Drying of Ionic Liquid

by

Che Fatin Humaira Binti Che Yusuf
(ID: 11907)

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

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(Dr. Lukman Bin Ismail)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

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.

CHE FATIN HUMAIRA BINTI CHE YUSUF

ABSTRACT

Room Temperature Ionic Liquids (RTILs) are salts in liquid phase. Continuous use of RTIL in a process may cause it to be contaminated with water and organic impurities over time making it necessary to regenerate and purify the RTIL for recycle purposes. Thus, drying is needed during pre-treatment and purification of IL solution before it can be used in any application to reduce weight, increase ease of handling and eliminate unwanted effects of moisture content towards IL properties. Drying process of ionic liquid is important since moisture levels that are too high may affect performance and reliability in most applications such as during synthesis of RTILs using aqueous solution to necessitate anion exchange and also in concentrating Benfield solution for recycles purposes during removal of CO_2. Therefore, to obtain the most optimum condition of drying for ionic liquids, the study on kinetic of drying is reported here by investigating the effects of drying temperatures, initial water content, types of ionic liquid cation and anion and different drying methods on drying curves and their subsequent kinetic parameters. Drying was done at 100, 120, 140, 160 and 180°C. The ratios of ionic liquid to water used were 1:4, 1:3, 1:2, 1:1 and 2:1. Ionic liquids containing [bmim] cation with $[SO_4]$- or Phosphate-containing anion were used and drying methods applied were halogen lamp and vacuum drying methods. Thermogravimetric analysis which measures change of mass over time throughout the drying process was used to generate primary drying curves which were then manipulated to get secondary kinetic data. The drying process mainly occurred during falling rate period. Samples dried under higher temperature using vacuum drying have higher maximum drying rates, lower final moisture contents, higher drying constants and shorter drying times. The same result is observed for samples containing smaller anion and higher ratio of IL to water.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

RTILs	Room-Temperature Ionic Liquids
GPU	Gas Permeation Unit
NA	Not Applicable
MR	Moisture Ratio
ppm	parts per million
[bmim][$MeSO_4$]	1-butyl-3-methylimidazolium methylsulfate
[emim][HSO_4]	1-ethyl-3-methylimidazolium hydrogensulfate
[bmim][$(C_2F_5)_3PF_3$]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate
[mmim][DMP]	1,3-dimethylimidazolium dimethylphosphate
[bmim][Cl]	1-butyl-3-methylimidazolium chloride
[bmim][DCA]	1-butyl-3-methylimidazolium dicyanamide
[bmim][$MeSO_4$]	1-butyl-3-methylimidazolium methylsulfate
[bmim][$(C_2F_5)_3PF_3$]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate

NOMENCLATURE

Symbol	**Definition [SI unit]**
K	Drying Rate Constant [min^{-1}]
E_a	Activation Energy [J/mol]
T	Temperature [^oC]
t	Time [min]
R	Gas Constant [J/mol]
$MC_{infinity}$	Final Moisture Content [%]

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ionic liquids are salts in the liquid state with a low melting point of below 100°C (Binnemans, 2006). The first ionic liquid, ethanolammonium nitrate, was discovered in 1888 by Gabriel and Weiner. In the 1970s and 1980s, ionic liquids based on alkyl-substituted imidazolium and pyridinium cations, with halide or tetrahalogenoaluminate anions, were initially developed for use as electrolytes in batteries. Two major drawbacks for some applications were moisture sensitivity and acidity/basicity which leads to the concern of removing the moisture content from the ionic liquids. As an overview, several types of ionic liquids are liquid at room temperature and they are usually referred to as Room-Temperature Ionic Liquids (RTILs). The cations of ionic liquids are often large organic cations, like imidazolium, pyridinium, pyrrolidinium, quaternary ammonium or phosphonium ions (Figure 1.1).

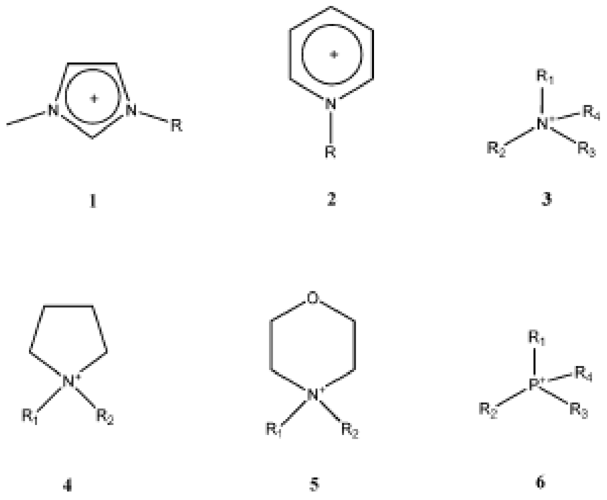


Figure 1.1 Common Cations in Ionic Liquids: (1) 1-alkyl-3-methylimidazolium; (2) 1-alkylpyridinium; (3) quaternary ammonium; (4) 1,1-dialkylpyrrolidinium; (5) 1,1-dialkylmorpholinium; (6) phosphonium (Binnemans, 2006)

The 1-alkyl-3-methylimidazolium ions are often used as the cationic part of ionic liquids. Cl- and Br- yield hydrophilic ionic liquids which are miscible with water and fluorinated anions like [PF_6]- allow preparation of hydrophobic ionic liquids that are immiscible with water. Hydrophobicity of ionic liquids containing [BF_4]- depends on the alkyl chain length of the associated cation whereby increasing alkyl chain length from butyl to hexyl to octyl increases hydrophobicity. Due to their hydrophobicity, they can be dried to very low final water contents. Recently, the studies on effect of water content in ionic liquids are getting increasing attention and several attempts to remove or reduce this moisture content have been done by incorporating the various methods of drying. In addition, we are also looking into the long-term stability of RTIL to identify the resulting decomposition products during the degradation due to thermal, mechanical, chemical or electrochemical stress. This is the basis for selection of appropriate processes for separation of decomposition products and regeneration of RTIL which is by using melt crystallization followed by subsequent drying process (Philipp, 2012).

Drying is a mass transfer process consisting of the removal of water or another solvent by evaporation from a solid, semi-solid or liquid. In some cases as described by Geankoplis (2003), water may be removed mechanically from solid materials by means of presses, centrifuging and other methods. This is cheaper than drying by thermal means for removal of water. A source of heat and an agent to remove the vapor produced by the process are often involved. Commonly, a gas stream such as air applies the heat by convection and carries away the vapor as humidity. Other possibilities are vacuum drying, where heat is supplied by conduction or radiation while the vapor produced is removed by the vacuum system.

1.2 Problem Statement

Molecular interactions that lead to the formation of aggregate structures in aqueous ionic liquid solutions have been the subject of recent studies. Water molecules can form hydrogen bonds with ionic liquid cations and anions. At low water concentrations, water molecules complex primarily with anions rather than with other water molecules and form clusters at high water concentrations. Complex formation can affect fluid properties, notably diffusivity. Although the anion is smaller than the cation, the anion diffusivity can be lower. This is attributed to water complexation.

Furthermore, ionic liquid’s properties can be highly dependent on water concentration, especially at low concentration. Additionally, solvation properties can change dramatically and necessitate careful control of water concentration.

Judging from the effects of water content in ionic liquid, drying or water removal is necessary to produce dry ionic liquid. The significance of producing dry ionic liquid is as an alternative to dry water and dry gel because they tend to collapse due to the temporal water vaporization in an open system. Dry ionic liquid is free from this undesirable defect due to its non-volatility. Based on literature review, there is only one paper which discussed about drying process of ionic liquid using membrane drying (Lipscomb, 2011) and it appears that there is not much development which deals with kinetic of drying for ionic liquids. Therefore, this work will contribute in the subject of drying kinetic for ionic liquid in order to analyze the optimum drying condition for ionic liquids based on drying curves analysis.

1.3 Aim and Objectives

The aim of this project is to study the kinetic of drying process for ionic liquids under different operating parameters and conditions. There are several objectives to be achieved in this study:

i. To study the effect of drying temperature on drying rate of ionic liquids
ii. To study the effect of different types of cation and anion on drying of ionic liquids
iii. To study the effect of moisture content on drying rate of ionic liquids
iv. To compare the performance of different drying methods in drying of ionic liquids

1.4 Scope of Study

In studying the kinetic of drying for ionic liquids, several parameters need to be set as the upper and lower boundary for the process. The first variable to be investigated is the temperature of drying for the ionic liquids. Lazzus (2011) points out that ionic liquid have favorable thermal stabilities and operate over large temperature ranges. The upper limit of the liquid range is usually bounded by the thermal decomposition temperature of the ionic liquid, since most ionic liquids are nonvolatile. In most cases, the decomposition occurs with complete mass loss and volatilization of the component fragments. Most ionic liquids will start to decompose above 300°C with thermal decomposition for imidazolium-based ionic liquids range between 225°C to 422°C (Lazzus, 2011). Moreover, since the ionic liquids to be dried contain significant amount of water, we have to note the boiling point of 100°C. Combining these two factors, the drying temperature will be varied between 100°C to 180°C.

Furthermore, in order to investigate the performance of different drying methods in drying ionic liquids, two different processes will be used in this study. The first method is by using halogen lamp drying whereby the heating element comprises of a glass tube filled with inert halogen gas containing a tungsten wire heating element. The second method will be vacuum drying whereby the ionic liquid sample is dried by means of hot circulating air under vacuum condition. Apart from different drying methods, different combination of ionic liquid anion and cation consisting of [bmim] cation, $[SO_4]^-$ and Phosphate-containing anion are also chosen since their molecular structures and diameters are different from each other and these may also affect the drying process and kinetic of the ionic liquid samples.

In drying of ionic liquids, solutions of ionic liquid samples will be prepared initially with different ionic liquid to water ratio. This is to study the effect of initial water content in ionic liquid samples on the drying performance. To select the ratio of water to ionic liquid, references were made on the application of Benfield Process whereby it is a thermally regenerated cyclical solvent process that uses a solution of amine sorbent in ionic liquid to remove CO_2, H_2S and other acid gas components (Baugh, 2012). Permeance of CO_2 increases at low water content and decreases after reaching a maximum value due to the hydrogen bond. The permeance of CO_2 increases from 11.5 to 13.8 GPU, where the water content increases from 0 to 0.10, and then decreases to 13.3 GPU at the water content of 0.15. Thus, for the purpose of my study, the range of ionic liquid to water content ratio will be between 1:4 and 2:1.

CHAPTER 2

LITERATURE REVIEW AND THEORY

This chapter will focus on the analytical, critical and objective review of written materials on kinetic study of drying for ionic liquids. It was found out that drying of ionic liquids have been done by many researchers for the purpose of purification of ionic liquid for their experiments. However, there is not much emphasis on the behavior of ionic liquid during the drying process itself especially on the kinetic part.

2.1 Chronological Development of Ionic Liquid Study

Table 2.1 Chronological Development of Ionic Liquid Study

No.	Development in Ionic Liquid	Year	Contributors
1.	Discovery of the first ionic liquid, ethanolammonium nitrate.	1888	Gabriel and Weiner
2.	Synthesis of earliest RTILs, ethylammonium nitrate.	1914	Paul Walden
3.	Ionic liquids based on alkyl-substituted imidazolium and pyridinium cations with halide or tetrahalogenoaluminate anions were developed for use as electrolytes in batteries.	1970 to 1980	NA
4.	Imidazolium is recognized as the most stable ionic liquid cation.	1982	Wilkes and Hussey
5.	A study on solution thermodynamics of imidazolium-based ionic liquids in water was conducted.	2001	Anthony, Maginn and Brennecke
6.	Relationship between water content and physical properties of aliphatic quaternary ammonium imide-type ionic liquid containing metal ions was established.	2005	Katase, Imashuku, Murase,Hirato and Awakura
7.	Interaction of ionic liquid with water with variation of water content in 1-butyl-3-methyl-imidazolium hexafluorophosphate was investigated.	2007	Seth, Chakraborty, Setua, and Sarkar
8.	Development of membrane drying of ionic liquid solutions by using reverse osmosis technique.	2011	Lipscomb and Du

2.2 The Drying Curve

The literatures being considered for this study will focus on drying process. Referring to an article by Traub (2002), for each and every product, there is a representative curve that describes the drying characteristics for that product at specific temperature, humidity, drying methods and conditions. Figure 2.1 represents a plot of total moisture content and drying rate versus time whereby drying occurs in three different periods (McCabe et al., 1993). The first phase or initial period is where sensible heat is transferred to the product and the contained moisture which enables the subsequent processes to take place. This is the heating up of the product from the inlet condition to the desired condition. During this period, the rate of evaporation increases dramatically with mostly free moisture being removed. Moving on to the second phase of constant rate period, free moisture persists on the surfaces and the rate of evaporation alters very little as the moisture content decreases. During this period, drying rates are high and higher inlet air temperatures than in subsequent drying stages can be used without detrimental effect to the product. There is a gradual and relatively small change in the product temperature during this period. The next stage will be falling rate period during which migration of moisture from the inner interstices of each particle to the outer surface becomes the limiting factor that reduces the drying rate.

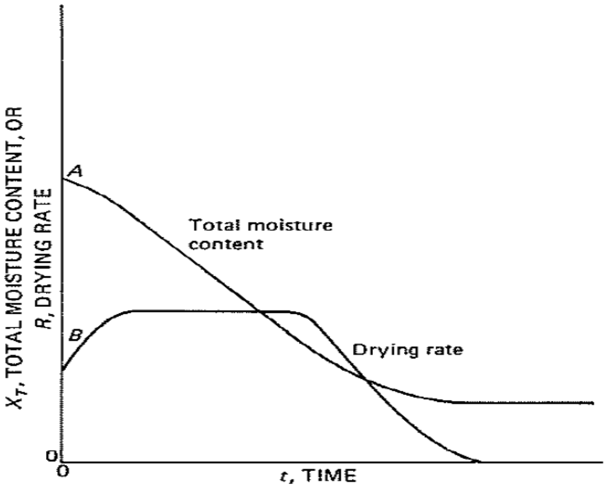


Figure 2.1 Total Moisture Content and Drying Rate versus Time (McCabe et al., 1993)

2.3 Kinetic of Drying

A series of work and studies on the kinetic of drying by thermal analysis have been performed previously by researchers to determine the kinetic data from the whole drying process of any materials. According to Pope et al. (1977), to extract the data for kinetic information, we have to recognize a reaction mechanism from the shape of the weight loss curve. Where a single mechanism predominates, as in the case of gas phase or solution reactions, it is often possible to describe the reaction by a general rate law:

$$\frac{dC}{dt} = k(1-C)^n$$

where: C = fractional conversion

t = time (min)

k = rate constant (min-1)

n = reaction order

Consider the reaction:

$$A \rightarrow \text{ Products}$$

If first order kinetic is followed, then the rate of the reaction is proportional to the concentration of A:

Rate = k (concentration A)

In the case of drying the reaction is:

$$(H_2O) \text{ absorbed} \rightarrow (H_2O) \text{ Gas}$$

Let α be the concentration of (H_2O) absorbed at t=0 and (α-x) be the concentration of (H_2O) absorbed at any other time denoted by t. The reaction rate for desorption is $\frac{dx}{dt} = k(\alpha - x)$. On integration, this equation becomes:

$$k = \frac{1}{t}\ln(\frac{\alpha}{\alpha - x})$$

The k values calculated can be used to plot a kinetic graph of ln k against 1/T (Figure 2.2) which will produce a reasonable straight line with gradient –E/R whereby R is the gas constant according to:

$$\ln k = \ln Z - \frac{E}{RT} \text{ (Z is Arrhenius frequency factor, min}^{-1}\text{)}$$

Thus, the activation energy, E (J/mol), can be directly obtained from the plot. Furthermore, all the kinetic value can also be used to approximate the theoretical drying time at any temperature via the following equation:

$$t\ (drying\ time) = \frac{4.5 \times 0.0113}{k_T}$$

where: t = drying time at the desired temperature (min)

k_T = calculated rate constant at the desired temperature, T (min^{-1})

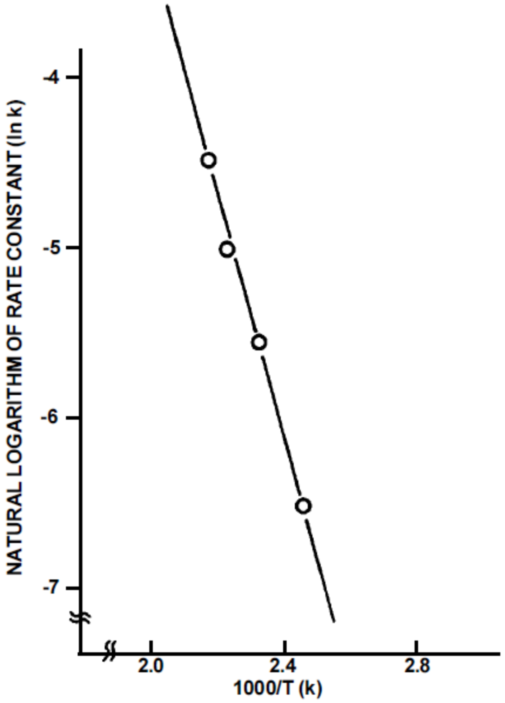
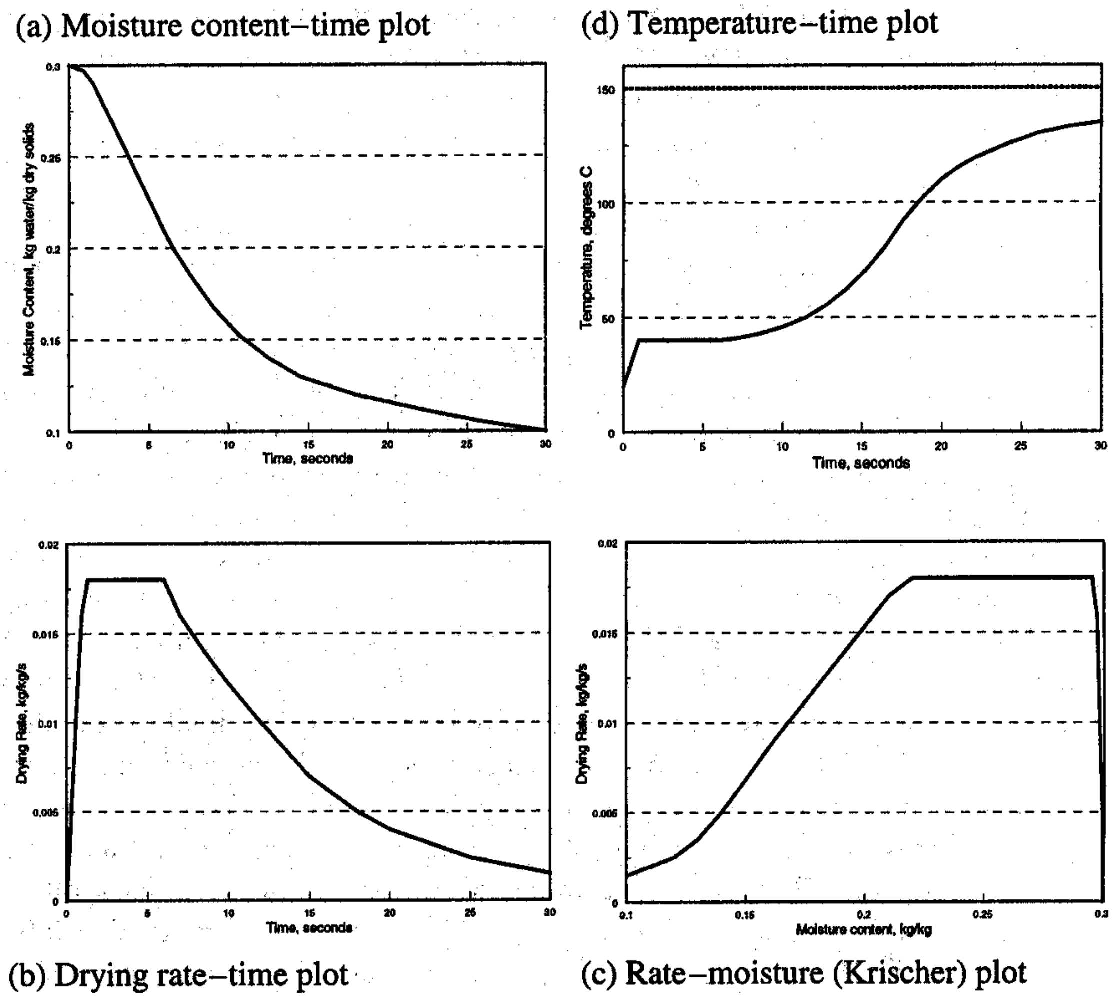


Figure 2.2 Kinetic of Drying (Pope et al., 1977)

Furthermore, an analysis done by Kemp et al. in 2001 suggested several methods for processing the kinetic data obtained from drying. Generally, the approach in analyzing the kinetic data will depend on several factors; particle size, initial and final moisture content, predominant drying regime (unhindered or falling-rate), air velocity, level of accuracy required for the data and availability of measuring equipment. All these data will be used to generate useful drying curves that are interrelated such as Figure 2.3 (a) showing drying curve obtained directly from weight loss-time data (moisture content vs. time). In addition, Figure 2.3 (b) plots drying rate curve obtained directly from humidity-time data (drying rate vs. time) while Figure 2.3 (c) represents time independent or Krischer curve derived from the combination of the previous curves (drying rate vs. moisture content). It is used as the basis for the characteristic curve scaling method. Finally, Figure 2.3 (d) shows a temperature-time plot representing how the sample temperature varies during the experiment.


(a) Moisture content–time plot

(d) Temperature–time plot

(b) Drying rate–time plot

(c) Rate–moisture (Krischer) plot

Figure 2.3 Drying rate and temperature curves for a particle (Kemp et al., 2001)

Figure 2.3 shows the four interrelated curves obtained by simulation of a single particle undergoing convective drying in a hot air stream at a constant 150°C. This approach can be applied to the drying of ionic liquids since under the chosen conditions, the material is assumed to show an induction (initial heating) stage, unhindered drying (constant rate) period and a hindered drying (falling rate) period.

2.4 Drying Kinetic Study by Thermogravimetric Analysis

A thermogravimetric approach was applied by Chen et al. (2012) to study the drying of powdered rice straw particles to determine the drying kinetic under isothermal drying conditions. The results obtained by Chen et al. (2012) are presented in forms of drying curve shown in Figure 2.4 and 2.5. Temperature significantly affected drying rate and drying time. More moisture can be removed with high temperature drying because it is the main driving force of moisture evaporation. As seen from Figure 2.5, there was no constant rate period. Thus, the drying process can be divided into two periods, the rising and falling rate period.

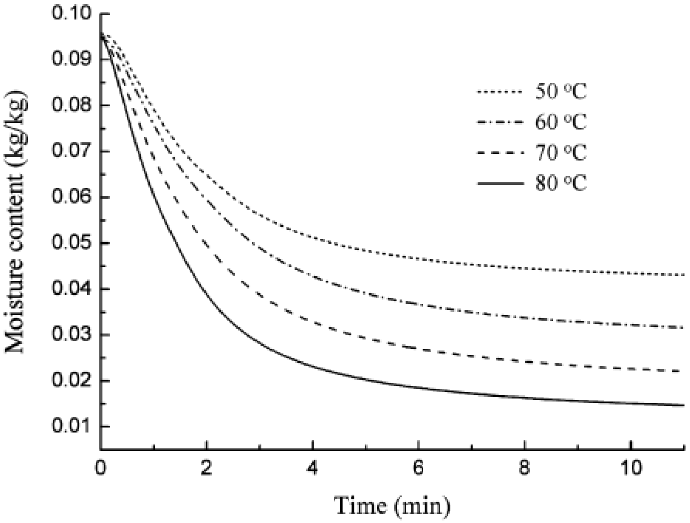


Figure 2.4 Drying Curve of Moisture Content versus Time (Chen et al., 2012)

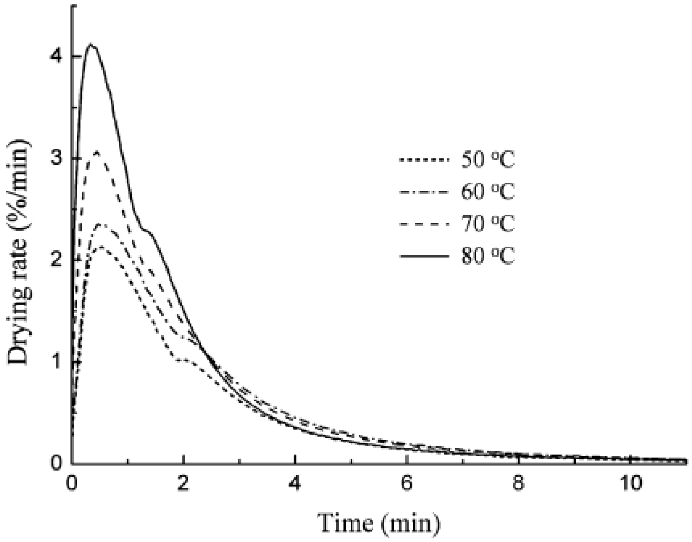


Figure 2.5 Drying Curve of Drying Rate versus Time (Chen et al., 2012)

By manipulating the thermogravimetric data as primary data, Ndukwu (2009) had calculated the drying constant, K (min^{-1}), by calculating moisture ratio of samples throughout the drying process by using the following equations:

$$MR = e^{-Kt}$$

$$MR = \frac{M - M_e}{M_i - M_e} = e^{-Kt}$$

$$K = -\frac{\ln MR}{t}$$

MR is moisture ratio, M_i is initial moisture content, M_e is equilibrium moisture content, M is moisture content at time t and K is drying constant. The drying constant was calculated from slope of negative natural log of moisture ratio against time (Figure 2.6).

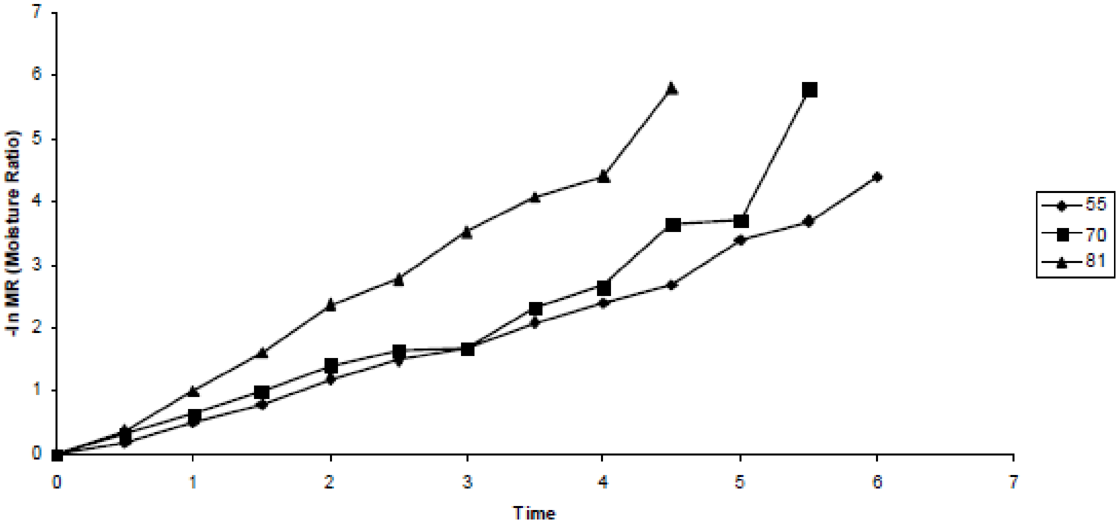


Figure 2.6 Drying Curve of –ln MR versus Time (Ndukwu, 2009)

2.5 Drying of Salt Solution

In the study of ionic liquid drying process, not much literature is available currently. However, considering the similar behaviour of ionic liquid with salt solution, we can determine several drying parameters by comparing them. As shown in Figure 2.7, the higher the salt concentration, the lower the decline in moisture. This was caused by higher moisture contents and lower salt contents in lower brine concentrations, allowing faster removal of water (Jason et al., 1992). The higher the salt, the lower the initial moisture of the solution and the faster it reaches equilibrium (Yu et al., 1982).

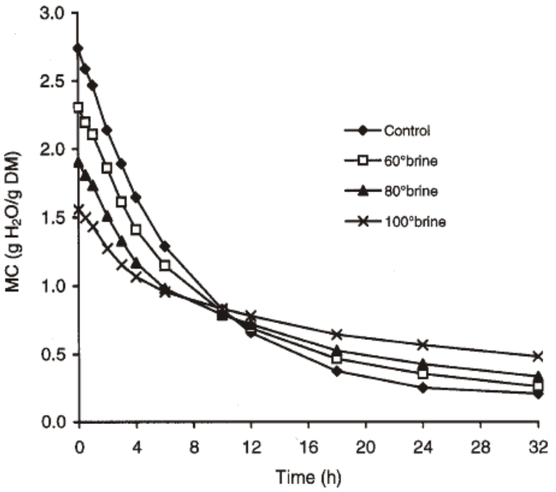


Figure 2.7 Drying Curve of Brines of Different Concentrations (Jason et al., 1992)

2.6 Application of Ionic Liquid in Removal of Carbon Dioxide

Ionic liquids are capable of acting as solvents for amine CO_2 absorbent compounds in CO_2 separation processes and it will enhance the sorption of the CO_2 by the amine. A cyclic sorption process for separating CO_2 in Benfield Process from a gas stream, such as flue gas or natural gas, brings the gas stream into contact with an absorbent solution of amine CO_2 sorbent in ionic liquid solvent followed by desorbing the CO_2 to regenerate the amine (Baugh, 2012). Referring to Figure 2.8, the performance of the process is affected by the water content whereby the optimum permeance of CO_2 is at 0.10 water content. From this data, we could expand the study to evaluate the performance of ionic liquids with different initial water content towards drying or water removal process in regenerating the ionic liquid.

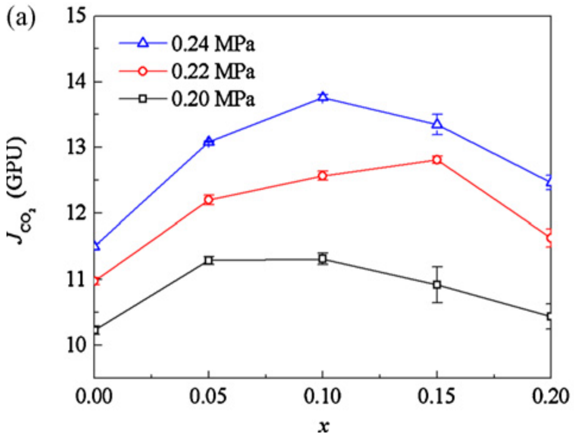


Figure 2.8 Permeance of CO_2 at Different Water Content (Baugh, 2012)

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Overview

This chapter will focus on methods and procedure used to achieve all the objectives of the project. In analyzing the kinetic of drying, moisture content measurement is done individually for effect of drying temperatures, types of cation/anion in ionic liquid sample, initial water contents and drying methods. Modern portable moisture balances are available with built in infrared heaters which directly measures the moisture content of the product and gives a profile of moisture content variations with time. The curve of moisture content as a function of time is then plotted. While different samples and different conditions of drying often give rise to curves of very different shapes in the falling rate period, the curve in Figure 3.1 occurs frequently and is expected for most of the experimental setups in this study.

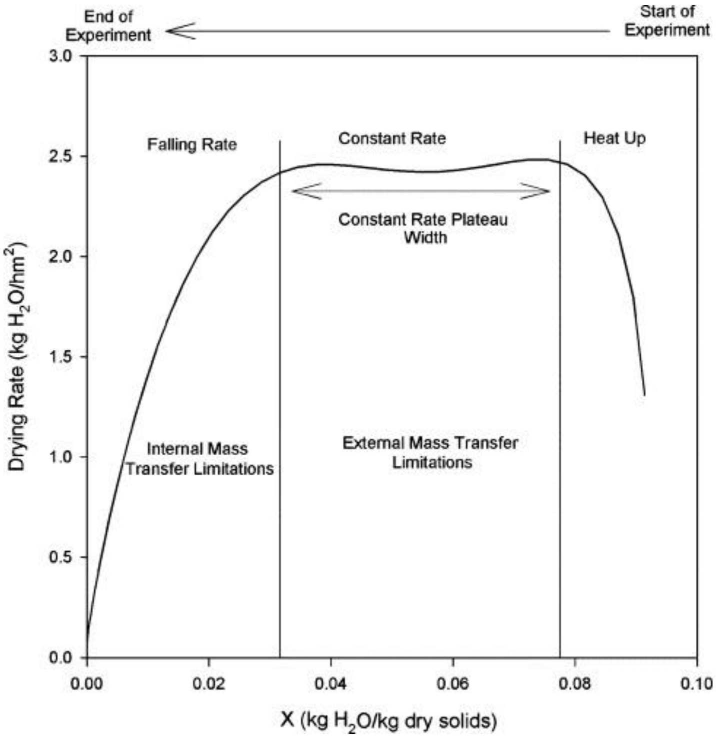


Figure 3.1 Expected Drying Curve from Moisture Analyzer

During the above measurements, the following conditions are followed:

1. The sample should be subjected to similar conditions of radiant heat transfer
2. Air should have the same temperature, humidity and velocity throughout the process

Electronic moisture balances with online data collection is used to establish drying curves of ionic liquid samples.

3.2 Effect of Drying Temperature

The initial water content of raw 1-butyl-3-methylimidazolium chloride is measured using Karl-Fischer titrator. Five samples of 0.5 g 1-butyl-3-methylimidazolium chloride mixed with 0.5 g distilled water (ionic liquid to water ratio of 1:1) are prepared and weighed in sample vials using mass balance. The heating temperature of Halogen Moisture Analyzer is set to 100°C for a period of 1 hour. Solution of ionic liquid sample is placed in the heating tray for the moisture analyzer to weight the initial mass and the heating process is started. After 1 hour, the ionic liquid sample is removed and the heating tray is cleaned. The result of overall moisture content over the period of 1 hour and final mass of sample is collected. The experiment is repeated at temperatures of 120°C, 140°C, 160°C and 180°C to generate different drying curves for each temperature.

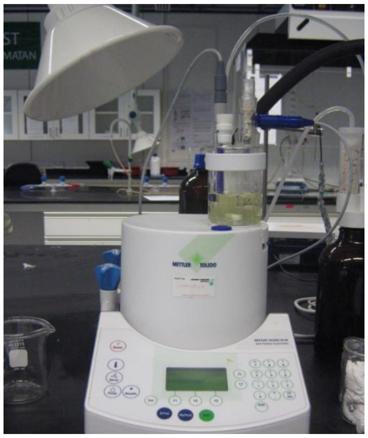


Figure 3.2 METTLER TOLEDO Karl Fischer Titrator

Figure 3.3 METTLER TOLEDO Halogen Moisture Analyzer

3.3 Effect of Different Types of Cation and Anion

The initial water contents of every raw ionic liquid samples are measured using Karl-Fischer titrator. Five samples of 0.5 g 1-butyl-3-methylimidazolium chloride mixed with 0.5 g distilled water (ionic liquid to water ratio of 1:1) are prepared and weighed in sample vials using mass balance. The heating temperature of Halogen Moisture Analyzer is set to 100°C for a period of 1 hour. Solution of ionic liquid sample is placed in the heating tray for the moisture analyzer to weight the initial mass and the heating process is started. After 1 hour, the ionic liquid sample is removed and the heating tray is cleaned. The result of overall moisture content over the period of 1 hour and final mass of sample is collected. The experiment is repeated using different types of ionic liquid to generate different drying curves for each ionic liquid samples.

To investigate the effects of different cation in ionic liquids, the following samples will be used:

i. 1-butyl-3-methylimidazolium methylsulfate, [bmim][$MeSO_4$]
ii. 1-ethyl-3-methylimidazolium hydrogensulfate, [emim][HSO_4]
iii. 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]
iv. 1,3-dimethylimidazolium dimethylphosphate, [mmim][DMP]

As for the anion part, we will use four different bmim-cation-based ionic liquids:

i. 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

ii. 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]
iii. 1-butyl-3-methylimidazolium methylsulfate, [bmim][$MeSO_4$]
iv. 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]

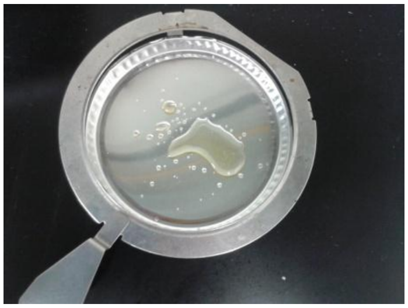


Figure 3.4 [bmim][Cl] Sample in Heating Tray

3.4 Effect of Initial Water Content

The initial water content of raw 1-butyl-3-methylimidazolium chloride is measured using Karl-Fischer titrator. A sample of 0.5 g 1-butyl-3-methylimidazolium chloride mixed with 2.0 g distilled water (ionic liquid to water ratio of 1:4) is prepared and weighed in a sample vial using mass balance. The heating temperature of Halogen Moisture Analyzer is set to 100°C for a period of 1 hour. Solution of ionic liquid sample is placed in the heating tray for the moisture analyzer to weight the initial mass and the heating process is started. After 1 hour, the ionic liquid sample is removed and the heating tray is cleaned. The result of overall moisture content over the period of 1 hour and final mass of sample is collected. The experiment is repeated with distilled water mass of 1.5 g, 1.0 g, 0.5 g and 0.25 g to generate different drying curves under different ratio.

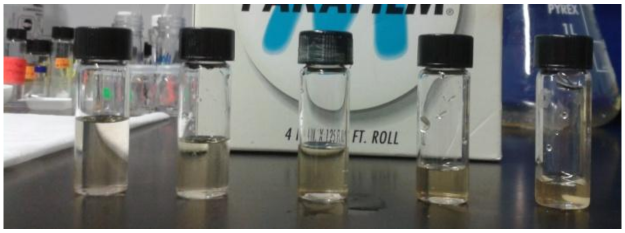


Figure 3.5 Samples of 1-butyl-3-methylimidazolium chloride with Different Ratio of Water

Figure 3.6 Weighing Mass of 1-butyl-3-methylimidazolium chloride

3.5 Effect of Drying Methods

The initial water content of raw 1-butyl-3-methylimidazolium chloride is measured using Karl-Fischer titrator. Six samples of 0.5 g 1-butyl-3-methylimidazolium chloride mixed with 0.5 g distilled water (ionic liquid to water ratio of 1:1) are prepared and their initial mass is weighed in a sample vial using mass balance to ensure uniform mass for all samples. The heating temperature of Vacuum Drying Oven is set to 100°C for 14 to 16 vacuum drying cycles (alternating between 50 and 900 millibar). After a stable temperature is achieved, solution of ionic liquid samples are placed in sample trays and left inside the oven before the vacuum pump is started. At 10 minutes interval, the vacuum pump is stopped and one ionic liquid sample is removed to weigh its current mass until a steady mass reading is achieved. The result of overall mass change over the period of 1 hour and final mass of samples are tabulated to generate drying curves for this method.

3.6 Research Methodology

From the raw data of moisture content readings over time obtained from moisture loss reading of the Halogen Moisture Analyzer and weight loss measurement from the Vacuum Drying Oven samples, a drying curve of Moisture Content against Time will be generated. Furthermore, by tabulating the weight loss data over time, the drying rate of ionic liquid samples can be calculated and plotted over time to produce another drying curve of Drying Rate against Time.

For analyzing kinetic of drying for ionic liquid, a graph of Negative Natural Log of Moisture Ratio against Time is plotted whereby the drying constant, K (min^{-1}), can be calculated from the slope of the graph. Further tabulation of different isothermal moisture loss curves can give us different K values and plotted as Natural Log of K against Inverse of Temperature to give a reasonable straight line with gradient E_a/R which enables us to get the activation energy of the drying process. All the data tabulated data and graphs will be explained in the next chapter.

3.7 Tools Required

The tools required for this study can be divided into three major parts which are equipment, apparatus and chemical. All the tools required have been summarized in Table 3.1.

Table 3.1 Tools Required

Equipment	• METTLER TOLEDO Halogen Moisture Analyzer • Thermo Scientific Vacuum Drying Oven • METTLER TOLEDO Karl Fischer Titrator • Mass Balance
Apparatus	• Sample Vials • Spatula • Pasteur pipette • Parafilm • Labelling Stickers
Chemical	• Ionic Liquids • Distilled Water

3.8 Gantt Chart

Table 3.2 Gantt Chart for Project Development

No.	Detail/Week (FYP I)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Preliminary research work on Ionic Liquid and Drying Process	■	■	■	■	■	■	■	■						
2.	Initial preparation of Ionic Liquid samples and required equipments									■	■				
3.	Tuning of parameters and operating conditions											■	■		
4.	Initial testing of experimental setup and data gathering													■	■

No.	Detail/Week (FYP II)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Determine the effect of temperature on drying of Ionic Liquid	■	■	■	■										
2.	Determine the effect cation/anion on drying of Ionic Liquid			■	■	■									
3.	Determine the effect of water amount on drying of Ionic Liquid				■	■	■	■							
4.	Determine the effect of drying methods on drying of Ionic Liquid							■	■	■	■				
5.	Data gathering, synthesis and analysis of drying curves for each parameter								■	■	■				
6.	Interpretation of drying curves for each parameter											■	■		
7.	Compilation of data analysis and Conclusion													■	■

CHAPTER 4

RESULT AND DISCUSSION

This chapter presents the finding and outcome of the project work done on kinetic of drying for ionic liquid. All the gathered data from the project work are presented in the form of tables and figures including graphs showing drying curves for all the objectives studied. The data had been analyzed and results had been discussed accordingly with regard to drying of ionic liquid and its kinetic data.

4.1 Overview

For the experiments described above, the raw data will be the total moisture content generated from the METTLER TOLEDO Halogen Moisture Analyzer (Figure 4.1) for a period of 60 minutes in 2 minutes interval for every reading. A period of 60 minutes is chosen due to the indication from initial samples testing whereby equilibrium moisture content for most ionic liquid samples are achieved in that duration. By taking into consideration the boiling point of water, the temperature is set at 100°C in order to dry the water content in the samples. In addition, the temperature settings are also increased gradually until 180°C to investigate the differences in their drying curves.

Thermogravimetric analysis (TGA), which can follow weight loss over a wide temperature range or over a long period of time at a specific temperature, on small (10-100 mg) samples, is a technique which rapidly provides data for understanding drying processes. The results yield not only quantitative information about the amount of moisture present, but also information about the rate of weight loss which can be used to determine kinetic parameters according to drying curves obtained.

Initially, all raw ionic liquid samples are tested by Karl Fischer Titration to determine its initial water content resulting in readings of less than 100 ppm (0.01%) for all samples and these small traces of water can be assumed as negligible. Thus, for the purpose of this experiment, water is mixed initially with all ionic liquid to produce a solution with ionic liquid to water ratio of 1:1 for most of the samples to be dried to ensure that drying process is possible despite the hygroscopic nature of ionic liquid.

⑤ Dimethylimim

```
ID                            1
Timer                 60:00 min
Drying temp.            100 °C
Weight                  1.045 g
                     100...0 %DC

  2:00 min          93.59 %DC
  4:00 min          86.32 %DC
  6:00 min          79.90 %DC
  8:00 min          73.97 %DC
 10:00 min          68.71 %DC
 12:00 min          64.21 %DC
 14:00 min          60.57 %DC
 16:00 min          57.70 %DC
 18:00 min          55.41 %DC
 20:00 min          53.78 %DC
 22:00 min          52.44 %DC
 24:00 min          51.48 %DC
 26:00 min          50.81 %DC
 28:00 min          50.33 %DC
 30:00 min          49.86 %DC
 32:00 min          49.47 %DC
 34:00 min          49.28 %DC
 36:00 min          49.09 %DC
 38:00 min          48.90 %DC
 40:00 min          48.71 %DC
 42:00 min          48.61 %DC
 44:00 min          48.61 %DC
 46:00 min          48.42 %DC
 48:00 min          48.42 %DC
 50:00 min          48.42 %DC
 52:00 min          48.33 %DC
 54:00 min          48.23 %DC
 56:00 min          48.33 %DC
 58:00 min          48.23 %DC

Total time          60:00 min
End result          48.23 %DC
```

Figure 4.1 Moisture Content Reading from Moisture Analyzer

4.2 Effect of Drying Temperature

The data obtained from the experiments are indicated in Figure 4.2 and 4.3 showing the change in moisture content and drying rate over time for temperature settings of 100°C, 120°C, 140°C, 160°C and 180°C with constant ratio of ionic liquid to initial water content (ratio of 1:1). The ionic liquid used is 1-butyl-3-methylimidazolium chloride for all samples. The moisture content is extracted directly from the moisture analyzer reading in percentage from 100% to equilibrium moisture content. Whereby the drying rate is calculated based on the initial and current weight of ionic liquid sample over a period of time using the formula below:

$$Drying\ rate\ (g/min) = \frac{Initial\ weight(g) - Current\ weight(g)}{time(\mathrm{min})}$$

4.2.1 Drying Curves

From the results obtained, Figure 4.2 resembles exactly that of typical moisture content plot for normal drying process whereby the graphs decrease at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content of the sample under the desired temperature. This is possible since the ionic liquid samples are prepared such that it is initially saturated with water content and thus, with sufficient heating under suitable temperature, the water content is gradually released to dry the ionic liquid. However, the final moisture content of the dried ionic liquid sample is not exactly 0%. There is still some percentage of moisture content available since it is well known that water is omnipresent in ionic liquids. Dry ionic liquid will absorb water from atmosphere especially when heat is applied to it. Imidazolium based ionic liquids in particular are extremely hygroscopic and they absorb water from atmosphere. These are the reasons why the ionic liquid samples need to be initially saturated with water and the final moisture content after drying is only between 40% and 50%.

For drying of all samples, the experiments are repeated twice to ensure data accuracy and repeatability. Error bars based on standard deviations between the first and second trials are presented in Figure 4.2. Since it is observable that the error bars are very small due to very low value of standard deviations, they can be assumed as negligible for all samples. The values of standard deviation for all samples are tabulated in APPENDIX A.

Referring to Figure 4.3, the shape of the drying rate curve is different to the typical drying rate curve shown in Chapter 2. There are only two phases of drying, initial period and falling rate period observed from the plots. It is highest at the first 5 minutes of continuous drying for all temperatures and decreases with time. This is a result of low internal resistance of moisture at the beginning of drying. Therefore, when energy is impacted, moisture can easily move to surface to be evaporated. As the drying progressed, more energy is needed due to the hygroscopic characteristic of ionic liquid which hinders the migration of moisture from the inner interstices of each particle to the outer surface. Consequently, the drying rate decreases gradually in the falling rate period and becomes zero.

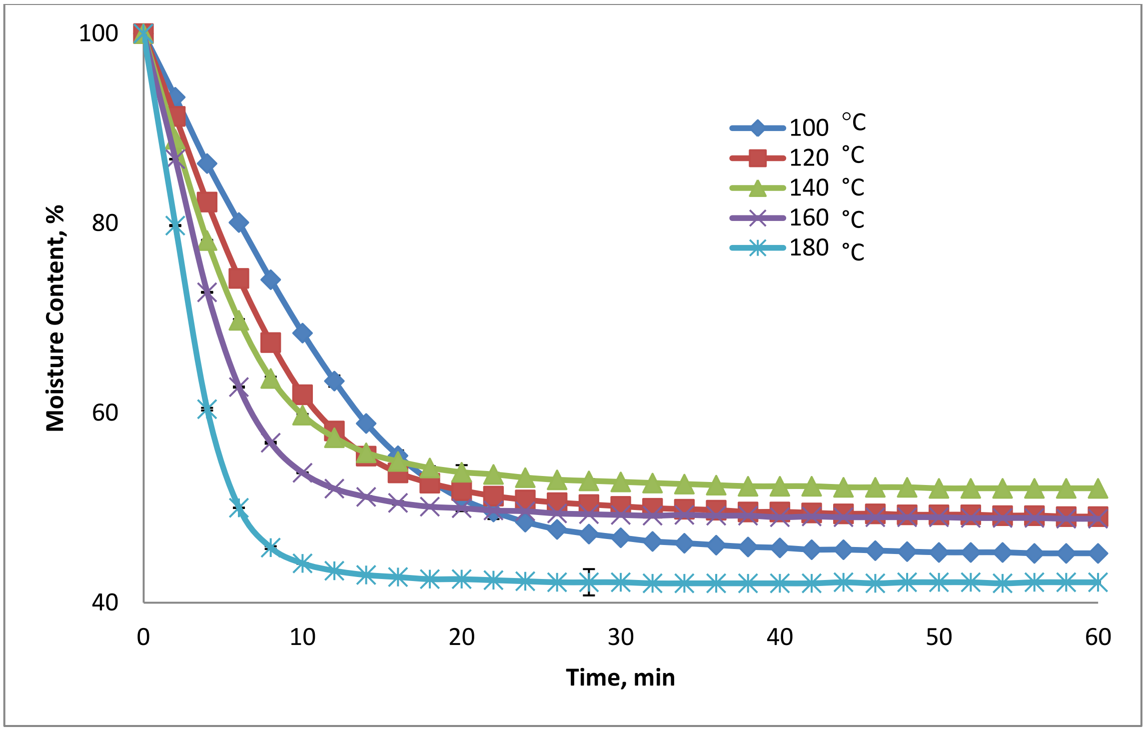


Figure 4.2 Drying Curve of Moisture Content versus Time at Different Temperatures

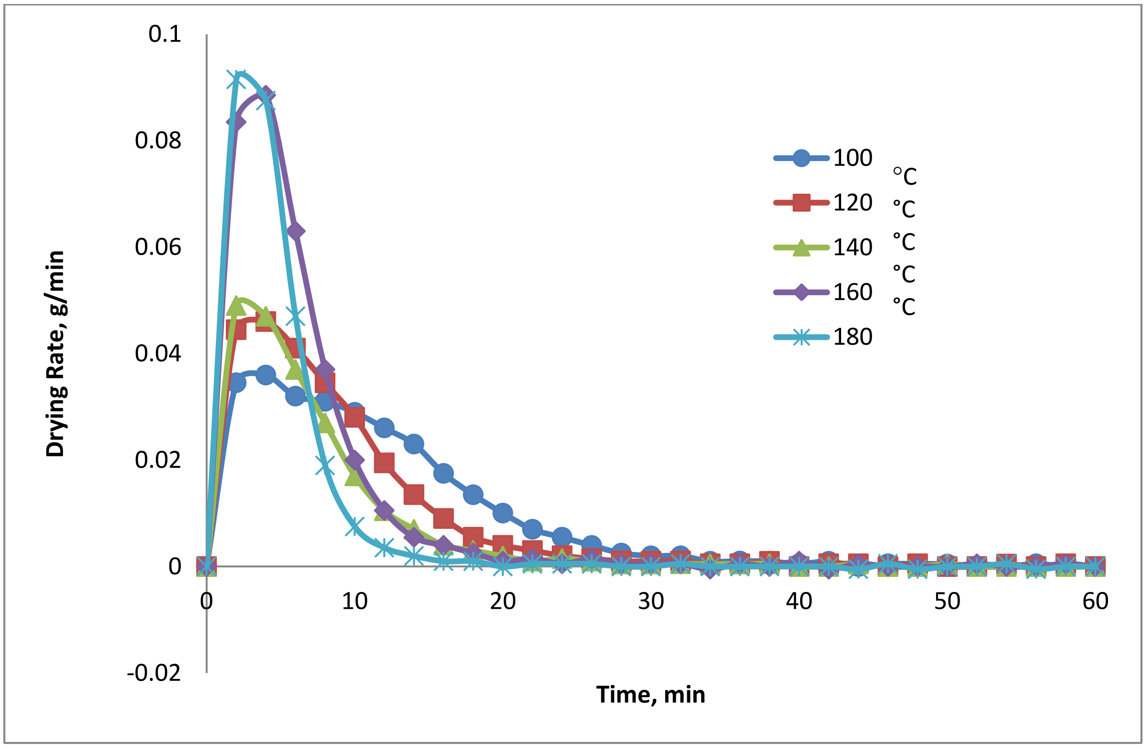


Figure 4.3 Drying Curve of Drying Rate versus Time at Different Temperatures

4.2.2 Analysis on Drying Kinetic

From both the moisture content and drying rate curves, it is observed that the moisture content decreases faster and in larger amount for higher drying temperature and the maximum drying rate is also higher (Table 4.1). The difference in vapour pressure between the inner interstices and surface of ionic liquid sample is the driving force causing the outward movement of moisture. The vapour pressure exerted by water rises very rapidly with increasing temperature and thus increases the drying rate. In addition, the use of high temperatures increases the capacity of air for holding water vapour from being reabsorbed by the ionic liquid and its drying potential which results in lower final moisture content ($MC_{infinity)}$ as indicated in Table 4.1. This can also be associated with the drying rate constant, k (min^{-1}), for each temperatures calculated by the method explained in Chapter 2.

Table 4.1 Experimental Data from Drying Curves

Temperature (°C)	Max Drying Rate (g/min)	$MC_{infinity}$ (%)
100	0.036	45.19
120	0.046	49.07
140	0.049	52.05
160	0.089	48.85
180	0.091	42.15

In order to obtain the drying constant, we have to know the moisture ratio of the ionic liquid samples throughout the drying process. Consequently, the drying constant can be obtained from the slope of negative natural log of moisture ratio against time (-ln MR versus time). The governing mathematical equations are as follows:

$$MR = \frac{M - M_e}{M_i - M_e} = e^{-Kt}$$

$$K = -\frac{\ln MR}{t}$$

Where MR is moisture ratio, M_i is initial moisture content, M_e is equilibrium moisture content, M is moisture content at time t and K is drying constant. Referring to Figure 4.4, for higher drying temperature, the slopes of the curve are steeper which also represent higher drying constant. This is due to drying under higher temperature leads to faster drying process and the reaction proceeds at greater speed with higher kinetic energy. The associated kinetic data are tabulated in Table 4.2.

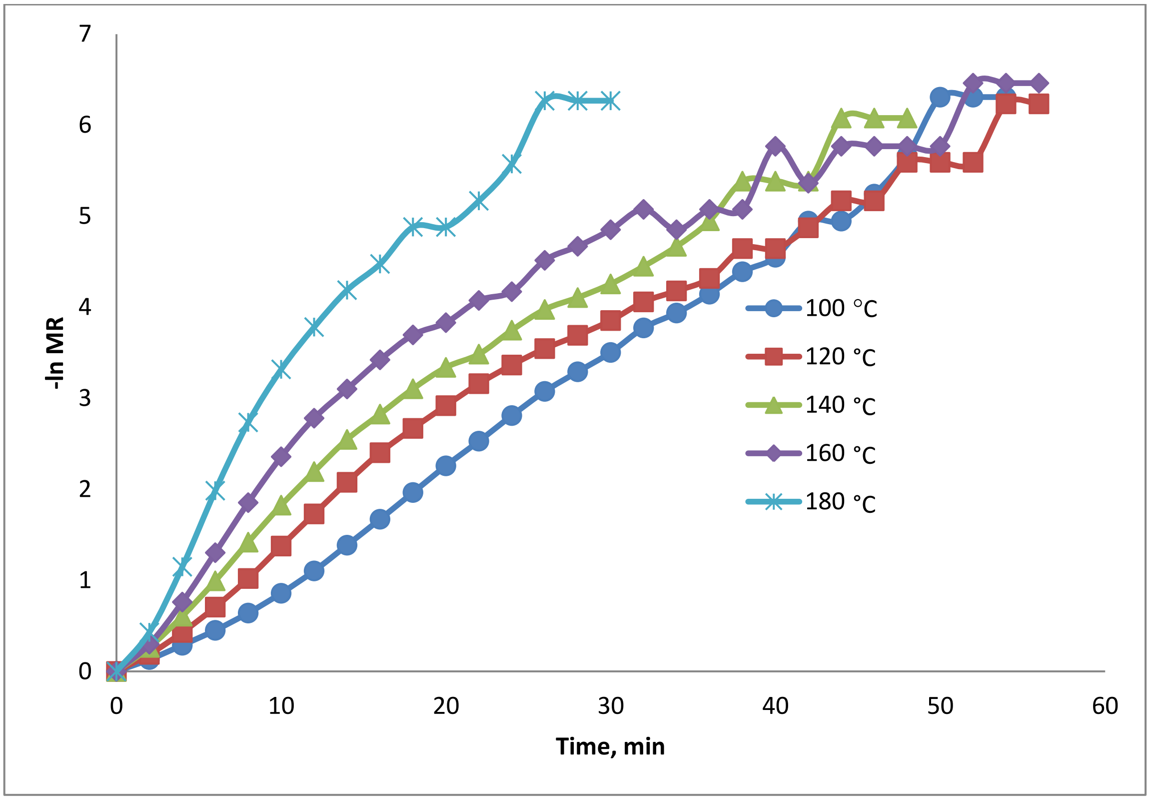


Figure 4.4 Drying Curve of Moisture Ratio at Different Temperature

Table 4.2 Kinetic Data

Temperature (°C)	k (min^{-1})	Drying Time (min)
100	0.1168	47
120	0.1284	38
140	0.1419	38
160	0.1617	32
180	0.2089	18

It is clear that the higher the drying temperature, the higher the rate constant obtained and drying time will consequently be shorter due to the higher reaction rate of the drying process. Furthermore, from the rate constants above, a plot of ln k against 1/T will give a reasonable straight line of gradient $–E_a/R$ (E is activation energy in J/mol and R is gas constant of 8.314 J/mol). Thus, the activation energy, E_a, needed to be overcome in order for the drying process to happen is measured from this line with a value of 989.03

J/mol for drying under temperature of 100°C to 180 °C which also indicates the sensitivity of the reaction rate to temperature.

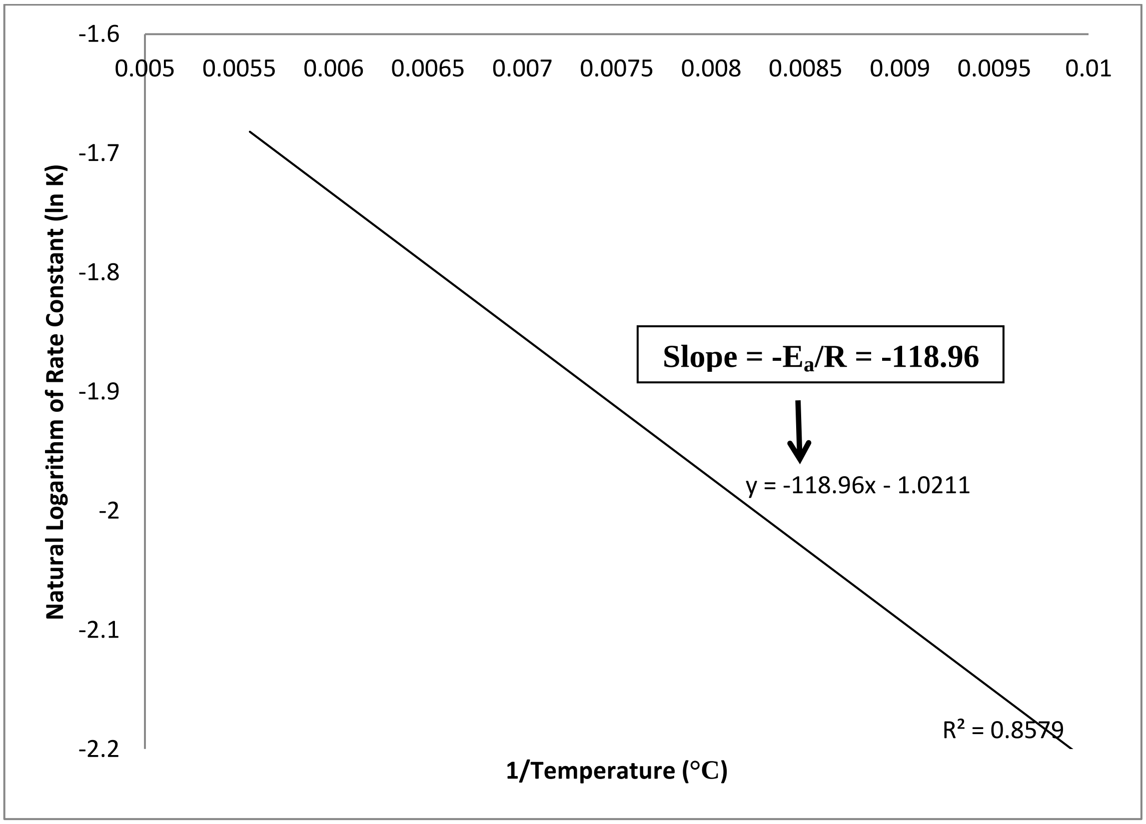


Figure 4.5 Plot of ln k against 1/T

4.3 Effect of Initial Water Content

The data obtained from the experiments are indicated in Figure 4.6 and 4.7 showing the change in moisture content and drying rate over time for different ionic liquid to initial water content ratio of 1:4, 1:3, 1:2, 1:1 and 2:1 with constant drying temperature settings of 100°C. The ionic liquid used is 1-butyl-3-methylimidazolium chloride for all samples.

4.3.1 Drying Curves

From the results obtained, Figure 4.6 is similar to that of typical moisture content plot for normal drying process whereby the graphs decrease at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content for all five samples of [bmim][Cl]. The reason behind this is as explained in previous section for the Effect of Drying Temperature. Referring to Figure 4.7, the shape of the drying rate curve is different to the typical drying rate curve shown in Chapter 2. There are only two phases of drying, initial period and falling rate period observed from the plots. The initial or rising rate period is very short and occurred just at the beginning of the drying process due to the rising temperature of the samples which directly improved the evaporation of free moisture on the ionic liquid surface. By increasing the initial water content in the [bmim][Cl] samples, more free moisture persists on the surface of ionic liquid. The falling rate period was the main drying process, during which internal diffusion dominated the moisture transfer in the samples.

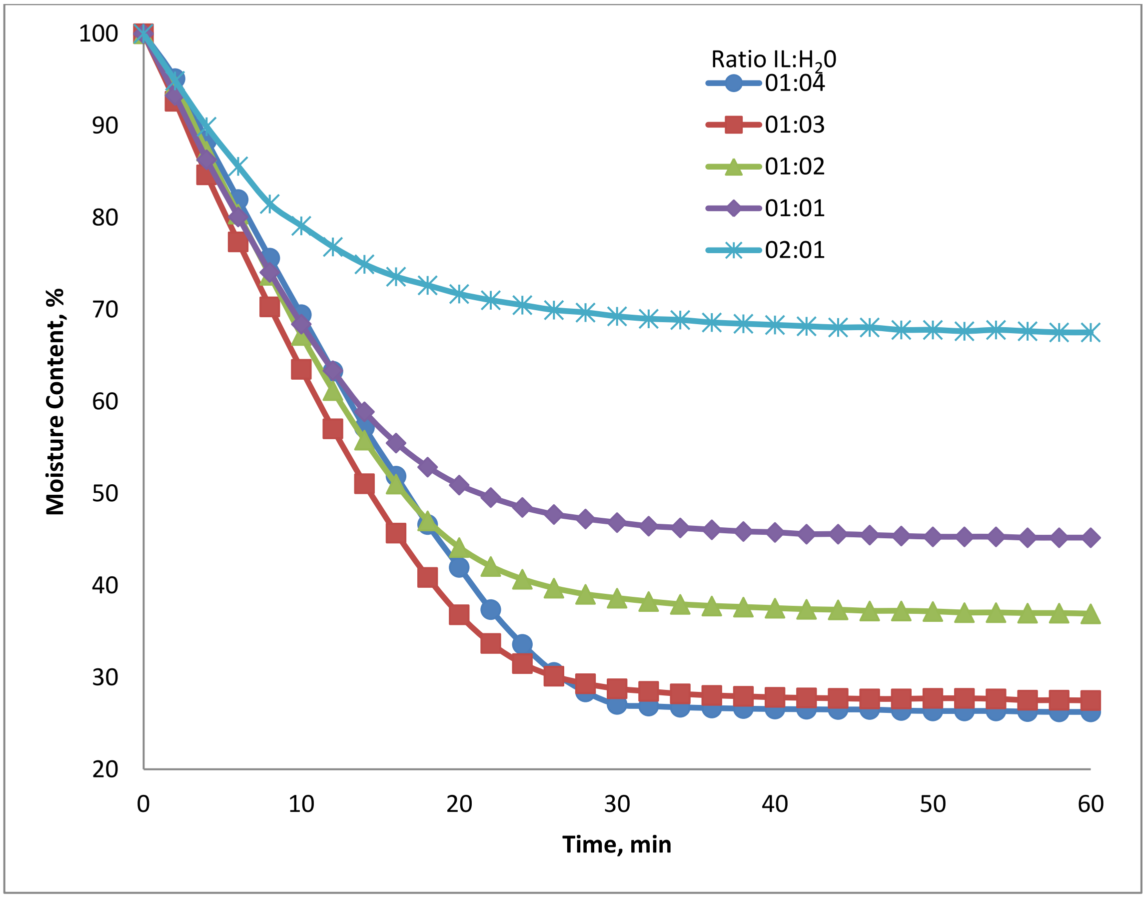


Figure 4.6 Drying Curve of Moisture Content versus Time at Different Water Content

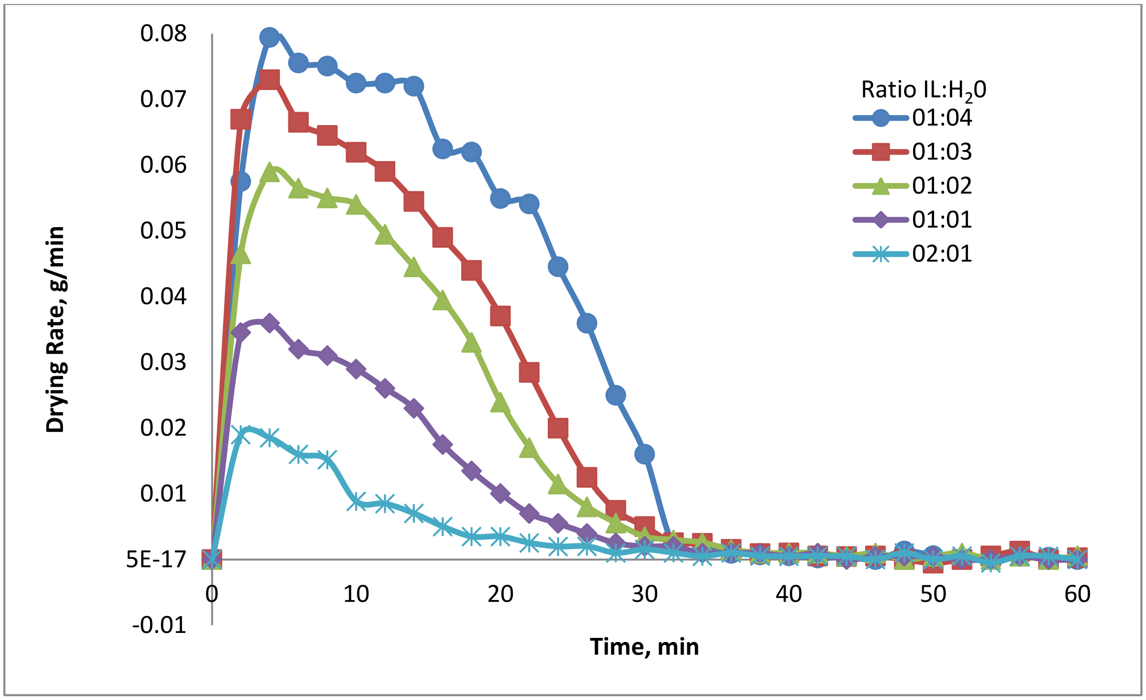


Figure 4.7 Drying Curve of Drying Rate versus Time at Different Water Content

Table 4.3 Experimental Data from Drying Curves

Ratio	Max Drying Rate (g/min)	$MC_{infinity}$ (%)
1:4	0.079	26.26
1:3	0.073	27.50
1:2	0.059	36.92
1:1	0.036	45.19
2:1	0.019	67.52

4.3.2 Analysis on Drying Kinetic

Furthermore, from both Figure 4.6 and 4.7, it is observed that the moisture content decreases faster and in larger amount for higher initial water concentration, the highest with ratio 1:4 and the lowest water content ratio is 2:1, with decreasing maximum drying rate (Table 4.3). This is because water molecules can form hydrogen bonds with ionic liquid cations and anions. At low water concentrations, water molecules complex primarily with anions rather than with other water molecules and form clusters at high water concentrations. Although the anion is smaller than the cation, the anion diffusivity can be lower. Thus, at low water concentrations, it is more difficult for the water molecules to evaporate to the atmosphere due to the stronger molecular interactions with ionic liquid anions. This also explains why the final moisture content is lowest for sample with ratio 1:4 (26.26%) and highest for sample of ratio 2:1 (67.52%). It can also be associated with the drying rate constant, k (min^{-1}). Higher rate constant is obtained for drying of ionic liquid sample with higher water concentration as can be seen from Figure 4.8 whereby the slope of the curve is higher. For higher initial water ratio, the drying process is faster and the reaction proceeds at greater speed.

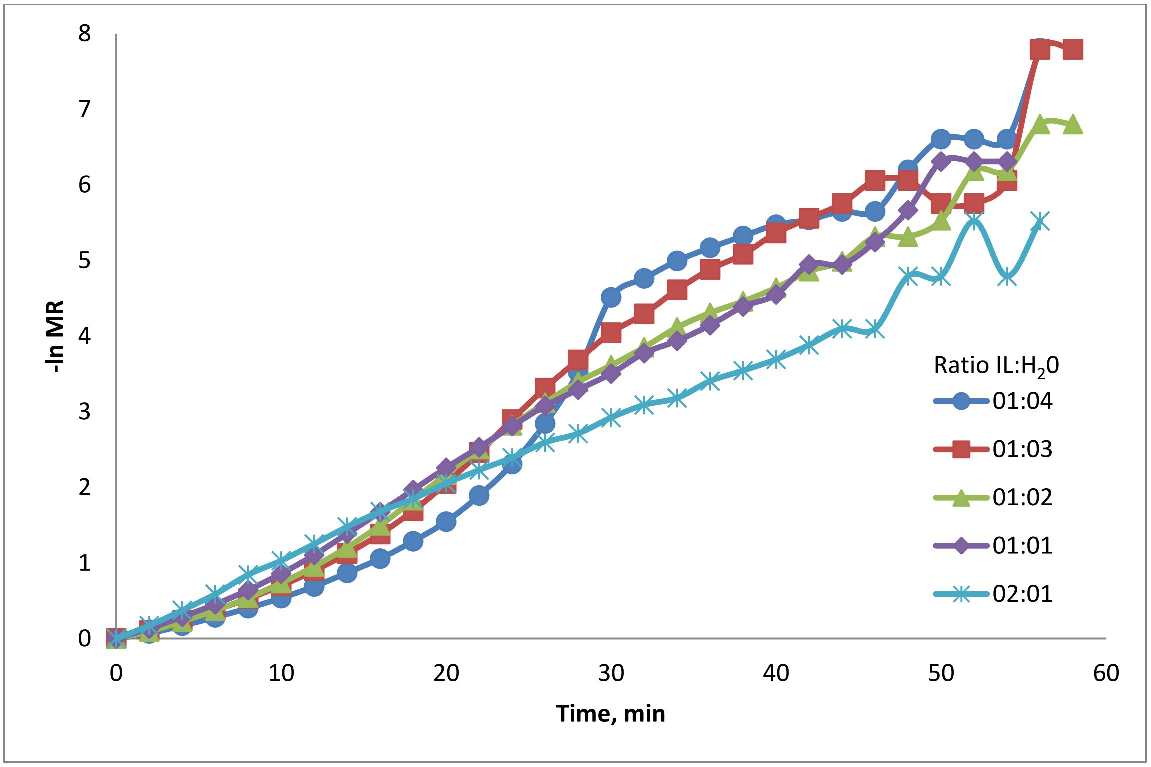


Figure 4.8 Drying Curve of Moisture Ratio at Different Ratio

Table 4.4 Kinetic Data

Ratio	k (min^{-1})	Drying Time (min)
1:4	0.1504	34
1:3	0.1348	36
1:2	0.1205	38
1:1	0.1168	47
2:1	0.0974	50

It is observed that the higher the initial water concentration, the higher the rate constant obtained and drying time will consequently be shorter due to the higher reaction rate of the drying process.

4.4 Effect of Different Types of Cation and Anion

The data obtained from the experiments are indicated in Figure 4.9, 4.10, 4.11, 4.12, 4.13 and 4.14 showing the change in moisture content and drying rate over time for different types of ionic liquid with constant ionic liquid to initial water content ratio of 1:1 and drying temperature settings of 100°C. The ionic liquids used are:

i. 1-butyl-3-methylimidazolium chloride, [bmim][Cl]
ii. 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]
iii. 1-butyl-3-methylimidazolium methylsulfate, [bmim][$MeSO_4$]
iv. 1-ethyl-3-methylimidazolium hydrogensulfate, [emim][HSO_4]
v. 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]
vi. 1,3-dimethylimidazolium dimethylphosphate, [mmim][DMP]

The different samples of ionic liquids are chosen based on their alkyl chain and size of anion. Different length of alkyl chain comprising of butyl, ethyl and dimethyl may affect many ionic liquid properties especially its size and density resulting in different abilities in holding and dissociating water molecules between ionic liquid particles. In addition, it is also desired to observe the behaviour of drying curve for different ionic liquid anion (SO_4 and phosphate) to see the extent of hydrogen bonding between the anion and water molecules inside the ionic liquid and the effect on its drying kinetic. To compare the effects of different types of cation and anion towards drying curve of these ionic liquid samples, the plots are separated into three categories based on similar cation or anion:

i. [bmim] cation (Figure 4.9 and 4.10)
ii. [SO_4]- anion (Figure 4.11 and 4.12)
iii. Phosphate-containing anion (Figure 4.13 and 4.14)

4.4.1 Drying Curves

From all the results obtained, the plot of moisture content is similar to that of typical moisture content plot for normal drying process whereby the graphs initially decrease at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content. The reason behind this is as explained in previous section for the Effect of Drying Temperature. Referring to the drying rate curve of all types of ionic liquid samples, the shape of the curve is different to the typical drying rate curve shown in Chapter 2. There are only two phases of drying, initial period and falling rate period observed from the plots similar to the previous results of different drying temperatures and initial water contents.

In addition, from Figure 4.9, the shapes of the graph are very similar to each other with final moisture content ranging around 45% for all four samples which shows the role of [bmim] cation in determining the extent to which water molecules can be stored and subsequently released in the ionic liquid samples. However, the moisture content decreases fastest with highest maximum drying rate and in largest amount for [bmim][$MeSO_4$] and the lowest amount of dehydration with minimum drying rate is observed for [bmim][$(C_2F_5)_3PF_3$] due to the different extent of hydrogen bonding between the water molecules and the anion in the four samples. When paired with the 1-butyl-3-methylimidazolium cation, the hydrogen-bond basicity of the anion determines the amount of energy needed to break the water molecules bond from ionic liquid particles and consequently this will also affect its kinetic of drying.

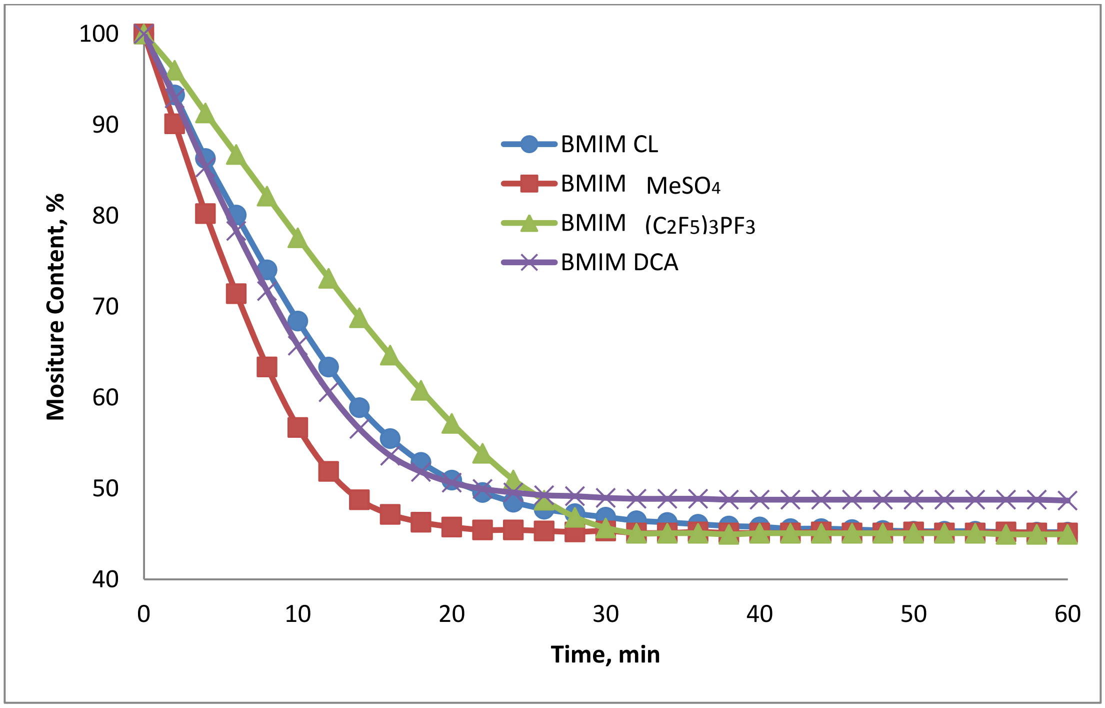


Figure 4.9 Drying Curve of Moisture Content versus Time for [bmim] Cation

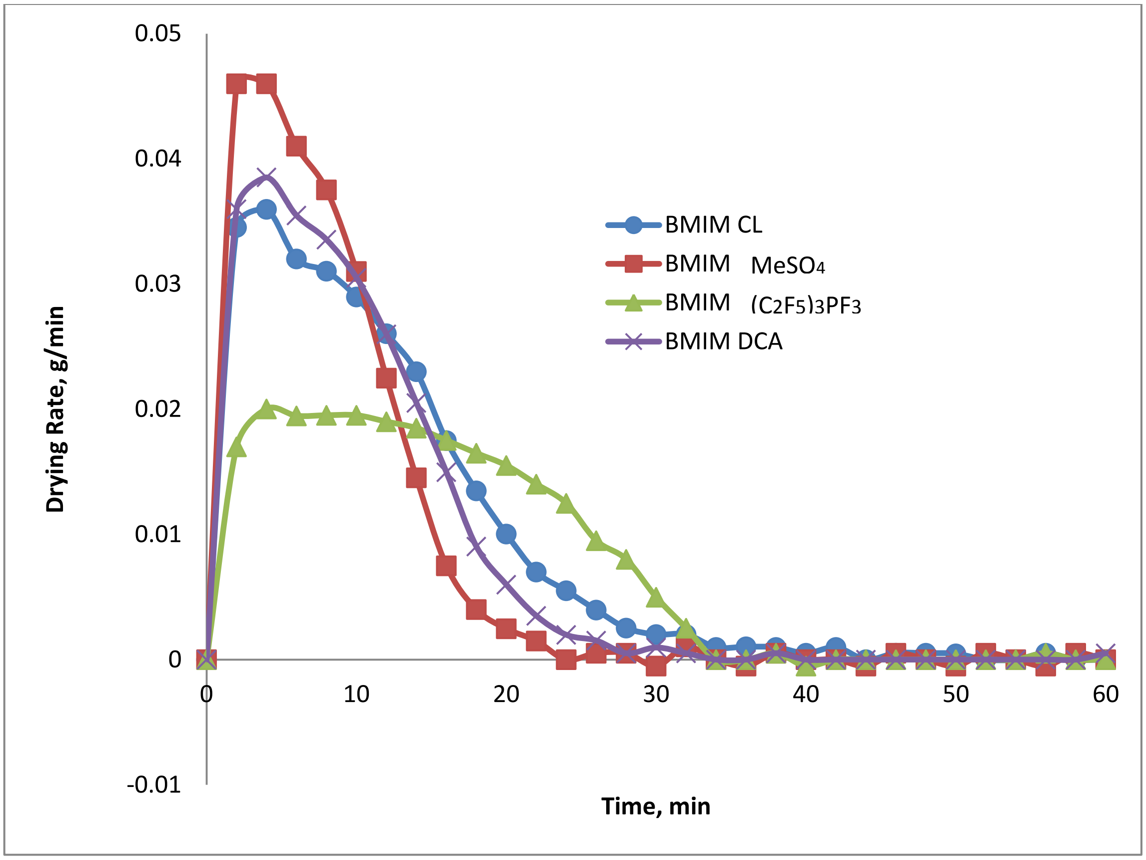


Figure 4.10 Drying Curve of Drying Rate versus Time for [bmim] Cation

Moving on to Figure 4.11 and 4.12, the shapes of the graph are very similar to each other. However, the moisture content decreases faster with higher maximum drying rate and in larger amount for [emim][HSO_4] compared to [bmim][$MeSO_4$] with final moisture content of 8.16% for [emim][HSO_4] and 45.11% for [bmim][$MeSO_4$]. This is due to the different length of alkyl chain whereby [emim][HSO_4] chain is shorter than [bmim][$MeSO_4$]. Longer alkyl chain has more free volume which enables more water molecules to be contained and bonded with the ionic liquid particles resulting in slower drying process. [emim][HSO_4] also shows the closest resemblance to the typical drying rate curve with all three phases of drying including the constant rate period. Furthermore, during the experiment, the sample of [emim][HSO_4] tends to vaporize especially when heat is applied to it resulting in greater reduction in its weight after drying. It is also observed that the drying process stops after 24 minutes for [emim][HSO_4] which is faster than [bmim][$MeSO_4$] (Table 4.7).

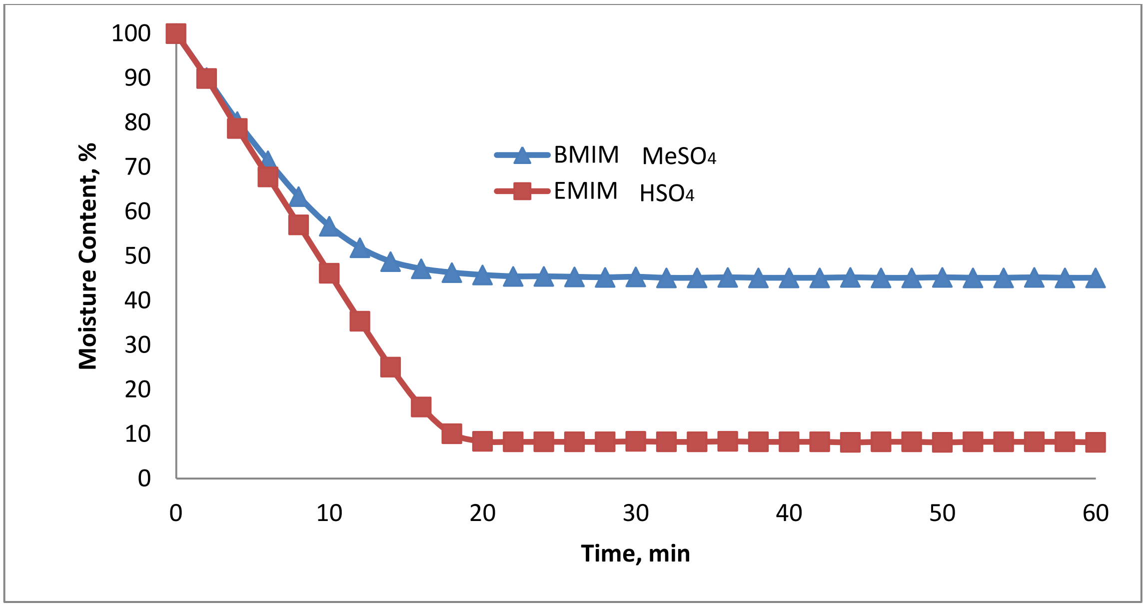


Figure 4.11 Drying Curve of Moisture Content versus Time for [SO_4]- Anion

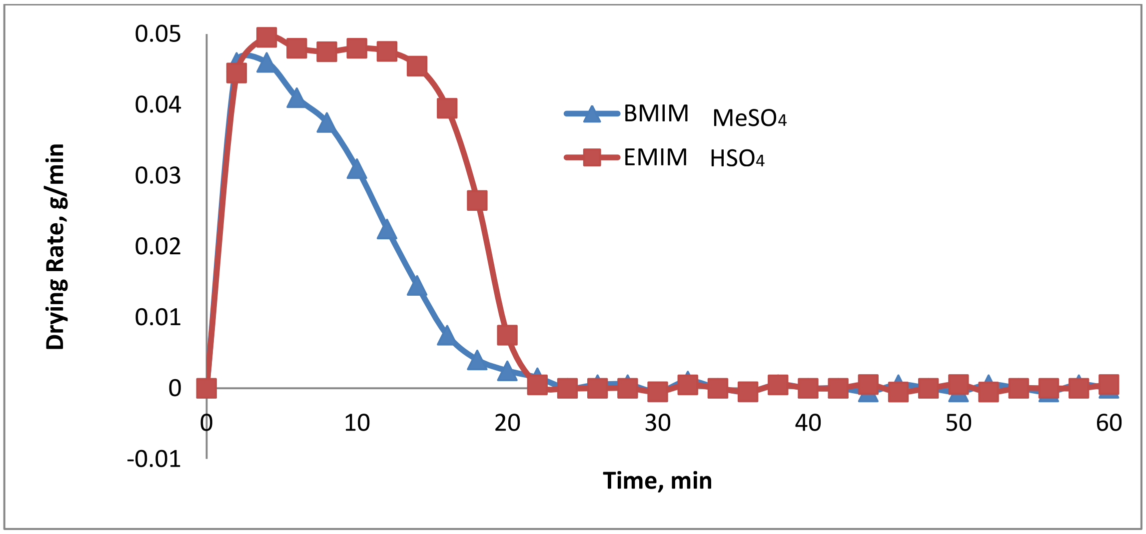


Figure 4.12 Drying Curve of Drying Rate versus Time for [SO_4]- Anion

Finally, referring to Figure 4.13 and 4.14, the shapes of the graph are very similar to each other with final moisture content of 44.95% for [bmim][$(C_2F_5)_3PF_3$] and 48.23% for [mmim][DMP]. Although the alkyl chain of [mmim][DMP] is shorter, it contains more water after the drying process due to the stronger hydrogen bonding between its anion and water molecules compared to [bmim][$(C_2F_5)_3PF_3$]. Initially, the moisture content decreases faster and in larger amount for [mmim][DMP] which shows the effect of shorter alkyl chain. However, after 15 minutes, the drying rate of [bmim][($C_2F_5)_3PF_3$] overcomes the drying rate of [mmim][DMP]. Besides, the drying process stops after 38 minutes for [bmim][($C_2F_5)_3PF_3$] which faster than [mmim][DMP] due to the stronger effect of anion hydrogen bonding (Table 4.7).

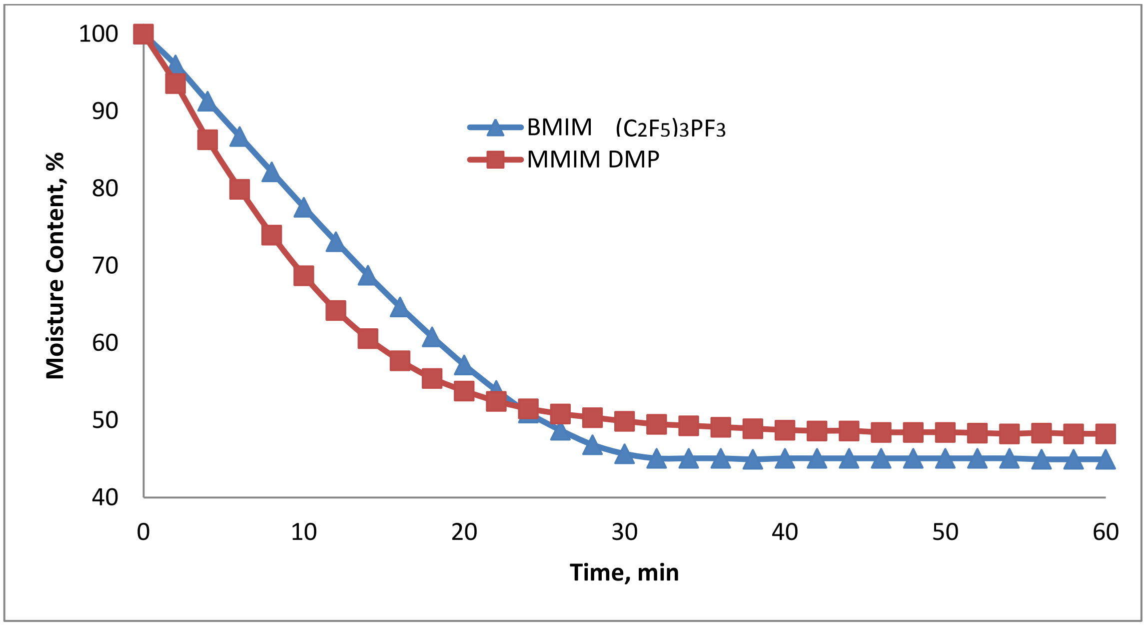


Figure 4.13 Drying Curve of Moisture Content versus Time for Phosphate Anion

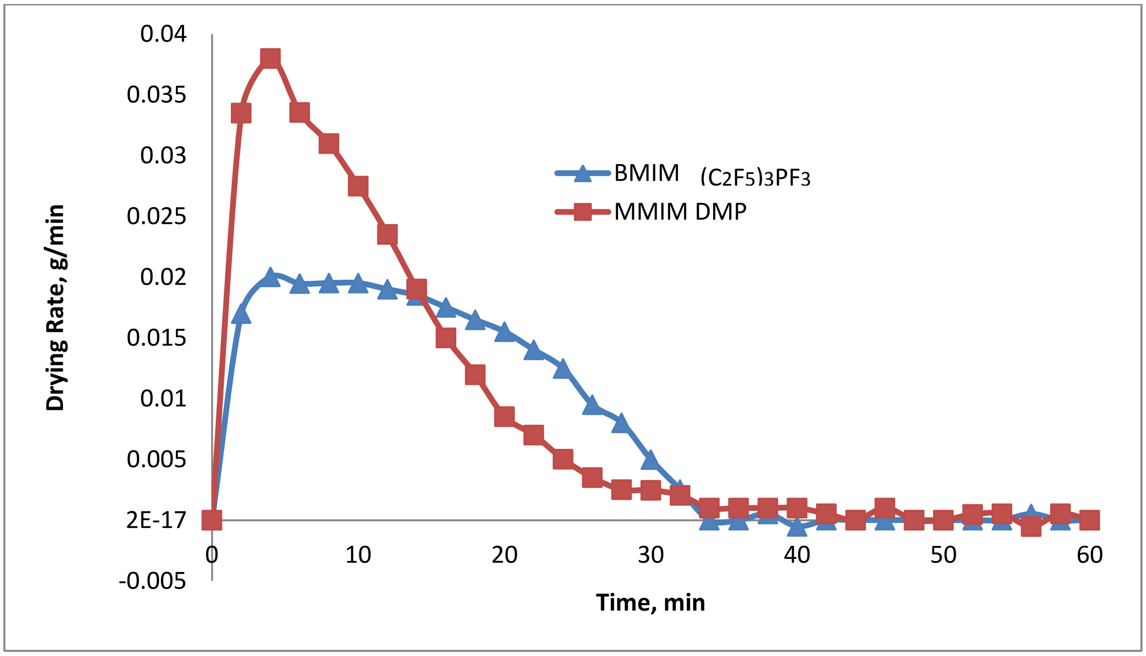


Figure 4.14 Drying Curve of Drying Rate versus Time for Phosphate Anion

Table 4.5 Experimental Data from Drying Curves

Ionic Liquid	Max Drying Rate (g/min)	$MC_{infinity}$ (%)
[emim][HSO_4]	0.050	8.16
[bmim][$MeSO_4$]	0.046	45.11
[bmim][DCA]	0.039	48.67
[mmim][DMP]	0.038	48.23
[bmim][Cl]	0.036	45.19
[bmim][$(C_2F_5)_3PF_3$]	0.020	44.95

4.4.2 Analysis on Drying Kinetic

Based on Table 4.7, drying rate constant and drying time is tabulated for different type of ionic liquid samples. It is observed that ionic liquid samples with [SO_4]- anion have higher drying constant value with steeper slope (Figure 4.15) and shorter drying time compared to other anion which leads to higher maximum drying rate and higher rate of reaction. The rate of reaction here refers to the transformation of water from liquid to gas during drying process. The effect of anion towards rate constant is more dominant than cation due to the stronger hydrogen bonding between water molecule and the anion particles which results in easier separation and evaporation of the water molecules for smaller size anions. Nevertheless, for bigger size anions, more energy is required to break the molecular bond of the moisture particles and since constant energy was supplied during the drying process, it took longer time to break, therefore maximum drying rate decreased (Table 4.5).

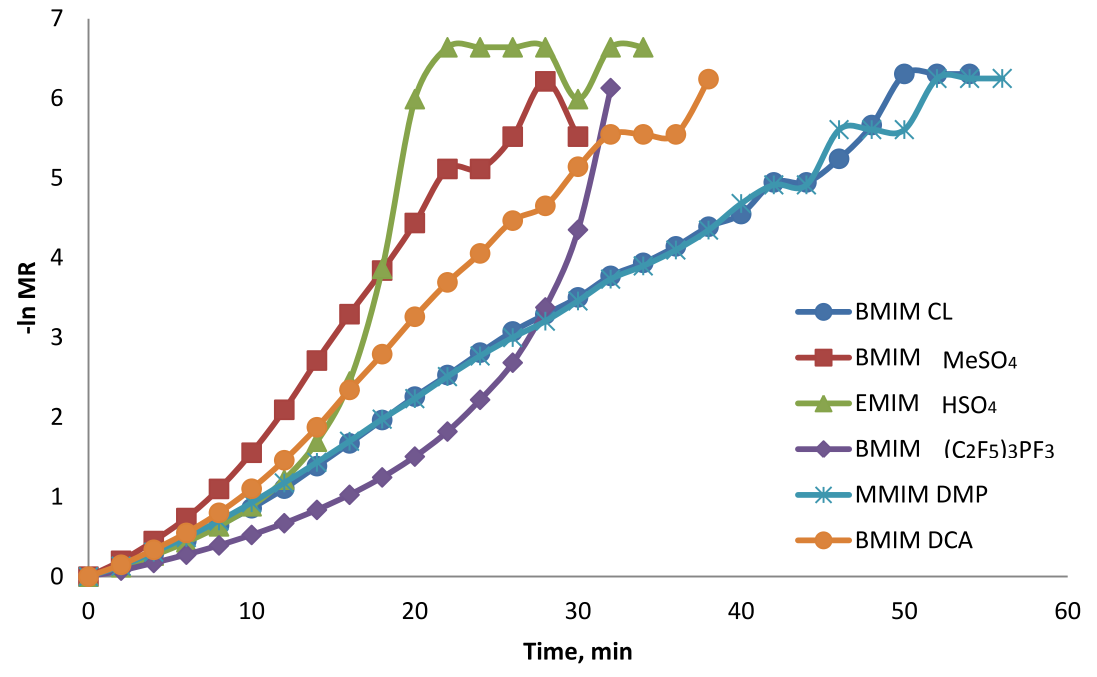


Figure 4.15 Drying Curves of Moisture Ratio for Different Ionic Liquid

Table 4.6 Molecular Structures of Ionic Liquid

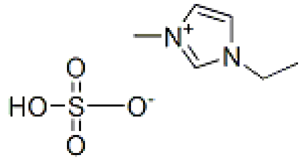
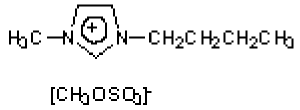
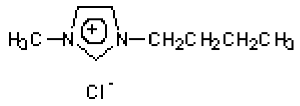
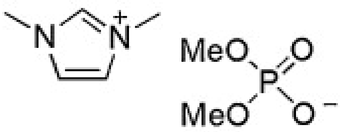
Ionic Liquid	Molecular Structure
[emim][HSO_4]	
[bmim][$MeSO_4$]	
[bmim][DCA]	
[bmim][$(C_2F_5)_3PF_3$]	
[bmim][Cl]	
[mmim][DMP]	

Table 4.7 Kinetic Data

Ionic Liquid	Molecular Formula	k (min^{-1})	Drying Time (min)
[emim][HSO_4]	$C_6H_{12}N_2O_4S$	0.1997	24
[bmim][$MeSO_4$]	$C_9H_{18}N_2O_4S$	0.184	28
[bmim][DCA]	$C_{10}H_{15}N_5$	0.1714	34
[bmim][$(C_2F_5)_3PF_3$]	$C_{14}H_{15}F_{18}N_2P$	0.145	38
[bmim][Cl]	$C_8H_{15}ClN_2$	0.1168	47
[mmim][DMP]	$C_7H_{15}N_2O_4P$	0.1153	48

It is observed from Table 4.6 and 4.7 that the bigger the molecular size of ionic liquid anion, the higher the rate constant obtained and drying time will consequently be shorter due to the higher reaction rate of the drying process.

4.5 Effect of Different Drying Methods

The data obtained from the experiments are indicated in Figure 4.16 and 4.17 showing the change in moisture content and drying rate over time for drying of 1-butyl-3-methylimidazolium chloride using vacuum drying compared with halogen lamp drying with constant drying temperature settings of 100°C and ionic liquid to water ratio of 1:1. The reason for choosing vacuum drying oven as an alternative method to dry ionic liquid samples is due to this method is a conventional and widely used method for drying laboratory samples since it is economical and less complex. In recent years, vacuum drying technology is also combined with microwave heating technology and other drying technologies. The results obtained from vacuum drying method will be compared with drying curves generated from the Halogen Moisture Analyzer mentioned earlier to analyze its efficiency and performance in drying process of ionic liquid samples.

4.5.1 Drying Curves

For vacuum drying method, the plot of moisture content is similar to that of typical moisture content plot for normal drying process whereby the graph initially decreases at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content. Referring to the drying rate curve, the shape of the curve using vacuum drying oven is different to the typical drying rate curve. There are only two phases of drying, initial period and falling rate period, whereby moisture transfer within ionic liquid particles is dominated by internal diffusion.

In addition, comparing the drying curves between vacuum drying and Halogen Moisture Analyzer at 100°C, the shapes of the graph are very similar to each other with lower final moisture content achieved for vacuum drying method (Table 4.8). Furthermore, the moisture content decreases fastest and in largest amount in vacuum drying (Table 4.8) since the maximum drying rate is higher than Halogen Moisture Analyzer. For vacuum drying, the thermal energy used to evaporate water is applied directly to the sample via the metallic shelf that it sits upon. There is an air inlet and outlet to carry the moisture lost from the sample out of the vacuum oven which prevents the accumulation of moisture within the oven so it can dry the samples to lower moisture content than the moisture analyzer. In addition, boiling point of water is also reduced when placed under vacuum. Thus, although the sample is heated at the same temperature, drying can be carried out much quicker in vacuum drying. Alternatively, lower temperatures can be used to remove the moisture (e.g. 70^{o}C instead of 100^{o}C). Thus, problems associated with decomposition of ionic liquid samples by heating under high temperature can be reduced.

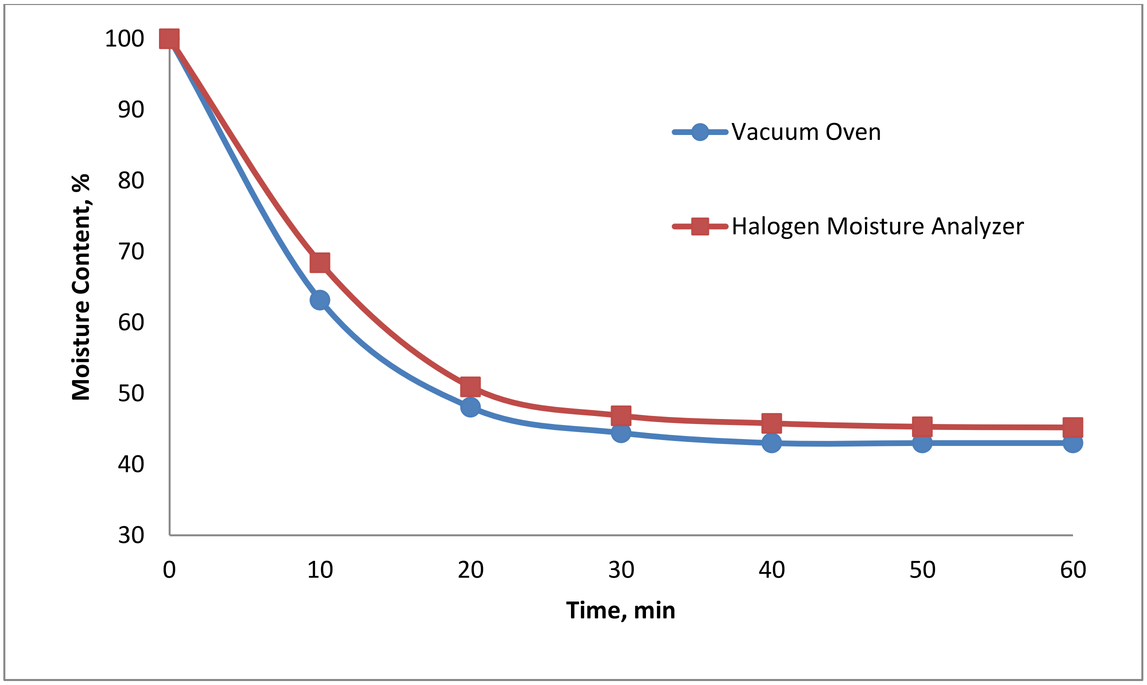


Figure 4.16 Comparison of Drying Curves for Moisture Content versus Time

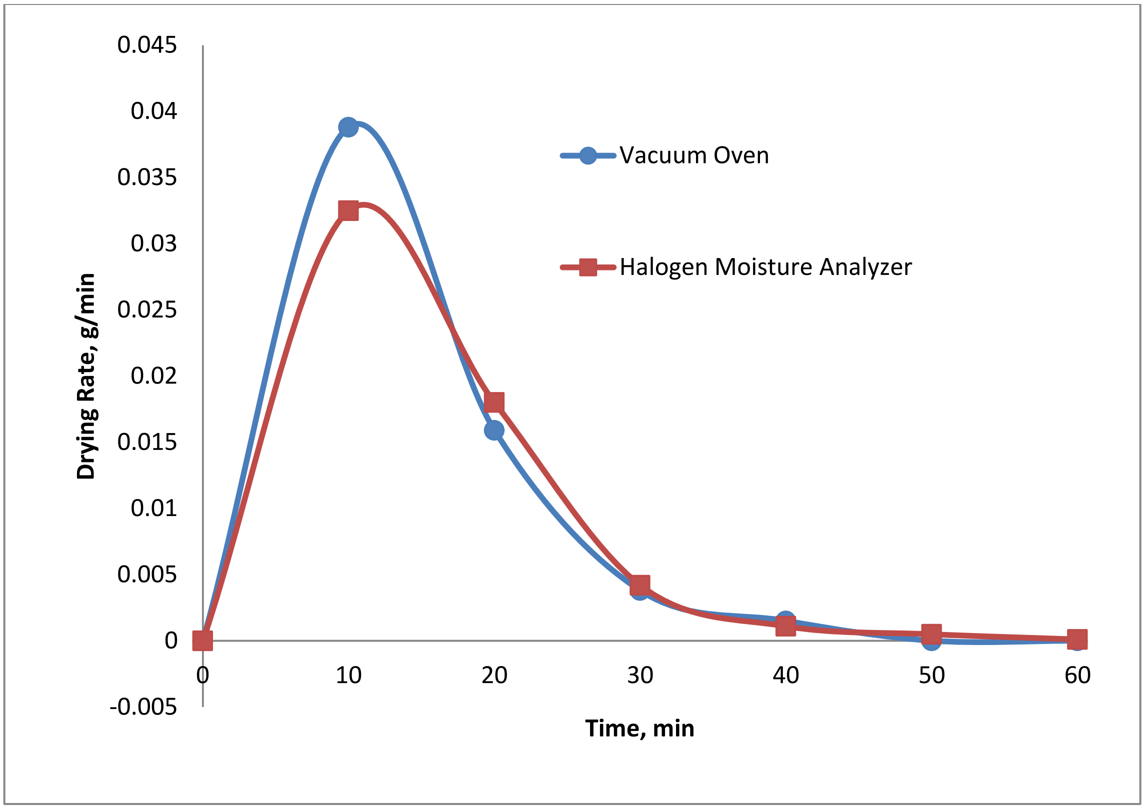


Figure 4.17 Comparison of Drying Curves for Drying Rate versus Time

Table 4.8 Experimental Data from Drying Curves

Drying Method	Max Drying Rate (g/min)	$MC_{infinity}$ (%)
Halogen Moisture Analyzer	0.036	45.19
Vacuum Drying Oven	0.039	43.02

4.5.2 Analysis on Drying Kinetic

The higher drying speed inside Vacuum Drying Oven can also be associated with the drying rate constant, k (min^{-1}). Relatively higher rate constant is obtained for vacuum drying method according to Figure 4.18 and Table 4.9 with shorter drying time achieved. For drying using halogen lamp, the drying process is slower and the reaction proceeds at lower speed since the Moisture Ratio changes which are related to change in sample mass are smaller throughout the process compared to vacuum drying method.

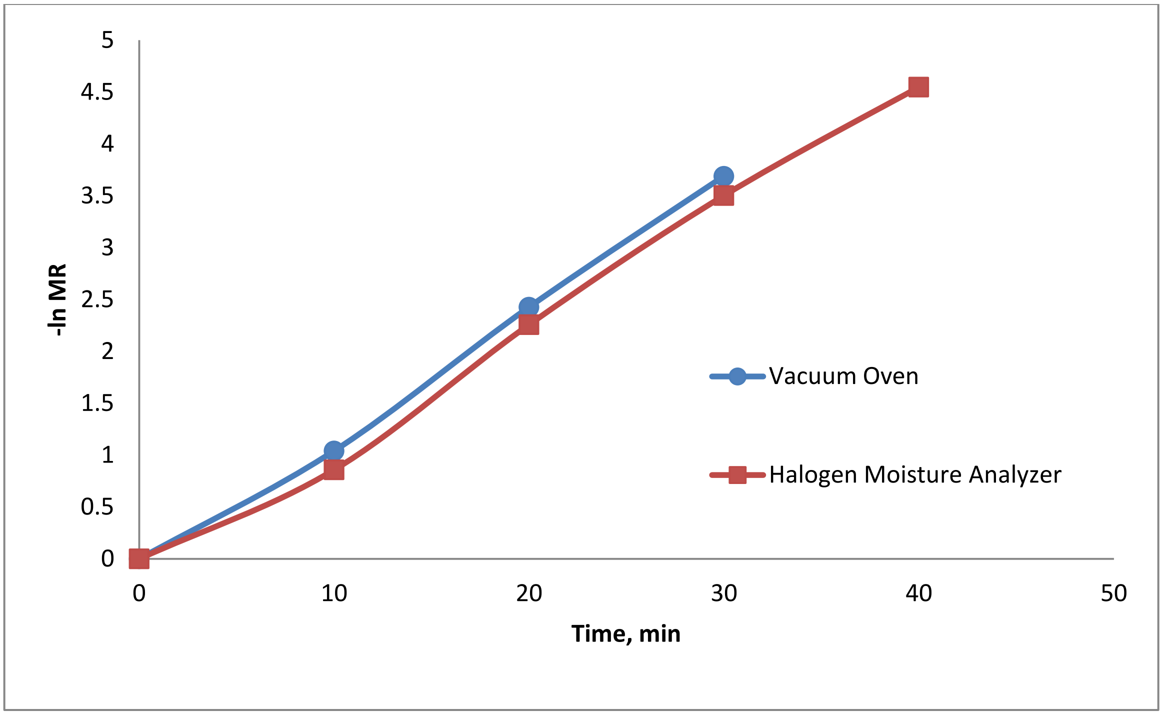


Figure 4.18 Drying Curves of Moisture Ratio for Vacuum Drying

Table 4.9 Kinetic Data

Drying Method	**k (min^{-1})**	**Drying Time (min)**
Halogen Moisture Analyzer	0.1168	47
Vacuum Drying Oven	0.123	40

It is observed that vacuum drying method has higher drying rate constant and drying time will consequently be shorter due to higher reaction rate governing the drying process which is also an indication that this method is more efficient and faster speed can be achieved in drying ionic liquid compared to Halogen Moisture Analyzer.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, the drying curves and kinetic of drying under each objectives outlined before which are drying temperatures, different combination of cation and anion, initial water content and drying methods have been analyzed in this paper. The effects of all those parameters are presented in the form of drying curves showing the change in moisture content percentage, drying rate over time and kinetic analysis are done to obtain their drying rate constant and drying time.

For the study on the effects of four different parameters on drying curves of ionic liquid, the following conclusion can be made. There are only two phases of drying in the drying rate curve of ionic liquid which are initial or rising rate period and falling rate period.

From the primary drying curves, manipulation of data which lead to secondary data for kinetic analysis can be made for all the different parameters with the following conclusion:

i. The higher the drying temperature, the higher the drying constant with shorter drying time achieved. Activation energy obtained is 989.03 J/mol for drying under temperature of 100°C to 180 °C.
ii. The higher the initial ratio of ionic liquid to water in sample solution, the higher the drying constant with shorter drying time achieved.
iii. The smaller the molecular size of ionic liquid anion, the higher the drying constant with shorter drying time achieved with fastest drying observed for samples containing $[SO_4]^-$ anion.
iv. Vacuum Drying Oven method has higher drying constant with shorter drying time which shows faster speed of drying compared to Halogen Moisture Analyzer.

Furthermore, the study on drying of ionic liquid is feasible in terms of its scopes and objectives whereby they are achievable and relevant to the scientific society. In addition, there are still some recommendations which can be made to expand the scope of study on drying of ionic liquid:

i. To investigate the effects of drying air velocity towards drying of ionic liquid.
ii. To investigate drying curves of ionic liquid under non-isothermal condition whereby the temperature is not constant throughout the drying period.
iii. To compare the final equilibrium moisture content obtained from drying of ionic liquid solution with original moisture content of dry ionic liquid.
iv. To repeat drying process of ionic liquid for different initial moisture content, types of cation and anion and drying methods at multiple temperatures. Thus, a graph of ln K against 1/T can be plotted to obtain the activation energy (E_a) for each parameters.

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APPENDIX A

EXPERIMENTAL AND KINETIC DATA

Temperature : 100°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	1.029	0	0
10	68.4	68.44	68.42	0.028284	0.704042	0.028966	0.858428
20	51.82	50.02	50.92	1.272792	0.523967	0.010033	2.258157
30	46.69	46.99	46.84	0.212132	0.481984	0.002007	3.503097
40	45.65	45.89	45.77	0.169706	0.470973	0.000514	4.5486
50	45.21	45.37	45.29	0.113137	0.466034	0.000463	6.306458
60	45.16	45.22	45.19	0.042426	0.465005	0	NA

Temperature : 120°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	1.019	0	0
10	61.79	62.05	61.92	0.183848	0.630965	0.028023	1.377108
20	51.62	52.02	51.82	0.282843	0.528046	0.003974	2.918851
30	50.06	50.24	50.15	0.127279	0.511029	0.000968	3.853491
40	49.47	49.65	49.56	0.127279	0.505016	0	4.643802
50	49.23	49.29	49.26	0.042426	0.501959	0	5.591183
60	49.06	49.08	49.07	0.014142	0.500023	0	NA

Temperature : 140°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	0.88	0	0
10	59.68	59.86	59.77	0.127279	0.525976	0.017028	1.826344
20	53.22	54.28	53.75	0.749533	0.473	0.00198	3.339531
30	52.62	52.84	52.73	0.155563	0.464024	0.000484	4.255821
40	52.26	52.28	52.27	0.014142	0.459976	0	5.384287
50	52.03	52.07	52.05	0.028284	0.45804	0.000484	NA
60	52.03	52.07	52.05	0.028284	0.45804	0	NA

Temperature : 160°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	1.261	0	0
10	53.66	53.72	53.69	0.042426	0.677031	0.019987	2.357848
20	49.9	50.02	49.96	0.084853	0.629996	0.001009	3.830402
30	49.23	49.27	49.25	0.028284	0.621043	0.000504	4.851053
40	48.99	49.03	49.01	0.028284	0.618016	0.001009	5.767344
50	49.01	49.01	49.01	0	0.618016	0	5.767344
60	48.83	48.87	48.85	0.028284	0.615999	0	NA

Temperature : 180°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	**Trial 1 (%)**	**Trial 2 (%)**	**Average (%)**	**Standard Deviation**	**Mass (g)**	**Drying Rate (g/min)**	**Moisture Ratio**
0	100	100	100	0	0.904	0	0
10	44.11	44.17	44.14	0.042426	0.399026	0.007503	3.317816
20	42.47	42.49	42.48	0.014142	0.384019	0	4.880734
30	42.13	42.17	42.15	0.028284	0.381036	0	6.267028
40	42.03	42.05	42.04	0.014142	0.380042	0	NA
50	42.15	42.15	42.15	0	0.381036	0	NA
60	42.17	42.13	42.15	0.028284	0.381036	0	NA

Temperature : 100°C

Ratio : 1:4

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	**Trial 1 (%)**	**Trial 2 (%)**	**Average (%)**	**Standard Deviation**	**Mass (g)**	**Drying Rate (g/min)**	**Moisture Ratio**
0	100	100	100	0	2.357	0	0
10	69.44	69.46	69.45	0.014142	1.636937	0.072478	0.534936
20	41.95	41.99	41.97	0.028284	0.989233	0.054918	1.546248
30	27.06	27.08	27.07	0.014142	0.63804	0.016028	4.511266
40	26.56	26.58	26.57	0.014142	0.626255	0.000589	5.471728
50	26.35	26.37	26.36	0.014142	0.621305	0.000589	6.60313
60	26.26	26.26	26.26	0	0.618948	0	NA

Temperature : 100°C

Ratio : 1:3

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	1.825	0	0
10	63.5	63.52	63.51	0.014142	1.159058	0.061959	0.69979
20	36.79	36.85	36.82	0.042426	0.671965	0.037048	2.051424
30	28.76	28.78	28.77	0.014142	0.525053	0.005019	4.04457
40	27.83	27.85	27.84	0.014142	0.50808	0.001004	5.362396
50	27.72	27.74	27.73	0.014142	0.506073	-0.00055	5.753263
60	27.51	27.49	27.5	0.014142	0.501875	0.000274	NA

Temperature : 100°C

Ratio : 1:2

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	1.652	0	0
10	67.17	67.21	67.19	0.028284	1.109979	0.05402	0.734247
20	44.11	44.15	44.13	0.028284	0.729028	0.023954	2.168935
30	38.61	38.63	38.62	0.014142	0.638002	0.003469	3.613776
40	37.52	37.54	37.53	0.014142	0.619996	0.000991	4.6387
50	37.16	37.18	37.17	0.014142	0.614048	0.000496	5.530698
60	36.89	36.95	36.92	0.042426	0.609918	0.000578	NA

Temperature : 100°C

Ratio : 2:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	0.742	0	0
10	79.1	79.12	79.11	0.014142	0.586996	0.00883	1.030482
20	71.69	71.71	71.7	0.014142	0.532014	0.003487	2.050313
30	69.26	69.28	69.27	0.014142	0.513983	0.001521	2.921009
40	68.31	68.35	68.33	0.028284	0.507009	0.000482	3.691346
50	67.8	67.78	67.79	0.014142	0.503002	0	4.789958
60	67.54	67.5	67.52	0.028284	0.500998	0	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium methylsulfate, [bmim][MeSO4]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	0.931	0	0
10	56.69	56.73	56.71	0.028284	0.52797	0.031002	1.554326
20	45.74	45.78	45.76	0.028284	0.426026	0.002467	4.436114
30	45.37	45.29	45.33	0.056569	0.422022	-0.00051	5.519459
40	45.11	45.11	45.11	0	0.419974	0	NA
50	45.27	45.17	45.22	0.070711	0.420998	-0.00051	NA
60	45.12	45.1	45.11	0.014142	0.419974	0	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1-ethyl-3-methylimidazolium hydrogensulfate, [emim][HSO4]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	0.882	0	0
10	46.1	46.2	46.15	0.070711	0.407043	0.047981	0.882725
20	8.38	8.4	8.39	0.014142	0.074	0.007497	5.989724
30	8.43	8.35	8.39	0.056569	0.074	-0.00049	5.989724
40	8.27	8.29	8.28	0.014142	0.07303	0	NA
50	8.13	8.19	8.16	0.042426	0.071971	0.000529	NA
60	8.17	8.15	8.16	0.014142	0.071971	0.000529	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]

Method : Halogen Moisture Analyzer

Time (min)	Trial 1 (%)	Trial 2 (%)	Average (%)	Standard Deviation	Mass (g)	Drying Rate (g/min)	Moisture Ratio
0	100	100	100	0	0.852	0	0
10	77.54	77.62	77.58	0.056569	0.660982	0.019511	0.52301
20	57.14	57.18	57.16	0.028284	0.487003	0.015506	1.505987
30	45.65	45.67	45.66	0.014142	0.389023	0.004984	4.350732
40	45.06	45.08	45.07	0.014142	0.383996	0	NA
50	45.06	45.08	45.07	0.014142	0.383996	0	NA
60	44.9	45	44.95	0.070711	0.382974	0	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1,3-dimethylimidazolium dimethylphosphate, [mmim][DMP]

Method : Halogen Moisture Analyzer

Time (min)	**Trial 1 (%)**	**Trial 2 (%)**	**Average (%)**	**Standard Deviation**	**Mass (g)**	**Drying Rate (g/min)**	**Moisture Ratio**
0	100	100	100	0	1.045	0	0
10	68.68	68.74	68.71	0.042426	0.71802	0.027484	0.927362
20	53.76	53.8	53.78	0.028284	0.562001	0.008517	2.233013
30	49.84	49.88	49.86	0.028284	0.521037	0.002456	3.458231
40	48.56	48.86	48.71	0.212132	0.50902	0.000993	4.68078
50	48.42	48.42	48.42	0	0.505989	0	5.607542
60	48.23	48.23	48.23	0	0.504004	0	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]

Method : Halogen Moisture Analyzer

Time (min)	**Trial 1 (%)**	**Trial 2 (%)**	**Average (%)**	**Standard Deviation**	**Mass (g)**	**Drying Rate (g/min)**	**Moisture Ratio**
0	100	100	100	0	1.015	0	0
10	65.64	65.78	65.71	0.098995	0.666957	0.030501	1.102712
20	50.61	50.67	50.64	0.042426	0.513996	0.005989	3.260242
30	48.95	48.99	48.97	0.028284	0.497046	0.000964	5.142248
40	48.76	48.78	48.77	0.014142	0.495016	0	NA
50	48.78	48.76	48.77	0.014142	0.495016	0	NA
60	48.68	48.66	48.67	0.014142	0.494001	0.000508	NA

Temperature : 100°C

Ratio : 1:1

Sample : 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

Method : Vacuum Drying

Time (min)	**Trial 1 (%)**	**Trial 2 (%)**	**Average (%)**	**Standard Deviation**	**Mass (g)**	**Drying Rate (g/min)**	**Moisture Ratio**
0	100	1.056	1.05	1.053	0.004243	0	0
10	63.1529	0.558	0.772	0.665	0.151321	0.0388	1.040343
20	48.05318	0.427	0.585	0.506	0.111723	0.0159	2.426637
30	44.44444	0.439	0.497	0.468	0.041012	0.0038	3.688877
40	43.01994	0.456	0.45	0.453	0.004243	0.0015	NA
50	43.01994	0.463	0.443	0.453	0.014142	0	NA
60	43.01994	0.463	0.443	0.453	0.014142	0	NA