 + 3.2865B^2 + 3.3333AB \dots (4)$$

Figure 8 shows Design-Expert plot for CO_2 adsorption capability, Y_2 of actual versus predicted value.

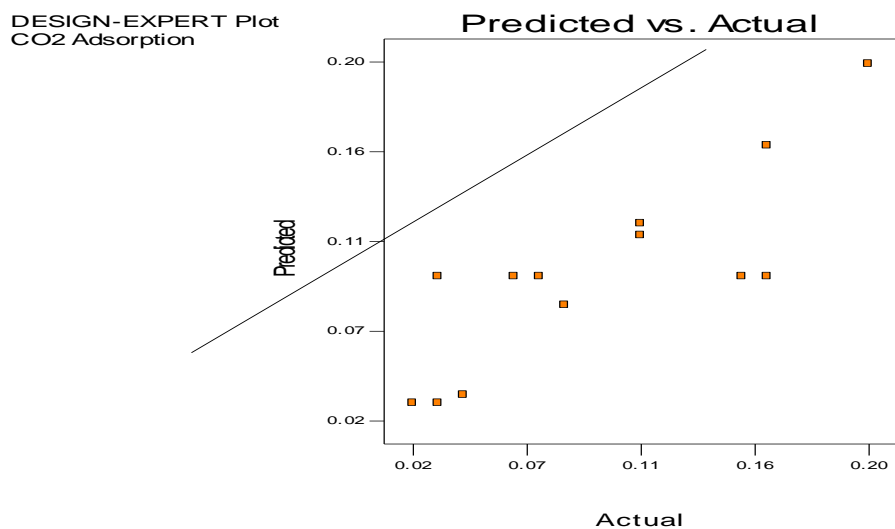


Figure 8: Actual versus predicted Design-Expert Plot of CO₂ adsorption capability

From the Figure 8, it shows that the actual values were scattered from the straight line (predicted value), however, most of the values located near the straight line. The effect of the operating variables to the CO₂ adsorption capability, Y₂ is plotted as shown in Figure 9.

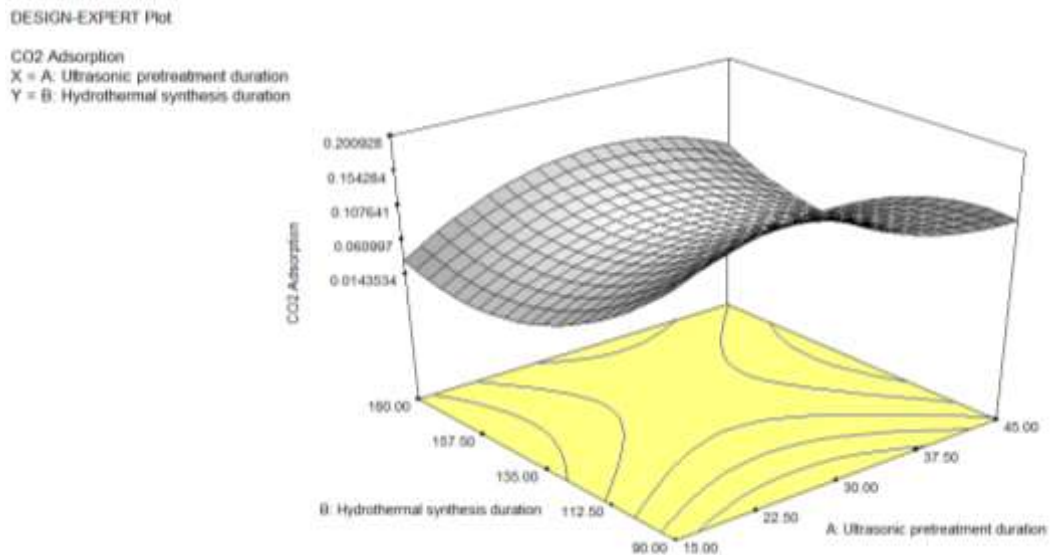


Figure 9: 3D surface Design-Expert Plot of CO₂ adsorption capability

From the 3D plot (Figure 9), it shows that the effect of the hydrothermal heating duration and ultrasonic pre-treatment duration to the CO₂ adsorption capability were inconsistent. The decrease in hydrothermal synthesis duration from 180 minutes to 135 minutes reduced the CO₂ adsorption capability. Further decrease of hydrothermal heating duration below 135 minutes to 90 minutes resulted in increased CO₂ adsorption capability.

Meanwhile, for ultrasonic pre-treatment duration ranged from 15 minutes to 37.5 minutes showed increasing pattern of CO₂ adsorption capability. For ultrasonic pre-treatment duration above 37.5 minutes up to 45 minutes, the CO₂ adsorption capability slightly decreased.

The inconsistent pattern of CO₂ adsorption capability for both variables is perhaps due to the incomplete crystallization. Although the size of particles was small, the crystallinity of the SAPO-34 will also affect the CO₂ adsorption capability.

4.1.2 Optimization

In this study, numerical optimization was chosen by using the DOE in order to optimize adsorption process. Goal was set for each criteria including operating variables and responses in order to get the optimum condition. Table 11 shows goal sets for each criteria.

Table 11: Goal of criteria for optimization

Criteria	Range		Goal set
	Lower	Upper	
Ultrasonic pre-treatment duration	15 minutes	45 minutes	Is in range
Hydrothermal synthesis duration	90 minutes	180 minutes	Is in range
Average particle size	10 nm	32 nm	Is minimum
CO ₂ adsorption capability	0.02 mmol/g	0.2 mmol/g	Is maximum

For ultrasonic pre-treatment duration and hydrothermal synthesis duration, the goal were set in range. Meanwhile, the average particle size is set minimum because, the smaller the size, the higher the surface area which resulted in better adsorption efficiency. The CO₂ adsorption capability was set as maximum in order to achieve maximum adsorption. From the goal set, there were two optimization solutions generated by the software. Table 12 shows the solutions of numerical optimization generated by the DOE.

Table 12: Solutions of numerical optimization by DOE

Solution	Ultrasonic pre-treatment duration	Hydrothermal synthesis duration	Average particle size	CO ₂ adsorption capability	Desirability

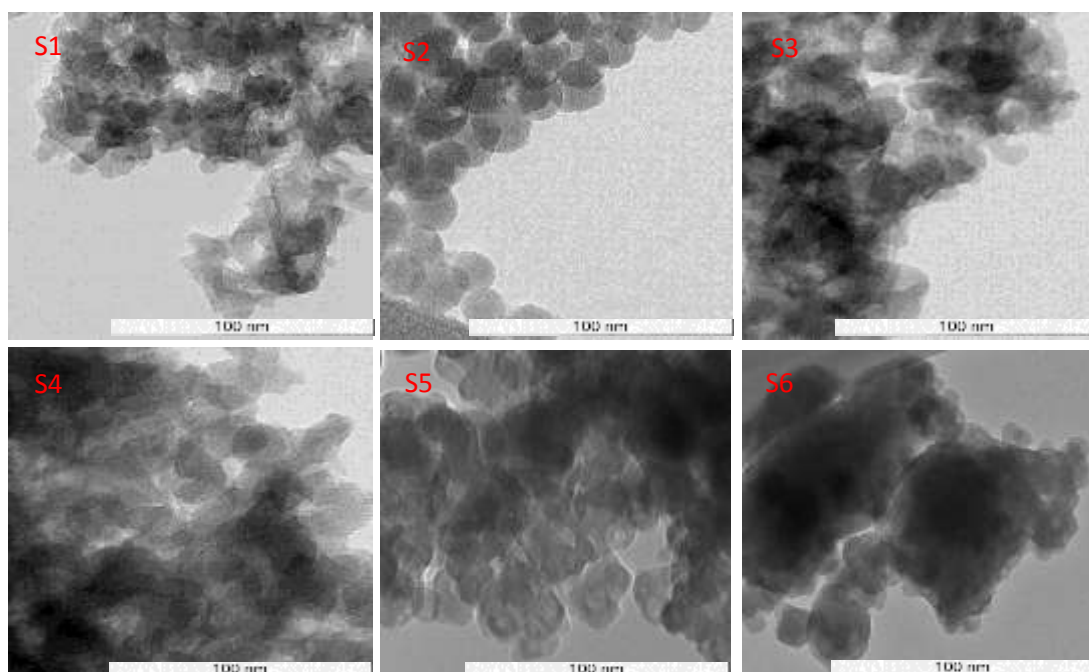
	(min)	(min)	(nm)	(mmol/g)	
1	32	90	12.92	0.20	0.919
2	39	180	25.72	0.11	0.374

From the solutions, Solution 1 was chosen as the optimum condition because of smaller average particle size and higher CO₂ adsorption capability compared to the Solution 2. Besides, the desirability of Solution 1 is 0.919 which practically higher.

4.2 CHARACTERIZATION OF SAPO-34 NANOPARTICLES

4.2.1 TRANSMITTANCE ELECTRON MICROSCOPE (TEM)

Figure 10 shows TEM images of all samples. Based on the Figure 10, it shows that the crystals have spherical shape nanoparticles. The higher the uniformity of the spherical shape of the particles means better crystal morphology. From all the samples, it shows that S2 has the best crystal morphology as uniform spherical shape was observed. This was because, the S2 sample was synthesized using longer hydrothermal heating duration that promotes particles growth in a well-defined shape with hydrothermal heating time of 180 minutes and ultrasonic time of 30 minutes. However, sample S6 should show the highest crystallinity instead of S2 because it has higher ultrasonic pretreatment duration (45 minutes) and same hydrothermal heating duration (180 minutes) compared to S2. However, the inconsistency of the results perhaps due to synthesis error or poor technique on TEM characterization.



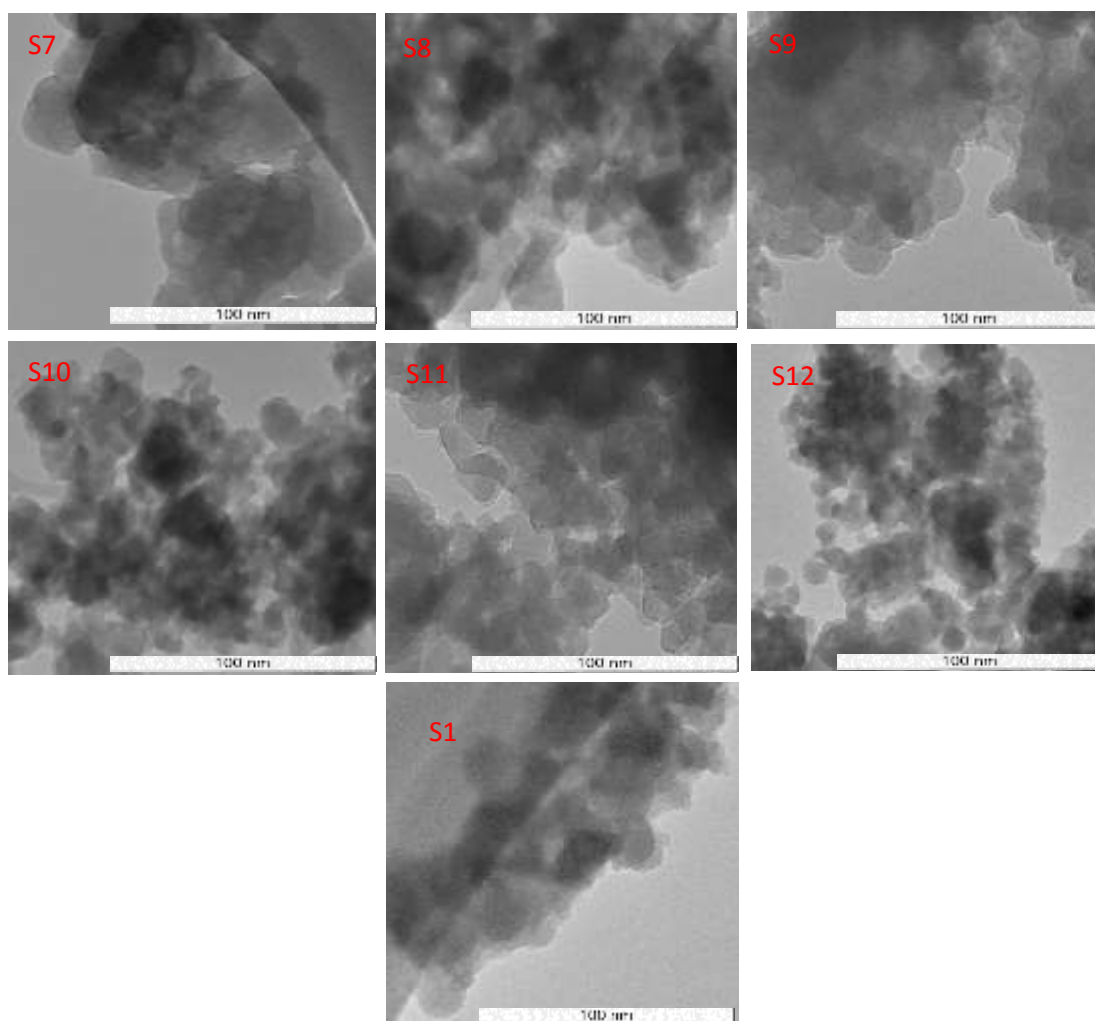


Figure 10: TEM images

The results of the particle size of each samples are shown in Table 8. As reported in literature, higher ultrasonic time can reduce the particle size of SAPO-34 and affect the morphology of the typical SAPO-34 which is in cubic shape to spherical shape.

Meanwhile, hydrothermal heating time can affect the particle growth whereby, by prolonging the heating time, it will lead to further crystal growth thus increasing the particle size (Askari et. al., 2012). However, based on literature, only 1.5 hours is needed to synthesize SAPO-34 with heating temperature of 200°C if ultrasonic pretreatment is applied (Askari et. al., 2012). In the present research, 3 hours hydrothermal heating duration was needed to obtain SAPO-34. The deviation of these results from literature was mainly attributed to different composition (Si, Al, P) of the synthesis solution and lower heating temperature of 160°C.

4.2.2 FOURIER TRANSFORM INFRA RED (FTIR)

Figure 11 shows the FTIR spectra for all the samples synthesized according to the synthesis parameters as listed in Table 8. FTIR spectra for all samples show almost similar peaks at 700, 1100, 1640 and 3450 cm^{-1} . Meanwhile, typical FTIR spectra of SAPO-34 show significant bands at 643, 1094, 1617 and 3450 cm^{-1} which related to O-H stretching vibrations, H-O-H bend, T-O-T asymmetric stretching vibrations and the vibrations in double ring ((Si-Al)-O₄, PO₄) region respectively (Liu et. al., 2008; Tan et. al., 2002 & Akolekar et. al., 1999).

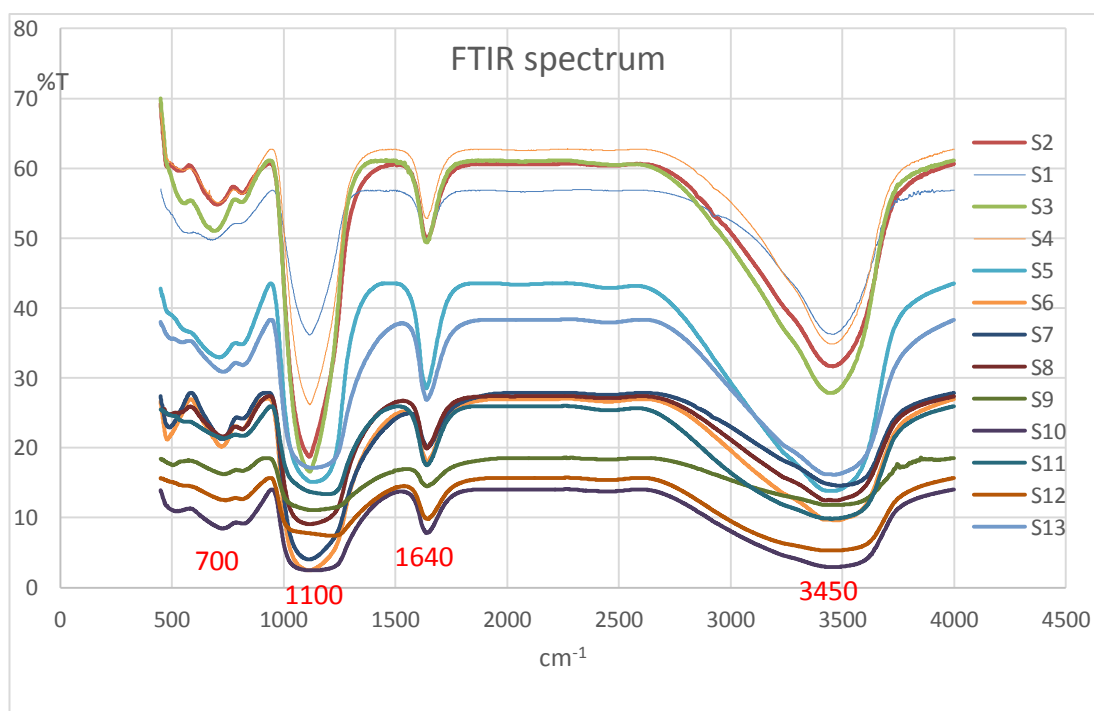


Figure 11: FTIR spectrum

Based on Figure 11, for the peaks around 650 and 1600 cm^{-1} corresponds to the TO bonding and –OH bonding in the SAPO-34 framework. These spectra correspond to SAPO-34 with chabazite (CHA) structure as reported in literature (Das et. al., 2012). For peak around 1100 cm^{-1} is due to the asymmetric stretching of T-O tetrahedral (T-Al, Si, P).

Meanwhile, peak around 3500 to 3600 cm^{-1} can be referred as absorption bands due to the bridging hydroxyl groups which attributed to –SiOHAl– groups from the interaction with the oxygen atoms of the framework and located inside the double-six rings (Izadbakhsh et. al., 2009). From these results, we can concluded here that all the samples synthesized in the present work showed SAPO-34 topology.

4.2.3 BET (N₂) SURFACE AREA

The specific surface areas of the samples were determined using Brunauer-Emmett-Teller (BET) method by nitrogen adsorption experiment. Figure 12 shows sorption-isotherm for samples S1, S2 and S3. BET surface area on samples S1, S2 and S3 are 122.8557 m^2/g , 56.2724 m^2/g and 97.1296 m^2/g respectively. As classification after IUPAC 1984, all samples exhibit Type II sorption-isotherm which shows that there is interaction between gas and adsorbent (“Determination of the Surface Area by the BET Method”, n.d.).

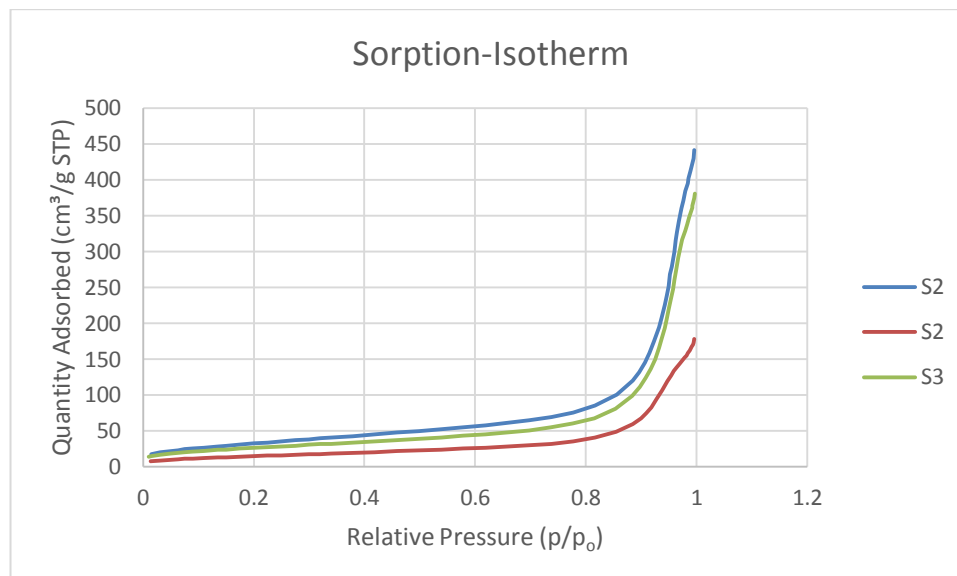


Figure 12: Sorption-Isotherm for S1, S2, and S3

Askari et. al., reported that the BET surface area were increased from 240.02 to 366.5 m²/g as the crystallization time increases. This was due to when the crystallization time increases, the crystallinity of the resulting SAPO-34 increased. Meanwhile, if the crystallization time is reduced, the crystallinity of the samples will partially lost and resulted in amorphous phase, and thus decreases the BET surface area (Askari et. al., 2012).

BET surface area for samples S1, S2 and S3 are 122.8557 m²/g, 56.2724 m²/g and 97.1296 m²/g respectively. These results show that the BET surface area decreases as the particle size increased which suggest that smaller particles lead to larger surface area. Furthermore, these results were consistent with the particle size measured using TEM (Figure 6). Table 9 shows BET results of sample corresponding to their average particle size.

Table 13: BET results of samples

Sample	BET Surface Area (m ² /g)	Average Particle Size (nm)
S1	122.8557	12.5
S2	56.2724	27.5
S3	97.1296	20.5

However, the surface area for these samples are not as high as reported in literature due to incomplete crystallinity.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In the present research, SAPO-34 were synthesized using ultrasonic pre-treatment and hydrothermal method as the methods are the most feasible and less time consuming. Meanwhile, to optimize the synthesis parameters like synthesis duration and ultrasonic duration, DoE software were used in order to design the experiment by generating minimum number of experimental runs. As per condition of experimental runs generated by the DoE software, synthesis of SAPO-34 were conducted. Lastly, the SAPO-34 particles were characterized using TEM and FTIR.

In order to determine the CO₂ adsorption of SAPO-34, BELSORP physisorption analyzer were used.

To summarize, based on the mentioned discussion of the results obtained from TEM, FTIR and BET surface area, the properties of each synthesized sample could be concluded as follows:

1. Based on TEM results, increasing hydrothermal duration time will increase particle size due to the growth of SAPO-34 particles and increasing in ultrasonic pre-treatment duration will reduce the particle size.
2. Based on FTIR results, the peak band of FTIR spectrum of all samples show similar results to a typical SAPO-34 FTIR spectrum which are 643, 1094, 1617 and 3450 that are related to O-H stretching vibrations, H-O-H bend, T-O-T asymmetric stretching vibrations and the vibrations in double ring ((Si-Al)-O₄, PO₄) region respectively
3. N₂-BET surface area of synthesized samples showed that increasing in particle size lead to decrease in BET surface area.
4. CO₂ adsorption capability with respect to particle size shows inconsistent results as the CO₂ adsorption capability should increase when the particle size decrease and not the other way around.
5. DOE results shows that the optimization condition for ultrasonic pretreatment duration of 32 minutes and hydrothermal heating duration of 90 minutes to get the minimum particle size (12.92 nm) and maximum CO₂ adsorption capability (0.20 mmol/g) within the range of the results.
6. Although optimization results were obtained, however, the model for the CO₂ adsorption capability, Y₂ was insignificant which shows that the effect of variables to CO₂ adsorption capability is not favorable for optimization using DOE software.

5.2 RECOMMENDATION

For further expansion of this project, the optimum condition should be proved by conducting another experiment using the optimum condition given by the DOE software.

REFERENCES

- [1] Hogue, C., Johnson, J. and Kemsley, J. (2012). Global-Warming Warnings. *Chemical & Engineering News*, 91(3). Retrieved from <http://cen.acs.org/articles/91/i3/Global-Warming-Warnings.html>
- [2] Li, S., Alvarado, G., Noble, R. D., & Falconer, J. L. (2005). Effects of impurities on CO₂/CH₄ separation through SAPO-34 membranes. *Journal of Membrane Science*, 251, 59-66.
- [3] Baker, R. (2001). Future directions of membrane gas separation technology. *Membrane Technology*, 138, 5-10.

- [4] Koros, W. J., & Mahajan, R. (2000). Pushing the limits on possibilities for large scale gas separation: which strategies? *Journal of Membrane Science*, 175, 181-196.
- [5] Li, S., Alvarado, G., Noble, R. D., & Falconer, J. L. (2004). SAPO-34 membranes for CO₂/CH₄ separation. *Journal of Membrane Science*, 241, 121-135.
- [6] Tsai, C. Y., Tam, S. Y., Lu, Y., & Brinker, C. J. (2000). Dual-Layer asymmetric microporous silica membrane. *Journal of Membrane Science*, 169, 255-268.
- [7] Asaeda, M., & Yamasaki, S. (2001). Separation of inorganic/organic gas mixtures by porous silica membranes. *Separation Purification Technology*, 25, 151-159.
- [8] Vu, D. Q., Koros, W. J., & Miller, S. J. (2002). Higher pressure CO₂/CH₄ separation using carbon molecular sieve hollow membranes. *Industrial & Engineering Chemistry Research*, 41, 367-380.
- [9] van den Broeke, L. J. P., Kapteijin, F., Mouljin, J. A. (1999). Transport and separation properties of a silicalite-1 membrane. *Chemical Engineering Science*, 54, 259-269.
- [10] Kusakabe, K., Kuroda, T., Murate, A., & Morooka, S. (1997). Formation of a Y-type zeolite membrane on a porous α -alumina tube for gas separation. *Industrial & Engineering Chemistry Research*, 36, 649-655.
- [11] Park, J., Lee, J. Y., Kim, K. S., Hong, S. B., & Seo, G. (2008). Product selectivity and catalytic deactivation of MOR zeolites with different acid site densities in methanol-to-olefin (MTO) reactions. *Applied Catalyst A*, 339, 36-44.

- [12] Li, S., Alvarado, G., Noble, R. D., & Falconer, J. L. (2008). SAPO-34 membranes for CO₂/CH₄ separations: Effect of Si/Al ratio. *Microporous and Mesoporous Materials*, 110, 310-317.
- [13] Razavian, M., Halladj, R., & Askari, S. (2011). Recent Advance in Silicoaluminophosphate Nanocatalyst Synthesis Techniques and Their Effects on Particle Size Distribution. *Review on Advance Material Science*, 29, 83-99.
- [14] Askari, S., & Halladj, R. (2012). Ultrasonic Pretreatment for Hydrothermal Synthesis of SAPO-34 nanocrystals. *Ultrasonic Sonochemistry*, 19, 554-559.
- [15] National Climate Assessment Development Advisory Committee. (2013). Federal Advisory Committee Draft Climate Assessment Report. Retrieved from <http://ncadac.globalchange.gov/>
- [16] Climate Commission. (2013). The Critical Decade: Extreme Weather. Retrieved from <http://climatecommission.gov.au/report/extreme-weather/>
- [17] U.S. Environmental Protection Agency. (2012). Sources of Greenhouse Gas Emissions. Retrieved from <http://www.epa.gov/climatechange/ghgemissions/sources.html>
- [18] International Panel on Climate Change, IPCC. (2005). IPCC Special Report on Carbon Dioxide Capture and Storage (1st ed.). New York, DC: Metz, B., Davidson, O., de Coninck, H. C., Loos, M., & Meyer, L. A.
- [19] Bellusi, G., Broccia, P., Carati, A., Millini, R., Pollesel, P., Rizzo, C., & Tagliabue, M. (2011). Silica-Aluminas for Carbon Dioxide Bulk Removal from Sour Natural Gas. *Microporous and Mesoporous Materials*, 146, 134-140.
- [20] Kohl, A. L., & Nielsen, R. (1997). *Gas Purification* (5th ed.). Houston, TX: Gulf Publication.

- [21] Seader, J. D., & Ernest, J. H. (2006). *Separation Process Principles* (2nd ed.). Wiley, India: Private Limited
- [22] Protea. (n.d.). Application: CO₂ capture by Amine Absorption. Retrieved from http://www.protea.ltd.uk/applications/co2_capture_anime_absorption.php
- [23] Rufford, T. E., Smart, S., Watson, G. C. Y., Graham, B. F., Boxall, J., Dinizda J. C., & May, E. F. (2012). The Removal of CO₂ and N₂ From Natural Gas: A Review of Conventional and Emerging Process Technologies. *Journal of Petroleum Science and Engineering*, 94, 123–154.
- [24] Songolzadeh, M., Ravanchi, M. T., & Soleimani, M. (2012). Carbon Dioxide Capture and Storage: A General Review on Adsorbents. *World Academy of Science, Engineering and Technology*, 70, 225-232.
- [25] Thiruvengkatachari, R., Su, S., An, H., & Yu, X. X. (2009). Post combustion CO₂ capture by carbon fibre monolithic adsorbents. *Progress in Energy and Combustion Science*, 35, 438-455.
- [26] Li, G., Xiao, P., Webley, P. A., Zhang, J., & Singh, R. (2009). Competition of CO₂/H₂O in adsorption based CO₂ capture. *Energy Procedia*, 1, 1123-1130.
- [27] Chaffee, A. L., Knowles, G. P., Liang, Z., Zhang, J., Xiao, P., & Webley, P. A. (2007). CO₂ capture by adsorption: Materials and process development. *International Journal of Greenhouse Gas Control*, 1, 11-18.
- [28] Hong, S. L., Funke, H. F., Falconer, J. L., & Noble, R. D. (2007). Ion-exchanged SAPO-34 membranes for light gas separations. *Microporous and Mesoporous Material*, 106, 140–146.
- [29] Peydayesh, M., Asarehpour, S., Bakhtiari, O., & Mohammadi, T. (2010). Preparation and characterization of SAPO-34 - Matrimid® 5218 mixed matrix

membranes for CO₂/CH₄ separation. *Chemical Engineering Research and Design*, 1163, 1-34.

[30] Mohammadi, T., Asarehpour, S., & Samei, M. (2012). Effects of Synthesis Temperature and Support Material on CO₂ and CH₄ Permeation through SAPO-34 Membranes. *Separation Science Technology*, 47, 2320-2330.

[31] Ashraf, T., & Siamak, S. (2010). Comparative Study of Carbon Dioxide and Methane Adsorption by Synthesized Fine Particles of SAPO-34 Molecular Sieve. *Oil and Gas Excellence*, 29, 37-45.

[32] Ertan, A. (2004). CO₂, N₂ and Ar Adsorption on Zeolites. (Unpublished doctoral dissertation). Izmir Institute of Technology, Izmir, Turkey.

[33] Yao, J., Wang, H., Ringer, H. P., Chan, K. Y., Zhang, L., & Xu, N. (2005). Growth of SAPO-34 in Polymer Hydrogels through Vapor-Phase Transport. *Microporous and Mesoporous Material*, 85, 267-272.

[34] van Heyden, H., Mintova, S., & Bein, T. (2006). AlPO-18 nanocrystals synthesized under microwave irradiation. *Journal of Materials Chemistry*, 16, 514-518.

[35] Chen, W., Zhang, J., & Cai, W. (2003). Sonochemical preparation of Au, Ag, Pd/SiO₂ mesoporous nanocomposites. *Scripta Materialia*, 48, 1061-1066.

[36] Buxton, R. (n.d.). Design Expert 7. Retrieved from Mathematics Learning Support Centre: mlsc.lboro.ac.uk/resources/statistics/design_expert_7.pdf

[37] Reimer, L. (1998) Scanning electron microscopy: Physics of image formation and microanalysis. Retrieved from http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html

- [38] Kumar, D. M. (2010). Electron Microscopy. Retrieved from <http://teacherschoice.files.wordpress.com/2010/12/electron-microscopy1.pdf>
- [39] Newport. (n.d.). Introduction to FTIR Spectroscopy. Retrieved from <http://www.newport.com/Introduction-to-FT-IRspectroscopy/405840/1033/content.aspx>
- [40] Dutrow, B. L., & Clark, C. M. (n.d.). XRD. Retrieved from http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html
- [41] Teamator. (n.d.). Volumetric instruments for sorption analysis. Retrieved from http://www.teamator.com/index.php?option=com_content&view=article&id=88:bel-products&catid=1:solids&Itemid=11
- [42] Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of American Chemical Society*, 60, 309-319.