CONVERSION OF GLYCEROL TO GLYCEROL CARBONATE VIA TRANSESTERIFICATION USING 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE CATALYST

ZATI ISMAH ISHAK

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2018

UNIVERSITY OF MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **ZATI ISMAH BINTI ISHAK**

Registration/Matric No: **SHC130032**

Name of Degree: **DOCTOR OF PHILOSOPHY (EXCEPT MATHEMATIC & SCIENCE PHILOSOPHY)**

Title of Project Paper/Research Report/Dissertation/Thesis (“this Work”):

CONVERSION OF GLYCEROL TO GLYCEROL CARBONATE VIA TRANSESTERIFICATION USING 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE CATALYST

Field of Study: **MATERIAL CHEMISTRY**

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya (“UM”), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate’s Signature Date:

Subscribed and solemnly declared before,

Witness’s Signature Date:

Name:

Designation:

CONVERSION OF GLYCEROL TO GLYCEROL CARBONATE VIA TRANSESTERIFICATION USING 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE CATALYST

ABSTRACT

In the present research, the synthesis of glycerol carbonate by transesterification of glycerol with diethyl carbonate in a green and efficient process catalyzed by ionic liquid was comparatively studied. A series of imidazolium and ammonium-based ionic liquids with different anions and conditions optimization (reaction temperature, reaction time, diethyl carbonate/glycerol ratio, solvent and catalyst loading) were screened for the best catalytic activity towards glycerol carbonate synthesis with respect to glycerol conversion and glycerol carbonate yield. It has been revealed that 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) remarks the highest activity towards glycerol conversion and glycerol carbonate yield of 93.5%, and 88.7%, respectively at 120 °C, 2.0 hours, molar ratio of diethyl carbonate/glycerol of 2, 0.50 mol% [Emim][Ac] loading with 2.0 wt.% water content. The peak intensities at 1262 cm^{-1} and 923 cm^{-1} corresponding to O-H bending and 3387 cm^{-1} corresponding to O-H stretching in glycerol were reduced indicate to glycerol being converted to glycerol carbonate. Meanwhile, the peak at 1750 cm^{-1} corresponding to C=O and also peaks between 1200 cm^{-1} to 1000 cm^{-1} corresponding to C–C and C–O stretching of 2-hydroxyethyl chain showed an increase in intensity. These supported the presence of glycerol carbonate while reaction was in progress. Glycerol carbonate peaks at 61.5 ppm, 67.0 ppm, and 77.5 ppm corresponding to $–CH_2–O-$, $–CH_2–OH$ and –CH–, respectively are gradually increased when the reaction solution turned into a single phase at 1.5 hours. Response surface methodology (RSM) showed the interactive effects between selected reaction parameters towards glycerol conversion and glycerol carbonate yield with 92.4% and 91.8%, respectively at optimum reaction conditions; reaction temperature of 118 °C, at 1.8 hours with 2.2 of diethyl carbonate/glycerol ratio and 0.42 mol% [Emim][Ac] loading. Recyclability study showed insignificant reduction of glycerol conversion from recovered [Emim][Ac] indicating that [Emim][Ac] could be reused for approximately three times. All the respective peaks of [Emim][Ac] can be comparably resolved with little variation in chemical shift of ^{1}H spectra NMR for each cycle, thus revealing that [Emim][Ac] was successfully recovered with no degradation on its structure. The result of the computational study using a General Atomic and Molecular Electronic Structure System (GAMESS) software clearly demonstrated that the activation of glycerol proceeds mainly through the hydrogen bonding interaction with $[Ac]^-$ anion. On the other hand, diethyl carbonate is also capable of forming hydrogen bonding with imidazolium ring proton at carbon 2 position and hydroxyl group of glycerol. The proposed mechanism of glycerol carbonate synthesis agreed well with the theoretical computational study.

PENUKARAN GLISEROL KEPADA GLISEROL KARBONAT MELALUI TRANSESTERIFIKASI MENGGUNAKAN MANGKIN 1-ETIL-3-METILIMIDAZOLIUM ASETAT

ABSTRAK

Dalam kajian ini, sintesis gliserol karbonat melalui tindak balas transesterifikasi gliserol dengan dietil karbonat dalam proses hijau dan cekap dimangkinkan oleh cecair ionik telah dikaji secara perbandingan dengan terperinci. Cecair ionik berasaskan kation imidazolium dan ammonium yang mempunyai anion yang berbeza serta pengoptimuman parameter-parameter keadaan (suhu tindak balas, masa tindak balas, nisbah molar dietil karbonat/gliserol, pelarut dan muatan pemangkin) telah disaring untuk memperoleh pemangkin yang memberi catatan aktiviti pemangkin yang terbaik terhadap penghasilan gliserol karbonat iaitu berdasarkan peratus penukaran gliserol dan gliserol karbonat terhasil. Keputusan mendapati, 1-etil-3-metilimidazolium asetat ([Emim][Ac]) memberi catatan aktiviti yang tinggi terhadap tindak balas penukaran gliserol dan gliserol karbonat terhasil, iaitu masing-masing sebanyak 93.5% dan 88.7% pada 120 °C, 2.0 jam, nisbah dietil karbonat/gliserol 2, 0.50 mol% muatan [Emim][Ac] dengan 2.0 wt.% kandungan air. Keamatan puncak-puncak iaitu pada 1262 cm^{-1} dan 923 cm^{-1} sesuai dengan O-H lentur dan 3387 cm^{-1} sesuai dengan O-H teregang pada gliserol berkurang menunjukkan gliserol ditukarkan kepada gliserol karbonat. Dalam pada itu, puncak pada 1750 cm^{-1} sesuai dengan C=O dan juga puncak antara 1200 cm^{-1} ke 1000 cm^{-1} merujuk kepada C-C dan C-O teregang pada 2-hidroksietil menunjukkan peningkatan keamatan. Ini menyokong kehadiran gliserol karbonat apabila tindak balas sedang berlaku. Puncak gliserol karbonat pada 61.5 ppm, 67.0 ppm dan 77.5 ppm bersesuaian dengan $–CH_2–O-$, $–CH_2–OH$ dan –CH–, masing-masing secara beransur-ansur meningkat apabila larutan tindak balas berubah menjadi fasa tunggal pada 1.5 jam. Kaedah tindak balas permukaan

(RSM) menunjukkan kesan interaksi antara parameter-parameter tindak balas terhadap tindak balas (penukaran gliserol dan gliserol karbonat terhasil) sebanyak 92.4% dan 91.8% gliserol karbonat terhasil, masing-masing diperolehi dibawah keadaan tindak balas optimum; suhu tindak balas 118 °C selama 1.8 jam dengan 2.2 nisbah dietil karbonat/gliserol dan 0.42 mol% muatan pemangkin [Emim][Ac]. Kajian kitar semula telah menunjukkan pengurangan yang tidak ketara terhadap penukaran gliserol melaui [Emim][Ac] yang dipulih semula dan [Emim][Ac] boleh digunakan semula sehingga kira-kira tiga kali kitaran. Semua puncak [Emim] [Ac] boleh dilihat dengan hanya sedikit variasi dalam peralihan kimia ^{1}H spektrum NMR untuk setiap kitaran, dengan itu mendedahkan bahawa [Emim][Ac] berjaya dipulihkan tanpa degradasi pada strukturnya. Hasil kajian teori komputer menggunakan perisian General Atomic and Molecular Electronic Structure System (GAMESS) jelas menunjukkan bahawa, gliserol diaktifkan melalui interaksi ikatan hidrogen dengan asetat anion. Sebaliknya, dietil karbonat juga mampu membentuk ikatan hidrogen dengan proton di kedudukan karbon 2 pada lingkaran imidazolium dan kumpulan hidroksil daripada gliserol. Oleh itu, mekanisma yang dicadangkan sepadan dengan kajian teori perisian komputer.

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisors, Dr. Nor Asrina Sairi and Prof. Dr. Yatimah Alias, who gave me the opportunity to join UMCIL group and guided me through this research work. By being very supportive, they always made my mind widely open. To my supporting research supervisors Prof. Dr. Mohamed Khaireddine Taieb Aroua and Prof. Madya Dr. Rozita Yusoff, thank you for your guidance. I would like to extend my heartfelt thanks to my labmates[1] (UM), colleagues (UPM) and *Gelep* buddies[2] for the bond of friendship and teamwork and also for making my stay in UM a bearable one with many sweet memories and experiences. Without all of you, I would not have made it this far. Special gratitude to my mentor, Sir Mohd Basyaruddin Abd. Rahman for his invaluable guidance and advices. A special thank you also goes to my mom (Gon Binti Daud) and housemate (Yusliza Yusof) for their patience, support and encouragement in every second. Words cannot express how grateful I am for their care and concern for me. Last but not least, I would also like to express my deepest gratitude for Ministry of Education Malaysia on MYBRAIN 15 scholarship, High Impact Research Grant (UM.C/625/1/HIR/MoE/ENG59) and PPP Grant (PG206-2014B) for the research expenses throughout the research period. Without their support, I would have never had the chance to complete this stressful journey with success.

Zati

---

[1] *Dazylah Darji, Nor Rahimah Said, Wan Melissa Wan Mazlan, Maizathul Akmam, Siti Mastura Mohd Zakaria, Kumuthini Chandrasekaram, Naimah Haron and labmates.*

[2] *Khairulazhar Jumbri, Emmy Maryati Omar, Asrul Farrish OKR Udaiyappan, Mohd Rizal Chumati, Nur Fariza Abdul Rahman, Siti Efliza Ashari and Intan Diana Mat Azmi*

TABLE OF CONTENTS

CHAPTER 1 : INTRODUCTION

CHAPTER 2 : LITERATURE REVIEW

CHAPTER 3 : MATERIAL AND METHOD

CHAPTER 4 : RESULTS AND DISCUSSION

CHAPTER 5 : GENERAL CONCLUSION AND FURTHER WORK

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF SYMBOLS AND ABBREVIATIONS

[Bmim][BF_4]	- 1-butyl-3-methylimidazolium tetrafluoroborate
[Bmim][Cl]	- 1-butyl-3-methylimidazolium chloride
[Bmim][Dca]	- 1-butyl-3-methylimidazolium dicyanamide
[Bmim][Im]	- 1-butyl-3-methylimidazolium imidazolide
[Ea][NO_3]	- ethylammonium nitrate
[Emim][Ac]	- 1-ethyl-3-methylimidazolium acetate
[Emim][DMP]	- 1-ethyl-3-methylimidazolium dimethyl phosphate
[Hea][Fmt]	- 2-hydrozyethylammonium formate
[HOEmim][$N(CN)_2$]	- 1-methyl-3-(2-hydroxylethyl)imidazolium dicyanamide
[Ma][NO_3]	- methylammonium nitrate
[$Mor_{1,4}$][$N(CN)_2$]	- N-methyl-N-butylmorpholinium dicyanamide
[$Mor_{1,g}$][$N(CN)_2$]	- N-methyl- N-glycerylmorpholinium dicyanamide
Atm	- atmosphere
ATR-FTIR	- Attenuated total reflection-fourier transform infrared
CaO	- calcium oxide
cP	- centipoise
DMF	- dimethylformamide
g	- gram
GAMESS	- General atomic and molecular electronic structure system
GC-FID	- Gas chromatography-flame ionization detector
GC-MS	- Gas chromatography-mass spectrometry
K	- kelvin
K_2CO_3	- potassium carbonate
KOH	- potassium hydroxide

ml	- milliliter
mmHg	- millimeter of mercury
mmol	- millimole
MPa	- megapascal
NaOH	- sodium hydroxide
NMR	- Nuclear magnetic resonance
°C	- degree Celsius
ppm	- parts per million
rpm	- rate per minute
TON	- turnover number
UV–VIS	- ultraviolet-visible
μl	- microliter

LIST OF APPENDICES

CHAPTER 1 : INTRODUCTION

1.1 Background

Since biodiesel production has increased rapidly around the world, a fundamental concern in biodiesel industry is the generated biodiesel by-product, glycerol (Figure 1.1). In general, it is estimated that, for 10 tons of biodiesel, 1 ton of glycerol is produced (10.0% of weight). It is predicted that by 2020 the global production of glycerol will reach 41.9 billion liters (Nanda et al., 2014). The surplus in glycerol decreased its price significantly which also reduced the profitability margins of biodiesel manufacturers.

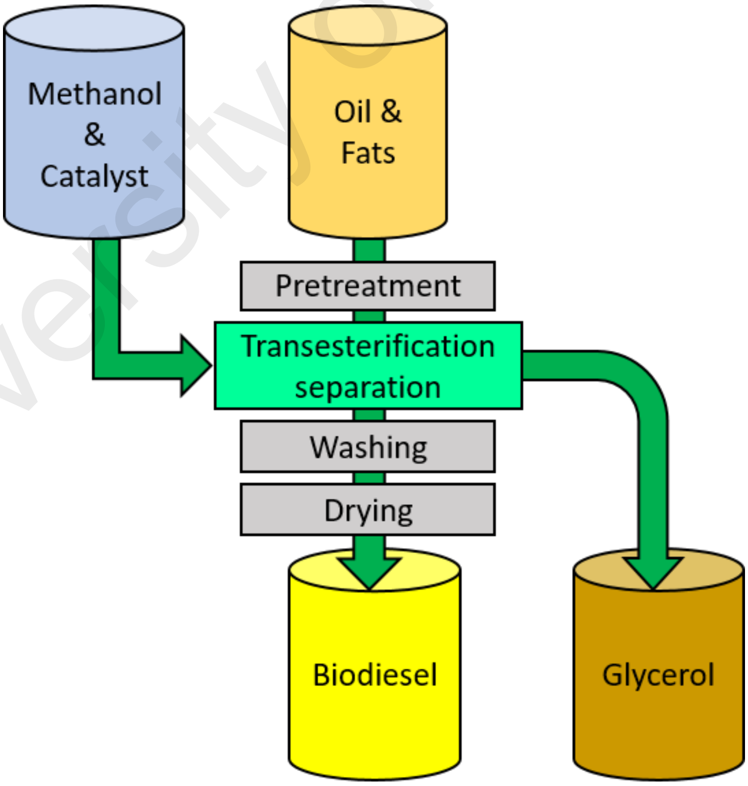


Figure 1.1: Biodiesel production process yielding glycerol as the main by-product.

The crude glycerol is about 80.0% pure and still contained contaminants like soap, methanol, and water. In order to turn this crude glycerol into a usable state for existing or emerging uses, a purification process must take place. During this refinement process residual organic matter, water, salt, methanol, and odors are removed. There are different types of glycerin grades ranging from crude glycerol to refined glycerol (pharmaceutical grade) as shown in Figure 1.2.

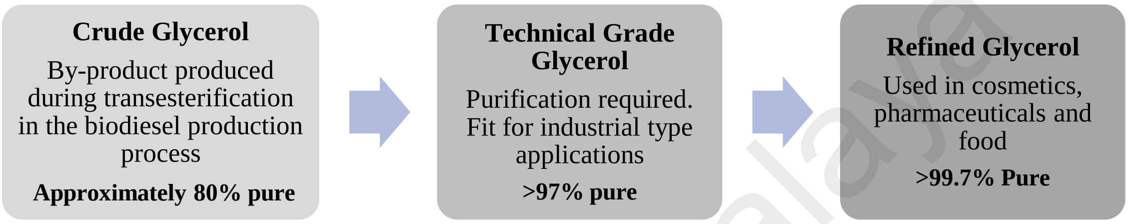


Figure 1.2: Different types of glycerol grades.

Utilization of glycerol for the synthesis of value-added chemicals is a theme of great industrial interest to overcome the surplus of glycerol which inevitably accumulated. As a non-toxic and biodegradable compound, glycerol will provide important environmental benefits to the new platform products. Via indirect transesterification reaction, glycerol can be converted to glycerol carbonate and this route has been proven to be the most promising one. Through this reaction, glycerol is reacted with carbon dioxide derivatives such as dimethyl carbonate and diethyl carbonate (Chiappe & Rajamani, 2012; Rokicki et al., 2005; Ochoa-Gómez et al., 2009) which have favored high glycerol carbonate yield.

Much effort has been devoted to the search for effective catalysts for the transesterification of glycerol. The catalyst can be divided into three types as shown in Figure 1.3 which each can be assigned through a wide spectrum of different catalyst properties categorized either acidic and basic catalysis. Furthermore, understanding of the catalyst property and the overall reaction mechanism is both practical and fundamental interest.

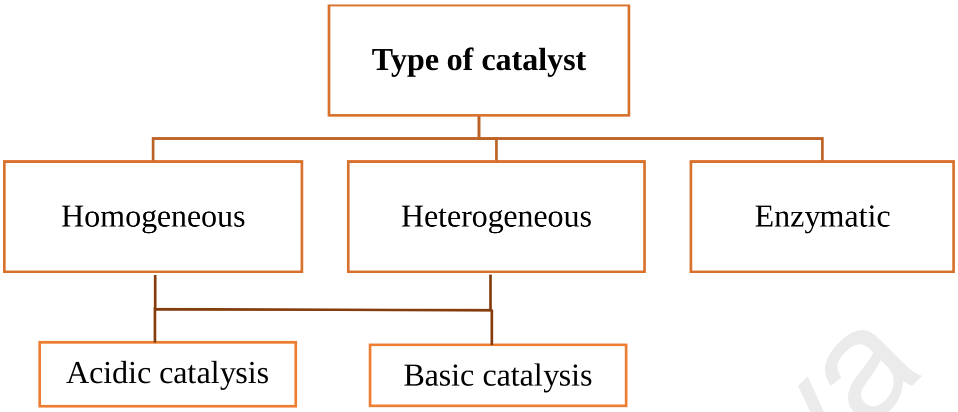


Figure 1.3: Type of catalyst use for transesterification reaction of glycerol with dialkyl carbonate.

The emergence of the green solvent such as ionic liquid with unique properties has gradually gained its versatile application as solvent and catalyst in the process synthesis (Mohammad Fauzi & Amin, 2012). The adjustable cation-anion pairing opens up the possibility of preparation of acidic or basic ionic liquids (Gong et al., 2008). Dual function of ionic liquids (catalyst and solvent) often leads to an increase in rate and/or reactivity compared to some of the catalysts that need the addition of solvent to enhance the reaction (Takagaki et al., 2010; Kumar et al., 2012). Thus, a huge interest on investigating the usefulness and the scope of ionic liquids as the catalyst in organic reactions and catalysis has been sufficiently reviewed (Wasserscheid & Welton, 2003; Olivier-Bourbigou et al., 2010), and still a lot of reported studies are expecting to come in foreseeable future.

1.2 Problem statement

The increasing demand of biodiesel makes glycerol as a by-product available in large quantities at decreasing prices. This has prompted the conversion of low-cost glycerol to value-added products (Teng et al., 2014; Sonnati et al., 2013; Ochoa-Gómez et al., 2012b). One of them is multifunctional glycerol carbonate which has increasing industrial attention based on its physical properties as well as on its reactivity. Transesterification of glycerol with dialkyl carbonate is one of the most direct and industrial feasible pathway to produce high glycerol carbonate yield. Catalyst plays a crucial role in the transesterification reaction of glycerol to glycerol carbonate. It is imperative to search for suitable catalysts that can attainably synthesize glycerol carbonate with regards to reducing the cost of operation and handling, bio-based, reusable through several cycles of reaction and involving chemical (catalytic) processes with reduced impacts on health, safety, environment, and energy.

Various heterogeneous catalysts have been reported for glycerol carbonate synthesis from glycerol and dimethyl carbonate. Many of them show a good catalytic activity for glycerol carbonate formation (Lu et al., 2013; Jiabo & Wang, 2011; Climent et al., 2010; Malyaadri et al., 2011). These catalysts are usually alkali metal oxide or mixed oxide catalysts. However, the preparation method of these catalysts usually is not environmentally friendly and it is time-consuming. Moreover, the catalyst such as calcium oxide (CaO) is deactivate more easily, evidenced by quick decrease of glycerol conversion during the catalyst recycling experiments (Ochoa-Gómez et al., 2009; Jiabo & Wang, 2011) which implies that, an expensive and troublesomely regeneration step following every reaction will be needed for CaO catalyst. Consequently, the cost associated with the preparation could affect the applicability of these catalysts in the industrial scale.

During the period from 2011 to 2016, more than 10,000 publications reported the great impacts of ionic liquids that can be designed to catalyze variety of reactions with excellent catalytic activity influencing the outcome of organic synthesis. It can be seen that less than 2000 publications have reported on ionic liquids as the catalysts in transesterification reactions of glycerol to glycerol carbonate (statistic from google scholar). Regardless of the reported excitements for transesterification reaction of glycerol using various homogeneous as well as heterogeneous catalysts, the limitations such as high catalyst loading (up to 10.00 mol%) and a large excess of substrate ratio between carbonylating source (dimethyl carbonate and diethyl carbonate) and glycerol (normally 3 to 10) need to be employed in order to achieve good glycerol conversions and high glycerol carbonate yield and selectivity in a reasonable time frame. Moreover, the factors governing the selectivity pattern such as the formation of glycerol carbonate or other possibility products are not well understood. Almost all the literature does investigate the pertinent factors influencing glycerol conversion and glycerol carbonate yield and/or selectivity, and just few studies focused on the detailed understanding of the fundamental underlying the reaction. These knowledge gaps constituted the starting point for experiments in this study.

1.3 Objectives of the research

The aim of this research is to investigate potential ionic liquids as catalyst for transesterification reaction of glycerol with diethyl carbonate and demonstrates the effect of reaction temperature, time, substrate molar ratio, catalyst loading, water content and basicity of catalyst towards glycerol conversion and glycerol carbonate yield and selectivity. Specific objectives of this research are as follows:

1) To explore potential ionic liquids as catalysts and evaluate the affecting parameters for transesterification of glycerol to glycerol carbonate.

2) To study the interactive effects between reaction parameters using Response Surface Methodology (RSM) approach.

3) To explore on recyclability of ionic liquid at optimum usage for transesterification of glycerol.

4) To elucidate the transesterification reaction mechanism theoretically using a computational method.

1.4 Scope of the research

In view of the recent interest in converting glycerol to glycerol carbonate, ionic liquid was used as catalyst for the transesterification reaction of glycerol and diethyl carbonate. Thus, the scope of the current research is divided into four main sections. For the first part, the performance of ionic liquid as catalyst towards transesterification of glycerol was measured by screening the potential ionic liquids. The approach was to use ionic liquid with targeted anion in order to obtain a satisfying glycerol conversion and glycerol carbonate yield and selectivity. Selection of ionic liquids was governed by the basicity value (β value) originated from the anion of the ionic liquids. Pertinent factors affecting the glycerol conversion and glycerol carbonate yield and selectivity such as the effect of temperature, reaction time, substrate ratio diethyl carbonate/glycerol, solvent, catalyst loading and water content of catalyst were evaluated individually. It was necessary to use Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) in order to corroborate the results obtained from product analysis using gas chromatography-flame ionization detector (GC-FID). Gas chromatography-mass spectrometry (GC-MS) was used to distinguish glycerol carbonate as the main product and also possible unknown products which have been formed along the reaction.

In the second part, statistical method, namely response surface methodology (RSM) was employed to determine the interactive effects between reaction parameters (factors that affect transesterification reaction of glycerol) that yielded the desired responses which are glycerol conversion and glycerol carbonate yield for a given measurement and described the responses near to optimum.

In the third part, the investigation on the possibility of recycling the ionic liquid employed for the consequence cycle of transesterification reaction was performed. The efficiency of recovery was examined along with the glycerol conversion and glycerol carbonate yield and selectivity.

In order to support the experimental findings, a computational study was also carried out in the last part. The mechanistic study was conducted by general atomic and molecular electronic structure system (GAMESS) software. In this study, the fundamental understanding of the role of anion and cation towards the transesterification reaction of glycerol and diethyl carbonate was achieved by prediction of the hydrogen bonding formed, thus help to stabilize the reaction during the reactants at initial state and transition states. The reaction mechanism was also proposed by means of the computational findings.

Therefore, it is important to gather overall understanding in the catalytic transesterification reaction of glycerol and diethyl carbonate using ionic liquid as catalyst as well as optimizing the catalytic reaction. The novelty of this study relies on the fundamental and practical levels as to gather overall understanding in the catalytic transesterification reaction of glycerol and diethyl carbonate using ionic liquid as catalyst. It is envisaged that this study could contribute towards creating a variety of new strategies for converting glycerol as a green building block glycerol together with ionic liquids for the more integrated process.

1.5 Outline of the thesis

In order to accomplish the objectives, this thesis is divided into five chapters which consist of the following chapters:

Chapter 1 describes the research background, problem statements, objectives, scope of work and the layout of the thesis.

Chapter 2 consists of relevant literature that motivates this study. It starts with a brief introduction of the background of the source of surplus glycerol and its properties. A broad literature review on the glycerol as a major chemical platform, glycerol carbonate and organic synthetic routes of converting glycerol to glycerol carbonate were presented in this chapter. Furthermore, it also reviews the properties of ionic liquids as catalysts, factors affecting transesterification reaction and reaction mechanism.

Chapter 3 provides the details of the materials, experimental and analytical apparatus including TLC, ATR-FTIR, NMR, GC-FID and GC-MS as well as methodology involved in the experiments.

Chapter 4 describes the results obtained from the transesterification of glycerol and diethyl carbonate by a screening of ionic liquids and reaction parameters such as temperature, time, substrate molar ratio and solvent, catalyst loading and water content. Glycerol conversion and glycerol carbonate yield and selectivity were measured by using GC-FID, while the results from ATR-FTIR, NMR and GC-MS were included to corroborate the GC-FID's results. The RSM was reported with the purpose of establishing the relationship between the reaction variables (reaction temperature, time, substrates ratio and catalyst loading) and the responses (glycerol conversion and glycerol carbonate yield) and determine how the responses are affected by the changes in the factors over a specified level of interest. Recyclability of ionic liquid catalyst was also reported for optimum glycerol conversion and glycerol carbonate yield and selectivity. Finally, this chapter also involves the results and the discussion on the computational study, which have been conducted by GAMESS and the discussion of the proposed mechanism.

Chapter 5 emphasizes and summarizes all the significant findings from this research. Furthermore, relevant suggestions for future work were also provided, which is essential and related to this work.

CHAPTER 2 : LITERATURE REVIEW

2.1 Glycerol

Today, as a result of the remarkable growth of biodiesel production produced from vegetable oils by transesterification processes with methanol or ethanol, the production of unavoidable glycerol increased very rapidly as well. The world outline of glycerol production is given in Figure 2.1. It is predicted that by 2020 the global production of glycerol will reach 41.9 billion liters (Nanda et al., 2014). Thus, crude glycerol disposal and utilization have become a serious issue and a financial and environmental liability for the biodiesel industry should be seriously reconsidered. A large amount of glycerol generated may become an environmental problem since it cannot be disposed in the environment. Economic utilizations of glycerol for value-added products are critically important for the sustainability of the biodiesel industry. Therefore, new methods for converting glycerol into high value-added chemicals are being developed.

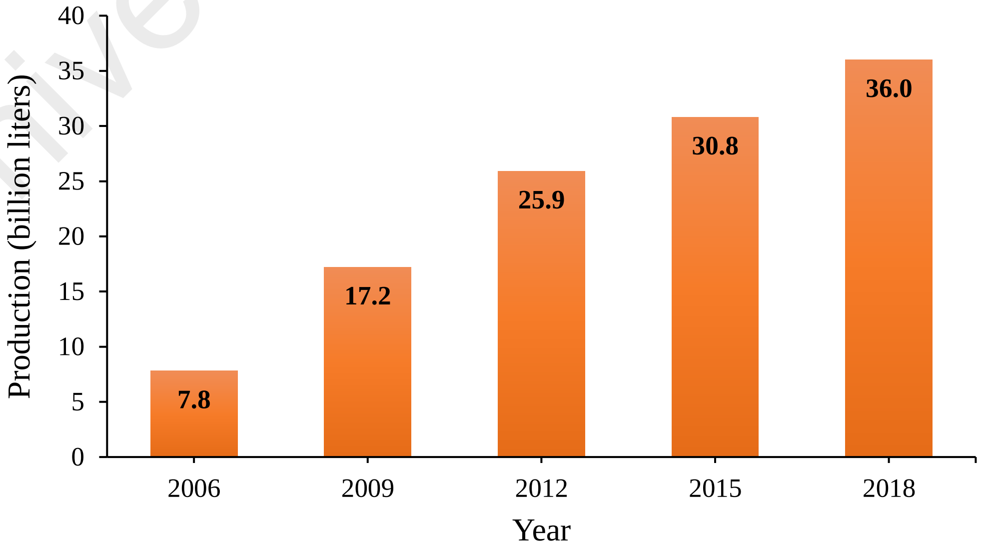


Figure 2.1: World outline of current surplus glycerol production (Nanda et al., 2014).

2.1.1. Physical and chemical properties of glycerol

Glycerol (glycerine or 1,2,3- propanetriol) is an organic compound and it has the chemical formula $C_3H_8O_3$ (Figure 2.2). Glycerol is virtually non-toxic to both human and environment. In pure form, glycerol is a clear, colorless, odorless, hygroscopic, vicious and sweet-taste liquid, which possesses a unique combination of physical and chemical properties. Table 2.1 shows physicochemical properties and toxicity data of glycerol.

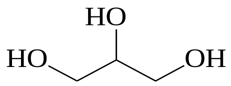


Figure 2.2: Chemical structure of glycerol.

Table 2.1: Some physicochemical properties and toxicity data of glycerol (Mario & Michele, 2010).

Properties	Toxicity data
Melting point	17.8 °C
Boiling point	290 °C
Molecular weight	92.09 g/mol
Viscosity (20 °C)	1200 cP
Vapour pressure (20 °C)	< 1mm Hg
Density (20 °C)	1.26 g cm^{-3}
Flash point	160 °C (closed cup)
Autoignition temperature	400 °C
Critical temperature	492.2 °C
Critical pressure	42.5 atm

Because it is a trihydric alcohol, glycerol is a polar protic solvent with a dielectric constant of 42.5 (at 25 °C) which is intermediate between that of water (78.5) and an ionic liquid such as 1-butyl-3-methylimidazolium hexafluorophosphate (11.4). The three-hydroxyl groups in glycerol dominate its solubility. Glycerol is completely soluble in water and short chain alcohols, sparingly soluble in many common organic solvents (ethyl acetate, dichloromethane, diethyl ether), and is insoluble in hydrocarbons (Mario

& Michele, 2010). Other than that, the extensive intermolecular hydrogen bonding is responsible for the high viscosity and boiling point of glycerol. Taking advantage of its high boiling point, reactions in glycerol can be carried out at high temperatures, thus allowing acceleration of the reaction.

Glycerol represents an important raw compound in numerous fine chemistry (e.g. food, drug, cosmetic and tobacco industry) and bulk industrial chemical processes due to its high chemical reactivity (Pagliaro et al., 2007). A highly functionalized nature exhibited by glycerol is due to the presence of primary and secondary hydroxyl groups that can be replaced with other chemical groups. The primary hydroxyl groups generally are more reactive than the secondary hydroxyl group, thus will preferably react first. In any reaction, however, the second and third hydroxyls will react to some extent before all the most reactive groups are exhausted. A large number of top-value added chemicals such as dihydroxyacetone, mesoxalic acid, 1,3-propane-diol, 1,3-dichloropropanol, glyceryl ethers, glycerol carbonate, and glyceryl esters can be obtained from glycerol by a variety of chemical reactions (Figure 2.3) (Zheng et al., 2008). There is a comprehensive literature and various research works are available on the glycerol valorization to value-added chemicals (Pagliaro et al., 2007; Pagliaro et al., 2009; Behr et al., 2008). Among them, the production of glycerol carbonate plays a prominent role as the monomer which could be used for the production of new functionalized polymers that might have an interesting new application (Ochoa-Gómez et al., 2012a).

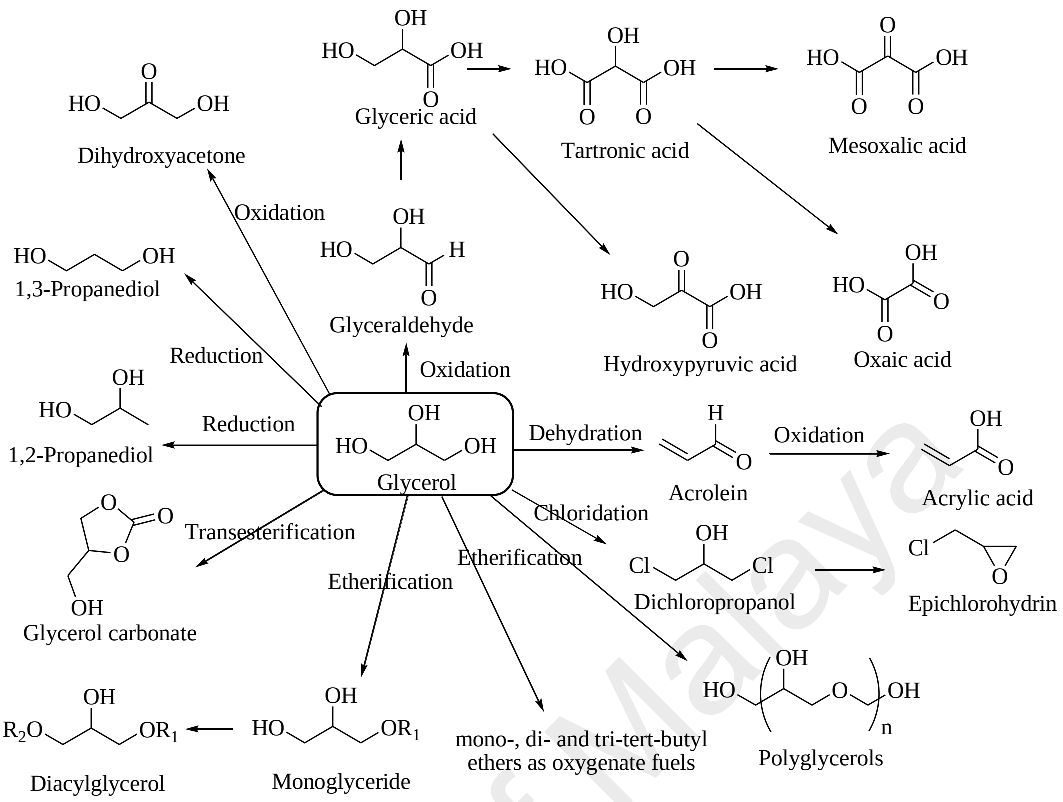


Figure 2.3: Value added chemicals from glycerol (Zheng et al., 2008).

2.2 Glycerol carbonate as a potential value-added chemical

With a focus on recent developments in the conversion of glycerol into value-added chemicals, production of glycerol carbonate is one of the glycerol derivatives that captures at present more scientific and industrial attention. The interest of glycerol carbonate as a bio-based product has broad spectrum of applications in several fields, mainly as a green solvent in analytical applications (Lameiras et al., 2011), Li-ion batteries (Ochoa-Gómez et al., 2012a) or as reaction media (Benoit et al., 2010; Ou et al., 2011). Glycerol carbonate could also serve as raw material for the production of glycidol (Yoo et al., 2001), which is widely being used in the textile, plastics, pharmaceutical and cosmetics industries. Due to its potential end uses, glycerol carbonate is a relatively new product for chemical industry for two main reasons: (1) its wide reactivity, implying numerous applications, (2) as a way to valorize glycerol, which is becoming widely available as a major bio-based by-product from the manufacturing of biodiesel and other chemicals (Behr et al., 2008) (Figure 2.4).

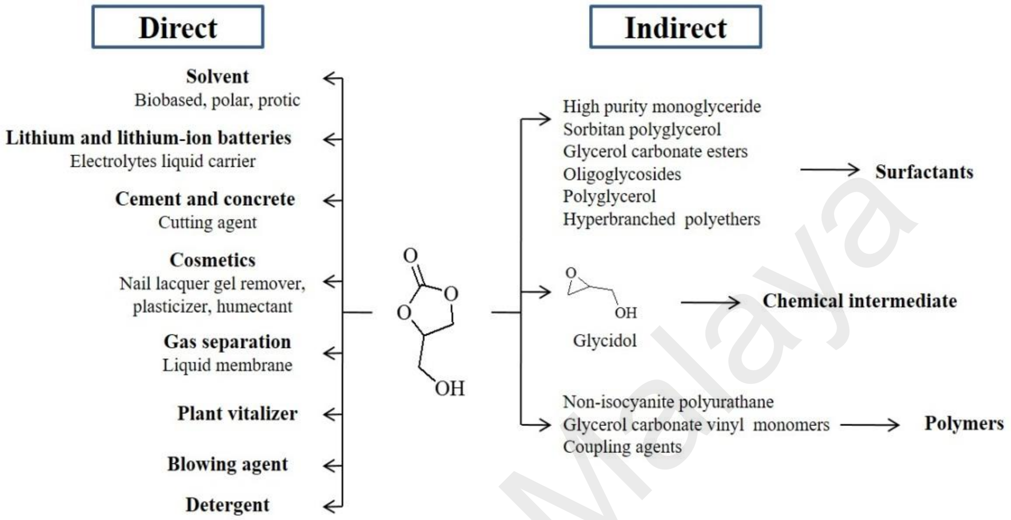


Figure 2.4: Direct and indirect application of glycerol carbonate (Ochoa-Gómez et al., 2012a; Pagliaro et al., 2007).

2.3 Synthesis routes of glycerol carbonate

Figure 2.5 enumerates six proposed synthesis routes of glycerol carbonate. These include direct carbonylation of glycerol with carbon dioxide and oxidative carbonylation of glycerol with the gaseous mixture of carbon monoxide. For indirect carbonylation, the routes include phosgenation, glycerolysis of urea and transesterification of alkyl carbonates and dialkyl carbonates. Their advantages and limitations are presented in Table 2.2 to exhibit the influence of catalyst on glycerol carbonate synthesis process.

Table 2.2: Advantages and disadvantages of conversion route with respect to glycerol carbonate yield.

Route	**Type**	**Catalyst**	**Advantages**	**Disadvantages**	**Glycerol carbonate yield (%)**	**Reference**
Direct route	Glycerol + Carbon dioxide	Sn, KOH/HCl, $La_2O_2CO_3$–ZnO, n-$Bu_2Sn(OMe)_2$, *n*-Bu_2SnO, $RhCl_3$ + PPh_3 + KI	Using bio-based reactant and commercially available at low price, no intermediate steps	Higher reaction temperature and pressure and longer heating time, poor carbon dioxide reactivity, thermodynamically limited, use of organic solvents to enhance the reaction rate and improve yield (from 7.0% to 35.0%), difficult recovery of products, formation of polyglycerols at higher temperature	7.0-90.0 (Free of solvent), 0.2-35.0 (Organic solvent)	Ma et al., 2012; Ochoa-Gómez et al., 2011
	Glycerol + Carbon monoxide	CuCl, $CuBr_2$, $PdCl_2$(1,10-phenanthroline) /KI (include addition of oxygen)	Straightforward synthetic method	Formation of large amount of by-products, toxicity of carbon monoxide, difficult in handling, higher reaction pressure	47.0 (Free of solvent), 83.0-96.0 (Organic solvent)	Hu et al., 2010; Mizuno et al., 1994; Wang et al., 2013

Continue…

Indirect route	Glycerol + Phosgene		Simple and effective way of reaction	Toxic gas, corrosive	-	Nemirowsky, 1885
	Glycerol + Urea	Zn/Ca/ Ma/ Zr/Al$_2$/La$_2$ oxide, ZnSO$_4$, MnSO$_4$, Zn hydrotalcite, γ-zirconium phosphate, gold, gallium, and zinc supported on oxides and Zeolite ZSM-5	Easy separable and recyclable of heterogeneous catalyst. Low cost raw material with low toxicity	Need low pressure, formation of ammonia as by-product, difficult purification	28.0-93.0	
	Glycerol + Alkylene carbonate (Ethylene carbonate/ Propylene carbonate)	Amberlyst A26 HCO$_3$, zeolite, Al/MgO hydrotalcite, Al/Mg, MgO, RNX-MCM41, Amberlyst A26 OH$^-$	Easy separable and recyclable of heterogeneous catalyst	Carbonylation agent expensive, difficult purification	68.0-92.0 (Free of solvent)	Cho et al., 2010; Vieville et al., 1998
	Glycerol + Dimethyl carbonate	Ammonium bromide, K$_2$CO$_3$, K$_2$CO$_3$/MgO, Sn, CaO,Ca(OH)$_2$, LiNO$_3$/Mg$_4$AlO$_{5.5}$,Mg-Al hydrotalcite, Mg/Al/Zr, hydrotalcite-hydromagnesite, lipase	Homogeneous catalyst enhanced reaction rate, non-corrosive, higher product obtained, for enzyme (ambient reactions condition, simplicity in purification of products)	Product yield decrease and polymerization of product at higher temperature, involve consecutive steps of catalyst preparation, costly	59.0-99.0 (Free of solvent), 79.0-99.0 (Organic solvent)	Kumar et al., 2012; Waghmare et al., 2015; Teles et al., 1994; Tudorache et al., 2014; Liu et al., 2014

Continue…

	Glycerol + Diethyl carbonate	1,3-dicholorodistannoxanes, Mg/Al hydrotalcite supported on Al_2O_3, lipase	Higher product obtained, non-polluting	Expensive and denaturation (for enzyme)	95.0-99.0 (Free of solvent), 84.0 (Organic solvent)	Álvarez et al., 2010; Álvarez et al., 2012; Wang & Cao, 2011

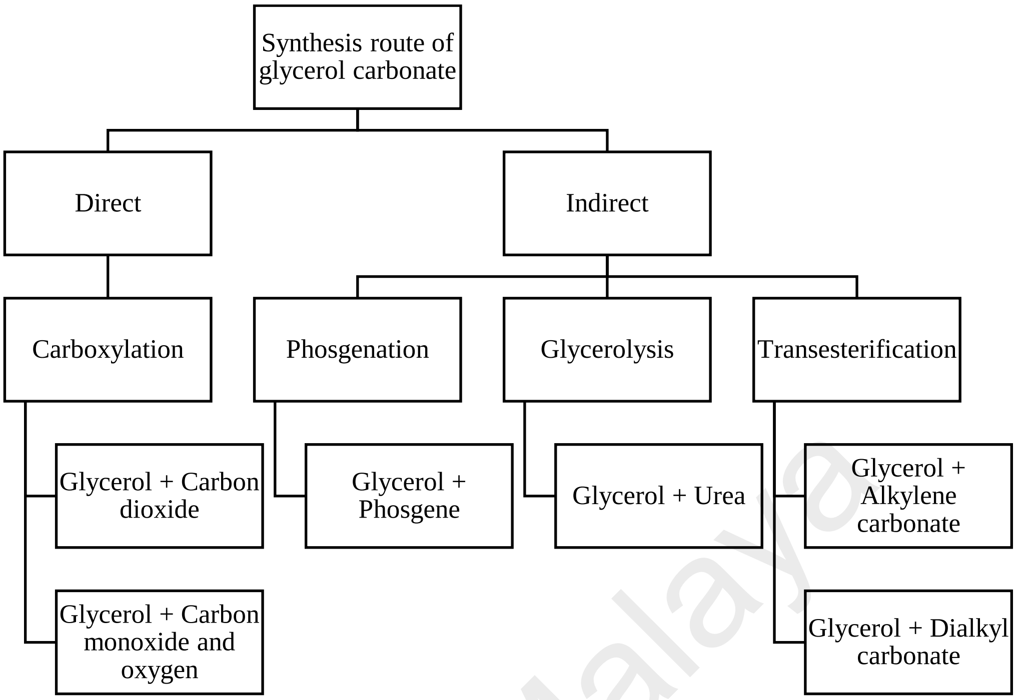
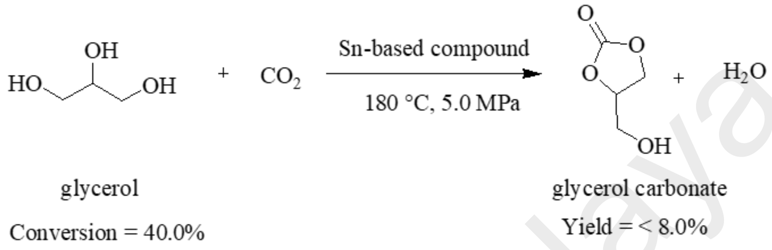


Figure 2.5: Various glycerol carbonate synthesis routes (Ramírez-López, & Belsué, 2012; Sonnati et al., 2013).

2.3.1 Direct synthetic route

2.3.1.1 Carboxylation of glycerol with carbon dioxide and carbon monoxide

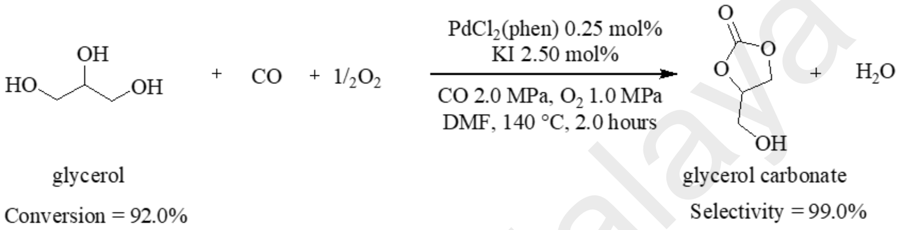
Direct carboxylation of glycerol by carbon dioxide could be considered as the most attractive and environmentally benign pathway leading to glycerol carbonate production because the process uses carbon dioxide, a global warming gas, as a raw material, and the only by-product is water (Scheme 2.1). Accordingly, a number of homogeneous and heterogeneous catalysts such as zeolites (under supercritical conditions), CeO_2/Al_2O_3, Sn-based compounds and rhodium complexes modified with phosphine ligands have been developed for the carboxylation of glycerol (Aresta et al., 2006; Dibenedetto et al., 2011; Ezhova et al., 2012; George et al., 2009; Vieville et al., 1998). However, the result has never been satisfactory in terms of glycerol carbonate yield and selectivity. Up to now, the poor carbon dioxide reactivity has led to yields lower than 8.0%, although a more promising yield of 32.0% has been reported by George et al. (2009). The low catalytic activities of catalyst were also reported even under high pressure because of the thermodynamic limitation (Aresta et al., 2006; Dibenedetto et al., 2011; Vieville et al., 1998).



Scheme 2.1: Synthesis of glycerol carbonate from glycerol and carbon dioxide.

Aresta et al. (2006) has reported the direct carboxylation of glycerol with carbon dioxide using tin complexes (n-$Bu_2Sn(OCH_3)_2$, n-Bu_2SnO and $Sn(OMe)_2$) as catalysts. The high temperature of 180 °C and a pressure of 50 atm were employed in the reaction. The conversion of glycerol was only 2.3% at 6.0 hours, 5.0 MPa and 453 K. In an attempt to increase the glycerol carbonate yield, molecular sieves were used to remove water from the gas phase and tetraethylene glycol dimethyl ether was used as a solvent. These have led to a slight increase of glycerol carbonate yield up to 35.0% at 4.0 hours, 13.8 MPa and 393 K. At higher pressure, carbon dioxide occurs in the liquid state thus required special expensive equipment to handle. Other than that, coupling agents (Tomishige et al., 2004), co-reactant such as ethylene carbonate (Vieville et al., 1998), solvents such as ethanol, n-butyl alcohol, acetone, tetrahydrofuran, pyridine, dimethyl sulfonate and dimethylformamide and dehydrating agent such as valeronitrile, benzonitrile, phenyl acetonitrile, 2-cyanopyridine (Liu et al., 2016) were also added to increase glycerol carbonate yield.

Carboxylation of glycerol with carbon monoxide and oxygen has also been previously reported (Scheme 2.2). Although it is a straightforward reaction, but this method has few drawbacks such as rigorous reaction conditions, formation of large number of by-products, toxicity of carbon monoxide and inherent difficulty to handle it safely both at laboratory and industrial scales (Hu et al., 2010; Mizuno et al., 2010; Teles et al., 1994; Wang et al., 2013).

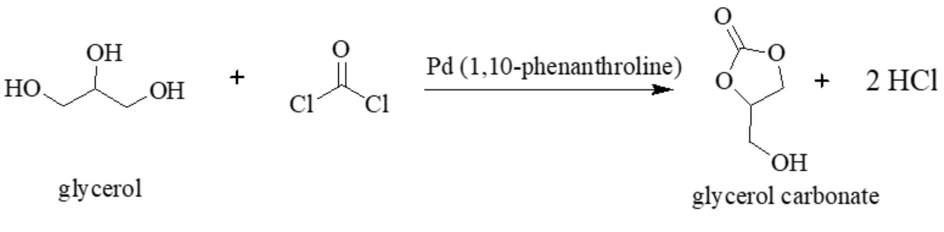


Scheme 2.2: Synthesis of glycerol carbonate from glycerol and carbon monoxide.

2.3.2 Indirect synthetic route

2.3.1.1 Phosgene

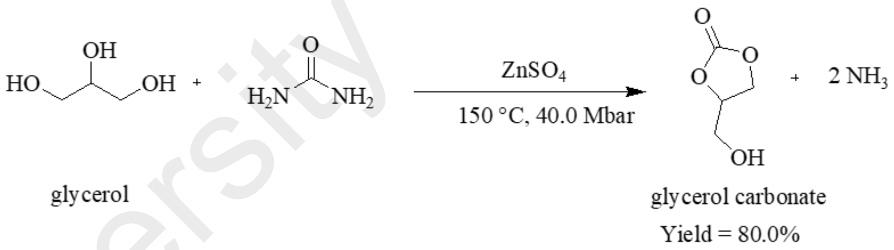
The indirect synthetic route involved phosgenation using phosgene shows to be a very simple and effective way to produce organic carbonates. Phosgenation reaction is somehow hazardous due to the toxicity of phosgene, thus the use of phosgene is limited (Climent et al., 2010; Sonnati et al., 2013) (Scheme 2.3).



Scheme 2.3: Phosgenation of glycerol carbonate from glycerol and phosgene.

2.3.1.2 Urea

As an alternative to carbon dioxide, urea has been extensively investigated as in indirect synthetic route (Scheme 2.4). This is a phosgene-free process that uses easily available and low-cost raw materials with low toxicity. Carbonylation of glycerol with urea are catalyzed by basic oxides; magnesium oxide (MgO) and calcium oxide (CaO), Al/Mg and Al/Li mixed oxides (Climent et al., 2010), samarium exchanged heteropoly acid (Ramesh Kumar & Jagadeeswaraiah, 2012), zirconium phosphate (Aresta et al., 2009), zinc compounds, lanthanum-based mixed oxide (Zhang & He, 2014), gold and palladium based supported (Ab Rahim et al., 2013), hydrotalcite based (Aresta et al., 2009; Climent et al., 2010; Park et al., 2012), boiler ash (Indran et al., 2014) and tin-tungsten mixed oxide (Jagadeeswaraiah et al., 2014).



Scheme 2.4: Carbonylation of glycerol carbonate with glycerol and urea.

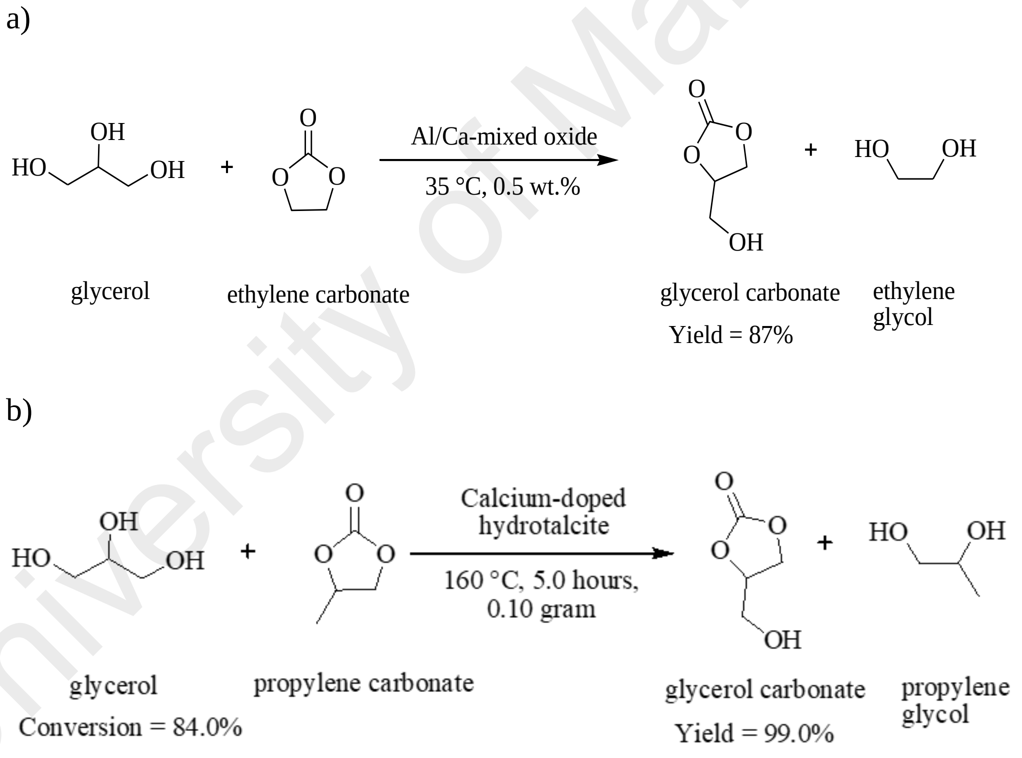
Mouloungui et al. (1996) patented the synthesis of glycerol carbonate by carbonylation of glycerol with urea in the presence of a catalyst bearing Lewis acid sites, in particular, metallic or organometallic salts or supported metallic compounds. Okutsu & Kitsuki (2001) have prepared glycerol carbonate by reacting glycerol with urea with zinc oxide (ZnO) in the presence of a dehydrating agent such as anhydrous magnesium sulfate ($MgSO_4$). After 6.0 hours of reaction time, the conversion of glycerol was 62.0% to 65.0% with a selectivity close to 92.0%. Catalysts based on zinc, $Zn(CH_3C_6H_4\text{-}SO_3)_2$, were used by Yoo & Mouloungui (2003) to synthesize glycerol carbonate from glycerol with urea and glycerol conversion achieved was 85.0% after 1.0 hour of reaction. A recent study by Nguyen-Phu et al. (2016) showed that Zn/Al mixed oxide was successfully impregnated into activated red mud which attained a glycerol carbonate yield of 59.8%, which is higher than 49.6% of the unsupported catalyst, $Zn_7Al_3O_x$.

Although the urea process is highly efficient for the production of glycerol carbonate, the reaction must be conducted at elevated temperature (Turney et al., 2013) and consumes a relatively longer reaction time about 1.0 hours to 8.0 hours (Sharath Babu et al., 2015). Moreover, the reaction is preferably carried out under vacuum, in particular at a pressure of between 10.0^3 Pa and 2.1^4 Pa, so as to displace the point of equilibrium of the reactions by continuously eliminating ammonia from the gaseous state.

2.3.1.3 Alkylene carbonate

Transesterifications are highly useful reactions for utilization of recent huge amount of glycerol production originated biodiesel synthesis from triglyceride and methanol (Andreani & Rocha, 2012). Transesterification of glycerol with alkylene carbonate (ethylene carbonate/propylene carbonate) is a safer and more effective method that involves much lower reaction temperature and high yield of glycerol carbonate (Alvarez et al., 2010; Climent et al., 2010; Mouloungui et al., 1996). Ethylene carbonate possesses interesting physical properties such as low toxicity, low evaporation rate, biodegradability and high solvency.

At present, potassium hydroxide (NaOH) (Esteban et al., 2016), Mg/Al hydrotalcite (Climent et al., 2010), Zn/Al hydrotalcite (Climent et al., 2010), potassium carbonate and MCM-41 based materials (Cho et al., 2010) have been used to catalyze the transesterification reaction of glycerol and ethylene carbonate. Moreover, the transesterification of glycerol in supercritical carbon dioxide using zeolites or strongly basic resins gives low glycerol carbonate yields (less than 25.0%) (Vieville et al., 1998). Through this route (Scheme 2.5 (a)), ethylene glycol was formed as a by-product with a high boiling point. Reducing the pressure is necessary during purification step to separate ethylene glycol from the glycerol carbonate production process.



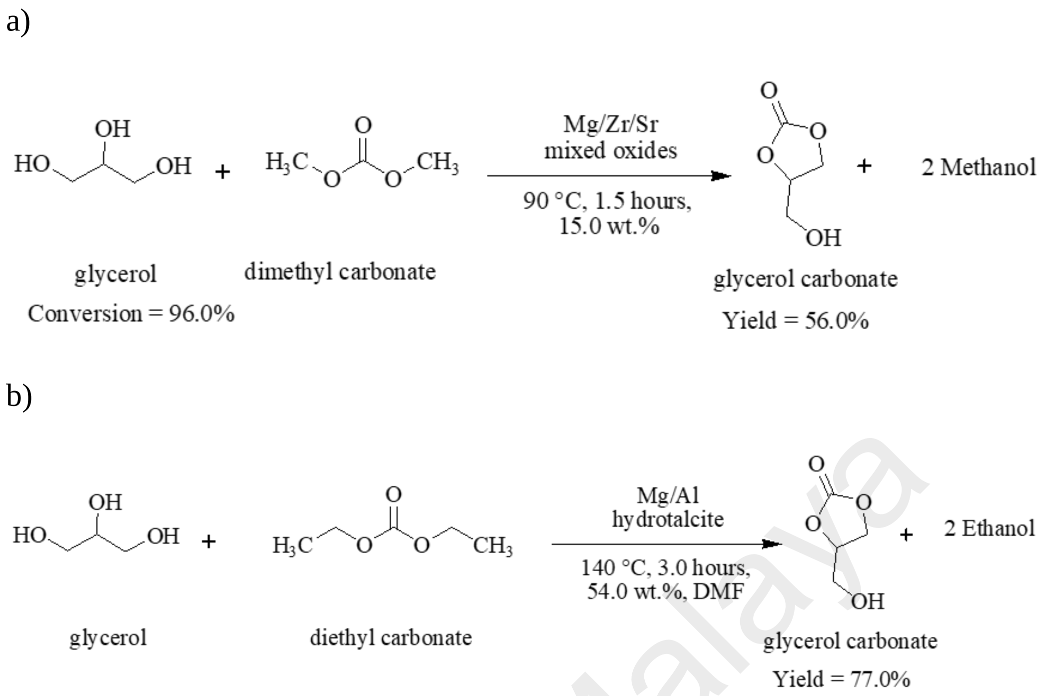
Scheme 2.5: Transesterification reaction of glycerol carbonate from glycerol and a) ethylene carbonate and b) propylene carbonate.

Despite promising metal-containing catalyst systems that have been developed for the synthesis of glycerol carbonate from glycerol and ethylene carbonate, ethylene carbonate is expensive. Thus, it is an urgent to find an efficient, inexpensive, and also environmental-friendly metal-free catalytic system for this interesting reaction.

2.3.1.4 Dialkyl carbonate

The most studied route for the synthesis of glycerol carbonate is via the environmentally benign transesterification of glycerol with dialkyl carbonate (Scheme 2.6). This is the most direct and industrial feasible pathways to produce high glycerol carbonate yield with safe or moderate reaction conditions (Ochoa-Gómez et al., 2012a). Dimethyl carbonate, diethyl carbonate or dibutyl carbonate (Tudorache et al., 2014) has been used as carbonate sources for transesterification reaction (Pasquier et al., 2009). Dimethyl carbonate is an environmentally-harmless chemical, which can be prepared from methanol and urea. It can also be synthesized by utilization of carbon dioxide, a readily available, inexpensive and environmentally acceptable starting material (La et al., 2007).

Likewise, diethyl carbonate is also an important commercial compound that can be prepared by ethanol and urea. It is non-toxic and readily more biodegradable (Tundo et al, 2002). Moreover, diethyl carbonate including ethoxy and carbonyl groups can be used as an effective carbonylating and ethylating agent as well as a raw material for manufacturing polycarbonates (Wang et al., 2007). Diethyl carbonate is also an excellent solvent and an intermediate for various pharmaceuticals such as antibiotic and phenobarbital. In addition, diethyl carbonate can be used as the electrolyte of lithium ion battery widely (Shaikh & Sivaram, 1996).



Scheme 2.6: Transesterification reaction of glycerol carbonate from glycerol and a) dimethyl carbonate and b) diethyl carbonate.

2.3.3 Summary on the synthesis routes of glycerol carbonate

As summary, two synthesis routes (direct and indirect routes) of glycerol carbonate have been well elaborated in section 2.3.1 and section 2.3.2. Among the routes for glycerol carbonate synthesis, transesterification of glycerol with dialkyl carbonate is one of the most direct and industrially feasible pathways to produce high glycerol carbonate yield. Moreover, this reaction offers facile separation of the product, by simple distillation of the methyl/ethyl alcohol co-product. With such transesterification reactions proving both efficient in catalysis and product isolation, the focus turned to substrate scope, and in particular to a substrate that had come to prominent attention due to the biodiesel boom at the end of the 20th century, glycerol. This synthesis route will be discussed systematically in the subsequent sub-chapter.

2.4 Homogeneous catalyst for transesterification reaction of glycerol with dialkyl carbonate

In this study, homogeneous catalyst system for transesterification reaction of glycerol is focused. Homogeneous catalyst can be defined as a catalyst that remains in the same phase (liquid) as the reactants enhancing reaction rate of a reaction without consuming itself. It provides an alternative way of lowering activation energy. Furthermore, it is non-corrosive which gives higher percentage of product while for the enzyme, it can perform well at an ambient reactions condition with simplicity in the purification of products. Due to the mentioned point, many studies have devoted attention to exploring the best homogeneous catalyst to enhance glycerol conversion and glycerol carbonate yield and selectivity. Consequently, Table 2.3 summarizes the reported homogeneous catalysts (not including ionic liquids) employed in transesterification reaction of glycerol with dialkyl carbonate.

Notably, a primary advantage of homogeneous catalysts is that the reaction rates are generally higher than those with heterogeneous catalysts. However, it has been reported that the homogeneous acidic catalysts are not suitable for glycerol carbonate synthesis as they indicate relatively weak catalytic activities (Ochoa-Gómez et al., 2012a). Less than 5.0% of glycerol carbonate yield has been reported using the strong acid such as *p*-toluenesulfonic or sulfuric acids in the catalytic reaction. Longer reaction time within 24.0 hours is needed in order to improve yield up to 50.0%.

Unlike acidic catalyst, homogeneous strong basic catalysts such as KOH, NaOH, $NaHCO_3$, calcium complex $Ca(C_3H_7O_3)(OCO_2CH_3)$, potassium carbonate (K_2CO_3) and ionic liquids have been employed in transesterification reaction which gave more than

90.0% glycerol carbonate yield (Chiappe & Rajamani, 2012; Jesus Esteban et al., 2015; Yi et al., 2014). However, the traditional synthesis of glycerol carbonate which involves the use of NaOH or $NaHCO_3$ has introduced several drawbacks such as the corrosion of the reactors and generation of basic aqueous effluents due to the neutralization of the base as well as the recovery of the product by distillation under reduced pressure (Arthur et al., 1959). In the view of this, pioneer works conducted by Herseczki et al. (2009), Rokicki et al. (2005) and Herseczki et al. (2011) have attempted to look on another catalyst for the transesterification reaction. From their findings, K_2CO_3 performed the best in catalyzing the transesterification of glycerol without the addition of any solvent. However, the formation of by-products was reported. Higher glycerol/dimethyl carbonate ratio over long reaction time (more than 48.0 hours) has led to the formation of glycerol dicarbonate about 34.0%. Glycerol dicarbonate can react further to form diglycerol tricarbonate, with relatively low yield about 18.0%. Progressive removal of methanol from the system was applied to reduce the percentage of by-products formed. On the other side, ring opening polymerization of glycerol carbonate to glycidol has significantly reduced glycerol carbonate selectivity. Aresta et al. (2006) discovered that n-$Bu_2Sn(OCH_3)_2$ has promoted transesterification reaction of equimolar glycerol/dimethyl carbonate of 1, resulting in a 65.0% glycerol conversion after 15.0 hours.

A study conducted by Naik et al. (2009) shows that organocatalyst; 1-n-butyl-3-methylimidazolium-2-carboxylate ([Bmim-2-CO_2]) is an effective catalyst for synthesizing glycerol carbonate. Interestingly, glycerol carbonate yield achieved 100.0% within 1.3 hours, thus exceeds the results achieved by K_2CO_3 claiming that glycerol carbonate can be obtained after 3.0 hours at 3.00 mol% of catalyst loading to get the comparable conversion (Rokicki et al., 2005).

Patel et al. (2009) has demonstrated that 1,3-dichlordistannoxanes have performed well as catalyst in the production of glycerol carbonate from transesterification of glycerol and diethyl carbonate without the addition of solvent. This is with regards to their earlier findings, which implied that ethylene carbonate and 1,2-propylene carbonate can be synthesized from respective polyols; ethylene glycol and 1,2-propylene glycol, using the same catalyst. Cyclic diamines such as, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were also found to exhibit high catalytic activities for the transesterification of glycerol with dimethyl carbonate (Munshi et al., 2014c).

As described above, conventional acid or base liquid catalysts for transesterification processes often entail several synthetic and environmental concerns. In this scenario, the need to find or implement the transesterification reaction based on innovative and possibly green catalysts and reaction pathway remains still a highly desirable target. One of the alternatives is using ionic liquids as catalysts as they are well known to be environmental-friendly and has driven their exploration and exploitation in countless fields among the physical and chemical sciences. The increased interest in ionic liquids by chemists and technologists clearly is also due to the utility of ionic liquids as solvents for reaction chemistry, including catalytic reactions. With this, scientists have made a concentrated effort to improve the performance of the ionic liquid catalysts (Welton, 1999). Ionic liquid as catalyst on transesterification reaction of glycerol and dialkyl carbonate will be discussed systematically in section 2.5 with more details focusing on its properties and performance upon the reaction.

Table 2.3: Comparison of reaction conditions and performance of various catalysts (except of ionic liquid) for glycerol transesterification.

Type of catalyst	Reaction conditions					Performance Y/C/S (%)	Reference
	Temperature (°C)	Molar ratio (carbonate/ glycerol)	Reaction time (hour)	Catalyst loading (wt.% or mol%)	Solvent		
Homogeneous base catalyst							
Potassium carbonate (K_2CO_3)	73-75	$3:1^a$	3.0	4.5 wt.%	nil	Y = 97.0	Rokicki et al., 2005
K_2CO_3	71-76	$3:1^a$	5.0	4.5 wt.%	nil	N.A.	Herseczki, Varga, & Marton, 2009
K_2CO_3	75	$5:1^a$	1.5	15.0 wt.%	nil	Y = 100.0	Ochoa-Gómez et al., 2009
K_2CO_3	73-75	$10:1^a$	48.0	4.5 wt.%	nil	Y = 18.0	Rokicki et al., 2005
K_2CO_3	73-75	$3:1^b$	4.0	3.00 mol%	nil	Y = 97.0	
K_2CO_3	70	$3:1^a$	1.0	1.0% w/w	nil	N.A	Esteban et al., 2015
Potassium hydroxide (KOH)	75	$5:1^a$	1.5	6.0 wt.%	nil	Y = 100.0	Ochoa-Gómez et al., 2009
Sodium hydroxide (NaOH)	75	$5:1^a$	1.5	4.0 wt.%	nil	Y = 98.5	Ochoa-Gómez et al., 2009
Triethylamine	68-88	$4:1^a$	2.5	10.00 mol%	nil	Y = 98.0	Ochoa-Gómez et al., 2012b
N-heterocyclic carbenes	Room temperature	$3.5:1^a$	0.33	2.60 mol%	nil	Y = 95.7	Hervert et al., 2014

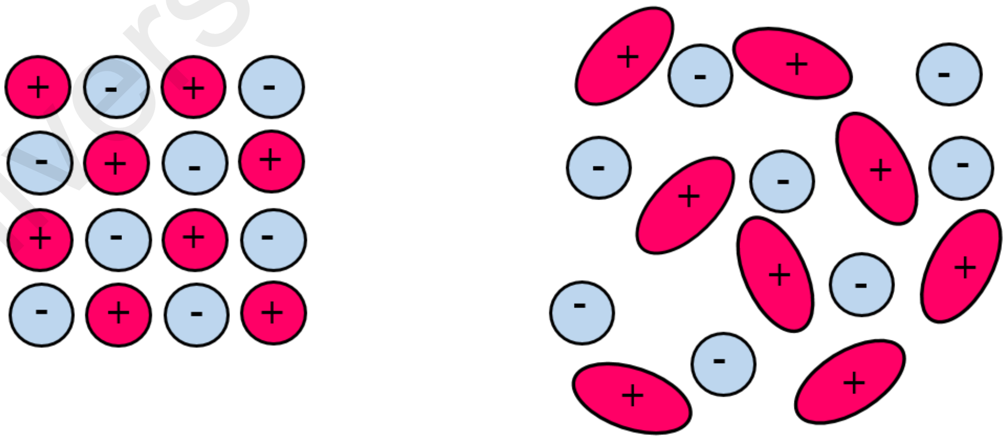
Continue…

1,3-Dichlorodistannoxanes	100	5:1[b]	2.0	0.50 mol%	nil	Y = 99.1	Patel et al., 2009
1-n-butyl-3-methylimmidazolium carboxylate	74	3.2:1	1.33	1.00 mol%	nil	Y = 100.0	Naik et al., 2009
1-n-butyl-3-methylimmidazolium carboxylate	74	3.2:1	5.0	5.00 mol%	nil	Y = 93.0	
Homogeneous acid catalyst							
Sulphuric acid (H_2SO_4)	75	5:1[a]	1.5	10.00 mol%	nil	Y = 3.5	Ochoa-Gómez et al., 2009
p-Toluenesulfonic acid	75	5:1[a]	1.5	10.00 mol%	nil	Y = 4.3	

Y = yield of glycerol carbonate, C = conversion of glycerol, S = selectivity of glycerol carbonate, N.A = not available, nil = not in list, [a] = use dimethyl carbonate as carbonate source, [b] = use diethyl carbonate as carbonate source, [c] = use ethylene carbonate as carbonate source

2.5 Ionic liquids

Ionic liquids are constituted of a wide range of organic cation and organic/inorganic anion and are liquid at or below 100 °C. In general, ionic compounds composed entirely of ions, are solids with high melting points, for example, above 450 °C. These solids are commonly known as 'molten salts' when heated to above their melting points. In contrast to "molten salt", ionic liquids have low melting points, from −100 °C to 200 °C. A simple example of a "molten salt" is molten sodium chloride (NaCl) which has a melting point of 801 °C (Figure 2.6). The considerable difference in the melting temperature between molten salt NaCl and ionic liquid, for example 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]) lies in the asymmetric and large cation of ionic liquids, leading to a difficult packing structure of the cations and anions as well as weak ionic bond between them as shown in Figure 2.6.



NaCl
(melting point 801 °C)

[Emim][Cl]
(melting point 87 °C)

Figure 2.6: Comparison between lattice energy of NaCl and [Emim][Cl] (Wilkes, Levisky, Wilson, & Hussey, 1982).

Some typical structures of ionic liquids are shown in Figure 2.7. Heteroatom cations such as alkylimidazolium, alkylpyridinium, alkylammonium and alkylphosphonium ions are the most widely used cations in the ionic liquids family. A wide range of physical characteristics of ionic liquids can be developed incorporating many different anions: including hexafluorophosphate, ethanoate, trifluoroethanoate, sulfate, hydrogensulfate, alkylsulfate, nitrate, biscyanamide ($[N(CN)_2]_2$), trifluoromethanesulfonate ($[CF_3SO_3]_2$), bis-trifluoromethylsulfonyl amide ($[N(CF_3SO_2)_2]_2$) and tris-trifluoromethylsulfonyl methanide ($[C(CF_3SO_2)_3]_2$). There are about one trillion (10^{18}) possible cation or anion combinations to produce ionic liquids, which can fit the needs of targeted properties and also specific reaction (Huddleston et al., 2001; Holbrey & Seddon, 1999).

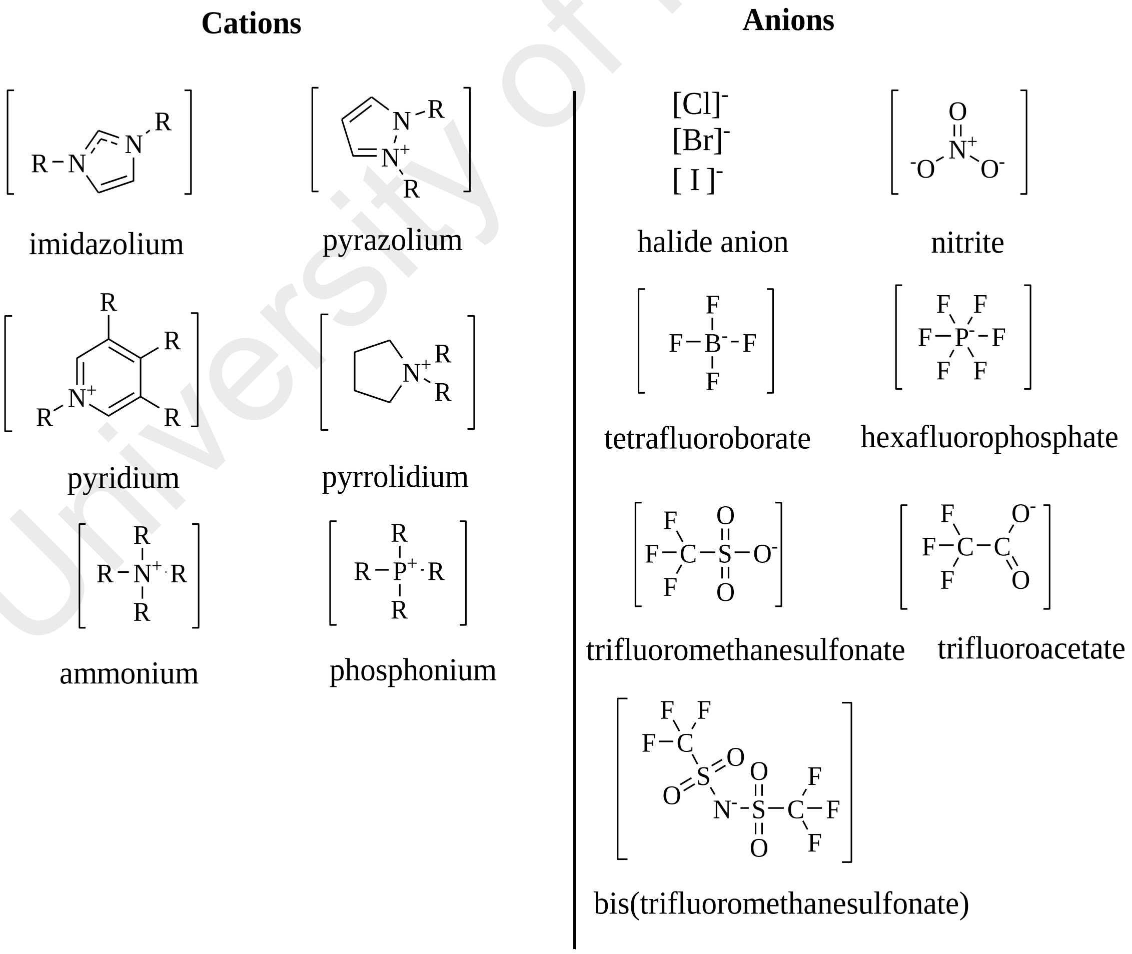


Figure 2.7: Examples of some typical cations and anions of ionic liquids.

Ionic liquids also exhibit high thermal stability, non-flammable, high electrical conductivity, low or negligible vapor pressure and low toxicity (Sheldon, 2001; Wasserscheid & Welton, 2008). Because of the unique properties of ionic liquids, they are integrated in many fields such as analytical chemistry (Joshi & Anderson, 2012), electrochemistry (Seddon, 1996), solvent for organic reaction (da Costa Lopes et al., 2013) and catalysis (Shu et al., 2014; Cheng et al., 2013). Besides, behaving as either solvent or catalyst in chemical processes, they could also act as both, thus drawn attention not only within academic area but also in industry.

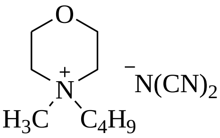
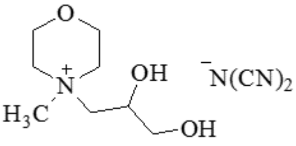
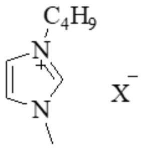
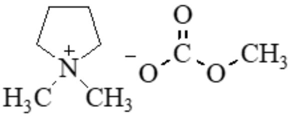
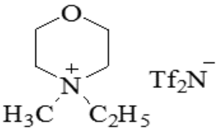
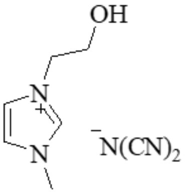
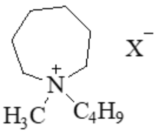
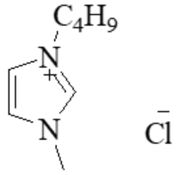
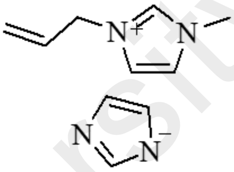
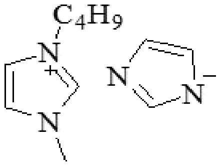
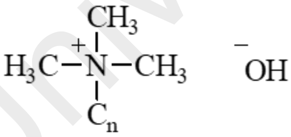
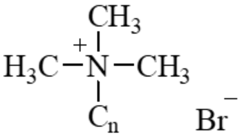
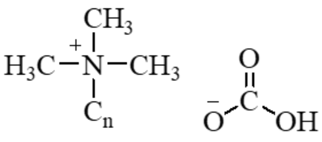
2.5.1 Ionic liquids as catalysts

The ability of ionic liquids to act as a solvent in chemical processes has never been argued before (Bose et al., 2010; Heinze et al., 2005; Sheldon, 2001). Yet, they also performed excellently as a catalyst and received considerable attention due to their prospects for 'green' catalysis (Rani et al., 2011). Ionic liquids can be designed to be used as a catalyst to accelerate the reaction and provide high catalytic activity as well as excellent chemical and thermal stability. It is evidenced that ionic liquids act as desirable catalysts for several organic synthetic reactions, including Diels-Alder reactions, hydrogenation, polymerization, cycloaddition, esterification and transesterification reaction (Anthofer et al., 2014; Lan et al., 2016; Welton, 1999; Welton, 2004). Anion and cation of ionic liquids can be change independently, allowing its properties such as solvation properties, polarity (Chiappe et al., 2009), viscosity and acidity or basicity of ionic liquids to be tuned to purpose. Furthermore, ionic liquids exhibited acidic or basic properties, which the combination of these unique properties emerges them as green reaction media and also catalyst (Gong et al., 2008). The acidity or basicity of reactive ionic liquids is governed by the strength of the cation, anion, or by the combination of the cation and anion.

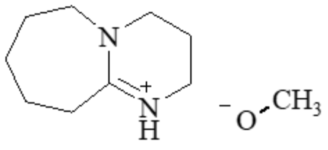
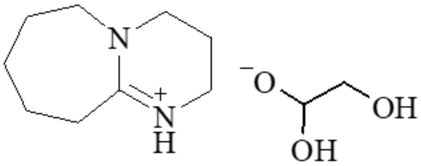
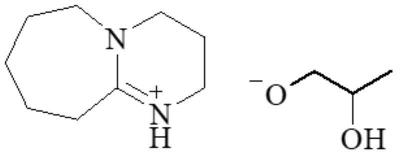
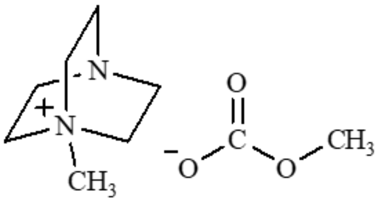
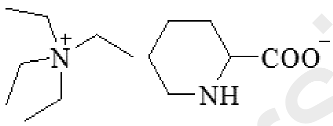
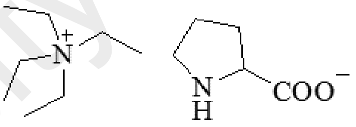
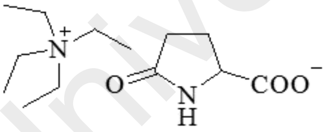
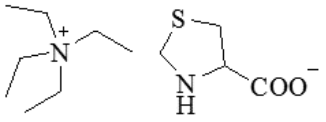
In another hand, the polarity of ionic liquids can be measured by means of polarity scales which describe the potential behaviors of the solvent in a relationship with the solute and that it is not an absolute property of the pure liquid (Rani et al., 2011). Kamlet & Taft (1976) introduced the multi-parameter polarity scales that comprises the complimentary scales of hydrogen bond acidity (α), (Taft & Kamlet, 1976) hydrogen bond basicity (β) and the dipolarity/ polarizability effects (π*) (Kamlet et al., 1977). These scales together provide greater sophistication when describing the polarity of a solvent than single parameter scales. Thus, the strength of cation and anion can be referred to the hydrogen bond acidity (α) and hydrogen bond basicity (β) value, respectively.

An efficient and realistic use of ionic liquids in catalysis requires the knowledge of their hydrogen bond acceptor of anion and hydrogen bond donor of cation ability. This will allow the preparation of acidic or basic ionic liquids. The common structures of ionic liquids used as the catalyst for transesterification reaction of glycerol are presented in Table 2.4. As a way of understanding the mechanism of transesterification reaction of glycerol and dialkyl carbonate for synthesizing glycerol carbonate, the roles of cation and anion of ionic liquids as catalysts were explored and further elaborate from section 2.5.1.1 to 2.5.1.3.

Table 2.4: Typical ionic liquids as catalysts use in transesterification reaction.

Ionic liquid	Reference
 $[Mor_{1,4}][N(CN)_2]$  $[Mor_{1,g}][N(CN)_2]$  X = Tf_2N $[Bmim][Tf_2N]$ X = PF_6 $[Bmim][PF_6]$  [Mmpyrr][$MeCO_3$]  $[Mor_{1,2}][Tf_2N]$  [HOEmim][$N(CN)_2$]  X = Tf_2N $[Hme_{1,4}][Tf_2N]$ X = $N(CN)_2$ $[Hme_{1,4}][N(CN)_2]$	Chiappe & Rajamani, 2012
 [Bmim][Cl]  [Amim][Im]  [bmim][Im]	Yi et al., 2014
 $H_3C-\overset{CH_3}{\underset{C_n}{\overset{+}{N}}}-CH_3 \quad {}^{-}OH$ [Tea][OH] C_n = methyl, ethyl, butyl, propyl  $H_3C-\overset{CH_3}{\underset{C_n}{\overset{+}{N}}}-CH_3 \quad Br^{-}$ [Tma][Br] C_n = methyl, butyl  [Tma][HCO_3] C_n = methyl, butyl	Gade et al., 2012

Continue…

 [DBU][methanol]  [DBU][glycerol]  [DBU][propylene glycol]	Munshi et al., 2014a
 [DABCO][Dmc]	Munshi et al., 2014b
 [N_{2222}][Pipe]  [N_{2222}][Pro]  [N_{2222}][H-pyr]  [N_{2222}][Thio]	Zhou et al., 2015

2.5.1.1 Effect of anion to transesterification reaction of glycerol

It is in general accepted that the strongest forces in ionic liquids are exhibited by basic anions which depends on their hydrogen bond acceptor ability (β) value to activate nucleophile, thus inflating the glycerol conversion. Choi et al. (2013) demonstrated that glycerol conversion increases with increasing β value of ionic liquid which is from 1.0 to 1.2. They suggested that the degree of the interaction between the anion and hydroxyl groups of glycerol through the hydrogen-bond is the most important factor in determining the activity of ionic liquids and selectivity pattern.

In another finding, Gade et al. (2012) reported that hydroxide and bicarbonate-based ionic liquids (tetraalkylammonium hydroxide; [Tea][OH], [Tba][OH], [Tma][OH]) and (tetraalkylammonium bicarbonate; [Tma][HCO_3], [Tba][HCO_3]) have been pointed out to effectively converted 77.0% to 95.0% of glycerol at 80 °C within 1.5 hours. The selectivity to glycerol carbonate after 1.5 hours of reaction time was reported with a range of 33.0% to 56.0% (Table 2.5). The higher basicity of hydroxide and bicarbonate counter ions best explains the higher activity achieved. They also reported that there was glycidol formation where its selectivity increased within the range of 26.0% to 70.0% as the catalyst loading increased. This could be due to the increase in the concentration of catalyst in the reaction mixture leading to an increase in glycerol carbonate decarboxylation. Halide-based ionic liquids such as [Tma][Br] and [Tba][Br] were not active for the reaction and only trace the amount of product was formed in these reactions.

Chiappe & Rajamani (2012) demonstrated that dicyanamide-based counteranion showed better catalytic activity, giving higher conversion and selectivity compared to neutral-based ionic liquids such as Tf_2N and PF_6 based counteranion. N-methyl-N-butylmorpholinium dicyanamide ($[Mor_{1,4}][N(CN)_2]$) give 95.0% glycerol conversion at 120 °C within 13.0 hours using a dimethyl carbonate/glycerol molar ratio of 3:1. Besides, highly basic ionic liquids N,N-dimethylpyrrolidinium methylcarbonate ($[mmPyrr][MeCO_3]$) gave complete glycerol conversion within 9.0 hours at 120 °C and a molar ratio of $[mmPyrr][MeCO_3]$/glycerol of 1:10.

Yi et al. (2014) demonstrated that 1-butyl-3-methylimidazolium imidazolide ([Bmim][Im]) gives better performance with higher conversion and selectivity compared to 1-butyl-3-methylimidazolium hydroxide ([Bmim][OH]) with 73.0% and 59.0% glycerol conversion, respectively. The differences of the catalysts performance can be attributed to the stronger basicity and dispersibility properties of the $[Im]^-$ anion relative to the $[OH]^-$ anion. $[Im]^-$ anion tends to undergo a stronger interaction with the hydroxyl group of glycerol resulting in the facile formation of the corresponding $[OH]^-$ anion followed by a nucleophilic attack on the carbonyl group of dimethyl carbonate. [Bmim][Im] was also found to give 73.4% glycerol conversion and 100.0% glycerol carbonate selectivity whereas neutral ionic liquid [Bmim][Cl] gave a lower glycerol conversion. These results were consistent with those described by Lin et al. (2013).

2.5.1.2 Effect of cation to transesterification reaction of glycerol

In general, the ability of cation to activate electrophile depends on their hydrogen bond donor (α) value. With respect to the effect of cation towards catalyst activity, Cho et al. (2010) demonstrated that increasing the alkyl chain length from ethyl to butyl of the cation of quaternary ammonium immobilized onto MCM-41 ionic liquids (heterogeneous catalyst) resulted in a significant increment of the conversion of glycerol of 93.0%, 79.0%

glycerol carbonate selectivity at 80 °C for 1.5 hours and turnover number (TON) in the range of 147 to 202. This is in good agreement with the previous reports on the effect of alkyl chain length of cation throughout the reaction (Ju et al., 2007). These findings were attributed to the stronger electron-donating ability of its butyl group compared with the other alkyl chain. Theoretically, increasing the bulkiness of alkyl chain may result in less electrostatic interaction between cation and anion which thereby forces anion away. The larger distance between cation and anion will lead to a higher mobility of anion. Therefore, anion will be much easier to initiate the reaction.

2.5.1.3 Synergistic effect of cation and anion to transesterification reaction of glycerol

In some studies, researchers have reported that synergistic catalytic effects of ionic liquids catalytic system play an important role in promoting the conversion of glycerol to glycerol carbonate. This is owing to the fact that the cation and anion of ionic liquids can cooperatively act as nucleophilic and electrophilic to catalyze various reactions which involve carbonyl activation (Zhang et al., 2011). They both work together by electrophile-nucleophile dual activation.

The plausible mechanisms also have been proposed by Munshi et al. (2014a) (as discussed in section 2.5.1.1) by considering the earlier proposed mechanism by Selva et al., (2012) and Gade et al. (2012) which reported on the parallel requirement of both anions and cations of ionic liquids for the activation of dimethyl carbonate and alcohols. Munshi et al. (2014a) reported on DBU-based ionic liquids in the transesterification reaction of glycerol with respect to the low TON which was reported in previous studies (Cho et al., 2010; Gade et al., 2012; Patel et al., 2009). They found that the 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)-methanol ionic liquid catalyst gave higher catalytic activity (TON = 9408). Then, the researchers have screened amidine-based ionic liquids; 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo [2.2.2] octane (DABCO), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), and 1,5- diazabicyclo[4.3.0]non-5-ene (DBN) for the transesterification reaction of dimethyl carbonate and glycerol (Munshi et al., 2014b). The results showed that, DBU performed better than DBN with 98.0% glycerol conversion and 96.0% glycerol carbonate selectivity at 100 °C within 7.5 hours and 0.01 mol% catalyst loading (TON = 9408) which is in line with their earlier reported work (Munshi et al., 2014a) (Figure 2.8).

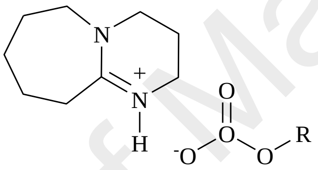


Figure 2.8: DBU based ionic liquid.

The synergistic effect of cation and anion on transesterification reaction of glycerol was also discussed by Cheng et al. (2013). They have found that hydrogen bonding originated from $C_{aromatic}$−H moieties of the cation has a positive effect on the ring-opening of epoxide to promote the synthesis of cyclic carbonate, while it may also weaken the nucleophilicity of the anions by limiting their movements to some extent (Cheng et al., 2013). Besides, the presence of hydroxyl groups on the cation did not affect the catalytic activity and nuclear magnetic resonance analysis of the reaction mixtures showed that the dihydroxyl-functionalized ionic liquids do not compete significantly with the glycerol in the reaction with dimethyl carbonate (Chiappe & Rajamani, 2012). Table 2.5 summarizes the ionic liquids that have been used as catalyst for transesterification of glycerol with dialkyl carbonate.

Table 2.5: Reaction conditions of ionic liquids as catalyst of glycerol carbonate synthesis.

	Reaction conditions					
Type of catalysts	**Temperature (°C)**	**Substrate ratio of glycerol/ Carbonate (equivalent molar)**	**Reaction time (hour)**	**Catalyst loading (wt., g or mol%)**	**Performance (C/Y/S) %**	**References**
Ionic liquid:						
Tetra-n-butylammonium bromide	120	1:2^{a}	6.0	3.30 mol%	Y = 92.0	Grey & Pa, 1999
[Tea][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 89.0, S = 56.0	Gade et al., 2012
[Tba][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 90.0, S = 47.0	
[Tma][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 95.0, S = 47.0	
[Tma][OH]	80	1:1^{a}	1.5	0.217 mmol	C = 45.0, S = 39.0	
[Tma][OH]	80	1:2^{a}	1.5	0.217 mmol	C = 74.0, S = 40.0	
[Tma][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 97.0, S = 46.0	
[Tma][OH]	80	2:1^{a}	1.5	0.217 mmol	C = 66.0, S = 30.0	
[Tma][OH]	80	3:1^{a}	1.5	0.217 mmol	C = 55.0, S = 51.0	
[Tpa][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 77.0, S = 42.0	
[Me-DABCO][OH]	80	1:3^{a}	1.5	0.217 mmol	C = 87.0, S = 46.0	
[Tma][HCO_3]	80	1:3^{a}	1.5	0.217 mmol	C = 83.0, S = 33.0	

Continue…

[Tba][HCO$_3$]	80	1:3^a	1.5	0.217 mmol	C = 86.0, S = 42.0	Gade et al., 2012
[Tma][Br]	80	1:3^a	1.5	0.217 mmol	C = very low	
[Tba][Br]	80	1:3^a	1.5	0.217 mmol	C = very low	
[Mor$_{1,4}$][N(CN)$_2$]	120	1:3^a	13.0	0.17 mmol	C = 95.0	Chiappe & Rajamani, 2012
[Mor$_{1,g}$][N(CN)$_2$]	120	1:3^a	13.0	0.16 mmol	C = 90.0	
[Hme$_{1,4}$][N(CN)$_2$]	120	1:3^a	13.0	0.16 mmol	C = 45.0	
[HOC$_2$mim][N(CN)$_2$]	120	1:3^a	13.0	0.2 mmol	C = 95.0	
[HOC$_2$mim][N(CN)$_2$]	120	1:3^a	13.0	0.4 mmol	C = 100.0	
[Mor$_{1,2}$][Tf$_2$N]	120	1:3^a	13.0	0.2 mmol	C = 0.0	
[Bmim][Tf$_2$N]	120	1:3^a	13.0	0.18 mmol	C = 0.0	
[Bmim][PF$_6$]	120	1:3^a	13.0	0.13 mmol	C = 0.0	
[Hme$_{1,4}$][Tf$_2$N]	120	1:3^a	13.0	0.2 mmol	C = 0.0	
[mmPyrr][MeOCO$_2$]	120	1:3^a	13.0	0.1 mmol	C = 100.0	
[Bmim][Im]	70	1:2^a	0.5	10.00 mol%	C = 73.4, S = 100.0	Yi et al., 2014
[Amim][Im]	70	1:2^a	0.5	10.00 mol%	C = 65.6, S = 100.0	
[Bmim][OH]	70	1:2^a	0.5	10.00 mol%	C = 59.0, S = 100.0	
[Amim][OH]	70	1:2^a	0.5	10.00 mol%	C = 53.0, S = 100.0	
[Bmim][HSO$_4$]	70	1:2^a	0.5	10.00 mol%	C = 15.0, S = 76.0	

Continue…

[Bsmim][HSO$_4$]	70	1:2^a	0.5	10.00 mol%	C = 11.0, S = 76.0	
[Bmim][Cl]	70	1:2^a	0.5	10.00 mol%	C = <10.0, S = 82.0	
[DBU][Methanol]	100	1:3^a	0.5	2.5 wt.%	C = 96.0, S = 82.0	Munshi et al., 2014a
[DBU][Methanol]	100	1:1^a	0.5	1.00 mol%	C = 62.0, S = 84.0	
[DBU][Methanol]	100	1:2^a	0.5	1.00 mol%	C = 71.0, S = 85.0	
[DBU][Methanol]	100	1:3^a	0.5	1.00 mol%	C = 96.0, S = 82.0	
[DBU][Methanol]	100	2:1^a	0.5	1.00 mol%	C = 78.0, S = 77.0	
[DBU][Methanol]	100	3:1^a	0.5	1.00 mol%	C = 68.0, S = 86.0	
[DBU][Propylene glycol]	100	1:3^a	0.5	2.5 wt.%	C = 87.0, S = 90.0	
[DBU][Glycerol]	100	1:3^a	0.5	2.5 wt.%	C = 85.0, S = 92.0	
Amidines based ionic liquids:						
4-dimethylaminopyridine (DMAP)	100	1:3^a	0.5	0.10 mol%	C = 5.0, S = 89.0	Munshi et al., 2014b
1,4-diazabicyclo[2.2.2]octane (DABCO)	100	1:3^a	0.5	0.10 mol%	C = 31.0, S = 93.0	
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	100	1:3^a	0.5	0.10 mol%	C = 51.0, S = 91.0	
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	100	1:3^a	7.5	0.01 mol%	C = 98.0, S = 96.0	

Continue…

1,5-diazabicyclo[4.3.0]non-5-ene (DBN)	100	1:3[a]	0.5	0.10 mol%	C = 44.0, S = 98.0	Munshi et al., 2014b
1,5-diazabicyclo[4.3.0]non-5-ene (DBN)	100	1:3[a]	7.5	0.01 mol%	C = 87.0, S = 99.0	
primary alkyl amine	100	1:3[a]	2.0	2.00 mol%	C = 37.0-53.0, S = 83.0-98.0	
primary, secondary, tertiary amine	100	1:3[a]	2.0	2.00 mol%	C = 76.0-97.0, S = 88.0-97.0	
[N$_{2222}$][Pipe]	130	1:2[a]	2.0	3.0 wt.%	C = 96.0, S = 18.0, S^{a}= 82.0	Zhou et al., 2015
[N$_{2222}$][Pro]	130	1:2[a]	2.0	3.0 wt.%	C = 94.0, S = 32.0, S^{a}= 68.0	
[N$_{2222}$][H-pyr]	130	1:2[a]	2.0	3.0 wt.%	C = 12.0, S = 75.0, S^{a}= 25.0	
[N$_{2222}$][Thio]	130	1:2[a]	2.0	3.0 wt.%	C = 11.0, S = 90.0, S^{a}= 10.0	
[N$_{2222}$][Ace]	130	1:2[a]	2.0	3.0 wt.%	C = 88.0, S = 42.0, S^{a}= 58.0	
Heterogeneous catalyst						
TEA-MCM41[e]	80	1:2 [b]	1.5	0.1 g	C = 93.0, S = 79.5	Cho et al., 2010
TPA-MCM41[e]	80	1:2 [b]	1.5	0.1 g	C = 93.3, S = 82.3	
TBA-MCM41[e]	80	1:2 [b]	1.5	0.1 g	C = 94.0, S = 83.8	

Continue…

THA-MCM41[e]	80	1:2 [b]	1.5	0.1 g	C = 92.8, S = 81.6

Y = yield of glycerol carbonate, C = conversion of glycerol, S = selectivity of glycerol carbonate

[a] use dimethyl carbonate as carbonate source

[b] use ethylene carbonate as carbonate source

[c] Selectivity of glycidol is reported

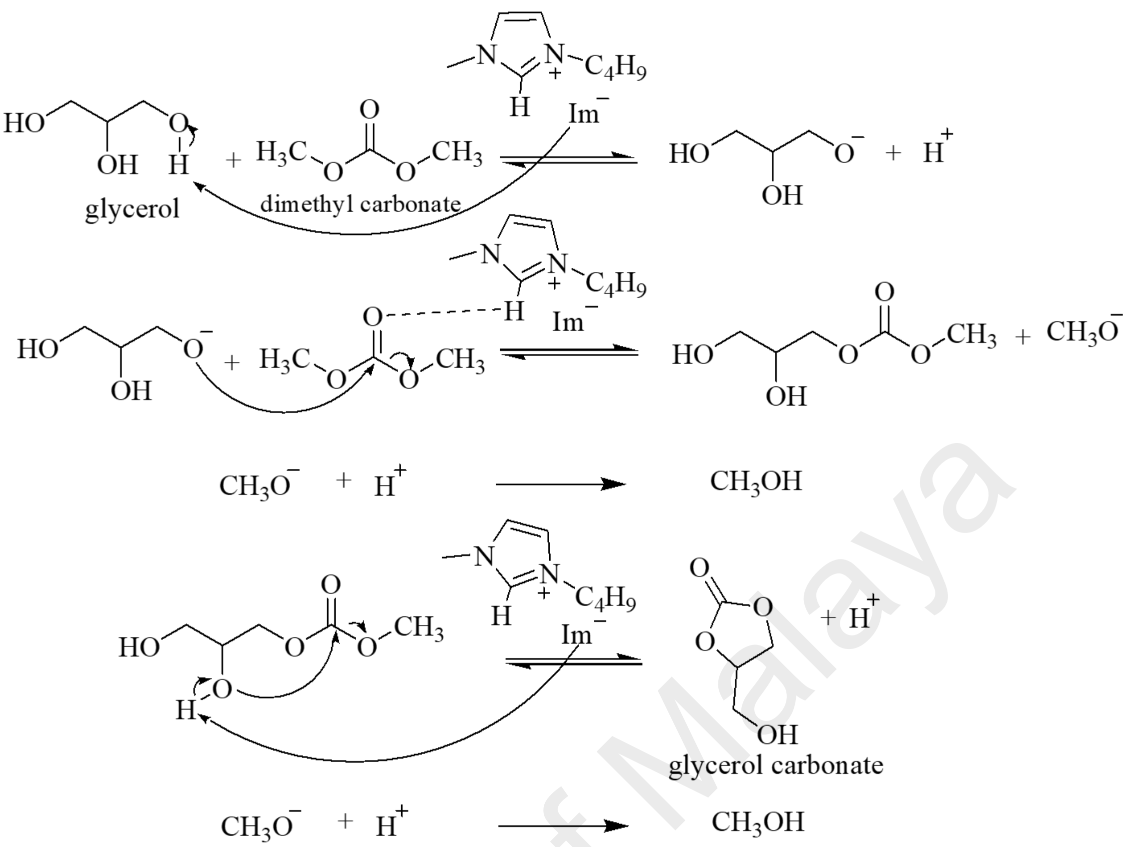
[d] Gas phase basicity (GPB) calculated using density functional theory (DFT)

[e] Immobilized onto mesoporous support

2.5.1.4 Reported mechanism

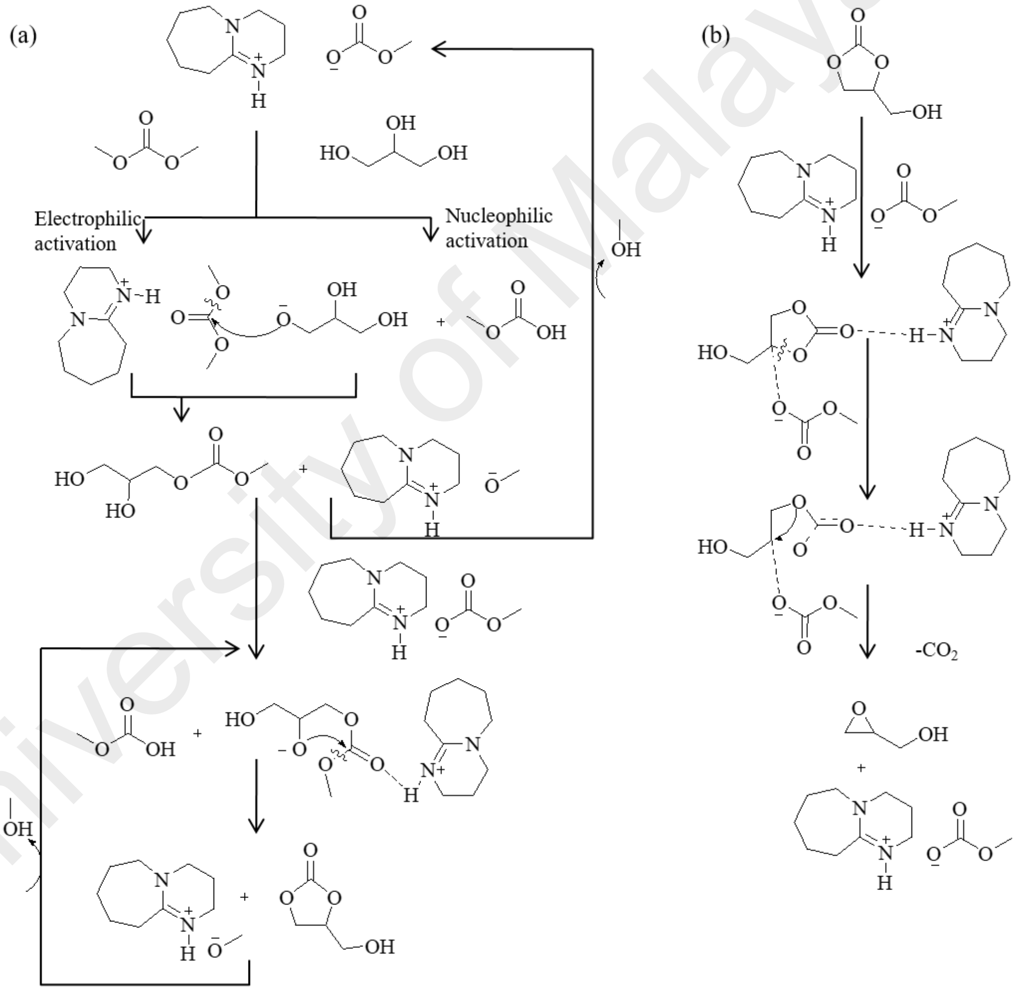
Another class of homogeneous catalysts that have been studied widely is that of the ionic liquids, which come in a range of guises. Ionic liquid, act as catalyst due to the adjustable cation-anion pairing which allows the preparation of acidic/basic ionic liquids. It is interesting to note that, the cation and anion in ionic liquids can activate electrophiles and nucleophiles respectively to catalyze various reactions involving carbonyl activation (Zhang et al., 2011). The ability of cation to activate electrophile depends on the ability of hydrogen bond donor while the ability of anion to activate nucleophile depends on the ability of hydrogen bond acceptor.

Scheme 2.7 illustrates the mechanism of the reaction for the formation of glyceroxide anion in step 1, initiated by nucleophilic attack of anion. The strength of nucleophile must be high enough to abstract the proton from the primary hydroxyl group of glycerol. Methanol is produced during the synthesis of glycerol carbonate (step 3). Furthermore, the glyceroxide anion reacts with dimethyl carbonate to produce methyl glyceryl carbonate as an intermediate (step 2) that converts to glycerol carbonate concomitantly through a fast-intramolecular cyclization (step 4) with the production of a second methanol molecule (step 5). The formation of methyl glyceryl carbonate was observed in only small quantities at low catalyst loading (0.01 mol%) (Munshi et al., 2014c). The close contacts between catalyst sites and glycerol are necessary to favor the reaction if there are no glycerol mass transport limitations from the bulk solution to the catalytic sites.



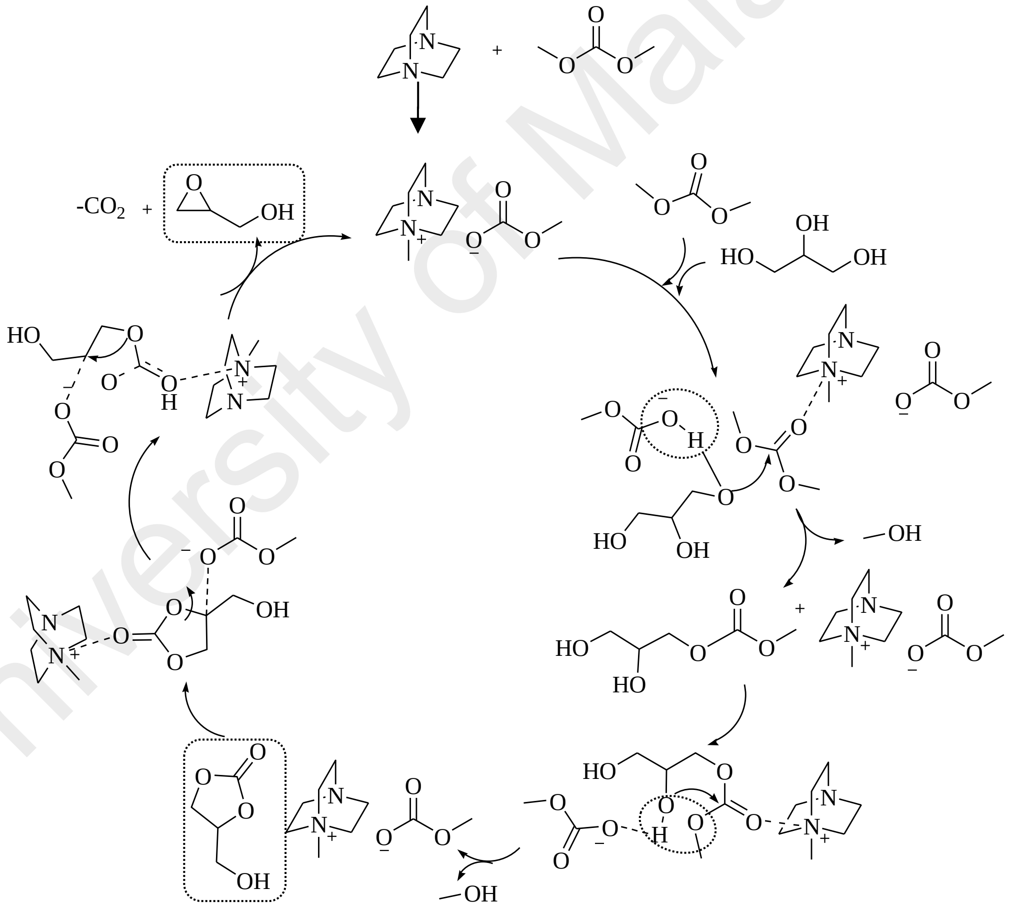
Scheme 2.7: Reaction mechanism of the transesterification of glycerol with dimethyl carbonate using 1-butyl-3-methylimidazolium imidazolide ([Bmim][Im]) catalyst.

There are a few of reported studies carried out on reaction mechanism with respect to the synergistic effect of cation and anion of ionic liquid which help in activating the reactants (Chakraborti & Roy, 2009; Lucchini at al., 2012; Selva et al., 2010). Selva et al. (2012) have proposed a mechanism for the synthesis of unsymmetrical carbonates involving parallel requirement of both anions and cations of ionic liquid for the activation of dimethyl carbonate and alcohols such as benzyl alcohol, cyclopentanol, cyclohexanol and menthol. Methyltrioctylphosphonium cation was coupled to weak basic anions such as bicarbonate, acetate, and phenolate was used as basic ionic liquid catalysts. Besides, Gade et al. (2012) have reported on direct synthesis of glycidol from glycerol via glycerol carbonate as an intermediate and also discussed the role of both cations as well as anion in decarboxylation of glycerol carbonate to glycidol over tetramethyl ammonium hydroxide ionic liquid as catalyst. Munshi et al. (2014a) have adapted the reaction mechanism proposed by Selva et al. (2012) and Gade et al. (2012) thereafter. A plausible reaction mechanism has been proposed for the transesterification of dimethyl carbonate with glycerol to glycerol carbonate and decarboxylation glycerol carbonate to glycidol over DBU-Methanol as catalyst as shown in Scheme 2.8.



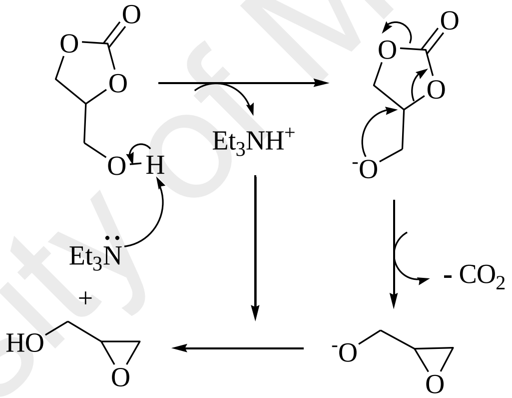
Scheme 2.8: The proposed reaction mechanism for (a) transesterification of dimethyl carbonate with glycerol and (b) decarboxylation of glycerol carbonate catalysed by ionic liquid (Munshi et al., 2014a).

Munshi et al. (2014c) also synthesized DABCO-based ionic liquids as a catalyst for transesterification of glycerol. DABCO functions as a nucleophilic catalyst, reacts with dimethyl carbonate and generates an ion pair. DABCO-Dimethyl carbonate ionic liquid is less basic than the parent DABCO giving the value of 11.0 and 9.1, respectively (measured at 17 °C). A plausible mechanism of transesterification reaction of glycerol and dimethyl carbonate using DABCO-Dimethyl carbonate catalyst has been proposed as in Scheme 2.9. The formation of glycidol was also reported.

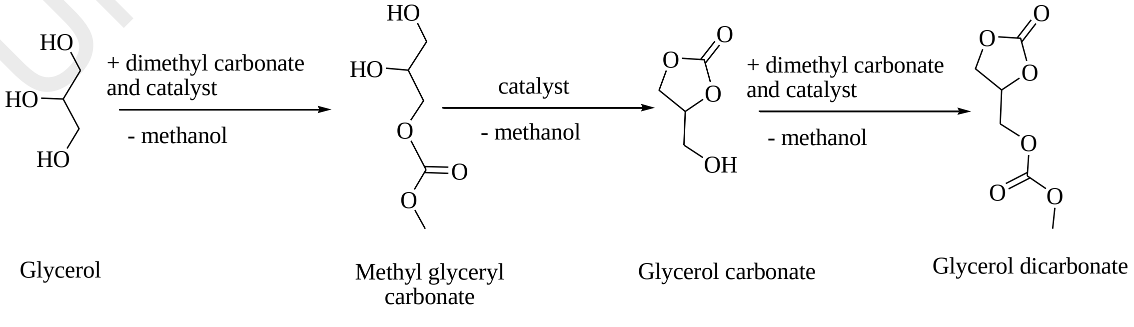


Scheme 2.9: Proposed reaction mechanism of transesterification reaction of glycerol and dimethyl carbonate using DABCO-Dimethyl carbonate catalyst (Munshi et al., 2014c).

As reactivity of glycerol carbonate lies not only in the ring but also in the pendant hydroxyl moiety, glycerol carbonate can react both as a nucleophile through its hydroxyl group, and as an electrophile through its ring carbon atoms. As being proposed by Ochoa-Gómez et al. (2012), at higher temperature of 135 °C, acidic primary hydroxyl pendant group of glycerol carbonate is deprotonated by tetraethylamine as catalyst resulting in a hydroxide ion which could initiate the glycerol carbonate ring opening polymerization. An intramolecular nucleophilic substitution reaction occurs, followed by ring-opening of the five-membered cyclic carbonate, to form glycidol (Scheme 2.10). Glycerol dicarbonate was also reported to form along the reaction (Scheme 2.11).



Scheme 2.10: Proposed mechanism for glycidol formation (Ochoa-Gómez et al., 2012b).



Scheme 2.11: Reaction mechanism of the transesterification of glycerol with dimethyl carbonate.

Through the literature in this area of study, it can be concluded that ionic liquids as catalyst can either contribute toward a single and synergistic effect of cation or/and anion on transesterification of glycerol. Reaction mechanism using heterogeneous catalysts were also proposed in several studies which signify the formation of other products such as glycidol and glycerol dicarbonate, rather than glycerol carbonate solely has been formed from the transesterification reaction of glycerol (Ochoa-Gómez et al., 2012b; Bai et al., 2013a; Bai et al., 2013b, Climent et al., 2010).

2.6 Factors influencing transesterification reaction of glycerol

The glycerol conversion, glycerol carbonate yield/selectivity and other possible products such as glycerol dicarbonate and glycidol in transesterification reaction are significantly altered by several reaction parameters such as reaction temperature, reaction time, substrates ratio and catalyst loading. Some of the studies have certainly explained the effect of solvent as well as impurity particularly in water content and methanol in the reaction mixture (Teng et al., 2014). The pertinent factors affecting the performance of ionic liquids catalyzing transesterification reaction of glycerol such as the effect of temperature, time, substrates ratio and catalyst loading will be elucidated individually in the section 2.6.1 to 2.6.4.

2.6.1 Effect of temperature

In most of the reported studies, the reaction temperature is obviously a critical parameter affecting the glycerol conversion and glycerol carbonate yield. This is mainly due to that higher temperature can improve the miscibility between hydrophobic dimethyl carbonate/diethyl carbonate and hydrophilic glycerol. The conversion of glycerol and the selectivity of glycerol carbonate increases as the reaction temperature increased (Chiappe & Rajamani, 2012; Cho et al., 2010; Gade et al., 2012; Grey, 1992) together with the chemical equilibrium constant (Li & Wang, 2011). The incomplete reaction was obtained at a very low temperature, indicated by two unchanged layers form, while one phase of reaction solution obtained can significantly indicate the complete reaction. Changes in temperature has increase the kinetic energy of the reactant molecules, thus affect on the rate of reaction. It can be correlated to the collision theory as well as the Arrhenius equation (Yadav & Chandan, 2014).

Nevertheless, the optimum reaction temperature in transesterification is closely dependent on the heat sensitive carbonates and catalysts used. Understanding the physical properties of the reactants can help in determining the optimum reaction condition of reaction. Dimethyl carbonate and glycerol are thermally stable and will not decomposed below 390 °C (Cross et al., 1976) and 150 °C (Benavides et al., 2013), respectively. It is therefore, the workable reaction temperature which is strongly encouraged to not exceeding the mentioned value. Besides, the high temperature must be avoided to eliminate the formation of highly flammable ethers resulting from undesired decomposition of dimethyl carbonate (Selva et al., 2011).

The synthesis route has been widely studied using different carbonate sources and catalysts at varying temperature range between 35 °C to 140 °C at atmosphere pressure. In the reaction involving ionic liquid as a catalyst, Zhou et al. (2015) has synthesized a series of tetraethylammoniumamino acid ionic liquids which show 96.0% glycerol conversion at an optimum reaction temperature of 130 °C. Li & Wang (2011) reported that increasing the temperature of the transesterification reaction should lead to a dramatic increase in the chemical equilibrium constant for the reaction of glycerol with dimethyl carbonate. Cho et al. (2010) have observed a similar trend in the transesterification of glycerol to glycerol carbonate using tetraalkylammonium salts immobilized on MCM-41 as the catalyst. At the higher temperature of 140 °C, a rapid darkening of the reaction mixture was reported by Chiappe & Rajamani (2012). This is due to the evaporation of dialkyl carbonates that exceeds their boiling points whereby excessive evaporation will cause partial decomposition of the reactants or catalyst.

Chiappe & Rajamani (2012) has reported obtaining a high glycerol conversion and glycerol carbonate selectivity at the reaction temperature of 120 °C. The reaction temperature can still be considered as it does not exceed the decomposition temperature of either/both of the reactants in the reaction. Dicyanamide based ionic liquids; N-methyl-N-butylmorpholinium dicyanamide, $[Mor_{1,4}][N(CN)_2]$, N-methyl- N-glycerylmorpholinium dicyanamide $[Mor_{1,g}][N(CN)_2]$ and 1-methyl-3-(2-hydroxylethyl)imidazolium dicyanamide, $[HOEmim][N(CN)_2]$ have given 90.0%, 95.0% and 95.0% glycerol conversion, respectively at 120 °C, 13.0 hours of reaction time with dimethyl carbonate/glycerol ratio of 3:1 and 0.16 to 0.20 mmol of catalyst loading.

In another study, 1-butyl-3-methylimidazolium imidazolide ([Bmim][Im]), 1-butyl-3-methylimidazolium hydroxide ([Bmim][OH]), 1-allyl-3-methylimidazolium imidazolide ([Amim][Im]), and 1-allyl-3- methylimidazolium hydroxide ([Amim][OH]) worked well as the catalysts in the reaction of glycerol with dimethyl carbonate at 70 °C, 0.5 hours, dimethyl carbonate/glycerol ratio of 2:1 and 10.00 mol% ionic liquid loading (Yi et al., 2014). The glycerol conversion increased by more than 65.4% when the reaction temperature increased from 25 °C to 70 °C. In contrast, the glycerol carbonate selectivity consistently less affected by the temperature, gives 100.0% its selectivity up to 70 °C, where it was decreased slightly with the increase of temperature. It is expected that the increase in the operating temperature beyond the optimum temperature might not improve the glycerol conversion but instead it would probably decrease the glycerol carbonate yield. This was witnessed with decarboxylation of glycerol carbonate to glycidol which decreases the glycerol carbonate selectivity while glycidol selectivity slightly increases as temperature increases (Munshi et al., 2014a).

An earlier finding by Rokicki et al. (2005) also have described the K_2CO_3-catalysed ring opening polymerization of glycerol carbonate at 170 °C which proceeds with carbon dioxide evolution and yields hyperbranched aliphatic polyethers. The reaction mechanism has been proposed as illustrated in Scheme 2.10 (described in section 2.5.1.4), motivated by earlier findings from Sandler & Berg (1966) who reported on vigorous polymerization of glycidol in the presence of triethylamine. The proposed mechanism has been supported by Ochoa-Gómez et al. (2012b), thereafter. In another study, Darensbourg & Yeung (2014) showed that decarboxylation is favored at high temperature, regardless of the acid or base-catalyzed system due to increasing reactivity of glycerol carbonate hydroxyl moiety with temperature. Formation of glycidol has also been reported in several studies with respect to homogeneous and heterogeneous catalyst (Zhou et al., 2015).

Therefore, it is crucial to control the optimum reaction temperature properly in achieving a maximum of glycerol carbonate yield and selectivity.

2.6.2 Effect of time

Higher reaction time could be advantageous as it allows more time for the glycerol to react in chemically catalyzed reaction. Furthermore, glycerol conversion rate and glycerol carbonate yield and selectivity are expected to increase with reaction time with respect to homogeneous or heterogeneous catalyst (Jagadeeswaraiah et al., 2014; Chiappe & Rajamani, 2012). Short reaction time is predictably attractive for industrial manufacturing of glycerol carbonate. In the absence of catalyst, transesterification was noted slow and gave only 20.0% glycerol conversion and 5.0% glycerol carbonate produced after 5.0 hours (Climent et al., 2010). Meanwhile, Yi et al. (2014) found that less than 5.0% of conversion was obtained at 0.5 hours of reaction without the presence of catalyst.

Generally, the reaction rate of base catalyzed transesterification is much faster than that of the acid catalysis due to higher catalytic activity (Ochoa-Gómez et al., 2009). Reaction time ranging from 0.5 hours to 13.0 hours have been reported for transesterification of glycerol using ionic liquids as catalysts. Many different types of base catalysts as previously mentioned (homogeneous and heterogeneous) are suitable for transesterification of glycerol as the reactions are rapid with no apparent induction period (Liu et al., 2013). Furthermore, the conversion rate of glycerol, glycerol carbonate yield and selectivity increase with reaction time (Chiappe & Rajamani, 2012; Yi et al., 2014). However, prolonged reaction time does not benefit the glycerol carbonate yield as there are further transesterification reaction of glycerol carbonate to formation glycerol dicarbonate (Álvarez et al., 2013; Yi et al., 2014) and also decarboxylation of glycerol carbonate to glycidol (Gade et al., 2012; Parameswaram et al., 2013; Choi et al., 2013). In order to achieve higher glycerol carbonate yield of more than 90.0%, optimum reaction time ranging from 30 minutes to 3.0 hours were applied in the homogeneous catalyzed transesterification (Ochoa-Gómez et al., 2009; Rokicki et al., 2005; Chiappe & Rajamani, 2012).

The transesterification of glycerol with DBU-methanol ionic liquid has given 89.0% glycerol conversion in 20 minutes reaction time, with 86.0% and 14.0% selectivity to glycerol carbonate and glycidol, respectively (Munshi et al., 2014a). The longest reaction time has been reported by Chiappe & Rajamani (2012) using N-methyl-N-butylmorpholinium dicyanamide, $[\mathrm{Mor}_{1,4}][\mathrm{N(CN)}_2]$, with 96.0% glycerol conversion at 13.0 hours reaction time. It was found that the glycerol conversion increased with an increase of the reaction time. However, this study has failed to report on glycerol carbonate yield or selectivity. Yi et al. (2014) have reported that continuous transesterification reaction has led to the formation of glycerol dicarbonate, thus decreases the glycerol carbonate selectivity. Glycerol conversion increase up to 99.3% was obtained when time is prolonged to 2.5 hours. However, glycerol carbonate achieved the highest yield of 98.4% at 1.5 hours, and slowly decreased to 91.0% as reaction time is reaching 2.5 hours.

2.6.3 Effect of substrate ratio

Theoretically, the ratio for transesterification reaction requires only 1.0 mol of carbonates and 1.0 mol of glycerol to produce 1.0 mol of glycerol carbonate and 1.0 or 2.0 mol of relevant by-product (methanol or ethanol). To ensure the operational feasibility, the molar ratio of reactants must be adjusted accordingly. No addition of solvents needed in order to cater the miscibility problem between hydrophilic glycerol and hydrophobic dialkyl carbonate when ionic liquids are used as catalyst. However, as compared to heterogeneous catalyst, the addition of solvent is necessary to promote the substrates miscibility as discussed earlier in section 2.4.2 (Takagaki et al., 2010; Kumar et al., 2012; Álvarez et al., 2012; Pan et al., 2012).

Furthermore, the transesterification of glycerol with carbonate source is a reversible reaction. With this in mind, carbonate source should be presented in an excess of stoichiometric proportion in order to shift the chemical equilibrium towards formation of glycerol carbonate, thus giving a positive effect on the glycerol conversion and glycerol carbonate yield. The carbonate source may play a role as substrate or solvent for the reaction.

As reported in the literature, the reactions were normally carried out at the molar ratio of carbonate source to glycerol in the range of 1.0 to 3.2 to shift the chemical equilibrium towards glycerol carbonate formation for greater glycerol conversion in a shorter time as shown in Table 2.5, using ionic liquids as catalysts. Low glycerol conversion and glycerol carbonate yield were observed when equimolar of reactants were used in the transesterification (Gade et al., 2012). The yield of glycerol carbonate increased when the carbonate source to glycerol ratio is raised beyond 2.0 and reached a maximum molar ratio of 3.2 (Naik et al., 2009). Even though an excess of carbonate source is beneficial to the formation of glycerol carbonate, the formation of glycerol dicarbonate and glycidol often take place (Zhou et al., 2015).

It is best to note that, ionic liquid has served not only as catalyst but also as cosolvent (dual function) in transesterification reaction (Chiappe & Rajamani, 2012). The results of high glycerol conversion and glycerol carbonate yield and selectivity using ionic liquid as catalyst are very interesting taking into account the moderate dimethyl carbonate/glycerol molar ratio. Other reported homogeneous catalysts have produced 90.0% to 100.0% glycerol carbonate yield with carbonate source to glycerol molar ratio between 2 and 5 (Ochoa-Gómez et al., 2009; Ochoa-Gómez et al., 2012b; Rokicki et al., 2005; Grey, 1992). By contrast, the ratio of diethyl carbonate/glycerol of 21 and 17 were reported when using Mg/Al hydrotalcite supported on α-Al_2O_3 and Mg/Al hydrotalcite supported on carbon nanofiber, respectively (Álvarez et al., 2012; Álvarez et al., 2013). Glycerol dicarbonate was reported to be formed as the by-product.

From economic and environmental viewpoint, the low molar ratio of carbonate source to glycerol and solvent free are preferable in the transesterification reaction. Nonetheless, high molar ratio or addition of solvent is essential to increase the miscibility of glycerol with dimethyl carbonate or diethyl carbonate.

2.6.4 Effect of catalyst loading

Generally, as the number of ionic liquids loading increased, there was significant increase in the glycerol conversion and the glycerol carbonate selectivity due to more glycerol molecules would be catalyzed in the desired reaction. Munshi et al. (2014a) have found that at very low catalyst loading; 0.01 and 0.03 mmol, the glycerol carbonate selectivity achieved was very high (>95.0%). However, with an increase in the catalyst loading, decarboxylation of glycerol carbonate leads to an increase in glycidol formation and 56.0% glycidol selectivity was obtained at the catalyst loading of 0.66 mmol. Glycerol carbonate selectivity decreased marginally with an increase in glycerol dicarbonate and glycidol selectivity (Yi et al., 2014; Munshi et al., 2014a). Their findings were in line with the findings reported by Gade et al. (2012) at which the interaction of cationic and anionic centres of ionic liquid with glycerol carbonate and increased in basicity of the reaction mixture due to increase in catalyst loading have led to decarboxylation of glycerol carbonate.

Proposed mechanism as discussed in section 2.5.1.4 can comprehend the understanding towards the effect of catalyst on transesterification reaction of glycerol. The pertinent factors affecting the performance of glycerol carbonate production have been summarized in Table 2.6.

Table 2.6: General comparison between homogeneous classic and ionic liquid catalyst.

Factor	Homogeneous catalyst system	
	Classic catalyst	**Ionic liquid**
Temperature (°C)	Room temperature - 100	70 - 130
Time (hour)	0.33 – 5.0	0.5 – 13.0
Substrate ratio of glycerol/carbonate (equivalent ratio)	1:2 - 1:10	1:1 - 1:3.2
Catalyst loading	0.01 – 15.0 wt% 0.50 – 10.00 mol%	0.1 - 0.217 mmol 0.01 – 10.00 mol%
Performance (C/Y/S), %	Y= 3.5 – 100.0	

Y = yield of glycerol carbonate, C = conversion of glycerol, S = selectivity of glycerol carbonate

2.7 Reusability of ionic liquids

The ionic liquid is separated from the product and can also be removed by decantation, presenting the advantages of cost and easiness compared to filtration (Seddon, 2003). It is economically viable for ionic liquids to be reused. [Mor$_{1,4}$][N(CN)$_2$] showed good recyclability of at least four recycles without any significant reduction in the glycerol conversion and glycerol carbonate selectivity (Chiappe & Rajamani, 2012). [Bmim][Im] could be reused three times with a slight decrease of glycerol conversion. The isolation of the product and catalyst can be done through liquid-liquid extraction method using diethyl ether (Yi et al., 2014), flash chromatography column with ethyl acetate and methanol as eluents (Chiappe & Rajamani, 2012) and easy catalyst filtration (Cho et al., 2010). Zhou et al. (2015) has reported that tetraethylammoniumamino acid ionic liquids can be extracted with deionized water, and the aqueous phase containing ionic liquids could be separated by simple decantation. Reusability of amidine-based ionic liquids has not been described by Munshi et al. (2014a) in their findings.

The heterogeneous catalyst TBA-MCM41 can be reused to at least up to three consecutive times without any considerable loss of its initial activity giving TON reduces only from 175.0 to 165.5 from fresh run until second recycle run, respectively (Munshi et al., 2014a). This type of catalyst showed additional advantages such as the reduction of the amount of ionic liquids employed and easy separation, as well as the recovery of catalyst from the reaction mixture. The conversion of glycerol and selectivity reported are comparable with the transesterification of glycerol using other types of heterogeneous catalysts (Climent et al., 2010; Ochoa-Gómez et al., 2009).

In summary, it can be seen that ionic liquids have performed well as catalyst, exhibited significant activity providing good to excellent yield of glycerol carbonate from transesterification of glycerol and carbonate source. This is due to their exclusive characteristics and special properties of anions and cations counterparts. Cation and anion counterparts can be tailored, in order to be used in organic reaction as catalyst and exert synergistic effects, thus help reaction rate enhancement. Moreover, ionic liquids can be recycled and reused, at least comparable to heterogeneous catalysts. Perhaps, a detail exploration and understanding of ionic liquid as catalyst can help in improving catalysis field. This area of study is still in its infancy though promising results have been reported. The reaction should be well explained through the fundamental point of view in order to capture the understanding of the whole reaction.

CHAPTER 3 : MATERIAL AND METHOD

3.1 Material and chemicals

All chemicals and solvents were commercially available and of analytical grade and were used without further purification, unless otherwise stated.

3.1.1 Chemicals for transesterification reaction of glycerol

Glycerol (99.5%), glycerol carbonate (99.5%), diethyl carbonate (99.5%) and glycidol (CAS: 556-52-5) were supplied by Aldrich and used without any further purification.

3.1.2 Source of ionic liquids

Ionic liquids namely methylammonium nitrate ([Ma][NO_3]), ethylammonium nitrate ([Ea][NO_3]), 2-hydrozyethylammonium formate ([Hea][Fmt]) were purchased from IoLiTec Inc. (USA). 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim][DMP]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), 1-butyl-3-methylimidazolium dicyanamide ([Bmim][Dca]) and 1-ethyl-3-methylimidazolium acetate ([Emim]][Ac]) were obtained from Merck. All ionic liquids were purchased having 99.0% of purity.

3.1.3 Solvents

Solvents; chloroform (AR grade), ethyl acetate (AR grade), methanol (AR grade) and methanol (GC grade-99.9%) were purchased from Fisher Scientific. Deuterated methanol-d_4 (99.8%) (Aldrich) was used as solvent in NMR analysis.

3.2 Experimental procedure

3.2.1 Drying of glycerol and ionic liquid

Glycerol and ionic liquids were dried using Schlenk technique to remove any water or volatile solvents content. This is necessary due to the highly hygroscopic behavior of glycerol and ionic liquids. Prior to drying, glycerol and ionic liquids were dried through continuous stirring under vacuum condition on a standard Schlenk line in order to minimize its water content (Figure 3.1). Water evaporation from the glycerol and ionic liquids were collected using cooling traps apparatus. A Karl Fischer Coulometric with ethanol-based hydranal reagents was used to measure the water content of glycerol and ionic liquids after drying and prior to use.

Figure 3.1: Drying of ionic liquid by Schenk line.

3.2.2 Transesterification reaction

3.2.2.1 Screening of ionic liquid as catalyst for transesterification reaction

The reaction was carried out using a 150.0 ml round bottom three-neck glass flask fitted with magnetic stirrer, reflux condenser, and sampling device. A constant heating energy was supplied to the glass flask in oil bath with nitrogen gas flow at atmospheric pressure using Schlenk line. In each experimental run, 13.7 mmol (1.2616 g) of glycerol was heated first, followed by the addition of an excess of diethyl carbonate into the flask. Then, each of the ionic liquids, methylammonium nitrate ([Ma][NO_3]), ethylammonium nitrate ([Ea][NO_3]), 2-hydrozyethylammonium formate ([Hea][Fmt]), 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim][Dmp]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), 1-butyl-3-methylimidazolium dicyanamide ([Bmim][Dca]) and 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) (0.50 mol% with respect to limiting substrate) was then added to the biphasic system as catalyst to start the reaction. The reaction was heated to the desired temperature and was stirred at speed of 1000 rpm to enhance mass transfer. The transesterification progress was monitored by analytical thin layer chromatography (TLC) with optimized developing solvent system of ethyl acetate/methanol (4.8:0.2). Alternatively, the formation of a sole phase could be taken as the end point of the reaction.

3.2.2.2 General procedure for transesterification reaction

The reaction was carried out using a 150.0 ml round bottom three-neck glass flask fitted with magnetic stirrer, reflux condenser, and sampling device. In a typical study, the reaction was initiated by introducing glycerol (13.7 mmol, 1.2616 g), followed with the addition of diethyl carbonate (13.7 mmol to 54.8 mmol) and ionic liquid (0.10 mol% to 10.00 mol%) with respect to limiting reactant. Ionic liquid with water content of 4 wt.% and 8 wt.% were prepared by addition of distilled water with respect to ionic liquid catalyst (wt./wt.%) used in the reaction. To start the reaction, the mixture was heated at temperature of 90 ºC to 140 ºC for the duration of 0.5 hours to 4.0 hours and was kept under nitrogen gas flow at atmospheric pressure. The reaction was stirred at speed of 1000 rpm to enhance the mixing. The temperature and stirring rate were controlled by using a temperature controller. The sample of liquid product produced was sampled at specific sampling time then subjected to analysis.

3.2.3 Recycle of ionic liquid

When the first run of experimental transesterification reaction procedure was completed, the reaction mixture was concentrated and dichloromethane (3x10.0 ml) was added to the residue in order to recover ionic liquid catalyst. Dichloromethane was earlier purified using water and sulphuric acid to remove any traces amount of water, ethanol, methanol (Armarego & Chai, 2009). Simple phase separation was performed to recover ionic liquid catalyst and calculated using the formula in equation 3.1. Later, the reaction was repeated again following the mentioned procedure using the recovered ionic liquid which has been dried using Schlenk line in order to get ≈2.0 wt.% water content. The recovered ionic liquid was analyzed with ^{1}H NMR to confirm its purity.

$$\text{Catalyst recovery (\%)} = \frac{\text{mass catalyst}_{final}}{mass\ catalyst_{\ initial}}\ x\ 100\% \quad \text{………………Equation 3.1}$$

3.2.4 Product analysis

3.2.4.1 Thin layer chromatography (TLC)

Analytical thin layer chromatography (TLC) was performed using Merck Kiesel 60 PF_{254} silica gel 60F254 plates with optimized developing a solvent system of ethyl acetate/methanol (4.8:0.2). Chromatograms were visualized by a heating plate that was dipped in potassium manganate (VII) ($KMnO_4$) reagent (3.0 g potassium permanganate, 20.0 g potassium carbonate, 5.0 ml NaOH (5.0%) and 300.0 ml distilled water). The transesterification progress was monitored by TLC.

3.2.4.2 Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometry

Infrared spectra were measured by attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR) with a built–in diamond ATR. ATR is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation. The sample needs to be free from impurities and solvents for infrared spectroscopy. The adsorption bands were measured in cm^{-1} at range 280 cm^{-1} to 4000 cm^{-1}.

3.2.4.3 Nuclear magnetic resonance (NMR) spectroscopy

Nuclear magnetic resonance (NMR) is a technique to determine the structure of organic compounds and provides detailed information on the three-dimensional structure of molecule in solution. $^{1}H/^{13}C$ NMR spectra were recorded at room temperature on NMR spectrometer. Deuterated methanol-*d4* solvent was obtained from Sigma-Aldrich. Time online analysis of products was analyzed using carbon (^{13}C) spectrum by sampling 150 µl of sample into the NMR tubes and then diluting with 500 µl of the deuterated methanol-*d4*. Recycled ionic liquid was also dissolved in deuterated methanol-*d4* solvent for ^{1}H/^{13}C analysis. For each sample, 32 scans and 2000 scans were accumulated for ^{1}H and ^{13}C analysis, respectively. Chemical shifts are quoted in parts per million (ppm) relative to residual solvent peak using tables of chemical shifts of solvents.

3.2.4.4 Gas chromatography-flame ionization detector (GC-FID)

A capillary column FFAP (30 m long, 0.25 mm internal diameter) was used as the stationary phase. The analysis of the sample was done by injecting a 1 µl aliquot in a splitless mode into the chromatography equipment. A good peak separation was achieved for all components under the conditions: the temperature of the column was programmed to have a 5-minutes initial hold at 60 ºC, a 5 ºC/minutes ramp from 60 ºC to 80 ºC and 1 minutes hold at 80 ºC, a 10 ºC/minutes ramp from 80 ºC to 230 ºC and a 10 minutes hold at 230 ºC. The carrier gas used was nitrogen and 1-butanol was added to each sample as an internal standard before the sample analysis. Standard glycerol and glycerol carbonate with a different range of concentration were used for calibration purpose and also by referring to the peak's retention time of their respective glycerol and glycerol carbonate standard. The conversions of glycerol and glycerol carbonate yield and selectivity were determined following equation 3.2 to equation 3.4, respectively:

$$\text{Conversion, C} = \frac{\text{initial mol}_{glycerol} - residual\ mol_{glycerol}}{initial\ mol_{glycerol}}\ x\ 100\%$$ …………Equation 3.2

$$\text{Yield, Y} = \frac{mol_{product\ formed}}{initial\ mol_{glycerol}}\ x\ 100\%$$ ....Equation 3.3

$$\text{Selectivity, S} = \frac{Yield\ _{product\ formed}}{Conversion_{glycerol}}\ x\ 100\%$$ ……………………………… Equation 3.4

The activity of ionic liquid towards the transesterification reaction was based on the glycerol conversion as limiting substrate measured under standard conditions of reaction. Other unknown by-products which total amount was ≤5.0% (by GC), were also detected. However, they were not quantified except for glycerol carbonate and glycidol.

3.2.4.5 Gas chromatography-mass spectrometry (GC-MS)

A capillary column DB-5 (30 m long, 0.25 mm internal diameter) was used as the stationary phase. Analysis of the sample was done by injecting a 3 µl aliquot in a splitless mode into the chromatography equipment. A good peak separation was achieved for all components under the conditions: temperature of the column was programmed to have a 5 minutes initial hold at 70 ºC, a 5 ºC /minutes ramp from 70 ºC to 120 ºC and 10 minutes hold at 120 ºC, a 10 ºC/minutes ramp from 120 ºC to 250 ºC and a 15 minutes hold at 250 ºC.

3.3 Modelling & optimization by response surface methodology (RSM)

3.3.1 Experimental design and statistical analysis

There are several designs available for fitting a second-order model. The most common one is the central composite design (CCD) that frequently works well for the process optimization (Bezerra et al., 2008). This design was presented by Box and Wilson (Box & Wilson, 1951). Generally, CCD requires a total of (2^k+2k+N_0) runs where k is the number of considered factors, 2^k are the points from the factorial design, $2k$ the axial points and N_0 the number of experiments carried out at the centre. A four-factor-three-level CCD was employed in this study, requiring 30 experiments. The fractional factorial design consisted of 16 factorial points, 8 axial points, and 6 centre points. The variables and their levels selected for the transesterification reactions of glycerol with [Emim][Ac] catalyst were: reaction temperature (110 ºC to 130 ºC); reaction time (1.5 hours to 2.5 hours), substrate ratio (1.5 to 2.5 equivalent ratio) and catalyst loading (0.30 mol% to 0.70 mol%). The experiments were produced in random order and triplicate measurements conversion and yield were run on each experiment by GC-FID. A software package by Design Expert Version 7.1.1 (State-Ease Inc., Statistics Made Easy, Minneapolis, MN, USA) was used to fit the second-order model to the independent variables using the following equation:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + \varepsilon \qquad \text{Equation 3.4}$$

where y is the dependent variable (percentage of response) to be modeled, x_i and x_j are the independent variables (factors), b_0, b_i, b_{ii} *and* b_{ij} are the regression coefficients of the model, and ε is the residual associated with the experiments. An analysis of variance (ANOVA) was used to determine the significance of the constructed model to describe the observed data. The R^2 (coefficient of determination) statistic indicates the percentage of the variability of the optimization parameters that is explained by the model. Three-dimensional surface plots were drawn to illustrate the main and interactive effects of the independent variables on the dependent ones.

3.4 Computational Methods

The interaction of reactants (glycerol and diethyl carbonate)-[Emim][Ac] at initial state and intermediate-[Emim][Ac] at transition states were theoretically investigated using the General Atomic and Molecular Electronic Structure System (GAMESS) software with hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31G basis sets approach (Munshi et al., 2014b). Avogadro version 7.3 was used to build up the starting geometry of glycerol, diethyl carbonate, intermediate, $[Emim]^+$ cation and $[Ac]^-$ anion. To confirm the connectivity between reactants-[Emim][Ac] (initial state) and intermediate-[Emim][Ac] (transition states), hydrogen bond distance was calculated.

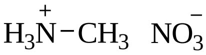
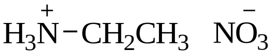
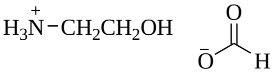
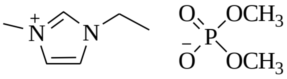
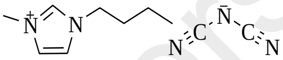
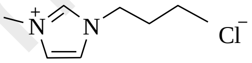
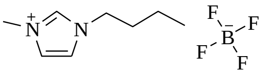
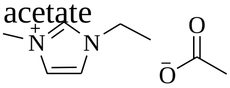
CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Screening of ionic liquid for transesterification reaction

Prior to start, a broader screening of ionic liquids seems necessary in order to select the best ionic liquid to catalyze the transesterification of glycerol and diethyl carbonate reaction. The role of anion as hydrogen bond acceptor has been a major consideration in choosing the ionic liquid in this study, with less attention on its cation. The strength of anion depends on the hydrogen bond basicity or the β value measured by reported Kamlet-Taff parameter (Kamlet et al., 1977; Taff & Kamlet, 1976; Kamlet & Taff, 1976). Kamlet–Taft model is used to elucidate the solvation parameters; which involves term α (hydrogen bond donor/hydrogen bond acidity), β (hydrogen bond acceptor/hydrogen bond basicity) and π* (polarizability or dipolarity). These α, β and π* values can be calculated by UV–VIS spectroscopy in the presence of solvatochromic dyes such as N,N-diethyl-4-nitroaniline and 4-nitroaniline (Seoud et al., 2011).

With this general approach in mind, a series of imidazolium and ammonium-based ionic liquids namely methylammonium nitrate ([Ma][NO_3]), ethylammonium nitrate ([Ea][NO_3]), 2-hydroxyethylammonium formate ([Hea][Fmt]), 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim][Dmp]), 1-butyl-3-methylimidazolium dicyanamide ([Bmim][Dca]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) were screened for transesterification reaction of glycerol and diethyl carbonate (Table 4.1).

Table 4.1: List of ionic liquids used as catalysts in transesterification reaction of glycerol and reported β value (Cláudio et al., 2014).

No.	Ionic liquid	Abbreviation	Molecular weight (g/mol)	Appearance	β value
1	Methylammonium nitrate  $H_3\overset{+}{N}-CH_3 \quad NO_3^-$	[Ma][NO3]	94.07	Liquid	0.460
2	Ethylammonium nitrate  $H_3\overset{+}{N}-CH_2CH_3 \quad NO_3^-$	[Ea][NO3]	107.09	Liquid	0.460
3	2-hydroxyethylammonium formate 	[Hea][Fmt]	107.11	Solid	0.730
4	1-ethyl-3-methylimidazolium dimethyl phosphate 	[Emim][Dmp]	236.21	Liquid	1.120
5	1-butyl-3-methylimidazolium dicyanamide 	[Bmim][Dca]	205.26	Liquid	0.596
6	1-butyl-3-methylimidazolium chloride 	[Bmim][Cl]	174.6	Liquid	0.950, 0.840[a]
7	1-butyl-3-methylimidazolium tetrafluoroborate 	[Bmim][BF4]	226.02	Liquid	0.550
8	1-ethyl-3-methylimidazolium acetate 	[Emim][Ac]	170.21	Liquid	1.201, 1.074[a]

[a] Vitz et al. (2009) and Brandt et al. (2010).

Table 4.2 shows the percentage of glycerol conversion and glycerol carbonate yield and selectivity for transesterification reaction of glycerol and diethyl carbonate using selected ammonium and imidazolium based ionic liquids. In general, there was a significant difference between selected ionic liquids in term of glycerol conversion, glycerol carbonate yield and phase changes at the end of the transesterification reaction. The reaction does proceed slowly even in the absence of any catalyst (blank) giving 5.0% of glycerol conversion and glycerol carbonate yield (Entry 1, Table 4.2). All ionic liquids screened were active showing moderate to high glycerol conversion for the transesterification reaction except for [Ma][NO_3], [Ea][NO_3], [Bmim][BF_4] having non-coordinating anion. These ionic liquids catalysts have weak abilities in forming hydrogen bonds with glycerol (Entry 2-3, Table 4.2).

Table 4.2: Catalyst screening of selected ionic liquid as catalyst for transesterification of glycerol. Reaction conditions: Temperature = 120 °C, Reaction time = 2.0 hours, Ratio diethyl carbonate/glycerol = 2 and Catalyst loading = 0.50 mol% based on limiting reactant.

Entry	Ionic liquid	Glycerol conversion (%)	Glycerol carbonate yield (%)	Glycerol carbonate selectivity (%)	Appearance of phase
1	Blank	5.0	5.0	100.0	2 phases[a]
2	[Ma][NO_3]	0.3	0.1	nc	2 phases[a]
3	[Ea][NO_3]	0.2	0.1	nc	2 phases[a]
4	[Bmim][Cl]	0.7	0.5	nc	2 phases[a]
5	[Bmim][BF_4]	0.0	0.0	0.0	2 phases[a]
6	[Hea][Fmt]	24.1	24.0	99.0	2 phases[a]
7	[Emim][Dmp]	22.2	22.0	99.0	2 phases[a]
8	[Bmim][Dca]	45.0	45.0	100.0	2 phases[a]
9	[Emim][Ac]	93.5	88.7	94.0	single phase

nc: not calculated; [a] Two phases of reaction mixture indicate incomplete glycerol conversion (even though 100% glycerol carbonate selectivity may achieve).

Besides, halide-based ionic liquid; [Bmim][Cl] gave 0.73% glycerol conversion and 0.46% glycerol carbonate in the reaction (Entry 4, Table 4.2). Similarly, Yi et al. (2014) reported low glycerol conversion (7.0%) when 81.5% glycerol carbonate selectivity were obtained when [Bmim][Cl] catalyzed the transesterification reaction of glycerol and dimethyl carbonate. Noting that, the observation of phase changes could be used as an indicative approach to visualize either incomplete or complete glycerol conversion achieved during ionic liquid catalyst screening.

As depicted in Table 4.2, [Bmim][Cl] (β = 0.950) (Entry 4) and [Emim][Dmp] (β = 1.1200) (Entry 7) gave lower glycerol conversion and glycerol carbonate yield. These ionic liquids were known to be categorized as the basic ionic liquids were considered inferior or similar to [Emim][Ac] as both anions have almost comparable β value to [Emim][Ac]. It could be related to the complexity of $[Dmp]^-$ anion structure (Mäki-Arvela et al., 2010) and incapable of forming hydrogen bonding with the hydroxyl group of glycerol with $[Cl]^-$ anion. Hydrogen of the glycerol hydroxyl group is much more preferred to form a bond to an electronegative O or N atom rather than a Cl atom (Swatloski et al., 2002). Unlike the results reported on [Bmim][Cl] (Entry 4, Table 4.2) activity towards glycerol conversion, [Bmim][Dca] (Entry 8, Table 4.2) shows better glycerol conversion and glycerol carbonate yield of 45.0%, respectively. The electronegativity of N atom consists in [Dca] anion could significantly explain this finding, even though [Bmim][Dca] shows lower β value (0.596) compared to [Bmim][Cl] (0.950). In contrast, Chiappe & Rajamani (2012) reported that glycerol conversion achieved using $[Mor_{1,4}][N(CN)_2]$ and $[HOEmim][N(CN)_2]$ were 95.0% and 100.0%, respectively. These could be related to the effect of alkyl length of morpholinium-based cation and substitution of hydroxyl group to the imidazolium-based cation that can influence the ionic liquids polarity and hydrogen bond donor ability, thus could cooperatively increase glycerol conversion (Lee & Prausnitz, 2010).

From the results, it is observed that the activity of the [Emim][Ac] is good giving 93.5% glycerol conversion and 88.7% glycerol carbonate yield at 2.0 hours with a ratio diethyl carbonate/glycerol of 2. It was believed that $[Ac]^-$ anion tends to form hydrogen bonds with the hydroxyl proton of glycerol, thus initiating the transesterification reaction. It is worth to mention that acetate-based ionic liquid shows as an excellent candidate not only as catalyst (this study) but also as solvent for pretreatment of lignocellulosic materials (Rahman et al., 2012; Rahman et al., 2016; Darji, 2015; Zakaria et al., 2017). Due to the proficiency of [Emim][Ac] to catalyze the reaction, [Emim][Ac] was taken up to evaluate in detail the effects of pertinent reaction parameters and will be discussed in section 4.1.1. Unless otherwise stated, all reactions were performed using standard Schlenk techniques, with nitrogen used to provide an inert atmosphere, in oven-dried Schlenk glassware.

4.1.1 Factors influencing transesterification reaction

As shown in section 4.1, [Emim][Ac] is revealed as a good candidate for catalyzing the transesterification reaction. Moreover, it is non-toxic, non-corrosive, biodegradable (Mäki-Arvela et al., 2010) and from the environmental point of view, [Emim][Ac] turned out as a potential catalyst for further organic synthesis as it is free of halogen. Therefore, in this section, the conditions optimization such as reaction temperature, reaction time, substrates ratio of diethyl carbonate/glycerol and solvent as well as catalyst loading with respect to the glycerol conversion and glycerol carbonate yield and selectivity were evaluated towards the transesterification reaction. Note that, glycidol selectivity is also reported along the study.

4.1.1.1 Effect of reaction temperature

In general, temperature increment during transesterification reaction should showed to a dramatic effect towards the glycerol conversion and glycerol carbonate yield and selectivity. This is mainly due to the fact that higher temperature can improve the miscibility between hydrophobic diethyl carbonate and hydrophilic glycerol (Yadav & Chandran, 2014). According to Arrhenius equation, an increase in reaction temperature can increase the collision rate between the reactants and thus change the reaction equilibrium towards the product yield. Nevertheless, the optimum reaction temperature in transesterification is closely dependent on the heat sensitive carbonates and catalysts used. Hence, the effect of temperature on conversion of glycerol to glycerol carbonate catalyzed by [Emim][Ac] was investigated at selected temperature of 35 °C and from 90 to 140 °C.

As depicted in Figure 4.1, less than 15.0% of the glycerol conversion and glycerol carbonate yield are measured at 35 °C and 90 °C. Meanwhile 18.6% of glycerol conversion and 18.0% glycerol carbonate yield were obtained at 100 °C. As shown in Figure 4.2, the reaction temperature less than 100 °C shows incomplete glycerol conversion (low glycerol carbonate yield) as two phases of reaction solution still remained after 2.0 hours as compared to its initial liquid–liquid biphasic solution. As the reaction proceeds with the increase of temperature (more than 100 °C), the initial liquid–liquid biphasic system transforms into a single-phase liquid, indicating that relatively complete glycerol conversion was achieved. This observation was in line with the reported study by Esteban et al. (2014) where a rapid increase of glycerol conversion and glycerol carbonate yield was observed when the temperature increases from 110 to 120 ºC, possibly due to the increase of collision energy.

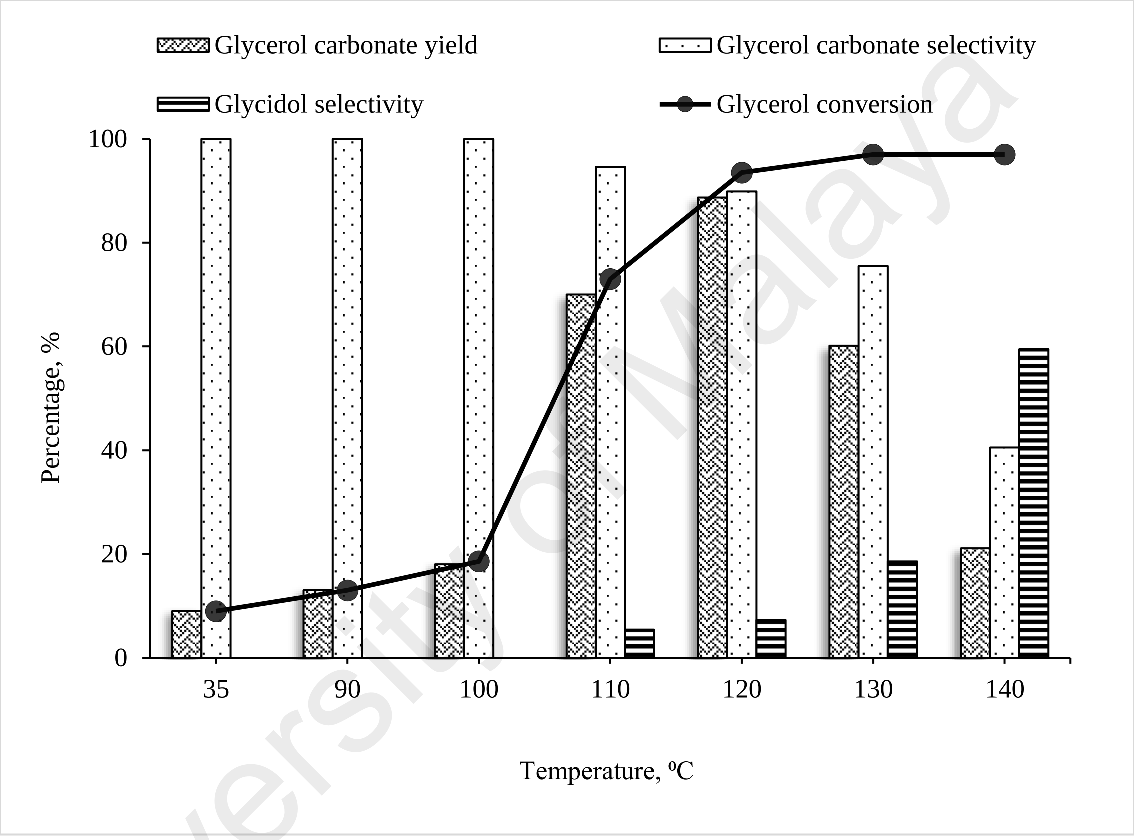


Figure 4.1: Effect of reaction temperature on the transesterification of glycerol with diethyl carbonate in the presence of [Emim][Ac] as catalyst. Reaction conditions: Reaction time = 2.0 hours, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading= 0.50 mol% based on limiting reactant.

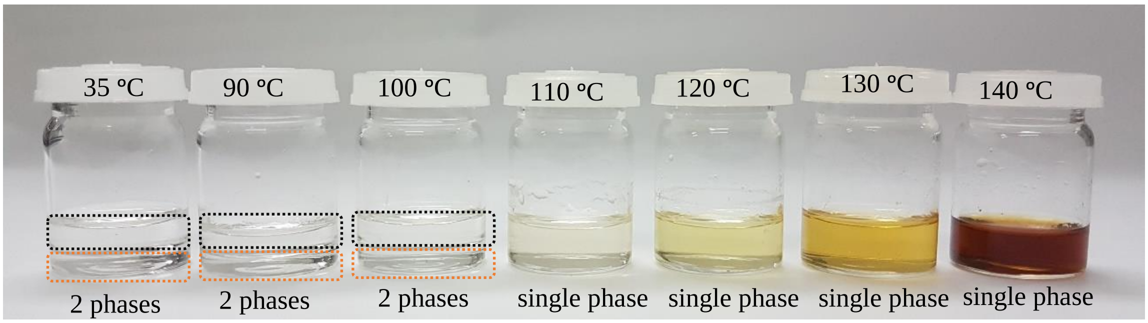


Figure 4.2: Changes of the colour of reaction solution with respect to the reaction temperature at 2.0 hours, Ratio of diethyl carbonate/glycerol of 2 and 0.50 mol% [Emim][Ac] loading.

As expected, the increase of reaction temperature from 100 to 110 ºC has significantly increased glycerol conversion (from 18.6% to 73.0%) and glycerol carbonate yield (from 18.0% to 70.0%) while 93.5% glycerol conversion and 88.7% glycerol carbonate yield were successfully obtained at 120 ºC (Figure 4.2). Further increase of reaction temperature at 130 ºC gives 97.0% glycerol conversion and glycerol carbonate yield was dropped to 60.2%. Even though the temperature plays a crucial role in increasing the reaction rate, severe temperature (140 ºC) has led to a rapid darkening of the reaction mixture which similarly observed by Chiappe and Rajamani (2012), using [$\text{Mor}_{1,4}$][N(CN)_2] as catalyst. At this stage, the dramatic decrease of glycerol carbonate yield (21.1%) and glycerol carbonate selectivity (40.5%) were probably due to the decarboxylation of glycerol carbonate to glycidol resulting from increasing the reactivity of its hydroxyl moiety with temperature, thus increased the glycidol selectivity (59.5%).

In the previous findings, Yi et al. (2014) demonstrated that [Bmim][Im] (10.00 mol%) has catalyzed the transesterification of glycerol with dimethyl carbonate and gave 73.4% glycerol conversion and 100.0% glycerol carbonate selectivity at the lowest temperature (70 °C) among other reported ionic liquids catalysts. Meanwhile, highest temperature of 130 °C has been reported by Zhou et al. (2015) using [N_{2222}][Pipe] with 96.0% glycerol conversion and 18.0% glycerol carbonate selectivity.

Theoretically, at high temperature, the primary hydroxyl pendant group of glycerol could react with the anion resulting in an hydroxide ion which could initiates the glycerol carbonate ring opening polymerization leading to a polymer (Chiappe & Rajamani, 2012; Ochoa-Gómez et al., 2011; Ochoa-Gómez et al., 2012b; Zhou et al., 2015). Besides, Rokicki et al. (2005) also have described the K_2CO_3-catalyzed ring opening polymerization of glycerol carbonate at 170 ºC which proceeds with carbon dioxide evolution and yields of hyper-branched aliphatic polyethers. These results suggest that, at a higher reaction temperature, the active catalysts could catalyze both transesterification reaction of glycerol to glycerol carbonate, which is absolutely dominant, and also glycerol carbonate decarboxylation to glycidol. Ochoa Gomez et al. (2012b) reported that 6.0% to 10.0% glycidol yield was additionally obtained despite of 99.0% glycerol conversion and a 98.0% glycerol carbonate yield at refluxing temperature of 68 to 88 °C, 2.5 hours of reaction time, dimethyl carbonate/glycerol ratio of 4 and 10.00 mol% of tetraethylamine loading.

It is agreeable that the formation of glycidol in one-pot reaction using [Emim][Ac] has somehow given an advantage to the overall reaction as glycidol can also be converted into value-added product. As an example, Gade et al. (2012) reported their pioneering work on the one-pot synthesis of glycidol using tetramethylammonium hydroxide as catalyst. However, this catalyst has some inherent drawbacks such as poor thermal ability and difficult reusability. Additionally, previously reported synthesis route of glycidol uses using non-environmentally friendly methods (Bolívar-Diaz et al., 2013).

According to the findings from this outcome, the reaction temperature of 120 ºC was chosen taking into account the glycerol conversion, glycerol carbonate yield and selectivity and glycidol selectivity. Even though this selected temperature was consistent with other research carried out by Grey & Pa (1999) and Chiappe & Rajamani (2012) (using ionic liquid as catalyst), however, in some extend the temperature was slightly higher if compared to classical basic catalyst (35 to 100 ºC) (Ochoa-Gómez et al., 2012b; Hervert et al., 2014).

4.1.1.2 Effect of reaction time

Reaction time also correlates with temperature. Higher reaction time could be advantageous as it allows more time for the glycerol to react in chemically catalyzed reaction. Furthermore, the conversion rate of glycerol, glycerol carbonate yield and selectivity are expected to increase with the reaction time. Figure 4.3 shows the influence of reaction time on the transesterification reaction catalyzed by [Emim][Ac], with respect to the glycerol conversion and glycerol carbonate yield and selectivity. It can be seen that in the early stages of the reaction (less than 0.5 hours), the formation of glycerol carbonate was negligible. However, the glycerol carbonate yield improved from 20.6% to 88.7% when the reaction time increased from 0.5 hours to 2.0 hours and then decreased over an extended time of reaction. It was also found that, one phase of solution was only obtained after 1.5 hours of heating, thus enhance the reaction rate thereafter. Besides, the glycerol conversion is enhanced with the reaction time prolonged from 1.0 to 4.0 hours, and it is maximized to 95.0% in 4.0 hours.

It is also seen from Figure 4.3 that glycerol carbonate selectivity decreased to 82.1% and glycidol selectivity improved substantially from 1.0% to 12.1% by prolonging reaction time up to 4.0 hours. This implies that the newly-formed glycerol carbonate is gradually converted to glycidol (Parameswaram et al., 2013). The results were consistent with those reported by Kondawar et al. (2017) and Song et al. (2017) where decarboxylation of glycerol carbonate to glycidol (glycidol formed less than 10.0%) become dominant after glycerol carbonate reaches equilibrium. Concurrently, there was also the formation of other unknown products including glycerol dicarbonate which was confirmed by ATR-FTIR, GC-FID and GC-MS analyses (discussed in section 4.1.2). It should be noted that, glycerol dicarbonate and other unknown products was not quantitatively measured in this study, except for glycerol, glycerol carbonate and glycidol.

From literature, the shortest reaction time of 0.5 hours using [Bmim][Im] (73.4% glycerol conversion and 100.0% glycerol carbonate selectivity) (Yi et al., 2014) and DBU-methanol (96.0% glycerol conversion and 82.0% glycerol carbonate selectivity) (Munshi et al., 2014) were reported whilst, the longest reaction time for maximum glycerol conversion (95.0%) was reported using [$Mor_{1,4}$][$N(CN)_2$] and [HOC_2mim][$N(CN)_2$] at 13.0 hours (Chiappe & Rajamani, 2012). Overall, the reaction time of 2.0 hours was selected for further evaluation.

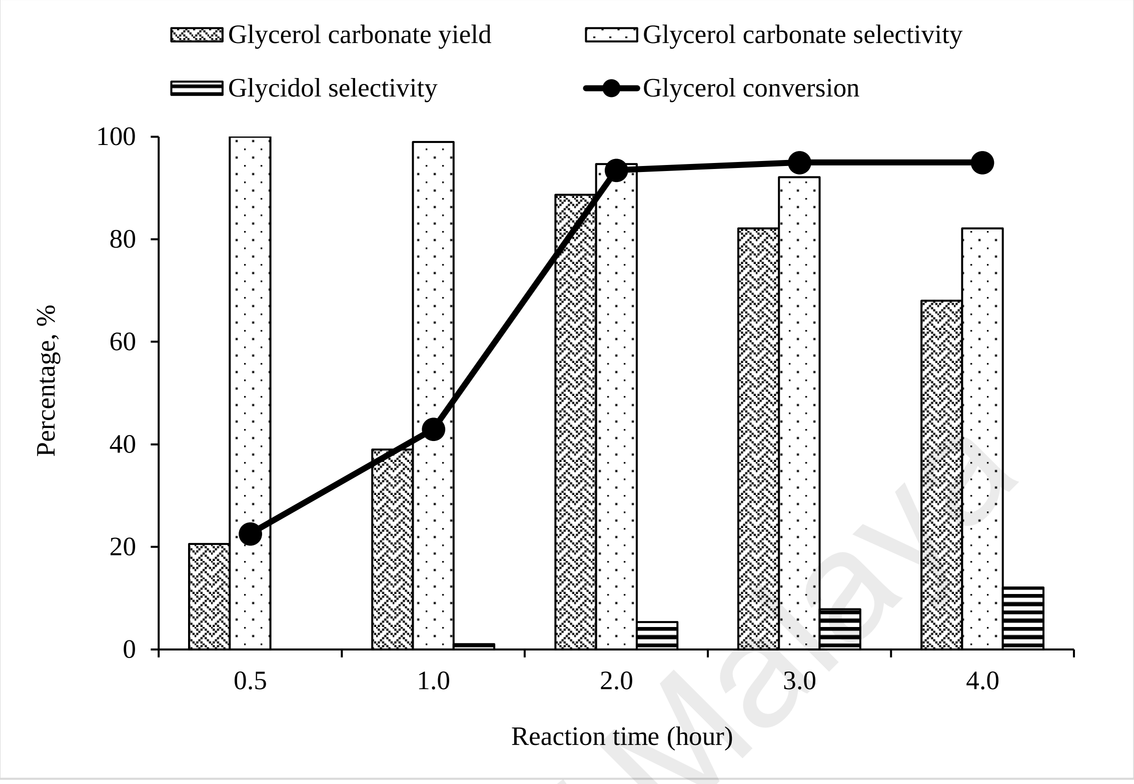


Figure 4.3: Effect of reaction time on the transesterification of glycerol with diethyl carbonate in the presence of [Emim][Ac] as catalyst. Reaction conditions: Temperature = 120 ºC, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading = 0.50 mol% based on limiting reactant.

4.1.1.3 Effect of substrate ratio and solvent

Since the rate of the reaction can be manipulated by varying the amount one of the reactant, the substrates ratio is an important parameter affecting the course of reaction. According to stoichiometric calculations, the ratio for transesterification reaction requires only 1 mol of carbonates and 1 mol of glycerol to produce 1 mol of glycerol carbonate and 2 mol of relevant by-product (methanol or ethanol). In the transesterification between the hydrophilic glycerol and hydrophobic carbonate source, the reactants are not miscible and the reaction is reversible which is in need of an excess carbonate source to give a positive effect on the glycerol conversion and glycerol carbonate yield (Chiappe & Rajamani, 2012).

As tabulated in Figure 4.4, low glycerol conversion and glycerol carbonate yield were observed when the equimolar of reactants were used in the transesterification giving 28.9% and 28.0%, respectively. This is expected since transesterification reaction is an equilibrium controlled reaction. The glycerol carbonate yield was increased (88.7%) when the diethyl carbonate/glycerol ratio is raised beyond 2 and kept slightly decreased to 78.1% at a molar ratio of 3. Glycerol conversion has gradually increased with the increase in diethyl carbonate/glycerol ratio from 1 to 3 indicating that the activity of [Emim][Ac] was dependent on the excess of diethyl carbonate to shift the reaction towards glycerol carbonate formation. However, glycerol conversion slightly decreased to 92.9% and also glycerol carbonate yield decreased to 72.9% at the molar ratio diethyl carbonate/glycerol of 4. This is expected due to the dilution of the reaction by diethyl carbonate (too excess of diethyl carbonate) which lessens the activity of [Emim][Ac] to initiate the reaction or glycerol carbonate was further reacted with the excess of diethyl carbonate to form glycerol dicarbonate.

From this study, the glycerol carbonate selectivity pattern was slightly affected by a change in the ratio of diethyl carbonate/glycerol. This finding was contradicted with the results reported by Munshi et al. (2014b) where glycerol carbonate selectivity pattern was not affected (in a range of 92.0% to 96.0%) by a change in molar ratio of dimethyl carbonate/glycerol of 0.3 to 3.0. From Ochoa-Gomez et al. (2012b) study, the formation of glycerol dicarbonate (8.0%) could not be prevented when catalyst/glycerol and dimethyl carbonate/glycerol molar ratios were increased. Hence, in subsequent reactions, the diethyl carbonate/glycerol ratio of 2 was fixed for further experiments.

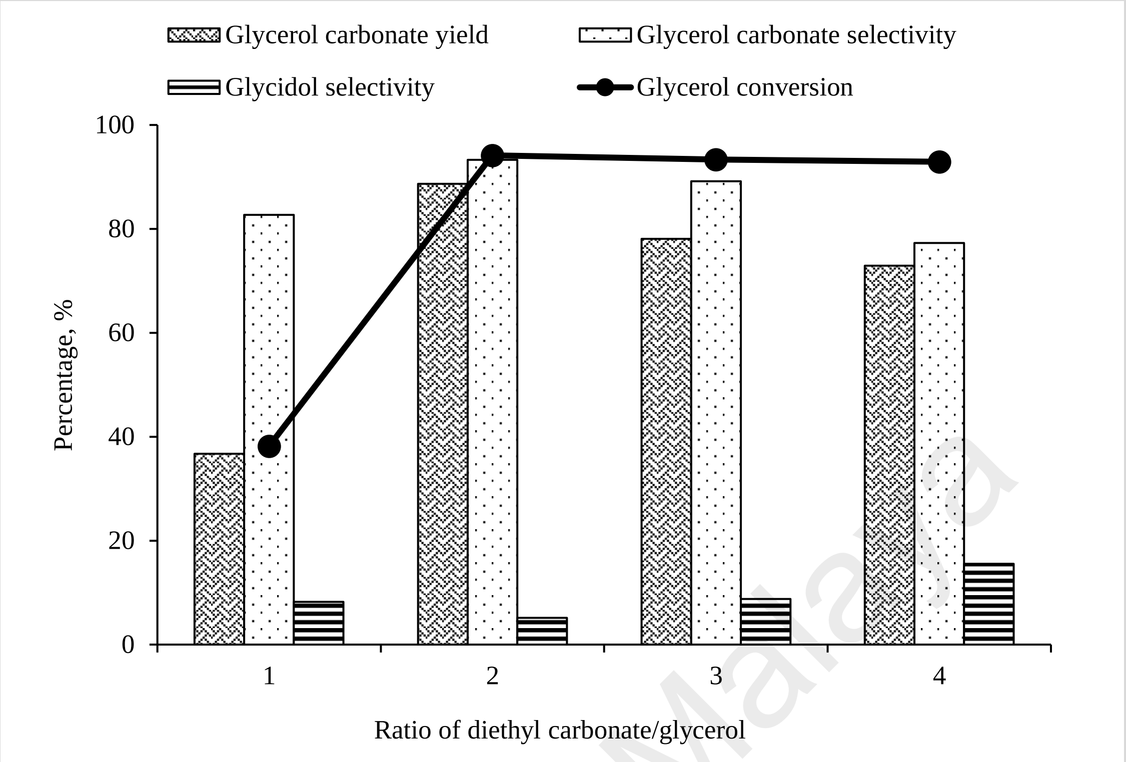


Figure 4.4: Effect of diethyl carbonate/glycerol ratio on conversion of glycerol and glycerol carbonate yield and selectivity. Reaction conditions: Temperature = 120 °C, Reaction time = 2.0 hours and [Emim][Ac] loading = 0.50 mol% based on limiting reactant.

Most ionic liquids are known to be hygroscopic to varying degrees, and that can be detrimental or useful depending upon the application in question. For instance, the effect of water content seems necessary to be conducted to affirm the reactivity of [Emim][Ac] towards catalyzing the transesterification reaction. At low water contents, 94.5% of glycerol conversion and 90.2% glycerol carbonate yield was achieved when water content was <1.0 wt.%, while 94.0% glycerol conversion and 89.2% glycerol carbonate yield was achieved with 2.0 wt.% of water content (Entry 1-2, Table 4.3). These findings show that low amount of water content traced in [Emim][Ac] (<1.0 wt.% to 2.0 wt.%) does not give negative effect towards [Emim][Ac] performance. It was expected that the traces amount of water content had helped to improve the solubility between hydrophilic glycerol and hydrophobic diethyl carbonate (Seong et al., 2011; Zhou et al., 2015).

However, the glycerol conversion and glycerol carbonate yield decreased with a water content more than 4.0 wt.% which has also been supported by Gade et al. (2012) findings (Entry 3-4, Table 4.3). When there was more than an optimum level of water, presumably it might lead to hydrolytic reactions, thus will significantly decreased the glycerol carbonate yield. Previously, Hammond et al. (2011) have found that for reaction of glycerol and urea with solid base catalysts, water has negative effect on the reaction.

Overall, it was found that, the transesterification reaction using [Emim][Ac] catalyst required no addition of solvents for the reaction to be initiated. Comparably, the transesterification reactions using heterogeneous catalyst were carried out with addition of organic solvent such as polar aprotic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile and hydrophilic solvents such as tetrahydrofuran (THF), tert-butanol, ethanol or methanol in order to compensate the low ratio of carbonate/glycerol (Álvarez et al., 2012; Kumar et al., 2012; Pan et al., 2012; Takagaki et al., 2010). Due to insignificant difference of glycerol conversion and glycerol carbonate yield between water content of [Emim][Ac] (Entry 1 and Entry 2), the optimum level of water content of [Emim][Ac] was fixed to 2.0 wt.%, considering the time consuming of drying [Emim][Ac] ionic liquid using Schlenk line, thus lead to inefficient use of energy.

Table 4.3: Effect of water contents in [Emim][Ac] on the glycerol conversion and glycerol carbonate yield.

Entry	Water content (wt.%)	Glycerol conversion (%)	Glycerol carbonate yield (%)
1	<1.0[a]	94.5	90.2
2	2.0[b]	94.0	89.2
3	4.0	87.9	84.4
4	>8.0	83.4	76.1

Reaction conditions: Temperature = 120 °C, Reaction time = 2.0 hours, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading= 0.50 mol% based on limiting reactant. [a] Dried using vacuum schlenk line for more than 72 hours. [b] Dried overnight in vacuum oven at 70 °C.

4.1.1.4 Effect of catalyst loading

An increase of catalyst loading led to a gradual increase in the glycerol carbonate yield because more glycerol molecules would be catalyzed in the desired reaction. Figure 4.5 displays the dependency of glycerol transesterification with diethyl carbonate to glycerol carbonate yield and selectivity on [Emim][Ac] loading ranging from 0.10 mol% to 10.00 mol%. At 0.10 mol%, [Emim][Ac] loading leads to a very slow reaction with 65.0% glycerol conversion and 59.6% glycerol carbonate yield, thus giving 90.3% glycerol carbonate selectivity. Maximum glycerol carbonate yield of 88.7% is accomplished with 0.50 mol% [Emim][Ac] loading, with 93.5% glycerol conversion. The increase of [Emim][Ac] loading up to 10.00 mol% has slightly increased the glycerol conversion while glycerol carbonate yield has decreased to 31.4%. The increased of catalyst concentration is believed to promote glycerol decarboxylation to glycidol due to the presence of strong bases catalyst (Gade et al., 2012) or glycerol dicarbonate formation (Ochoa-Gómez et al., 2012b) as described in ATR-FTIR and NMR studies (section 4.1.2.1 and 4.1.2.2). It has been reported that glycerol carbonate selectivity decreased as low as 15.0% when the concentration of [Tma][OH] catalyst increased to 6.00 mol% (Gade et al., 2012).

Monitoring on the glycerol carbonate selectivity pattern showed that selectivity was not much affected after 2.0 hours reaction time at lower [Emim][Ac] loading ranging from 0.10 mol% to 1.00 mol% (Figure 4.6). However, the increasing of [Emim][Ac] loading more than 1.00 mol% showed rapid decrease in glycerol carbonate selectivity. This observation was in agreement with findings reported by Gade et al. (2012), where decarboxylation of glycerol carbonate increased with the increase in the concentration of the [Tma][OH] ionic liquid catalyst in the reaction mixture. The lowest catalyst loading of 0.01 mol% has successfully converted 100.0% of glycerol using N,N-dimethylpyrrolidinium methylcarbonate (Chiappe & Rajamani, 2012). However, glycerol carbonate yield and selectivity have not been reported in their finding.

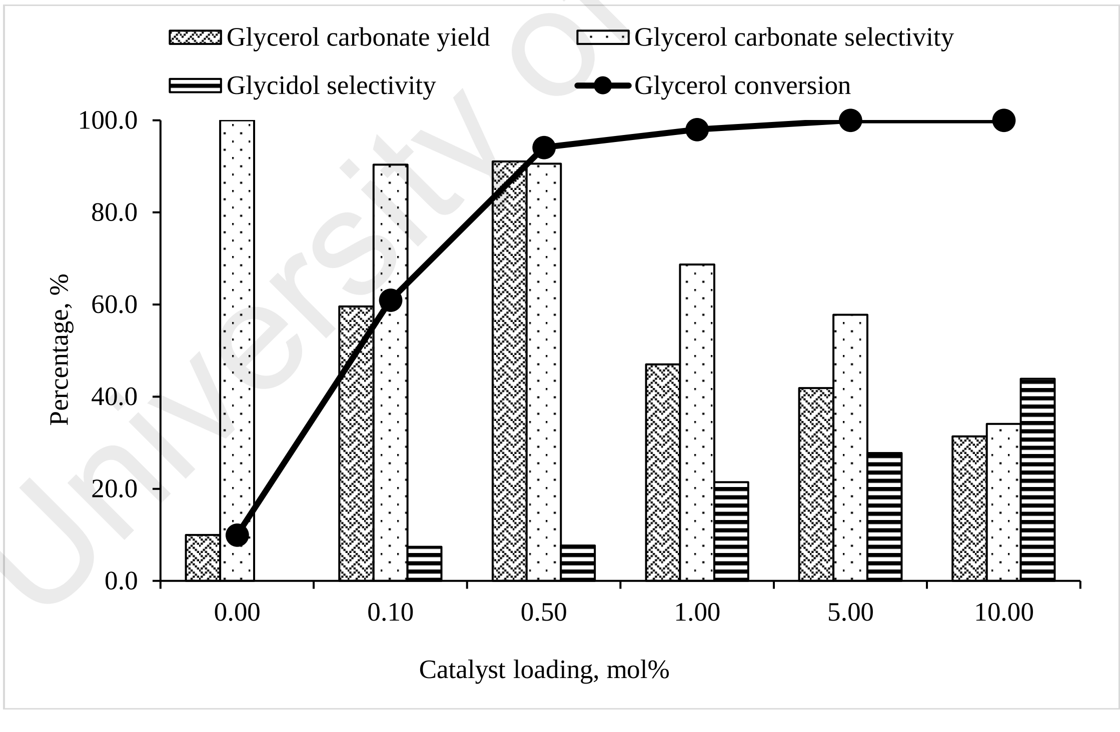


Figure 4.5: Effect of catalyst loading on the transesterification of glycerol with diethyl carbonate in the presence of [Emim][Ac] as catalyst. Reaction conditions: Temperature = 120 °C, Reaction time = 2.0 hours and Ratio of diethyl carbonate/glycerol = 2.

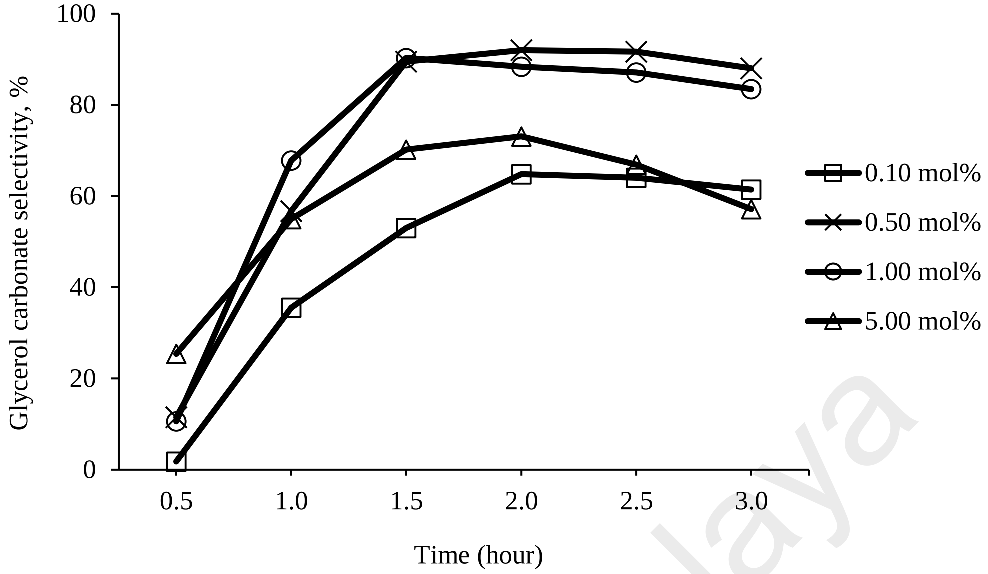


Figure 4.6: Effect of catalyst loading on glycerol carbonate selectivity with respect to time on transesterification of glycerol with diethyl carbonate. Reaction conditions: Temperature = 120 °C, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading = 0.50 mol% based on limiting reactant.

These results indicate that for maximization of glycerol carbonate yield and selectivity, the amount of the catalyst should be appropriate in order to minimize the formation of glycidol and other unknown compounds including glycerol dicarbonate. Therefore, 0.50 mol% of the [Emim][Ac] was selected as reference for further study.

4.1.2 Characterization of transesterification reaction of glycerol products

4.1.2.1 Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was carried out as a preliminary examination and confirmation of the presence of different functional groups of glycerol, glycerol carbonate as desired product and other possible products formed during transesterification reaction of glycerol and diethyl carbonate. Besides, ATR-FTIR analysis was conducted to corroborate with GC-FID analysis to clearly understand the interaction of ionic liquid catalysts with glycerol or glycerol carbonate. Table 4.4 tabulated the band assignments of glycerol, glycerol carbonate, glycidol and glycerol dicarbonate.

Hypothesesly, the degree of interaction between hydroxyl group of glycerol and anion of an ionic liquid is of pivotal importance in determining activity of the ionic liquids toward glycerol conversion and glycerol carbonate yield. This degree of interaction can be correlated in a form of hydrogen bond basicity of anion described by the β value (Table 4.1). Anion plays a major role in activating the hydroxyl group of glycerol through hydrogen-bonding interaction. The strength of nucleophile of the anion must be high enough to pull the proton from the hydroxyl group of glycerol, thus initiate the reaction.

Table 4.4: FTIR of absorption bands of functional groups of glycerol and possible products formed from transesterification reaction of glycerol and diethyl carbonate.

Band position (cm^{-1})	Functional groups	References
	Glycerol peaks[a]	
3350-3368	O-H stretching	Ochoa-Gómez et al., 2012b; Kongjao et al., 2010
2880 and 2930	C-H stretching	Kongjao et al., 2010
2100	C-O stretching	
1400-1460	C-O-H bending	
1450-1100	C-O stretching (primary and secondary alcohol)	
920	O-H bending	
	Glycerol carbonate peaks[a]	
3410-3435	O-H	Kim et al., 2014; Ochoa-Gómez et al., 2012b
1785-1790	C=O	
	Glycerol dicarbonate peaks	
1797	C=O cyclic	Ochoa-Gómez et al., 2012b
1755	C=O linear	
1445	OCH_3	
1397	CH_2	
1277	C(O)-O-C linear	
1171	C(O)-O-C cyclic	
	Glycidol peaks[a]	
3790	O-H stretching	Analysis using ATR-FTIR of glycidol standard
3000-3250	C-H stretching	
1300	O-H bend	
850-900	C-O bending	

[a] see APPENDIX A

The effect on the activity of screened ionic liquids specifically anions toward the transesterification reaction of glycerol was demonstrated in Figure 4.7. As shown in the spectra, it was clearly observed that when glycerol interacted with [Emim][Ac] which has a β values 1.201, the absorption band centered at 3287 cm^{-1} corresponding to the hydroxyl group of glycerol shifted to the lower frequency of 3195 cm^{-1} (Figure 4.7 (i)). Meanwhile, the O-H stretching frequency shifts to a slightly lower frequency when glycerol interacted with [Emim][Dmp], [Bmim][Dca] and [Hea][Fmt] of 3272 cm^{-1}, 3272 cm^{-1} and 3278 cm^{-}

^{1}, respectively (Figure 4.7 (f-h)). Upon the contact of glycerol with [Ma][NO_3], [Ea][NO_3], [Bmim][BF_4], [Bmim][Cl], the absorption band moved to a higher frequency of 3411 cm^{-1}, 3399 cm^{-1}, 3332 cm^{-1} and 3348 cm^{-1}, respectively (Figure 4.7 (b-e)). The higher O-H stretching frequency shift of glycerol upon interacting with [Ma][NO_3], [Ea][NO_3], [Bmim][BF_4] and [Bmim][Cl] indicates that there is no interaction between the hydroxyl group of glycerol and [NO_3]$^-$, [BF_4]$^-$ and [Cl]$^-$ anion. This can be ascribed to the straightening of intramolecular hydrogen-bonding interaction between glycerol molecules as the ionic liquids ([Bmim][BF_4] or [Bmim][Cl]) have weak ability to form hydrogen bonds during initiation step, thus only oriented between themselves (Omar, 2013).

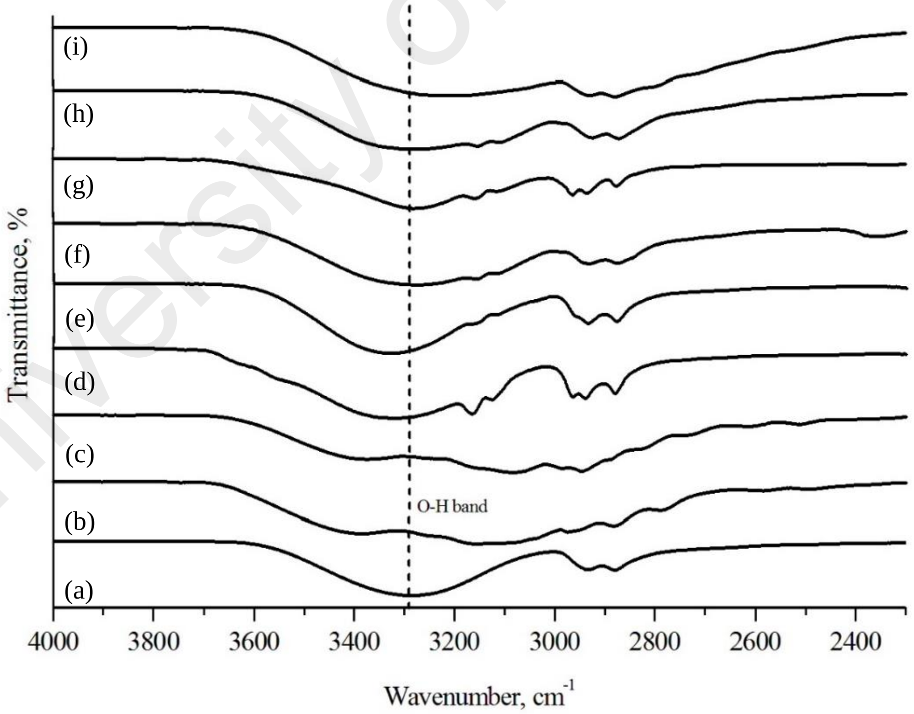


Figure 4.7: ATR-FTIR spectra showing the interactions of glycerol with ionic liquids: (a) glycerol, (b) glycerol-[Ma][NO_3], (c) glycerol-[Ea][NO_3], (d) glycerol-[Bmim][Cl], (e) glycerol-[Bmim][BF_4], (f) glycerol-[Emim][Dmp], (g) glycerol-[Bmim][Dca], (h) glycerol-[Hea][Fmt] and (i) glycerol-[Emim][Ac]. The ratio of glycerol to ionic liquid was set at 1.

Further study was conducted using [Emim][Ac] as it shows a good correlation between the hydroxyl group of glycerol and acetate ([Ac]$^-$) anion together with high glycerol conversion and glycerol carbonate yield and selectivity. [Ac]$^-$ anion tends to undergo a stronger interaction with the hydroxyl group of glycerol. The three hydroxyl groups of glycerol are active in the transesterification reaction. As the glycerol has a symmetrical structure, it is believed that [Ac]$^-$ anion can freely form hydrogen bonding between the primary hydroxyl group (carbon 1) and secondary alcohol (carbon 2) of glycerol (Figure 4.8). However, the primary hydroxyl group (carbon 1) is presumably more reactive than secondary hydroxyl group (carbon 2). Once the transesterification reaction of primary alcohol occurs, this will be resulting in the facile formation of the corresponding glyceroxide anion, and secondary alcohol that will further react with nearby carbonate group, which glycerol carbonate is formed.

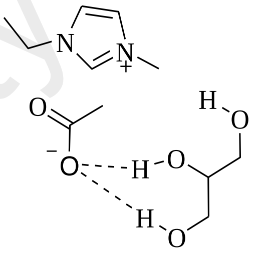


Figure 4.8: Hydrogen-bonding interaction between [Emim][Ac] and glycerol.

ATR-FTIR study was proceeded to investigate the formation of glycerol carbonate within selected time interval on the basis of peak intensity under reaction using [Emim][Ac] (Figure 4.9). Throughout the reaction, peaks intensity corresponds O–H bending in glycerol at 1262 cm^{-1} and 923 cm^{-1} (Indran et al., 2014) reduced significantly after 2 hours. The O–H bending is further supported by the –O–H stretching centered at 3387 cm^{-1} (Hazimah et al., 2003) that show a reduction in peak intensity, presumably due to glycerol being converted into glycerol carbonate. The peak at 1750 cm^{-1} corresponds to C=O of glycerol carbonate which increased in intensity when reaction time is prolonged up to 2 hours. The peaks at the range between 1200 cm^{-1} to 1000 cm^{-1} also support the presence of glycerol carbonate where these peaks indicate C–C and C–O stretching of 2-hydroxyethyl chain (Calvino-Casilda et al., 2011). All peaks correspond to glycerol carbonate showing an increase in the trend up to 2.0 hours of the reaction time and slightly decreased thereafter, indicated that the selectivity of glycerol carbonate was reduced. Apart of that, it was found that there was the formation of glycerol dicarbonate at peak 1264 cm^{-1} as the reaction time increases to 2.0 hours, however, this peak was not seen thereafter (Ochoa-Gómez et al., 2009). The formation of glycerol dicarbonate was confirmed by GC-FID spectra in Figure 4.13 (section 4.1.2.3).

It also can be seen from Figure 4.9 that the peak intensity at 923 cm^{-1} corresponded to O-H bending and 908 cm^{-1} were slightly broadened when the reaction proceeded (more than 3 hours). This peak was expected to be corresponded to C-O-C bond of glycidol or/and polyglycidol (Fischer & Ritter, 2013; Ochoa-Gómez et al., 2009). The formation of glycerol dicarbonate and glycidol were also reported in other studies indicated that it was difficult to stop the reaction at targeted molecule (Ochoa-Gómez et al., 2012b; Zhou et al., 2015). Further evaluation using GC-MS (further discussed in section 4.1.2.3) is necessary to confirm the formation of targeted product (glycerol carbonate) and other unknown compounds.

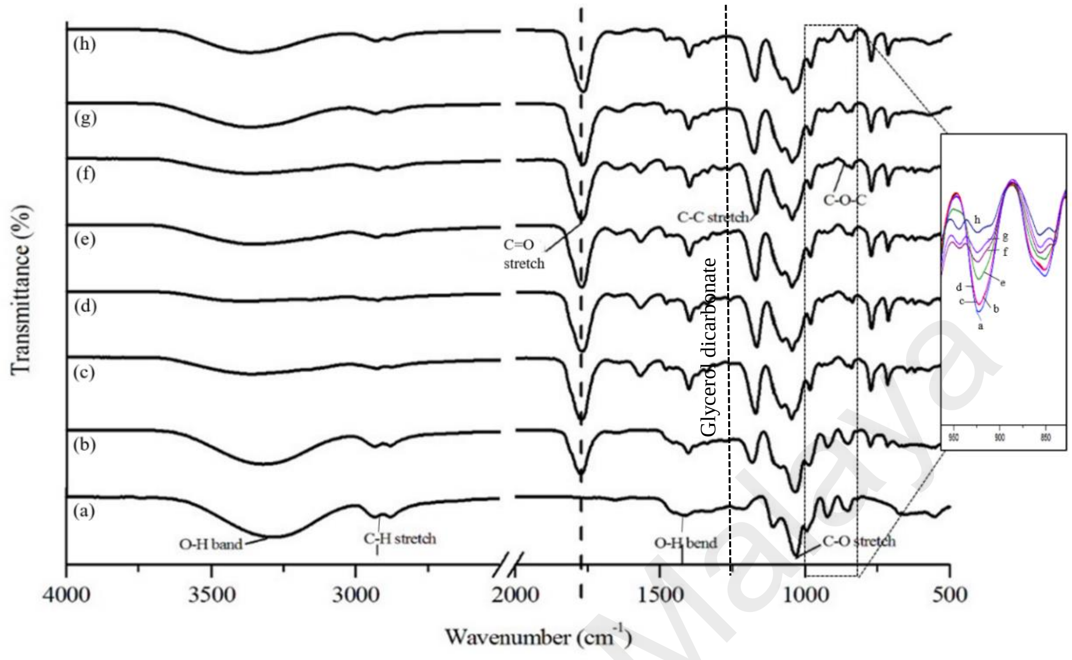


Figure 4.9: ATR-FTIR spectra of transesterification of glycerol using [Emim][Ac] as catalyst: (a) 30 minutes, (b) 1.0 hour, (c) 1.5 hours, (d) 2.0 hours, (e) 2.5 hours, (f) 3.0 hours, (g) 3.5 hours and (h) 4.0 hours. Reaction conditions: Temperature = 120 °C, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading= 0.50 mol% based on limiting reactant.

It would be reasonable to expect that the strength of [Emim][Ac] as nucleophile to initiate the formation of glyceroxide anion can somehow further react with glycerol carbonate, thus decreases its selectivity. Owing to this postulate, ATR-FTIR study on the effect of [Emim][Ac] loading towards the glycerol carbonate selectivity was investigated. As can be seen in Figure 4.10, a pronounced O-H stretching frequency shift of glycerol carbonate (from 3450 cm^{-1} to 3247 cm^{-1}) was observed to shift to a lower frequency when [Emim][Ac] loading (with respect to glycerol carbonate, mol%) increased from 0.10 mol% to 10.00 mol%, due to strong hydrogen bonding interaction between [Ac]$^-$ anion with hydroxyl end of glycerol carbonate.

[Emim][Ac] loading of 0.50 mol% has sufficient capability to catalyze the transesterification reaction with glycerol carbonate yield of 88.7% (Figure 4.10(c). The increase in [Emim][Ac] loading more than 0.50 mol% has adverse effects on glycerol carbonate selectivity, which helps to promote the formation of undesired products. It is evident by the decrease of peak intensity at 1750 cm^{-1} correspond to C=O of glycerol carbonate and the appearance of peak at 1264 cm^{-1} which is expected to belong to glycerol dicarbonate (discussed in Figure 4.9) (Figure 4.10(d-f)). This phenomenon is due to the activation of hydroxyl end of glycerol carbonate by [Ac]$^-$ anion which thus, leads to the further carbonylation of glycerol carbonate to form glycerol dicarbonate or decarboxylation of glycerol carbonate to form glycidol/polyglycidol. These results were paralleled to the other studies (Ochoa-Gómez et al., 2012b; Choi et al., 2013; Ochoa-Gómez et al., 2009; Munshi et al., 2014a). Additionally, ATR-FTIR result is consistent with the effect of [Emim][Ac] loading as discussed in section 4.1.2.1.

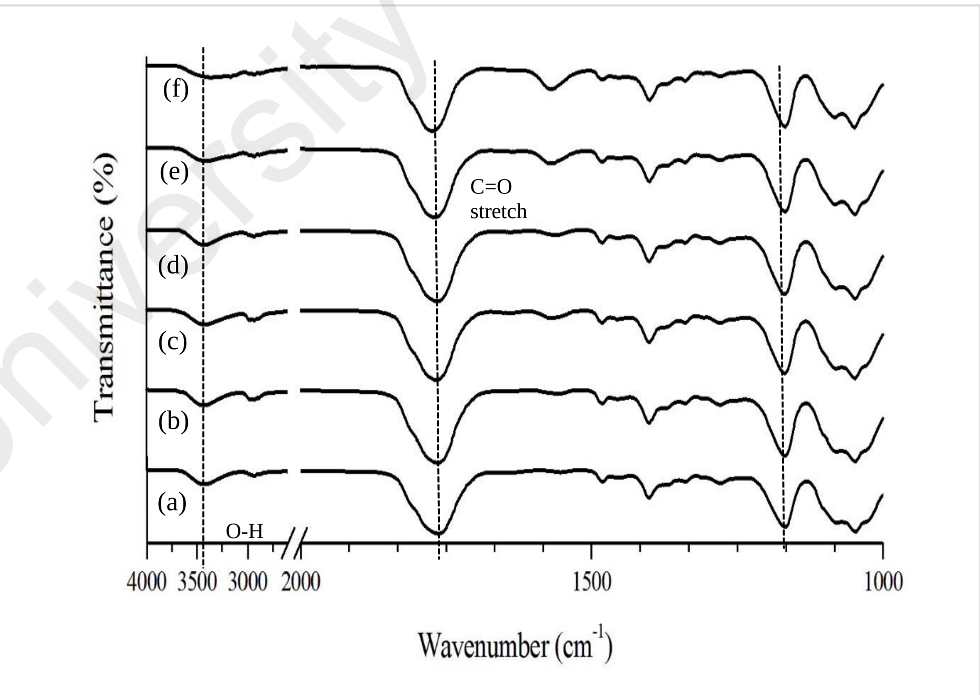


Figure 4.10: ATR-FTIR spectra of transesterification of glycerol and diethyl carbonate using [Emim][Ac] as catalyst: (a) glycerol carbonate and glycerol carbonate-[Emim][Ac] of (b), 0.10 mol%, (c) 0.50 mol%, (d) 1.00 mol%, (e) 5.00 mol% and (f) 10.00 mol%. Reaction conditions: Temperature = 120 °C, Reaction time = 2.0 hours and Ratio of diethyl carbonate/glycerol carbonate = 2.

From ATR-FTIR studies, it can be concluded that, the interaction of the anion of the ionic liquid (in this case $[Ac]^-$ anion) with glycerol should be strong enough and the interaction of anion with glycerol carbonate must be sufficiently weak in order to obtain high glycerol conversion, glycerol carbonate yield and selectivity.

4.1.2.2 Nuclear magnetic resonance (NMR) spectroscopy

^{13}C NMR spectroscopy was conducted to generate a reaction profile by time-on-time analysis for the transesterification reaction of glycerol. Deuterated methanol-*d₄* was used as solvent for NMR analysis. Figure 4.11(a-c) shows that, at the early stage of reaction, only glycerol peaks appeared at 72.0 ppm and 62.5 ppm which are attributed to the presence of –CH–O– and $–CH_2–O–$. Glycerol carbonate peaks at 61.5 ppm, 67.0 ppm, and 77.5 ppm correspond to $–CH_2–O-$, $–CH_2–OH$ and –CH–, respectively gradually increased when the reaction solution which initially liquid–liquid biphasic solution turned into single phase at 1.5 hours (Figure 4.11(d)). On the other hand, the small peaks at 54.2 ppm (-C=O-), 60.5 ppm ($-O-CH_2$), 69.0 ppm ($-O-CH_2-$), 70.5 ppm (O-CH-) and 79.5 ppm ($-CH_2-O$) correspond to glycerol dicarbonate while peaks at 43.9 ppm ($-CH_2-O$), 62.5 ppm (-CH-C) and 65.9 ppm ($-CH_2-OH$) corresponding to glycidol were observed as the reaction time is prolonged (Figure 4.11 (e-f)). These assumptions can be related well from the ATR-FTIR peaks pattern discussed in section 4.1.2.1, whereby the intensity of the respective peaks was influenced by reaction time. From Figure 4.11(f and g), it also reveals that there is progressive improvement of peaks that were assumed as unknown compounds observed when the reaction time was more than 2.0 hours. It should be noted that, the presence of these unknown compounds and glycerol dicarbonate was not quantitated in this study.

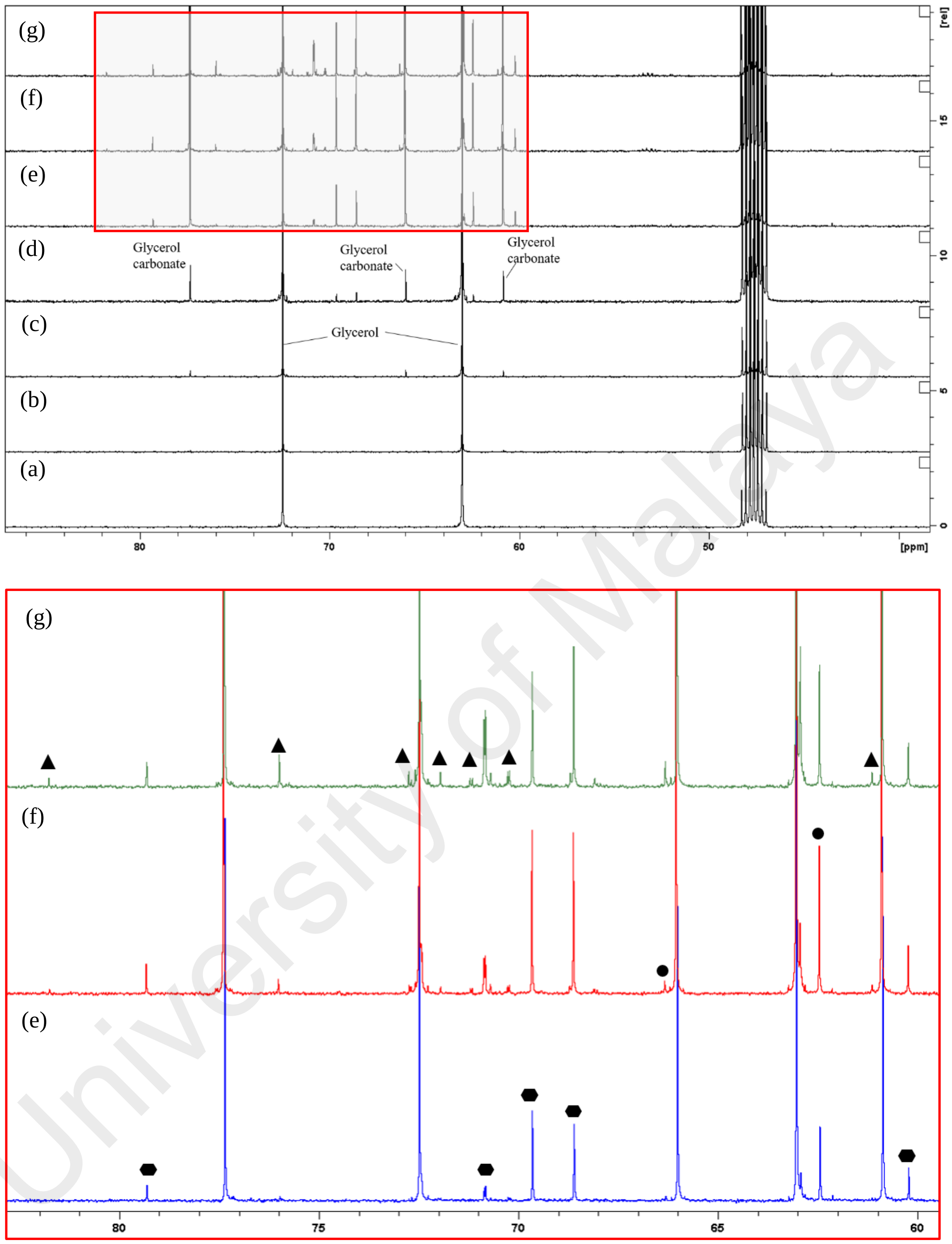


Figure 4.11: ^{13}C NMR of reaction mixture at selected time interval which is (a) 0 minute, (b) 30 minutes, (c) 1.0 hour, (d) 1.5 hours, (e) 2.0 hours, (f) 2.5 hours and (g) 3.0 hours (zooming at ≈ 60 ppm to 85 ppm for (e), (f) and (g)). Reaction conditions: Temperature = 120 °C, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading = 0.50 mol% based on limiting reactant. Deuterated methanol-d_4 (99.8%) was used as solvent in NMR analysis. The symbol depicted for (⬢) = glycerol dicarbonate, (●) = glycidol and (▲) = unknown compounds.

In order to partly support the prediction of the reaction mechanism (will be discussed in section 4.4), the interaction between [Emim][Ac] and glycerol as substrate was investigated using ^{1}H NMR. The ^{1}H NMR is a useful technique when it comes to obtain the message for the hydrogen bonding interaction, same as what ATR-FTIR spectra does (discussed in section 4.1.2.1). It is worth mentioning that, the effect of deuterated methanol-d_4 used as NMR solvent is neglected and is mainly focused on [Emim][Ac]/glycerol interaction. Based on the evidences from the ^{1}H NMR in Figure 4.12, the chemical shifts have slightly moved to downfield region attributed to the formation of hydrogen bonding between hydroxyl group of glycerol and [Emim][Ac] following the order; $\delta H2 > \delta H4 > \delta H5 > \delta H7 > \delta H6 > \delta Hb > \delta H8$. The trend was comparatively similar to the reported chemical shifts of [Emim][Ac] in common solvents (D_2O and CD_3OD) (Chen et al., 2014). The absolute change of ^{1}H NMR chemical shifts ($\Delta\delta$) for [Emim][Ac] and glycerol is tabulated in Table 4.5.

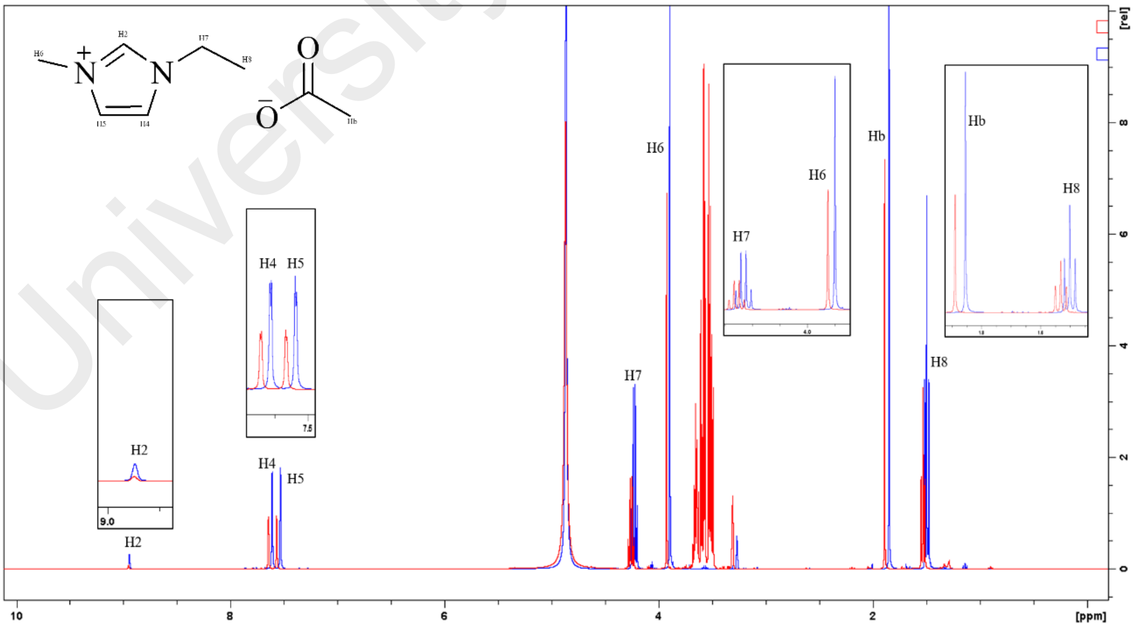


Figure 4.12: ^{1}H NMR spectra for [Emim][Ac] (indicates by blue spectrum) and [Emim][Ac]/glycerol mixture (indicates by red spectrum). [Emim][Ac]/glycerol mixture was prepared with ratio of 0.5:5. Deuterated methanol-d_4 (99.8%) was used as solvent in NMR analysis.

Table 4.5: Assignment ^{1}H NMR peak of [Emim][Ac]/glycerol mixture.

Assignments	**Chemical shift, δ (ppm)**		**Absolute change of chemical shift (Δδ, ppm)**
	Pure [Emim][Ac]	**[Emim][Ac]/glycerol**	
H2	8.9432	8.9492	0.0060
H4	7.6114	7.6452	0.0338
H5	7.5347	7.5680	0.0333
H7	4.2369	4.2844	0.0475
H6	3.8954	3.9251	0.0297
Hb	1.8495	1.8892	0.0397
H8	1.4962	1.5308	0.0346

4.1.2.3 Gas chromatography analysis

(a) Gas chromatography-flame ionization detector (GC-FID) spectroscopy

Identification and quantification of transesterification products were performed using gas chromatography-flame ionization detector (GC-FID) as well as comparison with mass spectroscopy spectra of the corresponding reference compounds which will be discussed in section 4.1.2.3 (b). Figure 4.13 shows the identification of glycidol, glycerol and glycerol carbonate standards which appeared at the retention time of 7.649 minutes, 16.640 minutes and 21.846 minutes, respectively. Retention time of glycerol dicarbonate was observed at 20.697 minutes (Ochoa-Gómez et al., 2012b).

It is best to notify that, through the observation of GC-FID chromatogram, glycidol standard shows several peaks, instead of single peak of glycidol at 7.649 minutes as depicted in Figure 4.14. As shown in Figure 4.15, glycidol molecule contains two reactive groups, namely epoxide and hydroxyl groups. The epoxide group is involved in propagation during anionic polymerization whereas the hydroxyl one is responsible for chain transfer reactions. Therefore, the polymerization of glycidol always leads to the formation of branched polymers (Gosecki et al., 2016). Presumably, the appearance of unknown peaks in glycidol standard from 16.625 minutes to 21.475 minutes could be assigned to the unavoidable formation of polyglycidols during synthesis reaction by the manufacturer. The analysis of GC-MS was conducted to further support this assumption.

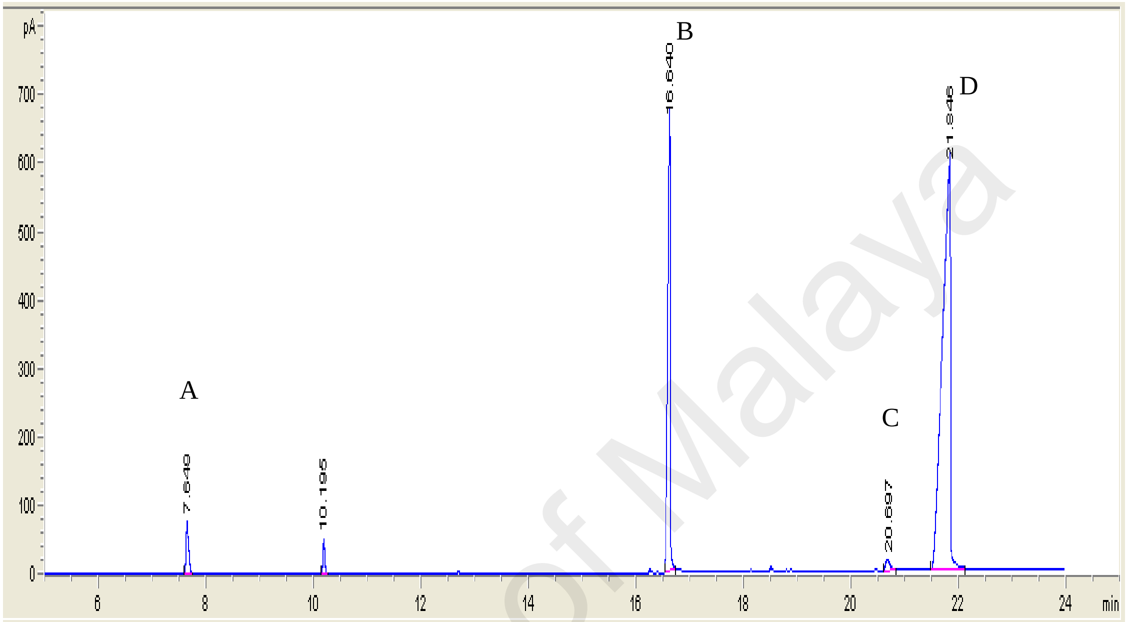


Figure 4.13: Gas chromatography of standard A = glycidol, B = glycerol, C = glycerol dicarbonate and D= glycerol carbonate. A solution of glycerol, glycerol carbonate and glycidol standard was prepared in equivalent ratio. Column FFAP (30 m x 0.25 mm). Injection volume: 1 µl. Oven: 60 ºC held 5 minutes, temperature ramp at 5 ºC/minutes from 60 ºC to 80 ºC, 1 minute hold at 80 ºC, a 10 ºC/minutes ramp from 80 ºC to 230 ºC and a 10 minutes hold at 230 ºC.

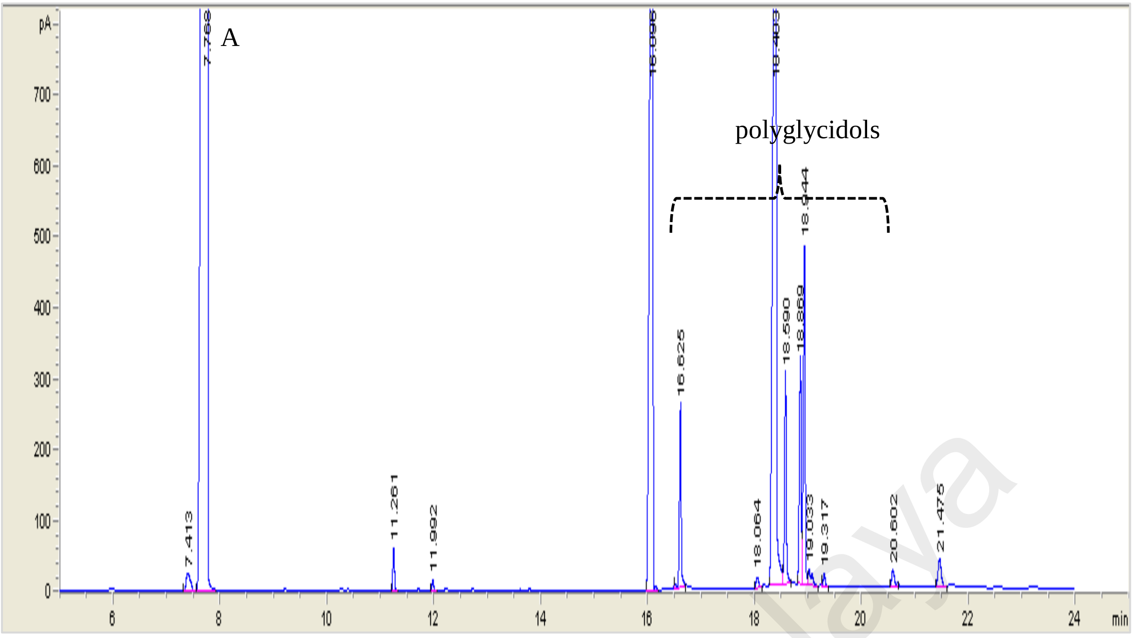


Figure 4.14: Gas chromatography of glycidol standard (97.0% purity). A = glycidol. Column FFAP (30 m x 0.25 mm). Injection volume: 1 µl. Oven: 60 ºC held 5 minutes, temperature ramp at 5 ºC/minutes from 60 ºC to 80 ºC, 1 minute hold at 80 ºC, a 10 ºC /minutes ramp from 80 ºC to 230 ºC and a 10 minutes hold at 230 ºC.

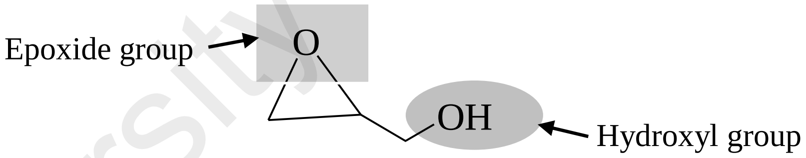


Figure 4.15: Glycidol functionalities.

The formation of the products as the transesterification reaction progress was evaluated as shown in Figure 4.16. Obviously, the formation of glycerol carbonate (88.7%) was observed as the reaction time increased at 2.0 hours, with 93.5% glycerol conversion. Moreover, the formation of glycidol and glycerol dicarbonate were slightly increased especially when initially biphasic transesterification reaction turned into one-phase mixture at 1.5 hours. Rapid decarboxylation of glycerol carbonate to glycidol and polyglycidols took place thereafter (more than 2.0 hours). This has led to the reduction of glycerol carbonate yield from 88.7% to 82.1% and the selectivity from 96.7% to 86.5%.

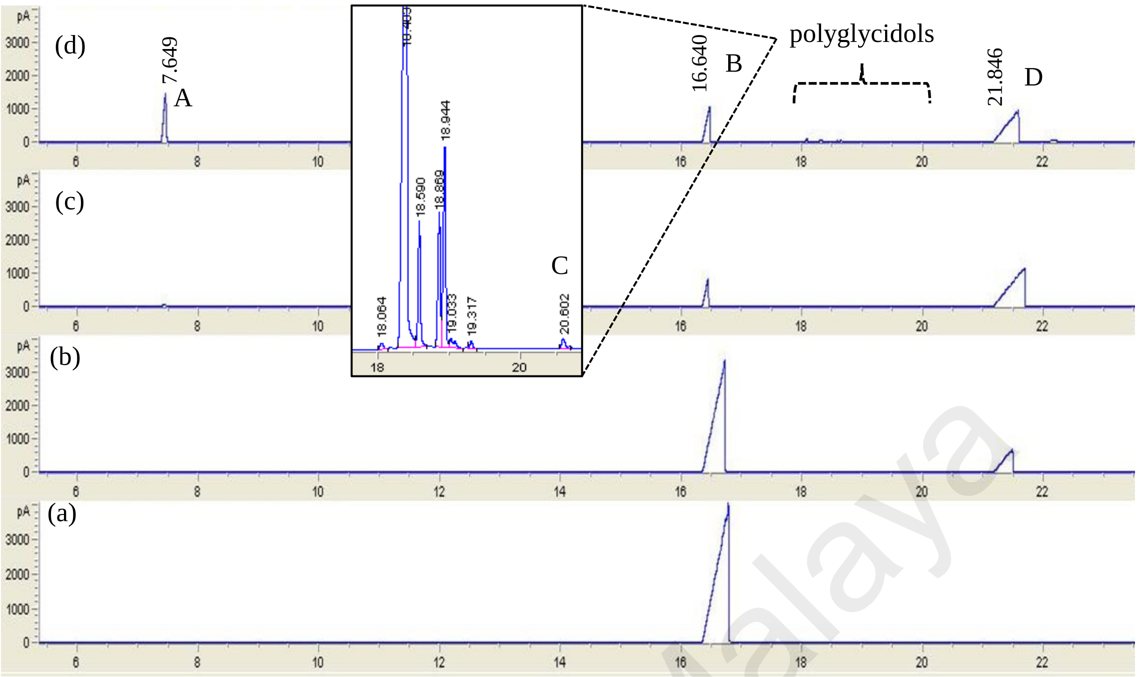


Figure 4.16: Gas chromatography-flame ionization detector spectra of transesterification reaction of glycerol and diethyl carbonate with respect to the reaction time: (a) 0 minute (b) 1.5 hours (c) 2.0 hours and (d) 3.0 hours. A = glycidol, B = glycerol, C = glycerol dicarbonate and D = glycerol carbonate. Reaction conditions: Temperature = 120 ºC, Ratio of diethyl carbonate/glycerol = 2 and [Emim][Ac] loading = 0.50 mol% based on limiting reactant. Column FFAP (30 m x 0.25 mm). Injection volume: 1 µl. Oven: 60 ºC held 5 minutes, temperature ramp at 5 ºC/minutes from 60 ºC to 80 ºC, 1 minute hold at 80 ºC, a 10 ºC/minutes ramp from 80 ºC to 230 ºC and a 10 minutes hold at 230 ºC.

(b) Gas chromatography-mass detector (GC-MS) spectroscopy

Gas chromatography-mass detector (GC-MS) was conducted to further confirm the formation of glycerol carbonate as a desired product for the transesterification of glycerol and diethyl carbonate using [Emim][Ac] as catalyst. Table 4.6 shows the GC-MS fragmentation patterns of transesterification products including glycerol as reactant. From Table 4.6, the formation of glycerol carbonate was confirmed with the abundant fragmentations ion of m/z = 31 attributed to the loss of -OCH_3, followed by the loss of -

OH and $-O_3C_3H_3$ with m/z = 18 and m/z = 87, respectively from glycerol carbonate molecule (Entry 2, APPENDIX B).

It is apparent from ^{13}C NMR (Figure 4.11) and GC-FID (Figure 4.16) spectra that there are more peaks present during the transesterification reaction than those which were anticipated (glycerol (reactant) and glycerol carbonate (desired product)). This suggests that, the side-products are formed in the reaction as well as glycerol carbonate. However, analysing and quantifying these side-products is difficult since the side-products are believed to contain similar functional groups to those of both the starting materials and glycerol carbonate. Therefore, they cannot be identified by ATR-FTIR. Furthermore, the compounds are not fluorescent, thus they cannot be analysed by ultraviolet-visible spectroscopy. This only leaves analysis by mass spectroscopy with the intention of identifying the unknown compounds that have been formed. However, as the side-products are likely to have the similar structure (cyclic carbonate containing structure), one should bear in mind those different compounds could produce similar mass fragments, especially since the compounds are quite bulky (polymer) and therefore likely to be broken up when ionized.

Generally, glycerol conversion and glycerol carbonate yield and selectivity will increase linearly upon time. However, as reaction time increased to more than 2.0 hours, the glycidol selectivity has increased which significantly decreased glycerol carbonate selectivity. The abundant fragmentations ion of m/z = 44 is attributed to the loss of $-OCH_3$ from glycidol molecule, followed by the loss of $-OC_2H_4$ and -OH, giving m/z = 31 and m/z = 18, respectively (Entry 3, APPENDIX B). From GC-FID analysis (Figure 4.14), the existence of polyglycidols in glycidol standard was further confirmed by GC-MS. It was revealed that, the mass spectrometry fragmentation patents were more likely attributed to aliphatic polyglycidols structure (Entry 4-7, APPENDIX B). From mass spectrometry pattern of 2-(propoxymethyl) oxirane, the abundant ion of m/z = 43 is attributed to cleavage of -C_3H_7. The ion species at m/z = 73 and m/z = 59 can derive from the cleavage of -$O_2C_3H_7$ and -OC_3H_7, respectively. While mass spectrometry pattern of 2-(ethoxymethyl) oxirane shows the highest abundant ion of m/z = 45 which corresponds to -OC_2H_5, followed by m/z = 43 and m/z =73 attributing to -OC_2H_3 and -$O_2C_3H_5$, respectively. Similar fragmentation pattern at m/z = 43 indicated to epoxide (-OC_2H_3) was observed for all glycidol's monomer and polymer. This can significantly explain how the collision between compounds will break the compound into smaller pieces or fragment which have similar m/z value, regardless to the bulkiness of the compound (Figure 4.17).

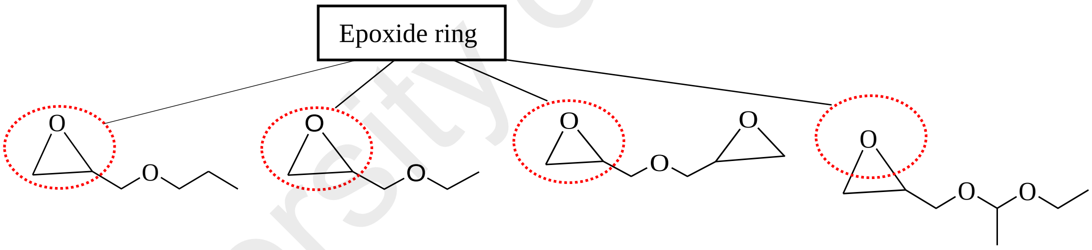


Figure 4.17: Possible aliphatic polyglycidol structures form during transesterification of glycerol and diethyl carbonate using [Emim][Ac] catalyst.

Furthermore, the abundant fragment ion of m/z = 73 which attributed to -$C_3H_5O_2$ (glycidol as monomer) has been predicted in several fragmentation patterns of mass spectrometry. It is best to note that, the formation of polyglycidols with higher molecular weight, supported by the spectrum shown in Figure 4.14 seems possible with the fact that, asymmetric glycidol (monomer) can undergo chain growth via an active chain end or via an activated monomer. This will yield different polymer structure as shown in Figure 4.18. Anionic ring-opening polymerization of the obtained glycerol carbonate has been well explained by Rokicki et al. (2005), which the polymerization proceeds with carbon dioxide liberation leading to a branched polyether/polyglycidol.

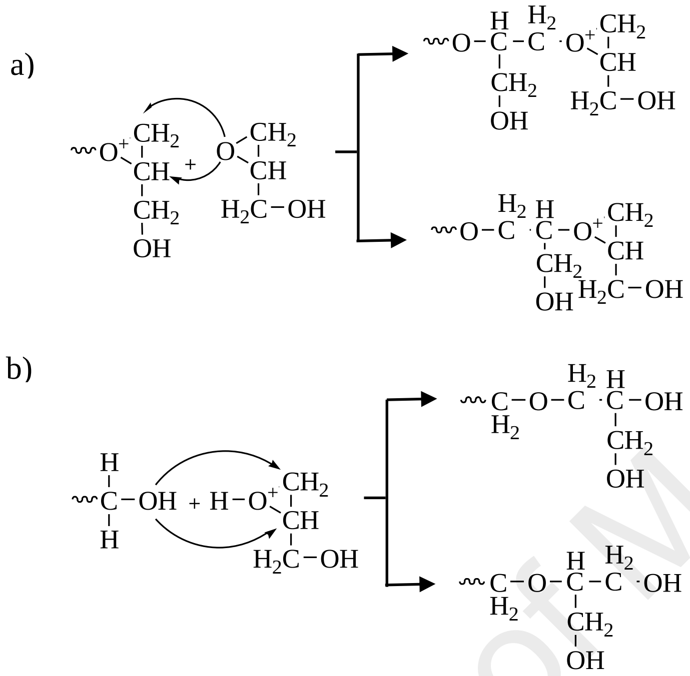
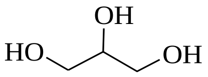
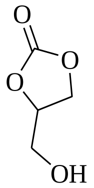
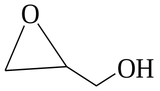
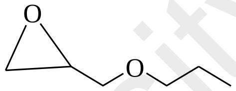
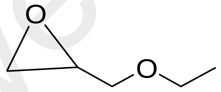
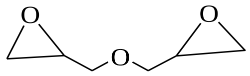
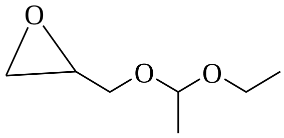


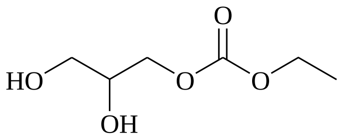
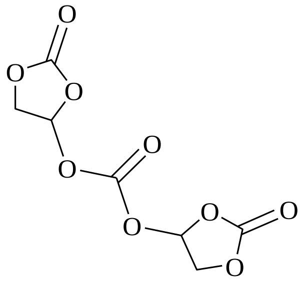
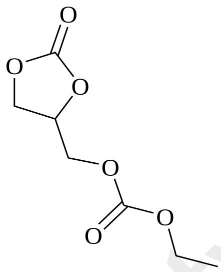
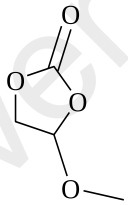
Figure 4.18: The structure of polyglycidol (a) Growth via an active chain end and (b) via an activated monomer mechanism (Nuyken & Pask, 2013).

It is notable to find out that the reaction intermediate present in GC-MS results, is indicated by ion species of m/z = 163 (Entry 8, APPENDIX B). Cleavage of -CH_3 and -C_2H_5 is attributed to ion species of m/z = 149 and m/z = 135, respectively. The ion species of m/z = 190 were observed due to fast cyclization of intermediate to form glycerol dicarbonate (Entry 10, APPENDIX B). This has suggested that glycerol dicarbonate could be formed during the transesterification reaction when there are longer reaction time and the presence of excess carbonate source (Ochoa-Gómez et al., 2012b). However, cyclization of intermediate to glycerol dicarbonate was not prominent as compared to glycerol carbonate.

Table 4.6: Synoptic table of major mass spectroscopy signals of transesterification reaction product.

Entry	Compound name and structure	Molecular weight (g/mol)	GC-MS fragmentation pattern
1	Glycerol ($C_3H_8O_3$) 	92	m/z: 92, $[M-OH]^+ = 17$, $[M-OCH_3]^+ = 31$, $[M-O_2C_5H_2]^+ = 61$
2	Glycerol carbonate ($C_4H_6O_4$) 	118	m/z: 118, $[M-OH]^+ = 17$, $[M-OCH_3]^+ = 31$, $[M-O_3C_3H_3]^+ = 87$, $[M-O_3C_4H_5]^+ = 101$
3	Glycidol ($C_3H_6O_2$) 	74	m/z: 74, $[M-OH]^+ = 17$, $[M-OC_2H_4]^+ = 31$, $[M-OCH_3]^+ = 44$
4	2-(propoxymethyl)oxirane ($C_6H_{12}O_2$) 	116	m/z: 116, $[M-CH_2CH_2CH_3]^+ = 43$, $[M-OC_2H_3]^+ = 43$, $[M-OC_3H_7]^+ = 59$, $[M-CH_2-OCH_2CH_2CH_3]^+ = 73$
5	2-(etoxymethyl)oxirane ($C_5H_{10}O_2$) 	102	m/z: 102, $[M-OC_2H_3]^+ = 43$, $[M-OC_2H_5]^+ = 45$, $[M-O_2C_3H_5]^+ = 73$
6	2,2'-oxybis(methylene)dioxirane ($C_6H_{10}O_3$) 	130	m/z: 130, $[M-C_2H_3O]^+ = 43$, $[M-OC_3H_5]^+ = 57$, $[M-O_2C_3H_5]^+ = 74$
7	Ethoxy ethyl glycidyl ether 	146	m/z: 146, $[M-O_2C_3H_5]^+= 73$, $[M-OC_4H_9]^+= 73$

Continue…

8	Intermediate 	164	m/z: 163, $[M-C_2H_5]^+$ = 135, $[M-CH_3]^+$ = 149
9	Diglycerol tricarbonate ($C_7H_6O_9$) 	234	m/z: 234, $[M-O_3C_3H_3]^+$ = 87, $[M-O_4C_3H_3]^+$ = 103, $[M-O_6C_4H_3]^+$ = 147
10	Glycerol dicarbonate 	190	m/z: 190, $[M-O_5C_5H_5]^+$ = 31, $[M-O_4C_4H_5]^+$ = 59, $[M-O_4C_3H_3]^+$ = 103, $[M-O_2C_3H_5]^+$ = 117, $[M-OC_2H_5]^+$ = 145
11	4-methoxy-1,3-dioxolan-2-one ($C_4H_6O_4$) 	118	m/z: 118, $[M-CH_3]^+$ = 15, $[M-OC_3H_7]^+$ = 59, $[M-O_3C_3H_3]^+$ = 87

4.2 Modelling and optimization by Response Surface Methodology (RSM)

The attempts to use ionic liquid as catalyst on transesterification of glycerol seemed to be reliable in this work. In principle, the formation of side products can be suppressed to a great extent through a suitable combination of cations and anions of ionic liquid. However, the optimal combination of reaction parameters seems hard to find. Understanding the interactive effects between reaction parameters will help to improve glycerol conversion and glycerol carbonate yield and selectivity. To date, neither specific interaction effect on reaction parameters nor detailed optimal conditions have been reported especially for homogeneous catalytic transesterification reaction of glycerol to glycerol carbonate using ionic liquid by statistical method, except in one study conducted by Ochoa-Gómez et al. (2009) using heterogeneous calcium oxide catalyst. Thus, it is necessary to conduct an optimization and evaluation on the interactive effects of selected critical parameters (reaction temperature, reaction time, substrates ratio and catalyst loading) using Response Surface Methodology (RSM) software.

4.2.1 Design of experiment (DOE)

4.2.1.1 Model fitting and analysis of variance (ANOVA)

The important characteristics of ionic liquids as catalyst are its reactivity toward high conversion and product yield and selectivity. The parameters and reaction conditions also seemed to influence the experimental result. As a result, the modelization technique from RSM was used to evaluate the relationship between experimental and observed results. Generally, a model is excessively complex, for instance having too many parameters relative to the number of observations, therefore overfitting occurs. In order to avoid overfitting, four main parameters that are assumed to be the critical parameters were selected to optimize the transesterification reaction of glycerol to glycerol carbonate. Before proceeding to RSM technique, experiment trials on the basis of studying one-to-one parameter at a time was conducted to at least acquire a knowledge about transesterification reaction pathway using selected ionic liquid. From the preliminary study as discussed in section 4.1.1, a range of corresponding parameter was selected; reaction temperature (110 °C to 130 °C), reaction time (1.50 hours to 2.50 hours), substrate ratio (1.50 to 2.50 equivalent molar) and catalyst loading (0.30 mol% to 0.70 mol%) as presented in Table 4.7. It should be noted that, the water content of [Emim][Ac] used as catalyst was fixed to 2.0 wt.%. The mean value was coded as zero while high and low levels of each variable were coded as 1 and -1.

Table 4.7: Range of variables for the central composite design (CCD).

Variable	**Level**		
	-1	**0**	**+1**
Temperature (°C), A	110	120	130
Time (hour), B	1.50	2.00	2.50
Substrate ratio (equivalent molar), C	1.50	2.00	2.50
Catalyst loading (mol%), D	0.30	0.50	0.70

The experimental design for both corresponding responses in conversion and yield for glycerol and glycerol carbonate, respectively is presented in Table 4.8. The predicted responses values were obtained by a model fitting technique correlated with the observed values using the software Design-Expert version 7.1. The best-fitting model was determined by regression analysis in second-order polynomial model using the equation 4.1.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + \varepsilon \qquad \text{Equation 4.1}$$

where y is the dependent variable (percentage of response) to be modeled, x_i and x_j are the independent variables (factors), b_0, b_i, b_{ii} *and* b_{ij} are the regression coefficients of the model, and ε is the residual associated to the experiments. An analysis of variance (ANOVA) was used to determine the significance of the constructed model to describe the observed data. The R^2 (coefficient of determination) statistic was used to check the adequacy of the developed model.

By fitting the data to various model (linear, two factorial, quadratic and cubic), the ANOVA showed that both the glycerol conversion and glycerol carbonate yield of transesterification reaction was fit to be described with a quadratic polynomial model. The final equation of the model (basically based on the coded values) is given by equation 4.2 and equation 4.3.

$$\text{Conversion (\%)} = +93.19 + 6.44A + 5.36B + 3.70C + 4.90D - 2.67AB + 0.25AC + 1.76AD - 3.13BC - 0.79BD - 0.64CD - 14.45A^2 - 0.28B^2 - 1.45C^2 - 0.073D^2 \quad \text{…… Equation 4.2}$$

$$\text{Yield (\%)} = +90.04 + 11.05A + 2.67B + 0.19C - 5.02D + 1.72AB - 0.065AC + 7.82AD - 1.76BC - 4.03BD + 1.46CD - 12.71A^2 - 4.34B^2 - 2.87C^2 - 9.71D^2 \quad \text{…… Equation 4.3}$$

Where A is the reaction temperature, B is the reaction time, C is the substrate ratio of diethyl carbonate/glycerol and D is the catalyst loading ([Emim][Ac]).

The ANOVA for the RSM is shown in Table 4.9 and Table 4.10. The computed F-value on the conversion is 13.31 and 24.23 on the yield of the model implying that the model is significant at the 95.0% confident level. The very small P-value of <0.0001 for both responses indicated that the obtained equations were appropriate and suitable after model reduction. According to the ANOVA, the lack-of-fit for conversion (0.2724) and yield (0.6664) implies that it is not significantly relative to the pure error. The significant and non-significant lack-of-fit indicate that the model for both responses is a good fit. The good quality of the equation was expressed by the determination coefficient, R^2 which normally has to be at least 80.0% in the model study (Muhamad et al., 2010). The R^2 of the quadratic model for conversion is 0.93 and the yield is 0.96 indicating that the model explains more than 80.0% of the variability and therefore sufficient to represent the actual relationship between the response and the significant variables. The quadratic polynomial model for conversion and the yield is also highly significant as compared to other suggested model by the Design Expert software which is linear ($R^2 = 0.4861$ (for conversion), $R^2 = 0.3005$ (for yield)) and two factorial interaction (2 FI) ($R^2 = 0.5241$ (for conversion), $R^2 = 0.4237$ (for yield)) model that have low in coefficient values.

Table 4.8: Composition of the various runs of the central composite design (CCD), actual and predicted responses.

Standard	**Independent variables**				**Responses**	
	Temperature (^{o}C)	**Time (hour)**	**Substrate (equivalent ratio)**	**Catalyst loading (mol%)**	**Conversion (%)**	**Yield (%)**
1	115	1.75	1.75	0.40	53.74	51.60
2	125	1.75	1.75	0.40	59.21	56.04
3	115	2.25	1.75	0.40	74.62	69.89
4	125	2.25	1.75	0.40	78.82	82.48
5	115	1.75	2.25	0.40	59.57	54.69
6	125	1.75	2.25	0.40	80.89	60.90
7	115	2.25	2.25	0.40	75.65	63.80
8	125	2.25	2.25	0.40	81.58	67.88
9	115	1.75	1.75	0.60	54.34	39.29
10	125	1.75	1.75	0.60	89.08	68.54
11	115	2.25	1.75	0.60	87.20	30.81
12	125	2.25	1.75	0.60	91.75	74.93
13	115	1.75	2.25	0.60	78.17	38.32
14	125	1.75	2.25	0.60	88.94	74.52
15	115	2.25	2.25	0.60	48.90	34.22
16	125	2.25	2.25	0.60	95.61	77.09
17	110	2.00	2.00	0.50	23.00	20.51
18	130	2.00	2.00	0.50	93.06	63.22
19	120	1.50	2.00	0.50	85.52	73.62
20	120	2.50	2.00	0.50	98.87	77.06
21	120	2.00	1.50	0.50	78.42	79.57
22	120	2.00	2.50	0.50	96.65	82.92
23	120	2.00	2.00	0.30	89.07	66.57
24	120	2.00	2.00	0.70	97.00	46.03
25	120	2.00	2.00	0.50	95.96	97.96
26	120	2.00	2.00	0.50	99.54	94.49
27	120	2.00	2.00	0.50	91.62	89.33
28	120	2.00	2.00	0.50	88.83	88.08
29	120	2.00	2.00	0.50	97.32	90.34
30	120	2.00	2.00	0.50	85.86	80.03

Table 4.9: Analysis of variance (ANOVA) and model coefficients on conversion.

Source	**Sum of squares**	**Degree of freedom**	**Mean square**	**F-Value**	***P*-value**
Model	7731.83	14	552.27	13.31	< 0.0001
Temperature (A)	623.45	1	623.45	15.02	0.0019
Time (B)	626.26	1	626.26	15.09	0.0019
Substrate ratio (C)	298.15	1	298.15	7.18	0.0189
Catalyst loading (D)	522.67	1	522.67	12.59	0.0036
AB	98.78	1	98.78	2.38	0.1469
AC	0.88	1	0.88	0.02	0.8867
AD	42.86	1	42.86	1.03	0.3281
BC	136.23	1	136.23	3.28	0.0932
BD	8.59	1	8.59	0.21	0.6567
CD	5.76	1	5.76	0.14	0.7156
A^2	3340.45	1	3340.45	80.48	< 0.0001
B^2	2.12	1	2.12	0.05	0.8247
C^2	55.38	1	55.38	1.33	0.2688
D^2	0.14	1	0.14	0.00	0.9542
Residual	539.57	13	41.51	-	-
Lack of fit	399.32	8	49.91	1.78	0.2724
Pure error	140.26	5	28.05	-	-
Corrected total	8271.41	27	-	-	-
R^2	0.93	-	-	-	-

[a] significant at “Prob>F” less than 0.05

[b] not significant at “Prob>F” more than 0.05

Table 4.10: Analysis of variance (ANOVA) and model coefficients on yield.

Source	Sum of squares	Degree of freedom	Mean square	F-Value	*P*-value
Model	10665.90	14	761.85	24.23	< 0.0001
Temperature (A)	2930.02	1	2930.02	93.17	< 0.0001
Time (B)	171.09	1	171.09	5.44	0.0351
Substrate ratio (C)	0.86	1	0.86	0.03	0.8711
Catalyst loading (D)	431.43	1	431.43	13.72	0.0024
AB	47.47	1	47.47	1.51	0.2395
AC	0.07	1	0.07	0.00	0.9637
AD	978.44	1	978.44	31.11	< 0.0001
BC	49.28	1	49.28	1.57	0.2312
BD	259.53	1	259.53	8.25	0.0123
CD	33.99	1	33.99	1.08	0.3161
A^2	4309.54	1	4309.54	137.03	< 0.0001
B^2	503.15	1	503.15	16.00	0.0013
C^2	219.27	1	219.27	6.97	0.0194
D^2	1509.71	1	1509.71	48.01	< 0.0001
Residual	440.28	14	31.45	-	-
Lack of fit	253.11	9	28.12	0.75	0.6664
Pure error	187.16	5	37.43	-	-
Corrected total	11106.18	28	-	-	-
R^2	0.96	-	-	-	-

[a] significant at "Prob>F" less than 0.05

[b] not significant at "Prob>F" more than 0.05

Figure 4.19 shows the correlation of actual experimental *versus* predicted conversion and yield and the normal probability plot that are obtained from equation 4.2 and equation 4.3. A linear distribution for both responses is indicative of a well-fitting model. The normal probability plot forms an approximately straight line and follows the linear distribution (Figure 4.19) (a_1) and (b_1)). The plot confirmed the assumption of ANOVA where the residuals are measured by the number of standard deviations between the actual and predicted value that satisfies the model very well. An adequate precision shows signal to noise ratio. Those ratios greater than four are suitable indicators to show that the model can be used to navigate the design space.

P-values less than 0.05 indicate that the model terms are significant. For the conversion, the parameters A, B, C, D, A^2, and C^2 are significant whereby the parameters A, B, D, AD, BD, A^2, B^2, C^2, and D^2 are significant for the yield. The other terms are not significant and so can be eliminated. Equation 4.2 and equation 4.3 were used then to study the effect of various parameters and their interactions on the conversion and yield of transesterification reaction.

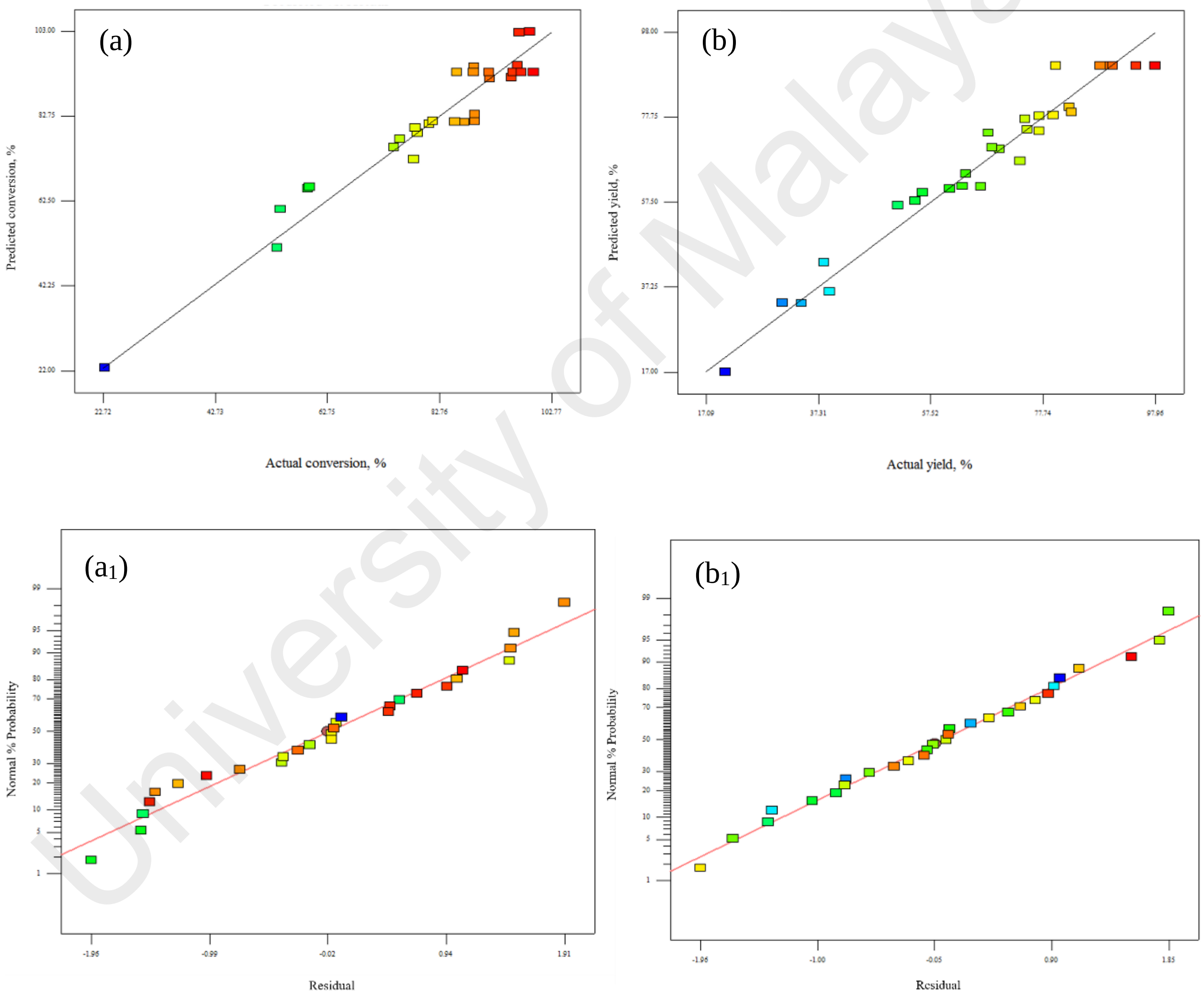


Figure 4.19: Plots showing correlation of actual and predicted values of conversion (a) and yield (b) by the model and normal probability of residuals conversion (a_1) and yield (b_1).

4.2.2 Interactive effects of variables on conversion

Conversion and yield reported in this optimization study are indicated to glycerol as limiting reactant and glycerol carbonate, respectively. Three-dimensional (3D) response surface plots were constructed by plotting one of the responses (conversion, %) on the Z-axis against other dependent variables while maintaining the other one at their optimum levels. This interaction involved between the effects of two parameters on percentage glycerol conversion as shown in Figure 4.20 to Figure 4.25.

Generally, an increase of reaction temperature and substrate molar ratio resulted in an increase of glycerol conversion. Increasing the reaction temperature had promoted more collisions between catalyst's and substrate's molecules. Moreover, the solubility between hydrophilic glycerol and hydrophobic diethyl carbonate can be improved by reducing mass transfer limitations. Apart from that, increasing the substrate ratio will shift the chemical equilibrium towards the formation of glycerol carbonate yield.

Figure 4.20 depicts the effect of temperature and substrate equivalent ratio on transesterification reaction at 2.00 hours and 0.50 mol% catalyst loading. The 3D response plot shows that the effect of temperature is more significant at higher substrate molar ratio. The glycerol conversion was observed to steadily increase as substrate ratio increased. This behaviour could be explained by the dependency of the reaction rate on temperature (Khayoon & Hameed, 2013). In such a case, the reaction can perform faster as the temperature increased. The percentage of conversion slightly decreased when the temperature increased from 122.5 to 125 ℃ at substrate ratio of 1.75. This shows that the transesterification reaction does need an excess of diethyl carbonate prior to shift the reaction towards glycerol carbonate even though high temperature is applied.

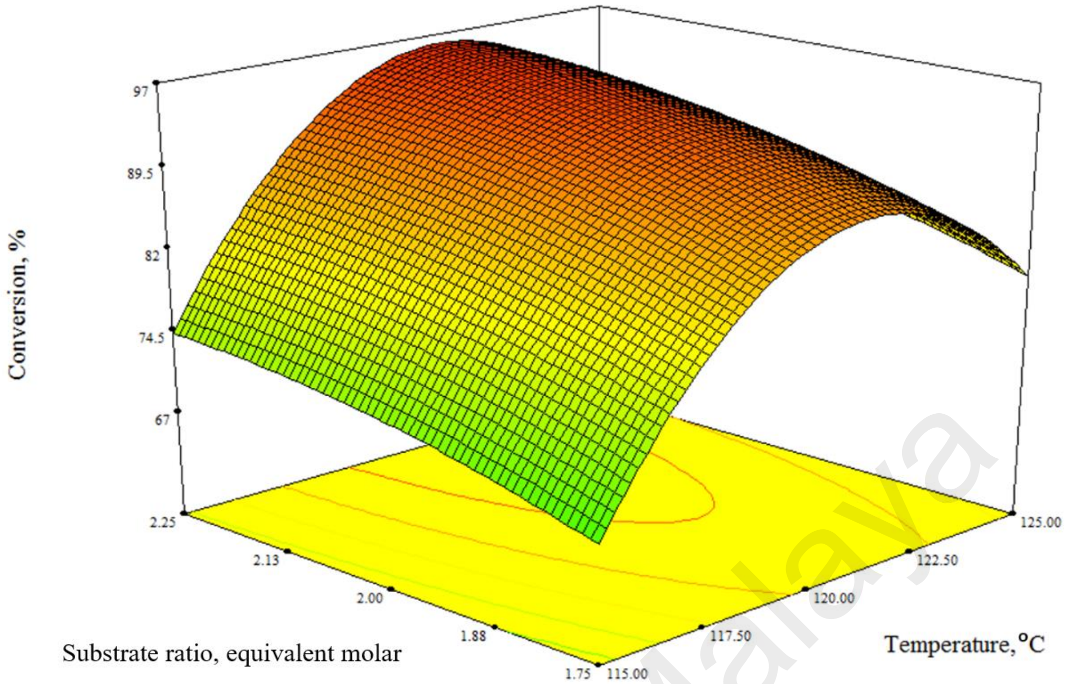


Figure 4.20: Response surface plot showing the interaction between two parameters, temperature and substrate ratio for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

Figure 4.21 shows the effect of varying reaction temperature and time on transesterification reaction at substrate ratio 2.00 and 0.50 mol% catalyst loading. It can be clearly seen that, there were linear increment of percentage glycerol conversion with increasing of reaction time at 115 °C. However, increasing reaction temperature to 122 °C, resulted in the increase of the glycerol conversion up to 83.0%. Increasing of reaction temperature thereafter significantly decreased the glycerol conversion. The use of high temperature exceeding the boiling point of the diethyl carbonate was not practical, as it might cause excessive evaporation thus led to the loss of substrate, even though reaction was run under closed system (Teng et al., 2015).

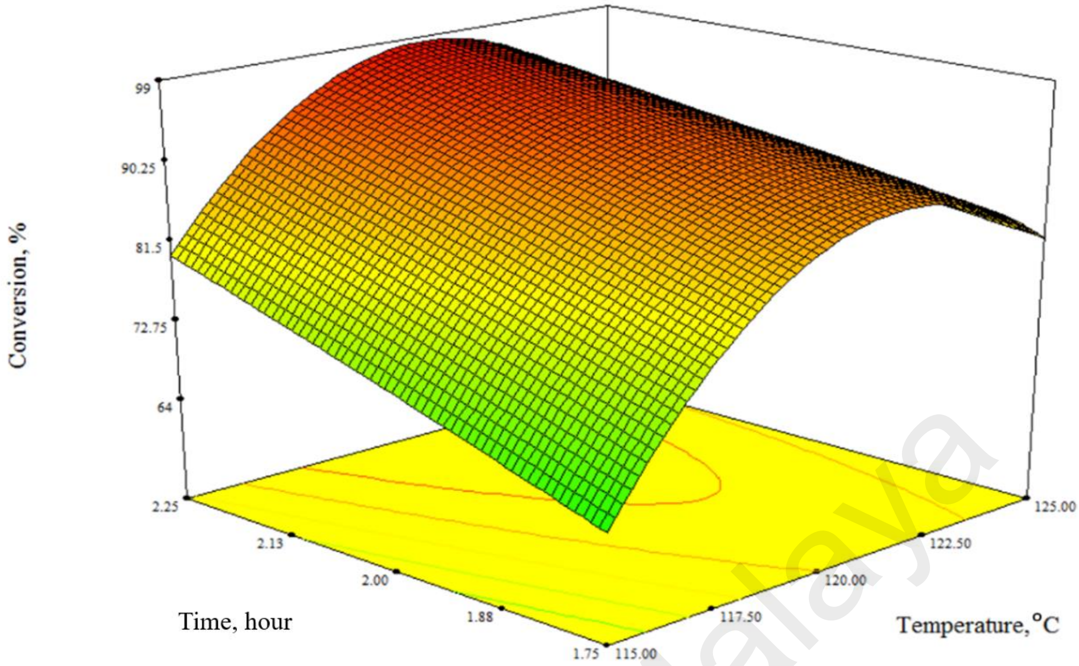


Figure 4.21: Response surface plot showing the interaction between two parameters, temperature and time for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

Figure 4.22 represents the effect of varying temperature and catalyst loading on the glycerol conversion for transesterification reaction. The reaction time and substrate molar ratio was fixed at 2.00 hours and 2.00, respectively. The 3D response surface plot indicates that as the reaction temperature increased, the percentage of glycerol conversion increased. While there is a linear increase of glycerol conversion at 115 °C with the increase of catalyst loading. Meanwhile, the glycerol conversion increased as the reaction temperature increased only up to an extent, which decreases thereafter. This indicates that a critical temperature is involved up to which percentage conversion is favoured and it is not so after that critical temperature. The percentage conversion was lower at temperature more than 120 °C. In this case, our first hypothesis was due to decomposition of catalyst at higher temperature. However, TGA analysis of [Emim][Ac] showed it stabled up to 245 °C (Darji, 2015). Regardless of it is well acclaimed of catalytic activity of [Emim][Ac], it is agreed to run the reaction under workable temperature to avoid exceeding the substrate’s boiling point temperature. The finding was in line with Ochoa-Gómez et al. (2009) where reaction temperature was selected based on the boiling point temperature of dimethyl carbonate, the maximum temperature achievable at atmospheric atmosphere.

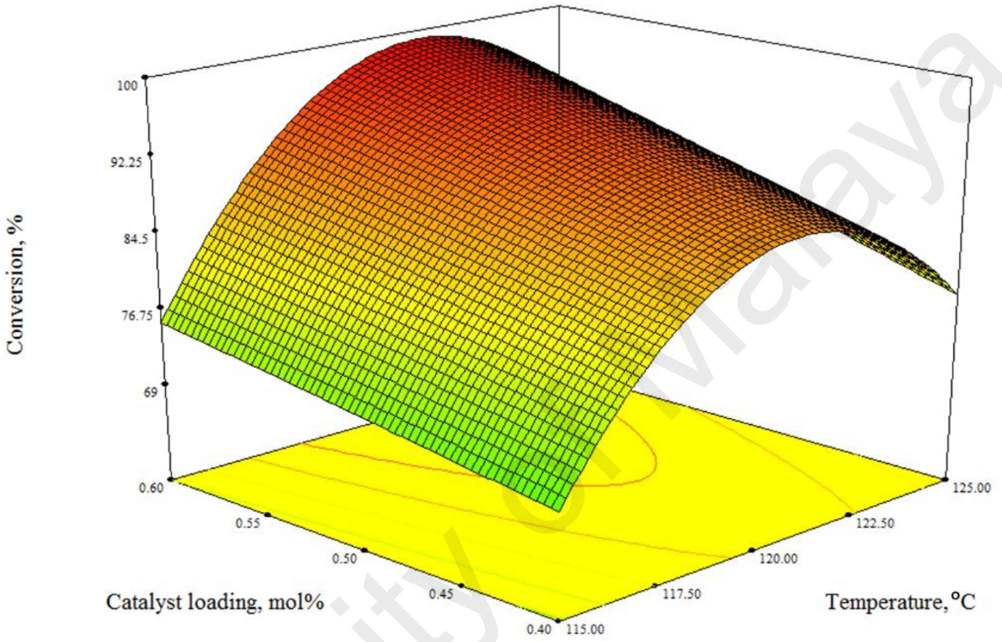


Figure 4.22: Response surface plot showing the interaction between two parameters, temperature and catalyst loading for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

Figure 4.23 depicts the effect of reaction time and catalyst loading, at temperature of 120 °C and substrate molar ratio of 2.00. It was observed that percentage conversion increased when the reaction time and catalyst loading increased. The optimization of reaction time is crucial to the transesterification process. When the reaction time is too short, the conversion will not come to completion, thus maintaining the two-phase reaction. Whereby, prolonging the reaction time provides enough time for reactants and catalysts to react. On the other hand, the increase of catalyst loading will increase the conversion rate of glycerol. When reaction time increased, rapid reaction with no induction period was observed, thus leads to complete conversion (Liu et al., 2013). Glycerol conversion attained maximum value of 100.0% at 2.25 hours and 0.60 mol% catalyst loading.

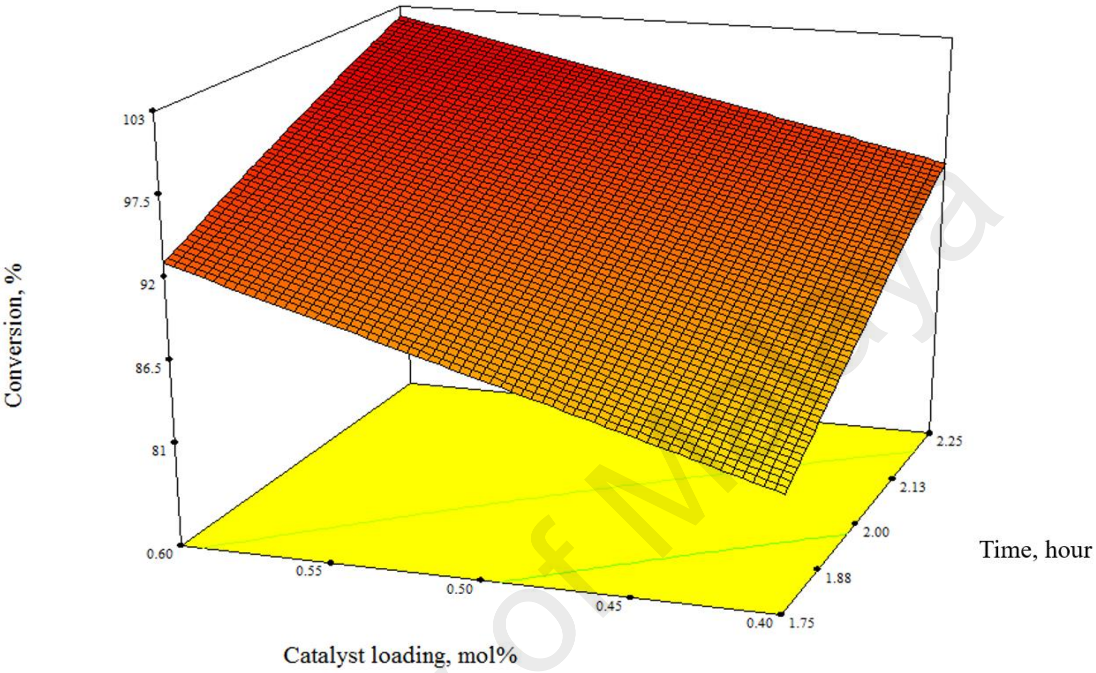


Figure 4.23: Response surface plot showing the interaction between two parameters, time and catalyst loading for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

Figure 4.24 represents the interactive effect of reaction time and substrate ratio for transesterification reaction at 120 °C and 0.50 mol% catalyst loading. It is shown that, as the increase of reaction time and substrate ratio, has led to increasing the percentage conversion more than 90.0%. At low reaction time and substrate ratio, the conversion was 79.0%, indicating that the transesterification reaction needs slightly longer reaction time upon the completion of conversion and sufficient substrate ratio of diethyl carbonate and glycerol in shifting to the forward reaction. Glycerol conversion of 98.0% was obtained at 2.25 hours and 2.25 substrate ratio.

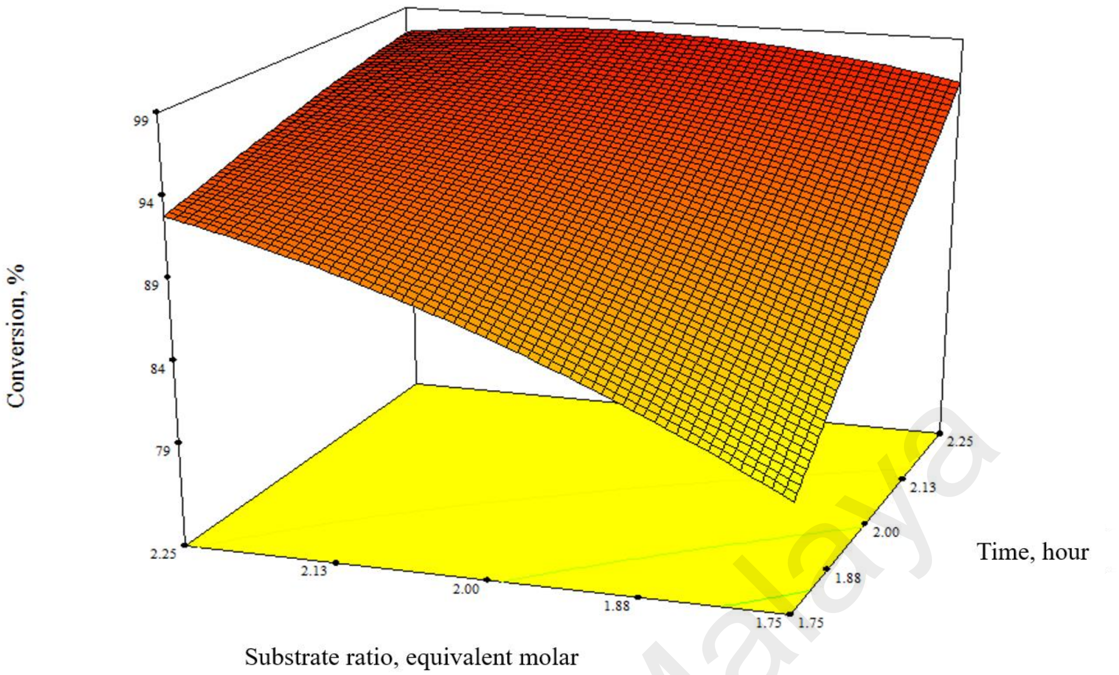


Figure 4.24: Response surface plot showing the interaction between two parameters, time and substrate ratio for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

Figure 4.25 depicts the effect of substrate ratio and catalyst loading on glycerol conversion of transesterification reaction at 120 °C and 2.00 hours. It was observed that glycerol conversion consistently increased with the increase in catalyst loading from 0.40 mol% to 0.60 mol%. Similarly, the same observation was also obtained as the substrate ratio of diethyl carbonate/glycerol increased. However, the effect of substrate ratio was less pronounced as compared to catalyst loading which can be clearly explained by ANOVA in Table 4.9, where the *P*-value (p>0.05) indicates that the substrate ratio (0.0189) was less significant compared to catalyst loading (0.0036). The reaction with substrate ratio 2.25 mol% and 0.60 mol% catalyst loading has led to the maximum percentage of conversion of nearly 100.0%.

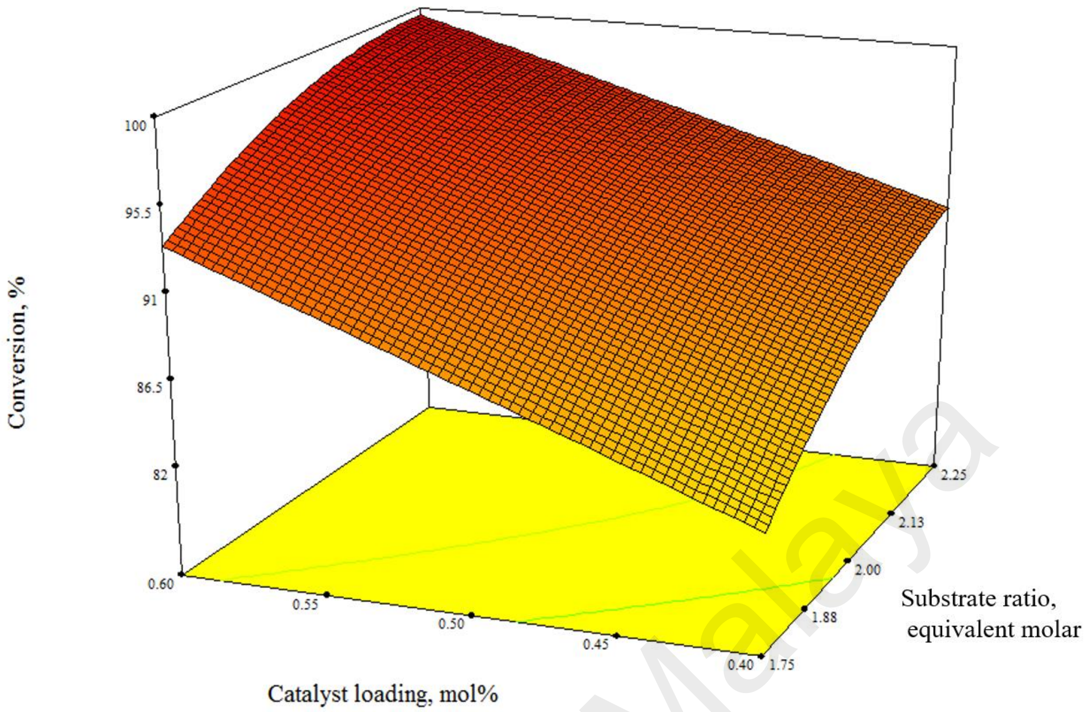


Figure 4.25: Response surface plot showing the interaction between two parameters, substrate ratio and catalyst loading for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the conversion (%) of glycerol in transesterification reaction.

4.2.3 Interactive effects of variables on yield

The quadratic polynomial equation of response surface methodology (Equation 4.3) was used to facilitate plotting on another response which is percentage yield (%) of glycerol carbonate. As similar to the percentage conversion, the yield plotting also was drawn on the Z-axis against two independent variables while other variables were on the same centre point values (coded level: 0). The response surface contours on the yield are shown in Figure 4.26 to Figure 4.30.

Figure 4.26 shows the combined effect reaction temperature and time and their interaction on glycerol carbonate yield at substrate ratio of 2.00 and 0.50 mol% catalyst loading. Reaction at low temperature and reaction time showed the lowest yield. As the temperature and time increased up to 122 °C and 2.13 hours, respectively, the percentage yield increased. It was observed that, when temperature increased more than 122.5 °C, percentage yield decreased, due to decarboxylation of glycerol carbonate to glycidol. Moderate temperature between 118 to 125 °C is necessary to provide enough energy for substrates and catalyst molecule to collide. Furthermore, positive interactive relationship between temperature and time shows good correlation with percentage yield.

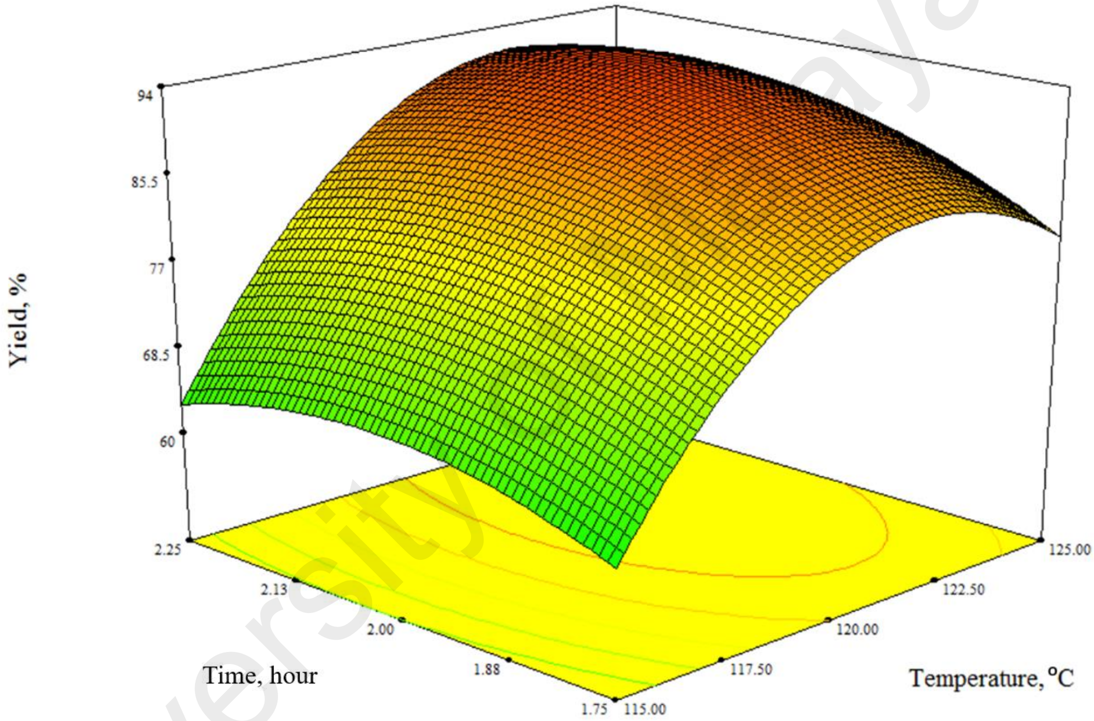


Figure 4.26: Response surface plot showing the interaction between two parameters, temperature and time for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the yield (%) of glycerol carbonate as product in transesterification reaction.

Generally, an increase in reaction temperature and substrate molar ratio resulted in an increase of glycerol carbonate yield (Figure 4.27). At 115 °C, slight increase of glycerol carbonate yield was observed even though substrate ratio increased. Increasing the reaction temperature promoted more collisions between catalyst's and substrate's molecules. Moreover, solubility between hydrophilic glycerol and hydrophobic diethyl carbonate can be improved by reducing mass transfer limitations. Reaction temperature between 118.5 to 125 °C and substrate ratio between 1.88 to 2.13 gave higher glycerol carbonate yield. However, the increase of reaction temperature more than 125 °C has slightly decreased glycerol carbonate yield, with respect to low and high substrate ratio of 1.75 and 2.25, respectively. High substrate ratio would incur additional cost for the reactants, thus are not preferable for industrial scale. Previously reported studies showed that substrate ratio in the range of 1.00 to 3.20 has given satisfied glycerol carbonate yield.

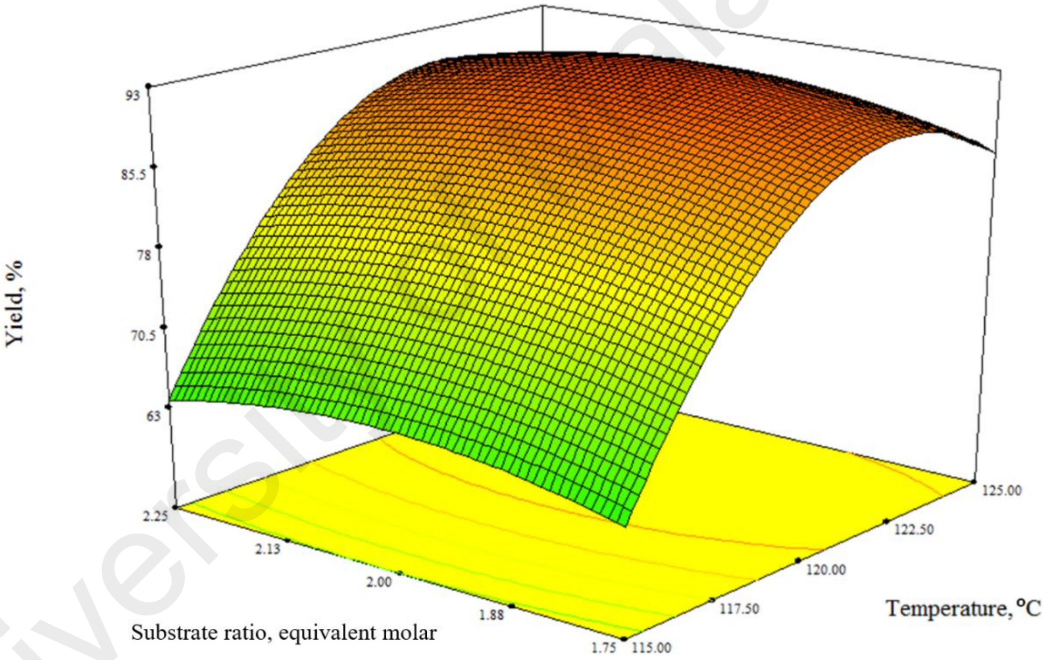


Figure 4.27: Response surface plot showing the interaction between two parameters, temperature and substrate ratio for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the yield (%) of glycerol carbonate as product in transesterification reaction.

The interactive effect between reaction time and substrate ratio was depicted in Figure 4.28 at 120 °C and 0.50 mol% catalyst loading. The glycerol carbonate yield increased with the increase of reaction time and substrate ratio. The positive interaction between reaction time and substrate ratio shows good correlation between these effects towards glycerol carbonate formation. The overall selectivity of [Emim][Ac] with time is high suggesting that the [Emim][Ac] is selective in the formation of glycerol carbonate. However, prolonging reaction time together with high substrate ratio has subsequently decreased glycerol carbonate yield. This was expected since high substrate ratio will lead to the formation of glycerol dicarbonate at long reaction time. Ochoa-Gómez et al. (2012b) reported uncontrollable formation of glycerol dicarbonate (8.0%) due to high ratio of dimethyl carbonate/glycerol.

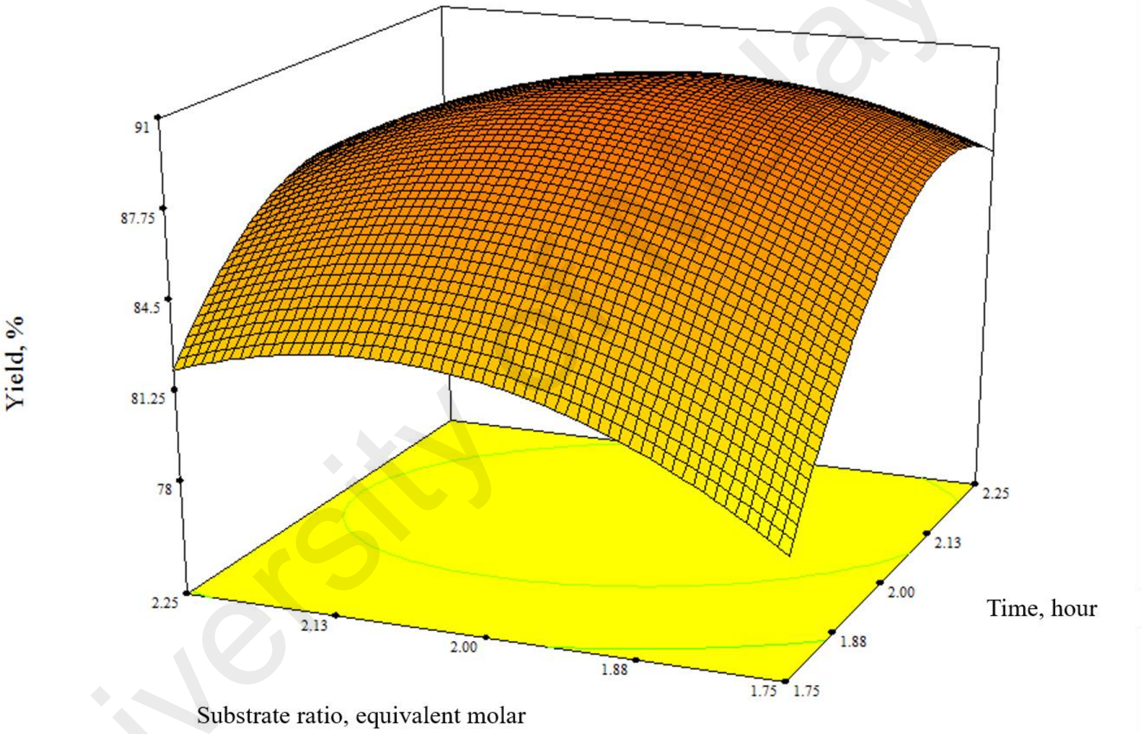


Figure 4.28: Response surface plot showing the interaction between two parameters, time and substrate ratio for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the yield (%) of glycerol carbonate as product in transesterification reaction.

Figure 4.29 depicts the effect of reaction temperature and catalyst loading on percentage yield at 2.00 hours and substrate ratio of 2.00. The 3D response plot shows that the percentage yield has gradually increased upon increasing temperature until reached optimum at 122 °C. However, the effect of temperature was observed as compared to catalyst loading. This result was consistent with ANOVA (Table 4.10) which indicated that by *P*-value of catalyst loading is 0.0024, which was slightly higher as compared to temperature of <0.0001. The increase of temperature and catalyst loading more than 122 °C and 0.48 mol% respectively, show the decrease of percentage yield thereafter. This can be attributed to the decarboxylation of glycerol carbonate to glycidol or polyglycidols. High temperature was reported to promote the formation of glycidol or polyglycidols, where the anion of ionic liquid helps to activate the hydroxyl group containing glycerol carbonate.

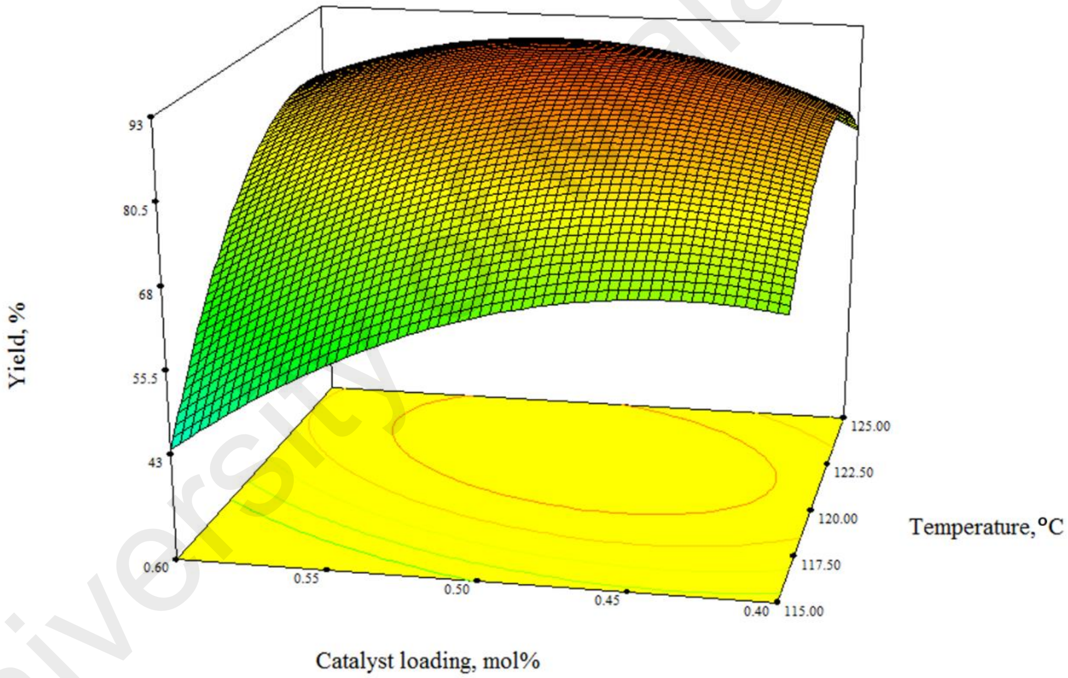


Figure 4.29: Response surface plot showing the interaction between two parameters, temperature and catalyst loading for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the yield (%) of glycerol carbonate as product in transesterification reaction.

The effect of varying time and catalyst loading at 120 °C and substrate ratio of 2.00 is shown in Figure 4.30. The 3D plot shows that at low catalyst loading and reaction time, percentage yield is low. As the reaction time increases up to 2.00 hours and catalyst loading reached optimum at 0.45 mol%, percentage yield increases. However, over 0.45

mol% catalyst loading has led to the decrease of percentage yield which would be best explained by the activity of [Emim][Ac] ionic liquid that influenced the decarboxylation of glycerol carbonate. This result can be corroborated with the result discussed on ATR-FTIR with respect to the increase of catalyst loading as shown in Figure 4.10.

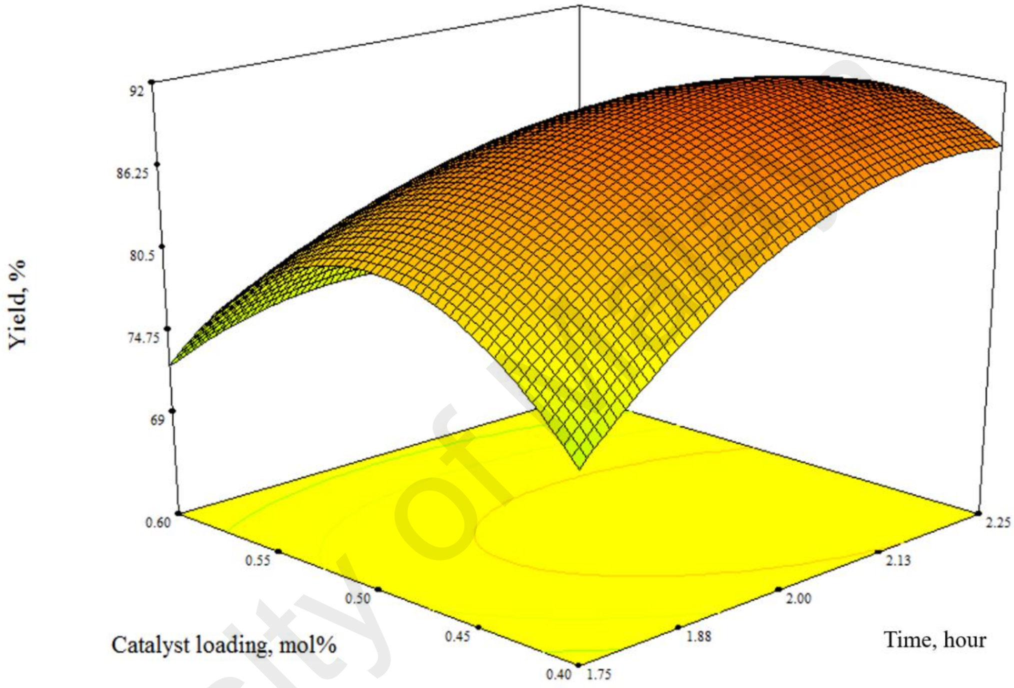


Figure 4.30: Response surface plot showing the interaction between two parameters, time and catalyst loading for transesterification reaction. Other variables are constant at their centre points. The numbers inside the contour plots indicate the yield (%) of glycerol carbonate as product in transesterification reaction.

From an economic viewpoint, it is desirable to use low catalyst loading to achieve a maximum conversion and yield. This report has successfully conveyed that, [Emim][Ac] has given good reactivity with least catalyst loading (0.42 mol%) in order to catalyse the transesterification of glycerol and diethyl carbonate. Comparably, 0.01 mol% of amidines basic ionic liquid; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been reported giving 98.0% glycerol conversion and 96.0% glycerol carbonate selectivity for transesterification of glycerol and dimethyl carbonate (Munshi et al., 2014b).

4.2.4 Optimization of transesterification reaction and model verification

In order to verify the prediction of the model, the optimal reaction conditions were applied to three independent replicates for transesterification of glycerol and diethyl carbonate. Table 4.11 represents three solutions with different desirability values which were used to predict the optimal condition for glycerol carbonate synthesis via catalytic transesterification of glycerol. From the software, catalyst loading should be minimized in order to tackle the industry needs, considering the price of ionic liquid while the conversion and yield were set to be maximized. In this case, the small number of significant responses value was given by the Design-Expert software. The experiments were then carried out and the resulting responses were compared to the predicted values.

The greatest glycerol conversion and glycerol carbonate yield were obtained in experiment 1 giving 92.41% and 91.80%, respectively. This demonstrated the validation of the RSM model. The good correlation between these results confirmed that the response models were adequate for reflecting the expected optimization.

Table 4.11: Optimum conditions for transesterification reaction of glycerol and diethyl carbonate generate from response surface model.

Exp	**Temperature (^{o}C)**	**Time (hour)**	**Substrate ratio (equivalent molar)**	**Catalyst loading (mol%)**	**Conversion (%)**		**Yield (%)**	
					Predicted	**Actual**	**Predicted**	**Actual**
1	118	1.8	2.20	0.42	92.59	92.41	91.33	91.80
2	116	2.2	1.85	0.44	93.66	91.90	90.12	90.10
3	122	2.3	2.00	0.50	98.26	96.47	83.36	84.17

4.3 Recyclability of ionic liquid catalyst

At optimum reaction conditions (discussed in section 4.2); 118 °C, 1.8 hours, substrate ratio of 2.2 and 0.42 mol% catalyst loading, [Emim][Ac] shows a good potential candidate as catalyst, at least comparable to the other reported homogeneous catalysts for the transesterification reaction with 92.4% glycerol conversion and 91.8% glycerol carbonate yield. However, the use of ionic liquid as either solvent or catalyst has created a big issue and has been an ongoing subject discussed in academic and industry and that is its relatively high cost. Therefore, recyclability study was critically essential for the economic feasibility of reaction and there is a need to reuse the catalyst after every cycle.

It is worth to mention that, recyclability of ionic liquid in transesterification reaction can be difficult to achieve in practice owing to the fact that [Emim][Ac] and glycerol are highly polar compounds. Only a few studies have reported on recycling of ionic liquid for example, through liquid-liquid extraction method using diethyl ether (Yi et al., 2014), deionized water (Zhou et al., 2015) and flash chromatography column with ethyl acetate and methanol as eluents (Chiappe & Rajamani, 2012). However, these studies failed to characterize the recovered ionic liquids or at least justify their findings. On the other studies, Darji (2015) and Zakaria et al. (2017) have successfully recycled [Emim][Ac] up to 4th recycles for dissolution of biomass.

The recovery and [Emim][Ac] performance profiles for every cycle were measured and supported by proton nuclear magnetic resonance (^{1}H NMR) in order to track the changes of [Emim][Ac] properties before (fresh) and after recycled for several times. As shown in Figure 4.31, the insignificant reduction of glycerol conversion from recovered [Emim][Ac] indicates that [Emim][Ac] could be recycled for approximately three times. The glycerol conversion using fresh [Emim][Ac] shows 92.4% (fresh), 92.6% (1st recycle), 89.1% (2nd recycle), 80.4% (3rd recycle) and slightly dropped to 69.1% after the 4th recycle. Meanwhile, the glycerol carbonate selectivity was slightly reduced after the 1st recycle (from 99.4% (fresh) to 91.8%) and slightly increased to 95.5%, 96.4% and 96.9% at 2nd, 3rd and 4th recycle, respectively. The increase of glycerol carbonate selectivity presumably due to a gradual loss of [Emim][Ac] through separation and decantation and accumulated amount of glycerol, thus [Ac]$^-$ anion has less tendency to activate the hydroxyl end of glycerol carbonate for further reaction (formation of either glycerol dicarbonate or glycidol). Zhou et al. (2015) reported that the recyclability of [N_{2222}][Pipe] was examined in five consecutive batch runs with glycerol conversion that was maintained 96.0%.

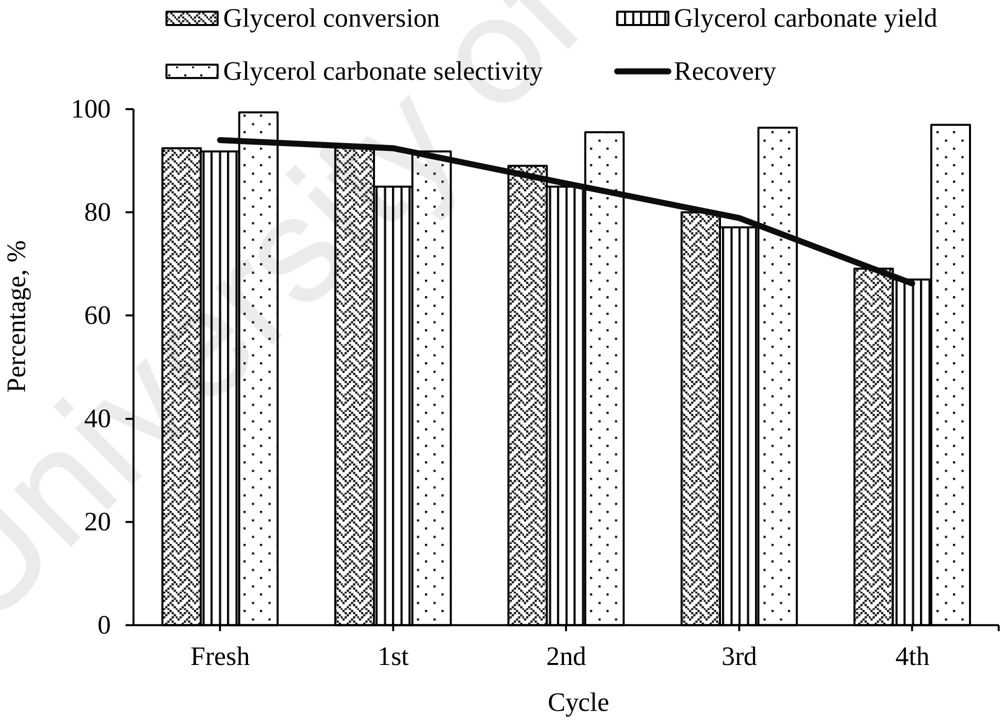


Figure 4.31: Recyclability study of [Emim][Ac] for transesterification reaction. Reaction conditions: Temperature = 118 °C, Reaction time = 1.8 hours, Ratio of diethyl carbonate/glycerol = 2.2 and [Emim][Ac] loading = 0.42 mol% based on limiting reactant (1st = first recycle, 2nd = second recycle, 3rd = third recycle and 4th = fourth recycle).

^{1}H spectra shown in Figure 4.32 revealed that there was insignificant peak shifting of the recovered [Emim][Ac] (after 3rd recycle, (Figure 4.32 (c)) as compared to the fresh [Emim][Ac] (Figure 4.32 (a)), despite the traces amount of glycerol which remained in the recovered [Emim][Ac]. All respective peaks of [Emim][Ac] are comparably resolved with little variation in chemical shift for each cycle despite the water peak at 3.35 ppm, indicated that [Emim][Ac] are successfully recovered with no degradation on its structure. Sun et al. (2009) reported that peaks at 62.7 ppm, 83.6 ppm and 86.2 ppm (observed by ^{13}C NMR) arise from minor degradation of [Emim][Ac] with increase in intensity due to longer heating time (16.0 hours) applied during the reaction. It should be noted that chemical shifts at 4.79 ppm represent the methanol-d_4 solvent. Table 4.12 tabulates the band assignment peaks of [Emim][Ac].

Overall, the recyclability study indicated that the 1st and the 2nd recycle of [Emim][Ac] were highly active to catalyze the transesterification reaction of glycerol with diethyl carbonate. The percentage of [Emim][Ac] recovered gradually decreased from 94.0% (fresh) to 66.2% (4th recycle) through separation and decantation processes thus lead to poor glycerol conversion and glycerol carbonate yield after the 3rd recycle.

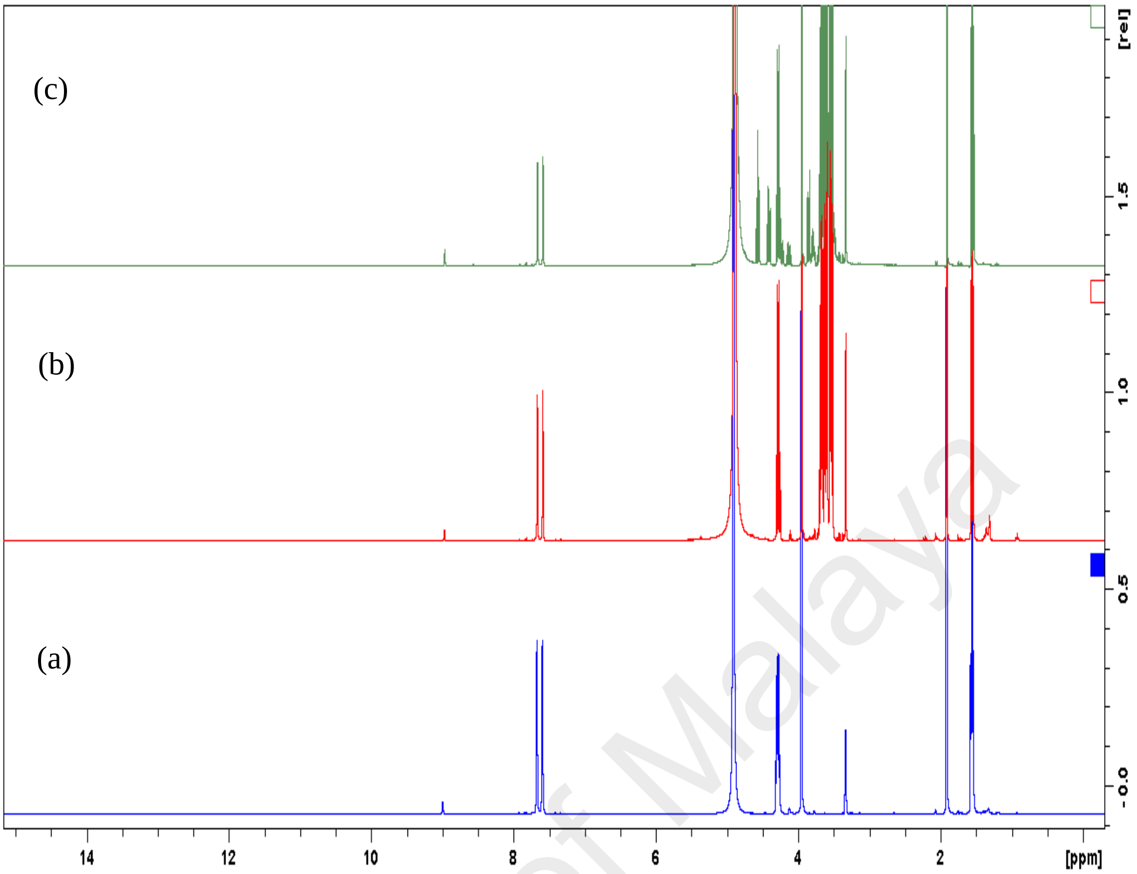


Figure 4.32: ^{1}H NMR analysis of (a) fresh [Emim][Ac], (b) recovered [Emim][Ac]-2nd recycle and (c) recovered [Emim][Ac]-3rd recycle. Reaction conditions: Heated at 118 °C at 1.8 hours, ratio of diethyl carbonate/glycerol 2.2 and 0.42 mol% [Emim][Ac] loading. Deuterated methanol-d_4 (99.8%) was used as solvent in NMR analysis.

Table 4.12: Assignment ^{1}H NMR peak of [Emim][Ac].

Assignments	Chemical shift, δ (ppm)			Multiplicity
	Fresh (This study)	**3rd recycle (This study)**	**Previous studies (Darji, 2015[a], Zakaria et al., 2017[b])**	
3H, CH_3	1.50	1.49	1.39, 1.45	Triplet
3H, CH_3CO	1.85	1.85	1.56, 1.70	Singlet
2H, CH_2	3.90	3.92	3.87, 3.89	Singlet
2H, NCH_2	4.21	4.24	4.20, 4.25	Triplet
1H, NCH	7.53	7.54	7.74, 7.73	Multiplet
1H, NCH	7.61	7.62	7.83, 7.83	Multiplet
1H, NCHN	8.94	8.97	9.72, 9.60	Singlet

[a] Assignment of [Emim][Ac] at 4th recycle. Deuterated DMSO-d_6 was used as solvent in NMR analysis.
[b] Assignment of [Emim][Ac] at 3rd recycle. Deuterated DMSO-d_6 was used as solvent in NMR analysis.

4.4 Mechanism of transesterification reaction

4.4.1 Computational study

It is difficult to predict the performance of ionic liquid in a given set of reaction conditions. Therefore, it is important to have a better understanding of synergistic catalytic between glycerol and diethyl carbonate as reactants with [Emim][Ac] catalyst, specifically on the role of $[Emim]^+$ cation and $[Ac]^-$ anion towards the transesterification reaction through computational study. Formation of intermolecular hydrogen bonding between reactants-[Emim][Ac] molecules play an important role in the catalysis. The computational study using a General Atomic and Molecular Electronic Structure System (GAMESS) software was conducted to support the experimental and spectroscopic results (ATR-FTIR and NMR) of the transesterification reaction.

Generally, the increasing of the hydrogen bond strength leads to a shorter bond distance (Abbott et al., 2011). The activation of glycerol by [Emim][Ac] proceeds mainly through the hydrogen bonding interaction with $[Ac]^-$ as clearly shown at the initial state of transesterification reaction (Figure 4.33). This is reasonable because $[Ac]^-$ anion is known as nucleophile, where its strength must be high enough to abstract the proton from the hydroxyl group of glycerol. It is best to note that, the primary ($H12_{(glycerol)}$) and secondary ($H25_{(glycerol)}$) hydroxyl groups of glycerol have the ability to form hydrogen bonding between $[Ac]^-$ anion (O8) with hydrogen bond distances of 1.706 Å ($H12_{(glycerol)}$---$O8_{([Ac]^-\ anion)}$) and 2.762 Å ($H25_{(glycerol)}$---$O8_{([Ac]^-\ anion)}$) respectively (Entry 1-2 (Figure 4.32)). However, the priority goes to primary ($H12_{(glycerol)}$---$O8_{([Ac]^-\ anion)}$), hydroxyl group presumably due to its reactivity more than the secondary ($H25_{(glycerol)}$---$O8_{([Ac]^-\ anion)}$) hydroxyl group even though all three hydroxyl groups of glycerol are active for the transesterification reaction. This has suggested that [Emim][Ac] can actively catalyze the transesterification reaction via two hydroxyl groups and was in line with Simanjuntak et al. (2015) findings. It was also predicted that, there is hydrogen bonding between O1 from diethyl carbonate and H1 from $[Emim]^+$ cation and O1 from diethyl carbonate and H29 from glycerol which is 2.254 Å and 3.762 Å, respectively (Entry 3-4 (Figure 4.33)) (Lan et al., 2016). These have demonstrated that diethyl carbonate is capable of interacting with imidazolium cation proton at carbon 2 position and hydroxyl group of glycerol in a cooperative manner. The strength of intramolecular hydrogen bonding between glycerol of $H29_{(glycerol)}$ and $O5_{(glycerol)}$ increase (1.842 Å), while $H25_{(glycerol)}$ and $O4_{(glycerol)}$ decrease (2.910 Å) due to intermolecular hydrogen bonding formed between $H12_{(glycerol)}$---$O8_{([Ac]^- anion)}$ and $H25_{(glycerol)}$---$O8_{([Ac]^- anion)}$ (Entry 5-6 (Figure 4.33)).

From the optimized transition state (TS1) the structure shown in Figure 4.34, hydrogen bond between O7 from $[Ac]^-$ anion and H12 from intermediate was formed, with the distance of 1.556 Å (Entry 7, Figure 4.34). The $[Ac]^-$ anion (O7) acts as proton acceptor from the secondary hydroxyl group (O3) of glycerol, thereby enhancing the nucleophilicity of the activated hydroxyl oxygen atom (O3). Meanwhile, there are corporative interaction of imidazolium cation (H1) with carbonyl oxygen of diethyl carbonate (O2) (O-H distance = 2.369 Å) by formation of hydrogen bonding and make the carbonyl carbon (C7) greatly positive charged. This has enhanced the nucleophilic attack of the activated hydroxyl oxygen atom (O3) on the carbonyl carbon (C7) of ethyl glyceryl carbonate intermediate and an ethanol was produced. Coincidently, the hydrogen bonding formed between the secondary oxygen (O5) and tertiary hydrogen of hydroxyl group (H29) of glycerol in the optimized reactants structure with [Emim][Ac] at initial state (Entry 5 (Figure 4.33)) is expected to brake, which is evidenced by the increased of hydrogen bond distances (3.268 Å) between oxygen atom (O3) with hydroxyl atom (H15) of ethyl glyceryl carbonate intermediate measured in the optimized transition state structure (TS1) (Entry 10 (Figure 4.34)).

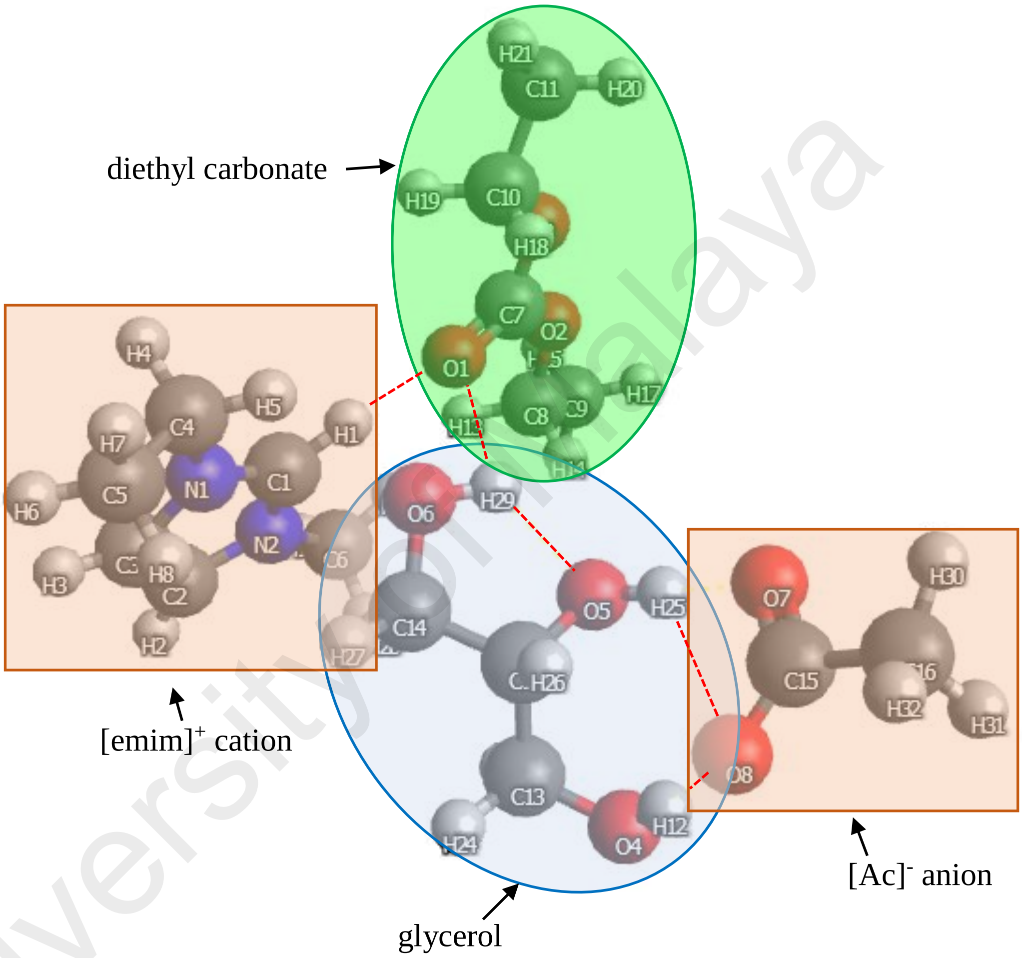


Figure 4.33: Optimized reactants structure with [Emim][Ac] at initial state of transesterification reaction using GAMESS software and visualized using Avogadro. Hydrogen bonds are represented by red dash line.

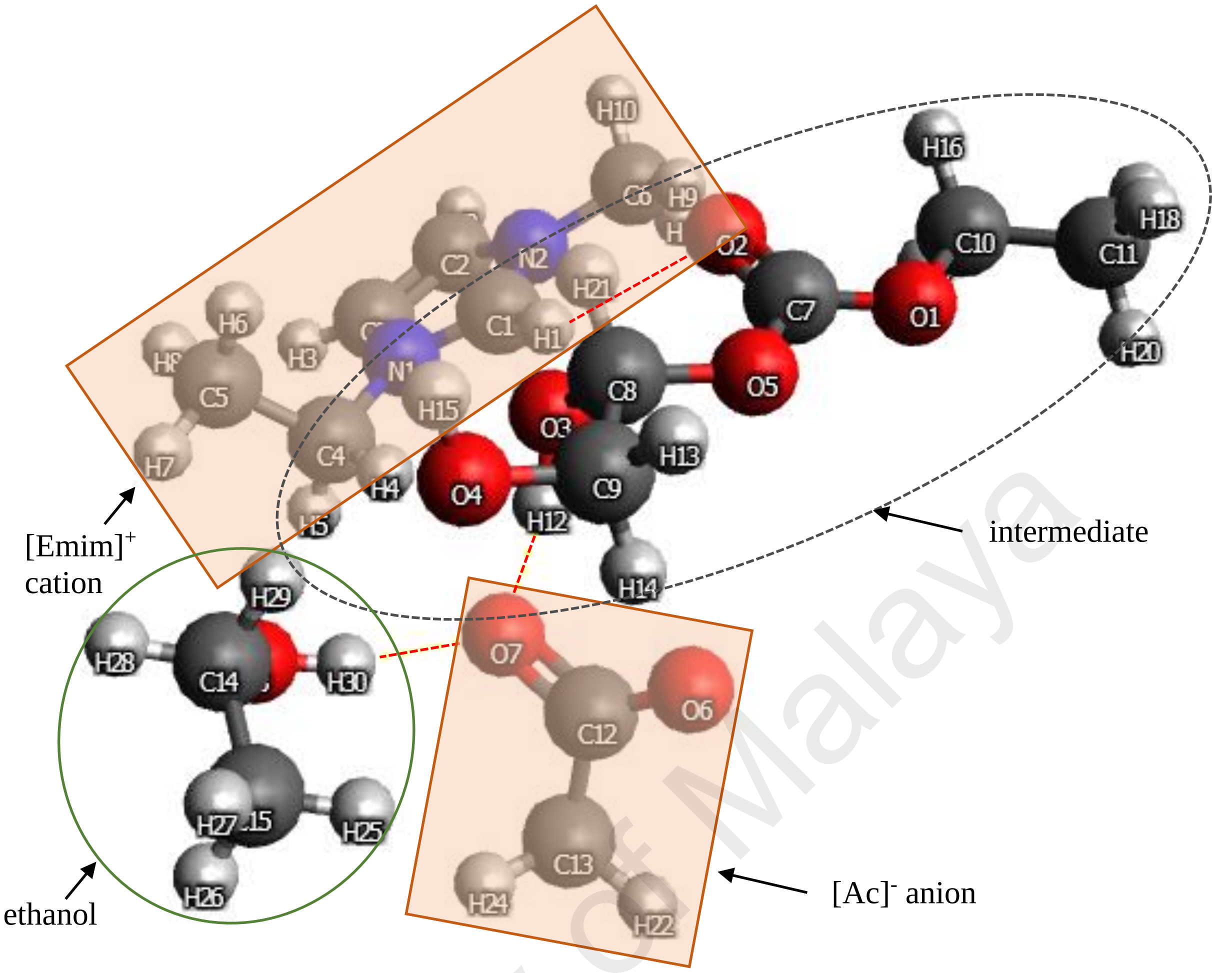


Figure 4.34: Optimized transition state (TS1) structure showing the interaction of [Emim][Ac] with ethyl glyceryl carbonate intermediate during transesterification reaction using GAMESS software and visualized using Avogadro. Hydrogen bonds are represented by red dash line.

Subsequently, as the intermediate losing a proton (H20) to [Ac]$^-$ anion (O6), the ethyl glyceryl carbonate intermediate species will undergo a fast-intramolecular cyclization between O4 and C7 of intermediate and the subsequent formation of glycerol carbonate might proceed together with the liberation of a second ethanol molecule (Figure 4.35). It is best to note that, at TS2, [Emim][Ac] catalyst regenerated evidence by the increase of hydrogen bonding between O6 ([Ac]$^-$ anion)---H20 (intermediate, TS2) (Entry 11,Figure 4.35) as compared to O7([Ac]$^-$ anion)---H12 (intermediate, TS1) (Entry 7, Figure 4.34) with 1.653 Å and 1.556 Å, respectively. This finding supports the results from recyclability study (discussed in section 4.3), where [Emim][Ac] can be recovered and recycled for at least three recycle.

Overall, the transesterification reaction of glycerol and diethyl carbonate could proceed in a cooperative manner, in which interaction between cation will activate the carbonyl group of the diethyl carbonate and anion will activate the glycerol, thus could be best explained that the high catalytic performance observed for [Emim][Ac] as the catalyst. Our finding was in agreement with Simanjuntak et al. (2015), taking into account the possibility of cation and anion to interact with glycerol and diethyl carbonate in a corporative manner. Table 4.13 summarizes the hydrogen bond interactions between reactants (glycerol and diethyl carbonate), transition state of TS1 and TS2.

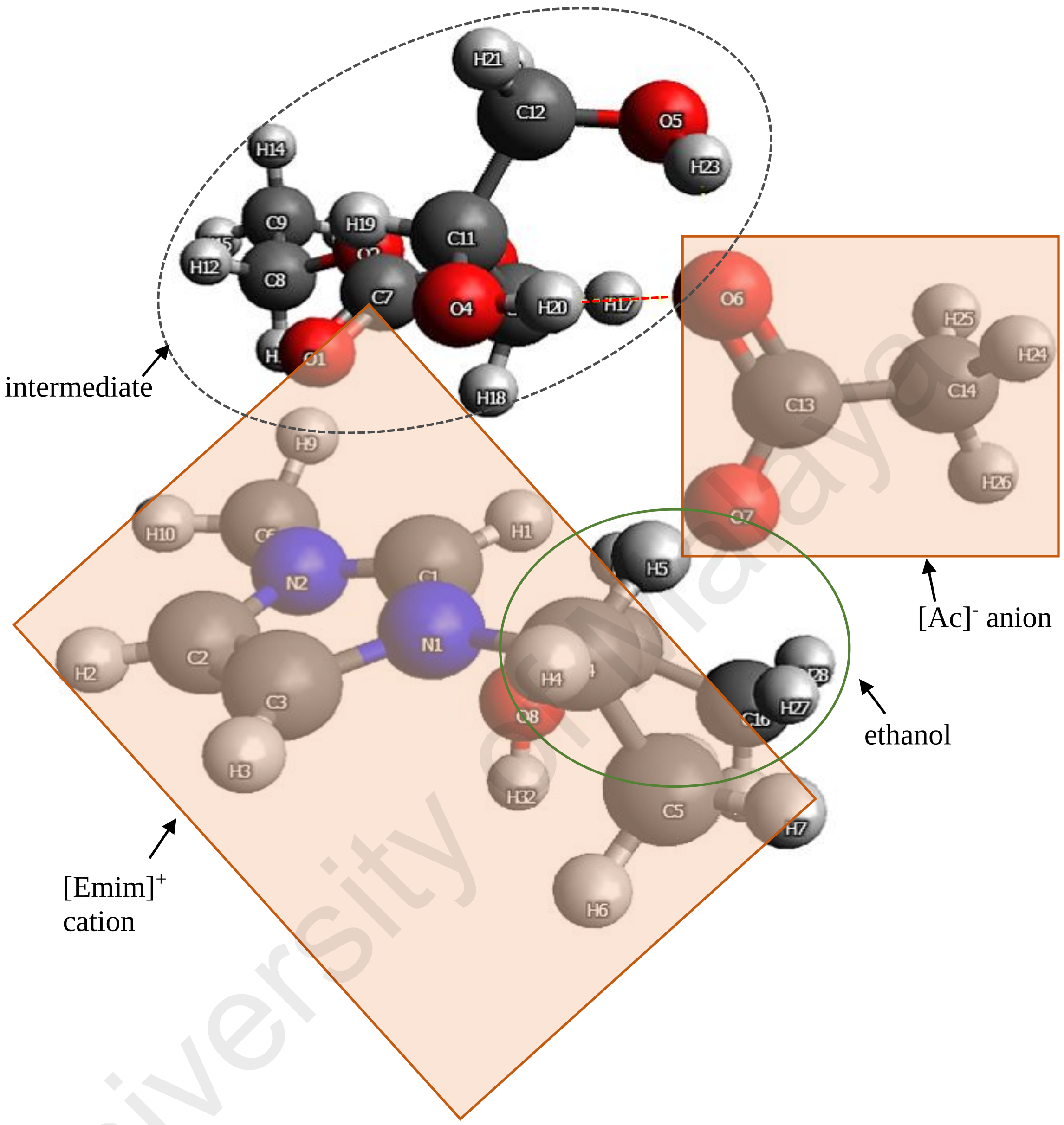


Figure 4.35: Optimized transition state (TS2) structure showing the interaction of [Emim][Ac] with ethyl glyceryl carbonate intermediate during transesterification reaction using GAMESS software and visualized using Avogadro. Hydrogen bonds are represented by red dash line.

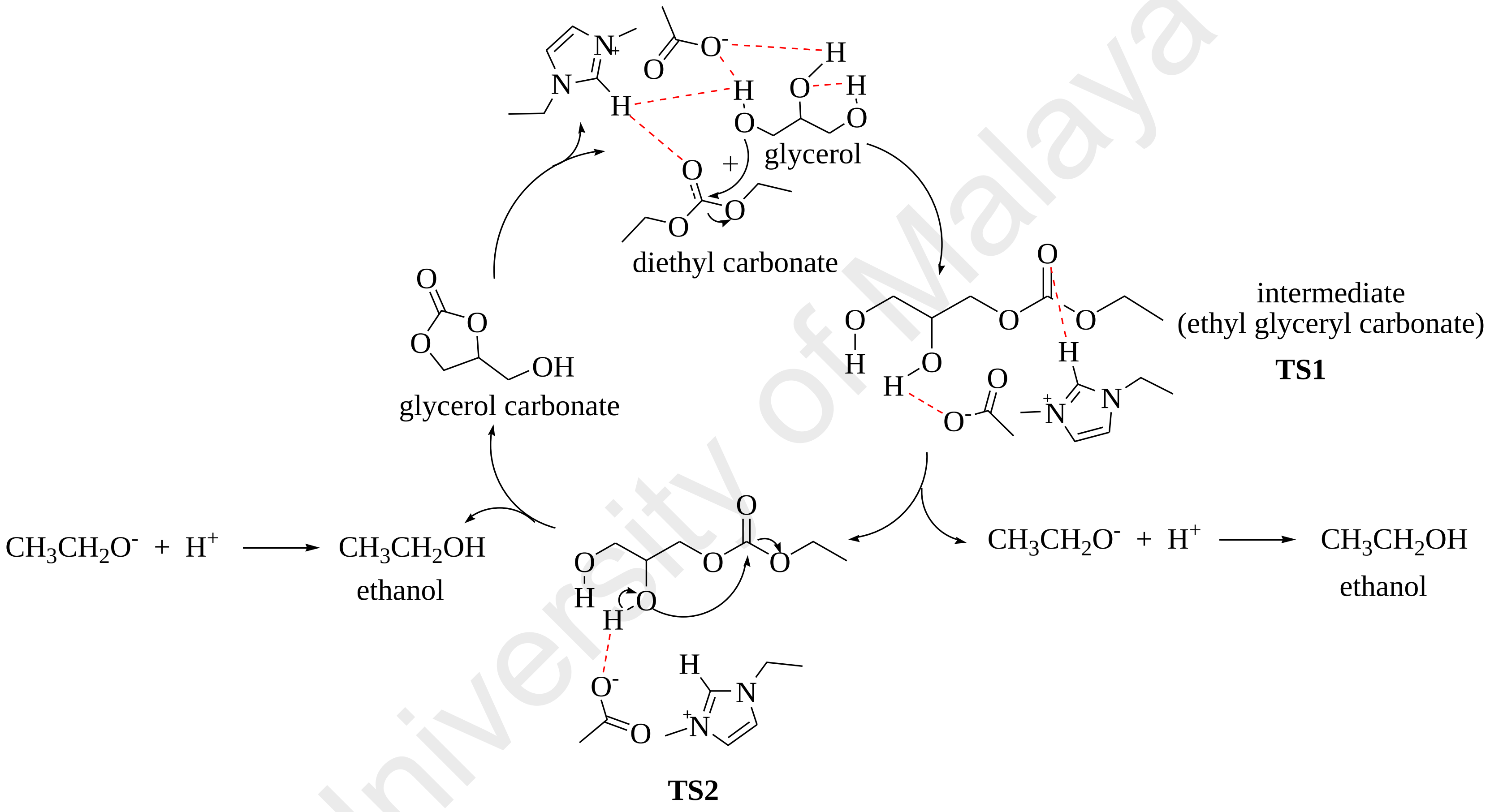
Table 4.13: Quantum mechanics calculation of reactants and transition states of intermediate and [Emim][Ac] catalyst with hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31G basis sets approach for the transesterification reaction of glycerol carbonate synthesis.

Entry	**Interaction**	**Distance [Å]**	
	Structure from reactants at initial state	**Before optimization[a]**	**After optimization**
1	H12$_{\text{(glycerol)}}$---O8$_{\text{([Ac]}^{-}\text{ anion)}}$	2.577	1.706
2	H25$_{\text{(glycerol)}}$---O8$_{\text{([Ac]}^{-}\text{ anion)}}$	3.517	2.762
3	O1$_{\text{(diethyl carbonate)}}$---H1$_{\text{([Emim]}^{+}\text{ cation)}}$	3.89	2.254
4	O1$_{\text{(diethyl carbonate)}}$---H29$_{\text{(glycerol)}}$	4.051	3.762
5	H29$_{\text{(glycerol)}}$---O5$_{\text{(glycerol)}}$	3.294	1.842
6	H25$_{\text{(glycerol)}}$---O4$_{\text{(glycerol)}}$	2.682	2.910
	Structure from intermediate of transition state (TS1)		
7	O7$_{\text{([Ac]}^{-}\text{ anion)}}$---H12$_{\text{(intermediate)}}$	2.874	1.556
8	O2$_{\text{(intermediate)}}$---H1$_{\text{([Emim]}^{+}\text{ cation)}}$	3.197	2.369
9	O5-H29$_{\text{(glycerol)}}$---O3-H15$_{\text{(intermediate)}}$	1.842	3.268
	Structure from intermediate of transition state (TS2)		
10	O6$_{\text{([Ac]}^{-}\text{ anion)}}$---H20$_{\text{(intermediate)}}$	3.748	1.653

[a] The structure of reactants at initial state and transition states (TS1 and TS2) before optimization can be found in APPENDIX D

4.4.2 Proposed mechanism

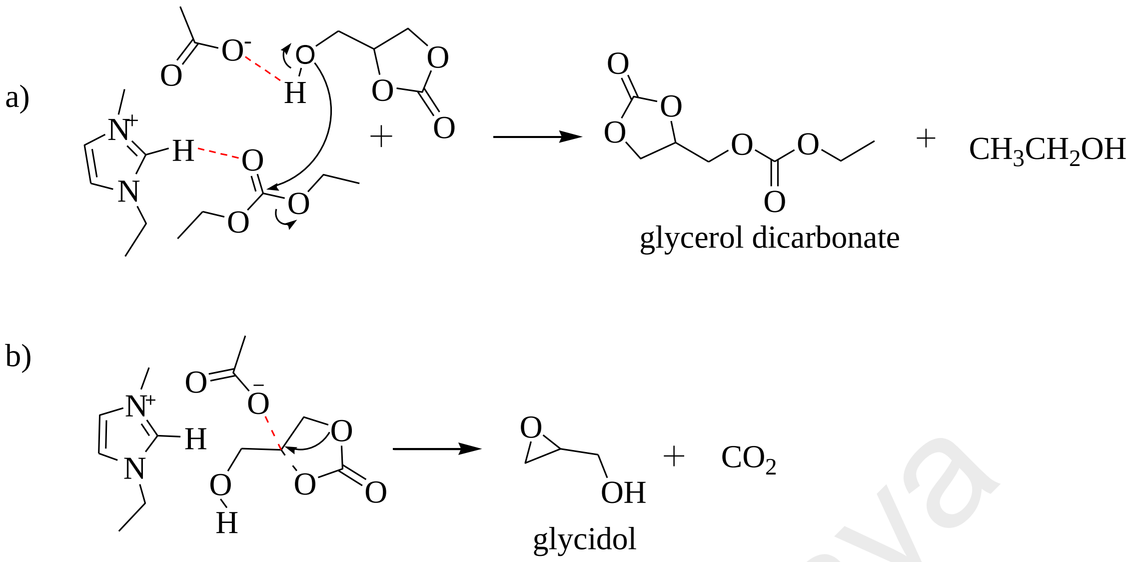
The computational results discussed in section 4.4.1 agreed well with the proposed mechanism of transesterification reaction of glycerol and diethyl carbonate catalyzed by [Emim][Ac] as illustrated in Scheme 4.1. The proposed mechanism gives the advantage of that [Emim][Ac] can work in cooperative manner by formation of hydrogen bonding to activate the transesterification reaction, thus leading towards the glycerol carbonate formation. There are also few reports on the use of ionic liquids as catalysts where both anion and cation help in activation of reactants (Selva et al., 2010).



Scheme 4.1: The proposed mechanism for glycerol carbonate synthesis through catalytic transesterification of glycerol with diethyl carbonate by [Emim][Ac].

The superior catalytic activity exhibited by [Emim][Ac] coincides with higher glycerol conversion and glycerol carbonate yield demonstrates in this study somehow has led to an unavoidable formation of glycerol dicarbonate and glycidol/polyglycidol. The glycerol dicarbonate and glycidol selectivity measured were 0.4% and 3.0%, respectively at reaction temperature of 118 °C, 1.8 hours, substrate ratio of diethyl carbonate/glycerol 2.2 and 0.42 mol% [Emim][Ac] loading. Theoretically, as the concentration of glycerol carbonate is high enough, the tertiary free hydroxyl group of glycerol can further react to initiate a new transesterification between glycerol carbonate and the diethyl carbonate leading to the formation of glycerol dicarbonate. Despite this, the probable reason for increase in glycidol selectivity could be mainly because of increase in basicity of the reaction mixture when there is an increase of [Emim][Ac] loading, favoring the decarboxylation of glycerol carbonate (Gade et al., 2012).

Thus, it is necessary to consummate the reaction mechanism of glycerol dicarbonate and glycidol formation as in Scheme 4.2. The mechanism of decarboxylation of glycerol to glycidol is somehow similar to the reaction of the carbon dioxide fixation reaction with alkylene oxides to produce cyclic carbonates (Takahashi et al., 2016). Moreover, there are some findings reported on the other potential by-products obtained throughout the transesterification reaction as discussed in section 4.1.2.3 (b), which significantly decreased the glycerol carbonate selectivity.



Scheme 4.2: The proposed mechanism for synthesis of possible by-products from glycerol carbonate, a) glycerol dicarbonate and b) glycidol, using [Emim][Ac] as catalyst.

CHAPTER 5 : GENERAL CONCLUSION AND FURTHER WORK

5.1 Conclusion

Among a number of homogeneous base catalysts such as potassium carbonate, potassium hydroxide, sodium hydroxide and trimethylamine, ionic liquids have come in a range of guises that have demonstrated facile glycerol conversion with dialkyl carbonate. As the benchmark, this research was embarked to gain and resemble an overall understanding in the catalytic transesterification reaction of glycerol and diethyl carbonate using ionic liquid as catalyst. Implementing ionic liquid catalyst system that avoid the use of metals as catalyst, solvents and harsh conditions are just the starting points for greener and more sustainable future.

The performance of ionic liquid as catalyst towards transesterification of glycerol was measured by screening the potential ionic liquids and evaluate the pertinent affecting parameters towards satisfied glycerol conversion and glycerol carbonate yield and selectivity. The results demonstrated 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) with the merits of 93.5% glycerol conversion and 88.7% glycerol carbonate yield at mild reaction conditions (reaction temperature of 120 °C at 2.0 hours, diethyl carbonate/glycerol ratio of 2 and 0.50 mol% [Emim][Ac] loading at the [Emim][Ac] water content of 2.0 wt.%. Characterization using ATR-FTIR revealed that, the peaks of O-H bending (1262 cm^{-1} and 923 cm^{-1}) and O-H stretching (3387 cm^{-1}) showed reduction in peak intensity as glycerol being converted to glycerol carbonate. Meanwhile, the peak at 1750 cm^{-1} corresponding to C=O of glycerol carbonate increased in intensity when the reaction time is prolonged up to 2.0 hours. This ATR-FTIR was also evidenced the formation of glycidol and glycerol dicarbonate at 908 cm^{-1} (C-O-C bond of glycidol) and

1264 cm^{-1}, respectively. These results are consistent with NMR and GC-MS analyses which affirmed that glycerol carbonate yield and selectivity decreased over the optimum reaction conditions due to further decarboxylation of glycerol carbonate to glycidol, polyglycidols or glycerol dicarbonate.

From the analysis of RSM, the optimum reaction conditions were predicted with high percentage yield (>90.0%) and low [Emim][Ac] loading. Furthermore, the interactive effects of the important parameters such as reaction temperature, reaction time, substrates ratio and [Emim][Ac] loading also were evaluated at fixed [Emim][Ac] water content of 2.0 wt.%. Glycerol conversion of 92.4% and glycerol carbonate yield of 91.8% were obtained under the optimum reaction conditions; reaction temperature of 118 °C, at 1.8 hours with 2.2 of diethyl carbonate/glycerol ratio and 0.42 mol% [Emim][Ac] loading. The comparison of the predicted and experimental values revealed that the models gave good correspondence between them, implying that empirical models derived from RSM can be used to adequately describe the relationship between the factors and responses (conversion and yield) in catalytic transesterification reaction of glycerol.

Recyclability study has revealed that [Emim][Ac] catalyst can be reused along with the increased batch of recycle number. Satisfying glycerol conversion and glycerol carbonate yield were successfully attained up to the 3rd recycle, with 80.4% and 77.1%, respectively, before it was dropped at 4th recycle giving 69.1% glycerol conversion and 67.3% glycerol carbonate yield. [Emim][Ac] ionic liquid turns to be superior to the traditional homogeneous catalyst with respect to the possibility of recovering. The recovery of the [Emim][Ac] after the 3rd recycle was maintained up to 78.9%, and showed a slight drop to 66.2% at 4th recycle. ^1H NMR spectroscopy showed that there are no properties changes in recovered [Emim][Ac], except for the leftover traces amount of glycerol.

The result in the computational study clearly demonstrates that, catalytic performance of ionic liquid catalyst does not depend only on basicity, but also cooperative role of imidazolium cation and anion appeared more suitable to predict the mechanism. [Emim][Ac] has successfully catalyzed the transesterification of glycerol and diethyl carbonate in cooperatives manner through the formation of hydrogen bonding. It is best to note that, [Emim][Ac] catalyst can be regenerated evidence by the increase of hydrogen bonding between the intermediate of TS2 as compared to intermediate of TS1. Therefore, the proposed mechanism agreed well with the theoretical computational study, thus provides an in-depth understanding of the overall transesterification reaction together with the valuable insight into the mechanisms of transesterification reaction of glycerol with dialkyl carbonate (in general).

In short, the overall findings of the research would be useful not only for laboratory-scale but also for the researchers in industry to find a way of designing of new and more efficient ionic liquid catalysts and optimal process development for the synthesis of cyclic carbonates (in general), thus attracts increasing attention in the future for ionic liquid-based industrial process development. Perhaps, this research can be as a reference in improving the needs and demands of transforming the surplus of glycerol to high value-added glycerol carbonate that grows in the fine chemicals industry.

5.2 Recommendation for further studies

The findings of the present research work are directive towards several areas which merit further studies, some of which are listed below: -

i. Investigation on the possibilities of using ionic liquid to catalyze the crude glycerol without any pretreatment deserved to be explored in detail.

ii. A further research effort needs to be devoted on the reaction kinetic of transesterification of glycerol catalyze by ionic liquid.

iii. Further investigation using other optimization and simulation studies such as Artificial Neural Network (ANN) would be necessary to predict the amount of desired product and by-product for transesterification of glycerol.

iv. The effect of cation could be experimentally and theoretically investigated for a deeper understanding of the whole catalytic transesterification reaction.

v. To prove the proposed mechanism experimentally by means of understanding the reaction process.

REFERENCES

Ab Rahim, M. H., Forde, M. M., Jenkins, R. L., Hammond, C., He, Q., Dimitratos, N., Lopez-Sanchez, J. A., Carley, A. F., Taylor, S. H., Willock, D. J., Murphy, D. M., Kiely, C. J. & Hutchings, G. J. (2013). Oxidation of methane to methanol with hydrogen peroxide using supported gold-palladium alloy nanoparticles. *Angewandte Chemie*, *125*(4), 1318–1322.

Abbott, A. P., Harris, R. C., Ryder, K. S., D'Agostino, C., Gladden, L. F. & Mantle, M. D. (2011). Glycerol eutectics as sustainable solvent systems. *Green Chemistry*, *13*, 82–90.

Álvarez, M., Frey, A., Bitter, J., Segarra, A., de Jong, K. & Medina, F. (2013). On the role of the activation procedure of supported hydrotalcites for base catalyzed reactions: Glycerol to glycerol carbonate and self-condensation of acetone. *Applied Catalysis B: Environmental*, *134-135*, 231–237.

Álvarez, M. G., Chimentão, R. J., Figueras, F. & Medina, F. (2012). Tunable basic and textural properties of hydrotalcite derived materials for transesterification of glycerol. *Applied Clay Science*, *58*, 16–24.

Álvarez, M., Plíšková, M., Segarra, A., Medina, F. & Figueras, F. (2012). Synthesis of glycerol carbonates by transesterification of glycerol in a continuous system using supported hydrotalcites as catalysts. *Applied Catalysis B: Environmental*, *113-114*, 212–220.

Alvarez, M., Segarra, A., Contreras, S., Sueiras, J., Medina, F. & Figueras, F. (2010). Enhanced use of renewable resources: Transesterification of glycerol catalyzed by hydrotalcite-like compounds. *Chemical Engineering Journal*, *161*, 340–345.

Andreani, L. & Rocha, J. D. (2012). Use of ionic liquids in biodiesel production: A review. *Brazilian Journal of Chemical Engineering*, *29*(01), 1–13.

Anthofer, M., Wilhelm, M., Cokoja, M., Markovits, I., Pöthig, A., Mínk, J., Herrmanna, W. A. & Kühn, F. (2014). Cycloaddition of CO_2 and epoxides catalyzed by imidazolium bromides at mild conditions: Influence of the cation on catalyst activity. *Catalysis Science & Technology*, *4*, 1749.

Aresta, M., Dibenedetto, A., Nocito, F. & Ferragina, C. (2009). Valorization of bio-glycerol: New catalytic materials for the synthesis of glycerol carbonate via glycerolysis of urea. *Journal of Catalysis*, *268*(1), 106–114.

Aresta, M., Dibenedetto, A., Nocito, F. & Pastore, C. (2006). A study on the carboxylation of glycerol to glycerol carbonate with carbon dioxide: The role of the catalyst, solvent and reaction conditions. *Journal of Molecular Catalysis A: Chemical*, *257*, 149–153.

Armarego, W. L. F. & Chai, C. L. L. (2009). Chapter 4-Purification of organic chemicals. In *Purification of laboratory chemicals* (Sixth Edition, pp. 88–444). Oxford: Butterworth-Heinemann.

Arthur, C. V, Bell, J. J. B. & David, M. J. (1959, December 1). Method for preparing glycerin carbonate. Google Patents. Retrieved from https://www.google.com/patents/US2915529.

Bai, R., Wang, Y., Wang, S., Mei, F., Li, T. & Li, G. (2013a). Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by NaOH/γ-Al_2O_3. *Fuel Processing Technology, 106*(0), 209–214.

Bai, R., Zhang, H., Mei, F., Wang, S., Li, T., Gu, Y. & Li, G. (2013b). One-pot synthesis of glycidol from glycerol and dimethyl carbonate over a highly efficient and easily available solid catalyst $NaAlO_2$. *Green Chemistry, 15*(10), 2929.

Behr, A., Eilting, J., Irawadi, K., Leschinski, J. & Lindner, F. (2008). Improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chemistry, 10*(1), 13.

Benavides, P. T., Salazar, J. & Diwekar, U. (2013). Economic comparison of continuous and batch production of biodiesel using soybean oil. *Environmental Progress and Sustainable Energy, 32*(1), 11–24.

Benoit, M., Brissonnet, Y., Guélou, E., De-Oliveira-Vigier, K., Barrault, J. & Jérôme, F. (2010). Acid-catalyzed dehydration of fructose and inulin with glycerol or glycerol carbonate as renewably sourced co-solvent. *ChemSusChem, 3*(11), 1304–1309.

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta, 76*(5), 965–977.

Bobbink, F. D. & Dyson, P. J. (2016). Synthesis of carbonates and related compounds incorporating CO_2 using ionic liquid-type catalysts: State-of-the-art and beyond. *Journal of Catalysis*. *343*, 52-61.

Bolívar-Diaz, C. L., Calvino-Casilda, V., Rubio-Marcos, F., Fernándes, J. F. & Bañares, M. A. (2013). New concepts for process intensification in the conversion of glycerol carbonate to glycidol. *Applied Catalysis B: Environmental, 129*, 575–579.

Bose, S., Armstrong, D. W. & Petrich, J. W. (2010). Enzyme-catalyzed hydrolysis of cellulose in ionic liquids: A green approach toward the production of biofuels. *Journal of Physical Chemistry B, 114*, 8221–8227.

Box, G. E. P. & Wilson, K. B. (1951). On the Experimental Attainment of Optimum Conditions. *Journal of the Royal Statistical Society. Series B (Methodological), 13*(1), 1–45.

Brandt, A., Hallett, J. P., Leak, D. J., Murphy, R. J. & Welton, T. (2010). The Effect of the ionic liquid anion in the pretreatment of pine wood chips. *Green Chemistry, 12*, 672–679.

Calvino-Casilda, V., Mul, G., Fernández, J. F., Rubio-Marcos, F. & Bañares, M. A. (2011). Monitoring the catalytic synthesis of glycerol carbonate by real-time attenuated total reflection FTIR spectroscopy. *Applied Catalysis A: General, 409-410*, 106–112.

Ch. Ramesh Kumar, Jagadeeswaraiah, K., Sai Prasad, P. S. & Lingaiah, N. (2012). Samarium exchanged heteropoly tungstate: An efficient solid acid catalyst for synthesis of glycerol carbonate from glycerol and for benzylation of anisole. *ChemCatChem*, *4*(9), 1360–1367.

Chakraborti, A. & Roy, S. (2009). On catalysis by ionic liquid. *Journal of the American Chemical Society*, *131*, 6902–6903.

Chen, Y., Cao, Y., Sun, X. & Mu, T. (2014). Hydrogen bonding interaction between acetate-based ionic liquid 1-ethyl-3-methylimidazolium acetate and common solvents. *Journal of Molecular Liquids*, *190*, 151–158.

Cheng, W., Su, Q., Wang, J., Sun, J. & Ng, F. (2013). Ionic liquids: The synergistic catalytic effect in the synthesis of cyclic carbonates. *Catalysts*, *3*, 878–901.

Chiappe, C., Malvaldi, M. & Pomelli, C. S. (2009). Ionic liquids: Solvation ability and polarity. *Pure and Applied Chemistry*, *81*(4), 767–776.

Chiappe, C. & Rajamani, S. (2012). Synthesis of glycerol carbonate from glycerol and dimethyl carbonate in basic ionic liquids. *Pure and Applied Chemistry*, *84*(3), 755–762.

Cho, H.-J., Kwon, H.-M., Tharun, J. & Park, D.-W. (2010). Synthesis of glycerol carbonate from ethylene carbonate and glycerol using immobilized ionic liquid catalysts. *Journal of Industrial and Engineering Chemistry*, *16*(5), 679–683.

Choi, J. S., Simanjuntaka, F. S. H., Oh, J. Y., Lee, K. I., Lee, S. D., Cheong, M., Kim, H. S. & Lee, H. (2013). Ionic-liquid-catalyzed decarboxylation of glycerol carbonate to glycidol. *Journal of Catalysis*, *297*, 248–255.

Cláudio, A. F. M., Swift, L., Hallett, J. P., Welton, T., Coutinho, J. A. P. & Freire, M. G. (2014). Extended scale for the hydrogen-bond basicity of ionic liquids. *Physical Chemistry Chemical Physics*, *16*, 6593–6601.

Climent, M. J., Corma, A., De Frutos, P., Iborra, S., Noy, M., Velty, A. & Concepción, P. (2010). Chemicals from biomass: Synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid-base pairs. *Journal of Catalysis*, *269*(1), 140–149.

Cross, J., Hunter, R. & Stimson, V. (1976). The thermal decomposition of simple carbonate esters. *Australian Journal of Chemistry*, *29*, 1477–1481.

Wang, D., Yang, B., Zhai, X. & Zhou, L. (2007). Synthesis of diethyl carbonate by catalytic alcoholysis of urea. *Fuel Processing Technology*, *88*, 807-812.

da Costa Lopes, A. M., João, K. G., Rubik, D. F., Bogel-Łukasik, E., Duarte, L. C., Andreaus, J. & Bogel-Łukasik, R. (2013). Pretreatment of lignocellulosic biomass using ionic liquids: Wheat straw fractionation. *Bioresource Technology*, *142*, 198–208.

Darensbourg, D. J. & Yeung, A. D. (2014). Kinetics and thermodynamics of the decarboxylation of 1,2-glycerol carbonate to produce glycidol: Computational insights. *Green Chemistry*, *16*(1), 247–252.

Darji, D. (2015). *Dissolution of rubber biomass in imidazolium-based ionic liquid for regeneration of cellulose*. (Unpublished PhD's thesis). University of Malaya, Kuala Lumpur, Malaysia.

Dibenedetto, A., Angelini, A., Aresta, M., Ethiraj, J., Fragale, C. & Nocito, F. (2011). Converting wastes into added value products: from glycerol to glycerol carbonate, glycidol and epichlorohydrin using environmentally friendly synthetic routes. *Tetrahedron*, *67*, 1308–1313.

Esteban, J., Fuente, E., Blanco, A., Ladero, M. & Garcia-Ochoa, F. (2015). Phenomenological kinetic model of the synthesis of glycerol carbonate assisted by focused beam reflectance measurements. *Chemical Engineering Journal*, *260,* 434–443.

Esteban, J., Ladero, M., Fuente, E., Blanco, Á. & García-Ochoa, F. (2016). Experimental and modelling approach to the catalytic coproduction of glycerol carbonate and ethylene glycol as a means to valorise glycerol. *Journal of the Taiwan Institute of Chemical Engineers*, *63,* 89–100.

Ezhova, N. N., Korosteleva, I. G., Kolesnichenko, N. V., Kuz'min, A. E., Khadzhiev, S. N., Vasil'eva, M. A. & Voronina, Z. D. (2012). Glycerol carboxylation to glycerol carbonate in the presence of rhodium complexes with phosphine ligands. *Petroleum Chemistry*, *52*(2), 91–96.

Fischer, J. & Ritter, H. (2013). Oligomeric epoxide–amine adducts based on 2-amino-N-isopropylacetamide and α-amino-ε-caprolactam: Solubility in presence of cyclodextrin and curing properties. *Beilstein Journal of Organic Chemistry*, *9*, 2803–2811.

Gade, S. M., Munshi, M. K., Chherawalla, B. M., Rane, V. H. & Kelkar, A. A. (2012). Synthesis of glycidol from glycerol and dimethyl carbonate using ionic liquid as a catalyst. *Catalysis Communications*, *27*, 184–188.

George, J., Patel, Y., Pillai, S. & Munshi, P. (2009). Methanol assisted selective formation of 1,2-glycerol carbonate from glycerol and carbon dioxide using nBu_2SnO as a catalyst. *Journal of Molecular Catalysis A: Chemical*, *304*(1-2), 1–7.

Go, A-. R., Lee, Y., Kim, Y. H., Park, S., Choi, J., Lee, J., Han, S. O., Kim, S. W. & Park, C. (2013). Enzymatic coproduction of biodiesel and glycerol carbonate from soybean oil in solvent-free system. *Enzyme and Microbial Technology*, *48*, 505–509.

Gong, K., Wang, H., Fang, D. & Liu, Z. (2008). Basic ionic liquid as catalyst for the rapid and green synthesis of substituted 2-amino-2-chromenes in aqueous media. *Catalysis Communications*, *9*, 650.

Gosecki, M., Gadzinowski, M., Gosecka, M., Basinska, T. & Slomkowski, S. (2016). Polyglycidol, its derivatives, and polyglycidol-containing copolymers-synthesis and medical applications. *Polymers*, *8*(6), 1–25.

Grey, R. A. (1992). Preparation of cyclic carbonates using alkylammonium and tertiary amine catalysts. *U.S* (https://www.google.com/patents/US5091543).

Hazimah, A. H., Ooi, T. L. & Salmiah, A. (2003). Recovery of glycerol and diglycerol from glycerol pitch. *Journal of Oil Palm Research*, *15*(1), 1–5.

Heinze, T., Schwikal, K. & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Technology*, *5*, 520–525.

Herseczki, Z., Arton, G. M. & Arga, T. V. (2011). Enhanced use of renewable resources: Transesterification of glycerol, the byproduct of biodiesel production. *Hungarian Journal of Industrial Chemistry*, *39*(2), 183–187.

Herseczki, Z., Varga, T. & Marton, G. (2009). Synthesis of glycerol carbonate from glycerol, a by-product of biodiesel production. *International Journal of Chemical Reactor Engineering*, *7*.

Hervert, B., McCarthy, P. D. & Palencia, H. (2014). Room temperature synthesis of glycerol carbonate catalyzed by N-heterocyclic carbenes. *Tetrahedron Letters*, *55*(1), 133–136.

Holbrey, J. D. & Seddon, K. R. (1999). The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates: Ionic liquids and ionic liquid crystals. *Journal of Chemical Society, Dalton Transactions*, 2133–2139.

Hu, J., Li, J., Gu, Y., Guan, Z., Mo, W., Ni, Y., Li, T. & Li, G. (2010). Oxidative carbonylation of glycerol to glycerol carbonate catalyzed by $PdCl_2$(phen)/KI. *Applied Catalysis A: General*, *386*(1-2), 188–193.

Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A. & Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry*, *3*, 156–164.

Indran, V. P., Syuhada Zuhaimi, N. A., Deraman, M. A., Maniam, G. P., Yusoff, M. M., Yun Hin, T.-Y. & Ab. Rahim, M. H. (2014). An accelerated route of glycerol carbonate formation from glycerol using waste boiler ash as catalyst. *RSC Advances*, *4*(48), 25257–25267.

Jagadeeswaraiah, K., Kumar, C. R., Prasad, P. S. S. & Lingaiah, N. (2014). Incorporation of Zn^{2+} ions into the secondary structure of heteropoly tungstate: Catalytic efficiency for synthesis of glycerol carbonate from glycerol and urea. *Catalysis Science & Technology*, *4*(9), 2969.

Jagadeeswaraiah, K., Kumar, C. R., Prasad, P. S. S., Loridant, S. & Lingaiah, N. (2014). Synthesis of glycerol carbonate from glycerol and urea over tin-tungsten mixed oxide catalysts. *Applied Catalysis A-General*, *469*, 165–172.

Jiabo, L. & Wang, T. (2011). On the deactivation of alkali solid catalysts for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. *Reaction Kinetics, Mechanisms and Catalysis*, *102*, 113–126.

Joshi, M. D. & Anderson, J. L. (2012). Recent advances of ionic liquids in separation science and mass spectrometry. *RSC Advances*, *2*, 5470–5484.

Ju, H.-Y., Manju, M. D., Kim, K., Park, S. & Park, D. (2007). Chemical fixation of carbon dioxide to dimethyl carbonate from propylene carbonate and methanol using ionic liquid catalysts. *Korean Journal of Chemical Engineering*, *24*(5), 917–919.

Kamlet, M. J., Abboud, J. L. & Taft, R. W. (1977). The solvatochromic comparison method. 6. The pi.* scale of solvent polarities. *Journal of the American Chemical Society*, *99*(18), 6027–6038.

Kamlet, M. & Taft, R. (1976). The solvatochromic comparison method. I. The β-scale of solvent hydrogen-bond acceptor (HBA) basicities. *Journal of American Oil Chemists' Society*, *98*(2), 337–383.

Khayoon, M. S. & Hameed, B. H. (2013). $Mg_{1+x}Ca_{1-x}O_2$ as reusable and efficient heterogeneous catalyst for the synthesis of glycerol carbonate via the transesterification of glycerol with dimethyl carbonate. *Applied Catalysis A: General*, *466*, 272–281.

Kim, D. W., Park, K. A., Kim, M. J., Kang, D. H., Yang, J. G. & Park, D. W. (2014). Synthesis of glycerol carbonate from urea and glycerol using polymer-supported metal containing ionic liquid catalysts. *Applied Catalysis A: General*, *473*, 31–40.

Kongjao, S., Damronglerd, S. & Hunsom, M. (2010). Purification of crude glycerol derived from waste used-oil methyl ester plant. *Korean Journal of Chemical Engineering*, *27*(3), 944–949.

Kumar, A., Iwatani, K., Nishimura, S., Takagaki, A. & Ebitani, K. (2012). Promotion effect of coexistent hydromagnesite in a highly active solid base hydrotalcite catalyst for transesterifications of glycols into cyclic carbonates. *Catalysis Today*, *185*(1), 241–246.

La, K. W., Jung, J. C., Kim, H., Baeck, I. S.-H. & Song, K. (2007). Effect of acid-base properties of $H_3PW_{12}O_{40}/Ce_xTi_{1-x}O_2$ catalysts on the direct synthesis of dimethyl carbonate from methanol and carbon dioxide: A TPD study of $H_3PW_{12}O_{40}/Ce_xTi_{1-x}O_2$ catalysts. *Journal of Molecular Catalysis A: Chemical*, *269*, 41–45.

Lameiras, P., Boudesocque, L., Mouloungui, Z., Renault, J.-H., Wieruszeski, J.-M. & Lip-pens, G. (2011). Glycerol and glycerol carbonate as ultraviscous solvents for mixture analysis by NMR. *Journal of Magnetic Resonance*, *212*, 161–168.

Lan, D. H., Fan, N., Wang, Y., Gao, X., Zhang, P., Chen, L., Au, C. T. & Yin, S. F. (2016). Recent advances in metal-free catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides. *Cuihua Xuebao/Chinese Journal of Catalysis*, *37*(6), 826–845.

Lee, J. M. & Prausnitz, J. M. (2010). Polarity and hydrogen-bond-donor strength for some ionic liquids: Effect of alkyl chain length on the pyrrolidinium cation. *Chemical Physics Letters*, *492*(1-3), 55–59.

Li, J. & Wang, T. (2011). Chemical equilibrium of glycerol carbonate synthesis from glycerol. *The Journal of Chemical Thermodynamics*, *43*(5), 731–736.

Lin, L., Yamaguchi, H. & Suzuki, A. (2013). Dissolution of cellulose in the mixed solvent of bmim]Cl-DMAc and its application. *RSC Advances*, *3*(34), 14379–14384.

Liu, J., Li, Y., Zhang, J. & He, D. (2016). Glycerol carbonylation with CO_2 to glycerol carbonate over CeO_2 catalyst and the influence of CeO_2 preparation methods and reaction parameters. *Applied Catalysis A: General*, *513*, 9–18.

Liu, P., Derchi, M. & Hensen, E. J. M. (2013). Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over MgAl mixed oxide catalysts. *Applied Catalysis A: General*, *467*, 124–131.

Lu, P., Wang, H. & Hu, K. (2013). Synthesis of glycerol carbonate from glycerol and dimethyl carbonate over the extruded CaO-based catalyst. *Chemical Engineering Journal*, *228*, 147–154.

Lucchini, V., Noe, M., Selva, M., Fabris, M. & Perosa, A. (2012). Cooperative nucleophilic-electrophilic organocatalysis by ionic liquids. *Chemical Communications*, *48*, 5178– 5180.

Ma, J., Song, J., Liu, H., Liu, J., Zhang, Z., Jiang, T., Fan, H. & Han, B. (2012). One-pot conversion of CO_2 and glycerol to value-added products using propylene oxide as the coupling agent. *Green Chemistry*, *14*, 1743.

Mäki-Arvela, P., Anugwom, I., Virtanen, P., Sjöholm, R. & Mikkola, J. P. (2010). Dissolution of lignocellulosic materials and its constituents using ionic liquids-A review. *Industrial Crops and Products*, *32*(3), 175–201.

Malyaadri, M., Jagadeeswaraiah, K., Prasad, P. S. S. & Lingaiah, N. (2011). Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over Mg/Al/Zr catalysts. *Applied Catalysis A: General General*, *401*(1-2), 153–157.

Mario, P. & Michele, R. (2010). *Future of glycerol* (Second Edition). London: Royal Society of Chemistry.

Mizuno, T., Nakai, T. & Mihara, M. (2010). New synthesis of glycerol carbonate from glycerol using sulfur-assisted carbonylation with carbon monoxide. *Heteroatom Chemistry*, *21*(2), 99–102.

Mohammad Fauzi, A. H. & Amin, N. A. S. (2012). An overview of ionic liquids as solvents in biodiesel synthesis. *Renewable and Sustainable Energy Reviews*, *16*(8), 5770–5786.

Mouloungui, Z., Yoo, J., Gachen, C., Gaset, A. & Vermeersch, G. (1996). Process for the preparation of glycerol carbonat from glycerol and a cyclic organic carbonat, especially ethylene or propylene carbonate. EP 0739888 A1.

Muhamad, N., Mohamad, R., Foo, H. L. & Abdul Rahim, R. (2010). Improvement of folate biosynthesis by lactic acid bacteria using response surface methodology. *Food Technology & Biotechnology*, *48*, 243.

Munshi, M. K., Biradar, P. S., Gade, S. M., Rane, V. H. & Kelkar, A. A. (2014a). Efficient synthesis of glycerol carbonate/glycidol using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) based ionic liquids as catalyst. *RSC Advances*, *4*, 17124–17128.

Munshi, M. K., Gade, S. M., Mane, M. V, Mishra, D., Pal, S., Vanka, K., Rane, V. H. & Kelkar, A. A. (2014b). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU): A highly efficient catalyst in glycerol carbonate synthesis. *Journal of Molecular Catalysis A: Chemical*, *391*, 144–149.

Munshi, M. K., Gade, S. M., Rane, V. H. & Kelkar, A. A. (2014c). Role of cation-anion cooperation in the selective synthesis of glycidol from glycerol using DABCO-DMC ionic liquid as catalyst. *RSC Advances*, *4*(61), 32127–32133.

Naik, P., Petitjean, L., Refes, K., Picquet, M. & Plasserauda, L. (2009). Imidazolium-2-carboxylate as an efficient, expeditious and eco-friendly organocatalyst for glycerol carbonate synthesis. *Advanced Synthesis & Catalysis*, *351*, 1753–1756.

Nanda, M. R., Yuan, Z., Qin, W., Ghaziaskar, H. S., Poirier, M.-A. & Xu, C. C. (2014). Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive. *Fuel*, *117*, 470–477.

Nanda M. R;, Yuan, Z., Qin, W., Poirier, M. & Chunbao, X. (2014). Purification of crude glycerol using acidification: Effects of acid types and product characterization. *Australian Journal of Chemistry*, *1*(1), 1004.

Nguyen-Phu, H., Park, C. Y. & Eun, W. S. (2016). Activated red mud-supported Zn/Al oxide catalysts for catalytic conversion of glycerol to glycerol carbonate: FTIR analysis. *Catalysis Communications*, *85*(3), 52–56.

Nuyken, O. & Pask, S. D. (2013). Ring-opening polymerization-An introductory review. *Polymers*, *5*(2), 361–403.

Ochoa-Gómez, J. R., Gómez-Jiménez-Aberasturi, O., Maestro-Madurga, B., Pesquera-Rodríguez, A., Ramírez-López, C., Lorenzo-Ibarreta, L., Torrecilla-Soria, J. & Villarán-Velasco, M. C. (2009). Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: Catalyst screening and reaction optimization. *Applied Catalysis A: General*, *366*(2), 315–324.

Ochoa-Gómez, J. R., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C. A., Nieto-Mestre, J., Maestro-Madurga, B. & Belsué, M. (2011). Synthesis of glycerol carbonate from 3-chloro-1,2-propanediol and carbon dioxide using triethylamine as both solvent and CO_2 fixation-activation agent. *Chemical Engineering Journal*, *175*(1), 505–511.

Ochoa-Gómez, J. R., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C. & Belsué, M. (2012a). A brief review on industrial alternatives for the manufacturing of glycerol carbonate, a green chemical. *Organic Process Research and Development*, *16*(3), 389–399.

Ochoa-Gómez, J. R., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C. & Maestro-Madurga, B. (2012b). Synthesis of glycerol 1,2-carbonate by transesterification of glycerol with dimethyl carbonate using triethylamine as a facile separable homogeneous catalyst. *Green Chemistry*, *14*(12), 3368.

Okutsu, M. & Kitsuki, T. (2001). Process for the preparation of glycerol carbonate.

Olivier-Bourbigou, H. & Magna, L. (2002). Ionic liquids: Perspective for organic and catalytic reactions. *Journal of Molecular Catalysis A: Chemical*, *419*, 182–183.

Olivier-Bourbigou, H., Magna, L. & Morvan, D. (2010). Ionic liquids and catalysis: Recent progress from knowledge to applications. *Applied Catalysis A: General*, *373*(1-2), 1–56.

Omar, E. M. (2013). *Development of proline-based chiral ionic liquid organocatalyst for asymmetric Michael reaction under microwave irradiation*. (Unpublished PhD’s thesis). Universiti Putra Malaysia, Serdang, Selangor.

Ou, G., He, B. & Yuan, Y. (2011). Lipases are soluble and active in glycerol carbonate as a novel biosolvent. *Enzyme and Microbial Technology*, *49*(2), 167–170.

Pagliaro, M., Ciriminna, R., Kimura, H., Rossi, M. & Della Pina, C. (2007). From glycerol to value-added products. *Angewandte Chemie-International Edition*, *46*(24), 4434-4440.

Pagliaro, M., Ciriminna, R., Kimura, H., Rossi, M. & Della Pina, C. (2009). Recent advances in the conversion of bioglycerol into value-added products. *European Journal of Lipid Science and Technology*, *111*(8), 788-799.

Pan, S., Zheng, L., Nie, R., Xia, S., Chen, P. & Hou, Z. (2012). Transesterification of glycerol with dimethyl carbonate to glycerol carbonate over Na–based zeolites. *Chinese Journal of Catalysis*, *33*(11-12), 1772–1777.

Parameswaram, M. S. G., Hari Babu, B., Sai Prasada, P. S. & Lingaiah, N. (2013). Transesterification of glycerol with dimethyl carbonate for the synthesis of glycerol carbonate over Mg/Zr/Sr mixed oxide base catalysts. *Catalysis Science & Technology*, *3*, 3242–3249.

Park, J., Choi, J. S., Woo, S. K., Lee, S. D., Cheong, M., Kim, H. S. & Lee, H. (2012). Isolation and characterization of intermediate catalytic species in the Zn-catalyzed glycerolysis of urea. *Applied Catalysis A-General*, *433-434*, 35–40.

Pasquier, N., Keul, H., Heine, E. & Moeller, M. (2007). From multifunctionalized poly(ethylene imine)s toward antimicrobial coatings. *Biomacromolecules*, *40*, 2874–2882.

Patel, Y., George, J., Pillai, S. M. & Munshi, P. (2009). Effect of liophilicity of catalyst in cyclic carbonate formation by transesterification of polyhydric alcohols. *Green Chemistry*, *11*(7), 1056.

Rahman, M. B. A., Ishak, Z. I., Abdullah, D. K., Astimar, A. A., Basri, M. & Salleh, A. B. (2012). Swelling and dissolution of oil palm biomass in ionic liquids. *Journal of Oil Palm Research*, *24*, 1267– 1276.

Rahman, M. B. A., Ishak, Z. I., Jumbri, K., Aziz, A. A., Basri, M. & Salleh, A. B. (2016). Effect of ionic liquids on oil palm biomass fiber dissolution, *Bioresources*, *11*, 7172–7190.

Rani, M. A. A., Brant, A., Crowhurst, L., Dolan, A., Lui, M., Hassan, N. H., Hallett, J. P., Hunt, P. A., Niedermeyer, H., Perez-Arlandis, J. M., Schrems, M., Welton, T. & Wilding, R. (2011). Understanding the polarity of ionic liquids. *Physical Chemistry Chemical Physics*, *13*, 16831–16840.

Rokicki, G., Rakoczy, P., Parzuchowski, P. & Sobiecki, M. (2005). Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: Glycerol carbonate. *Green Chemistry*, *7*(7), 529.

Sandler, S. R., & Berg, F. R. (1966). Room temperature polymerization of glycidol. *Journal of Polymer Science Part A-1: Polymer Chemistry*, *4*, 1253–1259.

Schols, E. (2014). Production of cyclic carbonates from CO_2 using renewable feedstocks. *CEOPS Workshop "R&D on CO_2 Utilization"*.

Seddon, K. R. (1996). Room-temperature ionic liquids: Neoteric solvents for clean catalysis. *Kinetics and Catalysis*, *37*, 693–697.

Seddon, K. R. (2003). Ionic liquids: A taste of the future. *Nature Materials*, *2*(6), 363–365.

Selva, M., Fabris, M., Lucchini, V., Perosa, A. & Noè, M. (2010). The reaction of primary aromatic amines with alkylene carbonates for the selective synthesis of bis-N-(2-hydroxy)alkylanilines: The catalytic effect of phosphonium-based ionic liquids. *Organic & Biomolecular Chemistry*, *8*(22), 5187–5198.

Selva, M., Fabris, M. & Perosa, A. (2011). Decarboxylation of dialkyl carbonates to dialkyl ethers over alkali metal-exchanged faujasites. *Green Chemistry*, *13*(4), 863.

Selva, M., Noe, M., Perosa, A. & Gottardo, M. (2012). Carbonate, acetate and phenolate phosphonium salts as catalysts in transesterification reactions for the synthesis of non-symmetric dialkyl carbonates. *Organic & Biomolecular Chemistry*, *10*, 6569.

Seoud, O. E., Silva, V., Possidonio, S., Casarano, R., Arêas, E. P. G. & Gimenes, P. (2011). Microwave-assisted derivatization of cellulose, 2-the surprising effect of the structure of ionic liquids on the dissolution and acylation of the biopolymer. *Macromolecular Chemistry and Physics*, *212*, 2541–2550.

Shaikh, A.-A. G. & Sivaram, S. (1996). Organic carbonates. *Chemical Reviews*, *96*(3), 951–976.

Sharath Babu, M., Srivani, A., Parameswaram, G., Veerabhadram, G. & Lingaiah, N. (2015). Understanding the role of tantalum in heteropoly tungstate catalysts for the synthesis of glycerol carbonate from glycerol and urea. *Catalysis Letters*, *145*(9), 1784–1791.

Sheldon, R. (2001). Catalytic reactions in ionic liquids. *Chemical Communications*, (23), 2399–2407.

Shu, C., T. Sun, T., Zhang, H., Jia, J. & Lou, Z. (2014). A novel process for gasoline desulfurization based on extraction with ionic liquids and reduction by sodium borohydride. *Fuel*, *121*, 72–78.

Simanjuntak, F. S. H., Choi, J. S., Lee, G., Lee, H. J., Lee, S. D., Cheong, M., Kim, H. S. & Lee, H. (2015). Synthesis of glycerol carbonate from the transesterification of dimethyl carbonate with glycerol using DABCO and DABCO-anchored Merrifield resin. *Applied Catalysis B: Environmental*, *165*, 642–650.

Sonnati, M. O., Amigoni, S., Darmanin, T. & Choulet, O. (2013). Glycerol carbonate as a versatile building block for tomorrow: Synthesis, reactivity, properties and applications. *Green Chemistry*, *15*, 283–306.

Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodríguez, H. & Rogers, R. D. (2009). Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chemistry*, *11*(5), 646–655.

Taft, R. W. & Kamlet, M. J. (1976). The solvatochromic comparison method. 2. The alpha-scale of solvent hydrogen-bond acceptor (HBA) basicities. *Journal of the American Chemical Society*, *98*(2), 377–383.

Takagaki, A., Iwatani, K., Nishimura, S. & Ebitani, K. (2010). Synthesis of glycerol carbonate from glycerol and dialkyl carbonates using hydrotalcite as a reusable heterogeneous base catalyst. *Green Chemistry*, *12*(4), 578–581.

Takahashi, T., Watahiki, T., Kitazume, S., Yasuda, H. & Sakakura, T. (2006). Synergistic hybrid catalyst for cyclic carbonate synthesis: Remarkable acceleration caused by immobilization of homogeneous catalyst on silica. *Chemical Communications*, (15), 1664–6.

Teles, J. H., Rieber, N. & Harder, W. (1994). Preparation of glycerol carbonate. US5359094 A.

Teng, W. K., Ngoh, G. C., Yusoff, R. & Aroua, M. K. (2014). A review on the performance of glycerol carbonate production via catalytic transesterification: Effects of influencing parameters. *Energy Conversion and Management*, *88*, 484–497.

Tomishige, K., Yasuda, H., Yoshida, Y., Nurunnabi, M., Li, B. & Kunimori, K. (2004). Catalytic performance and properties of ceria based catalysts for cyclic carbonate synthesis from glycol and carbon dioxide. *Green Chemistry*, *6*(4), 206–214.

Tudorache, M., Negoi, A., Protesescu, L. & Parvulescu, V. I. (2014). Biocatalytic alternative for bio-glycerol conversion with alkyl carbonates via a lipase-linked magnetic nano-particles assisted process. *Applied Catalysis B: Environmental*, *145*, 120–125.

Tundo, P., Selva, M. & Ambientali, S. (2002). The chemistry of dimethyl carbonate. *Accounts of Chemical Research*, *35*(9), 706–716.

Turney, T. W., Patti, A., Gates, W., Shaheen, U. & Kulasegaram, S. (2013). Formation of glycerol carbonate from glycerol and urea catalysed by metal monoglycerolates. *Green Chemistry*, *15*, 1925.

Vieville, C., Yoo, J., Pelet, S. & Mouloungui, Z. (1998). Synthesis of glycerol carbonate by direct carbonation of glycerol in supercritical CO_2 in the presence of zeolites and ion exchange resins. *Catalysis Letters*, *56*(4), 245–247.

Vitz, J., Erdmenger, T., Haensch, C. & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*, *11*(3), 417–424.

Wang, L., Liu, Y., Liu, C., Yang, R. & Dong, W. (2013). An efficient catalytic system for the synthesis of glycerol carbonate by oxidative carbonylation of glycerol. *Science China Chemistry*, *56*(10), 1455–1462.

Wasserscheid, P. & Welton, T. (2003). *Ionic liquids in synthesis*. Wiley-VCH Verlag GmbH & Co. KGaA.

Wasserscheid, P. & Welton, T. (2008). *Ionic liquids in synthesis* (Vol. 1). Wiley Online Library.

Welton, T. (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews*, *99*(1), 2071–2083.

Welton, T. (2004). Ionic liquids in catalysis, *Coordination Chemistry Reviews*, *248*, 2459–2477.

Wilkes, J. S., Levisky, J. A., Wilson, R. A. & Hussey, C. L. (1982). Dialkylimidazolium chloroaluminate melts: A new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. *Inorganic Chemistry*, *21*(3), 1263–1264.

Yadav, G. D. & Chandan, P. A. (2014). A green process for glycerol valorization to glycerol carbonate over heterogeneous hydrotalcite catalyst. *Catalysis Today, 237*, 47–53.

Yi, Y., Shen, Y., Sun, J., Wang, B., Xu, F. & Sun, R. (2014). Basic ionic liquids promoted the synthesis of glycerol 1,2-carbonate from glycerol. *Chinese Journal of Catalysis*, *35*(5), 757–762.

Yoo, J. W. & Mouloungui, Z. (2003). Catalytic carbonylation of glycerin by urea in the presence of zinc mesoporous system for the synthesis of glycerol carbonate. *Studies in Surface Science and Catalysis* (Vol. 146).

Yoo, J. W., Mouloungui, Z. & Gaset, A. (2001). Method for producing an epoxide, in particular of glycidol, and installation for implementation. US 6316641 B1.

Zakaria, S. M., Idris, A. & Alias, Y. (2017). Lignin extraction from coconut shell using aprotic ionic liquids. *BioResources*, *12*(3), 5749–5774.

Zhang, J. & He, D. (2014). Lanthanum-based mixed oxides for the synthesis of glycerol carbonate from glycerol and urea. *Reaction Kinetics, Mechanisms and Catalysis*, *113*(2), 375–392.

Zhang, L., Fu, X. & Gao, G. (2011). Anion-cation cooperative catalysis by ionic liquids. *ChemCatChem*, *3*, 1359–1365.

Zheng, Y., Chen, X. & Shen, Y. (2008). Commodity chemicals derived from glycerol, an important biorefinery feedstock. *Chemical Review*, *108*, 5253–5277.

Zhou, Y., Ouyang, F., Song, Z.-B., Yang, Z. & Tao, D.-J. (2015). Facile one-pot synthesis of glycidol from glycerol and dimethyl carbonate catalyzed by tetraethylammonium amino acid ionic liquids. *Catalysis Communications, 66*, 25–29.

LIST OF PUBLICATION AND PAPER PRESENTED

1. **Ishak, Z. I.**, Sairi, N. A., Alias, Y., Aroua, M.K.T. & Yusoff, R. (2017). A review of ionic liquids as catalysts for transesterification reactions of biodiesel and glycerol carbonate production. *Catalysis Reviews*, 1-50.

2. **Ishak, Z. I.**, Sairi, N. A., Alias, Y., Aroua, M.K.T. & Yusoff, R. (2016). Production of glycerol carbonate from glycerol with aid of ionic liquid as catalyst. *Chemical Engineering Journal*, *297*, 128-138.

3. **Ishak, Z. I.**, Sairi, N. A. & Alias, Y. (2015). Conversion of glycerol into glycerol carbonate catalyzed by ionic liquids, *Candidature Defense Postgraduate Student Research*, 18th November 2015, University of Malaya.

4. **Ishak, Z. I.**, Sairi, N. A. & Alias, Y. (2015). Optimization study of glycerol carbonate synthesis catalyzed by ionic liquids, 6th International Congress on Ionic Liquids, 15th-21st June 2015, Lotte Hotel Jeju, Korea.