Leaching Of Ionic Liquid From A Fixed Bed

By

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Bachelor of Engineering (Hons)

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Bandar Seri Iskandar

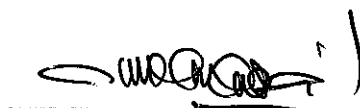31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

The Leaching Of Ionic liquid From A Fixed-Bed

By

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

_____

(Dr Lukman Bin Ismail)

UNIVERSITI TEKNOLOGI PETRONAS
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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.

AHMAD FAISAL BIN AHMAD SAZALI

ABSTRACT

The effect of hydrocarbon solvent, operating temperature and solid support on the leaching of supported ionic liquid phase is studied in this research project. Supported ionic liquid phase catalysis has already been applied in gas phase applications because to its stability, its application in liquid phase however requires coordination of the ionic liquid and reactants to avoid leaching. Leaching causes contamination of the product phase causing an increase in costs due to product purification and catalyst deactivation which is caused by cross solubility and mechanical removal. To adhere to the given project timeline and to make the project feasible only a certain number of variables are tested. The tested variable includes three types of hydrocarbon solvent, which are n-heptane, n-dodecane and toluene. The temperature at which the experiment is conducted is also manipulated at 25°C, 35°C, 45°C. The experiment was conducted in a batch operated method where hydrocarbon solvent is flowed from a reservoir to a glass column containing a constant amount of supported ionic liquid phase. Water is then washed with the hydrocarbon and analysed using the conductivity meter and atomic absorption spectrophotometer. The results showed that aromatics cause more leaching than n-alkanes. For n-alkane, varying operating temperature had a negligible effect on leaching.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ionic liquid are organic salts consisting of cation and anion in liquid form at room temperature (Camper et al., 2005). They are regarded as designer solvents due to their adjustable physical properties, and have been researched extensively for application in many areas such as lubrication, drug delivery, electrolysis and so forth. The area of interest in this project is its application in catalysis.

Although ionic liquids have adjustable properties, they usually possess high viscosity which limits their use as homogeneous catalyst. The high viscosity of the ionic liquid slows the diffusion of reactants through the catalyst phase therefore leading to a slow rate of reaction. Ionic liquids are also expensive, making their use in homogeneous catalysis uneconomical (Joni et al., 2009) due to the large volume required. The separation of the ionic liquid and product also poses difficulties which leads to increased costs.

A method of overcoming this problem is by coating or impregnating ionic liquid onto a solid support which results in what is called supported ionic liquid phase (SILP). The SILP reduces the amount of ionic liquid used and also allows for an easier separation of the product or reactant phase from the SILP (Virtanen et al., 2007).

SILP has been researched extensively for their use in gas phase due to their almost non-existent vapour pressure and high thermal stability and researched for use in alkylation, hydrogenation and hydroamination just to name a few (Joni et al., 2009).

The use of SILP in the liquid phase however is limited because of cross solubility problems, mechanical removal of ionic liquid film and catalyst leaching which leads to product contamination and catalyst deactivation (Werner et al., 2010). A better understanding of the parameters that influence the amount and rate ionic liquid leaching is needed before it can be used in liquid phase applications.

This project is aimed at studying the relation between several chosen variables and SILP leaching.

1.2 Problem Statement

The leaching of SILP causes product or reactant phase contamination resulting in catalyst deactivation ultimately leading to increased costs. The increased cost will be due to product purification later in the later stages of the process (Riisager et al., 2005). The ionic liquid and metal catalyst that leached needs to be separated from the product phase. The life span of SILP catalyst is also not known. Meaning that research on the long term stability of the ionic liquids in their respective operating conditions has not been done yet. This is true for the use of SILP in liquid hydrocarbon phases. The proposed research project will investigate the leaching of SILP in hydrocarbons.

1.3 Significance of Study

By knowing the relation between SILP leaching and the parameters that affect it, will lead to more knowledge for the application of SILP catalyst in liquid phase applications. This is because the factors that cause leaching are better understood. The industry prefers heterogeneous catalysts due to the ease of product separation and because reactions can be operated in a continuous way (Mikkola et al., 2007). The application of SILP in liquid phases requires careful coordination of all components to avoid cross solubility or unwanted reactions. The knowledge of SILP leaching will benefit industries that use catalysts in continuous mode, as this allows them to make better considerations when designing SILP in liquid phase applications especially for the hydrocarbon industry. An example of a hydrocarbon process using catalyst is hyroformylation (Riisager et al., 2003).

1.4 Scope of Study

The parameters tested in this project are hydrocarbon solvent type and operating temperature. The number of variables tested will be restricted as to adhere to the time allocation for the project. The planned experiments will be simulating fixed bed applications involving hydrocarbons in the industry, however there will be no metal catalyst suspended in the SILP phase implying that there are no planned reactions. The aim of the leaching study is to observe and analyse the relation between the manipulated variables and the rate and amount of ionic liquid leaching.

1.5 Aim and Objective

The aim of the study is to develop an understanding and establish a relation between the manipulated variables which includes hydrocarbon solvent type, operating temperature and its effect on leaching. The relation will be deducted from a graph of ionic liquid concentration versus batch pass number.

The following are objectives of the project

- To study the effect of alkanes of different types on ionic liquid leaching
- To study the effect of aromatics on ionic liquid leaching
- To study the effect of operating temperature on leaching

1.6 Relevancy and Feasibility of the Project

This proposed research will further increase the understanding of SILP leaching in hydrocarbons, which will be useful for industries that see the potential use of SILP in liquid phase conditions. This knowledge will improve the design and considerations of SILP in their potential applications. The project is feasible because the equipment and material required are available at PETRONAS Ionic Liquid Centre (PILC). The number of variables tested is also within the specified time constraint.

CHAPTER 2

THEORY

2.1 Introduction

The theory section will discuss on what is ionic liquid, supported ionic liquid phase and leaching.

2.2 Ionic Liquid

Ionic liquids are organic salts consisting of cation and anion at temperatures less than 100°C. They possess low volatility, high thermal stability and their properties can be manipulated through selection of anion and cation (Riisager et al., 2005). The adjustable properties include the ionic liquids density, conductivity, solubility and viscosity. Because of the reasons they have attracted attention in the scientific community. Figure 1 shows the possible applications of ionic liquids in the several disciplines.
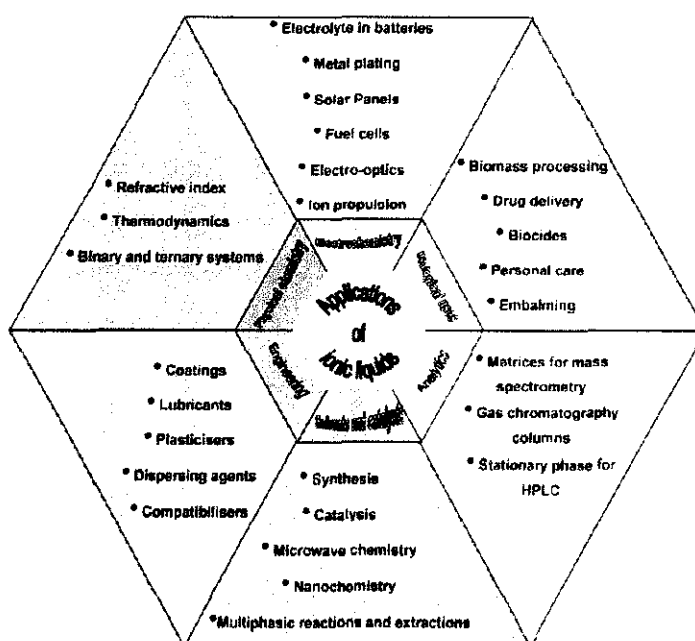
Figure 1: Application of Ionic Liquids

2.3 Supported Ionic Liquid Phase (SILP)

Ionic liquids consist entirely of ions and have no measurable vapour pressure which makes them attractive as alternative solvents for homogeneous catalysis. Their polar nature allows the stabilization of ionic transition metal complexes as well as complexes being susceptible to hydrolysis. However, beside their advantageous properties as solvents, ionic liquids are relatively expensive, even though being commercially available now (Olivier-Bourbigou et al., 2010).

Aside from that, ionic liquids are normally highly viscous solvents, thus having low diffusion coefficients. In case of fast chemical reactions this may result in mass transfer limitations, where only the catalyst is in the diffusion layer of the biphasic system. An ideal system for the use of ionic liquids is a small required amount of ionic liquid, ease of separation and high mass diffusivity (Chrobok et al., 2010). SILP tends to these problems.

SILP requires less ionic liquids compared to liquid-liquid biphasic ionic liquid catalysis and allows for easier separation. The thin ionic liquid film on the solid supports also allow for fast molecule diffusivity. This is why SILP are preferred over biphasic ionic liquid catalysis (Riisager et al., 2005). SILP however, behaves as a homogeneous catalyst although technically it is a heterogeneous catalyst, this is because there is no interaction between the support surface and homogeneous catalyst (Doorslaer et al., 2010). Therefore SILP possesses the advantages of homogeneous and heterogeneous catalyst.

Supported ionic liquid phase (SILP) are solid supports which have been coated or impregnated with ionic liquid. The ionic liquid film usually holds the transition metal catalyst which will increase the rate of reaction. The main use of SILP is in catalysis are continuous flow operated fixed bed. Figure 2 (Riisager et al., 2005) shows the principle of SILP.
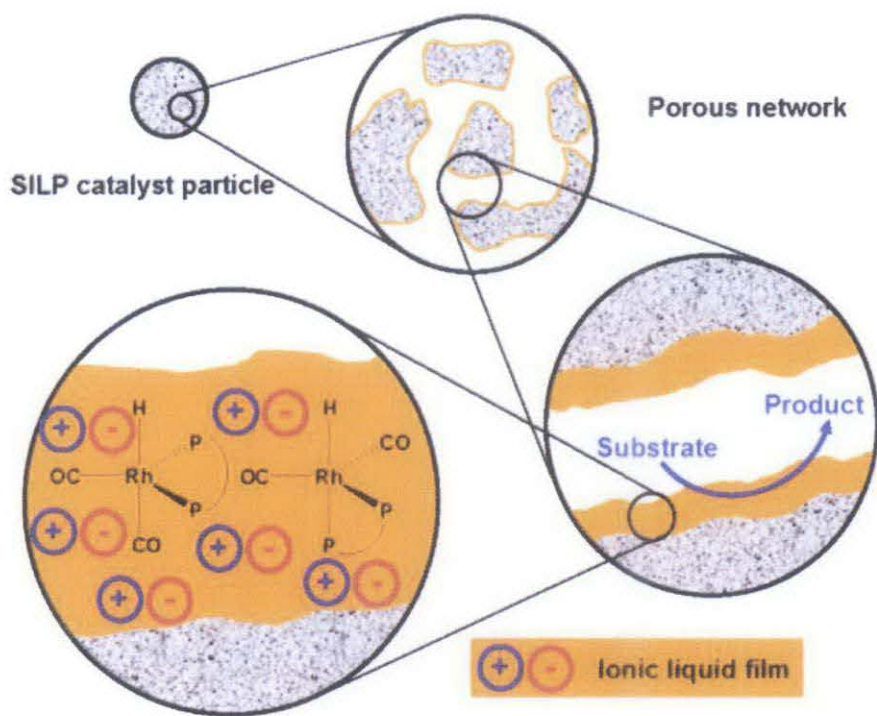
Figure 2: Schematic Principle of SILP Catalysis

The ionic liquid attaches itself onto the support through covalent bonding and physical adsorption (Riisager et al., 2005). This means that if the bond is broken, it would result in leaching of the ionic liquid film which holds the transition metal catalyst.

SILP are suitable for use in gas phase applications because they possess low volatility and high thermal stability, which is why they have been used in Friedel Crafts alkylation and methanol carbonylation (Olivier-Bourbigou et al., 2010). Figure 3 shows the application or current research of SILP technology.
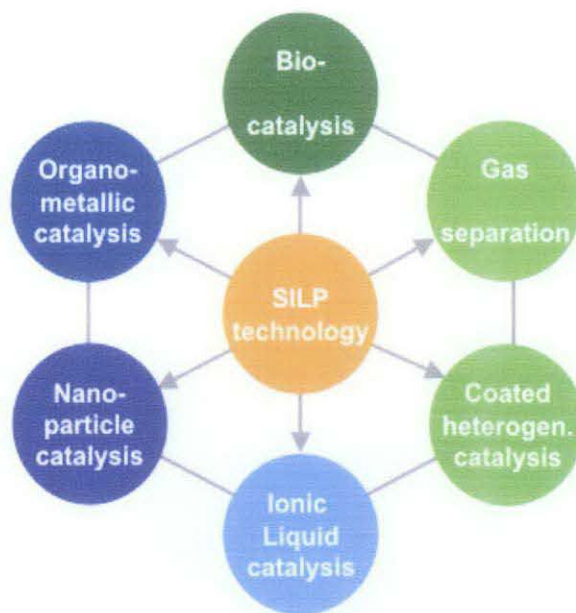
Figure 3: SILP Applications

SILP application in the liquid phase however requires a deeper understanding of the relation between ionic liquid and the other phases. This is to prevent the ionic liquid layer from dissolving into the reactant or product phase. Unnecessary reactions must also be avoided to prevent product contamination or ionic liquid disappearance which will lead to increased costs.

2.4 Ionic Liquid Leaching

Leaching occurs when the ionic liquid film detaches itself from the solid support and enters the reactant or product phase. Leaching causes product contamination and catalyst deactivation ultimately leading increased cost in the form of separation. Leaching of the ionic liquid is caused by cross solubility between the ionic liquid and the product phase and through mechanical removal of the ionic liquid film (Werner et al., 2010).

Leaching is generally caused by the ionic liquid dissolving into the liquid phase. Because ionic liquids are polar substances, their solubility varies with cation type and anion alkyl chain length (Ferreira et al., 2011). They can be hydrophobic or hydrophilic depending on the species, which is why it is difficult to generalize their

properties. This project however will investigate the leaching of SILP in hydrocarbons. This is to lead to the application of SILP in petroleum industries where the operation is continuous and ease of product separation is desired.

Based on a recent publication (Ferreira et al., 2011), the solubility of ionic liquids in hydrocarbon in decreasing order is aromatics followed by cycloalkanes and n-alkanes. The effect of the hydrocarbon chain on the solubility is, the longer the chain the lesser the solubility of ionic liquids in them. A detailed description of the findings can be seen in Table 1.

Table 1: Factors Affecting Solubility

Factor	Solubility
n-Alkane Alkyl Chain Length	$\uparrow C_n \rightarrow \downarrow$ Solubility
Aromatic Alkyl Chain Length	$\uparrow C_n \rightarrow \downarrow$ Solubility
Hydrocarbon Species	Aromatic > Cycloalkanes > n- Alkanes
Ionic Liquid Anion Alkyl Chain Length	$\uparrow C_n \rightarrow \uparrow$ Solubility

Based on the reported solubility of hydrocarbons and ionic liquids seen in Table 1, it is expected that in the leaching tests, the solvent that will cause the least amount of leaching is the alkane with the longest alkyl chain and solvent that will cause the most leaching is aromatic compounds with the least alkyl chain. The cross solubility between ionic liquids and hydrocarbons also increases when the ionic liquid is less polarized (Ferreira et al., 2011).

In testing the effect of flowrate on leaching the residence time the solvent flowing through the reactor will be manipulated. The residence time or space time is determined from the following equation.

$$\tau = \frac{V}{v_0}$$

where τ = space time v_0 = volume metric flowrate

        V = reactor volume

CHAPTER 3

METHDOLOGY

3.1 Introduction

This section describes the methodology used in the experiments. The SILP used in the experiments conducted is BMIM FeCl$_4$ on silica (20wt %) which has been pre-prepared by the research officers at PILC. All the experiments will use the silica solid support except for the testing of the solid support variable. The leach testing methodology has been slightly changed as new discoveries were made. In the leach testing stage, two parameters which are hydrocarbon solvent, and operating temperature will be manipulated and tested. The experiment is conducted in a batch operated method.

3.2 Equipment and Material Required

3.2.1 Equipment

Table 2: Equipment Required

Equipment	Purpose
Glass Column	To house the SILP
Rotary Evaporator	To remove excess ethanol on the SILP
Atomic Absorption Spectrophotometer	To analyse the solvent for ionic liquid content
Conductivity Meter	To analyse the solvent for ion content
Retort Stand	To hold the glass column
Magnetic Stirrer	To stir the water/hydrocarbon mixture
Separatory Funnel	To store the hydrocarbon solvent
Heater	To heat and circulate water

3.2.2 Material

Table 3: Material Required

Material	Purpose
BMIM FeCl$_4$	Ionic Liquid Species
Toluene	Solvent
N-Heptane	Solvent
N-Dodecane	Solvent
Silica Support	Ionic Liquid Solid Support
Glass Wool	To hold the SILP in place

3.3 SILP Leach Test

The leach experiment will investigate three variables and its relation to leaching. The three manipulated variables are as seen in Table 4.When testing a variable all other variables are set constant.

Table 4: Manipulated variables

Temperature Tested	Solid Support Type	Solvent
25°C (Room Temperature)	Silica	N-Heptane
35°C		N-Dodecane
45°C		Toluene

Table 5 shows the variables that are set constant for the experiment.

Table 5: Variables Set Constant

Variable	Amount
Amount of SILP tested	2.5 grams
Solvent Volume	50 millilitre
Ionic Liquid Tested	BMIM FeCl$_4$
Water Wash	50 milliliter (10 minutes at 700rpm)
Flowrate (Depends on glass wool packing)	-

3.3.1 Rig Design

The leaching test rig for the testing of the temperature variable setup is as in Figure 4.

Figure 4: Rig Design
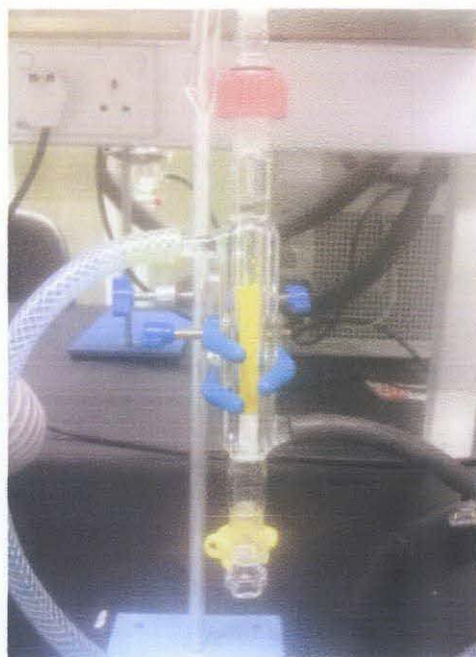
Figure 5: Glass Column Containing the SILP

As seen in Figure 4, a glass column is held in a vertical position by a retort stand. This is to allow the flow of hydrocarbon solvent through the column by gravity. The glass column houses the SILP which is held in place by glass wool. A separatory funnel is placed above the glass column which stores the hydrocarbon solvent.

The outer part of the glass column is connected to the heater which also functions as pump, as seen in Figure 5. The pump/heater will circulate heated water through outer part of the glass column. The temperature of the glass column is manipulated by controlling the temperature of the water set at the heater. The hydrocarbon that has passed the SILP is collected in a glass container which will be processed with de-ionized water and analysed.

The latter is the test rig design for the temperature variable using n-dodecane which is not very volatile, as for the testing of the solvent variable involving more volatile components such as toluene the experiment is conducted in a fume hood in the same manner without the heater as seen in Figure 6.

Figure 6: Experimental Rig Design without Heater

3.3.2 Leach Test Procedure for Solvent Variable

All other variables such as flow rate and temperature will be set constant except the hydrocarbon solvent type. The purpose of testing the solvent type is to see the effect of varying alkanes of different carbon chain lengths and aromatic on SILP leaching. The solvent types are chosen based on their type and alkyl chain. Based on (Ferreira et al., 2011), the solubility of hydrocarbon in ionic liquids in increasing order is n-alkane, cycloalkane followed by aromatics. The longer the alkyl chain the less soluble it is in ionic liquids. The experiment is conducted to see whether or not this is the same for leaching. The solvents tested in this project include n-heptane, n-dodecane and toluene.

Glass wool is place at one end of the glass column, SILP is then packed in the glass column through the other end and shaken to ensure an even packing. The experimental rig is then setup as seen in Figure 6. 50 milliliters of n-heptane is then poured into the separatory funnel and flowed slowly through the glass column. The level of hydrocarbon solvent inside the glass column is always kept above the SILP level as to ensure a maximum flowrate. Unfortunately the flowrate of the solvent

passing through the column cannot be controlled as the packing of the glass wool largely determines the flowrate. The hydrocarbon solvent is collected at the bottom for analysis later. This is repeated until six 50 milliliter batches of hydrocarbon are collected. The experiment is then repeated for n-dodecane and toluene.

3.3.3 Leach Test Procedure for Operating Temperature Variable

For the testing of operating temperature on leaching, the temperature of the SILP and hydrocarbon solvent is manipulated by controlling the temperature of the circulated water. The hydrocarbon solvent used for the temperature variable is n-dodecane. The experiment's purpose is to see the relation between leaching and operating temperature.

Figure 7: Control Interface for the Heater

Glass wool is place at one end of the glass column, SILP is then packed in the glass column through the other end. The experimental rig is then setup as seen in Figure 4. The circulated water's temperature is set at 35°C and left to stabilize for 30 minutes once reaching the set temperature, this is to allow time for all of the SILP to achieve a stable state at specified temperature. 50 milliliters of n-dodecane is then poured into the separatory funnel and flowed slowly through the glass column. The level of hydrocarbon solvent inside the glass column is always kept above the SILP level as

to ensure a maximum flowrate. Unfortunately the flowrate of the solvent passing through the column cannot be controlled as the packing of the glass wool largely determines the flowrate. The hydrocarbon solvent is collected at the bottom for analysis later. This is repeated until six 50 milliliter batches of hydrocarbon are collected. The experiment is then repeated at 45°C.

3.4 Analysis

The hydrocarbon samples collected is then mixed with 50 milliliters of de-ionized water and stirred using a magnetic stirrer at 700 rpm for 10 minutes to separate the leached ionic liquid from the hydrocarbon phase which is assumed to diffuse to the de-ionized water. This step is necessary as the conductivity meter and AAS analyzer can only analyze aqueous solution and not hydrocarbons. This is done separately to all samples. After the mixture has settled into two phases, the de-ionized water is separated from the two phase mixture using a pipette and stored in a test tube suitable for analysis using the atomic absorption spectrophotometer (AAS). The remaining samples are analyzed using a conductivity meter.

Figure 8: Conductivity Meter

Figure 9: Atomic Absorption Spectrophotometer

3.5 AAS Calibration

The AAS had to be calibrated every time it is used, this is to check for the accuracy of the equipment and whether or not it is functioning properly. The AAS first measures the standards prepared which in this case is zero, one, two and four ppm of iron in deionized water. If the calibration line is good only then will the analysis of the samples will be conducted. After the analysis of the samples, the iron standard will be measured again to check for consistency and accuracy.
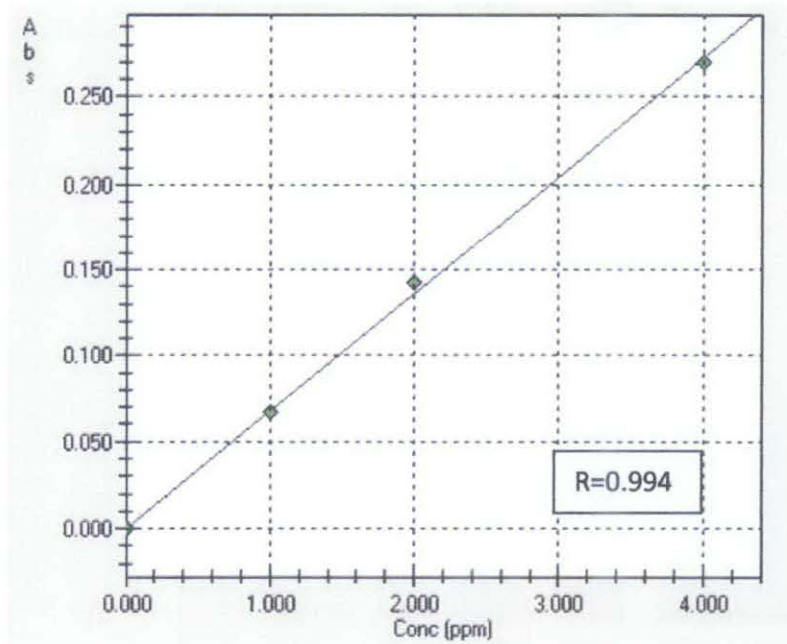
Figure 10: Calibration Line of the AAS

3.6 Difficulties Encountered

Several difficulties were encountered during the project's progress, among the very first is the availability of the peristaltic pump, due to the unavailability of a peristaltic pump the experiment had to be conducted in a batch manner, changing the initial methodology of the experiment.

The analyser planned for use which the ion chromatograph is not able to detect the species of ionic liquid leached which is BMIM $FeCl_4$ due to the unavailability of a iron column, this led to the use of the AAS for analysis.

The method of washing the hydrocarbon with de-ionized water also had to be changed. Initially the hydrocarbon and de-ionized water was mixed inside a test tube suitable for the vortex stirrer as seen in Figure 11, however after a period of time, the colour of the hydrocarbon phase turned blue following the colour of the test tube's cap, suggesting that the hydrocarbon dissolved the cap thus contaminating the sample. This caused a change in the method used to process the hydrocarbon sample. The hydrocarbon is now processed in a glass bottle with a more chemically resistant cap which is stirred using a magnetic stirrer.

Figure 11: Vortex Stirrer

Figure 12: N-Heptane Sample (Contaminated)

Changes also have been made to number and volume of hydrocarbon sample taken. Four batches were taken initially which has been increased to six, and the volume of hydrocarbon per pass has been increased from 10 millilitres to 15 millilitres due to results that is negative in value obtained using the AAS from n-heptane experiment. This caused repetition of the testing hydrocarbon solvent variable in order to obtain a set of experiment with the same methodology.

After increasing the amount of SILP tested using the revised methodology, the AAS still yielded results that are negative in value therefore a trend could not be established.

The reason for the imprecise conductivity meter reading is because of a discovery of partial solubility of hydrocarbon in water. After the hydrocarbon sample has been washed with water a portion of the hydrocarbon is still present in the water phase. When this water sample is analysed using the conductivity meter the hydrocarbon present in the water sample masks the ions present in the sample, causing errors in the reading. This can be seen in the following figure which shows the cloudy colour of the water phase of the bottom of the mixture.
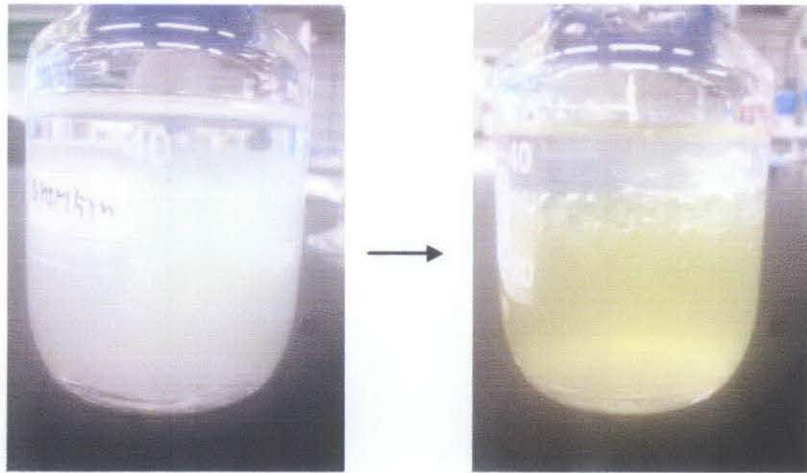
Figure 13: Leftover Hydrocarbon in the Water Phase after Settling

3.7 Project Activities

The activities conducted in this project include:

- Literature review
- SILP preparation
- Ionic liquid loading measurement
- SILP leach testing
- Analysis on the tested solvent for ionic liquid
- Processing of the obtained data
- Report Writing
- Presentations

3.8 Gantt Chart

The following are Gantt charts for FYP 1 and FYP 2

Task	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Mid Sem Break	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
Meeting with Supervisor															
Submission of Extended Proposal						○									
Oral Proposal Defence									○						
Preliminary Experiment															
Submission of Interim Draft Report														○	
Submission of Interim Report															○

Figure 14: FYP 1 Gantt Chart

Task	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Mid Sem Break	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15
Catalyst Preparation																
Catalyst Leach Testing																
Submission of Progress Report									○							
Data analysis										○						
Pre-EDX											○					
Submission of Draft Report												○				
Submission of Dissertation and Technical Paper													○			
Oral Presentation														○		
Submission of Project Dissertation																○

Figure 15: FYP 2 Gantt Chart

CHAPTER 4

RESULT AND DISCUSSION

The following section discusses the result obtained from the experiments performed so far. The parameters that have been tested include a preliminary test, the solvent variable and temperature variable. The SILP used for all experiments except for the solid support variable is BMIM FeCl$_4$ (20%wt) on silica.

4.1 Preliminary Test

The preliminary test is the very first experiment conducted in order to gain a better understanding and establishment of the research method. Three n-hexane passes were conducted in the preliminary test. The preliminary test's purpose is to evaluate the methodology of the experiment and to check for matters that may have gone unnoticed. This is because of a change in the original experiment's methodology. Many findings were discovered during the preliminary test and thus changes and improvements were made to the way the experiments are conducted. Figure 16 shows the experiments rig design.

Figure 16: Preliminary Test Rig

The following are the details of the preliminary test.

Table 6: Preliminary Test Detail

Variable	Amount
BMIM FeCl$_4$ (loaded)	1.7998 grams
n-Hexane (3 passes)	8 millilitre
Water (washed)	40 millilitre
Flowrate	-

One the things that was checked during the preliminary experiment is to see whether or not the hydrocarbon solvent would flow through the fine SILP material and glass wool without assistance of a pump, the experiment showed that flow was not a problem although the flowrate is slow. In the first run normal water was used to wash the n-hexane, however it was discovered later that normal water would cause significant errors when analysed using the conductivity meter since it measures all of the ion present in the sample and thus de-ionized water with a purity of 18.2 milliohms is used for the washing of all tested solvents.

The n-hexane that was passed through the fixed bed did not have any visible changes so the n-hexane was washed with water and then analysed using the conductivity meter to check for any changes in conductivity and resistivity. The results obtained were compared to pure deionized water to check for any changes.

Table 7: Preliminary Test Result

Measured Variable	Pure De-Ionized Water	Water Sample
Temperature (°C)	23.4	23.8
pH	7.56	7.22
TDS (ppm)	2.00	11.45
Conductivity (uS)	1.95	11.9
Resistivity (kilo ohms)	233.7	43.53

As seen in Table 7, the increased conductivity and the decreased resistivity of the water sample as compared to the pure de-ionized water suggested the increase of ions in the n-hexane after passing the SILP. The total dissolved solid (TDS) in the water sample also has increased compared to the pure de-ionized water, these findings suggest that there are more ions in that water sample than the pure de-ionized water, suggesting leaching of the SILP. The conductivity meter however is not very accurate as all ions in the water sample are measured including ions that are not BMIM FeCl$_4$. In the following experiments the samples are analysed using AAS to measure for iron content.

4.2 Solvent Parameter Test

The following section describes the results obtained from the testing of the hydrocarbon solvent variable. Three types of hydrocarbon were tested, they include n-heptane, n-dodecane and toluene.

4.2.1 N-Heptane

Table 8 and 9 shows the results obtained from the AAS and conductivity meter for the testing n-heptane solvent.

Table 8: N-Heptane AAS Result

Batch	Absolute	Concentration (PPM)
1	0.0011	0.0161
2	-0.0014	-0.0205
3	-0.0005	-0.0073
4	-0.0008	-0.0117
5	-0.0016	-0.0234
6	-0.0008	-0.0117

Table 9: N-Heptane Conductivity Meter Result

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	22.6	8.14	6.02	88.63	5.65
2	25.4	8.05	5.22	94.25	5.31
3	23.1	7.86	3.8	142.9	2.9
4	26.1	8.19	4.46	122.7	3.89
5	25.2	7.96	3.35	161.3	3.09
6	25.1	7.85	3.02	173.6	3.01

The results obtained from the AAS analysis except for the first batch indicate that there is no or very little iron present in the samples since the values are negative. The negative number however is due to the calibration of the AAS. The origin of the calibration line is not at zero, this causes any absolute reading below the point where the calibration line crosses the y-axis to be negative in value. The ionic liquid content which is BMIM $FeCl_4$ in the samples probably is in the parts per billion or ppb range making the detection by the AAS which can only measure till the ppm range not possible since the AAS is calibrated to measure iron at zero to four ppm accurately. This is caused by the sample having lower iron content than the zero iron standard.

The conductivity meter result shows a very low conductivity reading, which averages at around the 3 microsiemens mark which is similar to deionized water. The readings however are not very stable. The fluctuation in reading is caused by the hydrocarbon left in the water phase masking the ion reading of the conductivity meter therefore causing errors.

The conclusion that can be reached from the data gathered is that n-heptane causes no leaching or trace amounts of leaching. To determine whether or not n-heptane causes leaching the experiment has to be repeated and analyzed using equipment that is sensitive enough to measure ppb levels or conducted using more SILP.
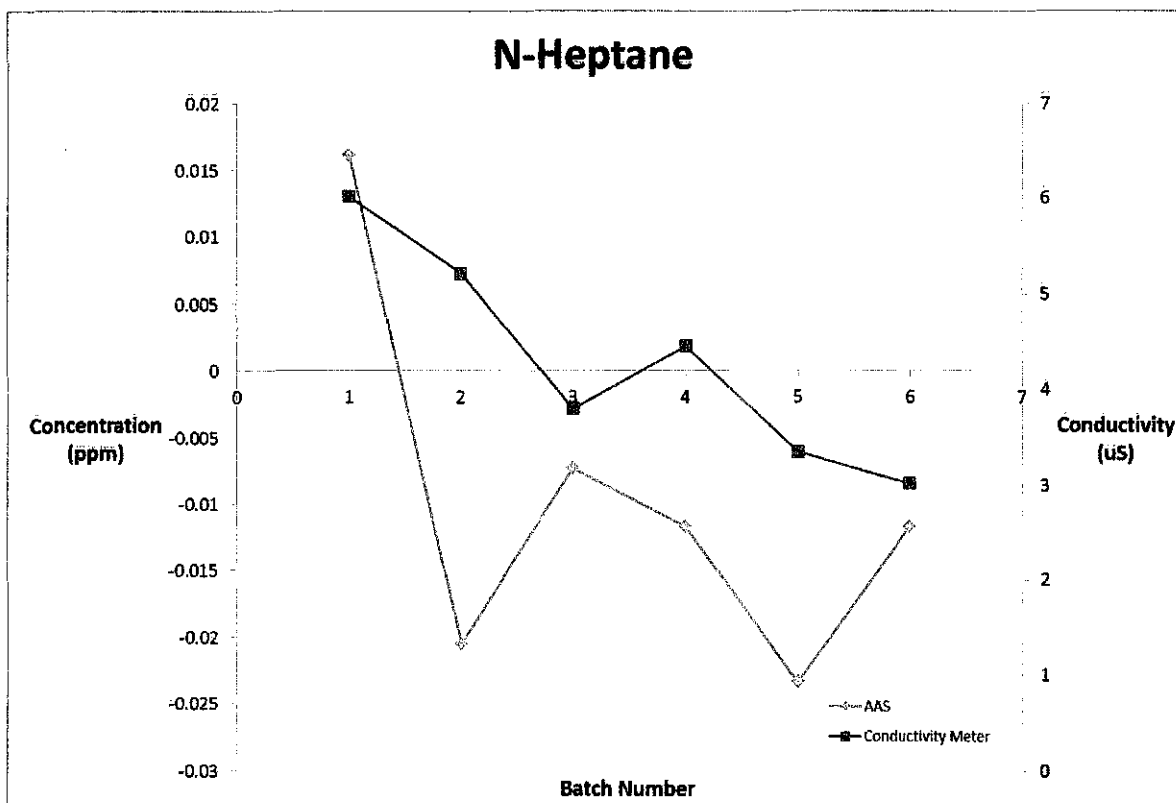
Figure 17: Comparison of AAS and Conductivity Meter Result for N-Heptane

Figure 17 depicts the results of the conductivity meter and AAS. The y-axis on the left is for the blue line which is the reading of the AAS in ppm. The y-axis on the right is for the red line which is the reading of the conductivity meter in microsiemens. The level of iron in the samples is past the limits of detection of the AAS analyzer, therefore yielding negative results.

Therefore it can be concluded that n-heptane does not cause the leaching of BMIM FeCl$_4$ on silica or the amount leaching is in ppb levels or trace amounts.

The following section will describe the results of n-heptane testing using an older methodology in which a lesser amount of solvent and SILP is used, changes have been made to however as the AAS yielded very small or negative values. Despite that, even after the modification of the experiments methodology as seen in section previously, results which showed a reducing trend could be obtained. The old experiment's details are as follows.

Table 10: N-Heptane Old Experiment Detail

Variable	Amount
BMIM FeCl$_4$ (loaded)	1.1834 grams
n-Heptane (4 passes)	10 millilitre
De-Ionized Water (washed)	25 millilitre
Flowrate	0.058 millilitre/second

Table 11: AAS Results

Batch	Concentration (ppm)
1	0.0000
2	0.0014
3	-0.0001
4	0.0003

Table 12: AAS Results (Repeated)

Batch	Concentration (ppm)
1	0.0003
2	0.0010
3	0.0001
4	-0.0004

As seen in Table 11 and 12, the results obtained were not conclusive, as the amount of iron leached is too little. This is due to the small amount of SILP tested and small

amount of solvent used per pass, to obtain a more conclusive result the amount of SILP tested and solvent passed will be increased in the following experiments. No physical changes were also observed on the n-heptane sample. The samples obtained could not be analysed using the conductivity meter due to contamination from the test tube.

4.2.2 N-Dodecane

Table 13 and 14 shows the results obtained from the AAS and conductivity meter for the testing n-heptane solvent.

Table 13: N-Dodecane AAS Result

Batch	Absolute	Concentration (PPM)
1	-0.002	-0.0293
2	-0.0018	-0.0264
3	-0.0024	-0.0352
4	-0.0018	-0.0264
5	-0.0016	-0.0234
6	-0.0011	-0.0161

Table 14: N-Dodecane Conductivity Meter Result

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	24.4	7.94	3.62	143.5	3.22
2	24.7	7.1	3.06	169.5	3.18
3	27.2	7.86	3.58	131.8	3.66
4	22.9	7.71	3.01	169.2	2.95
5	7.53	7.53	2.75	186	2.68
6	23.8	7.71	2.7	184.6	2.6

Similar to the results obtained from the n-heptane test, the AAS results for n-dodecane indicate a negative value for the concentration. This means that the concentration of ionic liquid in the sample is too low to be detected. The absolute

value detected by the AAS when referred to the calibration line turns to a negative value because the line's origin is not at zero.

The result obtained from the conductivity meter for the conductivity indicates that the ion detected in the sample is gradually decreasing apart from the third batch. The sudden increase in value for the third batch is because of impurities present in the sample. The trend displayed by the conductivity meter is what is expected. The amount of ions detected is supposed to decrease as the more hydrocarbons have passed. However the result obtained using the conductivity meter is doubted as hydrocarbons mask the ion reading.

As a conclusion the leaching caused by n-dodecane on SILP is in the parts per billion levels or it does not occur.
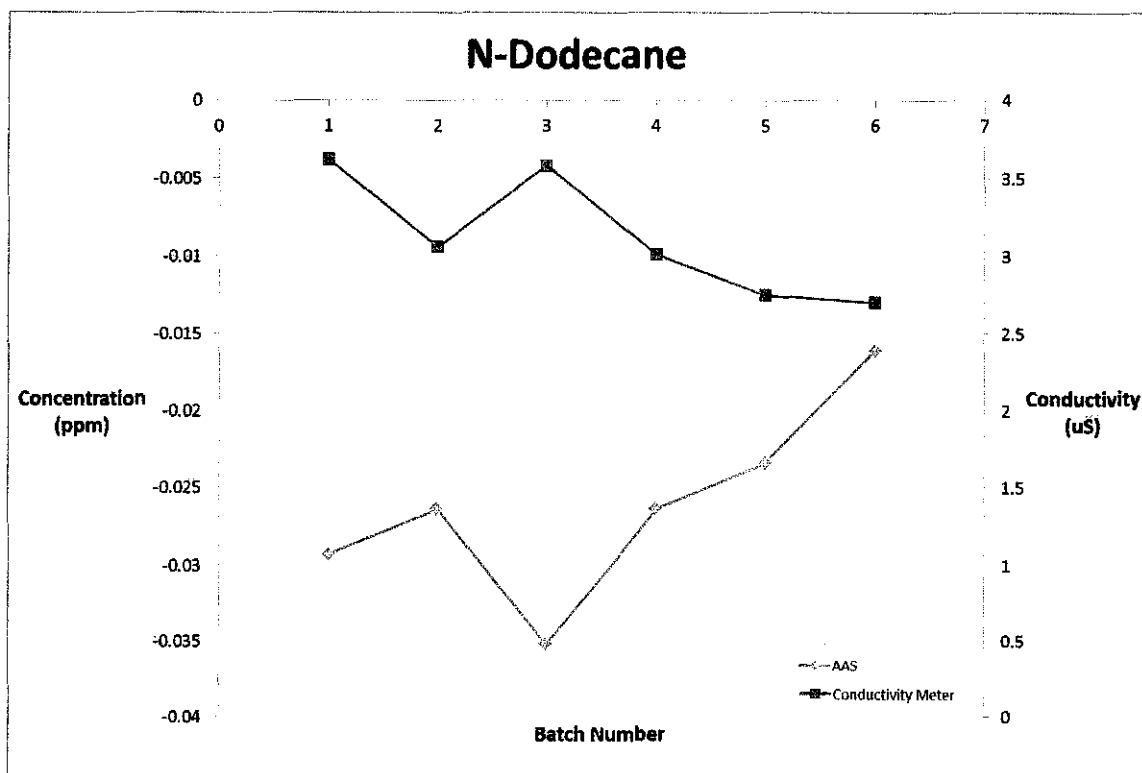

Figure 18: Comparison of AAS and Conductivity Meter Result for N-Dodecane

The figure above shows the trend of the results obtained by the AAS and conductivity meter. The conductivity meter displays a gradually reducing concentration of ion per batch as seen in the downward trend of the line, although errors may have occurred due to the hydrocarbon masking.

The AAS displays a gradually increasing value, the trend however can be neglected as the reading of the AAS is negative in value. This indicates that the concentration of ion in the sample is too low to be detected, implying that there no leaching of ionic liquid or there is trace amounts of leaching.

4.2.3 Toluene

The following are results of the toluene testing using the latest methodology as described in the methodology section, in which the amount of hydrocarbon solvent and SILP tested has been increased. This is so that the AAS can detect ionic liquid that may leached in the n-heptane and n-dodecane experiment because previous methodology employed small amounts of solvent and SILP which yielded a negative value however, even after increasing the amount of SILP and hydrocarbon solvent, the AAS values are still in the negative range as seen in the section previously. The testing of toluene is the only experiment which yielded positive readings, however this is seen to be obvious as there is colour change of the hydrocarbon solvent following the colour of the SILP indicating leaching.

Table 15: Toluene AAS Result

Batch	Absolute	Concentration (PPM)
1	0.3939	5.7716
2	0.8254	12.0942
3	0.6172	9.0435
4	0.6447	9.4465
5	0.6722	9.8494
6	0.3062	4.4866

Table 16: Toluene Conductivity Meter Result

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	24	3.9	177	3.381	149.1
2	23.4	3.69	322.3	1.574	309.1
3	24.5	3.96	203.9	2.53	200.1
4	23.5	3.8	252.3	2.07	241.4
5	23.6	4.11	194.3	2.67	187.4
6	25.4	3.92	268.4	1.871	260.3

The concentration of ionic liquid in the second batch as indicated by the AAS is higher than the first batch, this is most likely because the hydrocarbon that passed in the first batch did not have time to properly dissolve the ionic liquid coated onto the solid support. After the first batch however the SILP remains wet with toluene, allowing time for the second batch of toluene pass to bring down with it a lot more ionic liquid.

The AAS readings after that remain at around nine ppm till the last batch which is four ppm. The AAS is calibrated to detected zero to four ppm of iron accurately, however because toluene causes a large amount of leaching this caused a non-linearity in the results obtained. It must be kept in mind that for toluene analysis 5 milliliter of the original water sample has been diluted with 30 milliliter of de-ionized water following the results obtained in the old methodology, showing that the ionic liquid BMIM FeCl$_4$ is very soluble in toluene as compared to the alkanes tested previously. A downward trend in the amount of ionic liquid is present based on the concentration result.

The conductivity meter reading also detects a significantly higher reading than the ones obtained in the n-heptane and n-dodecane experiment. Toluene however is also more soluble in water than n-heptane and n-dodecane causing the reading of the conductivity meter to fluctuate. The toluene masks the ions that can be detected by conductivity meter probe therefore causing errors.

As a conclusion toluene which is an aromatic hydrocarbon species causes leaching of SILP which is considerably a lot more than that of n-alkanes.
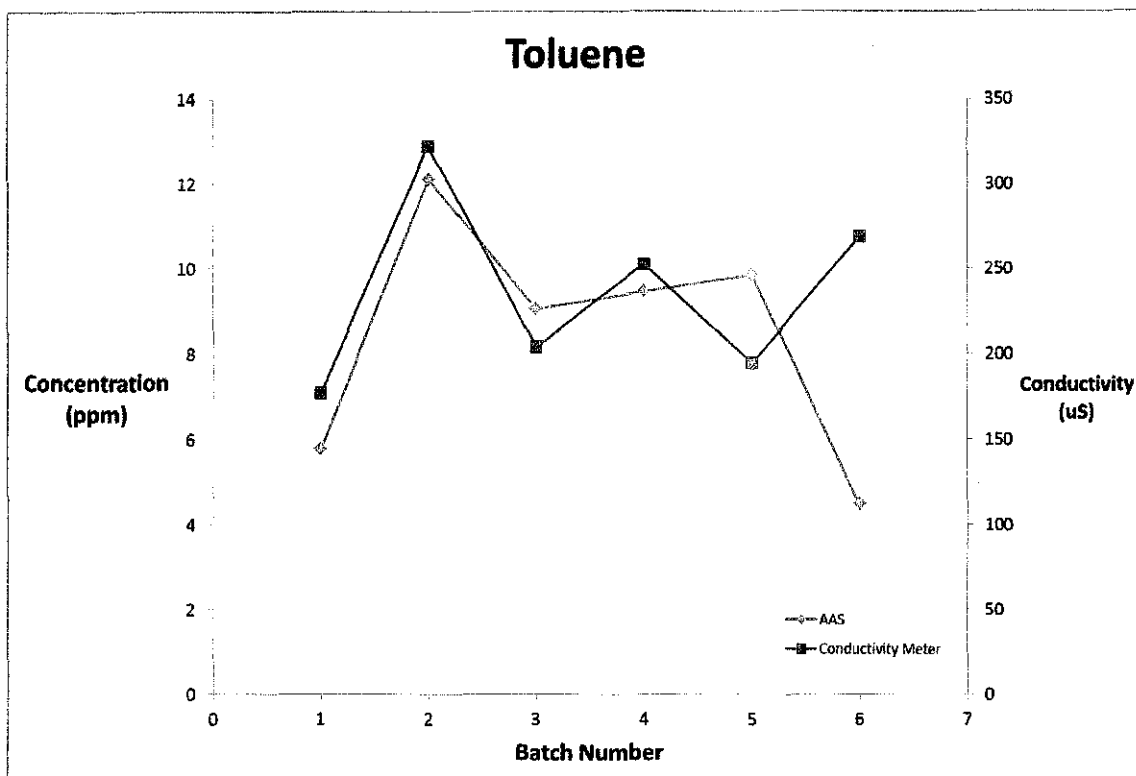
Figure 19: Comparison of AAS and Conductivity Meter Result for Toluene

The graph above shows the trend of the results obtained by the AAS and conductivity meter. Toluene by definitely causes a large amount of leaching compared to n–heptane and n-dodecane. This proves a finding in (Ferreira et al., 2011), which claims that the order of solubility of hydrocarbon in ionic liquid in increasing order is n-alkane, cycloalkane and aromatic hydrocarbon.

The points on the graph are roughly similar except for the last point, it is known that toluene masks the readings obtained by the conductivity meter. This causes errors in the reading.

The following are the results of the testing of toluene that used an old methodology.

Table 17: Toluene Old Experiment Detail

Variable	Amount
BMIM FeCl$_4$ (loaded)	2.8772 grams
n-Heptane (6 passes)	15 millilitre
De-Ionized Water (washed)	30 millilitre
Flowrate	0.02 millilitre/second

The figures below show the obvious colour leaching of the SILP caused by toluene.

Figure 20: Toluene Sample

As seen in Figure 20 the colour of the toluene has changed to a light brown colour following the colour of the SILP. Small ionic liquid droplets were also observed in the toluene samples. From the physical change alone, it can be concluded that toluene causes more leaching compared to n-heptane which showed no colour change. This is similar to findings in (Ferreira et al., 2011) which stated that the solubility of hydrocarbons in ionic liquid in general in increasing order is alkane followed by cycloalkane and aromatics.

Figure 21: Washing of Toluene

The washing of toluene has caused the de-ionized water to become cloudy, this is caused by the toluene forming an emulsion in the water which is due to its partial solubility.

Figure 22: After Settling

Figure 23: After Two Days of Settling

Table 18: Toluene AAS Result

Batch	Concentration (ppm)
1	27.09
2	15.98
3	24.06
4	27.05
5	27.92
6	27.04

As seen in Table 18 the results obtained from the AAS analysis is top standard, the values have way gone past the allowable range which is zero to four ppm of iron. Based on these findings the experiment which is repeated after this finding is diluted.

The peculiar reading which is the second batch is very cloudy as compared to the other samples, the high concentration of toluene in the sample may have affected the AAS masking the absolute amount detected.

Figure 24: Second Batch of Toluene Analysis after One Week

4.3 Temperature Parameter Test

The following are results of the experiment for n-dodecane at 25°C, 35°C and 45°C.

Table 19 : AAS Result for N-Dodecane at 25°C

Batch	Absolute	Concentration (PPM)
1	-0.002	-0.0293
2	-0.0018	-0.0264
3	-0.0024	-0.0352
4	-0.0018	-0.0264
5	-0.0016	-0.0234
6	-0.0011	-0.0161

Table 20: Conductivity Meter Result for N-Dodecane at 25°C

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	24.4	7.94	3.62	143.5	3.22
2	24.7	7.1	3.06	169.5	3.18
3	27.2	7.86	3.58	131.8	3.66
4	22.9	7.71	3.01	169.2	2.95
5	7.53	7.53	2.75	186	2.68
6	23.8	7.71	2.7	184.6	2.74

Table 21: AAS Result for N-Dodecane at 35°C

Batch	Absolute	Concentration (PPM)
1	-0.0027	-0.0396
2	-0.002	-0.0293
3	-0.0034	-0.0498
4	-0.0029	-0.0425
5	-0.0042	-0.0615
6	-0.0036	-0.0527

Table 22: Conductivity Meter Result for N-Dodecane at 35°C

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	23.1	7.39	3.22	179.4	2.92
2	24.6	7.8	3.36	144.6	3.61
3	23.7	7.64	3.49	150.1	3.31
4	23.5	7.44	3.7	136.9	3.92
5	24.5	8.2	2.82	193.1	2.88
6	22.4	7.5	3.21	162	3.09

Table 23: AAS Result for N-Dodecane at 45°C

Batch	Absolute	Concentration (PPM)
1	-0.0042	-0.0615
2	-0.0051	-0.0747
3	-0.002	-0.0293
4	-0.0012	-0.0176
5	-0.003	-0.044
6	-0.0022	-0.0322

Table 24: Conductivity Meter Result for N-Dodecane at 45°C

Batch	Temperature (°C)	pH	Conductivity (us)	Resistivity (k ohms)	TDS
1	22.7	7.54	3.12	168.6	3.28
2	22.3	8.45	4.19	117.8	4.03
3	24.3	6.9	3.47	145	3.5
4	24.1	7.07	3.46	146.6	3.64
5	24.6	7.23	3.85	131.9	3.36
6	23.5	7.11	3.64	140.7	3.48

The AAS result for all samples at all temperatures are in the negative range. Implying that there is no or trace amounts of leaching, as the AAS is only sensitive enough to measure till ppm levels of concentration. This result is similar to the experiment conducted on n-dodecane in the solvent variable.

The conductivity meter result, similar to the ones obtained in the n-dodecane test maintained an average reading of around three microsiemens. The effect of temperature on leaching cannot be seen as n-dodecane does not cause leaching in the ppm levels.
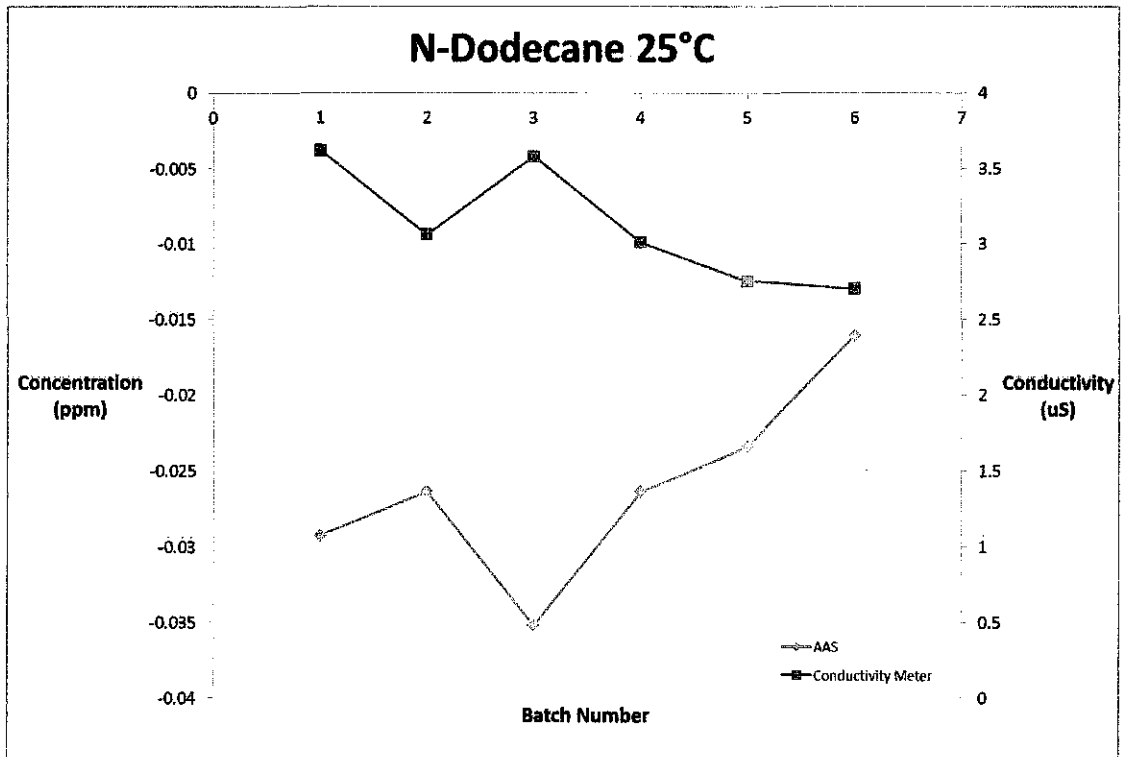
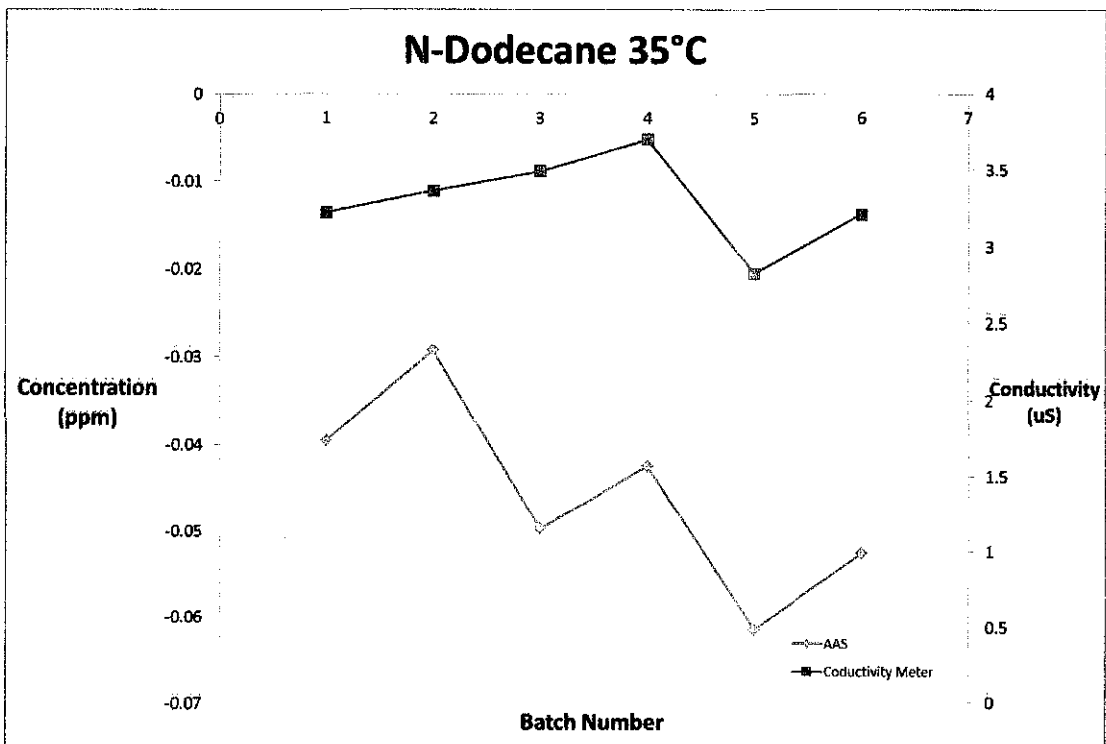Figure 25: AAS and Conductivity Meter Result for N-Dodecane at 25°C

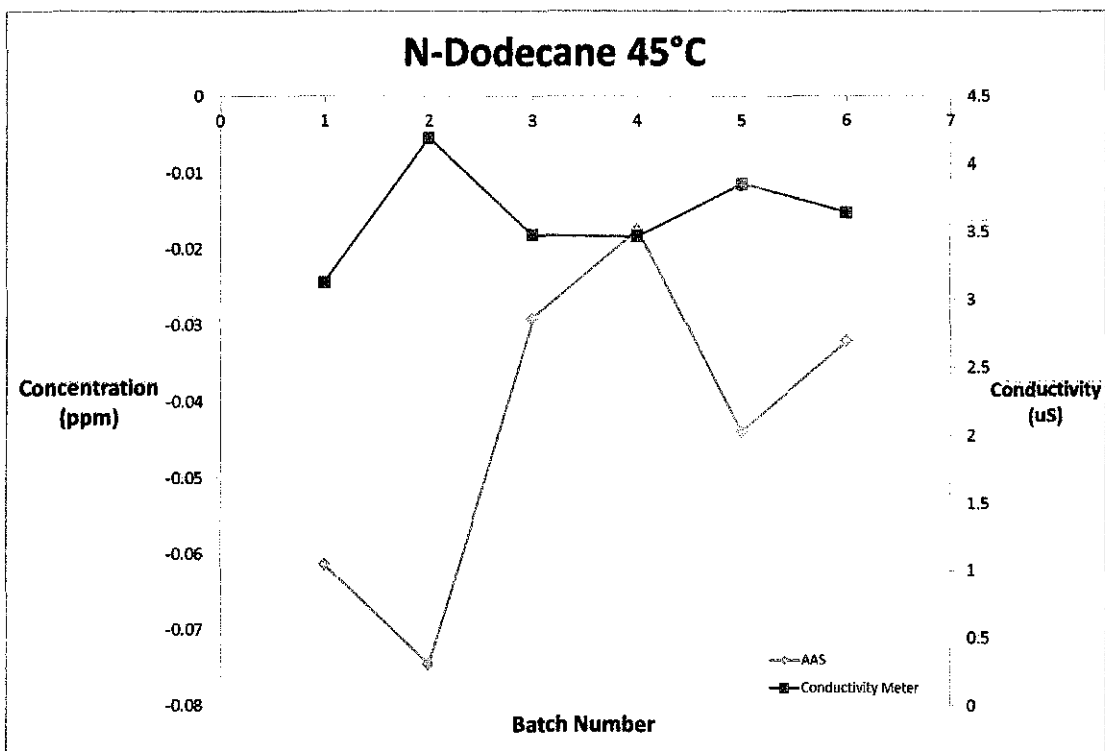Figure 26: AAS and Conductivity Meter Result for N-Dodecane at 35°C

Figure 27: AAS and Conductivity Meter Result for N-Dodecane at 45°C

The AAS results when plotted does not form any noticeable trends, the values are also negative in value. This indicates that the amount of iron in the sample is too little to be detected by the AAS. This is the reason why the effect of temperature on leaching cannot be detected. It cannot be confirmed yet as to the effect of temperature on leaching on a wide range, but for n-alkane species at lower temperatures, there is no significant effect on leaching.

This is also the same for the readings obtained by the conductivity meter. There are no noticeable trends in the graph, except for the downward trend observed at 25°C, which is expected of continuous passes of hydrocarbon. The reading for most of the samples is around 3 microsiemens.

4.4 Recommendation

The samples that is to be analysed using the conductivity meter is to be left idle for a longer period of time to allow the water and hydrocarbon phase to separate as much as possible. This is to minimize the effect of the hydrocarbon in the water which masks the reading of the conductivity meter and therefore causing errors.

To properly see the leaching trend of n-alkane if there is any, the amount of SILP tested should be increased or a more sensitive analyser which can detect ppb levels must be used. This is the reverse for toluene, an analyser which can detect ppm concentration at higher amounts accurately should be used. An alternative to this is to further dilute the sample. Unfortunately due to feasibility and project timeline experiments cannot be repeated using a different methodology.

CHAPTER 5

CONCLUSION

The result obtained from the solvent testing showed that aromatic hydrocarbon causes more leaching of supported ionic liquid phase as compared to n-alkanes. The effect of temperature on the leaching caused by n-alkanes is negligible at lower temperatures. Based on this information it can be concluded that n-alkanes do not cause leaching of supported ionic liquid phase at least in the ppm levels. The leaching of n-alkane at ppb levels is not known. Aromatics cause more leaching as compared to n-alkanes most likely because they are more polar due to the double bonds. Future experiments that can be conducted on this topic is the testing of the continuous passing of hydrocarbon over supported ionic liquid phase over a long period of time, to check for their stability and leaching. Different types of aromatic compounds should also be tested as to see its effect on leaching. The temperature variable should also be retested with aromatic compounds as to see the trend of varying temperature on leaching.

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Nomenclature

PILC – PETRONAS Ionic Liquid Center
SILP – Supported Ionic Liquid Phase
AAS – Atomic Absorption Spectrophotometer
BMIM – 1-Butyl-3-methylimidazolium