Synthesis of Polymer Ionic Liquid Incorporating Activated Carbon: Characterization and Carbon Dioxide (CO_2) Solubility Study

by

Muhammad Muhaimin Bin Abd Rahman

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Dissertation submitted in partial fulfilment of

the requirements for the

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr Muhammad Moniruzzaman)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2014

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 contain herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD MUHAIMIN BIN ABD RAHMAN

ABSTRACT

Carbon Dioxide (CO_2) is a type of greenhouse gases that being emitted to the environment through some industrial processes such as combustion of fossil fuels. CO_2 need to be separated in order to reduce global warming. There are several technique studied to separate CO_2. Among these, ionic liquids emerged as the best potential to separate CO_2 and are currently being studied. This method can still be improved to obtain a better CO2 separation capacity. This project aims to develop ionic liquids monomer as it then synthesized to become polymer ionic liquids incorporating activated carbon. Two types of polymer Ionic liquids were synthesized, which are Poly-(1-Vinyl-3-Ethylimidazolium Bromide), Poly-[Veim][Br] and Poly-(1-Vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide), Poly-[Veim][TF_2N]. Activated carbon was incorporated in the ionic liquid polymer. The polymer then are tested for characteristics using several equipment, which are Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and also using BET equipment (BET). The polymer materials were characterized for their morphology, composition and also the surface area that could be covered by CO_2. From the results, it is found out that the ionic liquid polymer incorporated with activated carbon gives higher amount of CO_2 adsorption compared to ionic liquid polymer without activated carbon. The result supports the study that activated carbon enhances the solubility of CO2 inside the polymer material.

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First and foremost, I would like to praise to Allah because of His help, I would be able to complete my Final Year Project successfully and beneficially. It also would not have been possible without help and support from various individuals and organizations.

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Thank you.

TABLE OF CONTENT

LIST OF FIGURE

LIST OF TABLE

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Carbon dioxide (CO_2) is a colourless and odourless gas. CO_2 is a type of gas that is naturally present in the Earth's atmosphere where it plays a part in the Carbon Cycle. Carbon Cycle is a natural circulation of Carbon among the atmosphere, oceans, soil, plants and animals (Overview of Greenhouse Gases, n.d.). Apart from that, CO_2 gas is also known as greenhouse gas that is emitted by various human activities. One of the main sources is from the burning of fossil fuel. Herzog (1993) says that fossil fuel supply 85% of the world main energy needs. It was predicted that emission of CO_2 will achieve up to 40.2 Gt by 2030 (Zhao, Dong, & Zhang, 2011).

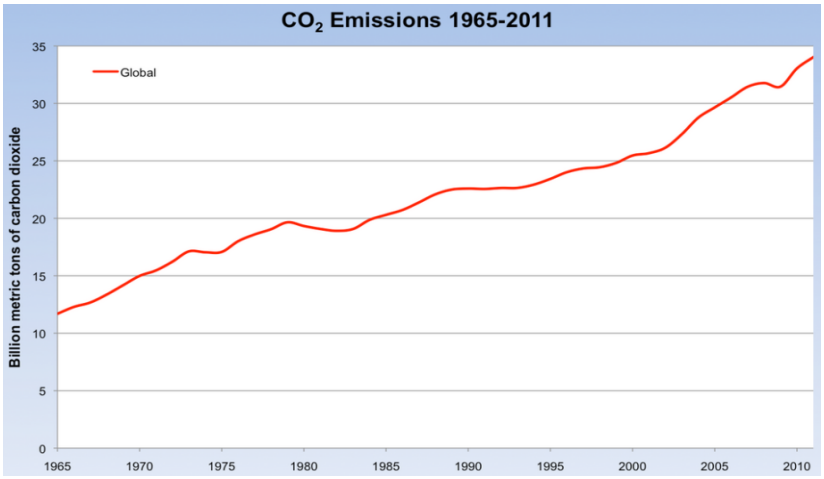


Figure 1.1: Global Amount of Carbon Dioxide Emission from 1965-2011 (Rapier, n.d.)

Figure 1.1 shows the CO_2 emission rate from 1965 up until 2011(Rapier, n.d.). This graph shows that the emission of CO_2 increases by year and it can be seen that the emission of CO_2 become more rapid after 2000. Up until 2002, the amount of CO_2 emission had never reached 1 billion metric tons of annual increment. Rapier (n.d.) says that however, after 2002, it was recorded three times which were during 2003, 2004 and 2010.

CO_2 emission to the atmosphere is a necessary as it helps in maintain the temperature that is suitable for living things on Earth (About CO_2 Emission, n.d.). However, excessive emission of CO_2 will causes more harm and will lead to Global Warming. In this modern era, the urge for a clean energy is something that is being highly studied with one of the main concern is regarding reducing CO_2 emission.

Nowadays, fossil fuels represent the majority of energy generation for daily purpose such as electricity and transportation. Even with the new types of technology that uses renewable sources to produce energy, it still cannot able to replace current fossil fuels combustion practice for energy generation. It might take several years or perhaps, several decades in order to replace fossil fuels combustion. Therefore, more and more research and studies are done in order to capture and separate CO_2 from being emitted to the atmosphere thus reducing the amount of greenhouse gases that are present in the atmosphere.

In order to capture and separate CO_2 from being emitted to atmosphere, there are numbers of CO_2 capture technology that are already practiced and studied. They are either in laboratory scale or industrial scale. Among the technologies are membrane separation, cryogenic separation, adsorption and also by using physical and chemical absorption (CO_2 Capture Project, 2008). Figure 1.2 shows the technologies that are currently existed in separating CO_2.

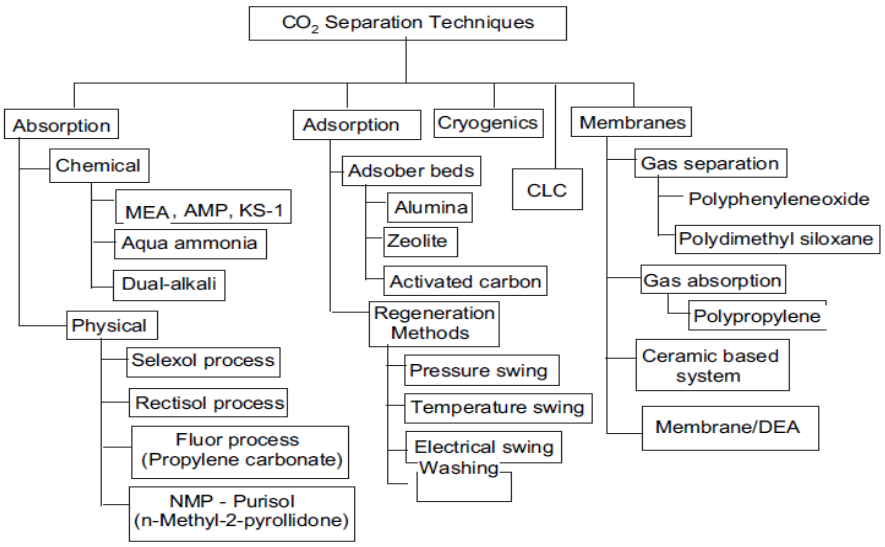


Figure 1.2: CO_2 Capture and Separation Technique (Olajire, 2010)

Among these technologies, amine physical absorption is the most used technology. Amine is widely used because of its stability, capacity and also its reactivity (Zhao, Dong, & Zhang, 2011). Monoethanolamine (MEA) is the most commonly used amine in CO_2 separation. It could capture 75-90% of CO_2, where it will produce a stream with high CO_2 content (Galán Sánchez, Meindersma, & de Haan, 2007)

However, despite good results given by MEA solvent on CO_2 separation, there are some drawbacks with this technology. Amine does not give good energy consumption as it consumes almost 30% of energy required to run a power plant (Zhao, Dong, & Zhang, 2011). Besides, the drawback of this technology is that the high rate of solvent losses due to evaporation and degradation, as well as having poor thermal stability. Therefore, a better solution in separating CO_2 is needed that will give better results in terms of economic and also energy efficiency.

There are recent researches where Ionic Liquids (ILs) was used in CO_2 separation. The separation of CO_2 using Ionic liquids was found in 1992 by Wilken and co-worker (Han & Armstrong, 2007). This draws attention from chemists as this type of separation was not being studied before the discovery. The properties of Ionic liquids such as low melting point (<373.15 K) and also having high thermal stability as well as other properties causes the attention are now more towards Ionic liquids. Nowadays, there are more types of Ionic liquids was studied in CO_2 capture. Therefore, this paper will be focusing on studying the capture of CO_2 using Ionic liquids.

1.2 Problem Statement

Ionic Liquids (ILs) is a combination of cation and anion. They are molten salts that are molten near ambient condition (Maginn, 2008). A lot of studies are done on Ionic liquids as it has good properties that could help in improving CO_2 separation. One of the properties is that it has a good CO_2 solubility. This attracts further studies on this technology.

Nowadays, many types of ionic liquids are studied in improving CO_2 separation. This is one of the main properties of ionic liquids which it has very wide range of combination of cation and anion. According to "The Research Progress of CO_2 Capture with Ionic Liquids", among the Ionic liquids that are studied are conventional Ionic liquids (CIL), functionalized Ionic liquids (FIL), supported Ionic liquids membranes (SILM), polymerized Ionic liquids (PIL) and also mixtures of Ionic liquids and also molecular solvent (Zhao, Dong, & Zhang, 2011).

However, despite having many type of ionic liquids and also having good CO_2 solubility in Ionic liquids, studies and reports suggested that the absorption capacity of Ionic liquids is still low, where it is much lower compared to MEA solutions [9]. But, due to its tuneable properties, ionic liquids can still be enhanced in order to improve CO_2 solubility. Therefore, this paper proposed in research to synthesize ionic liquid polymer incorporating activated carbon in order to increase the ionic liquids efficiency for CO_2 capture and separation.

1.3 Objective

The objective of this project is to synthesize ionic liquid based polymer incorporating activated carbon and test their capability in capturing and separating CO2. Polymer Ionic liquids are synthesized from an ionic liquids monomer and activated carbon is introduced while synthesizing the polymer. From this project, it is expected that the solubility of CO_2 for this polymer Ionic liquids will have a higher rate of CO_2 absorption capacity compared to the conventional Ionic liquids due to the mechanism of absorption and adsorption of polymer material that will enhance the solubility of CO_2.

1.4 Scope Of Study

In order to achieve the objective of this research project, there are some scopes of study that will be focused for this research. The scopes are:

1. Developing and synthesizing polymer ionic liquids incorporating activated carbon.
2. Studying the characteristics of the polymer material formed.
3. Studying the performance and efficiency of CO_2 solubility in the polymer ionic liquids.

1.5 Relevancy And Feasibility Of The Project Within The Scope And Time Frame

Synthesis of polymer Ionic Liquids incorporating activated carbon for the purpose of characterization and CO_2 solubility study is significant due to the amount of CO_2 emitted to the environment by various activities such as power generation using natural gas. Ionic Liquids known as a good CO_2 absorbent and by tuning the properties of Ionic Liquids by incorporating with activated carbon, it is expected that more amount of CO_2 could be absorbed and this could lead to many advantages towards the industry.

The author was given 28 weeks to conduct the research project under the supervision of Dr Muhammad Moniruzzaman from Chemical Engineering Department, Universiti Teknologi PETRONAS. A suitable Gantt chart has been developed in order that the project is possible to be conducted within the timeframe given by the university. All materials, apparatus, and equipment facilities are provided by the supervisor and the laboratory in Universiti Teknologi PETRONAS so that the project could be conducted. Regular meeting with supervisor while conducting the project helped the author in achieving the objective stated for this project.

CHAPTER 2

LITERATURE REVIEW

This chapter will review and discuss on the relevant theories regarding CO_2 capture and separation and also Ionic Liquids (ILs). This includes the importance of CO2 capture and separation, general characteristics of ionic liquids, CO2 capture and separation using Conventional ionic liquids and polymer ionic liquids, activated carbon for CO2 adsorption and previous research on Polymer ionic liquids incorporating activated carbon.

2.1 Importance Of Carbon Dioxide Capture And Separation

Nowadays, the amount of Carbon Dioxide (CO_2) is increasing in the Earth's atmosphere. The reason on increasing amount of CO_2 due to a lot of processes that releases CO_2. One of the processes is the combustion of fossil fuel (Herzog, n,d,). Combustion of fossil fuel is believed to be one of the major contributors to global warming. Therefore, there is an urge to capture CO_2 from flue gas before it is released.

Other than that, there are a number of large CO_2 emitting industrial sources. Herzog (n.d.) says that one of the examples is the natural gas operation where the amount of CO2 covers up to 20% by volume. Separations of CO_2 are important in this industry due to the nature of the CO_2. CO_2 is corrosive to the pipeline and ignoring the fact would give a big problem because the cost to replace new pipeline are more expensive compared to CO_2 removal.

Separation of CO_2 can benefit environmentally and also economically. Rather than it could help in slowing the greenhouse effect, the CO_2 that was captured can be used in some industrial areas that uses CO_2 as its material.

Enhanced Oil Recovery or EOR is a method where chemicals are introduced in order to improve oil mobility thus improving the amount of oil recovered from the reservoir. One of the EOR methods is called miscible EOR where miscible gases such as CO_2 are injected into the reservoir (Teledyne Isco, 2012). CO_2 that are removed from other industrial area can be used in this EOR method where the removed CO_2 can be utilized. Other than that, CO_2 can also be used in other area such as production of urea from ammonia.

Despite the importance of CO_2 separation, there are some perceptions towards this process as it was viewed as expensive. According to Howard J. Herzog, the reason towards CO_2 perceptions are that it will be more expensive to remove CO_2 rather than just emitting it to the atmosphere. Other than that is that the commercial MEA process is old and does not being fully optimized (Herzog, n.d.).

2.2 General Characteristics Of Ionic Liquids

Ionic Liquids (ILs) are solvents that usually made of large non-symmetrical organic cation and inorganic or organic anion. They are salts that exist in liquid condition at room temperature. Ionic liquids were extensively being studied after 1992 where before its discovery it was not under the attention of most scientists (Han & Armstrong, 2007). The study of Ionic liquids focuses on its application on many processes.

Ionic liquids possess unique properties compared to other solvent. They are generally colourless liquids with relatively high viscosity (Han & Ro, 2010). Ionic liquids also exhibit very low vapour pressure under ambient condition. This makes them effectively non-volatile. Other than that, Ionic liquids are good solvents for a broad spectrum of inorganic, organic and polymeric materials and immiscible with various type of organic solvent. In addition, the properties of ionic liquids varied for each IL where it depends on its cation and anion. The type of anion used will affect its thermal stability and miscibility while surface tension and density are depending on the length of the alkyl chain in the cation and/or shape or symmetry (Han & Ro, 2010). Figure 2.1 to 2.3 shows the typical cations and anions constituting Ionic liquids.

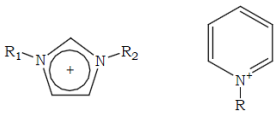


Figure 2.1: Typical Organic Cation (Maginn, 2008)

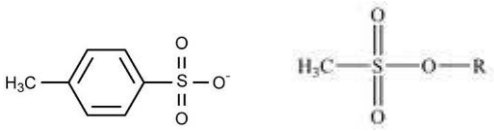


Figure 2.2: Typical Organic Anion (Maginn, 2008)

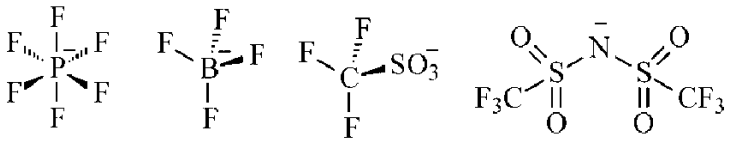
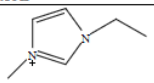
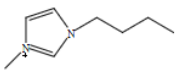
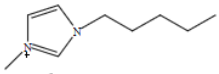
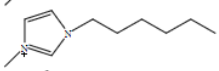
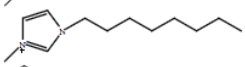
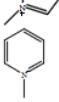
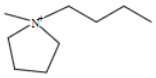


Figure 2.3: Typical Inorganic Anion (Han & Armstrong, 2007)

Table 2.1 shows the physical properties of some common ionic liquid.

Table 2.1: Physical properties of Ionic Liquids (Han & Ro, 2010)

Chemical formula		Abbreviation	Melting point, °C	Density (g mL^{-1}), 25 °C	Viscosity (cP), 25 °C	Molecular weight
Cation	Anion					
	$[BF_4]^-$	[EMIM][BF_4]	6	1.248	66	197.8
	$[PF_6]^-$	[EMIM][PF_6]	58-62	1.373	450	256.13
	$[BF_4]^-$	[BMIM][BF_4]	-82	1.208	233	225.80
	$[PF_6]^-$	[BMIM][PF_6]	10	1.373	400	284.18
	$[Br]^-$	[BMIM]Br	60	1.134	Solid	218.9
	$[Cl]^-$	[BMIM]Cl	89	1.120	Solid	146.50
	$[CF_3SO_3]^-$	[BMIM][CF_3SO_3]	16	1.290	90	260.0
	$[(CF_3SO_2)_2N]^-$	[BMIM] [$(CF_3SO_2)_2N$]	-4	1.420	52	487.9
	$[NTfO_2]^-$	[BMIM] [$NTfO_2$]	-8	1.404	48	433.0
	$[BF_4]^-$	[AMIM][BF_4]	-88	1.231	321	240.02
	$[BF_4]^-$	[HMIM][BF_4]	-82	1.075	211	254.08
	$[PF_6]^-$	[HMIM][PF_6]	-61	1.304	800	312.00
	$[BF_4]^-$	[OMIM][BF_4]	-79	1.11	440	281.8
	$[Cl]^-$	[OMIM][Cl]	0	1.000	16,000	230.50
	$[NTfO_2]^-$	[MPPyr] [$NTfO_2$]	0	1.44	39	416
	$[HCOO]^-$	BAF	-10	0.99	11.5	91
	$[NTfO_2]^-$	[BMPyrrol] [$NTfO_2$]	-50	1.4	71	422

Apart from having the interaction that exist in conventional organic solvents such as dipole-dipole interactions and van der Waals interaction, ionic liquids also have ionic interactions, which makes them very miscible with polar substances. In addition,

Han & Ro (2010) say that the presence of alkyl chain on the cation determines the solubility of ionic liquids in less polar fluid. Furthermore, this alkyl chain can change the properties of ionic liquids according to the length that are incorporated to cation and the types of anion.

According to "The Research Progress of CO_2 Capture with Ionic Liquids", the characteristics that make ionic liquids to become the best candidate to capture CO_2 are (Zhao, Dong & Zhang, 2011):

- Having negligible volatility
- Good thermal stability
- Strong dissolubility
- Tuneable structure and property.

2.3 CO_2 Capture With Conventional Ionic Liquids (CIL)

According to "The Research Progress of CO_2 Capture with Ionic Liquids", Blanchard *et al.* reported firstly that CO_2 is highly soluble in ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$). It reaches a mole fraction of 0.6 at 8MPa based on figure 6, while at 13.8MPa and 40°C, the solubility of $[C_4mim][PF_6]$ in CO_2 is less than 10^{-5} mole fraction (Zhao, Dong & Zhang, 2011).

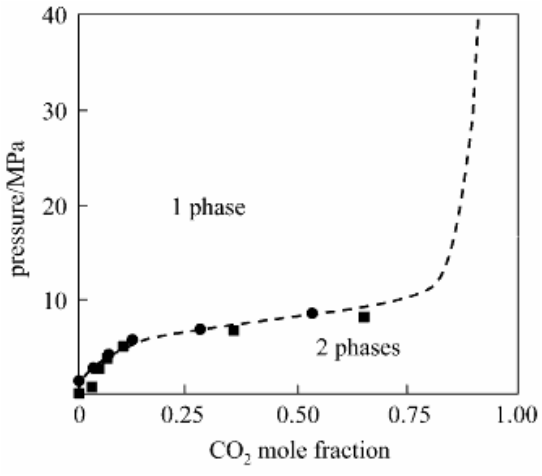


Figure 2.4: CO_2 Solubility in [C4mim][PF6] at 25°C (Zhao, Dong & Zhang, 2011)

It is also reported that in six types of Ionic liquids which are 1-n-butyl-3-methyl-imidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-n-octyl-3-methyl-imidazolium

hexafluorophosphate ($[C_8mim][PF_6]$), 1-n-octyl-3-methyl-imidazolium tetrafluoroborate ($[C_8mim][BF_4]$), 1-n-butyl-3-methyl-imidazolium nitrate ($[C_4mim][NO_3]$), 1-ethyl-3-methyl-imidazolium ethylsulfate ($[C_2mim][EtSO_4]$), and N-butyl pyridinium-tetrafluoroborate ([N-bupy][BF_4]) is found to able to dissolve large quantities of CO_2 at high pressure with no appreciable amount of ionic liquids solubilized in the CO_2 phase. This causes ionic liquids to receive much attention in CO_2 capture (Zhao, Dong & Zhang, 2011).

Another study, done by Baltus *et al.*, was on determining the solubility of CO_2 in a series of imidazolium-based Ionic liquids at low pressure (Zhao, Dong & Zhang, 2011). It is found that the solubility of CO_2 increases with the length of the alkyl side chain on the imidazolium ring but the CO_2 solubility in ionic liquids with phenyl groups was lower when compared to that with alkyl groups. It is also found that the CO_2 solubility is greater in ionic liquids with Tf_2N^- anions than that in ionic liquids with PF_6^- anions. Besides, the imidazolium-based ionic liquids with a fluorine-substituted C_8 side chain are higher than the corresponding ionic liquids shaving a non-fluorinated C_8 side chain (Zhao, Dong & Zhang, 2011).

A study was done by Anderson *et al.* on the selectivity of separating CO_2 from mixture gases. The solubility of CO_2, C_2H_4, C_2H_6, CH_4, CO, O_2, H_2 and N_2 was done in $[C_4mim][PF_6]$ and it is found out that CO_2 is the most soluble among these gases based on figure 7, and $[C_4mim][PF_6]$ can absorbs CO_2 selectively (Zhao, Dong & Zhang, 2011).

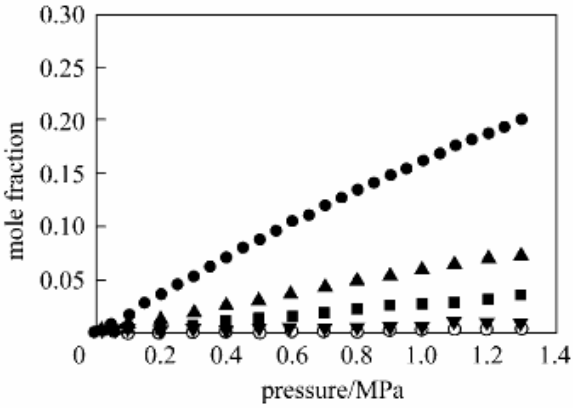


Figure 2.5: Solubility in $[C_4mim][PF_6]$ at 25°C (Zhao, Dong & Zhang, 2011)

Although studies suggested that the conventional IL can absorb and separate CO_2 effectively to a certain extent, it is just based on mechanism of physical adsorption. The disadvantage of this type of Ionic liquids is that the absorption capacity of CO_2

is far below that of the traditional alkanolamine solutions, even in the fluorinated Ionic liquids (Zhao, Dong & Zhang, 2011).

2.4 CO_2 Capture With Polymerized Ionic Liquids (PIL)

Based on previous parts, it can be said that CO_2 is sufficiently soluble in Conventional Ionic Liquid. However, it still not satisfying and the CO_2 absorption capacity for ionic liquids can still be further improved. One of the improvements, based on Tang *et al.* is to make ionic liquids into polymeric form which significantly increases the CO_2 sorption capacity compared to conventional ionic liquids (Zhao, Dong & Zhang, 2011).

The experiment done by tang *et al.* showed that the polymers of poly[p-vinylbenzyltrimethylammonium tetrafluoroborate] (P[VBTMA][BF_4]) has a CO_2 absorption capacity that about 7.6 times higher than [C_4mim][BF_4] which is the conventional IL. It is also found out that the absorption and desorption by this polymer are much faster than in IL. The polymer also can absorb CO_2 selectively in N_2/CO_2 mixed gas and did not absorb N_2 or O_2 at 78.97 kPa and 22°C (Zhao, Dong & Zhang, 2011).

Another study done by Tang *et al.* which is on the solubility of CO_2 in an ammonium-type ionic and other type polymers to study the effect of structure to the CO_2 sorption. It is found out that ammonium as the cation gives the highest CO_2 sorption capacity and the same was done on different anion with BF_4- have highest CO_2 sorption capacity.

The polymerized ionic liquids are found to be very viscous at room temperature and are easy to be applied as membrane materials. Bara *et al*. suggested that if the polymerized ionic liquids to be combed with another type of ionic liquids, which is supported ionic liquids membranes, it could produce higher CO_2 absorption capacity (Zhao, Dong & Zhang, 2011). It is summarized that the polymerized ionic liquids as a membrane materials is a relatively good option for separating and absorbing CO_2.

2.5 Activated Carbon For CO_2 Adsorption

Activated carbon, also known as activated charcoal, is a highly microporous material with a large surface area (Guo, Chang, & Xie, 2006). It is a charcoal that has been treated with oxygen in order to open up the tiny pores between carbon atoms (What is Activated Charcoal, n.d.). There are three main forms of activated carbon which are granular, powder and pelleted activated carbon (Activated Carbon, n.d.).

Figure 2.6: Activated Carbon (Activated Carbon, n.d.)

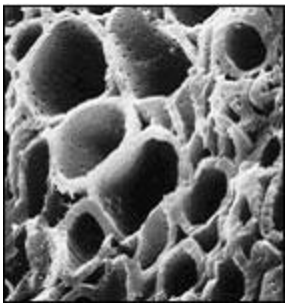


Figure 2.7: Activated Carbon under an Electron Microscope (Activated Carbon Filtration, n.d.)

Activated carbon was mainly used as adsorbent in desulfurization. Nowadays, there are researches that have shown that the activated carbon is suitable to be used in CO_2 capture and separation. Zhang et al. (n.d.) say that activated carbon have these meso-, micro- or macroporous carbonaceous structures have an advantage over other adsorbents, such as ease of regeneration, lesser sensitivity to moisture, and high CO_2 adsorption capacity at ambient pressure.

CO_2 adsorption capacity of Activated Carbon not only depends on its textural characteristics but also on its surface chemistry, which can be modified with different methodologies (Zhang et al., n.d.).

A study conducted by Siriwardane *et al.* (n.d.) on the adsorption and desorption on several solid sorbents including activated carbon. Four types of gases was studied which are CO_2 N_2 O_2 and H_2. The experiment was conducted at 25°C. From the results in figure 2.8, it is found out that the adsorption of CO_2 is the highest compared to other gas.

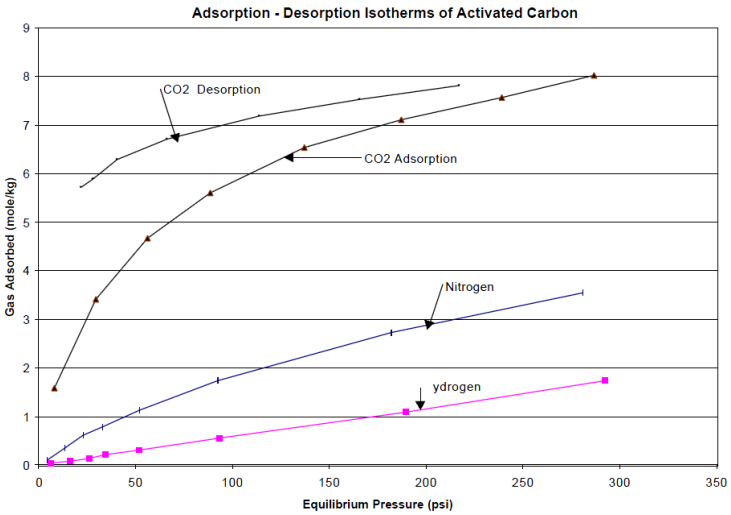


Figure 2.8: Adsorption-Desorption Isotherm of Activated Carbon (Siriwardane *et al.*, *n.d.*)

Another study conducted by Guo, Chang & Xie (2006) on the adsorption of CO_2 on activated carbon. In the experiment, the adsorption of CO_2 was studied on four samples, which are on the raw activated carbon and also activated carbon that was mixed with other chemicals. From the results in figure 2.9, it is found out that raw activated carbon have the lowest CO_2 adsorption compared with other materials (Guo, Chang & Xie, 2006).

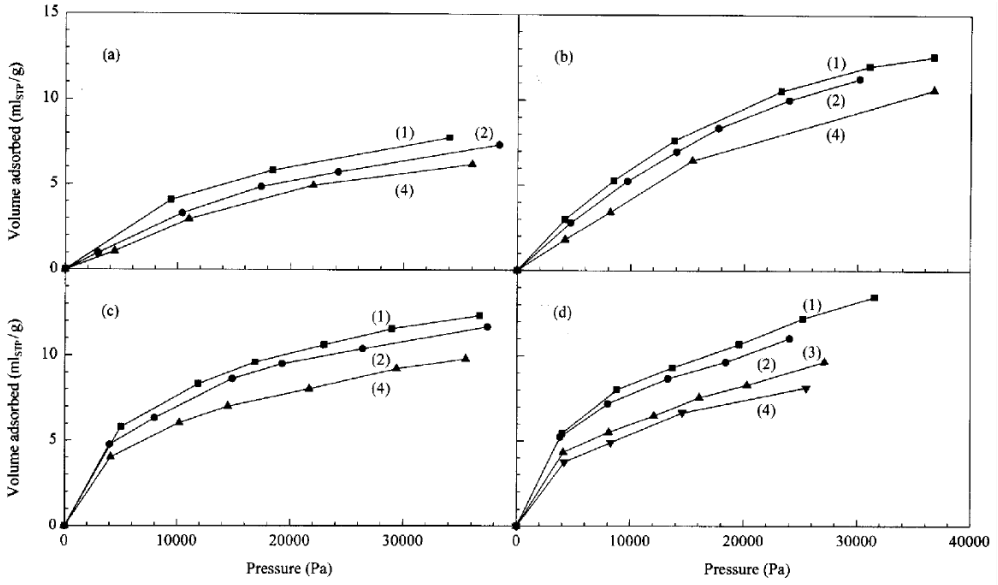


Figure 2.9: Adsorption Isotherms of CO_2 at different temperature on four activated carbon samples (Guo, Chang & Xie, 2006)

2.6 Synthesis Of Ionic Liquid Polymer Incorporating Activated Carbon

Synthesis of Ionic Liquids polymer incorporating activated carbon for CO_2 capture and separation is project conducted by a student of Universiti Teknologi PETRONAS, Muhammad Hafiz 'Arif bin Ahmad Sayukhi. The project mainly focuses on synthesizing polymer Ionic Liquid incorporating activated carbon for the purpose of studying the CO_2 capture and separation.

In this project, two types of polymer Ionic Liquid are synthesized from its monomer, which are Poly (1-Vinyl-3-Ethylimidazolium Bromide), Poly [Veim][Br] and also Poly (1-Vinyl-3-Ethylimidazolium bis(Trifluoromethylsulfonylimide)), Poly [Veim][TF_2N] and both types of Ionic Liquids are incorporated with activated carbon (Ahmad Sayukhi, 2013). Figure 2.10 and 2.11 shows the composition of the polymer Ionic Liquids formed studied using energy dispersive X-ray Spectroscopy (EDX).

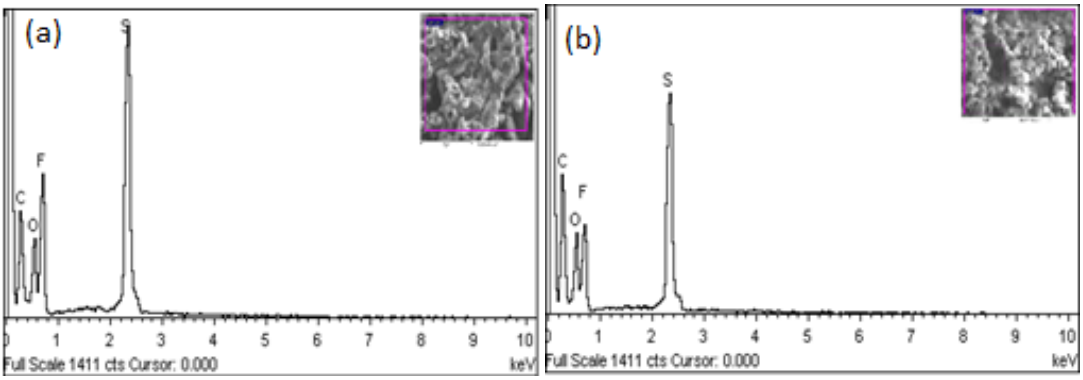


Figure 2.10: Composition of (a) Poly [Veim][Br] and (b) Poly [Veim][Br] Incorporating Activated Carbon (Ahmad Sayukhi, 2013)

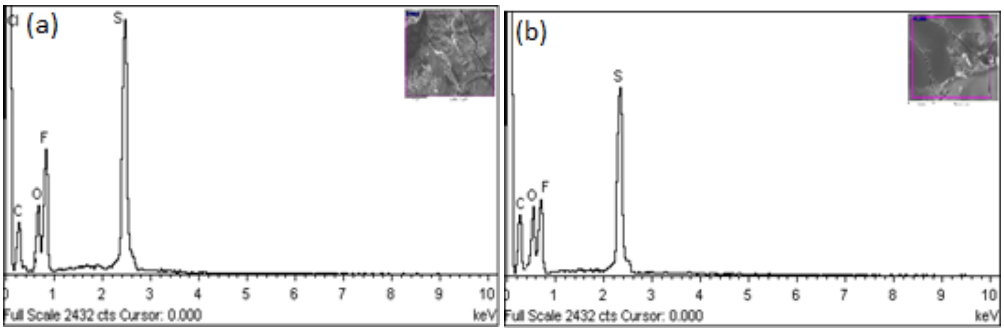


Figure 2.11: Composition of (a) Poly [Veim][TF_2N] and (b) Poly [Veim][TF_2N] Incorporating Activated Carbon (Ahmad Sayukhi, 2013)

From figure 2.10 and 2.11, the results show that the percentage of carbon is higher for both types of polymer Ionic Liquid incorporating activated carbon. This is due to activated carbon that added to the polymer which is successfully incorporated. Apart from studied using EDX, the surfaces of the two types of polymer material are also studied using the Scanning Electron Microscope (SEM) (Ahmad Sayukhi, 2013). The results are analysed at several magnifications which are at 200, 1000, 5000 and 10000, as shown in figure 2.12 until figure 2.15.

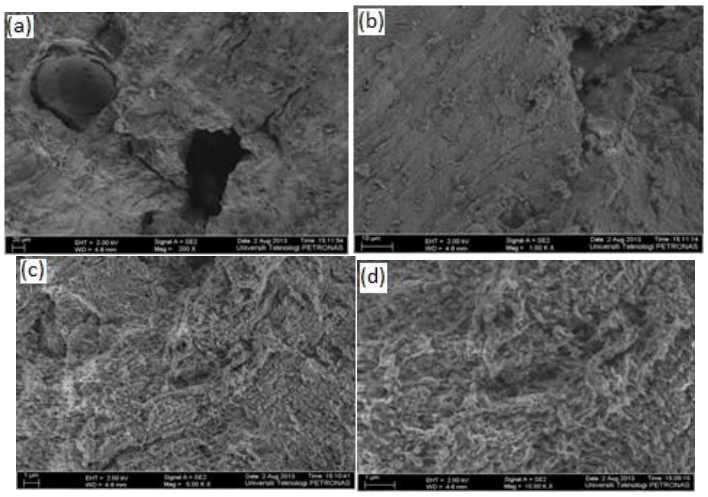


Figure 2.12: SEM images of Poly [Veim][Br] at magnification of (a) 200 (b) 1000 (c) 5000 (d)10000 (Ahmad Sayukhi, 2013)

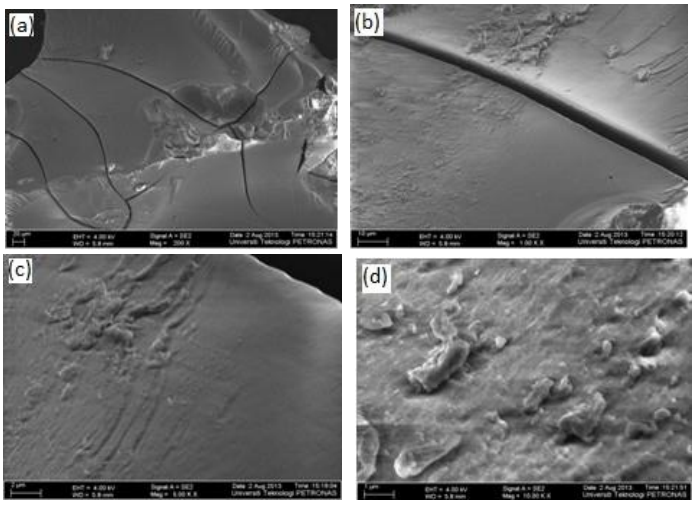


Figure 2.13: SEM images of Poly [Veim][Br] Incorporating Activated Carbon at magnification of (a) 200 (b) 1000 (c) 5000 (d)10000 (Ahmad Sayukhi, 2013)

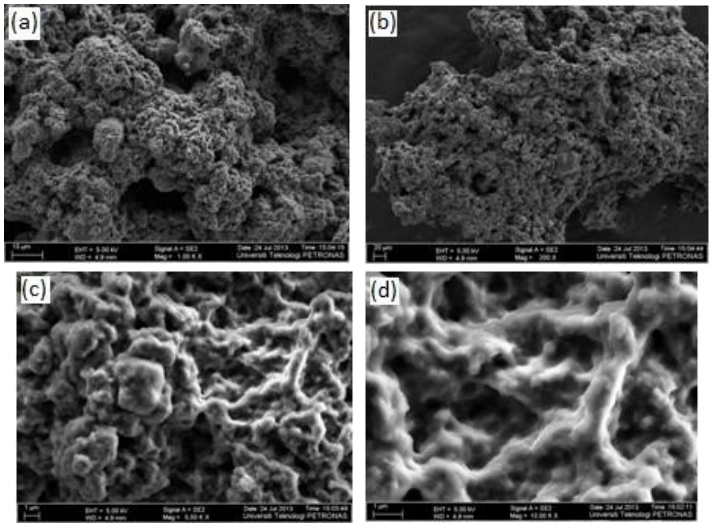


Figure 2.14: SEM images of Poly [Veim][TF_2N] at magnification of (a) 200 (b) 1000 (c) 5000 (d)10000 (Ahmad Sayukhi, 2013)

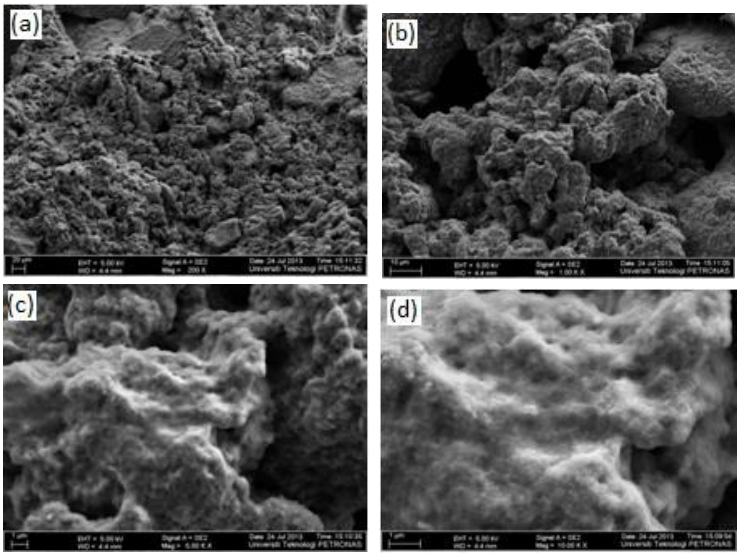


Figure 2.15: SEM images of Poly [Veim][TF_2N] Incorporating Activated Carbon at magnification of (a) 200 (b) 1000 (c) 5000 (d)10000 (Ahmad Sayukhi, 2013)

From the figure 2.12 and 2.13, it is found out that Poly [Veim][Br] incorporating activated carbon have less big pores and appear to be smoother compared to Poly [Veim][Br]. This could possibly due to the big pores in Poly [Veim][Br] is covered uniformly by activated carbon. The results are also the same for Poly [Veim][TF_2N] and Poly [Veim][TF_2N] incorporating activated carbon in figure 2.14 and 2.15.

The results shown in this project suggested that the activated carbon can be and has been successfully incorporated into the Ionic Liquid polymer. Therefore, this project will continue on further study regarding the effect of activated carbon in polymer Ionic Liquid on capturing and separating CO_2.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The methods that are used for conducting this project are mainly on research study and experiments. This includes reading related materials from various sources before conducting the experiments. The methodology has been divided into three main steps which are preliminary study, experimental works and also discussion and conclusion. Figure 3.1 show the diagram for the methodology.

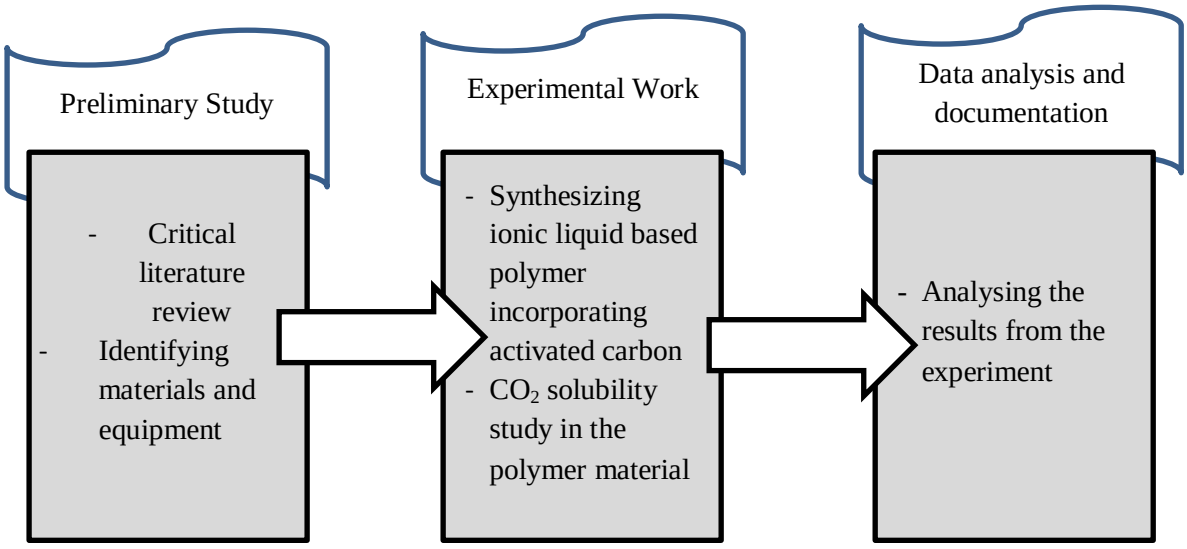


Figure 3.1: Schematic Diagram of Research Methodology

In preliminary study, critical literature review is done in order to narrow down the scope to synthesizing polymer Ionic Liquids (ILs) incorporating activated carbon for CO_2 so that it could be completed within the time scope of project.

After that, experiments can be conducted in order to achieve the objective of this experiment. Experiment will start by synthesizing Ionic liquids polymer and then followed by evaluating the solubility of CO_2 in polymer material formed. Finally, the results obtained from the experiment will be analysed to see if the objective of the project is achieved.

3.2 Project Activities

3.2.1 Requisition of Materials

Among the chemicals that will be used in the experimental works are:

1. 1-Vinyl Imidazole, $C_5H_6N_2$.
2. Ethyl Bromide, C_2H_5Br.
3. Ethyl Acetate $C_4H_8N_2$.
4. Lithium bis(Trifluoromethyl-sulfonyl) amide, $Li(TF_2N)$.
5. Trimethylolpropane tri-metacrylate, (TRIM).
6. 2, 2'- azobisisobutyronitrile, (AIBN).
7. Ammonium Persulfate
8. Activated Carbon.
9. Acetonitrile.
10. Ethanol.

3.2.2 Requisition of Equipment

Among the tools that will be used in the experimental works are:

1. Round Bottom Flux
2. Reflux system
3. Stirrer
4. Oil/Water Bath
5. Hot plate

Some equipment will also be used throughout the experiment works, which are:

1. Freeze-dryer
2. Scanning Electron Microscope (SEM)
3. B.E.T. Surface Area Analyser (BET)
4. X-Ray Spectroscopy (EDX)

3.2.3 Experimental Procedure

The procedures for this experiment are planned to be conducted in the Ionic Liquid lab in Universiti Teknologi PETRONAS. The procedures of this research can be divided into five main steps shown in figure 3.2:

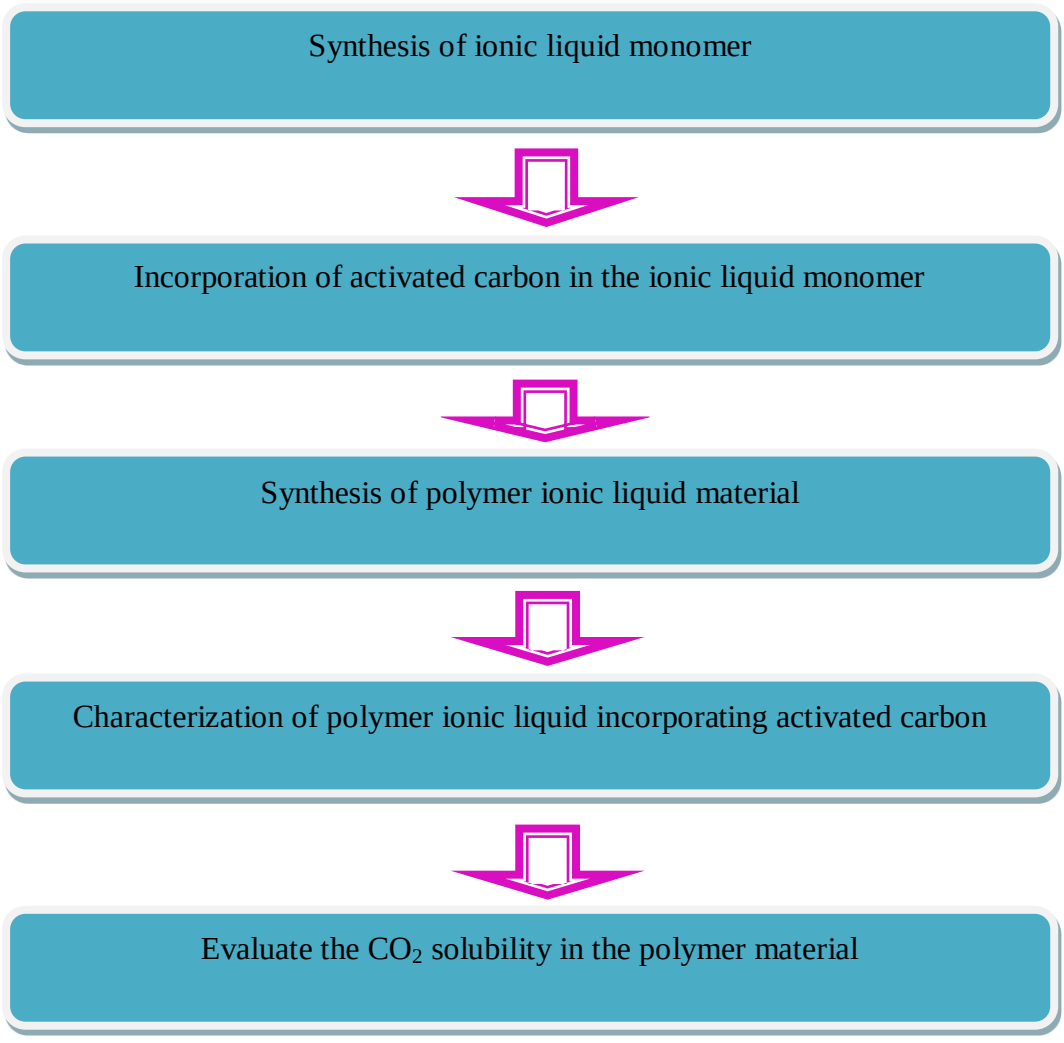


Figure 3.2: Flow chart of the experimental procedures

3.2.3.1 Synthesis of Ionic Liquid Monomer

This project will be using 1-Vinyl-3-ethylimidazolium bis(Trifluoromethylsulfonyl) imide, ([Veim][TF_2N]) as the Ionic Liquid monomer where it will be synthesized through anion exchange between 1-Vinyl-3-ethylimidazolium bromide ([Veim][Br]) and Lithium bis(Trifluoromethylsulfonyl) imide (Li[TF_2N]). [Veim][Br] is obtained through a reaction between Ethyl Bromide and 1-Vinylimidazole where the Ethyl Bromide will be added drop wise to 1-Vinylimidazole while being vigorously stirred in an ice-bath, following by heating in oil bath at 60°C for a few hours. The resulted [Veim][Br], which in white solid is going to be washed with Ethyl Acetate for several times to remove unreacted materials followed by rotary evaporator and after that freeze-drying for 24 hours. After that, anion exchange is conducted in molar ratio 1:1 between Li[TF_2N] and [Veim][Br] to obtain the monomer [Veim][TF_2N]. This product will be stored in a dessicator to avoid water absorption due to its hygroscopicity.

3.2.3.2 Synthesizing polymer IL incorporating activated carbon

In order to synthesize Ionic Liquid polymer incorporating activated carbon, activated carbon is first added into the IL monomer. It is microencapsulated in surfactant aggregates formed in Ionic liquids monomer where it is then incorporated into polymer framework through polymerization of [Veim][TF_2N]. The polymerization of [Veim][TF_2N] is started by adding 2, 2'- azobisisobutyronitrile, AIBN (3% mol based on IL monomer) as initiator at 30°C. Trimethylolpropane tri-metacrylate, TRIM act as cross linker is also added into the monomer. After a few hours, the polymer material will form and it is washed for a few times with Hexane and distilled water to remove unreacted substances.

3.2.3.3 Characterization of Polymer Material

The polymer material that is formed is then tested for characterization. Equipment such as Scanning Electron Microscope (SEM) is used in this part. The equipment will give signals that derive from electron-Ionic liquids polymer material interactions where the information regarding the material is revealed. This includes the external morphology (texture) making up the IL polymer material.

3.2.3.4 Evaluate the CO_2 solubility in the polymer material

Evaluation for CO_2 solubility efficiency and performance is going to be studied by analysing the surface area of the polymer material with CO_2. Equipment that will be used for this part is BET surface area analyser. The results obtained will be analysed to predict the solubility of CO_2 inside the polymer.

3.3 Key Milestones

For the completion of this project, several key milestones have been identified and listed as follows:

1. Understanding the purpose and the objective of the project.
2. Doing literature review to gather useful information from various sources such as journals and book regarding CO_2 separation, Ionic Liquids, activated carbon mechanism, and activated carbon in Ionic Liquids.
3. Designing and conducting experimental procedures to synthesize Ionic Liquid polymer incorporating activated carbon.
4. Designing and conducting experimental procedures to study the CO_2 solubility in the polymer material formed.
5. Analysing the data and results obtained from the experiment.
6. Documenting the analysed result from the experiment.

3.4 Gantt Chart

Table 3.1: Gantt chart for FYP

Week	FYP I														FYP II													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic	■	■	■																									
Preliminary Research Work (Critical Literature Review)			■	■	■	■	■	■	■	■	■	■																
Requisition for materials and equipment												■	■	■														
Synthesis of Ionic Liquid Polymer Incorporating Activated Carbon															■	■	■	■	■	■	■							
Characterization of Polymer Material																					■	■	■	■				
Evaluation of The Solubility Of CO_2 in Polymer Material																								■	■	■		
Data analysis and interpretation																									■	■	■	■

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis Of Polymer Ionic Liquid

4.1.1 Synthesis of Ionic Liquid Monomer 1-Vinyl-3-Ethylimidazolium Bromide

1-Vinyl-3-ethylimidazolium Bromide ($C_7H_{11}N_2Br$), known as [Veim][Br] is prepared by the reaction of 1-Vinyl imidazole with a halo-alkane compound where positively charged imidazolium ring is directly connected to a vynil group as shown in figure 4.1.

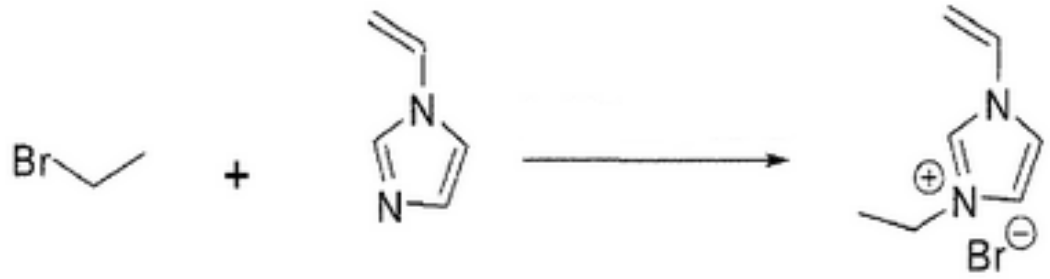


Figure 4.1: Synthesis of 1-Vinyl-3-ethylimidazalioum Bromide [Veim][Br]

1-Vinyl-3-ethylimidazalioum bromide Ionic Liquid monomer was synthesized in the reaction of 1-Vinylimidazole with Ethyl Bromide. Ethyl Bromide (33g, 0.3mol) was added drop wise into 1-Vinylimidazole (28g, 0.3mol) while vigorously stirred in ice bath. The mixture is followed by heating in oil bath at 40°C for 2 hours. The resulting white solid formed was washed with Ethyl Acetate several times to remove unreacted material. It is then dried using rotary evaporator at 79°C, followed by freeze drying for 24 hours and finally left in a vacuum oven for 2days. The synthesis steps are as shown in figure 4.2.

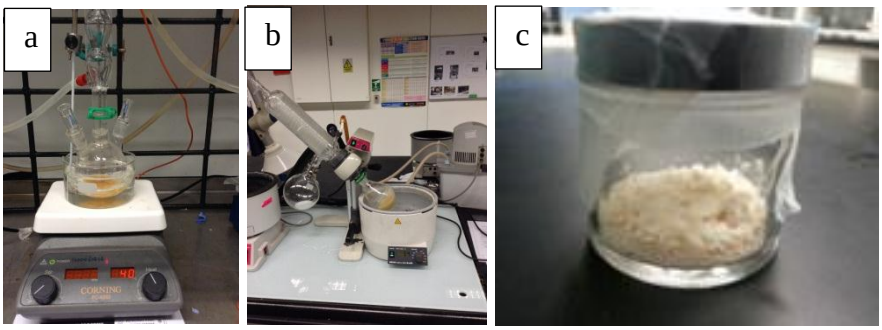


Figure 4.2: Synthesis steps of [Veim][Br] (a) Reaction at 40°C (b) Dried using rotary evaporator (c) Resulting white solids

4.1.2 Synthesis of Ionic Liquid Monomer 1-Vinyl-3-Ethylimidazolium Bis(Trifluoromethylsulfonyl)imide

1-Vinyl-3-ethylimidazalioum bis(trifluoromethylsulfonyl)imide ($C_9H_{11}F_6N_3O_4S_2$), which also known as [Veim][Tf_2N] is a viscous, yellowish ionic liquid and is prepared via anion exchange between the Ionic Liquid monomer 1-Vinyl-3-ethylimidazolium Bromide [Veim][Br] with Lithium bis(Trifluoromethylsulfonyl)imide Li[TF_2N] to produce [Veim][Tf_2N]. The synthesis is as shown in figure 4.3.

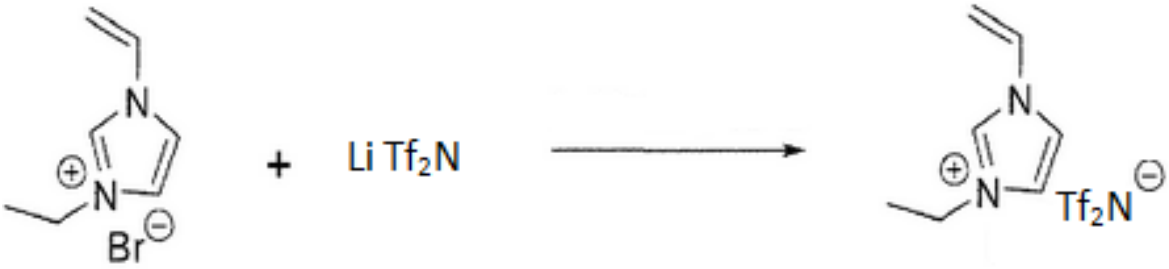


Figure 4.3: Synthesis route of 1-Vinyl-3-ethylimidazalioum bis(trifluoromethylsulfonylimide)

Ionic liquid monomer [Veim][Br] (12.788g, 0.063mol) was mixed with 6mL of distilled water. Li[TF_2N] (20g, 0.064mol) was added drop wise and constantly stirred at room temperature until the formation of two phase. The bottom phase and the top phase were contained [Veim][Tf_2N] and aqueous LiBr respectively. The top phase was decanted and

the Ionic Liquid was washed thoroughly with 5mL of distilled water for three times until all Br^- are removed. The distilled water used for washing is then removed from [Veim][TF_2N] with vacuum liner followed by lyophilisation in vacuum oven. The synthesis steps are as shown in figure 4.4.

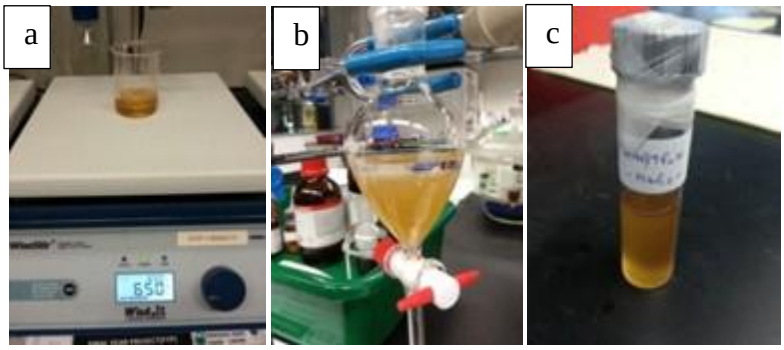


Figure 4.4: Synthesis steps of [Veim][TF_2N]] (a) Reaction at room temperature (b) Decanting the top phase (c) Resulting viscous, yellowish liquid

4.1.3 Synthesis of Ionic Liquid Polymer Poly-[Veim][Br] and Poly-[Veim][Br] Incorporating Activated Carbon

Polymer Ionic Liquid Poly-(1-Vinyl-3-ethylimidazolium Bromide), Poly-[Veim][Br] was synthesized by conventional free-radical polymerization. The polymerization of Ionic Liquid monomer [Veim][Br] was initiated by addition of 2,2'-azobis(isobutyronitirile) (AIBN) together with Trimethylolpropane tri-metacrylate (TRIM) as the cross linker. The synthesis route is as shown in figure 4.5.

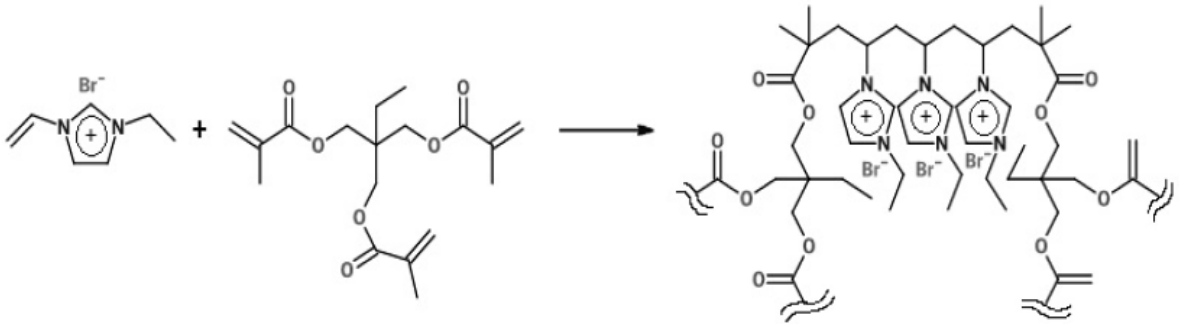


Figure 4.5: Synthesis Route of Poly-(1-Vinyl-3-ethylimidazalioum Bromide)

In the synthesis of the Poly-[Veim][Br], ionic liquid monomer [Veim][Br] (1g, 0.005mol) was added into ethanol (1g, 0.022mol). It was then purged with Nitrogen gas, N_2 for 30min. After then, AIBN (20mg, 0.12mmol) and TRIM (50mg, 0.15mmol) was added into the solution, and then purged with N_2 for another 10min. The mixture was stirred in an oil bath at 65 ℃ for 30 minutes.

After polymerization, the elastic gel particles formed was diluted with the reaction solvent and was poured into acetonitrile to precipitate the Poly-[VEIM][Br]. The polymer was washed three times with Acetonitrile before drying under vacuum at 70°C. The resulting solid formed which weigh 0.9g was stored in desiccator.

For the Poly-(1-Vinyl-3-ethylimidazalioum bromide) incorporating activated carbon, it was also synthesized by conventional free-radical polymerization. The synthesis steps are the same as in the synthesis of Poly-[Veim][Br] except that 50mg of activated carbon with 5 weight percent was introduced together with ionic liquid monomer [Veim][Br] in the ethanol. The resulting solid which weigh 0.96g was stored in dessicator. Figure 4.6 shows the polymer product of Poly-[Veim][Br] and figure 4.7 shows the polymer product of Poly-[Veim][Br] incorporating activated carbon.

Figure 4.6: Poly-(1-Vinyl-3-Ethylimidazolium Bromide)

Figure 4.7: Poly-(1-Vinyl-3-Ethylimidazolium Bromide) Incorporating Activated Carbon

4.1.4 Synthesis of Ionic Liquid Polymer Poly-[Veim][TF_2N] and Poly-[Veim][TF_2N] Incorporating Activated Carbon

Poly-(1-Vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide), Poly [Veim][TF_2N] was synthesized by conventional free-radical polymerization. The polymerization of ionic liquid monomer [Veim][TF_2N] was initiated by addition of 2,2'-azobis(isobutyronitirile) (AIBN) together with Trimethylolpropane tri-metacrylate (TRIM) as the cross linker. The synthesis route is as shown in figure 4.8.

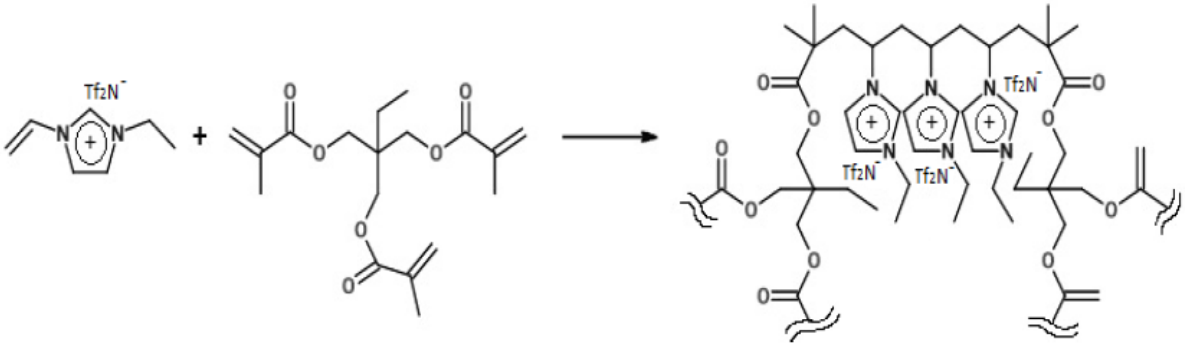


Figure 4.8: Synthesis Route of Poly-(1-Vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide).

In the synthesis of the Poly-[Veim][TF_2N], ionic liquid monomer [Veim][TF_2N] (1g, 0.003mol) was added into ethanol (1g, 0.022mol). It was then purged with Nitrogen gas, N_2 for 30min. After then, AIBN (20mg, 0.12mmol) and TRIM (50mg, 0.15mmol) was added into the solution, and then purged with N_2 for another 10min. The mixture was stirred in an oil bath at 65 °C for 30 minutes.

After polymerization, the elastic gel particles formed was diluted with the reaction solvent and was poured into distilled water to precipitate the Poly-[VEIM][TF_2N]. The polymer was washed three times with distilled water before drying under vacuum at 70°C. The resulting solids formed weigh 1.02g and was stored in desiccator.

For the Poly-(1-Vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide) incorporating activated carbon, it was also synthesized by conventional free-radical polymerization. The synthesis steps are the same as in the synthesis of Poly-[Veim][TF_2N] except that activated carbon with 5 weight percent was introduced

together with ionic liquid monomer [Veim][TF_2N] in the ethanol. The resulting solid weigh 1.04g was stored in the dessicator.

Figure 4.9 shows the polymer product of Poly-[Veim][Br] and figure 4.10 shows the polymer product of Poly-[Veim][Br] incorporating activated carbon.

Figure 4.9: Poly-(1-Vinyl-3-Ethylimidazolium Bis(Trifluoromethylsulfonyl Imide)

Figure 4.10: Poly-(1-Vinyl-3-Ethylimidazolium Bis(Trifluoromethylsulfonyl Imide) Incorporating Activated Carbon

4.2 Characterization Of Polymer Ionic Liquids Formed

4.2.1 Analysis using BET Machine

After successfully synthesizing similar polymer Ionic Liquid, the materials are then tested for it surface area. The surface area was studied using Belsorp Mini-II. The equipment will study the amount of CO_2 that can be covered by the polymer Ionic Liquid. Figure 4.11 shows the equipment used for the study.

Figure 4.11: Belsorp Mini-II

The experiment was started by heating the polymer ionic liquid up to 105°C for several hours. This is to remove any vapour formed by the ionic liquid. After that, the polymer material is added into a sample cell where the weight of the polymer ionic liquid is measured. The polymer material is once again being heated together with the sample cell for two hours before being weighed again. This is to ensure that the sample is totally dry before put into the machine.

The machine will first undergo system check before the sample cell is inserted into the machine for analysis. Both type of sample, Poly-[Veim][Br] and Poly-[Veim][TF_2N] are analysed using this equipment to study their surface are. The analyses are conducted at 101.33 kPa at 25°C. The results are as shown in figure 4.12 until 4.15.

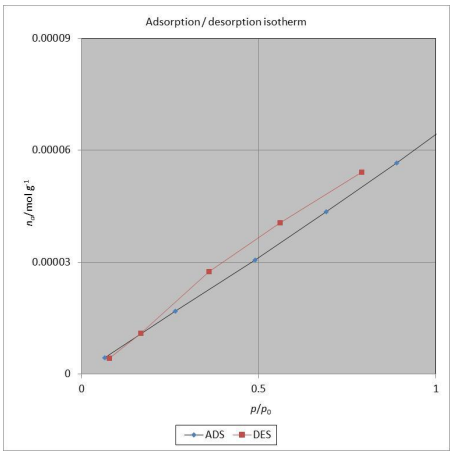


Figure 4.12: Adsorption/Desorption Isotherm of CO_2 on Poly-[Veim][TF_2N]

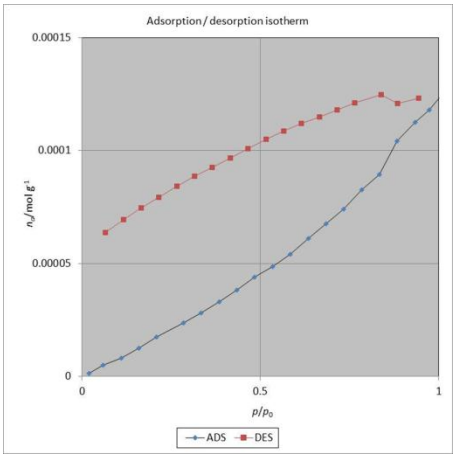


Figure 4.13: Adsorption/Desorption Isotherm of CO_2 on Poly-[Veim][TF_2N] Incorporating Activated Carbon

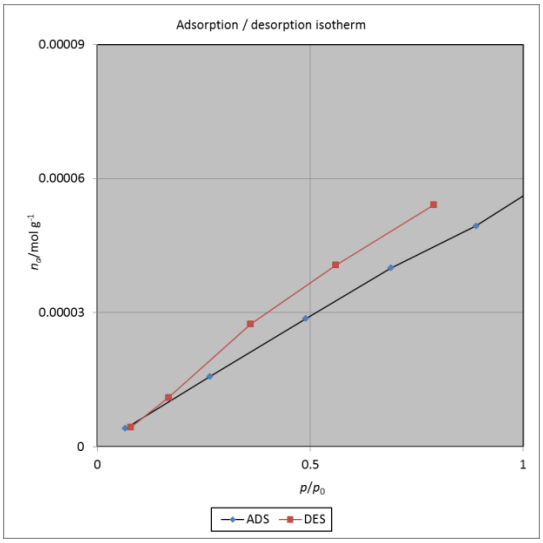


Figure 4.14: Adsorption/Desorption Isotherm of CO_2 on Poly-[Veim][Br]

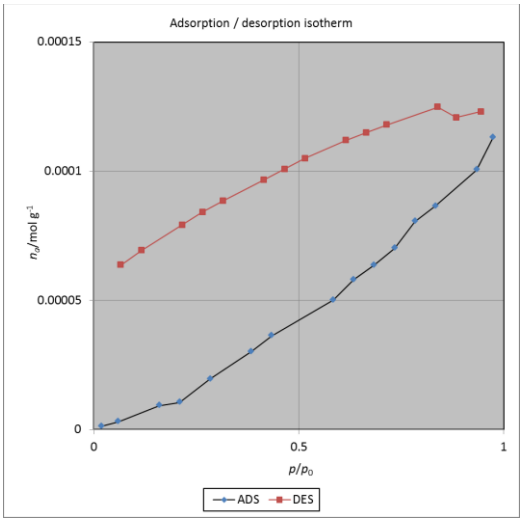


Figure 4.15: Adsorption/Desorption Isotherm of CO_2 on Poly-[Veim][Br] Incorporating Activated Carbon

The results from figure 4.12 until 4.15 are summarized in table 4.1 where the adsorption and desorption at highest pressure analysed is summed up into the table.

Table 4.1: Summary of Adsorption/Desorption Isotherm

Material	Adsorption		Desorption	
	Pressure (p/p_0)	Value (n_a/mol g^{-1})	Pressure (p/p_0)	Value (n_a/mol g^{-1})
Poly-[Veim][TF_2N]	1.0892	7.0438×10^{-5}	0.07833	4.309×10^{-6}
Poly-[Veim][TF_2N] + AC	1.0137	1.2564×10^{-4}	0.066177	6.3759×10^{-5}
Poly-[Veim][Br]	1.0892	6.1538×10^{-5}	0.07833	4.309×10^{-6}
Poly-[Veim][Br] + AC	1.0133	1.1864×10^{-4}	0.066177	6.3759×10^{-5}

From the table, it is found out that by comparing the polymer material with and without activated carbon, the value for adsorption and desorption are greater for material with activated carbon. This supports the study that by introducing activated carbon into the polymer material, it will increase the adsorption of polymer material. For the two different polymer material of [Veim][TF_2N] and [Veim][Br], it is found out that Poly-[Veim][TF_2N] gives the higher adsorption value. Further study is needed to analyse the behaviour of the isotherm trend.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As conclusion, the objective of this project which is to synthesize polymer ionic liquid incorporating activated carbon has been successfully achieved. Two types of ionic liquid polymer, which are Poly [Veim][Br] and Poly[Veim][TF_2N] were synthesized with activated carbon successfully incorporated into the polymer ionic liquid. It was done through free radical polymerization with AIBN and TRIM was used as cross linker and initiator.

The study of the polymer ionic liquids is still on-going whereas the polymer material was studied using Belsorp Mini-2 (BET). From the results in previous part, it is found out that the polymer material with activated carbon gives higher adsorption and desorption isotherm compared with the polymer material without activated carbon for both material. This supports the study that by introducing activated carbon into the material will increases the adsorption of the material.

In the future work, it is suggested that the polymer materials are studied for its solubility in CO_2 using equipment such as magnetic suspension balance (MSB). This equipment will study the solubility by weigh the samples contactless under nearly all measuring conditions. It is also suggested that the polymer ionic liquids are studied for its thermal stability to analyse the effect of activated carbon incorporated to the polymer material.

REFERENCE

Activated Carbon. Retrieved August 12, 2013 from http://activatedcarbonindia.in/.

Ahmad Sayukhi, M. H. A. (2013). *Synthesis of Ionic Liquid Polymer Incorporating Activated Carbon for Carbon Dioxide Capture and Separation*. Retrieved September 30, 2013 from http://utpedia.utp.edu.my/8449/1/FYP%20FINAL%20DISSERTATION%20MUHAMMAD%20HAFIZ%20ARIF%20BIN%20AHMAD%20SAYUKHI%2012734.pdf

AllerAir President Sam Teitelbaum on Activated Carbon Filtration. Retrieved August 12, 2013 from http://www.achooallergy.com/allerair-president-interview.asp

Bates, E.D., Mayton, R. D., Ntai, I., Davis, J. H. Jr., CO_2 Capture by a Task-Specific Ionic Liquid. 2001

Climate Change - About CO2 Emissions. Retrieved August 12, 2013 from: http://www.caring-planet.com/Page/title/About_CO2_Emissions/.

CO_2 Capture Project (2008). Three basic methods to separate gases. Retrieved June 18, 2013 from http://www,co2captureproject.com

EPA (n.d.). Overview of Greenhouse Gases. Retrieved August 12, 2013 from: http://www.epa.gov/climatechange/ghgemissions/gases/co2.html.

Galán Sánchez, L. M. (2008). *Functionalized Ionic Liquids: Absorption Solvents for Carbon Dioxide and Olefin Separation.*

Galán Sánchez, L. M., Meindersma, G. M., de Haan, A. B. (2007). Solvent Properties of Functionalized Ionic Liquids for CO_2 Absorption. *Trans IChemE, Part A, Chemical Engineering Research and Design,* 85(A1), 31-39 (2007).

Guo, B., Chang, L., & Xie, K. (2006). Adsorption of Carbon Dioxide on Activated Carbon. *Journal of Natural Gas Chemistry,* 15, 223-229 (2010).

Han, D. & Ro, K. H. (2010). Recent Applications of Ionic Liquids in Separation Technology. *Molecules,* 15, 2405-2426 (2010).

Han, X., & Armstrong, D. W. (2007). Ionic Liquids in Separations. *Accounts of Chemical Research,* 40(11), 1079-1086 (2007).

Herzog, H. J. (n.d.). The Economics of CO2 Separation and Capture. Retrieved June 18, 2013 from http://www.me.unm.edu/~mammoli/ME561_stuff/economics_in_technology.pdf

Li, P. Pramoda, K. P., & Chung, T. S. (2011). CO_2 Separation from Flue Gas Using Polyvinyl-(Room Temperature Ionic Liquid)-Room Temperature Ionic Liquid Composite Membranes. *Industrial & Engineering Chemistry Research*, 9344-9353 (2011).

Maginn, E. (2008, May 6). Evaluation of Ionic Liquids in Post-Combustion CO_2 Capture. Pittsburgh, PA.

Olajire, A.A., CO2 capture and separation technologies for end-of-pipe applications – A review. Energy, 2010. 35(6): p. 2610-2628.

Rapier, R. Global Carbon Dioxide Emissions - Facts and Figures. Retrieved August 12, 2013 from: http://www.energytrendsinsider.com/2012/07/02/global-carbon-dioxide-emissions-facts-and-figures/.

Siriwardane, R., Shen, M. Fisher, E., Poston, J., & Shamsi, A. (n.d.). Adsorption and Desorption of CO2 on Solid Sorbents (n.d.).

Teledyne Isco. (2012). *Enhanced Oil Recovery (EOR)*. Retrieved from http://www.isco.com/WebProductFiles/Applications/105/Application_Notes/Enhanced_Oil_Recovery.pdf

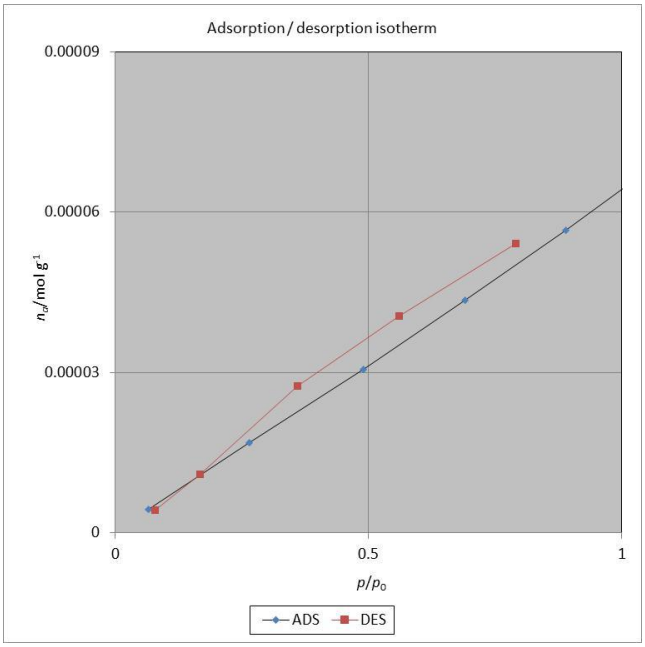
What is activated charcoal and why is it used in filters?. Retrieved August 12, 2013 from: http://science.howstuffworks.com/environmental/energy/question209.htm.

Zhang, C., Song, W., Sun, G., Xie, L., Wang, J., Li, K., Sun, C., Liu, H., Snape, C. E., & Drage, T. *CO_2 Capture with Activated Carbon Grafted by Nitrogenous Functional Groups*. June 28, 2013.

Zhao, Z., Dong, H., & Zhang, X. (2011). The Research Progress of CO_2 Capture with Ionic Liquids. *Chinese Journal of Chemical Engineering*, 20(1), 120-129 (2012).

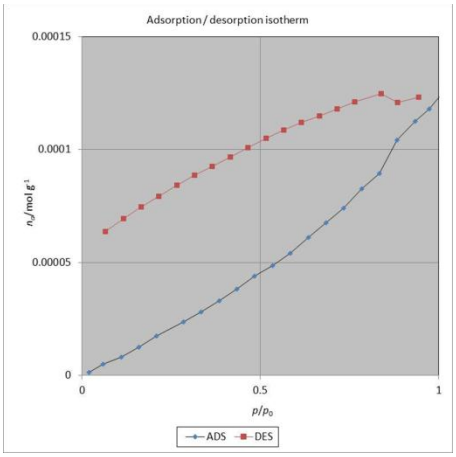
APPENDICE

APPENDIX 1: ANALYSIS OF POLY-[VEIM][TF_2N] USING BELSORP



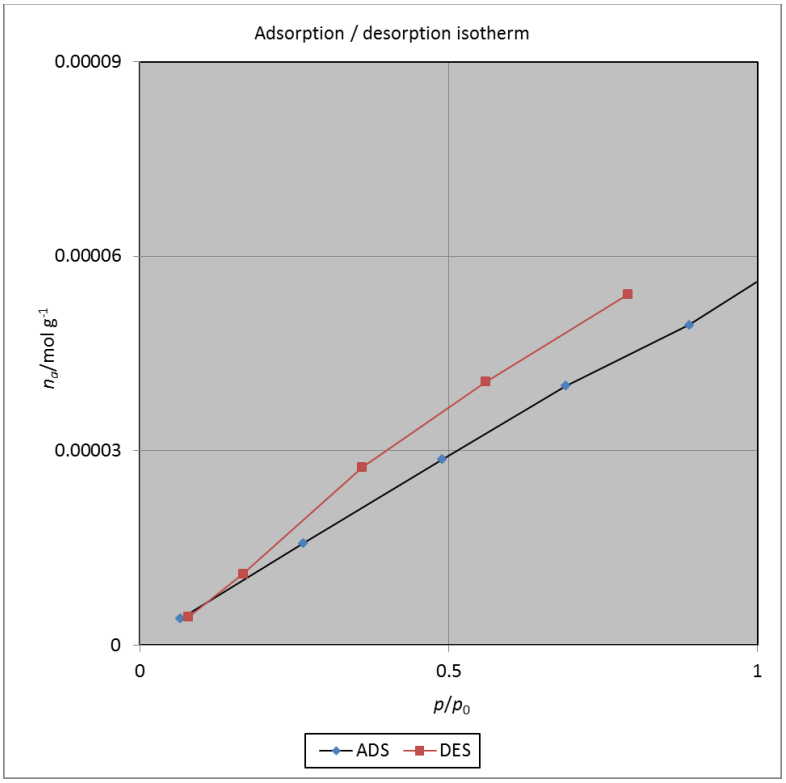
No	*pi*/kPa	*pe*/kPa	*pe*2/kPa	p_0/kPa	p/p_0	n_a/mol g^{-1}
ADS						
1	0	6.6336	0	101.33	0.065465	4.3567E-06
2	0	26.862	0	101.33	0.2651	0.000016854
3	0	49.576	0	101.33	0.4893	0.000030534
4	0	69.866	0	101.33	0.6895	0.000043561
5	0	90.155	0	101.33	0.8897	0.000056585
6	0	110.37	0	101.33	1.0892	0.000070438
DES						
1	0	80.15	0	101.33	0.791	0.000054149
2	0	56.74	0	101.33	0.56	0.00004057
3	0	36.519	0	101.33	0.3604	0.000027434
4	0	16.954	0	101.33	0.1673	0.000011019
5	0	7.9369	0	101.33	0.078327	0.000004309

APPENDIX 2: ANALYSIS OF POLY-[VEIM][TF_2N]+AC USING BELSORP



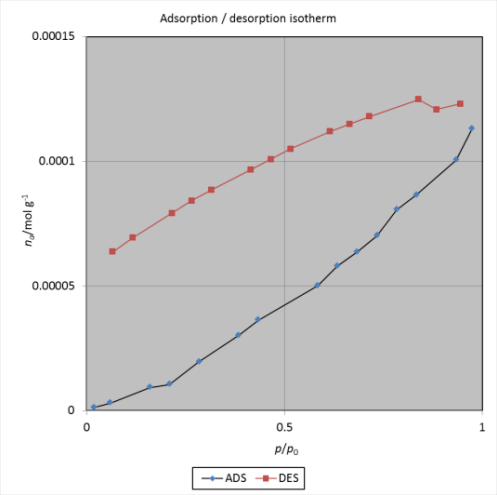
No	*pi*/kPa	*pe*/kPa	*pe*2/kPa	p_0/kPa	p/p_0	n_a/mol g^{-1}
ADS						
1	0	1.9344	0	101.33	0.01909	0.000001427
2	0	6.0137	0	101.33	0.059348	5.0152E-06
3	0	11.076	0	101.33	0.1093	8.0677E-06
4	0	16.135	0	101.33	0.1592	0.00001247
5	0	21.181	0	101.33	0.209	0.000017519
6	0	28.765	0	101.33	0.2839	0.000023574
7	0	33.844	0	101.33	0.334	0.000028186
8	0	38.903	0	101.33	0.3839	0.000033157
9	0	43.957	0	101.33	0.4338	0.00003831
10	0	49.02	0	101.33	0.4838	0.000044044
11	0	54.091	0	101.33	0.5338	0.000048742
12	0	59.157	0	101.33	0.5838	0.000054158
13	0	64.208	0	101.33	0.6337	0.000060971
14	0	69.27	0	101.33	0.6836	0.000067583
15	0	74.349	0	101.33	0.7337	0.000074128
16	0	79.396	0	101.33	0.7835	0.000082596
17	0	84.462	0	101.33	0.8335	0.000089502
18	0	89.505	0	101.33	0.8833	0.0001043
19	0	94.616	0	101.33	0.9337	0.00011247
20	0	98.675	0	101.33	0.9738	0.00011802
21	0	102.72	0	101.33	1.0137	0.00012564
DES						
1	0	95.688	0	101.33	0.9443	0.00012305
2	0	89.606	0	101.33	0.8843	0.00012079
3	0	85.025	0	101.33	0.8391	0.00012485
4	0	77.482	0	101.33	0.7647	0.00012108
5	0	72.419	0	101.33	0.7147	0.00011794
6	0	67.376	0	101.33	0.6649	0.00011494
7	0	62.318	0	101.33	0.615	0.00011189
8	0	57.271	0	101.33	0.5652	0.00010862
9	0	52.221	0	101.33	0.5154	0.00010493
10	0	47.162	0	101.33	0.4654	0.00010082
11	0	42.104	0	101.33	0.4155	0.000096672
12	0	37.041	0	101.33	0.3655	0.000092576
13	0	31.991	0	101.33	0.3157	0.000088565
14	0	26.932	0	101.33	0.2658	0.000084215
15	0	21.877	0	101.33	0.2159	0.000079192
16	0	16.819	0	101.33	0.166	0.000074498
17	0	11.764	0	101.33	0.1161	0.000069332
18	0	6.7057	0	101.33	0.066177	0.000063759

APPENDIX 3: ANALYSIS OF POLY-[VEIM][BR] USING BELSORP



No	*pi*/kPa	*pe*/kPa	*pe*2/kPa	p_0/kPa	p/p_0	n_a/mol g^{-1}
ADS						
1	0	6.6336	0	101.33	0.065465	4.0567E-06
2	0	26.862	0	101.33	0.2651	0.000015754
3	0	49.576	0	101.33	0.4893	0.000028634
4	0	69.866	0	101.33	0.6895	0.000039961
5	0	90.155	0	101.33	0.8897	0.000049385
6	0	110.37	0	101.33	1.0892	0.000061538
DES						
1	0	80.15	0	101.33	0.791	0.000054149
2	0	56.74	0	101.33	0.56	0.00004057
3	0	36.519	0	101.33	0.3604	0.000027434
4	0	16.954	0	101.33	0.1673	0.000011019
5	0	7.9369	0	101.33	0.078327	0.000004309

APPENDIX 4: ANALYSIS OF [VEIM][Br]+AC USING BELSORP



No	*pi*/kPa	*pe*/kPa	*pe*2/kPa	p_0/kPa	p/p_0	n_a/mol g^{-1}
ADS						
1	0	1.9344	0	101.33	0.01909	0.000001252
2	0	6.0137	0	101.33	0.059348	3.0152E-06
3	0	16.135	0	101.33	0.1592	0.000009247
4	0	21.181	0	101.33	0.209	0.000010519
5	0	28.765	0	101.33	0.2839	0.000019574
6	0	38.903	0	101.33	0.3839	0.000030157
7	0	43.957	0	101.33	0.4338	0.00003631
8	0	59.157	0	101.33	0.5838	0.000050158
9	0	64.208	0	101.33	0.6337	0.000057971
10	0	69.27	0	101.33	0.6836	0.000063583
11	0	74.349	0	101.33	0.7337	0.000070128
12	0	79.396	0	101.33	0.7835	0.000080596
13	0	84.462	0	101.33	0.8335	0.000086502
14	0	94.616	0	101.33	0.9337	0.00010047
15	0	98.675	0	101.33	0.9738	0.00011302
16	0	102.72	0	101.33		0.00011864
DES						
1	0	95.688	0	101.33	0.9443	0.00012305
2	0	89.606	0	101.33	0.8843	0.00012079
3	0	85.025	0	101.33	0.8391	0.00012485
4	0	72.419	0	101.33	0.7147	0.00011794
5	0	67.376	0	101.33	0.6649	0.00011494
6	0	62.318	0	101.33	0.615	0.00011189
7	0	52.221	0	101.33	0.5154	0.00010493
8	0	47.162	0	101.33	0.4654	0.00010082
9	0	42.104	0	101.33	0.4155	0.000096672
10	0	31.991	0	101.33	0.3157	0.000088565
11	0	26.932	0	101.33	0.2658	0.000084215
12	0	21.877	0	101.33	0.2159	0.000079192
13	0	11.764	0	101.33	0.1161	0.000069332
14	0	6.7057	0	101.33	0.066177	0.000063759
10	0	47.162	0	101.33	0.4654	0.00010082
11	0	42.104	0	101.33	0.4155	0.000096672
12	0	37.041	0	101.33	0.3655	0.000092576
13	0	31.991	0	101.33	0.3157	0.000088565
14	0	26.932	0	101.33	0.2658	0.000084215
15	0	21.877	0	101.33	0.2159	0.000079192
16	0	16.819	0	101.33	0.166	0.000074498
17	0	11.764	0	101.33	0.1161	0.000069332
18	0	6.7057	0	101.33	0.066177	0.000063759